

THEORY, RESEARCH AND DISCUSSIONS IN NATURAL SCIENCES AND MATHEMATICS

Editor

Assist. Prof. Dr. Elif ÜNAL ÇOKER



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Natural Sciences and Mathematics***

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Chapter 1

Stationarity And Structural Break Analysis of Turkish Republic Gold Coin Prices over the 1997–2026 Period

Harun YONAR¹, Mahmut IŞIK²

Abstract

Stationarity assessment in financial time series may be sensitive to the presence of structural breaks, the deterministic specification, and the sample period under examination. In this study, the monthly Turkish Republic Gold Coin price series for 1997:01–2026:05 was examined comparatively using conventional unit root tests and tests that explicitly account for structural breaks. The analysis first evaluated the 108-observation dataset covering 1997:01–2005:12; the series was then extended through May 2026, and unit root, structural break, and robustness analyses were conducted. Stationarity was assessed using the Augmented Dickey–Fuller (ADF), Phillips–Perron (PP), and Kwiatkowski–Phillips–Schmidt–Shin (KPSS) tests, whereas structural breaks were evaluated using a Perron-type Model A with an exogenously specified break and Zivot–Andrews Models A and C with an endogenously determined break. The ADF statistics obtained for 1997:01–2005:12 numerically matched the previously reported values. Perron-type Model A provided evidence in favor of stationarity under both the May 2001 exogenous-break specification and the February 2001 specification aligned with the exchange-rate regime change of 22 February 2001. In contrast, for the full 1997:01–2026:05 sample, the ADF and PP tests did not provide sufficient evidence that the level series was stationary, while the KPSS tests likewise did not support level or trend stationarity. The Zivot–Andrews models also failed to provide sufficient statistical evidence in favor of a one-break trend-stationary process. The findings indicate that the structural change around 2001 was pronounced in the 1997:01–2005:12 sample, whereas a single-break representation was insufficient to explain the long-run behavior of the series in the extended sample. Overall, the results demonstrate that stationarity assessment

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in financial time series should jointly consider the sample period, deterministic components, and the structure of potential breaks.

Keywords: Turkish Republic Gold Coin, stationarity, unit root, structural break, ADF, Phillips–Perron, KPSS, Perron, Zivot–Andrews

1. Introduction

Stationarity is a fundamental requirement for model selection and statistical inference in time-series analysis. Changes over time in the mean, variance, and covariance structure of a series can directly affect the reliability of regression, causality, and forecasting results. In financial and macroeconomic series in particular, major policy shifts, crises, exchange-rate regime changes, or market shocks may generate breaks in the deterministic structure and thereby reduce the power of conventional unit root tests. Accordingly, alongside augmented forms of the Dickey–Fuller approach and the Phillips–Perron test, methods that explicitly account for structural breaks, such as Perron (1989, 1997) and Zivot–Andrews (1992), occupy a central role in the analysis of financial time series. Empirical studies of gold and metal prices have likewise shown that structural breaks can affect assessments of long memory, volatility, and stationarity (Kirkulak Uludağ & Lkhamazhapov, 2014; Wahab & Adewuyi, 2021).

Using Turkish Republic Gold Coin prices, Yonar (2012) showed that conventional unit root tests and break-sensitive tests could lead to different inferences over the 1997–2005 period. Yonar and Işık (2014) emphasized that structural breaks should not be ignored when assessing stationarity. Yonar and Işık (2019) further showed that stationarity decisions that account for structural breaks may also affect causality assessments among macroeconomic indicators. Taken together, these studies indicate that stationarity assessment is sensitive not only to the test employed but also to potential structural changes in the series and to the sample period analyzed.

For Türkiye, the 2001 financial crisis constitutes a particularly relevant break candidate in this context. The transition of the Turkish lira to a floating exchange-rate regime on 22 February 2001 represented a regime change capable of generating level and slope shifts in domestically denominated asset prices (CBRT, 2001). However, the approximately 25 years following 2001 also encompassed the global financial crisis, fluctuations in international gold prices, exchange-rate shocks, and changing monetary-policy regimes, all of which may have introduced additional structural features into the same series. It is therefore necessary to test whether the single-break explanation that was prominent in the 1997–2005 period remains equally applicable to a substantially longer sample such as 1997–2026.

The objective of this study was to examine the relationship between stationarity and structural breaks in the Turkish Republic Gold Coin price series in two stages. In the first stage, ADF and structural-break results were evaluated using the 108-observation dataset for 1997:01–2005:12. In the second stage, the series was extended and analyzed using ADF, PP, KPSS, Perron-type, and Zivot–Andrews tests. This design enabled the stationarity and structural-break findings from the shorter and longer sample periods to be compared within a common analytical framework.

2. Materials and Methods

2.1. Data

The primary variable in this study was the monthly price of the Turkish Republic Gold Coin. The 108 monthly observations covering 1997:01–2005:12 were obtained from the dataset reported in Yonar (2012). Analyses for this period were conducted on the original observations without applying any scale transformation. For the monthly values, the Turkish Republic Gold Coin (TRY/unit) series listed under the “Gold Prices” data group in the Electronic Data Delivery System (EVDS) of the Central Bank of the Republic of Türkiye was used as the reference series (CBRT, 2026). The combined dataset comprised a total of 353 monthly observations covering 1997:01–2026:05.

Because the 1997–2005 data block reported in Yonar (2012) and the EVDS series were presented on different reporting scales, annual averages for the overlapping 1997–2005 period were compared when constructing the combined series. The ratio of the annual averages in the Yonar (2012) dataset to the corresponding EVDS annual averages ranged from 99,969.67 to 100,029.59, with a mean ratio of 100,000.44. Given the narrow range of these ratios, the 1997–2005 data block was converted to the EVDS scale using a constant scaling factor of 100,000. This constant scaling preserves the within-period logarithmic changes over 1997:01–2005:12. The simple price increase from 2005:12 to 2006:01 was 9.47% (log change: 9.05%); among the 352 monthly log-change observations in the full sample, 33 exhibited a larger absolute change. Thus, the change at the data-merging point did not constitute an extreme value in the sample distribution.

Because the May 2024 observation was markedly lower than the neighboring months, its influence on the results was examined through sensitivity analysis. The primary analyses were conducted using the observed data; in the sensitivity analysis, an alternative value based on the midpoint of the April and June 2024 log prices was used, and the ADF and Zivot–Andrews results were recalculated under this alternative value.

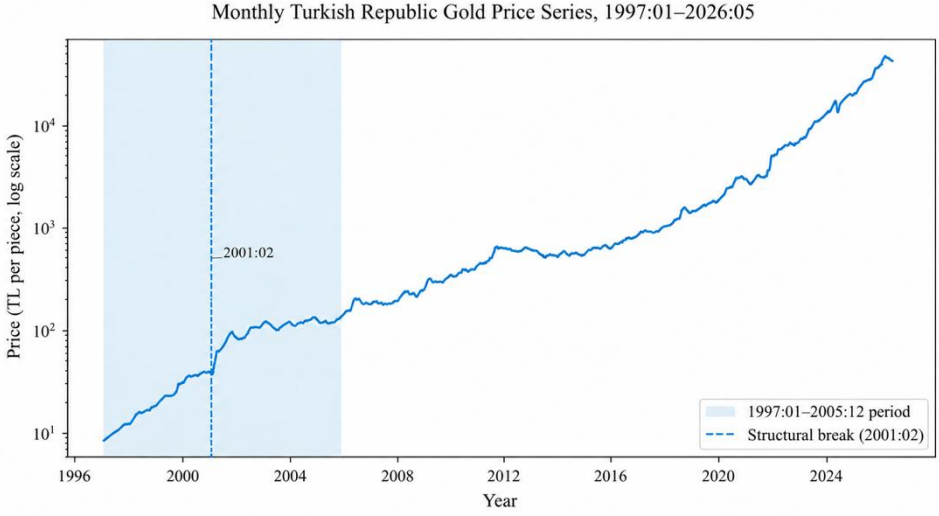


Figure 1. Monthly Turkish Republic Gold Coin price series, 1997:01–2026:05 (logarithmic scale).

2.2. Stationarity and Unit Root Tests

Weak stationarity is defined by a time series whose mean and variance are time-invariant and whose autocovariance depends only on the lag length. These conditions can be expressed mathematically as follows.

$$E(Y_t) = \mu, \quad \text{Var}(Y_t) = E[(Y_t - \mu)^2] = \sigma^2, \quad \text{Cov}(Y_t, Y_{t+k}) = \gamma_k \quad (1)$$

The starting point for unit root testing is the AR(1) representation: $Y_t = \rho Y_{t-1} + \varepsilon_t$. A value of $\rho = 1$ indicates a unit root, whereas $|\rho| < 1$ indicates stationarity. In practice, the ADF regression was specified in the following general form to control for serial correlation (Dickey & Fuller, 1979):

$$\Delta Y_t = \alpha + \beta t + \gamma Y_{t-1} + \sum_{i=1}^p \delta_i \Delta Y_{t-i} + \varepsilon_t \quad (2)$$

In the ADF test, $H_0: \gamma = 0$ denotes the presence of a unit root, whereas $H_1: \gamma < 0$ denotes stationarity. To preserve numerical comparability with the 1997:01–2005:12 period, analyses for this period used a fixed lag of $p = 1$ under three deterministic specifications (intercept + trend, intercept only, and no intercept/no trend). In the full sample, additional ADF tests were also conducted for the log-price series using AIC-based lag selection alongside the same fixed-lag specification.

The Phillips–Perron (PP) test evaluates the unit root null hypothesis and uses a nonparametric long-run variance correction for serial correlation and

heteroskedasticity (Phillips & Perron, 1988). In this study, the PP analysis was conducted using the $Z(\alpha)$ form of the pmdarima PPTest implementation, based on an auxiliary regression including an intercept and deterministic trend; the short bandwidth was used for the primary reporting, while the long bandwidth was used as a sensitivity check. In the KPSS test, by contrast, H_0 denotes stationarity: the intercept specification tests level stationarity, whereas the intercept + trend specification tests trend stationarity (Kwiatkowski et al., 1992). Accordingly, the ADF/PP and KPSS results were interpreted separately according to their respective null hypotheses.

2.3. Structural Break Models

Under the exogenous-break approach, the break date is specified in advance. Taking into account the Model A representation in Yonar (2012) and the augmented form used in the current application, the Perron-type regression with an exogenously specified break was formulated as follows:

$$\Delta Y_t = \alpha + \beta t + \theta_1 D(T^B)_t + \theta_2 DU_t + \gamma Y_{t-1} + \sum_{i=1}^p \delta_i \Delta Y_{t-i} + \varepsilon_t \quad (3)$$

Here, $D(T^B)_t$ takes the value 1 only when $t = T^B + 1$ and 0 otherwise, whereas DU_t takes the value 1 when $t > T^B$ and 0 otherwise. The break fraction is defined as $\lambda = T^B/T$. In the May 2001 specification used in Yonar (2012), $T^B = 2001:05$, $T = 108$, and $\lambda = 53/108 \approx 0.49$. This specification was included to preserve comparability with Yonar (2012). In addition, a second event-based exogenous-break specification was implemented in view of the Turkish lira's transition to a floating exchange-rate regime on 22 February 2001 (CBRT, 2001) and the selection of February 2001 as the endogenous break date by the Zivot–Andrews analyses. In this specification, $T^B = 2001:02$ and $\lambda = 50/108 \approx 0.46$; by model definition, DU_t was coded as 1 from March 2001 onward, while $D(T^B)_t$ was coded as 1 in 2001:03. A lag order of $p = 1$ was used in both Perron-type Model A specifications.

The Zivot–Andrews (1992) test selects the break date endogenously from the data. Model A allows for a break in the level only, whereas Model C allows for breaks in both the level and the trend. Models A and C are represented as follows:

$$\text{Model A: } Y_t = \mu + \beta t + \alpha Y_{t-1} + \theta DU_t(\lambda) + \sum_{i=1}^k c_i \Delta Y_{t-i} + \varepsilon_t \quad (4)$$

$$\text{Model C: } Y_t = \mu + \beta t + \alpha Y_{t-1} + \theta DU_t(\lambda) + \gamma DT_t(\lambda) + \sum_{i=1}^k c_i \Delta Y_{t-i} + \varepsilon_t \quad (5)$$

$DU_t(\lambda) = 1$ when $t > T\lambda$ and 0 otherwise. $DT_t(\lambda) = t - T\lambda$ when $t > T\lambda$ and 0 otherwise. In the Zivot–Andrews test, the unit root null hypothesis H_0 is tested against a trend-stationary alternative with a level and/or trend break at a single unknown date;

among the candidate dates, the test selects the date that yields the minimum t-statistic for the unit root coefficient. The implementation used 15% trimming, a maximum of 12 lags, and AIC-based lag selection; robustness was assessed using BIC- and t-statistic-based lag-selection procedures. In the statsmodels implementation, the lag length is selected once in the baseline model and then held constant across all candidate-break regressions.

2.4. Additional Robustness Analyses and Software

To assess the adequacy of the single deterministic-regime assumption in the long sample, a CUSUM parameter-stability test based on OLS residuals (Ploberger & Krämer, 1992) was applied to the log-price trend, and exploratory piecewise-linear trend segmentation was performed. The segmentation was descriptive in nature and was not treated as a formal multiple-break unit root test. Analyses were conducted in Python 3.13.5 and R 4.5.0. The Python environment used the NumPy, pandas, SciPy, statsmodels, and pmdarima packages. The datasets and analysis code were archived in machine-readable form. As a sensitivity assessment of data harmonization, the full-sample log-price ADF and Zivot–Andrews analyses were repeated using the minimum, mean, and maximum scaling ratios observed over the overlapping 1997–2005 period; the resulting hypothesis decisions and the candidate dates selected by Zivot–Andrews were then compared.

3. Results

3.1. ADF Results for 1997:01–2005:12

The ADF test was applied to the 108 observations for 1997:01–2005:12 under three deterministic specifications: intercept + trend, intercept only, and no intercept/no trend. The ADF statistics reported by Yonar (2012) and the results obtained in the present study for the same period are compared in Table 1.

Table 1. Comparison of ADF results for the 1997:01–2005:12 period.

Model	Reported ADF	Calculated ADF	p	5% critical value
Intercept + trend	-2.698206	-2.698206	0.237	-3.453
Intercept	-0.351053	-0.351053	0.918	-2.889
No intercept/no trend	1.518404	1.518404	0.968	-1.944

Note: In the ADF test, $H_0: \gamma = 0$ denotes the presence of a unit root, whereas $H_1: \gamma < 0$ denotes stationarity. At the 5% significance level, H_0 is rejected when the test statistic is more negative than the corresponding critical value. The 5% critical values shown in the table are based on the MacKinnon response-surface approximations (MacKinnon, 2010); the rounded values reported in Yonar (2012) are -3.45, -2.89, and -1.95, respectively. All absolute differences between the ADF statistics reported in Yonar (2012) and those obtained in the present study are smaller than 10^{-6} .

Across all three deterministic specifications, the ADF statistics obtained in the present study matched the values reported in Yonar (2012) to six decimal places. The unit root null hypothesis H_0 could not be rejected at the 5% significance level under any of the intercept + trend, intercept-only, or no-intercept/no-trend specifications. Thus, for the 1997:01–2005:12 dataset, the conventional ADF approach did not provide sufficient statistical evidence in favor of stationarity.

3.2. Structural Break Results for 1997:01–2005:12

To evaluate the effect of a structural break on unit root inference over the period examined, Perron-type Model A was applied using two exogenous-break definitions: the May 2001 specification used previously and an event-based February 2001 specification. In addition, Zivot–Andrews Models A and C with endogenously determined breaks were employed. Break dates, lag lengths, and test statistics are reported in Table 2.

Table 2. Structural-break unit root test results for the 1997:01–2005:12 period.

Model	Break date	Lag	Test statistic	5% critical value
Perron-type Model A (May 2001 break)	2001:05 (exogenous)	1	-5.1038	-3.760
Perron-type Model A (exchange-rate regime break)	2001:02 (exogenous)	1	-4.6712	-3.760
ZA Model A	2001:02 (endogenous)	1	-5.6886	-4.811
ZA Model C	2001:02 (endogenous)	1	-5.6412	-5.073

Note: In the Perron-type assessment, H_0 represents a unit root process, whereas the alternative hypothesis represents a trend-stationary process around the specified break. For Perron-type Model A, both break fractions ($\lambda \approx 0.46$ and $\lambda \approx 0.49$) were evaluated using the 5% critical value corresponding to $\lambda \approx 0.50$ (−3.760) reported by Perron (1989). In the February 2001 event-based specification, $T^B = 2001:02$, and the post-break dummy variables become effective from March 2001. In the Zivot–Andrews test, the unit root null hypothesis is tested against a trend-stationary alternative with a single endogenous break; a test statistic more negative than the corresponding critical value supports rejection of H_0 .

Under the May 2001 exogenous-break specification, the Perron-type Model A test statistic was −5.1038, and the unit root null H_0 was rejected relative to the 5% critical value of −3.760. When the exogenous break date was specified as February 2001, consistent with the exchange-rate regime change of 22 February 2001, the test statistic was −4.6712 and H_0 was again rejected. On the same 108 observations, Zivot–Andrews Models A and C, which search endogenously for the break, also selected February 2001 as the break date and rejected the unit root

null H_0 . These results show that the Perron-type hypothesis decision was unchanged across the two exogenous-break definitions examined and that the timing of the event-based February 2001 specification was consistent with the endogenous date identified by the Zivot–Andrews procedure.

3.3. ADF Results for 1997:01–2026:05

After extending the sample period to 1997:01–2026:05, the price-level and first-difference series were evaluated using a fixed-lag ADF test to preserve comparability with the 1997:01–2005:12 period. Results for the three deterministic specifications are presented in Table 3.

Table 3. Fixed-lag ($p = 1$) ADF results for the 1997:01–2026:05 period.

Transformation	Model	ADF statistic	p	5% critical value
Level	Intercept + trend	4.6171	>0.999	-3.423
Level	Intercept	6.0314	>0.999	-2.870
Level	No intercept/no trend	6.5441	>0.999	-1.942
First difference	Intercept + trend	-12.1029	<0.001	-3.423
First difference	Intercept	-11.0366	<0.001	-2.870
First difference	No intercept/no trend	-10.6513	<0.001	-1.942

Note: All ADF tests were conducted with a fixed lag of $p = 1$. H_0 denotes the presence of a unit root; a test statistic more negative than the corresponding critical value supports rejection of H_0 . The p-values and critical values are based on the MacKinnon response-surface approximations (MacKinnon, 1994, 2010).

When the observation window was extended through May 2026, the unit root null H_0 could not be rejected for the price level under any of the three ADF specifications. By contrast, H_0 was strongly rejected for the first difference under all specifications. These findings indicate that the full-sample price level did not provide sufficient evidence in favor of stationarity, whereas the first difference showed clear evidence of stationarity. The classification of the order of integration was considered jointly with the other stationarity tests and structural-break results.

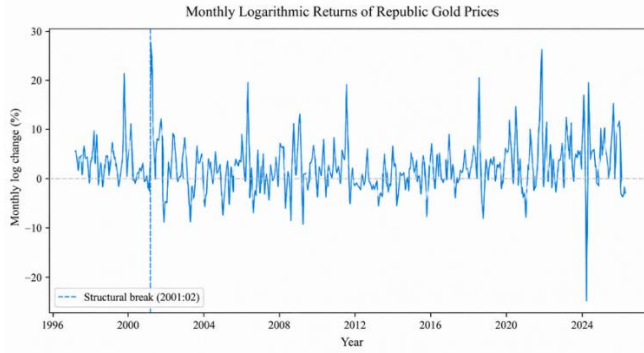


Figure 2. Monthly logarithmic changes in Turkish Republic Gold Coin prices, 1997:02–2026:05.

3.4. ADF, PP, and KPSS Results for 1997:01–2026:05

To examine the consistency of the stationarity findings across different testing approaches in the full sample, the ADF, Phillips–Perron, and KPSS tests were applied to the log-price and first log-difference series. Table 4 presents the results of these tests, which evaluate unit root and stationarity hypotheses in a complementary manner.

Table 4. ADF, PP, and KPSS results for the log price and first log difference over 1997:01–2026:05.

Transformation	Test / specification	Statistic	5% critical value	p
Log level	ADF (intercept)	0.6793	-2.870	0.989
Log level	ADF (intercept + trend)	-0.4768	-3.423	0.984
Log level	PP $Z(\alpha)$ (intercept + trend)	-1.0109	-21.382	0.987
Log level	KPSS (intercept)	2.8422	0.463	<0.010
Log level	KPSS (intercept + trend)	0.3575	0.146	<0.010
First log difference	ADF (intercept)	-9.6769	-2.870	<0.001
First log difference	ADF (intercept + trend)	-9.7042	-3.423	<0.001
First log difference	PP $Z(\alpha)$ (intercept + trend)	-261.7696	-21.381	<0.010
First log difference	KPSS (intercept)	0.4048	0.463	0.075
First log difference	KPSS (intercept + trend)	0.3413	0.146	<0.010

Note: In the ADF and PP tests, H_0 denotes the presence of a unit root; H_0 is rejected when the test statistic is more negative than the corresponding critical value and is accompanied by a small p-value. The PP results were obtained using the short-bandwidth setting of the pmdarima PPTest $Z(\alpha)$ implementation; the long-bandwidth setting yielded the same 5% decision. In the KPSS test, H_0 denotes stationarity, and H_0 is rejected when the test statistic exceeds the critical value. For the PP and KPSS implementations, p-values that reached the reporting bounds of the software are presented using inequalities.

At the log-price level, the unit root null H_0 could not be rejected by the ADF or PP tests, whereas the stationarity null H_0 was rejected by the KPSS tests. Despite their different null hypotheses, the joint implication of these tests does not support treating the level series as stationary. For the first log difference, the ADF and PP tests strongly rejected the unit root null H_0 . In the KPSS specification with an intercept, the stationarity null H_0 was not rejected ($p = 0.075$), whereas trend stationarity was rejected under the intercept + trend specification ($p < 0.010$). Thus, the first log difference provides strong evidence in favor of stationarity, although the finding remains sensitive to the deterministic specification.

3.5. Zivot–Andrews and Stability Results for 1997:01–2026:05

The effect of a potential single structural break on the unit root results in the full sample was examined using Zivot–Andrews Models A and C for both the log-price and price-level series. Test statistics, lag lengths, and candidate dates selected by the algorithm are shown in Table 5.

Table 5. Zivot–Andrews Model A and Model C results for the 1997:01–2026:05 period.

Series	Model	ZA stat.	p	k	Candidate date
Log price	A (level)	-3.1454	0.862	3	2021:10
Log price	C (level + trend)	-3.3206	0.887	3	2018:08
Price	A (level)	6.3196	>0.999	11	2021:09
Price	C (level + trend)	3.0421	>0.999	11	2022:01

Note: In the Zivot–Andrews test, the unit root null H_0 is evaluated against a trend-stationary alternative with a single unknown break. The 5% critical values are -4.811 for Model A and -5.073 for Model C. “Candidate date” denotes the date at which the ZA statistic is minimized, while k denotes the selected lag length. When H_0 is not rejected, candidate dates should not be interpreted as confirmed structural breaks. The primary results were obtained using 15% trimming, a maximum of 12 lags, and AIC-based lag selection.

In the full sample, neither Model A nor Model C rejected the unit root null H_0 for either the log-price or price-level series. Accordingly, the dates selected between 2018 and 2022 were interpreted not as confirmed structural-break dates but as candidate dates at which the ZA statistic reached its minimum. The fact that the hypothesis decision was unchanged between the logarithmic and level transformations indicates that the conclusion of insufficient evidence for a one-break trend-stationary alternative was robust to data transformation.

The CUSUM test based on OLS residuals from the linear log-price trend regression rejected the null hypothesis of parameter stability (statistic = 3.447, $p <$

0.001). In exploratory piecewise-linear trend segmentation, BIC selection under a minimum segment length of 48 months identified five slope-change candidates at 2001:04, 2007:06, 2011:08, 2015:08, and 2021:11. Because the number and timing of the candidates changed when the minimum segment length was reduced to 36 and 42 months, these dates were treated as descriptive candidates rather than confirmed structural breaks; the analysis was not a formal multiple-break unit root test. In the Zivot–Andrews sensitivity analyses, varying the trimming proportion across 0.10, 0.15, and 0.20 and the lag-selection method across AIC, BIC, and the t-statistic did not lead to rejection of the unit root null H_0 under any Model A/C specification. When the alternative value was used for the May 2024 observation, the ADF intercept + trend statistic changed from -0.4768 to -0.4676 ($p = 0.9843$ to 0.9847), while the ZA Model C statistic changed from -3.3206 to -3.3490 ($p = 0.8866$ to 0.8758); the ZA candidate date remained 2018:08. This sensitivity analysis indicates that the full-sample findings were not driven by this single observation. Likewise, when the minimum, mean, and maximum ratios observed over the overlapping 1997–2005 period were used as the harmonization coefficient, the hypothesis decisions from the full-sample ADF and Zivot–Andrews tests remained unchanged, and the candidate dates selected by Zivot–Andrews were preserved.

3.6. Comparative Assessment Across Sample Periods

To provide an integrated assessment of the findings from the 1997:01–2005:12 and 1997:01–2026:05 samples, the testing approaches used in each period and their analytical focus are summarized together. The comparative framework across periods and methods is presented in Table 6.

Table 6. Comparison of the methods applied over the 1997:01–2005:12 and 1997:01–2026:05 periods.

Period	Method	Analytical focus
1997–2005	Conventional ADF	Unit root testing without accounting for a break
1997–2005	Perron-type / ZA	Single-break unit root testing
1997–2026:05	ADF / PP / KPSS	Complementary assessment of level and difference stationarity
1997–2026:05	ZA Model A/C	Unit root testing with a single endogenous break

Note: In the 1997–2005 period, the unit root null H_0 was not rejected by the ADF tests that did not account for a break, whereas H_0 was rejected in the Perron-type and Zivot–Andrews analyses incorporating a break around 2001. In the full 1997–2026:05 sample, the ADF and PP tests did not reject the unit root null H_0 for the level series, the KPSS test rejected stationarity, and ZA Models A/C did not provide sufficient evidence in favor of a one-break trend-stationary alternative. These findings show that the statistical evidence concerning stationarity can vary according to the test specification and the sample period.

4. CONCLUSION AND EVALUATION

Examining the Turkish Republic Gold Coin price series over two different sample horizons showed that the assessment of stationarity was sensitive to the sample period and the definition of the structural break. For 1997:01–2005:12, conventional ADF tests did not provide sufficient evidence in favor of stationarity, whereas the Perron-type and Zivot–Andrews models that accounted for the regime change around 2001 produced evidence consistent with stationarity. In Perron-type Model A, the May 2001 and February 2001 exogenous-break specifications yielded conclusions in the same direction, indicating that the findings were robust to these two alternative definitions of the break date. Moreover, the numerical agreement between the ADF statistics obtained from the same 108 observations and the values reported previously supports the interpretation that the difference in inference is associated with model specification and the way the structural break is modeled rather than with the underlying dataset.

When the series was extended through May 2026, however, the single-break models did not provide sufficient evidence in favor of trend stationarity for the full sample. The unit root null H_0 could not be rejected for the price level in the ADF and PP tests, stationarity was rejected by the KPSS tests, and the unit root null H_0 was likewise not rejected in the Zivot–Andrews Model A/C results. The CUSUM test for the linear trend regression rejected parameter stability, while exploratory trend segmentation indicated several candidate slope changes. These findings suggest that an approximately 30-year series may not be adequately represented by a single break; however, they do not substitute for formal multiple-break unit root tests.

The results for the 1997:01–2005:12 and 1997:01–2026:05 samples should be considered jointly in light of differences in sample composition and model assumptions. In the 1997–2005 period examined by Yonar (2012) and Yonar and Işık (2014), the break around 2001 was a pronounced feature, whereas the sample extending to 2026 includes a larger number of economic regimes and shocks. In the Perron-type and Zivot–Andrews analyses applied in the present study to the same 108 observations, break-sensitive models rejected H_0 , whereas the one-break ZA model did not reach the same conclusion in the full sample. The methodological framework emphasized by Yonar and Işık (2019)—namely, that stationarity decisions may affect subsequent econometric inference—is also consistent with this sample sensitivity.

These findings indicate that stationarity assessment in financial time series should not be based on a single test result or a single sample window. The choice of deterministic components, lag length, whether the break date is specified a

priori or determined from the data, the potential number of breaks, and the data transformation should be considered jointly. In long-horizon nominal price series in particular, single-break tests can be diagnostically useful, but where multiple regime changes are plausible, they should be complemented by multiple-break and break-adjusted unit root methods.

This study has several limitations. Because the 1997:01–2005:12 and 2006:01–2026:05 data blocks were reported on different scales, scale harmonization was required to construct the combined series. The scaling coefficient was determined from annual averages over the overlapping 1997–2005 period; sensitivity analyses based on the minimum, mean, and maximum ratios did not alter the primary hypothesis decisions or the Zivot–Andrews candidate dates. The Zivot–Andrews approach permits only a single structural break, which is an important limitation when multiple regime changes may occur in long-horizon series. Accordingly, additional assessments of multiple breaks were treated as descriptive robustness analyses and were not interpreted as formal multiple-break unit root tests. Because of the reporting limits of the PP implementation used, extreme p-values were presented as inequalities. In addition, observations for 2026 were available only through May.

Note: This book chapter was derived from Harun Yonar’s master’s thesis entitled “**Investigation of Stationarity Using Time Series Analysis with Structural Breaks and an Application**”, completed under the supervision of Mahmut Işık at the Graduate School of Natural and Applied Sciences, Fırat University. A portion of the findings for the 1997–2005 period was presented by Yonar and Işık (2014) as a conference abstract at IECMSA 2014.

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Degradation Mechanism of Three Natural Dyes That Give a Red Colour Using the DFT Method

Bahar EREN¹

ABSTRACT

Natural products are of great importance due to the presence of many secondary metabolites in their structure and their use in a wide variety of aspects of life. Their use in the food, pharmaceutical, and dye industries, as well as the fact that many are obtained synthetically, further increases their importance. During dye production and dyeing, active compounds such as alizarin, purpurin, and other anthraquinone derivatives can be transported to aquatic environments via wastewater. Furthermore, compounds contained in plants containing dyes can reach groundwater and streams through precipitation and surface runoff in areas where they are agriculturally cultivated.

From an atmospheric chemistry perspective, it is thought that organic compounds released during drying, processing, and dyeing processes can mix with the atmosphere and react with OH• radicals. The investigated degradation mechanisms and energy parameters revealed that the compounds in question tend to decompose spontaneously in both aqueous and atmospheric conditions. Negative ΔG (Gibbs Free Energy) values obtained at all degradation steps indicate that the process is thermodynamically spontaneous and that natural dyes can participate in the cycle without creating a polluting effect. The modelling results show that the molecules can be gradually incorporated into the natural cycle.

The degradation mechanisms of three dyes, namely Alizarin red S, Alizarin, and Purpurin, were investigated using Quantum Mechanical Density Functional Theory (DFT) molecular modelling. The theoretical study elucidated both the initial molecules reacting with OH radicals and the fragments involved in the degradation mechanism. The traces of these molecules in nature were examined from the perspective of atmospheric chemistry and water chemistry. The fate of both the original molecule and its hydroxylated fragments in natural cycles, when mixed with surface waters, was theoretically elucidated.

Keywords: DFT, Alizarin red S, Alizarin, Purpurin, dye, OH radical

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INTRODUCTION

Natural anthraquinones most commonly have a 9,10-anthraquinone structure, as shown in Figure 1. Anthraquinones are polycyclic compounds with an unsaturated diketone structure (containing a quinoid group). As important secondary metabolites in plants, anthraquinones play an effective role in many biological processes and responses to environmental factors. Widely found in human nutrition, anthraquinones contribute to reducing disease risk through various biological activities such as anticancer, antibacterial, and antioxidant properties. (Wang et al., 2024).

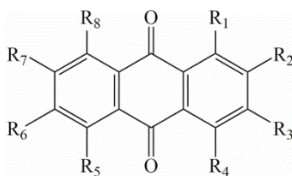


Figure 1. General structure of the anthraquinone group (Wang et al., 2024)

Purpurin, alizarin, munjistin, pseudopurpurin, rubiadin, and kinizarin are common naturally occurring anthraquinone compounds (Zhao and Zheng, 2023). Due to their structural variations, bioavailability, and versatile biological activities, anthraquinone compounds are of great importance in both plant biochemistry and pharmaceutical research. The reason for selecting the molecules shown in Figure 2. (a-c) in this study is that they all have an anthraquinone structure and are used as natural red dyes.

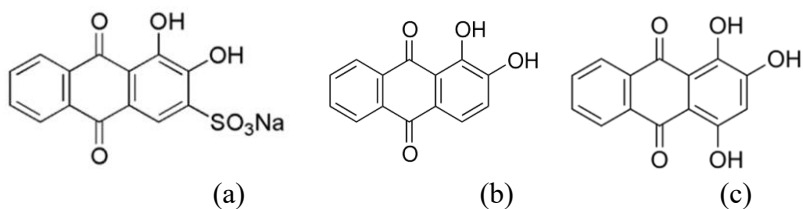


Figure 2. Two-dimensional shapes of (a) Alizarin red S (AKS), (b) Alizarin (AL), and (c) Purpurin (PP) molecules

Alizarin Red S, also called Mordant Red 3 or Alizarin Carmine, is a water-soluble sodium salt of sulfonic acid (Lillie, 1977; Legan et al., 2016). Alizarin Red S is used in histology to stain calcium deposits in tissues, and in geology to stain and distinguish carbonate minerals. In the presence of calcium, it binds to calcium to form an orange to red pigment. All specimens can be stained with this

substance, especially to show bone distribution in developing embryos (Puchtler et al., 1969; Bancroft and Stevens, 1982).

Alizarin, also known as Mordant Red 11 or 1,2-dihydroxyanthraquinone, is an organic compound that has also been given the name "Turkish Red." It has been used as a red dye, particularly for colouring textile fabrics, and is obtained from the roots of madder plants. The primary madder species from which alizarin is obtained is *Rubia tinctorum* (Vankar et al., 2008). Alizarin is a staining agent used in biological research. It stains free calcium and some calcium compounds red or light purple (Vankar et al., 2008; Bien, 2000). Free (ionic) calcium undergoes a precipitation reaction with alizarin. When a tissue block containing calcium is immersed in alizarin, it immediately turns red. Thus, both pure calcium and calcium in bones and other tissues can be stained. These alizarin-stained elements can be better visualized under fluorescent lights stimulated at 440-460 nm (Smith et al., 2018).

Purpurin is found in the roots of the madder plant (*Rubia tinctorum*), along with alizarin (1,2-dihydroxyanthraquinone). The root contains the colourless glycosides of the dyes. Purpurin is a crystalline solid that forms orange-red needles melting at 259 °C (Haynes, 2016). It turns red when dissolved in ethanol and yellow when dissolved in boiling water with alkalis (Vankar et al., 2008). Unlike alizarin, purpurin is dissolved by boiling in an aluminium sulphate solution where it can be precipitated with acid. This procedure can be used to separate the two dyes (Fay, 1919).

In this research, molecules containing electronegative atoms such as O were preferred. The necessity of water-soluble particles was considered, as the interactions of the molecules with the OH radical would be investigated, and studies would be conducted in both the gas and water phases. During the degradation of the molecules, the structures around the electronegative atom within the molecule, the presence of stable closed rings, double bonds, hydrophobic or hydrophilic structures at the molecular ends, and easily separable groups were examined individually.

All dyes to be studied theoretically are organic. It is also known that low concentrations of organic pollutants are present in surface waters. Hydroxyl radicals are degraders and specific detectors that attack biomolecules at different rates. A hydroxyl radical attack on an aromatic compound leads to the formation of a new hydroxylated product. (Eren and Yalçın Gürkan, 2017). The initial aim was to track new products that might be even more dangerous than the product released into nature and to elucidate the degradation reaction. Biomolecules, which are hydroxyl scavengers at various rates, are specific detectors for hydroxyl radicals due to their hydroxylation capabilities. Any hydroxyl radical

attacking an aromatic compound leads to the formation of a hydroxylated product, and these newly formed products can be far more harmful than the original products at the beginning of the process, therefore monitoring these products is crucial. The OH radical acts as an electrophile in its reaction with any organic molecule and therefore readily binds to unsaturated bonds, whereas the O radical is a nucleophile and therefore cannot interact with these bonds. If an aliphatic side chain is attached to an aromatic molecule, the OH radical prefers the aromatic ring for binding. (Anbar and Neta, 1967; Buxton et al., 1988; Halliwell et al., 1998; Aschmann et al., 2005, 2010; Ashmann and Atkinson, 2006; Atkinson et al., 1988; Atkinson and Arey, 2003; Eren and Yalçın Gürkan, 2017).

MATERIAL and METHODS

To determine all possible reaction pathways of the theoretically studied molecules, geometric optimizations were performed using the DFT/B3LYP/6-31G(d) basis set of Quantum Mechanical Density Functional Theory (DFT), an electronic structure method. For all fragments, the Gauss View 6 molecular representation program and the Gaussian 16 program were used for orbital calculations (Gaussian 16, 2009). The fragmentation reaction energy is affected by the water molecules in the aqueous medium. In addition, the geometric stretching in solutions is induced by H₂O. That is, the presence of a dielectric medium such as H₂O causes relaxation in the geometry related to the solute and has a stabilizing effect that reduces the energy for this mechanism (Eren and Gürkan, 2017). Therefore, in this study, the CPCM solvent model from the COSMO (conductor-like screening solvation model) software package in Gaussian 16 was used to explain the solvent effect of H₂O on the Molecule + ·OH reaction energy (Gaussian 16, 2009).

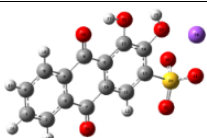
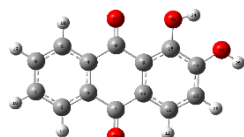
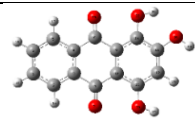
The Gaussian 16 program was used to calculate the energies of atoms and molecules and to perform geometric optimizations. Gauss View 6 visualizes molecules, allowing us to rotate, move, and modify them as desired. It enables us to graphically examine the results calculated by the Gaussian program. These results can be categorized as optimized molecular structures, molecular orbitals, electrostatic potential surfaces, atomic charges, IR, Raman, and NMR spectra, and normal mode animations depending on vibration frequencies (Gaussian 16, 2009).

If it is predicted that the longest bond and the widest bond opening will break first in the fragmentation pathway for any given molecule, this is determined by observing the energy values and environments of electronegative atoms. It should be remembered that double-bonded or closed-loop structures are more stable than

others, and that in the event of fragmentation, breaking from these stable structures will occur in the final stage (Eren and Gürkan, 2023a,b). The energy values of the possible reaction pathways for each studied molecule and its fragments have been calculated in both the gas phase and in water phases. Each fragment is included in the study as a result of the interaction of the parent molecules with the OH radical. The reason why the energy values calculated for each molecule are presented in atomic mass units (Au) is that when converted to SI units, the part after the decimal point makes it difficult to observe the energy difference between the fragments.

RESEARCH FINDING

Table 1. Optimized forms, molecular formulas, common names, and IUPAC names of the studied molecules, in order (C is represented in grey, O in red, S in yellow, Na atom in purple, and H atom in white)

Optimized Forms	Molecular Formulas	Common Names	IUPAC Names
 AKS	$C_{14}H_7O_7S.Na$	Alizarin red S	Sodium; 3,4-dihydroxy-9,10-dioxoanthracene-2-sulfonate
 AL	$C_{14}H_8O_4$	Alizarin	1,2-dihydroxyanthraquinone
 PP	$C_{14}H_8O_5$	Purpurin	1,2,4-trihydroxyanthraquinone

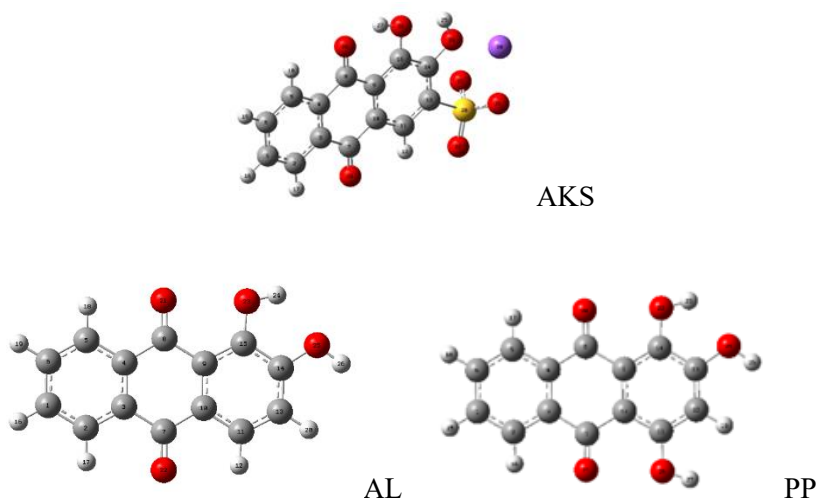
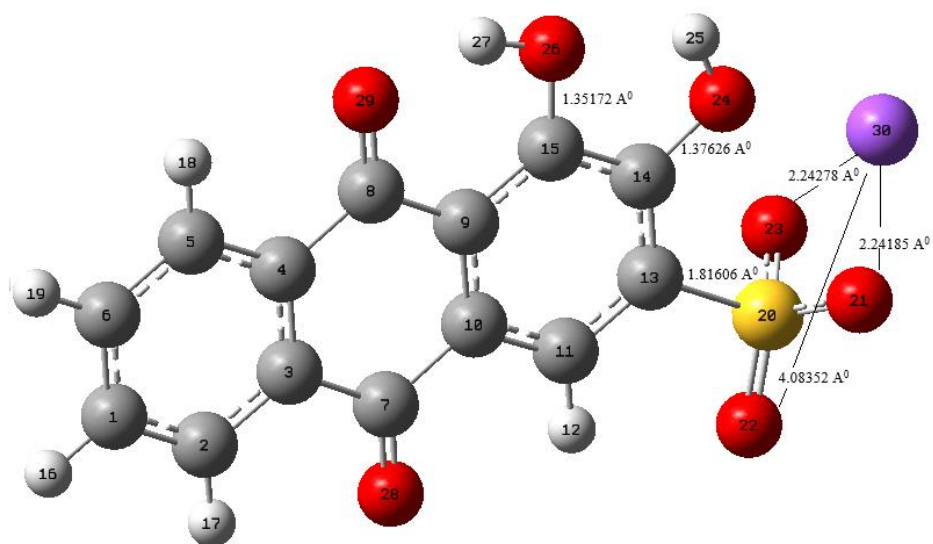
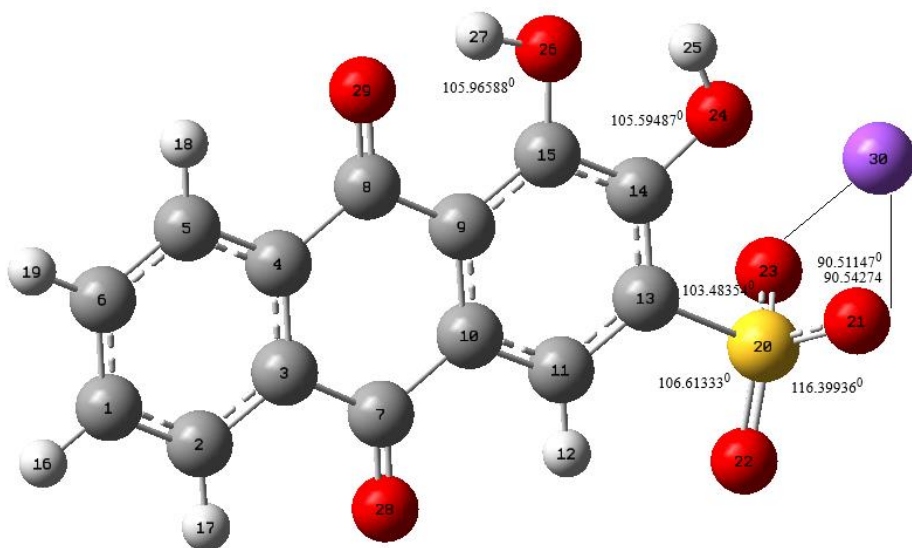


Figure 3. Optimized DFT shapes of Alizarin Red S (AKS), Alizarin (AL), and Purpurin (PP) molecules (C is represented in grey, O in red, S in yellow, Na atom in purple, and H atom in white)



(a)



(b)

Figure 4. Bond lengths (a) and bond angles (b) between atoms of the AKS molecule

The AKS molecule has a structure containing C=O, C-OH, P=O, P-O---Na bonds, as shown in Figure 4. Although it is predicted that the longest bond and the widest bond angle will break first for any molecule, the cleavage path is determined by observing the energy values and environments of electronegative atoms. It should be remembered that structures containing double bonds or closed rings are more stable than others, and if cleavage occurs, breaking from these stable structures will be the final stage (Eren and Yalçın Gürkan, 2023a, b).

If only bond length were considered, the bonds should be separated from the molecule in the following order, from longest to shortest, as shown in Figure 4(a): O₂₃Na₃₀, O₂₁Na₃₀, C₁₃S₂₀, C₁₄O₂₄ and C₁₅O₂₆. It should be noted that the stable bonds C₈=O₂₉, C₇=O₂₈ and S₂₀=O₂₂, shown in Figures 1, 4, and 5, will be the last to be separated in the cleavage pathway.

If a cleavage path is determined solely based on bond angles, according to Figure 4(b), starting with the widest bond angle, the atoms that should be separated from the molecule are O₂₁S₂₀O₂₂, C₁₃S₂₀C₂₂, C₁₅O₂₆H₂₇, C₁₄O₂₄H₂₅, C₁₃S₂₀O₂₃, S₂₀O₂₁Na₃₀ or S₂₀O₂₃Na₃₀ in that order.

If we wanted to determine the decay path based solely on electronegative atoms, examining the Mulliken charges in Table 4 reveals that, in order of electronegativity (the most electronegative atoms are shown in dark), O₂₄, O₂₆, O₂₁, O₂₃, O₂₉, O₂₂, O₂₈ and the surrounding atoms are noteworthy. As shown in Figures 1, 4, and 5, C₈=O₂₉, C₇=O₂₈, and S₂₀=O₂₂ have double bonds; therefore, decomposition does not prefer to start around these bonds due to the presence of stable bonds.

Table 2. Calculated energy values in gas phase, water, methanol, and chloroform solvent (C is represented in grey, O in red, S in yellow, Na atom in purple and H atom in white)

	Gas phase	Water phase	Methanol	Chloroform
AKS	-1624.593089	-1624.649240	-1624.647193	-1624.635781
	-1624.592145	-1624.648296	-1624.646248	-1624.634837
	-1624.658295	-1624.716304	-1624.714064	-1624.703334
AL	-839.003928	-839.020852	-839.020481	-839.016894
	-839.002984	-839.019908	-839.019537	-839.015950
	-839.057709	-839.074776	-839.074400	-839.070774
PP	-914.202253	-914.227540	-914.226997	-914.220810
	-914.201309	-914.226596	-914.226053	-914.219866
	-914.259281	-914.281554	-914.281014	-914.278443

Table 3. Calculated energy values in gas phase, water, methanol, and chloroform solvent of AKS and Fragments from the Molecules Studied

	AKS	A3	A7	A1	A2
Gas phase	-1624.593089	-1549.370864	-1474.147564	-1462.793956	-1387.561006
	-1624.592145	-1549.369920	-1474.146620	-1462.793012	-1387.560061
	-1624.658295	-1549.436433	-1474.211251	-1462.856724	-1387.622045
Water phase	-1624.649240	-1549.427480		-1462.812867	-1387.579523
	-1624.648296	-1549.426536		-1462.811922	-1387.578579
	-1624.716304	-1549.493560		-1462.875906	-1387.641107
Methanol	-1624.647193	-1549.426014	-1474.201164	-1462.812447	-1387.579122
	-1624.646248	-1549.425070	-1474.200220	-1462.811503	-1387.578178
	-1624.714064	-1549.492454	-1474.266509	-1462.875479	-1387.640684
Chloroform	-1624.635781	-1549.417887	-1474.193558	-1462.808408	-1387.575214
	-1624.634837	-1549.416943	-1474.192614	-1462.807464	-1387.574270
	-1624.703334	-1549.483492	-1474.257864	-1462.871386	-1387.636570
	A8	A9	A6	A5	
Gas phase	-1312.354632	-1237.124186	-688.587199	-763.811882	
	-1312.353688	-1237.123241	-688.586254	-763.810938	
	-1312.415481	-1237.181674	-688.635688	-763.861929	
Water phase	-1312.371662	-1237.124186	-688.595298	-763.804418	
	-1312.370718	-1237.123241	-688.594354	-763.803474	
	-1312.431691	-1237.181674	-688.643931	-763.855770	
Methanol		-1237.140404	-688.595128	-763.804113	
		-1237.139460	-688.594183	-763.803169	
		-1237.198051	-688.643757	-763.855463	
Chloroform	-1312.367648	-1237.136916	-688.593457	-763.818064	
	-1312.366704	-1237.135972	-688.592512	-763.817119	
	-1312.428098	-1237.194641	-688.642053	-763.868198	

In addition to the gas and water phases with similar energy values, methanol, and chloroform, one hydrophilic and one hydrophobic solvent, were also added.

Table 4. Mulliken Charges of AKS, AL, PP, and their fragments from the molecules studied

AKS		A1		A2		A3		A5	
C ₁	-0.121207	C ₁	-0.120409	C ₁	-0.120555	C ₁	-0.123760	C ₁	-0.123696
C ₂	-0.173943	C ₂	-0.172773	C ₂	-0.173148	C ₂	-0.172420	C ₂	-0.173029
C ₅	-0.170104	C ₅	-0.168876	C ₅	-0.168999	C ₅	-0.172202	C ₅	-0.172106
C ₆	-0.126492	C ₆	-0.125524	C ₆	-0.125807	C ₆	-0.125117	C ₆	-0.125056
C ₁₁	-0.245691	C ₁₁	-0.214571	C ₁₁	-0.204192	C ₁₁	-0.204294	C ₁₁	-0.183057
C ₁₃	-0.171669	C ₁₃	-0.215007	C ₁₃	-0.224638	C ₁₃	-0.131173	C ₁₃	-0.128007
S ₂₀	1.348986	S ₂₀	1.223682	S ₂₀	0.973733	C ₁₄	-0.183067	C ₁₄	-0.149150
O₂₁ -0.635184		O ₂₁	-0.489502	O ₂₁	-0.488872	S ₂₀	1.294787	O ₂₀	-0.640990
O₂₂ -0.515549		O ₂₂	-0.483626	O ₂₂	-0.504257	O ₂₁	-0.648981	O ₂₂	-0.476343
O₂₃ -0.635036		O ₂₃	-0.637073	O ₂₃	-0.631051	O ₂₂	-0.501601	O ₂₃	-0.554858
O₂₄ -0.703921		O ₂₄	-0.663578	O ₂₅	-0.682228	O ₂₃	-0.646012		
O₂₆ -0.701018		O ₂₆	-0.684830	O ₂₇	-0.470020	O ₂₄	-0.641143		
O₂₈ -0.467292		O ₂₈	-0.467630	O ₂₈	-0.551848	O ₂₆	-0.471355		
O₂₉ -0.559886		O ₂₉	-0.551431			O ₂₇	-0.555307		
Na ₃₀	0.564372					Na ₂₈	0.611851		
A6		A7		A8		A9		PP	
C ₁	-0.124756	C ₁	-0.124865	C ₁	-0.123467	C ₁	-0.123390	C ₁	-0.126158
C ₂	-0.172384	C ₂	-0.171708	C ₂	-0.170002	C ₂	-0.170028	C ₂	-0.174814
C ₅	-0.172383	C ₅	-0.172413	C ₅	-0.170726	C ₅	-0.170617	C ₅	-0.173088
C ₆	-0.124756	C ₆	-0.124240	C ₆	-0.123381	C ₆	-0.123322	C ₆	-0.127478
C ₁₁	-0.172379	C ₁₁	-0.201261	C ₁₁	-0.179618	C ₁₁	-0.181850	C ₉	-0.001996
C ₁₃	-0.124758	C ₁₃	-0.115459	C ₁₃	-0.152568	C ₁₃	-0.165167	C ₁₂	-0.271398
C ₁₄	-0.124745	C ₁₄	-0.146337	C ₁₄	-0.136196	C ₁₄	-0.131533	O ₂₀	-0.462793
C ₁₅	-0.172378	C ₁₅	-0.168756	C ₁₅	-0.168458	C ₁₅	-0.166629	O ₂₁	-0.471880
O ₂₀	-0.478186	S ₂₀	1.293132	S ₂₀	1.207994	S ₂₀	0.955806	O ₂₂	-0.612265
O ₂₁	-0.478115	O ₂₁	-0.632579	O ₂₁	-0.526616	O ₂₁	-0.507602	O ₂₄	-0.673694
		O ₂₂	-0.522082	O ₂₂	-0.478578	O ₂₂	-0.500568	O ₂₆	-0.601692
		O ₂₃	-0.649499	O ₂₃	-0.633033	O ₂₃	-0.467332		
		O ₂₄	-0.483327	O ₂₄	-0.466585	O ₂₄	-0.467989		
		O ₂₅	-0.474828	O ₂₅	-0.469220				
		Na ₂₆	0.612501						
AL									
C ₁	-0.126475								
C ₂	-0.173405								
C ₅	-0.173405								
C ₆	-0.126475								
C ₁₂	-0.188922								
C ₁₃	-0.188924								
O ₂₀	-0.462284								
O ₂₁	-0.462284								
O ₂₂	-0.600545								
O ₂₄	-0.600545								

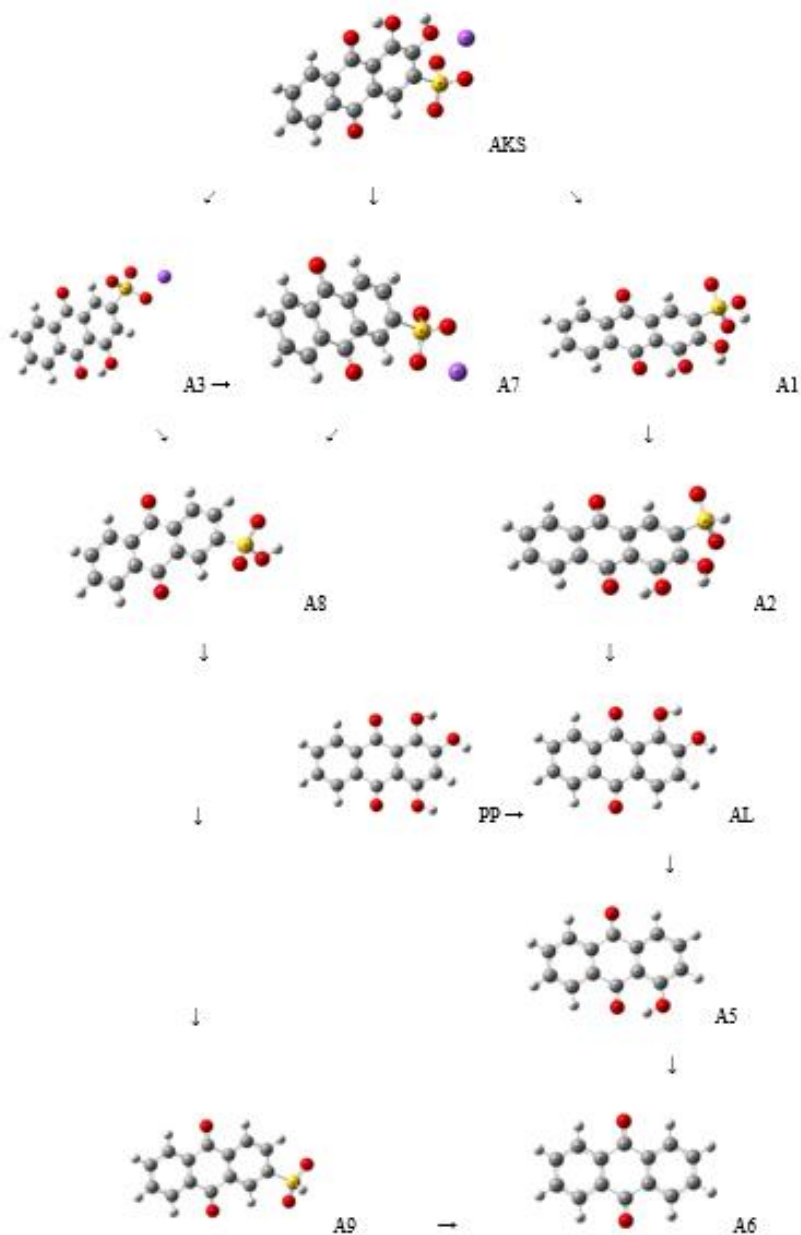


Figure 5. Degradation mechanisms of AKS, AL and PP molecules and their fragments by DFT (C is represented in grey, O in red, S in yellow, Na atom in purple and H atom in white)

CONCLUSION and DISCUSSION

The optimized form of the Quantum Mechanical Density Functional Theory (DFT) of the Alizarin Red S (AKS), using the DFT/B3LYP/6-31G(d) basis set, is shown in Figure 3; the bond lengths (a) and bond angles (b) between the atoms of the molecule are shown in Figure 4; and the ΔE (energy), ΔH (enthalpy), ΔG (Gibbs free) energy values (Au), and Mulliken charges of electronegative atoms in the gas and water phases of the molecule are given in Table 2-4. The energy values calculated for each molecule studied are given in atomic mass units (Au) because, when converted to SI units, the numbers after the decimal point are very close to each other, and the energy differences between them cannot be easily observed. Figure 4 and Table 3,4 serve as references at the beginning of the theoretical work, as the entire study is structured accordingly.

Table 2 and 3 shows in the gas phase, water phase, methanol, and chloroform solvent, energy (ΔE), enthalpy (ΔH), and free energy (ΔG) values (Au) for the studied molecules and their fragments. The energy values of the AKS molecule and its fragments are the most important reference source for estimating the fragmentation path. Negative values indicate that these fragments separated spontaneously, without any external energy input. Fragmentation requires writing the results starting from the smallest of these negative values. It is important to note that energy calculations are performed for each broken bond. Failure to calculate the energy for any broken fragment represents an incomplete fragmentation path.

After examining the bond lengths, bond angles, Mulliken charges of the electronegative atoms, and energy values individually in Figure 4 and Table 2-4, the degradation mechanism of the AKS molecule and its fragments using DFT, as shown in Figure 5, was determined. The first three branches were formed by the successive breaking of the C₁₄-O₂₄, C₁₅-O₂₆, and O₂₁-Na₃₀ bonds. The degradation pathway will continue from these A3, A7 and A1 branches. After these three main branches, the energy values for each fragment were examined, and using the same approach, the degradation mechanism of the AKS molecule and its fragments using DFT, as shown in Figure 5, was written.

Acknowledgment

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Theoretical Degradation Mechanisms of Selected Chemical Nerve Agents Using the DFT Method

Bahar EREN¹

ABSTRACT

In this study, seven organophosphorus-based chemical nerve agents were examined. The seven molecules studied were three molecules from the G series of chemical nerve agents: Tabun (GA), Sarin (GB), and Soman (GD); VX, a representative of the V series; and three molecules from the Novichok series: A 230, A-232, and A 234. The chemical and theoretical structural properties of these seven molecules have been investigated. Nerve agents belonging to these three series pose a serious threat to public health due to their high acute toxicity and environmental persistence. Therefore, the environmental fate of nerve agents is related to a detailed understanding of the degradation mechanisms of these compounds.

The limitation of experimental studies due to high toxicity has led researchers to theoretical methods, especially Quantum Mechanical Density Functional Theory (DFT).

The aim of this study is to theoretically explain the fate of both the starting molecules of nerve agents and their hydroxylated fragments in nature, which enter the natural cycle as a result of their release into the atmosphere, and to provide a comprehensive, scientific and up-to-date reference source for researchers working in the fields of both theoretical chemistry and public health. Because the reactions of molecules calculated in the DFT/B3LYP/6-31G(d) basis set with the OH radical are important for both surface water and atmospheric chemistry, calculations were performed using modeling techniques in both the gas and water phases. As a result of the theoretical calculations, degradation mechanisms were determined for each starting molecule.

Keywords: DFT, Tabun, Sarin, Soman, VX, Novichok series (A-230, A-232, A-234)

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INTRODUCTION

Organophosphorus compounds chemically, they can be considered esters of phosphoric acid (H_3PO_4), and share a general structure represented by $\text{O}=\text{P}(\text{OR})_3$. The methoxy (OCH_3) or ethoxy (OC_2H_5) esters are usually attached to the phosphorus atom as two ester groups. The third ester group can be aliphatic, homocyclic, or heterocyclic and can be attached to the phosphorus atom via ester (P-O-R) or thioester (P-S-R) bonds. This weak bond enhances the electrophilic property of the phosphorus atom and gives it electron-attracting capabilities. Each chemical agent has an organophosphate skeleton containing a phosphorus atom. This central atom is usually surrounded by a leaving group (e.g., F^- or alkyl), an alcohol or amine functional group, and an oxygen or sulphide atom. The physicochemical properties of active substances in different subgroups, such as evaporation, water solubility, penetration into plant tissues, and movement within plant tissues, differ significantly. This difference is primarily due to the $\text{P}=\text{O}$ or $\text{P}=\text{S}$ structure and the organic structures in the third ester group. (Aschmann et al., 2005a, 2005b; Aschmann and Atkinson, 2006, Aschmann et al., 2010; Eren and Yalçın Gürkan, 2021, 2022, 2023a, 2023b; Goodman et al., 1988a, 1988b; Haziri et al., 2024).

Organophosphorus-based nerve agents inhibit the enzymes acetylcholinesterase and butyrylcholinesterase in insects, as well as in humans and many other animals. As a result, the breakdown of acetylcholine stops, it accumulates, and the clinical condition known as cholinergic syndrome develops. Depending on the toxic strength of the agent, clinical symptoms can range from mild to severe, even leading to death within minutes. In this study, seven organophosphorus-based chemical nerve agents were examined. The seven molecules studied were three molecules from the G series of chemical nerve agents: Tabun (GA), Sarin (GB), and Soman (GD); VX, a representative of the V series; and three molecules from the Novichok series: A 230, A-232, and A 234.

Organophosphorus nerve agents exhibit significant differences in chemical stability, reactivity, and bioaccumulation potential due to the presence of different functional groups. The toxicity level of these compounds is directly related to the nature of the functional groups attached to the phosphorus centre and the electron-withdrawing/electron-repelling properties of these groups (Dökmeci, 2025a, 2025b; Eren ve Yalçın Gürkan, 2021, 2022, 2023b). In G-series agents (Tabun, Sarin, Soman), phosphorus-bound fluoride or cyanide groups provide high volatility and relatively low environmental persistence; these agents act rapidly and tend to degrade quickly. In contrast, V-series agents such as VX, due to their P-S (thioester) bond, are resistant to both hydrophilic and lipophilic environments and can remain on surfaces and biological tissues for extended

periods (Dökmeci, 2025c). In the Novichok series of agents (A 230, A 232, and A 234), a fundamentally different structural feature stands out: a nitrogen (P–N) bond directly attached to the phosphorus atom and large, branched alkyl substituents. These phosphoramidites structures both provide resistance to nucleophilic attacks by redistributing the electron density at the phosphorus centre and kinetically slow down hydrolysis and oxidation reactions through steric hindrance (Zhang et al., 2023; Türker, 2024).

Hydrolysis reactions in aquatic environments lead to the breaking of phosphorus–fluorine (P–F) or phosphorus–sulphide (P–S) bonds in organophosphorus compounds, forming less toxic products; while oxidation processes (e.g., activation of the P–S bond as a result of oxidation of the thioether group in VX to sulfoxide/sulfone derivatives) play a significant role in the environmental degradation of particularly resistant agents (Noga and Jurowski, 2023; Noga et al., 2024). A DFT study at the M06-2X/SMD level reported that P–F bond cleavage is the main pathway in the neutral hydrolysis of the A-234 Novichok agent, and its activation energy is higher than that of Sarin, therefore A-234 is more persistent in the environment (Burns, et al., 2019). Therefore, elucidating these reactions at the molecular level is crucial for both environmental risk assessments and the development of effective decontamination strategies.

Theoretical Method

Understanding reaction mechanisms and structural interactions at the molecular level is critical for the disposal of highly toxic compounds such as chemical warfare agents. Since experimental investigation of such agents is highly limited due to both ethical and safety concerns, theoretical chemistry and computer-aided modelling techniques are prominent in this field. In this context, Quantum Mechanical Density Functional Theory (DFT) is a widely preferred method. Computational chemistry examines all chemical structures and reactions at the molecular level, aiming to determine all physical and chemical properties by using the geometric parameters where the molecular structure is most stable (Parr and Yang, 1994; Foresman and Frish, 1996; Hinchliffe, 1996, 1999; Hush et al., 2005).

To determine all possible reaction pathways of the seven molecules studied, geometric optimizations were performed using the DFT/B3LYP/6-31G(d) basis set of Quantum Mechanical Density Functional Theory (DFT) from electronic structure methods. GaussView 6 molecular representation program and Gaussian 16 program were used for all molecular orbital calculations. With Gaussian 16 program, the energies of atoms and molecules can be calculated, geometric optimizations can be performed, and energy-dependent vibration frequencies,

force constants, and dipole moments can be calculated. (Gaussian 16, 2009). Gauss View 6 is a graphical interface designed for preparing input files and visualizing outputs for Gaussian software packages. It allows for the visualization of molecules, enabling their rotation, movement, and modification. It also facilitates the creation of input files, even for complex calculations. It allows for the graphical examination of results calculated by the Gaussian program (Gaussian 16, 2009). Since the reactions of the seven molecules studied with the OH radical are important for both water purification and atmospheric chemistry, all calculations were performed both in the gas phase and in the water phase, modelling the solvent effect. In addition, geometric stretching in solutions is induced by H₂O (Eren and Gürkan, 2015, 2017; Hinchliffe, 1996, 1999; Hush et al., 2005). Therefore, in this study, to explain the solvent effect of H₂O on the reaction energy of seven nerve agent molecules with the + ·OH radical; Calculations were performed using the DFT/B3LYP/6-31G(d) method. Using the CPCM in the COSMO (conductor-like screening solvation model) solvent model of this software package, the water phase was also modelled by selecting water as the solvent medium (Gaussian 16, 2009).

Research Findings

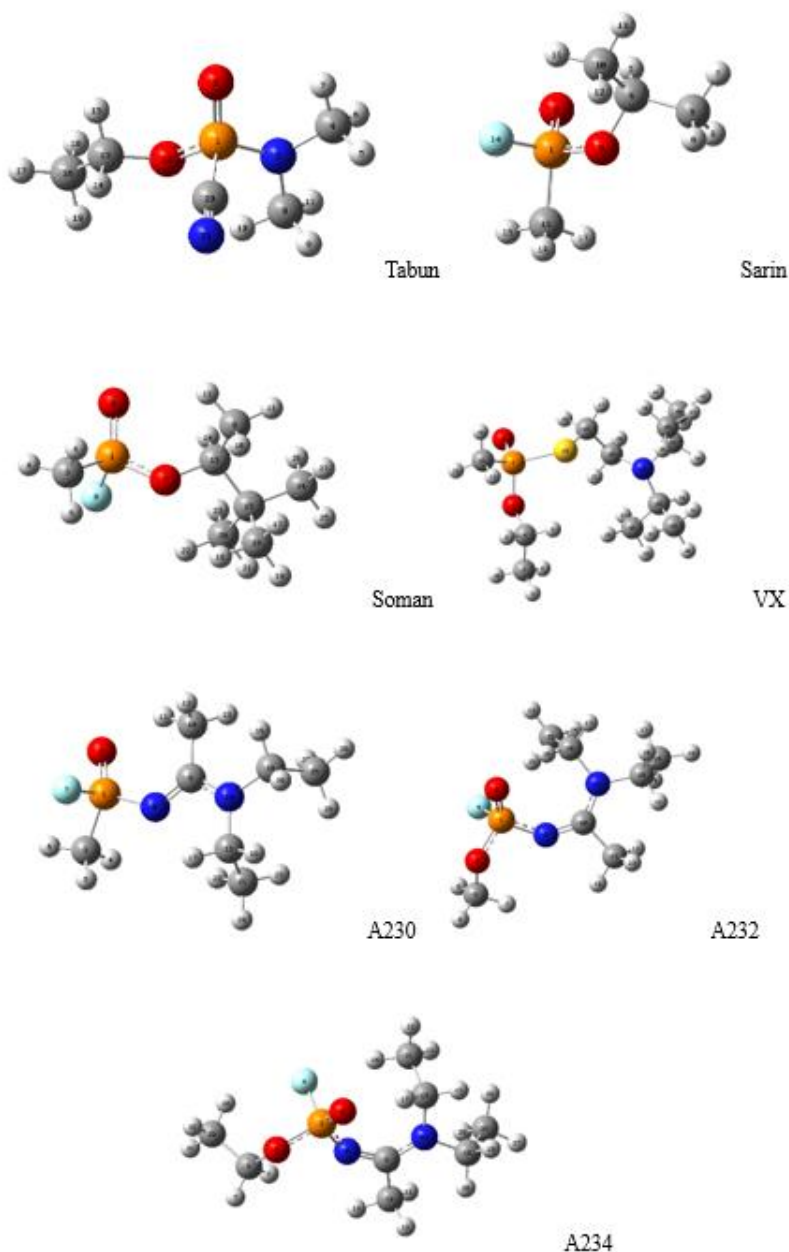
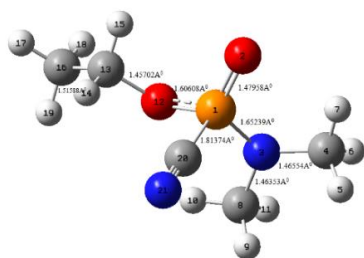
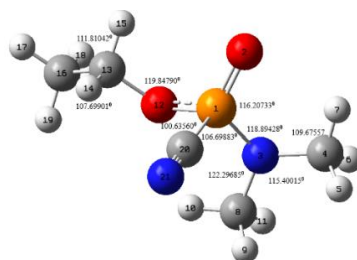


Figure 1. Optimized shapes of Tabun, Sarin, Soman, VX, A230, A232 and A234 molecules, respectively, using the DFT method (C is represented in grey, O in red, N in dark blue, P in orange, F in light blue, S in yellow and H atom in white)

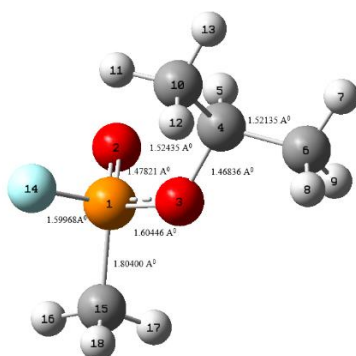


(a)

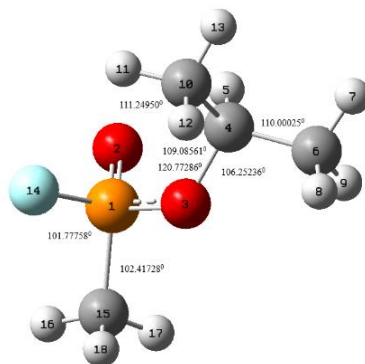


(b)

Figure 2. Bond lengths (a) and bond angles (b) between atoms of the Tabun molecule, respectively (C is represented in grey, O in red, N in dark blue, P in orange and H in white)

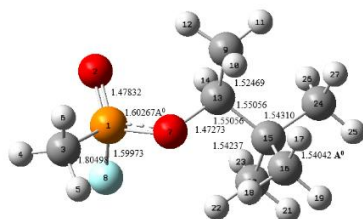


(a)

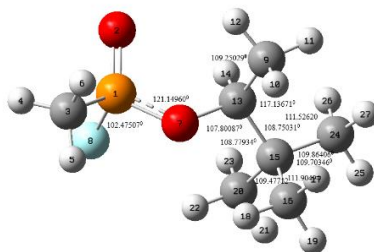


(b)

Figure 3. Bond lengths (a) and bond angles (b) between atoms of the Sarin molecule, respectively (C is represented in grey, O in red, F in light blue, P in orange, and H in white)



(a)



(b)

Figure 4. Bond lengths (a) and bond angles (b) between atoms of the Soman molecule, respectively (C is represented in grey, O in red, F in light blue, P in orange, and H in white)

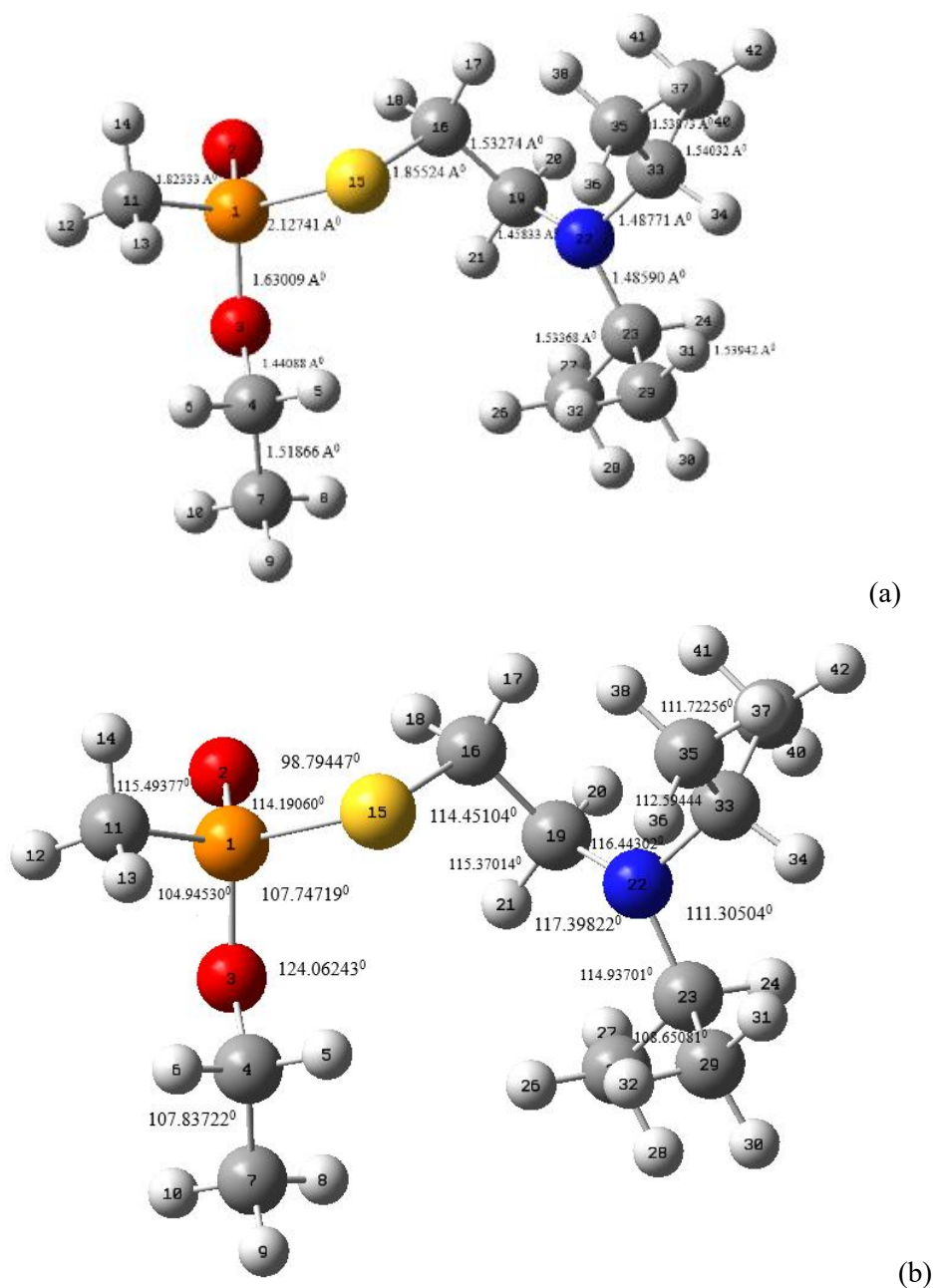
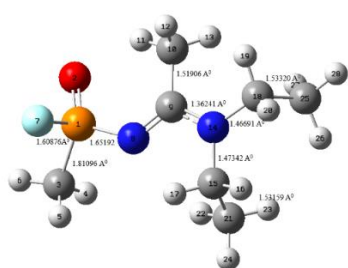
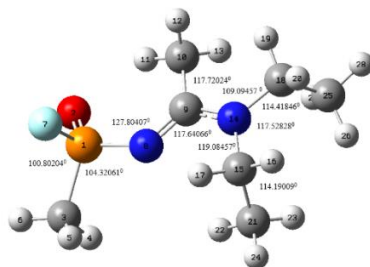


Figure 5. Bond lengths (a) and bond angles (b) between atoms of the VX molecule, respectively (C is represented in grey, O in red, P in orange, N in dark blue, S in yellow, and H in white)

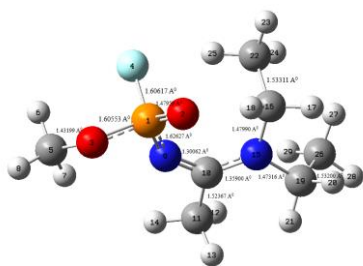


(a)

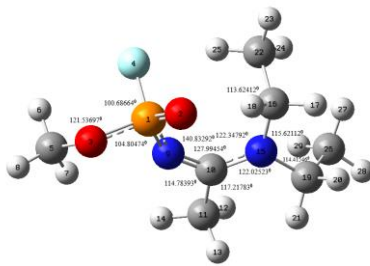


(b)

Figure 6. Bond lengths (a) and bond angles (b) between atoms of the A230 molecule, respectively (C is represented in grey, O in red, F in light blue, N in dark blue, P in orange and H in white)

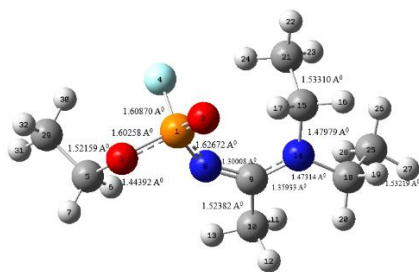


(a)

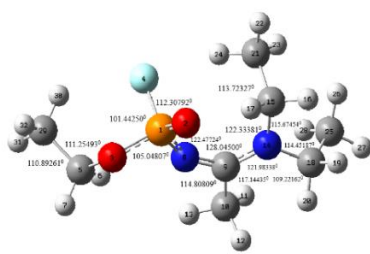


(b)

Figure 7. Bond lengths (a) and bond angles (b) between atoms of the A232 molecule, respectively (C is represented in grey, O in red, F in light blue, N in dark blue, P in orange and H in white)



(a)



(b)

Figure 8. Bond lengths (a) and bond angles (b) between atoms of the A234 molecule, respectively (C is represented in grey, O in red, N in dark blue, F in light blue, P in orange, and H in white) Images were taken from different angles due to the twisted structure of the figure.

Table 1. ΔE (energy), ΔH (enthalpy), ΔG (Gibbs free) energy values (Au) for the studied molecules in gas and water phases; bond lengths (Å), bond angles ($^\circ$), and Mulliken charges of electronegative atoms (For each molecule, the longest bonds, widest bond angles, and Mulliken charges of the most electronegative atoms are indicated in bold)

Molecules	(Au)	Bond Lengths	(Å)	Bond Angles	($^\circ$)	Mulliken Charges
Tabun		N ₃ -C ₄	1.46554	C₈N₃C₄	115.40015	P ₁ 1.113678
	Gas Phase	N ₃ -C ₈	1.46353	P₁N₃C₄	118.89428	O₂ -0.528685
	ΔE	P₁-N₃	1.65239	P₁N₃C₈	122.29685	N₃ -0.490690
	ΔH	P₁-C₂₀	1.81374	N ₃ P ₁ C ₂₀	106.69883	C ₄ -0.320856
	ΔG	P₁-O₁₂	1.60608	C ₁₆ C ₁₃ O ₁₂	107.69901	C ₈ -0.318525
	Water Phase	O ₂ -P ₁	1.47958	P ₁ O ₁₂ C ₁₃	119.84790	O₁₂ -0.537355
	ΔE	C ₁₃ -O ₁₂	1.45702	O ₁₂ P ₁ C ₂₀	100.63560	C ₁₃ -0.057087
	ΔH	C₁₃-C₁₆	1.51588	N₃P₁O₂	116.20733	C₁₆ -0.457156
	ΔG			C ₁₆ C ₁₃ H ₁₅	111.81042	N₂₁ -0.356437
				N ₃ C ₄ H ₇	109.67557	
Sarin		C ₄ -C ₆	1.52135	C₄C₆H₇	110.00025	P ₁ 1.118555
		C ₄ -C ₁₀	1.52435	O ₃ C ₄ C ₆	106.25236	O₂ -0.541015
	Gas Phase	C ₄ -O ₃	1.46836	P₁O₃C₄	120.77286	O₃ -0.540707
		P₁-C₁₅	1.80400	O ₃ P ₁ C ₁₅	102.41728	C₆ -0.448138
	Water Phase	P₁-F₁₄	1.59968	F ₁₄ P ₁ C ₁₅	101.77758	C ₁₀ -0.452954
		P₁-O₃	1.60446	C₄C₁₀H₁₁	111.24950	F ₁₄ -0.323946
		P ₁ -O ₂	1.47821	C₁₀C₄O₃	109.08561	C ₁₅ -0.665410
		P₁-C₃	1.80498	F ₈ P ₁ O ₇	102.47507	P ₁ 1.131863
Soman		P₁-F₈	1.59973	P₁O₇C₁₃	121.14960	O₂ -0.547032
		P ₁ -O ₂	1.47832	C ₁₆ C ₁₅ C ₂₄	109.70346	C₃ -0.665815
	Gas Phase	P₁-O₇	1.60267	C ₁₃ C ₁₅ C ₂₄	108.75031	O₇ -0.560495
		O ₇ -C ₁₃	1.47273	O ₇ C ₁₃ C ₁₅	107.80087	F ₈ -0.322089
		C ₉ -C ₁₃	1.52469	C ₁₃ C ₁₅ C ₂₀	108.77934	C ₉ -0.469545
		C ₁₃ -C ₁₅	1.55056	C ₂₀ C ₁₅ C ₁₆	109.47712	C ₁₆ -0.454503
	Water Phase	C ₁₅ -C ₂₄	1.54310	C ₁₃ C ₁₉ H ₁₂	109.25029	C ₂₀ -0.457429
		C ₁₅ -C ₁₆	1.54042	C₉C₁₃C₁₅	117.13671	C ₂₄ -0.456847
		C ₁₅ -C ₂₀	1.54237	C₁₅C₂₄H₂₆	111.52620	
				F ₈ P ₁ C ₃	101.56706	
				C ₁₅ C ₂₄ H ₂₅	109.86406	
				C₁₅C₁₆H₁₇	111.90494	
VX		C ₄ -C ₇	1.51866	O₂P₁C₁₁	115.49377	P ₁ 0.938894
		O ₃ -C ₄	1.44088	O ₃ P ₁ C ₁₁	104.94530	O₂ -0.543201
		O₃-P₁	1.63009	O ₃ P ₁ C ₁₅	107.74719	O₃ -0.520875
	Gas Phase	P₁-C₁₁	1.82333	O₂P₁C₁₅	114.19060	C ₄ -0.051241
		P₁-S₁₅	2.12741	P ₁ S ₁₅ C ₁₆	98.79447	C ₇ -0.456353
		S₁₅-C₁₆	1.85524	P₁O₃C₄	124.06243	C₁₁ -0.674848
	Water Phase	C₁₆-C₁₉	1.53274	O ₃ C ₄ C ₇	107.83722	S ₁₅ -0.112670
		C ₁₉ -N ₂₂	1.45833	S₁₅C₁₆C₁₉	114.45104	C ₁₆ -0.452872
		N ₂₂ -C ₃₃	1.48771	C₁₆C₁₉N₂₂	115.37014	C ₁₉ -0.120946

		C₃₃-C₃₅	1.53873	C₁₉N₂₂C₂₃	117.39822	N ₂₂	-0.394782
		C₃₃-C₃₉	1.54032	C₁₉N₂₂C₃₃	116.44302	C ₂₅	-0.484763
		N ₂₂ -C ₂₃	1.48590	C ₂₃ N ₂₂ C ₃₃	111.30504	C ₂₉	-0.432851
		C₂₃-C₂₉	1.53942	N ₂₂ C ₃₃ C ₃₅	112.59444	C ₃₅	-0.436911
		C₂₃-C₂₅	1.53368	C ₃₅ C ₃₃ C ₃₉	111.72256	C ₃₉	-0.460268
		P ₁ -O ₂	1.48853	C ₂₅ C ₂₃ C ₂₉	108.65081		
				N₂₂C₂₃C₂₅	114.93701		
A230		P₁-F₇	1.60876	C ₃ P ₁ N ₈	104.32061	P ₁	1.021399
	-902.136924	P₁-C₃	1.81096	P₁N₈C₉	127.80407	O₂	-0.568342
Gas Phase	-902.135979	P₁-N₈	1.65192	C₉N₁₄C₁₅	119.08457	C₃	-0.650840
	-902.194468	C₉-C₁₀	1.51906	N₈C₉N₁₄	117.64066	F₇	-0.325614
		N ₁₄ -C ₁₅	1.47342	C₁₀C₉N₁₄	117.72024	N₈	-0.598369
Water Phase		N ₁₄ -C ₁₈	1.46691	N ₁₄ C ₁₈ H ₁₉	109.09457	C₁₀	-0.566684
	-902.150654	C ₉ -N ₁₄	1.36241	N ₁₄ C ₁₈ C ₂₅	114.41846	N₁₄	-0.393349
	-902.149710	C₁₅-C₂₁	1.53159	C₁₅N₁₄C₁₈	117.52828	C ₁₅	-0.129261
	-902.208436	C₁₈-C₂₅	1.53320	C ₃ P ₁ F ₇	100.80204	C ₁₈	-0.154160
					114.19009	C ₂₁	-0.448698
						C ₂₅	-0.445216
A232		P₁-F₄	1.60617	N ₁₅ C ₁₆ C ₂₂	113.62412	P ₁	1.151748
	-977.348728	P₁-O₃	1.60553	C₁₀N₁₅C₁₆	122.34792	O₂	-0.552224
Gas Phase	-977.347784	O ₃ -C ₅	1.43199	N₉C₁₉N₁₄	127.99454	O₃	-0.493368
	-977.408593	P ₁ -O ₂	1.47959	P₁N₉C₁₀	140.83292	F₄	-0.339224
		P₁-N₉	1.62627	F ₄ P ₁ O ₃	100.68664	C ₅	-0.214251
Water Phase		N ₉ -C ₁₀	1.30062	P₁O₃C₅	121.53697	C₁₁	-0.530690
	-977.364548	C ₁₀ -N ₁₅	1.35900	O ₃ P ₁ N ₉	104.80474	N₁₅	-0.383319
	-977.363604	C₁₀-C₁₁	1.52367	N ₉ C ₁₀ C ₁₁	114.78393	C ₁₆	-0.209149
	-977.424636	N ₁₅ -C ₁₉	1.47316	C₁₁C₁₀N₁₅	117.21783	C ₁₉	-0.157528
		N ₁₅ -C ₁₆	1.47990	C₁₀N₁₅C₁₉	122.02523	C ₂₂	-0.455398
		C₁₆-C₂₂	1.53311	C₁₆N₁₅C₁₉	115.62112	C ₂₆	-0.447543
		C₁₉-C₂₆	1.53200	N ₁₅ C ₁₉ C ₂₆	114.41546		
A234		C₅-C₂₉	1.52159	H ₇ C ₅ C ₂₉	110.89261	P ₁	1.154638
	-1016.637845	C ₅ -O ₃	1.44392	O ₃ C ₅ C ₂₉	111.25493	O₂	-0.553480
Gas Phase	-1016.636901	O₃-P₁	1.60258	O ₃ P ₁ N ₈	105.04807	O₃	-0.502544
	-1016.701020	P₁-F₄	1.60870	O ₃ P ₁ F ₄	101.44250	F₄	-0.340410
		P₁-N₈	1.62672	O ₂ P ₁ F ₄	112.30792	C ₅	-0.042381
Water Phase		N ₈ -C ₉	1.30008	O₂P₁N₈	122.47724	N₈	-0.594663
	-1016.661098	C₉-C₁₀	1.52382	N₈C₉N₁₄	128.04500	C₁₀	-0.530907
	-1016.660154	C ₉ -N ₄	1.35933	N ₈ C ₉ C ₁₀	114.80809	N₁₄	-0.384281
	-1016.725185	N ₄ -C ₁₈	1.47314	C₁₀C₉N₁₄	117.14435	C ₁₅	-0.208098
		N ₄ -C ₁₅	1.47979	C₉N₁₄C₁₈	121.98338	C ₁₈	-0.156902
		C₂₂-C₂₁	1.53310	C₉N₁₄C₁₅	122.33381	C₂₁	-0.455613
		C₁₈-C₂₅	1.53219	N ₁₄ C ₁₅ C ₂₁	113.72327	C₂₅	-0.447497
				C ₁₅ N ₁₄ C ₁₈	115.67454	C₂₉	-0.455538
				N ₁₄ C ₁₈ H ₂₀	109.22162		
				N ₁₄ C ₁₈ C ₂₅	114.45187		

Table 2. Gas phase ΔE (energy), ΔH (enthalpy), ΔG (Gibbs free) energy values (Au) of the studied molecules and their fragments

Tabun	Sarin	Soman	VX	A230	A234
-798.300736	-750.029816	-867.879135	-1379.222372	-902.136924	-1016.637845
-798.299792	-750.028872	-867.878191	-1379.221427	-902.135979	-1016.636901
-798.354123	-750.076075	-867.934573	-1379.296457	-902.194468	-1016.701020
T1	Sa1	So1	VX1	VR1	A232
-759.021440	-710.739790	-828.596233	-1339.942491	-862.852177	-977.348728
-759.020496	-710.738846	-828.595289	-	-862.851233	-977.347784
-759.071775	-710.782922	-828.649189	1339.941547 -1340.012401	-862.907374	-977.408593
T2	Sa4	So11	VX5	VR4	A2322
-759.010567	-710.719886	-828.593380	-1339.931928	-862.853811	-938.074193
-759.009623	-710.718942	-828.592436	-1339.930984	-862.852867	-938.073249
-759.060427	-710.763582	-828.645598	-1340.003977	-862.908185	-938.130112
T11	Sa2	So4	VX4	VR3	A2321
-719.744314	-671.444432	-828.574632	-1339.920628	-862.834462	-938.065517
-719.743370	-671.443488	-828.573688	-1339.919683	-862.833518	-938.064573
-719.790642	-671.484368	-828.626251	-1339.991968	-862.889064	-938.122253
T21	Sa5	So2	VX6	VR2	A2323
-719.732639	-671.431134	-789.312506	-1300.666257	-823.577678	-938.063867
-719.731694	-671.430190	-789.311562	-	-823.576733	-938.062922
-719.777566	-671.470587	-789.362239	1300.665313 -1300.733475	-823.630170	-938.120672
T22	Sa7	So12	VX2	VR42	A21
-719.731546	-650.732876	-789.308115	-1300.660409	-823.568664	-898.801703
-719.730601	-650.731932	-789.307171	-1300.659465	-823.567720	-898.800759
-719.778077	-650.776941	-789.357353	-1300.728788	-823.620505	-898.856732
T3	Sa3	So5	VX3	VR31	A23221
-706.056608	-632.174776	-789.291796	-1261.386734	-823.549471	-898.790378
-706.055664	-632.173832	-789.290852	-1261.385790	-823.548526	-898.789434
-706.104682	-632.210194	-789.341134	-1261.453413	-823.601312	-898.843701
T23	Sa51	So41	VX7	VR41	A23231
-680.454652	-632.140646	-789.288780	-1261.363426	-823.545301	-898.779171
-680.453708	-632.139702	-789.287836	-1261.362482	-823.544357	-898.778227
-680.496730	-632.176736	-789.337183	-1261.427058	-823.596464	-898.833529
T12	Sa71	So3	VX31	VR21	A23222
-680.454128	-611.443441	-750.023661	-1143.537806	-784.291163	-859.517392
-680.453184	-611.442496	-750.022716	-1143.536862	-784.290219	-859.516448
-680.496636	-611.484969	-750.070421	- 1143.592935	-784.340875	-859.569502
T31	Sa72	So42	VX32	VR32	A23232
-666.778810	-611.429395	-750.003554	-1088.216304	-784.274866	-859.511006
-666.777866	-611.428450	-750.002610	-	-784.273921	-859.510061
-666.824181	-611.469628	-750.049178	1088.215360 -1088.269646	-784.323718	-859.562197

T32	Sa6	So8	VX321	VR22	A23233
-666.766859	-592.868918	-710.739750	-1048.931525	-784.259913	-820.223816
-666.765914	-592.867974	-710.738806	-1048.930580	-784.258968	-820.222872
-666.811393	-592.900823	-710.783134	-1048.981467	-784.308501	-820.271468
T4	Sa73	So43	VX33	VR23	A22
-641.177366	-572.147547	-710.718879	-1009.647267	-744.978902	-820.236949
-641.176422	-572.146603	-710.717934	-1009.646323	-744.977958	-820.236005
-641.215964	-572.185917	-710.761785	-1009.693102	-745.024436	-820.286043
T5	Sa74	So7	VX331	VR33	A221
-627.488997	-572.139627	-671.449712	-970.345146	-705.707069	-780.961935
-627.488053	-572.138682	-671.448768	-970.344202	-705.706125	-780.960991
-627.530727	-572.177361	-671.489737	-970.387506	-705.749122	-781.006682
T6	Sa75	So44	VX10	VR5	A222
-588.215400	-532.844300	-671.434832	-931.055114	-689.648697	-780.942767
-588.214456	-532.843356	-671.433888	-931.054170	-689.647752	-780.941823
-588.252492	-532.878825	-671.474408	-931.093941	-689.691024	-780.986411
T7	Sa76	So45	VX11	VR6	A223
-588.212458	-493.573928	-632.144496	-891.785046	-650.348331	-764.869520
-588.211514	-493.572984	-632.143552	-891.784102	-650.347386	-764.868576
-588.250328	-493.603751	-632.180932	-891.819486	-650.386701	-764.914959
T71	Sa6		VR7		A225
-548.937958	-592.868918		-611.046201		-741.665212
-548.937014	-592.867974		-611.045256		-741.664268
-548.971123	-592.900823		-611.080701		-741.705730
Sa76			VR24		
-493.573928			-666.410245		
-493.572984			-666.409301		
-493.603751			-666.448551		

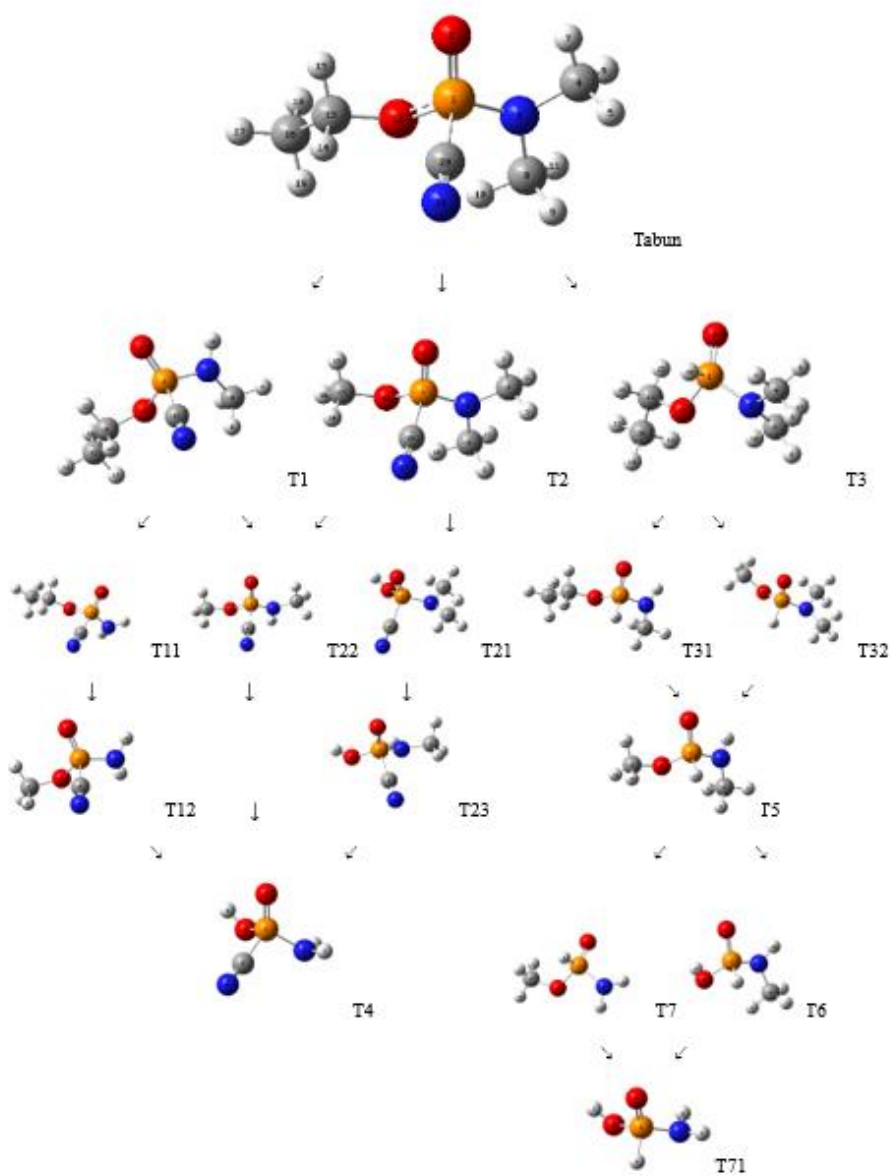


Figure 9. Degradation mechanism of tabun molecule and its fragments by DFT (C is represented in grey, O in red, N in dark blue, P in orange and H atom in white)

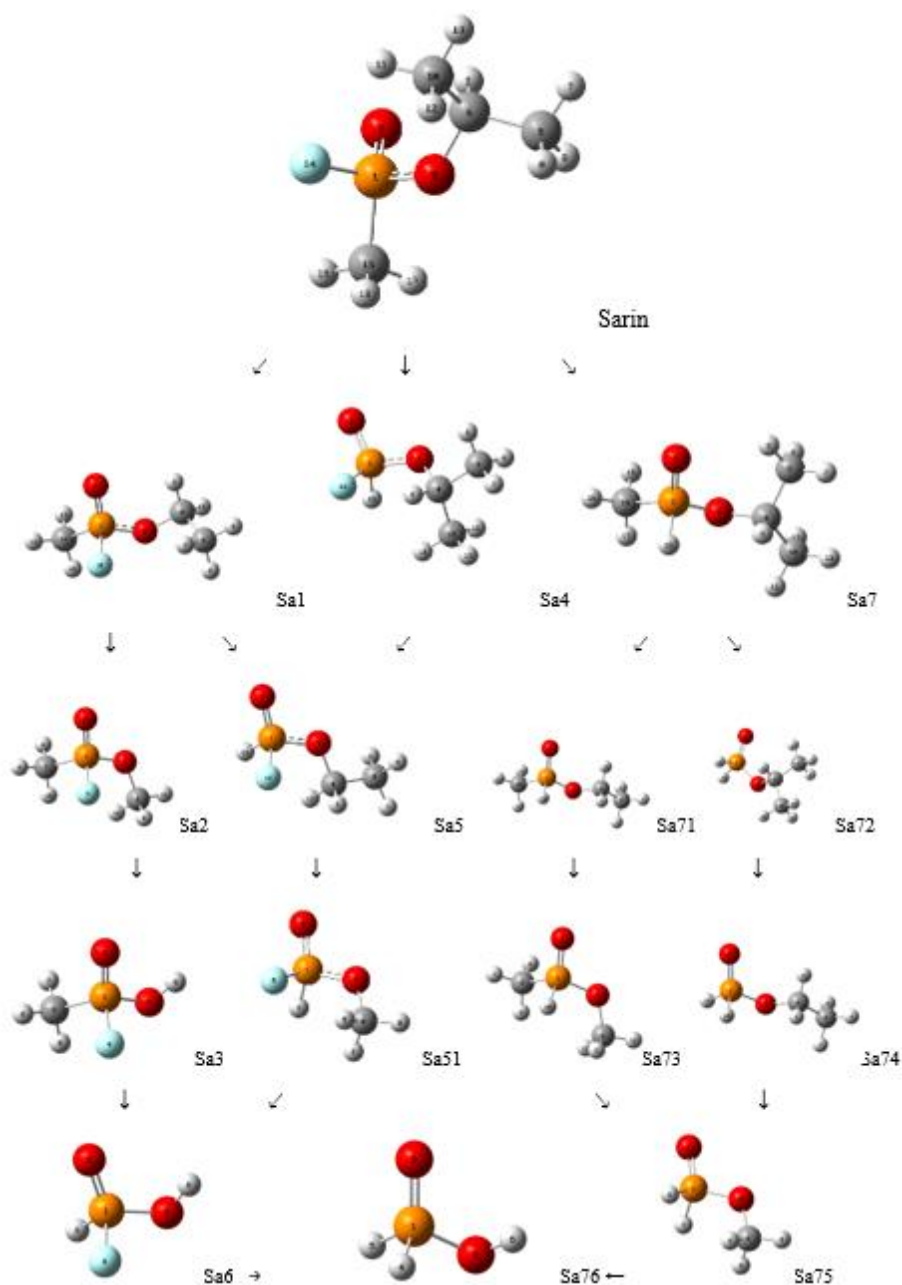


Figure 10. Degradation mechanism of sarin molecule and fragments by DFT (C is represented in grey, O in red, F in light blue, P in orange and H atom in white)

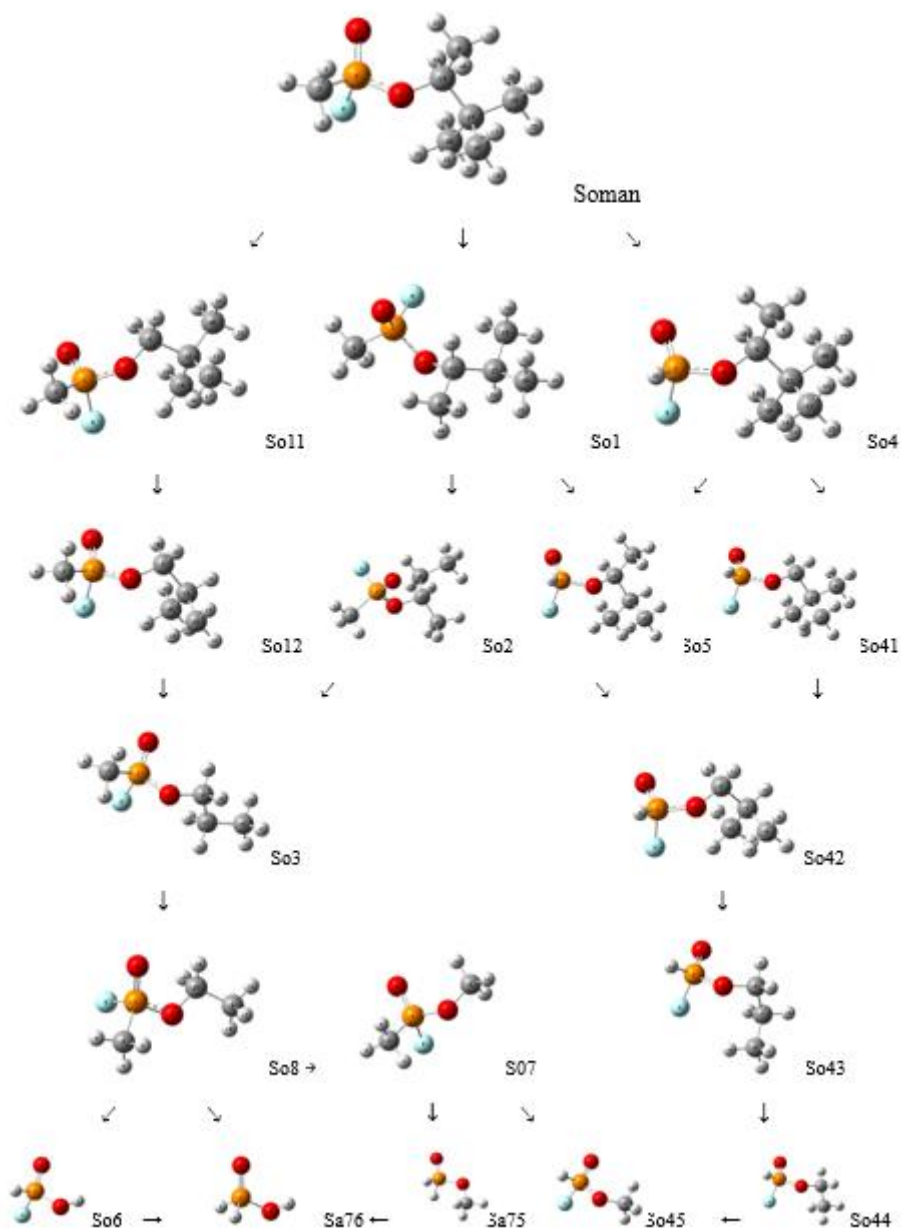


Figure 11. Degradation mechanism of Soman molecule and its fragments by DFT (C is represented in grey, O in red, F in light blue, P in orange and H atom in white)

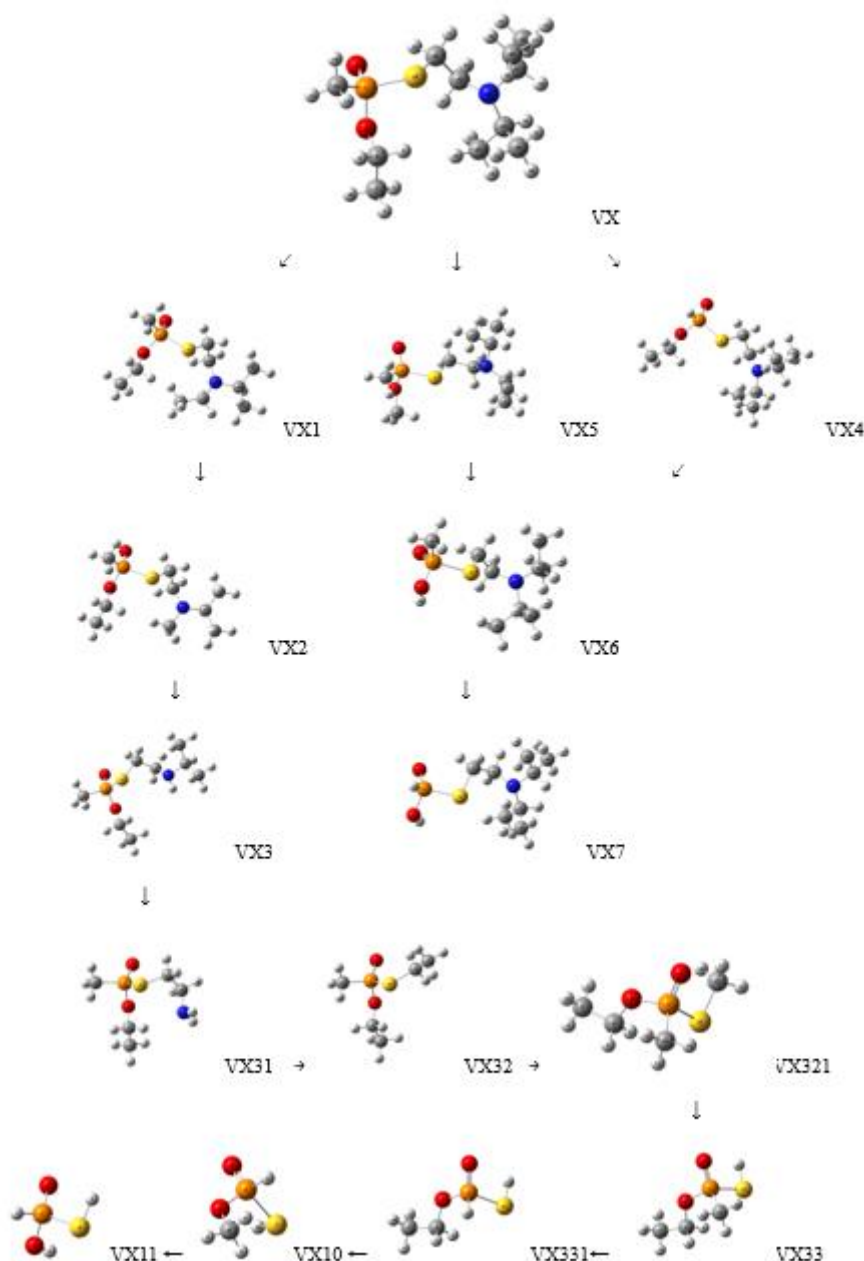


Figure 12. Degradation mechanism of VX molecule and its fragments by DFT (C is represented in grey, O in red, N in dark blue, S in yellow, P in orange and H atom in white)

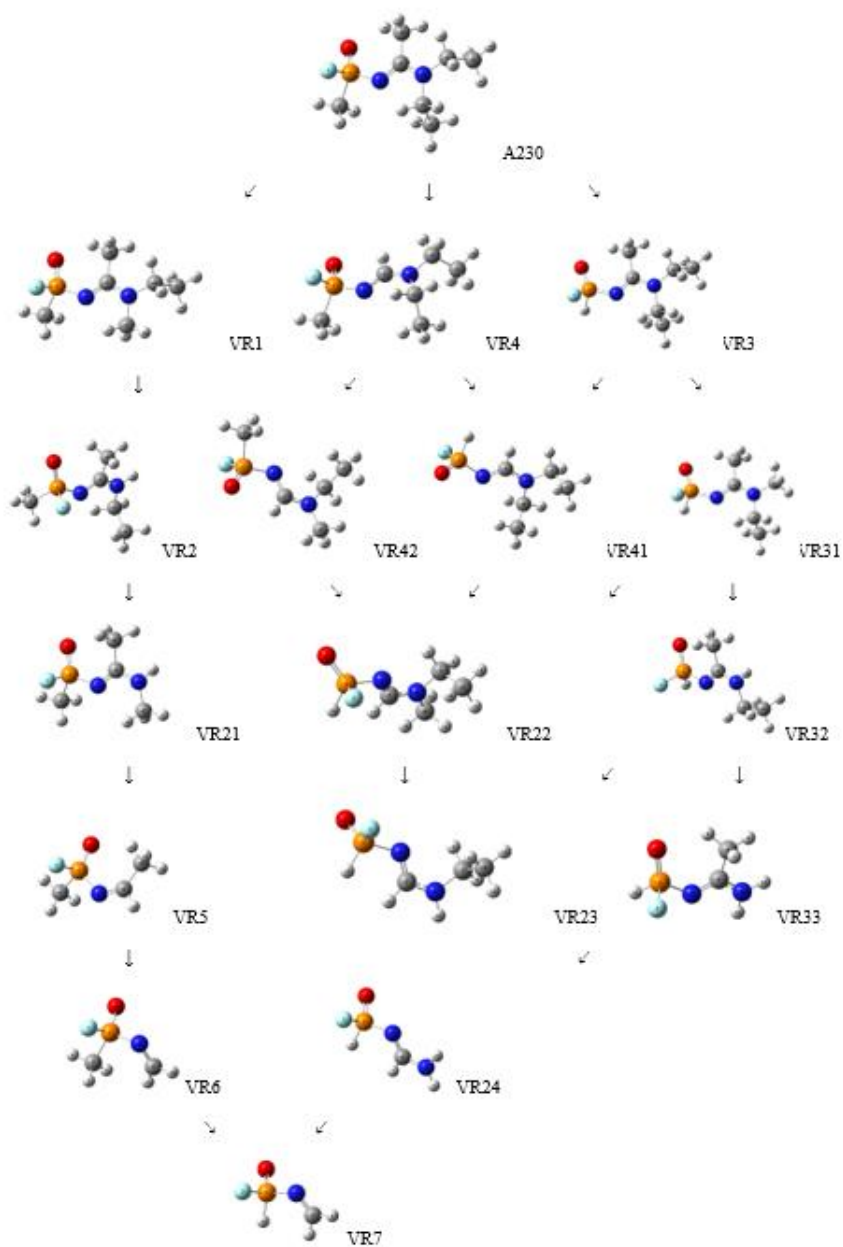


Figure 13. Degradation mechanism of A230 molecule and its fragments by DFT (C is represented in grey, O in red, N in dark blue, F in light blue, P in orange and H atom in white)

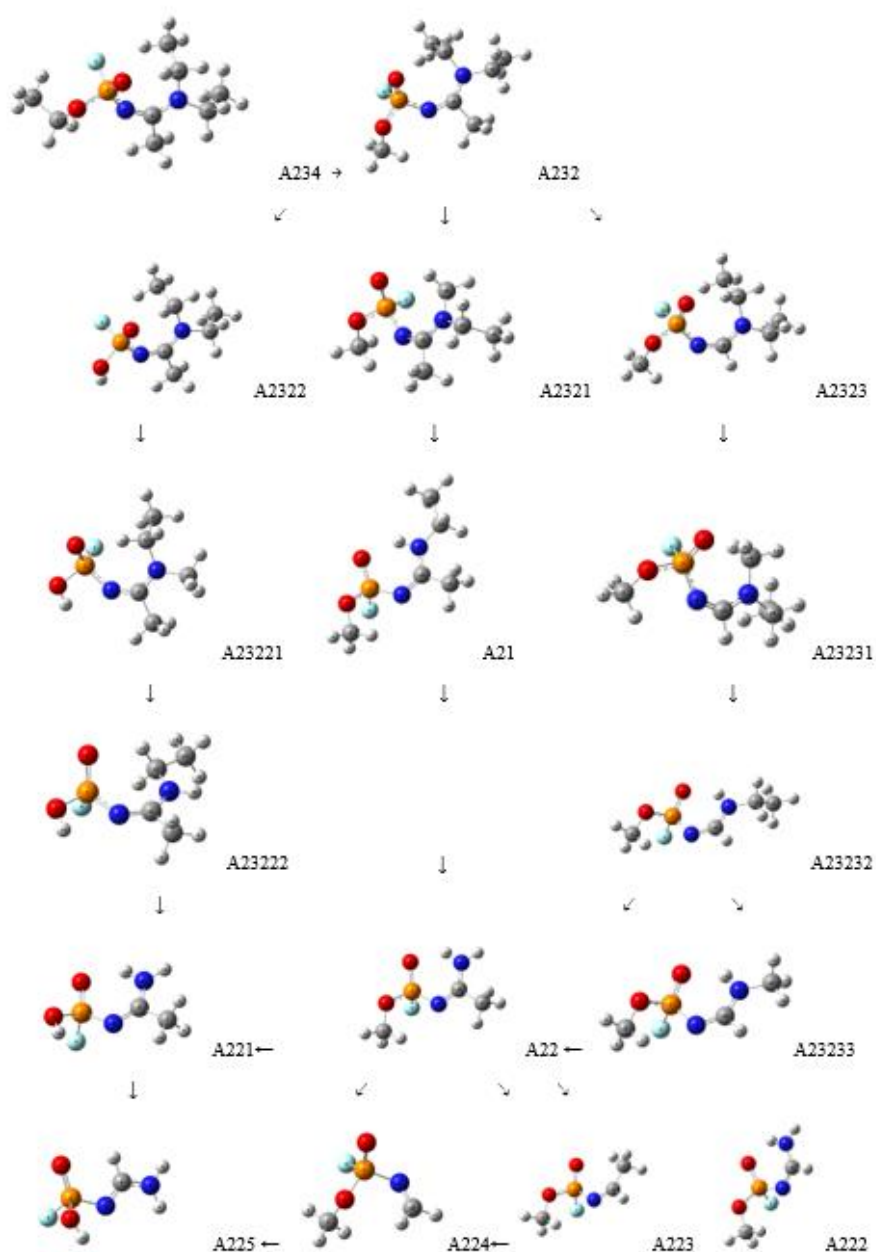


Figure 14. Degradation mechanism of A232, A234 molecules and its fragments by DFT (C is represented in grey, O in red, N in dark blue, F in light blue, P in orange and H atom in white)

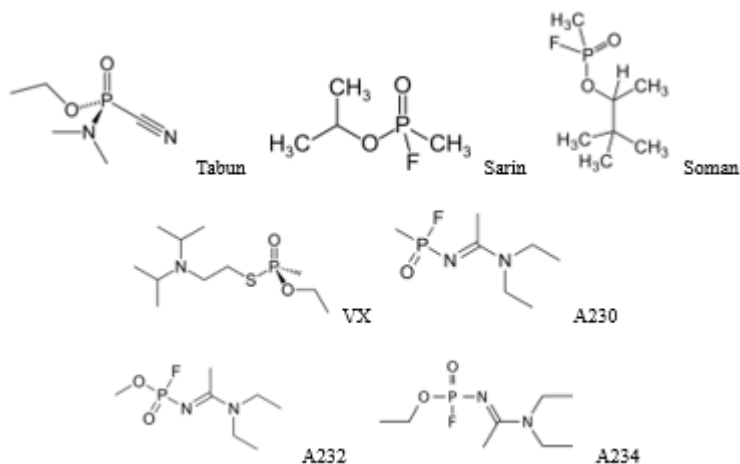


Figure 15. Two-dimensional representation of the G series nerve agents, namely Tabun, Sarin and Soman; the V series, VX; and the Novichok series, namely A230, A232 and A234 molecules

The optimized form of the Quantum Mechanical Density Functional Theory (DFT) of the Tabun or GA molecule, a G nerve agent with the chemical formula $C_5H_{11}N_2O_2P$, using the DFT/B3LYP/6-31G(d) basis set, is shown in Figure 1; the bond lengths (a) and bond angles (b) between the atoms of the molecule are shown in Figure 2; and the ΔE (energy), ΔH (enthalpy), ΔG (Gibbs free) energy values (Au), bond lengths (A^0), bond angles ($^\circ$), and Mulliken charges of electronegative atoms in the gas and water phases of the molecule are given in Table 1. The energy values calculated for each molecule studied are given in atomic mass units (Au) because, when converted to SI units, the numbers after the decimal point are very close to each other, and the energy differences between them cannot be easily observed. Figure 1 and Table 1 serve as references at the beginning of the theoretical work, as the entire study is structured accordingly.

The Tabun molecule has a structure containing $P=O$, $P-OC_2H_5$, $P-N(CH_3)_2$, and $P-C\equiv N$ bonds, as shown in Figure 15. Although it is predicted that the longest bond and the widest bond angle will break first for any molecule, the cleavage path is determined by observing the energy values and environments of electronegative atoms. It should be remembered that structures containing double bonds or closed rings are more stable than others, and if cleavage occurs, breaking from these stable structures will be the final stage (Eren and Yalçın Gürkan, 2023b).

Therefore, considering only bond length, and ordering from longest to shortest bond (the longest bonds are indicated in bold in Table 1), the bonds should be

separated from the molecule in the following order, as seen in Figure 2(a) and Table 1: P₁-C₂₀, P₁-N₃, P₁-O₁₂, C₁₃-C₁₆, O₂-P₁, N₃-C₄, N₃-C₈, C₁₃-O₁₂. It should be noted that the stable bonds P₁=O₂ and C₂₀≡N₂₁, shown in Figures 1, 2, and 9, will be the last to be separated in the cleavage pathway.

If a cleavage path is determined solely based on bond angles, according to Figure 2(b) and Table 1, starting with the widest bond angle (which are indicated in bold in Table 1), the atoms that should be separated from the molecule are P₁N₃C₈, P₁O₁₂C₁₃, P₁N₃C₄, N₃P₁O₂, C₈N₃C₄, C₁₆C₁₃O₁₂ in that order.

If we wanted to determine the decay path based solely on electronegative atoms, examining the Mulliken charges in Table 1 reveals that, in order of electronegativity (the most electronegative atoms are shown in dark), O₂, O₁₂, N₃, N₂₁ and the surrounding atoms are noteworthy. As shown in Figures 1, 2, and 9, O₂ and N₂₁ have double and triple bonds (P₁=O₂ and C₂₀≡N₂₁), therefore decay does not begin around these bonds.

Table 2 shows the gas-phase energy (ΔE), enthalpy (ΔH), and free energy (ΔG) values (Au) for the studied molecules and their fragments. The energy values of the Tabun molecule and its fragments are the most important reference source for estimating the fragmentation path. Negative values indicate that these fragments separated spontaneously, without any external energy input. Fragmentation requires writing the results starting from the smallest of these negative values. It is important to note that energy calculations are performed for each broken bond. Failure to calculate the energy for any broken fragment represents an incomplete fragmentation path.

After examining the bond lengths, bond angles, Mulliken charges of the electronegative atoms, and energy values individually in Table 1, the degradation mechanism of the Tabun molecule and its fragments using DFT, as shown in Figure 9, was determined. The first three branches were formed by the successive breaking of the N₃-C₄ or N₃-C₈, C₁₃-C₁₆, and P₁-C₂₀ bonds. The degradation pathway will continue from these T1 (-759.021440 Au), T2 (-759.010567 Au), and T3 (-706.056608 Au) branches. After these three main branches, the energy values for each fragment were examined, and using the same approach, the degradation mechanism of the Tabun molecule and its fragments using DFT, as shown in Figure 9, was written.

The degradation pathway mechanism is described only for Tabun, a representative example from the G series of nerve agents. The data in Tables 1 and 2, along with the visual representation of bond lengths and bond angles in Figures 2, 3, and 4, and the description of the Tabun molecule, allow for easy understanding of the degradation mechanisms shown in Figures 10 and 11. Figure 16 shows the initial and final stages of the DFT-optimized degradation pathways for Tabun (GA), Sarin (GB), and Soman

(GD) molecules, belonging to the G series of nerve agents, respectively, thus presenting the results for these three molecules from the same series.

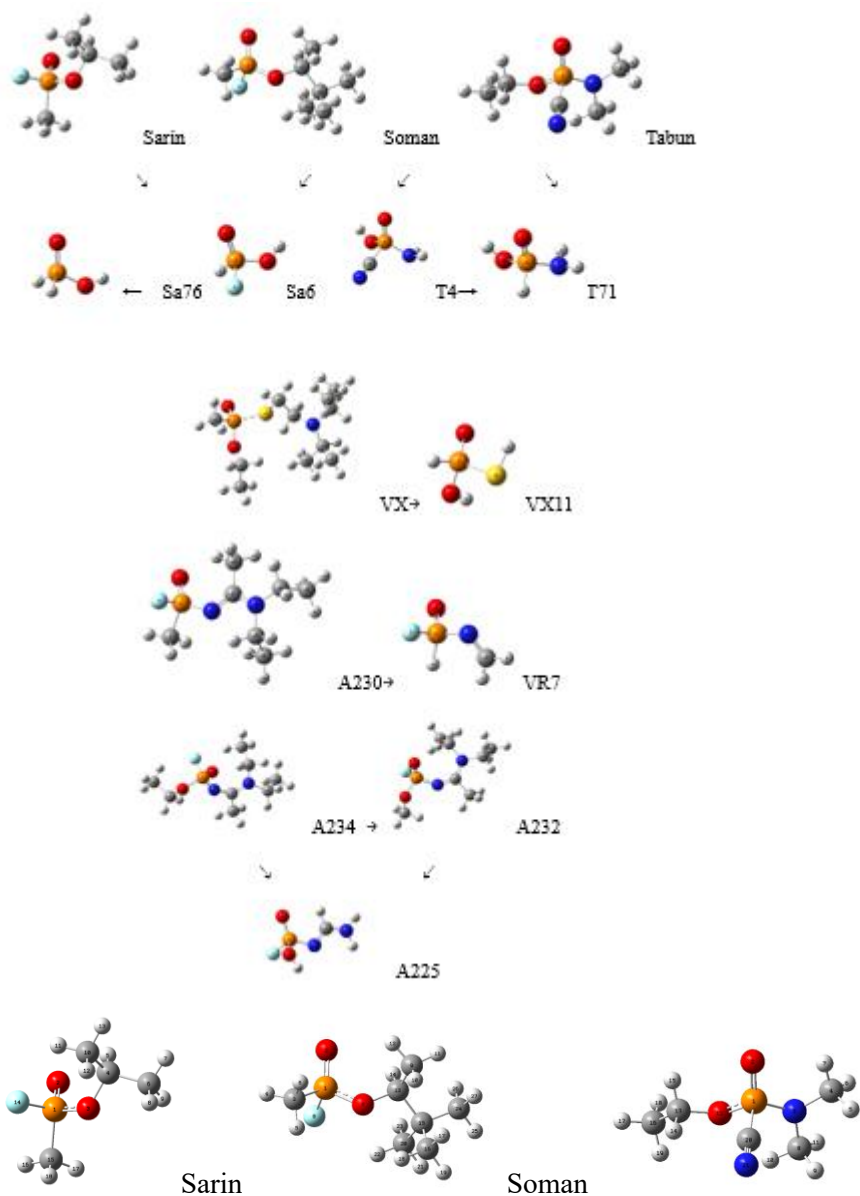


Figure 16. DFT-optimized representations of the initial and final stages of the degradation pathways of nerve agents belonging to the G series (Tabun (GA), Sarin (GB), and Soman (GD)); the V series (VX); and the Novichok series (A230, A232, and A234), respectively (C is represented in grey, O in red, N in dark blue, F in light blue, S in yellow, P in orange, and H in white)

Following the same line of thought, the degradation pathways in Figures 12-14 were written, and in Figure 16, the initial and final stages of the DFT-optimized degradation pathways of the VX and Novichok series nerve agents, respectively, and the results for these four molecules are clearly shown.

Conclusion and Discussion

The environmental persistence and toxicity of nerve agents necessitate an understanding of their degradation mechanisms at the molecular level. The molecular behaviour of seven nerve agents from three different series was studied in detail by optimizing them with the DFT/B3LYP/6 31G(d) basis set and modelling their degradation mechanisms. The geometric structures, bond lengths, bond angles, Mulliken charge distributions, and energy (ΔE), enthalpy (ΔH), and Gibbs free energy (ΔG) values in both gas and water phases of these optimized agents are visualized in Figures 1-16 and presented in Tables 1 and 2. These quantum chemical data reveal that the negative energy values in Tables 1 and 2 for each agent indicate that the reactions will occur spontaneously, meaning no external energy input is required. The initial and final states of each nerve agent are clearly shown in Figure 16.

This study not only describes the structural and chemical properties of nerve agents but also reveals their degradation mechanisms, molecular-level toxicity trends, and critical interaction sites for antidote design. Thus, a multidimensional assessment combining quantum chemical data with toxicological observations is provided; and it is believed that this approach will create a strong theoretical foundation for future research in the fields of chemical defence systems, health safety, and environmental risk management.

G-series agents have lower structural stability and are more easily degraded but reactive according to DFT analyses. These agents typically initiate their first cleavage from P–O, P–F, or P–C bonds, producing short-lived fragments with high inhibitory activity. Due to these characteristics, although their acute effects are strong, they offer a more advantageous treatability profile compared to Novichok agents in terms of their degradation rates and response to treatment. The VX agent is positioned between the G-series and Novichok agents in terms of toxicity and stability. VX's degradation pathways appear to form more stable intermediates, most of which retain their toxic character. VX's high lipophilicity and low volatility pose a significant threat in terms of absorption through the skin and diffusion to the central nervous system. At the same time, the fragments formed after degradation can maintain their long-term biological activity. Novichok agents tend to form irreversible and rapidly aging bonds with the acetylcholinesterase (AChE) enzyme. This significantly limits the effectiveness

of current antidotes and complicates treatment. Mulliken charge analyses also show that negative charges, concentrated especially around nitrogen and oxygen atoms, can cause strong and persistent interactions with the enzyme (Dökmeci and Dökmeci, 2009; Eddleston et al., 2008; Eyer, 2003).

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Theoretical modelling was done with Gaussian16 & Gauss View 6 & TCP Linda Programs, (2009) TRUBA.

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Normal Helices in The Multiplicative Euclidean Space $\mathbb{E}_*^3$

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Abstract

Multiplicative (bigeometric) calculus replaces the additive structure of the real line by the multiplicative one, and it gives rise to a differential geometry of curves in which curves of exponential type become elementary objects. In this chapter we study, in the multiplicative Euclidean space $\mathbb{E}_*^3$, a class of curves that generalizes the classical helices. Following a recent Euclidean approach of Lucas and Ortega-Yagües, a curve is regarded as a helix when some vector field with constant coordinates with respect to its Frenet frame (a Frenet-constant, or F-constant, vector field) makes a constant angle with a fixed direction. We first develop the tools that are needed: the arithmetic of positive numbers, the multiplicative derivative and integral, the vector algebra of $\mathbb{E}_*^3$, the multiplicative Frenet–Serret apparatus, the multiplicative Darboux vector of an arbitrary moving frame and a multiplicative transport theorem. We then concentrate on normal helices, for which the F-constant vector field lies in the normal plane and is orthogonal to the axis. We obtain their natural equation, prove that they are exactly the curves on multiplicative cylinders whose principal normal keeps a constant angle with the normal of the cylinder, compute the curvature and torsion of such curves and construct an explicit family on a multiplicative circular cylinder. Each characterization is stated twice, in multiplicative notation and with ordinary operations.

Keywords: Normal helix; Frenet-constant vector field; multiplicative Darboux vector; transport theorem; natural equation; multiplicative cylinder; non-Newtonian calculus.

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1 Introduction

In the classical differential geometry of space curves, a helix (also called a general helix, a cylindrical helix or a curve of constant slope) is a curve whose tangent lines make a constant angle with a fixed direction. By the theorem of Lancret, these are exactly the curves along which the ratio of torsion to curvature is constant [21, p. 33]. Many variations of this notion have been proposed by replacing the unit tangent with another natural vector field along the curve; a well-known example is given by the slant helices, defined by the analogous condition on the principal normal lines [10, 12]. Slant helices have also been investigated in other ambient spaces, such as the dual space $\mathbb{D}^3$ [14] and the dual Lorentzian space $\mathbb{D}_1^3$ [16].

Lucas and Ortega-Yagües [13] recently suggested a point of view that contains these variations as particular cases. For a curve α with Frenet frame $\mathcal{F} = \{T, N, B\}$, a vector field along α is called $\mathcal{F}$ -constant if its coordinates with respect to $\mathcal{F}$ do not depend on the parameter. The tangent, the principal normal and the binormal are $\mathcal{F}$ -constant, and so is every combination of them with constant coefficients. The curve is then declared a helix if one of its $\mathcal{F}$ -constant vector fields makes a constant angle with a fixed direction, which plays the role of an axis. When the $\mathcal{F}$ -constant vector field lies in the normal, osculating or rectifying plane, the curve is called a normal, osculating or rectifying helix, respectively. In [13] the natural equations of these curves are obtained when the $\mathcal{F}$ -constant field is orthogonal to the axis, and the curves are described geometrically by means of cylinders. This point of view has since been extended beyond the Euclidean 3-space: timelike normal, osculating and rectifying helices in the Minkowski space $\mathbb{E}_1^3$ were characterized in [15], and helices with $\mathcal{F}$ -constant vector fields in the Euclidean space $\mathbb{E}^4$ were studied in [17].

A second source for the present chapter is non-Newtonian calculus. Grossman and Katz [8] observed that the arithmetic of the real line can be replaced by the arithmetic generated by any bijection of the real line onto a subset of itself, and that every such choice produces a complete calculus with its own derivative and integral. The multiplicative calculus, in which sums and differences are replaced by products and quotients, is the most studied of these systems; see [7, 20] for its early development and [2, 3] for applications to differential equations and to modeling. Georgiev built multiplicative versions of the differential geometry of curves and surfaces [5, 6], and this framework has been used to investigate multiplicative rectifying curves [1] and multiplicative general and slant helices [9].

Our aim is to develop the theory of normal helices in the multiplicative Euclidean space $\mathbb{E}_*^3$ along the lines of [13]. Section 2 gathers the multiplicative tools; in addition to standard material, it contains the multiplicative Darboux vector of an arbitrary moving frame, a multiplicative transport theorem and the elementary properties of multiplicative $\mathcal{F}$ -constant vector fields. Section 3 contains the main results: the natural equation of multiplicative normal helices (Theorem 3.2), their characterization by means of multiplicative cylinders (Theorem 3.5), the curvature and torsion of curves lying on such cylinders (Proposition 3.6 and Corollary 3.7), and an explicit family of examples on a multiplicative circular cylinder (Section 3.4 and Figure 1). The other classes of helices mentioned above can be treated with the same tools; here we restrict our attention to the normal ones, which are the most closely related to cylinders. Section 4 contains some concluding comments.

We point out from the beginning that the coordinatewise logarithm $\Lambda: \mathbb{E}_*^3 \rightarrow \mathbb{R}^3$ carries each multiplicative structure used below onto the corresponding Euclidean one (Lemma 2.2 and Remark 2.9). Consequently, the results of this chapter correspond, through Λ , to the Euclidean statements of [13] applied to the logarithmic image of the curve, and they should not be regarded as logically independent of them. Our proofs, however, are carried out entirely within multiplicative calculus, and every characterization is also written in ordinary arithmetic, which is the convenient form for explicit computations with exponential curves such as the one shown in Figure 1(a). In the discussion of the example we also clarify an orientation issue in the corresponding Euclidean example of [13].

2 Preliminaries

2.1 Arithmetic of positive real numbers

Let $\mathbb{R}_* = (0, \infty)$. Following [1, 5, 6], for $a, b \in \mathbb{R}_*$ we put

$$\begin{aligned} a +_* b &= e^{\ln a + \ln b} = ab, & a -_* b &= e^{\ln a - \ln b} = \frac{a}{b}, \\ a \cdot_* b &= e^{\ln a \ln b}, & a /_* b &= e^{\ln a / \ln b} \quad (b \neq 1). \end{aligned}$$

With these operations $\mathbb{R}_*$ becomes a field whose zero element is $0_* = 1$ and whose unit is $1_* = e$; moreover, the natural logarithm is an order preserving field isomorphism from $(\mathbb{R}_*, +_*, \cdot_*)$ onto $(\mathbb{R}, +, \cdot)$. In particular, inequalities keep their usual meaning, and $a > 0_*$ simply means $a > 1$. The additive inverse of a is $-_* a = 0_* -_* a = 1/a$. For $n \in \mathbb{R}$ we write $n_* = e^n$, so that $2_* = e^2$, $3_* = e^3$ and $(1/2)_* = e^{1/2}$; the multiplicative powers are $a^{n_*} = e^{(\ln a)^n}$ whenever the

right-hand side makes sense, so that $a^{2*} = a \cdot_* a = e^{(\ln a)^2}$ and $a^{(1/2)*} = e^{\sqrt{\ln a}}$ for $a \geq 0_*$. The multiplicative absolute value is $|a|_* = e^{|\ln a|}$. We adopt the usual conventions: $\cdot_*$ and $/_*$ are performed before $+_*$ and $-_*$, and a unary $-_*$ affects the whole product written after it.

Every real function $F: J \subset \mathbb{R} \rightarrow \mathbb{R}$ induces a multiplicative function

$$F_*(x) = e^{F(\ln x)}, \quad x \in e^J = \{e^y: y \in J\}. \quad (1)$$

In this way one obtains $\sin_*$, $\cos_*$, $\tan_*$, $\cot_*$, $\sec_*$, $\csc_*$, $\sinh_*$, $\cosh_*$, $\arctan_*$, arsinh_* and $\exp_* x = e^{e^{\ln x}} = e^x$. Powers of these functions are written as $\cos_*^2 \theta = (\cos_* \theta)^{2*}$, and similarly in the other cases. Since $\ln$ is an isomorphism of fields, every identity between elementary functions remains valid after its operations have been replaced by their multiplicative counterparts; for example, $\sin_*^2 \theta +_* \cos_*^2 \theta = 1_*$ and $\sec_*^2 \theta = 1_* +_* \tan_*^2 \theta$. Angles are also measured multiplicatively: $\pi_* = e^\pi$, the interval between $-(\pi/2)_*$ and $(\pi/2)_*$ is $(e^{-\pi/2}, e^{\pi/2})$, and a condition such as “ $\theta \neq 0$ ” becomes $\theta \neq 0_*$, that is, $\theta \neq 1$.

2.2 Multiplicative derivative and integral

Let $f: I \subset \mathbb{R}_* \rightarrow \mathbb{R}_*$ be defined on an open interval. The multiplicative derivative of f at $x \in I$ is [1, 7]

$$f^*(x) = \lim_{h \rightarrow 0_*} (f(x +_* h) -_* f(x)) /_* h = \lim_{h \rightarrow 1} \left(\frac{f(hx)}{f(x)} \right)^{1/\ln h},$$

and, when f is differentiable in the ordinary sense, this limit exists and equals $e^{x(\ln f)'(x)}$. This is the bigeometric derivative of [7, 8]; it should not be confused with the geometric multiplicative derivative $e^{(\ln f)'(x)}$ used in [2, 3, 20], of which it is the x -th power. Higher order derivatives are denoted by f^{**} , f^{***} , and so on. The computations become transparent if one associates with f its logarithmic representative

$$\hat{f}(u) = \ln f(e^u), \quad u \in \ln I.$$

A direct substitution shows that, for functions f, g and h and a real function F ,

$$\begin{aligned} \widehat{f^*} &= \hat{f}', & \widehat{f +_* g} &= \hat{f} + \hat{g}, & \widehat{f \cdot_* g} &= \hat{f} + \hat{g}, \\ \widehat{f \circ h} &= \hat{f} \circ \hat{h}, & \widehat{F_* \circ f} &= F \circ \hat{f}. \end{aligned} \quad (2)$$

The multiplicative integral of f over $[a, b] \subset I$ is

$$\begin{aligned} * \int_a^b f(x) \cdot_* d_* x &= \exp \left(\int_a^b \frac{\ln f(x)}{x} dx \right) \\ &= \exp \left(\int_{\ln a}^{\ln b} \hat{f}(u) du \right), \end{aligned} \quad (3)$$

and an indefinite multiplicative integral $* \int f \cdot_* d_* x$ stands for any multiplicative primitive of f , that is, any function whose multiplicative derivative equals f . The rules of multiplicative calculus that will be used are collected in the next lemma (see [1, 6, 7]).

Lemma 2.1. *Let $f, g: I \rightarrow \mathbb{R}_*$ be multiplicatively differentiable, let $c \in \mathbb{R}_*$, and let $h: J \rightarrow I$ be multiplicatively differentiable.*

(a) $(c \cdot_* f)^* = c \cdot_* f^*$ and $(f \cdot_* g)^* = f^* \cdot_* g^*$, $(f /_* g)^* = f^* /_* g^*$; moreover, $f^* \equiv 0_*$ on I if and only if f is constant.

(b) $(f \cdot_* g)^* = f^* \cdot_* g +_* f \cdot_* g^*$, and $(f /_* g)^* = (f^* \cdot_* g -_* f \cdot_* g^*) /_* g^2$ whenever g never takes the value 0_* .

(c) (Chain rule) $(f \circ h)^* = (f^* \circ h) \cdot_* h^*$.

(d) $(F_*)^* = (F')_*$ for every differentiable real function F . In particular $(\sin_*)^* = \cos_*$, $(\cos_*)^* = -_* \sin_*$, $(\tan_*)^* = \sec_*^2$, $(\sinh_*)^* = \cosh_*$, $(\cosh_*)^* = \sinh_*$, $(\exp_*)^* = \exp_*$, $(\arctan_*)^*(x) = 1_* /_* (1_* + x^2)$, $(\operatorname{arsinh}_*)^*(x) = 1_* /_* (1_* + x^2)^{(1/2)}$, and the identity map satisfies $\operatorname{id}^* = 1_*$.

(e) $(* \int_a^x f(u) \cdot_* d_* u)^* = f(x)$ and $* \int_a^b f^*(x) \cdot_* d_* x = f(b) -_* f(a)$.

(f) If g is continuous, the solutions of the linear equation $\mu^* = g \cdot_* \mu$ are the functions $\mu = c \cdot_* \exp_*(* \int g \cdot_* d_* x)$, $c \in \mathbb{R}_*$. If $c \neq 0_*$, such a solution never takes the value 0_* .

Proof. By (2) and (3), each assertion is the image under $f \mapsto \hat{f}$ of a familiar rule of ordinary calculus. For instance, (c) is the chain rule for $\hat{f} \circ \hat{h}$, and (d) follows from $\widehat{F_*} = F$. In (f), the equation $\mu^* = g \cdot_* \mu$ reads $\hat{\mu}' = \hat{g} \hat{\mu}$, whose solutions are $\hat{\mu} = C \exp(\int \hat{g} du)$ with $C \in \mathbb{R}$; going back through the hat map we get $\mu = c \cdot_* \exp_*(* \int g \cdot_* d_* x)$ with $c = e^C$, and $\hat{\mu}$ has no zeros when $C \neq 0$. $\square$

2.3 The multiplicative Euclidean space

We denote by $\mathbb{E}_*^3$ the set $\mathbb{R}_*^3$ equipped with the operations [1, 5]

$$\begin{aligned} x +_* y &= (x_1 y_1, x_2 y_2, x_3 y_3), \\ a \cdot_* x &= (e^{\ln a \ln x_1}, e^{\ln a \ln x_2}, e^{\ln a \ln x_3}), \quad a \in \mathbb{R}_*, \end{aligned}$$

whose zero vector is $0_* = (1, 1, 1)$ and whose canonical basis is formed by $e_1 = (e, 1, 1)$, $e_2 = (1, e, 1)$ and $e_3 = (1, 1, e)$. Inner products, norms and cross products are defined multiplicatively by

$$\begin{aligned} \langle x, y \rangle_* &= x_1 \cdot_* y_1 +_* x_2 \cdot_* y_2 +_* x_3 \cdot_* y_3 = e^{\ln x_1 \ln y_1 + \ln x_2 \ln y_2 + \ln x_3 \ln y_3}, \\ \|x\|_* &= \langle x, x \rangle_*^{(1/2)*}, \\ x \times_* y &= (e^{\ln x_2 \ln y_3 - \ln x_3 \ln y_2}, e^{\ln x_3 \ln y_1 - \ln x_1 \ln y_3}, e^{\ln x_1 \ln y_2 - \ln x_2 \ln y_1}), \end{aligned}$$

and the multiplicative determinant is $\det_*(x, y, z) = \langle x \times_* y, z \rangle_*$. Two vectors are multiplicatively orthogonal when $\langle x, y \rangle_* = 0_*$, a vector is unit when $\|x\|_* = 1_*$, and the multiplicative angle $\theta \in [0_*, \pi_*]$ between two nonzero vectors is determined by $\cos_* \theta = \langle x, y \rangle_* / (\|x\|_* \cdot_* \|y\|_*)$. A multiplicative orthonormal basis $\{u_1, u_2, u_3\}$ is positively oriented if $u_3 = u_1 \times_* u_2$. The multiplicative line through P in the direction of $v \neq 0_*$ is $\{P +_* z \cdot_* v : z \in \mathbb{R}_*\}$, and the multiplicative plane through P orthogonal to v is $\{Q : \langle Q -_* P, v \rangle_* = 0_*\}$.

Lemma 2.2. *The map $\Lambda : \mathbb{E}_*^3 \rightarrow \mathbb{R}^3$, $\Lambda(x) = (\ln x_1, \ln x_2, \ln x_3)$, is a bijection satisfying*

$$\begin{aligned} \Lambda(x +_* y) &= \Lambda x + \Lambda y, & \Lambda(a \cdot_* x) &= (\ln a) \Lambda x, \\ \Lambda(x \times_* y) &= \Lambda x \times \Lambda y, & \ln \langle x, y \rangle_* &= \langle \Lambda x, \Lambda y \rangle, & \ln \|x\|_* &= |\Lambda x|, \end{aligned}$$

and $\ln \det_*(x, y, z) = \det(\Lambda x, \Lambda y, \Lambda z)$. Moreover, $\ln \theta$ is the Euclidean angle between Λx and Λy . As a result, any identity of vector algebra in $\mathbb{R}^3$ yields a valid identity in $\mathbb{E}_*^3$ after each operation is replaced by its multiplicative analogue; for instance,

$$\begin{aligned} x \times_* (y \times_* z) &= \langle x, z \rangle_* \cdot_* y -_* \langle x, y \rangle_* \cdot_* z, \\ \|x \times_* y\|_*^{2*} &= \|x\|_*^{2*} \cdot_* \|y\|_*^{2*} -_* \langle x, y \rangle_*^{2*}. \end{aligned}$$

Proof. All the formulas follow at once from the definitions; the vector identities are the images under Λ^{-1} of their Euclidean versions. $\square$

2.4 Curves and the multiplicative Frenet apparatus

A multiplicative curve is a map $\alpha: I \subset \mathbb{R}_* \rightarrow \mathbb{E}_*^3$, $s \mapsto (\alpha_1(s), \alpha_2(s), \alpha_3(s))$, whose components are multiplicatively differentiable, and its multiplicative derivative is $\alpha^* = (\alpha_1^*, \alpha_2^*, \alpha_3^*)$. We call α regular when α^* never equals 0_* ; if moreover $\|\alpha^*\|_* \equiv 1_*$, we say that s is a multiplicative arc length parameter, and every regular curve admits such a parameter [1, 5]. We write $\mathfrak{X}_*(\alpha)$ for the space of multiplicatively differentiable vector fields along α ; their derivatives are taken coordinate by coordinate. With α we associate its logarithmic image, the Euclidean curve

$$\hat{\alpha}: \ln I \rightarrow \mathbb{R}^3, \quad \hat{\alpha}(u) = \Lambda(\alpha(e^u)),$$

and $\hat{X}$ is defined in the same way for $X \in \mathfrak{X}_*(\alpha)$. By (2), $\widehat{X^*} = \hat{X}'$.

Lemma 2.3. *Let $X, Y \in \mathfrak{X}_*(\alpha)$, $f: I \rightarrow \mathbb{R}_*$ and $h: J \rightarrow I$ be multiplicatively differentiable. Then*

$$\begin{aligned} (X +_* Y)^* &= X^* +_* Y^*, & (f \cdot_* X)^* &= f^* \cdot_* X +_* f \cdot_* X^*, \\ \langle X, Y \rangle_*^* &= \langle X^*, Y \rangle_* + \langle X, Y^* \rangle_*, \\ (X \times_* Y)^* &= X^* \times_* Y +_* X \times_* Y^*, & (X \circ h)^* &= (X^* \circ h) \cdot_* h^*. \end{aligned}$$

Moreover, $X^* \equiv 0_*$ if and only if X is constant.

Proof. Apply (2) componentwise and use Lemma 2.2. $\square$

Assume that α is parametrized by multiplicative arc length and that α^{**} never vanishes. Its multiplicative Frenet apparatus is defined by [1]

$$\begin{aligned} T_\alpha &= \alpha^*, & \kappa_\alpha &= \|\alpha^{**}\|_*, & N_\alpha &= (1_*/\kappa_\alpha) \cdot_* \alpha^{**}, \\ B_\alpha &= T_\alpha \times_* N_\alpha, & \tau_\alpha &= \langle N_\alpha^*, B_\alpha \rangle_*. \end{aligned}$$

These three fields constitute a positively oriented orthonormal moving frame in the multiplicative sense. Through each point $\alpha(s)$ pass the multiplicative osculating plane, perpendicular to $B_\alpha(s)$, the normal plane, perpendicular to $T_\alpha(s)$, and the rectifying plane, perpendicular to $N_\alpha(s)$.

Proposition 2.4. *Suppose that s is a multiplicative arc length parameter of α and that $\kappa_\alpha > 0_*$.*

(i) *The multiplicative Frenet–Serret equations hold:*

$$\begin{aligned} T_\alpha^* &= \kappa_\alpha \cdot_* N_\alpha, \\ N_\alpha^* &= -_* \kappa_\alpha \cdot_* T_\alpha +_* \tau_\alpha \cdot_* B_\alpha, \\ B_\alpha^* &= -_* \tau_\alpha \cdot_* N_\alpha. \end{aligned} \quad (4)$$

(ii) *The logarithmic image $\hat{\alpha}$ is a unit speed curve in $\mathbb{R}^3$ with Frenet frame $\{\hat{T}_\alpha, \hat{N}_\alpha, \hat{B}_\alpha\}$, curvature $\hat{\kappa}_\alpha$ and torsion $\hat{\tau}_\alpha$.*

(iii) *For an arbitrary regular parametrization with $\alpha^* \times_* \alpha^{**} \neq 0_*$, the curvature and torsion are given by*

$$\begin{aligned} \kappa_\alpha &= \| \alpha^* \times_* \alpha^{**} \|_* /_* \| \alpha^* \|_*^3, \\ \tau_\alpha &= \det_*(\alpha^*, \alpha^{**}, \alpha^{***}) /_* \| \alpha^* \times_* \alpha^{**} \|_*^2. \end{aligned}$$

(iv) $\tau_\alpha \equiv 0_*$ *exactly when α lies in some multiplicative plane.*

Proof. For (i) we refer to [1, Section 3] and [5]. For (ii), recall that $\widehat{\alpha^*} = \hat{\alpha}'$ and that Λ preserves all the operations (Lemma 2.2). Hence $\hat{T}_\alpha = \hat{\alpha}'$ is a unit vector field, $\hat{\alpha}'' = \hat{\kappa}_\alpha \hat{N}_\alpha$, and the images of the equations (4) under the hat map are the Frenet–Serret equations of $\hat{\alpha}$. Statements (iii) and (iv) are then consequences of their Euclidean analogues; they can also be proved directly by imitating the classical arguments with Lemma 2.3. $\square$

From now on every curve is assumed to be given by a multiplicative arc length parameter and to have $\kappa_\alpha > 0_*$. Unless the contrary is stated they are also nonplanar, which here means that $\tau_\alpha(s) \neq 0_*$ for every s . For such a curve we call $\rho_\alpha = \tau_\alpha /_* \kappa_\alpha$ its multiplicative Lancret curvature.

2.5 Darboux vectors of moving frames and Frenet-constant fields

Consider a moving multiplicative orthonormal frame $\mathcal{F} = \{F_1, F_2, F_3\}$ along α , that is, $\langle F_i, F_j \rangle_* = \delta_{ij}^*$ with $\delta_{ii}^* = 1_*$ and $\delta_{ij}^* = 0_*$ for $i \neq j$, and assume that it is positively oriented, $F_3 = F_1 \times_* F_2$. Expanding the derivatives of its vectors in the frame itself we get $F_i^* = \omega_{i1} \cdot_* F_1 +_* \omega_{i2} \cdot_* F_2 +_* \omega_{i3} \cdot_* F_3$, where $\omega_{ij} = \langle F_i^*, F_j \rangle_*$.

Proposition 2.5. *There is exactly one vector field $D_{\mathcal{F}} \in \mathfrak{X}_*(\alpha)$ such that*

$$F_1^* = D_{\mathcal{F}} \times_* F_1, \quad F_2^* = D_{\mathcal{F}} \times_* F_2, \quad F_3^* = D_{\mathcal{F}} \times_* F_3. \quad (5)$$

It is given by

$$\begin{aligned} D_{\mathcal{F}} &= \omega_{23} \cdot_* F_1 +_* \omega_{31} \cdot_* F_2 +_* \omega_{12} \cdot_* F_3 \\ &= (1/2)_* \cdot_* (F_1 \times_* F_1^* +_* F_2 \times_* F_2^* +_* F_3 \times_* F_3^*). \end{aligned}$$

In particular, for the Frenet frame of α we have $D_{\alpha} = \tau_{\alpha} \cdot_ T_{\alpha} +_* \kappa_{\alpha} \cdot_* B_{\alpha}$ and $\|D_{\alpha}\|_* = (\kappa_{\alpha}^{2_*} +_* \tau_{\alpha}^{2_*})^{(1/2)_*}$.*

Proof. Differentiating $\langle F_i, F_j \rangle_* = \delta_{ij}^*$ with Lemma 2.3 gives $\omega_{ij} +_* \omega_{ji} = 0_*$; thus the matrix (ω_{ij}) is multiplicatively skew-symmetric and, in particular, $\omega_{ii} = 0_*$. Let D denote the combination $\omega_{23} \cdot_* F_1 +_* \omega_{31} \cdot_* F_2 +_* \omega_{12} \cdot_* F_3$. Using $F_2 \times_* F_1 = -_* F_3$ and $F_3 \times_* F_1 = F_2$ (Lemma 2.2) we find

$$D \times_* F_1 = -_* \omega_{31} \cdot_* F_3 +_* \omega_{12} \cdot_* F_2 = \omega_{12} \cdot_* F_2 +_* \omega_{13} \cdot_* F_3 = F_1^*,$$

and in the same way $D \times_* F_2 = F_2^*$ and $D \times_* F_3 = F_3^*$. If another field D' satisfies (5), then $(D -_* D') \times_* F_i = 0_*$ for $i = 1, 2, 3$; a vector which is collinear with three linearly independent vectors is zero, so $D = D'$. For the second expression of D , Lemma 2.2 gives $F_i \times_* (D \times_* F_i) = D -_* \langle F_i, D \rangle_* \cdot_* F_i$, and adding over i we obtain $F_1 \times_* F_1^* +_* F_2 \times_* F_2^* +_* F_3 \times_* F_3^* = 3_* \cdot_* D -_* D = 2_* \cdot_* D$; since $(1/2)_* \cdot_* 2_* = 1_*$, the formula follows. Finally, for the Frenet frame (4) yields $\omega_{12} = \kappa_{\alpha}$, $\omega_{23} = \tau_{\alpha}$ and $\omega_{13} = 0_*$. $\square$

The field $D_{\mathcal{F}}$ is the multiplicative Darboux vector of $\mathcal{F}$ (for the Euclidean notion see [11, pp. 43–45]). For the Frenet frame, D_{α} plays the role of the multiplicative angular velocity of the frame, and $\|D_{\alpha}\|_*$ is the multiplicative total curvature of α .

Let $W \in \mathfrak{X}_*(\alpha)$ and write $W = w_1 \cdot_* F_1 +_* w_2 \cdot_* F_2 +_* w_3 \cdot_* F_3$ with $w_i = \langle W, F_i \rangle_*$. The multiplicative derivative of W relative to $\mathcal{F}$ is the field obtained by differentiating only the coordinates,

$$\frac{d_*^{\mathcal{F}} W}{d_* s} = w_1^* \cdot_* F_1 +_* w_2^* \cdot_* F_2 +_* w_3^* \cdot_* F_3.$$

Differentiating W with Lemma 2.3 and using (5) we arrive at the multiplicative transport theorem

$$W^* = \frac{d_*^{\mathcal{F}} W}{d_* s} +_* D_{\mathcal{F}} \times_* W. \quad (6)$$

Its meaning is the same as in the Euclidean setting (see [19, p. 11]): the rate of change of W seen from the fixed frame $\{e_1, e_2, e_3\}$ is the rate of change measured inside the moving frame plus the contribution due to the rotation of the frame itself.

Definition 2.6. A vector field $W \in \mathfrak{X}_*(\alpha)$ is called $\mathcal{F}$ -constant (multiplicatively constant with respect to $\mathcal{F}$) if $d_*^{\mathcal{F}} W / d_* s = 0_*$; by (6) this happens if and only if $W^* = D_{\mathcal{F}} \times_* W$. The set of $\mathcal{F}$ -constant vector fields along α is denoted by $\mathfrak{X}_*^{\mathcal{F}}(\alpha)$.

In the Euclidean literature such fields have been described as vectors rigidly attached to the moving points of the curve [18]; from a kinematic point of view, if α is thought of as the path of a rigid body carrying the frame $\mathcal{F}$, an $\mathcal{F}$ -constant field is a vector fixed in the body [19].

Proposition 2.7. *Let $\mathcal{F}$ be as above.*

- (1) *If W is $\mathcal{F}$ -constant, then $\|W\|_*$ is constant.*
- (2) *If W_1 and W_2 are $\mathcal{F}$ -constant, then so is $W_1 +_* W_2$.*
- (3) *If W is $\mathcal{F}$ -constant and never zero, and $h: I \rightarrow \mathbb{R}_*$ is multiplicatively differentiable, then $h \cdot_* W$ is $\mathcal{F}$ -constant if and only if h is constant.*
- (4) *W is $\mathcal{F}$ -constant if and only if $W = a_1 \cdot_* F_1 +_* a_2 \cdot_* F_2 +_* a_3 \cdot_* F_3$ with constants $a_1, a_2, a_3 \in \mathbb{R}_*$. Hence $\mathfrak{X}_*^{\mathcal{F}}(\alpha)$ is a vector space of dimension three over the field $\mathbb{R}_*$.*

Proof. Statement (4) is a consequence of (6) and Lemma 2.1(a), and (2) follows from (4).

For (1),

$$\langle W, W \rangle_*^* = 2_* \cdot_* \langle W^*, W \rangle_* = 2_* \cdot_* \langle D_{\mathcal{F}} \times_* W, W \rangle_* = 0_*.$$

For (3),

$$(h \cdot_* W)^* = h^* \cdot_* W +_* h \cdot_* (D_{\mathcal{F}} \times_* W) = h^* \cdot_* W +_* D_{\mathcal{F}} \times_* (h \cdot_* W),$$

so $h \cdot_* W$ is $\mathcal{F}$ -constant exactly when $h^* \cdot_* W = 0_*$, that is, when $h^* = 0_*$. $\square$

2.6 Multiplicative helices

We say that a nonzero field $W \in \mathfrak{X}_*(\alpha)$ lies in the normal, rectifying or osculating plane when it is everywhere perpendicular to T_α , to N_α or to B_α , respectively. From now on the frame $\mathcal{F}$ is always the Frenet frame $\{T_\alpha, N_\alpha, B_\alpha\}$.

By Proposition 2.7, the $\mathcal{F}$ -constant vector fields are the combinations $W = a \cdot T_\alpha + b \cdot N_\alpha + c \cdot B_\alpha$ with constant coefficients $a, b, c \in \mathbb{R}_*$, or, equivalently, the solutions of $W^* = D_\alpha \times_* W$. In particular T_α , N_α and B_α themselves are $\mathcal{F}$ -constant.

Definition 2.8. Let W be an $\mathcal{F}$ -constant field along α and $V \neq 0_*$ a constant vector. If the multiplicative angle between $W(s)$ and V is independent of s , the curve is called a multiplicative helix and the direction of V an axis. Depending on the plane that contains W , one speaks of multiplicative normal, osculating or rectifying helices.

There is no loss of generality in assuming $\|W\|_* = 1_*$. Taking $W = T_\alpha$ one obtains the multiplicative general (cylindrical) helices, and $W = N_\alpha$ gives the multiplicative slant helices; both classes were investigated in [9] as counterparts of the classical curves of constant slope [21, p. 33] and slant helices [10, 12]. The term osculating helix used here has nothing to do with the circular helix having high-order contact with a curve at a given point [21, p. 42]. In this chapter we deal with the normal case of the following question, which was answered in [13] in the Euclidean setting:

How can one characterize the multiplicative helices whose $\mathcal{F}$ -constant vector field W is multiplicatively orthogonal to the axis, $\langle W, V \rangle_ = 0_*$?*

If W coincides with T_α or B_α , the condition $\langle W, V \rangle_* = 0_*$ forces α to be planar, while for $W = N_\alpha$ it characterizes the multiplicative cylindrical helices (see Remark 3.3). Hence only fields that combine two or three Frenet vectors lead to new curves.

Remark 2.9 (Transfer principle). By Lemma 2.2, (2) and Proposition 2.4(ii), the logarithmic image of the multiplicative Darboux vector is the Darboux vector of the logarithmic image, $\widehat{D}_\alpha = D_{\widehat{\alpha}}$. Therefore W is $\mathcal{F}$ -constant along α if and only if $\widehat{W}$ is $\mathcal{F}$ -constant along $\widehat{\alpha}$, and $\langle W, V \rangle_* = 0_*$ if and only if $\langle \widehat{W}, \Lambda V \rangle = 0$. Accordingly, Λ maps the multiplicative helices of each of the three types with axis V onto the Euclidean helices of [13] of the same type with axis ΛV . In the same manner, the multiplicative cylinders used in Section 3 correspond to Euclidean cylinders, and each scalar identity below turns into the corresponding identity of [13] for $\widehat{\kappa}_\alpha$ and $\widehat{\tau}_\alpha$ after taking logarithms. Table 1 summarizes this correspondence. The results of the present chapter could thus also be obtained from [13] by means of Λ ; we have preferred to give multiplicative proofs and to add, for every characterization, its form in ordinary arithmetic, using that $\ln f^*(s) = s (\ln f)'(s)$ for every positive function f .

Table 1. Correspondence between Euclidean notions, their multiplicative counterparts and their values in ordinary arithmetic.

Euclidean	Multiplicative	In ordinary arithmetic
0, 1	$0_*, 1_*$	1, e
$a + b, a - b$	$a +_* b, a -_* b$	$ab, a/b$
$ab, a/b$	$a \cdot_* b, a /_* b$	$e^{\ln a \ln b}, e^{\ln a / \ln b}$
$a^2, \sqrt{a}$	$a^{2_*}, a^{(1/2)_*}$	$e^{(\ln a)^2}, e^{\sqrt{\ln a}}$
$\cos \theta, \tan \theta$	$\cos_* \theta, \tan_* \theta$	$e^{\cos(\ln \theta)}, e^{\tan(\ln \theta)}$
$f'(s)$	$f^*(s)$	$e^{s(\ln f)'(s)}$
$\int_a^b f(s) ds$	$* \int_a^b f(s) \cdot_* d_* s$	$e^{\int_a^b \ln f(s) ds / s}$
$x + y, a x \text{ in } \mathbb{R}^3$	$x +_* y, a \cdot_* x \text{ in } \mathbb{E}_*^3$	$(x_i y_i)_i, (x_i^{\ln a})_i$
$\langle x, y \rangle, \ x\ $	$\langle x, y \rangle_*, \ x\ _*$	$e^{\sum_i \ln x_i \ln y_i}, e^{(\sum_i \ln^2 x_i)^{1/2}}$
$x \times y$	$x \times_* y$	$\Lambda^{-1}(\Lambda x \times \Lambda y)$
$D = \tau T + \kappa B$	$D_\alpha = \tau_\alpha \cdot_* T_\alpha +_* \kappa_\alpha \cdot_* B_\alpha$	$\Lambda^{-1}(\ln \tau_\alpha \Lambda T_\alpha + \ln \kappa_\alpha \Lambda B_\alpha)$
$W' = D \times W$	$W^* = D_{\mathcal{F}} \times_* W$	$(e^{s(\ln W)'(s)})_i = \Lambda^{-1}(\Lambda D_{\mathcal{F}} \times \Lambda W)$
cylinder $\beta(t) + zV$	$\beta(t) +_* z \cdot_* V$	$(\beta_i(t) z^{\ln V})_i$

3 Normal helices

In this section $\alpha: I \rightarrow \mathbb{E}_*^3$ denotes a nonplanar curve parametrized by multiplicative arc length, with multiplicative Frenet apparatus $\{\kappa_\alpha, \tau_\alpha; T_\alpha, N_\alpha, B_\alpha\}$ and multiplicative Lancret curvature $\rho_\alpha = \tau_\alpha /_* \kappa_\alpha$. A unit normal $\mathcal{F}$ -constant vector field has constant coordinates with respect to N_α and B_α and none along T_α ; hence it can be written as

$$W_\theta = \cos_* \theta \cdot_* N_\alpha +_* \sin_* \theta \cdot_* B_\alpha \quad (7)$$

for a constant multiplicative angle θ . Replacing W_θ by $-_* W_\theta$ does not affect its orthogonality to a given vector, so we may and do assume that $\cos_* \theta \geq 0_*$, that is, $e^{-\pi/2} \leq \theta \leq e^{\pi/2}$.

3.1 An adapted frame and the natural equation

Together with W_θ we shall use the unit normal field

$$U_\theta = \sin_* \theta \cdot_* N_\alpha -_* \cos_* \theta \cdot_* B_\alpha. \quad (8)$$

Lemma 3.1. *The fields T_α , U_θ , W_θ are $\mathcal{F}$ -constant and form a positively oriented multiplicative orthonormal frame along α . Their multiplicative derivatives are*

$$\begin{aligned} T_\alpha^* &= \kappa_\alpha \cdot \sin_* \theta \cdot U_\theta + \kappa_\alpha \cdot \cos_* \theta \cdot W_\theta, \\ U_\theta^* &= -\kappa_\alpha \cdot \sin_* \theta \cdot T_\alpha + \tau_\alpha \cdot W_\theta, \\ W_\theta^* &= -\kappa_\alpha \cdot \cos_* \theta \cdot T_\alpha - \tau_\alpha \cdot U_\theta. \end{aligned} \quad (9)$$

Proof. Both U_θ and W_θ have constant coordinates in the Frenet frame, so they are $\mathcal{F}$ -constant by Proposition 2.7(4). Orthonormality is checked directly, and $T_\alpha \times_* U_\theta = \sin_* \theta \cdot B_\alpha + \cos_* \theta \cdot N_\alpha = W_\theta$ gives the orientation. Inverting (7) and (8) we obtain $N_\alpha = \sin_* \theta \cdot U_\theta + \cos_* \theta \cdot W_\theta$ and $B_\alpha = -\cos_* \theta \cdot U_\theta + \sin_* \theta \cdot W_\theta$, so that the Darboux vector of the Frenet frame becomes

$$\begin{aligned} D_\alpha &= \tau_\alpha \cdot T_\alpha + \kappa_\alpha \cdot B_\alpha \\ &= \tau_\alpha \cdot T_\alpha - \kappa_\alpha \cdot \cos_* \theta \cdot U_\theta + \kappa_\alpha \cdot \sin_* \theta \cdot W_\theta. \end{aligned}$$

Every $\mathcal{F}$ -constant field X satisfies $X^* = D_\alpha \times_* X$ (Definition 2.6), and computing the three products $D_\alpha \times_* T_\alpha$, $D_\alpha \times_* U_\theta$, $D_\alpha \times_* W_\theta$ with the orientation rules $T_\alpha \times_* U_\theta = W_\theta$, $U_\theta \times_* W_\theta = T_\alpha$ and $W_\theta \times_* T_\alpha = U_\theta$ yields (9). $\square$

In other words, the adapted frame $\{T_\alpha, U_\theta, W_\theta\}$ rotates with the same multiplicative angular velocity D_α as the Frenet frame. We are now ready to state the first main result.

Theorem 3.2. *Let α be a nonplanar curve in $\mathbb{E}_*^3$ parametrized by multiplicative arc length, with $\kappa_\alpha > 0_*$, and let θ be a constant with $e^{-\pi/2} < \theta < e^{\pi/2}$. The following conditions are equivalent.*

(a) *Some constant vector $V \neq 0_*$ satisfies $\langle W_\theta, V \rangle_* = 0_*$; that is, α is a multiplicative normal helix with an axis V perpendicular to its $\mathcal{F}$ -constant field W_θ .*

(b) *The multiplicative curvature and torsion of α satisfy*

$$\left(\kappa_\alpha /_* (\cos_*^2 \theta \cdot \kappa_\alpha^{2*} + \tau_\alpha^{2*}) \right) \cdot \rho_\alpha^* = -\tan_* \theta. \quad (10)$$

When these conditions hold, V is a constant multiple of

$$\begin{aligned} V_\theta &= \mu \cdot (U_\theta - \sec_* \theta \cdot \rho_\alpha \cdot T_\alpha), \\ \mu &= \exp_* (\tan_* \theta \cdot \int \tau_\alpha \cdot d_* s). \end{aligned} \quad (11)$$

In ordinary arithmetic, equation (10) reads

$$\frac{\ln \kappa_\alpha}{\cos^2(\ln \theta) \ln^2 \kappa_\alpha + \ln^2 \tau_\alpha} s \frac{d}{ds} \left(\frac{\ln \tau_\alpha}{\ln \kappa_\alpha} \right) = -\tan(\ln \theta). \quad (12)$$

Proof. Let V be any vector field along α satisfying $\langle W_\theta, V \rangle_* = 0_*$. By Lemma 3.1 we can expand $V = \lambda \cdot_* T_\alpha +_* \mu \cdot_* U_\theta$, where $\lambda = \langle V, T_\alpha \rangle_*$ and $\mu = \langle V, U_\theta \rangle_*$. Differentiating with Lemma 2.3 and (9) we get

$$\begin{aligned} V^* &= (\lambda^* \cdot_* \mu \cdot_* \kappa_\alpha \cdot_* \sin_* \theta) \cdot_* T_\alpha \\ &\quad +_* (\mu^* +_* \lambda \cdot_* \kappa_\alpha \cdot_* \sin_* \theta) \cdot_* U_\theta \\ &\quad +_* (\lambda \cdot_* \kappa_\alpha \cdot_* \cos_* \theta +_* \mu \cdot_* \tau_\alpha) \cdot_* W_\theta. \end{aligned}$$

Consequently V is constant exactly when the three scalar equations

$$\lambda^* = \mu \cdot_* \kappa_\alpha \cdot_* \sin_* \theta, \quad (13)$$

$$\mu^* = -_* \lambda \cdot_* \kappa_\alpha \cdot_* \sin_* \theta, \quad (14)$$

$$\lambda \cdot_* \kappa_\alpha \cdot_* \cos_* \theta +_* \mu \cdot_* \tau_\alpha = 0_* \quad (15)$$

hold simultaneously.

(a) $\Rightarrow$ (b). Assume that V is constant and nonzero. Since $\kappa_\alpha > 0_*$ and $\cos_* \theta > 0_*$, equation (15) can be solved for λ :

$$\lambda = -_* \sec_* \theta \cdot_* \rho_\alpha \cdot_* \mu. \quad (16)$$

Substituting this expression into (14) we obtain the linear equation $\mu^* = \tan_* \theta \cdot_* \tau_\alpha \cdot_* \mu$. By Lemma 2.1(f), $\mu = c \cdot_* \exp_*(\tan_* \theta \cdot_* \int \tau_\alpha \cdot_* d_* s)$ for a constant $c \in \mathbb{R}_*$, and $c \neq 0_*$, since $c = 0_*$ would give $\mu \equiv 0_*$, then $\lambda \equiv 0_*$ by (16), and finally $V = 0_*$. In particular μ never vanishes, and $V = c \cdot_* V_\theta$. Next we differentiate (16):

$$\begin{aligned} \lambda^* &= -_* \sec_* \theta \cdot_* (\rho_\alpha^* \cdot_* \mu +_* \rho_\alpha \cdot_* \mu^*) \\ &= -_* \sec_* \theta \cdot_* \mu \cdot_* (\rho_\alpha^* +_* \tan_* \theta \cdot_* \tau_\alpha \cdot_* \rho_\alpha). \end{aligned}$$

Comparing with (13) and cancelling the nonvanishing factor μ , we find

$$\begin{aligned}\rho_\alpha^* &= -_* \sin_* \theta \cdot \cos_* \theta \cdot \kappa_\alpha -_* \tan_* \theta \cdot \tau_\alpha \cdot \rho_\alpha \\ &= -_* \tan_* \theta \cdot (\cos_*^2 \theta \cdot \kappa_\alpha^2 +_* \tau_\alpha^2) /_* \kappa_\alpha,\end{aligned}\tag{17}$$

where we used $\sin_* \theta \cdot \cos_* \theta = \tan_* \theta \cdot \cos_*^2 \theta$ and $\tau_\alpha \cdot \rho_\alpha = \tau_\alpha^2 /_* \kappa_\alpha$. Because α is nonplanar, $\cos_*^2 \theta \cdot \kappa_\alpha^2 +_* \tau_\alpha^2 > 0_*$, and multiplying (17) by $\kappa_\alpha /_* (\cos_*^2 \theta \cdot \kappa_\alpha^2 +_* \tau_\alpha^2)$ gives (10).

(b) $\Rightarrow$ (a). Now assume (10), define μ by (11), λ by (16) and put $V = \lambda \cdot T_\alpha +_* \mu \cdot U_\theta$, which is precisely V_θ . Equation (15) holds by the choice of λ , and (14) holds because $\mu^* = \tan_* \theta \cdot \tau_\alpha \cdot \mu = -_* \lambda \cdot \kappa_\alpha \cdot \sin_* \theta$. The computation made in the first part shows that, for these λ and μ , equation (13) is equivalent to (17), that is, to (10). Therefore $V^* = 0_*$. Since μ has no zeros, $V \neq 0_*$, and $\langle W_\theta, V \rangle_* = 0_*$ by construction.

Finally, (12) is obtained by taking logarithms in (10): multiplicative products, quotients and sums become ordinary products, quotients and sums of logarithms, $\ln \rho_\alpha = \ln \tau_\alpha / \ln \kappa_\alpha$, and $\ln f^*(s) = s (\ln f)'(s)$ for every positive differentiable function f . $\square$

Remark 3.3. (1) *The value $\theta = 0_*$.* In this case $W_\theta = N_\alpha$ and $U_\theta = -_* B_\alpha$, the function μ in (11) is constant, and $V_\theta = -_* \mu \cdot (\rho_\alpha \cdot T_\alpha +_* B_\alpha)$. Equation (10) reduces to $\rho_\alpha^* = 0_*$, so the multiplicative normal helices with $W = N_\alpha$ are exactly the multiplicative cylindrical helices, in agreement with the multiplicative theorem of Lancret [9, Theorem 4.12]. Notice that in this case V is parallel to the Darboux vector $D_\alpha = \kappa_\alpha \cdot (\rho_\alpha \cdot T_\alpha +_* B_\alpha)$.

(2) *The values $\theta = e^{\pm \pi/2}$.* Then $W_\theta = \pm B_\alpha$ and no nonplanar curve can have such a field orthogonal to a nonzero constant vector: equation (15) becomes $\mu \cdot \tau_\alpha = 0_*$, whence $\mu \equiv 0_*$, and then (14) forces $\lambda \equiv 0_*$. This justifies the restriction $e^{-\pi/2} < \theta < e^{\pi/2}$ in Theorem 3.2. Together with the normalization $\cos_* \theta \geq 0_*$, it follows that α is a multiplicative normal helix with $\mathcal{F}$ -constant field orthogonal to the axis if and only if (10) holds for some constant $\theta \in (e^{-\pi/2}, e^{\pi/2})$.

(3) *Uniqueness of the axis.* The proof shows that the constant vectors orthogonal to W_θ form the one-dimensional space $\{c \cdot V_\theta : c \in \mathbb{R}_*\}$. Thus the axis of a multiplicative normal helix is determined by W_θ .

(4) *Monotonicity of ρ_α .* If $\theta \neq 0_*$, the right-hand side of (17) never vanishes, so the Lancret curvature of a multiplicative normal helix with $\theta \neq 0_*$ is strictly monotone. In particular, such a curve is never a multiplicative cylindrical helix.

3.2 Normal helices on multiplicative cylinders

Let V be a unit vector and let $\beta: J \rightarrow \mathbb{E}_*^3$ be a curve parametrized by multiplicative arc length, with $\kappa_\beta > 0_*$, lying in a multiplicative plane orthogonal to V . The multiplicative cylinder over β with rulings parallel to V is the surface

$$\mathcal{C}_{\beta,V}: X(t, z) = \beta(t) +_* z \cdot_* V, \quad (t, z) \in J \times \mathbb{R}_*,$$

which in ordinary arithmetic is $X(t, z) = (\beta_i(t) z^{\ln V_i})_{i=1,2,3}$. Its partial multiplicative derivatives are $X_t^* = T_\beta(t)$ and $X_z^* = V$, which are orthonormal, so the cylinder is regular. Since β lies in a plane orthogonal to V , its binormal is $\pm V$; reversing the orientation of β if necessary, we assume $B_\beta = -_* V$. Then $T_\beta \times_* V = N_\beta$, so that $N_\beta(t)$ is the unit normal of $\mathcal{C}_{\beta,V}$ at $X(t, z)$, and the Frenet–Serret equations of β reduce to $T_\beta^* = \kappa_\beta \cdot_* N_\beta$ and $N_\beta^* = -_* \kappa_\beta \cdot_* T_\beta$.

Lemma 3.4. *Let $\alpha(s) = X(t(s), z(s))$, $s \in I$, be a curve on $\mathcal{C}_{\beta,V}$ parametrized by multiplicative arc length.*

(i) *There is a multiplicatively differentiable function φ on I such that $t^* = \cos_* \varphi$ and $z^* = \sin_* \varphi$; consequently $T_\alpha = \cos_* \varphi \cdot_* T_\beta(t) +_* \sin_* \varphi \cdot_* V$.*

(ii) *Put $U = -_* \sin_* \varphi \cdot_* T_\beta(t) +_* \cos_* \varphi \cdot_* V$. Then T_α , U and $N_\beta(t)$ form, in this order, a positively oriented orthonormal frame along α , and $N_\beta(t(s))$ is the unit normal of the cylinder at $\alpha(s)$.*

(iii) $T_\alpha^* = \varphi^* \cdot_* U +_* \cos_*^2 \varphi \cdot_* \kappa_\beta(t) \cdot_* N_\beta(t)$.

Proof. By the chain rule (Lemma 2.3), $\alpha^* = t^* \cdot_* T_\beta(t) +_* z^* \cdot_* V$. As T_β and V are orthonormal and $\|\alpha^*\|_* = 1_*$, we get $(t^*)^{2*} +_* (z^*)^{2*} = 1_*$. In logarithmic terms, $(\hat{t}', \hat{z}')$ is a differentiable map into the unit circle, and it therefore admits a differentiable angle function; its image under the hat correspondence is the required φ . This proves (i). The orthonormality in (ii) is immediate, and Lemma 2.2 gives $T_\alpha \times_* U = \cos_*^2 \varphi \cdot_* (T_\beta \times_* V) -_* \sin_*^2 \varphi \cdot_* (V \times_* T_\beta) = N_\beta$. For (iii), we differentiate T_α and use $(T_\beta \circ t)^* = t^* \cdot_* \kappa_\beta(t) \cdot_* N_\beta(t)$ together with $t^* = \cos_* \varphi$. $\square$

Theorem 3.5. *Let $V \neq 0_*$ be a constant vector. A curve α in $\mathbb{E}_*^3$ is a multiplicative normal helix with axis V and $\mathcal{F}$ -constant field perpendicular to V exactly when two conditions hold: α is contained in a multiplicative cylinder whose rulings have the direction of V , and the multiplicative angle between N_α and the unit normal of that cylinder does not vary along α .*

Proof. Assume first that α is such a helix, with field W_θ . By Theorem 3.2 we may take $V = V_\theta$ in (11), and then the surface $X(s, z) = \alpha(s) +_* z \cdot_* V$ is a

multiplicative cylinder with rulings parallel to V which contains α . Along α we have $X_S^* = T_\alpha$, $X_Z^* = V$, and by Lemma 3.1

$$X_S^* \times_* X_Z^* = T_\alpha \times_* (\mu \cdot_* U_\theta \cdot_* \mu \cdot_* \sec_* \theta \cdot_* \rho_\alpha \cdot_* T_\alpha) = \mu \cdot_* W_\theta.$$

Because μ vanishes nowhere, this cylinder has no singular points on α , and $\pm W_\theta$ is its unit normal there. Hence $\langle N_\alpha, \pm W_\theta \rangle_* = \pm \cos_* \theta$ does not depend on s , which is the second condition. Moreover, after normalizing V , this cylinder is of the form $\mathcal{C}_{\beta, V}$ considered above. Indeed, since μ vanishes nowhere, T_α is never parallel to V , so the multiplicative orthogonal projection β of α onto a multiplicative plane orthogonal to V is a regular curve, and X parametrizes the cylinder over β with rulings parallel to V . Parametrize β by multiplicative arc length and write $\alpha(s) = \beta(t(s)) \cdot_* z(s) \cdot_* V$. Along α the unit normal $T_\beta \circ t \times_* V$ of this cylinder equals $\pm W_\theta$, and by (9) the coordinate of W_θ^* along T_α is $-\kappa_\alpha \cdot_* \cos_* \theta \neq 0_*$; hence $(T_\beta \circ t)^*$ never vanishes, so that $\kappa_\beta > 0_*$. Reversing the orientation of β if necessary, we also have $B_\beta = -_* V$.

Conversely, suppose that α lies on $\mathcal{C}_{\beta, V}$ and that N_α makes a constant multiplicative angle θ with $N_\beta(t)$. Because N_α is orthogonal to T_α , it lies in the plane spanned by U and $N_\beta(t)$ (Lemma 3.4(ii)), and, orienting the angle suitably, $N_\alpha = \sin_* \theta \cdot_* U +_* \cos_* \theta \cdot_* N_\beta(t)$. Using $T_\alpha \times_* U = N_\beta$ and $T_\alpha \times_* N_\beta = -_* U$ we obtain

$$B_\alpha = T_\alpha \times_* N_\alpha = -_* \cos_* \theta \cdot_* U +_* \sin_* \theta \cdot_* N_\beta(t), \quad (18)$$

and therefore $W_\theta = \cos_* \theta \cdot_* N_\alpha +_* \sin_* \theta \cdot_* B_\alpha = N_\beta(t)$. The field W_θ is $\mathcal{F}$ -constant because θ is constant, and $\langle N_\beta(t), V \rangle_* = 0_*$ because N_β is tangent to the plane of β , which is orthogonal to V . Hence α is a multiplicative normal helix with axis V . $\square$

The proof also shows that, along a normal helix lying on $\mathcal{C}_{\beta, V}$, the field W_θ is nothing but the unit normal $N_\beta \circ t$ of the cylinder. For $\theta = 0_*$ the principal normal of α is everywhere normal to the cylinder; equivalently, the multiplicative acceleration $\alpha^{**} = \kappa_\alpha \cdot_* N_\alpha$ is normal to the surface, which means that α is a multiplicative geodesic of $\mathcal{C}_{\beta, V}$. By Remark 3.3(1) these curves are the multiplicative cylindrical helices, so Theorem 3.5 contains the multiplicative form of the classical description of cylindrical helices as geodesics of cylinders.

3.3 Curvature and torsion of normal helices on a cylinder

The next result describes the curves of a multiplicative cylinder whose principal normal keeps a constant angle with the normal of the surface, and computes their curvature and torsion in terms of the curvature of the base curve.

Proposition 3.6. *Let $\alpha(s) = X(t(s), z(s))$ be a curve on $\mathcal{C}_{\beta, V}$ parametrized by multiplicative arc length, and let $\theta \in (e^{-\pi/2}, e^{\pi/2})$ be constant. Then $N_\alpha = \sin_* \theta \cdot_* U +_* \cos_* \theta \cdot_* N_\beta(t)$, i.e. the multiplicative angle from the normal of the cylinder to N_α is the constant θ , if and only if there exists a multiplicatively differentiable function φ , with $\cos_* \varphi$ never equal to 0_* , such that*

$$t^*(s) = \cos_* \varphi(s), \quad (19)$$

$$z^*(s) = \sin_* \varphi(s), \quad (20)$$

$$\varphi^*(s) = \tan_* \theta \cdot_* \cos_*^2 \varphi(s) \cdot_* \kappa_\beta(t(s)). \quad (21)$$

In this case the multiplicative curvature and torsion of α are

$$\begin{aligned} \kappa_\alpha &= (\cos_*^2 \varphi /_* \cos_* \theta) \cdot_* \kappa_\beta(t), \\ \tau_\alpha &= -_* \sin_* \varphi \cdot_* \cos_* \varphi \cdot_* \kappa_\beta(t). \end{aligned} \quad (22)$$

In ordinary arithmetic, (19)–(22) become

$$\begin{aligned} \frac{s t'(s)}{t(s)} &= \cos(\ln \varphi), & \frac{s z'(s)}{z(s)} &= \sin(\ln \varphi), \\ \frac{s \varphi'(s)}{\varphi(s)} &= \tan(\ln \theta) \cos^2(\ln \varphi) \ln \kappa_\beta(t(s)), \\ \ln \kappa_\alpha &= \frac{\cos^2(\ln \varphi)}{\cos(\ln \theta)} \ln \kappa_\beta(t(s)), \\ \ln \tau_\alpha &= -\sin(\ln \varphi) \cos(\ln \varphi) \ln \kappa_\beta(t(s)). \end{aligned}$$

Proof. Equations (19) and (20) hold for the function φ of Lemma 3.4(i). Suppose that $N_\alpha = \sin_* \theta \cdot_* U +_* \cos_* \theta \cdot_* N_\beta(t)$. Comparing $T_\alpha^* = \kappa_\alpha \cdot_* N_\alpha$ with Lemma 3.4(iii) we get

$$\varphi^* = \kappa_\alpha \cdot_* \sin_* \theta, \quad \cos_*^2 \varphi \cdot_* \kappa_\beta(t) = \kappa_\alpha \cdot_* \cos_* \theta. \quad (23)$$

As $\kappa_\alpha > 0_*$ and $\cos_*\theta > 0_*$, the second identity shows that $\cos_*\varphi$ never vanishes and gives the value of κ_α in (22); substituting it into the first identity yields (21). To compute the torsion we differentiate (18). Writing $T_\beta = \cos_*\varphi \cdot T_\alpha - \sin_*\varphi \cdot U$, a short computation gives

$$\begin{aligned} U^* &= -_*\varphi^* \cdot T_\alpha - \sin_*\varphi \cdot \cos_*\varphi \cdot \kappa_\beta \cdot N_\beta, \\ (N_\beta \circ t)^* &= -_*\cos_*\varphi \cdot \kappa_\beta \cdot T_\beta \\ &= -_*\cos_*^2\varphi \cdot \kappa_\beta \cdot T_\alpha + \sin_*\varphi \cdot \cos_*\varphi \cdot \kappa_\beta \cdot U, \end{aligned}$$

where κ_β and N_β are evaluated at $t(s)$. Therefore

$$\begin{aligned} B_\alpha^* &= (\cos_*\theta \cdot \varphi^* - \sin_*\theta \cdot \cos_*^2\varphi \cdot \kappa_\beta) \cdot T_\alpha \\ &\quad + \sin_*\varphi \cdot \cos_*\varphi \cdot \kappa_\beta \cdot (\sin_*\theta \cdot U + \cos_*\theta \cdot N_\beta). \end{aligned}$$

By (23) the coefficient of T_α vanishes, and the last bracket is N_α . Comparing with $B_\alpha^* = -_*\tau_\alpha \cdot N_\alpha$ we obtain the torsion in (22).

Conversely, assume (19)–(21). Lemma 3.4(iii) and (21) give

$$\begin{aligned} T_\alpha^* &= \cos_*^2\varphi \cdot \kappa_\beta \cdot (\tan_*\theta \cdot U + N_\beta) \\ &= (\cos_*^2\varphi / \cos_*\theta) \cdot \kappa_\beta \cdot (\sin_*\theta \cdot U + \cos_*\theta \cdot N_\beta). \end{aligned}$$

The scalar factor is positive, because $\kappa_\beta > 0_*$, $\cos_*\theta > 0_*$ and $\cos_*\varphi \neq 0_*$, and the vector in the last bracket is unit. Hence this factor is κ_α and $N_\alpha = \sin_*\theta \cdot U + \cos_*\theta \cdot N_\beta$. The expressions in ordinary arithmetic follow as in Theorem 3.2. $\square$

In the direct part of Proposition 3.6 the restriction on θ is in fact automatic: if $\cos_*\theta \leq 0_*$, the second identity in (23) forces $\cos_*\varphi \equiv 0_*$, so that α would run along a ruling of $\mathcal{C}_{\beta,V}$, which is impossible because $\kappa_\alpha > 0_*$. The assumption on θ is needed only in the converse part.

Corollary 3.7. *Under the hypotheses of Proposition 3.6, the multiplicative Lancret curvature of α is $\rho_\alpha = -_*\cos_*\theta \cdot \tan_*\varphi$, and*

$$\rho_\alpha^*(s) = -_*\sin_*\theta \cdot \kappa_\beta(t(s)). \quad (24)$$

Consequently, if $\theta \neq 0_*$, then α is congruent to a multiplicative rectifying curve precisely when the base curve β is (an arc of) a multiplicative circle, i.e. when $\mathcal{C}_{\beta,V}$ is a multiplicative circular cylinder.

Proof. The first formula is the quotient of the two expressions in (22). By Lemma 2.1(d) and (21), $(\tan_* \varphi)^* = \sec_*^2 \varphi \cdot_* \varphi^* = \tan_* \theta \cdot_* \kappa_\beta(t)$, and (24) follows because $\cos_* \theta \cdot_* \tan_* \theta = \sin_* \theta$. Multiplicative rectifying curves, whose position vector always lies in the rectifying plane, are the multiplicative analogues of the curves introduced by Chen [4]. Proposition 4.2 of [1] states that, for $\kappa_\alpha > 0_*$, congruence to a multiplicative rectifying curve amounts to a relation $\rho_\alpha = c \cdot_* s +_* d$ with constants $c \neq 0_*$ and d , which by Lemma 2.1 means that ρ_α^* is a nonzero constant. For $\theta \neq 0_*$, by (24) this means that κ_β is constant along $t(s)$; since $t^* = \cos_* \varphi$ never vanishes, t is strictly monotone and κ_β is constant on an interval. A plane curve with constant multiplicative curvature has an arc of a circle as its logarithmic image, which proves the claim. $\square$

Remark 3.8. Proposition 3.6 gives an independent check of Theorem 3.2. Indeed, from (22) we get $\cos_*^2 \theta \cdot_* \kappa_\alpha^{2*} +_* \tau_\alpha^{2*} = \cos_*^2 \varphi \cdot_* \kappa_\beta^{2*}$, so that $\kappa_\alpha /_* (\cos_*^2 \theta \cdot_* \kappa_\alpha^{2*} +_* \tau_\alpha^{2*}) = 1 /_* (\cos_* \theta \cdot_* \kappa_\beta)$, and multiplying by (24) we recover the natural equation (10).

3.4 An explicit family on a multiplicative circular cylinder

We now apply Proposition 3.6 to the simplest base curve. Let β be the multiplicative unit circle centered at 0_* in the multiplicative plane orthogonal to e_3 (see [1, Section 3]):

$$\beta(t) = (\cos_* t, \sin_* t, 0_*) = (e^{\cos(\text{Int})}, e^{\sin(\text{Int})}, 1), \quad t \in \mathbb{R}_*.$$

It is parametrized by multiplicative arc length, with $\kappa_\beta = 1_*$, $T_\beta = (-_* \sin_* t, \cos_* t, 0_*)$, $N_\beta = (-_* \cos_* t, -_* \sin_* t, 0_*)$ and $B_\beta = e_3$. The convention $B_\beta = -_* V$ of Section 3.2 therefore requires $V = -_* e_3 = (1, 1, e^{-1})$, and the corresponding cylinder is $X(t, z) = (e^{\cos(\text{Int})}, e^{\sin(\text{Int})}, 1/z)$.

Since $\kappa_\beta = 1_*$, equation (21) becomes $(\tan_* \varphi)^* = \tan_* \theta$. Choosing the integration constants suitably (which amounts to a multiplicative translation of the parameter s), we obtain

$$\begin{aligned} \varphi(s) &= \arctan_*(\tan_* \theta \cdot_* s), \\ t(s) &= \cot_* \theta \cdot_* \text{arsinh}_*(\tan_* \theta \cdot_* s) +_* t_0, \\ z(s) &= \cot_* \theta \cdot_* (1 +_* \tan_*^2 \theta \cdot_* s^{2*})^{(1/2)*} +_* z_0, \end{aligned}$$

with constants $t_0, z_0 \in \mathbb{R}_*$. The resulting multiplicative normal helices are

$$\alpha(s) = (\cos_* t(s), \sin_* t(s), -_* z(s)), \quad (25)$$

or, in ordinary arithmetic, writing $\vartheta = \ln \theta$ and $\theta(s) = \cot \vartheta \operatorname{arsinh}(\tan \vartheta \ln s) + \ln t_0$,

$$\alpha(s) = (e^{\cos \vartheta(s)}, e^{\sin \vartheta(s)}, e^{-\cot \vartheta \sqrt{1 + \tan^2 \vartheta \ln^2 s} - \ln z_0}).$$

Since $\cos_*^{2*} \varphi = 1_* /_* (1_* +_* \tan_*^{2*} \theta \cdot_* s^{2*})$, formulas (22) give

$$\begin{aligned} \kappa_\alpha(s) &= \cos_* \theta /_* (\cos_*^{2*} \theta +_* \sin_*^{2*} \theta \cdot_* s^{2*}), \\ \tau_\alpha(s) &= -_* \sin_* \theta \cdot_* \cos_* \theta \cdot_* s /_* (\cos_*^{2*} \theta +_* \sin_*^{2*} \theta \cdot_* s^{2*}), \end{aligned} \quad (26)$$

that is, $\ln \kappa_\alpha = \cos \vartheta / (\cos^2 \vartheta + \sin^2 \vartheta \ln^2 s)$ and $\ln \tau_\alpha = -\sin \vartheta \cos \vartheta \ln s / (\cos^2 \vartheta + \sin^2 \vartheta \ln^2 s)$. In particular $\rho_\alpha = -_* \sin_* \theta \cdot_* s$, in accordance with Corollary 3.7: these curves are congruent to multiplicative rectifying curves. The torsion vanishes only at $s = 0_* = 1$, so Theorem 3.2 applies separately on $0 < s < 1$ and on $s > 1$.

A simpler description is obtained with the new parameter v defined by $\tan_* \theta \cdot_* s = \sinh_*(\tan_* \theta \cdot_* v)$, i.e. $\tan \vartheta \ln s = \sinh(\tan \vartheta \ln v)$. Then $t = v +_* t_0$ and $z = \cot_* \theta \cdot_* \cosh_*(\tan_* \theta \cdot_* v) +_* z_0$, so that

$$\begin{aligned} \alpha(v) &= (\cos_*(v +_* t_0), \sin_*(v +_* t_0), \\ &\quad -_*(\cot_* \theta \cdot_* \cosh_*(\tan_* \theta \cdot_* v) +_* z_0)), \end{aligned} \quad (27)$$

that is, $\alpha(v) = (e^{\cos(\ln v + \ln t_0)}, e^{\sin(\ln v + \ln t_0)}, e^{-\cot \vartheta \cosh(\tan \vartheta \ln v) - \ln z_0})$.

This parameter is not the multiplicative arc length, and Proposition 2.4(iii) yields

$$\begin{aligned} \kappa_\alpha(v) &= \sec_* \theta /_* \cosh_*^{2*}(\tan_* \theta \cdot_* v), \\ \tau_\alpha(v) &= -_* \sinh_*(\tan_* \theta \cdot_* v) /_* \cosh_*^{2*}(\tan_* \theta \cdot_* v), \end{aligned} \quad (28)$$

or $\ln \kappa_\alpha = \sec \vartheta / \cosh^2(\tan \vartheta \ln v)$ and $\ln \tau_\alpha = -\sinh(\tan \vartheta \ln v) / \cosh^2(\tan \vartheta \ln v)$. Figure 1 shows a curve of this family together with its logarithmic image; the exponential character of the curve in the actual coordinates of $\mathbb{E}_*^3$ contrasts with the simple shape of its logarithmic image.

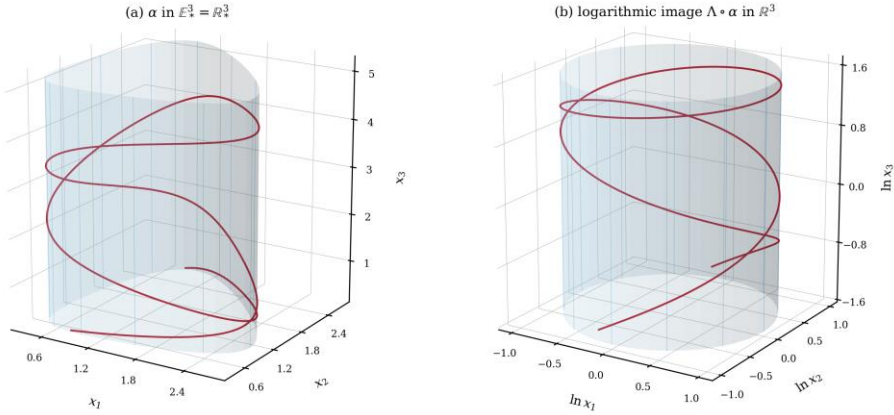


Figure 1. The multiplicative normal helix (27) with $\theta = e^{\pi/36}$, $t_0 = 0_*$, $\ln z_0 = -\cot(\pi/36) - 3/2$ and $e^{-8} \leq v \leq e^8$, drawn on the multiplicative circular cylinder that carries it. (a) The curve in the actual coordinates of $\mathbb{E}_*^3 = \mathbb{R}_*^3$. (b) Its logarithmic image $\Lambda \circ \alpha$, a Euclidean normal helix on a circular cylinder of $\mathbb{R}^3$.

Remark 3.9 (Orientation in the Euclidean example of [13]). The logarithmic image of (27) is the Euclidean curve $\gamma(u) = (\cos(u + u_0), \sin(u + u_0), -\cot\vartheta \cosh(ut\vartheta) - w_0)$, where $u = \ln v$, $u_0 = \ln t_0$ and $w_0 = \ln z_0$, and its curvature and torsion are the logarithms of (28). In [13, Section 2.3] the corresponding Euclidean curves are printed with the opposite sign in the third coordinate, namely with $+\cot\vartheta \sqrt{1 + \tan^2\vartheta s^2} + z_0$ in the arc length parametrization and with $+\cot\vartheta \cosh(t\tan\vartheta) + z_0$ after the change of parameter; that is, they are drawn on the cylinder $\beta(t) + zV$ with $V = e_3$. For the counterclockwise unit circle one has $B_\beta = e_3$, so the convention $T_\beta \times V = N_\beta$ adopted in [13, Section 2.2] actually requires $V = -e_3$. A direct computation shows that the printed curves have the curvature stated in [13], but their torsion is $+\sin\vartheta \cos\vartheta s / (\cos^2\vartheta + \sin^2\vartheta s^2)$ and $+\sinh(t\tan\vartheta) / \cosh^2(t\tan\vartheta)$ respectively, the opposite of the values displayed there; for them the normal $\mathcal{F}$ -constant field orthogonal to the axis is $\cos\vartheta N - \sin\vartheta B$, so that they correspond to the angle $-\vartheta$ rather than ϑ . The formulas of [13] are correct for the reflected curves, whose third coordinate carries a minus sign, which are exactly the logarithmic images of (25) and (27). Accordingly, the curve of $\mathbb{E}_*^3$ obtained from (27) by deleting the outer $_*$ in the third coordinate has torsion $\sinh_*(\tan_*\theta \cdot_* v) /_* \cosh_*^2(\tan_*\theta \cdot_* v)$. The discrepancy is confined to the example and does not affect any theorem of [13]. We have also checked every formula of this section numerically, working directly with the definitions of the multiplicative operations and derivative.

4 Concluding remarks

We have presented the multiplicative counterpart, in $\mathbb{E}_*^3$, of the theory of normal helices associated with Frenet-constant vector fields. The multiplicative Darboux vector and the transport theorem show that the $\mathcal{F}$ -constant fields are precisely the solutions of $W^* = D_\alpha \times_* W$; using a frame adapted to the normal field W_θ , we derived the natural equation of multiplicative normal helices (Theorem 3.2), identified these curves with the curves of multiplicative cylinders whose principal normal keeps a constant angle with the normal of the surface (Theorem 3.5), computed their curvature and torsion (Proposition 3.6) and described explicitly the normal helices of a multiplicative circular cylinder, which turn out to be congruent to multiplicative rectifying curves (Corollary 3.7). The same machinery applies to the osculating and rectifying helices and to $\mathcal{F}$ -constant fields with three nonzero components, which were studied in the Euclidean case in [13].

As explained in Remark 2.9, the coordinatewise logarithm turns the multiplicative theory into the Euclidean one, and the statements above are faithful non-Newtonian counterparts of those in [13]. Their interest lies in the fact that the multiplicative language describes exponential-type curves like the helix in Figure 1(a) by very simple invariants, and in the connection it provides with the recent research on multiplicative curves [1, 5, 9]. Two natural continuations are the study of multiplicative normal helices whose $\mathcal{F}$ -constant field forms with the axis a constant angle different from the multiplicative right angle $e^{\pi/2}$ (in logarithmic terms W_θ describes a curve on the unit sphere, and such a curve makes a constant angle with a fixed direction exactly when its geodesic curvature is constant, which yields the natural equation also in this case), and the analysis of analogous problems in other non-Newtonian geometries [8].

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Chapter 5

Exact and Reproducible Computation of Degree Based Topological Indices

Edge Partitions, M Polynomials, and Validation Methods

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Abstract

Degree-based topological indices are among the most extensively used numerical graph invariants in chemical graph theory. Their definitions are compact, but their reliable evaluation on parametrized graph families is often less straightforward than the final formulas suggest. Incorrect edge partitions, hidden restrictions on parameters, inappropriate use of M-polynomial operators, premature floating-point evaluation, and the absence of independent checks can all produce plausible yet false expressions. This chapter develops a unified and reproducible treatment of seven representative indices: the first and second Zagreb indices, the general Randić index, the atom–bond connectivity index, the geometric–arithmetic index, the Sombor index, and Albertson irregularity. All are placed in the established bond-incident-degree framework generated by a symmetric edge kernel. Four mutually reinforcing representations are examined: direct edge sums, edge-degree partitions, M-polynomials, and adjacency-matrix formulas. A general coefficient-evaluation functional is used to express uniformly both the indices accessible through the standard differential–integral M-polynomial calculus and nonlinear radical kernels requiring extended operators or direct coefficient evaluation. Consistency identities for edge partitions are proved and converted into practical validation tests. Closed formulas are derived for regular and semiregular bipartite graphs, and canonical graph families are used as exact test cases. The principal contribution is an auditable validation methodology comprising structural certificates, independent computational routes, symbolic and numerical checks, common failure modes, and a reproducibility checklist. The central methodological claim is that a closed formula should be regarded as established only after the underlying partition and the resulting value have survived independent structural and computational checks.

Keywords: chemical graph theory; degree-based topological index; edge-degree partition; M-polynomial; Zagreb index; Randić index; Sombor index; graph irregularity; exact computation; reproducibility

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1. Introduction

A molecular graph represents atoms by vertices and covalent bonds by edges, with chemical qualifications added or suppressed according to the modelling objective. Once a molecular structure has been converted into a graph, a topological index assigns a numerical invariant to that graph. The resulting number is intended to compress selected structural information and may subsequently be used in classification, extremal analysis, or quantitative structure–property and structure–activity investigations. The classical literature contains distance-based, spectral, information-theoretic, and degree-based descriptors; the present chapter concerns the last class.

Vertex degree is local information. Nevertheless, the distribution of degrees across adjacent vertices encodes branching, local heterogeneity, and the way high- and low-degree sites are connected. This observation lies behind the Zagreb indices, the Randić index, the atom–bond connectivity (ABC) index, the geometric–arithmetic (GA) index, and many later descriptors. The Sombor index recasts the two endpoint degrees as a Euclidean vector, while Albertson irregularity measures their absolute disparity. These indices have different mathematical forms and different historical motivations, but they share a single edge-local architecture.

The computational literature often proceeds graph family by graph family: vertices are classified, edges are partitioned by endpoint degrees, and the desired sums are evaluated. That approach is efficient when correct. It is also fragile. A missing edge class changes every index derived from the same partition; an incorrect boundary count may remain invisible after algebraic simplification; and a formula verified only numerically for one parameter value may conceal an exceptional case. The M-polynomial provides a powerful compression of the edge-degree partition, but it does not remove the need to establish that partition. Moreover, statements that “all degree-based indices follow by operators” require qualification: ordinary differential and integral operators naturally realize polynomial and certain rational functions of the endpoint degrees, whereas radical kernels require a broader coefficient-evaluation mechanism.

The bond-incident-degree (BID) terminology is not introduced here. It belongs to the established bond-additive modelling tradition initiated systematically by Vukičević and Gašperov [26] and subsequently developed in a substantial extremal literature; see the recent survey by Ali, Gutman, and Furtula [29]. The present chapter uses that existing framework as its common language rather than claiming it as a new construction.

This chapter has four objectives. First, it places seven important indices inside the established BID functional. Second, it proves equivalence among

direct, partition, polynomial, and matrix formulations. Third, it separates exact symbolic derivation from numerical approximation and develops independent validation identities. Fourth, and most importantly, it turns these results into a reproducible workflow that can be implemented in any transparent graph-computation environment.

The emphasis is therefore methodological rather than encyclopedic. No finite chapter can reproduce the full literature on degree-based descriptors. The references selected here cover the foundational definitions, major unifying treatments, and computational tools directly needed for the framework. Newer variants—such as reduced, average, and elliptic Sombor-type indices or neighborhood-degree polynomials—can be incorporated by extending the kernel and the underlying local data, but they are deliberately kept outside the main set so that the central theory remains precise.

2. Preliminaries and the BID Framework

Throughout, $G = (V, E)$ denotes a finite, simple, undirected graph with $n = |V|$, $m = |E|$, minimum degree δ , and maximum degree Δ . The degree of $v \in V$ is denoted by $d(v)$. Unless stated otherwise, isolated vertices are allowed in the graph but do not contribute to an edge sum. When a kernel contains division by degrees, its arguments are endpoint degrees and hence are positive.

Following the established BID convention [26,29], let $f: \{1, \dots, \Delta\}^2 \rightarrow \mathbb{R}$ be symmetric, so that $f(i, j) = f(j, i)$. The BID index generated by f is

$$I_f(G) = \sum_{uv \in E(G)} f(d(u), d(v)).$$

The symmetry of f makes the definition independent of an orientation of the edges. Equation (1) is the common computational core of the indices considered below.

2.1 Seven representative indices

The first Zagreb index may be written in vertex or edge form:

$$M_1(G) = \sum_{v \in V} d(v)^2 = \sum_{uv \in E} (d(u) + d(v)).$$

The second Zagreb index is

$$M_2(G) = \sum_{uv \in E} d(u)d(v).$$

The general Randić index, for real α , is

$$R_\alpha(G) = \sum_{uv \in E} (d(u)d(v))^\alpha.$$

The classical connectivity index corresponds to $\alpha = -1/2$. The atom–bond connectivity index is

$$ABC(G) = \sum_{uv \in E} \sqrt{\frac{d(u) + d(v) - 2}{d(u)d(v)}}.$$

The geometric–arithmetic index is

$$GA(G) = \sum_{uv \in E} \frac{2\sqrt{d(u)d(v)}}{d(u) + d(v)}.$$

The Sombor index is

$$SO(G) = \sum_{uv \in E} \sqrt{d(u)^2 + d(v)^2}.$$

Finally, Albertson irregularity is

$$Alb(G) = \sum_{uv \in E} |d(u) - d(v)|.$$

Thus (2)–(8) arise from the following kernels.

The corresponding edge kernels are

- $M_1: f(i, j) = i + j$;
- $M_2: f(i, j) = ij$;
- $R_\alpha: f(i, j) = (ij)^\alpha$;
- $ABC: f(i, j) = \sqrt{(i + j - 2)/(ij)}$;
- $GA: f(i, j) = 2\sqrt{ij}/(i + j)$;
- $SO: f(i, j) = \sqrt{i^2 + j^2}$;
- $Alb: f(i, j) = |i - j|$.

The list reveals a computational distinction. Polynomial kernels can be obtained from differential operators acting on a generating polynomial. Reciprocal monomials can be obtained by integral operators. The radical and absolute-value kernels are equally legitimate BID kernels, but they generally fall outside a finite calculus made solely of those standard operators.

3. Edge-Degree Partitions

For integers $1 \leq i \leq j \leq \Delta$, define

$$m_{ij}(G) = |\{uv \in E: \{d(u), d(v)\} = \{i, j\}\}|.$$

The collection $\{m_{ij}\}$ is the edge-degree partition of G . It records how many edges join each unordered pair of degree classes.

Theorem 1 (partition evaluation). For every symmetric kernel f ,

$$I_f(G) = \sum_{1 \leq i \leq j \leq \Delta} m_{ij}(G) f(i, j).$$

Proof. The sets of edges counted by m_{ij} are pairwise disjoint and their union is E . On every edge in the (i, j) -class, the summand in (1) equals $f(i, j)$. Summing the constant contribution over each class and then over all classes gives (10). ▀

Theorem 1 turns seven separate computations into one structural task: determine m_{ij} correctly. Once the partition is known, every BID index follows by changing only the kernel.

3.1 Necessary consistency identities

Let

$$n_i = |\{v \in V: d(v) = i\}|.$$

The following identities are essential audit conditions.

Proposition 2 (partition consistency). Every valid edge-degree partition satisfies

$$\sum_{1 \leq i \leq j \leq \Delta} m_{ij} = m,$$

and, for each $i \geq 1$,

$$in_i = 2m_{ii} + \sum_{j < i} m_{ji} + \sum_{j > i} m_{ij}.$$

Consequently,

$$\sum_{i=1}^{\Delta} i n_i = 2m.$$

Proof. Equation (12) follows because the edge classes partition E . To prove (13), count incidences between degree- i vertices and edges. There are in_i such incidences. Every (i, i) -edge contributes two incidences, while every (i, j) -edge with $j \neq i$ contributes one. Summing (13) over i counts each edge twice and yields (14), the handshaking lemma. ▀

Equations (12)–(14) are necessary, not sufficient. A fabricated nonnegative table can satisfy all three and still fail to be graph-realizable. Nevertheless, they detect most transcription and boundary-count errors encountered in formula derivations. A stronger check compares a proposed partition with one produced independently from an explicit adjacency representation for several admissible parameter values.

3.2 Direct formulas from the partition

Substitution into (10) gives

$$\begin{aligned} M_1(G) &= \sum_{i \leq j} m_{ij} (i + j), \\ M_2(G) &= \sum_{i \leq j} m_{ij} ij, \\ R_\alpha(G) &= \sum_{i \leq j} m_{ij} (ij)^\alpha, \\ ABC(G) &= \sum_{i \leq j} m_{ij} \sqrt{\frac{i + j - 2}{ij}}, \\ GA(G) &= \sum_{i \leq j} m_{ij} \frac{2\sqrt{ij}}{i + j}, \\ SO(G) &= \sum_{i \leq j} m_{ij} \sqrt{i^2 + j^2}, \\ Alb(G) &= \sum_{i \leq j} m_{ij} |i - j|. \end{aligned}$$

Equation (15) should normally be the first displayed result after a partition table. It makes the substitution transparent and reduces the risk introduced by expanding radicals or rational expressions too early.

4. The M-Polynomial and General Coefficient Evaluation

Deutsch and Klavžar introduced the M-polynomial

$$M(G; x, y) = \sum_{1 \leq i \leq j \leq \Delta} m_{ij}(G) x^i y^j.$$

It is a lossless encoding of the edge-degree partition. In particular, the coefficient of $x^i y^j$ is m_{ij} , and $M(G; 1, 1) = m$.

4.1 Coefficient evaluation

For a symmetric kernel f , define a linear functional on polynomials supported on positive bidegrees by

$$\mathcal{L}_f \left(\sum_{i \leq j} a_{ij} x^i y^j \right) = \sum_{i \leq j} a_{ij} f(i, j).$$

Theorem 3 (coefficient-functional M-polynomial representation). For every BID kernel f ,

$$I_f(G) = \mathcal{L}_f[M(G; x, y)].$$

Proof. Apply (17) to (16) and invoke Theorem 1. ▀

The importance of (18) is conceptual. The M-polynomial determines every degree-based index whose summand depends only on the unordered pair of endpoint degrees. No special differential identity is required for this determinacy. Operator formulas are convenient realizations of $\mathcal{L}_f$ for particular kernels, not the definition of what the polynomial contains.

4.2 Differential and integral operator calculus

Let

$$D_x = x \frac{\partial}{\partial x}, \quad D_y = y \frac{\partial}{\partial y},$$

and

$$S_x F(x, y) = \int_0^x \frac{F(t, y)}{t} dt, \quad S_y F(x, y) = \int_0^y \frac{F(x, t)}{t} dt.$$

On a monomial, these operators satisfy

$$D_x(x^i y^j) = i x^{i-1} y^j, \quad S_x(x^i y^j) = \frac{1}{i} x^i y^j,$$

with analogous formulas in y . Hence

$$\begin{aligned} M_1(G) &= (D_x + D_y)M \Big|_{x=y=1}, \\ M_2(G) &= D_x D_y M \Big|_{x=y=1}, \end{aligned}$$

and, for a positive integer k ,

$$R_k(G) = (D_x D_y)^k M \Big|_{x=y=1}.$$

For reciprocal integer powers,

$$R_{-k}(G) = (S_x S_y)^k M \Big|_{x=y=1}.$$

The classical Randić index $R_{-1/2}$ is not produced by an integer iteration of $S_x S_y$. It is, however, recovered exactly through (17) with $f(i, j) = (ij)^{-1/2}$. The same coefficient-functional method gives ABC , GA , SO , and Alb without requiring a separate derivation operator for each kernel.

Remark 4 (standard and extended operator calculi). The operators D_x, D_y, S_x, S_y and their use in extracting degree-based indices are part of the original M-polynomial calculus of Deutsch and Klavžar [7]. A finite expression built only from these operators, addition, scalar multiplication, and evaluation at $(1,1)$ naturally produces kernels assembled from integral powers of i and j . This limitation has already motivated extended constructions. In particular, Kumar and Das [27] developed closed derivation formulas for Sombor-type indices by augmenting the M-polynomial operator apparatus, while Barman and Das [28] used fractional and composite operators for the hyperbolic Sombor index. The coefficient functional $\mathcal{L}_f$ in (17) is not presented as the first attempt to address radical kernels. Its role here is different: it provides a direct, kernel-independent evaluation map that covers arbitrary symmetric endpoint-degree functions without designing a new operator chain for every radical expression. Extended operators may be preferable when an explicit operational formula is

the objective; coefficient evaluation is preferable when generality, transparency, and computational auditability are the primary concerns.

5. Matrix Representations

Let $A = (a_{uv})$ be the adjacency matrix of G , let $\mathbf{d} = (d_1, \dots, d_n)^T = A\mathbf{1}$, and let $D = \text{diag}(d_1, \dots, d_n)$. Since every undirected edge appears twice in a double sum,

$$I_f(G) = \frac{1}{2} \sum_{u=1}^n \sum_{v=1}^n a_{uv} f(d_u, d_v).$$

This representation is useful because it is derived from an object—the adjacency matrix—that can be constructed independently of a symbolic edge partition. For the Zagreb indices,

$$M_1(G) = \mathbf{d}^T \mathbf{d} = \text{tr}(D^2),$$

And

$$M_2(G) = \frac{1}{2} \mathbf{d}^T A \mathbf{d}.$$

Similarly,

$$\text{Alb}(G) = \frac{1}{2} \sum_{u,v} a_{uv} |d_u - d_v|,$$

and

$$SO(G) = \frac{1}{2} \sum_{u,v} a_{uv} \sqrt{d_u^2 + d_v^2}.$$

Equation (26) is not computationally intended as a dense n^2 procedure. With adjacency lists or sparse matrices it is evaluated over nonzero entries and therefore has linear time in $n + m$, including degree construction. Its primary methodological value is independence: matrix-based code need not reuse the same partition routine whose output is being tested.

6. Closed Results for Structurally Important Graph Classes

The general framework becomes especially transparent on regular and semiregular bipartite graphs.

6.1 Regular graphs

Suppose G is r -regular on n vertices. Then $m = nr/2$ and the only edge class is (r, r) .

Corollary 5. For an r -regular graph,

$$\begin{aligned} M_1(G) &= nr^2, \\ M_2(G) &= \frac{nr^3}{2}, \\ R_\alpha(G) &= \frac{nr}{2} r^{2\alpha}, \\ ABC(G) &= \frac{n}{2} \sqrt{2r-2}, \\ GA(G) &= \frac{nr}{2}, \\ SO(G) &= \frac{nr^2}{\sqrt{2}}, \\ Alb(G) &= 0. \end{aligned}$$

Proof. Substitute $m_{rr} = nr/2$ into (15). For example, $ABC = (nr/2)\sqrt{(2r-2)/r^2} = (n/2)\sqrt{2r-2}$. ▫

The identity $GA(G) = m$ for regular graphs also follows from the arithmetic–geometric mean inequality: every edge term in (6) equals one precisely when its endpoint degrees are equal. More generally, $GA(G) \leq m$, with equality if every connected component containing an edge is regular.

6.2 Semiregular bipartite graphs

Let $G = (X, Y; E)$ be bipartite, with every vertex in X of degree r and every vertex in Y of degree s . Then all m edges have degree pair (r, s) .

Corollary 6. For an (r, s) -semiregular bipartite graph,

$$\begin{aligned}
M_1(G) &= m(r + s), \\
M_2(G) &= mrs, \\
R_\alpha(G) &= m(rs)^\alpha, \\
ABC(G) &= m \sqrt{\frac{r + s - 2}{rs}}, \\
GA(G) &= m \frac{2\sqrt{rs}}{r + s}, \\
SO(G) &= m\sqrt{r^2 + s^2}, \\
Alb(G) &= m|r - s|.
\end{aligned}$$

Complete bipartite graphs and stars are immediate special cases. These formulas are also valuable unit tests because each graph has a one-term M-polynomial, yet the two endpoint degrees need not coincide.

6.3 Bounds and diagnostic consequences

Several elementary inequalities provide additional checks. For every edge with positive endpoint degrees,

$$0 < \frac{2\sqrt{d(u)d(v)}}{d(u) + d(v)} \leq 1,$$

so $0 < GA(G) \leq m$ whenever $m > 0$. Furthermore,

$$\sqrt{d(u)^2 + d(v)^2} \geq \frac{d(u) + d(v)}{\sqrt{2}},$$

which yields

$$SO(G) \geq \frac{M_1(G)}{\sqrt{2}}.$$

Equality in (34), and hence in (35), holds exactly when the endpoint degrees are equal on every edge. Finally,

$$|d(u) - d(v)| \leq \sqrt{d(u)^2 + d(v)^2},$$

implies $Alb(G) \leq SO(G)$. These inequalities are not substitutes for exact verification, but a computed value violating one of them is certainly wrong.

7. Canonical Test Graphs

A reproducible implementation should be tested on graph families whose partitions and indices can be derived by inspection. Let $P_n, C_n, K_n, S_n = K_{1,n-1}$, and $K_{p,q}$ denote the path, cycle, complete graph, star, and complete bipartite graph, respectively.

For $n \geq 3$,

$$M(P_n; x, y) = 2xy^2 + (n - 3)x^2y^2.$$

The two terminal edges are of type (1,2); the remaining $n - 3$ edges are of type (2,2). For $n \geq 3$,

$$M(C_n; x, y) = nx^2y^2.$$

For $n \geq 2$,

$$M(K_n; x, y) = \binom{n}{2} x^{n-1} y^{n-1},$$

And

$$M(S_n; x, y) = (n - 1)xy^{n-1}.$$

Finally,

$$M(K_{p,q}; x, y) = pq x^{\min(p,q)} y^{\max(p,q)}.$$

These expressions expose boundary cases. Formula (37) is valid for P_3 , where the coefficient $n - 3$ vanishes, but P_2 instead has $M(P_2; x, y) = xy$. A formula stated without its parameter range is incomplete even if its algebra is otherwise correct.

7.1 Exact values for selected tests

The following exact benchmark values use $\alpha = -1/2$:

- P_4 : $M_1 = 10$, $M_2 = 8$, $R_{-1/2} = \sqrt{2} + 1/2$, $ABC = 3/\sqrt{2}$, $GA = 4\sqrt{2}/3 + 1$, $SO = 2\sqrt{5} + 2\sqrt{2}$, and $Alb = 2$.
- C_5 : $M_1 = 20$, $M_2 = 20$, $R_{-1/2} = 5/2$, $ABC = 5/\sqrt{2}$, $GA = 5$, $SO = 10\sqrt{2}$, and $Alb = 0$.
- K_4 : $M_1 = 36$, $M_2 = 54$, $R_{-1/2} = 2$, $ABC = 4$, $GA = 6$, $SO = 18\sqrt{2}$, and $Alb = 0$.

- S_5 : $M_1 = 20$, $M_2 = 16$, $R_{-1/2} = 2$, $ABC = 2\sqrt{3}$, $GA = 16/5$, $SO = 4\sqrt{17}$, and $Alb = 12$.
- $K_{2,3}$: $M_1 = 30$, $M_2 = 36$, $R_{-1/2} = \sqrt{6}$, $ABC = 6/\sqrt{2}$, $GA = 12\sqrt{6}/5$, $SO = 6\sqrt{13}$, and $Alb = 6$.

For P_4 , the ABC entry simplifies further: the two (1,2)-edges each contribute $1/\sqrt{2}$, and the single (2,2)-edge also contributes $1/\sqrt{2}$, hence $ABC(P_4) = 3/\sqrt{2}$. The class-by-class expression is intentionally diagnostic, and its simplified and unsimplified forms must agree. This example illustrates why retaining a partition-level expression before simplification improves auditability.

8. Exact Algorithms and Computational Complexity

Assume that a graph is supplied by adjacency lists. Degrees are computed in $O(n + m)$ time. A single traversal of the undirected edges then produces the partition dictionary keyed by $(\min(d(u), d(v)), \max(d(u), d(v)))$.

Algorithm 1: Edge-degree partition

```

input: simple undirected graph  $G=(V,E)$ 
degree[v] <- length(adjacency[v]) for every v
partition <- empty map with default value 0
for each undirected edge {u,v} in E do
  i <- min(degree[u], degree[v])
  j <- max(degree[u], degree[v])
  partition[(i,j)] <- partition[(i,j)] + 1
return partition

```

The running time is $O(n + m)$, and the map contains at most $\Delta(\Delta + 1)/2$ keys and at most m nonzero keys. Once the partition contains t nonzero classes, any one index in (15) is computed in $O(t)$ time. Thus computing many indices from one partition is substantially cheaper than repeatedly traversing all edges.

Algorithm 2: Independent direct evaluation

```

input: graph  $G=(V,E)$ , symmetric kernel f
degree[v] <- length(adjacency[v]) for every v
value <- 0
for each undirected edge {u,v} in E do
  value <- value + f(degree[u], degree[v])
return value

```

The two algorithms should not call a shared “class contribution” function during validation. Otherwise, an error in that shared function can make both

routes agree incorrectly. Independence is a design property, not merely the fact that two printed expressions look different.

8.1 Exact arithmetic

The counts n_i, m_{ij}, M_1, M_2 , and Alb are integers. They should remain integers throughout the computation. Rational exponents and square-root kernels often produce algebraic numbers. When degrees are symbolic parameters, an expression such as $\sqrt{(r+s-2)/(rs)}$ should not be converted to decimal form. When degrees are concrete integers, a computer algebra system can simplify radicals exactly, subject to correct assumptions.

Floating-point values are appropriate for presentation or for comparison with external software, not as the primary derivation. Equality tests should combine absolute and relative tolerances:

$$|a - b| \leq \varepsilon_{\text{abs}} + \varepsilon_{\text{rel}} \max(|a|, |b|).$$

The tolerance must be reported, together with the numeric precision and software version. A fixed absolute tolerance alone is unsuitable when graph size and index magnitude vary widely.

9. A Layered Validation Protocol

Reliable closed formulas require checks at several logically distinct levels.

9.1 Structural validation

Before evaluating any index, verify:

1. all partition counts are nonnegative integers for every admissible parameter value;
2. the counts sum to (m) as in (12);
3. every degree-class incidence equation (13) holds;
4. the degree counts satisfy the handshaking identity (14);
5. boundary parameter values do not merge, remove, or create edge classes unexpectedly.

The incidence equations are especially informative. If the total edge count is correct but an edge has been moved from class (i, j) to (i, k) , equation (12) will not detect the mistake, whereas equations (13) for classes j and k generally will.

9.2 Representation-level validation

For a graph instance constructed independently, compare at least three routes:

$$\text{edge loop} \quad \leftrightarrow \quad \text{partition sum} \quad \leftrightarrow \quad \mathcal{L}_f[M].$$

For M_1 and M_2 , also compare the vertex and matrix formulas (27)–(28). Agreement among algebraically equivalent formulas is meaningful only if their input data were generated independently. For example, an M-polynomial assembled from the same incorrect partition is not an independent validation of that partition; it validates only the subsequent substitution.

9.3 Family-level validation

For a parametrized family G_k , test:

- the smallest admissible (k);
- the next one or two values, where boundary structure may still be exceptional;
- at least one moderate value;
- random admissible values when graph generation is available.

Symbolic identity checking should follow numeric spot checks, not replace them. A computer algebra system can confirm that two formulas simplify to zero under stated assumptions, but it cannot determine that the original combinatorial partition represented the intended graph.

9.4 Cross-index diagnostics

The same partition produces all seven indices, so relations such as (33)–(36) become inexpensive sanity checks. Other useful identities include

$$M_1(G) = \sum_i i^2 n_i$$

And

$$M_1(G) = \sum_{i \leq j} m_{ij} (i + j).$$

These two expressions depend on different summaries—vertex degree counts and edge-degree counts—and their agreement is therefore structurally informative.

9.5 Validation certificate

For reproducible publication, each reported family can be accompanied by a compact certificate containing:

- the admissible parameter domain;
- n , m , and the nonzero n_i ;

- the complete nonzero list of m_{ij} ;
- residuals of (12)–(14);
- the M-polynomial;
- exact outputs of (15);
- test instances and graph-generation rules;
- software, version, precision, and source-code checksum.

This certificate is small compared with the article itself, yet it exposes nearly every piece of information needed to reproduce the calculation.

10. Reproducible Computational Design

Reproducibility is not achieved merely by attaching code. The code must be organized so that it does not silently reproduce the same assumption through every route.

10.1 Recommended software architecture

A transparent implementation can be divided into four modules:

1. **Graph construction.** Generates vertices and edges from explicit parameters and rejects inadmissible inputs.
2. **Structural extraction.** Computes n_i , m_{ij} , n , and m from the graph instance.
3. **Index evaluation.** Contains one direct edge evaluator and a separate partition evaluator implementing the kernels defined in Section 2.1.
4. **Validation and reporting.** Tests identities, compares exact expressions, evaluates controlled decimal approximations, and exports a machine-readable certificate.

The partition should be stored with canonical unordered keys (i, j) where $i \leq j$. A common implementation error is to count (i, j) and (j, i) separately. Edge iteration must likewise ensure that each undirected edge is visited exactly once.

10.2 Symbolic assumptions

Computer algebra systems simplify radicals according to assumptions. For positive integers r, s , one may simplify $\sqrt{r^2} = r$, but without positivity the correct result is $|r|$. Therefore parameter declarations belong to the mathematical model, not merely to software syntax. Every symbolic derivation should state integrality, positivity, ordering, and lower bounds explicitly.

10.3 Machine-readable output

A minimal JSON-like record for one graph instance is

```
{
  "graph_family": "family name",
  "parameters": { ... },
  "order": n,
  "size": m,
  "degree_counts": { "i": n_i, ... },
  "edge_degree_counts": { "i,j": m_ij, ... },
  "indices_exact": { ... },
  "indices_numeric": { ... },
  "checks": { "edge_sum": true, "incidences": true, ... },
  "software": { "language": ..., "version": ... }
}
```

Exact values should be serialized as unambiguous strings when the interchange format lacks symbolic algebra. Decimal approximations should be additional fields rather than replacements.

10.4 Reproducibility checklist

Before submission, the following questions should all receive affirmative answers:

- Is the graph simple, finite, and undirected, or are departures explicitly defined?
- Are the parameter range and exceptional cases stated?
- Are vertex and edge counts proved or independently checked?
- Does the partition satisfy every incidence equation?
- Is the M-polynomial written with canonical exponents $i \leq j$?
- Are exact expressions preserved through derivation?
- Are at least two genuinely independent computational routes used?
- Are tolerances, precision, package versions, and random seeds reported?
- Can a reader regenerate every table from supplied data and code?
- Are claims about chemical predictivity separated from purely graph-theoretic computation?

The final question is important. An index can be computed correctly without being empirically useful for a particular property. Predictive performance requires a separate statistical design, molecular data, descriptor comparison, validation split, and uncertainty analysis. Exact graph computation is a necessary foundation, not evidence of QSPR efficacy by itself.

11. Common Failure Modes

11.1 Correct totals with an incorrect partition

Checking only $\sum m_{ij} = m$ is inadequate. Two edge classes can be miscounted by equal and opposite amounts. Degree-incidence equations and independent enumeration are needed.

11.2 Circular M-polynomial verification

Constructing $M(G; x, y)$ from a proposed partition and then recovering the same index from that polynomial proves only algebraic consistency. Since the coefficients are the partition counts, this route contains no new combinatorial evidence.

11.3 Undefined operator notation

Writing a formal square root of a differential operator without specifying its domain and action is not a derivation. Radical indices are evaluated rigorously by the coefficient functional (17), or by a carefully defined functional calculus beyond the elementary M-polynomial operators.

11.4 Premature decimalization

Replacing radicals by decimals hides simplifications and makes equality dependent on tolerance. Exact and approximate columns should be distinct.

11.5 Missing boundary cases

Parametrized structures often change at their smallest sizes. Edge classes may disappear, coincide, or acquire negative symbolic “counts” if a generic expression is extrapolated too far. The admissible domain must be derived from the construction.

11.6 Unsupported chemical interpretation

Historical use of a descriptor in chemical modelling does not establish predictive validity for a new molecular family or target property. A mathematically rigorous chapter should describe structural sensitivity—such as branching or degree imbalance—without converting it into an untested empirical claim.

12. Further Extensions

The framework extends immediately to any symmetric endpoint-degree kernel. Modified Sombor variants, the symmetric division-degree index, forgotten index, inverse degree indices, and many other BID descriptors require only a new f in (1) and (17). Two qualifications are necessary.

First, indices depending on neighbor-degree sums, distances, eccentricities, edge neighborhoods, or spectral data are not determined by the ordinary edge-degree partition. They require enriched polynomials or different structural summaries. Second, two nonisomorphic graphs may have the same M-polynomial and hence the same value for every BID index. Thus the polynomial is complete for endpoint-degree sums but not a complete graph invariant.

This limitation can be stated formally. If $M(G; x, y) = M(H; x, y)$, then Theorem 3 implies

$$I_f(G) = I_f(H) \quad \text{for every symmetric endpoint-degree kernel } f.$$

Consequently, adding more BID indices cannot distinguish such a pair. Descriptor selection should therefore consider informational redundancy: several indices derived from the same small partition may be strongly dependent, even when their formulas appear different.

A promising computational direction is to treat the partition vector

$$\mathbf{m}(G) = (m_{11}, m_{12}, \dots, m_{\Delta\Delta})$$

as the primary exact representation. Every fixed BID index is then a linear functional of $\mathbf{m}$, although its kernel values may be nonlinear functions of i, j . This viewpoint separates graph enumeration from descriptor choice, facilitates vectorized evaluation, and makes sensitivity to each edge class explicit.

13. Conclusion

Degree-based topological indices share a simple but powerful structure: they aggregate a symmetric function of the degrees at the ends of each edge. Within the established BID framework, the edge-degree partition is the decisive combinatorial object, the M-polynomial is its algebraic encoding, and the adjacency representation supplies an independent computational route. The coefficient-evaluation functional used here makes the relation explicit for arbitrary BID kernels and clarifies the relationship between the standard differential–integral calculus, recent extended operators for radical kernels, and direct coefficient evaluation.

The mathematical results lead directly to a validation discipline. A proposed formula should satisfy edge and incidence identities, agree with direct evaluation on independently generated graphs, preserve exact arithmetic, respect parameter boundaries, and pass cross-index inequalities. Regular and semiregular bipartite graphs supply closed benchmark families, while paths, cycles, complete graphs, stars, and complete bipartite graphs furnish compact unit tests.

The broader lesson, and the principal contribution of this chapter, is methodological. Concise closed forms are the end of a calculation, not evidence of its correctness. Reproducible degree-based graph computation requires the derivation, structural data, implementation, and verification record to support one another without circularity. When those components are made explicit, the resulting topological-index analysis becomes easier to audit, extend, and reuse across chemical graph families.

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