RJC

RASĀYAN *J. Chem.*
Vol. 18 | No. 2 |1083-1089| April - June | 2025
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

INVESTIGATION OF SILYLMETHANOL UNDERGOING REARRANGEMENT REACTIONS USING DFT

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ABSTRACT

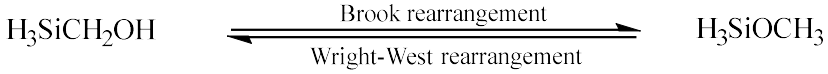
The present study sheds light on the two rearrangement reactions of silylmethanol using the B3LYP hybrid functional at the 6-311++G(d,p) basis set. Two paths, the formation of methoxysilane and methylsilanol from the two isomeric conformers of silylmethanol, are studied. The transition states for the two conformers of silylmethanol and the two paths that are studied in detail are obtained with only one negative frequency. In both paths, a penta-coordinated (Si) transition state with two three-membered rings is obtained. Our calculations of electronic charge density and Laplacian density supported the observations of bond formation as well as dissociation in the two rearrangement reactions. Natural atomic charges obtained after calculations also emphasized the electron density redistribution among the various atoms. The reaction profile along the IRC is calculated for both paths. Energetics of the two rearrangement reactions show that the formation of methylsilanol is more exothermic as compared to that of methoxysilane. The results of our study are in accordance with the previous theoretical calculations of the ab initio method.

Keywords: B3LYP, Isomeric Conformers, Methoxysilane, Methylsilanol, Organosilicon, Transition State, Intrinsic Reaction Coordinate.

RASĀYAN *J. Chem.*, Vol. 18, No. 2, 2025

INTRODUCTION

The chemistry of organosilicon compounds, i.e., a group of compounds that consist of a functional group bonded to an organic part of a molecule that is attached to silicon through a Si-C bond, plays a key role in organosilicon chemistry.[1] These carbofunctional organosilicon compounds are vital building blocks in a variety of materials. They are used in the synthesis of novel organosilicon compounds, polymers, and adjuvants in the agricultural industry, etc.[2] They are also used comprehensively as intermediates in various synthesis processes. Moreover, they also act as effective catalysts in different types of chemical reactions such as isomerization, polymerization, and reduction.[3] Since it is known that these compounds can either undergo [1,2] rearrangement or decomposition under different chemical conditions, such as the presence of a strong base or a reaction initiated by peroxide.[4-7] So, understanding rearrangement reactions in these compounds becomes important for their effective control and use in organosilicon chemistry. Brook and Wright-West rearrangements are well-known [1, n] silyl migration reactions from carbon to oxygen in α-silyl alcohol and from oxygen to carbon in alkoxy silanes, respectively.



The [1,2] rearrangements of silylmethanol have been the subject of experimental and theoretical studies.[8-11] The ab initio studies of the silylmethanol have suggested the formation of penta-coordinated Si with two three-membered rings as an intermediate.[8-10,12,13] However, DFT studies for the silylmethanol rearrangements are not reported. The present study investigates the two rearrangement reactions of silylmethanol via DFT calculations to shed more light on the energetics and to understand bonding characteristics in the considered reactions.

EXPERIMENTAL

Method of Calculations

In the present study, density functional calculations were performed using B3LYP, a hybrid functional. All the geometry optimizations of the reactants, transition states (TS), and products were carried out at the

http://doi.org/10.31788/RJC.2025.1829264

B3LYP/6-311++G(d,p) level.[14-16] To understand the reaction mechanism of the two rearrangement reactions under study, bonding characteristics, i.e., ρ_c (electronic charge density) and $\nabla^2\rho_c$ (Laplacian density), were calculated.[17] Harmonic vibrational frequencies (scaled by a factor of 0.9679) were calculated to determine the type of stationary points.[18] Activation energy (E_a) and energy of reaction (ΔE) were calculated at three different levels of calculations, viz., B3LYP, HF, and MP2, with the same basis set that has been employed at the B3LYP level of theory.[19-22] Investigation of two reaction paths was carried out via intrinsic reaction coordinate (IRC) at the B3LYP/6-311++G(d,p) level. NBO analysis was carried out, and natural atomic charges were also reported to analyze the charge transfer between the different atoms during the reaction. All the calculations were done using the GAUSSIAN-09 package, based on quantum chemistry.

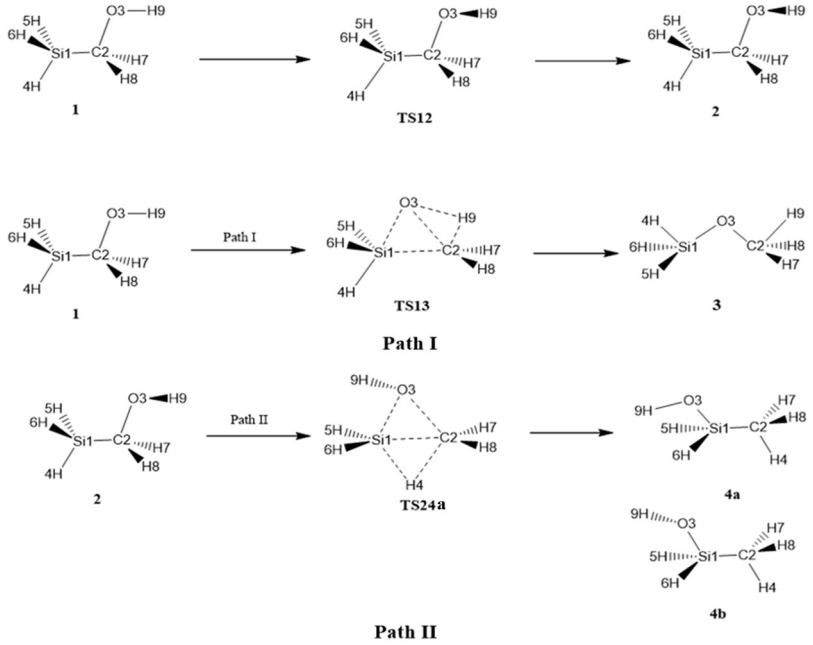


Fig.-1: [1,2] Rearrangement of Silylmethanol to Methoxysilane and Methylsilanol

RESULTS AND DISCUSSIONS

Structures of Reactants, Transition States, and Products

Geometrical parameters of all the reactants, TS, and products are tabulated in Table-1, that are obtained after fully optimizing the geometries of the same. The silylmethanol rearrangement reactions could be proposed by two paths (I and II) as shown in Fig.-1. Silylmethanol, the reactant, is found to be present in two stable geometries (‘1’ and ‘2’), which are isomeric conformers. Geometry ‘1’ is more stable than ‘2’, but only by 0.7 kcal mol^{-1}. ‘1’ isomerizes to ‘2’ through ‘TS12’ with a small energy barrier of 0.9 kcal mol^{-1} (Table-6). ‘TS12’ will not be discussed in detail as we are more interested in the two rearrangement reactions of silylmethanol. In path I, a Brook rearrangement has taken place with the migration of the silyl group of ‘1’ from C to O atom via ‘TS13’, forming methoxysilane (‘3’). In path II, migration of the hydroxyl group of ‘2’ from C to Si atom through ‘TS24’ has taken place with the formation of methylsilanol (‘4a’). The two reaction paths have been discussed in detail concerning structural changes and bonding characteristics.

Table-1: Selected Geometric Parameters using B3LYP/6-311++G(d,p)

System[b]	1	2	3	4a	4b	TS12	TS13	TS24a
Lengths (in Å)								
Si1-O3	-	-	1.662	1.674	1.674	2.755	1.704	1.841
Si1-C2	1.901	1.907	-	1.866	1.876	1.905	2.688	1.818
C2-O3	1.435	1.438	1.421	-	-	1.443	1.654	2.226
Si1-H4	1.488	1.488	1.478	-	-	1.490	1.474	1.618
O3-H9	0.962	0.962	-	0.959	0.959	0.960	1.113	0.966
C2-H9	-	-	1.091	-	-	1.978	1.405	2.796

C2-H7	1.099	1.092	1.097	1.093	1.093	1.100	1.087	1.090
C2-H8	1.099	1.099	1.097	1..093	1.094	1.100	1.080	1.090
Si1-H5	1.484	1.484	1.489	1.490	1.480	1.484	1.481	1.487
Si1-H6	1.484	1.489	1.489	1.490	1.490	1.486	1.483	1.480
C2-H4	-	-	-	1.094	1.095	-	-	2.228
Angles (in Degrees)								
Si1-O3-C2	-	-	124.7	-	-	40.5	106.4	52.1
Si1-C2-O3	108.0	113.0	-	-	-	110.0	37.5	53.0
H4-Si1-C2	107.9	110.0	-	-	110.8	109.4	88.6	80.6
H5-Si1-C2	110.4	108.8	-	111.1	110.8	110.1	89.2	120.0
H6-Si1-C2	110.4	108.8	-	111.1	109.0	109.7	94.4	121.1
H7-C2-Si1	109.4	109.6	-	110.8	111.2	110.4	94.4	123.1
H8-C2-Si1	109.4	110.8	-	110.8	111.7	110.4	135.5	123.4
C2-O3-H9	109.2	108.9	-	-	-	109.1	57.1	116.7
H9-O3-Si1	-	-	-	120.0	119.8	119.6	133.4	120.2
Dihedral Angles (in Degrees)								
H4-Si1-C2-O3	180.0	-176.9	-	-	-	177.7	-121.3	-178.0
H5-Si1-C2-O3	60.8	61.8	-	120.1	116.8	57.7	126.5	91.3
H7-C2-Si1-O3	121.4	-117.5	-	-60.0	-57.1	123.4	-111.1	-94.1
H8-C2-Si1-O3	-121.4	125.5	-	60.1	63.7	-119.2	42.3	88.6
H9-O3-C2-Si1	180.0	64.3	-	-	-	113.5	-131.5	-108.7

Formation of Methoxysilane (Path I)

In the formation of methoxysilane ('3') via 'TS13', bond angles, Si1-C2-O3 and C2-O3-H9, decrease considerably as one goes from the reactant ('1') to 'TS13'. The C2-O3 and O3-H9 bonds weaken (bond length increases) as we go from '1' to 'TS13' (Table-1). These changes are consistent with the decrease in the ρ (r_c) values for these two bonds. Furthermore, from $\nabla^2\rho_c$ values, one can see that the covalent nature of the C2-O3 and O3-H9 bonds changes to non-covalent in 'TS13' (Table-2). In the reactant '1', the Si1-C2 bond elongates from 1.901 to 2.688 Å, and the ρ (r_c) value for the same bond was not observed in the 'TS13' as well as in product '3', indicating dissociation of the Si-C bond in the TS itself. The Si1-O3 and C2-H9 bond formations were observed in the 'TS13' structure, supported by the bond distances of 1.704 and 1.405 Å, respectively. The observation for the Si1-O3 bond was also reinforced by the ρ (r_c) and $\nabla^2\rho_c$ values. All these changes in the reactant '1' lead to the formation of 'TS13', a penta-coordinated Si and C atom with two three-membered rings. However, our results slightly differ from the previous theoretical calculations concerning pentacoordinate TS in the formation of methoxysilane since no electronic charge density was observed for the Si-C bond, and the bond distance between the two atoms was also very large (Table-1 and 2).[12] The 'TS13', saddle point of first-order, was confirmed from the IRC calculations (Fig.-2) with only one imaginary vibrational frequency indicating an acceptable TS. To analyze the rearrangement reaction, natural atomic charges were also calculated and tabulated in Table-3. In the process of the formation of 'TS13', the negative charge on the O atom increases by 0.177, the Si atom becomes more positive, and the C atom becomes slightly more negative. These observations of charge redistribution suggest that now electrons are shared between Si and O atoms more as compared to between C and O atoms. When the product ('3') forms, the Si-C bond dissociates, and the charge on C increases by 0.402 as compared to that in 'TS13'. Furthermore, the charge on the Si and O atoms in '3' as compared to that in '1' suggests that more transfer of valence electrons from Si to the O atom.

Formation of Methylsilanol (Path II)

In Path II, when methylsilanol ('4a') formation takes place via 'TS24a' from the reactant '2', it was observed that the Si1-C2-O3 angle decreases considerably in 'TS24a'. Also, the Si1-O3-C2 angle of 52.1° was observed in the same leading to suggest the O atom is moving towards the Si atom. The C2-O3 and Si1-H4 bond lengths increase as we go from '2' to 'TS24a'. Furthermore, distances of 1.841 and 2.228 Å were observed between Si1-O3 and C2-H4, respectively (Table-1). All these observations of bond lengthening and proximity of Si and O atoms, and C2 and H4, were supported by the ρ (r_c) and $\nabla^2\rho_c$ values. It can be seen from Table-2 that ρ (r_c) and $\nabla^2\rho_c$ values for the Si-O in 'TS24a' are 0.084 and 0.382,

respectively, and that for C-O there are no values, indicating bond formation in the former and bond dissociation in the latter. Furthermore, it can be noted that the ρ (r_c) value for Si1-H4 decreases, indicating bond weakening. All these observations in the process of forming 'TS24a' lead to the formation of a pentacoordinated (Si atom) TS with two three-membered rings. Only one negative frequency for the 'TS24a' (Table-5) confirmed the valid structure of the same. Now, when the reaction moves from 'TS24a' to '4a', Si1-O3 and C2-H4 bond distances further decrease, and C2-O3 and Si1-H4 bond dissociation takes place.

These observations in '4a' were reinforced by the ρ (r_c) and $\nabla^2\rho_c$ values, reported in Table-2. Natural atomic charge analysis suggested transfer of partial valence electrons from Si to the O atom in the TS, thereby increasing the negative charge from -0.726 to -0.965, and that on the Si atom positive charge increased by 0.162. Also, there was a slight decrease in negative charge on the C atom (Table-3). Now, when the product '4a' forms from the 'TS24a', there is an increase of negative charge on the C atom by 0.68, suggesting transfer of charge from Si to the C atom.

Also, there is an increase of positive charge on Si and negative charge on O that leads to sharing of more electron charge density from Si to O. It should be noted that the charge on H4 changes from negative to positive, indicating a shift of H4 from Si to C.

Table-2: Some Selected Bonding Characteristics of Reaction Paths using B3LYP/6-311++G(d,p) Optimized Geometry

1 ⟶ 3 (Path I)						
System[a]	1		TS13		3	
	ρ (r_c)	$\nabla^2\rho_c$	ρ (r_c)	$\nabla^2\rho_c$	ρ (r_c)	$\nabla^2\rho_c$
Si1- C2	-	-	0.115	0.695	0.128	0.828
Si1- C2	0.118	0.199	-	-	-	-
C2-O3	0.245	-0.440	0.138	0.019	0.245	-0.362
O3-H9	0.368	-2.487	0.227	-0.665	-	-
2 ⟶ 4a (Path II)						
System[a]	2		TS24a		4	
	ρ (r_c)	$\nabla^2\rho_c$	ρ (r_c)	$\nabla^2\rho_c$	ρ (r_c)	$\nabla^2\rho_c$
Si1- C2	0.118	0.180	0.122	0.426	0.124	0.218
C2-O3	0.244	-0.446	-	-	-	-
H4-Si1	0.118	0.217	0.088	0.113	-	-
Si1-O3	-	-	0.084	0.382	0.125	0.792
O3-H9	0.368	-2.496	0.358	-2.385	0.362	-2.470

a. See Fig.1, ρ_c in e/au^3 and $\nabla^2\rho_c$ in e/au^5

Table-3: Natural Atomic Charges

System[a]	1	2	3	4a	4b	TS12	TS13	TS24a
Si1	0.862	0.831	1.196	1.413	1.411	0.850	1.193	0.993
C2	-0.436	-0.435	-0.190	-1.08	-1.090	-0.437	-0.592	-0.400
O3	-0.740	-0.726	-0.893	-1.064	-1.061	-0.740	-0.917	-0.965
H4	-0.172	-0.166	-0.189	0.229	0.230	-0.173	-0.167	-0.183
H5	-0.160	-0.158	-0.213	-0.227	-0.206	-0.158	-0.193	-0.166
H6	-0.160	-0.172	-0.213	-0.227	-0.227	-0.168	-0.197	-0.143
H7	0.174	0.174	0.160	0.234	0.232	0.179	0.182	0.193
H8	0.174	0.198	0.160	0.234	0.225	0.187	0.192	0.200
H9	0.458	0.453	0.182	0.488	0.485	0.461	0.499	0.472

Harmonic Vibrational Frequencies

For all the considered reactants, TS, and products, harmonic vibrational frequencies are calculated using B3LYP/6-311++G(d,p) and reported in Table-4 and 5. All the reactants and products possess positive values of vibrational frequencies, indicating stable geometries of all the structures. The frequency data corresponds to the respective molecular structures. For all three TS, viz., TS12, TS13, and TS24a, a single imaginary frequency was observed, suggesting an acceptable TS. Our results for vibrational frequencies are in good

agreement with the previous theoretical calculations.[11] The zero-point vibrational energies (ZPVE) were also reported at the B3LYP/6-311++G(d,p) level.

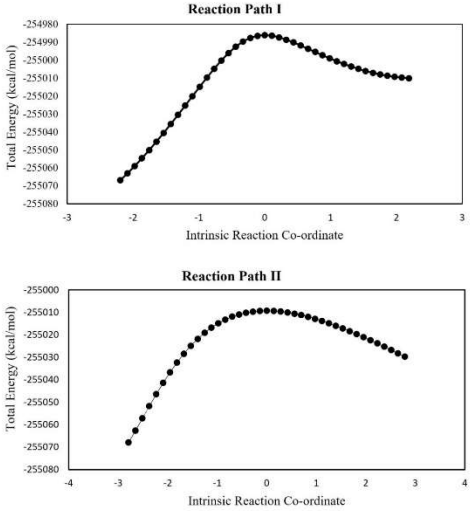


Fig.-2: Potential Energy Profile (PES) for Two Reaction Paths (using B3LYP/6-311G++(d,p) basis set). The Transition State is Represented by the Zero Point Along the IRC. The Reactant and Products are towards the Negative and Positive Directions, respectively.

Table-4: Calculated Harmonic Vibrational Frequencies[b] (cm^{-1}) and ZPVE (kcal mol^{-1}) using B3LYP/6-311G++(d,p) Optimized Geometry

System[a]	1	TS13	3	TS12
	245 (123)	1523i (934)	688 (63)	245i (96)
	505 (30)	136 (940)	696 (23)	560 (25)
	568 (28)	280 (30)	728 (69)	710 (41)
	694 (57)	568 (151)	918 (81)	818 (49)
	901 (230)	638 (138)	934 (182)	899 (247)
	922 (55)	685 (57)	956 (243)	921 (52)
	926 (32)	702 (112)	1085 (184)	925 (28)
	994 (66)	768 (33)	1162 (43)	976 (81)
	1147 (28)	891 (123)	2126 (176)	1108 (29)
	2143 (109)	934 (105)	2132 (97)	1304 (10)
	2163 (82)	946 (158)	2192 (110)	2136 (117)
	2167 (122)	2157 (162)	2892 (68)	2154 (107)
	2878 (46)	2165 (62)	2943 (48)	2167 (107)
	2912 (35)	2182 (114)	2999 (30)	2910 (35)
	3699 (31)	2219 (78)		3742 (50)
ZPVE	41.5	36.9	41.9	41.1

a. See Fig.1 b. Scaled by 0.9679
c. Values in the parentheses are intensities in km/mol

Table-5: Calculated Harmonic Vibrational Frequencies[b] (cm^{-1}) and ZPVE (kcal mol^{-1}) using B3LYP/6-311G++(d,p) Optimized Geometry

System[a]	2	TS24a	4a	4b
	272 (150)	603i (124)	184 (116)	182 (114)
	552 (25)	407 (115)	696 (141)	243 (36)
	826 (47)	447 (52)	705 (57)	666 (71)
	900 (242)	546 (84)	798 (143)	738 (59)
	919 (49)	660 (75)	861 (46)	785 (167)
	925 (36)	797 (122)	933 (245)	869 (57)
	988 (76)	849 (97)	965 (144)	920 (249)
	1108 (46)	914 (99)	1259 (31)	942 (129)

	1325 (25)	1574 (192)	2120 (207)	1258 (30)
	2136 (89)	2124 (92)	2128 (135)	2123 (169)
	2143 (133)	2171 (98)	3778 (83)	2176 (128)
	2165 (104)	3689 (55)		3777 (80)
	2890 (43)			
	3706 (31)			
ZPVE	41.5	38.0	42.2	42.2

a. See Fig.1 b. Scaled by 0.9679
c. Values in the parentheses are intensities in km/mol

Energetics of the Two [1,2] Rearrangement Reactions

The energy of the reaction (ΔE) for 1→ 2, 1→ 3, and 2→ 4a, and activation energy (E_a) for all three TS viz., TS12, TS13, and TS24a, are calculated and tabulated in Table-6 using the HF, MP2, and B3LYP methods at the 6-311++G(d,p) basis set. The magnitude of E_a is found to be higher by 22.7 kcal mol^{-1} for path I, i.e., the formation of methoxysilane, as compared to path II, i.e., methylsilanol formation using the B3LYP method. The same trend is observed for the HF and MP2 methods. Path II is more exothermic as compared to path I. Inclusion of electron correlation decreases the E_a considerably and decreases the energy of reaction (ΔE) by a small amount for both paths. Our results are in good agreement with the results of other theoretical studies.[11] PES, i.e., potential energy surface, is plotted (Fig.-2) along the IRC (intrinsic reaction coordinate) which is calculated using B3LYP/6-311++G(d,p). The two plots of the IRC suggest that products for both paths lie on the PES. The maxima in the two plots (Fig.-2) at zero value of IRC (x-axis) correspond to TS.

Table-6: Calculated Activation Energies (E_a) and Energy of Reaction (ΔE) (in kcal mol^{-1}) for [1,2] Rearrangement Reactions of Silylmethanol

Reaction[a]		A	B	C	Others[b]
1 → 2	E_a	2.7	2.5	0.9	1.0
	ΔE	1.3	1.1	0.7	0.4
1 → 3 (Path I)	E_a	101.3	73.5	80.0	84.3
	ΔE	-23.9	-20.5	-20.8	-28.0
2 → 4a (Path II)	E_a	66.4	68.0	57.3	68.7
	ΔE	-46.3	-46.5	-44.1	-48.3

Energy values are considered after zero-point vibration energy correction.
a. See Fig.-1 b. Taken from reference [12]
A. Using HF/6-311++G(d,p), B. Using MP2/6-311++G(d,p), C. Using B3LYP/6-311++G(d,p)

CONCLUSION

The rearrangement reactions of silylmethanol via two different paths (I and II) are investigated using the B3LYP functional at the 6-311G++(d,p) basis set. In the path I, methoxysilane ('3') forms from one of the isomeric conformers of silylmethanol ('1') via a pentacoordinated (Si atom) transition state. In path II, methylsilanol formation takes place from another conformer of silylmethanol ('2') again through a transition state that is pentacoordinated (Si atom) with two three-membered rings. The TS structures obtained in our study are confirmed by the single negative frequency. The activation energy for path I is found to be high when compared to the alternative potential path II by 22.7 kcal mol^{-1}. The formation of methylsilanol is more exothermic (by 23.3 kcal mol^{-1}) as compared to the methoxysilane formation. The magnitude of ρ_c and $\nabla^2\rho_c$ supported the observations of bond formation and dissociation in the two TS during the course of the reaction. Natural atomic charges on the different atoms also reinforced the observation of bond breaking and formation. Our results are in good agreement with the previously reported calculations at the MP2 level. From the present study, we conclude that DFT calculations effectively include exchange and correlation at an economical computational cost.

ACKNOWLEDGEMENTS

Both the authors are grateful to Zakir Husain Delhi College and University of Delhi for providing the necessary resources for the present work.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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REFERENCES

1. H. Mollabagher, M.M. Mojtahedi, and S.A.H.S. Mousavi, *Journal of the Iranian Chemical Society*, **21**, 1795(2024), https://doi.org/10.1007/s13738-024-03041-7
2. M.A. Pigaleva, I.V. Elmanovich, M.N. Temnikov, M. O. Gallyamov and A. M. Muzafarov, *Polymer Science Series B*, **58**, 235(2016), https://doi.org/10.1134/S1560090416030118
3. K. M. Lewis and S. Couderc, *Molecules*, **27(14)**, 4341(2022), https://doi.org/10.3390/molecules27144341
4. A. G. Brook, *Accounts of Chemical Research*, **7(3)**, 77(1974), https://doi.org/10.1021/ar50075a003
5. M. D. Paredes and R. Alonso, *Tetrahedron Letters*, **40(20)**, 3973(1999), https://doi.org/10.1016/S0040-4039(99)00646-2
6. M. D. Paredes and R. Alonso, *The Journal of Organic Chemistry*, **65(8)**, 2292(2000), https://doi.org/10.1021/jo9912855
7. S. Shuto, M. Kanazaki, S. Ichikawa, N. Minakawa and A. Matsuda, *The Journal of Organic Chemistry*, **63(3)**, 746 (1998), https://doi.org/10.1021/jo971703a
8. P. Antoniotti and G. Tonachini, *The Journal of Organic Chemistry*, **58(14)**, 3622(1993), https://doi.org/10.1021/jo00066a011
9. P. Antoniotti, C. Canepa and G. Tonachini, *The Journal of Organic Chemistry*, **59(14)**, 3952(1994), https://doi.org/10.1021/jo00093a029
10. Y. Wang and M. Dolg, *Tetrahdron*, **55(44)**,12751(1999), https://doi.org/10.1016/S0040-4020(99)00751-6
11. C. H. Schiesser and M. L. Styles, *Journal of the Chemical Society, Perkin Transactions 2*, **2(11)**, 2335(1997), https://doi.org/10.1039/A702587D
12. Y. Yu and S. Feng, *The Journal of Physical Chemistry A*, **108(36)**, 7468(2004), https://doi.org/10.1021/jp048197v
13. Y. Yu and S. Feng, *International Journal of Quantum Chemistry*, **107(1)**, 105(2007), https://doi.org/10.1002/qua.21018
14. A. D. Becke, *Physical Review A*, **38**, 3098(1988), https://link.aps.org/doi/10.1103/PhysRevA.38.3098
15. A. D. Becke, *Journal of Chemical Physics*, **98(7)**, 5648(1993), https://doi.org/10.1063/1.464913
16. C. Lee, W. Yang and R. G. Parr, *Physical Review B*, **37**, 785(1988), https://doi.org/10.1103/PhysRevB.37.785
17. R. F. W. Bader, *Accounts of Chemical Research*, **18(1)**, 9(1985), https://doi.org/10.1021/ar00109a003
18. M. P. Andersson and P. Uvdal, *The Journal of Physical Chemistry A*, **109(12)**, 2937(2005), https://doi.org/10.1021/jp045733a
19. W. J. Hehre, L. Radom, P. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, John Wiley, New York, pp. 548 (1986), https://doi.org/10.1002/jcc.540070314
20. R. G. Parr and W. Yang, Density Functional theory of Atoms and Molecules, Oxford University Press, New York, Oxford, pp. IX+333 (1989), https://doi.org/10.1002/qua.560470107
21. J. K. Labanoeski and J. W. Andzelin, "Density Functional Methods in Chemistry," Springer Verlag, New York (1991), https://doi.org/10.1007/978-1-4612-3136-3
22. S. H. Vosko, L. Wilk, and M. Nusair, *Canadian Journal of Physics*, **58(8)**, 1200(1980), https://doi.org/10.1139/p80-159

[RJC-9264/2025]