[G009]

The investigation of transition state in the conversion of 3-cyclopropylmethoxy-3-chloro diazirine to various products by ab initio method

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Abstract

Optimized geometry and the corresponding electronic structure, vibrational frequencies and thermodynamic properties of cyclopropylmethoxychlorocarbene (**cpmcc**), 3-cyclopropylmethoxy-3-chlorodiazirine have been calculated using ab initio methods DFT-B3LYP with 6-311++G** basis set. Results show that **cpmcc** is transition state with a first order TS saddle point. The displacement matrix of the negative mode of vibration of the TS specie shows that the reaction path follows in the direction of the elimination of the CO group which is consistent with the mechanism proposed upon experimental data. Calculations were also carried out for reactants and products at the same levels of theory. Nuclear quadrupole coupling constants (NQCC), χ, and asymmetry parameter, η, of the ^{2}H, ^{35}Cl nuclei have been calculated for reactants, transition states and products.

Introduction

Identification and characterization of intermediate complexes are the master keys in the pathways for organic reactions. Accurate information about structural and electronic properties of possible intermediates and products are needed in order to shed light on the possible decomposition or combination pathways [1]. Detailed information about the intermediates of a reaction can also be used to interpret the existence and to estimate and predict the kinetic and thermodynamic controlled products of a certain reaction [2-4]. This information is crucial, especially, in the industrial design of chemical reactors.

In spite of the great advances in the instrumental methods of identification and characterization, it is not always possible to trace all intermediates and pathways of all chemical reactions, particularly the fast reactions [5-8]. For this type of reactions, ab initio computations are the only alternative sources of the required information.

The aim of this research is to study in detail the electronic structure and stability of cyclopropylmethoxychloro carbene **cpmcc** introduced recently as a transition state in the two-step conversion (Fig. 1) of 3-cyclopropylmethoxy-3-chloro diazirine **2** to cyclopropylmethyl chloride **5** during fragmentation process in the mass spectroscopy experiments [9-11]. The experimental studies show that fragmentation of cyclopropylmethoxychlorocarbene in MeCN at 25°C affords cyclopropylmethyl chloride, cyclobutyl chloride and 3-butenyl chloride in a distribution of 73.3:17.1:9.6 [12].

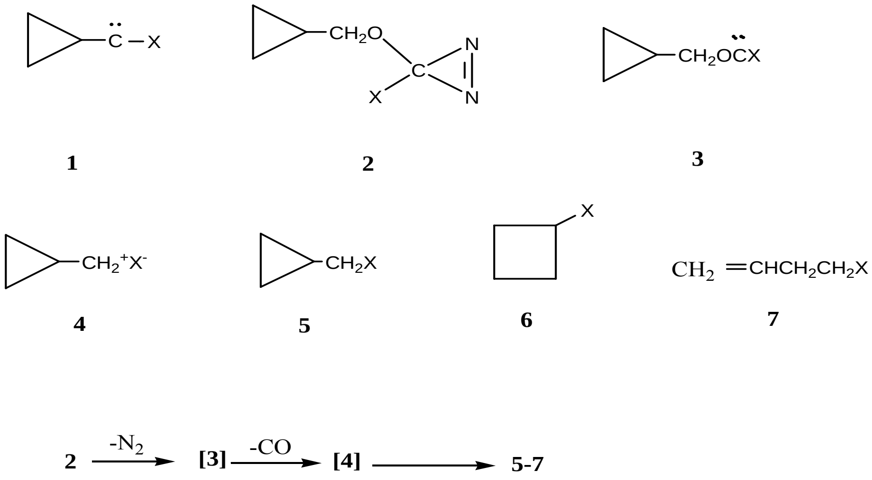


Figure. 1

In this article, DFT-B3LYP level with 6-311++G** basis set are used to study: **cpmcc**, **3** and different products **5**, cyclobutyl chloride **6** and 3-butenyl chloride **7** (Fig. 1). At the result, for these molecules investigated optimized geometry, negative modes, and parameters of NMR, NQR spectra.

The specie of **cpmcc** was generated from 3-cyclopropyl 3-chloro diazirine with eliminating N_2 according to Fig. 1 [13]. Next, by eliminating the CO group is converted to the ion pair cyclopropylmethylium chloride **4**. Geometry optimization starting from different points around the equilibrium geometry of **4**, leads to different equilibrium geometries **5** to **7** [14]. It can therefore be predicted that rearrangement of **4** will result in a mixture of **5** to **7** as shown in Fig. 1. The theoretical studies of McKee [15], Schleyer [16] and Hehre [17] have showed that cyclopropylcarbinylcation has an imaginary frequency.

NQR spectroscopy is based on the interaction between nuclear electric quadrupole moments of quadrupolar nuclei (having spin $I > ½$) with the local molecular electric field gradient (EFG) [18, 19]. The EFG at a nucleus in molecular environment is a one-electron property and can be obtained with a reasonable effort using ab initio computations. Since, it involves only the ground state wave function, calculation of EFG should be easier and faster than the calculation of the NMR chemical shifts. Therefore, theoretical efforts needs to devote to the interpretation of NQR spectroscopy are less than that of NMR spectroscopy [20, 21].

2. Computations

The fully optimized geometries and the corresponding electronic structures, vibrational frequencies and thermochemical properties of compounds **2** to **7** have been calculated using ab initio density function theory (DFT) using Becke's three-parameter hybrid functional combined with the Lee-Yang-Parr correlation functional (B3LYP) level of theory with 6-311++G** basis set [22,23]. All ab initio calculations were performed using GAUSSIAN 98 package [24]. Furthermore, electron spin density distribution over the entire molecule and NMR chemical shielding for all nuclei of the compound have been calculated based on the optimized geometry.

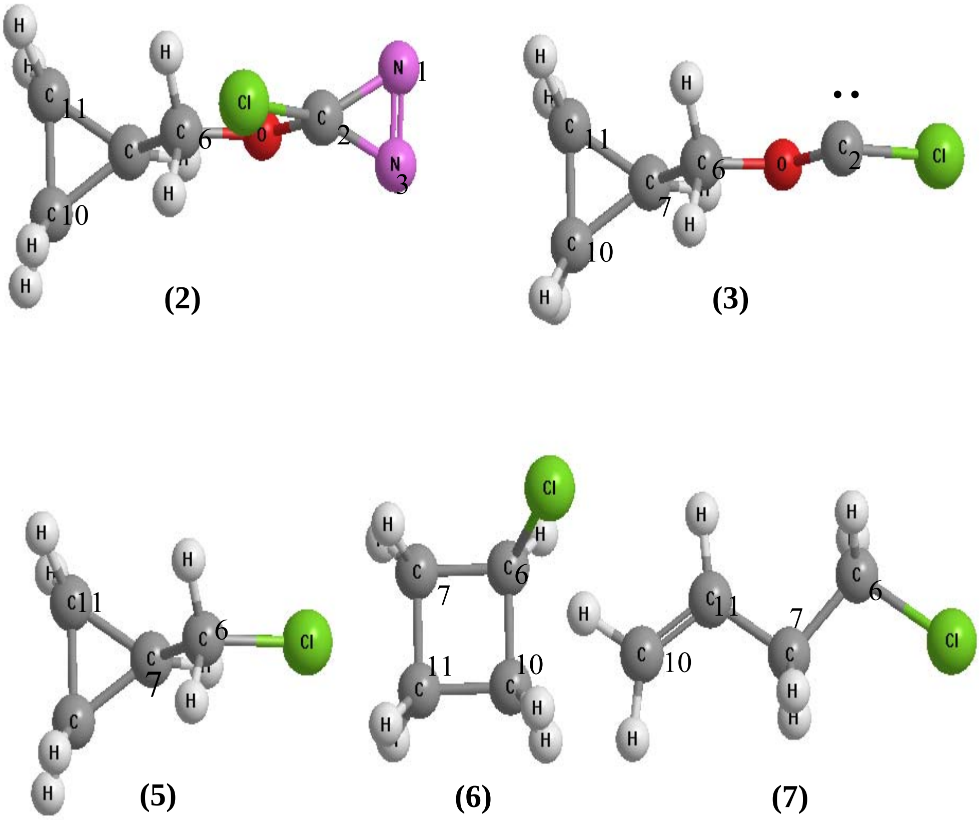
3. Results and discussion

3.1. Structural analysis

The optimized geometrical parameters obtained for compounds **1** to **7** with different substituents are tabulated in Table 1. These data Results show that transient species **3** is formed from one cyclopropyl group with a tetrahedral structure around the C_2 carbene center. Similar to other known carbenes, the carbene bonds in **cpmcc** is non-linear.

The optimized geometry of **cpmcc** is demonstrated in Fig. 2. The bond angles reported in Table 1 show that CH_2 group has been connected by tetrahedral angle similar to methane to cyclopropyl. A comparative study shows that angels ∠O-C-X and ∠C6-O-C2 in intermediate **3** are smaller than there corresponding values in reactant **2** (Table 1). In other words, the intermediate **3** is under strain and thus is converted to the products with less strain. The N=N bond length is shorter than the C-N bond length in the reactant **2**. This shows that the N_2 elimination proceeds via elongation of the C-N bonds. Since the C2-O bond length is shorter in **cpmcc** reactant compound **2**, and at the same time C6-O bond length in **cpmcc** is longer than that in the reactant, it can thus be said that the reaction path follows via the shortening of the C2-O and lengthening of the C6-O bond which allows eventually elimination of the CO group. These structural data are consistent with what Graham [12]. The investigations showed that C2-O bond length is shorter and C6-O bond length is longer in **cpmcc** with more electronegative substituent.

The results of Table 1 show ring angel strain in compound of **6** is lower because this compound has quartet ring. Also, the computations were carried out for **cpmcc** transition stat with multiplicities singlet and triplet for carbene. Also, the results of Table 1 show that transition state with singlet multiplicity is more stable than transition state with triplet multiplicity.



(2) **(3)**

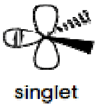
(5) **(6)** **(7)**

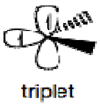
Figure 2: The optimized structures of cyclopropylmethoxychloro carbene (cpmcc) (3), reactant (2) and its CO elimination products (5, 6, 7).

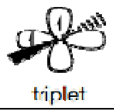
Table 1. The optimized Bond lengths and angles computed at DFT-B3LYP/6-311++G** levels of theory for reactant (2), transition state (3) and products (5, 6 and 7). (See Fig. 2 for the numbering scheme).

Structural Parameters	**2**	**3**		**5**	**6**	**7**
		[a]**m=1**	**m=3**			
R(C_2-N)	1.432	—	—	—	—	—
R(C_2-Cl)	1.782	1.800	1.749	—	—	—
R(C_6-Cl)	—	—	—	1.823	1.816	1.818
R(C_2-O)	1.347	1.282	1.306	—	—	—
R(C_6-C_7)	1.507	1.495	1.497	1.510	1.539	1.522
R(C_2-H_8)	—	—	—	1.089	1.089	1.089
∠OC_2Cl	115.890	106.208	125.086	—	—	—
∠XC_6C_7	—	—	—	114.199	118.169	111.541
∠C_2OC_6	115.681	115.249	117.908	—	—	—
Stability energy(Hartree)	—	-730.157	-730.096	—	—	—

[a]Multiplicity of carbon atom in carbene (: CH_2)







3.2. Transition state

Transition state structures of **cpmcc** has been found and optimized by B3LYP/6-311++G** level of theory. Results show that **cpmcc** have one imaginary frequency and thus one negative mode. Existence of a single negative mode shows that **cpmcc** have a first order saddle point which requires a single product. The only negative mode of **cpmcc** TS structure is shown in Fig. 3. This figure clearly shows that the reaction path follows the elimination of the CO group. Since **cpmcc** is transient specie, it cannot be probed experimentally by routine methods. This is why no experimental data is reported for **cpmcc** TS in the literature. Also, Fig. 3 clearly confirmed results of section 3.1.

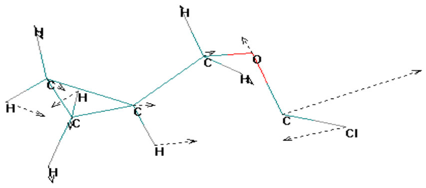


Figure 3. The only negative mode of **cpmcc (**imaginary frequency).

3.3. NMR Spectra

NMR Spectrum of molecule of cyclopropylmethoxychloro carbene (**cpmcc**) also has been studied with B3LYP/6-311++G** method.

To better understand bonding and electronic structure in **cpmcc** isotropic and anisotropic NMR chemical shieldings have been calculated for the ^{13}C nuclei using GIAO method for the optimized structure of intermediate **cpmcc** at B3LYP level of theory using 6-311++G** basis set and the results tabulated in Table 2. To convert σ_{ii} (^{17}O, ^{35}Cl, ^{13}C and ^{1}H) to chemical shifts, δ_{ii}, H_2O, $CHCl_3$ and TMS were chosen as the reference, $\delta_{ii} = \sigma_{ii,r} - \sigma_{ii,s}$, where the subscripts "r" and "s" refer to the reference and sample, respectively.

The investigation of the results in Table 2 shows that δ_{nn} values describe the shape of an ellipsoid in three dimensions in the principal axis system of the chemical shift tensor. This shape is related to the topology of the electronic wave function at the site of the nucleus and can therefore lead to details about chemical bonding. The difference between δ_{nn} values for particular site is a strong function of the symmetry and structure of the bonding environment.

δ_{11} and δ_{33} correspond to the minimum and maximum values of the chemical shift or the minimum and maximum electron density along orthogonal directions in the principal axis system of the chemical shift tensor. With regard to the structure of carbene which has both an empty p-orbital and lone electron pair, it is most likely that the 11 direction lies along the symmetry axis of the empty p-orbital whereas the 33 direction involves the hybrid orbital

TABLE 2: The calculated Chemical Shielding Tensors and [a]chemical shifts of the various atoms B3LYP/6-311++G** in CPMXC.

	$^{1}\sigma_{11}$	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$	δ11	δ22	δ33	δiso	Δδ
Cl	-422.11	406.34	806.44	263.55	814.32	554.7291	17.8139	157.499	243.3473	-128.773
C2	-552.61	-55.87	25.30	-194.39	329.55	733.2559	236.559	165.5582	378.4577	-319.349
C6	43.06	74.69	144.05	87.27	85.17	137.58	105.9983	46.8189	96.79907	-74.9703
O	-567.42	-58.96	172.56	-151.27	485.75	863.7805	372.5633	184.0111	473.4516	-434.161
H	23.76	28.05	31.66	27.82	5.76	4.4073	1.5694	6.448	4.141567	3.45965

[1] Calculated σ_{iso}, σ_{11}, σ_{22}, σ_{33} and $\Delta\sigma$ values in ppm.

[2] X= The various substitutions in CPMXC.

[a] To convert σ_{ii} (^{17}O, ^{35}Cl, ^{13}C and ^{1}H) to chemical shifts, δ_{ii}, H_2O, $CHCl_3$ and TMS were chosen as the reference, $\delta_{ii} = \sigma_{ii,r} - \sigma_{ii,s}$, where the subscripts "r" and "s" refer to the reference and sample, respectively.

containing the lone electron pair. The structure of carbene indicates essentially zero electron density along the 11 direction. Therefore, one would expect δ_{11} for **cpmcc** to tend toward bare nucleus value.

3.4. NQR spectra

Table 3 lists the computed NQR parameters (χ,η) for the ^{35}Cl and ^{2}H nuclei for the series compounds appeared in Fig. 1. As no experimental NQR spectra is reported for these compounds, present NQR data serve as prediction to be confirmed by future experiments. It can be seen from Table 6 that the NQR parameters are not sensitive to the computational methods. These results show that the NQCC of ^{35}Cl has the largest value in compound **2** as compared to other compounds, but the value of η is very small indicating the high symmetry around Cl atom in compound **2**. From the expression ofχ, it is obvious that NQCC of a nucleus is directly proportional to q_{zz}. There are two factors controlling the value of q_{zz} in a nucleus, charge density on the nucleus and the symmetry of EFG around the nucleus. It is evident that increase in the charge density causes the q_{zz} and consequently χ to be increased. If charge distribution is such that the asymmetry of EFG around the nucleus increases, then q_{zz} and consequently χ would be decreased.

Since the contribution of nonbonding electrons (lone pairs p and d) in the nonspherical charge distribution is greater than that of the bonding electrons. Therefore in atoms with nonbonding electron pairs, the EFG is more asymmetric due to increase in the charge density. Therefore, in these cases, the χ and η values decreases and increases with the increase of charge density, respectively. The smallest value of the ^{35}Cl NQCC in compound **3** compared to other compounds indicates that the EFG is more asymmetric due to the lone pairs located on C atom. On the other hand, the observed change in the value of η for ^{35}Cl can be recorded as an evidence for the much larger distortion of the electron distribution around Cl in compound **3**. It is noticeable that the NQR parameters of three products **5**, **6**, and **7** are approximately the same. The computed NQR parameters of ^{2}H in the conversion of the reactants to products do not change significantly.

The NQCC parameter is a measure of the interaction between the nuclear quadrupole moment and the EFG at the quadrupole nucleus site due to the nonspherical and noncylindrical (anisotropic) charge distribution in the system. Such as interaction can be measured either in the gas phase (using microwave spectroscopy) or in the solid phase (mostly by NQR spectroscopy). The EFG is a traceless, symmetric second rank tensor whose principal axes are chosen so that its components satisfy $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$ in which $q_{ij} = \frac{\partial^2 V}{\partial i \partial j}$ with i, j = x, y, z and V is the external electrostatic potential).Since relative values of the q_{ii} elements (the diagonal components of the EFG tensor represent symmetry of the charge distribution in molecule, therefore NQCC values are extremely sensitive to the atomic and chemical bonds arrangements and are excellent probes for the identification of bonding conformations and molecular structure. In this research, NQR parameters have been calculated and analysed for 2,3,4,…

Table 3. Nuclear quadrupole coupling constants (NQCC), χ, and asymmetry parameters calculated for 2H and X=^{35}Cl ,^{19}F ,^{2}H nuclei for different compounds (2), (3), (5), (6) and (7) using DFT-B3LYP/6-311++G** level.

	2	3	5	6	7
	B3LYP/6-311++G**				
χ Cl	69.58	54.16	64.27	65.30	68.63
η	0.064	0.571	0.018	0.031	0.021
χ^2H(H-C$_{10}$)^b	103.46	199.39	211.38	206.55	197.51
χ^2H(H-C$_{12}$)	106.77	199.76	-	-	-
χ^2H(H-C$_{16}$)	209.16	209.53	216.41	206.56	213.98
χ^2H(H-C$_{14}$)	108.54	209.27	216.44	204.86	208.62
χ^2H(H-C$_8$)	-	-	202.55	202.50	202.38
χ ^{14}N^a	3.98	-	-	-	-
η	0.448	-	-	-	-

^{a} χ of (X=^{35}Cl ,^{19}F) and ^{14}N in MHz and for X=^{2}H in KHz
^{b}χ of ^{2}H in KHz

4. Conclusion

The optimized geometries obtained from different methods are slightly different. However, all of them predict that **cpmcc** is a stable intermediate with a first-order saddle point (having only one negative mode). The displacement matrix of the negative mode of vibration shows that the reaction path follows in the direction of the elimination of CO group; corresponding to the mechanism proposed previously by Graham [12].

The calculated shielding constants are in good agreement with the values reported for carbenes. Electron spin density distributions and NQR results show that the chlorine atom has critical role in the stabilization of the free electrons on **cpmcc**.

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