



Scholars Research Library
(<http://scholarsresearchlibrary.com/archive.html>)



ISSN : 2231- 3176
CODEN (USA): JCMMDA

A DFT Study of the [1+2] cycloaddition reactions of 2-[1, 3]dioxolan-2-ylidene-malononitrile, TCE and chlorocarbene

Abdellah Zeroual*, Redouan Hammal and Abdeslam El Hajbi

Physical Chemistry Laboratory, Department of Chemistry, Faculty of Science, Chouaib Doukkali University, El Jadida, Morocco

ABSTRACT

A theoretical study of the molecular mechanism and regioselectivity of the [1+2] cycloaddition reaction between 2,3-Dicyano-but-2-enedinitrile (TCE: R_1), 2-[1, 3]Dioxolan-2-ylidene-malononitrile (R_2) and chlorocarbene. has been carried out at the B3LYP/6-31(d) level of theory. The calculation of activation and reaction energies indicates that the attack at the double bond of 2-[1, 3]Dioxolan-2-ylidene-malononitrile is favored both kinetically and thermodynamically, which is in agreement with the experimental data.

Keywords: carbene, regioselectivity, nucleophilicity, DFT, Parr functions.

INTRODUCTION

Carbenes are neutral species containing a carbon atom with only six valence electrons. Carbenes are usually formed from precursors by the loss of small, stable molecules (α -elimination) a strong base removes an acidic proton adjacent to an electron withdrawing group to give a carbanion. Loss of a leaving group from the carbanion creates a carbene. One of the best known elimination reactions occurs when chloroform or dichloromethane are treated with base, forming a dichlorocarbene (chlorocarbene). In particular, several methods exist for converting alkenes to cyclopropane rings using carbene type reagents, [1-3] the reaction is said to progress through a concerted mechanism as all bonds are formed and broken in concert, [4-7] not by a radical mechanism. [8-9]

Our aim in this work is to present a theoretical study of cycloaddition [1+2], (Figure 1) and compared the results of our calculations with experimental results available in the literature. [10]

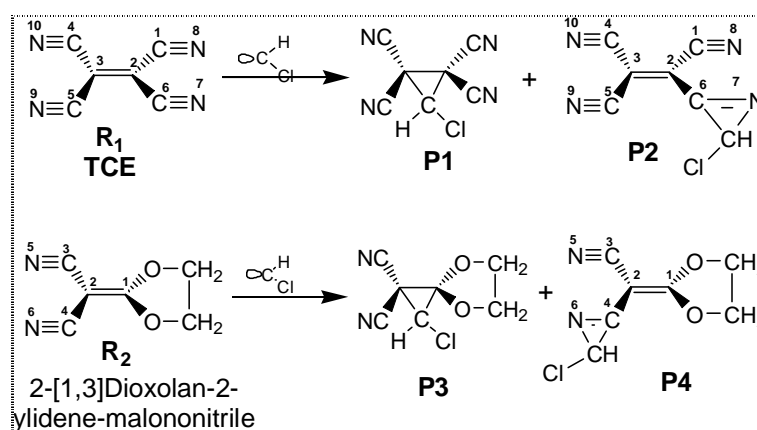


Fig. 1

MATERIALS AND METHODS

DFT computations were carried out using the B3LYP functional, [11] together with the standard 6-31G(d) basis set. [12] The optimizations were carried out using the Beryn analytical gradient optimization method. [13] The stationary points were characterized by frequency computations in order to verify that TSs have one and only one imaginary frequency. The IRC paths [14] were traced in order to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism using the second order González–Schlegel integration method. [15]

The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method. [16] All computations were carried out with the Gaussian 09 suite of programs. [17] The global electrophilicity index [18] ω , is given by the following expression, $\omega = (\mu^2/2\eta)$, in terms of the electronic chemical potential μ and the chemical hardness η . Both quantities may be approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO, e_H and e_L , as $\mu = (e_H - e_L)/2$ and $\eta = (e_L - e_H)$, respectively. [19] Recently, we introduced an empirical (relative) nucleophilicity index N , [20] based on the HOMO energies obtained within the Kohn–Sham scheme, [21] and defined as $N = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE})$. The nucleophilicity is referred to tetracyanoethylene (TCE), because it presents the lowest HOMO energy in a large series of molecules already investigated in the context of polar cycloadditions. This choice allows us to handle conveniently a nucleophilicity scale of positive values. Electrophilic P_k^+ and nucleophilic P_k^- Parr functions, [22] were obtained through the analysis of the Mulliken atomic spin density (ASD) of the radical anion and radical cation of the reagents. The local electrophilicity indices and local nucleophilicity indices were evaluated using the following expressions: $\omega_k = \omega \cdot P_k^+$, $N_k = N \cdot P_k^-$. [22]

RESULTS AND DISCUSSION

3.1. Analysis of the reactivity indices of the reactants.

The static global properties, namely electronic chemical potential μ , chemical hardness η , global electrophilicity index ω and global nucleophilicity index N of R_1 , R_2 and chlorocarbene are the chemical properties which we used to analyse reactivity at the various sites in the reactants (Table1).

Table 1: DFT/B3LYP/6-31G(d) Electronic chemical potential, μ , chemical hardness, η , electrophilicity ω , and nucleophilicity N values, in eV

	μ	η	N	ω
HCCl (carbene)	-5.00	3.40	2.31	3.68
R1 (T.CE)	-6.98	4.06	0	6.01
R2	-4.03	5.55	2.21	1.46

We can deduce from table 1 that:

- The electronic chemical potential of **carbene** is greater than that of the R_1 (TCE) and R_2 (2-[1, 3]Dioxolan-2-ylidene-malonitrile) which implies that electron transfer takes place from carbene to the R_1 and R_2 .
- The nucleophilicity index of the carbene (2.31 eV) is greater than that of the R_1 and R_2 (0.0 and 2.21 eV respectively), implying that in these reactions the carbene behaves as a nucleophile while the R_1 and R_2 behave as electrophiles.

3.2. Prediction of the regioselectivity of the reaction using local electrophilicity and local nucleophilicity indices.

According to Chattaraj's polar model, the local philicity indices (ω_k and N_k) can be used to reliably predict the most favoured interaction between two polar centres.[24, 25] The most favourable attack is that which is associated with the highest local electrophilicity index ω_k of the electrophile and the highest local nucleophilicity index N_k of the nucleophile. We calculated the values N_k and ω_k for carbene, R_1 and R_2 in order to predict the most likely electrophile/nucleophile interaction throughout the reaction pathway and so explain the regioselectivity of the reaction.

Table 2: Local nucleophilicity N_k (eV) and local electrophilicity ω_k (eV) of the R1, R2 and chlorocarbene

TCE	N_k (a)	ω_k
C ₃ =C ₂	0	2.04
C ₁ =C ₄ =C ₅ =C ₆	0	-0.30
N ₇ =N ₈ =N ₉ =N ₁₀	0	0.78
Reactif 2	N_k (a)	ω_k
C ₁	0.04	0.87
C ₂	0.90	0.06
C ₃ =C ₅	-0.19	0.03
N ₄ =N ₆	0.44	0.04
HCCl	N_k (a)	ω_k
C1	1.84	4.96

From table 2, we can deduce that:

The carbon atoms C₂ and C₃ of the TCE are the most electrophilic active site ($\omega_c = 2.04$ eV). The carbon C₁ and C₂ of the R₂ (C₁ = 0.87 and C₂ = 0.06 eV) are the most electrophilic centers. We can therefore deduce that the most favored interaction will take place between the double bond of R₁ and R₂ and the carbon atom of carbene.

3.3. Kinetic study of the two modes of attack (Determination of the kinetic parameters).

Relative enthalpies (ΔH), entropies (ΔS), and Gibbs free energies (ΔG) for the species involved in the [1+2] reaction between R₁, R₂ and are displayed in Table 3.

Table 3: B3LYP/6-31G(d) relative ^a enthalpies, ΔH in kcal mol⁻¹, entropies, ΔS in cal mol⁻¹ K⁻¹ and Gibbs free energies, ΔG in kcal mol⁻¹, for the species involved in the [1+2] cycloaddition between TCE and CHCl, (R₂ and CHCl)

	ΔH	ΔS	ΔG
TS1	4.3	-36.1	15.0
TS2	81.5	-43.4	94.1
P1	-64.6	-45.7	-114.2
P2	-36.3	-41.0	-64.6
TS3	0.62	-27.8	8.1
TS4	1.9	-32.4	11.3
P3	-58.3	-45.5	-45.2
P4	+1.8	-22.5	+8.7

^a: relative to TCE+CHCl and R₂+CHCl

The activation enthalpies associated with the reactions of TCE and chlorocarbene yielding cyclic products P1, P2 are 4.3 (TS1) and 81.5 (TS2) kcal mol⁻¹, respectively. These high activation enthalpies indicate that these reactions are very unfavorable. Addition of entropies to the enthalpies raises the activation free energy of TS1 to 15.0 kcal mol⁻¹, and decreases the activation free energy of TS2 to 94.1 kcal mol⁻¹. These changes are due to the favorable activation entropy associated with these retro cycloadditions ($\Delta S = -36.1$ and -43.4 cal mol⁻¹ K, respectively).

The activation enthalpies associated with the reactions of: 2-[1, 3]Dioxolan-2-ylidene-malononitrile and chlorocarbene yielding cyclic products P₃, P₄ are 0.62 (TS3) and 1.9 (TS4) kcal mol⁻¹, respectively. These activation enthalpies indicate that these reactions are very favorable. In addition the formation of the product P₄ is unfavorable because the reaction enthalpy is positive (thermodynamically unfavorable). These results agree with experimental reports, where only the product P₃ is obtained. While a schematic representation for the reactions profile of these cyclizations are given in Figure 2

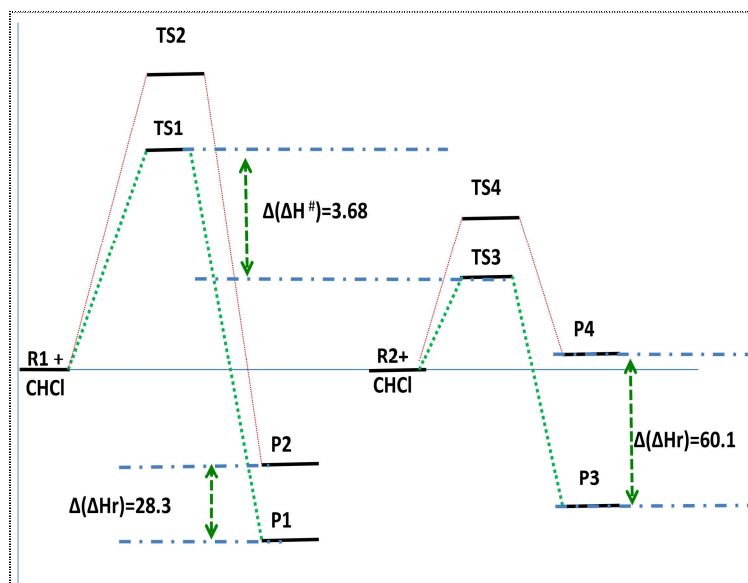


Fig.2: B3LYP/6-31G(d) energy profile (ΔH , in kcal/mol) of the reaction between TCE, 2-[1, 3]Dioxolan-2-ylidene-malononitrile and chlorocarbene

Therefore, four TSs, TS1, TS2, TS3 and TS4, and four cycloadducts, P1, P2, P3 and P4, associated to the C=C and C \equiv N, have been located and characterized. The different stationary points of this cycloaddition have been depicted in Figure 1. The optimized geometries of the TSs are depicted in Figure 3.

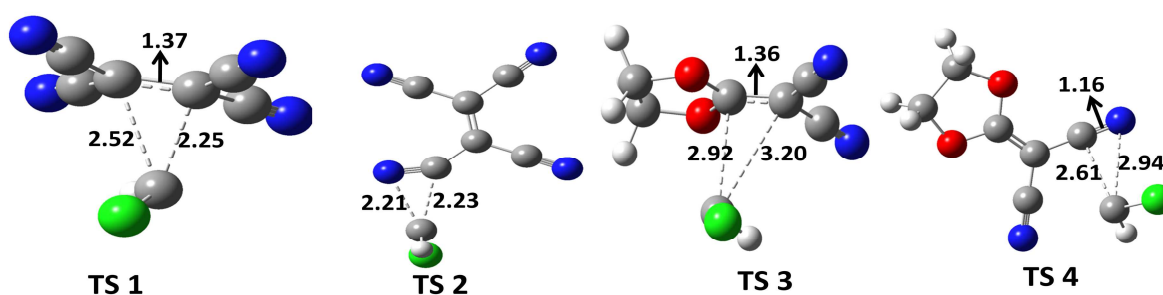


Fig. 3: Geometries of the TSs involved in the regioisomeric pathways associated between R₁, R₂ and chlorocarbene. Distances are given in Angstroms

CONCLUSION

The regioselectivity of the reaction between TCE, 2-[1, 3]Dioxolan-2-ylidene-malononitrile and chlorocarbene were studied using DFT/B3LYP/6-31G(d). Analysis of the global electrophilicity and nucleophilicity indices showed that TCE and 2-[1, 3]Dioxolan-2-ylidene-malononitrile behaves as a nucleophiles, while chlorocarbene behaves as an electrophile. The regioselectivity found experimentally was confirmed by local indices of electrophilicity and nucleophilicity ω_k and N_k . Calculation of the transition states shows that the formation of the product P4 is most favored than author products.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

CONTRIBUTION OF THE AUTHORS

Redouan Hammal analyzed the data. Abdeslam El Hajbi analyzed the data and revised the draft paper. Abdellah Zeroual carried out the localization of transition state analysed the data and revised the paper.

REFERENCES

- [1] V. Franzen, *Chemische Berichte*, **1962**, 95, 571-573.
- [2] H. M. Frey, *Trans. Faraday Soc.*, **1962**, 58, 516-528.

- [3] P. Kadaba, J. Edwards, *J. Org. Chem.*, **1960**, 25 (8), 1431–1433.
- [4] H. Fujimoto, R. Hoffmann, *J. Phys. Chem.*, **1974**, 78, 1167–1173.
- [5] W. W. Schoeller, E. Yurtsever, *J. Am. Chem. Soc.*, **1978**, 100, 7548–7550.
- [6] Nathan L. Bauld and David Wirth, *J. Comput. Chem.*, **1981**, 2, 1–6
- [7] W. S. Wolfgang, A. Nevzat, *J. Chem. Soc., Chem. Commun.*, **1982**, 1, 20–22.
- [8] A.G. Anastassiou, R.P. Cellura, E. Ciganek, *Tetrahedron Lett.*, **1970**, 11, 5267–5270.
- [9] Weitao Pan, Michael E. Hendrick, Maitland Jones Jr., *Tetrahedron Lett.*, **1999**, 40, 3085–3088.
- [10] O. Pelletier, K. Jankowski, *Can. J. Chem.*, **1982**, 60, 2383–2386.
- [11] Y. Zhao, D.G. Truhlar, *J. Phys. Chem.* **2004**, A 108, 6908–6918.
- [12] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- [13] H.B. Schlegel, *J. Comput. Chem.* **1982**, 2, 214–218
- [14] K. Fukui, *J. Phys. Chem.* **1970**, 74, 4161–4163
- [15] C. González, H.B. Schlegel, *J. Chem. Phys.* **1991**, 95, 5853–5860.
- [16] A.E. Reed, R.B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, 83, 735–746;
- [17] M.J. Frisch et al., *Gaussian 09, Revision A 02*, Gaussian Inc., Wallingford CT, 2009.
- [18] R.G. Parr, L. von Szentpaly, S. Liu, *J. Am. Chem. Soc.* **1999**, 121, 1922–1924.
- [19] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc.* **1983**, 105, 7512–7516.
- [20] L.R. Domingo, P. Pérez, *Org. Biomol. Chem.* **2011**, 9, 7168–7175
- [21] G. Kresse, J. Fuethmuller, *Computat. Mater. Sci.*, **1996**, 6, 15–50.
- [22] A. Zeroual, .A. Benharref, A. El Hajbi, *J Mol Model.* **2015**, 21, 2594–2599.
- [23] L.R. Domingo, M.J. Aurell, P. Pérez, R. Contreras, *J. Phys. Chem. A*, **2002**, 106, 6871–6875.
- [24] D.H. Ess; G.O. Jones; K.N. Houk, *Adv. Synth. Catal.*, **2006**, 348, 2337–2361.
- [25] PK Chattaraj; U Sarkar; DR Roy, *Chem. Rev.*, **2006**, 106, 2065–2091.