A DFT exploration of the [3+2] cycloaddition of RCNO (R = H, Me and F) with carbon flatland mimicking graphene

Lydia Rhyman[a], Luis R. Domingo[b], John A. Joule[c] and Ponnadurai Ramasami[a*]

[a] *Computational Chemistry Group, Department of Chemistry, University of Mauritius, Réduit, Mauritius*

[b] *Departamento de Química Orgánica, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*

[c] *The School of Chemistry, The University of Manchester, Manchester M13 9PL, UK*
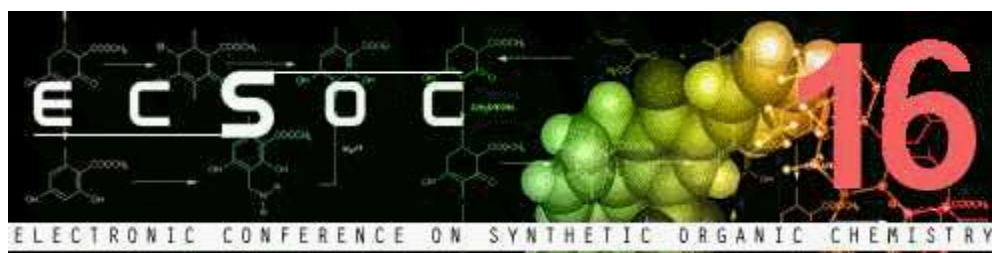
Author for correspondence e-mail: ramchemi@intnet.mu

This paper is presented for

ECSOC-16

International Electronic Conference on Synthetic Organic Chemistry

1-30 November 2012

"This presentation is part of the PhD research work of Miss Lydia Rhyman (lyd.rhyman@gmail.com, http://www.uom.ac.mu/sites/ccuom/). Her research is based on the theoretical study of cycloaddition reactions and eludication of the reaction mechanisms including different stereo- and regiochemical pathways and to predict the thermodynamic and kinetic parameters of the reactions."

A video presentation of this work is available at
http://www.youtube.com/channel/UCn3Yd8sgd7k9-cfpSSZAffQ?feature=watch

Abstract

Graphene is the latest allotrope of carbon to be under the spotlight ever since its discovery by Novoselov and coworkers in 2004. Owing to its fascinating structural, electrical, optical, mechanical and thermal properties, graphene can be regarded as a rapidly rising star in various fields such as supercapacitors, biosensors and batteries. The organic chemistry of graphene has stimulated a great deal of research and is gaining considerable attention. Among the various experimental studies that have been carried out on graphene, it was found that [3+2] cycloadditions (32CA) can be achieved on graphene sheets and the resulting functionalized graphenes are dispersible in polar organic solvents and water. The outstanding properties of graphene inspire fundamental studies and within the context of our recent publication on the 32CA of nitrile oxides with fullerene, we now explore the 32CA of unsubstituted (**HCNO**) and substituted nitrile oxides (**FCNO** and **MeCNO**) to model of graphenes. We seek to rationalize the energetic, thermodynamic and kinetic parameters of these reactions. To the best of our knowledge this is the first time that transition state structures (TSs) for 32CA on graphene models have been reported. Our interest lies in gaining a better insight into the reaction mechanism such as its synchronicity, the nature of the TS, charge transfer, analysis of the reactivity indices and the rate constants. An unexpected behaviour (lowest activation energy) was found for the 32CA involving **FCNO**, as these reactions have some pseudodiradical character. The findings of our research should be helpful to experimentalists in their quests for functionalized graphenes.

1.0 Introduction

- The [3+2] cycloaddition (32CA) has proved to be a versatile method for the construction of five-membered rings [1-3].

- Over the past decades, the 32CA has found broad applicability especially in the functionalization of fullerene and carbon nanotubes [4-6].

- Since its discovery by Novoselov and coworkers in 2004 [7], graphene, which is a monolayer of carbon atoms densely packed into a two dimensional hexagonal crystal lattice, has sparked a general interest from the experimental community [7-11].

- A couple of experimental studies have been performed on the reaction of graphene with azomethine ylides and it was reported that the sheet edges are the most reactive sites even though the center region can also be functionalized [12-15].

- Recently, Cao and Houk [16] theoretically studied the 32CA of an azomethine ylide and a carbonyl ylide to models of graphene using density functional theory (DFT). They explored the three types of bonds: at the center, corner and edge, and reported that the outer layer of graphene is more reactive than center areas, Figure 1.

- The reactions on corner and edge bonds are exothermic with both 1,3-dipoles. On the other hand, azomethine ylide reactions on center bonds of graphenes are endothermic while carbonyl ylide reactions on center bonds have free energies around 0 kcal/mol.

\
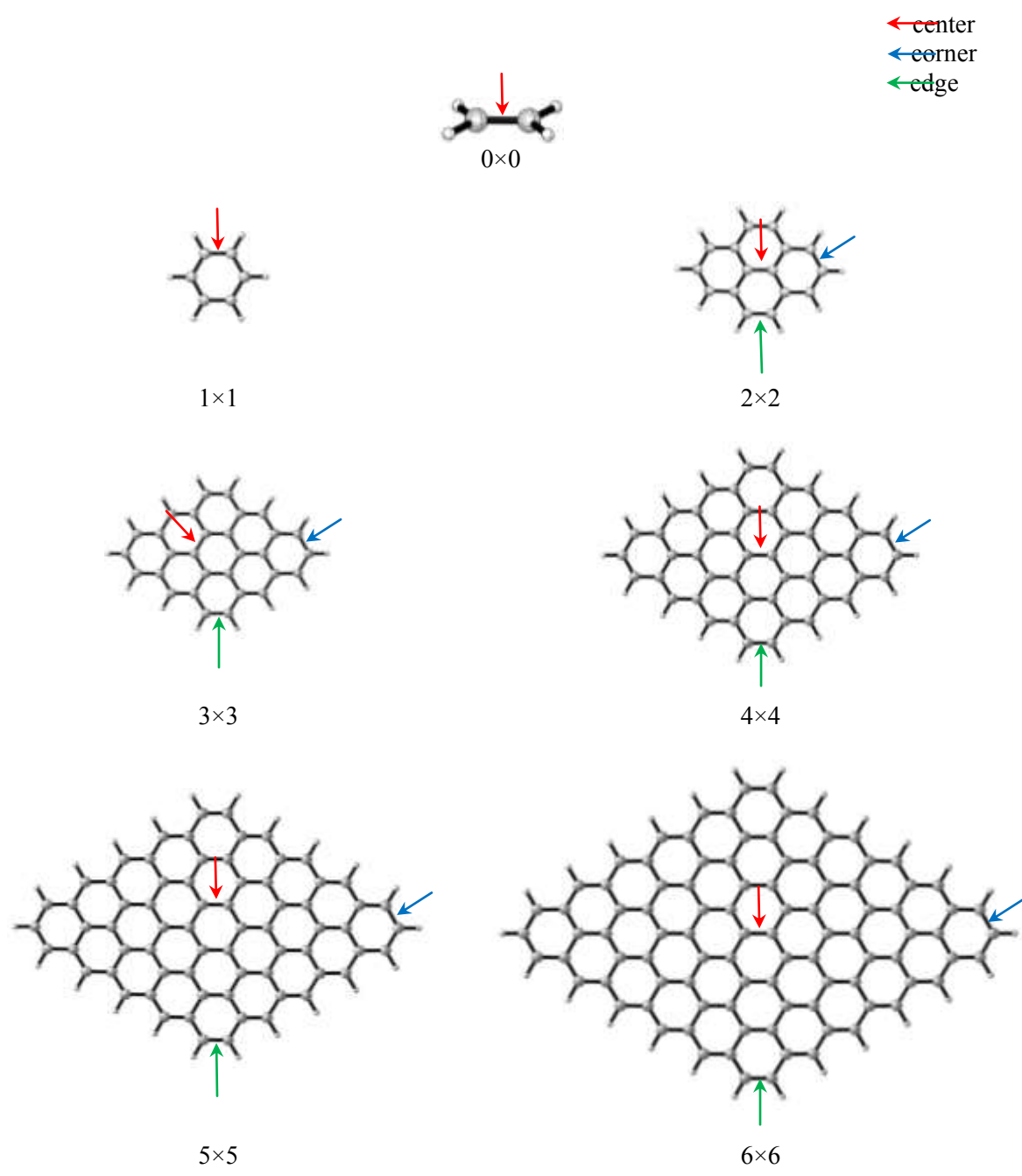
Figure 1: Graphene models (ethene, benzene, 2×2, 3×3, 4×4, 5×5 and 6×6) showing the types of bonds that are explored; center, corner and edge.

1.1 Objectives

- The outstanding properties of graphene inspire fundamental studies and within the context of our recent publication on the 32CA of nitrile oxides with fullerene [17], we now explore the 32CA of unsubstituted (**HCNO**) and substituted nitrile oxides (**FCNO** and **MeCNO**) to model of graphenes.

- In this work, we seek to rationalize the energetic, thermodynamic and kinetic parameters of these reactions.

- To the best of our knowledge this is the first time that transition state structures (TSs) for 32CA on graphene models have been reported.

- Our interest lies in gaining a better insight into the reaction mechanism such as:

    (i) its synchronicity,

    (ii) the nature of TSs and

    (iii) charge transfer (CT).

    The results obtained are critically analyzed and discussed.

2.0 Methodology

- Optimizations were carried out with the Gaussian 09 suite of programs [18], at the B3LYP [19,20] density functional with the 6-31G(d) basis set [21]. Previous work showed that B3LYP/6-31G(d) is relatively accurate, although the reaction exothermicities are underestimated by about 5 kcal/mol [22,23].

- Full geometry optimizations were computed with restricted and unrestricted B3LYP/6-31G(d) methods.

- The graphene models, as illustrated in Figure 1, include polybenzenoid hydrocarbons and we found that there are many types of double bonds but only three of them will be taken into consideration namely center, corner and edge as per the publication by Cao and Houk [9].

- The center bonds of the 5×5 and 6×6 systems will behave most like graphene as they are surrounded by more benzene rings compared to smaller systems even though graphene consists of thousands of carbon atoms.

- Every stationary point identified was characterized by the number of negative eigenvalues of their Hessian matrix; 0 for minima and 1 for any true TS. The imaginary frequencies also exhibit the expected motion.

- The reported electronic energies include zero-point energies (ZPE) corrections.

- Further, the intrinsic reaction coordinate [24,25] (IRC) path was traced, at the same level of theory, to ensure that the TSs led to the expected reactants and products.

- Natural bond orbital (NBO) analysis was performed on the electronic structures of the critical points according to Weinhold and coworkers [26,27] as implemented in Gaussian 09.

3.0 Results and Discussion

3.1 Energetics

- Table 1 lists the relative energies of the 32CA reactions of **RCNO** with ethene (0×0, see Figure 2), the simplest dipolarophile. This reaction has the lowest activation energy and is most exothermic as supported by literature [9].

Table 1: Relative energies[a] (ΔE, kcal mol^{-1}) including ZPE for the gas phase reactions of **RCNO (R = H, F and Me)** with ethene (0×0) and benzene (1×1).

	(0×0)		(1×1)	
	TS	CA	TS	CA
HCNO	13.30	-39.84	24.20	-1.15
FCNO	1.58	-64.70	8.02	-26.62
MeCNO	13.91	-38.33	26.00	0.34

[a] *Relative to **RCNO** + 0×0 and 1×1.*

- On comparing the three nitrile oxides studied, it was found that the reaction with **FCNO** has the lowest activation energy and thus, indicates its ability to stabilize a radical mechanism.

- Benzene (1×1, see Figure 2) is the simplest aromatic system and unit of graphene which is used as dipolarophile. The 32CA reactions with **RCNO** disrupt the aromaticity of the benzene ring and hence the reaction has higher activation energy and is less exothermic than the reaction with ethene.

HCNO + 0×0   **FCNO** + 0×0   **MeCNO** + 0×0

HCNO + 1×1   **FCNO** + 1×1   **MeCNO** + 1×1
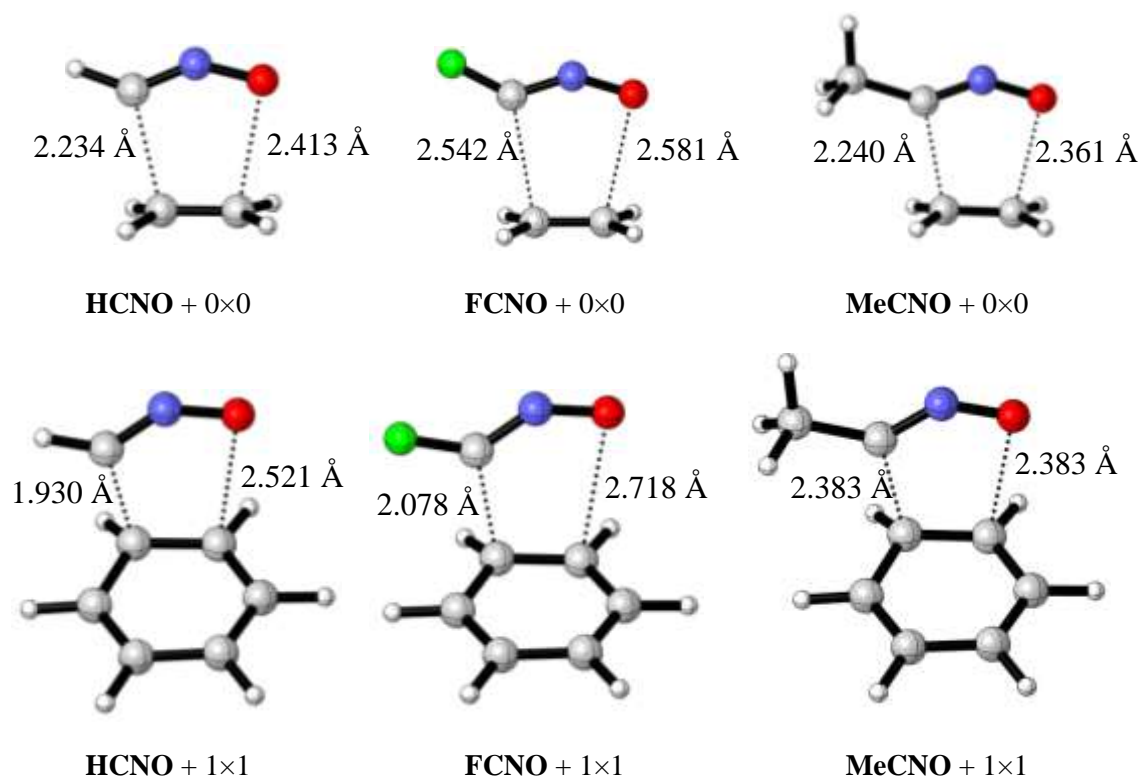
Figure 2: TSs obtained from the 32CA of **RCNO** with 0×0 and 1×1.

- Generally, the activation energy for the 32CA of **RCNO** with 2×2 up to 6×6 systems follows the same trend as illustrated in Figure 3(a). So far, we have not yet been able to locate the TS for the reaction of MeCNO with the 6×6 graphene model.

- The activation energy at the center bonds is kinetically unfavourable compared to the corner and edge bonds. This is because reactions at the center bond have a direct effect on the surrounding benzene rings because their aromaticity are lost, thereby weakening the π-π conjugation and distorting the planar morphology of the graphene models.

9
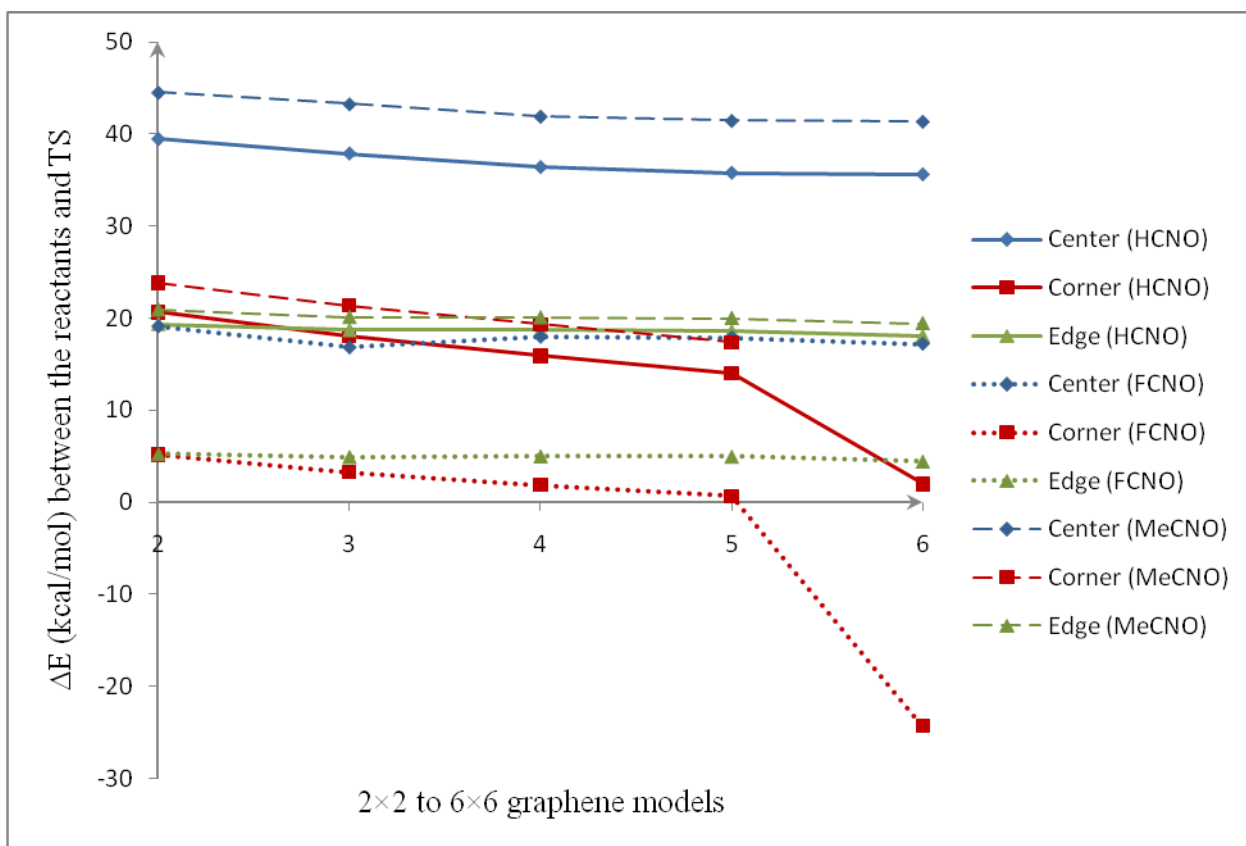
Figure 3(a) Relative energies of the transition states involved in the 32CAs of **RCNO** with graphene models at the RB3LYP/6-31G(d) level.

- An analysis of Figure 3(b) indicates that the reactions at the corner and edge bonds are more favoured kinetically as well as thermodynamically, with a preference for reaction at the edge bond, since only the ring in which reaction occurred is distorted while the other areas are unaffected.
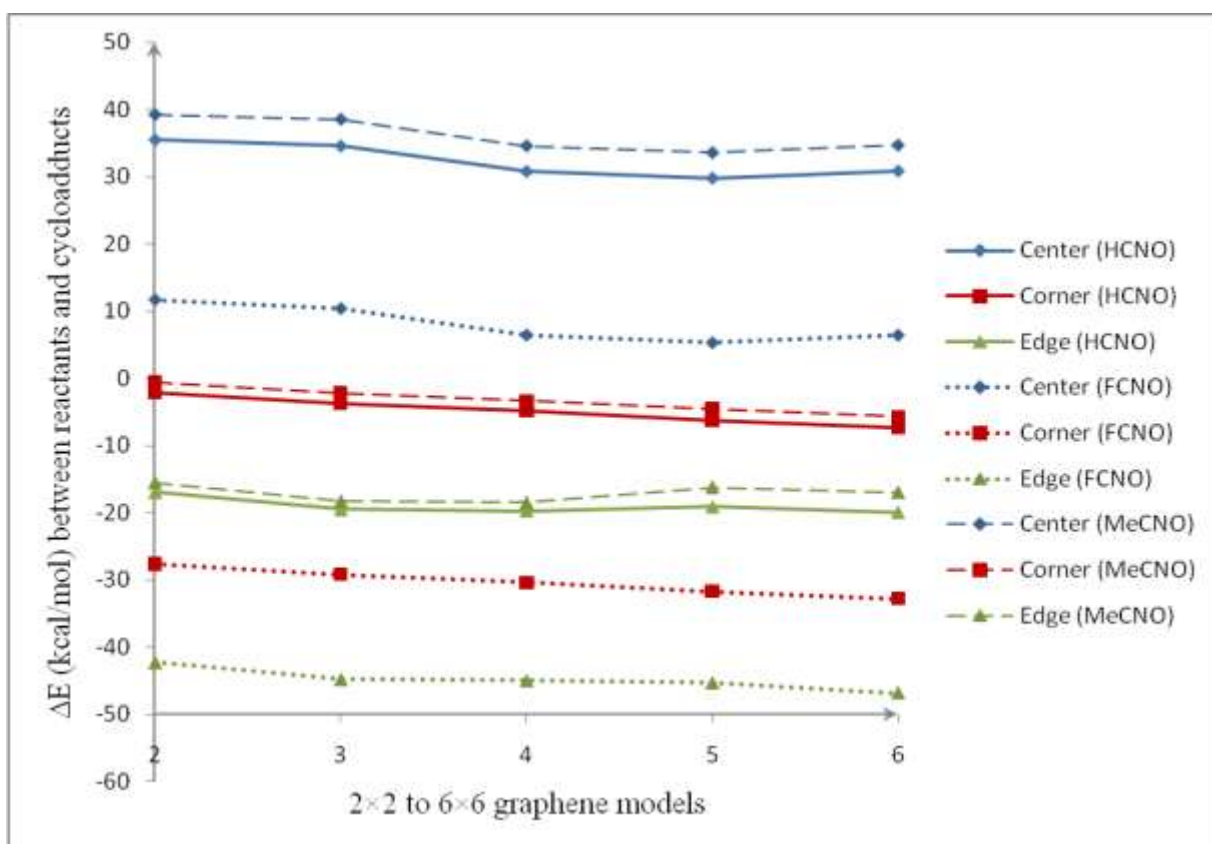
Figure 3(b) Relative energies of cycloadducts involved in the 32CA of **RCNO** with graphene models at the RB3LYP/6-31G(d) level.

- It is interesting to note that as from the 4×4 system, the activation energy and the relative energies between the reactants and cycloadducts become almost same as the reactive sites are shared by the same number of benzene rings.

- Moreover, reaction with **MeCNO** yields a higher activation energy followed by **HCNO** and **FCNO**. The activation energy for the 32CA of **FCNO** with all the graphene models decreases drastically which is in conformity with the activation energy obtained for its reaction with [60]fullerene [17].

- Furthermore, we suspect that the results for the 6×6 system as the 32CA of the nitrile oxides to the 6×6 graphene model at the corner bond yielding a negative activation energy are
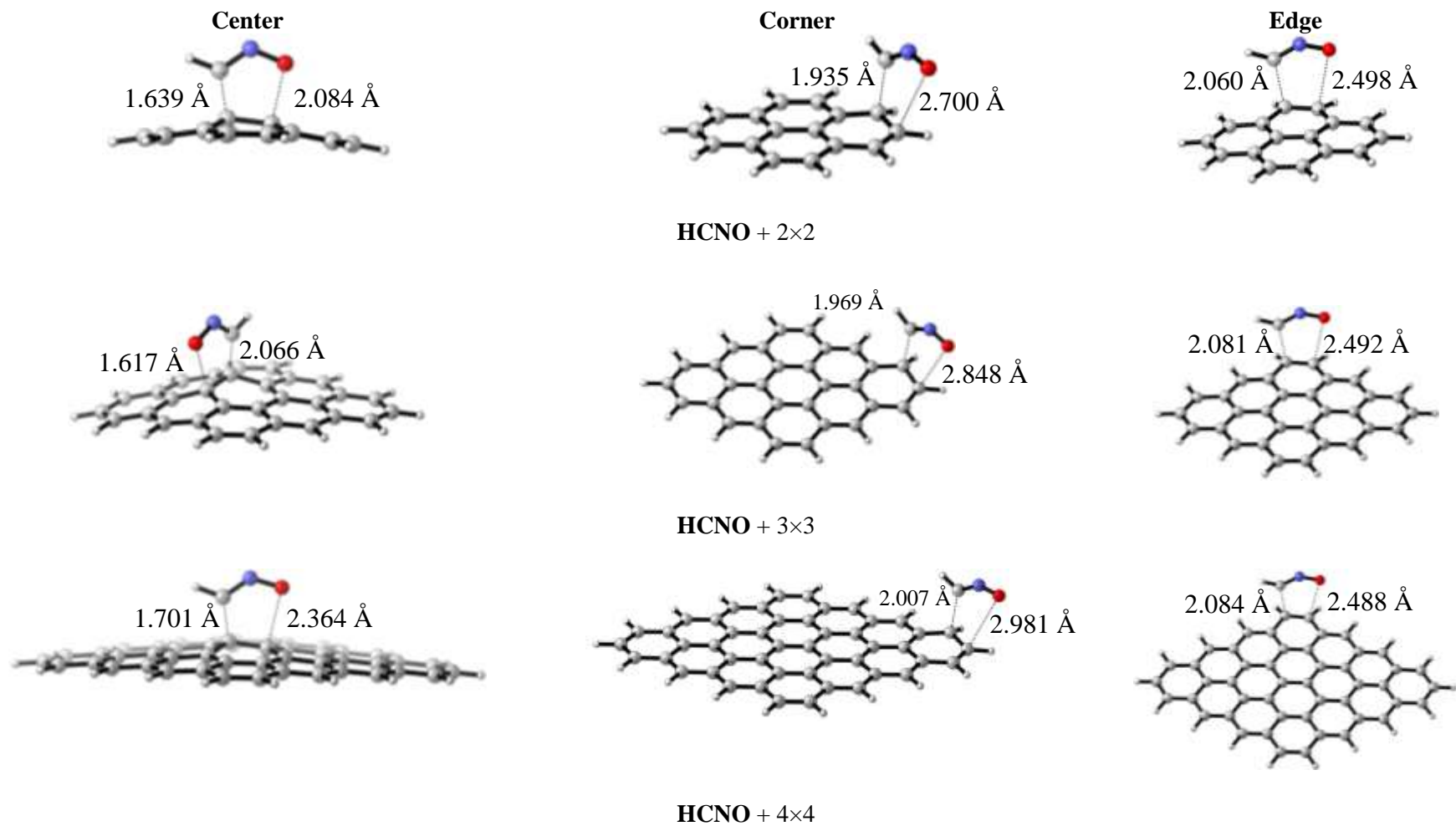
spurious. In contrast to the smaller systems, the trend obtained for the restricted and unrestricted reactions of the 6×6 system is not conserved.
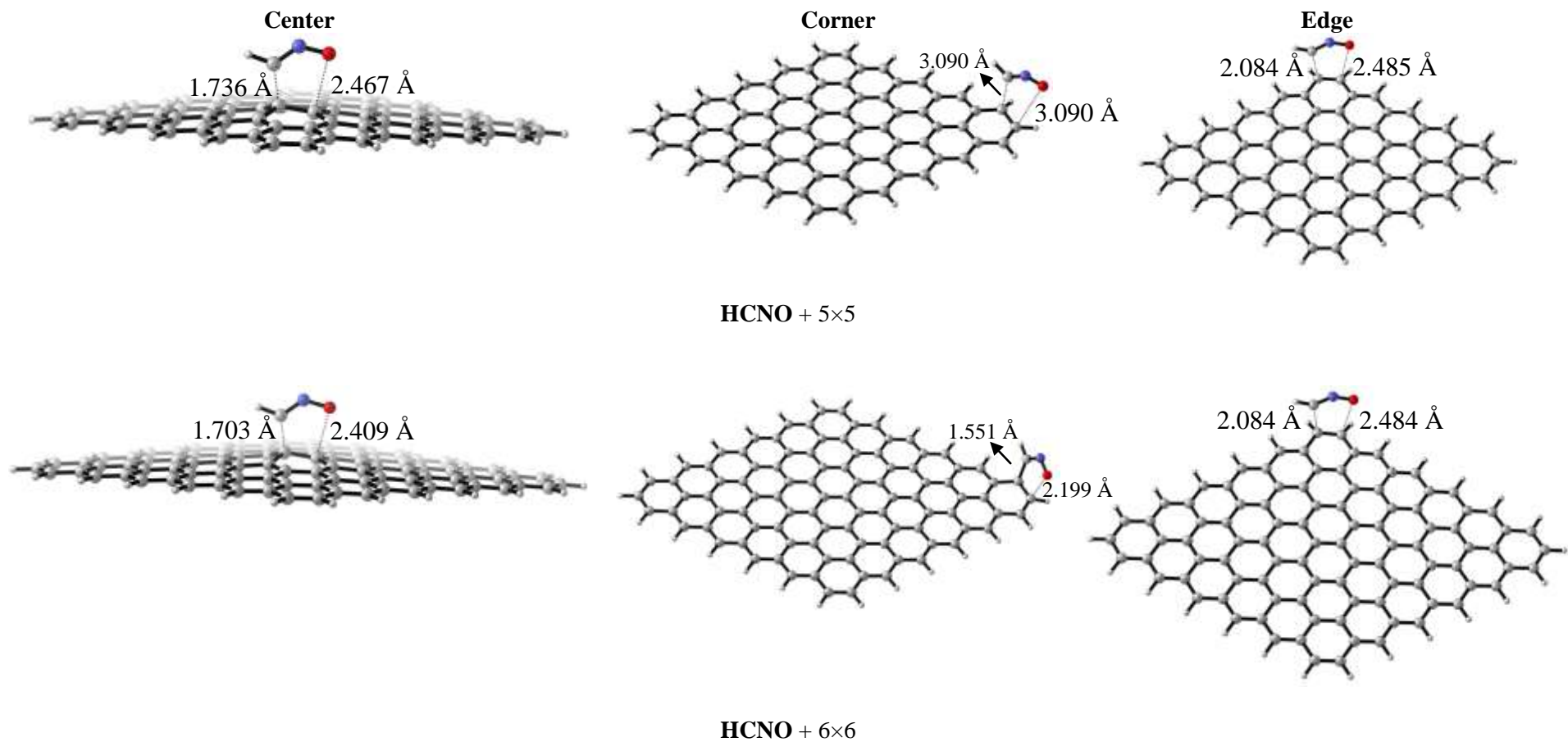
3.2 Geometrical Parameters

- An analysis of the geometries of the TSs (Figure 4) associated with these 1,3-DCs show that these reactions are asynchronous one-step processes.

- Analysis of the lengths of the two forming bonds at the TSs indicates that the length of the C–O forming bond is longer than the C–C bond, suggesting that the formation of C–C bond is more advanced than the C–O bond.

- The degree of asynchronicity, Δd, can be determined by considering the ratio of difference between the lengths of the two forming bonds such that $\Delta d = [d(C–O) – d(C–C)]$ as shown in Table 2.

Table 2: Δd at the TSs.

R	center	corner	edge
		2×2	
H	0.45	0.77	0.44
F	0.83	0.78	0.41
Me	0.39	0.53	0.30
		3×3	
H	0.45	0.88	0.41
F	0.92	0.89	0.36
Me	0.44	0.62	0.17
		4×4	
H	0.66	0.97	0.40
F	0.81	0.98	0.36
Me	0.45	0.68	0.16
		5×5	
H	0.73	1.05	0.40
F	0.82	1.07	0.35
Me	0.46	0.72	0.16
		6×6	
H	0.71	0.65	0.40
F	0.84	0.69	0.35
Me	0.47	-	0.16

Center **Corner** **Edge**

1.639 Å 2.084 Å

1.935 Å 2.700 Å

2.060 Å 2.498 Å

HCNO + 2×2

1.617 Å 2.066 Å

1.969 Å 2.848 Å

2.081 Å 2.492 Å

HCNO + 3×3

1.701 Å 2.364 Å

2.007 Å 2.981 Å

2.084 Å 2.488 Å

HCNO + 4×4

Figure 4(a): TSs obtained from the 32CA reactions of **HCNO** with 2×2, 3×3 and 4×4 at the RB3LYP/6-31G(d) level.

Center

1.736 Å   2.467 Å

Corner

3.090 Å

3.090 Å

Edge

2.084 Å   2.485 Å

HCNO + 5×5

1.703 Å   2.409 Å

1.551 Å

2.199 Å

2.084 Å   2.484 Å

HCNO + 6×6

Figure 4(b): TSs obtained from the 32CA reactions of **HCNO** with 5×5 and 6×6 at the RB3LYP/6-31G(d) level.

- Greater asynchronicity is observed for the reaction of nitrile oxides at the corner bonds of the graphene models followed by the reaction at the edge bonds. However, the asynchronity decreases for the reaction of **RCNO** with the 6×6 graphene model at the corner bond compared to the smaller models as the C–C bond is already formed in the TSs involving the 6×6 model.

- Moreover, a comparison of the Δd for these 32CAs indicates that Δd is largest when $\mathbf{R} = \mathbf{F}$ and hence, it is the most asynchronous. The corresponding reactions have a two-stage one-step mechanism. On the other hand, the most synchronous TS arises from the reaction of **MeCNO** with the graphene models.

- It can be concluded that the presence of fluorine on the nitrile oxide produces a cycloadduct through more asynchronous TSs ($\mathbf{R} = \mathbf{F}$), while the presence of an electron-releasing group on the nitrile oxide affords more synchronous TSs ($\mathbf{R} = \mathbf{Me}$). We also found that moving from 2×2 to 6×6 graphene models, the synchronicity difference increases considerably.

3.3 Bond Order and Charge Transfer

- The Wiberg bond indices [28] have been computed to follow the nature of the cycloaddition process using NBO analysis.

- The BO values of the two forming bonds at the TSs for the 32CA are reported in Table 3.

Table 3: Wiberg Bond Orders of the TSs involved during the 32CA of nitrile oxides with models of graphene at the RB3LYP/6-31G(d) level.

R	center		corner		edge	
	C-O	C-C	C-O	C-C	C-O	C-C
	2×2					
H	0.34	0.77	0.11	0.48	0.19	0.38
F	0.10	0.58	0.07	0.31	0.13	0.25
Me	0.30	0.70	0.16	0.48	0.23	0.37
	3×3					
H	0.35	0.80	0.08	0.45	0.19	0.37
F	0.06	0.52	0.05	0.28	0.13	0.23
Me	0.29	0.74	0.12	0.46	0.23	0.36
	4×4					
H	0.20	0.69	0.06	0.42	0.19	0.37
F	0.09	0.49	0.03	0.24	0.13	0.23
Me	0.24	0.63	0.07	0.44	0.24	0.35
	5×5					
H	0.16	0.65	0.05	0.40	0.19	0.37
F	0.09	0.47	0.02	0.21	0.13	0.23
Me	0.22	0.61	0.07	0.42	0.24	0.36
	6×6					
H	0.18	0.69	0.26	0.92	0.19	0.37
F	0.08	0.48	0.25	0.94	0.13	0.23
Me	0.22	0.64	-	-	0.24	0.36

- For the 32CAs at the center, corner and edge bonds, the BO values for the C-O and C-C bonds decrease and eventually become comparable as from the 4×4 graphene model.

- The electronic nature of these 32CAs is evaluated by analyzing the CT at the TSs. The natural atomic charges are shared between the nitrile oxides and the models of graphene, and these data are shown in Table 4.

Table 4: Charge transfer (CT, in e) of TSs at the RB3LYP/6-31G(d) level.

R	center	corner	edge
		2×2	
H	-0.10	-0.09	-0.05
F	-0.13	-0.11	-0.07
Me	-0.06	-0.06	-0.02
		3×3	
H	-0.12	-0.08	-0.04
F	-0.13	-0.11	-0.06
Me	-0.09	-0.05	-0.01
		4×4	
H	-0.11	-0.07	-0.03
F	-0.12	-0.11	-0.05
Me	-0.05	-0.04	-0.01
		5×5	
H	-0.09	-0.07	-0.03
F	-0.07	-0.12	-0.05
Me	-0.05	-0.03	0.00
		6×6	
H	-0.10	-0.20	-0.03
F	-0.12	-0.25	-0.05
Me	-0.06	-	0.00

- For the reactions with ethene, the natural population analysis gives a negligible CT, which takes place from ethene to the nitrile oxides (CT = -0.03, -0.03 and -0.01 for **HCNO**, **FCNO** and **MeCNO**, respectively).

- Similarly, the 32CAs of the nitrile oxides with benzene have insignificant CT being -0.08, -0.09 and -0.06 for **HCNO**, **FCNO** and **MeCNO**, respectively. These low CTs point to non-polar processes with some pseudoradical character [29,30]. It is to be noted that CT increases slightly with the presence of fluorine on the nitrile oxide.

- The reactions with the graphene models (2×2 to 6×6), also present very low CT; however, in all these cycloadditions, the flux of the electron density depends on the nature of the substituent

present on the nitrile oxide. The reaction of **MeCNO** with the graphene models shows that there is no CT between the reactants.

- All the computed TSs have only one imaginary vibrational frequency, corresponding to the atomic motion along the direction of the newly forming bonds. The values for the imaginary frequencies are reported in Table 5.

Table 5: Dipole moment (Debye) and imaginary frequency (cm^{-1}) of the TSs at the RB3LYP/6-31G(d) level.

	Dipole moment (Debye)			Imaginary frequency (cm^{-1})		
R	center	corner	edge	center	corner	edge
	2×2					
H	3.163	3.698	3.431	-333.7	-417.3	-448.3
F	3.584	3.761	3.350	-318.0	-377.0	-355.9
Me	3.864	3.380	3.575	-353.1	-433.3	-450.1
	3×3					
H	3.346	4.436	2.079	-212.2	-435.8	-452.3
F	3.595	4.761	2.023	-307.1	-250.8	-252.9
Me	2.877	3.541	2.177	-199.0	-433.0	-448.9
	4×4					
H	2.677	5.245	1.926	-148.0	-452.6	-454.0
F	3.095	5.884	1.998	-322.8	-225.0	-254.3
Me	1.951	3.780	1.886	-304.8	-451.8	-450.4
	5×5					
H	2.572	6.039	1.883	-193.8	-460.9	-455.0
F	3.072	7.004	2.022	-346.5	-197.6	-254.7
Me	1.707	3.922	1.735	-334.3	-464.9	-450.8
	6×6					
H	2.661	11.156	1.884	-132.9	-155.6	-455.4
F	3.087	15.233	2.057	-341.2	-156.4	-255.1
Me	1.776	-	1.680	-296.7	-	-451.2

- The imaginary frequency values of the TSs involving **MeCNO** are slightly lower than those involving **FCNO**. These low values indicate that these processes are associated with heavy atom motions and are also related to the earlier TSs.

4.0 Conclusions and Future Work

- In order to gain a better insight into the reaction mechanism, we also report the synchronicity, the nature of the TS and the charge transfer of the 32CA reaction.

- An unexpected behaviour (lowest activation energy) has been observed for the 32CA involving **FCNO** as these reactions have some pseudodiradical character.

- Generally, the geometrical parameter and BO analysis reveal that the TSs are concerted and asynchronous. However, the high asynchronicity found in the 32CA reactions of **FCNO** indicate that these reactions take place via a two-stage one step mechanism.

- The low CT found at the TSs, indicates that these 32CA reactions have non-polar character.

- We anticipate that the aforementioned data will be helpful to experimentalists in their attempts for the synthesis and characterization of these novel compounds.

- In future work, we will analyze the reactivity indices and the rate constants of these 32CA reactions and discuss their relative stabilities.

Acknowledgements

References

1. R. Huisgen, Angew. Chem., Int. Ed. Engl., 1963, 2, 565.

2. B. I. Kharisov, O. V. Kharissova, M. J. Gomez and U. O. Mendez, Ind. Eng. Chem. Res., 2009, 48, 545.

3. G. Ghini, L. Luconi, A. Rossin, C. Bianchini, G. Giambastiani, S. Cicchi, L. Lascialfari, A. Brandi and A. Giannasi, Chem. Commun., 2010, 46, 252.

4. Z. Markovic and V. Trajkovic, Biomaterials, 2008, 29, 3561.

5. D. M. Guldi, F. Zerbetto, V. Georgakilas, and M. Prato, Acc. Chem. Res., 2005, 38, 38.

6. R. Maeda-Mamiya, E. Noiri, H. Isobe, W. Nakanishi, K. Okamoto, K. Doi, T. Sugaya, T. Izumi, T. Homma and E. Nakamura, Proc. Natl. Acad. Sci., 2010, 107, 5339.

7. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 2004, 306, 666.

8. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, Nature, 2005, 438, 197.

9. Y. B. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, Nature, 2005, 438, 201.

10. K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim and A. K. Geim, Science, 2007, 315, 1379.

11. R. Ruoff, Nat. Nanotechnol., 2008, 3, 10.

12. V. Georgakilas, A. B. Bourlinos, R. Zboril, T. A. Steriotis, P. Dallas, A. K. Stubos and C. Trapalis, Chem. Commun., 2010, 46, 1766.

13. M. Quintana, K. Spyrou, M. Grzelczak, W. R. Browne, P. Rudolf and M. Prato, ACS Nano, 2010, 4, 3527.

14. T. T. Lin, W. D. Zhang, J. C. Huang and C. B. He, J. Phys. Chem. B, 2005, 109, 13755.

15. D. E. Jiang, B. G. Sumpter and S. Dai, J. Chem. Phys., 2007, 126.

16. Y. Cao and K. N. Houk, J. Mater. Chem., 2011, 21, 1503.

17. L. Rhyman, S. Jhaumeer-Laulloo, L. R. Domingo, J. A. Joule and P. Ramasami, Heterocycles, 2012, 84, 719.

18. Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

19. A. D. Becke, J. Chem. Phys., 1988, 38, 3098.

20. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.

21. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab initio Molecular Orbital Theory; Wiley and Sons: New York, 1986.

22. E. Goldstein, B. Beno and K. N. Houk, J. Am. Chem. Soc., 1996, 118, 6036.

23. L. R. Domingo, M. Arnó and J. Andrés, J. Am. Chem. Soc., 1998, 120, 1617.

24. C. Gonzalez and H. B. Schlegel, J. Chem. Phys., 1989, 90, 2154;

25. C. Gonzalez and H. B. Schlegel, J. Phys. Chem., 1990, 94, 5523.

26. A. E. Reed, R. B. Weinstock, and F. Weinhold, J. Chem. Phys., 1985, 83, 735.

27. A. E. Reed, L. A. Curtiss, and F. Weinhold, Chem. Rev., 1988, 88, 899.

28. K. B. Wiberg, Tetrahedron, 1968, 24, 1083.

29. L. R. Domingo, M. T. Picher, P. Arroyo, and J. A. Saez, J. Org. Chem., 2006, 71, 9319

30. L. R. Domingo, E. Chamorro, P. Pérez, Eur. J. Org. Chem., 2009, 3036.

Kindly visit:

7th Workshop on Computational Chemistry and Its Applications (7th CCA)
part of The International Conference on Computational Science
5 – 7 June, 2013, Barcelona, Spain

Workshop website: http://sites.uom.ac.mu/cca/