Theoretical study of the Diels-Alder reaction between o-benzoquinone and norbornadiene

To cite this article: Ramiro F Quijano-Quiñones et al 2013 IOP Conf. Ser.: Mater. Sci. Eng. 45 012029

View the article online for updates and enhancements.

You may also like

- Advances in the chemical modification of epitaxial graphene
  E Bekyarova, S Sarkar, S Niyogi et al.

- Umpolung Diels-Alder Reactions By Electrocatalysis
  Yohei Okada, Atsushi Ozaki, Yusuke Yamaguchi et al.

- A review on Diels-Alder based self-healing polymer composites
  N I Khan, S Halder, S B Gunjan et al.
Theoretical study of the Diels-Alder reaction between o-benzoquinone and norbornadiene

Ramiro F Quijano-Quiñones¹, M Quesadas-Rojas¹, Gabriel Cuevas² and Gonzalo J Mena-Rejón¹

¹Laboratorio de Química Farmacéutica, Facultad de Química, Universidad Autónoma de Yucatán, calle 41 No. 421 x 26 y 28 col. Industrial C.P. 97150. Mérida, Yucatán, México
²Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, Ciudad Universitaria, C.P. 04510 México D.F., México

E-mail: ramiro.quijano@uady.mx

Abstract. The reaction between norbornadiene and o-benzoquinone is an important step in polyalicyclic rigid structures synthesis. It has been considered that this reaction is an example of Diels-Alder (DA) and hetero-Diels-Alder (HDA) cycloadditions with o-benzoquinone acting as diene (forming C-C bonds) and heterodiene (forming O-C bonds). We have performed a Density Functional Theory study of this reaction, employing B3LYP, mPW1PW91, and B1B95 functionals and 6-31G(d,p) and 6-31+G(d,p) Gaussian type basis sets. The results indicate that Diels-Alder is a feasible mechanism for both reactions, but should not be the main route to the formation of products with C-C bonds.

1. Introduction

The Diels-Alder (DA) and Hetero-Diels-Alder (HDA) reactions are [4+2] π electrons cycloadditions of great importance for organic chemistry and represent one of the most powerful methods in synthetic chemistry. In particular, the Diels-Alder reaction of o-benzoquinone as a diene and norbornadiene as a dienophile has been used to produce rigid polyalicyclic structures [1-3] with the ability to act as supramolecular hosts by acting as molecular tweezers, clamps, and clips for synthetic receptors [4] and have been employed in host-guest studies [5-6].

Margetić et al. [7] have studied the reaction of o-benzoquinone (R=H, Figure 1) and o-chloranil (R=Cl, Figure 1) with norbornadiene. Experimentally, they have found that o-chloranil gave six adds 1-6. In contrast, the similar reaction with o-benzoquinone only gives four adds 1-4 with the adduct 1 being the dominant product, while adds 2 and 3 were found in smaller amounts, and adduct 4 was detected by spectroscopy, but not isolated. In order to explain the experimentally observed stereospecificities, the author performed a theoretical study of these Diels-Alder reactions using ab initio methods at DFT level using a Gaussian type basis set 6-31G(d,p) and the B3LYP hybrid functional for the exchange-correlation potential. Given their failure to locate concerted transition structure for the HDA cycloaddition of o-benzoquinone (adds 5 and 6), they proposed a second, nonconcerted biradical mechanism leading to formation of the products 5 and 6. However, the performance of the theoretical method was not evaluated, which is important to establish the reliability of theoretical results, since there are evidence that B3LYP [8] method usually underestimates barrier heights [9, 10] and there are several hybrid functionals developed to increase B3LYP performance.
incorporating kinetic energy of electrons and/or changing the amount of exact HF exchange in the exchange-correlation functional form [11]. This is the case of mPW1PW91 [12] which incorporates 25% of exact HF exchange (in contrast with 20% included in B3LYP), and B1B95 [13] which includes kinetic energy of electrons. Both exchange-correlation potentials have demonstrated a better performance than B3LYP in prediction of energy barriers of some organic reactions [14-16]. In order to get a better understanding of the reaction nature, we have performed a systematic study using different Gaussian basis sets and different approximations to the exchange-correlation functional, to evaluate changes in the transition state structure and the activation energy of this reaction with respect to the method of calculation.

![Figure 1. Reaction between o-benzoquinone (R=H) and o-chloranil (R = Cl) with norbornadiene.](image)

2. Computational Details
All the quantum chemical calculations were performed with Gaussian 09 [17]. Geometrical optimization, including transition-structure searches, was carried out with Gaussian type 6-31G(d,p) and 6-31+G(d,p) basis sets, using Density Functional Theory (DFT) hybrid methods with B3LYP, mPW1PW91, and B1B95 functionals for evaluate the exchange-correlation potential, employing the following convergence criteria: Maximum force on each atom < 0.023 eV/Å, mean root square of the maximum force on each atom < 0.0153 eV/Å, maximum displacement of each atom < 0.0095 Å, and mean root square of maximum displacement of each atom < 0.00064 Å.

Transition-structures search was carried out with Synchronous Transit-Guided Quasi-Newton (STQN) Method, which was developed by Schlegel and co-workers [18], and uses a linear synchronous transit or quadratic synchronous transit approach to get closer to the quadratic region around the transition state and then uses a quasi-Newton or eigenvector-following algorithm to complete the optimization.

Transition states were verified by vibrational analysis, confirming the presence of one imaginary frequency corresponding to a movement in the direction of the reaction coordinate. The values of the activation energies have been calculated on the basis of the total energies of the stationary points.

3. Results and Discussion
All the transition states were located and their degree of asynchronicity (Δd) and activation energy (ΔE) are collected in tables 1 and 2, while transition state structures at B3LYP/6-31+G(d,p) are depicted in figure 2.

Our results (table 1) shows that the transition states TS1, TS5, and TS6 are highly synchronous, with Δd values below 0.05. On the other hand TS2 and TS3 were slightly asynchronous with values up to 0.135, whereas TS4 was highly asynchronous, with Δd up to 0.466. All our attempts to locate a synchronous TS4 were unsuccessful and converged to a non-synchronous TS4.

As we expected from previously reports [7, 14, 16], the size of the barrier depends on the calculation method. Table 2 shows that with mPW1PW91 and B1B95 exchange-correlation functionals, we obtain lower activation barriers than with B3LYP. Taking into account that B3LYP
underestimates activation barriers [9, 10] we can conclude that mPW1PW91 and B1B95 are poor candidates for the study of this reaction. Furthermore, the effect of adding diffuse functions is increase all activation energies about 1-2 kcal/mol as well as the degree of asynchronicity.

Table 1. Degree of asynchronicity\textsuperscript{a} for the conversion of o-benzoquinone and norbornadiene to adducts 1-6.

| Level of calculation | 1     | 2     | 3     | 4     | 5     | 6     |
|----------------------|-------|-------|-------|-------|-------|-------|
| B1B95/6-31G(d,p)     | 0.001 | 0.002 | 0.039 | 0.241 | 0.000 | 0.003 |
| B1B95/6-31+G(d,p)    | 0.001 | 0.011 | 0.041 | 0.331 | 0.001 | 0.003 |
| B3LYP/6-31G(d,p)     | 0.001 | 0.040 | 0.095 | 0.316 | 0.001 | 0.006 |
| B3LYP/6-31+G(d,p)    | 0.000 | 0.135 | 0.116 | 0.466 | 0.000 | 0.006 |
| mPW1PW91/6-31G(d,p) | 0.000 | 0.001 | 0.001 | 0.245 | 0.001 | 0.004 |
| mPW1PW91/6-31+G(d,p)| 0.002 | 0.041 | 0.100 | 0.298 | 0.000 | 0.001 |

\textsuperscript{a}TS/P, defined as the difference between the ratios of the forming bond lengths in the TS and the corresponding bond lengths in the product [19].

Table 2. Calculated activation energies for the conversion of o-benzoquinone and norbornadiene to adducts 1-6 (kcal/mol).\textsuperscript{a}

| Level of calculation | TS1 | TS2 | TS3 | TS4 | TS5 | TS6 |
|----------------------|-----|-----|-----|-----|-----|-----|
| B1B95/6-31G(d,p)     | 13.8| 15.2| 15.5| 20.3| 9.5 | 12.6|
| B1B95/6-31+G(d,p)    | 15.0| 16.7| 16.8| 21.8| 11.6| 14.3|
| B3LYP/6-31G(d,p)     | 18.3| 20.0| 20.8| 24.4| 9.6 | 12.8|
| B3LYP/6-31+G(d,p)    | 20.2| 22.0| 22.9| 26.6| 12.3| 15.1|
| mPW1PW91/6-31G(d,p) | 13.1| 15.0| 15.3| 19.9| 8.6 | 11.7|
| mPW1PW91/6-31+G(d,p)| 14.5| 16.5| 16.8| 21.5| 10.7| 13.5|

\textsuperscript{a}Label TS\textsubscript{i} refers to the transition state for the formation of adduct i.

Figure 2. Transition states (B3LYP/6-31+G(d,p)) for the reaction between o-benzoquinone and norbornadiene to form adducts 1-6.

All the levels of calculation predict the following order on the activation energies, TS5 < TS6 < TS1 < TS2 < TS3 < TS4, which is not according to the experimental selectivity found for products 1-6 [1, 7]. However, the fact that transition states TS5 and TS6 exist, means that reaction producing...
adducts 5 and 6 is viable, and could operate by DA mechanism, in contrast with the findings in a previous report [7].

4. Conclusions

We find the transition states TS5 and TS6, nevertheless we are not according with observed experimental selectivity. These results suggest that Diels-Alder is a feasible mechanism for both reactions, but should not be the main route to the formation of products with C-C bonds. There are other alternatives mechanistic paths: ionic or radical mechanism.

Acknowledgments

The financial support was provided by Facultad de Química of Universidad Autónoma de Yucatán, México (PIFI-FOMES 2007).

References

[1] Warrener R N, Johnston M R and Gunter M J 1998 Synlett. 593-6.
[2] Johnstom M R, Gunter M J and Warrener R N 2002 Tetrahedron 58 3445-51.
[3] Warrener R N, Johnston M R, Schultz A C, Golic M, Houghton M A and Gunter M J. 1998 Synlett 590-2.
[4] Klärner F G, Panitzky J, Preda D and Scott L T 2000 J. Mol. Model. 6 318-27.
[5] Yamaguchi T, Ishii N, Tashiro K and Aida T 2003 J. Am. Chem. Soc. 125 13934-5.
[6] Dudi´c M, Lhoták P, Stibor I, Pet´ríˇcková H and Lang K 2004 New J. Chem. 28 85-90.
[7] Margetić D, Johnston M R and Warrener R N 2001 Molecules 5 1417-28.
[8] Becke A D 1988 Phys. Rev. A 38 3098-3100.
Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785-789.
Stephens P J, Devlin F J, Chabalowski C F and Frisch M J 1994 J. Phys. Chem. 98 11623-7.
[9] Durant J L 1996 Chem. Phys. Lett. 256 595-602.
[10] Lynch B J, Fast P L, Harris M and Truhlar D G 2000 J. Phys. Chem. A 104 4811-5.
[11] Cohen A J, Mori-Sánchez P, Yang W 2012 Chem. Rev. 112 289-320.
[12] Adamo C and Baron V 1998 J. Chem. Phys. 108 664-675.
[13] Becke A D 1996 J. Chem. Phys. 104 1040-6.
[14] Barquera-Lozada J E and Cuevas G 2009 J. Org. Chem.74 874-83.
[15] Matsuda S P T, Wilson W K and Xiong Q 2006 Org. Biomol. Chem. 4 530-43.
[16] Zao Y, Pu J, Lynch B J and Truhlar D G 2004 Phys. Chem. Chem. Phys. 6 673-6.
[17] Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Seuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
[18] Peng C and Schlegel H B 1993 Isr. J. Chem. 33 449-54.
[19] Legnani L, Lunghi C, Albini M F, Nativi C, Richichi B and Toma L 2007 Eur. J. Org. Chem. 2007 3547-54.