

[G002]

DFT Study Of The Addition Of SO₂ To 1, 3-Butadiene And Derivatives

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Abstract

Addition reactions of SO₂ to 1,3-butadiene and heteroderivatives were studied by performing density functional theory (DFT) calculations together with the 6-311+G* basis set. Reactants, products, and transition states for each reaction were localized and the IRC connecting reactants and products was also obtained. Magnetic properties were evaluated along the reaction path to elucidate the characteristics of the reactions studied with respect to their aromaticity and pericyclic character.

The addition can proceed by means of a cheletropic reaction giving a five-membered cycle as a product or via a cycloaddition resulting on a six-membered cycle. The results thus obtained indicate that for most reactions studied the energy barrier is smaller for the cycloaddition process, whereas the most stable product comes from cheletropic reaction.

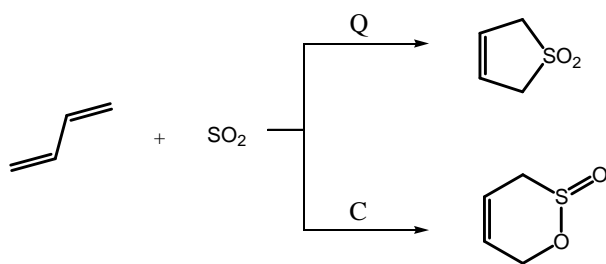
From the analysis of the magnetic properties along the reaction path, all reactions exhibit aromaticity enhancement near the transition state and, therefore, show pericyclic character.

Introduction

According to the original definition of Lemal, a pseudopericyclic reaction is a concerted transformation whose primary changes in bonding encompass a cyclic array of atoms, at one or more of which nonbonding and bonding atomic orbitals interchange roles.[1] Although Lemal's definition is seemingly clear, there is some ambiguity in it as the orbital description is not unique. As a consequence, no universally accepted clear-cut, absolute criterion exists for distinguishing a pseudopericyclic reaction from a normal pericyclic one.

In this respect, magnetic criteria seemed to be the most useful ones. In a normal pericyclic reaction, a cyclic loop of orbitals is formed in the transition state, leading to aromaticity, whereas in pseudopericyclic reactions, the orbital disconnection prevents the transition state for being aromatic.[2,3] Therefore, an analysis of magnetic properties (which reflect to some extent the presence of aromaticity) can be used as a criterion for distinguishing both reaction mechanisms.[3-5]

In a recent work, we have studied several thermal cheletropic decarbonylations, having found that several of these reactions exhibit pseudopericyclic character.[6] Following this line, in the present work, we present a study of SO₂ addition to 1,3-butadiene and derivatives. The addition can proceed by means of a cycloaddition (C) or a cheletropic reaction (Q), as shown in scheme 1. The reactions studied are shown in Figures 1 and 2.



Scheme 1

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- [1] J. A. Ross, R. P. Seiders, y D. M. Lemal, *J. Am. Chem. Soc.*, **98** (14) (1976) 4325.
[2] H. E. Zimmermann, *Acc. Chem. Res.*, **4** (1971) 272.
[3] R. Herges, H. Jiao, y P. v. R. Schleyer, *Angew. Chem. Int. Ed.*, **33** (1994) 1376.
[4] E. M. Cabaleiro-Lago, J. Rodríguez-Otero, y J. M. Hermida-Ramon, *J. Phys. Chem. A*, **107** (24) (2003) 4962.
[5] J. Rodríguez-Otero y E. M. Cabaleiro-Lago, *Chem. Eur. J.*, **9** (8) (2003) 1837.
[6] J. Rodríguez Otero, E. M. Cabaleiro Lago, J. M. Hermida-Ramón, y A. Peña-Gallego, *J. Org. Chem.*, **68** (2003) 8823.

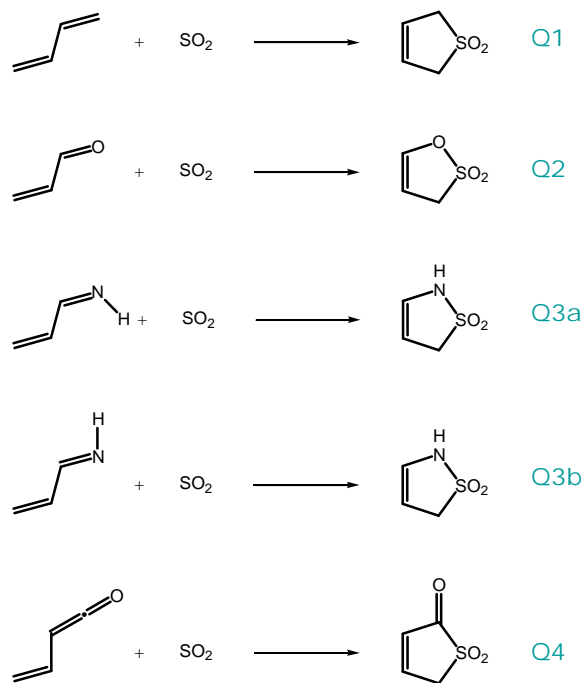


Figure 1. Cheletropic reactions studied in this work.

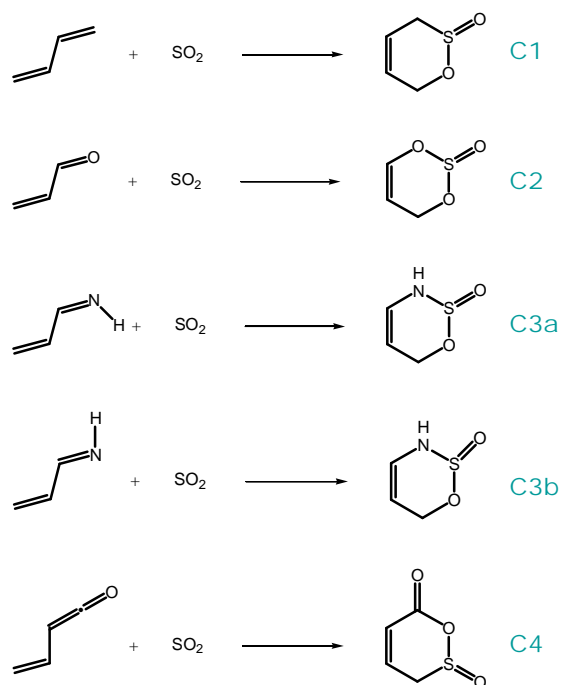


Figure 2. Cycloaddition reactions studied in this work.

Computational details

The geometry of each stationary point was fully optimized using the 6-311+G* basis set and the B3LYP functional. All points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies. Calculations with the G2MP2 method were also performed to obtain a better description of energies. Also, the pathway for each reaction was obtained by using the intrinsic reaction coordinate (IRC) with mass-weighted coordinates. The anisotropy of the magnetic susceptibility was then obtained at different points along the reaction path by computing the NMR shielding tensors at the B3LYP/6-311+G* level with the IGAIM method. Also, Nucleus Independent Chemical Shift (NICS) was obtained along the path in four different points of the system, as shown in Figure 3. NICS values were evaluated at the same level of calculation.

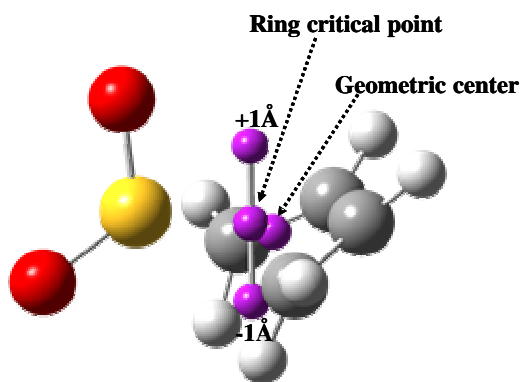


Figure 3. Points where NICS was calculated along the reaction path of each reaction studied.

Results

As noted from Table 1, all reactions present a considerable energy barrier, though it is usually smaller for the cycloaddition path. However, the most stable product is obtained from the cheletropic path in all cases except for reaction 4, where the cycloaddition product is more stable than the five-membered ring obtained from the cheletropic path. Also, all cheletropic reactions are neatly exothermic, except reaction 2 which is slightly endothermic, whereas in the group of cycloaddition reactions, only reaction 4 shows a clearly exothermic behaviour.

Table 1. Energies in kJ/mol relative to the reactants for the reactions studied.

	R_{cis} ^(a)	TS_{chel}	P_{chel}	TS_{endo} ^(b)	TS_{exo} ^(b)	P_{cyclo} ^(c)
Reaction 1	12.35	77.19	-43.32	75.64	78.04	-8.42
Reaction 2	8.60	119.57	2.88	90.28	74.62	20.00
Reaction 3a	11.06	117.53	-26.14	110.98	110.19	-1.86
Reaction 3b	10.98	86.53	-22.66	67.31	47.91	2.44
Reaction 4	6.30	72.55	-28.46	36.34	49.23	-72.30

(a) Energies of the butadiene in *s-cis* conformation.

(b) Endo and exo refer to the orientation of the free S-O bond with respect to the butadiene.

(c) Only the most stable conformation of the product is listed.

Figures 4 and 5 show how the anisotropy of the magnetic susceptibility changes along the reaction path for the reactions studied. It can be clearly appreciated the presence of minima in the vicinity of the transition states for all cycloaddition reactions, indicating aromatization in the transition state and therefore pericyclic character. In the case of cheletropic reactions the behaviour is not as clear, and only for reactions **Q1** and **Q3a** a clear minimum is observed. For reactions **Q2** and **Q3b** a not so defined minimum can be observed. Finally, for reaction **Q4** it seems that no minimum is present, which in principle indicates non-pericyclic mechanism.

NICS results allow a more clear interpretation. In this case, all reactions exhibit minima in the transition states in all points considered in the calculations (See Figures 6 and 7). Even reaction **Q4** exhibits a defined minimum thus indicating its pericyclic character. In any case, the aromaticity enhancement is much larger for cycloaddition reactions than for the corresponding cheletropic reactions for all cases studied.

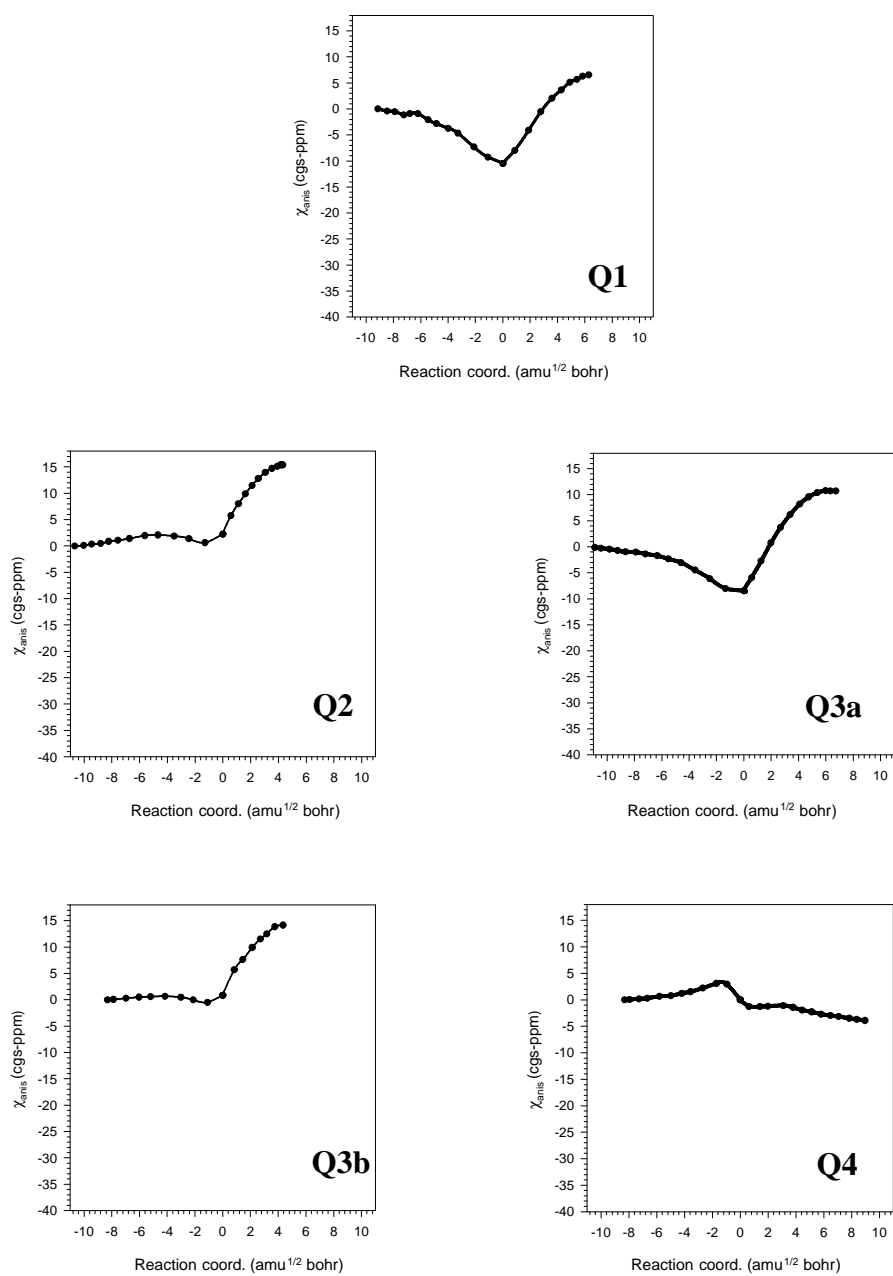


Figure 4. Variation of the anisotropy of the magnetic susceptibility along the reaction path relative to the reactants.

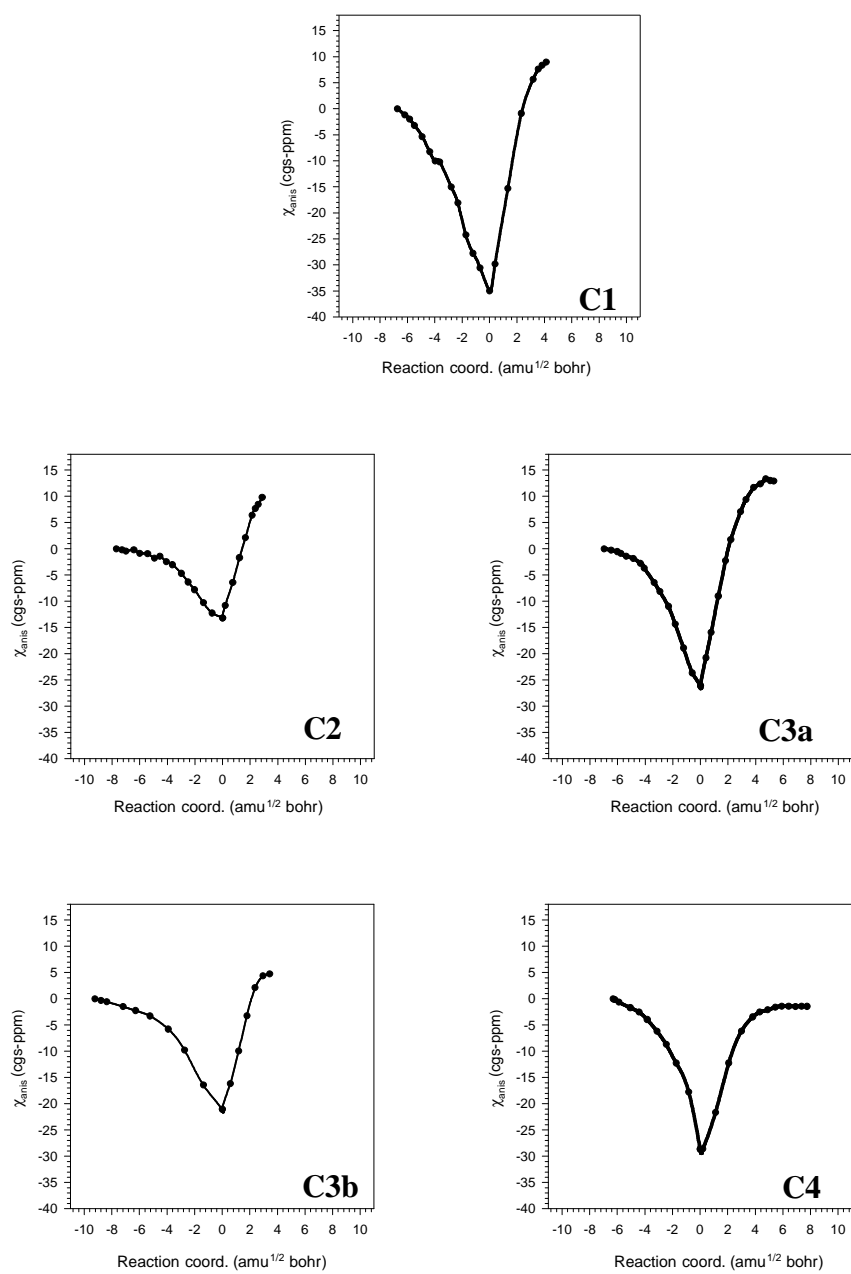


Figure 5. Variation of the anisotropy of the magnetic susceptibility along the reaction path relative to the reactants.

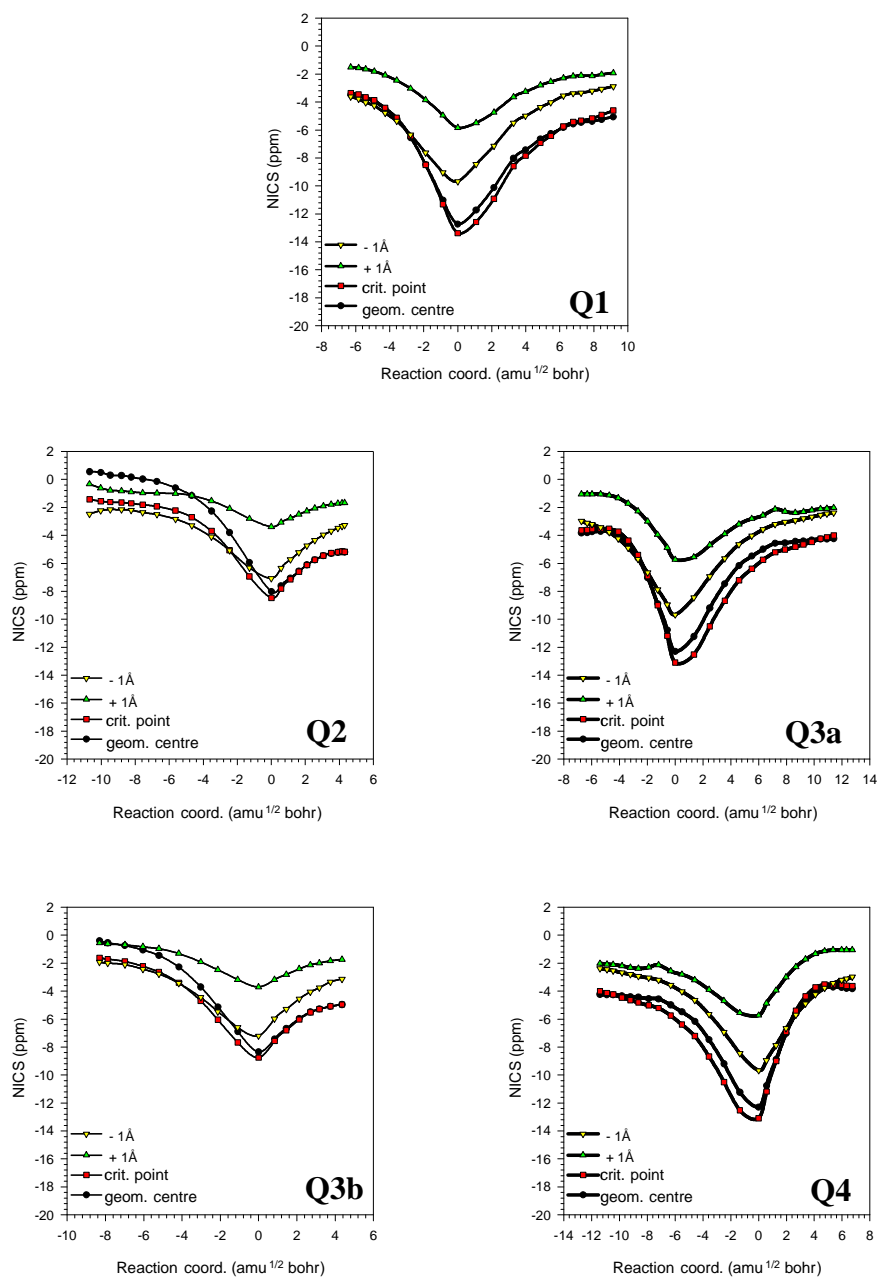


Figure 6. Variation of NICS along the reaction path as calculated in the points shown in figure 3.

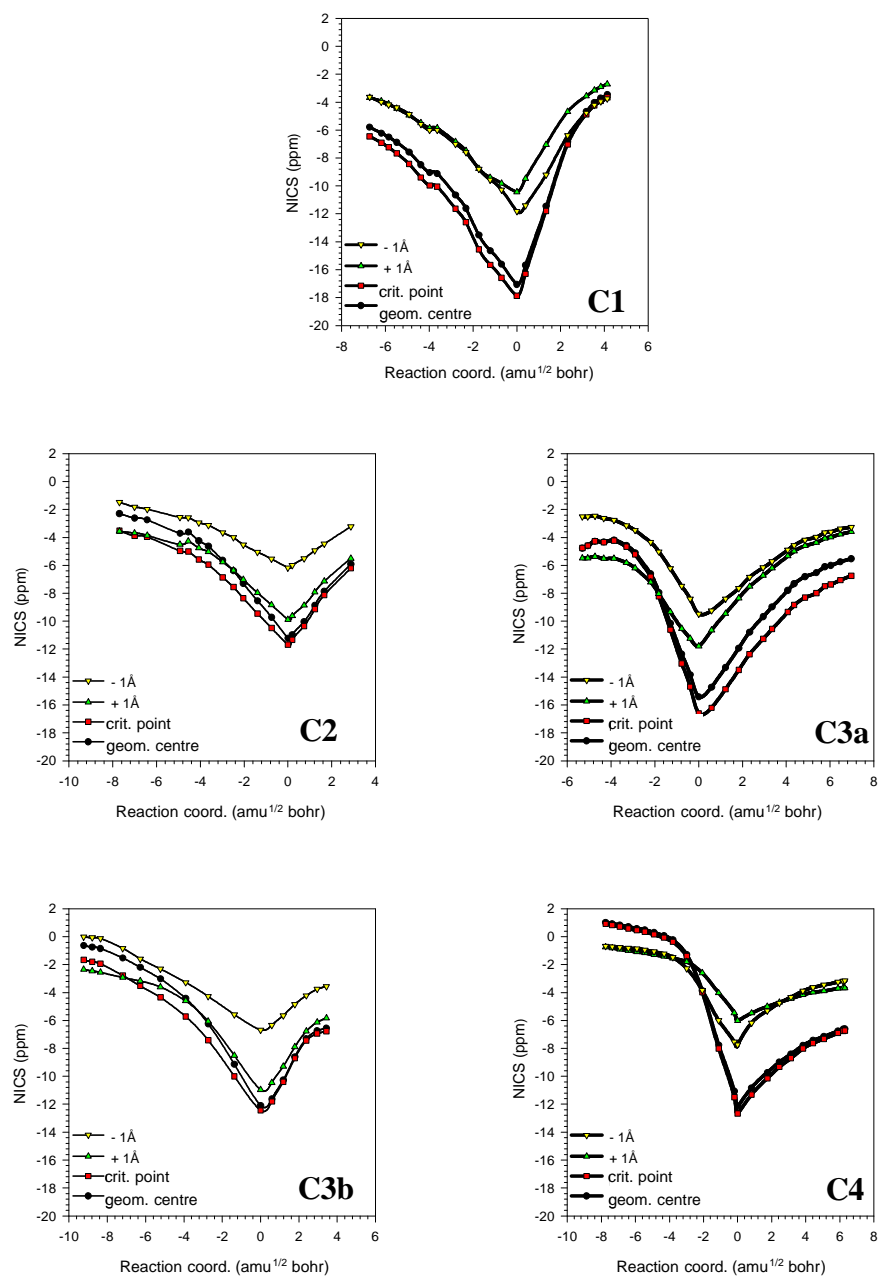


Figure 7. Variation of NICS along the reaction path as calculated in the points shown in figure 3.