

[g010] **Theoretical study of the pericyclic/pseudopericyclic character of the automerization of Perfluorotetramethyl (Dewar thiophene) *exo*-S-oxide.**

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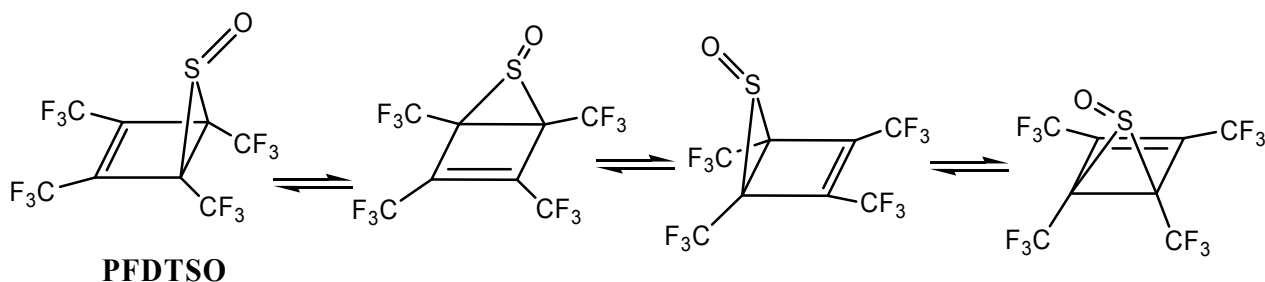
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Abstract

A theoretical study of the "walk" rearrangement in bicyclo[2.1.0]pentene and perfluorotetramethyl (Dewar thiophene) *exo*-S-oxide has been carried out. In order to analyze the pericyclic character of these two reactions, some magnetic properties (NICS and ACID) have been calculated in the reactant/product and in the transition state of each reaction. Despite the differences between them, the results for both reactions show an enhancement of aromaticity in the transition state, which is consistent with a pericyclic behavior. NBO calculations show that the small activation energy for the second reaction can be interpreted in terms of a strongly stabilization of the transition state by the *exo*-oxide substituent. No evidence of any pseudopericyclic character has been found. Although the walk rearrangement in perfluorotetramethyl (Dewar thiophene) *exo*-S-oxide has special characteristics, the process of [1,3]-sigmatropic shift remains with a fundamental role in its mechanism. So, the mechanism proposed by Lemal et al, should be revised.

Introduction

In 1976 Lemal and co-workers¹ defined the term "pseudopericyclic reaction" as 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. This means a "disconnection" in the cyclic array of overlapping orbitals, because the atomic orbitals switching functions are mutually orthogonal. Hence, pseudopericyclic reactions cannot be orbital symmetry forbidden. Their definition was based in the experimental behavior of Perfluorotetramethyl (Dewar thiophene) *exo*-S-oxide (**PFDTSO**), which undergoes an extraordinarily facile automerization



Pseudopericyclic reactions fell into oblivion until Birney²⁻¹⁰ first and several other authors¹¹⁻²⁰ later revived interest in them by showing that a number of organic syntheses involve this type of process. However, until now, no universally accepted clear-cut, absolute criterion exists for distinguishing a pseudopericyclic reaction from a normal pericyclic reaction. This has raised some controversy in classifying some reactions.²¹⁻²⁵

Evaluation of magnetic properties can be very useful to assess aromatization along the reaction. This relies on the fact that the cyclic loop of a pericyclic reaction yields an aromatic transition state,²⁶ as quantitatively confirmed for various reactions.²⁷⁻³⁰ Thus, Herges et al. showed that, in the vicinity of the transition state in the Diels–Alder reaction, the magnetic susceptibility χ and its anisotropy χ_{anis} exhibit well defined minima with respect to the reactant and product.²⁷ On the other hand, the typical disconnection of pseudopericyclic reactions would have prevented this enhanced aromatization, as shown by us for the unequivocally pseudopericyclic cyclization of 5-oxo-2,4-pentadienal to pyran-2-one.²⁴ This reaction involves in-plane attack of the electron lone pair of the carbonyl oxygen atom on the electrophilic allene carbon atom.

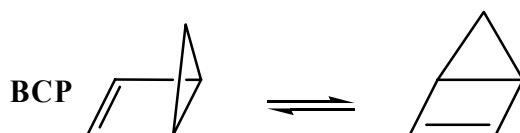
Another method that uses the magnetic properties is ACID (anisotropy of the current-induced density), recently developed by Herges and Geuenich.³¹ This method has been used for the quantitative study of delocalization in molecules. It has also been used to study several pericyclic reactions and to distinguish coarctate from pseudocoarctate reactions.³²⁻³³ This seems to indicate that this method could be useful for the study of pseudopericyclic reactions. Recently, we have shown that evaluation of magnetic properties along the whole reaction is a useful tool to study the

pericyclic/pseudopericyclic character of a mechanism. This analysis, together with ACID plots, allows the classification of reactions with acceptable certainty.³⁴⁻⁴¹

Although the automerization of compound **PFDTSO** was the first defined pseudopericyclic reaction, no significant theoretical study has been carried out until now.⁴² For this reason, in this paper we present a comprehensive theoretical study of this process and, moreover, an analysis of the parent pericyclic reaction (sigmatropic methylene shift in bicyclo[2.1.0]pentene) was done as well. The principal mechanism that govern the fluxional behavior of these compounds is controlled by [1,3]-sigmatropic shifts of a migrating group to the adjacent position of the ring. The rearrangements of this type are classified as "walk" rearrangements.

Results

For a better understanding of the automerization of **PFDTSO**, first we analyzed a reaction which could be considered the parent pericyclic reaction: the [1,3]-sigmatropic shift of methylene in bicyclo[2.1.0]pentene (**BCP**).



According to Skancke *et al.* (UHF, CASSCF, Møller-Pleset calculations) this thermal walk rearrangement goes via inversion at the migrating center.⁴³ The rearrangement is likely a two-step process passing through a diradical intermediate. However, later, Jensen using a multiconfigurational self-consistent field (MCSCF) found that the Woodward-Hoffman allowed reaction is a concerted process with a C_s symmetry transition structure.⁴⁴ The electronic structure of this transition state was approximately 50% biradical. According to Jensen calculations, the use of spin contaminated unrestricted Hartree-Fock and Møller-Pleset wave functions is found to give deviating results, both for energies and for characterization of stationary points of the PES. Thus the results and conclusions drawn on the basis of spin contaminated UHF and UMP wave functions (Skancke *et al.*) should be viewed with skepticism. Recent results of Reyes *et al.* showed evidence at the CASPT2//CASSCF level of theory for pericyclic transition structure of the ring-walk rearrangement with inversion of configuration.⁴⁵ Later, in the study of the isomerization of **BCP** into cyclopenta-1,3-diene, Ozkan *et al.* showed that the UB3LYP functional performed well despite the high contamination that was present in the singlet biradicaloid transition state; so B3LYP functional is quite resistant to the possible consequences of spin contamination.⁴⁶ Both Jensen and Reyes *et al.* only perform calculations on the transition state for the [1,3]-sigmatropic shift in **BCP**. So, no activation energy was supplied for these authors. For this reason, we have performed calculations to obtain the activation energy at different levels of calculation (Table 1).

Table 1. Activation energy (kcal/mol) at 0 K for the [1,3]-sigmatropic shift in **BCP**.

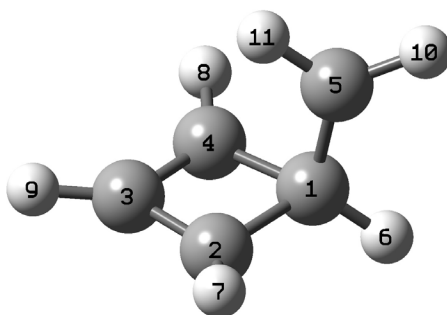
CCSD(T)/6-311+G**//MP2/6-311+G**	28.50
CCSD(T)/6-311+G**//B3LYP/6-31G*	28.80
CCSD(T)/6-311+G**//UB3LYP/6-31G*	28.48
CBS-QB3	25.76
CASSCF(4,4)/6-31G*// CASSCF(4,4)/6-31G*	17.31
CASPT2(4,4)/6-31G*// CASSCF(4,4)/6-31G*	27.43
CASSCF(6,6)/6-31G*// CASSCF(6,6)/6-31G*	12.27
CASPT2(6,6)/6-31G*// CASSCF(6,6)/6-31G*	27.91
B3LYP/6-31G*	31.06
UB3LYP/6-31G*	28.98

Table 1 shows that all methods (except CASSCF without taking into account the dynamical correlation) predict an energy barrier about 30 kcal/mol. Despite its low cost, DFT theory perform reasonably well; even the restricted version B3LYP gives only an error about 10 % relative to the most expensive calculations. As regard geometry, concordance for all methods is very good at the minimum and only small differences appear at the transition state (Table 2).

Table 2. Selected geometrical parameters of the transition structure for the [1,3]-sigmatropic shift in **BCP**. Distances in Å, angles in degrees.

	C1-C5	C1-C2 C1-C4	C2-C3 C4-C3	C2-C5 C4-C5	C3C1C5	ν_{imag} (cm ⁻¹)
CAS(4,4)/STO-3G ^a	1.506	1.541	1.410	2.542	118.9	479
B3LYP/6-31G*	1.451	1.523	1.401	2.293	102.3	288
UB3LYP/6-31G*	1.466	1.534	1.399	2.418	111.1	none
MP2/6-311+G**	1.461	1.520	1.409	2.279	99.9	278
CASSCF(4,4)/6-31G* ^b	1.474	1.526	1.400	2.436	112.0	none
CASSCF(6,6)/6-31G*	1.497	1.522	1.400	2.432	110.4	none

^a Jensen (ref. 44). ^b The results of Reyes et al (ref. 45) have been exactly reproduced for us.



According to Table 2, RB3LYP results are in general very close to those of more expensive methods; the main difference is the position of methylene, somewhat more closed regarding the four membered ring (C1C2C3C4), which is reflected in a smaller distance C2-C5 (or C4-C5) and a smaller angle C3-C1-C2. Restricted MP2 method performs very similar to RB3LYP, although slightly worse. It could be surprising the nonexistence of any imaginary frequency for the CASSCF/6-31G* and UB3LYP transition structures. However, it was already mentioned by Reyes et al.⁴⁵ and they concluded (and our results support their statement) that ZPE and CASPT2 corrections remove the minimum character and restore a more traditional description of the reaction as a concerted process.

To assess aromatization during the [1,3]-sigmatropic shift in **BCP**, two magnetic procedures were chosen: the Schleyer's nucleus-independent chemical shift (NICS)⁴⁷ and the above commented ACID method.

For electrocyclizations the choice of the points to calculate NICS is quite clear: in the center of the forming ring and/or 1 Å above or below this point to avoid spurious effects associated to σ bonds.⁴⁸ The choice for sigmatropic shifts is not so obvious; for that reason we decided to calculate NICS not only in particular points but in a set of points defined by a line which passes through the geometrical center of the four-member ring (see Figure 1). This calculation was done for the transition state and for the reactant/product to observe the differences between them. The results (Figure 2), obtained at the B3LYP/6-31+G** level using the GIAO (Gauge-Independent Atomic Orbital) method,⁴⁹ show the enhanced aromaticity which takes place at the transition state: the more negative value is -11.8 ppm, and it corresponds to a position 0.8 Å above the plane formed by the four-member ring. If we compare the region above this plane, in transition state and in reactant/product, we can conclude that transition state shows a greater aromaticity which is consistent with the pericyclic character of this reaction. As it would be expected, the more negative NICS values are concentrated in the region where methylene undergoes the [1,3]-sigmatropic shift.

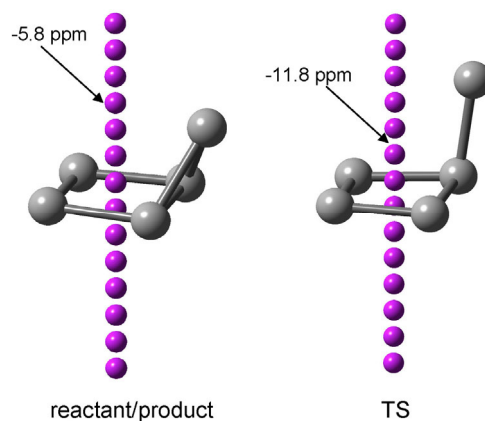


Figure 1. [1,3]-sigmatropic shift in **BCP**. NICS values were calculated in a set of points defined by a line which passes through the geometrical center of the four-member ring. The maximum values are indicated in each case.

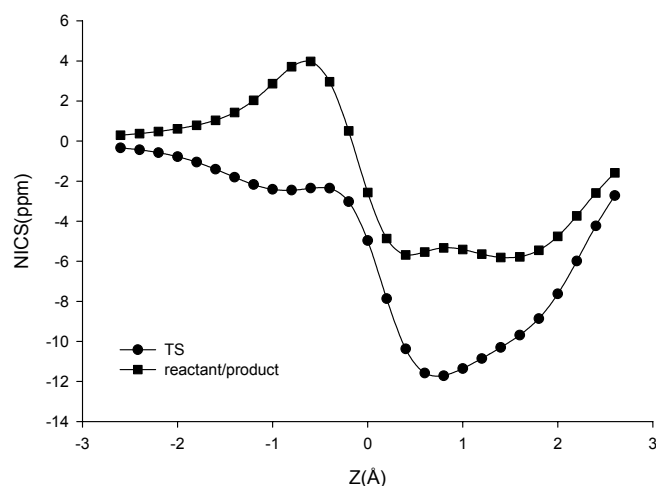


Figure 2. [1,3]-sigmatropic shift in **BCP**. Variation of NICS along the line of points showed in Figure 1.

The ACID method is an efficient tool for the investigation and visualization of delocalization and conjugation. In principle a cyclic topology in an ACID plot indicates a pericyclic reaction. Disconnections that are characteristic for pseudopericyclic systems are immediately visible as a disconnection in the continuous system of the ACID boundary. Figure 3 show the results, obtained at the B3LYP/6-31+G** level and the CGST (continuous set of gauge transformations) method.^{50,51} For the transition state the current density vectors show the pericyclic nature of the delocalized system: the strong diatropic ring current forms a closed loop, as expected for an aromatic system. In the reactant/product, by contrast, no appreciable ring current is observed.

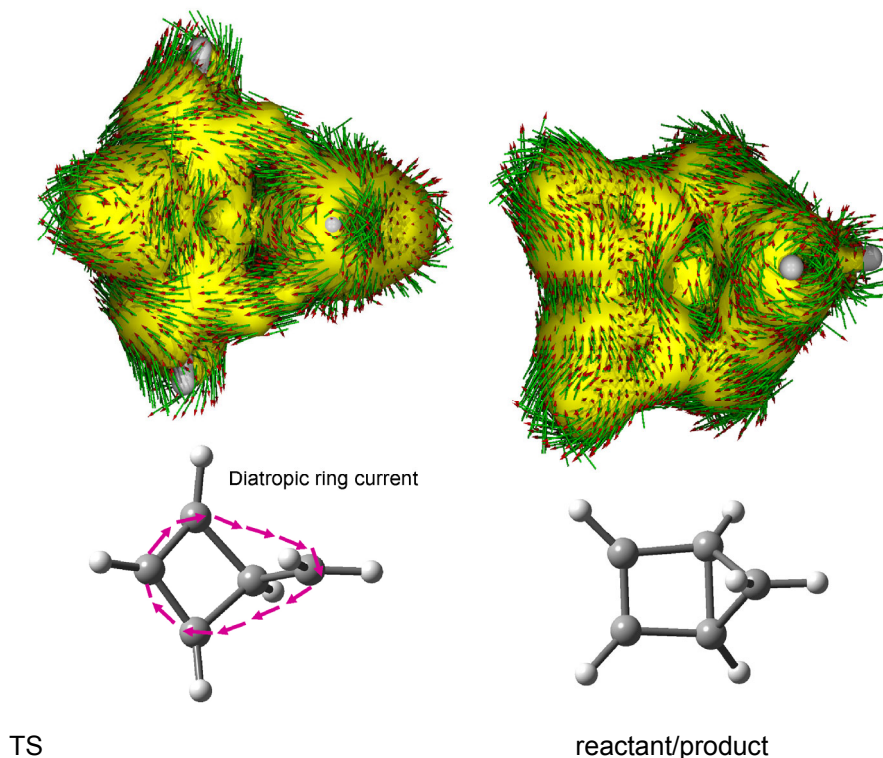


Figure 3. ACID plots for the TS and reactant/product of [1,3]-sigmatropic shift in **BCP**. Current density vectors (green arrows with red tips) are plotted on the isosurface of value 0.025, and the magnetic field points from the paper to the reader. In TS the current density vectors exhibit a closed circle.

In the ACID method, the extent of conjugation can be quantified by the critical isosurface value (CIV) at which the topology of the ACID boundary surface changes. In the transition state, for the forming/breaking bonds (C5-C2 and C5-C4) a CIV of 0.030 is calculated. Although this value is not very high, it involves a considerable conjugation, especially if it is taken into account the long bond distance (2.3 Å).

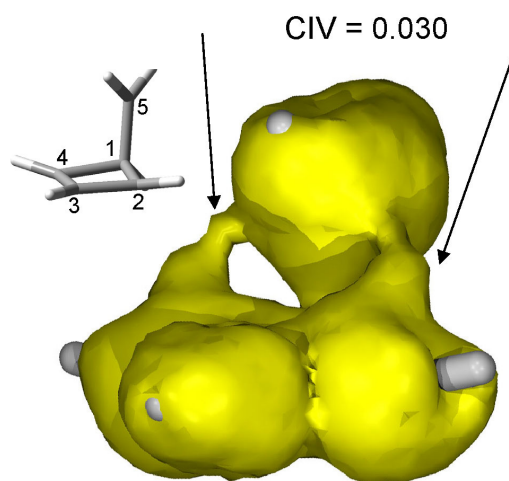
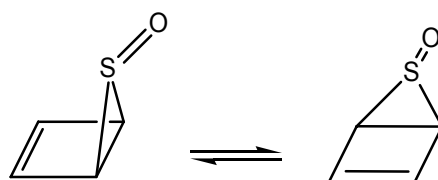


Figure 4. ACID plot for the transition state of [1,3]-sigmatropic shift in **BCP**, at an isosurface value of 0.029. For the bonds C5-C2 and C5-C4, a value of 0.030 breaks the connection.

B3LYP/6-31G* calculations also perform fairly well for the automerization of (Dewar thiophene) *exo*-S-oxide (**DTSO**), the unsubstituted parent of the compound purpose of our study. So, the calculated activation energy (including ZPE) was 4.85 kcal/mol, reasonably close to 5.86 kcal/mol (CCSD(T)/6-311+G**//MP2/6-311+G**) and 5.10 kcal/mol (CBS-QB3).



DTSO

The good results obtained using the B3LYP/6-31G* method for the two previous reactions, allow us to rely on this calculation level in order to analyze the behavior of **PFDTSO**, a compound whose size prevents the use of more sophisticated methods. The calculated activation energy was 5.38 kcal/mol, slightly higher than that of its unsubstituted parent. So, a first outstanding result is that both the automerization of the substituted and the unsubstituted compounds show an activation energy very much lower than that of the parent pericyclic reaction (**BCP**): the decrease is greater than 80%. It properly reproduces the experimental findings of Lemal et al,¹ who found an extraordinarily facile automerization.

As in the case of [1,3]-sigmatropic shift in **BCP**, to assessing aromatization during the reaction, NICS and ACID methods were used with the above mentioned calculation levels.

NICS results, calculated along a set of points analogous to those figure 1, are shown in Figure 5.

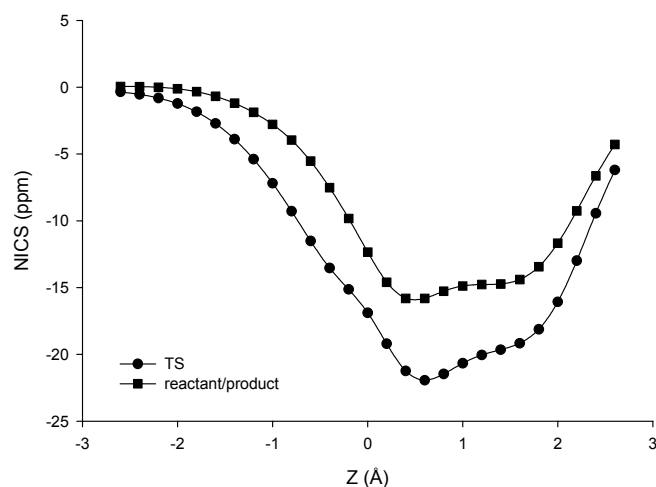


Figure 5. Automerization in **PFDTSO**. Variation of NICS along the line of points analogous to those showed in Figure 1.

Figure 5 shows a behavior very similar to that of figure 2: an enhanced aromaticity takes place at the transition state. Even the magnitude of the enhancement is similar, so a decrease of about 6 ppm is obtained for the TS relative to the values for reactant/product. For TS, the minimum NICS value is -21.94 ppm and it corresponds to a position 0.6 Å above the plane formed by the four-member ring (0.8 Å for TS in **BCP**). It is remarkable that minimum values in figure 5 are substantially more negative than those of figure 2. However, the evaluation of the absolute aromaticity of a compound remains a controversial matter, but we are interested in its variation along the reaction and not in an absolute value. This is the reason why can we conclude that aromatization in the transition state of the automerization of **PFDTSO** is an evidence of the pericyclic character of this reaction.

Figure 6 shows the ACID plot for the transition state of the reaction. Although the current density is considerably smaller than that of figure 3, a closed loop with diatropic ring current can be observed, displaying the aromatic character of this structure. In the reactant/product, by contrast, no appreciable ring current is observed. The calculated CIV for the forming/breaking bonds (C5-C2 and C5-C4) is 0.029 (figure 7); a value only slightly smaller than that for TS of [1,3]-sigmatropic shift in **BCP**. Moreover, in this case the bond distance is somewhat longer (2.4 Å)

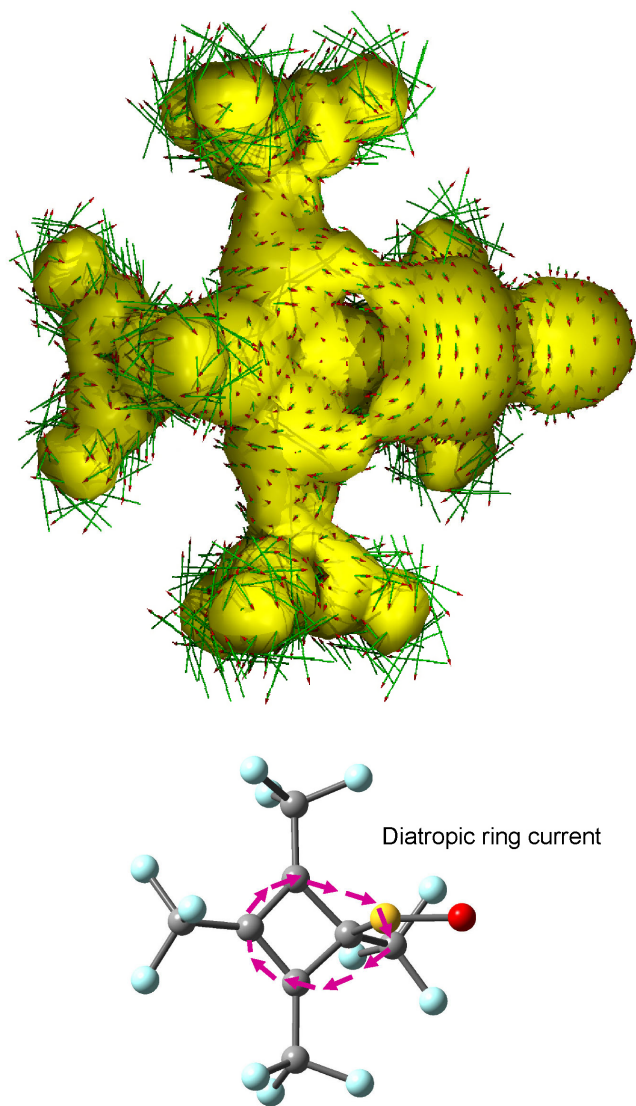


Figure 6. ACID plot for the transition state of automerization of **PFDTSO** Current density vectors (green arrows with red tips) are plotted on the isosurface of value 0.025, and the magnetic field points from the paper to the reader. The current density vectors exhibit a closed circle.

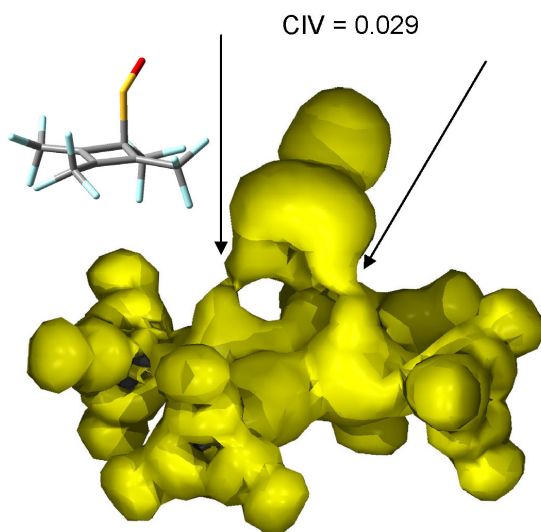
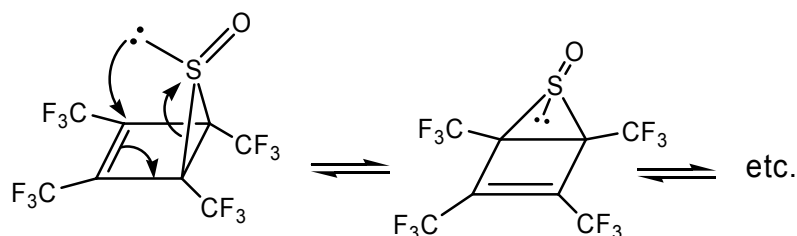
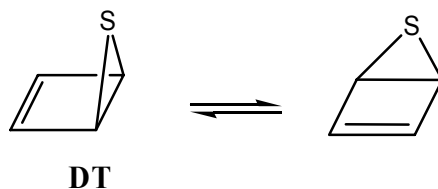


Figure 7. ACID plot for the transition state of automerization of **PFDTSO**, at an isosurface value of 0.028. For the bonds C5-C2 and C5-C4, a value of 0.029 breaks the connection.

In summary, magnetic properties (NICS and ACID) show that behavior of both reactions (automerization of **PFDTSO** and **BCP**) is basically the same, which is the expected for a pericyclic reaction. Then, which is the reason for the huge decrease of activation energy in the former reaction? Lemal *et al.*¹ proposed the next mechanism to answer this question and to support the pseudopericyclic character.



In this mechanism the sulfur lone pair forms the new bond to carbon, and the electrons of the cleaving C-S bond become a lone pair. This mechanism was used to define the name *pseudopericyclic* to describe reactions where nonbonding and bonding atomic orbitals interchange roles. However, this proposed mechanism disagrees with several facts. First, for the automerization of Dewar thiophene (**DT**), Dorogan *et al.* calculated an activation energy of about 16 kcal/mol at the MP2 and B3LYP levels;⁵² that is, three times the value calculated for **PFDTSO** and **DTSO**. If the mechanism was a nucleophilic attack of the lone pair of sulfur to carbon, the reaction for **DT** should have an small activation energy as well (even smaller than that for **PFDTSO** and **DTSO**, since in these compounds the nucleophilic character in the sulfur atom must be reduced due the effect of the adjacent oxygen atom).



Another more important point is that, actually, sulfur atom has not any nucleophilic character. In fact, according to NBO calculations,⁵³⁻⁵⁵ in the best Lewis structure of the reactant/product the sulfur atom is +1, the oxygen atom is -1 and the bond between them is only single. The calculated NBO charges are +1.23 (S), -0.82 (O) and -0.10 (the supposedly attacked C). To support the conclusions obtained from NBO calculations, the molecular electrostatic potential, MEP, has been computed. Figure 8 clearly shows (in agreement with NBO charges) that only the region surrounding O atom has negative MEP values.

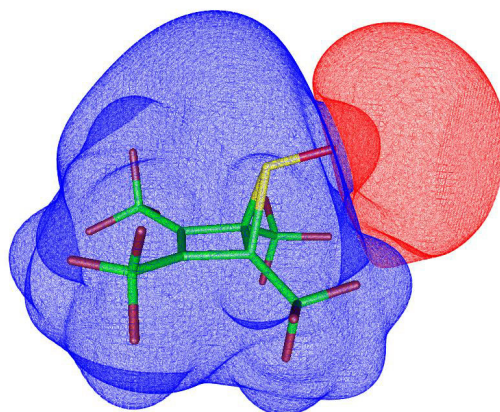


Figure 8. Computed MEP for **PFDTSO** The isosurfaces represented are -0.01 (red) and +0.01 (blue) a.u.

With those NBO and MEP results, it is unlikely that a mechanism with a nucleophilic attack from the sulfur atom takes place.

Using semiempirical MINDO/3 and the approximate ab initio PRDDO method, Snyder and Halgren suggested that the small activation energy for the automerization of **PFDTSO** arises primarily from a preferential stabilization of the transition state.⁴² Moreover, these authors found no evidence for the lone pair participation implied by the pseudopericyclic concept. Our calculations agree with this hypothesis. First, as we commented above, the nucleophilic attack of the lone pair of the sulfur atom is not very probable. Moreover, a more detailed observation of NBO results confirms these conclusions by means of the second order perturbation analysis. This analysis supplies the energies of delocalization of electrons from filled NBOs into empty NBOs - so that they do not finish up quite filled or quite empty. Table 3 shows the most important values of the second order perturbation energy for the transition state of the automerization of **PFDTSO**. The participation of the lone pair of S is insignificant: lower than 2.6 kcal/mol. However, a high value (64.43 kcal/mol) corresponds to a donation from one of the lone pairs of O (LP-3 in Figure 9) to the σ^* NBO of the forming/breaking bonds (σ^* (S5-C2) in Figure 9). For the reactant/product of **PFDTSO**, this donation is important, but lower than 20 kcal/mol, so, (and in agreement with the conclusions of Snyder and Halgren), the transition state for the automerization of **PFDTSO** is strongly stabilized by the exo-oxide substituent. In addition to this, a noteworthy fact is the high energy of the two donations $\sigma \leftrightarrow \pi$ (41.75 and 65.38 kcal/mol), of similar magnitude to that in the transition state of [1,3]-sigmatropic shift of methylene in **BCP** (50.67 and 55.43 kcal/mol); this indicates that character of [1,3]-sigmatropic shift is fundamental in the mechanism of the reaction of automerization of **PFDTSO**.

Table 3. Stabilization energies (kcal/mol), $E^{(2)}$, for the transition states of the reactions as obtained by second order analysis using the NBO method. X=S (**PFDTSO**), X=C(**BCP**).

donor	acceptor	TS (PFDTSO)	TS (BCP)
σ (X5-C2)	π^* (C3-C4)	41.75	50.67
π (C3-C4)	σ^* (X5-C2)	65.38	55.43
LP-2 (O)	σ^* (X5-C1)	26.78	-
LP-3 (O)	σ^* (X5-C2)	64.43	-

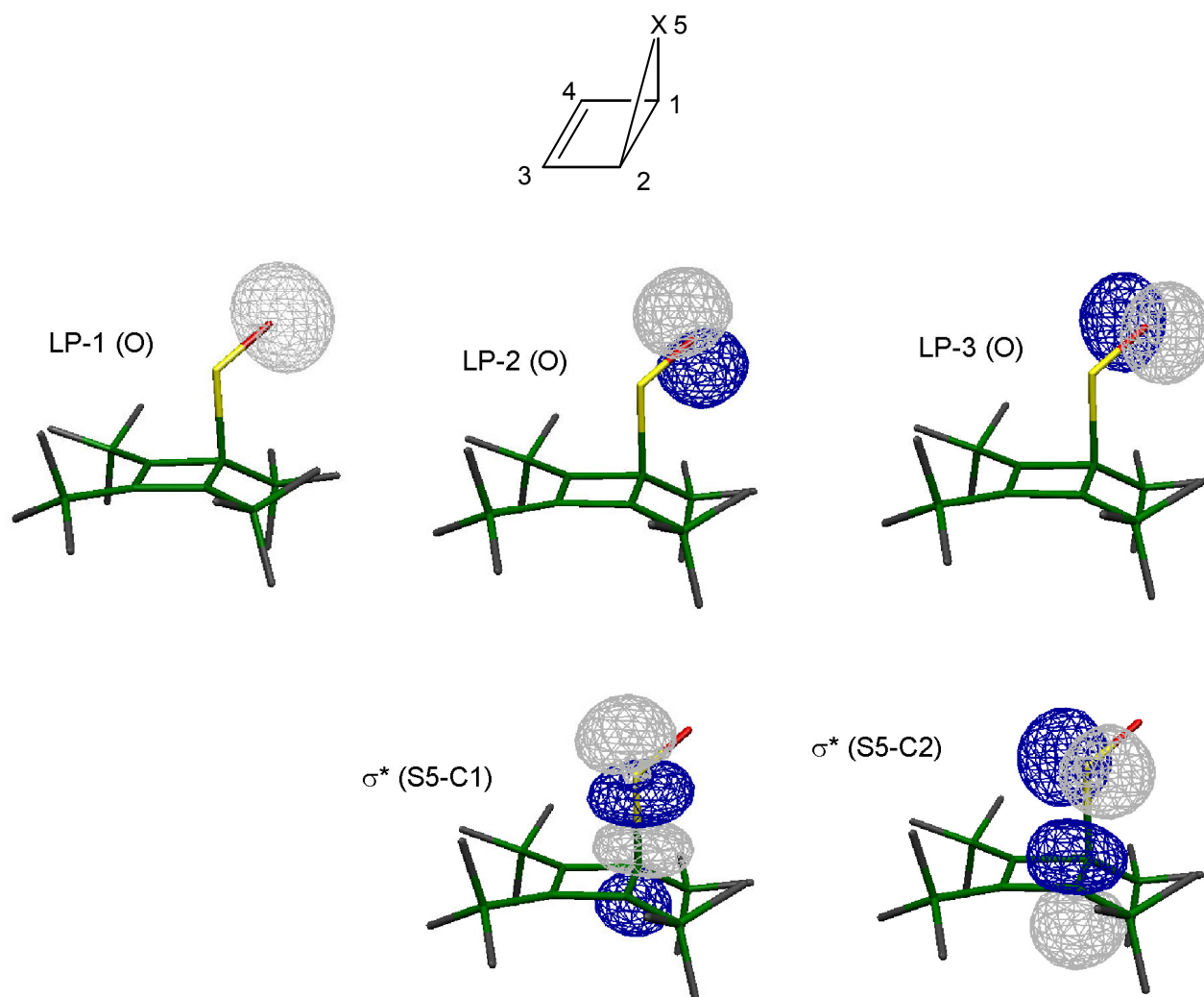


Figure 9. Representation of some NBOs in the transition state for the automerization of **PFDTSO**.

Conclusions

The walk rearrangement of **BCP** is a pericyclic reaction which consists in a [1,3]-sigmatropic shift of methylene. By the use of magnetic properties (NICS and ACID methods), the enhancement of aromaticity which takes place in the transition state of this reaction has been confirmed. This enhanced aromaticity is caused by the cyclic loop of interacting orbitals; this fact has been quantitatively confirmed for several pericyclic reactions.²⁹⁻³³

For the walk rearrangement of **PFDTSO**, Lemal et al. proposed a mechanism totally different which consists in a nucleophilic attack from the sulfur lone pair to a carbon atom and in a conversion of the electrons of the cleaving C-S bond in a lone pair.¹ This mechanism was used to define the name *pseudopericyclic* to describe reactions where nonbonding and bonding atomic orbitals interchange roles. However, according to our calculations this proposed mechanism seems to be unlikely. First, NBO charges and MEP values show that sulfur atom has not any nucleophilic character. Moreover, the analysis of magnetic properties for this reaction show an enhancement of aromaticity similar to that for the unequivocally pericyclic reaction of **PFDTSO**.

In agreement with previous findings,⁴⁵ our calculations seem to explain the very low activation for the walk rearrangement in **PFDTSO**.

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