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Theoretical study of the walk rearrangement in perfluorotetramethyl (Dewar thiophene) *exo*-*S*-oxide

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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. 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 strong stabilization of the transition state by the *exo*-oxide substituent. So, the mechanism proposed in the past should be revised.

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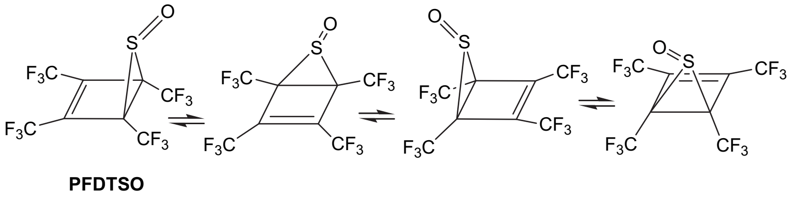
1. Introduction

In 1976 Lemal et al.[1] 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. Their definition was based on the experimental behavior of perfluorotetramethyl (Dewar thiophene) *exo*-*S*-oxide (**PFDTSO**), which undergoes an extraordinarily facile automerization (Scheme 1).

Pseudopericyclic reactions fell into oblivion until Birney[2–10] first and several other authors[11–20] 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 fact can be interesting to study the pericyclic character of a reaction since the cyclic loop of a pericyclic reaction yields an aromatic transition state,[26] as quantitatively confirmed for various reactions;[27–30] e.g., 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,



Scheme 1.

Keywords: Ab initio calculations; Density functional calculations; Pericyclic reactions; Reaction mechanisms; Aromaticity.

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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.

Although the automerization of compound **PFDTSO** was the first defined pseudopericyclic reaction, no significant theoretical study has been carried out until now. 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 governs 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.

2. Computational details

For the study of the sigmatropic methylene shift in bicyclo-[2.1.0]pentene (**BCP**) several high-level ab initio calculations were performed. Coupled cluster CCSD(T) single point calculations were calculated at the MP2, B3LYP, and CCSD optimized geometries. The composite ab initio method CBS-QB3 was also used. The possibility of some biradical character in the transition state could suggest the use of a multiconfigurational SCF (MCSCF) method like CASSCF. Nondynamical correlation has been included through the calculations at the CASSCF level of theory using the two following sets of orbitals in the active space: (4,4) (4 electrons on 4 orbitals) and (6,6). Using CASSCF geometries, the dynamical correlation was taken into account in a perturbative way through CASPT2 calculations. As regards activation energy, all these accurate ab initio calculations generate very similar results. On the other hand, the much less expensive B3LYP method was able to reproduce these results in a reasonable way. In the case of the walk rearrangement of (Dewar thiophene) *exo*-*S*-oxide (**DTSO**) B3LYP results were also reasonably close to those of CCSD(T) and CBS-QB3 methods. These facts, together with the large size of **PFDTSO** support the use of B3LYP method for the study of the walk rearrangement in this compound.

The standard 6-31G(d) and 6-311+G(d,p) basis sets have been used for calculations.

All points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies, using analytical (B3LYP, MP2, and CASSCF) or numerical (CCSD) second derivatives.

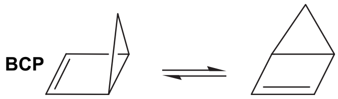
Aromaticity was evaluated by means of the analysis of magnetic properties. The most widely used magnetic-based index is the NICS (nucleus-independent chemical shift) index,[31] which is defined as the negative value of the shielding, computed at a ring center (NICS(0)) or at some other interesting point of the system. NICS values were calculated at the B3LYP/6-31+G(d,p) level using the GIAO (gauge-independent atomic orbital) method.[32] Another method that uses the magnetic properties is ACID (anisotropy of the current-induced density), recently developed by Herges and Geuenich.[33] 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.[34,35] 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.[36–43] In the present work, ACID calculations were performed at the B3LYP/6-31+G(d,p) level and the CSGT (continuous set of gauge transformations) method.[44,45]

Calculations were carried out with Gaussian03[46] and MOLCAS 6.0[47] (for CASSCF/CASPT2) programs.

3. Results and discussion

3.1. Walk rearrangement in bicyclo[2.1.0]pentene (BCP)

For a better understanding of the walk rearrangement of **PFDTSO**, first we analyzed a reaction, which could be considered as the parent pericyclic reaction: the [1,3]-sigmatropic shift of methylene in **BCP** (Scheme 2).



Scheme 2.

According to Skancke et al. this thermal walk rearrangement goes via inversion at the migrating center.[48] 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.[49] 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 in configuration.[50] Both Jensen and Reyes et al. only performed calculations on the transition state for the [1,3]-sigmatropic shift in **BCP**. Therefore, 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 shows that all methods (except CASSCF without taking into account the dynamical correlation) predict an energy barrier of about 30 kcal/mol. Despite its low cost, DFT

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**//CCSD/6-31G*	28.17
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

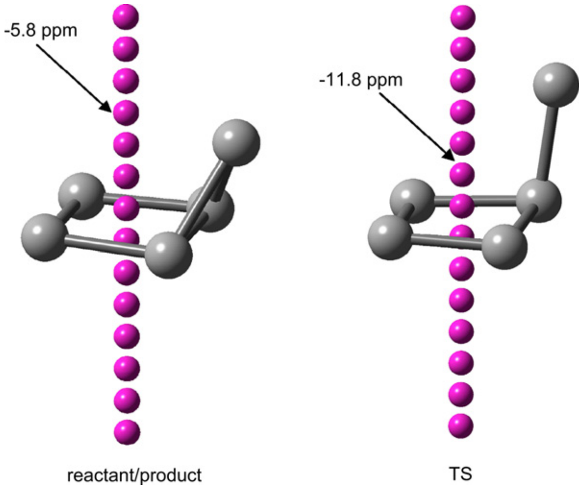
theory performs reasonably well: only an error of about 10% relative to the most expensive calculations is found.

As regards geometry, concordance for all methods is very good at the reactant/product and only small differences appear at the transition state (Table 2). According to Table 2, B3LYP 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 (C1–C2–C3–C4), which is reflected in a smaller distance C2–C5 (or C4–C5) and a smaller angle C3–C1–C5. MP2 method performs very similar to B3LYP, although slightly worse. It could be surprising the nonexistence of any imaginary frequency for the CASSCF/6-31G* transition structure. However, it was already mentioned by Reyes et al.[50] 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: NICS and ACID.

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.[51] The choice for sigmatropic shifts is not so obvious; for that reason we decided to calculate NICS not only in a particular point but in a set of points defined by a line, which passes through the geometrical center of the four-membered ring (see Fig. 1). This calculation was done for the transition state and for the reactant/product to observe the differences between them. The results (Fig. 2) 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-membered 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.

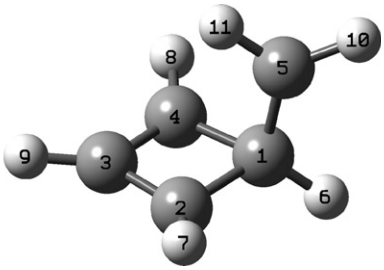
The ACID method is an efficient tool for the investigation and visualization of delocalization and conjugation. In principle a cyclic topology in an ACID plot indicates a pericyclic reaction. Disconnections that are characteristic for



reactant/product TS

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-membered ring. The maximum values are indicated in each case.

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



	C1–C5	C1–C2, C1–C4	C2–C3, C4–C3	C2–C5, C4–C5	C3–C1–C5	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
MP2/6-311+G**	1.461	1.520	1.409	2.279	99.9	278
CCSD/6-31G*	1.458	1.519	1.404	2.297	101.8	324
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] See Ref. 49.

[b] The results of Reyes et al. (Ref. 50) have been exactly reproduced by us.

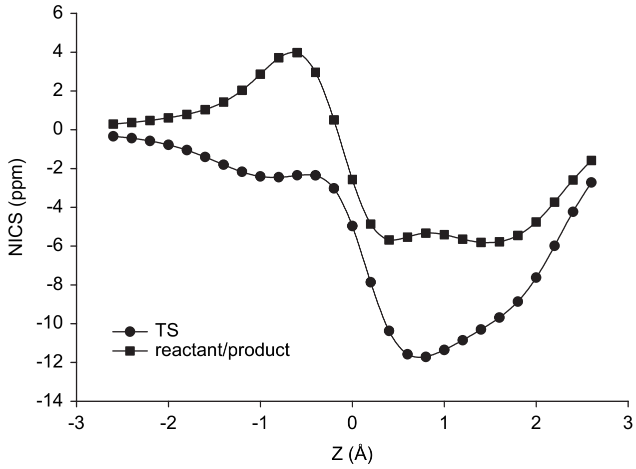


Figure 2. [1,3]-Sigmatropic shift in **BCP**. Variation of NICS along the line of points showed in Figure 1.

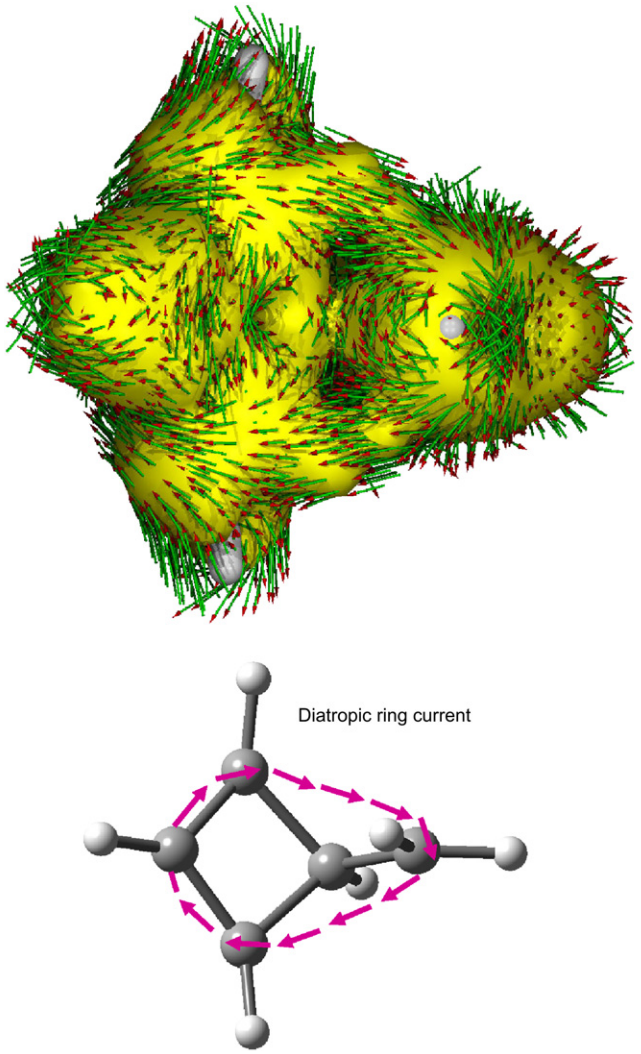


Figure 3. ACID plot for the TS of the [1,3]-sigmatropic shift in **BCP**. Current density vectors (green arrows with red tips) are plotted on the isosurface value of 0.025, and the magnetic field points from the paper to the reader. The current density vectors exhibit a closed circle.

pseudopericyclic systems are immediately visible as a disconnection in the continuous system of the ACID boundary. Figure 3 shows our results. In the transition state the current density vectors show the pericyclic nature of the delocalized system: a strong diatropic ring current forms a closed loop, as expected for an aromatic system. In an analogous illustration for reactant/product, by contrast, no appreciable ring current is observed.

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 (Fig. 4). Although this value is not very high, it involves a considerable conjugation, especially if the long bond distance is taken into account (2.3 Å).

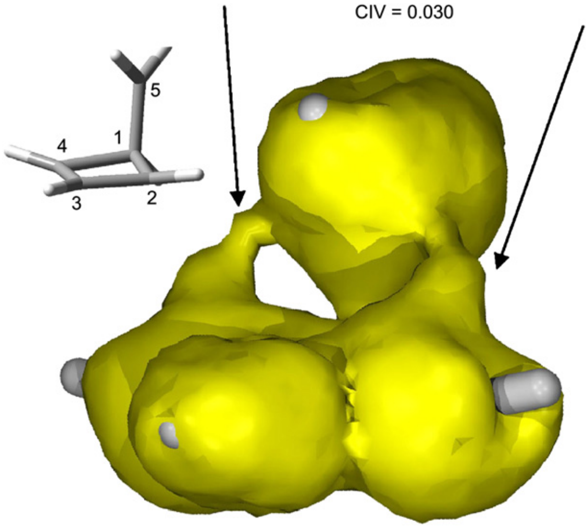
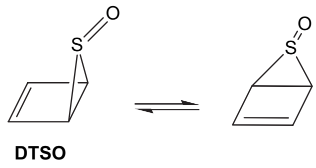


Figure 4. ACID plot for the transition state of [1,3]-sigmatropic shift in **BCP**, at an isosurface value of 0.029. For the bonds C5–C2 and C5–C4, a value of 0.030 breaks the connection.

3.2. Walk rearrangement in perfluorotetramethyl (Dewar thiophene) *exo*-*S*-oxide, PFDTSO

B3LYP/6-31G* calculations also perform fairly well for the automerization of (Dewar thiophene) *exo*-*S*-oxide (**DTSO**, Scheme 3), 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).



Scheme 3.

The good results obtained using the B3LYP/6-31G* method for the two previous reactions, allow us to rely on this level of calculation 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 compound. So, a first outstanding result is that the walk rearrangement of both the substituted and the unsubstituted compounds shows 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 assess the 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 of Figure 1, are shown in Figure 5. This figure 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-membered ring (0.8 Å for TS in **BCP**). So, we can conclude that aromatization in the transition state of the walk rearrangement of **PFDTSO** is an evidence for the pericyclic character of this reaction. 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.

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; a value only slightly smaller than that for TS of [1,3]-sigmatropic shift in **BCP**, even though in this case the bond distance is somewhat longer (2.4 Å).

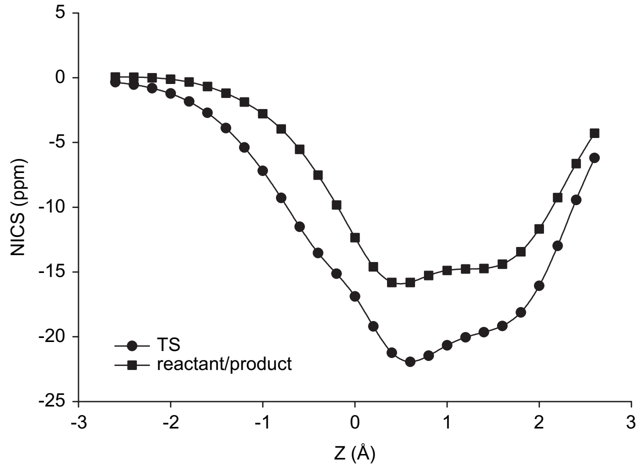


Figure 5. Walk rearrangement in **PFDTSO**. Variation of NICS along a line of points analogous to those showed in Figure 1.

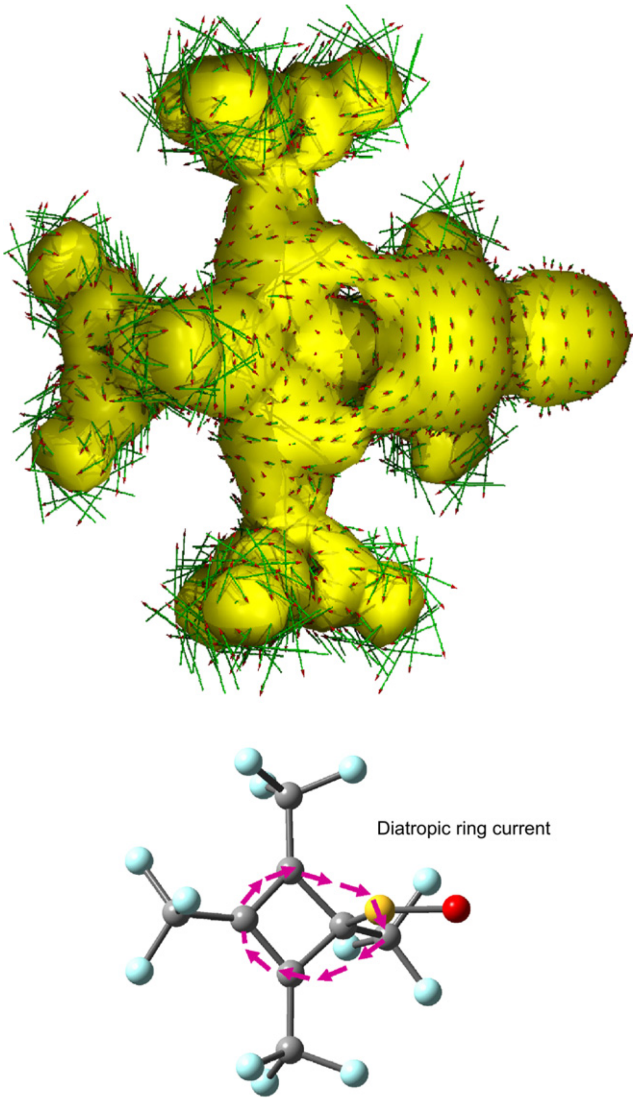
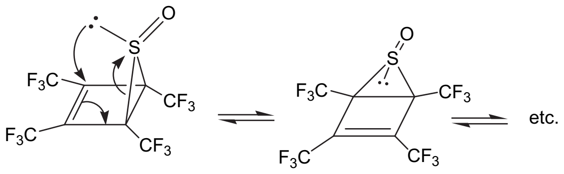


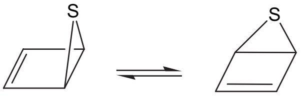
Figure 6. ACID plot for the transition state of walk rearrangement of **PFDTSO**. Current density vectors (green arrows with red tips) are plotted on the isosurface value of 0.025, and the magnetic field points from the paper to the reader. The current density vectors exhibit a closed circle.

In summary, magnetic properties (NICS and ACID) show that the behavior of both reactions (walk rearrangement of **PFDTSO** and **BCP**) is basically the same, which is expected for a pericyclic reaction. Then, which is the reason for the huge decrease in activation energy in the former reaction? Lemal et al.[1] proposed the following mechanism to answer this question and to support the pseudopericyclic character (Scheme 4).



Scheme 4.

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 walk rearrangement of Dewar thiophene (**DT**, Scheme 5), 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 on carbon, the reaction for **DT** should have a 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 does not have any nucleophilic character. In fact, according to NBO calculations,[53–55] in the best Lewis structure of the reactant/product of **PFDTSO**, 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 charges, the molecular electrostatic potential, MEP, has been computed. Figure 7 clearly shows (in agreement with NBO charges) that only the region surrounding O atom has negative MEP values. With these NBO and MEP results, it is unlikely that a mechanism with a nucleophilic attack from the sulfur atom takes place.



DT

Scheme 5.

Using semiempirical MINDO/3 and the approximate ab initio PRDDO method, Snyder and Halgren suggested that the small activation energy for the walk rearrangement of **PFDTSO** arises primarily from a preferential stabilization of the transition state.[56] 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 walk rearrangement 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 Fig. 8) to the σ^* NBO of the forming/breaking bonds (σ^* (S5–C2) in Fig. 8). 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 walk rearrangement 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), with a similar magnitude to those in the transition state of the walk rearrangement in **BCP** (50.67 and 55.43 kcal/mol); this indicates that the mechanism of the walk rearrangement of **PFDTSO** still retains the pericyclic [1,3]-sigmatropic shift character.

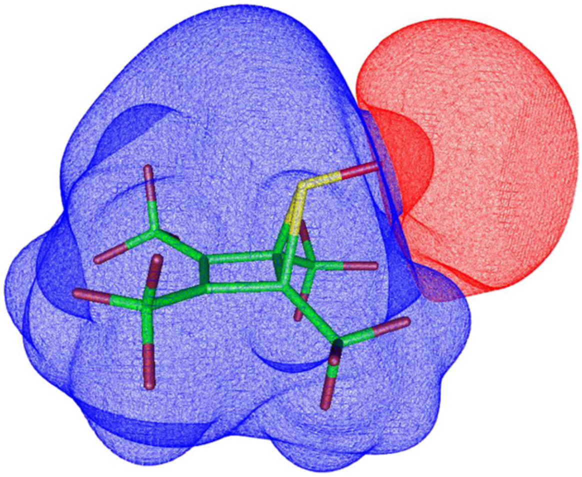
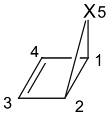


Figure 7. Computed MEP for **PFDTSO** The isosurfaces represented are −0.01 (red) and +0.01 (blue) a.u.

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	—

4. 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.[26–30]

For the walk rearrangement of **PFDTSO**, Lemal et al. proposed a mechanism that is 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*, which refers to 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 does not have any nucleophilic

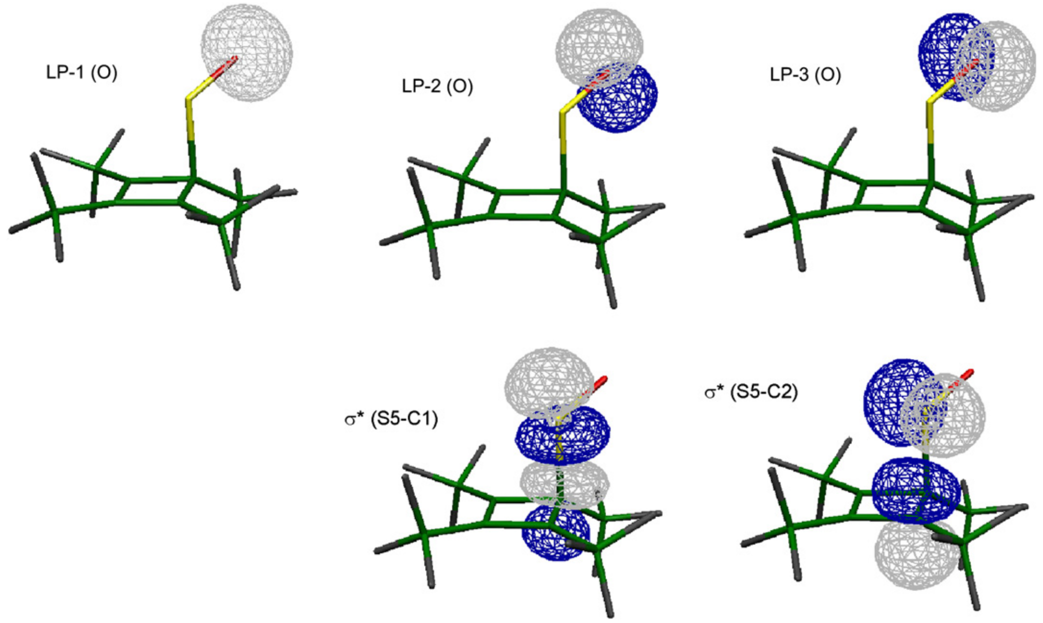


Figure 8. Representation of some NBOs in the transition state for the walk rearrangement of **PFDTSO**.

character. Moreover, the analysis of magnetic properties for this reaction shows an enhancement of aromaticity in the transition state similar to that for the unequivocally pericyclic reaction of **BCP**.

In agreement with previous findings,[56] our calculations seem to explain the very low activation for the walk rearrangement in **PFDTSO** by means of a preferential stabilization of the transition state by the *exo*-oxide substituent.

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