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A Density Functional Theory Study on the Electrocyclization of 1,2,4,6-Heptatetraene Analogues: Converting a Pericyclic to a Pseudopericyclic Reaction

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Abstract: A comprehensive B3LYP/6-31+G* study on the electrocyclization of 1,2,4,6-heptatetraene analogues was conducted. Starting from the cyclization of (2*Z*)-2,4,5-hexatrienal, a pericyclic disrotatory process favored by the assistance of a electron lone pair, we incorporated small modifications in its molecular structure to obtain a truly pseudopericyclic process. To this purpose electronegative atoms (fluorine and nitrogen) were added to give a more electrophilic character on the carbon atom which is attacked by the electron lone pair of the oxygen atom. The complete pathway for each reaction was determined, and changes in magnetic properties were monitored with a view to estimating the aromatization associated with each process. This information, together with the energetic and structural results, allowed us to classify the reactions as pseudopericyclic or pericyclic. Among all studied reactions only one was a truly pseudopericyclic process and another was a borderline case. The features of this unequivocally pseudopericyclic case were analyzed in depth.

Keywords: aromaticity · density functional calculations · electrocyclic reactions · transition states

Introduction

According to the original definition of Lemal and co-workers, 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] 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. Recently, Birney et al.[2–10] and others[11–20] showed that a number of organic syntheses involve this type of process. Although Lemal's definition is seemingly quite clear, there is some ambiguity as the orbital description is not unique; thus, any unit transformation of canonical molecular orbitals can be used to reproduce molecular properties.

Until now, no universally accepted, clear-cut, absolute criterion exists for distinguishing a pseudopericyclic reaction from a normal pericyclic reaction. This has led to controversy in classifying some reactions.[21–24] In addition to using structural criteria and natural bonding orbitals (NBOs),[25–27] we examined magnetic properties with a view to assessing aromatization during the processes. This relies on the fact that the cyclic loop of a pericyclic reaction yields an aromatic transition state,[28] as quantitatively confirmed for various reactions.[29–32] 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.[29] On the other hand, the typical disconnection of pseudopericyclic reactions would have prevented this enhanced aromatization, as shown by us for the unequivocally pseudopericy-

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clic 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. The way χ and especially χ_{anis} change along the reaction coordinate reveals that the process involves no appreciable aromatization. This clearly departs from the typical aromatization of pericyclic processes.

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. Nevertheless, its systematic application to a substantial number of pseudopericyclic reactions is still necessary to confirm its general validity in this field.

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.[36,37]

The electrocyclization of 1,2,4,6-heptatetraene (reaction 1 in Figure 1) is an unequivocally pericyclic reaction: p_z orbitals of C1 and C2 rotate in a disrotatory way to close the ring.[21–24] For reaction 2 the results suggest that, although the electron lone pair on the oxygen atom seemingly plays a crucial role in the reaction mechanism, it does not suffice to deprive the reaction from the essential features of a pericyclic disrotatory electrocyclization.[20,22,24] The stabilization of the transition state due to the interaction of the lone pair with the π system already has been shown by Houk et al. for the ring opening of 1,2-dihydroazete.[38] Because of this interaction, in reaction 2 the molecule need not undergo as much geometrical distortion as in a prototypical pericyclic reaction. Notwithstanding its special features, reaction 2 retains the essential characteristic of a pericyclic mechanism: enhanced aromaticity near the transition state. Evidently, there is a mechanistic continuum between a pure pericyclic and a pure pseudopericyclic reaction; reaction 2 (and many other reactions) behaves in a manner intermediate between the two extremes. The involvement of the lone pair in reaction 2 seemingly “pushes” the reaction mechanism towards pseudopericyclic character, so this reaction may be a borderline case. However, the results show that the borderline is not crossed (no disconnection is apparent) and that reaction 2 is a pericyclic disrotatory electrocyclization favored by the assistance of an electron lone pair. We think that in these cases it is appropriate to use the term “pericyclic reactions favored by the assistance of a lone pair”, or simply “assisted pericyclic reactions”.

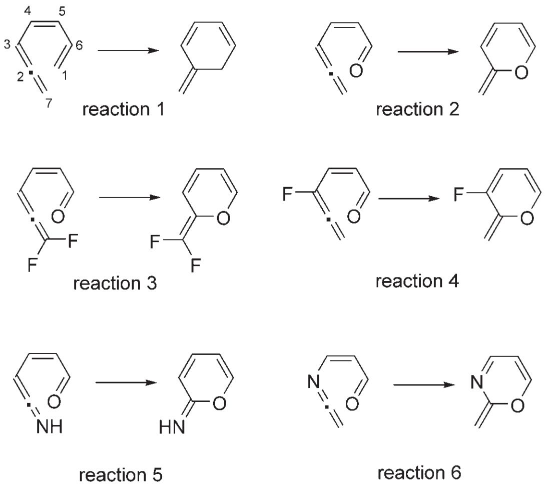

Figure 1. Reaction scheme for the studied electrocyclizations.

Abstract in Spanish: *Se ha llevado a cabo un exhaustivo estudio B3LYP/6-31+G* de la electrociclación de análogos del 1,2,4,6-heptatetraeno. Partiendo de la ciclación del (2Z)-2,4,5-hexatrienal, un proceso pericíclico disrotatorio favorecido por la ayuda de un par electrónico solitario, hemos incorporado pequeñas modificaciones en su estructura molecular con el fin de obtener un proceso verdaderamente pseudopericíclico. Con este propósito se añadieron átomos electronegativos (flúor y oxígeno) para conseguir un mayor carácter electrofílico en el átomo de carbono que es atacado por el par electrónico solitario del átomo de oxígeno. Se han determinado los caminos de reacción completos y se ha observado la variación de las propiedades magnéticas con el fin de estimar la aromatización asociada a cada proceso. Esta información, junto con los resultados energéticos y estructurales, nos han permitido clasificar las reacciones como pseudopericíclicas o pericíclicas. De todas las reacciones estudiadas sólo una resultó ser realmente pseudopericíclica y otra resultó ser un caso límite. Las características de este caso inequívocamente pseudopericíclico han sido analizadas en profundidad.*

The purpose of the present paper is modifying reaction 2 to push it across the borderline and to obtain a pseudopericyclic mechanism. To reach this target, electronegative atoms (N and F) were added (reactions 3–6 in Figure 1) to increase the positive charge at C2. Thus, in-plane attack of the electron lone pair of O1 on this electrophilic carbon atom will be favored. This occurs when $C7H_2$ is replaced by an oxygen atom, in the unequivocally pseudopericyclic cyclization of 5-oxo-2,4-pentadienal to pyran-2-one.[24]

Based on the foregoing, we conducted a comprehensive DFT study on the reactions of Figure 1. The pathways for the reactions were elucidated, and the variation of magnetic properties along each was examined to classify them as pericyclic or pseudopericyclic processes.

The knowledge of the conditions which can help to obtain a pseudopericyclic mechanism is interesting since pseudopericyclic reactions take place with small (or even zero) activation energies; this is an important result for synthetic organic chemistry.

Computational Methods

The geometry of each stationary point was fully optimized using the Gaussian 98 software package[39] with the 6-31+G* basis set and density functional theory (B3LYP functional).[40,41] All points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies by using analytical second derivatives. The pathway for each reaction was obtained by using the intrinsic reaction coordinate (IRC) with mass-weighted coordinates.[42–44] Although the evaluation of the absolute aromaticity of a compound remains a controversial, relatively obscure issue,[45] we were primarily interested in its variation during the reaction, and the evaluation of magnetic properties can be a useful tool for this purpose. Changes in magnetic properties along the IRC were monitored at different points, for which the magnetic susceptibility χ and its anisotropy χ_{anis} were calculated. Magnetic susceptibility values were calculated by computing the NMR shielding tensors using the IGAIM (individual gauges for atoms in molecules) method,[46,47] which is a slight variation of the CSGT (continuous set of gauge transformations) method.[46,48] The variation of the NICS[49] (nucleus-independent chemical shift) was also monitored along the IRC. We also carried out some ACID calculations (anisotropy of the current-induced density) with the program supplied by Herges.[33]

Results and Discussion

Figure 2 shows the energy profiles obtained from the IRC calculations. The whole reaction pathway from reactants to products was determined in all cases.[50] According to this figure, reactions 2, 3, and 4 have an energy barrier only slightly smaller than that for the prototypical pericyclic reaction 1. Only reaction 6 and, especially, reaction 5 have substantially smaller energy barriers. The calculated values (at 0 K, including zero-point vibrational energies) were 11.4, 8.6, 10.2, 9.8, 1.0, and 5.3 kcal mol^{-1} for reactions 1–6, respectively. These are not true overall barrier heights as their computation was based on the *cZc* conformation of the reactant, which is the most unstable, rather on the most stable one, generally *tZt*. The overall barrier heights thus were 20.5, 14.9, 16.4, 13.9, 3.3, and 7.3 kcal mol^{-1}, respectively. Pseudopericyclic reactions are known to exhibit low activation energies.[2–10] This conclusion should be interpreted in a relative rather than absolute manner as, in fact, pseudopericyclic reactions have low activation energies with respect to analogous pericyclic reactions. Thus, the pseudopericyclic Boulton–Katritzky rearrangement of (5*R*)-4-nitrosobenz[*c*]-isoxazole and its anion have activation energies higher than 30 kcal mol^{-1}.[37] The difficulty arises when we are looking for "the analogous pericyclic reaction", since it is sometimes a not easy task. For these reasons, the barrier heights can reveal some trends or clues, but they do not constitute proof of the pericyclic/pseudopericyclic character of the reactions.

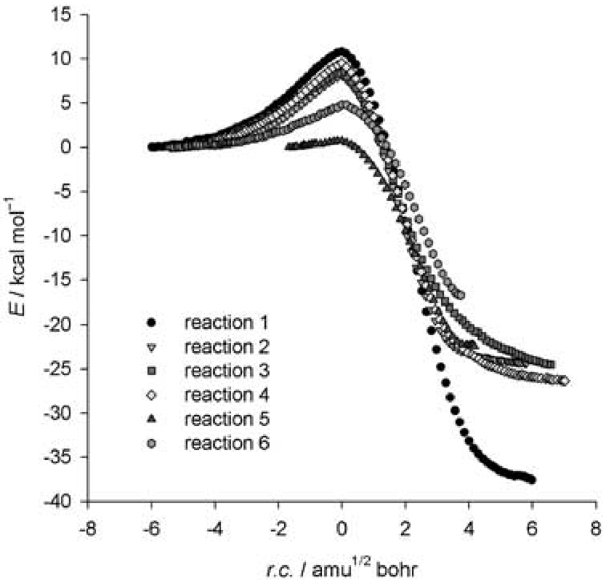

Figure 2. Energy profiles for the reactions.

According to Birney et al. pseudopericyclic reactions have planar transition states.[2–10] As can be seen in Figure 3 (which includes the normal vibrational frequency corresponding to each imaginary frequency) and Table 1, there are substantial differences in the planarity of the transition structures. Thus, TS$_1$, TS$_2$, and TS$_3$ have geometries strongly distorted from planarity, whereas the remaining transition structures, especially TS$_5$, show more planar geometries. On the whole, TS$_6$ is less planar than TS$_5$; however, in TS$_6$ the H atoms of C7 show a spatial arrangement that does not point to a disrotatory electrocyclization. The dihedral angles of these H atoms are very close to planarity: 169.2° and −12.5° (see Table 1). An almost total lack of rotation of these H atoms is observed when we display the animation of the imaginary frequency for TS$_6$. In TS$_5$ the situation is very

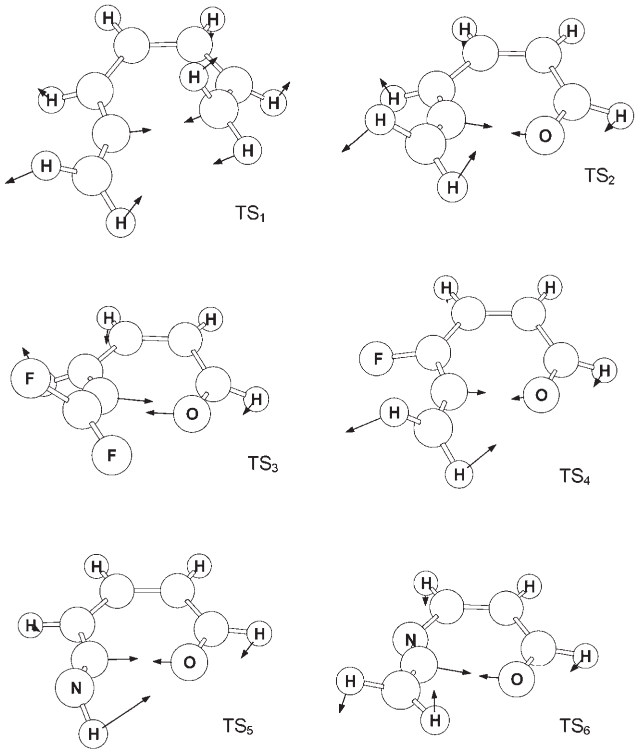

Figure 3. Transition structures and normal mode eigenvectors for the coordinate frequency.

Table 1. Bond lengths [Å], angles [°] and dihedral angles [°] at the transition states.

	TS_1	TS_2	TS_3	TS_4	TS_5	TS_6
X1−C6	1.380	1.257	1.257	1.261	1.254	1.252
C6−C5	1.413	1.418	1.422	1.413	1.418	1.426
C5−C4	1.387	1.388	1.389	1.388	1.383	1.382
C4−C3	1.426	1.411	1.413	1.402	1.411	1.343
C3−C2	1.360	1.365	1.362	1.364	1.369	1.259
C2−X1	2.274	2.041	2.009	2.008	2.127	2.120
X7−C2	1.326	1.316	1.315	1.317	1.218	1.319
C3-C2-X1	101.1	103.7	107.7	102.2	100.6	103.4
C4-C3-C2	129.2	124.6	121.9	128.5	127.9	129.1
C5-C4-C3	126.0	124.9	123.3	124.5	128.1	124.4
C6-C5-C4	122.1	119.6	120.2	119.3	120.5	121.0
X1-C6-C5	120.9	125.3	126.8	124.2	123.6	125.3
C2-X1-C6	105.8	114.2	110.6	117.1	117.8	111.0
X7-C2-C3	148.6	152.6	147.8	149.8	155.7	154.7
X7-C2-C1	108.2	103.6	103.8	107.8	105.8	101.9
C4-C3-C2-X1	−1.5	−27.8	−30.2	−17.6	−12.4	−27.6
C5-C4-C3-C2	20.5	19.2	19.5	13.7	9.4	23.6
C6-C5-C4-C3	-8.2	10.3	12.1	8.2	4.4	2.5
X1-C6-C5-C4	−30.6	−21.6	−26.1	−20.5	−9.2	−13.0
C2-X1-C6-C5	42.5	7.6	10.3	13.0	3.3	4.1
C3-C2-X1-C6	−27.7	16.0	16.9	5.1	7.0	14.4
ring distortion[a]	131.0	102.5	115.1	78.1	45.7	85.1
X7-C2-C3-C4	157.8	146.2	138.1	155.7	155.7	152.5
C2-X1-C6-H	−130.2	−166.8	−162.7	−161.6	−174.5	−173.2
H-X7-C2-C3	151.5	157.4	163.7	150.1	143.9	169.2
	−32.5	−26.4	−19.6	−33.4		−12.5

[a] This is a simple way of quantifying the nonplanarity of the six-membered ring. It is calculated merely by adding the absolute values of the previous six dihedral angles.

different: the dihedral angle H-N7-C2-C3 is 143.9°, and the animation clearly shows a rotatory movement.

If we take TS_6 and carry out an optimization (search for a TS) with enforcement of a planar geometry for the six-membered ring (all the atoms of the molecule were constrained to a plane except for the two H atoms of C7), we obtain a structure which is not true TS, since an additional imaginary frequency appears (corresponding to deformation of the enforced plane, as expected). This structure with full C_s symmetry (at the end of the optimization the H atoms were placed in the molecular plane, too) has an energy (including ZPE) only 0.19 $\text{kcal}\,\text{mol}^{-1}$ above that of the true transition structure. An analogous calculation for TS_5 gives a value of 1.22 $\text{kcal}\,\text{mol}^{-1}$ (H atom out of plane), although TS_5 is more planar than TS_6. For the remaining transition structures much larger values are obtained (e.g., 5.89 $\text{kcal}\,\text{mol}^{-1}$ for TS_2 and 4.82 $\text{kcal}\,\text{mol}^{-1}$ for the rather planar TS_4). In summary, although TS_6 does not have the greater planarity, its geometrical and energetical characteristics point to a pseudopericyclic reaction. The same holds to a lesser extent for reaction 5.

Figures 4 and 5 show the variation of the magnetic properties during the reactions. Reactions 1–4 show the typical pattern expected for a pericyclic reaction: marked aromatization near the transition state that is reflected in the presence of well-defined minima in the curve for both magnetic susceptibility χ and its anisotropy χ_{anis}. Reaction 6 shows an absolute pseudopericyclic pattern, that is, no aromatization near the transition state: χ and χ_{anis} rise continuously. Reaction 5 is the most difficult to interpret; although there are slight minima in the plots, the behavior is very different from that of the four clearly pericyclic reactions.

Figure 6 shows the behavior of the NICS along the reaction coordinates. For each point of the IRC the NICS value was calculated at two points: at the geometric center of the six-membered ring and at the ring critical point (3,+1), RCP, as defined by Bader's theory.[51] No appreciable differences are found for these two curves (because the geometric centres and the RCPs are rather close), so the choice of the geometrical center is appropriate to save computation time (at least for cases similar to these). In any case, Figure 6 leads to the same conclusions as Figures 4 and 5: clearly pericyclic behavior for

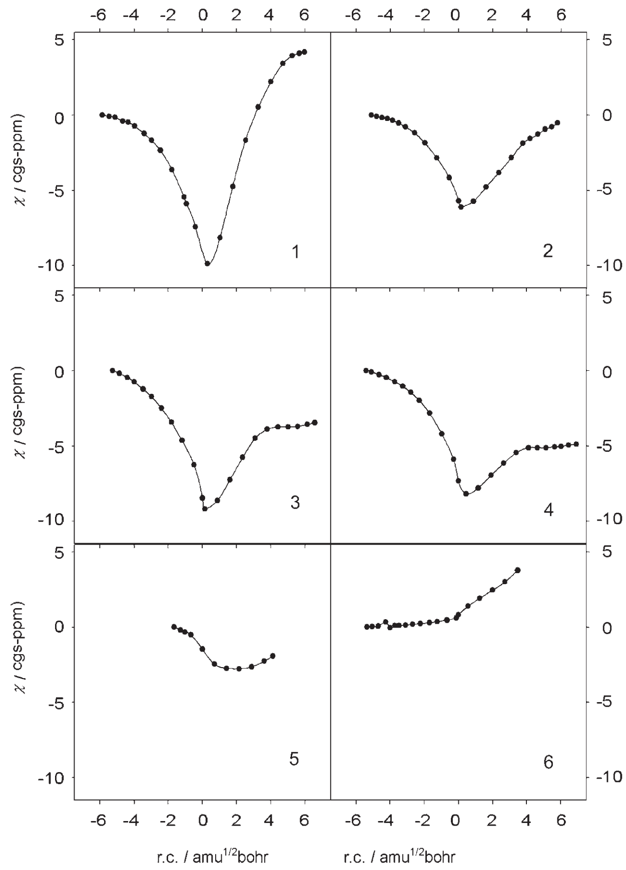

Figure 4. Variation of magnetic susceptibility relative to the reactant.

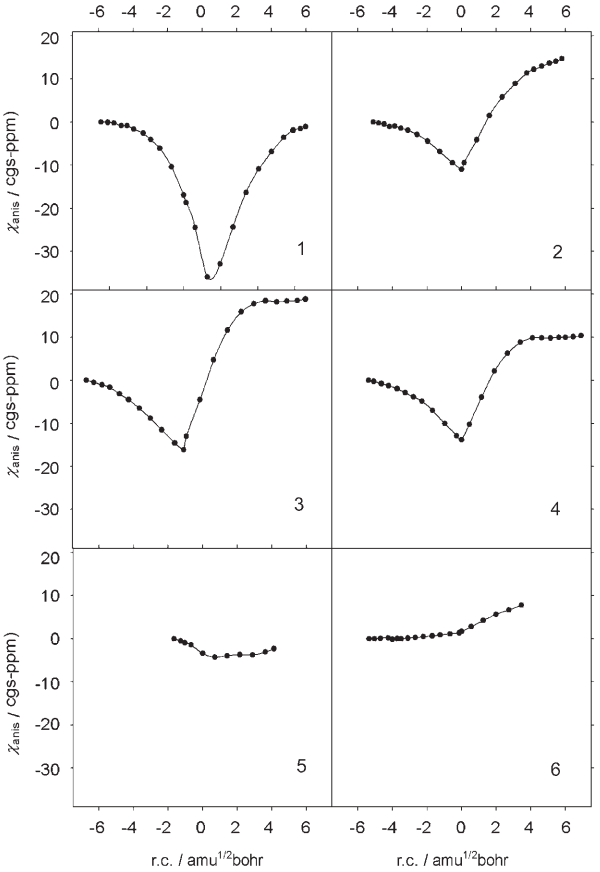

Figure 5. Variation of anisotropy of the magnetic susceptibility relative to the reactant.

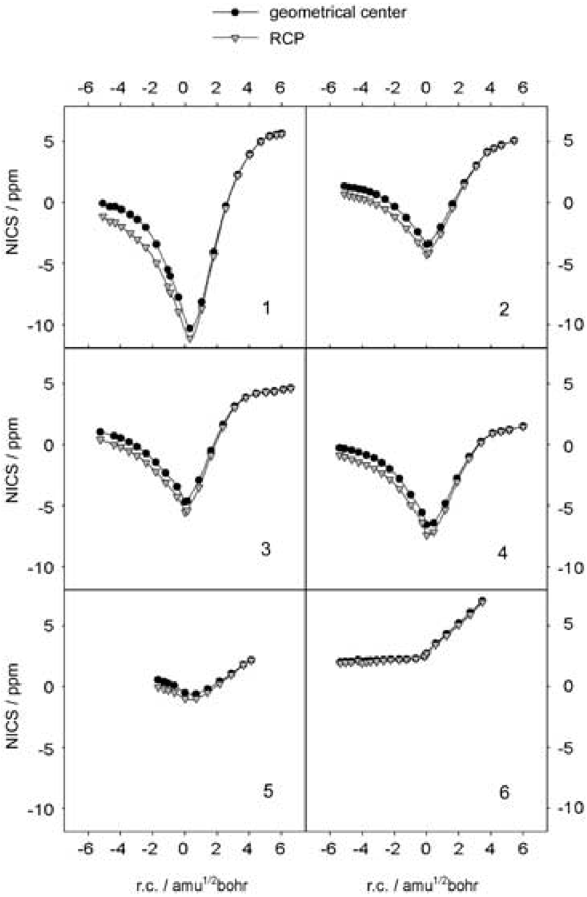

Figure 6. Variation of NICS.

reactions 1–4, clearly pseudopericyclic behavior for reaction 6 and a behavior that is very difficult to classify for reaction 5. Figure 7 shows the variation of NICS along a normal axis for the six transition structures (positive *Z* values above the molecules as they are shown in Figure 3). For pericyclic reactions 1–4 a deep minimum appears. As expected, these minima are located under the molecule, since on this side the disrotatory movement allows close proximity between the terminal p_z atomic orbitals (of X1 and C2). For this situation de Lera et al. proposed the term π^1 aromaticity.[21] No appreciable minimum appears for reaction 6, and a very shallow minimum is observed for reaction 5. In this figure we can observe a progression in the form of the curve going from the most pericyclic reaction 1 up to the pseudopericyclic behavior of reaction 6. As the progression advances, the minimum at the lower side disappears and a maximum in the upper side appears.

To investigate the existence of disconnections (typical of pseudopericyclic reactions) we also applied the ACID method.[33–35] This 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 surface. Figure 8 presents the ACID isosurface of each transition structure (an isosurface of anisotropy 0.030 was chosen). The figure shows the lower side of the molecule

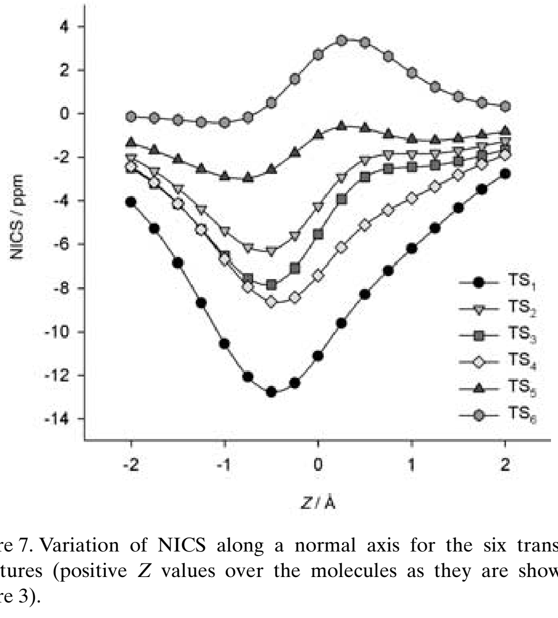

Figure 7. Variation of NICS along a normal axis for the six transition structures (positive *Z* values over the molecules as they are shown in Figure 3).

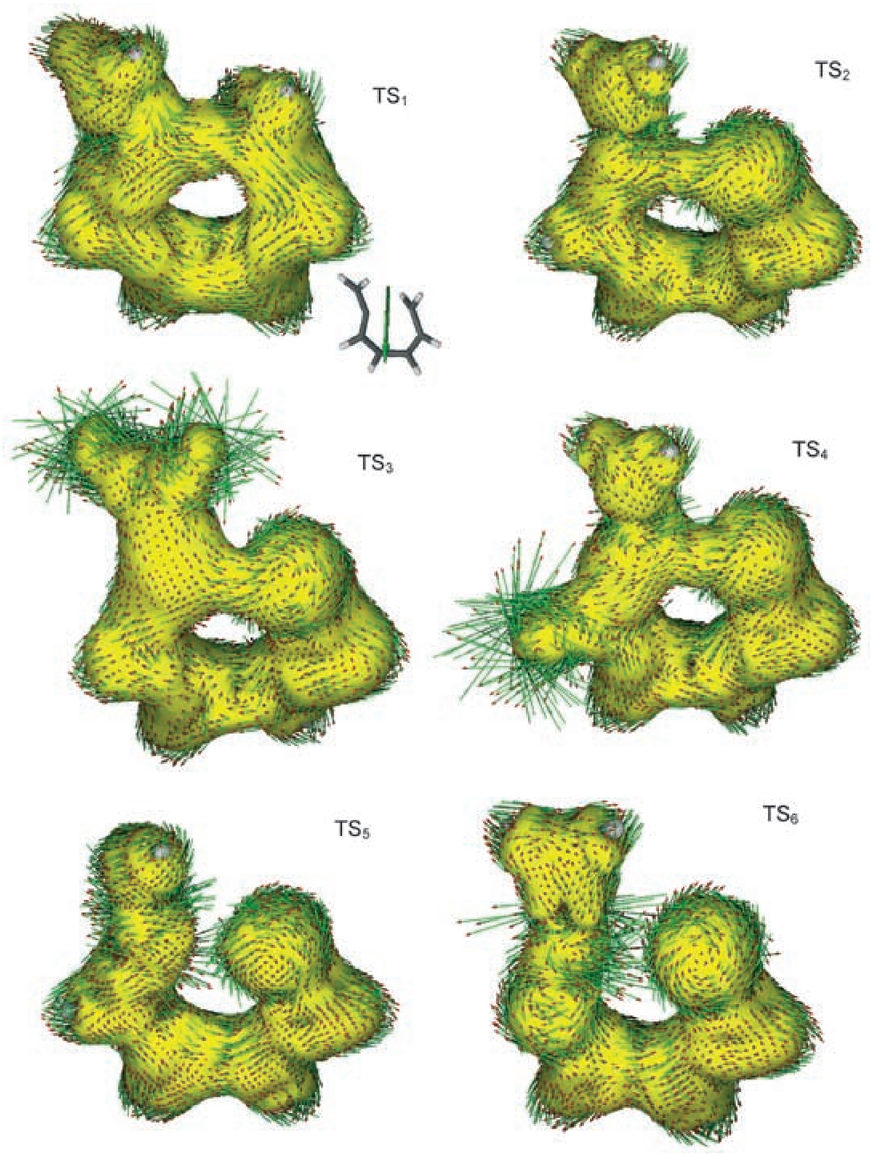

Figure 8. ACID plots for the transition states of reactions 1–6. The current density vectors (green arrows with red tips) are plotted on the isosurface of value 0.030. The vector of the magnetic field is shown for TS_1. In TS_{1-4} the current density vectors exhibit a closed circle in the six-membered ring and no disconnection. In $TS_{5,6}$ the topology of delocalized electrons exhibits one disconnection.

where the ring current is basically located. The vector of the magnetic field points downwards. The transition structures for reactions 1–4 do not exhibit any disconnection. Moreover, plotting the current density vectors onto the isosurface shows the pericyclic nature of the delocalized system: the strong diatropic ring current forms a closed loop around the six-membered ring, as expected for an aromatic system. The behavior of TS_5 and TS_6 is markedly different: a disconnection seems to exist in bond O1−C2, and a diatropic ring current is not observed. The extent of conjugation can be quantified by the critical isosurface value (CIV) at which the topology of the ACID boundary surface changes: 0.064, 0.050, 0.062, 0.059, 0.025, and 0.017 for reactions 1–6, respectively. Again, reactions 1–4 behave in a pericyclic manner (large CIV), while the values for reactions 5–6 point to a pseudopericyclic behavior. However, if we analyse these two reactions in depth, several differences can be found between them. First, CIV for TS_5 is not as small as the usual pseudopericyclic values. Moreover, an ACID plot for TS_5 at a smaller isovalue (≤ 0.020) reveals a small diatropic ring current flowing around the loop. However, for reaction 6, when the isovalue was lower than the CIV (0.017), no ring current could be observed. This reaffirms the pseudopericyclic character of reaction 6, but adds more doubt about the classification of reaction 5.

One purposes of this work is modifying reaction 2 to obtain a pseudopericyclic mechanism. We thought that this should be possible by increasing the electrophilic character of C2. Hence, electronegative atoms (N and F) were added in reactions 3–6. Table 2 lists point charges at C2 obtained by NBO calculations and by means of electrostatic potential-derived charges (Merk-Singh–Kollmam scheme). The charges correspond to reactants in their "reactive" conformation (*cZc*). Considering the limited predictive ability of point charges, only for reactants 5 and 6 is a significant positive charge achieved. The inclusion of F atoms (reactions 3 and 4) even reduces the positive charge, probably because they are placed in the position β to C2 and affect the contiguous C atoms.

Table 2. Point charges at C2 obtained by NBO calculations and by means of electrostatic potential-derived charges (Merk-Singh–Kollmam (MK) scheme).

	NBO	MK
reactant 1	+0.09	+0.22
reactant 2	+0.16	+0.27
reactant 3	−0.07	−0.19
reactant 4	+0.05	+0.10
reactant 5	+0.50	+0.59
reactant 6	+0.46	+0.43

However, for reactants 5 and 6 the N atom can withdraw charge from C2 since it is located contiguously. The point charges for these two reactants lead to the next question: why is reaction 6 more clearly pseudopericyclic than reaction 5 although the positive charge on C2 is similar or even smaller? The answer seems clear: there are influencing factors other than charge on C2. An exhaustive analysis of the characteristics of the reactant corresponding to reaction 6 allowed us to find the reasons for the pseudopericyclicity of this reaction.

For reactants 1–5 there is conjugation between bonds π-(2–3), π(4–5) and π(6–1); hence, because of the allene moiety, bond π(2–7) adopts a perpendicular arrangement relative to the other three π bonds (in the reaction bond π-(2–7) must rotate to become coplanar with the rest of the molecule). However, reactant 6 has a rather unexpected geometry (Figure 9). The positions of the hydrogen atoms of C7 do not agree with the expected structure. Accordingly, bond π(2–3), which must be perpendicular to bond π(2–7), would be out of conjugation (the dihedral angle C2-N3-C4-C5 is 70.4°). To explain this surprising behavior we carried out an NBO calculation on reactant 6, which allowed us to understand all these facts: The reason for the “anomaly” is the position of the nitrogen lone pair (LP), the NBO of which has a p character greater than expected (81 % instead of the typical 67 % for an sp^2 hybrid) and does not point outwards from the molecule; it is practically normal to the structure. This is corroborated by molecular electrostatic potential (MEP) calculations: Figure 9 reveals a negative isosurface (0.035 a.u., dotted) which shows the position of the oxygen LPs (the larger region) and the nitrogen LP (the smaller region). Thus, it is this LP and not bond π(2–3) which conjugates with bonds π(4–5) and π(6–1). Figure 10 a and b clearly show this situation. However, for reactant 5 (and for all the others) the expected structure is found (see Figure 10 c). The peculiar structure of reactant 6 favors the pseudopericyclic character of the electrocyclization, since bond π(2–3) no longer needs to rotate and the H atoms of C7 are practically in their final position already. Thus, basically, reaction 6 consists only of bringing together O1 with C2, which takes place by attack of the O1 LP on positively charged C2. Figure 11 shows that the rotation of the H atoms of C7 along the reaction coordinate is very smooth, but this rotation is much more noticeable for reaction 5.

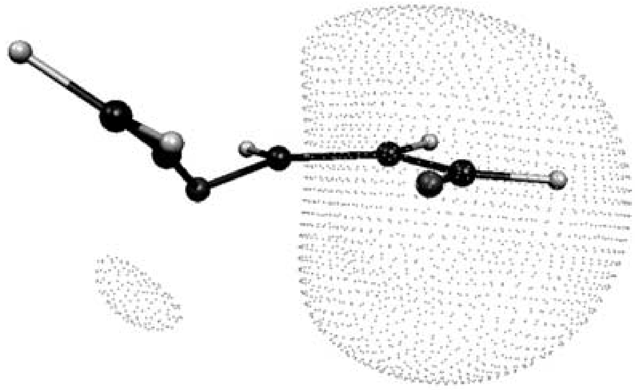

Figure 9. Optimized geometry of reactant 6 in its “reactive” conformation *cZc*. The dots correspond to an isosurface (−0.035 a.u.) of molecular electrostatic potential (MEP).

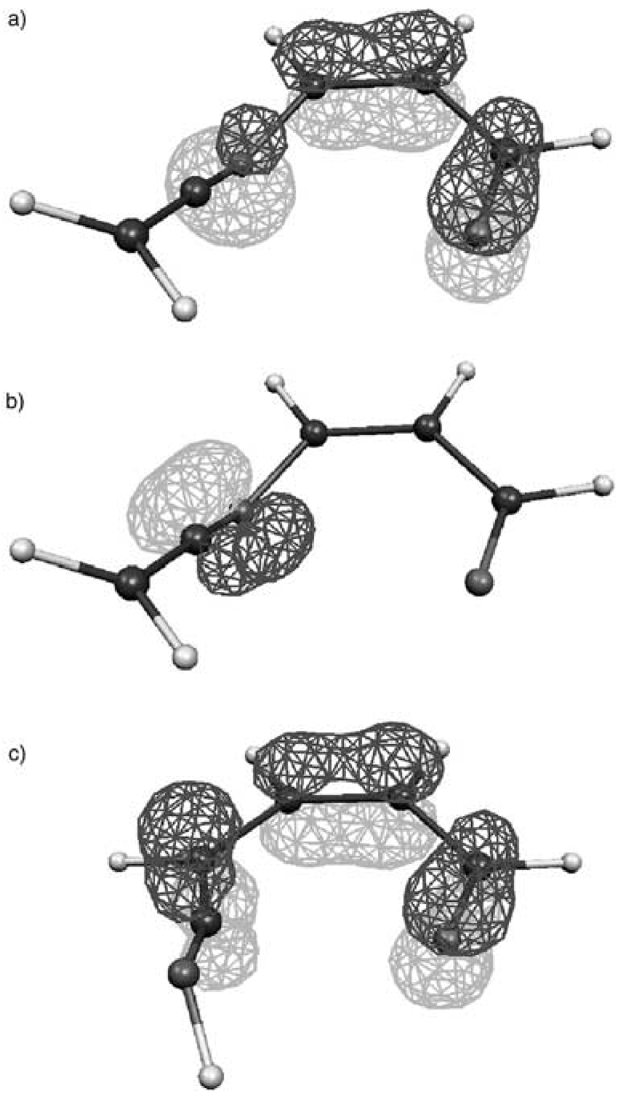

Figure 10. NBOs. a) π(4–5), π(1–6) and LP(N3) for reactant 6. b) π(2–3) for reactant 6. c) π(2–3), π(4–5) and π(1–6) for reactant 5.

Conclusion

According to previous calculations, the electrocyclization of (2*Z*)-2,4,5-hexatrienal (reaction 2) is a pericyclic disrotatory process favored by the assistance of an electron lone pair.[20,22,24] Although the evidence reported is suggestive of an essentially pericyclic mechanism, its features are in-between those of a prototypical pericyclic reaction and a prototypical pseudopericyclic reaction. We investigated how we could modify reactant 2 to achieve a pseudopericyclic process. To this purpose, electronegative atoms (N and F) were

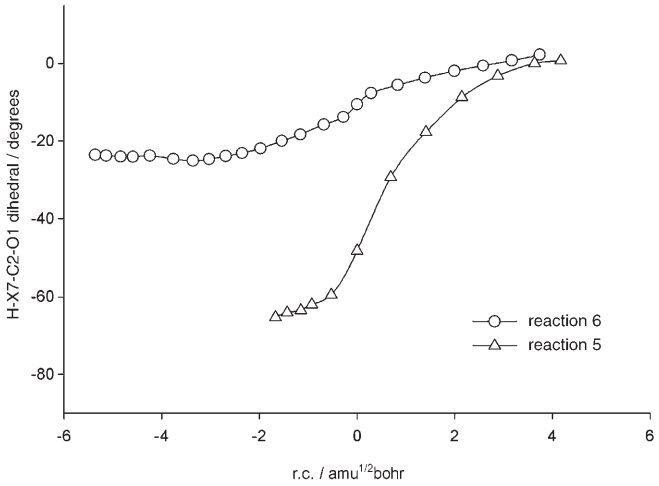

Figure 11. Variation of the H-X7-C2-O1 dihedral angle during reactions 5 and 6.

added to favor the electrophilic character of carbon atom C2 and hence attack of the electron lone pair of O1 (reactions 3–6).

We used the variation of energy, structural and magnetic parameters along the reaction pathway with a view to examining all the reactions. Based on the results, reactions 3 and 4 behave similarly to pericyclic reaction 2. In these two reactions, substitution by fluorine atoms does not achieve the purpose of increasing the positive charge on C2, probably because the F atoms are not located contiguously with C2. On the contrary, for reactants 5 and 6 the N atom can withdraw charge from C2. The examination of structural and magnetic parameters along the reaction pathway allows us to conclude that reaction 6 follows a pseudopericyclic mechanism. The classification of reaction 5 as pericyclic or pseudopericyclic is a very challenging task. All the results indicate that this reaction is a borderline case; its behavior is far from those of the other pericyclic reactions, but it retains some features typical of the pericyclic pattern (albeit in an almost imperceptible manner). Thus, minima appear in the plots of susceptibility χ, anisotropy of susceptibility χ_{anis} and NICS, but these minima are very smooth, virtually nonexistent. Something similar happens with ACID results: although the behavior of TS_5 is very different from those of pericyclic TS_{1-4}, an ACID plot with a small isovalue reveals a small diatropic ring current flowing around the loop (typical of a pericyclic TS). For TS_6, under no circumstances does the ring current appear.

In conclusion, reaction 6 can definitely be classified as pseudopericyclic. However, reaction 5, although it possesses features of pseudopericyclic nature, is preferably designated as very weakly pericyclic. However, this is a borderline case and perhaps only a nomenclature issue. More important is why reaction 5 is less pseudopericyclic than reaction 6 although in both cases the electrophilic character of C2 of the reactants is similar (even higher for reactant 5). A detailed examination of reactant 6 allows us to explain this: the geometry is not as expected, due to the "anomalous" position of the nitrogen LP. According to NBO calculations this LP has a high p character and conjugates with two π bonds. The peculiar structure of reactant 6 favors the pseudopericyclic character of the electrocyclization, since an important portion of the molecule is nearly in its final position already, and rotation of the allene part is unnecessary.

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[50] In principle two different transition states should be found for reaction 5 (to generate the *Z* and *E* configuration in the imine, respectively). However, calculations at the B3LYP/6-31+G* level only gave the TS which leads to the *Z* configuration of the product (exocyclic NH towards the ring oxygen atom). An exhaustive search for a TS which leads to the *E* configuration was not successful: all attempts always led to the same TS_5 which is shown in Figure 3. This unexpected situation could be explained by analyzing the geometry of the reactant. In the most stable conformation (*tZt*) the iminic H atom adopts the expected geometry: absolutely normal to the allene moiety. However, in the reactive conformation (*cZc*) the H atom loses this geometry and has already substantially moved towards the ring oxygen atom: the C1-C2-N7-H dihedral is −62.1°, very close to −48.2° in TS_5.
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