Criteria for the Elucidation of the Pseudopericyclic Character of the Cyclization of (*Z*)-1,2,4,6-Heptatetraene and Its Heterosubstituted Analogues: Magnetic Properties and Natural Bond Orbital Analysis

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Abstract: The electrocyclization of heterosubstituted derivatives of (*Z*)-1,2,4,6-heptatetraene, (2*Z*)-2,4,5-hexatrien-1-imine and (2*Z*)-2,4,5-hexatrienal exhibit some features which suggest a pseudopericyclic mechanism. In order to examine this, a comprehensive study including the determination of magnetic properties to estimate aromaticity and an NBO analysis throughout the reaction path was conducted. The cyclization of 5-oxo-2,4-pentadienal, a process of unequivocal pseudopericyclic nature, was studied for comparison. The results suggest that, although the lone electron pair on the heteroatom in the heptatetraene derivatives 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.

Keywords: ab initio calculations • aromaticity • density functional calculations • electrocyclic reactions • transition states

Introduction

Pseudopericyclic reactions were originally defined by Lemal as a concerted transformation where the primary changes in bonding compass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles.[1, 2] The role interchange 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. Although this definition is seemingly quite clear, some ambiguity remains as the orbital description is not unique.

Birney and co-workers[3–12] have examined a large number of pseudopericyclic reactions, which as they have found possess three essential features, namely: very low or zero activation energies, planar transition states and that no pseudopericyclic reaction can be forbidden. One such reaction is the cyclization of 5-oxo-2,4-pentadienal to pyran-2-one (reaction D in Figure 1).[6] This reaction involves the in-plane attack of the lone electron pair on the carbonyl oxygen on the electrophilic allene carbon; there is a lack of overlap between σ and π orbitals, and no barrier to ring closure. The 1,5-electrocyclizations of iminodiazomethanes and conjugated nitrile ylide exhibit similar features.[13, 14] Another pseudopericyclic processes have been described recently.[15–17]

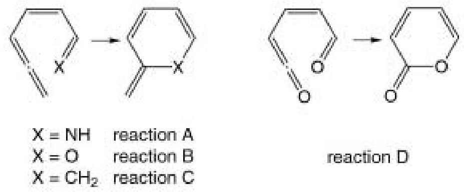

Figure 1. Reaction schemes for the electrocyclizations studied. Reaction A represents the *E* configuration of the imine. The *Z* configuration is studied by means of reaction A2.

(*Z*)-1,2,4,6-Heptatetraene and its heterosubstituted derivatives undergo electrocyclizations similar to that of 5-oxo-2,4-pentadienal. Recently, Lera et al.[18] hypothesized that, while the cyclization of the parent compound (reaction C in Figure 1) is pericyclic, those of its derivatives (2*Z*)-2,4,5-hexatrien-1-imine (reaction A in Figure 1) and (2*Z*)-2,4,5-hexatrienal (reaction B in Figure 1) involve a nucleophilic addition that is pseudopericyclic in nature. In our minds, however, the evidence provided by these authors is not sufficient to unequivocally establish the pseudopericyclic nature of these processes; rather, our calculations suggest that reactions A

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and B are essentially pericyclic, even though they are favored (or assisted) by the lone electron pair on the heteroatom.[19] In previous work, we found the energies of activation for such reactions not to be too low and the corresponding transition states to be far from planar. Also, the mere observation of the nuclear motion corresponding to the imaginary frequency of the transition state suggests no appreciable difference among the transition states TS_A, TS_B and TS_C. Although the lone pair on the heteroatom plays a prominent role—it decreases the energy of activation—there is no in-plane attack on the allene carbon as deviations are quite substantial. Thus, for the transition state of reaction A, the lone pair is at an angle of 57° with respect to the N1-C2-C3 plane. One of the arguments used by Lera et al. was based on the increased aromaticity of the transition state in reaction C relative to those in A and B. The cyclic loop of pericyclic reactions is known to give rise to aromatic transition states;[20–24] additionally the typical disconnection of pseudopericyclic reactions prevents this aromaticity. Based on our magnetic susceptibility anisotropy (χ_{anis}) calculations, the transition states TS_A and TS_B (with χ_{anis} values of -36.54 and -31.37 cgs ppm, respectively) are less aromatic than TS_C ($\chi_{anis} = -46.44$ cgs ppm) but still aromatic to some extent. It should be noted, however, that these data are of limited value, as it seems more logical to examine the cyclization process as a whole than the transition structures involved. Moreover aromaticity and its quantitation remain controversial subjects.[25, 26] For this reason, in this work we conducted a careful study of the whole cyclization process in reactions A, B and C rather than its transition states alone; to this end, we examined aromaticity in terms of both χ_{anis} and the nucleus-independent chemical shifts (NICS) reported by Schleyer.[27] The reactions were also studied using the natural bonding orbital (NBO) analysis[28–30] and all the results compared with those for a similar, unequivocally pseudopericyclic process (namely the cyclization of 5-oxo-2,4-pentadienal, reaction D). The combination of these data enabled a more accurate assessment of the character of these reactions.

It is necessary to indicate that in the present work we have not only studied the *E* configuration of the imine of the reaction A, but that we have also analyzed the behavior of *Z* configuration (reaction A2). In the (*Z*)-imine the lone pair position of the N atom (outwards of the ring) precludes its involvement in the new bond formed. Cossio and Lera have demonstrated that (*E*)-imine gives rise to a transition state less aromatic than the (*Z*)-imine.[31] However, we think that this is not a conclusive demonstration of that electrocyclization of the (*E*)-imine is a pseudopericyclic process. Thus, it is evident that the (*Z*)-imine must give rise to a pericyclic process very similar to the reaction C, since the lone pair cannot participate in an efficient way. It is with the (*E*)-imine where doubts arise, since the position of the lone pair is the one that could give rise to a pseudopericyclic reaction as it is the case of 1,5-electrocyclization of (*E*)-iminodiazomethane: for this reaction Fabian et al.[13] showed the pseudopericyclic character of the absolutely planar transition state.

Abstract in Spanish: *La electrociclación de los derivados heterosustituidos del (2Z)-1,2,4,6-heptatetraeno, el (2Z)-2,4,5-hexatrien-1-imine y el (2Z)-2,4,5-hexatrienal presentan características que podrían sugerir un mecanismo de tipo pseudopericíclico. Para examinar esta circunstancia se ha realizado un exhaustivo estudio que incluye el cálculo de propiedades magnéticas (para estimar la aromatización) y el análisis NBO a lo largo de todo el camino de reacción. A efectos comparativos, también se ha realizado el estudio de la ciclación del 5-oxo-2,4-pentadienal, proceso inequívocamente de naturaleza pseudopericíclica. Los resultados obtenidos parecen indicar que aunque en los análogos del heptatetraeno la participación del par electrónico solitario del heteroátomo es de vital importancia en el mecanismo de reacción, no es suficiente para que estas reacciones pierdan las características esenciales correspondientes a una electrociclación disrotatoria pericíclica.*

Computational Methods

The geometries of all stationary points were fully optimized using the Gaussian 98 software package[32] with the 6-31G** basis set and the density functional theory (specifically, the Becke3LYP functional).[33, 34] In other electrocyclizations this method had previously provided results comparable to those obtained with computationally much more expensive methods.[35] All points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies, using analytical second derivatives. Also, the whole path for each reaction was obtained by using the intrinsic reaction coordinate (IRC)[36–38] with mass-weighted cartesian coordinates. Changes in magnetic properties along the IRC were monitored at different points for which the nucleus-independent chemical shift (NICS), magnetic susceptibility (χ) and magnetic susceptibility anisotropy (χ_{anis}) were calculated. NICS values were obtained by using a slightly larger basis set (namely B3LYP/6-31+G**) in conjunction with the GIAO (Gauge-Independent Atomic Orbital) method.[39] Magnetic susceptibility values were calculated by computing the NMR shielding tensors at the 6-311+G(2d,p) level as they required a much more powerful basis set. Because the GIAO method provides no information about magnetic susceptibility; this was calculated using the IGAIM (Individual Gauges for Atoms in Molecules) method,[40, 41] which is a slight variation of the CSGT (Continuous Set of Gauge Transformations) method.[40–42] Processes were also monitored by applying the NBO (Natural Bond Orbital) method[28–30] along the IRC, using the B3LYP/6-31G** electron densities.

Results and Discussion

Reaction paths: Figure 2 shows the reaction profiles for the five processes studied. Consistent with previous findings of Birney et al.,[6] the B3LYP/6-31G** method revealed no energy barrier for the pseudopericyclic reaction D. Consequently, the reactant as depicted in Figure 1 could not be located at this computational level. On the other hand, the HF/6-31G** method allowed its identification and provided an energy barrier of only 1.52 kcal mol^{-1}. For this reason, we chose to monitor the IRC at the Hartree – Fock level and perform B3LYP/6-31G** single-point calculations at different points of the reaction path. This was the computational level used to obtain the graph in Figure 2, which reveals no energy barrier either.

The other four processes exhibited moderate energy barriers, namely: 6.13 kcal mol^{-1} for reaction A, 17.15 kcal mol^{-1} for reaction A2, 8.04 kcal mol^{-1} for reaction B and 11.05 kcal mol^{-1} for reaction C. In any case, these

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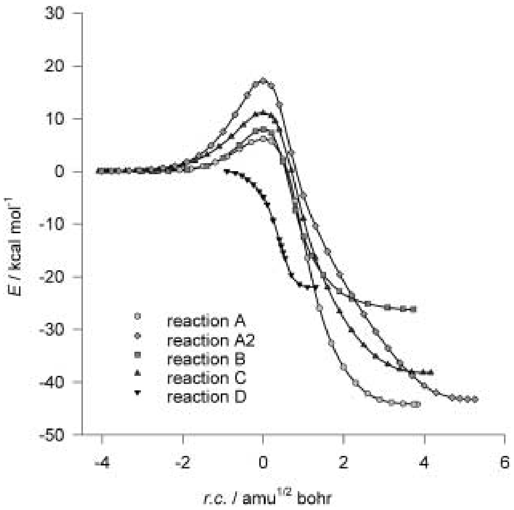

Figure 2. Energy profile for the reactions.

are not true energies of activation as their computation should not have relied on the *cZc* conformation of the reactant—which is the most unstable—but rather on the most stable one, generally *tZt*. The energies of activation thus obtained (at 0 K, including zero-point vibrational energies, scaled by 0.9806)[43] were 13.75, 24.14, 14.41 and 19.97 kcal mol^{-1} for reaction A, A2, B and C, respectively. The previously calculated energies of activation for the cyclization of (*Z*)-1,3,5-hexatriene and its heterosubstituted analogues were 20.58, 37.12, 21.52 and 30.11 kcal mol^{-1} (including ZPVE).[35] A comparison of these values with those for reactions A, A2, B and C reveals that the replacement of the terminal double bond with an allene group results in marked decreases in the energy of activation (namely 6.83 kcal mol^{-1} for reaction A, 12.98 kcal mol^{-1} for reaction A2, 7.11 kcal mol^{-1} for reaction B and 10.14 kcal mol^{-1} for reaction C).

Anisotropy along the reaction path: Table 1 shows the χ_{anis} values obtained at the singular points of the reactions. As can be seen, the transition state of reactions A2 and C exhibited an abrupt decrease in anisotropy with respect to both the reactant and product. This is the behavior to be expected from a typical pericyclic reaction[21] since, as stated by Zimmerman, thermally allowed pericyclic reactions are considered to take place preferentially through concerted aromatic transition states that are energetically favored.[20] This is not the case with pseudopericyclic reaction D; rather, χ_{anis} decreases monotonically from the reactant to the product and there is no appreciable aromatization in the transition state. In reactions A and B, the aromatization of the transition state is more than appreciable and, though not so strongly as in reactions A2 and C; this suggests that both reactions take place via an essentially pericyclic path. Figure 3 reflects these conclusions in a more graphical manner; it shows not only the singular points, but also the whole reaction path (as the variation of χ_{anis} with respect to the reactant). As can be seen, the curves for reactions A, A2, B and C are similar. To a different extent, the four exhibit a central sink (near the transition state, but slightly shifted to the products) that reflects the aromatization inherent in a pericyclic reaction. On the contrary, in reaction D, χ_{anis} decreases continuously from the reactants to the product; although the latter appears to be somewhat more aromatic, there is no appreciable sink suggestive of a specially favored aromatic transition state.

Table 1. Anisotropies and NICS at the singular points of reactions.

		χ_{anis} [cgs ppm]	NICS [ppm]
	reactant	−17.67	1.27
reaction A	TS	−36.54	−5.73
	product	−3.71	4.20
	reactant	−18.65	−0.01
reaction A2	TS	−47.85	−11.88
	product	−3.71	4.20
	reactant	−19.55	1.08
reaction B	TS	−31.37	−4.47
	product	−4.40	5.05
	reactant	−15.49	−0.34
reaction C	TS	−46.44	−10.98
	product	−14.67	5.10
	reactant	−16.33	−0.75
reaction D	TS	−21.08	−1.64
	product	−26.98	−0.14

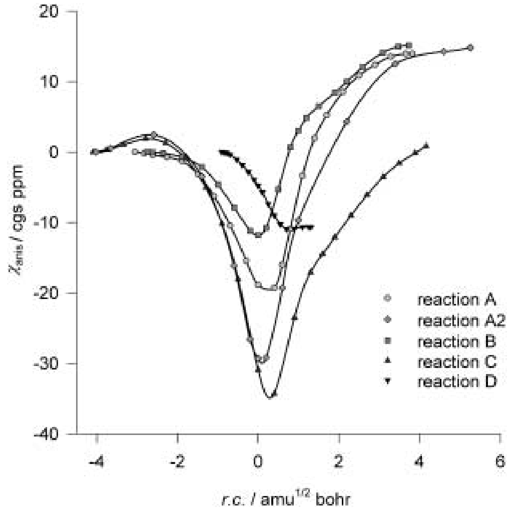

Figure 3. Variation of anisotropy of the magnetic susceptibility relative to the reactant.

The magnetic susceptibility (Figure 4) varies identically with anisotropy. The only difference is that the curve for the pseudopericyclic process D exhibits a very small minimum—much smaller than those for the other four reactions.

NICS along the reaction path: Although, originally, Schleyer et al.[27] calculated NICS at the geometric center of the ring, they subsequently[44] chose to use the ring critical point (3,+1) obtained using Bader's "theory of atoms in molecules"[45] as implemented in the AIMPAC suite of programs.[46] This choice, based on the topology of the electron density, constitutes an unambiguous characterization of a ring, so we used it to obtain NICS at selected points along the reaction path. The results (Table 1 and Figure 5) suggest that NICS behaves identically with magnetic susceptibility. Thus, the transition states of reactions A, A2, B and C exhibit markedly decreased NICS values and hence increased aromaticity; on

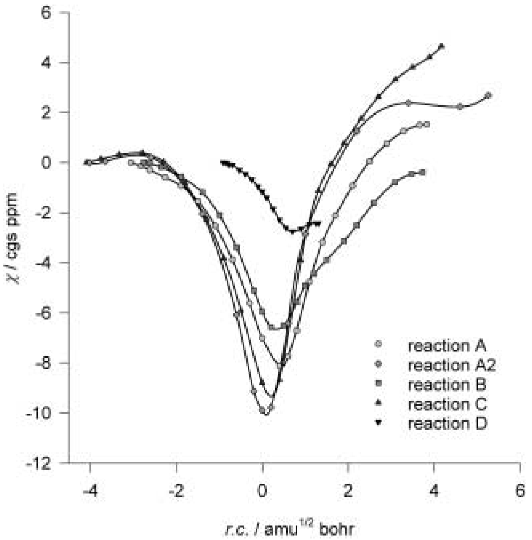

Figure 4. Variation of magnetic susceptibility relative to the reactant.

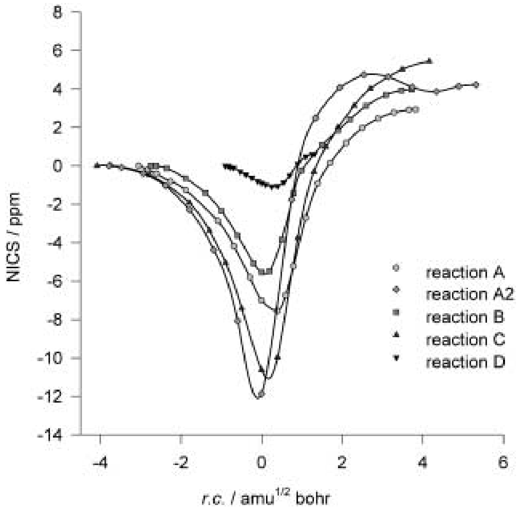

Figure 5. Variation of nucleus-independent chemical shift (NICS) relative to the reactant.

Table 2. Wiberg bond orders at the transition states.

	TS_A	TS_{A2}	TS_B	TS_C	TS_D
X1−C6	1.69	1.49	1.54	1.57	1.52
C6−C5	1.23	1.38	1.29	1.32	1.28
C5−C4	1.58	1.46	1.49	1.53	1.51
C4−C3	1.27	1.37	1.33	1.29	1.34
C3−C2	1.61	1.52	1.53	1.61	1.41
C2−X1	0.29	0.41	0.31	0.33	0.30
X7−C2	1.90	1.89	1.93	1.89	2.00

Table 3. Bond lengths [Å], angles and dihedral angles [°] at the transition states.

	TS_A	TS_{A2}	TS_B	TS_C	TS_D
X1−C6	1.298	1.336	1.254	1.377	1.226
C6−C5	1.427	1.401	1.418	1.411	1.414
C5−C4	1.373	1.396	1.384	1.385	1.362
C4−C3	1.425	1.410	1.411	1.424	1.407
C3−C2	1.353	1.371	1.362	1.359	1.364
C2−X1	2.186	2.091	2.047	2.271	1.985
X7−C2	1.319	1.322	1.314	1.324	1.138
C3-C2-X1	99.4	105.0	103.6	101.1	100.6
C4-C3-C2	129.2	126.8	124.9	129.2	127.8
C5-C4-C3	126.9	124.9	125.0	126.1	128.4
C6-C5-C4	121.4	119.7	119.6	122.1	118.2
X1-C6-C5	121.3	124.0	125.5	120.9	122.7
C2-X1-C6	115.7	108.1	114.1	106.0	122.3
X7-C2-C3	151.0	147.2	152.5	148.8	154.6
X7-C2-C1	109.3	106.5	103.8	108.2	104.8
C4-C3-C2-X1	−17.2	−5.6	−26.8	−1.5	0.0
C5-C4-C3-C2	20.8	19.6	18.9	20.4	0.0
C6-C5-C4-C3	2.3	−4.7	9.8	−8.1	0.0
X1-C6-C5-C4	−23.0	−29.5	−21.6	−30.2	0.0
C2-X1-C6-C5	21.1	38.2	8.5	42.1	0.0
C3-C2-X1-C6	−2.6	−20.9	14.7	−27.5	0.0
X7-C2-C3-C4	156.3	158.7	148.0	158.1	180.0
C2-X1-C6-H	−155.3	−132.7	−165.9	−130.6	180.0
H-X1-C6-C2[a]	−148.0	75.3	–	−127.0, 78.4	–
H-X1-C6-C5	169.1	−37.1	–	169.9, −36.3	–
H_1-X7-C2-C3	−41.1	−26.1	−28.0	−32.5	–
H_2-X7-C2-C3	144.5	158.2	155.9	151.4	–

[a] Deviation of the H atom with respect to the plane formed by atoms X1, C6 and C2.

the other hand, the curve for the pseudopericyclic reaction D exhibits a small sink but NICS remains virtually constant throughout the reaction, so the process involves negligible aromatization.

Although the minimum is indeed more shallow for A and B than for A2 and C, its appearance is seemingly consistent with a pericyclic aromatic process.

The only salient difference between the χ_{anis} and NICS results lies in the pseudopericyclic reaction D: while χ_{anis} predicts greater aromaticity in the product than in the reactant, NICS suggests similar aromaticity in both. In any case, this has no effect on our discussion, which is focussed on the aromatization near the transition states.

NBO analysis: The transition state and whole path of each reaction were subjected to a comprehensive NBO analysis. Tables 2 and 3 show the Wiberg bond orders and structural parameters, respectively, for the transition states. Table 3 shows that TS_A and TS_B are far from planar although not as much as TS_{A2} and TS_C. The length of the incipient bond (C2−X1) differs appreciably among the reactions, but the differences have small effect on bond orders (which range from 0.29 to 0.33), except for TS_{A2} (0.41) which represents a transition state somewhat closer to the product, which also happened in the parent compound (without allene group).[35] One of the few salient features is probably the bond order of the X7−C2 exocyclic bond. Thus, it is highest for the pseudopericyclic reaction D (2.00) and somewhat lower for the other four reactions (1.90, 1.89, 1.93 and 1.89). The bond orders for the natural localized molecular orbitals (NLMOs) involved in the interaction between atoms X1 and C2 in the transition states (Table 4) are of greater interest as they allow one to identify the localized orbitals most actively involved in the C2−X1 bond formed in the cyclization process. As expected, the lone pair on the heteroatom plays a crucial role (bond order of 0.147) in the pseudopericyclic process D--much more so than the π bonds in the molecule. On the other hand, the X7−C2 exocyclic bond takes virtually no part

Table 4. Bond orders of the natural localized molecular orbitals (NLMOs) for the interaction between atoms X1 and C2 in the transition states.

	TS$_A$	TS$_{A2}$	TS$_B$	TS$_C$	TS$_D$
π(X1–C6)	0.033	0.118	0.035	0.098	0.007
π(C2–C3)	0.027	0.050	0.025	0.041	0.020
π(C4–C5)	0.039	0.069	0.033	0.057	0.014
π(C2–C7)	0.009	0.031	0.007	0.031	<0.002
LP(X1)	0.077	0.003	0.092	–	0.147

in the process, which is consistent with the above-mentioned Wiberg bond order (2.00). In reactions A2 and C, which are unequivocally pericyclic in nature, the π(X1–C6) bond play a prominent role, although the other π orbitals also participate in outstanding way. In these transition states TS$_{A2}$ and TS$_C$, the exocyclic bond is involved nearly to the same extent as the other π orbitals (0.031). The transition states for reactions A and B lie in an intermediate behavior, albeit closer to TS$_{A2}$ and TS$_C$: although the most important role is that played by the lone pair on the heteroatom, the π orbitals are also strongly involved. On the other hand, the π orbital of the exocyclic bond is only slightly involved (0.007 and 0.009). Regarding the similarity of TS$_A$ and TS$_B$ to TS$_{A2}$ and TS$_C$, the lack of a properly oriented lone pair in reactions A2 and C is partly offset by the participation of the exocyclic bond. The most salient features of the unequivocally pseudopericyclic reaction D are an overwhelming predominance of the lone pair and a nearly zero involvement of the exocyclic bond.

The analysis of the transition states is completed with the data of Table 5, which shows the results of the second order perturbation analysis as the energies of delocalization of electrons from filled NBOs into empty NBOs—so that they do not finish up quite filled or quite empty. De Lera et al.[31] suggested a pseudopericyclic nature for reaction A on the basis that the lone pair on N1 donates to the localized orbitals π*(C2–C7) and π*(C2–C3) with associated second-order perturbation energies of about 17 and 8 kcal mol^{-1}, respectively; we obtained 16.43 and 7.89 kcal mol^{-1} as a result of the different basis set used. These authors stated that "… in sharp contrast, the interactions between the π(C2–C3) and π(N1–C6) localized orbitals, which would be associated with the disrotatory process, are only of ca. 3 kcal mol^{-1} …". As can be seen from Table 5, our results for such interactions were 2.79 and 2.52 kcal mol^{-1}. According this Table, we believe that the previous assertion by de Lera et al. is unwarranted. Based on the values for TS$_C$, the disrotatory character of which is unquestionable, the π(C2–C3)–π(X1–C6) interactions also exhibit low energies (4.81 and 6.25 kcal mol^{-1}), much smaller than the interactions π(C4–C5)–π(X1–C6) and π(C2–C3)–π(C4–C5) (15–17 kcal mol^{-1}). Although in TS$_A$ and TS$_B$ the interactions of the lone pair of X1 with π*(C2–C7) and π*(C2–C3) are important, they are less so than some of the π–π* interactions. Thus, the strongest interaction in both TS$_A$ and TS$_B$ is π(C4–C5) → π*(X1–C6) (24.66 and 35.52 kcal mol^{-1}, respectively). The pseudopericyclic reaction D behaves rather differently from the previous reactions; thus, the interaction of the lone pair occurs almost exclusively with the π*(C2–C7) exocyclic bond and the magnitude of this interaction, 54.12 kcal mol^{-1}, is the largest by far.

Table 5. Stabilization energies [kcal mol^{-1}], $E^{(2)}$, for the transition states of the reactions as obtained by second order analysis using the NBO method.

Donor	Acceptor	TS$_A$	TS$_{A2}$	TS$_B$	TS$_C$	TS$_D$
π(X1–C6)	π*(C4–C5)	7.61	10.46	4.41	15.25	3.88
π(C4–C5)	π*(X1–C6)	24.66	25.76	35.52	17.24	35.97
π(C2–C3)	π*(C4–C5)	21.22	21.29	27.25	16.19	29.68
π(C4–C5)	π*(C2–C3)	11.78	16.40	10.64	16.89	9.71
π(C2–C3)	π*(X1–C6)	2.79	6.49	2.37	4.81	0.58
π(X1–C6)	π*(C2–C3)	2.52	11.49	3.99	6.25	1.00
LP(X1)[a]	π*(C2–C7)	16.43	<0.50	15.11	–	54.12
LP(X1)[a]	π*(C2–C3)	7.89	2.76	13.84	–	<0.50

[a] The inner lone pair of O1 atom in reactions B and D.

As with the magnetic properties, the whole reaction path is more informative than are the individual transition states. In fact, it allows the course of the reaction to be monitored and the restrictions arising from focussing on a single point to be avoided. As can easily be seen from the variation of NBOs along the reaction path, reactions A, A2, B and C behave rather differently from the unequivocally pseudopericyclic reaction D. In the latter, one of the two lone pairs on O1 attacks C2 in a direct manner, so, at a given point in the process (close to TS) where the reaction coordinate is about 0.04 amu$^{1/2}$ bohr, the lone pair becomes the σ bond between O1 and C2, and, simultaneously, the NBO π(C6–O1) becomes the lone pair of O1. This situation can be associated with the definition of Lemal: nonbonding and bonding atomic orbitals exchange roles. Thus, a p_z orbital of atom O1 that previously formed a π bond with C6 becomes the nonbonding orbital corresponding to the lone pair. The situation is different for reactions A, A2, B and C. Thus, the NBOs corresponding to the lone pairs in reactions A and B form no other type of bond at any time; they preserve their identity throughout the reaction and, as this proceeds, they undergo a rotation (computed from the directionality of NBOs) which is highly similar to that experienced by C1–H bonds in reaction C and result in disrotation with respect to the terminal CH_2 group in the allene. In reactions A, A2, B and C, the σ bond between X1 and C2 result from the transformation of π bonds in the molecule, so no exchange between non-bonding and bonding atomic orbitals takes place (i.e., no disconnection occurs), so the reactions are seemingly of pericyclic nature. Figure 6 illustrates the rotation of the lone pairs through the variation of the Y-X1-C6-C5 dihedral, Y denoting a lone pair in A, B and D reactions, and the inner H atom on C1 in reaction C. For clarity, we have omitted the graph corresponding to the A2 reaction, because although the behavior is very similar to the one of reaction C, the rotation of the H atom on N1 ranges a great interval (from 0 to $-180°$). As can be seen, the rotation is roughly similar for reactions A, B and C, specially at the beginning of the cyclization. The only salient difference between the rotation in A and B with respect to C is that, in the last, the H-C1-C6-C5 dihedral reaches a value of $-106.2°$ at the end of the IRC by virtue of the NBO corresponding to the C–H bond being formed by an sp^3 hybrid orbital of C1. In reactions A and B, the final dihedral angle is $-90.0°$ by effect of the lone pair, which starts as a hybrid of roughly sp^2 character, ending as a virtually pure p_z orbital normal to the molecular plane in order to increase π delocalization. In pseudopericyclic reaction D rotation of the lone pair is absent,

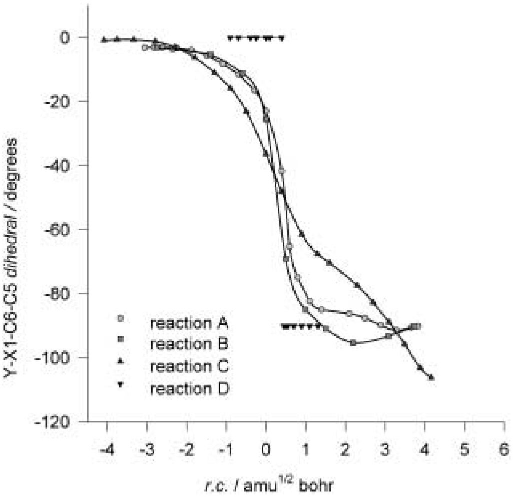

Figure 6. Change of the Y-X1-C6-C5 dihedral angle along the reaction path. Y denotes a lone pair in reactions A, B and D; and the inner H atom on C1 in reaction C.

so the lone pair is initially coplanar with X1-C6-C5 but adopts a normal orientation immediately after the transition state since, as stated above, it forms a p_z orbital in O1, when the orbital interchange occurs (r.c. 0.04 amu$^{1/2}$ bohr).

Conclusion

The magnetic properties (χ_{anis} and NICS) calculated along the reaction path for the electrocyclization process examined in this work suggest that reactions A, A2, B and C involve a strong aromaticity increase, which is typical of pericyclic reactions. By contrast, the pseudopericyclic reaction D exhibits no appreciable aromaticity maximum: χ_{anis} decreases monotonically from the reactant to the product and NICS remains virtually constant throughout the reaction path.

The NBO analysis leads to the same conclusions and exposes the clear-cut differences between the pseudopericyclic and pericyclic mechanism. Thus, the former involves the exchange between non-bonding and bonding orbitals (specifically, between the lone pair on X1 and a bonding pair), whereas the latter involves no exchange as the lone pairs on X1 preserve their identity throughout reactions A and B, and experience a clear-cut disrotatory rotation with respect to the other end of the cyclic loop.

The reaction A2 is clearly pericyclic and displays a behavior very similar to reaction C in all the aspects analyzed. Although the evidence reported in this work is suggestive of an essentially pericyclic mechanism for reactions A and B, their characteristics are in between those of reactions C and D, which are unequivocally pericyclic and pseudopericyclic, respectively. This is no doubt the result of the prominent role of the lone pair on X1 in the cyclization process. This substantially decreases the energy of activation and provides a reaction path where the aromatic stabilization is not necessary to be too high. 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.[47] Because of this interaction, in reactions A and B the molecules need not undergo as much geometrical distortion as in a prototypical pericyclic reaction. Notwithstanding their special features, reactions A and B retain the essential characteristics of a pericyclic mechanism.

At this point, the following question arises: is a more or less pseudopericyclic reaction feasible? Based on the definition of Lemal, we believe a reaction is either pseudopericyclic or non-pseudopericyclic since at least one orbital disconnection is needed to meet the requirements of the former. The involvement of the lone pair in reactions A and B seemingly "pushes" the reaction mechanism to the pseudopericyclic end, so these two reactions might be borderline cases. However, our results suggest that the borderline is not crossed—no disconnection is apparent—and that both reactions are pericyclic disrotatory electrocyclizations favored by the assistance of a lone electron pair.

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