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A DFT study of the [4 + 2] cycloadditions of conjugated ketenes (vinylketene, imidoylketene and formylketene) with formaldimine. The pericyclic or pseudopericyclic character from magnetic properties

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Abstract—A comprehensive B3LYP/6-31+G* study of the nature of the [4+2] cycloadditions of conjugated ketenes, vinylketene, imidoylketene and formylketene, with formaldimine was conducted. For each reaction, the complete pathway was determined and changes in different magnetic properties (magnetic susceptibility, χ, magnetic susceptibility anisotropy, χ_{anis}, and the nucleus-independent chemical shift, NICS) were monitored along the reaction profile with a view to estimate the aromatization associated to the process. We have also applied the ACID (anisotropy of the current-induced density) method with the same purpose. The deep analysis of the results indicates the existence of both disrotatory and conrotatory pericyclic paths for the cyclization step of the cycloaddition of vinylketene with formaldimine and the pseudopericyclic character of reactions with imidoylketene and formylketene.

1. Introduction

Since Staudinger discovered ketenes in 1905,[1] their structures, reactions and use in organic synthesis have been widely studied.[2] The [2+2] cycloadditions of ketenes have been of great usefulness in synthetic methodology, as in the case of the cycloaddition of ketenes to imines in order to obtain β-lactam antibiotics.[3] In the last years, the [4+2] cycloadditions, where the ketene has a dienophile behaviour, have been investigated. Yamabe et al. have provided NMR evidence for [4+2] cycloadditions involving the carbonyl of the ketene with dienes.[4]

In this paper, we are interested in the study of the [4+2] cycloadditions of conjugated ketenes (vinylketene, imidoylketene and formylketene) with formaldimine, and especially in their pericyclic or pseudopericyclic behaviour. Zhou and Birney[5] have found a concerted pathway for the three reactions, but also a stepwise pathway for the two later reactions. As indicated by the calculations performed by these authors at B3LYP/6-31G* level, the stepwise pathways are the lowest energy paths for these reactions. On the basis of the geometric and electronic structure of the transition state and the energy barrier, these authors concluded a pericyclic nature of the [4+2] concerted cycloaddition for the vinylketene with formaldimine. On the other hand, they found a pseudopericyclic behaviour for both concerted and stepwise reactions for the imidoylketene and formylketene with formaldimine.

Pseudopericyclic reactions were originally defined by Lemal as concerted transformations whose primary changes in bonding encompass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbital interchange roles.[6,7] This role interchange means a disconnection in the cyclic array of overlapping orbitals. The problem of this definition seems to be in that the orbital description is not unique.

Birney and co-workers have studied a large number of pseudopericyclic reactions,[8–14] finding three common characteristics: very low activation energies, planar transition states and impossibility of being symmetry forbidden regardless of the number of electrons involved.

Other studies[15] have employed the aromatic character of the transition states as an argument to explain the differences between pericyclic and pseudopericyclic reactions. The cyclic

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loop formed in the transition states of pericyclic reactions is known to give rise to aromatic transition states,[16–20] whereas the orbital disconnection in the pseudopericyclic reactions prevents this transition states from being aromatic.

However, the aromatic character of a transition state does not imply the impossibility of pseudopericyclic reaction, as we have demonstrated in the previous paper.[21] This fact indicated the need to study the whole process and not only the transition structure in order to define a process as pericyclic or pseudopericyclic. In addition, we have stood out the importance of the study of the magnetic properties along the reaction profile in this controversial matter.[22] For this reason, in this work we carried out a comprehensive study of the aromaticity along the reaction profile of the whole processes of [4+2] cycloaddition of formaldimine to vinylketene, imidoylketene and formylketene. The aromaticity was examined in terms of magnetic susceptibility, χ, its anisotropy, χ_{anis}, and the nucleus-independent chemical shift, NICS, reported by Schleyer et al.[23]

Herges and Geuenich[24] have recently developed a method based on magnetic properties, which seems to be a good tool in order to distinguish between coarctate and pseudocoarctate and pericyclic and pseudopericyclic reactions as we have indicated in other papers.[21,22,25] This method is referred as ACID (anisotropy of the current-induced density) method and it will be also employed in this study.

2. Results and discussion

2.1. Reactions paths

According to our calculations (B3LYP/6-31+G*) no concerted path is found for any of these reactions (Scheme 1). However, working at B3LYP/6-31G* level Zhou and Birney[5] found a concerted transition state for A reaction. To clarify this discrepancy we tested other large basis sets: in most cases the calculations lead to a two-step process (see Supplementary data). In any case, for a better comparison with reactions B and C (which follow a two-step process according to all tests), the results obtained from B3LYP/6-31+G* calculations seem appropriate. The study of the cyclization process (step from IntA to 3A) in reaction A deserves a special attention. We have found two possible transition states with similar energy (the difference of energy is less than 2 kcal mol^{-1}). The basic difference between the two structures is its conrotatory (TS2Aconr) or disrotatory (TS2Adisr) nature. The application of Woodward–Hoffman rules about orbital symmetry in this reaction indicates that the disrotatory process is thermally allowed while the conrotatory one is forbidden. According to the theory of aromaticity in pericyclic reactions,[16] the transition state for disrotatory path will be aromatic and the transition state for conrotatory path will be antiaromatic. So, the deep analysis of the cyclization and the variation of the aromaticity along the process have a special interest. The transition state for a hypothetical concerted process in reaction B and C proposed by Zhou and Birney[5] does not link reactant and product (see Supplementary data).

The relevant stationary points found in the potential energy surfaces for the three processes and their energies are shown in Table 1. As we have commented above, for reaction A, at B3LYP/6-31+G* level, we have obtained a two stepwise path but with two different transition states for the cyclization step: one for a conrotatory reaction (TS2Aconr) and another for a disrotatory process (TS2Adisr). Figure 1 shows the structures for these transition states and normal mode eigenvectors for the coordinate frequency.

Figure 2 shows the energy profiles obtained from the IRC calculations for the cyclizations (from Inty to 3y). Pseudopericyclic reactions possess low activation energies with

Table 1. Calculated relative energies of the stationary points

Structure	Relative energy	
	B3LYP/6-31G*[a]	B3LYP/6-31+G*
TS1A		8.92 (10.90)
IntA		8.67 (11.33)
TS2Aconr	12.0 (14.7)	11.40 (14.28)
TS2Adisr		9.51 (12.45)
3A	−57.5 (−50.8)	−56.13 (−49.50)
TS1B	1.2 (2.9)	3.02 (4.49)
IntB	−3.8 (−0.2)	−3.49 (0.03)
TS2B	−2.5 (0.9)	−3.07 (0.31)
3B	−49.7 (−43.3)	−49.09 (−42.77)
TS1C	−1.5 (−0.7)	0.54 (1.88)
IntC	−6.1 (−2.5)	−5.41 (−1.80)
TS2C	−5.2 (−1.8)	−5.17 (−1.74)
3C	−37.6 (−31.4)	−36.21 (−29.89)

The values are relative to the more stable conformation of the corresponding reactants. ZPE corrected values in brackets.

[a] From Ref. 5.

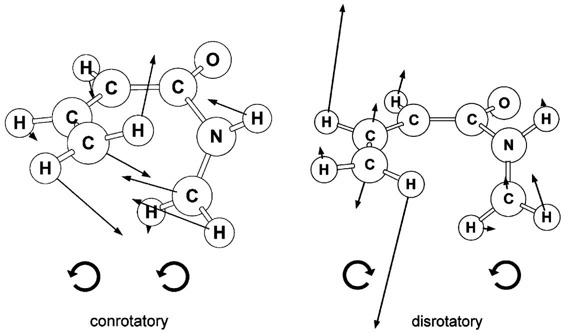
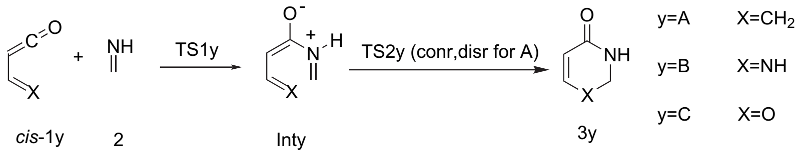


Figure 1. Transition structures for cyclization of process A and normal mode eigenvectors for the coordinate frequency.



Scheme 1. Reaction paths for the processes.

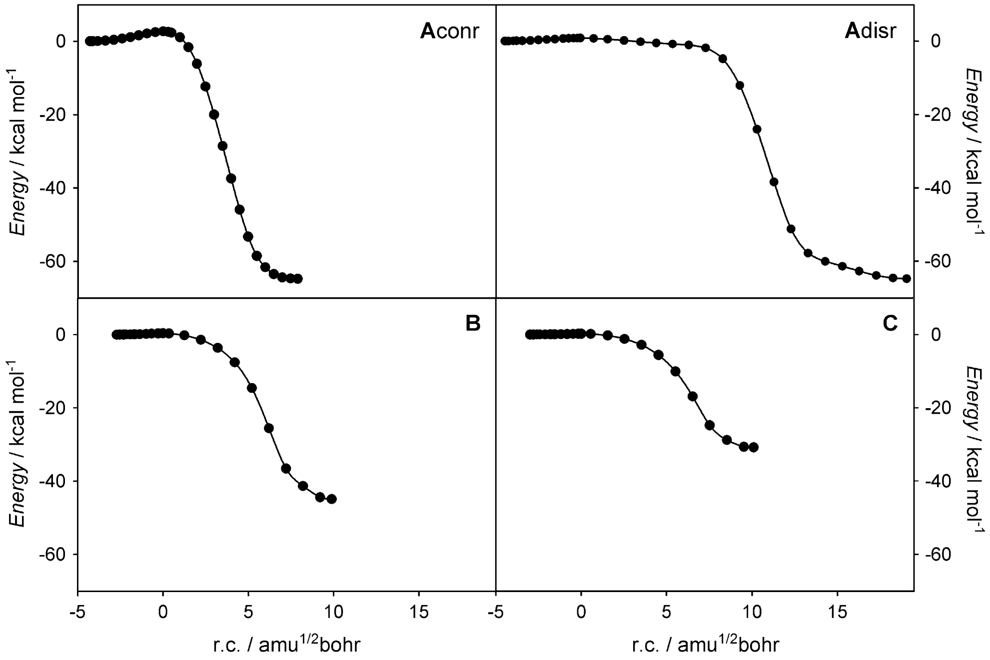


Figure 2. Energy profiles for the four cyclizations.

respect to analogous pericyclic reactions. All reactions studied in this work present small barriers (2.95 for conrotatory A, 1.12 for disrotatory A, 0.28 for B and 0.06 kcal mol^{-1} for C), but as we have shown in previous works,[25] energies are not a good criterion. Therefore, in this work, the pericyclic or pseudopericyclic character will be proved on the basis of magnetic properties.

2.2. Magnetic properties along the reaction path: susceptibility, anisotropy and NICS

Figures 3–5 show the variation of magnetic susceptibility (χ), magnetic susceptibility anisotropy (χ_{anis}) and nucleus-independent chemical shift (NICS), respectively, during the cyclization process. The NICS values along the reaction path were calculated in four different points. These points correspond to the geometrical centre of the new ring, to the ring critical point, RCP, as defined by Bader[26] and to points 1 Å above and below the critical plane. Schleyer has cautioned against the use of NICS in the plane of the ring due to spurious effects associated to σ bonds.[27] For pericyclic reactions, a marked minimum is observed near the transition structure, indicating its enhanced aromaticity. For the studied reactions, three different behaviours are observed: The isotropic magnetic susceptibility for the conrotatory A cyclization presents a maximum near the transition

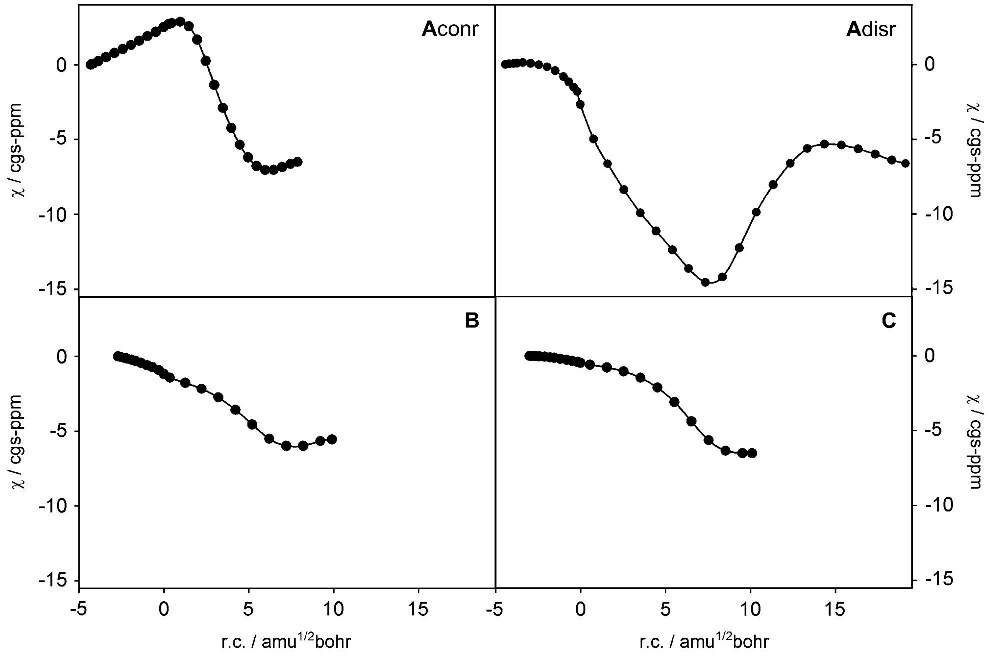


Figure 3. Variation of isotropic magnetic susceptibility along the reaction path (relative to Inty).

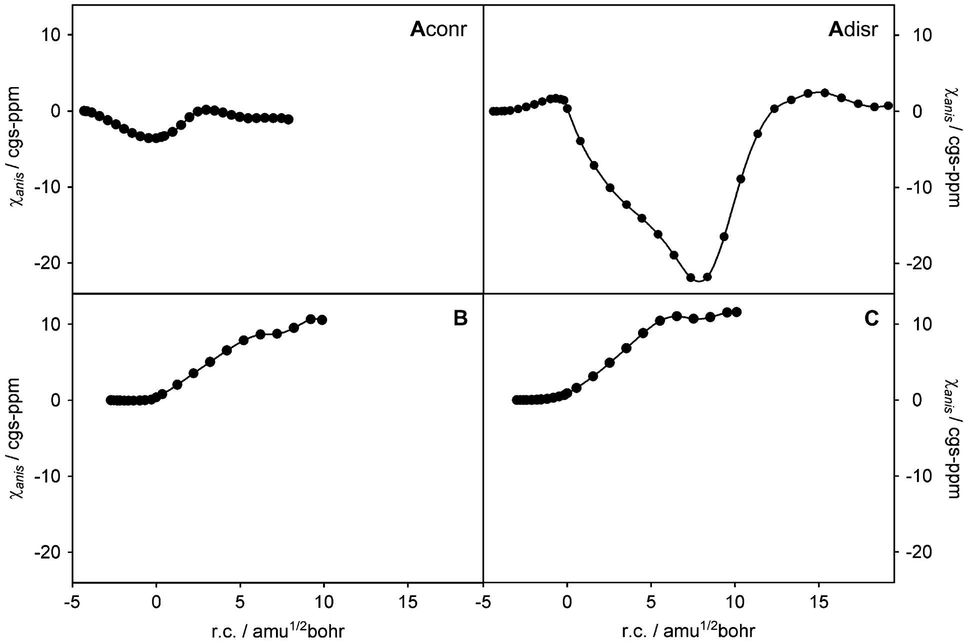


Figure 4. Variation of anisotropy of magnetic susceptibility along the reaction path (relative to Inty).

state. Moreover, positive NICS values are found near the transition state, which points out its antiaromatic character. These facts agree with the forbidden character of this conrotatory reaction. The magnetic properties for the disrotatory A reaction present a marked minimum. It is very usual that pericyclic reactions to show a minimum of the magnetic properties (maximum of aromaticity) in the vicinity of the transition state. However, the minimum found for the A disrotatory cyclization does not appear near the transition state (it occurs at a reaction coordinate of about 8 amu$^{1/2}$ bohr). This apparent discrepancy can be explained if we take into account the characteristics of this process: the disrotatory cyclization A has a very early transition state with a very large C–X distance (3.20 Å), hindering the electronic delocalization yet. But, in the course of the reaction, when the distance is closer to the typical transition state distance for cyclizations, we can observe this minimum. So, the maximum of aromaticity for this reaction takes place for a length of the forming C–X bond similar to that of the other transition states of the present study (about 2.7 Å). Therefore, this behaviour points out to a pericyclic character for this disrotatory cyclization. For the B and C cases, no noticeable minimum is found for any of the properties, indicating the absence of special aromaticity in the transition state.

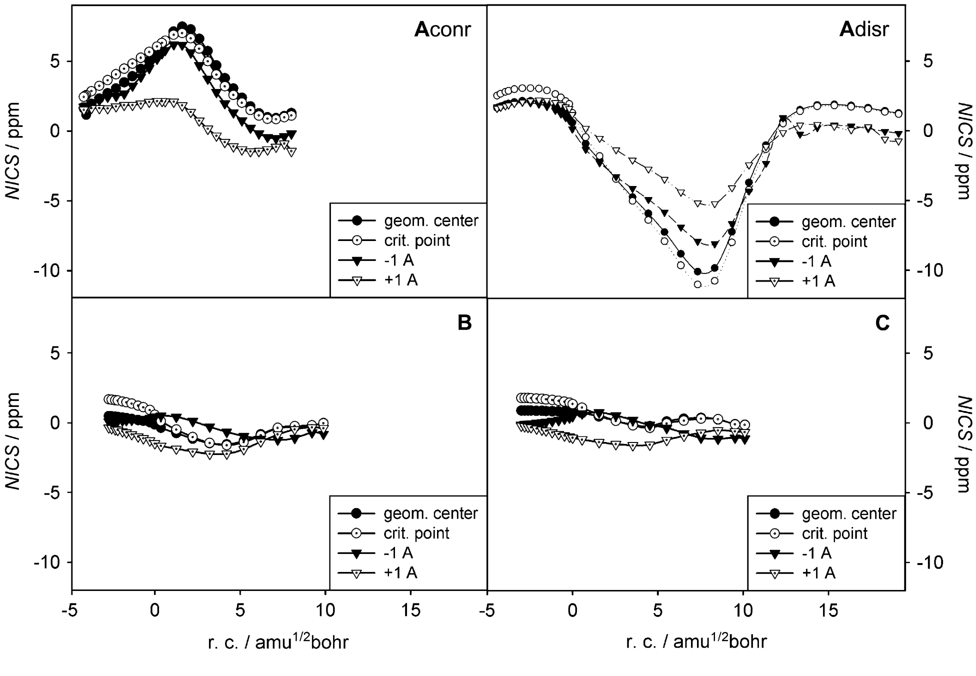


Figure 5. Variation of NICS along the reaction path.

On the basis of this behaviour, the reactions B and C should be classified as pseudopericyclic reactions.

2.3. ACID (anisotropy of the current-induced density) method

In order to carry out a deeper study of the nature of the second step of these reactions (electrocyclization), the ACID method[24] was employed. This is a recently published method to investigate the delocalization and conjugation effects in molecules. It provides a powerful way to visualize the density of delocalized electrons and quantify conjugation effects. The ACID approach has several advantages: it is a scalar field, which is invariant with respect to the relative orientation of the magnetic field and the molecule; it is not a simple function of the overall electron density; it has the same symmetry as the wave function, and it can be plotted as an isosurface. Some examples have demonstrated the applicability of this method to distinguish between pericyclic/pseudopericyclic and coarctate/pseudocoarctate reactivity.[21,22,24,25,28,29]

When a magnetic field is applied to an aromatic molecule, an induced current density is generated. For an aromatic system, if the magnetic field vector is orthogonal with respect to the ring plane, the induced current follows the left hand rule and it is called *diatropic* (clockwise current in the ACID figures if the magnetic field points upwards). For an antiaromatic system, the induced current is called *paratropic* (counterclockwise current). Moreover, in a nonaromatic system, no cyclic current is observed.

Figure 6 presents the ACID isosurface of the transition states for the studied cyclizations at an isosurface value of 0.03 au. For a more useful comparison, in the disrotatory case for reaction A, the ACID isosurface corresponds to a structure with similar C–X distance to the other transition states (2.7 Å). Current density vectors are plotted onto the ACID isosurface. The transition states for reactions B and C do not exhibit the cyclic topology, which characterize aromatic structures. This is a new proof of the pseudopericyclic character of these reactions. The ACID isosurface for TS2Aconr helps us to understand the nature of this process. Instead of the typical disconnection of pseudopericyclic reactions, it shows a paratropic ring current. This points out an antiaromatic character of the transition state and explains the higher barrier with respect to the disrotatory process and the maximum of the magnetic properties. Finally, for the structure corresponding to the disrotatory reaction path of process A, we may observe a diatropic ring current, indicating an aromatic character and a pericyclic behaviour.

The presence of disconnections in the ring current can also be quantified by means of the critical isosurface value (CIV), which indicates the isosurface value at which the topology changes from cyclic to noncyclic. Large CIV values indicate aromaticity or antiaromaticity and small CIV values indicate disconnection. In the studied cyclizations, the values for the CIV in the structures analyzed are 0.040, 0.032, 0.011, and 0.008 for reactions Aconr, Adisr, B and C, respectively. The small values for reactions B and C indicate the presence of a disconnection.

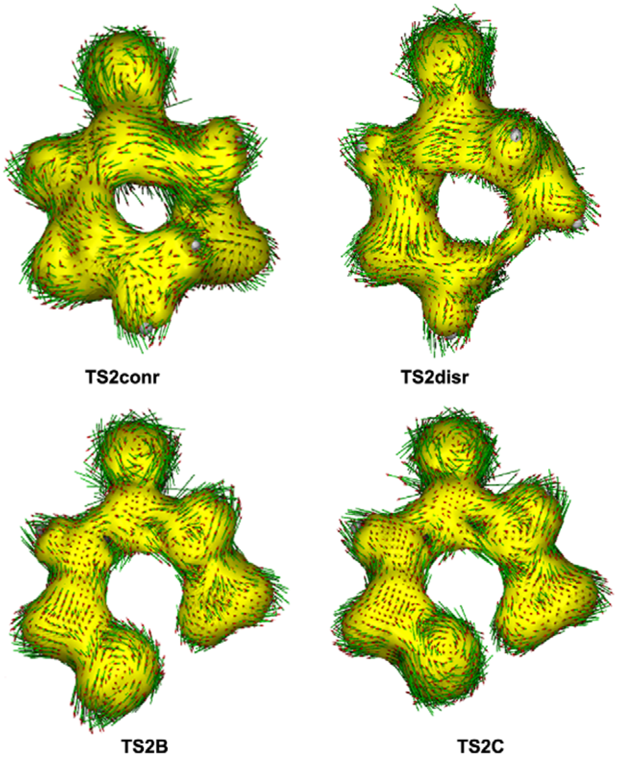


Figure 6. ACID plots for the transition structures of the studied reactions (isosurface value 0.03 a.u.). For a more useful comparison, in the disrotatory case for reaction A, the ACID isosurface corresponds to a structure with similar C–X distance to the other transition states (2.7 Å).

3. Conclusions

The [4+2] cycloadditions of vinylketene, imidoylketene and formylketene with formaldimine were studied by performing B3LYP/6-31+G* calculations. Reactants, intermediates, products and transition states were located and characterized by means of a vibrational analysis. Also, intrinsic reaction coordinate calculations have been performed and the changes in magnetic properties along the reaction path were studied for the cyclization process.

For the three reactions, we have found stepwise pathways but not concerted ones. For the A reaction, two pathways were obtained with a shared first step but with different nature of the cyclization (IntA to 3A): conrotatory and disrotatory. By means of a magnetic properties analysis, we are able to conclude an antiaromatic character for the conrotatory transition state and aromatic character for the disrotatory one. In order to define the cyclization process as pericyclic or pseudopericyclic, the variation of magnetic properties along the IRC was analyzed. Only for the reaction Adisr, the magnetic properties present a minimum. This minimum (maximum of aromatic character) is a characteristic of the typical pericyclic reactions and an important distinction between pericyclic and pseudopericyclic processes. The ACID isosurface for a structure of the reaction path of cyclization Adisr with similar C–X distance to the other transition states shows a diamagnetic ring current, showing its aromatic character in agreement with an allowed pericyclic behaviour. For these reasons, we have concluded a pericyclic behaviour for this reaction.

For reaction Aconr, the ACID isosurface of the transition state shows a paramagnetic ring current, indicating an antiaromatic character. This fact together with the minimum of aromaticity found near the transition state (obtained from magnetic susceptibility and NICS along the IRC) allows us to classify this reaction as pericyclic but following an 'a priori' forbidden path.

Both conrotatory and disrotatory processes present very small barriers, being the disrotatory the smallest one, as expected. So, both channels are possible for this reaction. The possibility of the 'forbidden' path can be explained from the scarce stability of intermediate IntA.

For the B and C cases, no appreciable minimum or maximum is found for the magnetic properties along the path, showing the absence of special aromaticity near the transition state. Moreover, the ACID isosurfaces of the transition states for these two reactions do not have the cyclic topology, which characterizes the aromatic structures, presenting a clear disconnection. These facts allow us to classify these two reactions as pseudopericyclic in agreement with Zhou and Birney.[5]

In summary, the different behaviour is given by the X-substituent: for the cases where heteroatoms with electron lone pairs (nitrogen or oxygen) are present, the reactions are pseudopericyclic, whereas when X is a methylene group the reaction is pericyclic. This involvement of lone pairs ('pushing' the reaction mechanism to a pseudopericyclic character) is quite usual and it was previously stated,[22,25] though not always implies a pseudopericyclic character.

4. Computational methods

Geometries of the relevant stationary points in the reaction paths for the three studied reactions were optimized at the B3LYP theoretical level[30,31] employing the 6-31+G* basis set. All points were confirmed as minima or transition states by calculating the harmonic vibrational frequencies at the B3LYP/6-31+G* level, using analytical second derivatives. In addition, the path for the reactions was obtained using the intrinsic reaction coordinate (IRC)[32–34] at the same theoretical level.

Magnetic properties: nucleus-independent chemical shift (NICS), magnetic susceptibility (χ) and magnetic susceptibility anisotropy (χ_{anis}) were calculated at different points along the IRC. In the magnetic susceptibility calculations, the NMR shielding tensors have been computed with a larger basis set (6-311+G(2d,p)). In order to obtain the NICS along the reaction path at the B3LYP/6-31+G* level, we have employed the GIAO (gauge-independent atomic orbital) method[35] but this method does not provide information about magnetic susceptibility, so χ, and χ_{anis} were calculated using the IGAIM (individual gauges for atoms in molecules) method,[36,37] which is a slight variation of the CSGT (continuous set of gauge transformations) method.[36–38] Finally, CSGT method at the B3LYP/6-31+G* level of theory was employed in ACID calculations, carried out with the programme supplied by Herges and Geuenich.[24]

All calculations were performed with the Gaussian98 software package.[39]

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Supplementary data

Listings of optimized geometries of reactants, products, intermediates, and transition states for the three reactions and the IRCs from the transition state for a hypothetical concerted process in reaction B and C proposed by Birney et al. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.142.

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