J. Phys. Chem. A **2007,** *111,* 2935−2940

A Comparative Theoretical Study of the Pericyclic-pseudopericyclic Character in a Group of Cyclizations of Dienylketenes to Cyclohexadienones

A. Peña-Gallego* and J. Rodríguez-Otero*

Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, Avenida das Ciencias s/n, 15782 Santiago de Compostela, Spain

E. M. Cabaleiro-Lago

Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus de Lugo, Avenida Alfonso X El Sabio s/n, 27002 Lugo, Spain

Received: December 20, 2006; In Final Form: February 14, 2007

A comprehensive B3LYP/6-31+G* study of the nature of 6π electrocyclizations of four different dienylketenes (2-furanyl, 2-pyrrolyl, cyclopenta-1,3-dienyl, and 2-thiophenyl-substituted ketenes) to corresponding cyclohexadienones was carried out. An analogous system ((3Z)-4-(3H-pyrrol-2-yl)buta-1,3-dien-1-one) was also analyzed. For this purpose, the complete pathways were determined (reactants, products, transition states, and the IRC connecting reactants and products), and changes in different magnetic properties (magnetic susceptibility, χ, magnetic susceptibility anisotropy, χ_{anis}, and the nucleus-independent chemical shifts, NICS) were monitored along the reaction profiles with a view to estimating the aromatization associated to the processes. We have also applied the ACID (anisotropy of the current-induced density) method with the same intention. The deep analysis of the results indicates a pericyclic character of the processes for the dienylketenes despite the relatively small NICS values in the transition states. Only the reaction of (3Z)-4-(3H-pyrrol-2-yl)buta-1,3-dien-1-one presents pseudopericyclic character due to the in-plane attack of the lone pair on nitrogen.

1. Introduction

Since Staudinger discovered ketenes in 1905,[1] their structures, reactions and use in organic synthesis have been widely studied.[2] Ketenes are known as one of the most versatile organic synthetic intermediates.

The cyclizations of dienylketenes to cyclohexadienones have been widely employed in the synthesis of polycyclic aromatic compounds.[3] However, the kinetic and theoretical aspects of these reactions are not very studied. Birney[4] has examined the cyclization of 5-oxo-2,4-pentadienal to pyran-2-one, obtaining a pseudopericyclic pathway. In our group,[5] we have analyzed the same reaction in depth. Alajarin and co-workers[6] have shown a pseudopericyclic character in the conversion of *N*-acylimidoylketenes to 2-substituted 1,3-oxazin-6-ones. Zora[7] has recently presented a study about the transitions structures and energetics of processes in which the terminal vinyl group of the dienylketenes is embedded into a cyclic olefin or an aromatic moiety, or is replaced by an allene or imine group. Zora argued the lowering of activation energy with respect to the totally carbonated compound (4*Z*)-1,3,5,6-heptatetraene and the not so negative NICS values obtained in the transition states to conclude a pseudopericyclic character of these reactions.

However, we believe that a deeper study of these processes is necessary to know their behavior, analyzing not only the transition states but all the reaction path. This point was recently demonstrated in a study of cyclizations of (3*Z*)-1,3,5-hexatrienone and nitrogen derivatives.[8] For this reason, in this paper, we are interested in the study of the 6π electrocyclizations of four different dienylketenes (2-furanyl, 2-pyrrolyl, cyclopenta-1,3-dienyl, 2*H*-pyrro-2-yl, and 2-thiophenyl-substituted ketenes) to corresponding cyclohexadienones, and the analogous system (3Z)-4-(3H-pyrrol-2-yl)buta-1,3-dien-1-one. This study has concentrated on their pericyclic or pseudopericyclic behavior. The reactions analyzed and the numbering scheme followed in this work are shown in Figure 1. For reactants, the reactive conformation is shown.

Pseudopericyclic reactions were originally defined by Lemal as concerted transformations whose primary changes in bonding compass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbital interchange roles.[9,10] This 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.[4,11−16] They have found three common characteristics: very low activation energies, planar transition states, and a pseudopericyclic reaction is always orbital symmetry allowed, regardless of the number of electrons involved.

Other studies[17] have employed the aromatic character of the transition states as an argument to explain the difference between pericyclic and pseudopericyclic reactions. The cyclic loop of pericyclic reactions is known to give rise to aromatic transition states,[18−22] and the orbital disconnection in the pseudopericyclic reactions prevents this aromaticity. The aromatization affects magnetic properties as magnetic susceptibility and anisotropy, leading to especially negative values. These magnetic properties are molecular properties and they can be affected by parts of the molecule not implicated in the reaction process. To avoid

---

* Corresponding authors. E-mails: qfpena@usc.es (A.P.-G.); qftjesus@usc.es (J.R.-O.).

10.1021/jp068772q CCC: $37.00

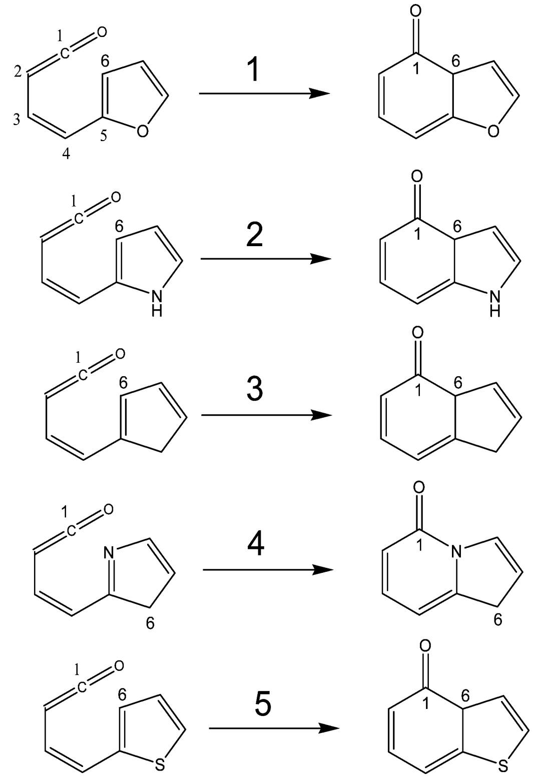

Figure 1. Reactions studied and numbering scheme.

this, a useful property is the Nucleus Independent Chemical Shift proposed by Schleyer et al.[23] This magnitude can be evaluated at any point of the molecule and presents very negative values in the center of aromatic rings.

However, an aromatic character of a transition state does not imply the impossibility of pseudopericyclic reaction, as we have demonstrated in a previous paper.[24] This statement indicates the necessity 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 magnetic properties along the reaction profile in this controversial matter.[25] For this reason, this work carries out a comprehensive study of the aromaticity along the reaction profile of the whole process for the above indicated electrocyclizations. This aromaticity was examined in terms of magnetic susceptibility, χ, magnetic susceptibility anisotropy, χ_{anis}, and the nucleus-independent chemical shifts, NICS, reported by Schleyer.[23]

Herges and Geuenich[26] have recently developed a method based on magnetic properties, which seems to be a good tool in distinguishing between coarctate and pseudocoarctate and pericyclic and pseudopericyclic as we have indicated in other papers.[23,24,27] This method is referred as ACID (anisotropy of the current-induced density) method and it has be employed in this study.

2. Computational Methods

The geometry of each stationary point was optimized at the density functional theory (DFT) level with the 6-31+G* basis set. Becke's three-parameter exchange functional (B3)[28] was employed in conjunction with the Lee−Yang−Parr correlation functional (LYP).[29] All points were confirmed as minima or transition states by calculating the harmonic vibrational frequencies using analytical second derivatives. In addition, the path for each reaction was obtained using the intrinsic reaction coordinate (IRC)[30−32] at the same theoretical level. All calculations were performed with the Gaussian98 software package.[33]

The evaluation of the absolute aromaticity of a molecule remains a controversial matter,[34] but we were interested in its variation during the reaction and not in a absolute value. This is the reason why the evaluation of magnetic properties is a useful tool for our study. 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 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 B3LYP/6-31+G* level of theory was employed in ACID calculations, carried out with the program supplied by Herges.[26]

3. Results and Discussion

3.1. Reactions Paths. Table 1 summarizes the energies of the species involved in the reactions analyzed. It is necessary to indicate that reactants can present different conformations. The nomenclature chosen is referred to atoms 2−3−4−5 as they are named in Figure 1, being the bonds 2−3 and 4−5 single bonds and the bond 3−4, a double bond. As regard single bonds, *s*-cis or *s*-trans conformations have been taken into account (*s* or *t*), and configuration *Z* was considered for the double bond. Figure 1 shows the conformations which are able to produce the electrocyclation process: *cZt* for reactions 1, 2, and 5; *cZc* for reactions 3 and 4.

For reactions 1, 4, and 5, the most stable conformation of reactants corresponds to *tZc* structure whereas for reaction 2 and 3 the most stable conformation is the *tZt*. For all reactants, the energies in Table 1 are referred to the most stable conformer.

Figure 2 shows the energy profiles for these reactions obtained from IRC calculations. Consistent with previous findings for other pseudopericyclic reactions,[5] B3LYP method revealed no energy barrier for the reaction 4. Consequently, the reactant as depicted in Figure 1 could not be located at this computational level. On the other hand, the HF/6-31+G* method allowed its identification and provided an negligible energy barrier of only 0.04 kcal mol^{-1}. For this reason, we have chosen to monitor the IRC at the Hartree−Fock level and perform B3LYP single-point calculations at different points of the reaction path in order to obtain the magnetic properties.

3.2. Magnetic Properties. Figure 3 shows the variation of mean magnetic susceptibility along the reaction path of the processes studied. For pericyclic reactions, a marked minimum in the magnetic susceptibility would be expected near the transition structure, indicating its special aromaticity.[19] For the studied reactions, no minimum close to transition state is observed. The behavior for reactions 1, 2, 3, and 5 is similar with a sigmoid variation of the susceptibility and a continuous increasing from reactants to products without any sign of special aromatization. The representation for reaction 4 is quite different (a nearly constant value is obtained along the reaction path), and this can indicate a different character of reaction 4. In any case, as regarding susceptibility, there is no special aromatization in the transition states of all the reactions, in agreement with a nonpericyclic behavior. However, the mean magnetic suscep-

TABLE 1: Calculated Relatives Energies in kcal Mol^{-1} of the Stationary Points[a]

reaction	*tZc*	*tZt*	*cZc*	*cZt*	TS	product
1	0.00	1.90 (1.85)	1.81 (1.87)	4.64 (4.58)	16.30 (16.04)	−3.98 (−2.64)
2	0.47 (0.50)	0.00	2.58 (2.51)	2.88 (2.81)	12.74 (12.59)	−5.79 (−4.54)
3	1.06 (0.94)	0.00	3.78 (3.62)	3.40 (3.34)	12.57 (12.28)	−17.13 (−15.25)
4[b]	0.00	2.91 (2.97)	0.27 (0.36)	6.19 (6.22)	0.31 (0.35)	−41.63 (−38.99)
5	0.00	0.70 (0.81)	3.85 (3.77)	3.38 (3.42)	14.22 (14.05)	−6.97 (−5.44)

[a] The values are relative to the most stable conformation of reactants and the values in parenthesis are corrected with ZPE. [b] HF/6-31+G* (see text).

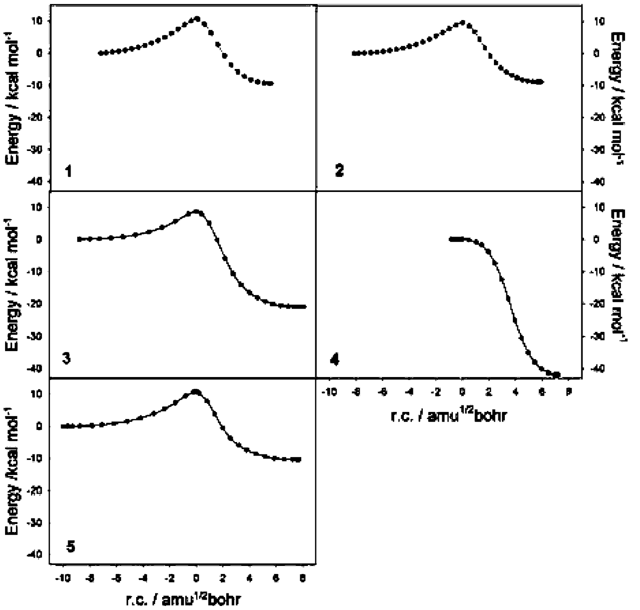

Figure 2. Variation of energy along the reaction path for the reactions studied.

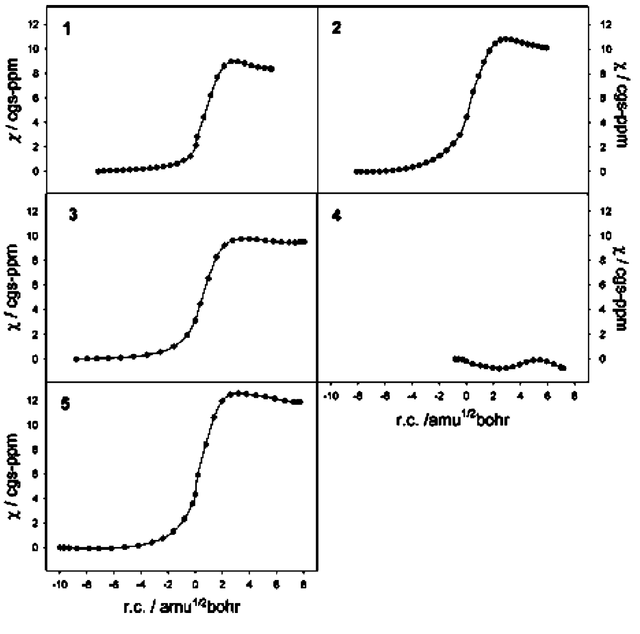

Figure 3. Variation of isotropic magnetic susceptibility along the reaction path and relative to the reactant.

tibility is not a good tool to assess aromaticity for large molecules where only local aromaticity is expected.[27,39]

The same problem can happen with the anisotropy of the magnetic susceptibility, although in a lesser extent. So Figure 4, which presents the variation of anisotropy of the magnetic susceptibility along the reaction path, shows a different behavior. A shallow minimum appears near the transition state for reactions 1, 2, 3, and 5. This minimum, which is specially evident for reactions 3 and 5, indicates an enhancement of aromaticity and a possible pericyclic nature of the process. Again, the graphic for reaction 4 is clearly different. For this reaction an almost negligible minimum appears; however, it cannot be associated with any aromatization since it happens very far from the transition state (the length of the forming bond, C1-N, is already 1.68 Å).

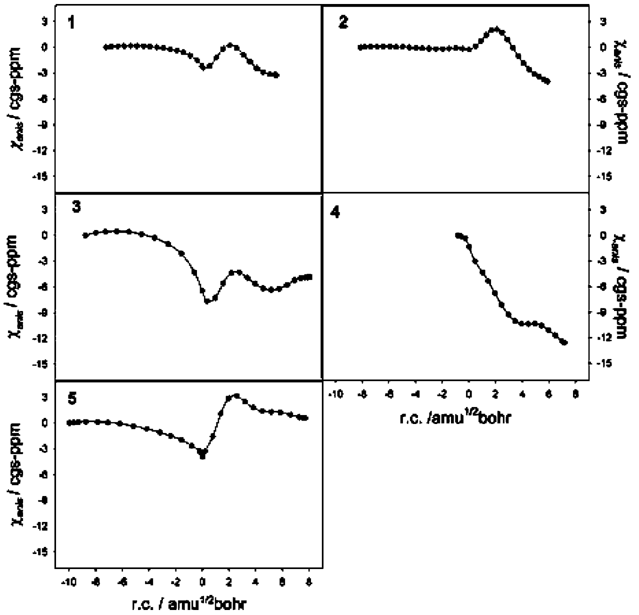

Figure 4. Variation of anisotropy of magnetic susceptibility along the reaction path and relative to the reactant.

We have also employed another way of measuring aromaticity: the NICS index proposed by Schleyer, which is defined as the negative value of the magnetic shielding.[23] This property can be evaluated at a single point of the molecule, avoiding some of the problems related to global properties as susceptibility and anisotropy. Figure 5 shows the variation of NICS along the reaction path in four different points. These points correspond to the geometrical center of the new ring, to the ring critical point, RCP, as defined by Bader[40] 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.[41]

Zora considered that the relative small NICS(0) values observed for the transition states of reactions 1, 2, and 5 indicated a pseudopericyclic behavior.[7] However, it is important to emphasize that the variation of the NICS values along the reaction path should be analyzed, not only the values in the transition states.

Figure 5, like Figures 3 and 4, shows clearly two different behaviors. For reactions 1, 2, 3, and 5, a minimum appears near the transition state, indicating special aromatization. This minimum is not observed for the points above the plane (+1 Å) and not so deep for those located in the plane (geometric

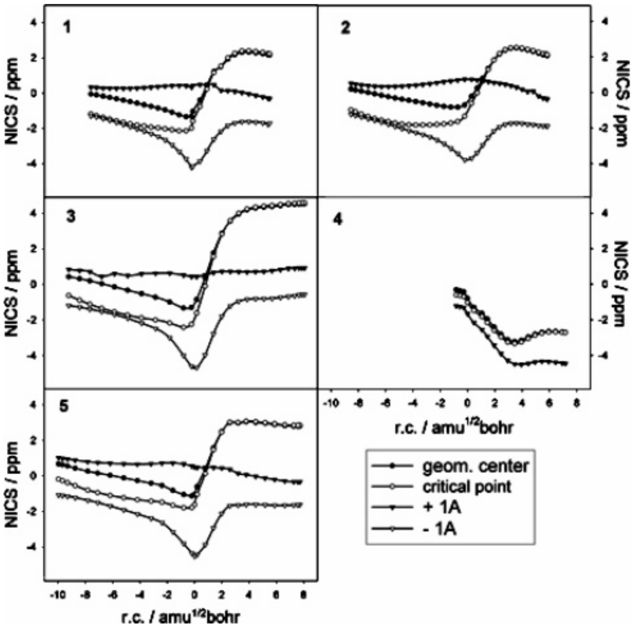

Figure 5. Variation of NICS along the reaction path and relative to the reactant.

center and critical point). However, for points placed below this plane, the NICS are more negative, and with a quite marked minimum. That fact is consistent with a ring current circulating on the side where disrotatory movement allows a closed loop of atomic interacting *p* orbitals. It indicates a substantial aromatization and a pericyclic character of these reactions.

For reaction 4, no significant minimum is presented at any point along the reaction path, consistent with a pseudopericyclic behavior. Only a negligible minimum appears for the curves calculated at the plane and, moreover, at the end of the reaction path, very close to products. In adittion, the curve for +1 Å and −1 Å are the same since the complete planarity of the molecule is maintained along the whole reaction path.

3.3. ACID. We have also employed the method ACID to evaluate aromaticity. This method, developed by Herges and Geuenich, allows investigation of the delocalization and conjugation effects in molecules. It provides a powerful way to visualize the density of delocalized electrons and evaluate conjugation effects. A cyclic topology with diatropic ring current implies aromaticity, and a noncyclic (presence of disconnections) topology implies nonaromaticity. 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.[3,5,26,27,39] Also, the presence of disconnections can be tested by means of the critical isosurface value (CIV). This value indicates the isosurface value at which the topology changes from cyclic to noncyclic. Large CIV's indicate aromaticity or antiaromaticity and small CIV's indicate disconnection.

The values obtained for the CIV in the transition state of the reactions studied are 0.052, 0.052, 0.048, 0.011, and 0.053 for reactions 1, 2, 3, 4, and 5, respectively. The very small CIV of reaction 4 indicates the presence of a disconnection.

Figure 6 presents the ACID isosurface of transition states for the five reactions studied at an isosurface value of 0.04. The length of the forming bond at the transition state of reaction 4 (2.301 Å) is close to that of the reactant (2.437 Å). For that reason, and in order to obtain a better comparison, to represent the behavior of reaction 4 in Figure 6, we have chosen a point of the reaction path when the length of the forming bond is similar to that of the corresponding bond in the other transition states (2.15 Å). Current density vectors are plotted onto the ACID isosurface. For reactions 1, 2 ,3 and 5, a diatropic ring current is observed. On the contrary, reaction 4 exhibits a marked disconnection between N and C1 atoms, being impossible a ring current (accoding to our calculations, this discon-

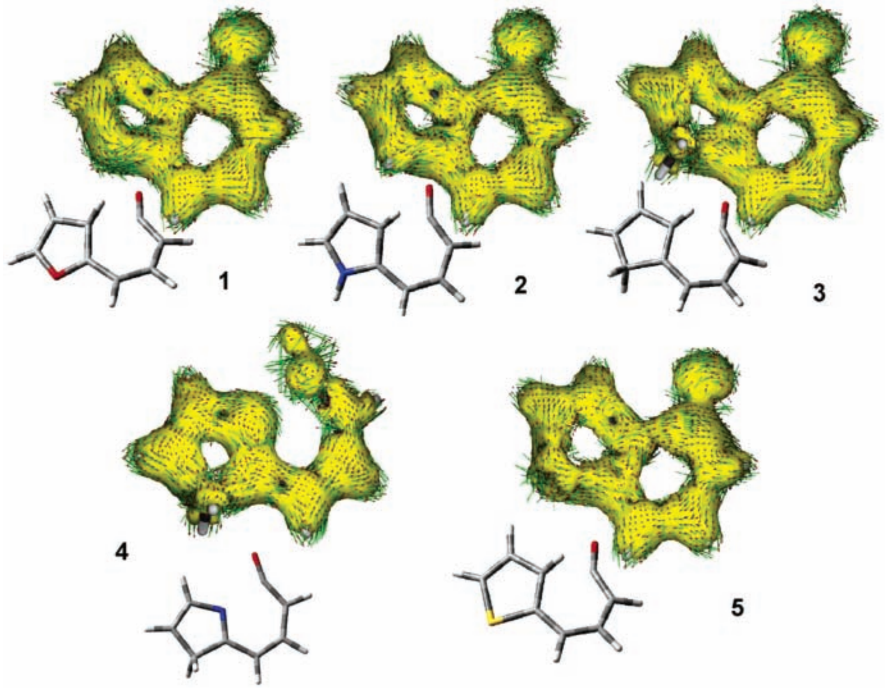

Figure 6. ACID plots for the transition structures of the studied reactions at an isosurface value of 0.04. The magnetic field points from the paper to the reader. For reaction 4, a different point of the reaction path was selected as we have indicated in the text.

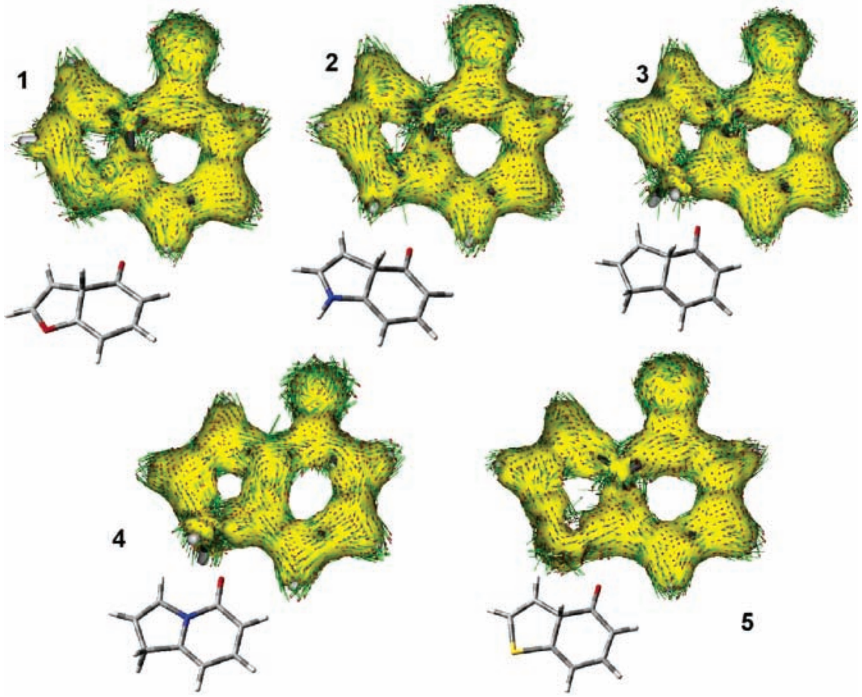

Figure 7. ACID plots for the products of the studied reactions at an isosurface value of 0.04. The magnetic field points from the paper to the reader.

nection is even more noticeable in the transition state). In Figure 7, for comparison, the ACID isosurface of products for the five reactions studied at an isosurface value of 0.04 are showed. For the products of reactions 1, 2 , 3, and 5, the ACID results indicate a smaller aromaticity than in their respective transition states, while the ACID isosurface for the product of reaction 4 does not show the disconnection between N and C1 atoms found in the ACID isosurface for its transition state.

Therefore, ACID method supports the pericyclic character of reactions 1, 2, 3, and 5 and the pseudopericyclic character of reaction 4.

4. Conclusions

The main conclusion of this work is the pericyclic character of reactions 1, 2, 3, and 5, with an increase of aromaticity in the vicinity of the transition states and the pseudopericyclic character of reaction 4.

We have demonstrated that it is useful to study the whole process and not only the transition state in order to define a process as pericyclic or non-pericyclic. The absolute value of NICS in the transition states of these reactions can lead to erroneous results. Therefore, Zora[7] considered that the relative small NICS(0) values observed for the transition states of reactions 1, 2, and 5 indicated a pseudopericyclic behavior. However, the variation of magnetic properties along the IRC presents a minimum near the transition state structure for these three reactions and for reaction 3. This minimum (maximum of aromatic character) is characteristic of a pericyclic reaction and an important distinction between pericyclic and pseudopericyclic processes.

The ACID isosurfaces of the transition states for reactions 1, 2, 3, and 5 have the cyclic topology which characterizes aromatic structures. The comparison of these ACID isosurfaces with that of reaction 4 supports the pseudopericyclic character of this reaction 4. This is a new example of the applicability of the ACID method in order to distinguish pericyclic and pseudopericyclic reactions.

Acknowledgment. The authors thank Xunta de Galicia (Project PGIDT04PXIC20904PN) and Ministerio de Ciencia y Tecnología (BQU2003-01104) for financial support. The authors express their deep gratitude to Dr. Herges for his assistance and for the ACID program. A. P.-G. thanks Xunta de Galicia for "Isidro Parga Pondal" contract. We are also thankful to Centro de Supercomputación de Galicia (CESGA) for the use of their computers.

Supporting Information Available: Listings of optimized geometries of reactants, products and transition states for the species participating in the five reactions. Figure of transition states of reaction 1. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Staudinger, H. *Chem. Ber.* **1905**, *38*, 1735−1739.

(2) Tidwell, T. T. *Ketenes*; John Wiley & Sons: New York, 1995.

(3) Moore, H. W.; Benjamin, R. Y. *Chemtracts: Org. Chem.* **1992**, *5*, 273 and references therein.

(4) Birney, D. M. *J. Org. Chem.* **1996**, *61*, 243.

(5) Rodriguez-Otero, J.; Cabaleiro-Lago, E. M. *Chem. Eur. J.* **2003**, *9*, 1837.

(6) Alajarin, M.; Vidal, A.; Sanchez-Andrada, P.; Tovar, F.; Ochoa, G. *Org. Lett.* **2000**, *2*, 965.

(7) Zora, M. *J. Org. Chem.* **2004**, *69*, 1940.

(8) Cabaleiro-Lago, E. M.; Rodriguez-Otero, J.; Varela-Varela, S. M.; Peña-Gallego, A.; Hermida-Ramon, J. M. *J. Org. Chem.* **2005**, *70*, 3921.

(9) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325.

(10) Bushweller, C. H.; Ross, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 629.

(11) Birney, D. M.; Wagenseller, P. E.; *J. Am. Chem. Soc.* **1994**, *116*, 6262.

(12) Birney, D. M.; Ham, S.; Unruh, G. R. *J. Am. Chem. Soc.* **1997**, *119*, 4509.

(13) Birney, D. M.; Xu, X.; Ham, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 189.

(14) Birney, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 10917.

(15) Shumway, W.; Dalley, N. K.; Birney, D. M. *J. Org. Chem.* **2001**, *66*, 5832.

(16) Shumway, W.; Ham, S.; Moer, J.; Whittlesey, B. R.; Birney, D. M. *J. Org. Chem.* **2000**, *65*, 7731.

(17) de Lera, A. R.; Alvarez, R.; Lecea, B.; Torrado, A.; Cossio, F. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 557.

(18) Zimmerman, H. E.; *Acc. Chem. Res.* **1971**, *4*, 272.

(19) Herges, R.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1994**, *33*, 1376.

(20) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655.

(21) Manoharan, M.; De Proft, F.; Geerlings, P. *J. Org. Chem.* **2000**, *65*, 7971.

(22) Manoharan, M.; De Proft, F.; Geerlings, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1767.

(23) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(24) Peña-Gallego, A.; Rodriguez-Otero, J.; Cabaleiro-Lago, E. M. *J. Org. Chem.* **2004**, *69*, 7013.

(25) Peña-Gallego, A.; Rodriguez-Otero, J.; Cabaleiro-Lago, E. M. *Eur. J. Org. Chem.* **2005**, 3228.

(26) Herges, R.; Geuenich, D. *J. Phys. Chem. A* **2001**, *105*, 3214.

(27) Rodriguez-Otero, J.; Cabaleiro-Lago, E. M.; Hermida-Ramon, J. M.; Peña-Gallego, A. *J. Org. Chem.* **2003**, *68*, 8823.

(28) A. D. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(29) Lee, C.; Yang, W.; Parr, R. J. *Phys. Rev. B* **1988**, *37*, 785.

(30) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(31) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(32) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5223.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*; Gaussian, Inc., Pittsburgh, PA, 1998.

(34) See special issues dedicated to aromaticity: *Chem. Rev.* **2001**, *5*, 101, Geunich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.

(35) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(36) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223.

(37) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1.

(38) Cheeseman, J. R.; Frisch, M. J.; Trucks, G. W.; Keith, T. A. *J. Chem. Phys.* **1996**, *104*, 5497.

(39) Cabaleiro-Lago, E. M.; Rodriguez-Otero, J.; Hermida-Ramon, J. M. *J. Phys. Chem. A* **2003**, *107*, 4962.

(40) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(41) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.