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An analysis of the changes in aromaticity and planarity along the reaction path of the simplest Diels–Alder reaction. Exploring the validity of different indicators of aromaticity

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Abstract

In this work, we analyze the changes in aromaticity and planarity along the reaction path of the Diels–Alder reaction between ethene and 1,3-butadiene. To this end, a new index that quantifies the planarity of a given ring is defined. As expected, the planarity of the ring being formed in the Diels–Alder cycloaddition increases along the reaction path from reactants to product. On the other hand, the aromaticity of the ring formed is measured using several well-established indices of aromaticity such as the nucleus independent chemical shift (NICS), the harmonic oscillator model of aromaticity (HOMA), and the *para*-delocalization index (PDI), as well as a recently defined descriptor of aromaticity: the aromatic fluctuation index (FLU). The results given by the NICS and PDI indices, at variance with those obtained by means of the HOMA and FLU indicators of aromaticity, confirm the existence of an aromatic transition state for this reaction. The reasons for the failure of some of the descriptors of aromaticity employed are discussed. The results support the multidimensional character of aromaticity.

Keywords: Aromaticity; Nucleus independent chemical shift (NICS); *Para*-delocalization index (PDI); Harmonic oscillator model of aromaticity (HOMA); Aromatic fluctuation index (FLU); Planarity; Atoms in Molecules theory (AIM); Diels–Alder reaction

1. Introduction

The well-known Diels–Alder (DA) [1–3] reaction between ethene and 1,3-butadiene to yield cyclohexene is the prototype of a thermally allowed 4s + 2s cycloaddition. This reaction has been extensively investigated using different theoretical methods. It is now well-recognized that this reaction takes place via a synchronous and concerted mechanism through an aromatic boatlike transition state (TS) [2,4]. By 1938 [5], the analogy between the π electrons of benzene and the six delocalized electrons in the cyclic TS of the DA reaction was already recognized. The aromatic nature of this TS has been later confirmed theoretically using magnetic-based indices such as the nucleus independent chemical shifts (NICS) and the magnetic susceptibility exaltations [3,6].

Aromaticity is a concept of central importance in physical organic chemistry [7–10]. It has been very useful in the rationalization of the structure, stability, and reactivity of many molecules. Even though this concept was introduced in 1865 by Kekulé [11], it has no precise and collectively assumed definition yet. Probably the most widely accepted description of aromaticity was formulated by Schleyer and Jiao in 1996 [9]. These authors defined aromatic systems as conjugated cyclic π-electron compounds that exhibit a cyclic electron delocalization leading to bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as energetic stabilization. According to this definition, aromaticity manifests itself through a variety of phenomena, which can be quantified to have a measure of aromaticity. Thus, the evaluation of aromaticity is usually performed by analyzing its manifestations and this leads to the classical structural, magnetic, energetic, and reactivity-based measures of

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aromaticity [10,12]. At this point, we must note that, as found by Katritzky-Krygowski and co-workers by means of principal component analyses, aromaticity is a multidimensional property and, as a consequence, aromatic compounds cannot be fully characterized using a single index [12–16]. In fact, different studies have confirmed that different indices of aromaticity can afford divergent answers [17,18]. Consequently, to make reliable comparisons restricted to groups of relatively similar compounds it is usually recommended to employ a set of aromaticity descriptors [16–18].

Aromaticity in DA reactions has been until now analyzed using only magnetic-based indices. Because of the multidimensional character of this phenomenon, we believe that it is convenient to discuss the aromaticity in DA cycloadditions using descriptors based on different properties. Since not all aromaticity indices give the same results, it is worth analyzing certain particular cases in which the behavior of aromaticity is well-established, such as in the DA reaction, to detect possible limitations and failures of commonly used indicators of aromaticity. Thus, the goal of the present work is to quantify the aromaticity along the reaction path of the simplest DA reaction between 1,3-butadiene and ethene (see Scheme 1) using several indicators of aromaticity, to discuss their behavior for this particular reaction.

As a structure-based measure, we have made use of the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as [19]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{\mathrm{opt}} - R_i)^2, \tag{1}$$

where n is the number of bonds considered, and α is an empirical constant (for C–C bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model non-aromatic system, and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt} (1.388 Å for C–C bonds), assumed to be achieved for fully aromatic systems. R_i stands for a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity [7,13].

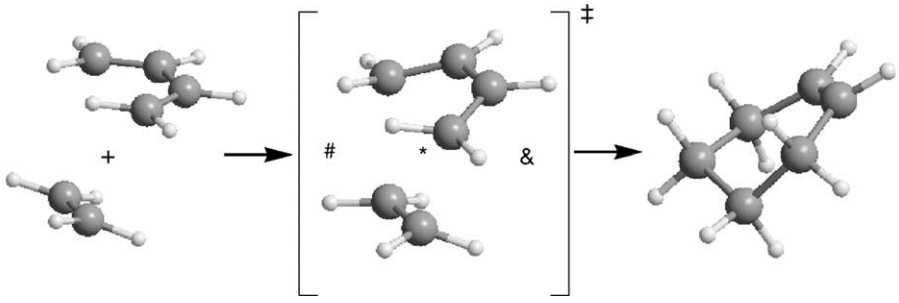
Magnetic indices of aromaticity are based on the π-electron ring current that is induced when the system is exposed to external magnetic fields. In this work, we have used the NICS, proposed by Schleyer and co-workers [9,20], as a magnetic descriptor of aromaticity. This is one of the most widely employed indicators of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS value, the more aromatic the ring is.

As an aromaticity criterion based on electron delocalization, we have employed the *para*-delocalization index (PDI) [21], which is obtained using the delocalization index (DI) [22,23] as defined in the framework of the Atoms in Molecules (AIM) theory of Bader [24]. The PDI is an average of all DI of *para*-related carbon atoms in a given six-membered ring. The DI value between atoms A and B, δ(A,B), is obtained by double integration of the exchange–correlation density ($\Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)$) over the basins of atoms A and B, which are defined from the condition of zero-flux gradient in the one-electron density, $\rho(\vec{r})$ [24]:

$$\begin{aligned}\delta(\mathrm{A},\mathrm{B}) &= -\int_{\mathrm{A}}\int_{\mathrm{B}}\Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2 - \int_{\mathrm{B}}\int_{\mathrm{A}}\Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2 \\ &= -2\int_{\mathrm{A}}\int_{\mathrm{B}}\Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2. \end{aligned} \tag{2}$$

δ(A,B) provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B. Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous works [21] have shown that for a series of planar and curved polycyclic aromatic hydrocarbons there is a satisfactory correlation between NICS, HOMA, and PDI. In general, larger PDIs go with larger absolute values of NICS and larger HOMA values.

Another electronically based criterion of aromaticity has been recently defined by Matito et al. [25], the aromatic fluctuation index (FLU), which describes the fluctuation of electronic charge between adjacent atoms in a given ring. The FLU index is based on the fact that aromaticity is related to the cyclic delocalized circulation of π electrons, and it is constructed not only considering the amount of electron sharing between contiguous atoms, which should



Scheme 1. Schematic representation of reactants, transition state and product of the Diels–Alder reaction between ethene and 1,3-butadiene. The position of the symbol (#) corresponds approximately to the position where NICS(1) has been calculated; (*) for NICS(0); and (&) for NICS(−1) (see text for details).

be substantial in aromatic molecules, but also taking into account the similarity of electron sharing between adjacent atoms. It is defined as

$$\mathrm{FLU} = \frac{1}{n}\sum_{\mathrm{A-B}}^{\mathrm{RING}}\left[\left(\frac{\mathrm{Flu(A\rightarrow B)}}{\mathrm{Flu(B\rightarrow A)}}\right)^{\delta}\left(\frac{\delta(\mathrm{A,B})-\delta_{\mathrm{ref}}(\mathrm{A,B})}{\delta_{\mathrm{ref}}(\mathrm{A,B})}\right)\right]^2, \tag{3}$$

with the sum running over all adjacent pairs of atoms around the ring, n being equal to the number of members in the ring, $\delta_{\mathrm{ref}}(\mathrm{C,C})=1.4$ (the δ(C,C) value in benzene at the HF/6-31G(d) level [25]), and the fluctuation from atom A to atom B reading as follows

$$\mathrm{Flu(A\rightarrow B)} = \frac{\delta(\mathrm{A,B})}{\sum_{B\neq A}\delta(\mathrm{A,B})} = \frac{\delta(\mathrm{A,B})}{2(N(\mathrm{A})-\lambda(\mathrm{A}))}, \tag{4}$$

where δ(A,B) is the DI between basins of atoms A and B, N(A) is the population of basin A, and λ(A) is the number of electrons localized in basin A. FLU is close to 0 in aromatic species, and differing from it in non-aromatic ones.

Finally, another characteristic of an aromatic species is its planarity that facilitates the delocalization of the π-electrons around the ring. This is the reason why we have also tried to evaluate the aromaticity through an analysis of the planarity of the system along the reaction path. To this end, we have devised a procedure that finds the best fitted plane π to a given ring. The methodology followed is detailed in the next section.

2. Obtention of best fitted plane π

Our purpose is to find the best fitted plane π to a certain cloud of points $\mathbf{P}\equiv\{P_i\}_{i=1,m}$. We use the well-known Eq. (5) that gives the distance between a given point P_i to a plane π.

$$\mathrm{d}(\pi,P_i) = |\alpha^{\mathrm{T}}P_i + \alpha_0|. \tag{5}$$

In this equation, α is the normalized plane's normal vector. This restriction on the modulus of the vector α makes no loss of generalization. The best fitted plane is obtained by minimizing the error function $\Phi(\alpha,\mathbf{P})$ that measures the sum of the square distances $d(\pi,P_i)$ from the set of points $\mathbf{P}\equiv\{P_i\}_{i=1,m}$ to the plane π.

$$\begin{aligned}\Phi(\alpha,\mathbf{P}) &= \sum_i^m d(\pi,P_i)^2 = \sum_i^m(\alpha^{\mathrm{T}}P_i+\alpha_0)^2\\ &= \sum_i^m[\alpha_1x_1^i+\cdots+\alpha_nx_n^i+\alpha_0]^2.\end{aligned} \tag{6}$$

First, let us find the minimum according to α_0:

$$\frac{\partial\Phi(\alpha,\mathbf{P})}{\partial\alpha_0} = 0 \tag{7}$$

$$2\sum_{i=1}^m[\alpha^{\mathrm{T}}P_i+\alpha_0] = 0, \quad \frac{\alpha^{\mathrm{T}}\sum_{i=1}^m[P_i]}{m} = \alpha^{\mathrm{T}}\bar{P} = -\alpha_0. \tag{8}$$

Thus, now we can write $\Phi(\alpha,\mathbf{P})$ as

$$\begin{aligned}\Phi(\alpha,\mathbf{P}) &= \sum_i^m(\alpha^{\mathrm{T}}(P_i-\bar{P}))^2\\ &= \sum_i^m[\alpha_1(x_1^i-\bar{x}_1)+\cdots+\alpha_n(x_n^i-\bar{x}_n)]^2.\end{aligned} \tag{9}$$

Forcing the α vector to have modulus 1 as stated on Eq. (5), we look for the minima of the above expression under this normalization restriction that is included in the minimization through a Lagrange multiplier in the following way:

$$\begin{aligned}L(\alpha;\lambda) &= \Phi(\alpha,\mathbf{P})-\lambda(||\alpha||^2-1)\\ &= \sum_i^m(\alpha^T(P_i-\bar{P}))^2-\lambda(\alpha^T\alpha-1)\\ &\frac{\partial L(\alpha;\lambda)}{\partial\alpha_j} = 0.\end{aligned} \tag{10}$$

We obtain the following set of equations:

$$\sum_{i=1}^m[\alpha^{\mathrm{T}}(P_i-\bar{P})](x_j^i-\bar{x}_j) = \lambda\alpha_j. \tag{11}$$

On the other hand, the covariance matrix reads:

$$\Sigma = \left\{\sigma_{ij} = \frac{\sum_{k=1}^m(x_i^k-\bar{x}_i)(x_j^k-\bar{x}_j)}{m}\right\}. \tag{12}$$

Hence, we can write the equation above in terms of the covariance matrix elements:

$$\alpha_1\sigma_{1j}+\cdots+\alpha_j(\sigma_{nj}-\lambda')+\cdots+\alpha_n\sigma_{nj} = 0 \quad 0\leq j\leq n, \tag{13}$$

where $\lambda'=\lambda/m$. The last set of equations can be easily recognized as the following secular formula:

$$\Sigma\mathbf{A} = \mathbf{A}\Lambda. \tag{14}$$

$\mathbf{A}$ is the matrix that collects eigenvectors (i.e. normal vectors of different planes) of covariance matrix Σ, and Λ is a diagonal matrix with the eigenvalues (corresponding to the $\Phi(\alpha,\mathbf{P})$ values). The lowest eigenvector is the vector perpendicular to the best fitted plane in the way stated above. The corresponding eigenvalue is an unambiguous measure of the planarity for the set of points $\mathbf{P}$, since its

value quantify in an unequivocal way how far the points are from the best fitted plane. A similar derivation and an alternative one can be found in Ref. [26].

The best fitted plane is usually mistaken as the plane obtained in a typical multiregression method. Our best fitted plane is found in the basis of minimizing the distances of **P** to π. On the other hand, the multiregression methods lead to the best plane in order to do predictions on a certain variable X, i.e. the minimization is over a function resulting of the difference between the X values and its expectation values according to π.

The quantity $\Phi(\alpha,\mathbf{P})$ obtained for the best fitted plane π, from each set of points **P**—corresponding to a molecular geometry determined by the nuclear positions of the atoms in the ring—will be given as a measure of molecular planarity; hereafter these quantities will be referred to as the Root-Summed-Square (RSS) values.

3. Computational details

All calculations have been performed with the GAUSSIAN 98 [27] and AIMPAC [28] packages of programs, at the B3LYP level of theory [29] with the 6-31G* basis set [30]. The intrinsic reaction path (IRP) [31] for the DA reaction has been computed with the GAUSSIAN 98 package [27], going downhill from the TS in mass-weighted coordinates using the algorithm by Gonzalez and Schlegel [32]. The TS of the DA reaction was characterized by the existence of a unique imaginary frequency corresponding to the C–C bond formation and breaking. All aromaticity criteria have also been evaluated at the same B3LYP/6-31G* level of theory.

The GIAO method [33] has been used to perform calculations of NICS at 1 Å (NICS(1)) above the ring center, which is determined by the non-weighted mean of the heavy atoms coordinates, following the direction given by the normal vector corresponding to the best fitted plane. Integrations of DIs were performed by use of the AIMPAC [28] collection of programs. Calculation of these DIs with the density functional theory (DFT) cannot be performed exactly because the electron-pair density is not available at this level of theory [34]. As an approximation, we have used the Kohn–Sham orbitals obtained from a DFT calculation to compute HF-like DIs through the expression:

$$\delta(\mathrm{A},\mathrm{B}) = 4\sum_{i,j}^{N/2} S_{ij}(\mathrm{A})S_{ij}(\mathrm{B}). \tag{15}$$

The summations in Eq. (15) run over all the $N/2$ occupied molecular orbitals. $S_{ij}(\mathrm{A})$ is the overlap of the molecular orbitals i and j within the basin of atom A. Eq. (15) does not account for electron correlation effects. In practice, the values of the DIs obtained using this approximation are generally closer to the HF values than correlated DIs obtained with a configuration interaction method [34]. The numerical accuracy of the AIM calculations has been assessed using two criteria: (i) the integration of the Laplacian of the electron density ($\nabla^2\rho(\vec{r})$) within an atomic basin must be close to zero; (ii) the number of electrons in a molecule must be equal to the sum of all the electron populations of the molecule, and also equal to the sum of all the localization indices and half of the delocalization indices in the molecule. For all atomic calculations, integrated absolute values of ($\nabla^2\rho(\vec{r})$) were always less than 0.001 a.u. For all molecules, errors in the calculated number of electrons were always less than 0.01 a.u.

4. Results and discussion

The present work analyzes the aromaticity along the DA reaction between 1,3-butadiene and ethene to yield cyclohexene (boat conformation), which is often taken as a prototype of a pericyclic concerted reaction. As said in Section 1, this reaction is characterized by an aromatic TS, thus along the reaction path we expect a peak of aromaticity around the TS, which, in principle, should be shown by the different aromaticity criteria.

Table 1 lists all values obtained from the different aromaticity criteria applied to the analysis of the DA reaction, while Fig. 1 depicts the NICS(1), PDI, FLU, HOMA, and RSS values along the reaction path. From Table 1, it is seen that only the magnetic NICS(1) and the electronic PDI criteria find the most aromatic point along the reaction path around the TS of the reaction. Because of the lack of a symmetry plane, the NICS(1) computed at 1 Å above the ring center determined by the non-weighted mean of the heavy atoms coordinates, following the positive direction of the normal vector corresponding to the best fitted plane does not coincide with the NICS computed at 1 Å below the ring center (NICS(−1)) (see Scheme 1). However, all definitions of NICS, and in particular NICS(0) and NICS(−1), also find that a structure close to the TS is the most aromatic species along the reaction path of this DA reaction. For this reason, only NICS(1) values are discussed in this work. On the other hand, both the HOMA and the electronic FLU indices consider the cyclohexene molecule (product), as the most aromatic species in the reaction. The RSS measure of the planarity shows that the cyclohexene species is the flattest system along the DA reaction path. In principle, the flatter a structure, the easier the π-electron delocalization. Therefore, likewise the HOMA and FLU indices, the RSS measure also fails in considering the cyclohexene as the most aromatic species along the DA reaction. We see in this example that the study of the planarity along a reaction path may fail to account for the aromaticity of the species involved, since the most planar structures are not necessarily those having the most extended π-electron delocalization. Thus, in this case, an aromaticity analysis only based on geometrical indices such as HOMA and RSS gives a wrong answer. However, it is also true that these indices can be very useful when dealing

Table 1
Reaction coordinate (IRP in amu$^{1/2}$ bohr), RSS, HOMA, NICS(1) (ppm), PDI (electrons), and FLU for different points along the reaction path of the DA reaction between 1,3-butadiene and ethene

IRP	RSS	HOMA	NICS(1)	PDI	FLU
−3.491	0.865	−170.116	−2.335	0.055	0.339
−2.892	0.848	−150.941	−2.967	0.058	0.327
−2.293	0.829	−132.591	−3.803	0.063	0.313
−1.694	0.807	−115.002	−4.951	0.069	0.293
−1.094	0.782	−98.287	−6.534	0.077	0.266
−0.496	0.758	−82.619	−8.669	0.086	0.231
−0.296	0.750	−77.671	−9.489	0.089	0.218
−0.099	0.742	−72.925	−10.293	0.091	0.204
0.000	0.732	−66.285	−11.416	0.094	0.183
0.099	0.721	−59.981	−12.251	0.096	0.163
0.397	0.711	−53.819	−16.975	0.095	0.144
0.697	0.700	−47.992	−16.449	0.092	0.128
1.297	0.678	−37.455	−13.830	0.081	0.106
1.897	0.654	−28.388	−10.812	0.067	0.095
2.497	0.625	−20.773	−8.421	0.053	0.091
3.097	0.593	−14.589	−6.755	0.043	0.089
3.397	0.575	−12.021	−6.140	0.039	0.089
3.597	0.563	−10.497	−5.792	0.037	0.088

Negative values of the IRP correspond to the reactants side of the reaction path, positive values to the product side, and IRP = 0.000 corresponds to the TS of the DA cycloaddition.

with the aromaticity in structurally similar compounds. Finally, it is worth noting that the species with the highest slope of RSS (see Table 1 and Fig. 1) along the IRC corresponds to the most aromatic structure on the reaction path, the TS.

HOMA and FLU values measure variances of the structural and electronic patterns, respectively, around the ring. Therefore, HOMA and FLU might fail if they are not applied to stable species because, while reactions are occurring, structural and electronic parameters suffer major changes. The larger the difference between the standard bond lengths for aromatic species and the average bond lengths, the lower aromaticity predicted with HOMA (lower HOMA values). And, the higher the differences between the standard in aromatic systems and the actual electronic sharing, the lower aromaticity predicted by FLU (higher FLU values). For this reason, in general, HOMA and FLU can not be used to compare the aromaticity between species which undergo large structural or electronic changes.

The present study has shown that FLU and HOMA indices are not suitable for the study of aromaticity along a reaction path because they give wrong aromaticity differences when applied to species that are structurally or electronically very different. In principle, we expect that any criterion to quantify aromaticity that is defined using a reference model of aromaticity will have problems to find the TS of the DA reaction as the most aromatic species along the reaction path. However, FLU and HOMA indices have proven to behave properly in aromaticity studies of systems having the usual aromatic structures [13,25]. In these circumstances, changes in aromaticity of the different species analyzed are less dramatic and are well quantified by variance-like indices. Although both FLU and HOMA present the same wrong behavior in this DA reaction, this result cannot be generalized for all cases. For instance, in a recent work, Matito et al. [25] have studied the change of aromaticity along the series: cyclohexane, cyclohexene, cycohexa-1,4-diene, cyclohexa-1,3-diene, and benzene, a set of molecules with increasing π-conjugated character from non-aromatic cyclohexane to aromatic benzene. These authors found

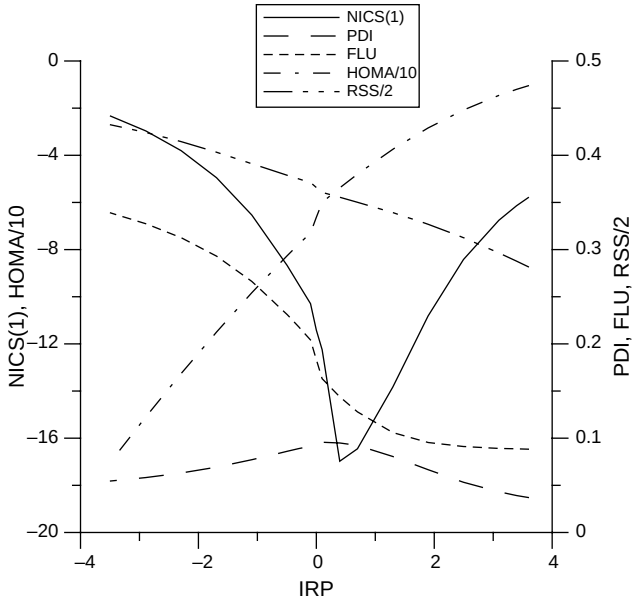


Fig. 1. Plot of NICS(1) (ppm), PDI (electrons), FLU, HOMA (values divided by 10), and RSS (values divided by 2) versus the reaction coordinate (IRP in amu$^{1/2}$ bohr). Negative values of the IRP correspond to the reactants side of the reaction path, positive values to the product side, and IRP = 0.000 corresponds to the TS of the DA cycloaddition.

that while FLU correctly reproduces the predicted steady increase of the aromatic character along the series, the HOMA index fails to account for the expected continuous intensification in aromaticity.

Finally, although NICS behaves correctly for the DA reaction, it has been recently shown that it fails to recognize the decrease of aromaticity that takes place when going from planar to pyramidalized pyracylene [18], at variance with PDI and HOMA values that correctly account for this reduction of aromaticity. NICS is also known to overestimate the local aromaticity of inner rings in linear polyacenes [10,35]. On the other hand, HOMA and PDI fail to correctly account for the increase of aromaticity [36] when going from C_{60} to C_{60}^{+10} [37]. Indeed, there is no single descriptor of aromaticity that behaves correctly for all situations. This fact reinforces the idea of aromaticity as being a multidimensional property [12–14,16]. For this reason, we also strongly recommend the use of more than a single parameter for aromaticity studies.

5. Conclusions

In the present study, the paradigmatic DA reaction between 1,3-butadiene and ethene, presenting an aromatic TS, has been analyzed to show that some aromaticity indices may fail to describe aromaticity in chemical reactions. The NICS and PDI indicators of aromaticity correctly predict that a structure close to the TS is the most aromatic species along the reaction path. On the contrary, we have found that HOMA and FLU indices are unsuccessful to account for the aromaticity of the TS. The same is true for the new defined geometric RSS index, which quantifies the planarity of a given structure. This index shows that the most planar species along the reaction path of the DA reaction between 1,3-butadiene and ethene is cyclohexene, the final product.

Inclusion of electron correlation effects will obviously change the quantitative values of the indices, but we do not expect that it may alter in a significant way the qualitative conclusions of this work. In particular, with respect to the PDI and FLU results, it has been found that the Hartree–Fock (HF) values of DIs represent upper bounds to the number of electron pairs shared between atoms [22,34,38]. Consequently, inclusion of correlation energy will reduce the values of the PDI index (the effect on the FLU indices is less clear). However, we think that conclusions obtained from the comparison of the different values will remain unchanged. This is the case, for instance, of the relation between the DIs of *meta* and *para* related carbon atoms in benzene. These values are 0.068 and 0.106 e at the HF/3-21G* level, respectively, and 0.048 and 0.071 e at the CISD/3-21G* level, respectively [39]. Thus, although the values of DIs are quite different, both the HF and the CISD levels of calculation qualitatively agree in assigning a larger DI for the carbon atoms in *para* position.

Finally, the failure of some indices to detect the aromaticity of the TS in the simplest DA cycloaddition reinforces the idea of the multidimensional character of aromaticity and the need for using several criteria to quantify the aromatic character of a given species. The results presented in this paper clearly confirm the necessity of finding new indices of aromaticity that can be successfully applied to a series of well-defined situations, as far as the aromatic behavior is concerned, such as the DA reaction. More research is underway in our laboratory concerning this particular issue.

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References

[1] K.N. Houk, Y. Li, J. Slorer, L. Raimondi, F. Beno, J. Chem. Soc., Faraday Trans. 90 (1990) 1599; F. Bernardi, P. Celani, M. Olivucci, M.A. Robb, G. Suzzi-Valli, J. Am. Chem. Soc. 117 (1995) 10531; R. Herges, H. Jiao, P.v.R. Schleyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 1376.
[2] K.N. Houk, J. Gonzalez, Y. Li, Acc. Chem. Res. 28 (1995) 81.
[3] H. Jiao, P.v.R. Schleyer, J. Phys. Org. Chem. 11 (1998) 655.
[4] R.B. Woodward, R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970; H. Zimmermann, Acc. Chem. Res., 33272; M.J.S. Dewar, Angew. Chem., Int. Ed., 10761; S. Sakai, J. Phys. Chem. A, 104922; O. Wiest, K.N. Houk, Top. Curr. Chem., 1831; H. Lischka, E. Ventura, M. Dallos, Chem. Phys. Chem., 51365.
[5] M.G. Evans, E. Warhurst, Trans. Faraday Soc. 34 (1938) 614.
[6] C. Corminboeuf, T. Heine, J. Weber, 5 (2003) 1127.M. Manoharan, F. De Proft, P. Geerlings, J. Org. Chem. 65 (2000) 7971; M. Manoharan, F. De Proft, P. Geerlings, J. Chem. Soc., Perkin Trans. 2 (2000) 1767; M. Manoharan, F. De Proft, P. Geerlings, J. Org. Chem. 65 (2000) 6132.
[7] P.v.R. Schleyer, Chem. Rev. 101 (2001) 1115.
[8] P.J. Garrat, Aromaticity, Wiley, New York, 1986; V.I. Minkin, M.N. Glukhovtsev, B.Y. Simkin, Aromaticity and Antiaromaticity: Electronic and Structural Aspects, Wiley, New York, 1994.
[9] P.v.R. Schleyer, H. Jiao, Pure Appl. Chem. 68 (1996) 209.
[10] T.M. Krygowski, M.K. Cyranski, Z. Czarnocki, G. Häfelinger, A.R. Katritzky, Tetrahedron 56 (2000) 1783.
[11] A. Kekulé, Bull. Soc. Chim. Fr. (Paris) 3 (1865) 98.
[12] A.R. Katritzky, K. Jug, D.C. Oniciu, Chem. Rev. 101 (2001) 1421.
[13] T.M. Krygowski, M.K. Cyranski, Chem. Rev. 101 (2001) 1385.

[14] A.R. Katritzky, M. Karelson, S. Sild, T.M. Krygowski, K. Jug, J. Org. Chem. 63 (1998) 5228.
[15] A.R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano, M. Szafran, J. Am. Chem. Soc. 111 (1989) 7.
[16] M.K. Cyranski, T.M. Krygowski, A.R. Katritzky, P.v.R. Schleyer, J. Org. Chem. 67 (2002) 1333.
[17] J. Poater, I. García-Cruz, F. Illas, M. Solà, Phys. Chem. Chem. Phys. 6 (2004) 314.
[18] J. Poater, M. Solà, R.G. Viglione, R. Zanasi, J. Org. Chem. 69 (2004) 7537.
[19] J. Kruszewski, T.M. Krygowski, Tetrahedron Lett. 13 (1972) 3839; T.M. Krygowski, J. Chem. Inf. Comput. Sci. 33 (1993) 70.
[20] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R. van Eikema Hommes, J. Am. Chem. Soc. 118 (1996) 6317.
[21] J. Poater, X. Fradera, M. Duran, M. Solà, Chem. Eur. J. 9 (2003) 400; J. Poater, X. Fradera, M. Duran, M. Solà, Chem. Eur. J. 9 (2003) 1113.
[22] X. Fradera, M.A. Austen, R.F.W. Bader, J. Phys. Chem. A 103 (1999) 304.
[23] X. Fradera, J. Poater, S. Simon, M. Duran, M. Solà, Theor. Chem. Acc. 108 (2002) 214.
[24] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon, Oxford, 1990; R.F.W. Bader, Acc. Chem. Res., 189; R.F.W. Bader, Chem. Rev., 91893.
[25] E. Matito, M. Duran, M. Solà, J. Chem. Phys. 122 (2005) 014109.
[26] G. Menczel, Acta Chim. Acad. Sci. Hung. 60 (1969) 135.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, R. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A11, Gaussian, Inc., Pittsburgh, PA, 1998.
[28] F.W. Biegler-König, R.F.W. Bader, T.-H. Tang, J. Comput. Chem. 3 (1982) 317.
[29] A.D. Becke, J. Chem. Phys. 98 (1993) 5648; C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785; P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[30] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257; P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213; M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. Frees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
[31] K. Fukui, J. Phys. Chem. 74 (1970) 4161; K. Fukui, Acc. Chem. Res. 14 (1981) 363.
[32] C. Gonzalez, H.B. Schlegel, J. Chem. Phys. 90 (1988) 2154.
[33] K. Wolinski, J.F. Hilton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 821.
[34] J. Poater, M. Solà, M. Duran, X. Fradera, Theor. Chem. Acc. 107 (2002) 362.
[35] M.V. Zhigalko, O.V. Shishkin, L. Gorb, J. Leszczynski, J. Mol. Struct. (Theochem) 693 (2004) 153.
[36] A. Hirsch, Z. Chen, H. Jiao, Angew. Chem., Int. Ed. 39 (2000) 3915; Z. Chen, H. Jiao, A. Hirsch, W. Thiel, J. Mol. Model. 7 (2001) 161.
[37] J. Poater, M. Solà, unpublished results.
[38] R.F.W. Bader, D. Bayles, J. Phys. Chem. A 104 (2000) 5579.
[39] X. Fradera, J. Poater, M. Solà, unpublished results.