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Can Substituted Cyclopentadiene Become Aromatic or Antiaromatic?

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Abstract: Cyclopentadiene derivatives with electronegative (F, Cl) or electropositive (H_3Si, Me_3Si) bis-5,5-substituents were studied at the B3LYP/6-311G* level of theory. It was found that there is no special stabilization or destabilization for any of the derivatives; the energetic effects that were previously attributed to aromatic stabilization or antiaromatic destabilization are the result of interactions in the reference systems. A nucleus-independent chemical shift (NICS) scan study at the HF-GIAO/6-311+G* theoretical level of these and similar derivatives suggest that they all show different magnitudes of diamagnetic ring current. None of the derivatives shows a paramagnetic ring current. Thus, cyclopentadienes are neither aromatic nor antiaromatic. It is also concluded that a diamagnetic ring current is perhaps necessary but certainly not a sufficient condition for aromaticity. The NICS scan procedure describes the type of ring current in the system, whereas a single isotropic NICS value (i.e., NICS(1)) may wrongly assign the type of ring current. It is shown that neither NICS(1) nor the NICS scan procedure can be used as a single aromaticity criterion.

Keywords: aromaticity · cyclopentadienes · density functional calculations · NICS scan · stabilization

Introduction

Cyclopentadiene and its derivatives are well known compounds that are used mainly as dienes and as sources for cyclopentadienyl anions. The NICS scan procedure[1] shows a behavior for cyclopentadiene that is similar to that of aromatic systems (Figure 1), that is, both the isotropic NICS[2] values and the out-of-plane component of the chemical shifts show minima upon increasing the distance (r) of the NICS probe (bq)[3] from the molecular plane. The NICS scan shape therefore suggests the presence of a diamagnetic ring current, which should be manifest in the chemical shift of the protons (assuming that the RCM is correct[4]). Indeed, when comparing the chemical shifts of the dienic protons of cyclopentadiene to other dienes, one finds a clear downfield shift: the average chemical shifts of the dienic protons in 1,3-butadiene and 1,3-cyclohexadiene are $\delta = 5.45$ and 5.84 ppm, respectively, whereas the respective average chemical shift of the protons in cyclopentadiene is $\delta = 6.36$ ppm.[5] This can be explained by considering the molecular orbitals (MOs) of cyclopentadiene (Figure 2). The first orbital that allows cyclic conjugation is a bonding combina-

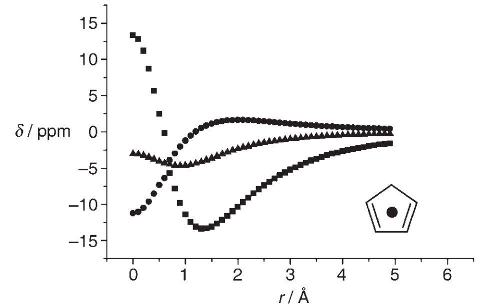

Figure 1. NICS values as a function of distance for cyclopentadiene: ■ out-of-plane component; ● in-plane component; ▲ isotropic chemical shift.

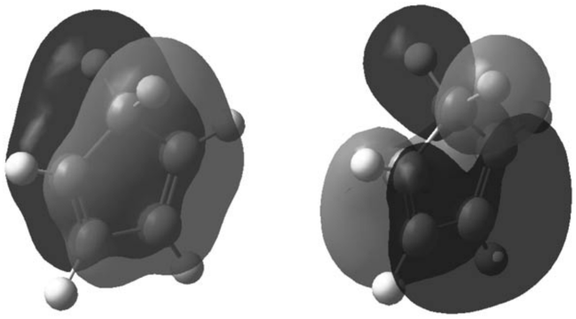

Figure 2. HOMO−6 (left) and HOMO−1 (right) of cyclopentadiene.

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tion between the lowest π orbital of the butadienic fragment (the "all bonding" combination) and the π(CH_2) orbital of the CH_2 fragment. This MO is topologically identical to the lowest π orbital of benzene. The second MO that is involved in the cyclic conjugation is the antibonding combination of the above-mentioned two fragment orbitals. These orbitals allow cyclic conjugation in the system, which is not formally conjugated, and, with six π electrons, for it to show a diamagnetic ring current. However, because the two orbitals are occupied (HOMO−6 and HOMO−1), there is a "no bond" (i.e., no π bond) situation. The alternative name for this phenomenon is hyperconjugation, which was invoked for cyclopentadiene as early as 1939.[6]

Hyperconjugation in cyclopentadiene should become more efficient if electropositive substituents are placed at the 5-position, and less effective if electronegative substituents are used.[7] Recently, Nyulászi and Schleyer claimed that, based on NICS(1),[8] magnetic exaltation, and energy criteria, electropositively substituted cyclopentadienes (e.g., 5,5-$(H_3M)_2$-cyclopentadiene, M = Si, Ge, Sn) are aromatic, whereas analogous derivatives substituted with electronegative substituents (i.e., 5,5-X_2-cyclopentadiene, X = F, Cl) are antiaromatic.[9] There are, however, no experimental confirmations of these claims, that is, there are no reports that these compounds undergo typical aromatic or antiaromatic chemistry. Moreover, if these compounds become aromatic one should expect a downfield shift of the protons relative to nonsubstituted cyclopentadiene. In fact, for nine different Si, Ge, and Sn 5,5-disubstituted cyclopentadienes the two extreme cases show an upfield shift of $\delta = 0.42$ ppm (for 5-trimethylsilyl-5-trihydroxysilylcyclopentadiene) and a downfield shift of $\delta = 0.39$ ppm (for 5,5-bis(dimethylchlorosilyl)cyclopentadiene and 5,5-bis(dimethylchlorogermyl)cyclopentadiene) relative to cyclopentadiene. The majority of the chemical shifts are $\delta = 6.5$–6.6 ppm, that is, a downfield shift of $\delta = 0.15$–0.25 ppm relative to cyclopentadiene.[10] Furthermore, the calculated average proton chemical shifts of the 5,5-dichloro and -disilyl cyclopentadienes (GIAO-HF/6-311+G*//B3LYP/6-311G*) suggest that the protons of the dichloro derivative resonate at $\delta = 0.06$ ppm downfield from the disilyl derivative—certainly not consistent with these derivatives being antiaromatic and aromatic, respectively. Additionally, there is a principle point that is troublesome: If cyclopentadiene can become aromatic through enhanced hyperconjugation, which can be achieved with electropositive substituents at the 5-position, and electronegative substituents diminish the hyperconjugation, than at the limit of high electronegativity the hyperconjugation should become zero. This should result in electronegatively substituted cyclopentadiene systems approaching usual diene systems (e.g., *s-cis*-1,3-butadiene), not antiaromatic systems.

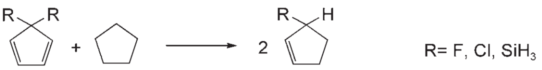
The above-mentioned inconsistencies prompted this study.[11] Energy criteria and the NICS scan[1] procedure are used here to determine if indeed cyclopentadienes can become aromatic or antiaromatic, and what the validity of a single NICS value (i.e., NICS(1)) as a criterion for aromaticity is.

Computational Methods

The Gaussian 03 program was used.[12] The molecules and ions were structurally optimized at the B3LYP/6-311G* level of theory and analytical frequency calculations were carried out to ensure real minima (i.e., $N_{\mathrm{imag}} = 0$).[13] The NICS probes (bqs) were placed above the geometrical center of the systems (namely, the average values of the in-plane coordinates of the carbon atoms of the five-membered ring) at distances ranging from 0.0 Å (i.e., at the molecular plane) to 4.9 Å at a step size of 0.1 Å. All the NICS values used were obtained at the 6-311+G* basis set at the Hartree–Fock (HF) level, using the GIAO[14] procedure at B3LYP/6-311G* geometry. The NICS values are the isotropic chemical shifts of the respective bqs, and the eigenvalues of the chemical-shift tensors were used to separate the isotropic NICS values into their in-plane and out-of-plane components. Because NICS values are distance dependent, the abbreviation *N@r* will be used throughout the paper, to denote the NICS value (ppm) at a distance *r* (Å) from the molecular plane. The energies of the equations that are discussed in the text are given in kcal mol^{-1} for zero-point-corrected total energies. Table 1 in the Results and Discussion summarizes the results of the equations for total energies, zero-point-corrected total energies, and Δ*H*.

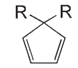
Results and Discussion

Energies: Nyulászi and Schleyer[9] used Equation (1) to determine the stabilization and destabilization effects of the substituents, for which the results were −9.53, −5.13, and 9.87 kcal mol^{-1} for R = F, Cl, and SiH_3, respectively, at B3LYP/6-311+G**.



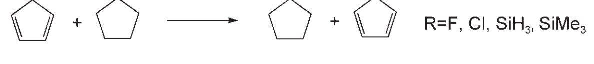
(1)

This equation measures a few effects (for example, *gem*-substitution relative to single substitution, changing from a bisallylic system to a monoallylic system), and thus we decided to study each effect separately. Systems **1**–**4** were chosen for



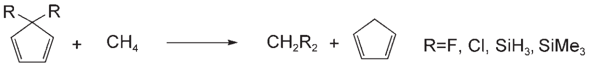
1: R=F. **2**: R=Cl. **3**: R=SiH_3. **4**: R=$SiMe_3$. **5**: R=$^+NH_3$.

the current study; **1**–**3** for the electronic effects[15] and **4** to introduce a more realistic system that exists experimentally. Equation (2) measures the transfer of the disubstitution from cyclopentadiene to the saturated cyclopentane.



(2)

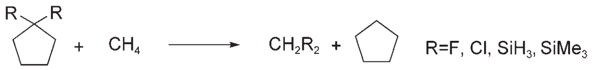
The results are consistent with Nyulásszi and Schleyer's conclusions.[9] Thus, **1** and **2** are destabilized by 14.1 and 8.3 kcal mol^{-1}, respectively, whereas **3** and **4** are stabilized by 11.0 and 14.6 kcal mol^{-1}, respectively, relative to their saturated analogues. The interpretation, namely, that these values represent aromatic and antiaromatic stabilizations and destabilizations, respectively, contains a built-in assumption, which is that the substituents interact mainly with the π skeleton, and that there are no significant interactions between the substituents and the skeleton of the five-membered ring. Equation (3), which compares the substituted cyclopentadienes to methane, tests this hypothesis. If the above-mentioned hypothesis is correct, then the results for Equations (2) and (3) should be similar.



(3)

However, the results are 3.3, 1.8, 7.3, and 5.9 kcal mol^{-1} for **1**–**4**, respectively. Thus, in all of the cases the *gem*-disubstituted cyclopentadienes are more stable than the respective *gem*-disubstituted methanes. Both the endothermicity and the magnitudes of the energies of Equation (3) do not support the assignment of antiaromaticity to **1** and **2** and of aromaticity to **3** and **4**.

In order to understand from where the differences between cyclopentane and methane as reference systems arise, Equation (4), which compares the *gem*-disubstituted cyclopentanes and methanes directly, was calculated. The results are 17.4, 10.0, −5.1, and −9.6 kcal mol^{-1} for the R = F, Cl, SiH$_3$, and SiMe$_3$ derivatives, respectively.



(4)

These results suggest that electronegatively substituted cyclopentanes are more stable than their methane analogues, and electropositively substituted cyclopentanes are less stable than their methane analogues. By considering the frontier orbitals of the systems, these differences in stabilities can be explained. Figure 3 shows the HOMO of 1,1-difluorocyclopentane, difluoromethane, 1,1-bis(silyl)cyclopentane, and disilylmethane. In both fluoride derivatives, the HOMO has an in-phase combination of two lone pairs of the F atoms. However, in difluoromethane the other part is an orthogonal $\pi(CH_2)$, whereas in the cyclopentane derivative it is a σ^* orbital that can accept electron density from the F atom lone pair. In the silyl derivatives, the HOMO part on the silyl atoms is similar for the two systems, but in the cyclopentane derivative there is an antibonding interaction with the neighboring $\pi(CH_2)$, and no interaction with the CH_2 in the methane derivative. In other words, the difference between the *gem*-disubstituted methane and cyclopentane analogues results from the presence of CH_2 fragments adjacent to the substituted carbon in the latter, which stabilize the F and Cl derivatives and destabilize the SiR$_3$ derivatives.

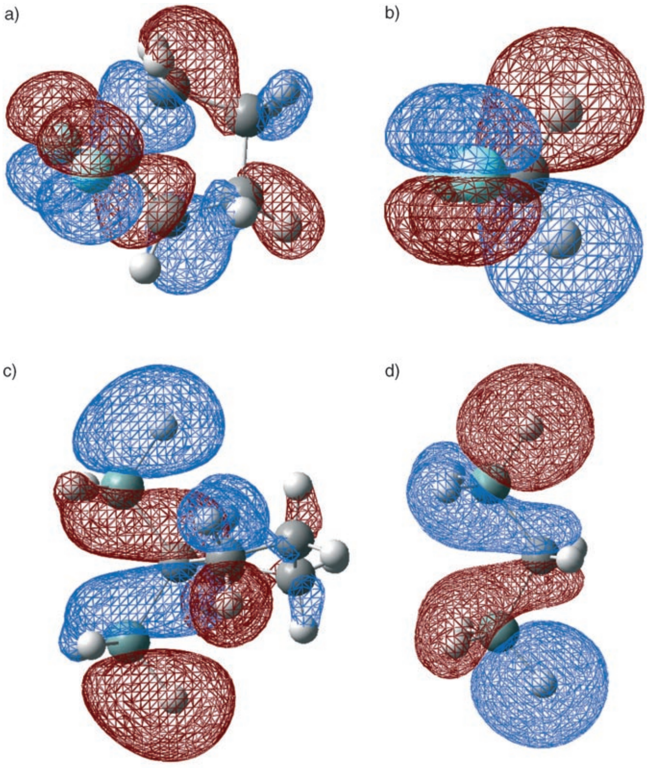
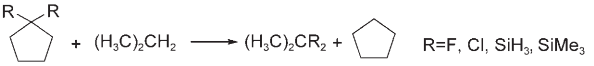


Figure 3. The HOMO orbitals of a) 1,1-difluorocyclopentane, b) difluoromethane, c) 1,1-bis(silyl)cyclopentane, and d) disilylmethane.

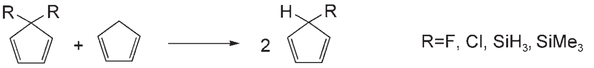
If indeed the analysis presented above is correct, that is, that the energies of Equations (1) and (2) are the results of interactions between the substituents and the α-CH_2 fragments, then the comparison between cyclopentane and propane analogues should be (close to) thermoneutral. Equation (5) describes this comparison, and its results are indeed almost thermoneutral: −0.5, 0.3, 0.9, and 0.8 kcal mol^{-1} for R = F, Cl, SiH$_3$, and SiMe$_3$, respectively.



(5)

It can be therefore concluded that the results of Equations (1) and (2) are due to interactions of the substituents with α-CH_2 fragments in cyclopentane, interactions that do not exist in methane and cyclopentadiene.

To further check this conclusion, Equation (6), which describes the effect of *gem*-disubstitution relative to single substitution on cyclopentadiene, was calculated.



(6)

Aromatic and antiaromatic interactions should have preserved the trends observed by Nyulászzi and Schleyer,[9] but the results (11.8, −1.8, 0.7, and −2.7 kcal mol^{-1} for R = F, Cl,

SiH_3, and $SiMe_3$, respectively) do not support such interactions.

The Hückel-based notion is that triplet antiaromatic systems should be almost as stable as their singlet systems. Indeed, at B3LYP/6-311G*, triplet cyclobutadiene is only approximately 5 kcal mol^{-1} less stable than singlet cyclobutadiene. In addition, it was shown that triplet antiaromatic systems are stabilized by aromatic-type interactions.[16] Table 1 (right column) lists the singlet–triplet energy gaps for **1**–**4**, the values of which are all high. The energy gaps for **1** and **2** (ca. 39 kcal mol^{-1}) and for **3** and **4** (ca. 61–62 kcal mol^{-1}) can be understood by considering the HOMO–LUMO gaps of the singlet systems (111.9, 105.7, 128.7, and 129.8 kcal mol^{-1} for **1**–**4**, respectively), which are in all cases larger than that for cyclobutadiene (84.8 kcal mol^{-1}), smaller than that for benzene (155.3 kcal mol^{-1}), and in the same range as that for *s-cis*-1,3-butadiene (123.7 kcal mol^{-1}) at the same theoretical level. Thus, the singlet–triplet energy gaps and the HOMO–LUMO gaps in **1**–**4** also do not support aromaticity or antiaromaticity characters for **1**–**4**.

Table 1. Energies [kcal mol^{-1}] for Equations (1) to (6) and singlet–triplet energy differences [kcal mol^{-1}]. For Equation (1), the numbers in parentheses are taken from reference [9].

R		[Eq. (1)]	[Eq. (2)]	[Eq. (3)]	[Eq. (4)]	[Eq. (5)]	[Eq. (6)]	S→T
F	ΔE[a]	−2.4 (−9.5)	−14.0	1.1	15.0	−0.6	11.3	41.7
	ΔE(ZPE)[b]	−2.0	−14.1	3.3	17.4	−0.5	11.8	39.6
	ΔH[c]	−2.0	−14.2	2.6	16.8	−0.6	11.8	39.9
Cl	ΔE[a]	−10.3 (−5.1)	−8.2	−0.2	8.0	0.2	−2.5	41.1
	ΔE(ZPE)[b]	−9.7	−8.3	1.8	10.0	0.3	−1.8	38.9
	ΔH[c]	−9.7	−8.4	0.8	9.2	0.1	−1.8	38.8
H_3Si	ΔE[a]	13.2	11.8	6.7	−5.1	0.9	0.7	65.0
	ΔE(ZPE)[b]	12.4 (9.9)	11.0	7.3	−3.7	0.9	0.7	61.2
	ΔH[c]	12.5	10.9	6.6	−4.4	0.9	0.5	61.5
Me_3Si	ΔE[a]	11.6	14.8	5.1	−9.6	0.9	−2.2	65.5
	ΔE(ZPE)[b]	10.7	14.6	5.9	−8.7	0.8	−2.7	62.1
	ΔH[c]	10.8	14.2	4.8	−9.4	0.8	−2.5	62.7

[a] Based on total energies. [b] Based on nonscaled zero-point-corrected total energies. [c] At 298.15 K.

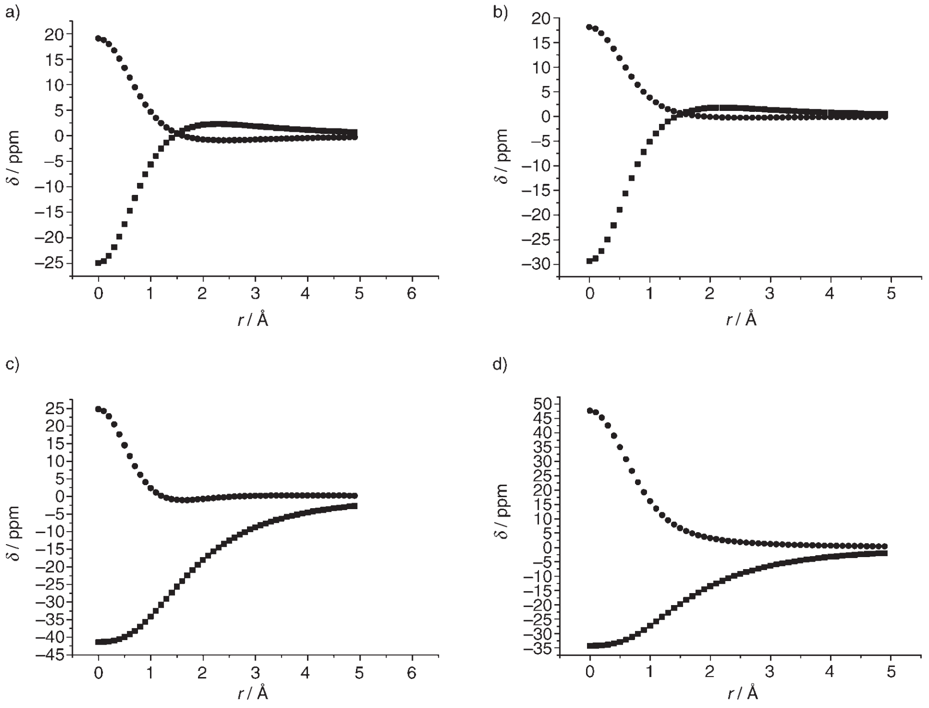


Figure 4. Diamagnetic (■) and paramagnetic (●) contributions to the in-plane components of the NICS scan in a) benzene and b) cyclopentadiene, and to the out-of-plane components in c) benzene and d) cyclopentadiene.

NICS scan: As mentioned above, attenuation of the hyperconjugation should result in a smaller diamagnetic ring current, but not in a paramagnetic ring current. NICS(1) has large positive values for electronegatively substituted cyclopentadienes, and large negative values for electropositively substituted cyclopentadienes,[9] indicating antiaromaticity and aromaticity, respectively.[17] We recently introduced a modified way of using NICS, which is based on scanning the NICS values over a distance and dissecting them into in-plane and out-of-plane components. The shapes of the curves (NICS and its components as a function of the distance) are indicative of the existence of a diamagnetic or paramagnetic ring current. This NICS-based method is much safer to use than a single isotropic NICS value (e.g., NICS(1)).[1]

To get a better insight into the factors governing the NICS scan pictures, the in-plane and out-of-plane tensors of the NICS scan of cyclopentadiene were dissected into their diamagnetic and paramagnetic contributions, and compared with those of benzene[1] (Figure 4). It can be observed that the NICS scan behaviors of the two systems are very similar. The magnitudes, however, are somewhat different. Thus, the diamagnetic component of the in-plane contribution of cyclopentadiene is somewhat larger than that of benzene at short distances but decreases faster with increasing distance (e.g., −29.3@0 and −3.5@1.0 in cyclopentadiene versus −25.0@0 and −5.6@1.0 in benzene). The paramagnetic components are similar at short distances and also decrease faster with the distance in cyclopentadiene (18.1@0, 3.8@1.0 in cyclopentadiene; 19.0@0, 4.7@1.0 in benzene). The differences in the out-of-plane contributions are larger. Thus, benzene shows a higher diamagnetic component (−41.1@0, −34.2@1.0) than cyclopentadiene (−34.2@0, −27.3@1.0) and a smaller paramagnetic component (24.8@0, 2.4@1.0 in benzene; 47.7@0, 16.2@1.0 in cyclopentadiene). Thus, it may be concluded that benzene and cyclopentadiene show the same type of ring current, however, it is less diamagnetic and more paramagnetic in the out-of-plane component for cyclopentadiene. The smaller diamagnetic ring current in cyclopentadiene is mainly due to the larger paramagnetic contribution in cyclopentadiene (a difference of 22.9@0 and 13.8@1.0) and less so due to a reduced diamagnetic contribution (a difference of 7.1@0 and 6.9@1.0). In benzene, the diamagnetic contribution is larger than the paramagnetic contribution to the out-of-plane component, whereas in cyclopentadiene the diamagnetic contribution to the out-of-plane component is smaller than the paramagnetic contribution at short distances, larger at longer distances, becoming equal at about 0.55 Å.

Figure 5 shows the NICS scan for **1**–**3** and **5**.[18] The last system was chosen because it contains positively charged substituents that mimic highly electronegative substituents. All the NICS scan plots show minima for the isotropic NICS values and for the out-of-plane components, indicating diamagnetic ring currents. The location and magnitude of the minima change for the different derivatives. For **1**, the isotropic and out-of-plane component minima are −0.46@1.8 and −3.90@2.3, respectively. As the substituent becomes less electronegative (or more electropositive) the minima of the isotropic and out-of-plane curves become more negative and appear at shorter distances from the molecular plane. Thus, for the Cl derivative **2** the respective numbers are −2.02@1.3 and −6.02@2.1, and for the SiH_3 derivative **3** the values are −9.2@0.7 and −21.9@1.1. The ammonium-substituted derivative **5** is an exception, showing a relatively shallow and remote minimum for the isotropic NICS values (−0.63@3.4) but deep and close minimum for the out-of-plane component (−22.5@1.0). Thus, the NICS scan values indicate that indeed the more electronegative the substituents are, the smaller the diatropic ring currents are, as shown by shallower minima at larger distances. The exceptional behavior of **5**, which, on the one hand shows a remote and shallow minimum for the isotropic NICS values but a close and deep minimum for the out-of-plane component, is the result of a large effect on the in-plane component of the chemical shift, as observed before in charged species.[1] This NICS scan behavior is also manifest in the proton chemical shifts. The calculated chemical shifts of the protons of **1**–**4** are within ±0.7 ppm from the respective protons of cyclopentadiene. For **5**, the 1,4-protons are shifted upfield by $\delta = 2.1$ ppm, and the 2,3-protons are shifted downfield by $\delta = 5.0$ ppm relative to the respective protons in cyclopentadiene. This indicates the effect of the electronegativity on the one hand and the enhanced diamagnetic ring current on the other. It is worth noting that none of the derivatives show a typical antiaromatic (i.e., paratropic ring current) NICS scan curve.[1]

How do the substituents affect the diamagnetic and paramagnetic contributions to each of the chemical-shift tensors? The general shape of all the derivatives is similar to that of the unsubstituted cyclopentadiene (and benzene, see Figure 4). However, the values are different, and some points along the distance scan are given in Table 2. Clearly, the in-plane components are only affected a little by the substituents. The more pronounced effect is found in the out-of-plane component. It can be observed that for **1** the largest effect is the enhancement of the paramagnetic contribution, whereas for **3** it is the enhancement of the diamagnetic contribution. This behavior is very different from that found for

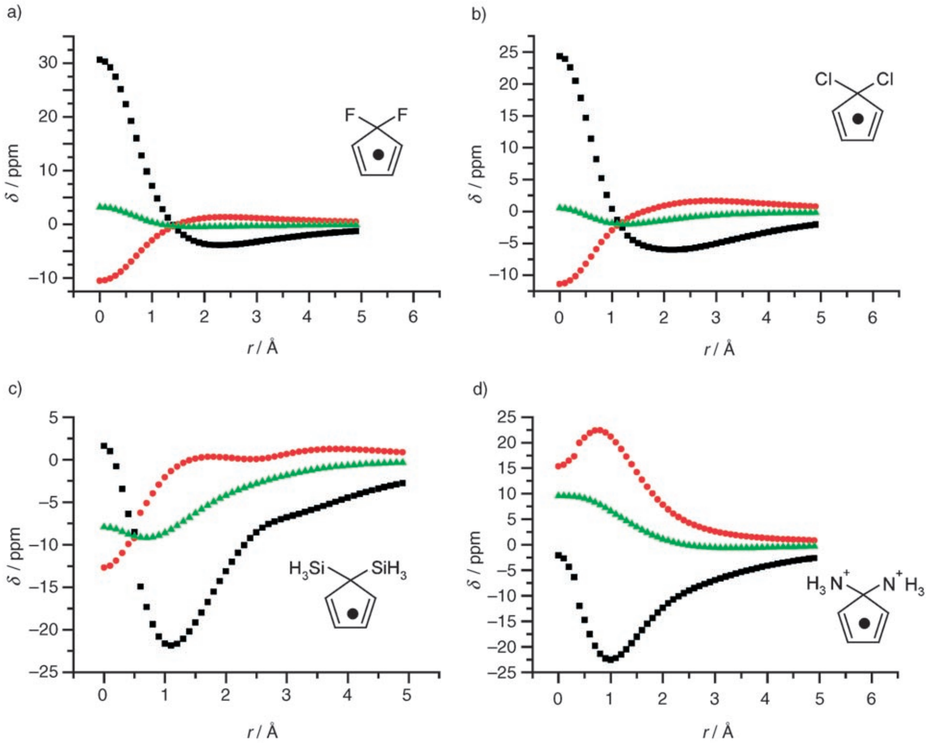


Figure 5. NICS values as a function of distance for a) 5,5-difluorocyclopentadiene, b) 5,5-dichlorocyclopentadiene, c) 5,5-disilylcyclopentadiene, and d) 5,5-bis(ammonium)cyclopentadiene: ■ out-of-plane component; ● in-plane component; ▲ isotropic chemical shift.

Table 2. Diamagnetic (dia) and paramagnetic (para) contributions to the in-plane and out-of-plane components of the NICS of cyclopentadiene, **1**, and **3** at the molecular plane and 1 Å above it.

		Cyclopentadiene	**1**	**3**
in-plane	dia@0	−29.3	−30.1	−31.3
	para@0	18.1	19.5	18.6
	dia@1.0	−5.1	−5.5	−8.3
	para@1.0	3.8	2.5	6.1
out-of-plane	dia@0	−34.3	−39.0	−48.5
	para@0	47.7	69.6	50.1
	dia@1.0	−27.3	−29.9	−37.4
	para@1.0	16.2	37.0	16.0

cyclobutadiene, which shows that the diamagnetic contribution to the out-of-plane component is almost identical to that in benzene, but the paramagnetic contribution is tremendously enhanced (by 137.3@0 and 89.2@1.0),[1] thus arguing against the aromaticity and antiaromaticity of cyclopentadiene derivatives.

Current density analysis: The ACID (anisotropy of the induced current density) method developed by Herges et al. is a method to quantify and visualize the density of the delocalized electrons in molecules[19] and has been used to investigate delocalization and conjugation in a number of organic molecules and transition states.[20] Figure 6 shows the current density vectors for **1** and **3**, which are plotted onto the ACID isosurface (isosurface value 0.05), where the magnetic field vector is orthogonal to the ring plane and pointing towards the viewer (i.e., diamagnetic and paramagnetic ring currents are clockwise and anticlockwise, respectively) and the lengths of the current vectors are proportional to the strength of the current. Both systems show paratropic ring current in the inner circumference of the ring, which is strongest in the ring plane, and diatropic ring current in the periphery, qualitatively similar to the picture obtained for benzene.[19,21] The differences are in the magnitudes of the currents. There is only a weak diatropic current in the π system of **1** (short vectors) and a paratropic ring current of similar strength inside the ring. In **3** it can be observed that the diatropic ring current is significantly stronger (longer vectors) and the paratropic current is weaker. Thus, the picture obtained from current density analysis is essentially identical to that obtained from the NICS scan and contradicts the picture obtained from a single isotropic NICS value.

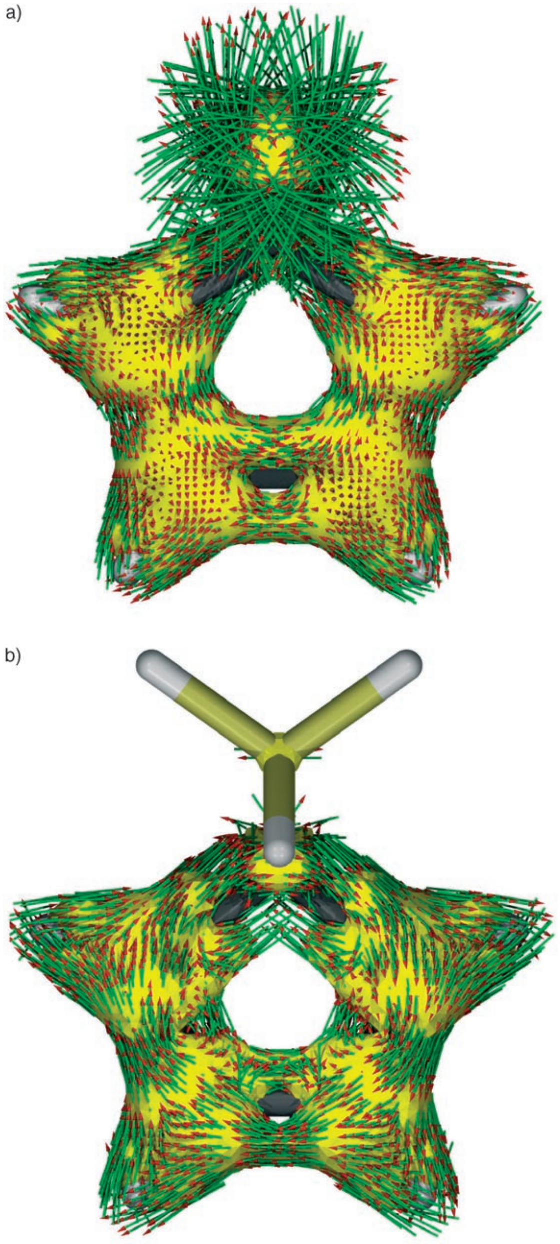


Figure 6. ACID current density plot of a) 5,5-difluorocyclopentadiene and b) 5,5-disilylcyclopentadiene. See text for the plot details.

Conclusions

It was shown by means of energy criteria that the derivatives of cyclopentadiene are neither aromatic nor antiaromatic. These systems are nonaromatic conjugated dienes, in accordance with the experimental information that exists in the literature. NICS scans show that all the derivatives under study have different magnitudes of diatropic ring currents, and thus none of the compounds is antiaromatic. Current density analysis gives a very similar (if not identical) picture. Together with the energy criteria, it must be concluded that the fact that diamagnetic ring currents exist (at different magnitudes) does not necessarily mean that the molecule is aromatic. Thus, it may well be that diamagnetic and paramagnetic ring currents (as observed, for example, in the NICS scan) are necessary but not sufficient conditions to determine aromaticity and antiaromaticity. It was also clearly shown that a single NICS value (e.g., NICS(1)) can give a wrong answer regarding the type of ring current in the system under study, and thus can certainly wrongly assess the aromaticity, antiaromaticity, and nonaromaticity of compounds.

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[2] Nucleus-independent chemical shift, see: P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[3] The probe for the NICS calculations is a ghost atom which is called "bq" in the Gaussian package after Banquo, the ghost that hunts Macbeth. This naming will be used throughout the paper.

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[10] For 5,5-R,R′-cyclopentadienes the average chemical shifts of the butadienic units are as follows: a) $R = Me_2Si\text{-}CH_2CH_2C_8F_{17}$, $R' = Me_3Sn$, $\delta = 6.50$ ppm; b) $R = Me_2Si\text{-}CH_2CH_2C_8F_{17}$, $R' = Me_3Si$, $\delta = 6.56$ ppm, see: J. Čermák, L. Šťastná, J. Sýkora, J. Kvíčala, *Organometallics* **2004**, *23*, 2850; c) $R = Me_2Si\text{-}SiMe_3$, $R' = Me_3Si$, $\delta = 6.53$–6.58 ppm, see: A. Klipp, S. H. A. Petri, B. Neumann, H.-G. Stammler, P. Jutzi, *J. Organomet. Chem.* **2001**, *620*, 20; d) $R = Me_3Si$, $R' = Si(OH)_3$, $\delta = 5.94$ ppm; e) $R = R' = Me_2SiOMe$, $\delta = 6.5$ ppm; f) $R = R' = Me_2SiCl$, $\delta = 6.75$ ppm, see: P. Jutzi, M. Schneider, H.-G. Stammler, B. Neumann, *Organometallics* **1997**, *16*, 5377; g) $R = Me_2SiCl$, $R' = Me_3Ge$, $\delta = 6.35$ ppm; h) $R = Me_2GeCl$, $R' = Me_3Si$, $\delta = 6.65$ ppm; i) $R = R' = Me_2GeCl$, $\delta = 6.75$, see: J. M. Rozell, Jr., P. R. Jones, *Organometallics* **1985**, *4*, 2206; j) $R = Me_2Si\text{-}t\text{Bu}$, $R' = Me_3Si$, $\delta = 6.3$ ppm; k) $R = Me_2SiCl$, $R' = Me_3Si$, $\delta = 6.4$ ppm, see: P. R. Jones, J. M. Rozell, Jr., B. M. Campbell, *Organometallics* **1985**, *4*, 1321.

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[18] The NICS scan of **4** is not indicative because the bq probe feels the effect of the hydrogen atoms of the trimethylsilyl groups. A similar effect (which, however, is remote enough and thus does not interfere with the shape close to the minima) can be observed in **3**.

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