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Ground- and Excited-State Aromaticity and Antiaromaticity in Benzene and Cyclobutadiene

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The aromaticity and antiaromaticity of the ground state (S_0), lowest triplet state (T_1), and first singlet excited state (S_1) of benzene, and the ground states (S_0), lowest triplet states (T_1), and the first and second singlet excited states (S_1 and S_2) of square and rectangular cyclobutadiene are assessed using various magnetic criteria including nucleus-independent chemical shifts (NICS), proton shieldings, and magnetic susceptibilities calculated using complete-active-space self-consistent field (CASSCF) wave functions constructed from gauge-including atomic orbitals (GIAOs). These magnetic criteria strongly suggest that, in contrast to the well-known aromaticity of the S_0 state of benzene, the T_1 and S_1 states of this molecule are antiaromatic. In square cyclobutadiene, which is shown to be considerably more antiaromatic than rectangular cyclobutadiene, the magnetic properties of the T_1 and S_1 states allow these to be classified as aromatic. According to the computed magnetic criteria, the T_1 state of rectangular cyclobutadiene is still aromatic, but the S_1 state is antiaromatic, just as the S_2 state of square cyclobutadiene; the S_2 state of rectangular cyclobutadiene is nonaromatic. The results demonstrate that the well-known "triplet aromaticity" of cyclic conjugated hydrocarbons represents a particular case of a broader concept of excited-state aromaticity and antiaromaticity. It is shown that while electronic excitation may lead to increased nuclear shieldings in certain low-lying electronic states, in general its main effect can be expected to be nuclear deshielding, which can be substantial for heavier nuclei.

1. Introduction

The idea that the concepts of aromaticity and antiaromaticity apply to molecules in other than their electronic ground states can be traced back to Baird,[1] who argued that the well-known $4n + 2$ and $4n$ rules for ground-state aromaticity in cyclic conjugated hydrocarbons are reversed in their lowest triplet states: rings with $4n$ π electrons become aromatic while $4n + 2$ systems should be regarded as antiaromatic. The existence of "triplet aromaticity" was confirmed by Gogonea et al.[2] who carried out extensive ab initio and density functional theory (DFT) studies of the lowest triplet states of annulenes with $4n$ π electrons and showed that this phenomenon manifests itself in ring planarization, equalization of bond lengths, low singlet−triplet energy gaps, sizable aromatic stabilization energies (with respect to triplet reference states), negative nucleus-independent chemical shifts (NICS),[3] downfield ^{1}H NMR chemical shifts, and significant diamagnetic susceptibility exaltations. Fowler et al. [4] provided additional insights into the triplet aromaticity of cycles with $4n$ π electrons by analyzing the ring currents in these systems within a qualitative open-shell adaptation of the ipsocentric approach.

In a recent paper,[5] Soncini and Fowler introduced a more general set of rules for the aromaticity of the subset of electronic states of C_NH_N conjugated rings of D_{Nh} symmetry containing even numbers of π electrons which can be accommodated by a single closed-shell or high-spin open-shell Slater determinant. According to these rules, the lowest-energy states with even total spin (singlet, quintet, etc.) of rings with $4n + 2$ π electrons and the lowest-energy states with odd total spin (triplet, septet, etc.) of rings with $4n$ π electrons should be aromatic. In an interesting demonstration of the validity of these ideas, Soncini and Fowler showed that both the closed-shell ground state and the single-determinant approximation to the first quintet state of azulene exhibit strong perimeter diatropic currents consistent with aromaticity. In an attempt to extend their aromaticity rules, Soncini and Fowler also argued that, in general, the lowest electronic states with odd total spin of rings with $4n + 2$ π electrons, as well as the lowest electronic states with even total spin of rings with $4n$ π electrons, should be antiaromatic. However, none of these electronic states can be described by a single Slater determinant, and thus the problem lies outside the scope of applicability of the restricted open-shell Hartree−Fock (ROHF) methodology used in ref 5. Any attempt to carry out a ROHF calculation on an electronic state of this type is bound to converge to a wave function exhibiting a symmetry lower than that of the nuclear framework, the analysis of which is most likely to indicate nonaromatic character. In view of this fact, it is not surprising that Soncini and Fowler did not provide even a single computational example illustrating their ideas about antiaromaticity.

While there is a convincing array of ab initio results in favor of triplet aromaticity in conjugated rings containing $4n$ π electrons, Baird's notion of triplet antiaromaticity in cycles with $4n + 2$ π electrons has not been scrutinized using similar theoretical techniques. The additional complication in this case is that, due to the nature of the problem, it is necessary to use wavefunctions containing at least two Slater determinants. One indication that the lowest triplet state T_1 of D_{6h} benzene may, indeed, be antiaromatic is provided by the experimental and theoretical evidence[6,7] that in this state the regular hexagonal structure is unstable toward a quinoidal distortion leading to a D_{2h} geometry.

The first systematic ab initio study of the geometries of the low-lying excited states of cyclobutadiene carried out by Fratev

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et al.[8] showed that, in contrast to the antiaromatic singlet ground state S_0, which is well-known to prefer a rectangular D_{2h} geometry with alternating carbon−carbon bond lengths, the first and second singlet excited states S_1 and S_2, as well as the lowest triplet state T_1, assume square geometries of D_{4h} symmetry. These findings have been confirmed at higher levels of theory.[9,10] The bond-length equalization observed in the S_1, S_2, and T_1 states of cyclobutadiene led Fratev et al.[8] to suggest that these states may have some aromatic character, which was assumed to be less pronounced than that of the ground state of benzene, as the latter has shorter carbon−carbon bond lengths. Fratev et al. pointed out that this suggestion was consistent with the fact that when obtained photochemically, cyclobutadiene decomposes relatively slowly upon prolonged irradiation to acetylene while, in its ground state, it dimerizes rapidly upon heating.[11] On the basis of the experimental data available at the time, which were indicating that both the lowest triplet and first singlet excited states of benzene, T_1 and S_1, retained D_{6h} symmetry but featured longer carbon−carbon bonds, Fratev et al. made a further conjecture that the ground-state aromaticity of benzene should be expected to decrease upon excitation to T_1 or S_1. While this conjecture needs to be revised in view of the fact that later research points out that the T_1 state of benzene has a D_{2h} geometry (see above), the intriguing concept of a more general excited-state aromaticity, which encompasses the better-known triplet aromaticity, as well as the high-spin open-shell aromaticity discussed by Soncini and Fowler,[5] deserves further attention. A closer look at the S_1 state of benzene shows that the proof of this concept requires more than a simple examination of bond length alternation patterns and bond length changes.

The modern valence-bond (VB) description of the first singlet excited state of benzene within the spin-coupled VB (SCVB) approach is dominated by an out-of-phase combination of the two Kekulé structures,[12] unlike that of S_0, which is very well approximated by an in-phase combination of these structures.[13] This makes the SCVB description of the S_1 state of benzene similar to the VB wavefunctions for the ground-state of square cyclobutadiene obtained within the generalized resonating VB (GRVB) approach[14] and spin-coupled (SC) theory (when using atom-centered semilocalized orbitals),[15] both of which represent out-of-phase combinations of the two Kekulé structures for this molecule. In addition to this, high-level computational results[16] on *s*-indacene, a formally antiaromatic highly reactive tricyclic hydrocarbon with 12 π electrons, strongly suggest that it adopts a "delocalized" ground-state geometry which does not exhibit alternation of carbon−carbon single and double bonds. Thus, there is a distinct possibility that the S_1 state of benzene is not just less aromatic than the ground state S_0—it may very well be antiaromatic, despite its bond-equalized D_{6h} geometry.

The aim of this paper is to assess the aromaticity and antiaromaticity of the S_0, T_1, and S_1 states of D_{6h} benzene and the S_0, T_1, S_1, and S_2 states of square and rectangular cyclobutadiene using various magnetic criteria including NICS values, proton shieldings, and magnetic susceptibilities. In order to treat the different geometries and electronic states of the two molecules at very much the same qualitatively correct level of theory, the calculations have been carried out using complete-active-space self-consistent field (CASSCF) wavefunctions constructed from gauge-including atomic orbitals (GIAOs). The influence of the nondynamic correlation effects included in the CASSCF wavefunction on the ground-state magnetic properties of aromatic and antiaromatic conjugated rings is highlighted by comparing the corresponding CASSCF-GIAO results for benzene and rectangular cyclobutadiene to those coming from HF-GIAO (Hartree−Fock method using GIAOs) and MP2-GIAO (second-order Møller−Plesset perturbation theory with GIAOs) calculations. For the lowest triplet states of square and rectangular cyclobutadiene, the CASSCF-GIAO results are juxtaposed with their unrestricted HF-GIAO (UHF-GIAO) counterparts. The ^{1}H and ^{13}C shieldings for different electronic states reported in this paper provide insights into the extent to which nuclear shieldings can be affected by electronic excitation.

2. Computational Procedure

The CASSCF-GIAO calculations reported in this paper were performed using the DALTON 2.0 program package,[17] which implements the MCSCF-GIAO (multiconfigurational SCF with GIAOs) methodology developed in refs 18 and 19. The S_0 (1^1A_{1g}), T_1(1^3B_{1u}), and S_1 (1^1B_{2u}) states of D_{6h} benzene were described using π-space CASSCF wavefunctions with "6 electrons in 6 orbitals" [CASSCF(6,6)]. For the S_0 (1^1B_{1g}), T_1 (1^3A_{2g}), S_1 (1^1A_{1g}), and S_2 (1^1B_{2g}) states of square (D_{4h}) cyclobutadiene and the S_0 (1^1A_g), T_1 (1^3B_{1g}), S_1 (2^1A_g), and S_2 (1^1B_{1g}) states of rectangular (D_{2h}) cyclobutadiene use was made of π-space CASSCF wavefunctions with "4 electrons in 4 orbitals" [CASSCF(4,4)]. The HF-GIAO, UHF-GIAO, and MP2-GIAO results were obtained with GAUSSIAN03.[20] The basis set used throughout this work was 6-311++G(2d,2p).

The calculations on benzene were carried out at the experimental D_{6h} gas-phase ground-state geometry established through analysis of the ν_4 vibration−rotation bands of C_6H_6 and C_6D_6,[21] with C−C and C−H bond lengths of 1.3964 and 1.0831 Å, respectively. For square and rectangular cyclobutadiene use was made of the optimized geometries obtained by means of multireference averaged quadratic coupled cluster (MR-AQCC) calculations employing orbitals coming from state-averaged π -space CASSCF(4,4) wavefunctions including S_0, T_1, S_1, and S_2 (SA-4-CASSCF), within the cc-pVTZ basis.[10] At this level of theory, square D_{4h} cyclobutadiene, which can be viewed as the transition structure in the ground-state automerization reaction connecting the two equivalent D_{2h} rectangular structures, is characterized by C−C and C−H bond lengths of 1.447 and 1.076 Å, respectively. The MR-AQCC/SA-4-CASSCF/cc-pVTZ geometry reported for D_{2h} rectangular cyclobutadiene exhibits C−C bond lengths of 1.349 and 1.562 Å, a C−H bond length of 1.077 Å, and a H−C−C bond angle of 134.9° (with the longer C−C bond). According to ref 10, the optimized geometries remain the same within a larger aug′-cc-pVTZ basis (which omits the carbon *f* and hydrogen *d* functions from the standard aug-cc-pVTZ specification). As a consequence of the employment of ground-state geometries for the excited states, the results of the current work can be considered to account for the effects of vertical excitations.

As the S_1 (2^1A_g) state of rectangular cyclobutadiene has the same symmetry as the ground state S_0 (1^1A_g), its wavefunction was calculated by instructing the CASSCF procedure to use the second configuration interaction (CI) root.

The range of NICS indices reported in this paper includes Schleyer's original NICS(0)$_{iso}$ (isotropic shielding with reversed sign, $-\sigma_{iso}$, calculated in the center of the ring),[3] NICS(1)$_{iso}$ ($-\sigma_{iso}$ calculated 1 Å above the ring center),[22,23] NICS(0)$_{zz}$ (the out-of-plane component of the shielding tensor with reversed sign, $-\sigma_{zz}$, calculated in the center of the ring)[24,25] and NICS(1)$_{zz}$ ($-\sigma_{zz}$ calculated 1 Å above the ring center).[26] No "dissected" NICS indices (see ref 26) have been calculated, as this is not currently possible within the main approach used in this work, CASSCF-GIAO. In principle, the MC individual gauge for localized orbitals (MC-IGLO) method of van Wüllen and

TABLE 1: Energies of the S_0, T_1, and S_1 States of Benzene and the S_0, T_1, S_1, and S_2 States of Cyclobutadiene and Vertical Excitation Energies from the Current Work (ΔE) and the Literature ($\Delta E_{\mathrm{lit.}}$)[a]

molecule	state	method	energy (au)	ΔE (eV)	$\Delta E_{\mathrm{lit.}}$ (eV)
C_6H_6 (D_{6h})	S_0 (1^1A_{1g})	HF	−230.766 572	-	-
		MP2[b]	−231.760 795	-	-
		CASSCF	−230.838 459	0.00	-
	T_1 (1^3B_{1u})	CASSCF	−230.696 661	3.86	3.95[c]/3.85[d]
	S_1 (1^1B_{2u})	CASSCF	−230.656 017	4.96	4.90[e]/4.94[d]
C_4H_4 (D_{4h})	S_0 (1^1B_{1g})	CASSCF	−153.740 906	0.00	-
	T_1 (1^3A_{2g})	UHF	−153.694 926	-	-
		CASSCF	−153.724 602	0.44	0.55[f]/0.23[g]
	S_1 (1^1A_{1g})	CASSCF	−153.658 522	2.24	2.42[f]/1.33[g]
	S_2 (1^1B_{2g})	CASSCF	−153.613 040	3.48	4.14[f]/1.80[g]
C_4H_4 (D_{2h})	S_0 (1^1A_g)	HF	−153.685 831	-	-
		MP2[b]	−154.347 164	-	-
		CASSCF	−153.752 529	0.00	-
	T_1 (1^3B_{1g})	UHF	−153.661 046	-	-
		CASSCF	−153.692 048	2.74	~1.5[h]
	S_1 (2^1A_g)	CASSCF	−153.591 373	4.38	~4.0[h]
	S_2 (1^1B_{1g})	CASSCF	−153.581 218	4.66	~3.3[h]

[a] For further details, see text. [b] MP2(Full) results. [c] Electron-impact spectroscopy from ref 33. [d] SCVB theory.[12] [e] Electron-impact spectroscopy from ref 34. [f] CASSCF(4,4)/6-31G.[32] [g] MR-AQCC/SA-4-CASSCF/aug′-cc-pVTZ, S_0, T_1, and S_1 at their optimized geometries.[10] [h] MR-AQCC/SA-4-CASSCF/aug-pVTZ differences at the S_0 geometry from Figure 2 in ref 10.

Kutzelnigg[27,28] should be capable of computing dissected NICS values for the S_0, T_1, and S_1 states of benzene and the S_0, T_1, S_1, and S_2 states of cyclobutadiene, but its code is not available at this moment in free or commercial form. The conclusion of an extensive comparison of the performance of various NICS indices calculated using density functional theory (DFT, PW91-IGLO/IGLO-III)[26] was that while the most reliable index was of the "dissected" type, NICS(0)$_{\pi zz}$ [the π-orbital contribution to NICS(0)$_{zz}$], NICS(1)$_{zz}$ was not far behind.

In line with previous work on NICS[2] and ring currents[4] in triplet systems, the CASSCF-GIAO and UHF-GIAO magnetic properties of the T_1 states of benzene and cyclobutadiene computed in this paper include the contributions arising from the perturbation to the wavefunction only (these are often referred to as "orbital" contributions in single-reference approaches). The omission of the large terms associated with the interaction of the electronic spin angular momentum and the magnetic field[29,30] means that the reported numbers will exhibit considerable differences from experimental measurements when and if these become available. On the other hand, this makes the values reported for triplet states directly comparable to those for singlet states.

3. Results and Discussion

The energies of the various wavefunctions for the S_0, T_1, and S_1 states of benzene and the S_0, T_1, S_1, and S_2 states of cyclobutadiene computed in this paper are shown in Table 1. As expected from the work of other authors (see, e.g., ref 31), the CASSCF(6,6)/6-311++G(2d,2p) $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ vertical excitation energies of benzene agree very well with experimental data and higher-level theoretical estimates. In the case of square cyclobutadiene, the CASSCF(4,4)/6-311++G(2d,2p) $T_1 \leftarrow S_0$, $S_1 \leftarrow S_0$, and $S_2 \leftarrow S_0$ vertical excitation energies show some improvement over the CASSCF(4,4)/6-31G results[32] but remain somewhat higher than the more accurate MR-AQCC/SA-4-CASSCF/aug′-cc-pVTZ values.[10] The reason for this is in the limited sizes of the singlet and triplet "4 in 4" active spaces which are comprised of just 20 and, respectively, 15 configuration state functions (CSFs), before any use of spatial symmetry. A similar situation is observed for rectangular cyclobutadiene, with one additional detail: While the current CASSCF(4,4)/6-311++G(2d,2p) calculations indicate that the S_1 state is 2^1A_g, at higher levels of theory the lowest singlet excited state switches to 1^1B_{1g}.[9,10]

The UHF calculations on the lowest triplet states of square and rectangular cyclobutadiene employed $M = 1$ wave functions; in both cases the spin contamination was observed to be close to insignificant ($\langle \hat{S}^2 \rangle$ values of 2.0177 and 2.0179, respectively). In addition to the HF and UHF wavefunctions reported in Table 1, it is possible to obtain a closed-shell HF wavefunction for square cyclobutadiene and a UHF ($M = 1$) wavefunction for triplet benzene. However, both of these exhibit D_{2h} symmetry and correspond to "broken-symmetry" solutions.

Each of the CASSCF-GIAO NICS(0), NICS(1), and NICS(1)$_{zz}$ values for the ground state of square cyclobutadiene is approximately two times larger than the corresponding value for rectangular cyclobutadiene (see Table 2). In the case of NICS(0)$_{zz}$ the increase is smaller but still substantial. This clearly shows that the ground state of square cyclobutadiene is significantly more antiaromatic than that of rectangular cyclobutadiene. While the increase of the antiaromaticity of the ground state of cyclobutadiene on passing from the rectangular to the square geometry is not unexpected, the magnitudes of the differences between the CASSCF-GIAO NICS values calculated at the two geometries come as a surprise. The numbers suggest that the difference between the S_0 aromaticities of square and rectangular cyclobutadiene is not much smaller than the difference between the S_0 aromaticities of rectangular cyclobutadiene and benzene. For example, the S_0 NICS(1)$_{zz}$ values for square and rectangular cyclobutadiene differ by ca. 49 ppm, while those for rectangular cyclobutadiene and benzene are ca. 67 ppm apart.

The ground-state HF-GIAO, MP2-GIAO, and CASSCF-GIAO NICS values for benzene are reasonably similar and suggest that the introduction of electron correlation effects leads to a relatively minor decrease of the ground-state aromaticity. Dynamic correlation (included in the MP2 construction) affects the value of NICS(0) more than nondynamic correlation (included in the CASSCF wavefunction); all other NICS indices are influenced to a greater extent by the inclusion of nondynamic

TABLE 2: NICS Values for the S_0, T_1, and S_1 States of Benzene and the S_0, T_1, S_1, and S_2 States of Cyclobutadiene (ppm)[a]

molecule	state	method	NICS(0)	NICS(1)	NICS(0)$_{zz}$	NICS(1)$_{zz}$
C_6H_6 (D_{6h})	S_0 (1^1A_{1g})	HF	−9.35	−10.83	−17.45	−32.45
		MP2	−7.60	−9.97	−15.56	−30.39
		CASSCF	−8.17	−9.53	−12.21	−27.83
	T_1 (1^3B_{1u})	CASSCF	39.63	30.10	130.54	90.61
	S_1 (1^1B_{2u})	CASSCF	45.81	34.67	145.90	102.76
C_4H_4 (D_{4h})	S_0 (1^1B_{1g})	CASSCF	36.41	28.23	145.91	88.14
	T_1 (1^3A_{2g})	UHF	−5.48	−7.95	20.50	−19.87
		CASSCF	−3.74	−6.54	24.26	−16.47
	S_1 (1^1A_{1g})	CASSCF	3.44	−4.28	24.61	−16.38
	S_2 (1^1B_{2g})	CASSCF	22.10	12.86	77.09	31.24
C_4H_4 (D_{2h})	S_0 (1^1A_g)	HF	31.46	22.72	124.46	68.78
		MP2	29.94	19.81	120.72	61.22
		CASSCF	18.42	12.33	91.55	39.27
	T_1 (1^3B_{1g})	UHF	−2.91	−6.85	27.16	−16.85
		CASSCF	−1.20	−5.41	31.11	−13.26
	S_1 (2^1A_g)	CASSCF	68.55	50.05	214.60	144.08
	S_2 (1^1B_{1g})	CASSCF	17.26	7.44	59.45	12.94

[a] For further details, see text.

correlation. The S_0 HF-GIAO, MP2-GIAO, and CASSCF-GIAO NICS(0) and NICS(0)$_{zz}$ values for benzene obtained in the current work (see Table 2) are in very good agreement with those reported by Jensen et al.[35] who used a modified version of the standard cc-pVTZ basis in which the *f* functions on carbon and the *d* functions on hydrogen were omitted.

The comparison of the ground-state HF-GIAO, MP2-GIAO, and CASSCF-GIAO NICS values for rectangular cyclobutadiene shows that its S_0 antiaromaticity is significantly overestimated at the HF and MP2 levels of theory. This clearly demonstrates that the single-reference closed-shell HF wavefunction for cyclobutadiene remains markedly inferior to the π-space CASSCF(4,4) wavefunction even at a D_{2h} geometry with well-defined carbon−carbon "single" and "double" bonds and that the inclusion of dynamic correlation through the MP2 construction is unable to compensate for its deficiencies, at least so far as magnetic properties are concerned.

If one takes into account the ranges of variation of the NICS indices included in Table 2, it becomes obvious that all CASSCF-GIAO NICS values for the T_1 and S_1 states of benzene are reasonably close to their counterparts for the S_0 state of square cyclobutadiene. This is a strong indication that the T_1 and S_1 states of benzene are antiaromatic. The magnitudes of the NICS indices suggest that the higher-energy state S_1, despite its preference for a geometry of D_{6h} symmetry, is a little more antiaromatic than T_1.

Interestingly, the evidence for the better-studied aromaticity of the T_1 state of square cyclobutadiene[2,4] provided by the NICS values in Table 2 is not as emphatic as that for the antiaromaticity of the T_1 and S_1 states of benzene. Just as in the case of the S_0 state of benzene, the introduction of additional nondynamic correlation is observed to make the T_1 state of square cyclobutadiene less aromatic (compare the UHF-GIAO and CASSCF-GIAO results). The positive NICS(0)$_{zz}$ values should not be viewed as an indication that this index fails to recognize the aromaticity of the system, as the CASSCF-GIAO NICS(0)$_{zz}$ values for the ground states of benzene and square cyclobutadiene are well apart, at −12.21 and 145.91 ppm, respectively, and the NICS(0)$_{zz}$ values for the lowest triplet state of square cyclobutadiene are obviously much closer to the aromatic end of this range.

At the rectangular geometry, the T_1 state of cyclobutadiene becomes less aromatic than at the square geometry. This finding is consistent with the existing computational evidence that the equilibrium geometry of the T_1 state of cyclobutadiene exhibits D_{4h} symmetry.[9,10] While the reduction of the magnitude of the T_1 CASSCF-GIAO NICS(0) on passing from the square to the rectangular geometry is more than 3-fold, the smaller changes in the other three NICS indices suggest that the decrease in aromaticity is not that dramatic.

In the case of the S_1 state of square cyclobutadiene, two of the CASSCF-GIAO NICS indices, NICS(0)$_{zz}$ and NICS(1)$_{zz}$, are almost the same as the corresponding indices for the T_1 state of this molecule, while the S_1 NICS(1) amounts to ca. 65% of the T_1 value. The S_1 NICS(0) value (3.44 ppm) is positive, but significantly closer to the benzene ground-state NICS(0) (−8.17 ppm) than to the S_0 NICS(0) (36.41 ppm). These observations indicate that the S_1 state of square cyclobutadiene has some aromatic character which, however, is less pronounced than that of the T_1 state. The CASSCF-GIAO NICS values for the S_2 state of square cyclobutadiene imply that this state is antiaromatic, to a similar extent as the ground-state of rectangular cyclobutadiene. Thus, the S_2 state of square cyclobutadiene provides another example of a system which prefers a bond-equalized geometry but exhibits an antiaromatic set of NICS indices.

According to its NICS values, at the rectangular geometry the S_1 state of cyclobutadiene should be even more antiaromatic than the ground-state at the square geometry. While initially this might seem implausible, high-level calculations[9,10] have shown that the energy of the S_1 state increases much faster with the introduction of bond alternation than the energies of the T_1 and S_2 states. As a consequence, the S_1 state should be very unstable at the rectangular geometry and the antiaromatic NICS values may be one manifestation of this instability. Having in mind the ranges of variation of the NICS indices included in Table 2, at the rectangular geometry the S_2 state can be classified as nonaromatic or slightly antiaromatic.

The carbon and proton shieldings and the magnetic susceptibilities for the S_0, T_1, and S_1 states of benzene and the S_0, T_1, S_1, and S_2 states of cyclobutadiene computed in this paper are shown in Table 3. This table includes isotropic shieldings, $\sigma_{iso} = (1/3)(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, out-of-plane shielding tensor components, σ_{zz}, isotropic magnetic susceptibilities, $\chi_{iso} = (1/3)(\chi_{xx} + \chi_{yy} + \chi_{zz})$, and out-of-plane components of the magnetic susceptibility tensor, χ_{zz}. While Table 3 does not contain

TABLE 3: Carbon and Proton Shieldings (ppm) and Magnetic Susceptibilities (ppm cm^3 mol^{-1}) for the S_0, T_1, and S_1 States of Benzene and the S_0, T_1, S_1, and S_2 States of Cyclobutadiene[a]

molecule	state	method	$\sigma_{iso}(^{13}C)$	$\sigma_{zz}(^{13}C)$	$\sigma_{iso}(^{1}H)$	$\sigma_{zz}(^{1}H)$	χ_{iso}	χ_{zz}
C_6H_6 (D_{6h})	S_0 (1^1A_{1g})	HF	57.76	187.96	24.20	20.62	−60.58	−106.27
		MP2	67.37	187.52	23.92	20.47	-	-
		CASSCF	73.52	186.58	24.90	21.07	−59.33	−99.67
	T_1 (1^3B_{1u})	CASSCF	81.89	145.31	29.31	32.20	−6.16	56.93
	S_1 (1^1B_{2u})	CASSCF	78.69	139.92	29.54	33.28	2.43	78.97
C_4H_4 (D_{4h})	S_0 (1^1B_{1g})	CASSCF	68.24	124.97	27.60	30.34	−12.20	12.88
	T_1 (1^3A_{2g})	UHF	55.67	160.04	24.42	24.04	−32.20	−50.90
		CASSCF	71.75	159.29	25.15	24.27	−32.16	−48.42
	S_1 (1^1A_{1g})	CASSCF	54.80	158.66	23.96	24.27	−28.78	−48.80
	S_2 (1^1B_{2g})	CASSCF	15.85	143.84	22.88	26.44	−17.43	−24.19
C_4H_4 (D_{2h})	S_0 (1^1A_g)	HF	42.17	123.76	26.11	28.87	−14.28	2.81
		MP2	58.59	121.90	26.30	28.41	-	-
		CASSCF	71.19	133.49	26.70	27.46	−21.76	−13.85
	T_1 (1^3B_{1g})	UHF	45.77	150.60	23.90	24.12	−29.96	−47.37
		CASSCF	65.42	149.88	24.87	24.37	−30.32	−44.68
	S_1 (2^1A_g)	CASSCF	27.73	94.97	26.09	33.31	7.54	51.51
	S_2 (1^1B_{1g})	CASSCF	5.58	140.69	21.59	25.30	−17.26	−32.38

[a] For further details, see text.

shielding and magnetic susceptibility anisotropies, the $\Delta\sigma$ and $\Delta\chi$ values corresponding to the definitions which are most useful when discussing the aromaticities of planar ring systems, $\Delta\sigma = \sigma_{zz} - (1/2)(\sigma_{xx} + \sigma_{yy})$ and $\Delta\chi = \chi_{zz} - (1/2)(\chi_{xx} + \chi_{yy})$, can be calculated readily, if required, through the expressions $\Delta\sigma = (3/2)(\sigma_{zz} - \sigma_{iso})$ and $\Delta\chi = (3/2)(\chi_{zz} - \chi_{iso})$. The $\sigma_{iso}(^{13}C)$, $\sigma_{zz}(^{13}C)$, $\sigma_{iso}(^{1}H)$, $\sigma_{zz}(^{1}H)$, and χ_{iso} values for the ground states of square and rectangular cyclobutadiene obtained in the current work are in very good agreement with the HF-IGLO and MC-IGLO results reported by van Wüllen and Kutzelnigg.[27]

The carbon isotropic shielding $\sigma_{iso}(^{13}C)$ is the only quantity included in Table 3 which does not carry information about the aromatic properties of the different electronic states of benzene and cyclobutadiene. However, the $\sigma_{iso}(^{13}C)$ values obtained in the current work are of considerable interest for other reasons. The first of these is associated with the significant increases of the carbon isotropic shieldings upon inclusion of electron correlation effects. The MP2-GIAO and CASSCF-GIAO $\sigma_{iso}(^{13}C)$ values for the ground state of benzene were found to be ca. 10 and ca. 16 ppm, respectively, above the HF-GIAO result. Surprisingly, the theoretical value which is in best agreement with the experimental absolute ^{13}C shielding in gas-phase benzene, 57.2 ppm (300 K, extrapolated to zero pressure),[36] is the one obtained at the HF-GIAO level of theory. The basis set used in the current work is sufficiently large, and it is unlikely that extrapolation to the basis set limit will introduce any significant changes in the data reported in Table 3. The series of HF, MP2, CCSD (coupled-cluster with singles and doubles), and CCSD(T) (CCSD including a perturbative treatment of triple excitations) GIAO calculations on ethene (C_2H_4) and ethyne (C_2H_2) carried out by Auer et al.[37] indicate that at the CCSD(T) level of theory the carbons in unsaturated hydrocarbons are even more shielded than at the MP2 level of theory. Thus, further improvement of the wavefunction is unlikely to bring the theoretical $\sigma_{iso}(^{13}C)$ value for the ground state of benzene below the MP2 level. The discrepancy between experiment and theory can be reduced but not completely eliminated by taking into account the zero-point vibrational correction to the ^{13}C shielding constant as, according to the results of Auer et al.,[37] this correction can be expected to be in the region of −0.5 to −4.5 ppm. Having in mind the existing computational evidence, it seems reasonable to allow for the possibility that the ^{13}C shielding for benzene on the absolute ^{13}C shielding scale[36] may be at least 5 ppm too low.

The separations between the ^{13}C isotropic shieldings in the ground state of rectangular cyclobutadiene calculated at the HF-GIAO, MP2-GIAO, and CASSCF-GIAO levels of theory are considerably larger than in benzene. This is another indication of the already mentioned insufficiently good quality of the closed-shell HF wavefunction, the impact of which can be also noticed in the MP2 results. The tendency of the CASSCF-GIAO approach to predict higher ^{13}C isotropic shieldings is continued in the lowest triplet states of square and rectangular cyclobutadiene in which the CASSCF-GIAO $\sigma_{iso}(^{13}C)$ values lie ca. 16 and ca. 20 ppm, respectively, above their UHF-GIAO counterparts.

Another interesting aspect of the ^{13}C and ^{1}H isotropic shieldings included in Table 3 is the extent to which these quantities are affected by electronic excitation. A HF-level study of the electronic excitation effects on NMR shieldings carried out by Augspurger and Dykstra,[38] in which the excited-state energies were approximated by adding molecular orbital energy differences to the HF ground-state energy, reached the conclusion that the single electron promotion from one of the higher-energy occupied orbitals to one of the lower-energy unoccupied orbitals could change the ^{13}C shieldings by −10 to 31 ppm, and the proton shieldings by less than 1 ppm. The results of the current work show that while the carbon nuclei in an excited state of an unsaturated hydrocarbon can be more shielded than in the ground state, any increase in the ^{13}C isotropic shielding is likely to be more modest—the largest increase observed in Table 3, between the S_0 and T_1 states of benzene, is less than 9 ppm. As demonstrated by the $\sigma_{iso}(^{13}C)$ values for cyclobutadiene included in Table 3, the carbon nuclei in higher excited states of unsaturated hydrocarbons can become significantly deshielded.

The influence of electronic excitation on the ^{1}H isotropic shieldings in benzene and cyclobutadiene is much more profound than anticipated by Augspurger and Dykstra,[38] but this is largely due to the associated changes in aromaticity. In line with the expected switch from an aromatic to an antiaromatic system, the proton shieldings in benzene increase by more than 4 ppm on passing from the ground state S_0 to the lowest triplet state T_1 or the first excited state S_1. Changes in the opposite direction, but on a smaller scale, are observed when passing from the S_0 state to the T_1 or S_1 state in square cyclobutadiene, and from the S_0 state to the T_1 state in rectangular cyclobutadiene. The higher $\sigma_{iso}(^1H)$ value observed in the S_1 state of rectangular cyclobutadiene can be viewed as a confirmation of its antiaromaticity. The low ^1H isotropic shieldings in the S_2 states of square and rectangular cyclobutadiene parallel the low $\sigma_{iso}(^{13}C)$ values and reflect an overall excited-state nuclear deshielding rather than aromatic character. In contrast to the ^{13}C isotropic shieldings, the inclusion of electron correlation effects leads to relatively minor changes (under 1 ppm) in the $\sigma_{iso}(^1H)$ values.

The out-of-plane components of the ^{13}C shielding tensors for the various electronic states of benzene and cyclobutadiene fall into two distinct groups which largely coincide with the aromaticity classification suggested by the NICS indices. The "aromatic" CASSCF-GIAO $\sigma_{zz}(^{13}C)$ values are systematically higher than the "antiaromatic" ones, and the only case which shows a discrepancy with the NICS-based predictions is that of the S_2 state of rectangular cyclobutadiene, for which the out-of-plane component of the ^{13}C shielding tensor implies antiaromatic, rather than nonaromatic, character. The out-of-plane components of the ^1H shielding tensors offer an even clearer distinction between electronic states that can be deemed to be aromatic or antiaromatic. Once again, there are two well-separated groups of values, but this time around the aromatic CASSCF-GIAO $\sigma_{zz}(^1H)$ values are systematically lower than the antiaromatic ones. There is no problem with the S_2 state of rectangular cyclobutadiene, as its $\sigma_{zz}(^1H)$ value of 25.30 ppm is right between the aromatic and antiaromatic ranges. The out-of-plane component of a nuclear shielding tensor which is most significantly affected by the inclusion of electron correlation effects is $\sigma_{zz}(^{13}C)$ in the ground state of rectangular cyclobutadiene, for which the CASSCF-GIAO value is considerably larger than its HF-GIAO and MP2-GIAO counterparts.

The CASSCF-GIAO χ_{iso} and χ_{zz} values for benzene obtained in the current work are in very good agreement with the experimental data reported by Schmalz et al., $(1/2)(\chi_{xx} + \chi_{yy}) = -34.9 \pm 2.0$ and $\chi_{zz} = -94.9 \pm 2.5$, which combine to give $\chi_{iso} = -54.9 \pm 1.5$ (all in ppm cm^3 mol^{-1}). The HF-GIAO χ_{iso} and χ_{zz} values for benzene from Table 3 almost coincide with the "near-Hartree−Fock-limit" HF-IGLO results of Fleischer et al.[39] of −60.7 and −106.7 ppm cm^3 mol^{-1}, respectively, which vindicates the decision to use the 6-311++G(2d,2p) basis in all calculations of magnetic properties reported in this paper and provides an example of the near-equivalence of the IGLO and GIAO approaches. One interesting observation is that while nondynamic electron correlation has relatively little effect on the isotropic (or average) magnetic susceptibility of benzene, it is essential for proper evaluation of the out-of-plane component of the magnetic susceptibility tensor. As expected, there are also considerable differences between the χ_{iso} and χ_{zz} values for the ground state of rectangular cyclobutadiene calculated at the HF-GIAO and CASSCF-GIAO levels of theory. The χ_{iso} and χ_{zz} values included in Table 3 allow an unambiguous differentiation between the aromatic, antiaromatic, and nonaromatic electronic states of benzene and cyclobutadiene, which is in complete agreement with the NICS-based classification. The large range of variation of the out-of-plane component of the magnetic susceptibility tensor suggests that this quantity, which is closely related to the exaltation of the isotropic magnetic susceptibility (see, e.g., ref 39), can be viewed as one of the most sensitive aromaticity indices.

4. Conclusions

The magnetic properties of the low-lying electronic states of benzene and cyclobutadiene studied in this paper strongly suggest that the lowest triplet state and the first singlet excited state of benzene are antiaromatic, the lowest triplet state and the first singlet excited-state of square cyclobutadiene are aromatic, the lowest triplet state of rectangular cyclobutadiene is aromatic, the second singlet excited state of square cyclobutadiene and the first singlet excited state of rectangular cyclobutadiene are antiaromatic and, finally, the second singlet excited state of rectangular cyclobutadiene is nonaromatic. These findings have very interesting implications for the theory of pericyclic reactions as, according to them, in concerted pericyclic reactions which would involve a cyclobutadiene-like transition state (TS), this TS can be expected to experience antiaromatic destabilization in thermal conditions and aromatic stabilization in photochemical conditions, while, in concerted reactions which would involve a benzene-like TS, this TS can be expected to experience aromatic stabilization in thermal conditions and antiaromatic destabilization in photochemical conditions. As a consequence, the current results about the aromaticity and antiaromaticity of the low-lying electronic states of benzene and cyclobutadiene can be considered to provide a reasonably rigorous CASSCF-level vindication of the most important subset of the Woodward−Hoffmann rules.

The changes in the magnetic properties of benzene and cyclobutadiene upon electronic excitation indicate that aromaticity is mainly a ground-state phenomenon, which is less well-expressed in low-lying excited states and is unlikely to be detectable in higher excited states. Antiaromaticity does not seem to "decrease" in a similar way upon electronic excitation, but this is most likely a consequence of the presence of various additional destabilizing factors within the wavefunctions of higher excited states.

Despite the fact that the isotropic nuclear shieldings may increase in some low-lying excited states, in general electronic excitation should be expected to result in deshielding of all nuclei, which can be to a significant extent for heavier nuclei.

The inclusion of nondynamic electron correlation effects through an appropriate CASSCF or MCSCF wavefunction is essential for a balanced analysis of the aromaticity or antiaromaticity of cyclic conjugated hydrocarbons through their magnetic properties. While there are certain magnetic properties of the ground and lowest triplet states of benzene and cyclobutadiene which are described reasonably well at the HF and UHF levels of theory, to assume that these would be equally well-described at the same levels of theory in other molecules, and especially in antiaromatic systems, would be pure guesswork.

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