Aromaticity and Antiaromaticity in the Low-Lying Electronic States of Cyclooctatetraene

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The levels of aromaticity of the most important geometries on the ground-state (S_0), lowest triplet-state (T_1), and first singlet excited-state (S_1) potential energy surfaces (PESs) for cycloocta-1,3,5,7-tetraene (COT) are assessed using a wide range of magnetic criteria including nucleus-independent chemical shifts (NICSs), proton shieldings, and magnetic susceptibilities calculated using complete-active-space self-consistent-field (CASSCF) wave functions constructed from gauge-including atomic orbitals (GIAOs). It is shown that the ground state of D_{8h} COT (transition state for the π-bond-shift process on the S_0 PES) is markedly antiaromatic, even more so than the classical example of an antiaromatic system, the ground state of square cyclobutadiene. The CASSCF-GIAO magnetic properties of the ground state of D_{4h} COT (transition state for the ring-inversion process on the S_0 PES) strongly suggest that it is much less antiaromatic than the ground state of D_{8h} COT, whereas those of the ground state of D_{2d} COT (local minimum on the S_0 PES) indicate that it is decidedly nonaromatic. The lowest triplet state and the first singlet excited state of D_{8h} COT (local minima on the T_1 PES and the S_1 PES, respectively) exhibit surprisingly similar magnetic properties. These, in turn, are very close to the magnetic properties of benzene, which is a strong indication of a high degree of aromaticity.

1. Introduction

In contrast to the prediction of elementary Hückel molecular orbital (HMO) theory, cycloocta-1,3,5,7-tetraene (COT), a $4n$ π-electron system with $n = 2$, is not antiaromatic but rather nonaromatic, as it adopts a nonplanar tub-shaped geometry of D_{2d} symmetry that involves four equivalent largely noninteracting olefinic π bonds. However, the ring-inversion and π-bond-shift processes on the ground-state (S_0) potential energy surface (PES) of COT have been shown to pass through planar transition states of D_{4h} and D_{8h} symmetry (see ref 1 and references therein), which create better opportunities for π-electron conjugation and possible antiaromatic behavior. A modern valence-bond (VB) study of the electronic structure of COT,[2] which made use of spin-coupled (SC) theory, concluded that the presence of singlet biradical character within the π-space SC wave function for COT at its D_{8h} geometry on the ground-state PES was an indication of antiaromaticity, whereas the absence of resonance within the SC wave functions at the D_{4h} and D_{2d} geometries was considered to imply nonaromatic behavior. Whereas the most popular magnetic aromaticity probe, Schleyer's nucleus-independent chemical shift (NICS),[3] indicates that D_{2d} COT is, indeed, nonaromatic,[4] the NICS values for D_{4h} COT suggest that it is markedly antiaromatic, even more so than rectangular (D_{2h}-symmetry) cyclobutadiene.[3] The current NICS-based picture of the ground-state aromaticity of COT is incomplete, as there are no results for the D_{8h} geometry, at which the antiaromaticity of the system should manifest itself to the fullest extent. The reason behind this omission is that, as a rule, NICS values are calculated using single-determinant Hartree–Fock (HF) or density functional theory (DFT) wave functions, whereas D_{8h} COT, the ground state of which is an open-shell singlet (see, e.g., ref 1), requires at least a two-determinant wave function. (Although it is possible to obtain a closed-shell single-determinant wave function for D_{8h} COT, it would have only D_{4h} symmetry, which is lower than that of the nuclear framework.)

One of the aims of this work is to highlight the differences between the aromaticities of the D_{8h}, D_{4h}, and D_{2d} geometries on the ground-state PES of COT through the use of a range of magnetic criteria including NICS values, proton shieldings, and magnetic susceptibilities calculated using complete-active-space self-consistent-field (CASSCF) wave functions constructed from gauge-including atomic orbitals (GIAOs).

The importance of nondynamic correlation effects, which are included in the CASSCF wave function, for the proper description of the magnetic properties of antiaromatic systems was recently demonstrated on the example of cyclobutadiene.[5] It was found that, at the lowest-energy rectangular ground-state geometry (D_{2h} symmetry), the HF-GIAO level of theory overestimated the NICS(0) value by more than 70% in comparison to the CASSCF-GIAO result and that the CASSCF-GIAO-level NICS(0) value for square (D_{4h}) C_4H_4 was approximately twice that for rectangular (D_{2h}) C_4H_4, which is an indication of the sharp decline in the antiaromaticity of the system on passing from the square to the rectangular geometry. The results of the current work show that the use of CASSCF wave functions is equally important for obtaining reliable theoretical estimates of the magnetic properties of COT.

The first piece of evidence suggesting that the lowest triplet state (T_1) of COT is aromatic was provided by its Dewar resonance energy, which was calculated by Baird in his pioneering work on triplet aromaticity.[6] The unrestricted DFT (UB3LYP/6-311+G**) geometry optimization of the T_1 state of COT carried out by Gogonea et al.[4] produced a structure of D_{8h} symmetry with a C–C bond length close to that in benzene. The NICS, proton chemical shift, magnetic susceptibility, and magnetic susceptibility exaltation of the lowest triplet state of COT reported by these authors are also entirely consistent with aromatic behavior.

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The CASSCF/6-31G* geometry of the first singlet excited state (S_1) of COT obtained by Garavelli et al.[7] has much in common with that of the lowest triplet state: It exhibits D_{8h} symmetry, and once again, the C—C bond length is reasonably close to that in benzene. Garavelli and co-workers attributed the planarization of the S_1 state of COT to "a kind of aromatic effect", but so far, the possibility that this state might be aromatic has not been investigated using magnetic criteria.

Recent analyses of the aromaticities of the low-lying electronic states of benzene and cyclobutadiene utilizing NICS values, proton shieldings, and magnetic susceptibilities calculated at the CASSCF-GIAO level of theory concluded that the T_1 and S_1 states of D_{6h} benzene are antiaromatic, whereas the T_1 and S_1 states of D_{4h} cyclobutadiene are aromatic.[5] In the present work, these magnetic criteria are employed to deduce the aromaticities of the lowest triplet state and the first singlet excited state of COT. Wherever appropriate, the CASSCF-GIAO results are compared to results obtained using the HF-GIAO and MP2-GIAO (second-order Møller−Plesset perturbation theory with GIAOs) approaches.

The same set of magnetic criteria are used to probe the possibility that, as implied by a set of ring-current-based rules formulated by Soncini and Fowler,[8] in addition to the lowest triplet state of D_{8h} COT (total spin $S = 1$), the lowest septet state of this system, which corresponds to the next odd total spin value, $S = 3$, might also be aromatic.

2. Computational Procedure

The CASSCF wave functions for COT utilized in this work incorporate active spaces with "eight electrons in eight orbitals" [CASSCF(8,8)]. The S_0, T_1, and S_1 states of D_{8h} COT were formed from the π-orbital configuration $(a_{2u})^2(e_{1g})^4(e_{2u})^2$ (the remaining active π orbitals were a doubly degenerate e_{3g} orbital and a b_{2u} orbital). The symmetries of the singlet and triplet states associated with the direct product $e_{2u} \times e_{2u}$ are determined by the compositions of its symmetric part $[e_{2u} \times e_{2u}]$ and antisymmetric part $\{e_{2u} \times e_{2u}\}$ ($e_{2u} \times e_{2u} = [e_{2u} \times e_{2u}] + \{e_{2u} \times e_{2u}\}$), which are given by $[e_{2u} \times e_{2u}] = a_{1g} + b_{1g} + b_{2g}$ and $\{e_{2u} \times e_{2u}\} = a_{2g}$[9] (for details of the procedure that can be used to calculate the characters of the symmetric and antisymmetric components of a direct product, see refs 10−12). Thus, $e_{2u} \times e_{2u}$ gives rise to three singlet states, $^1A_{1g}$, $^1B_{1g}$, and $^1B_{2g}$, and one triplet state, $^3A_{2g}$. Although some authors label the lowest triplet state of D_{8h} COT as $^3A_{2u}$ (see, e.g., refs 1, 4, and 13), it is clear that the $(a_{2u})^2(e_{1g})^4(e_{2u})^2$ configuration does not include a state of A_{2u} symmetry. For the lowest septet state of D_{8h} COT, use was made of the "doubly excited" π-orbital configuration $(a_{2u})^2(e_{1g})^2(e_{2u})^2(e_{3g})^2$ (the remaining active-space π orbital was a b_{2u} orbital). As $\{e_{1g} \times e_{1g}\} = \{e_{2u} \times e_{2u}\} = \{e_{3g} \times e_{3g}\} = a_{2g}$, the associated septet state is $^7A_{2g}$. The construction of the other required CASSCF(8,8) wave functions, for the S_0 states of D_{4h} and D_{2d} COT, followed the usual, rather straightforward recipe.

The geometries of the 1^1B_{1g} state of D_{8h} COT (transition state for the π-bond-shift process on the S_0 PES), the 1^1A_{1g} state of D_{4h} COT (transition state for the ring-inversion process on the S_0 PES), the 1^1A_1 state of D_{2d} COT (local minimum on the S_0 PES), the 1^3A_{2g} state of D_{8h} COT (local minimum on the T_1 PES), the 1^1A_{1g} state of D_{8h} COT (local minimum on the S_1 PES), and the 1^7A_{2g} state of D_{8h} COT (saddle point on the lowest septet-state PES) were optimized at the CASSCF(8,8)/6-31G** level of theory. The geometry of the lowest septet state of D_{8h} COT was also optimized using the restricted high-spin open-shell HF (ROHF) and unrestricted HF (UHF) wave functions within the 6-31G** basis. To prepare the grounds for a comparison between the magnetic properties of COT and those of other molecules, the geometries of the ground states of benzene (1^1A_{1g}, D_{6h} symmetry), square cyclobutadiene (1^1B_{1g}, D_{4h} symmetry), and (*E*)-hexa-1,3,5-triene (1^1A_g, C_{2h} symmetry) were optimized at the CASSCF(6,6)/6-31G**, CASSCF(4,4)/6-31G**, and CASSCF(6,6)/6-31G** levels of theory, respectively. All geometry optimizations were carried out using Gaussian 03[14] under the "Tight" convergence criteria; the local-minimum or saddle-point nature of each optimized geometry was investigated through diagonalization of the corresponding nuclear Hessian. Gaussian 03 was also used to obtain all HF-GIAO and MP2-GIAO results. The CASSCF-GIAO calculations made use of active spaces identical to those used in the geometry optimizations and were performed using the Dalton 2.0 program package,[15] which implements the MCSCF-GIAO (multiconfigurational SCF with GIAOs) methodology developed in refs 16 and 17. The basis set used in all magnetic-property calculations included in this work was 6-311+G*. All reported total energies of various electronic states were computed within the same basis.

This work makes use of four NICS indices: Schleyer's original $\mathrm{NICS}(0)_{\mathrm{iso}} = -\sigma_{\mathrm{iso}}(0)$, where the isotropic shielding $\sigma_{\mathrm{iso}}(0) = {}^1/_3[\sigma_{xx}(0) + \sigma_{yy}(0) + \sigma_{zz}(0)]$ is calculated in the center of the ring;[3] $\mathrm{NICS}(1)_{\mathrm{iso}} = -\sigma_{\mathrm{iso}}(1)$, with $\sigma_{\mathrm{iso}}(1)$ calculated 1 Å above the ring center;[18,19] $\mathrm{NICS}(0)_{zz} = -\sigma_{zz}(0)$; [20,21] and $\mathrm{NICS}(1)_{zz} = -\sigma_{zz}(1)$.[22] "Dissected" NICS indices (see ref 22) were not calculated, as this is not currently feasible within the main approach used in this work, CASSCF-GIAO. It should be possible to obtain "dissected" NICS values at a level of theory very close to CASSCF-GIAO by means of the multiconfigurational individual gauge for localized orbitals (MC-IGLO) method of van Wüllen and Kutzelnigg,[23,24] but at this moment, its code is not available in free or commercial form. Even though an extensive comparison of the performance of various NICS indices calculated using density functional theory (PW91-IGLO/IGLO-III)[22] reached the conclusion that the most reliable index was of the "dissected" type, $\mathrm{NICS}(0)_{\pi zz}$ [the π-orbital contribution to $\mathrm{NICS}(0)_{zz}$], $\mathrm{NICS}(1)_{zz}$ was found to be only slightly inferior.

In line with previous work on NICS[4] and ring currents[25] in triplet systems, the CASSCF-GIAO and UHF-GIAO magnetic properties of the T_1 and the lowest septet states of COT computed in this work include the contributions arising from the perturbation to the wave function only (these are often referred to as "orbital" contributions in single-determinant approaches). Although this choice is convenient for the purposes of the current study, as the values reported for a triplet or a septet state become directly comparable to those for singlet states, a more rigorous treatment would need to take into account the large terms associated with the interaction between the electronic spin angular momentum and the magnetic field.[26,27]

3. Results and Discussion

The optimized carbon−carbon bond lengths and total energies for the electronic states of COT, benzene, cyclobutadiene, and hexatriene discussed in this work are summarized in Table 1. It is worth noting that the carbon−carbon bond length in the S_0 state of D_{8h} COT, which is widely accepted to be antiaromatic, does not change appreciably in the T_1 and S_1 states of this molecule and is much closer to the carbon−carbon bond length in the aromatic S_0 state of D_{6h} benzene than to that in the antiaromatic S_0 state of D_{4h} cyclobutadiene. The carbon−carbon bond length in the 1^7A_{2g} state of D_{8h} COT suggests that the

TABLE 1: Carbon−Carbon Bond Lengths and Total Energies for the S_0, T_1, S_1, and Lowest Septet States of COT and the S_0 States of Benzene, Square Cyclobutadiene, and (*E*)-Hexa-1,3,5-triene[a]

molecule	state	R(C−C) (Å)	method	energy (au)
C_8H_8 (D_{8h})	S_0, 1^1B_{1g}	1.4081[b]	CASSCF(8,8)	−307.663 411
	T_1, 1^3A_{2g}	1.4063[c]	UHF[d]	−307.542 913
			CASSCF(8,8)	−307.638 857
	S_1, 1^1A_{1g}	1.4074[c]	CASSCF(8,8)	−307.612 618
	1^7A_{2g}	1.4850[e]	UHF[f]	−307.172 313
			CASSCF(8,8)	−307.237 934
C_8H_8 (D_{4h})	S_0, 1^1A_{1g}	1.3510, 1.4718[b]	HF	−307.558 891
			MP2[g]	−308.763 781
			CASSCF(8,8)	−307.674 646
C_8H_8 (D_{2d})	S_0, 1^1A_1	1.3436, 1.4794[c]	HF	−307.581 494
			MP2[g]	−308.789 261
			CASSCF(8,8)	−307.691 721
C_6H_6 (D_{6h})	S_0, 1^1A_{1g}	1.3961[h]	HF	−230.745 430
			MP2[g]	−231.652 533
			CASSCF(6,6)	−230.817 488
C_4H_4 (D_{4h})	S_0, 1^1B_{1g}	1.4434[i]	CASSCF(4,4)	−153.707 337
C_6H_8 (C_{2h})	S_0, 1^1A_g	1.3449, 1.4608, 1.3509[j]	HF	−231.853 091
			MP2[g]	−232.761 115
			CASSCF(6,6)	−231.934 938

[a] All energies calculated within the 6-311+G* basis. [b] CASSCF(8,8)/6-31G** transition-state geometries. [c] CASSCF(8,8)/6-31G** local-minimum geometries. [d] $M = 1$ wave function, $\langle \hat{S}^2 \rangle = 2.0152$. [e] CASSCF(8,8)/6-31G** geometry corresponding to a 14th-order saddle point. [f] $M = 3$ wave function, $\langle \hat{S}^2 \rangle = 12.0964$. [g] MP2-(Full) results. [h] CASSCF(6,6)/6-31G** local-minimum geometry. [i] CASSCF(4,4)/6-31G** transition-state geometry. [j] CASSCF(6,6)/6-31G** local-minimum geometry; consecutive carbon−carbon bond lengths from one end of the chain.

bonds making up the ring are largely single bonds. The instability of the D_{8h} geometry of this state is highlighted by the fact that it corresponds to a saddle point at which the nuclear Hessian has 14 negative eigenvalues. The UHF/6-31G** and ROHF/6-31G** geometries for the lowest septet state of D_{8h} COT exhibit slightly shorter carbon−carbon bond lengths of 1.4684 and 1.4682 Å, respectively. The UHF/6-31G** geometry (at which the spin contamination of the $M = 3$ wave function is insignificant, $\langle \hat{S}^2 \rangle = 12.0534$) represents a ninth-order saddle point; the ROHF/6-31G** geometry represents a seventh-order saddle point. The large numbers of negative eigenvalues of the nuclear Hessian obtained at three different levels of theory demonstrate clearly that, while the D_{8h} geometry of the lowest septet state of COT can be of some interest as a model in abstract discussions of the aromaticity of high-spin electronic states, it cannot be associated with any structural rearrangement that might take place on the lowest septet-state PES for COT and is devoid of physical relevance.

While finding accurate theoretical estimates of the separations between the various electronic states of COT is not among the aims of the current work, it should be noted that the differences between the CASSCF(8,8)/6-311+G*//CASSCF(8,8)/6-31G** energies included in Table 1 agree well with the CASSCF-level results of other authors.[9,13]

As expected, the CASSCF-GIAO-level NICS indices for the S_0 state of D_{8h} COT included in Table 2 provide strong evidence for its antiaromatic character. In fact, the NICS(0), NICS(1), and NICS$(1)_{zz}$ values suggest that this state is even more antiaromatic than the ground state of square cyclobutadiene. Thus, despite the fact that one should expect the extent of antiaromaticity of $4n$ π-electron cycles to decrease with the increase of the size of the ring, the current data show no distinct signs of a decrease of this type on passing from $n = 1$ to $n = 2$. Another interesting observation is that the significantly shorter carbon−carbon bond length in the S_0 state of D_{8h} COT, in comparison to that in the S_0 state of D_{4h} cyclobutadiene (see Table 1), is not associated with a reduction in antiaromatic character.

The presence of bond alternation within the D_{4h} geometry of COT leads to a marked decrease in the ground-state antiaromaticity of the system: The CASSCF-GIAO NICS values for the S_0 state of COT at the D_{4h} geometry turn out to be significantly smaller (by factors between ca. 2.3 and 2.7) than those at the bond-equalized D_{8h} geometry. The use of the CASSCF-GIAO level of theory is essential for observing this effect. The HF method cannot produce a symmetry-adapted wave function for the ground state of D_{8h} COT, which also affects the MP2 construction, as it is based on a HF reference. In addition, the HF-GIAO and MP2-GIAO NICS indices for the ground state of D_{4h} COT are considerably higher than their CASSCF-GIAO counterparts. Thus, despite the relatively large coefficient (0.897 380) with which the closed-shell Slater determinant $|(\sigma\ \text{core})(a_{2u})^2(e_g)^4(b_{2u})^2|$ enters the CASSCF(8,8)/6-311+G* construction for D_{4h} COT [(σ core) is a shorthand for the 24 doubly occupied orbitals σ], a wave function ansatz based on this determinant only lacks the flexibility required for the proper description of some of the magnetic properties of the system. In this particular case, the introduction of MP2 corrections leads to even more unrealistic NICS values. Similar observations were made in a discussion of the HF-GIAO, MP2-GIAO, and CASSCF-GIAO NICS indices for the ground state of rectangular (D_{2h}) cyclobutadiene.[5] All of this suggests that the HF-GIAO and MP2-GIAO approaches are not suitable for NICS calculations on antiaromatic systems.

The low magnitudes of the NICS(0), NICS(1), and NICS$(1)_{zz}$ indices produced by all three levels of theory at the D_{2d} ground-state geometry of COT are in line with the expected nonaromatic character of this nonplanar structure, which exhibits significant carbon−carbon bond-length alternation. The "0" and "1" NICS values at this geometry were calculated with respect to the center of the rectangle defined by the midpoints of the carbon−carbon "single" bonds. The HF-GIAO, MP2-GIAO, and CASSCF-GIAO NICS$(0)_{zz}$ indices for D_{2d} COT are reasonably close, and the comparison of the CASSCF-GIAO NICS$(0)_{zz}$ index for D_{2d} COT to the other CASSCF-GIAO NICS$(0)_{zz}$ indices in Table 2 shows that it is safe to interpret its value as a further indication of nonaromatic character.

The differences between the CASSCF-GIAO NICS(0), NICS(1), NICS$(0)_{zz}$, and NICS$(1)_{zz}$ values for the lowest singlet and lowest triplet states of D_{8h} COT shown in Table 2 are surprisingly small, even though the energies of the two states (see Table 1) are ca. 16.5 kcal mol^{-1} apart. Three of these values, the CASSCF-GIAO NICS(0), NICS(1), and NICS$(1)_{zz}$, are also very close to the corresponding CASSCF-GIAO results for the ground state of benzene, the archetypal example of an aromatic system. The CASSCF-GIAO values for the T_1 and S_1 states of D_{8h} COT of the remaining index, NICS$(0)_{zz}$, are significantly more negative than that for the S_0 state of benzene. Thus, all four NICS indices, calculated at the CASSCF-GIAO level of theory, suggest that the lowest singlet and lowest triplet states of D_{8h} COT should be almost equally aromatic. According to the two "in-plane" indices, NICS(0) and NICS$(0)_{zz}$, the T_1 and S_1 states of D_{8h} COT should be more aromatic than the ground state of benzene, whereas according to the two "out-of-plane"

TABLE 2: NICS Values (in ppm) for the S_0, T_1, S_1, and Lowest Septet States of COT and the S_0 States of Benzene and Square Cyclobutadiene[a]

molecule	state	method	NICS(0)	NICS(1)	$\text{NICS}(0)_{zz}$	$\text{NICS}(1)_{zz}$
C_8H_8 (D_{8h})	S_0, 1^1B_{1g}	CASSCF(8,8)	40.71	32.23	128.71	98.22
	T_1, 1^3A_{2g}	UHF	−12.14	−11.92	−31.72	−35.08
		CASSCF(8,8)	−8.93	−8.98	−20.64	−25.60
	S_1, 1^1A_{1g}	CASSCF(8,8)	−8.87	−9.02	−21.52	−26.34
	1^7A_{2g}	UHF	−8.47	−8.07	−15.16	−20.09
		CASSCF(8,8)	−1.20	−1.72	4.55	−3.37
C_8H_8 (D_{4h})	S_0, 1^1A_{1g}	HF	29.27	22.71	92.87	68.92
		MP2	39.05	30.72	121.48	92.46
		CASSCF(8,8)	16.10	11.98	55.40	37.62
C_8H_8 (D_{2d})	S_0, 1^1A_1	HF	1.91	−1.41	15.92	5.33
		MP2	3.09	−0.49	19.00	7.57
		CASSCF(8,8)	1.16	−1.57	14.08	4.21
C_6H_6 (D_{6h})	S_0, 1^1A_{1g}	HF	−9.42	−11.25	−16.45	−31.84
		MP2	−7.55	−10.14	−14.28	−29.78
		CASSCF(6,6)	−8.26	−9.86	−11.23	−27.23
C_4H_4 (D_{4h})	S_0, 1^1B_{1g}	CASSCF(4,4)	35.79	27.30	144.46	86.22

[a] For further details, see text.

indices, NICS(1) and $\text{NICS}(1)_{zz}$, these two states should be slightly less aromatic than the ground state of benzene.

The UHF-GIAO NICS indices for the lowest triplet state of D_{8h} COT are more negative than those calculated at the CASSCF-GIAO level of theory (see Table 2), in agreement with an analogous observation made in an analysis of the aromaticities of the lowest triplet states of square and rectangular cyclobutadiene.[5] The differences between the UHF-GIAO and CASSCF-GIAO NICS indices for the T_1 state of D_{8h} COT are larger than the corresponding differences for the T_1 states of square and rectangular cyclobutadiene. This suggests that the tendency of UHF-GIAO NICS indices to predict exaggerated degrees of aromaticity is likely to become more pronounced in larger cyclic conjugated systems.

According to the ring-current-based rules formulated by Soncini and Fowler,[8] the lowest septet state of D_{8h} COT should be aromatic. This notion is supported by the NICS indices for this state calculated at the UHF-GIAO level of theory (see Table 2), which imply a degree of aromaticity slightly lower than that for the ground state of benzene. However, the CASSCF-GIAO NICS indices tell a different story, suggesting that, although the 1^7A_{2g} state of D_{8h} COT is slightly more aromatic than the decidedly nonaromatic ground state of D_{2d} COT, the degree of its aromaticity is close to negligibly low.

The carbon and proton isotropic shieldings, $\sigma_{\text{iso}} = {}^1/_3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, and out-of-plane shielding tensor components, σ_{zz}, as well as the isotropic magnetic susceptibilities, $\chi_{\text{iso}} = {}^1/_3(\chi_{xx} + \chi_{yy} + \chi_{zz})$, and out-of-plane components of the magnetic susceptibility tensor, χ_{zz}, for the S_0, T_1, S_1, and lowest septet states of COT and the S_0 states of benzene, cyclobutadiene, and hexatriene computed in this work are reported in Table 3. This table does not contain shielding and magnetic susceptibility anisotropies, but the $\Delta\sigma$ and $\Delta\chi$ values corresponding to the definitions that are most useful when analyzing 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 in a very straightforward manner as $\Delta\sigma = {}^3/_2(\sigma_{zz} - \sigma_{\text{iso}})$ and $\Delta\chi = {}^3/_2(\chi_{zz} - \chi_{\text{iso}})$.

Before discussing the significance of the data presented in Table 3 in detail, it is appropriate to draw attention to the surprisingly close similarity between all CASSCF-GIAO magnetic properties of the T_1 and S_1 states of D_{8h} COT, which reinforces a similar observation made in the preceding discussion of the NICS indices for these two states shown in Table 2.

The most widely used source of information about aromaticity and antiaromaticity among the data included in Table 3 is provided by the proton isotropic shieldings $\sigma_{\text{iso}}(^1\text{H})$. As expected, the protons in the aromatic ground state of benzene are deshielded with respect to the protons from the central —CH═CH— unit in the nonaromatic ground state of hexatriene, whereas the protons in the antiaromatic ground state of cyclobutadiene are more shielded than those in hexatriene (compare the corresponding CASSCF-GIAO results shown in Table 3). The protons in the S_0 state of D_{8h} COT are significantly more shielded than the protons in the S_0 state of cyclobutadiene, which represents an additional indication of strong antiaromatic character. The CASSCF-GIAO proton shieldings decrease by ca. 2.8 ppm at the bond-alternating D_{4h} COT geometry, in line with the expected decrease in antiaromaticity suggested by the NICS indices. The differences between the CASSCF-GIAO $\sigma_{\text{iso}}(^1\text{H})$ values for the ground state of D_{2d} COT, the lowest septet state of D_{8h} COT, and the ground state of hexatriene are small, which suggests that these two states of COT are essentially nonaromatic. The very close proton isotropic shieldings for the T_1 and S_1 states of D_{8h} COT calculated at the CASSCF-GIAO level of theory, which, in turn, are very similar to the CASSCF-GIAO $\sigma_{\text{iso}}(^1\text{H})$ value for the ground state of benzene, provide strong evidence of the well-expressed, almost-equal aromaticities of the two states.

The differences between the $\sigma_{\text{iso}}(^1\text{H})$ values calculated at different levels of theory are relatively small, but because the deshielding and shielding effects associated with aromatic or antiaromatic character are also small, it is important to compare ^{1}H isotropic shieldings calculated at the same level of theory. The fact that the HF-GIAO and MP2-GIAO results suggest that the protons in the ground-state D_{4h} COT are more shielded than those at the CASSCF-GIAO level of theory can be viewed as another manifestation of the insufficiently good quality of the closed-shell HF wave function for this state, as discussed in the analysis of the corresponding NICS indices.

For planar geometries, the out-of-plane components of the ^{1}H shielding tensors $\sigma_{zz}(^1\text{H})$, which cover a wider range of values than the ^{1}H isotropic shieldings $\sigma_{\text{iso}}(^1\text{H})$, offer an even more

TABLE 3: Carbon and Proton Shieldings (in ppm) and Magnetic Susceptibilities (in ppm cm^3 mol^{-1}) for the for the S$_0$, T$_1$, S$_1$, and Lowest Septet States of COT and the S$_0$ States of Benzene, Square Cyclobutadiene, and (*E*)-Hexa-1,3,5-triene[a,b]

molecule	state	method	σ_{iso}(^{13}C)	σ_{zz}(^{13}C)	σ_{iso}(^{1}H)	σ_{zz}(^{1}H)	χ_{iso}	χ_{zz}
C_8H_8 (D_{8h})	S_0, 1^1B_{1g}	CASSCF(8,8)	70.21	133.92	31.70	37.07	20.87	171.83
	T_1, 1^3A_{2g}	UHF	66.82	182.18	24.64	17.63	−96.17	−183.88
		CASSCF(8,8)	81.93	178.88	25.57	18.94	−88.55	−157.62
	S_1, 1^1A_{1g}	CASSCF(8,8)	80.01	179.14	25.43	18.84	−88.38	−160.23
	1^7A_{2g}	UHF	101.36	169.60	26.29	19.86	−85.01	−157.86
		CASSCF(8,8)	111.17	163.81	27.59	22.54	−64.25	−98.32
C_8H_8 (D_{4h})	S_0, 1^1A_{1g}	HF	57.79	143.52	29.78	32.46	−4.09	93.22
		MP2	66.19	133.55	30.44	35.41	–	–
		CASSCF(8,8)	79.48	154.57	28.91	28.23	−33.10	11.19
C_8H_8 (D_{2d})	S_0, 1^1A_1	HF	56.06	65.53	26.66	24.75	−58.70	−54.60
		MP2	65.39	74.08	26.17	24.50	–	–
		CASSCF(8,8)	76.57	87.05	27.26	25.35	−61.51	−62.21
C_6H_6 (D_{6h})	S_0, 1^1A_{1g}	HF	59.34	189.25	24.95	21.45	−60.85	−106.40
		MP2	70.47	189.18	24.44	20.92	–	–
		CASSCF(6,6)	75.07	187.85	25.62	21.89	−59.64	−99.95
C_4H_4 (D_{4h})	S_0, 1^1B_{1g}	CASSCF(4,4)	70.15	127.64	28.28	31.04	−12.37	12.59
C_6H_8 (C_{2h})	S_0, 1^1A_g	HF	55.39	152.54	26.02	24.67	−52.31	−68.93
		MP2	64.65	147.94	25.67	24.42	–	–
		CASSCF(6,6)	73.24	152.57	26.77	24.92	−53.46	−68.67

[a] The hexatriene shieldings are for the nuclei within the central —CH=CH— unit. [b] For further details, see text.

straightforward way of distinguishing between aromatic, nonaromatic, and antiaromatic states. The only difference from the state classification following from the CASSCF-GIAO NICS indices and proton isotropic shieldings is associated with the CASSCF-GIAO value of σ_{zz}(^{1}H) for the 1^7A_{2g} state of D_{8h} COT, which is closer to the σ_{zz}(^{1}H) value for the aromatic ground state of benzene than to that for the nonaromatic ground state of hexatriene. Despite the fact that the σ_{zz}(^{1}H) values for the ground state of the nonplanar D_{2d} COT suggest nonaromatic behavior, it is not appropriate to compare these values to those for planar systems, as the *z* axis at the D_{2d} geometry is perpendicular to the plane defined by the midpoints of the carbon−carbon "single" bonds and not to one of the planes defined by the carbon atoms participating in a carbon−carbon "double" bond and the attached hydrogen atoms. The same applies to the σ_{zz}(^{13}C) values for the ground state of the nonplanar D_{2d} COT, which differ considerably from the corresponding values for planar systems. On the whole, the level of theory affects the σ_{zz}(^{1}H) values similarly to the ^{1}H isotropic shieldings, but some differences, for example, those between the HF-GIAO, MP2-GIAO, and CASSCF-GIAO results for D_{4h} COT, are more pronounced.

Even though the out-of-plane components of the ^{13}C shielding tensors σ_{zz}(^{13}C) are not among the traditional aromaticity criteria, the differences between the values of these quantities for the electronic states with planar geometries included in Table 3 are sufficiently well-manifested to allow the classification of most states as aromatic or antiaromatic. The only case in which a σ_{zz}(^{13}C) value fails to reflect the antiaromaticity of a state is for the ground state of the bond-alternating D_{4h} COT: The CASSCF-GIAO out-of-plane component of the ^{13}C shielding tensor for this state is close to that for the nonaromatic ground state of hexatriene. Whereas the UHF-GIAO σ_{zz}(^{13}C) value for the 1^7A_{2g} state of D_{8h} COT is closer to the aromatic region, the value calculated at the CASSCF-GIAO level of theory falls in between the antiaromatic and aromatic regions, which suggests mostly nonaromatic behavior.

The relatively small gap of ca. 5 ppm between the CASSCF-GIAO carbon isotropic shieldings σ_{iso}(^{13}C) for the ground states of benzene and square cyclobutadiene and the wide spread of the σ_{iso}(^{13}C) values included in Table 3 show that these quantities are not affected in a systematic fashion by the aromaticities of the states to which they pertain. Within the 6-311+G* basis, the ^{13}C isotropic shielding in the ground state of benzene calculated at the CASSCF-GIAO level of theory is 4.60 ppm higher than that obtained at the MP2-GIAO level of theory, which, in turn, is 11.13 ppm higher than the HF-GIAO shielding (see Table 3). The separations between the CASSCF-GIAO and MP2-GIAO and between the MP2-GIAO and HF-GIAO ^{13}C isotropic shieldings in the ground state of benzene obtained within the larger 6-311++G(2d,2p) basis (and at a slightly different geometry) amount to 6.15 and 9.61 ppm, respectively.[5] Thus, whereas in the larger basis the MP2-GIAO shielding shifts in the direction of the HF-GIAO result, the gap between the CASSCF-GIAO and HF-GIAO shieldings remains very much the same. The results included in Table 3 reinforce the observation made in ref 5 that the ^{13}C isotropic shieldings in the low-lying electronic states of small conjugated rings are strongly influenced by the inclusion of electron correlation effects. Although some of the particularly large differences between the carbon isotropic shieldings calculated at the CASSCF-GIAO and MP2-GIAO levels of theory, for example, those for the ground states of D_{4h} and D_{2d} COT, can be attributed to the insufficiently good quality of the HF wave function used as a reference in the MP2 construction, it is also possible that, in other cases, the CASSCF-GIAO approach can overestimate the σ_{iso}(^{13}C) values. The fact that, on their own, both the nondynamic and dynamic correlation effects, included in the CASSCF and MP2 wave functions, respectively, increase the calculated ^{13}C isotropic shieldings suggests that a more rigorous theoretical assessment of these quantities in conjugated systems would require the development of a GIAO or IGLO implementation of a many-body perturbation theory treatment based on a CASSCF reference, such as CASPT2.[28]

The isotropic (or average) magnetic susceptibilities, χ_{iso}, listed in Table 3 show marked differences between the most aromatic states (the ground state of benzene and the T_1 and S_1 states of D_{8h} COT) and the most antiaromatic states (the ground states of cyclobutadiene and D_{8h} COT), but they do not distinguish sufficiently well between aromatic and nonaromatic states (compare the HF-GIAO and CASSCF-GIAO χ_{iso} values for the ground states of benzene and D_{2d} COT). The out-of-plane components of the magnetic susceptibility tensor, χ_{zz}, allow clearer differentiation between aromatic, nonaromatic, and antiaromatic states. According to both the χ_{iso} and χ_{zz} values, the 1^7A_{2g} state of D_{8h} COT should be aromatic. The effect of nondynamic electron correlation on the χ_{iso} and χ_{zz} values for the ground state of hexatriene is relatively small, especially in so far as χ_{zz} is concerned. The same holds for the χ_{iso} value for the ground state of benzene, but there is a gap of more than 6 ppm cm^3 mol^{-1} between the HF-GIAO and CASSCF-GIAO estimates of χ_{zz}. For all other electronic states of cyclic systems included in Table 3, the differences between the isotropic magnetic susceptibilities and out-of-plane components of the magnetic susceptibility tensor evaluated at the HF-GIAO or UHF-GIAO and CASSCF-GIAO levels of theory are more substantial. As expected from the preceding discussion of other magnetic properties, these differences are particularly large for the ground state of the bond-alternating D_{4h} COT. The significant differences between the UHF-GIAO and CASSCF-GIAO χ_{iso} and χ_{zz} values for the 1^7A_{2g} state of D_{8h} COT suggest that the $M = 3$ UHF wave function for this state is of a rather modest quality. The HF-GIAO and CASSCF-GIAO χ_{iso} and χ_{zz} values for the ground states of benzene and square cyclobutadiene listed in Table 3 are very similar to the corresponding values reported in ref 5 where use was made of a larger 6-311++G(2d,2p) basis and slightly different geometries: The largest difference, between the CASSCF-GIAO χ_{iso} values for the ground state of benzene, amounts to just 0.31 ppm cm^3 mol^{-1}. As a consequence, despite the use of the smaller 6-311+G* basis, the CASSCF-GIAO χ_{iso} and χ_{zz} values for benzene obtained in the current work are still in very good agreement with the experimental data reported by Schmalz et al.,[29] $^1/_2(\chi_{xx} + \chi_{yy}) = -34.9 \pm 2.0$ and $\chi_{zz} = -94.9 \pm 2.5$, which combine to give $\chi_{\mathrm{iso}} = -54.9 \pm 1.5$ (all in ppm cm^3 mol^{-1}), whereas their HF-GIAO counterparts remain very close to the "near-Hartree-Fock-limit" HF-IGLO results of Fleischer et al.[30] of -60.7 and -106.7 ppm cm^3 mol^{-1}.

4. Conclusions

The values of the NICS(0), NICS(1), NICS(0)$_{zz}$, and NICS(1)$_{zz}$ indices for the ground state of D_{8h} COT calculated at the CASSCF-GIAO level of theory strongly suggest that this state is markedly antiaromatic, even more so than the classical example of an antiaromatic system, the ground state of square cyclobutadiene. This finding is supported by the values of the proton isotropic shieldings, $\sigma_{\mathrm{iso}}(^1\mathrm{H})$, the out-of-plane components of the ^{1}H and ^{13}C shielding tensors, $\sigma_{zz}(^1\mathrm{H})$ and $\sigma_{zz}(^{13}\mathrm{C})$, the isotropic magnetic susceptibilities, χ_{iso}, and the out-of-plane components of the magnetic susceptibility tensor, χ_{zz}, for the ground states of D_{8h} COT and D_{4h} cyclobutadiene obtained at the same level of theory. The changes in the values of these magnetic properties, calculated at the CASSCF-GIAO level of theory, on passing to the ground states of the bond-alternating planar D_{4h} COT and nonplanar D_{2d} COT show clearly that the ground state of D_{4h} COT is much less antiaromatic than the ground state of D_{8h} COT, whereas the ground state of D_{2d} COT is decidedly nonaromatic.

The antiaromaticity of the ground state of D_{4h} COT is very significantly overestimated at the HF-GIAO level of theory and, especially, at the MP2-GIAO level of theory, which produce NICS(0) values that are more than 80% higher and more than 142% higher, respectively, than the CASSCF-GIAO result. In combination with the recently established fact that, at the lowest-energy rectangular ground-state geometry of cyclobutadiene (D_{2h} symmetry), the HF-GIAO level of theory overestimates the NICS(0) value by more than 70% in comparison to the CASSCF-GIAO result,[5] these findings lead to the conclusion that the HF-GIAO approach, as well as the MP2-GIAO approach, which uses a wave function based on a HF reference, are largely unsuitable for NICS calculations on antiaromatic systems, even when obtaining a symmetry-adapted closed-shell HF wave function for the system is a completely straightforward task. Inspection of the HF-GIAO, MP2-GIAO, and CASSCF-GIAO results for the ground state of D_{4h} COT included in Table 3 suggests that the same holds for a number of other magnetic properties.

The magnetic properties of the lowest triplet state and the first singlet excited state of D_{8h} COT evaluated at the CASSCF-GIAO level of theory are surprisingly similar even though these two states have different spin multiplicities and their energies are separated by a gap of ca. 16.5 kcal mol^{-1}. The comparison of the magnetic properties of these states to those of the ground state of benzene strongly suggest that both states display levels of aromaticity very close to that of the ground state of benzene.

Although, according to the ring-current-based rules formulated by Soncini and Fowler,[8] the lowest septet state (total spin $S = 3$) of D_{8h} COT should be aromatic, the magnetic properties of this state calculated at the CASSCF-GIAO level of theory do not provide unambiguous evidence about the level of its aromaticity. The NICS indices suggest that the 1^7A_{2g} state of D_{8h} COT might be aromatic, but only slightly so. Judging by its isotropic proton shielding, $\sigma_{\mathrm{iso}}(^1\mathrm{H})$, and out-of-plane component of the ^{13}C shielding tensor, $\sigma_{zz}(^{13}\mathrm{C})$, this state should be nonaromatic; however, the out-of-plane component of the proton shielding tensor, $\sigma_{zz}(^1\mathrm{H})$, indicates a certain degree of aromaticity. Finally, the values of the isotropic magnetic susceptibility, χ_{iso}, and the out-of-plane component of the magnetic susceptibility tensor, χ_{zz}, suggest that the 1^7A_{2g} state of D_{8h} COT should be almost as aromatic as the ground state of benzene. The fact that the D_{8h} geometry represents a saddle point on the CASSCF(8,8)/6-31G** PES for the lowest septet state of COT at which the nuclear Hessian has 14 negative eigenvalues shows clearly that the magnetic aromaticity criteria to be trusted when assessing the relative aromaticity of this highly unstable geometry are the NICS indices, the isotropic proton shielding, and the out-of-plane component of the ^{13}C shielding tensor.

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