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# Aromaticity reversals and their effect on bonding in the low-lying electronic states of cyclooctatetraene†

Peter B. Karadakov \* and Nicholas Preston

Aromaticity reversals and their effect on chemical bonding in the low-lying electronic states of cyclooctatetraene (COT) are investigated through a visual approach which examines the variations in isotropic magnetic shielding in the space surrounding the molecule. The ground state ( $S_0$ ) of COT is shown to be strongly antiaromatic at the  $\pi$ -bond-shifting transition state (TS), a regular octagon of  $D_{8h}$  symmetry;  $S_0$  antiaromaticity decreases at the  $D_{4h}$  planar bond-alternating tub-to-tub ring-inversion TS but traces of it are shown to persist even at the tub-shaped  $D_{2d}$  local minimum geometry. The lowest triplet ( $T_1$ ) and first singlet excited ( $S_1$ ) states of COT are found to have very similar  $D_{8h}$  geometries and visually indistinguishable shielding distributions closely resembling that in benzene and indicating similarly high levels of aromaticity. Unexpectedly, COT diverges from its antiaromatic predecessor, cyclobutadiene, in the properties of the second singlet excited state ( $S_2$ ): In cyclobutadiene  $S_2$  is antiaromatic but in COT this state turns out to be strongly aromatic, with a shielding distribution closely following that around  $S_2$  benzene.

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## Introduction

Cyclooctatetraene ( $C_8H_8$ , COT) has been aptly described as “one of the decisive molecules in the history of chemistry”.<sup>1</sup> It has been the subject of numerous experimental and theoretical studies; a comprehensive account of pre-2012 research has been provided by Schleyer and co-workers.<sup>1</sup> The ground-state ( $S_0$ ) potential energy surface (PES) of COT has been examined in considerable detail<sup>2–8</sup> and has been found to include symmetry-equivalent tub-shaped local minima of  $D_{2d}$  symmetry connected through planar tub-to-tub ring-inversion transition states (TS) of  $D_{4h}$  symmetry; these, in turn, are connected through a planar  $\pi$ -bond-shifting TS in the form of a regular octagon of  $D_{8h}$  symmetry. In its electronic ground state  $D_{8h}$  COT is a singlet diradical and its full-symmetry description requires at least a two-determinant wavefunction; the attempt

to use the standard single closed-shell Slater determinant results in a “broken-symmetry” wavefunction which suggests energetically favourable distortions of the nuclear framework to one of the two bond-alternating  $D_{4h}$  geometries. As shown by Hrovat and Borden,<sup>3</sup> the ground-state PES of COT can be described with high accuracy using a complete active-space self-consistent field (CASSCF) wavefunction with “8 electrons in 8 orbitals”, CASSCF(8,8), accounting for the eight electrons involved in the bond rearrangements linking the  $D_{2d}$ ,  $D_{4h}$  and  $D_{8h}$  stationary points; CASSCF(8,8) wavefunctions have been also found to work well in studies of several low-lying electronic states of COT.<sup>4,6,9,10</sup>

Hückel molecular orbital (HMO) theory depicts the ground electronic state of  $D_{8h}$  COT as an antiaromatic triplet which is incorrect in more than one way: Firstly, at this geometry COT has an antiaromatic singlet ground electronic state which violates Hund’s rule and secondly, the lowest triplet state ( $T_1$ ) of  $D_{8h}$  COT has been shown to be aromatic.<sup>10–13</sup>  $D_{8h}$  COT was used by Baird as an example of a molecule featuring an aromaticity reversal on excitation from  $S_0$  to  $T_1$ ,<sup>11</sup> subsequent research revealed that  $D_{8h}$  COT experiences a similar aromaticity reversal on excitation from  $S_0$  to the first singlet excited state ( $S_1$ ).<sup>10</sup> Recent experimental work has demonstrated that cyclooctatetraene-fused acene dimers exhibit remarkable conformational flexibility associated with the change in aromaticity of the central COT moiety on excitation from  $S_0$  to  $S_1$ ; such “flapping” fluorophores (FLAP) provide a versatile platform for designing novel photofunctional systems.<sup>14–16</sup>

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† Electronic supplementary information (ESI) available: Isotropic shielding contour plots for the  $S_0$  (at  $D_{4h}$  and  $D_{8h}$  geometries),  $T_1$ ,  $S_1$  and  $S_2$  (at  $D_{8h}$  geometries) electronic states of COT in planes 1 Å above the respective molecular planes and in planes perpendicular to the molecular planes; computational details and  $D_{2d}$   $S_0$  and  $D_{4h}$   $S_0$  optimised geometries; details of the compositions of the CASSCF wavefunctions for the  $S_0$ ,  $S_1$ ,  $S_2$  and  $T_1$  electronic states of  $D_{8h}$  COT (PDF). Zip archive of Gaussian cube files with isotropic shielding values for the  $S_0$  (at  $D_{2d}$ ,  $D_{4h}$  and  $D_{8h}$  geometries),  $T_1$ ,  $S_1$  and  $S_2$  (at  $D_{8h}$  geometries) electronic states of COT (ZIP). See DOI: 10.1039/d1cp04394c



In this paper we investigate aromaticity and chemical bonding at all stationary points of the ground-state PES of COT, including the  $D_{2d}$  tub-shaped,  $D_{4h}$  bond-alternating and  $D_{8h}$  geometries, as well as at the  $D_{8h}$  geometries of the lowest triplet and first and second singlet ( $T_1$ ,  $S_1$  and  $S_2$ ) electronic excited states by analysing, for each geometry and electronic state, the changes in the off-nucleus isotropic shielding,  $\sigma_{\text{iso}}(\mathbf{r}) = 1/3[\sigma_{xx}(\mathbf{r}) + \sigma_{yy}(\mathbf{r}) + \sigma_{zz}(\mathbf{r})]$ , within the space surrounding the molecule. All  $\sigma_{\text{iso}}(\mathbf{r})$  calculations make use of state-specific CASSCF(8,8) wavefunctions constructed from gauge-including atomic orbitals (GIAOs). The aromaticities of the  $S_0$ ,  $T_1$  and  $S_1$  states of COT have been examined at the CASSCF(8,8)-GIAO level<sup>10</sup> with several types of nucleus-independent chemical shifts (NICS),<sup>17–22</sup> proton shieldings and magnetic susceptibilities. However, when applying NICS in order to assess the aromaticity of a larger ring such as COT, it is logical to ask to what extent we can trust predictions based on a single shielding value calculated at or above the centre of this ring. In contrast to NICS and other single-value aromaticity criteria,  $\sigma_{\text{iso}}(\mathbf{r})$  isosurfaces and contour plots provide somewhat more detailed and, arguably, more reliable information about aromaticity and its effect on chemical bonding.<sup>23–27</sup> Representing off-nucleus magnetic isotropic shielding as a function of position in the space surrounding a molecule requires a very large number of closely spaced data points which addresses potential deficiencies of single-point NICS such as the need to choose, in a more or less arbitrary manner, locations at which these quantities are calculated (NICS can exhibit strong positional dependence and, in certain situations, standard choices can be inappropriate<sup>28,29</sup>), and the argument that a single number might not be sufficient to characterise all aspects of aromatic behaviour, supported by the observation that different ring current maps can produce nearly indistinguishable single-point NICS values.<sup>30,31</sup> The application of this approach to the low-lying electronic states of the archetypal examples of aromatic and antiaromatic systems, benzene ( $C_6H_6$ ) and square cyclobutadiene ( $C_4H_4$ )<sup>24</sup> has shown that the profoundly different shielding distributions in the  $S_0$  states of  $C_6H_6$  and  $C_4H_4$  can be viewed as aromaticity and antiaromaticity “fingerprints” which are reproduced in other electronic states of the two molecules and allow classification of these states as aromatic ( $S_0$  and  $S_2$  for  $C_6H_6$ ,  $T_1$  and  $S_1$  for  $C_4H_4$ ) or antiaromatic ( $S_0$  and  $S_2$  for  $C_4H_4$ ,  $T_1$  and  $S_1$  for  $C_6H_6$ );  $S_2$   $C_6H_6$  was predicted to be even more aromatic than  $S_0$   $C_6H_6$ . Whether or not the low-lying electronic states of  $D_{8h}$  COT follow a pattern similar to that observed in its antiaromatic cyclic conjugated predecessor with  $4n$   $\pi$  electrons, square cyclobutadiene, is one of the questions targeted through the research reported in this paper.

## Computational procedure

The active spaces in the state-specific CASSCF(8,8) wavefunctions for the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  states of  $D_{8h}$  COT studied in this paper were formed from the  $\pi$ -orbital configuration  $(a_{2u})^2(e_{1g})^4(e_{2u})^2$  and two higher-energy  $\pi$  orbitals, a doubly-degenerate  $e_{3g}$  and a  $b_{2u}$ . As explained in ref. 10, the

symmetries of the singlet and triplet states associated with the direct product  $e_{2u} \times e_{2u}$  follow from the compositions of its symmetric and antisymmetric parts,  $[e_{2u} \times e_{2u}] = a_{1g} + b_{1g} + b_{2g}$  and  $\{e_{2u} \times e_{2u}\} = a_{2g}$ , respectively. Thus  $e_{2u} \times e_{2u}$  gives rise to three singlet states,  $1^1A_{1g}$  ( $S_1$ ),  $1^1B_{1g}$  ( $S_0$ ) and  $1^1B_{2g}$  ( $S_2$ ), and one triplet state,  $1^3A_{2g}$  ( $T_1$ ). The largest subgroup of the  $D_{8h}$  point group supported by one of the program packages we used for CASSCF(8,8) calculations, Dalton,<sup>32</sup> is  $D_{2h}$ , therefore in that subgroup the  $S_0$ ,  $S_1$ ,  $S_2$  and  $T_1$  states of  $D_{8h}$  COT were treated as the  $1^1B_{1g}$ ,  $1^1A_g$ ,  $2^1A_g$  and  $1^3B_{1g}$  states, respectively. The  $2^1A_g$  state was accessed by requesting the second root of the CASSCF(8,8) configuration interaction (CI) problem in that symmetry. In the CASSCF(8,8) calculations carried out with Gaussian16<sup>33</sup> the  $S_1$  and  $S_2$  states were accessed by requesting the second and third roots, respectively, of the CASSCF(8,8) CI problem. The selection of active-space orbitals for the CASSCF(8,8) wavefunctions for the  $S_0$  states of  $D_{4h}$  and  $D_{2d}$  COT was, in each case, a straightforward task.

The CASSCF(8,8)/6-31G\*\* optimised geometries of the  $1^1B_{1g}$  state of  $D_{8h}$  COT (TS for the  $\pi$  bond shift process on the  $S_0$  PES), the  $1^1A_{1g}$  state of  $D_{4h}$  COT (TS 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) and the  $1^1A_{1g}$  state of  $D_{8h}$  COT (local minimum on the  $S_1$  PES) were taken from an earlier study of COT.<sup>10</sup> Additionally, the geometry of the  $1^1B_{2g}$  state of  $D_{8h}$  COT (local minimum on the  $S_2$  PES) was optimised at the same CASSCF(8,8)/6-31G\*\* level, and then the geometries of all stationary points on the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  PES of COT studied in this paper were reoptimised at the CASSCF(8,8)/cc-pVTZ level. As the differences between the CASSCF(8,8)/6-31G\*\* and CASSCF(8,8)/cc-pVTZ optimised geometries were observed to be minor, all subsequent magnetic shielding calculations were carried out at the CASSCF(8,8)/6-31G\*\* geometries; according to our experience with calculations of this type, off-nucleus shieldings are relatively insensitive to minor changes in molecular geometry. All of the additional geometry optimizations were carried out using Gaussian16<sup>33</sup> and the local minimum or saddle point nature of each optimised geometry was verified through an analytic harmonic frequency calculation.

All CASSCF(8,8)-GIAO calculations were performed by means of the MCSCF-GIAO (multiconfigurational SCF with GIAOs) methodology<sup>34,35</sup> that is implemented in the Dalton program package;<sup>32</sup> the basis set used in these calculations was 6-311+G\*. All reported total energies of various electronic states at CASSCF(8,8)/6-31G\*\* geometries were also computed within the 6-311+G\* basis, with both Gaussian16 and Dalton. Following previous work on NICS<sup>10,12,24,36</sup> and ring currents<sup>37</sup> in triplet systems, the CASSCF-GIAO isotropic shieldings in the lowest triplet electronic state of COT reported in this paper include only contributions that arise from the perturbation to the wavefunction. With this choice, the values reported for a triplet state can be compared directly with those for singlet states. For comparisons to experimental data when and if such data becomes available, one will need to take into account the large terms associated



with the interaction between the electronic spin angular momentum and the magnetic field.<sup>38,39</sup>

The grids of points used in the construction of  $\sigma_{\text{iso}}(\mathbf{r})$  isosurfaces and contour plots for the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT studied in this paper are regular, with a spacing of 0.05 Å, in the shape of rectangular boxes centred at the origins of centre-of-mass right-handed Cartesian coordinate systems in which the  $z$  axes are oriented along the respective principal symmetry axes and the  $x$  and  $y$  axes are oriented along the  $C_2'$  axes ( $D_{2d}$  geometry) or the  $C_2''$  axes ( $D_{4h}$  and  $D_{8h}$  geometries). The grid for the  $S_0$  state of  $D_{2d}$  COT consists of  $133^2 \times 81$  points, and the grids for all other states consist of  $161^2 \times 101$  points. In order to reduce computational effort, the  $\sigma_{\text{iso}}(\mathbf{r})$  values for each electronic state were calculated only at symmetry-unique grid points (1/4 of all points for  $D_{2d}$  COT and 1/8 of all points for  $D_{4h}$  and  $D_{8h}$  COT, respectively) and data were then replicated by symmetry. For visualization purposes, all  $\sigma_{\text{iso}}(\mathbf{r})$  values obtained for the electronic states of COT were assembled into Gaussian cube files.<sup>40</sup>

## Results and discussion

The carbon–carbon and carbon–hydrogen bond lengths in the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT from geometries optimised using state-specific CASSCF(8,8) wavefunctions in the 6-31G\*\* and cc-pVTZ basis sets are shown in Table 1 together with the lowest harmonic frequencies and total energies of these states. The carbon–carbon and carbon–hydrogen bond lengths calculated in the cc-pVTZ basis set are slightly shorter; the largest difference between 6-31G\*\* and cc-pVTZ bond lengths of 0.0052 Å is observed for the carbon–carbon “double” bond in  $D_{2d}$  COT.

The results for the electronic states of  $D_{8h}$  COT obtained in the cc-pVTZ basis provide further indication that the antiaromatic  $S_0$  and aromatic  $T_1$  and  $S_1$  geometries can be expected to be very similar, with carbon–carbon bond lengths closer to that in benzene and significantly shorter than that in cyclobutadiene, 1.3961 Å and 1.4434 Å, respectively, from CASSCF(6,6)/6-31G\*\* and CASSCF(4,4)/6-31G\*\*  $S_0$  geometry optimizations of

$D_{6h}$  benzene and  $D_{4h}$  cyclobutadiene.<sup>10</sup> The carbon–carbon bond length in the  $S_2$   $D_{8h}$  COT geometry is almost identical to that in  $S_0$  benzene, with a difference of just 0.0004 Å (in the 6-31G\*\* basis), which suggests an increase in aromaticity in comparison to  $T_1$  and  $S_1$  COT.

The variations in isotropic shielding around the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT at the CASSCF(8,8)/6-31G\*\* geometries reported in Table 1 are illustrated in Fig. 1. The isovalues of  $\sigma_{\text{iso}}(\mathbf{r}) = \pm 16$  ppm and the molecular orientations were chosen so as to show reasonable levels of detail. Other orientations and isosurfaces for other isovalues can be examined using the Gaussian cube files with isotropic shielding values for the different geometries and electronic states of COT that are included in the ESI.† Further information about the behaviour of the isotropic shielding in the electronic states of COT at the planar  $D_{4h}$  and  $D_{8h}$  geometries is provided by contour plots in three planes: the molecular plane (Fig. 2), a plane 1 Å above it, and a plane perpendicular to the molecular plane (Fig. S1 and S2 in the ESI†).

The shielding along the carbon framework in the  $S_0$  electronic ground state at the  $D_{2d}$  tub-shaped geometry outlines a sequence of alternating “single” and “double” carbon–carbon bonds similar to those reported in the magnetic shielding study of bonding in *trans*-1,3-butadiene.<sup>41</sup> It is interesting to observe that this clearly non-aromatic picture retains a minor hint of antiaromaticity in the form of a small deshielded region surrounded by the yellow  $\sigma_{\text{iso}}(\mathbf{r}) = -1$  ppm isosurface in the centre of the ring. Note that other parts of this isosurface at -1 ppm can be seen as larger “halos” over the smaller orange “halos” at -16 ppm surrounding carbon atoms familiar from previous magnetic shielding studies of conjugated systems involving  $sp^2$  and  $sp$  hybridised carbon atoms and other  $sp^2$  hybridised first main row atoms.<sup>23,24,27,42,43</sup> A recent study of magnetically induced currents in  $D_{2d}$  COT reported a weak paratropic global molecular ring current,<sup>8</sup> an indication of a very low level of antiaromaticity, which is in line with the findings of the current work. The shielding along the carbon framework does not show signs of additional conjugation over that in *trans*-1,3-butadiene<sup>41</sup> which suggests that the interesting concept of “two-way” (double) hyperconjugation in  $D_{2d}$  COT<sup>1</sup> is

**Table 1** Carbon–carbon and carbon–hydrogen bond lengths (Å), lowest harmonic frequencies ( $\text{cm}^{-1}$ ) and total energies ( $E_h$ ) for the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT from CASSCF(8,8) calculations in the 6-31G\*\*, cc-pVTZ and 6-311 + G\* basis sets; “6-31G\*\*” rows show CASSCF(8,8)/6-311 + G\*/CASSCF(8,8)/6-31G\*\* total energies.  $S_0$ ,  $T_1$  and  $S_1$  data at CASSCF(8,8)/6-31G\*\* geometries from ref. 10.  $D_{4h}$  and  $D_{8h}$   $S_0$  TS geometries; local minimum geometries for all other states

Geometry	State	Basis	$R(\text{CC})$	$R(\text{CH})$	$\nu_1$	Energy
$D_{2d}$	$S_0$ ( $1^1A_1$ )	6-31G**	1.3436, 1.4794	1.0791	179.8 ( $a_1$ )	-307.691 721
		cc-pVTZ	1.3384, 1.4767	1.0767	180.5 ( $a_1$ )	-307.735 840
$D_{4h}$	$S_0$ ( $1^1A_{1g}$ )	6-31G**	1.3510, 1.4718	1.0777	112.6i ( $b_{2u}$ )	-307.674 646
		cc-pVTZ	1.3454, 1.4705	1.0753	144.4i ( $b_{2u}$ )	-307.718 937
$D_{8h}$	$S_0$ ( $1^1B_{1g}$ )	6-31G**	1.4081	1.0774	2304.0i ( $b_{2g}$ )	-307.663 411
		cc-pVTZ	1.4044	1.0750	2595.3i ( $b_{2g}$ )	-307.707 176
	$T_1$ ( $1^3A_{2g}$ )	6-31G**	1.4063	1.0773	159.5 ( $e_{2u}$ )	-307.638 857
		cc-pVTZ	1.4026	1.0750	162.4 ( $e_{2u}$ )	-307.682 884
	$S_1$ ( $1^1A_{1g}$ )	6-31G**	1.4074	1.0772	157.7 ( $e_{2u}$ )	-307.612 618
		cc-pVTZ	1.4036	1.0748	160.1 ( $e_{2u}$ )	-307.656 593
	$S_2$ ( $1^1B_{2g}$ )	6-31G**	1.3957	1.0773	162.8 ( $e_{2u}$ )	-307.557 953
		cc-pVTZ	1.3927	1.0749	166.0 ( $e_{2u}$ )	-307.603 528



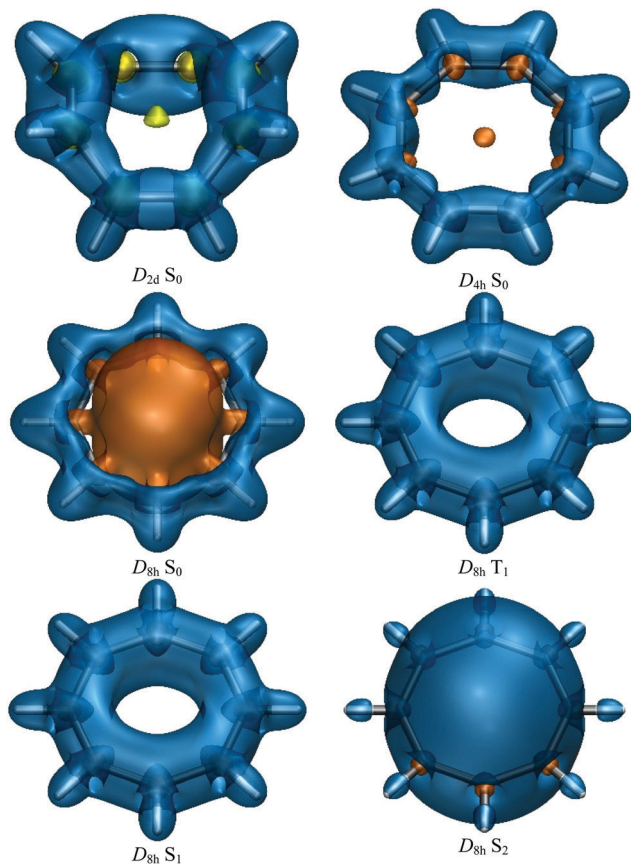


Fig. 1 Isotropic shielding isosurfaces at  $\sigma_{\text{iso}}(\mathbf{r}) = \pm 16$  ppm (“+” in blue, “-” in orange) for the electronic states of COT studied in this paper; additional  $\sigma_{\text{iso}}(\mathbf{r}) = -1$  ppm isosurface (yellow) included for  $S_0$  ( $D_{2d}$  geometry). For details, see text.

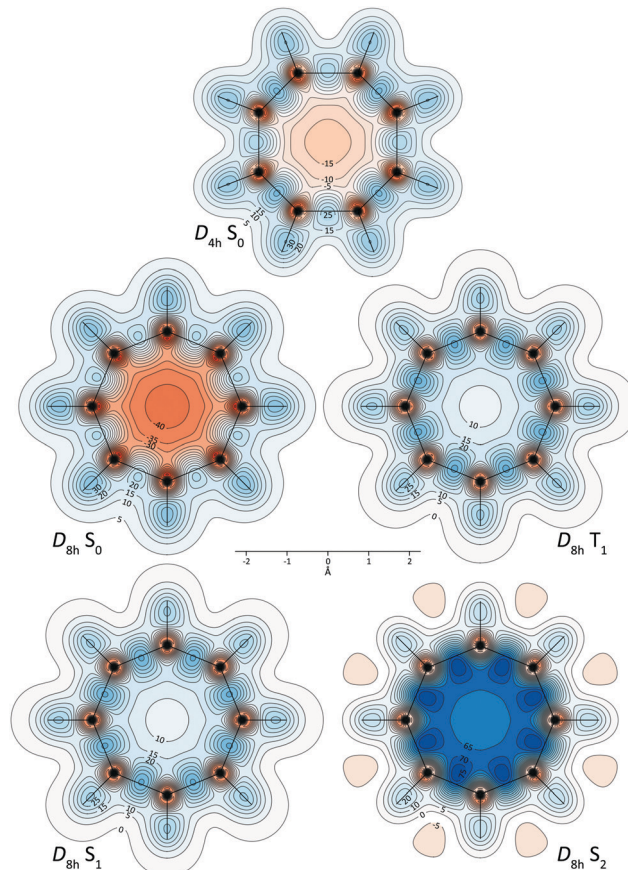


Fig. 2 Isotropic shielding contour plots in the molecular (horizontal) planes for the  $S_0$  state of  $D_{4h}$  COT and the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  states of  $D_{8h}$  COT. Contour levels at  $-75(5)75$  ppm, orange (deshielded) to blue (shielded).

likely to make only a minor contribution to bonding in this molecule.

The differences between the shielding around “single” and “double” carbon–carbon bonds are still obvious but somewhat less pronounced at the  $S_0$  planar geometry of  $D_{4h}$  symmetry. There is some more evidence of antiaromaticity at the ring centre, in the form of a small almost spherical deshielded region with a boundary at  $-16$  ppm. In fact, the  $D_{4h}$   $S_0$   $\sigma_{\text{iso}}(\mathbf{r})$  contour plot in Fig. 2 indicates that most of the interior of the carbon ring is moderately deshielded, including a sizeable region deshielded by more than 10 ppm. Antiaromaticity is also manifested by the weakened shielding around carbon–carbon bonds, the bulk of which is displaced away from the ring centre; this affects more the four “single” bonds.

The ground-state antiaromaticity of COT is most pronounced at the  $D_{8h}$  planar geometry, at which the shielding picture is dominated by a large strongly deshielded dumbbell-shaped region in the centre of the molecule. The presence of this strongly deshielded region leads to further reduction of the shielding around carbon–carbon bonds and further displacement of this shielding towards the exterior of the ring. The variations in isotropic shielding around  $S_0$   $D_{8h}$  COT resemble closely those observed for the paradigm of antiaromaticity,

the electronic ground state of square cyclobutadiene.<sup>24</sup> It has been suggested, on the basis of NICS values, that the  $S_0$  state of  $D_{8h}$  COT is more antiaromatic than the respective state of square cyclobutadiene.<sup>10</sup> Indeed, the deshielding of the ring interior shown in Fig. 1, 2 and Fig. S1, S2 (ESI†) is more intensive than that seen in analogous contour plots for square cyclobutadiene<sup>23,24</sup> but, at the same time, in COT the extent to which the central deshielded region disrupts the shielding around carbon–carbon bonds is smaller. It would be correct to say that while the  $S_0$  state of  $D_{8h}$  COT is undoubtedly strongly antiaromatic, antiaromaticity affects bonding along the carbon framework to a lesser degree than in the respective state of square cyclobutadiene. This is in line with the similarity between the antiaromatic  $S_0$  and aromatic  $T_1$  and  $S_1$   $D_{8h}$  COT geometries illustrated by the data in Table 1.

Clearly,  $\sigma_{\text{iso}}(\mathbf{r})$  isosurfaces and contour plots differentiate between the levels of aromaticity of ground-state COT at its  $D_{8h}$ ,  $D_{4h}$  and  $D_{2d}$  geometries in a more nuanced way than modern valence bond (VB) theory: According to a spin-coupled generalised valence-bond (SCGVB) study,<sup>44</sup> antiaromaticity at the  $D_{8h}$  geometry follows from the singlet biradical character of the wavefunction (triplet pairs coupled to an overall singlet), whereas the absence of resonance within the wavefunctions



**Table 2** Carbon and proton isotropic shieldings and NICS values for the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT. CASSCF(8,8)-GIAO/6-311 + G\*\*/CASSCF(8,8)/6-31G\*\* results, all in ppm

Geometry	State	$\sigma_{\text{iso}}(^{13}\text{C})$	$\sigma_{\text{iso}}(^1\text{H})$	NICS(0)	NICS(1)	NICS(0) <sub>zz</sub>	NICS(1) <sub>zz</sub>
$D_{2d}$	$S_0$ ( $1^1A_1$ )	76.57	27.26	1.16	-1.57	14.08	4.21
$D_{4h}$	$S_0$ ( $1^1A_{1g}$ )	79.48	28.91	16.10	11.98	55.40	37.62
$D_{8h}$	$S_0$ ( $1^1B_{1g}$ )	70.21	31.70	40.71	32.23	128.71	98.22
	$T_1$ ( $1^3A_{2g}$ )	81.93	25.57	-8.93	-8.98	-20.64	-25.60
	$S_1$ ( $1^1A_{1g}$ )	80.01	25.43	-8.87	-9.02	-21.52	-26.34
	$S_2$ ( $1^1B_{2g}$ )	86.02	18.88	-61.55	-52.97	-181.20	-159.09

at the  $D_{4h}$  and  $D_{2d}$  geometries was taken as a sign of non-aromatic behaviour.

It is difficult to tell apart the isotropic shielding pictures observed in the  $T_1$  and  $S_1$  electronic states of COT (Fig. 1, 2 and Fig. S1, S2, ESI<sup>†</sup>); both of these bear surprisingly close resemblance to the doughnut-shaped region of increased shielding enveloping the carbon framework in the electronic ground state of benzene,<sup>23,24</sup> extended over a ring of eight rather than six carbons atoms. This observation provides compelling visual evidence that the  $T_1$  and  $S_1$  electronic states of COT exhibit levels of aromaticity very similar to that of the electronic ground state of benzene.

The negligible change in the level of aromaticity between the  $T_1$  and  $S_1$  electronic states of COT is one of the differences between the aromaticity characteristics of the low-lying excited states of COT and square cyclobutadiene: In square cyclobutadiene  $T_1$  is noticeably more aromatic than  $S_1$ .<sup>24</sup> A second, more important and somewhat unexpected difference is associated with the aromaticity of the second singlet excited state  $S_2$ . In square cyclobutadiene  $S_2$  is antiaromatic but less so than  $S_0$ .<sup>24</sup> In stark contrast, in the  $S_2$  of COT the interior of the carbon ring is intensively shielded all over (Fig. 1, 2 and Fig. S1, S2, ESI<sup>†</sup>), in close resemblance to the shielding picture observed in the  $S_2$  state of benzene.<sup>24</sup>

The conclusion that can be drawn from this unexpected finding is that the  $S_2$  electronic state of COT, similarly to the corresponding state of benzene, exhibits a significant level of aromaticity, surpassing that of benzene in its electronic ground state.

Carbon and proton isotropic shieldings and various NICS indices for the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT, calculated at the same level of theory as the data for the shielding isosurfaces and contour plots, are collected in Table 2. The NICS indices include the original NICS index  $\text{NICS}(0) = -\sigma_{\text{iso}}(\text{at ring centre})$ ,<sup>17</sup> as well as  $\text{NICS}(1) = -\sigma_{\text{iso}}(\text{at } 1 \text{ \AA above ring centre})$ ,<sup>18,19</sup>  $\text{NICS}(0)_{zz} = -\sigma_{zz}(\text{at ring centre})$ ,<sup>20,21</sup> and  $\text{NICS}(1)_{zz} = -\sigma_{zz}(\text{at } 1 \text{ \AA above ring centre})$ .<sup>22</sup> The position at which  $\text{NICS}(1)$  was evaluated for the non-planar  $D_{2d}$  ground state of COT was 1 Å away from the ring centre along the  $S_4$  improper rotation axis. The data for states other than the  $S_2$  electronic state of COT were found to be identical to those reported earlier<sup>10</sup> and have been included in order to facilitate comparison with the rather unexpected magnetic features of this state. According to the  $\text{NICS}(0)$ ,  $\text{NICS}(1)$ ,  $\text{NICS}(0)_{zz}$  and  $\text{NICS}(1)_{zz}$  values for the  $S_2$  electronic state of COT, this state of COT is decidedly more aromatic than the corresponding state

of benzene.<sup>24</sup> This conclusion is reinforced by the very significant proton deshielding observed in  $S_2$  COT: the corresponding  $\sigma_{\text{iso}}(^1\text{H})$  value is more than 8 ppm lower than that in the  $D_{2d}$  ground state. Despite the fact that NICS carry much less information than the shielding isosurfaces and contour plots shown in Fig. 1, 2 and Fig. S1, S2 (ESI<sup>†</sup>), the data included in Table 2 demonstrates that they provide reasonably accurate assessments of the aromaticities of the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT. Of course, due to their single-point nature, NICS are unable to provide any of the insights into the influence of aromaticity and antiaromaticity on bonding in the  $S_0$ ,  $T_1$ ,  $S_1$  and  $S_2$  electronic states of COT that can be analysed and visualised through the respective isotropic shielding isosurfaces and contour plots.

## Conclusions

The analysis of the spatial variations in isotropic shielding,  $\sigma_{\text{iso}}(\mathbf{r})$ , at all stationary points of the ground-state PES of COT, including the  $D_{2d}$  tub-shaped,  $D_{4h}$  bond-alternating and  $D_{8h}$  geometries, as well as at the  $D_{8h}$  geometries of the lowest triplet and first and second singlet ( $T_1$ ,  $S_1$  and  $S_2$ ) electronic excited states reveals both expected and unexpected features of bonding and aromaticity, some of which change dramatically between electronic states.

As expected, the intense antiaromaticity of the electronic ground state at the  $D_{8h}$  planar regular octagon geometry experiences rapid decrease on passing, through the lower-energy  $D_{4h}$  planar geometry, to the lowest-energy  $D_{2d}$  non-planar tub-shaped geometry. Interestingly, even at the  $D_{2d}$  geometry, in which the alternating “single” and “double” carbon-carbon bonds are clearly outlined by the changes in isotropic shielding, ground-state COT retains a hint of antiaromaticity in the form of a small deshielded region surrounding the geometric centre of the molecule.

The features of the first and second singlet excited states of COT revealed by the current magnetic shielding study indicate that Hückel-antiaromatic rings with eight  $\pi$  electrons can be expected to behave differently from square cyclobutadiene in their first and second singlet excited states, with  $S_1$  becoming as aromatic as  $T_1$  and  $S_2$  turning out as strongly aromatic rather than antiaromatic.

The shielding isosurfaces and contour plots suggest that  $\pi$  bonding in the  $S_2$  state of COT (as well as in the  $S_2$  state of benzene<sup>24</sup>) is strengthened, which is associated with increased



shielding within, above and below the ring; this increased shielding creates the perception of a substantially higher level of aromaticity. However, all of this is at the expense of the shielding over the  $\sigma$  framework and the strength of the  $\sigma$  bonds, hence the higher energy of this state. These findings can have important implications for the design of novel photo-functional materials involving flapping molecules<sup>14–16</sup> and suggest that researchers in the area should be advised to examine not only the first singlet excited state of a flapping molecule but also the second singlet excited state—annulation can enhance the  $\sigma$  bond framework, decrease the energy of this state and make it more accessible.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- J. I. Wu, I. Fernández, Y. Mo and P. v. R. Schleyer, *J. Chem. Theory Comput.*, 2012, **8**, 1280–1287.
- M. J. S. Dewar and K. M. Merz, Jr., *J. Phys. Chem.*, 1985, **89**, 4739–4744.
- D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 5879–5881.
- P. G. Wenthold, D. A. Hrovat, W. T. Borden and W. C. Lineberger, *Science*, 1996, **272**, 1456–1459.
- F.-G. Klärner, *Angew. Chem., Int. Ed.*, 2001, **40**, 3977–3981.
- J. L. Andrés, O. Castaño, A. Morreale, R. Palmeiro and R. Gomperts, *J. Chem. Phys.*, 1998, **108**, 203–207.
- A. Schild and B. Paulus, *J. Comput. Chem.*, 2013, **34**, 1393–1397.
- R. J. F. Berger and A. Viel, *Z. Naturforsch., B: J. Chem. Sci.*, 2020, **75**, 327–339.
- M. Garavelli, F. Bernardi, A. Cembran, O. Castaño, L. M. Frutos, M. Merchan and M. Olivucci, *J. Am. Chem. Soc.*, 2002, **124**, 13770.
- P. B. Karadakov, *J. Phys. Chem. A*, 2008, **112**, 12707–12713.
- N. C. Baird, *J. Am. Chem. Soc.*, 1972, **94**, 4941–4948.
- V. Gogonea, P. v. R. Schleyer and P. R. Schreiner, *Angew. Chem., Int. Ed.*, 1998, **37**, 1945–1948.
- F. Feixas, J. Vandenbussche, P. Bultinck, E. Matito and M. Solà, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20690–20703.
- T. Yamakado, S. Takahashi, K. Watanabe, Y. Matsumoto, A. Osuka and S. Saito, *Angew. Chem., Int. Ed.*, 2018, **57**, 5438–5443.
- S. Saito, *Flapping Molecules for Photofunctional Materials, in Molecular Technology: Materials Innovation*, ed H. Yamamoto and T. Kato, Wiley-VCH, Weinheim, 2019, vol. 3, pp 17–51.
- R. Kimura, H. Kuramochi, P. Liu, T. Yamakado, A. Osuka, T. Tahara and S. Saito, *Angew. Chem., Int. Ed.*, 2020, **59**, 16430–16435.
- P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
- P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin and O. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669–12670.
- P. v. R. Schleyer, M. Manoharan, Z. X. Wang, B. Kiran, H. Jiao, R. Puchta and N. J. R. van Eikema Hommes, *Org. Lett.*, 2001, **3**, 2465–2468.
- I. Cernusak, P. W. Fowler and E. Steiner, *Mol. Phys.*, 2000, **98**, 945–953.
- E. Steiner, P. W. Fowler and L. W. Jenneskens, *Angew. Chem., Int. Ed.*, 2001, **40**, 362–366.
- H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.*, 2006, **8**, 863–866.
- P. B. Karadakov and K. E. Horner, *J. Phys. Chem. A*, 2013, **117**, 518–523.
- P. B. Karadakov, P. Hearnshaw and K. E. Horner, *J. Org. Chem.*, 2015, **81**, 11346–11352.
- P. B. Karadakov, M. A. H. Al-Yassiri and D. L. Cooper, *Chem. – Eur. J.*, 2018, **24**, 16791–16803.
- P. B. Karadakov, *Org. Lett.*, 2020, **22**, 8676–8680.
- P. B. Karadakov, M. Di and D. L. Cooper, *J. Phys. Chem. A*, 2020, **124**, 9611–9616.
- C. Foroutan-Nejad, S. Shahbazian, F. Feixas, P. Rashidi-Ranjbar and M. Solà, *J. Comput. Chem.*, 2011, **32**, 2422–2431.
- C. Foroutan-Nejad, *Theor. Chem. Acc.*, 2015, **134**(8), 1–9.
- S. Fias, P. W. Fowler, J. L. Delgado, U. Hahn and P. Bultinck, *Chem. – Eur. J.*, 2008, **14**, 3093–3099.
- S. Van Damme, G. Acke, R. W. A. Havenith and P. Bultinck, *Phys. Chem. Chem. Phys.*, 2016, **18**, 11746–11755.
- K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, R. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansík, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawłowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Snegov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski and H. Ågren, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2014, **4**, 269–284, Dalton, a molecular electronic structure program, Release Dalton2018.1, 2019, see <http://daltonprogram.org>.



- 33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.
- 34 K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K. L. Bak and H. J. A. Jensen, *J. Chem. Phys.*, 1994, **100**, 8178–8185.
- 35 K. Ruud, T. Helgaker, K. L. Bak, P. Jørgensen and J. Olsen, *Chem. Phys.*, 1995, **195**, 157–169.
- 36 P. B. Karadakov, *J. Phys. Chem. A*, 2008, **112**, 7303–7309.
- 37 P. W. Fowler, E. Steiner and L. W. Jenneskens, *Chem. Phys. Lett.*, 2003, **371**, 719–723.
- 38 Z. Rinkevicius, J. Vaara, L. Telyatnyk and O. Vahtras, *J. Chem. Phys.*, 2003, **118**, 2550–2561.
- 39 J. Vaara, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5399–5418.
- 40 See <https://gaussian.com/cubegen/> (checked on 24 September 2021).
- 41 P. B. Karadakov and K. E. Horner, *J. Chem. Theory Comput.*, 2016, **12**, 558–563.
- 42 K. E. Horner and P. B. Karadakov, *J. Org. Chem.*, 2013, **78**, 8037–8043.
- 43 K. E. Horner and P. B. Karadakov, *J. Org. Chem.*, 2015, **80**, 7150–7157.
- 44 P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, *J. Phys. Chem.*, 1995, **99**, 10186–10195.

