Electronic Supplementary Information

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

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1. Additional Figures

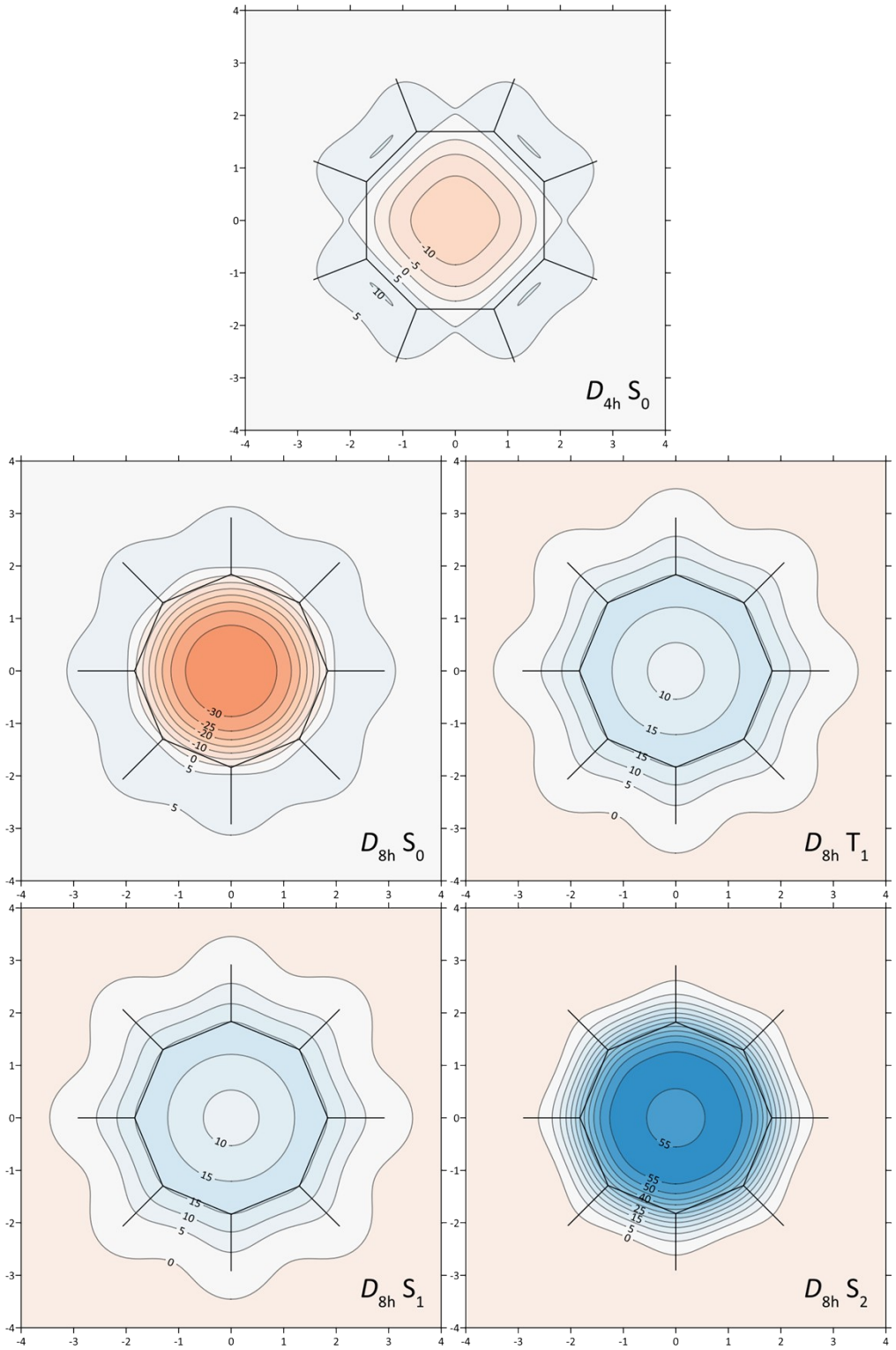

Fig. S1. Isotropic shielding contour plots for the S_0 (at D_{4h} and D_{8h} geometries), T_1, S_1 and S_2 (at D_{8h} geometries) electronic states of COT in planes 1 Å above the respective molecular planes. CASSCF(8,8)-GIAO/6-311+G*//CASSCF(8,8) /6-31G** level of theory, $\sigma_{iso}(\mathbf{r})$ in ppm, distances in Å.

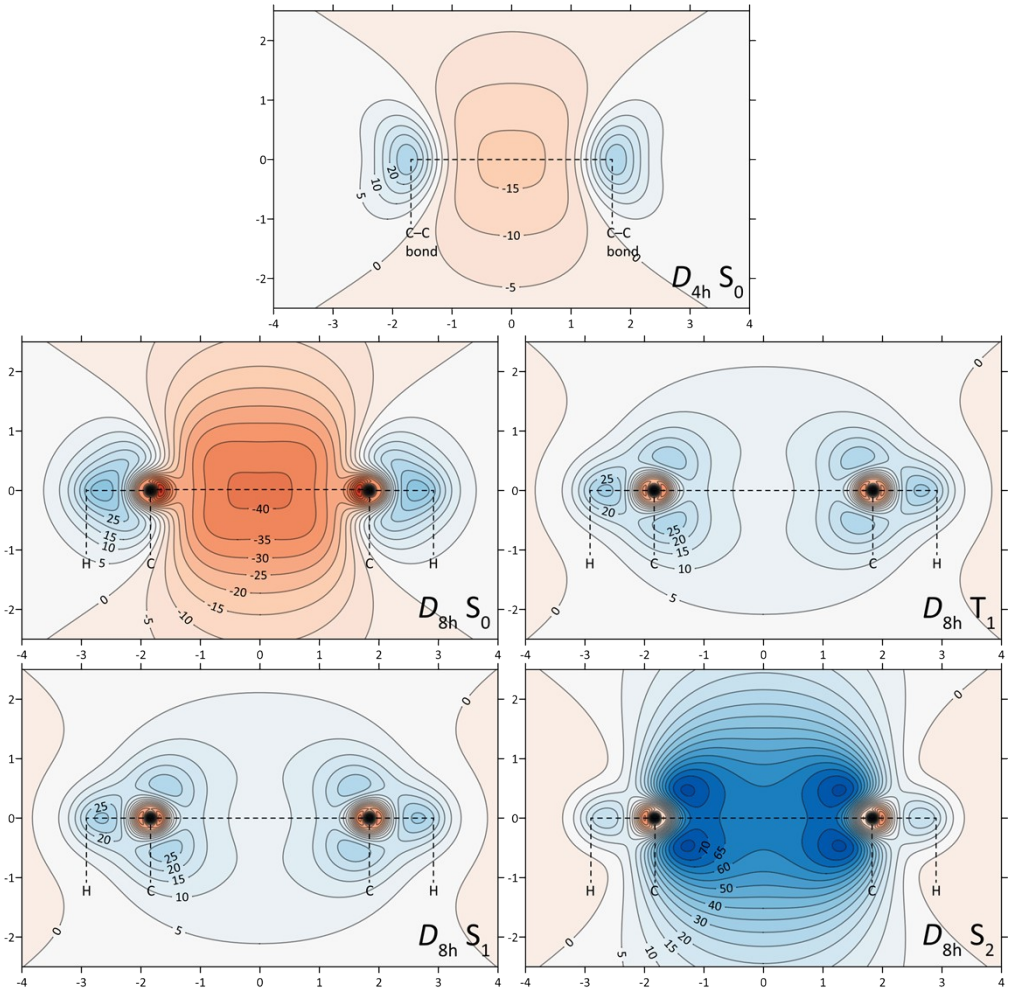

Fig. S2. Isotropic shielding contour plots for the S_0 (at D_{4h} and D_{8h} geometries), T_1, S_1 and S_2 (at D_{8h} geometries) electronic states of COT in vertical planes perpendicular to the respective molecular planes. The vertical plane for the S_0 state at the D_{4h} geometry is passing through the midpoints of two opposite C–C bonds; for all other states the vertical planes are passing through two opposite C–H unites. Other details as for Figure S1.

2. Gaussian Cube Files with Isotropic Shielding Values

A 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 is available as a separate download. These files can be examined with several programs, including GaussView (see https://gaussian.com/gaussview6/) and Visual Molecular Dynamics (VMD, see https://www.ks.uiuc.edu/Research/vmd/). Both URLs were checked on 24 September 2021.

3. Additional Computational Details

All GAUSSIAN CASSCF(8,8)/6-31G** and CASSCF(8,8)/cc-pVTZ geometry optimizations reported in this paper were carried out using the option “Opt(VeryTight)”.

All DALTON CASSCF(8,8)-GIAO/6-311+G* NMR shielding tensor calculations were run without changes to the default program options.

4. Optimised Geometries

The geometries of all states of COT of D_{8h} symmetry are defined completely by the data included in Table 1.

For the geometries below, all coordinates are in Å.

CASSCF(8,8)/6-31G** optimised geometry of D_{2d} S_0 COT.

C	-0.671777	1.562419	0.387958
C	-1.562419	0.671777	-0.387958
C	-1.562419	-0.671777	-0.387958
C	-0.671777	-1.562419	0.387958
C	0.671777	-1.562419	0.387958
C	1.562419	-0.671777	-0.387958
C	1.562419	0.671777	-0.387958
C	0.671777	1.562419	0.387958
H	-1.172715	2.323498	0.966126
H	-2.323498	1.172715	-0.966126
H	-2.323498	-1.172715	-0.966126
H	-1.172715	-2.323498	0.966126
H	1.172715	-2.323498	0.966126
H	2.323498	-1.172715	-0.966126
H	2.323498	1.172715	-0.966126
H	1.172715	2.323498	0.966126

CASSCF(8,8)/cc-pVTZ optimised geometry of D_{2d} S_0 COT.

C	-0.669177	1.560748	0.384289
C	-1.560748	0.669177	-0.384289
C	-1.560748	-0.669177	-0.384289
C	-0.669177	-1.560748	0.384289
C	0.669177	-1.560748	0.384289
C	1.560748	-0.669177	-0.384289
C	1.560748	0.669177	-0.384289
C	0.669177	1.560748	0.384289
H	-1.168154	2.323977	0.956803
H	-2.323977	1.168154	-0.956803
H	-2.323977	-1.168154	-0.956803
H	-1.168154	-2.323977	0.956803
H	1.168154	-2.323977	0.956803
H	2.323977	-1.168154	-0.956803
H	2.323977	1.168154	-0.956803
H	1.168154	2.323977	0.956803

CASSCF(8,8)/6-31G** optimised geometry of D_{4h} S_0 COT.

C	0.675524	1.716236	0.000000
C	1.716236	0.675524	0.000000
C	1.716236	-0.675524	0.000000
C	0.675524	-1.716236	0.000000
C	-0.675524	-1.716236	0.000000
C	-1.716236	-0.675524	0.000000
C	-1.716236	0.675524	0.000000
C	-0.675524	1.716236	0.000000
H	1.107408	2.703584	0.000000

```
H    2.703584    1.107408    0.000000
H    2.703584   -1.107408    0.000000
H    1.107408   -2.703584    0.000000
H   -1.107408   -2.703584    0.000000
H   -2.703584   -1.107408    0.000000
H   -2.703584    1.107408    0.000000
H   -1.107408    2.703584    0.000000
```

CASSCF(8,8)/cc-pVTZ optimised geometry of D_{4h} S_0 COT.

```
C    0.672701    1.712477    0.000000
C    1.712477    0.672701   -0.000000
C    1.712477   -0.672701    0.000000
C    0.672701   -1.712477   -0.000000
C   -0.672701   -1.712477    0.000000
C   -1.712477   -0.672701   -0.000000
C   -1.712477    0.672701    0.000000
C   -0.672701    1.712477   -0.000000
H    1.103917    2.697556    0.000000
H    2.697556    1.103917   -0.000000
H    2.697556   -1.103917    0.000000
H    1.103917   -2.697556   -0.000000
H   -1.103917   -2.697556    0.000000
H   -2.697556   -1.103917   -0.000000
H   -2.697556    1.103917    0.000000
H   -1.103917    2.697556   -0.000000
```

5. Additional Information about the CASSCF(8,8) Wavefunctions for the S_0, S_1, S_2 and T_1 States of D_{8h} COT

As explained in the section Computational procedure, the largest subgroup of the D_{8h} point group supported by the Dalton program package is D_{2h}, therefore 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 data included below provides details of the compositions of the respective CASSCF(8,8)/6-311+G*//CASSCF(8,8)/6-31G** wavefunctions taken from the Dalton output files. Note that due to the use of state-optimized CASSCF wavefunctions, the natural orbitals for all four states are different; we include information for the active-space natural orbitals only. The numbering of the active-space natural orbitals in CSFs corresponds to the order in which these orbitals appear in the lists showing their occupancies.

S_0 (1^1B_{1g}) state

```
 Occupancies of natural orbitals
 -------------------------------

 Symmetry 5  ( B1u) -- Total occupation in this symmetry is   2.998517251

   1.939910483   1.001987233   0.056619535

 Symmetry 6  ( B2g) -- Total occupation in this symmetry is   1.999747757

   1.892943453   0.106804304

 Symmetry 7  ( B3g) -- Total occupation in this symmetry is   1.999747756

   1.892943458   0.106804298
```

```
Symmetry 8  ( Au ) -- Total occupation in this symmetry is   1.001987236

  1.001987236

Printout of CI-coefficients abs greater than 0.05000 for root  1
*** NOTE: this root is the reference state ***

Printout of coefficients in interval  3.1623E-01 to  1.0000E+00
============================================================

 Coefficient of CSF no.        39 is      0.89412239    8.94122394E-01
 Orbital          1   4   6   2   8
 Spin coupling    2   2   2   1  -1
```

The S_0 data shows that the largest contribution to the S_0 wavefunction (79.9%) is provided by a single configuration state function (CSF), in which the active-space natural orbitals 1, 4 and 6 are doubly-occupied, and the spins of the singly-occupied active-space natural orbitals 2 and 8 are coupled to a singlet.

S_1 (1^1A_g) state

```
Occupancies of natural orbitals
-------------------------------

Symmetry 5  ( B1u) -- Total occupation in this symmetry is   3.018022301

  1.928102895   1.038015577   0.051903830

Symmetry 6  ( B2g) -- Total occupation in this symmetry is   1.971970668

  1.867502612   0.104468055

Symmetry 7  ( B3g) -- Total occupation in this symmetry is   1.971970647

  1.867502600   0.104468047

Symmetry 8  ( Au ) -- Total occupation in this symmetry is   1.038036384

  1.038036384

Printout of CI-coefficients abs greater than 0.05000 for root  1
*** NOTE: this root is the reference state ***

Printout of coefficients in interval  3.1623E-01 to  1.0000E+00
============================================================

 Coefficient of CSF no.         7 is      0.62102063    6.21020633E-01
 Orbital          1   2   4   6
 Spin coupling    2   2   2   2

 Coefficient of CSF no.        49 is      0.62102879    6.21028795E-01
 Orbital          1   4   6   8
 Spin coupling    2   2   2   2
```

The S_1 data shows that the largest contribution to the S_1 wavefunction (77.1%) is provided by two CSFs, in which all active-space natural orbitals are doubly-occupied (orbitals 1, 2, 4 and 6 in the first CSF, and orbitals 1, 4, 6 and 8 in the second CFS, respectively).

S_2 (2^1A_g) state

```
 Occupancies of natural orbitals
 -------------------------------

 Symmetry 5  ( B1u) -- Total occupation in this symmetry is   2.997965956

   1.981221666   1.002561542   0.014182748

 Symmetry 6  ( B2g) -- Total occupation in this symmetry is   1.999730938

   1.963059419   0.036671518

 Symmetry 7  ( B3g) -- Total occupation in this symmetry is   1.999730939

   1.963059471   0.036671468

 Symmetry 8  ( Au ) -- Total occupation in this symmetry is   1.002572167

   1.002572167

 Printout of CI-coefficients abs greater than 0.10000 for root  2
 *** NOTE: this root is the reference state ***

 Printout of coefficients in interval  3.1623E-01 to  1.0000E+00
 ================================================================

  Coefficient of CSF no.         7 is     -0.68519088   -6.85190880E-01
  Orbital          1   2   4   6
  Spin coupling    2   2   2   2

  Coefficient of CSF no.        49 is      0.68519464    6.85194641E-01
  Orbital          1   4   6   8
  Spin coupling    2   2   2   2
```

The S_2 data shows that the largest contribution to the S_2 wavefunction (93.9%) is provided by two CSFs, in which all active-space natural orbitals are doubly-occupied (orbitals 1, 2, 4 and 6 in the first CSF, and orbitals 1, 4, 6 and 8 in the second CFS, respectively). These CSFs are similar to those dominating the S_1 wavefunction but their combined weight in S_2 is larger, and the coefficients for these CSFs are of opposite signs.

T_1 (1^3B_{1g}) state

```
 Occupancies of natural orbitals
 -------------------------------

 Symmetry 5  ( B1u) -- Total occupation in this symmetry is   3.001154697

   1.945715406   1.005938179   0.049501112

 Symmetry 6  ( B2g) -- Total occupation in this symmetry is   1.996453559
```

```
  1.894918303   0.101535256

 Symmetry 7  ( B3g) -- Total occupation in this symmetry is   1.996453557

  1.894918283   0.101535274

 Symmetry 8  ( Au ) -- Total occupation in this symmetry is   1.005938187

  1.005938187

 Printout of CI-coefficients abs greater than 0.05000 for root  1
 *** NOTE: this root is the reference state ***

 Printout of coefficients in interval  3.1623E-01 to  1.0000E+00
 ================================================================

  Coefficient of CSF no.        39 is      0.89784048    8.97840483E-01
  Orbital          1   4   6   2   8
  Spin coupling    2   2   2   1   1
```

The T_1 data shows that the largest contribution to the T_1 wavefunction (80.6%) is provided by a single configuration state function (CSF), in which the active-space natural orbitals 1, 4 and 6 are doubly-occupied, and the spins of the singly-occupied active-space natural orbitals 2 and 8 are coupled to a triplet. This is similar to the composition of the S_0 wavefunction, and the main difference between the CSFs dominating the S_0 and T_1 wavefunctions is in the mode of coupling of the spins of the singly-occupied active-space natural orbitals 2 and 8.