

Is Free Cyclooctatetraene Dianion an Aromatic System? A Quantum Chemistry Study

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To investigate whether free cyclooctatetraene dianion (COT²⁻) is aromatic, quantum chemistry methods were used to optimize its structure. Based on the optimized structures, the natural population analysis (NPA) charge, bond order, delocalization energy, nucleus-independent chemical shift (NICS), and harmonic oscillator model of aromaticity (HOMA) values were computed by DFT-B3LYP method with basis set 6-311++G**, which shows that COT²⁻ is not aromatic as it is not planar and has different bond lengths and bond orders, smallest delocalization energy and positive NICS values. To further confirm the finding, the changes of NICS and energy against ring distortion angle were scanned. The COT²⁻ has positive NICS values all along the angle from 180° to 120° while other aromatic systems always have negative values. The energy scanning suggests that COT²⁻ should have the weakest capability to maintain its planar structure. All the calculations strongly indicate that COT²⁻ is not aromatic. This study also suggests that NICS scan might be a good approach to judge aromaticity.

Keywords cyclooctatetraene, aromaticity, NICS, HOMA, dianion

Introduction

1,3,5,7-Cyclooctatetraene, with molecular formula C₈H₈ (COT, hereinafter) and four single and four double carbon-carbon bonds alternately arranged in its 8-membered ring structure, is an interesting molecule as it is neither planar nor aromatic. However, COT moiety shows aromaticity with planar structure in its complex with alkaline earth metal, *e.g.*, COT-Ca, which is formed by COT and calcium.^{1,2} The cause is that about 2 electrons are transferred from Ca to COT to form a planar structure with 10- π -electrons, demonstrating essential effect of charge on the COT property. Then, an old question arises again whether cyclooctatetraene dianion (COT²⁻ hereinafter) is an aromatic system. To the best of our knowledge, no publication is found to date on systematic study of the aromaticity of COT²⁻ by quantum chemistry methods.

The concept of aromaticity forms in the developing process of organic chemistry. Those compounds have some general characteristics as planar ring structures, (4*n*+2) delocalized π electrons,^{3,4} lower energy, and special property of magnetism and spectrality. With the development of theory and experimental techniques,

people put forward more standards to predict whether a compound has the characteristics of aromaticity, *e.g.*, nucleus-independent chemical shift (NICS)^{5,6} that is nowadays a widely used magnetic index.^{7,8} When NICS is less than zero, the compound is aromatic while the compound is anti-aromatic if NICS is greater than zero. Another method is called harmonic oscillator model of aromaticity (HOMA) put forward by Kruszewski and Krygowski⁹ with the formula of

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{opt}} - R_i)^2$$

where *n* is the number of bonds considered, and α is an empirical constant fixed (for C—C bonds $\alpha=257.7$), R_{opt} is 1.388 Å and R_i is the computed bond length. An aromatic ring has HOMA value = 1 whereas a non-aromatic compound has value 0. Other criteria include delocalization energy, enthalpy of hydrogenation and so on.

To explore structural and aromatic properties, the geometries of COT and COT²⁻ were fully optimized. On the basis of the optimized structures, atomic charge, bond order, NICS, HOMA, delocalization energy, and

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the changes of NICS and energy against ring distortion were calculated. The results show that free COT^{2-} with D_{2d} symmetry is anti-aromatic although the COT^{2-} moiety with C_{8v} symmetry in the complex COT-Ca is aromatic.²

Computational details

The geometries of COT and COT^{2-} were fully optimized without any symmetry constraint using the DFT-B3LYP^{10,11} method with basis set 6-311++G**. The reason why the diffuse functions were employed in this study is that COT^{2-} is a dianion. Then, vibrational frequency analysis was carried out for the optimized structures to validate whether they are minima on the potential energy surfaces. The natural population analysis (NPA) atomic charge, bond order, electron density (ρ) at bond critical point (BCP), NICS and HOMA values, delocalization energy, and the changes of NICS and energy against ring distortion were then calculated at the same level of the theory based on the optimized structures. All the calculations were performed on an SGI3800 supercomputer with Gaussian 03¹² and AIM2000.^{13,14}

Results and discussion

Optimized geometries of COT and its ions

The optimized geometries of COT and its dianion are depicted in Figure 1. It was observed that both COT and COT^{2-} had two different carbon-carbon bond lengths that are between typical single and double bond lengths with the same symmetry of D_{2d} , indicating that COT^{2-} should not be an aromatic structure. Interestingly, if symmetry of D_{8h} was forced to keep during the geometrical optimization for COT^{2-} , identical optimized bond length was found in the structure. But the frequency calculation revealed imaginary frequencies, indicating that COT^{2-} would not adopt the geometry with D_{8h} symmetry. Therefore, the geometry with D_{2d} symmetry should be a minimum structure, which has two different carbon-carbon bond lengths (1.420 and 1.412 Å). To confirm this observation, the MP2 method with basis set 6-311++G** was used to optimize the structure of COT^{2-} , which reveals again that COT^{2-} would not adopt the geometry with D_{8h} symmetry.

Atomic charge and bond order

Table 1 shows the NPA charge and bond order calculated at B3LYP/6-311++G** level. As expected, all carbon atoms have the same atomic charge, indicating that the eight carbon atoms have the same chemical environment. However, the bond orders of C(1)—C(2) and C(2)—C(3) in COT are 1.067 and 1.857, respectively, corresponding to the single and double bond lengths of the carbon-carbon bonds in COT . While the bond orders of C(1)—C(2) and C(2)—C(3) in COT^{2-} are also different from each other, and are obviously less than that in benzene. These observations suggest

again that the COT^{2-} might not be an aromatic system.

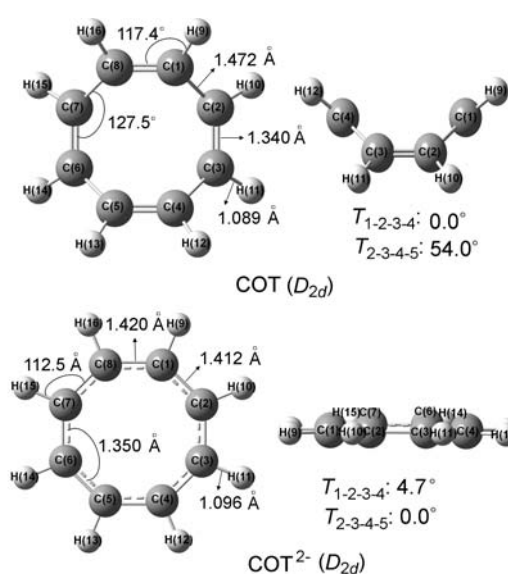


Figure 1 Optimized structures and point groups of COT and COT^{2-} at B3LYP/6-311++G** level.

Table 1 Calculated NBO atomic charge (a.u.) and bond order at B3LYP/6-311++G** level

		COT	COT^{2-}	C_6H_6
Atomic charge	C(1)	-0.200	-0.374	-0.204
	H(16)	0.200	0.124	0.204
Bond order	C(1)—C(2)	1.067	1.337	1.438
	C(2)—C(3)	1.857	1.379	1.438

To further explore the bond strength, electron density ρ of bond critical point (BCP) was calculated at the B3LYP/6-311++G** level. The data in Table 2 show that the BCP densities of C(1)—C(2) (0.288 a.u.) and C(2)—C(3) (0.291 a.u.) in the dianion are different, and are between the typical single bond (0.268 a.u.) and double bond (0.337 a.u.) in COT , suggesting repeatedly that COT^{2-} is not a well delocalized system, which is in consistent with the optimized bond length and bond order.

Table 2 Electron density ρ (a.u.) of the bond critical points in COT , COT^{2-} and C_6H_6 at B3LYP/6-311++G** level

	COT	COT^{2-}	C_6H_6
C(1)—C(2)	0.268	0.288	0.309
C(2)—C(3)	0.337	0.291	0.309

Estimated NICS and HOMA values

Table 3 lists the estimated NICS and HOMA values at B3LYP/6-311++G** level. Benzene is of negative NICS value. The COT and its dianion have positive values, accordingly, COT and its dianion are anti-aromatic. This conclusion is in agreement with the

deduction based on the optimized geometrical parameters, bond order and electron density values. However, the HOMA values of COT^{2-} is 0.797, accordingly COT^{2-} is somewhat aromatic. This is somewhat contradicted with the findings from NICS and other calculated results discussed above. Thus, these two aromaticity criteria lead to different conclusion of a specific system. Therefore, more calculation should be performed to clarify the aromaticity of COT^{2-} .

Table 3 NICS and HOMA of COT, COT^{2-} (D_{2d} symmetry) and C_6H_6 at B3LYP/6-311++G** level

	COT	COT^{2-}	C_6H_6
NICS (0 Å) ^a	4.652	8.703	-8.045
NICS (1 Å) ^a	0.938	6.825	-10.216
HOMA	-0.214	0.80	0.989

^a The distance from the centroid along the D_{2d} axis.

Planar distortion energy scanning

We thought that a good aromatic system should be very rigid against ring distortion, in other words, it should have strong capability to keep its planar geometry. Thus, a scan study of the planar distortion energy of COT^{2-} and benzene was performed at the B3LYP/6-311++G** level. Distortion energy, ΔE as shown in Figure 2a, is defined as the difference between the fully minimized energy and the energy corresponding to a specific dihedral ($T_{2-1-4-5}$, $T_{2-1-5-6}$), which reveals that COT^{2-} has the weakest capability to maintain its planar structure among the four calculated systems. The $\Delta\Delta E$ is the energy change against dihedral per 10° as shown in Figure 2b. Indeed, the slope of the regression formula of $\Delta\Delta E$ against dihedral for benzene is 1.87 with an intercept of $115 \text{ kJ}\cdot\text{mol}^{-1}$, while it is 1.20 for COT^{2-} with an intercept of $71 \text{ kJ}\cdot\text{mol}^{-1}$. The other two well-known aromatic systems pyridine and pyrazine also have larger slope and intercept than COT^{2-} . Thus, good aromatic system, such as benzene, has stronger capability to maintain its planar structure.

NICS versus planar distortion

We also thought that a good aromatic system should still have aromaticity if its geometry is perturbed. Thus, a scan of NICS value of both benzene and COT^{2-} against dihedral was performed. As showed in Figure 3, the NICS values of COT^{2-} are always positive except a specific geometry with a dihedral angle of 180° . However, the planar COT^{2-} has imaginary frequencies, therefore, is not stable. For validation again, the scan of NICS value against distortion angle for other two systems, *viz.*, pyridine and pyrazine, was performed, which reveals a similar result that all NICS values are always negative for aromatic systems. Accordingly, free COT^{2-} is anti-aromatic in general though it might adopt another symmetry, *e.g.* D_{8h} symmetry, if different optimization

methods and basis sets were employed.

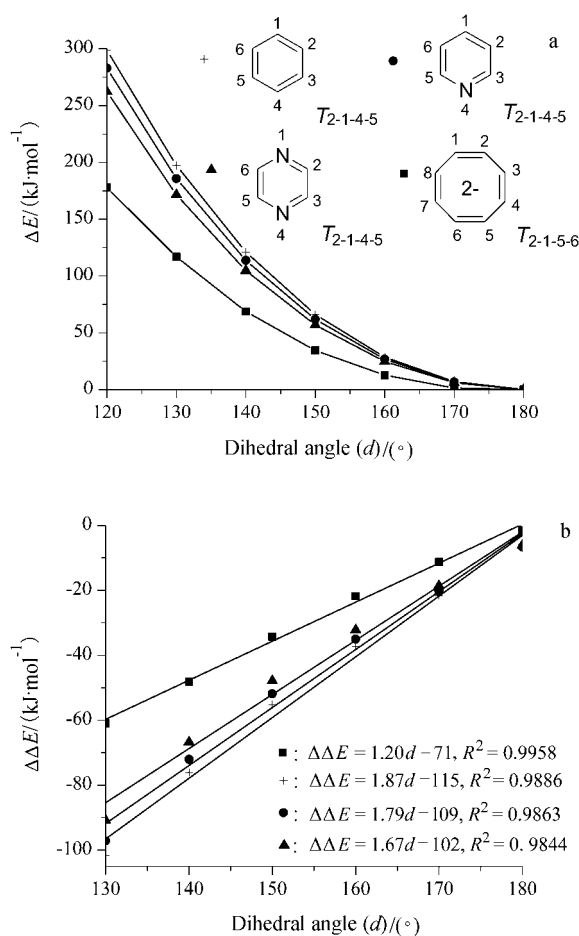


Figure 2 (a) The ΔE versus the dihedral angle; (b) The $\Delta\Delta E$ versus the dihedral angle.

Delocalization energy

The conjugative effect can cause delocalization energy. The delocalization energy of C_6H_6 is equal to the difference between enthalpy of hydrogenation of C_6H_6 and three times of that of the cyclohexene.¹⁵⁻¹⁷ Compound is more stable when its delocalization energy is greater. Table 4 shows that the delocalization energy of COT^{2-} is 30.4 or $3.8 \text{ kJ}\cdot\text{mol}^{-1}$ per bond, while the other aromatic systems are of much higher delocalization energy than COT^{2-} . For instance, the delocalization energy of benzene is 157.3 or $26.2 \text{ kJ}\cdot\text{mol}^{-1}$ per bond, therefore, COT^{2-} should not be an aromatic system.

Table 4 Delocalization energy (ΔE_{deloc} in $\text{kJ}\cdot\text{mol}^{-1}$)

System	ΔE_{deloc}	ΔE_{deloc} (per bond)
benzene	157.3 (exp 151)	26.2 (exp 25.2)
pyridine	134.2	22.4
pyrazine	109.5	18.3
COT^{2-}	30.4	3.8

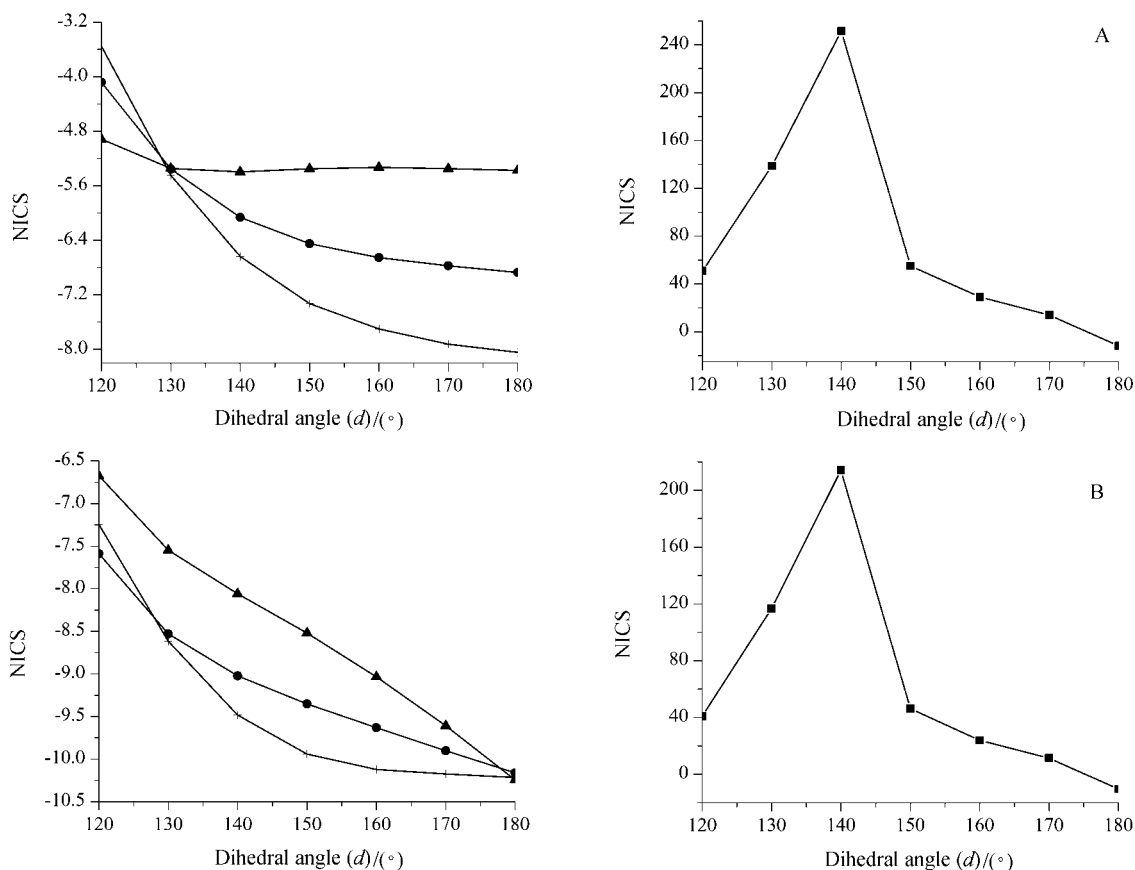


Figure 3 NICS values versus planar distortion angle. (A) at 0 Å from the centroid along the main axis; (B) at 1 Å from the centroid along the main axis (refer to Figure 2 for system sign).

Conclusion

To study structural and aromatic properties of free cyclooctatetraene dianion (COT^{2-}), density functional theory B3LYP was applied to optimize the structures of COT and COT^{2-} with basis set 6-311++G**, followed by calculation of NBO atomic charge, bond order, electron density ρ of bond critical point (BCP), nucleus-independent chemical shifts (NICS), HOMA, delocalization energy, and the changes of NICS and energy against ring distortion angle. The calculation results show free COT^{2-} with D_{2d} symmetry as its lowest energy structure is anti-aromatic in nature. This study also suggests that NICS scan against ring distortion angle might be a good criterion for evaluating aromaticity.

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