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Dithieno[3,4-*b*:3′,4′-*d*]thiophene-Annelated Antiaromatic Planar Cyclooctatetraene with Olefinic Protons

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ABSTRACT

The design and synthesis of a new planar cyclooctatetraene (COT) with protons directly connected to the COT ring was attained by mono-annelation with dithieno[3,4-*b*:3′,4′-*d*]thiophene. The planar structure of the COT core was unambiguously confirmed by X-ray crystallography. The magnetic antiaromaticity of the COT core was found to be higher than that of the previously synthesized planar COTs with olefinic protons, according to the results of ^{1}H NMR and absorption spectra as well as NICS calculations.

Modern theoretical studies of the magnetic criteria of aromaticity have predicted that the antiaromaticity of planar cyclooctatetraene (COT) in the singlet state is quite high,[1,2] although, given its energetic properties, the antiaromaticity of COT, even in its planar form, has long been known to be negligibly small.[3] Thus, it was shown that D_{4h} COT has the largest nucleus independent chemical shift (NICS)[4] value among bond-alternated 4nπ-annulenes.[2d] However, the bond-alternated planar COTs are the transition states for ring inversion[3a,5] and are difficult to access by spectroscopic means. To experimentally study the magnetic criteria of the antiaromaticity of planar COT, it is necessary to employ structural modifications that force the inherently tub-shaped COT ring into a planar structure. Various molecular designs have been proposed for this purpose,[1,3a,6−11] but only a few derivatives have realized a completely planar COT structure with substantial antiaromatic paratropicity. In particular, derivatives isolated having protons directly connected to the planar COT core, which are potentially useful to investigate the

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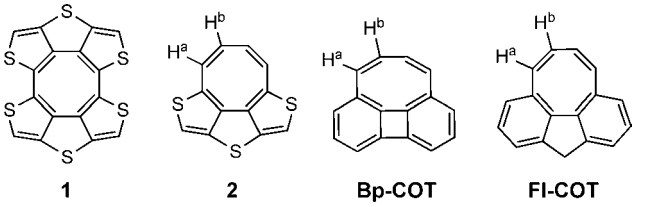
paratropic ring current by ^{1}H NMR spectroscopy, have been limited to biphenylene-[10] and fluorene-annelated[11] ones, abbreviated here as **Bp-COT** and **Fl-COT**, respectively.

Recently, we reported the synthesis and properties of the dithienothiophene cyclic dimer **1** having a planar COT core.[7b] The NICS antiaromaticity of the COT ring in **1** is approximately 70% of that of the hypothetical D_{4h} COT, which has top-class NICS-based antiaromaticity among existing COT derivatives. The principal reason for the 30% reduction of the NICS value was considered to be the annelation of the aromatic thiophene ring, as further reduction of the NICS value was observed when the planar COT core was annelated with benzene having greater aromaticity than thiophene. These results prompted us to synthesize COT **2**, which was monoannelated with dithienothiophene and is expected to exhibit greater antiaromaticity in its COT core. In this study, we report the synthesis, structure, and properties of the planar COT **2** together with the results of DFT calculations. From these investigations, the COT ring in **2** was shown to have a higher magnetic antiaromaticity than **Bp-COT** or **Fl-COT**.



In general, the synthesis of a COT ring is not straightforward.[12] In fact, the double Wittig reaction in the final step for **Bp-COT** gave quite a low yield (~1%).[10b] Furthermore, preparation of the corresponding precursor dithienobenzene for **2**, as prepared for **Fl-COT** from cyclopenta[*def*]phenanthrene,[11] appeared to be difficult. Recently, Mitchell et al. reported the preparation of dimethyldihydropyrene-annelated COT by using ring-closing metathesis as the key step.[13] Thus we chose a similar route, although we needed to prepare an asymmetrically arranged dialkene precursor unlike in the previous route. As shown in Scheme 1, the first alkene unit was introduced via formylation of dithieno[3,4-*b*:3′,4′-*d*]thiophene **3**[7b] followed by Wittig reaction. Because of the low stability of the vinyl analogue of **5**, the preparation of a propylene derivative was necessary. The second alkene unit was then introduced by formylation followed by reaction with vinyl magnesium bromide. The cyclooctatriene precursor **8** was obtained by ring-closing metathesis using Grubbs second generation catalyst, and the final dehydration was achieved with Martin sulfurane and potassium *tert*-butoxide to give **2**.

To predict the planarity of **2**, geometry optimization at the B3LYP/6-31G(d,p) level was conducted. As shown in Figure 1a, the completely planar C_{2v} structure was obtained as the most stable conformer, which was in contrast to slightly and significantly bent structures of **1**[7b] and

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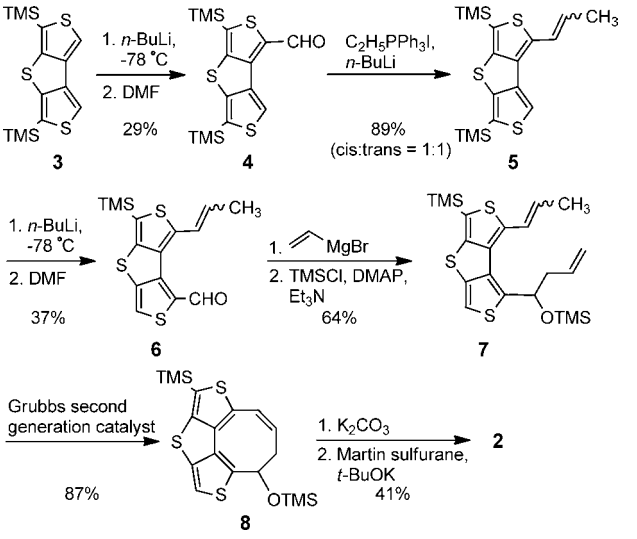
Scheme 1. Synthesis of **2**



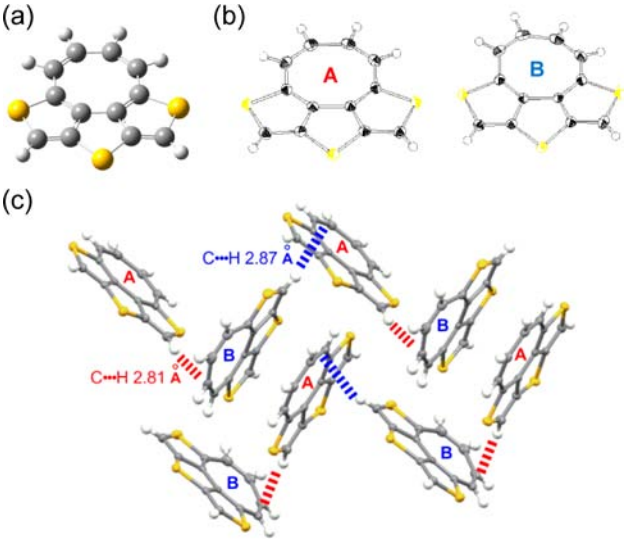


Figure 1. (a) Optimized and (b) X-ray (ORTEP 50% probability) structures and (c) crystal packing of **2**.

Fl-COT (Figure S1, Supporting Information), respectively. In an ideal D_{4h} octagon, all inner angles are 135°, and the COT ring in the optimized structure of **2** showed only small deviations, with angles ranging from 133.2° to 136.8°. The deviation was much smaller than in the deformed planar COT (angle range: 124.0−143.5°) of **Bp-COT** (Figure S1, Supporting Information). Thus, the structure and planarity of the COT ring is in a delicate balance between the bond lengths and angles of the surrounding units, and **2** has the least deformed planar COT ring among them. As for the bond lengths in the COT ring, a significant deviation from standard values was not observed, suggesting that the magnetic

criteria of antiaromaticity described below is not correlated with the bond length alternation.

A single crystal of **2** suitable for X-ray analysis was obtained from isopropyl ether cooled in a refrigerator. In the X-ray structure, which was the first observed for planar COT derivatives with olefinic protons, two crystallographically independent conformers were observed (Figure 1b). One (denoted by A in Figure 1) has a planar structure, while the other (B) has a slightly bent COT ring. The bending in the latter conformer is considered to be due to crystal packing forces because there are shorter intermolecular C···H contacts (2.81 Å) between the COT carbons in the B form and a thiophene proton in the A form (Figure 1c). The observed bond lengths of the butadienylene moiety in the COT ring ranged from 1.343(3) to 1.347(3) Å for the *double bond* portion and 1.463(3) to 1.466(3) Å for the *single bond* portion. These bond lengths are typical for 1,3-butadiene. Therefore, the magnetic criteria of antiaromaticity is not correlated with the bond length alternation as predicted by DFT calculations. The bond angles in the COT ring in the A form ranged from 132.6(2)° to 137.8(2)°, which were also very close to the calculated values.

For comparisons of magnetic (anti)aromaticity, NICS[4] has become one of the most popular measures in recent years. In NICS calculations using the Gaussian program, the gauge including atomic orbitals (GIAO) model through the HF or B3LYP methods was usually selected. However, in the parent D_{4h} COT, GIAO−HF and GIAO−B3LYP gave quite different NICS(0)$_{iso}$ (NICS(1)$_{zz}$) values[2a] (GIAO/HF/6-311+G(d,p): 26.6 (62.5), GIAO/B3LYP/6-311++G(d,p): 41.3 (99.3)). This discrepancy is due to the large difference in the calculated HOMO−LUMO gap (HF: 7.89 eV, B3LYP: 2.36 eV), as the ring current of the COT ring is dominated by the HOMO−LUMO transition caused by the external magnetic field.[14,15] Thus, we investigated which method is better for NICS calculations of (4n)π-electron systems. For this purpose, we compared the calculated and observed ^{1}H NMR shifts of other (4n)π (dehydro)annulenes that have inner ring protons,[16] which are much more sensitive to the ring current effect than the outer protons. As a result,[16] the chemical shifts for the inner ring protons calculated with the B3LYP method were too low field, while those with the HF method were in reasonable agreement with the experimental values, suggesting that the HF method is better for NICS calculations of antiaromatic rings.[17,18] In comparison among **2**, **Bp-COT** and **Fl-COT** (Table 1 for the HF method and Table S2, Supporting Information, for the B3LYP method), **2** has the largest NICS(0)$_{iso}$ (NICS(1)$_{zz}$) value (21.1 (51.0)). This value is approximately 80% of that of the parent D_{4h} COT.

Table 1. NICS(0)$_{iso}$ and NICS(1)$_{zz}$ (ppm)[a] Values of Planar COTs

compd	NICS(0)$_{iso}$	NICS(1)$_{zz}$
1	17.4	44.8
2	21.1	51.0
COT (D_{4h})	26.6	62.5
Bp-COT	13.8	32.5
Fl-COT	8.6	19.5

[a] GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d,p).

Antiaromatic COT should be accompanied by a narrow HOMO−LUMO gap, and the gaps of **2** calculated at the B3LYP/6-31G(d,p) level (2.5 eV)[17] and estimated by cyclic voltammetry (CV) (2.4 eV, Figure S2, Supporting Information) and UV−vis spectra (650 nm (λ_{max} (beginning of vibrational steps)) 1.9 eV, Figure 2) were comparable

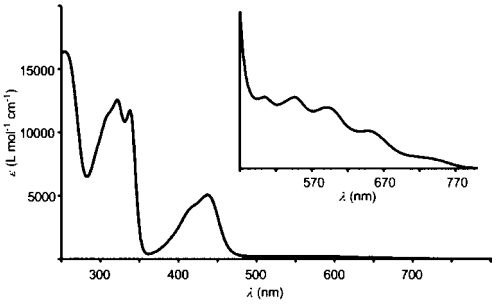


Figure 2. UV−vis spectrum of **2** in CH_2Cl_2.

to those of **1** (calc: 2.6 eV) and its tetra-TMS derivative (calc: 2.6 eV, CV: 2.3 eV, UV−vis: 2.0 eV)[7] despite of the reduction of the π-system from **1** to **2**. Note that the longest absorption maximum of **2** was 19 nm longer than that of **Bp-COT**,[10b] indicating **2** has a narrower HOMO−LUMO gap than **Bp-COT**.

The observed and calculated NMR chemical shifts of the olefin protons (H^a and H^b) in the COT rings are summarized in Table 2. The observed chemical shifts of H^b in **2** (δ 4.41 ppm), which are less affected by the ring current of annelated thiophene ring, were 1.4−1.5 ppm in the higher field than those of the corresponding H^b in **8** (δ 5.94) and olefinic protons in the parent COT (δ 5.8). The magnitude of upfield shifts are comparable to that of downfield shifts of the alkenyl protons from 1,3-cyclohexadiene (δ 5.7−5.8) to benezene (δ 7.3). Accordingly, a substantial paratropic

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(15) A similar discrepancy was also observed for planar COT with the CTOCD-DZ (continuous transformation of the origin of the current density-diamagnetic zero) method. See ref 2c.

(16) The experimental data were obtained from the following studies. [16]Annulene: Oth, J. F. M.; Gilles, J.-M. *Tetrahedron. Lett.* **1968**, *9*, 6259–6264. Trisdehydro[16]annulene: Nakatsuji, S.; Morigaki, M.; Akiyama, S.; Nakagawa, M. *Tetrahedron. Lett.* **1975**, *16*, 1233–1236. Trisdehydro[20]annulene: Nakatsuji, S.; Nakagawa, M. *Tetrahedron. Lett.* **1975**, *16*, 3927–3930. Trisdehydro[24]annulene: Nakatsuji, S.; Akiyama, S.; Nakagawa, M. *Tetrahedron. Lett.* **1976**, *17*, 2623–2626. See Table S1 in Supporting Information for the numerical results.

(17) Despite the overestimation of paratropic ring current with the B3LYP method, which partly stems from the calculated narrower HOMO−LUMO gap, the B3LYP method gave the better estimation of observed HOMO−LUMO gap.

(18) The similar conclusion was also drawn for the magnetic properties of aromatic annulenes. See: Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopandhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495–13505.

Table 2. Observed and Calculated ^{1}H NMR Chemical Shifts (ppm) of H^a and H^b in Planar COTs

	obsd		calcd[a]	
compd	H^a	H^b	H^a	H^b
2	4.71	4.41	4.22	4.00
8	6.73	5.94	6.88	6.18
Bp-COT	4.74	4.61	4.99	4.61
Fl-COT	5.90	5.68	6.12	5.70

[a] GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d,p).

ring current is present in **2**.[19] In comparison among **2**, **Bp-COT** and **Fl-COT**, the chemical shift of H^b in **2** was in the highest field consistent with the larger NICS value of **2**. Thus, these experimental results, i.e., the narrower HOMO−LUMO gap and the higher field chemical shift of H^b of **2**, supported the conclusion that the COT ring of **2** has a higher magnetic atiaromaticity than **Bp-COT** or **Fl-COT**, as predicted by the NICS calculations.

As shown in Figure 1c, one of the two thiophene protons of **2** was located near the border between the shielding and deshielding regions of the adjacent antiaromatic COT ring, with relatively short distances (2.8−2.9 Å) in the solid state. Thus it is interesting to observe the shift in the ^{1}H NMR signal in the solid state due to a paratropic ring current in the COT ring. GIAO−HF calculations using the X-ray packing structure showed that the thiophene protons of the A and B forms located near the COT rings in the B and A forms are shifted to a lower field by 3.2 and 3.5 ppm in comparison with the other thiophene protons, respectively.[20] Thus the theoretical calculations predicted that the thiophene protons are in the strongly deshielding region. In contrast, high-resolution solid-state ^{1}H NMR spectrum by the combined rotation and multiple-pulse spectroscopy (CRAMPS) method (Figure 3) revealed that the signals of the thiophene protons appeared at δ 7.2 and 6.9 ppm, indicating that the downfield shift from that in solution (δ 6.61 ppm) was 0.6 ppm at the most. We confirmed by X-ray crystallography that the crystal packing of **2** was maintained before and after the measurements. Therefore, one explanation for this large discrepancy between the theoretical predictions and the experimental results is that the GIAO−HF calculations overestimate the deshielding shift caused by the paratropic ring current at the region where the observed thiophene protons are located. To our knowledge, experimental data revealing the spatial distribution of paratropic ring current are still rare,[8b] and the collection of such data would be important for estimating the accuracy of theoretical methods dealing with magnetic properties.

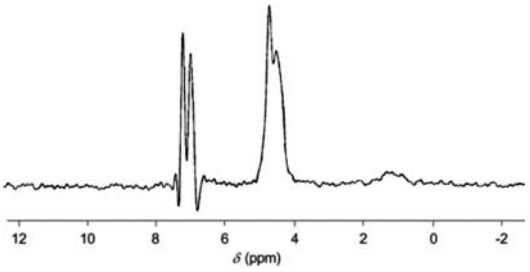

Figure 3. High-resolution solid-state ^{1}H NMR spectrum of single crystals of **2** accquired using the CRAMPS method.

In summary, we have succeeded in the synthesis of a new planar COT derivative **2** with olefinic protons that enable the experimental observation of antiaromatic paratropicity by ^{1}H NMR. The combined experimental and theoretical investigation demonstrated that the COT ring of **2** has substantial magnetic antiaromaticity. The antiaromaticity was accompanied by a considerable narrowing of the HOMO−LUMO gap, which is potentially useful for organic materials such as unique semiconductors for electronic[7a] and optoelectronic[21] applications.

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Supporting Information Available. Experimental procedures and characterization data for **2**. Figures S1 and S2. Tables S1−S10. Cartesian coordinates of the optimized structures. Crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

(19) Not only π-ring current but also σ-electrons affect ^{1}H NMR chemical shifts of ring protons. Therefore, the similar upfield and downfield shifts do not necessarily warrant the equivalency of the ring currents in the different π-systems. See: (a) Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 605–608. (b) Viglione, R. G.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 2265–2267.

(20) See Table S3 in Supporting Information for the detailed results.

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The authors declare no competing financial interest.