

# Molecular, Crystal, and Thin-Film Structures of Octathio[8]circulene: Release of Antiaromatic Molecular Distortion and Lamellar Structure of Self-Assembling Thin Films

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Carbon–sulfur compounds<sup>[1]</sup> have been studied extensively as key materials in organic/molecular electronics. A variety of poly- and oligothiophenes have been synthesized by organic synthesis and electrochemistry to elucidate their electronic properties.<sup>[2–4]</sup> TTF (=1,4,5,8-tetrathiafulvalene) is a very important molecular skeleton as a donor for organic metals and superconductors; [TTF][TCNQ (7,7,8,8-tetracyanoquinodimethane)] was the first organic metal to be developed into organic superconductors in the salts of TMTSF (=tetramethyltetraselenafulvalene), BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene).<sup>[5]</sup> In these materials, intermolecular S··S contacts play a crucial role in bringing about multidimensional electronic structures that are advantageous to electrical conduction. Cyclic oligothiophenes and thiocirculenes possess promising molecular structures from this perspective; the sulfur atoms are exposed to the outside of the molecular rings. Intermolecular S··S contacts are naturally expected in their crystals. In addition, their molecular structures are of considerable interest because they involve the radialene framework that has been a theoretical and experimental matter of concern with regard to exocyclic double bonds, aromaticity, and  $\pi$ -conjugation.<sup>[6–13]</sup>

Recently, Nenajdenko et al. synthesized octathio[8]circulene (**2**) from the parent compound, tetrathiophene (**1**), and **2** named “sulflower”.<sup>[14]</sup> They obtained **2** as a red powder and estimated molecular and crystal structures from powder X-ray diffraction data, concluding the presence of a closed packing structure in the solid state with short intermolecular S··S contacts.<sup>[14]</sup> Although the synthesis of **2** has attracted much attention, there is no single-crystal X-ray analysis; the

molecular structure of **2** is open to debating on bond lengths, antiaromaticity.

In our previous work, we carried out crystal growths and thin-film fabrications of a planar macrocyclic molecule, tetrakis(thiadiazole)porphyrizine, with strong self-assembling capabilities due to electrostatic S··N contacts and  $\pi$ - $\pi$  interactions. The investigations revealed a highly ordered molecular arrangement in the thin films, which is nearly the same as that in the bulk crystals.<sup>[15]</sup> In the present work, we prepared the single crystals and thin films of the sulflower **2**. The molecular, crystal, and thin-film structures of **2** are described in detail, on the basis of the results of X-ray single-crystal analysis, in comparison with those of **1**.

Single crystals of the parent compound **1** were grown by slow evaporation of the Et<sub>2</sub>O solution at room temperature. While the X-ray structure of **1** has been reported previously,<sup>[16]</sup> we obtained a new polymorph belonging to the monoclinic *P*2<sub>1</sub>/*c* space group.<sup>[17]</sup> In this new polymorph, there are two crystallographically independent molecules, whereas their molecular structures are nearly the same. Figure 1 shows top and side views of one of the two molecules. The bond lengths of **1** are shown in Figure S1 (Supporting Information) and Table 1, where the *endo* bond is the one shared

Table 1. Averaged values of the bond lengths for **1** and **2** [Å].

	<i>endo</i> shorter	<i>exo</i> longer	cyclic <i>exo</i>	C–S
<b>1</b>	1.436(4)	1.477(4)	1.369(4)	1.708(2)
<b>2</b>	1.412(1)	1.430(4)	1.372(7)	1.753(6)

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by the eight- and five-membered rings, the *exo* bond is connecting two thiophene rings, and the *exocyclic* C=C bond is exocyclic to the eight-membered ring. The eight-membered inner ring of **1** exhibits a tub conformation, in contrast to the planar molecular structure of a six-membered-ring derivative, benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]trithiophene.<sup>[13]</sup> The C–C bond lengths in the central eight-membered ring are be-

tween the typical ones of C–C (1.54 Å) and C=C (1.34 Å), and exhibit a clear bond alternation; the *endo* bonds are shorter than the *exo* bonds by 0.04 Å, reflecting the anti-aromaticity of 8 $\pi$ -electron systems.

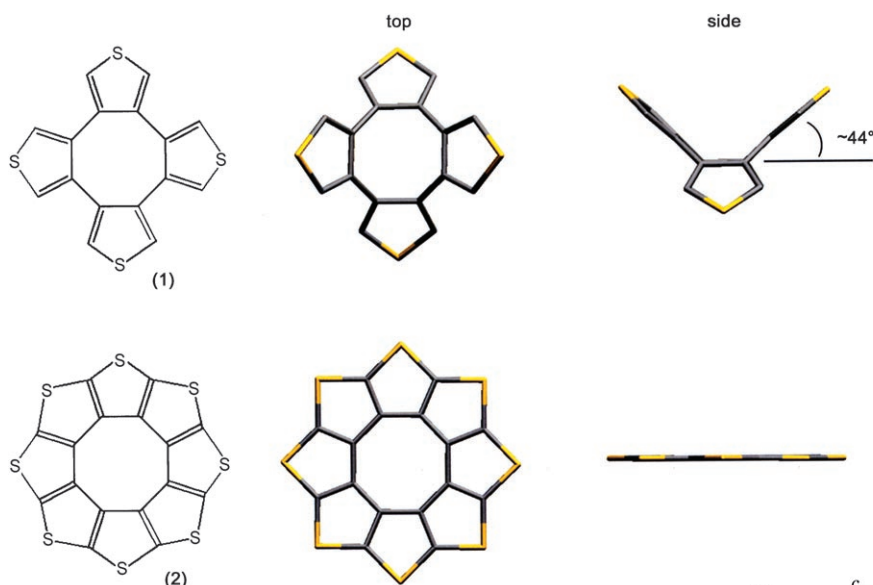


Figure 1. Top and side views of the molecular structures of **1** and **2**.

Figure 2a shows the third HOMO of **1**, which was obtained by means of the DFT B3LYP method with a 6-31G(d) basis set (see also Figure S2 and, Tables S1 and S2 in the Supporting Information). This orbital clearly indicates a  $\pi$ -bonding character between the facing thiazole rings on opposite sides of the eight-membered ring. This must be the reason for the tub formation in **1**, in addition to the intramolecular steric effect between the hydrogen atoms on the neighboring thiophene rings.

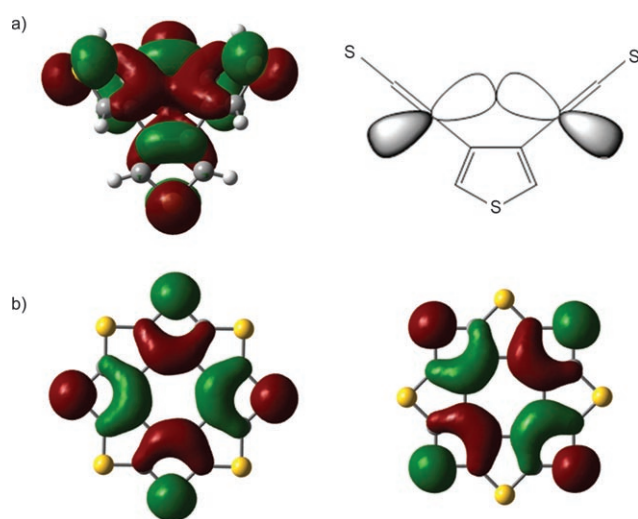


Figure 2. Characteristic molecular orbitals of **1** and **2**: a) the third HOMO of **1**; b) the nearly degenerated third and fourth HOMOs of **2**.

Figure 3a depicts a view of the unit cell of **1**. The molecules, denoted as A and B, are crystallographically independent. Their intermolecular arrangement includes short distances between the thiophene rings with C...C distances of 3.50–3.74 Å, where the thiophene rings are arranged to be nearly perpendicular with each other. This arrangement is indicative of the C–H... $\pi$  interactions. Other than these contacts, there is no significant  $\pi$ – $\pi$  overlaps or short S...S contacts in **1**.

Single crystals of **2** were obtained as red needles by vacuum sublimation, and X-ray crystal analysis was carried out at 173 K. The space group was found to be the monoclinic  $P2_1/n$ ,<sup>[17]</sup> while it was assigned to the non-centrosymmetric  $P2_1$  in the previous Rietveld analy-

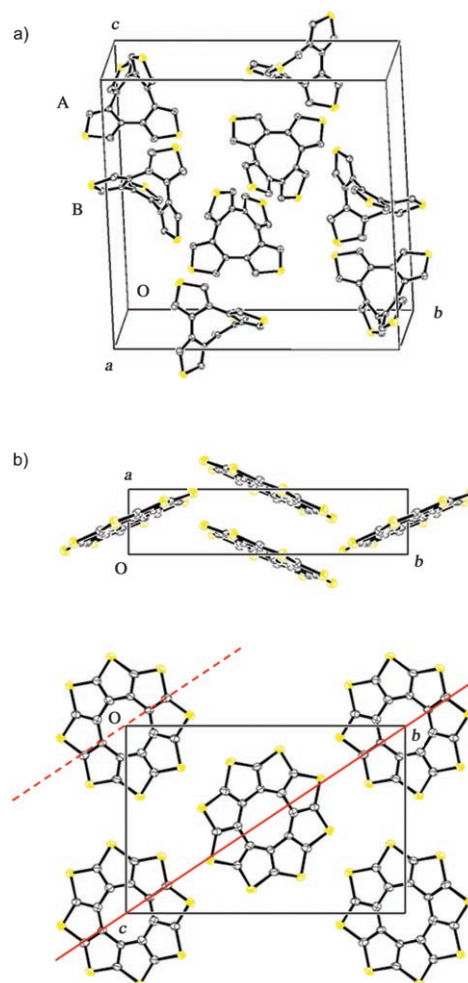


Figure 3. a) A view of the unit cell of **1**; b) projections of the crystal structure of **2** along the *c* and *a* axes. The red line shows the (011) plane.

sis.<sup>[14]</sup> The symmetry, obtained in the present re-determination of the crystal structure of **2**, reduced the size of the asymmetric unit to one-half molecule. Regarding the molecular packing, that obtained in the present work was essentially the same as that in the powder X-ray study.<sup>[14]</sup>

Figure 1 shows top and side views of the molecular structure of **2**. In contrast to the tub formation in **1**, the molecule **2** has a very planar structure, as theoretically predicted previously.<sup>[14]</sup> The inner eight-membered ring exhibits an obvious bond alternation, but it is much less significant than that in **1**. Although the *endo* and *exo* bonds cannot be defined in the molecular skeleton of **2**, the values of the shorter and longer bond lengths are listed in the columns of the *endo* and *exo* bonds, respectively, in Table 1. The C–C bond lengths on the inner ring of **2** are found to be shorter than those of **1**, suggesting an enhancement of the double-bond character, but still longer than those in benzene (1.399 Å). The distances of the exocyclic C=C bonds in **2** are similar to those in **1**, while those of the C–S bond are longer in **2**. It is notable that there is no bond alternation on the outer C–S sixteen-membered ring in **2**.

Figure 2b shows the nearly degenerated third and fourth HOMOs of **2**, which were calculated with the same method used for compound **1**. One can be superimposed on the other by the rotation of 45° around the molecular axis. Each orbital alternately provides  $\pi$ -bonding character to the C–C bonds on the inner eight-membered ring. It is considered that the presence of these two molecular orbitals makes the bond alternation on the inner ring less significant; the structural distortion caused by the  $8\pi$ -electron antiaromaticity of **2** is released by the pseudo- $C_8$  symmetry in the outer ring.

Figure 3b shows projections of the unit cell of **2** along the *a* and *c* axes. There is a one-dimensional  $\pi$ -stacking column along the *a* axis, which is surrounded by six neighbors with short S...S contacts. These features were reported in ref. [14]. Figure 4a depicts the intermolecular overlap of the two neighboring molecules in the  $\pi$ -stacking column. This figure indicates a shifted overlap so as to release electrostatic repulsions between the sulfur atoms. Figure 4b shows a space-filling view of the intercolumnar arrangement. The shifted  $\pi$ -stacking makes small cavities into which the sulfur atoms in the neighboring columns are inserted, creating an interdigitated structure.

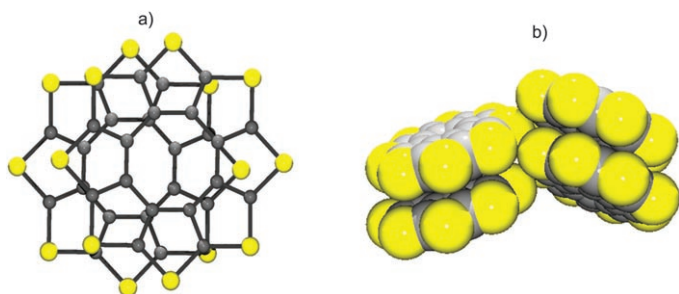


Figure 4. a) Intermolecular overlap between two neighboring molecules in the stacking column of **2**; b) space-filling view of the intercolumnar arrangement in **2**.

Thin films of **2** (500 nm in thickness) were prepared on Si(100) and ITO by vacuum vapor deposition. Figure 5 shows the X-ray diffractions (XRD) for this thin film on Si(100). The out-of-plane measurements (bold line) indicate several diffraction peaks, whose assignments are shown in this figure. Since the diffraction from the (011) plane ( $d=0.929$  nm) at  $2\theta=9.5^\circ$  ( $d=0.913$  nm) is much stronger than those of the others, the thin film is considered to have a lamellar structure, in which the (011) plane is parallel to the substrate. The red line in Figure 3 shows the (011) plane. It is reasonable to conclude that the molecular planes of **2** are all perpendicular to the substrate in this thin film. This type of perpendicular molecular plane alignment is typical for the thin films of organic  $\pi$  molecules because it is advantageous for gaining both  $\pi$ - $\pi$  stacking stabilization and a high density on a unit area of the substrates.<sup>[18]</sup> The in-plane XRD pattern (thin line) shows very weak diffractions; there is no characteristic diffraction. This suggests little long-range periodicity in the in-plane structure. The XRD patterns of the thin films of **2** on ITO are essentially the same as those on Si(100).

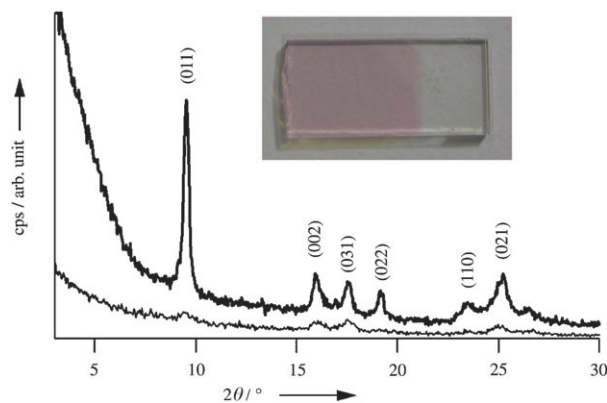


Figure 5. XRD patterns of **2** on Si(100). The bold and thin lines show the results of the out-of-plane and in-plane scans, respectively. The inset shows a photograph of the thin film on ITO.

In summary, the molecular and crystal structures of **1** and **2** were accurately determined by X-ray single-crystal analysis. In contrast to the significant tub-shape distortion in **1**, the molecule **2** has a very planar structure, in which the structural distortion caused by the  $8\pi$  antiaromaticity is released. Crystalline thin films of **2** were obtained by vacuum vapor deposition, and thin-film XRD indicated a lamellar structure in which the molecular planes are nearly perpendicular to the substrates.

## Experimental Section

Compounds **1** and **2** were prepared by the methods given in references [19] and [14], respectively. The thin films of **2** with a thickness of 500 nm were prepared by vacuum vapor-deposition at 400 °C under  $3 \times 10^{-4}$  Pa at a rate of 2–6 nm min<sup>-1</sup>, using a ULVAC VPC-260FN. The film

thickness was monitored during deposition by a quartz crystal microbalance located adjacent to the sample position within the bell jar.

Single-crystal X-ray diffraction data were collected on a Rigaku RA-Micro007 CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.710690 \text{ \AA}$ ). The structures were solved by direct methods and refined by the full-matrix least squares method on  $F^2$  using SHELXL97. All hydrogen atoms were placed at calculated positions.

Out-of-plane and in-plane X-ray diffractions of the thin-films were recorded on a Rigaku SmartLab X-ray diffractometer.

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**Keywords:** aromaticity • molecular structures • self-assembly • thin films

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- [16] H. Inrgartinger, U-Huber-Patz, H. Rodewald, *Acta Crystallogr. Sect. C* **1985**, *41*, 1088–1089.
- [17] Crystal Data: **1**  $\text{C}_{16}\text{H}_8\text{S}_4$ ,  $M_r = 328.48$ , colorless block, monoclinic,  $P2_1/c$ ,  $a = 7.3506(8)$ ,  $b = 19.502(2)$ ,  $c = 19.558(2) \text{ \AA}$ ,  $\beta = 90.5427(15)^\circ$ ,  $V = 2803.6(6) \text{ \AA}^3$ ,  $Z = 8$ ,  $T = 173 \text{ K}$ , final  $R = 0.0496$  (all data),  $wR2 = 0.1362$  (all data),  $\text{GOF} = 0.986$ . **2**  $\text{C}_{16}\text{S}_8$ ,  $M_r = 448.66$ , red needle, monoclinic,  $P2_1/n$ ,  $a = 3.869(2)$ ,  $b = 16.529(9)$ ,  $c = 11.146(6) \text{ \AA}$ ,  $\beta = 94.023(10)^\circ$ ,  $V = 711.0(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 173 \text{ K}$ , final  $R = 0.0842$  (all data),  $wR2 = 0.1681$  (all data),  $\text{GOF} = 1.069$ . CCDC 673455 (**1**) and 673454 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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