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### 3,4-Dimethyltetrathiafulvalene†

CALVIN E. UZELMEIER,<sup>a</sup> MARC FOURMIGUÉ<sup>b</sup> AND KIM R. DUNBAR<sup>a</sup>

<sup>a</sup>Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA, and <sup>b</sup>Institut des Matériaux (IMN, UMR CNRS 110), 2 rue de la Houssinière, F-44072 Nantes CEDEX 03, France. E-mail: dunbar@cem.msu.edu

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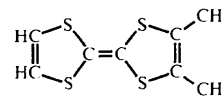
#### Abstract

The title compound consists of C<sub>3</sub>H<sub>8</sub>S<sub>4</sub> molecules where the tetrathiafulvalene backbone is nearly planar, and bond angles and distances are in accord with other TTF derivatives. The C—S—C angles for the five-membered rings of the TTF moiety average 95.83 (15)° for the ring containing the methyl groups and 94.37 (17)° for the unsubstituted ring. The molecules are stacked in pairs about an inversion center, with intermolecular S··S distances of 3.932 (2) Å between adjacent molecules.

#### Comment

Organic molecules such as tetrathiafulvalene (TTF) and its derivatives are important precursors in the design of new conducting, optical and magnetic materials. These planar molecules can be readily oxidized both chemically and electrochemically to produce radical cations which, when associated with suitable electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), form segregated stacks that allow for electrical conductivity due to the overlap of their  $\pi$  orbitals (Ferraris *et al.*, 1973). These donor molecules have also been observed to form salts with large metal-

based cluster anions that exhibit remarkably variable properties, differences that are attributed to the size and shape of the organic donor and inorganic acceptors, as well as their redox properties. Fourmigué & Batail (1992) have shown that methyl-TTF derivatives such as the title compound can be used to prepare a series of multidentate TTF–phosphine ligands, including 3,4-dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene (*ortho*-P2). The structure of 3,4-dimethyltetrathiafulvalene, (I), has been undertaken in order to compare the geometrical features with those of related TTF derivatives and the structures of the *ortho*-P2 ligand and its metal complexes (Uzelmeier *et al.*, 1998).



(I)

The central core (S1–S4, C3 and C4) of the title molecule is nearly planar, with a maximum deviation of 0.016 (2) Å for C3, and an r.m.s. deviation of 0.010 Å. The dihedral angle between planes C5, C6, S4, S3 and S1–S4, C3, C4 is 0.60 (13)°, while the angle between planes C1, C2, S2, S1 and S1–S4, C3, C4 is 1.88 (16)°. This is in contrast to the analogous dihedral angles in the neutral and cationic TTF crystal structures, where both fulvalene rings exhibit the same out-of-plane bend. For neutral tetrathiafulvalene, the value is 2.1° for both five-membered rings (Cooper *et al.*, 1971), whereas for cationic TTF, the corresponding dihedral angles between the planes are 2.2° (Kistenmacher *et al.*, 1974). Bond distances and angles within the TTF core of (I) are comparable to other TTF molecules. The C=C bond at the center of the molecule is 1.340 (4) Å, and S··S distances within the molecule are 2.967 (2) Å for S1··S2 and 2.945 (1) Å for S3··S4. It should be noted that this value for the central C=C distance is equivalent to that in neutral TTF [1.349 (3) Å], but shorter than that found in cationic TTF [1.369 (4) Å]. The bond lengths of the external C atoms in (I) are 1.308 (5) Å for C1=C2 and 1.338 (4) Å for C5=C6. This lengthening of C5=C6 renders it indistinguishable from C3=C4, a situation that has also been observed in 3,3'-dimethyl-4,4'-bis(diphenylphosphino)tetrathiafulvalene (Fourmigué *et al.*, 1997). Another manifestation of the presence of methyl substituents is differences in the S—C distances. The five-membered ring that contains the methyl groups exhibits S—C distances that are essentially all equivalent, but on the opposite side of the molecule; the sulfur to bridging-carbon distances are longer than the sulfur to exterior-carbon distances by 0.024 (4) Å.

Typically, neutral TTF stacks in a parallel orientation with respect to the *b* axis, with intermolecular S··S contacts of 3.62 Å; the TTF cation in TTF–TCNQ also

† Alternative name: 2-(2*H*-1,3-dithiol-2-ylidene)-4,5-dimethyl-2*H*-1,3-dithiole.

stacks parallel to the *b* axis, but with a much shorter TTF...TTF distance of 3.47 Å (Kistenmacher *et al.*, 1974). In contrast, (I) 'dimerizes' into stacked pairs. These pairs [TTF...TTF<sup>i</sup>; symmetry code (i) 1 - *x*, -*y*, -*z*] pack with significantly longer intermolecular contacts of 3.932 (2) Å and furthermore align themselves in a head-to-tail fashion, as clearly seen in the packing diagram (Fig. 2). This distance is significantly greater than twice the van der Waals radius of sulfur (3.6 Å; Bondi, 1964). Adjacent pairs are approximately perpendicular to each other, forming a dihedral angle [between planes S1-S4, C3, C4 and S1<sup>ii</sup>-S4<sup>ii</sup>, C3<sup>ii</sup>, C4<sup>ii</sup>; symmetry code: (ii)  $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ] of 83.03 (4)°, where one of the H atoms (H2) of the unsubstituted dithiole ring system of each molecule points towards the S4<sup>ii</sup> *p* orbital of a molecule in an adjacent pair. The C2...S4<sup>ii</sup> intermolecular distance is 4.46 (1) Å, which is greater than the sum of the van der Waals radii of carbon and sulfur (3.55 Å), indicating no significant interaction is present.

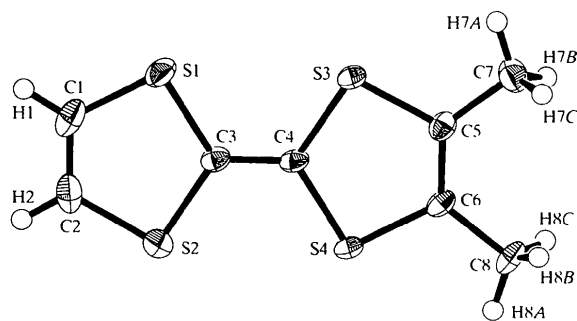


Fig. 1. ORTEP (Johnson, 1965) drawing of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

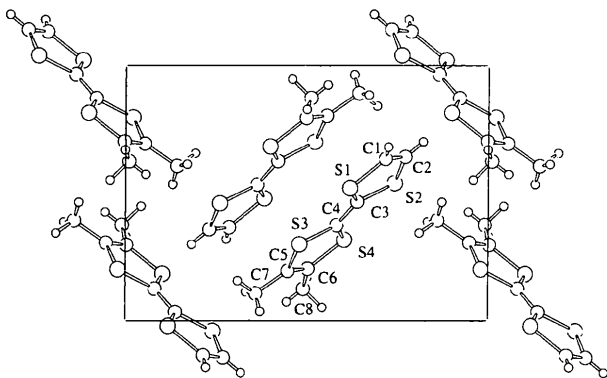


Fig. 2. Packing diagram of (I) viewed down the *a* axis.

## Experimental

The synthesis of the title compound was carried out according to methods previously published by Lerstrup *et al.* (1988). Crystals were obtained by dissolving the product in the

minimum amount of hot toluene, allowing the solution to cool slowly to room temperature, and then chilling at 258 K for 12 h.

## Crystal data

C<sub>8</sub>H<sub>8</sub>S<sub>4</sub>  
*M<sub>r</sub>* = 232.39  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 7.425 (2) Å  
*b* = 9.568 (3) Å  
*c* = 14.035 (4) Å  
 $\beta$  = 97.13 (2)°  
*V* = 989.4 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>v</sub>* = 1.560 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

## Data collection

Siemens P3/V diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction:  
 $\psi$  scan (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.543, *T<sub>max</sub>* = 0.770  
 2530 measured reflections  
 1481 independent reflections  
 1188 reflections with  
*I* > 2 $\sigma$ (*I*)

## Refinement

Refinement on *F*<sup>2</sup>  
*R* = 0.035  
*wR* = 0.093  
*S* = 1.068  
 1481 reflections  
 142 parameters  
 Only H-atom *U*'s refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.2448P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 24 reflections  
 $\theta$  = 2.58–11.78°  
 $\mu$  = 0.900 mm<sup>-1</sup>  
*T* = 163 (1) K  
 Platelet  
 0.68 × 0.60 × 0.29 mm  
 Orange

*R<sub>int</sub>* = 0.045  
 $\theta_{max}$  = 23.58°  
*h* = -8 → 8  
*k* = 0 → 10  
*l* = -15 → 15  
 3 standard reflections  
 every 150 reflections  
 intensity decay: -1.2%

( $\Delta/\sigma$ )<sub>max</sub> = 0.002  
 $\Delta\rho_{max}$  = 0.32 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.46 e Å<sup>-3</sup>  
 Extinction correction:  
 SHELXL93  
 Extinction coefficient:  
 0.0081 (17)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.743 (4)	S4—C4	1.762 (3)
S1—C3	1.765 (3)	C1—C2	1.308 (5)
S2—C2	1.739 (4)	C3—C4	1.340 (4)
S2—C3	1.767 (3)	C5—C6	1.338 (4)
S3—C4	1.753 (3)	C5—C7	1.500 (5)
S3—C5	1.755 (3)	C6—C8	1.503 (5)
S4—C6	1.758 (3)		
C1—S1—C3	94.42 (17)	S1—C3—S2	114.27 (17)
C2—S2—C3	94.31 (17)	C3—C4—S3	123.3 (3)
C4—S3—C5	96.14 (15)	S3—C4—S4	113.89 (17)
C6—S4—C4	95.51 (15)	C6—C5—C7	127.0 (3)
C2—C1—S1	118.2 (3)	C6—C5—S3	116.9 (2)
C1—C2—S2	118.7 (3)	C5—C6—C8	126.8 (3)
C4—C3—S2	122.9 (3)	C5—C6—S4	117.6 (2)

All non-H atoms were refined with anisotropic displacement parameters. Methyl and aromatic H atoms were refined without restraints.

Data collection: P3/V (Siemens, 1989). Cell refinement: Siemens P3/V. Data reduction: TEXSAN (Molecular Structure Corporation, 1996). Program(s) used to solve structure:

*MITHRIL* (Gilmore, 1983) in *TEXSAN*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1086). Services for accessing these data are described at the back of the journal.

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## Benzophenone Crown Ether Acetals with 14- and 17-Membered Rings

HATSUE TAMURA,<sup>a</sup> SHINYA UENO,<sup>a</sup> KAZUhide OGAWA,<sup>b</sup> TOSHIKAZU NAGAI<sup>a</sup> AND TAKUMI OSHIMA<sup>a</sup>

<sup>a</sup>Department of Applied Chemistry, Faculty of Engineering, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560, Japan, and <sup>b</sup>Institute of Chemistry, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560, Japan. E-mail: tamura@ch.wani.osaka-u.ac.jp

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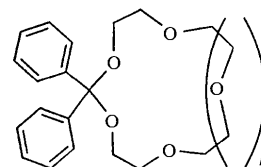
## Abstract

The 14-membered ring of 2,2-diphenyl-1,3,6,9,12-pentaoxacyclotetradecane, C<sub>21</sub>H<sub>26</sub>O<sub>5</sub>, is greatly distorted from a rectangular structure. By contrast, the homologous 17-membered ring of 2,2-diphenyl-1,3,6,9,12,15-hexaoxacycloheptadecane, C<sub>23</sub>H<sub>30</sub>O<sub>6</sub>, with an additional oxyethylene unit, adopts an approximately rectangular structure and the cavity has an unsymmetrical shape.

## Comment

Crown ether acetals have ring-contracted structures, each containing one methylene unit, as compared with usual crown ethers possessing the same number of O atoms. In view of the cation-binding capability, several workers have examined the alkali metal ion extractability of these macrocyclic polyethers (Kawakami *et al.*, 1978; Ouchi *et al.*, 1984). However, little is known about their structural details because of their intrinsic acid-sensitive properties coupled with a lack of general and useful synthetic methods (Pedersen, 1970; Kawakami *et al.*, 1977; Oshima *et al.*, 1982).

In our previous paper, we reported that the 11-membered-ring benzophenone crown ether acetal 2,2-diphenyl-1,3,6,9-tetraoxacycloundecane, (I), adopts a planar–chiral conformation for the largely twisted macrocyclic ring (Tamura *et al.*, 1997). We have extended the X-ray crystal structure analyses to the higher homologues, namely the 14- and 17-membered benzophenone crown ether acetals 2,2-di-



- (I)  $n=0$   
 (II)  $n=1$   
 (III)  $n=2$