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N-Methylthiocarbamoyltetrathiafulvalene at 150 K

JUDITH A. K. HOWARD, ANDREI S. BATSANOV,† MARTIN R. BRYCE AND JULIE N. HEATON

Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England

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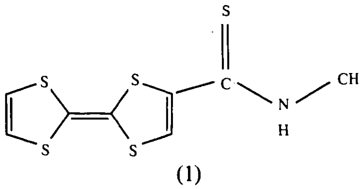
Abstract

The crystal structure of the title compound, 4-(*N*-methylthiocarbamoyl)-2,2′-bi(1,3-dithiolylidene), C_8H_7-NS_5, has been re-determined at 150 K and is compared with that determined by an ambient-temperature study, showing essentially the same motif (κ packing of dimers) and strongly anisotropic thermal expansion.

Comment

Recently we studied the crystal structure of *N*-methylthiocarbamoyltetrathiafulvalene, (1), at ambient temperature (Batsanov, Bryce, Cooke, Heaton & Howard, 1993; Batsanov *et al.*, 1994), which provided the first example of κ-phase packing of neutral TTF (TTF = tetrathiafulvalene) donor molecules. Herein we report the re-investigation of the structure of (1) at 150 K.



(1)

The structure is essentially the same as at 293 K. Parallel (inversionally equivalent) molecules form dimers with close contacts between the central, almost planar C_2S_4 moieties. The interplanar separation between the molecules [3.32 (5) Å] is slightly shorter than at 293 K [3.41 (4) Å], as is the shortest C(4)···C(4′) distance [3.338 (5) *versus* 3.401 (7) Å]. The peripheral C═C moieties of the TTF molecules are bent outwards from the dimer slightly more than at 293 K. The substituted and unsubstituted rings are folded along the S···S vectors with angles of 23.6 (1) and 14.5 (1)°, compared with 22.8 (1) and 13.9 (1)°, respectively, at 293 K.

The dimers are packed in a κ fashion, *i.e.* with the longest axes of the molecules parallel and their

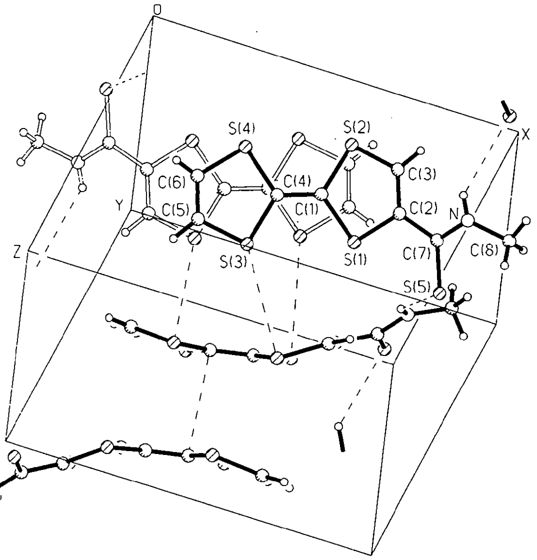


Fig. 1. A view of the dimers of the title compound in the unit cell. Short intermolecular contacts, hydrogen bonds and the atomic numbering scheme in the reference molecule are shown.

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† On leave from the Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia.

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planes perpendicular. The shortest interdimer S···S contacts are 3.550 (1), 3.686 (1) and 3.770 (1) Å, compared with 3.570 (2), 3.649 (2) and 3.850 (2) Å, respectively, at 293 K. The κ packing is stabilized by hydrogen bonds [N—H···S5(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 3.496 (3) Å]. It is noteworthy that from 293 to 150 K the unit-cell volume and the axes b and c decrease by 1.9, 2.0 and 1.8%, respectively, but the a axis increases by 1.9%. Thus on cooling the structure becomes denser in the direction of the S···S interactions, but expands in the direction of the longest axis of the molecule, together with slight elongation of the molecule itself; the intramolecular C5···C8 distance is 9.731 (5) Å at 150 K compared with 9.682 (8) Å at 293 K.

Experimental

Crystal data

$C_8H_7NS_5$
$M_r = 277.45$
Monoclinic
$P2_1/c$
$a = 11.947$ (3) Å
$b = 8.300$ (3) Å
$c = 11.031$ (3) Å
$\beta = 90.74$ (2)°
$V = 1093.7$ (6) Å^3
$Z = 4$
$D_x = 1.685$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 13.6$–15.0°
$\mu = 1.015$ mm^{-1}
$T = 150$ (2) K
Plate
0.46 × 0.43 × 0.21 mm
Black
Crystal source: crystallized from CH_3CN

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical
$T_{\min} = 0.853$, $T_{\max} = 1.000$
2448 measured reflections
2317 independent reflections
1842 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.023$
$\theta_{\max} = 27.50°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0290$
$wR(F^2) = 0.0722$
$S = 1.068$
2310 reflections
156 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0320P)^2 + 0.9896P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.400$ e Å^{-3}
$\Delta\rho_{\min} = -0.276$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.70583 (5)	0.24833 (8)	0.41090 (6)	0.0222 (2)
S2	0.62551 (6)	−0.00325 (8)	0.24133 (6)	0.0238 (2)
S3	0.45335 (6)	0.27483 (8)	0.52132 (6)	0.0253 (2)
S4	0.37148 (6)	0.04362 (9)	0.33602 (6)	0.0277 (2)
S5	0.94172 (6)	0.40710 (10)	0.38440 (6)	0.0331 (2)
N	0.9344 (2)	0.3074 (3)	0.1569 (2)	0.0261 (5)
C1	0.5916 (2)	0.1330 (3)	0.3573 (2)	0.0201 (5)
C2	0.7831 (2)	0.2165 (3)	0.2773 (2)	0.0187 (5)
C3	0.7458 (2)	0.0991 (3)	0.2034 (2)	0.0200 (5)
C4	0.4865 (2)	0.1485 (3)	0.3988 (2)	0.0207 (5)
C5	0.3086 (2)	0.2629 (4)	0.4948 (3)	0.0310 (6)
C6	0.2727 (2)	0.1602 (4)	0.4121 (3)	0.0330 (7)
C7	0.8872 (2)	0.3083 (3)	0.2645 (2)	0.0200 (5)
C8	1.0431 (3)	0.3780 (5)	0.1334 (3)	0.0362 (7)

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.763 (3)	S5—C7	1.680 (3)
S1—C2	1.769 (2)	N—C7	1.321 (3)
S2—C3	1.726 (3)	N—C8	1.450 (4)
S2—C1	1.758 (3)	C1—C4	1.348 (3)
S3—C5	1.753 (3)	C2—C3	1.343 (3)
S3—C4	1.760 (3)	C2—C7	1.467 (3)
S4—C6	1.749 (3)	C5—C6	1.317 (5)
S4—C4	1.761 (3)		
C1—S1—C2	92.83 (12)	C7—C2—S1	117.0 (2)
C3—S2—C1	93.47 (12)	C2—C3—S2	118.7 (2)
C5—S3—C4	93.98 (14)	C1—C4—S3	122.5 (2)
C6—S4—C4	93.77 (14)	C1—C4—S4	123.0 (2)
C7—N—C8	123.5 (2)	S3—C4—S4	114.49 (14)
C4—C1—S2	122.2 (2)	C6—C5—S3	117.7 (2)
C4—C1—S1	123.7 (2)	C5—C6—S4	118.3 (2)
S2—C1—S1	114.10 (14)	N—C7—C2	117.2 (2)
C3—C2—C7	126.4 (2)	N—C7—S5	122.9 (2)
C3—C2—S1	116.2 (2)	C2—C7—S5	119.9 (2)

A Cryostream open-flow gas cryostat (Cosier & Glazer, 1986) was used. An empirical absorption correction (North, Phillips & Mathews, 1968) was applied using *TEXSAN* (Molecular Structure Corporation, 1989), giving only minor improvement. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined by full-matrix least squares using *SHELXL*93 (Sheldrick, 1993). All H atoms were refined independently with isotropic displacement factors. Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: HA1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(methylethylenedithio)tetrathiafulvalene

K. Swaminathan and Patrick J. Carroll

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

Jai D. Singh and Harkesh B. Singh

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

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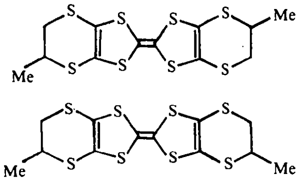
Abstract

The crystal of the title compound, $C_{12}H_{12}S_8$, is a mixture of the 7,7′-dimethylbis(ethylenedithio)tetrathiafulvalene and 7,8′-dimethylbis(ethylenedithio)tetrathiafulvalene isomers, in an almost 60:40 ratio. The crystal is disordered with respect to the position of one of the methyl substituents. The S atoms are involved in three-dimensional intermolecular S···S contacts with distances within 3.703 Å.

Comment

The organic π-donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has been the subject of numerous studies owing to the superconducting properties of several of its cation radical salts (Williams *et al.*, 1991; Bryce, 1991). The presence of two-dimensional S···S networks and C—H···(anion) interactions in the cation radical salts is important in determining the solid-state properties. Consequently, much synthetic effort has been devoted to systematically varying the structure of BEDT-TTF with consequential 'fine tuning' of the ionization potential, symmetry, size and S···S intermolecular contacts (Kumar, Singh, Das, Sinha & Mishnev, 1991; Moore & Bryce, 1992). The crystal of neutral BEDT-TTF is composed of pairs of BEDT-TTF molecules having a side-by-side arrangement, similar to that found in superconducting ion radical salts (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986).

The title compound, BMeEDT-TTF, a π-donor closely related to BEDT-TTF, has been reported previously (Papavassiliou, Zambounis & Yiannopoulos, 1987); however, no systematic investigations have been carried out. Recently, a modified synthesis and detailed characterization of the title compound have been reported (Singh & Singh, 1992) and ^{1}H NMR studies indicate it to be an isomeric mixture. In fact, in the 300 MHz spectrum of the compound, the proton resonances are split in a 60:40 ratio due to the presence of these isomers. The first ($^1E_{1/2}$) and second ($^2E_{1/2}$) ionization potentials of the present compound are slightly lower than those of BEDT-TTF. In this paper, we report the crystal structure and compare it with those of related compounds.



BMeEDT-TTF

The reaction of 4,5-dimercapto-1,3-dithiole-2-thione with (±)-1,2-dibromopropane at 198 K afforded 4,5-(methylethylenedithio)-1,3-dithiole-2-thione. The thione was coupled in the presence of triethylphosphite to give the title compound. The compound was purified by recrystallization from dichloromethane to give orange crystals.

The molecule is disordered near the C(3)—C(4) region, as expected. The C(3)—C(3*M*) and C(4)—C(4*M*) bond lengths [1.720 (20) and 1.643 (22) Å, respectively] are longer than the normal C—C bond length. The disorder of the methyl groups located at the C(3) and C(4) atoms makes the C(3)—C(3*M*) and C(4)—C(4*M*) bond lengths, the C(3)···C(4*M*) and C(4)···C(3*M*) distances, and also distances involving some of the H atoms, deviate significantly from the corresponding ideal values. Also, the C(3), C(3*M*), C(4) and C(8*M*) atoms have higher temperature factors. Contrary to expectation, the molecule shown in Fig. 1(*b*) does not have any centre of symmetry as the ring formed by the atoms C(2), S(2), C(3), C(4), S(3) and C(5) is planar within 0.101 (11) Å, whereas the equivalent ring formed by the other ethylenedithio moiety has a half-chair conformation with a dihedral angle of 45.8 (4)° between the planes formed by C(7), C(10), S(7), S(6) and S(6), S(7), C(9), C(8). The S atoms are involved in intermolecular S···S contacts: S(3)···S(2^{i}) 3.533 (3), S(4)···S(2^{i}) 3.434 (3), S(7)···S(6^{i}) 3.703 (3), S(1)···S(5^{ii}) 3.572 (2),