

## Structure of the Organic Semiconducting Radical Cation Salt Tris[2,6-dimethoxy-3,7-bis(methylthio)naphthalene] Diperchlorate

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**Abstract.**  $(C_{14}H_{16}O_2S_2)_3^{2+} \cdot 2ClO_4^-$ ,  $M_r = 1040.13$ , monoclinic,  $C2/m$ ,  $a = 22.040$  (5),  $b = 10.295$  (4),  $c = 11.827$  (3) Å,  $\beta = 120.57$  (2)°,  $V = 2311$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.495$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 4.63$  cm<sup>-1</sup>,  $F(000) = 1084$ ,  $T = 295$  K. Final  $R(F^2) = 0.068$  for 2081 unique reflections. Triads of planar 2,6-DMbTN molecules ( $C_{14}H_{16}O_2S_2 = 2,6\text{-DMbTN}$ ) form stacks along the **b** direction. The two S atoms in each 2,6-DMbTN molecule are part of infinite close to linear (174–177°) chains of S atoms along the *b* axis, with S··S distances 3.401 (2), 3.401 (2) and 3.503 (3) Å, respectively. The two S-atom chains are related by a twofold axis.

**Introduction.** This work is part of a series of studies into the structures and physical properties of electrochemically prepared cation radical salts (c.r.s.) with chalcogen-substituted aromatic hydrocarbons as donors. Three other substituted naphthalene compounds with 3:2 stoichiometry have already been studied in this series: the isomeric compound tris[2,7-dimethoxy-3,6-bis(methylthio)naphthalene] diperchlorate,  $(2,7\text{-DMbTN})_3(\text{ClO}_4)_2$  (Olovsson & Olovsson, 1992*a*), tris[2,3,6,7-tetramethoxynaphthalene] bis[hexafluoroarsenate],  $(\text{TMN})_3(\text{AsF}_6)_2$  (Olovsson & Olovsson, 1991) and the corresponding perchlorate compound,  $(\text{TMN})_3(\text{ClO}_4)_2$  (Olovsson & Olovsson, 1992*b*).

**Experimental.** Black crystals of  $(2,6\text{-DMbTN})_3(\text{ClO}_4)_2$  with a bluish black metallic lustre were prepared by electrolytic oxidation of 2,6-DMbTN in  $\text{CH}_2\text{Cl}_2$  solution in the presence of  $(n\text{Bu}_4\text{N})\text{ClO}_4$  at a constant current density of a few  $\mu\text{A cm}^{-2}$  at room temperature. A somewhat irregularly shaped crystal of maximum dimensions  $0.20 \times 0.15 \times 0.11$  mm was chosen for measurements on a MicroVAX II controlled Stoe 4-circle diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation in  $\omega/2\theta$  scan mode [scan width  $\Delta\omega = 0.7^\circ$ ; scan time varied to maintain constant  $\sigma(I)/I = 0.017$ ; 70 steps, with minimum and maximum scan times 0.3 and 2.5 s step<sup>-1</sup>, respectively]. The range of *h*, *k*, *l* was  $-29 \leq h \leq 29$ ,  $-13 \leq k \leq 0$ ,  $0 \leq l \leq 15$  with  $[(\sin\theta)/\lambda]_{\max} =$

$0.671$  Å<sup>-1</sup>. Unit-cell dimensions were determined from a least-squares refinement of the setting angles of 24 reflections in the  $2\theta$  range 15–23°. Five standard reflections were measured every 240 min of X-ray exposure time; their intensities decreased by less than 2% during the data collection. A linear scaling derived from the standard reflections was used to correct the measured intensities; a contribution taking account of instability in the measurement and of uncertainty in the scaling was added to the standard deviations estimated on the basis of counting statistics (McCandlish, Stout & Andrews, 1975). The raw intensities were corrected for background using the profile-analysis method of Lehmann & Larsen (1974). The intensities were corrected for Lorentz and polarization effects. Absorption correction was performed by the Gaussian integration method using a  $10 \times 12 \times 12$  grid. The crystal was described by nine faces. Transmission factors were in the range 0.936 to 0.953 for the 3621 collected intensities. Averaging symmetry-equivalent reflections ( $R_{\text{int}} = 0.015$ ) and deleting space-group extinctions left 3094 unique intensities.

From the diffraction symmetry and extinctions the space groups  $C2$ ,  $Cm$  and  $C2/m$  were possible. The structure was solved and refined in  $C2/m$ . We also tried to lower the symmetry to  $C2$  or  $Cm$ , but this gave no significant improvement in the *R* factors. The major parts of the 2,6-DMbTN molecules were found using direct methods in the *MULTAN80* program package (Main *et al.*, 1980); the rest of the structure (except for H atoms) was found in successive Fourier syntheses. All H-atom positions were first calculated using the program *SHELX76* (Sheldrick, 1976), using a C—H distance of 1.08 Å. These positions were subsequently refined without constraints. Reflections with  $F_o^2 \leq 0$  were excluded in refinements. Neutral atomic and anomalous scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–100, 102, 149). For H atoms, the spherical bonded scattering factor was used. The function minimized in the full-matrix least-squares program *DUPALS* (Lundgren, 1982) was  $\sum w(|F_o|^2 - |F_c|^2)^2$  where  $w^{-1}$

$= \sigma_{\text{count}}^2(F_o^2) + (0.060F_o^2)^2$ . In the final cycle, 1013 reflections with  $F_o^2 < \sigma(F_o^2)$  were excluded, leaving 2081 reflections for the refinement of 216 parameters. These were one scale factor, 92 positional parameters, 108 anisotropic displacement parameters (non-H atoms), 14 isotropic displacement parameters (H atoms) and one isotropic extinction coefficient. Final agreement factors:  $R(F) = 0.067$ ,  $R(F^2) = 0.068$ ,  $wR(F^2) = 0.126$ ,  $S(F^2) = 1.28$ .  $(\Delta/\sigma)_{\text{max}} < 0.1$  in the final cycle. A final  $\Delta\rho$  map gave maximum and minimum peak heights of 0.6 and  $-0.4 \text{ e } \text{\AA}^{-3}$ . The secondary isotropic type I extinction coefficient was refined to 2873 (1350) [Becker & Coppens (1974, 1975), Lorentzian mosaic-spread distribution]. After the final refinement, all H-atom positions were recalculated (C—H = 1.08 Å). The molecular plots were made using ORTEPII (Johnson, 1976); other computer programs used are described by Lundgren (1982).

**Discussion.** Final atomic parameters are given in Table 1.\* The crystal packing is shown in Fig. 1, bond distances, displacement ellipsoids and bond angles in Fig. 2. The asymmetric unit consists of one quarter of a 2,6-DMbTN(1) molecule, half a 2,6-DMbTN(2) molecule and half a  $ClO_4^-$  ion. The twofold axis runs through the centre of all the 2,6-DMbTN molecules (Fig. 2). The 2,6-DMbTN(1) molecule lies in a mirror plane, as well as two O atoms and the Cl atom of the  $ClO_4^-$  ion. All other atoms are in general positions. Deviations from planarity in 2,6-DMbTN(2) were calculated relative to the least-squares plane defined by atoms C(21)—C(25) [coplanar within 0.007 (4) Å]: C(26) +0.105 (6), C(27) +0.178 (7), S(2) -0.011 (1) and O(2) +0.014 (3) Å. The methyl groups of the 2,6-DMbTN(2) molecule are in this way displaced towards the 2,6-DMbTN(1) molecule to avoid collisions with the methyl groups of the neighbouring 2,6-DMbTN(2) molecule in the stack (cf. Fig. 1). As expected, the displacement parameters of the methyl C and perchlorate O atoms are significantly larger than those of the other atoms (cf. Fig. 1 and Table 1). The bond distances in the  $ClO_4^-$  ion are: Cl—O(1Cl) 1.398 (6), Cl—O(2Cl) 1.358 (6) and Cl—O(3Cl) 1.415 (6) Å; bond angles are 107.7–113.0° with standard deviations 0.3–0.5°. The expected Cl—O distance is about 1.42 Å, making two bonds significantly foreshortened. This can, at least partly, be explained by the unusually large displacement

\* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54999 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0262]

Table 1. Atomic fractional coordinates and displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}$
C(1)	0.9147 (2)	0.00000	0.3432 (4)	0.032 (2)
C(2)	0.9367 (2)	0.00000	0.2525 (4)	0.031 (2)
C(3)	1.0111 (2)	0.00000	0.2982 (4)	0.035 (2)
C(4)	1.0588 (2)	0.00000	0.4278 (4)	0.033 (2)
C(5)	1.0367 (2)	0.00000	0.5218 (4)	0.031 (2)
C(6)	0.7938 (3)	0.00000	0.0672 (5)	0.050 (3)
C(7)	1.0974 (3)	0.00000	0.2354 (7)	0.081 (6)
S(1)	0.87966 (6)	0.00000	0.08381 (10)	0.0415 (7)
O(1)	1.0255 (2)	0.00000	0.1981 (3)	0.049 (2)
C(21)	0.9897 (2)	0.3280 (4)	0.3346 (3)	0.0377 (16)
C(22)	0.9169 (2)	0.3290 (3)	0.2550 (3)	0.0395 (16)
C(23)	0.8741 (2)	0.3274 (3)	0.3140 (3)	0.0412 (16)
C(24)	0.9036 (2)	0.3282 (3)	0.4465 (3)	0.0400 (17)
C(25)	0.9782 (2)	0.3277 (3)	0.5290 (3)	0.0374 (15)
C(26)	0.9401 (2)	0.3189 (6)	0.0472 (4)	0.056 (2)
C(27)	0.7570 (2)	0.3107 (6)	0.2766 (5)	0.070 (3)
S(2)	0.87186 (5)	0.32986 (11)	0.08549 (8)	0.0514 (5)
O(2)	0.80321 (11)	0.3269 (3)	0.2262 (2)	0.0565 (15)
Cl	0.67094 (8)	0.00000	0.31513 (14)	0.0711 (11)
O(1Cl)	0.6319 (3)	-0.1132 (6)	0.2962 (5)	0.182 (5)
O(2Cl)	0.7254 (4)	0.00000	0.4412 (5)	0.147 (5)
O(3Cl)	0.6950 (3)	0.00000	0.2246 (5)	0.096 (4)

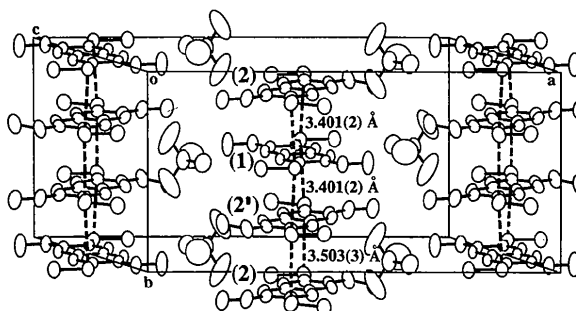


Fig. 1. Molecular packing. H atoms have been omitted for clarity. Linear S...S chains are formed along the stacking axis *b*. The distances are between the S atoms in the chains.

parameters for these O atoms (cf. Table 1). We did not attempt to look for possible orientational disorder of the  $ClO_4^-$  ion. From the stoichiometry it follows that, on average, each 2,6-DMbTN molecule has a charge of  $+\frac{2}{3}$ . The bond distances in 2,6-DMbTN(1) and 2,6-DMbTN(2) were compared in order to check for possible charge differences between molecules (1) and (2); no significant difference was found, in agreement with the ESR experiment showing that the charge cannot be treated as localized on specific 2,6-DMbTN molecules in the stack (Söderholm, von Schütz, Noreland, Olovsson & Hellberg, 1992). The same result was also found in the 2,7-DMbTN salt (Olovsson & Olovsson, 1992a).

**Stacking arrangement.** The 2,6-DMbTN molecules are packed in stacks along the *b* axis, with the  $ClO_4^-$  ions surrounding them (Fig. 1). Within a stack, one 2,6-DMbTN(1) molecule and two 2,6-DMbTN(2) molecules form a triad with interplanar distances 3.38 (1) and 3.38 (1) Å; between these triads the

interplanar distance is 3.54 (1) Å (the stacking is illustrated in Fig. 1 where the S...S distances are given). The molecular overlap is shown in Fig. 3. The S atoms are part of infinite close to linear (174–177°) chains of S atoms along the *b* axis, with S...S distances 3.401 (2), 3.401 (2) and 3.503 (3) Å, respectively. These intermolecular S...S contacts are all shorter than the sum of the van der Waals radii, 3.6 Å (Bondi, 1964). In the corresponding 2,7-DMbTN salt (Olovsson & Olovsson, 1992*a*) there is only one S...S chain passing through a given molecule, making the stacking pattern less uniform and the crystal structure more sensitive to perturbations during the electrocrystallization. The ClO<sub>4</sub><sup>-</sup> ion has 12 O...H contacts ≤ 3.0 Å to the H atoms of 2,6-DMbTN(2) [the shortest is 2.55 (4) Å], but no such short contacts to 2,6-DMbTN(1) [the shortest is 3.07 (3) Å]. The same type of distribution is found in the 2,7-DMbTN salt, where the number of short contacts is 17 and 4, respectively.

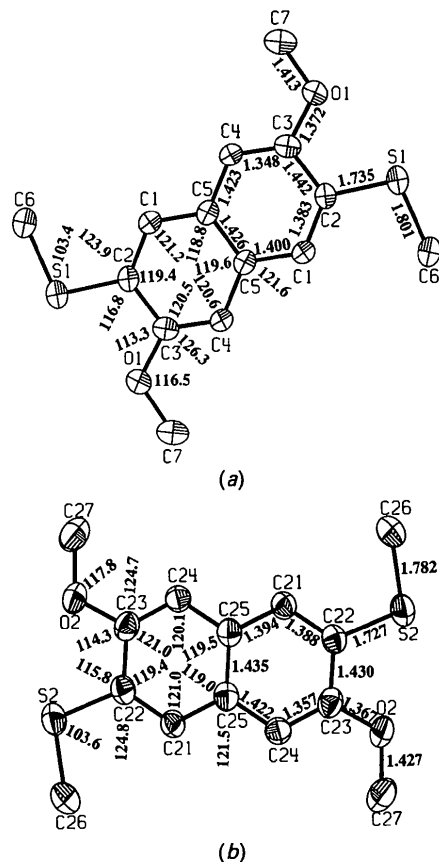


Fig. 2. Bond distances (Å), bond angles (°) and atomic notation for the 2,6-DMbTN molecules. The orientation is the same as in Fig. 3. H atoms are not included. (a) 2,6-DMbTN(1), (b) 2,6-DMbTN(2). All thermal ellipsoids are plotted at 50% probability. E.s.d.'s for C—S distances are 0.003–0.004 Å; for C—C and C—O distances they are 0.004–0.007 Å, and for corresponding angles 0.2–0.5°.

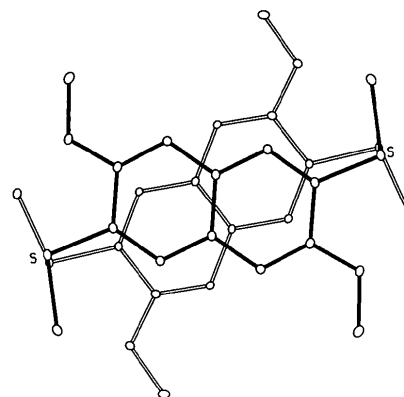


Fig. 3. Overlap of the 2,6-DMbTN molecules within the triad, viewed along the stacking axis *b*. A 2,6-DMbTN(1) molecule (unfilled bonds) is situated between two 2,6-DMbTN(2) molecules (filled bonds) which completely overlap each other in the figure.

**Physical properties.** The temperature dependence of the conductivity is characteristic of a semiconductor, and the room-temperature conductivity along the stacking direction is 40–70 Sm<sup>-1</sup>, with a band gap of 0.5 eV. The conductivity is almost three orders of magnitude higher than in the 2,7-DMbTN salt, while the activation energies are about the same. This indicates that there are less defects in the 2,6-DMbTN salt. The semiconducting behaviour is caused by the trimerization of the stacks. For further details of the electronic and magnetic properties see Söderholm *et al.* (1992).

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## Structure of 2-(6-Bromo-3-methyl-4-oxo-4*H*-1-benzopyran-2-yl)-1-(2-oxocyclopentyl)-1-phenylethane

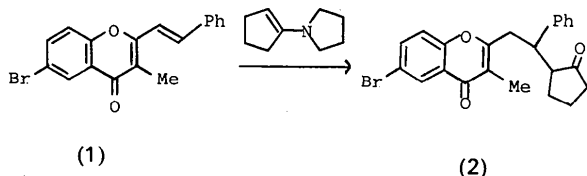
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**Abstract.**  $C_{23}H_{21}BrO_3$ ,  $M_r = 425.32$ , monoclinic,  $P2_1/c$ ,  $a = 10.656(2)$ ,  $b = 12.167(2)$ ,  $c = 15.508(2)$  Å,  $\beta = 98.42(1)^\circ$ ,  $V = 1988.9(1.0)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.420$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 20.63$  cm<sup>-1</sup>,  $F(000) = 872$ ,  $T = 295$  K,  $R = 0.041$ ,  $wR = 0.039$  for 1630 reflections. This work unambiguously establishes the position of the 2-oxocyclopentyl group in the molecule.

**Introduction.** The addition of cyclopentanone-pyrrolidine enamine to (*E*)-6-bromo-3-methyl-4-oxo-2-styryl-4*H*-1-benzopyran (1) gave a nitrogen-free crystalline product, which from <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Letcher & Yue, 1992) was shown to be 2-(6-bromo-3-methyl-4-oxo-4*H*-1-benzopyran-2-yl)-1-phenylethane with a 2-oxocyclopentyl substituent attached at either the 1- or 2-position of ethane. In order to determine the exact position of the substituent, the structure of the product was determined by a single-crystal X-ray analysis; the structure has been found to be that represented by (2).



**Experimental.** The title compound (2) was obtained in 50% yield from the reaction between (1) and cyclopentanone-pyrrolidine enamine, and was crystallized from 95% ethanol.

A colourless crystal of dimensions  $0.15 \times 0.25 \times 0.2$  mm was selected for intensity measurement on an

Enraf-Nonius CAD-4 diffractometer, with graphite-monochromated Mo  $K\alpha$  radiation, and scintillation counter. Cell parameters were determined by least squares from setting angles of 25 reflections ( $10 < 2\theta < 16^\circ$ ), measured on the diffractometer. The intensities of 6611 reflections ( $2\theta_{\text{max}} = 48^\circ$ ), in the range  $-12 \leq h \leq 12$ ,  $0 \leq k \leq 13$ ,  $-17 \leq l \leq 17$ , were measured using the  $\omega$ - $2\theta$  scan,  $\omega$ -scan angle  $(0.75 + 0.344 \tan \theta)^\circ$  at  $0.92$ – $5.49$  min<sup>-1</sup>, extended 25% on each side for background measurement. Three standard reflections measured every 2 h showed no decay. Systematic absences indicated  $P2_1/c$  and this was confirmed in the structure solution. The intensity data were corrected for Lorentz and polarization effects only. After equivalent reflections were averaged, the 6611 measured data gave 3280 independent reflections, of which 1630 reflections with  $I > 1.0\sigma(I)$ , where  $\sigma^2(I) = S + 4(B1 + B2)$ ,  $S = \text{scan}$ ,  $B1$  and  $B2$

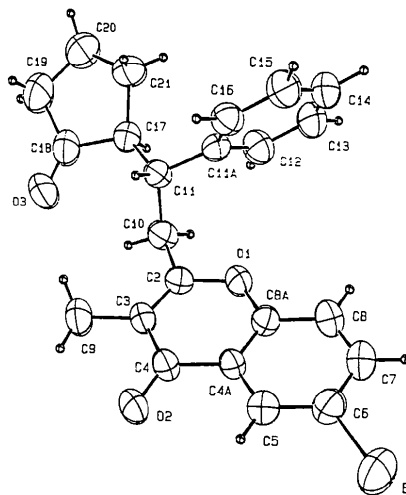


Fig. 1. ORTEP (Johnson, 1976) drawing of the molecule (2) with numbering of atoms.

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