The Crystal Structures of Three Precursors to Organic Donors based on BEDT–TTF

Sine Larsen,[a,*] Thorstein Thorsteinsson,[a] Søren Bøwadt,[b] Thomas K. Hansen,[b] Karikath S. Varma,[c] Jan Becher[b] and Allan E. Underhill[c]

[a] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, [b] Department of Chemistry, University of Odense, Campusvej 55, DK-5230 Odense M, Denmark and [c] Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, UK

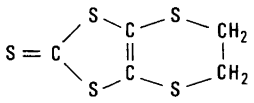
Larsen, S., Thorsteinsson, T., Bøwadt, S., Hansen, T. K., Varma, K. S., Becher, J. and Underhill, A. E., 1991. The Crystal Structures of Three Precursors to Organic Donors based on BEDT–TTF. – Acta Chem. Scand. 45: 709–715.

Three precursors to organic donors based on BEDT–TTF have been prepared, 2,3-dihydro-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione (**1**), 2,3-dihydro-2-oxo-3-phenyl-1,3-dithiolo[4,5][1,4]dithiin-6-thione (**2**) and 2,3-dihydro-2-phenyl-1,3-dithiolo-[4,5-*e*][1,4]dithiin-6-one (**3**). The crystal structures have been determined from low-temperature X-ray diffraction data. They crystallize in monoclinic space groups as follows. Compound **1** in $P2_1/n$ with a = 10.600(2), b = 5.7887(8), c = 13.436(3) Å, β = 93.03(2)°, Z = 4; 2801 reflections gave R = 0.030. Compound **2** in $P2_1/c$ with a = 10.0792(13), b = 6.059(2), c = 20.578(5) Å, β = 105.87°, Z = 4; 2490 reflections gave R = 0.031. Compound **3** in $C2/c$ with a = 15.735(13), b = 9.1996(9), c = 16.487(14) Å, β = 96.85(3)°, Z = 8; 3510 reflections gave R = 0.044. Compound **3** displays disorder of the ethylene group. The molecular geometries of these compounds are similar to those found in the salts of the related dimers BEDT–TTF. Short S–S intermolecular interactions influence the packing in **1–3**. These interactions are comparable to and even shorter than those found in BEDT–TTF salts.

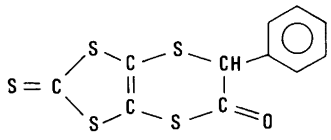
The discovery of superconductivity in single crystals of β-(BEDT–TTF)$_2$I$_3$ with a transition temperature of 1.4 K at atmospheric pressure has prompted a great deal of research into the preparation and properties of related multi-sulphur π-donors.[1] It has been demonstrated that stabilization of the metallic state at low temperature in this type of system is dependent upon the extent of intermolecular S–S interactions.[2] Clearly in derivatives of bis(ethylendithio)tetrathiafulvalene (BEDT–TTF) these interactions will be influenced by two factors; the changes in electron density on the sulphur atoms due to the effect of the substituent and the steric effects of the substituents on the packing of the donor molecules in the solid state. An understanding of these effects is crucial to the rational design of new organic donors.

As part of a study involving the synthesis of new organic multi-sulphur π-donors we have studied molecules which can give information concerning the influence of substituents on the BEDT–TTF structure. With this aim in mind, we have investigated suitable precursor molecules which were expected to show significant steric and electronic effects in the solid state. Here results are presented from the crystal structure determinations of three such moelcules **1–3** shown in Fig. 1, and a discussion is given of the structural data with regard to substituent effects on BEDT–TTF-based donors.

(1)



(2)



(3)

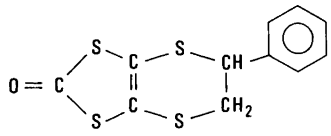


Fig. 1. Schematic drawings of the three precursors: (**1**) 2,3-dihydro-1,3-dithiolo[4,5-e][1,4]dithiin-6-thione, (**2**) 2,3-dihydro-2-oxo-3-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione and (**3**) 2,3-dihydro-2-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-one.

Experimental

Preparation and analyses. 2,3-Dihydro-1,3-dithiolo-[4,5-*e*][1,4]dithiin-6-thione (**1**) was synthesized by a recently reported procedure (m.p. 119–121 °C).[3] Spectral and analytical data of compound **1** were in agreement with values given in the literature.[3,4] Crystals suitable for X-ray data collection were obtained by recrystallization from absolute ethanol.

* To whom correspondence should be addressed.

2,3-Dihydro-2-oxo-3-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione (**2**) was synthesized by a modification of a reported procedure.[4] A solution of 14.37 g (0.02 mol) of bis(tetraethylammonium)-bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate(II) in dry THF (400 ml) and a solution of 7.56 g (0.04 mol) of 2-chloro-2-phenylacetylchloride in dry THF (400 ml) both were seperately placed in two dropping funnels whereupon these two solutions were added simultaneously to 600 ml of dry THF at −40 °C with stirring. The addition took place over 4 h at −40 °C. The mixture was left stirring overnight while the temperature was allowed to rise to room temperature.

The reaction mixture was filtered and the resulting yellow–orange solution concentrated *in vacuo*. The product was recrystallized from $CHCl_3$ to yield 11.25 g (89 %) of yellow crystals of compound **2** (mp. 165–166 °C). When the THF in the above procedure was replaced by dry acetone compound **2** separated out immediately as yellow crystals.

IR: (KBr): 1688 (C=O), 1064 (C=S) cm^{-1}. MS ([−]; 70 eV): *m/z* (% relative intensity) 314 (32) M^+, 121 (24), 118 (100), 90 (52), 89 (29), 76 (17). ^1H NMR: 250 MHz [$^2H_6$]DMSO.* 7.36 (s, 5 H), 5.38 (s, 1 H). ^{13}C NMR: 62.9 MHz [$^2H_6$]DMSO:* 210.1 (C=S), 169.6 (C=O), 135.1 (Ph–C), 128.8 (Ph–CH), 128.7 (Ph–CH), 128.4 (Ph–CH), 129.3 (C=C), 132.7 (C=C), 56.7 (CH).

Microanalysis calculated for $C_{11}H_6OS_5$: C: 42.01, H: 1.92 %. Found: C: 42.03, H: 1.92 %.

2,3-Dihydro-2-phenyl-1,3-dithio-[4,5-*e*][1,4]-dithiin-6-one (**3**) was synthesized from 2,3-dihydro-2-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione.[5] To the thione (3 g) in a mixture of chloroform (100 cm^3) and glacial acetic acid (130 cm^3) was added mercury(II) acetate (11.15 g). The mixture was stirred at room temperature for 30 min whereupon it was filtered and the organic phase was washed repeatedly with saturated sodium bicarbonate solution and finally with water. Drying (sodium sulphate) and concentration *in vacuo* afforded pale yellow crystals. Recrystallization from ethanol–chloroform (3:1) gave good quality crystals suitable for X-ray data collection. Yield: 90–93 %; m.p. 88–89 °C; IR: (KBr): 1624 (C=O) cm^{-1}. MS ([−]; 70 eV): *m/z* (% relative intensity) 284 (43) M^+, 224 (2), 180 (2), 135 (2), 104 (100), 88 (3), 78 (4). ^1H NMR: 250 MHz, $CDCl_3$: 7.40 (m, 5 H), 4.80 (m, 1 H), 3.5 ppm (m, 2 H). ^{13}C NMR: 62.5 MHz $CDCl_3$: 188.6 (C=O), 137.8 (Ph–C), 128.9 (Ph–C), 128.7 (Ph–C), 127.3 (Ph–C), 114.8 (C=C), 112.0 (C=C), 49.4 (CH), 36.7 ppm (CH_2). Microanalysis calculated for $C_{11}H_8OS_4$: C: 46.45, H: 2.84 %. Found: C: 45.83, H: 2.66 %.

X-Ray crystallography. The crystal structures were determined from low-temperature X-ray diffraction data. A CAD4 diffractometer was used for the data collections using Mo*K*α radiation and a graphite monochromator. The crystals were cooled with an Enraf–Nonius gas-flow low-

Table 1. Crystal data and a summary of data collection and refinement results.

	(1)	(2)	(3)
Formula	$C_5H_4S_5$	$C_{11}H_6OS_5$	$C_{11}H_8OS_4$
Formula weight/g mol^{-1}	224.41	314.49	284.44
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
Cell parameters at 110 K:			
a/Å	10.600(2)	10.0792(13)	15.735(3)
b/Å	5.7887(8)	6.059(2)	9.1996(9)
c/Å	13.436(3)	20.578(5)	16.487(14)
β/°	93.03(2)	105.87(15)	96.85(3)
V/Å^3	823.3(5)	1208.9(10)	2369.5(10)
Z	4	4	8
D_c/g cm^{-3}	1.810	1.728	1.595
μ(Mo*K*α)/cm^{-1}	12.72	8.98	7.44
Crystal size/mm	0.06×0.3×0.5	0.07×0.25×0.50	0.15×0.20×0.60
Scan mode	ω−2θ	ω	ω−2θ
Scan range, Δω	1.2+0.35 tan θ	2.0	1.0+0.35 tan θ
θ-range/°	1–35	1–30	1–35
No. of independent reflections	3631	3472	5213
No. of observed [$\|F\|^2 \geq 3\sigma(\|F\|^2)$] reflections, *n*	2801	2490	3510
w^{-1}[a]	$\sigma^2_{CS}(F)+0.0004\|F\|^2$	$\sigma^2_{CS}(F)+0.0006\|F\|^2$	$\sigma^2_{CS}(F)+0.0006\|F\|^2$
No. of variables, *m*	107	178	178
$S = \Sigma w\Delta F^2/(n-m)$	1.4	1.3	1.9
R	0.030	0.031	0.044
R_w	0.037	0.041	0.063

[a] σ_{CS} is the standard deviation calculated from counting statistics.

*The material decomposes on standing in DMSO.

temperature device. The temperature, 110 K, monitored with a thermocouple placed a few centimetres above the crystal in the exhaust pipe, remained constant within 1 K during the experiments. Crystal data for the three compounds are listed in Table 1 with a summary of data reduction and refinement results. An analysis of reflection profiles provided the basis for the selection of scan mode and scan interval for the data collections. The intensities of three standard reflections were measured after every 10000 s. The orientation of the crystal was checked after every 300 reflections.

Compound **1** crystallizes as yellow plates. The systematically absent reflections $h0l$: $h+l = 2n+1$ and $0k0$: $k = 2n+1$, uniquely determine the space group to be $P2_1/n$, a nonstandard setting of $P2_1/c$. Unit-cell parameters were determined from 18 reflections with $16.7 < \theta < 23.7°$. Data reduction included corrections for Lorentz, polarization and background effects, and symmetry-related reflections were averaged. The intensity control reflections showed that no degradation of the crystal had occurred.

The structure was solved by direct methods (MULTAN)[6] and refined by full matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$. After anisotropic thermal parameters were introduced a difference Fourier map clearly showed all the hydrogen atoms in the structure. The positional and isotropic thermal parameters for the hydrogen atoms were included in the refinement. After the final refinement cycle the maximum shift was 0.6σ. The peaks in the final difference Fourier were in the range 0.8 to -0.5 e Å^{-3}. The positional parameters are listed in Table 2.

Compound **2** forms platelike crystals belonging to the monoclinic system. The space group was established to be $P2_1/c$ from the systematically absent reflections; $h0l$: $l = 2n+1$ and $0k0$: $k = 2n+1$. 22 reflections in the range $13.5 < \theta < 21.0°$ were used for the determination of unit-cell parameters. The data reduction, structure solution and refinement follow the same pattern as described above for **1**. The hydrogen atoms had their positional parameters included in the refinement, but they were given a fixed isotropic thermal parameter, $B = 2.0$ Å^2. The maximum shift in the final cycle was 0.08σ. The difference Fourier had peaks in the range 0.5 to -0.5 e Å^{-3}. The positional parameters are listed in Table 3.

Table 2. Positional parameters and equivalent isotropic temperature factors for compound **1**, 2,3-dihydro-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione.

Atom	*x*	*y*	*z*	B_{iso}[a]/Å^2
S1	0.793 47(3)	0.228 53(6)	0.350 83(3)	1.037(5)
S2	0.946 49(3)	−0.180 78(6)	0.353 15(2)	0.969(5)
S3	0.868 03(3)	−0.360 01(6)	0.546 32(3)	1.110(5)
S4	0.681 80(3)	0.141 12(6)	0.546 19(3)	1.296(5)
S5	0.958 30(3)	0.141 73(7)	0.181 92(3)	1.243(5)
C1	0.903 0(1)	0.069 7(2)	0.290 6(1)	0.92(2)
C2	0.857 4(1)	−0.139 2(2)	0.457 5(1)	0.84(2)
C3	0.758 6(1)	−0.266 8(3)	0.638 0(1)	1.19(2)
C4	0.643 2(1)	−0.142 1(3)	0.593 3(1)	1.23(2)
C5	0.786 0(1)	0.055 3(2)	0.456 5(1)	0.94(2)

[a] $B_{iso} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij}\, \boldsymbol{a}_i \cdot \boldsymbol{a}_j\, a_i^* a_j^*$.

Table 3. Positional parameters and equivalent isotropic temperature factors for compound **2**, 2,3-dihydro-2-oxo-3-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione.

Atom	*x*	*y*	*z*	B_{iso}[a]/Å^2
S1	0.568 61(5)	0.193 84(9)	0.067 80(3)	1.117(9)
S2	0.863 98(5)	0.171 10(9)	0.128 47(3)	0.990(8)
S3	0.846 27(5)	−0.241 23(9)	0.208 38(3)	0.927(8)
S4	0.508 25(5)	−0.235 72(9)	0.124 34(3)	1.097(9)
S5	0.761 00(6)	0.531 30(9)	0.031 70(3)	1.278(9)
C1	0.729 1(2)	0.309 0(4)	0.073 0(1)	1.02(4)
C2	0.765 9(2)	−0.039 8(3)	0.150 2(1)	0.87(3)
C3	0.710 5(2)	−0.274 4(3)	0.251 4(1)	0.84(3)
C4	0.582 2(2)	−0.373 1(4)	0.202 8(1)	0.99(4)
C5	0.628 3(2)	−0.030 5(4)	0.120 8(1)	0.95(4)
C6	0.767 9(2)	−0.419 7(4)	0.312 2(1)	0.89(3)
C7	0.818 8(2)	−0.629 6(4)	0.304 1(1)	1.05(4)
C8	0.877 6(2)	−0.759 5(4)	0.360 5(1)	1.18(4)
C9	0.883 4(2)	−0.683 0(4)	0.424 9(1)	1.21(4)
C10	0.830 7(2)	−0.476 3(4)	0.433 2(1)	1.26(4)
C11	0.772 5(2)	−0.344 7(4)	0.377 1(1)	1.07(4)
O	0.525 9(2)	−0.539 1(3)	0.213 17(8)	1.52(3)

[a] See Table 2.

Compound **3** forms yellow spearhead-shaped crystals which belong to the monoclinic system. The systematically absent reflections hkl: $h+k = 2n+1$ and $h0l$: $l = 2n+1$ are consistent with the space groups $C2/c$ or Cc. 22 reflections in the range $15.3 < \theta < 19.4°$ were used for the determination of unit-cell parameters. Data reduction was performed as described above. As attempts to solve the structure by direct methods did not provide a solution, Patterson search methods were employed instead. Introducing the fragment from **1** in the space group $C2/c$, the PATSEE program gave coordinates for the four sulphur atoms. The remaining non-hydrogen atoms in the structure were found in a subsequent difference Fourier map. As refinements progressed it became apparent that the ethylene moiety of the six-membered ring is disordered. The crystal contains this group in two different conformations which were assigned as four partly populated atomic sites in the following structure refinement. The population parameters of these atoms were included in the refinements; when convergence was obtained the population parameters were scaled to give the sum 1.0 and fixed at these values in the final refinement cycles.

Owing to the disorder of the ethylene group it was only possible to localize with certainty the hydrogen atoms of the phenyl group. They were included in the refinement with a fixed isotropic temperature factor of 3.0 Å^2. The maximum shift after the final cycle is 0.03σ and the peaks in the final difference Fourier were between 1.2 and -0.6 e Å^{-3}. The positional parameters are listed in Table 4.

The crystallographic computations were performed with the Enraf–Nonius structure determination package.[8] The

Table 4. Positional parameters and equivalent isotropic temperature factors for compound **3**, 2,3-dihydro-2-phenyl-1,3-dithiolo[4,5-*e*][1,4]dithiin-6-thione.

Atom	*x*	*y*	*z*	B_{iso}[a]/Å^2
S1	0.396 95(3)	0.752 62(6)	0.983 48(3)	2.271(9)
S2	0.415 71(3)	0.481 61(6)	0.892 69(4)	2.132(8)
S3	0.508 57(3)	0.558 99(7)	0.836 37(4)	2.609(9)
S4	0.557 28(3)	0.885 52(6)	0.944 52(4)	2.357(9)
O	0.286 6(1)	0.536 1(2)	0.976 8(1)	2.78(3)
C1	0.353 2(1)	0.580 3(3)	0.955 6(1)	2.11(3)
C2	0.496 5(1)	0.612 5(2)	0.890 7(1)	1.80(3)
C31(0.59)[b]	0.662 3(2)	0.699 9(4)	0.869 4(2)	1.59(5)
C41(0.59)[b]	0.627 1(2)	0.854 3(4)	0.866 2(2)	2.03(5)
C32(0.41)[b]	0.634 7(3)	0.719 8(5)	0.832 4(3)	1.62(7)
C42(0.41)[b]	0.650 7(3)	0.798 2(7)	0.913 8(4)	2.38(9)
C5	0.487 4(1)	0.736 8(2)	0.932 0(1)	1.76(3)
C6	0.728 3(1)	0.686 7(3)	0.809 7(2)	2.72(4)
C7	0.728 6(1)	0.742 7(3)	0.731 7(2)	2.79(4)
C8	0.800 3(2)	0.734 1(3)	0.692 0(2)	3.00(5)
C9	0.873 6(1)	0.668 6(3)	0.730 8(2)	3.31(5)
C10	0.873 7(2)	0.611 0(3)	0.807 8(2)	3.56(5)
C11	0.800 7(2)	0.619 2(3)	0.846 8(2)	3.37(5)

[a]See Table 2. [b]Population parameters different from 1 are shown in parenthesis.

atomic scattering factors including corrections for anomalous dispersion from the tabulation of Cromer and Waber[9] were used as contained in the program. The anisotropic thermal parameters for the non-hydrogen atoms and lists of observed and calculated structure factors are available from one of the authors (S.L).

Results and discussion

The molecular geometries of the three molecules are illustrated by the bond lengths and angles listed in Table 5 and by Fig. 2. The conformational disorder of the ethylene moiety in **3** is similar to the disorder observed in the a I_3^- salt of BEDT–TTF.[10] The population parameters are similar in magnitude, but in contrast to β-(BEDT–TTF)I_3 the diffraction pattern of **3** does not show any indication of a modulated structure. The phenyl group is placed symmetrically relative to the two conformations, S3–C31–C41–S4 and S3–C32–C42–S4, which have torsion angles of 70 and −75°, respectively.

An inspection of the bond lengths and angles reveals that in **1** and **3** they are related by twofold symmetry within the experimental accuracy. Compound **2** deviates only from twofold symmetry in the six-membered ring owing to the change of an sp^3 carbon atom to an sp^2 carbon atom. **2** and **3** display similarities with respect to the relative orientation of the phenyl group. In **2** the phenyl group and the five-membered ring are perpendicular. Although C4 does not have any substituents, the corresponding interplanar angle is 86° in **3**.

BEDT–TTF has been shown to be an excellent electron donor, and this molecule and its salt have been subject to extensive structural investigations.[10–13] A recent review article contains a survey of the crystal and molecular structures of different BEDT–TTF compounds.[2] It is of obvious interest to make comparisons with the structural results for the present compounds, which are related to half a BEDT–TTF molecule. Compounds **1–3** have a planar five-membered ring. The interplanar angles between this ring and the S3–C2–C5–S4 moiety are 2.4° in **1**, 2.3° in **2** and 2.6° in **3** comparable to the equivalent angles in the BEDT–TTF structures. The comparison also reveals that the overall geometry of the part of the molecule defined by S1, S2, C2, C5, S3, C3, C4 and S4 remains unperturbed by both the dimerization and the variation of charge in BEDT–TTF. The only significant variation is found in the S1–C1–S2 fragment. The C1–S1 and C1–S2 bond lengths are in the range 1.716–1.765 Å in **1–3**, which is similar to the variations in the BEDT–TTF compounds.

The replacement of S5 with oxygen is accompanied by a significant increase in the C1–S1 and C1–S2 bond lengths. They average to 1.765 Å in compound **3**, compared with 1.716 Å in **1** and 1.735 Å in **2**. This could indicate that conjugation within the ring system is less pronounced in **3**

Table 5. Bond lengths (in Å) and bond angles (in °) in the three compounds.

	(**1**)	(**2**)	(**3**)[a]
C1–S5/O	1.6559(13)	1.670(2)	1.215(2)
C1–S1	1.7157(13)	1.738(2)	1.767(2)
C1–S2	1.7264(13)	1.732(2)	1.763(2)
S1–C5	1.7431(13)	1.744(2)	1.7477(14)
S2–C2	1.7489(12)	1.747(2)	1.7538(15)
C2–C5	1.356(2)	1.354(3)	1.347(2)
C2–S3	1.7474(12)	1.746(2)	1.7541(15)
S3–C3	1.8163(13)	1.833(2)	1.861(3)
C3–C4	1.517(2)	1.525(3)	1.524(3)
C4–S4	1.8118(14)	1.788(2)	1.815(3)
S4–C5	1.7494(12)	1.751(2)	1.753(2)
C3–C6	–	1.510(3)	1.518(3)
C4–O	–	1.202(3)	–
S1–C1–S5/O	124.10(8)	126.73(12)	123.26(14)
S1–C1–S2	113.00(7)	113.33(11)	112.82(8)
S2–C1–S5/O	122.86(8)	119.94(12)	123.92(14)
C1–S1–C5	97.85(6)	96.80(9)	96.48(7)
C1–S2–C2	97.64(6)	97.15(9)	96.54(7)
S2–C2–C5	115.46(9)	115.95(14)	116.87(11)
S1–C5–C2	115.94(9)	116.62(15)	117.28(12)
C2–C5–S4	126.87(10)	125.95(15)	128.25(11)
C5–C2–S3	129.13(10)	124.19(15)	128.93(12)
C2–S3–C3	102.96(6)	98.07(9)	101.09(9)
S3–C3–C4	113.82(9)	109.72(13)	113.8(2)
C3–C4–S4	112.10(10)	118.66(14)	111.8(2)
C4–S4–C5	98.41(6)	104.24(9)	102.54(10)
S1–C5–S4	117.09(7)	117.09(10)	114.42(8)
S2–C2–S3	115.35(7)	119.83(11)	114.17(9)
S3–C3–C6	–	107.30(12)	104.9(2)
C4–C3–C6	–	112.3(2)	109.1(2)
S4–C4–O	–	116.73(15)	–

[a]The dimensions given involve the more populated (C31–C41) conformer.

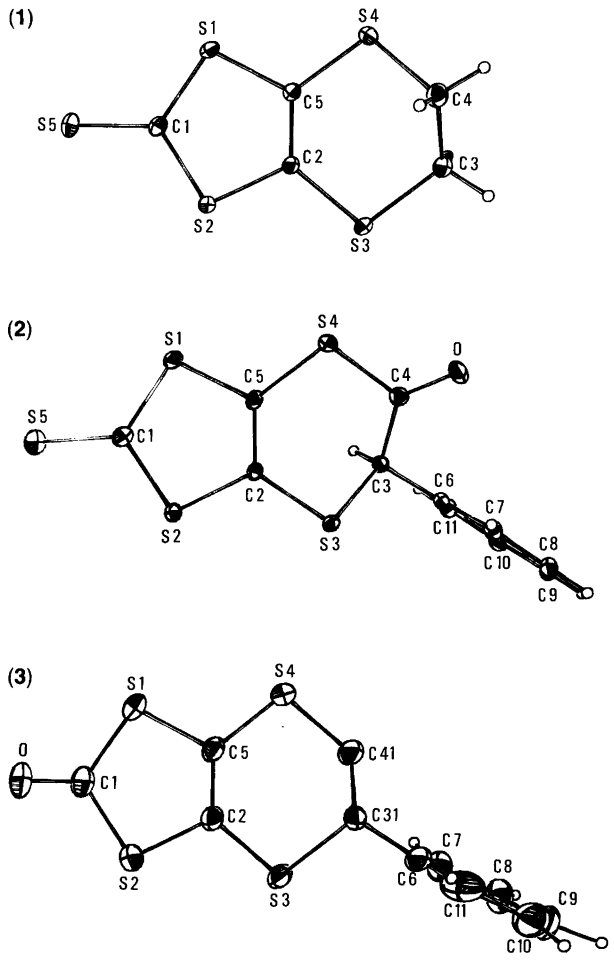


Fig. 2. Ortep drawings of the three precursors (**1**)–(**3**) illustrating atomic labelling. The more populated conformer is shown of compound **3**. The thermal ellipsoids are drawn to enclose 50 % probability. The hydrogen atoms are drawn as spheres with an arbitrary radius.

than in the other molecules. However, in the calculation of least-squares planes for the C1, S1, S2, C2 and C5 moiety compound **3** has the smallest deviations from planarity, the maximum deviation from the plane being 0.006 Å. In **1** and **2** the ring is significantly more puckered, with deviations up to 0.024 Å from the plane. It is also remarkable that **1**, with the shortest C1–S1 and C1–S2 bonds, also has a shorter [1.656(1) Å] C=S double bond than **2** [1.670(2) Å]. This may be a consequence of the short intermolecular contacts in **1** (*vide infra*).

Short intermolecular S–S distances have been considered to be an essential feature of the conducting of BEDT–TTF salts.[2] Table 6 lists some short intermolecular contacts in the present structures. One notes that the number of short S–S distances in **1** is remarkable and comparable to those found in the BEDT–TTF salts. Four of the S–S distances in **1** are in the range 3.5–3.7 Å, close to the sum of van der Waals radii, 3.6 Å.[14] The short S4–S5 contact of 3.313 Å in **1** is indicated on the stereo pair shown in Fig. 3. It cannot be excluded that this interaction is repulsive and may explain the short C1–S5 bond in **1**. There is only one S–S interaction in **2** less than 3.7 Å, and the packing in **2** seems to be influenced by a C3–H···O hydrogen bond, which is indicated on the stereo pair in Fig. 4. Compound **3** has three S–S contacts shorter than 3.6 Å, and the short S4–S4 contact is marked on Fig. 5.

The packing diagrams of the three monomers **1**–**3** reveal that even though these compounds have significant S–S interactions the relative orientations of the molecules differ internally and from the arrangements found in the BEDT–TTF compounds.

Conclusions

The present structure determinations have shown that these BEDT–TTF monomers have molecular dimensions that are similar to those oberved in BEDT–TTF compounds. The structural variations due to the substitution in **2** and **3** are comparable to the variations caused by the variation of charge of the dimer in the BEDT–TTF salts. These non-conducting monomers have intermolecular S–S interactions that are similar to those observed in the conducting BEDT–TTF salts. Consequently it may be concluded that not only the S–S contacts but also the relative orientation (stacking) of the BEDT–TTF molecules are important for the conducting properties of the salt. From these results it would appear that the short S–S intermolecular distances in the conducting BEDT–TTF salts are not a result of the electron delocalization, but are a feature of the neutral species that may facilitate of delocalized electrons in the cationic compounds.

Table 6. Short intermolecular contact distances (in Å).

(1)		(2)		(3)	
S1–S2[a]	3.6770(5)	S1–S1[d]	3.6205(10)	S1–S4[f]	3.5784(6)
S1–S5[a]	3.5933(5)	C3–H···O[e]	3.032(2)	S3–S3[g]	3.5799(9)
S4–S5[b]	3.3133(5)			S4–S4[f]	3.4380(8)
S2–S3[c]	3.5321(4)				
S3–S3[c]	3.5166(6)				

[a](1½−x, ½+y, ½−z). [b](x−½, ½−y, z+½). [c](2−x, −y−1, 1+z). [d](1−x, −y, −z). [e](1−x, ½+y, ½−z). [f](1−x, 2−y, 2−z). [g](1−x, y, 1½−z).

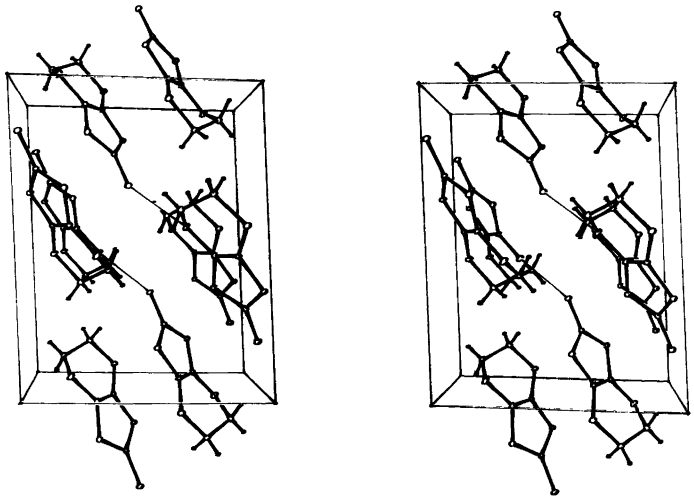


Fig. 3. Packing in the crystals of compound **1** seen along the crystallographic *b*-axis. The short S4–S5 intermolecular contacts are indicated by thin lines.

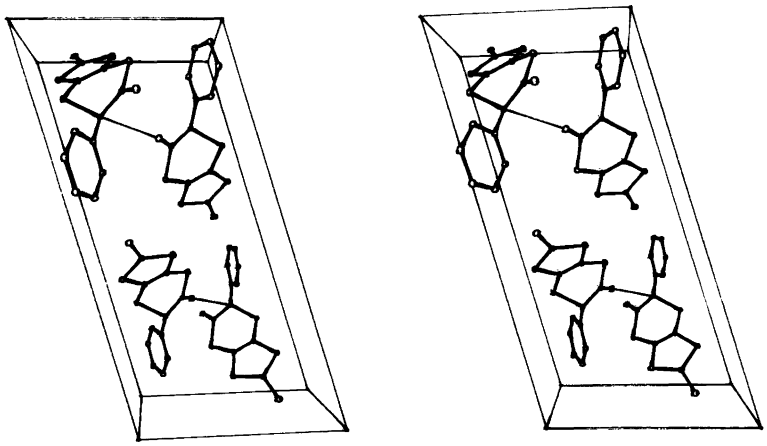


Fig. 4. Packing in the crystals of compound **2** seen along the crystallographic *b*-axis. The short C–H···O hydrogen bond is shown as thin lines.

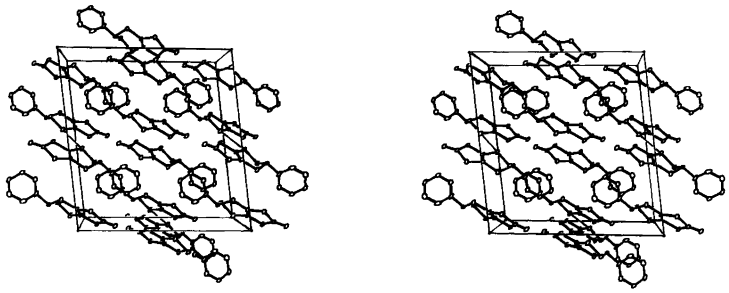


Fig. 5. Packing in compound **3** seen along the *b*-axis the short S4–S4 intermolecular distance is illustrated as in Fig. 3. The more populated conformer is shown in the drawing.

Acknowledgements. The authors are grateful to Mr. F. Hansen for help with the experimental crystallographic work. We are also grateful for support from the SERC (UK) (To K.S.V. and A.E.U.) and from the Danish Natural Science Research Council (to S.L.).

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Received February 26, 1991.