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Structure of 3,4;3′,4′-Bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene–Tetrabromoindate (2:1), $(BEDT\text{-}TTF)_2InBr_4$, $(C_{10}H_8S_8)_2InBr_4$

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Abstract. $M_r = 1203\cdot83$, triclinic, $P\bar{1}$, $a = 6\cdot618\,(1)$, $b = 16\cdot040\,(3)$, $c = 17\cdot470\,(3)$ Å, $\alpha = 95\cdot29\,(2)°$, $\beta = 92\cdot43\,(1)$, $\gamma = 99\cdot12\,(1)°$, $V = 1819\cdot9$ Å^3, $Z = 2$, $D_x = 2\cdot20$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71073$ Å) $= 5\cdot89$ mm^{-1}, $F(000) = 1162$, $T = 298$ K, $R(F) = 0\cdot095$ for 2965 observed reflections ($F_o > 0\cdot0$). The structure consists of dimerized stacks of BEDT-TTF ($C_{10}S_8H_8$) molecules separated by sheets of tetrahedral $InBr_4^-$ anions. Different, and short ($d \leq 3\cdot6$ Å) S—S contacts occur normal to the molecular-stacking direction for the two independent BEDT-TTF molecules. Short anion–sulfur non-bonding contacts, and dimerization of the BEDT-TTF molecules within the stacks, may be responsible for this behavior. An activated conductivity ($E_a = 0\cdot15$ e V) with a room-temperature value of $0\cdot05$–$0\cdot5$ Ω^{-1} cm^{-1} is observed along the needle (crystal a^*) axis.

Introduction. The family of organic conductors based on BEDT-TTF includes $(BEDT\text{-}TTF)_2X$ charge-transfer salts where X is a monovalent anion with tetrahedral or octahedral geometry. Crystals of these materials derived from tetrahedral anions include the first sulfur-based organic superconductor $(BEDT\text{-}TTF)_2ReO_4$ [$T_c \simeq 2$ K at 0·4 GPa pressure (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983)] and $(BEDT\text{-}TTF)_2ClO_4\,(TCE)_{0\cdot5}$ (TCE = 1,1,2-trichloroethane) which is metallic to 1·4 K (Kobayashi, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1983). Both of these derivatives contain segregated stacks of donor and acceptor molecules having significant intermolecular S—S interactions between the organic molecules both along and normal to the stacking direction (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1983; Parkin *et al.*, 1983) and as a result have been characterized as two-dimensional electrical conductors (Kobayashi, Kato *et al.*, 1983). In contrast, salts containing octahedral anions, *e.g.* α- and β-$(BEDT\text{-}TTF)_2PF_6$ (Kobayashi, Kato *et al.*, 1983;

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Kobayashi, Mori, Kato, Kobayashi, Sasaki, Saito & Inokuchi, 1983) and (BEDT-TTF)$_2$AsF$_6$ (Leung, Beno, Blackman, Coughlin, Miderski, Joss, Crabtree & Williams, 1984), either are semiconducting, or undergo metal–insulator transitions near ambient temperatures, and are structurally more 'one-dimensional' possessing short S—S contacts normal to the stacking direction only. Structural data for (BEDT-TTF)$_2$InBr$_4$ show that this large tetrahedral anion produces intermolecular S—S interactions similar to those observed in the octahedral anion salts, consistent with our observation of activated conductivity.

Table 1. *Fractional coordinates and thermal parameters*

The complete temperature factor is $\exp[-U_{eq}(\sin^2\theta)/(\lambda^2 8\pi^2)]$, where $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$ in units of Å^2.

	x	*y*	*z*	$U_{eq}(\times 10^3)$
S(1)	0·3197 (8)	0·3624 (3)	0·9275 (3)	41 (2)
S(2)	0·7639 (8)	0·4232 (3)	0·9491 (3)	43 (2)
S(3)	0·2549 (8)	0·5267 (3)	0·8467 (3)	42 (2)
S(4)	0·6961 (8)	0·5917 (3)	0·8645 (3)	41 (2)
S(5)	0·3335 (10)	0·1984 (4)	0·9892 (4)	76 (3)
S(6)	0·8523 (9)	0·2655 (3)	1·0127 (3)	54 (2)
S(7)	0·1591 (9)	0·6585 (4)	0·7510 (3)	59 (3)
S(8)	0·6782 (10)	0·7354 (4)	0·7718 (4)	78 (3)
S(11)	0·2770 (8)	0·4810 (3)	0·6034 (3)	42 (2)
S(12)	0·7199 (8)	0·5470 (3)	0·6143 (3)	44 (2)
S(13)	0·1936 (8)	0·6474 (3)	0·5214 (3)	45 (2)
S(14)	0·6373 (8)	0·7110 (3)	0·5341 (3)	47 (2)
S(15)	0·3081 (8)	0·3394 (3)	0·6972 (3)	51 (2)
S(16)	0·8337 (9)	0·4195 (4)	0·7103 (3)	63 (3)
S(17)	0·0789 (9)	0·7941 (3)	0·4522 (3)	54 (2)
S(18)	0·6070 (9)	0·8722 (3)	0·4683 (3)	51 (2)
C(1)	0·5274 (30)	0·4419 (11)	0·9162 (10)	36 (8)
C(2)	0·4965 (27)	0·5118 (10)	0·8808 (9)	29 (8)
C(3)	0·4720 (34)	0·2937 (12)	0·9679 (10)	37 (8)
C(4)	0·6732 (34)	0·3228 (12)	0·9777 (10)	40 (9)
C(5)	0·3516 (31)	0·6167 (11)	0·8008 (10)	33 (8)
C(6)	0·5489 (33)	0·6458 (12)	0·8064 (11)	41 (9)
C(7)	0·5215 (32)	0·1303 (12)	1·0004 (13)	61 (10)
C(8)	0·7310 (32)	0·1603 (11)	0·9701 (12)	51 (9)
C(9)	0·2733 (36)	0·7710 (12)	0·7615 (15)	77 (12)
C(10*A*)	0·4650 (71)	0·7810 (31)	0·7220 (41)	23 (23)
C(10*B*)	0·5007 (96)	0·8038 (44)	0·7622 (59)	76 (26)
C(11)	0·4782 (27)	0·5614 (11)	0·5850 (9)	30 (7)
C(12)	0·4326 (29)	0·6305 (11)	0·5502 (10)	37 (8)
C(13)	0·4305 (35)	0·4284 (12)	0·6598 (10)	40 (9)
C(14)	0·6367 (36)	0·4568 (11)	0·6630 (10)	39 (9)
C(15)	0·2771 (33)	0·7465 (11)	0·4911 (10)	36 (8)
C(16)	0·4791 (31)	0·7768 (11)	0·4956 (9)	29 (8)
C(17*A*)	0·5113 (60)	0·2767 (29)	0·7029 (47)	25 (18)
C(17*B*)	0·5304 (73)	0·2932 (35)	0·7388 (58)	20 (23)
C(18*A*)	0·7172 (59)	0·3343 (31)	0·7566 (41)	48 (19)
C(18*B*)	0·7133 (76)	0·3101 (37)	0·7150 (50)	29 (26)
C(19)	0·4007 (31)	0·9121 (11)	0·4162 (11)	40 (8)
C(20)	0·2090 (32)	0·9061 (11)	0·4593 (12)	47 (9)
In(1)	0·1000 (2)	0·0147 (1)	0·7767 (1)	40 (1)
Br(1)	−0·0390 (4)	−0·0803 (1)	0·6582 (1)	71 (1)
Br(2)	−0·0330 (4)	−0·0471 (2)	0·8931 (1)	73 (1)
Br(3)	0·0194 (4)	0·1594 (1)	0·7672 (1)	71 (1)
Br(4)	0·4806 (4)	0·0275 (2)	0·7839 (2)	78 (1)

Table 2. *Selected short intermolecular contact distances* (Å)

		Symmetry
S(2)···S(3)	3·595 (7)	$1-x,1-y,2-z$*
S(5)···S(6)	3·547 (8)	$x-1,y,z$
S(7)···S(8)	3·611 (9)	$x-1,y,z$
S(11)···S(16)	3·599 (8)	$x-1,y,z$
S(14)···S(17)	3·439 (8)	$x+1,y,z$
S(15)···S(16)	3·583 (8)	$x-1,y,z$
S(17)···S(18)	3·556 (8)	$x-1,y,z$
S(5)···Br(2)	3·716 (6)	$-x,-y,2-z$
S(15)···Br(3)	3·546 (5)	$x-1,y,z$
Br(2)···Br(2)	3·877 (5)	$-x,-y,2-z$
Br(3)···Br(4)	3·884 (4)	$x-1,y,z$

* *Intra*stack S···S distances shown between molecules *A* and *A′* in Fig. 1.

Experimental. Crystals of (BEDT-TTF)$_2$InBr$_4$ prepared by the electrolytic oxidation of BEDT-TTF in 1,1,2-trichloroethane solution in the presence of (n-Bu$_4$N)InBr$_4$ (Gislason, Lloyd & Tuck, 1971) at a constant current (0·5 µA) and controlled temperature (296·6 K). D_m not determined. Thin black needle 0·034 × 0·074 × 0·283 mm. Syntex $P2_1$ automated four-circle diffractometer. Unit-cell dimensions determined from a least-squares refinement of the setting angles of 25 reflections ($18° < 2\theta < 30°$). Intensity data collected using the ω-scan technique with variable scan rates of 2·0 to 12·0° min^{-1} to $\sin\theta/\lambda = 0{\cdot}48$ Å^{-1} ($h = 0$ to 6, $k = -15$ to 15, $l = -16$ to 16). Four standard reflections measured at an interval of 100 reflections, small (2-3%) random variations. Data corrected for absorption effects using a Gaussian integration procedure; $T_{\min} = 0{\cdot}676$, $T_{\max} = 0{\cdot}828$. For the 4000 reflections collected, standard reflections and duplicate $0kl$ reflections were averaged to yield 3437 unique data with $R_{av}(F_o) = 0{\cdot}020$ and $R_{av}(wF_o) = 0{\cdot}015$; 2965 with $F_o > 0{\cdot}0$ retained for further calculations. Intensity statistics indicated the centrosymmetric space group, and this choice was later confirmed by the successful structure solution and least-squares refinement. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which provided the positions of all S atoms. The C atoms, and the InBr$_4^-$ anion atom positional parameters, were derived using Fourier methods. Atomic- and anomalous-scattering factors from *International Tables for X-ray Crystallography* (1974). All computations carried out using a local modification of the *UCLA Crystallographic Program Package* (Strouse, 1978). The exocyclic C atoms of the BEDT-TTF molecules, C(10) and C(17)–C(18), were found to possess large thermal motion normal to the plane of the BEDT-TTF molecules and were treated as separate atomic sites [*e.g.* C(17) is C(17*A*) and C(17*B*)] and refined with isotropic temperature factors and site populations of 0·5. The attempted refinement of the structure in the noncentrosymmetric space group $P1$ did not eliminate this disorder and resulted in higher agreement factors. Anisotropic temperature factors were used for all S atoms and C atoms which were not disordered. H atoms not located. $\sum w|F_o - F_c|$ minimized, where $w = 1/\sigma(F_o)$ and $\sigma(F_o) = 1/(2F_o)[\sigma(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}$, with the value of $\sigma(F_o^2)$ based on counting statistics. $\Delta/\sigma = 0{\cdot}04$ in final least-squares cycle which resulted in the agreement factors $R(F_o) = 0{\cdot}095$, $wR(F_o) = 0{\cdot}063$, and $S = 2{\cdot}21$. No correction for

Table 3. *Interatomic distances* (Å) *and angles* (°)

Within the BEDT-TTF molecule

S(1)–C(1)	1·75 (2)	S(1)–C(3)	1·78 (2)	S(2)–C(1)	1·72 (2)
S(2)–C(4)	1·75 (2)	S(3)–C(2)	1·74 (2)	S(3)–C(5)	1·76 (2)
S(4)–C(2)	1·74 (2)	S(4)–C(6)	1·76 (2)	S(5)–C(3)	1·73 (2)
S(5)–C(7)	1·80 (2)	S(6)–C(4)	1·74 (2)	S(6)–C(8)	1·83 (2)
S(7)–C(5)	1·77 (2)	S(7)–C(9)	1·83 (2)	S(8)–C(6)	1·73 (2)
S(8)–C(10*B*)	1·74 (5)	S(8)–C(10*A*)	1·90 (5)	S(11)–C(13)	1·75 (2)
S(11)–C(11)	1·76 (2)	S(12)–C(11)	1·72 (2)	S(12)–C(14)	1·77 (2)
S(13)–C(12)	1·71 (2)	S(13)–C(15)	1·74 (2)	S(14)–C(16)	1·76 (2)
S(14)–C(12)	1·77 (2)	S(15)–C(13)	1·72 (2)	S(15)–C(17*A*)	1·81 (3)
S(15)–C(17*B*)	1·90 (5)	S(16)–C(14)	1·73 (2)	S(16)–C(18*A*)	1·74 (4)
S(16)–C(18*B*)	1·82 (5)	S(17)–C(15)	1·76 (2)	S(17)–C(20)	1·86 (2)
S(18)–C(16)	1·74 (2)	S(18)–C(19)	1·84 (2)	C(1)–C(2)	1·37 (2)
C(3)–C(4)	1·34 (2)	C(5)–C(6)	1·31 (2)	C(7)–C(8)	1·53 (3)
C(9)–C(10*A*)	1·46 (4)	C(9)–C(10*B*)	1·51 (6)	C(11)–C(12)	1·38 (2)
C(13)–C(14)	1·37 (2)	C(15)–C(16)	1·34 (2)	C(17*A*)–C(18*B*)	1·36 (6)
C(17*A*)–C(18*A*)	1·71 (9)	C(17*B*)–C(18*B*)	1·29 (7)	C(17*B*)–C(18*A*)	1·32 (7)
C(19)–C(20)	1·50 (3)				
C(10*A*)–C(10*B*)	0·77 (6)	C(17*A*)–C(17*B*)	0·66 (5)	C(18*A*)–C(18*B*)	0·79 (5)

C(1)–S(1)–C(3)	94·8 (10)	C(1)–S(2)–C(4)	95·4 (10)
C(2)–S(3)–C(5)	93·7 (9)	C(2)–S(4)–C(6)	96·0 (9)
C(3)–S(5)–C(7)	104·8 (10)	C(4)–S(6)–C(8)	97·9 (10)
C(5)–S(7)–C(9)	99·6 (10)	C(6)–S(8)–C(10*B*)	106·4 (19)
C(6)–S(8)–C(10*A*)	103·1 (15)	C(10*B*)–S(8)–C(10*A*)	23·9 (23)
C(13)–S(11)–C(11)	95·0 (10)	C(11)–S(12)–C(14)	95·2 (9)
C(12)–S(13)–C(15)	95·1 (10)	C(16)–S(14)–C(12)	94·7 (9)
C(13)–S(15)–C(17*A*)	101·6 (13)	C(13)–S(15)–C(17*B*)	102·4 (15)
C(17*A*)–S(15)–C(17*B*)	20·3 (15)	C(14)–S(16)–C(18*A*)	105·8 (15)
C(14)–S(16)–C(18*B*)	99·7 (17)	C(18*A*)–S(16)–C(18*B*)	25·50 (16)
C(15)–S(17)–C(20)	99·9 (9)	C(16)–S(18)–C(19)	102·0 (9)
C(2)–C(1)–S(2)	124·3 (15)	C(2)–C(1)–S(1)	119·9 (15)
S(2)–C(1)–S(1)	115·7 (10)	C(1)–C(2)–S(4)	122·7 (14)
C(1)–C(2)–S(3)	122·6 (14)	S(4)–C(2)–S(3)	114·8 (9)
C(4)–C(3)–S(5)	129·9 (15)	C(4)–C(3)–S(1)	116·1 (15)
S(5)–C(3)–S(1)	114·1 (12)	C(3)–C(4)–S(6)	124·2 (15)
C(3)–C(4)–S(2)	118·1 (15)	S(6)–C(4)–S(2)	117·7 (13)
C(6)–C(5)–S(3)	119·9 (15)	C(6)–C(5)–S(7)	127·0 (16)
S(3)–C(5)–S(7)	113·1 (12)	C(5)–C(6)–S(8)	128·6 (16)
C(5)–C(6)–S(4)	115·1 (15)	S(8)–C(6)–S(4)	116·0 (12)
C(8)–C(7)–S(5)	115·9 (13)	C(7)–C(8)–S(6)	113·8 (14)
C(10*A*)–C(9)–S(7)	108·8 (25)	C(10*B*)–C(9)–S(7)	124·6 (27)
C(9)–C(10*A*)–S(8)	113·7 (32)	C(9)–C(10*B*)–S(8)	120·5 (38)
C(12)–C(11)–S(12)	125·1 (14)	C(12)–C(11)–S(11)	119·2 (14)
S(12)–C(11)–S(11)	115·8 (10)	C(11)–C(12)–S(13)	126·3 (15)
C(11)–C(12)–S(14)	118·1 (14)	S(13)–C(12)–S(14)	115·6 (10)
C(14)–C(13)–S(15)	126·8 (15)	C(14)–C(13)–S(11)	116·6 (14)
S(15)–C(13)–S(11)	116·3 (13)	C(13)–C(14)–S(16)	129·6 (14)
C(13)–C(14)–S(12)	116·7 (14)	S(16)–C(14)–S(12)	113·6 (13)
C(16)–C(15)–S(13)	119·0 (15)	C(16)–C(15)–S(17)	127·1 (14)
S(13)–C(15)–S(17)	113·8 (12)	C(15)–C(16)–S(18)	129·2 (14)
C(15)–C(16)–S(14)	115·6 (14)	S(18)–C(16)–S(14)	115·2 (12)
C(18*B*)–C(17*A*)–S(15)	124·0 (38)	C(18*A*)–C(17*A*)–S(15)	109·6 (36)
C(18*B*)–C(17*B*)–S(15)	122·0 (45)	C(18*A*)–C(17*B*)–S(15)	126·0 (32)
C(17*B*)–C(18*A*)–S(16)	124·4 (43)	C(17*A*)–C(18*A*)–S(16)	111·9 (35)
C(17*B*)–C(18*B*)–S(16)	120·4 (48)	C(17*A*)–C(18*B*)–S(16)	127·8 (34)
C(20)–C(19)–S(18)	112·1 (13)	C(19)–C(20)–S(17)	109·8 (13)

Within the $\mathrm{InBr_4^-}$ anion

In(1)–Br(1)	2·504 (3)	In(1)–Br(2)	2·478 (3)	In(1)–Br(3)	2·481 (3)
In(1)–Br(4)	2·491 (3)				

Br(2)–In(1)–Br(3)	112·39 (10)	Br(2)–In(1)–Br(4)	108·70 (10)
Br(2)–In(1)–Br(1)	110·28 (10)	Br(3)–In(1)–Br(4)	106·93 (10)
Br(3)–In(1)–Br(1)	110·01 (10)	Br(4)–In(1)–Br(1)	108·39 (10)

secondary extinction. A difference Fourier synthesis based on the structure factors derived from the final parameter values produced random variations of $\pm 0·6$ e Å^{-3} with the largest peaks 1·0–0·75 e Å^{-3} associated with the disordered ethylene-group C atoms. The electrical conductivity was measured below room temperature along the needle (crystal a^*) axis on two specimens. The measurements were made using the four-probe, low-frequency AC technique, with contacts applied by silver paint. A room-temperature conductivity of 0·05 Ω^{-1} cm^{-1} was observed in one case, 0·5 in the other. The same activation energy, 0·15 e V, was seen for both.

Discussion. Final positional and thermal parameters are presented in Table 1.* The intermolecular S–S, S–Br and Br–Br contact distances less than the sum of the van der Waals radii (3·6, 3·8 and 4·0 Å, respectively) are summarized in Table 2. Intramolecular distances and angles are given in Table 3. The asymmetric unit contains two independent BEDT-TTF molecules (labeled *A* and *B* in Fig. 1) and one $\mathrm{InBr_4^-}$ anion. As is shown in Fig. 1, the BEDT-TTF molecules form a zigzag stack along the *c* axis. This stack is dimerized with the interplanar spacings being $A\cdots A' = 3·43$, $A\cdots B = 3·87$ and $B\cdots B' = 3·47$ Å. In addition, the BEDT-TTF molecules are bowed away from the short interplanar interactions (*i.e.* the dimeric $A\cdots A'$ and $B\cdots B'$) resulting in an average deviation of the exocyclic S atoms from the molecular plane of 0·3 Å. As a result only one short intrastack S···S intermolecular contact distance is observed (Table 2 and Fig. 1). A similar dimerization of the molecular stack, and distortion of the molecules away from the dimeric counterparts, has been observed in dibenzotetrathiafulvalene–tetrafluorotetracyano-*p*-quinodimethane (DBTTF-TCNQ4) (Emge, Bryden, Wiygul, Cowan, Kistenmacher & Bloch, 1982). The intermolecular S···S contacts in the planes of the BEDT-TTF molecules, and the numbering scheme used, are pictured in Fig. 2. The interstack (in-plane) S···S

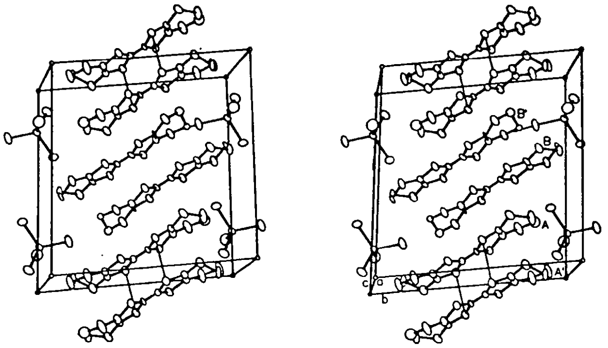

Fig. 1. The unit cell of $(\text{BEDT-TTF})_2\mathrm{InBr_4}$ viewed down the *a* axis. The zigzag stacks of BEDT-TTF molecules are dimerized with the interplanar spacings $A\cdots A' = 3·43$, $A\cdots B = 3·87$ and $B\cdots B' = 3·47$ Å. The thermal ellipsoids are drawn at the 50% probability level. The symmetry operations which produce molecules A' and B' are $(1-x, 1-y, 1-z)$ and $(1-x, 1-y, 2-z)$, respectively.

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39358 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contact distances for molecule A and molecule B are quite different (see Fig. 2 and Table 2) and may reflect the differing anion interactions which are observed for the BEDT-TTF molecules. For molecule A only weak intra- and interstack S···S ($d > 3{\cdot}55$ Å) contacts are observed and no S···Br interactions occur while molecule B has no intrastack S···S contact interactions but is involved in short in-plane S···S and S···Br contacts. For comparison, the structures of (BEDT-TTF)$_2X$ salts containing octahedral anions, α- and β-(BEDT-TTF)$_2$PF$_6$ (Kobayashi, Kato *et al.*, 1983) and (BEDT-TTF)$_2$AsF$_6$ (Leung *et al.*, 1984), possess interstack side-by-side contact distances nearly identical to those observed for molecule B, but lack out-of-plane S···S contacts, and are either semiconducting or metallic only near ambient temperatures. The structures of the metallic (BEDT-TTF)$_2X$ salts, $X = \mathrm{ReO_4^-}$ and $X = \mathrm{ClO_4^-}$, however, contain both (short) side-by-side and out-of-plane S···S contacts similar to those observed for molecule A. Our conductivity results, which are similar to those on the octahedral-anion salts, suggest that the sulfur orbitals are not directed so as to take advantage of the short side-by-side molecular contacts. The $\mathrm{InBr_4^-}$ anion is tetrahedral, with an average Br—In—Br angle of 109·5° and average In—Br distance of 2·49 Å, in good agreement with those previously reported (Khan & Tuck, 1982). The short Br···Br contact distances result in sheets of anions in the ac plane interleaving the sheets of organic BEDT-TTF molecules.

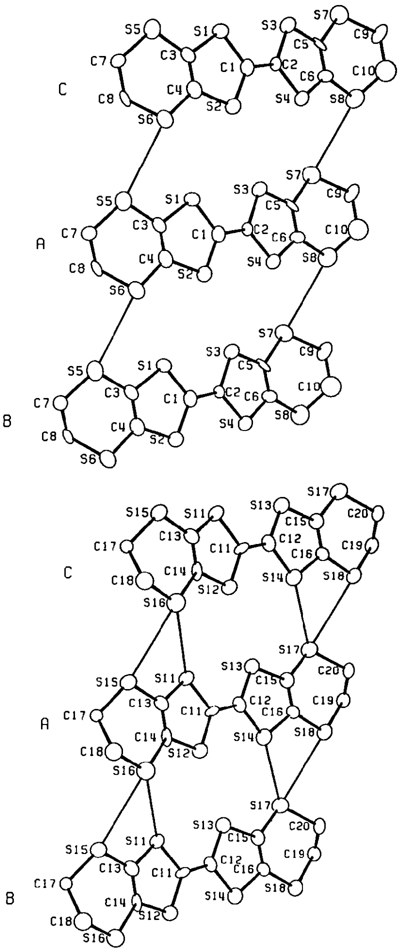

Fig. 2. *ORTEP* drawing (Johnson, 1965) of the molecular packing in the ab plane (50% probability level) for the BEDT-TTF molecule A (top) and molecule B (bottom). The intermolecular S···S contacts less than the sum of the van der Waals radii (3·60 Å) are indicated. The symmetry operations which produce each of the molecules are A (x, y, z); B ($x, y, z-1$); and C ($x, y, z+1$).

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