Structure of Anthra[9,1-*cd*:10,5-*c'd'*]bis[1,2]diselenole (TSA) and of its Partially Oxidized, Metallic Polyiodide TSA I$_{1.2}$

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Abstract

'Tetraselenaanthracene' (TSA), $C_{14}H_6Se_4$, $M_r = 490.04$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.318 (3)$, $b = 4.111 (1)$, $c = 16.035 (4)$ Å, $\beta = 90.43 (2)°$, $V = 614.3$ Å^3, $Z = 2$, $d_c = 2.65$ Mg m^{-3}. $R = 0.030$ for 1039 observed reflections. The planar molecules form stacks along **b** with an interplanar separation of 3.59 Å. The normals to the molecular planes are inclined at 29° to the stacking axis. Short intermolecular Se–Se contacts exist between adjacent stacks, the shortest one being 3.467 (1) Å. 'Tetraselenaanthracenium iodide' (TSA I$_{1.2}$), $C_{14}H_6I_{1.20}Se_4$, $M_r = 642.32$, is monoclinic, $P2_1/c$, with $a = 18.644 (12)$, $b = 3.856 (2)$, $c = 19.746 (12)$ Å, $\beta = 93.36 (5)°$, $V = 1417.1$ Å^3, $d_c = 3.01$ Mg m^{-3}. $R = 0.118$ for 1080 observed reflections. The structure contains two crystallographically inequivalent stacks of partially oxidized 'tetraselenaanthracenium' cations (interplanar distances 3.44 and 3.56 Å, respectively) and linear triiodide chains (proved by resonance Raman spectra) ordered in one dimension only. TSA I$_{1.2}$ behaves as a metal down to 220 K with $\sigma(300$ K) between 200 and 400 Ω^{-1} cm^{-1} measured parallel to the stacking axis.

Introduction

Planar organic heterocyclic molecules – especially those containing S, Se and N as ring atoms – have met with considerable recent interest in the field of materials science. Some of these compounds can be oxidized to highly conducting materials, so-called organic metals. [For recent reviews see Keller (1977), Miller & Epstein (1978), Hatfield (1979), Alcacer (1980), Carneiro (1981).] Even superconductors have been discovered recently (Bechgaard, Carneiro, Olsen, Rasmussen & Jacobsen, 1981; Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981). From a structural point of view two aspects are worth mentioning:

(i) Three-dimensional correlations between atoms of different chains should enhance the electrical con-

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ductivity and should help to suppress the metal–insulator transitions common in these solids at lower temperatures.

(ii) Iodine oxidation very often leads to segregated stacked compounds containing additional one-dimensionally ordered polyiodide chains. These might support the conduction process and are of structural interest in themselves (Endres, Pouget & Comès, 1982).

To investigate 'three-dimensionally correlated' solids we prepared anthra[9,1-cd:10,5-c'd']bis[1,2]diselenole ('tetraselenaanthracene' TSA) and anthra[9,1-cd:10,5-c'd']bis[1,2]dithiole ('tetrathiaanthracene' TTA). Hoping to find new polyiodide chains we oxidized these species and discovered a partially oxidized iodide, TSA I$_{1.2}$, which turned out to be metallic down to 220 K. The details of the synthetic procedure were described earlier (Endres, Keller, Queckbörner, Veigel & Schweitzer, 1982). Here we report the results of resonance Raman and of single-crystal X-ray investigations.

Experimental

Preparation

TSA and TSA I$_{1.2}$ were prepared as described earlier (Endres, Keller, Queckbörner, Veigel & Schweitzer, 1982). The crystals of TSA and TSA I$_{1.2}$ used for the investigations reported here were grown by a diffusion method. The solid obtained in this manner is a mixture of TSA and TSA I$_{1.2}$ crystals. The former occur as black platelets (or prisms) with a greenish lustre, the latter are usually needles with a remarkable golden 'metallic' reflection. On this basis the crystals of the different compounds can be separated by inspection under a microscope.

Structure solutions

(1) TSA. Lattice parameters were derived from the setting angles of 25 reflections centred on a diffractometer (Syntex R3, monochromatic Mo Kα radiation). Data collection (θ–2θ scans background–peak–background, $2\theta \leq 60°$) yielded 1039 independent observed reflections with $I > 1·5\,\sigma(I)$. An empirical absorption correction (ψ scans) was applied. An Se position was derived from a Patterson synthesis, and subsequent Fourier syntheses revealed the other non-H atoms. Refinement with anisotropic temperature factors converged with a weighted (unweighted) R factor of 0·035 (0·043). A difference Fourier map revealed the positions of the three H atoms of the asymmetric unit. Refining them with isotropic temperature factors and the non-H atoms with anisotropic ones by 'cascade matrix' least squares resulted in a weighted (unweighted) R of 0·030 (0·040). The weighting scheme was $w = 1/\sigma^2(F)$.

(2) TSA I$_{1.2}$. Rotation photographs around the long axis of the column-like crystals (crystallographic b axis) showed, in addition to the usual rows of Bragg peaks, diffuse continuous lines with a spacing incommensurate with the Bragg lattice. These diffuse lines indicate that the iodine is arranged in chains of polyiodide anions which are ordered in one dimension only, and with a repeat distance incommensurate with the unit-cell length of the cation lattice. As the projection gives an ordered two-dimensional array, the polyiodide ions contribute to the intensities of the h0l reflections, but not to those with $k \neq 0$. Hence the intensities of all the Bragg reflections contain information about the three-dimensional array of the organic cations, and of the *projection* of the polyiodide chains. Lattice parameters of the Bragg lattice were derived from the setting angles of 23 reflections centred on a diffractometer (Siemens AED, Zr-filtered Mo Kα radiation). Data collection (ignoring the diffuse sheets) with the 'five-value method', $2\theta \leq 50°$, yielded 1080 observed independent intensities with $I > 3·0\sigma(I)$, comprising 280 h0l reflections. An absorption correction was not applied (crystal size approximately $0·045 \times 0·05 \times 0·15$ mm, $\mu = 129$ cm^{-1}).

Attempts to solve the structure started with the *ac* projection. The iodine sites were derived from a Patterson map, and most of the other non-H atoms could be found in Fourier syntheses. To reveal the three-dimensional structure of the organic cations, only reflections with $k \neq 0$ were taken in the next step, as these do not contain iodine contributions. The y coordinate of the Se atoms in addition to the x and z coordinates detected in the projection were found by 'trial-and-error': by shifting the atoms one after another along the b axis and calculating R factors, four Se positions were found. (In an alternative approach, direct methods were applied to the reflections with $k \neq 0$. Four Se positions were finally revealed as well, equivalent to those detected above.) Subsequent Fourier syntheses clearly resolved the positions of all the non-H atoms of one of the two independent molecules in the unit cell. The second molecule turned out to be disordered: two molecules statistically occupy the same site such that the position of the central six-membered ring is common to both molecules. The
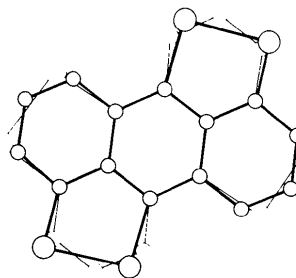

Fig. 1. TSA I$_{1.2}$: the two statistically disordered molecules II of 'tetraselenaanthracenium iodide'.

five-membered heterocyclic rings of one molecule correspond to the lateral six-membered rings of the other. This type of disorder is illustrated in Fig. 1. From the heights of the peaks in a Fourier map the occupancy ratio was estimated to be $0.75:0.25$.

In the next step we determined the cation to anion ratio. (Analytical data were not available, as the sample was a mixture of the unoxidized tetraselenaanthracene and of the oxidized product.) For this, we returned to the ac projection and varied the site occupation factor (s.o.f.) of iodine, until the best value of R was reached. This was the case for s.o.f. approximately 1.3. This number is in reasonable agreement with the value obtained from the ratio of the repeat distance of the cation stack [3.856 (2) Å] and the mean I–I spacing along the polyiodide chains [3.22 (10) Å]. The latter value is obtained from the spacing of the most prominent pair of diffuse lines on a rotation photograph. The cation:iodine ratio can be calculated by dividing the two distances, $3.856:3.22$, which yields $1:1.20$.

Now refinement with all reflections was started. To allow for iodine contributing to reflections with $k = 0$ only, an artificial 'iodine chain' was constructed with five equally spaced iodine sites along $\mathbf{b}$, with fixed values for y and constrained values for the site occupation factors of $1.3:5 = 0.26$. This artificial chain has the consequence that the iodine contributions to all reflections with $k \neq 0$ cancel. In the refinement cycles either the site occupation factors or the temperature factors were allowed to vary. A large scatter in C—C distances of the ring system, especially of the disordered species, made it advisable to constrain the lateral six-membered rings to regular hexagons. The positions of Se and of the C atoms of the central ring which bind to Se were not constrained. For the statistically occupied molecular sites one molecule was held fixed when the other was refined. Finally, H positions were calculated (in the disordered species for the 'major component' only) and refined with fixed isotropic temperature factors $U = 0.08$ Å^2 and coupled with the constrained C-atom positions. Se atoms were refined with anisotropic temperature factors, the other atoms with isotropic ones. Refinement of the site occupation factors of the disordered cations (constrained to be identical within each molecule, and to sum to one for both molecules) resulted in a ratio 0.775 (7)$:0.225$ (7). The site occupation factor of the I atoms of the artificial chain refined to 0.241 (3) for each of the five 'positions', giving a tetraselenaanthracene to iodine ratio of $1:1.205$ (3). This is in excellent agreement with the value derived from the spacing of the diffuse lines on the film. R was 0.118, taking unit weights for all reflections.

Calculations were carried out on a NOVA 3 computer, connected with a Tektronix plotter. The SHELXTL program system (Sheldrick, 1979) was

applied, which uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account.

Resonance Raman spectra

The RR spectra of a KBr pellet (TSA I$_{1.2}$:KBr = 1:10) were recorded at 1.3 K. The sample was glued with silicon grease to a flat brass holder and placed directly in the liquid-helium bath of a cryostat (Leybold) in which the temperature could be lowered to 1.3 K by pumping.

As an excitation source an argon ion laser (Coherent CR 6) tuned to the 5145 Å line in combination with a monochromator (Anaspec 300 S) and an interference filter (Schott 514 nm) was used. The incident power of about 70 mW was focused with a lens on the sample. The emission was monitored at right angles to the excitation path with a 0.85 m double monochromator (Spex 1402) equipped with holographic gratings (2400 gratings per mm) and spatial filtering option. A cooled (223 K) photomultiplier (RCA 31034A02) and a photon-counting system (PAR 1121, 1109) were used as detector system.

Description of the structures

(1) TSA

Atomic coordinates are listed in Table 1,* the numbering scheme, bond distances and angles in the centrosymmetric molecule are shown in Fig. 2. The

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* Lists of anisotropic temperature factors and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36996 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *for 'tetraselenaanthracene' and isotropic temperature factors* ($\times 10^3$) *equivalent to the refined anisotropic values (except for* H *atoms which were refined isotropically)*

U is defined as $U = \frac{1}{3}$trace $\tilde{U}$, $\tilde{U}$ signifying the diagonalized U matrix.

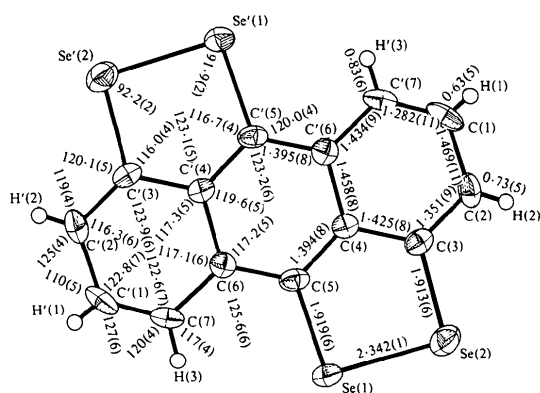|	x	y	z	U (Å^2)
Se(1)	2895.3 (7)	2476.9 (20)	1523.2 (4)	30.1 (2)
Se(2)	4876.5 (8)	432.2 (17)	2261.9 (4)	32.7 (2)
C(1)	8497 (8)	1999 (20)	774 (6)	34 (3)
C(2)	7584 (7)	976 (17)	1470 (5)	27 (2)
C(3)	6172 (7)	1673 (15)	1398 (4)	25 (2)
C(4)	5553 (6)	3339 (14)	705 (4)	21 (2)
C(5)	4089 (7)	4000 (15)	635 (4)	24 (2)
C(6)	3483 (6)	5655 (15)	−41 (4)	23 (2)
C(7)	1995 (7)	6479 (17)	−135 (5)	29 (2)
H(1)	9129 (56)	1479 (138)	826 (37)	6 (20)
H(2)	7830 (53)	43 (125)	1831 (30)	0 (15)
H(3)	1467 (60)	6188 (131)	276 (36)	19 (18)

Fig. 2. TSA: the 'tetraselenaanthracene' molecule with numbering scheme, bond distances (Å) and angles (°). H atoms are drawn with an arbitrary temperature factor, while thermal ellipsoids are at 50% probability.
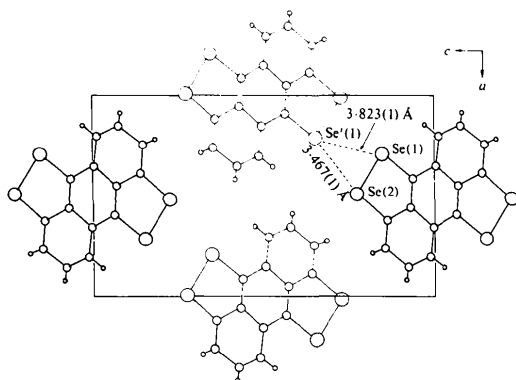

Fig. 3. TSA: projection of the structures onto the *ac* plane. The molecules drawn with thin lines are around *y* = 0; those drawn with thick lines around *y* = ½.

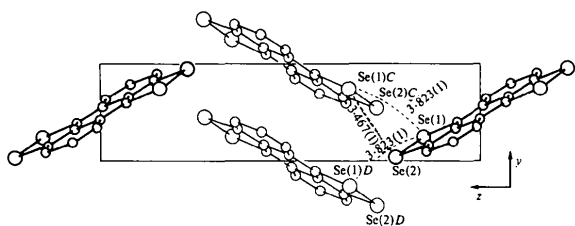

Fig. 4. TSA: projection of the structure onto the *bc* plane. Thin lines are drawn for molecules at *x* = 0, thick lines for those at *x* = ½. H atoms are omitted.

molecule is essentially planar. The mean [maximum] deviation of a non-H atom from the least-squares plane through these atoms amounts to 0·018 (17) Å [0·05 (1) Å]. The centre of gravity of the molecule coincides with the crystallographic inversion centre at ½,½,0. The symmetry operations of space group $P2_1/n$ generate another molecule around 0,0,½. Their mutual arrangement is shown in Fig. 3, a perpendicular
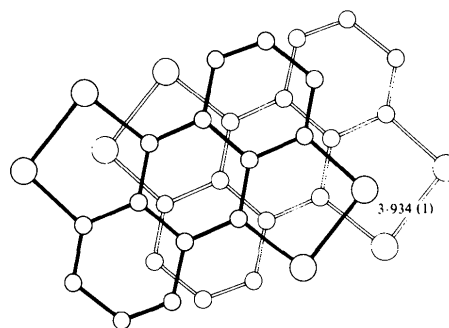

Fig. 5. TSA: perpendicular projection of two adjacent molecules of a stack. H atoms are omitted.

projection onto the *ac* plane. The molecules are arranged in stacks along **b** with an interplanar distance of 3·59 (2) Å and a tilt angle to the *b* axis of 29·0 (5)°. The molecules at ½,½,0 and at 0,0,½ are tilted in opposite directions, so that the typical 'herring-bone' pattern results. An impression of this is given in Fig. 4, a projection of the structure onto the *bc* plane. The mode of overlap of two molecules of a stack is shown in Fig. 5.

The shortest Se–Se contact within a stack is 3·934 (1) Å. Shorter intermolecular Se–Se contacts occur between the stacks, the shortest being 3·467 (1) Å. Se–Se contacts shorter than 4·1 Å are indicated in Figs. 3–5.

(2) TSA I$_{1·2}$

The structure consists of two crystallographically independent stacks of organic molecules, and polyiodide chains ordered in one direction only. The mean I–I spacing can be derived from the separation of the most intense pair of diffuse lines on a rotation photograph; it amounts to 3·22 (10) Å. The inner pair of diffuse lines corresponds to a repeat distance of the iodine chains of 19·3 (7) Å, six times the mean I–I separation. This could mean either that the chains contain hexaiodide ions – a very improbable assumption – or that the repeat distance comprises two triiodide anions. More detailed information about the polyiodide chain cannot be derived from routine rotating-crystal photographs. Only a detailed investigation of the diffuse scattering, as has been carried out, for example, for the polyiodides of *N,N'*-disubstituted phenazines (Endres, Pouget & Comès, 1982) could provide more information.

To resolve this problem, we undertook a resonance Raman (RR) investigation. This method has proved to be very useful for characterizing the different iodine species in solids containing polyiodide ions (Phillips, Scaringe. Hoffman & Ibers, 1980; Teitelbaum, Ruby & Marks, 1979, 1980). The RR spectrum obtained from a polycrystalline sample of TSA I$_{1·2}$ (Fig. 6) shows the typical I$_3^-$ pattern (sharp line at 113 cm^{-1} with overtone
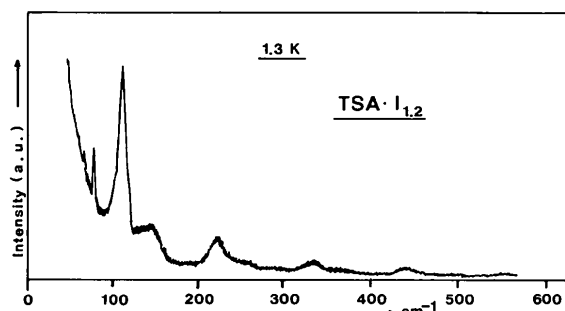
Fig. 6. Resonance Raman spectrum of polycrystalline TSA $I_{1.2}$ at 1·3 K.

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\times 10^3$) *for 'tetraselenaanthracenium iodide'*

For Se, isotropic temperature factors equivalent to the refined anisotropic values are given: U is defined as $U = \frac{1}{3}$trace $\tilde{U}$, $\tilde{U}$ signifying the diagonalized U matrix. For C atoms refined isotropic temperature factors are indicated. Site occupation factors (s.o.f.) of the statistically disordered molecule II are also included (if left blank, s.o.f. = 1).

	s.o.f.	x	y	z	U (Å^2)
Se(1)	0·775 (7)	1681 (4)	2180 (20)	5421 (3)	36 (2)
Se(2)	0·775 (7)	1846 (4)	3968 (21)	4304 (3)	41 (3)
Se(5)	0·225 (7)	−506 (12)	2388 (83)	2438 (15)	44 (9)
Se(6)	0·225 (7)	674 (16)	4092 (76)	3270 (19)	47 (10)
C(1)		872 (13)	3242 (94)	4066 (14)	38 (11)
C(2)		712 (20)	791 (117)	5195 (14)	37 (12)
C(3)		442 (13)	1540 (94)	4516 (14)	42 (12)
C(4)		−276 (13)	829 (94)	4328 (14)	19 (9)
C(5)	0·775 (7)	−564 (13)	1821 (94)	3689 (14)	34 (26)
C(6)	0·775 (7)	−135 (13)	3522 (94)	3239 (14)	19 (12)
C(7)	0·775 (7)	583 (13)	4233 (94)	3427 (14)	85 (67)
C(8)	0·225 (7)	1416 (20)	1673 (117)	5403 (14)	18 (16)
C(9)	0·225 (7)	1855 (20)	3317 (117)	4953 (14)	23 (41)
C(10)	0·225 (7)	1589 (20)	4078 (117)	4295 (14)	11 (61)
H(5)	0·775 (7)	−571 (13)	−342 (94)	4638 (14)	
H(6)	0·775 (7)	−1058 (13)	1332 (94)	3560 (14)	
H(7)	0·775 (7)	−333 (13)	4205 (94)	2799 (14)	
Se(3)		3688 (2)	1940 (15)	3873 (2)	38 (2)
Se(4)		4511 (3)	3771 (16)	3102 (2)	39 (2)
C(11)		6016 (12)	3415 (85)	3556 (10)	25 (9)
C(12)		6582 (12)	2716 (85)	4030 (10)	51 (14)
C(13)		6441 (12)	1420 (85)	4668 (10)	27 (10)
C(14)		5735 (12)	822 (85)	4833 (10)	43 (13)
C(15)		5168 (12)	1521 (85)	4360 (10)	26 (10)
C(16)		5309 (12)	2817 (85)	3721 (10)	22 (9)
C(17)		4399 (23)	754 (138)	4532 (21)	36 (11)
H(11)		6113 (12)	4307 (85)	3117 (10)	
H(12)		7068 (12)	3127 (85)	3917 (10)	
H(13)		6831 (12)	939 (85)	4994 (10)	
I		2347 (2)	y	2500 (2)	63 (2)

progressions at 224 cm^{-1}, 334 cm^{-1} and 442 $\pm$ 5 cm^{-1}). The additional weak I–I line is due to impurities. The comparatively high wavenumber for the first line (113 cm^{-1} compared to 107 cm^{-1} in many other triiodide solids) indicates rather small interactions between I_3^- ions and rather large separations. The presence of

triiodide ions leads to a formulation of the compound as $TSA(I_3)_{0.4}$, with an average positive charge of 0·4 per organic molecule. Due to the existence of two inequivalent stacks of TSA, an unequal charge distribution or even the presence of a neutral stack cannot be ruled out.

Atomic coordinates are listed in Table 2.* For iodine, no value for the y coordinate can be given, as the Bragg reflections contain no information about it. The asymmetric unit consists of iodine and two halves of the tetraselenaanthracene molecules, with their centres of gravity at $\frac{1}{2},0,\frac{1}{2}$ (molecule I) and at $0,0,\frac{1}{2}$, respectively (molecule II). The unconstrained bond distances and angles are shown in Fig. 7. In the following discussion only the major component of molecule II is considered. Each of the two crystallographically different tetraselenaanthracene species forms stacks along **b**. Interplanar distances (defining molecular planes as the planes through the condensed carbon rings) are 3·56 (3) Å in species I and 3·44 (3) Å in species II, respectively. Tilt angles to the stacking axis are 26·8 (5)° in II and 22·5 (5)° in I. The dihedral
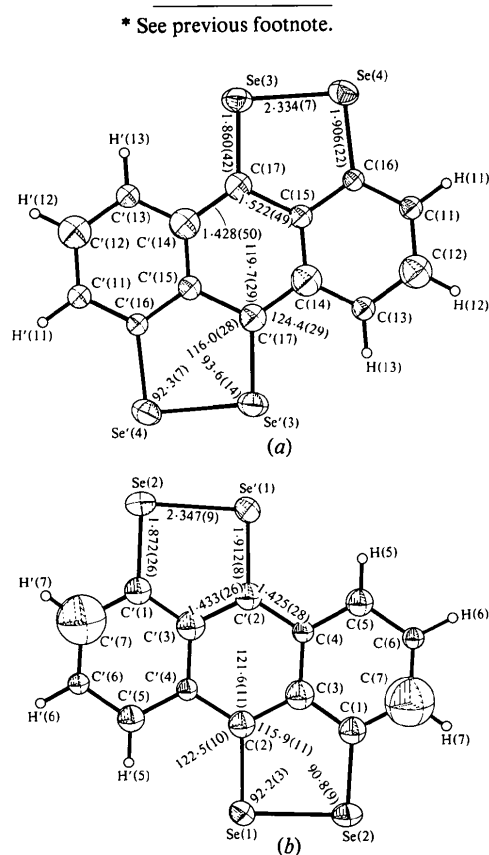
* See previous footnote.

Fig. 7. (a) TSA $I_{1.2}$: 'tetraselenaanthracene' molecule I around $\frac{1}{2},0,\frac{1}{2}$, in the iodination product. Only the unconstrained bond distances and angles are given. Thermal ellipsoids are at 50% probability. (b) TSA $I_{1.2}$: analoguous to (a). The major component of the disordered molecules II (cf. Fig. 1) is shown.
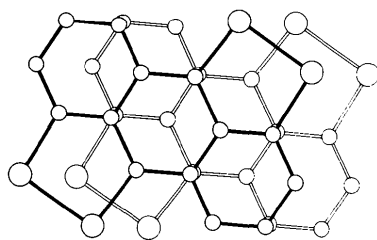
Fig. 8. TSA $I_{1.2}$: perpendicular projection of two molecules I of a stack.
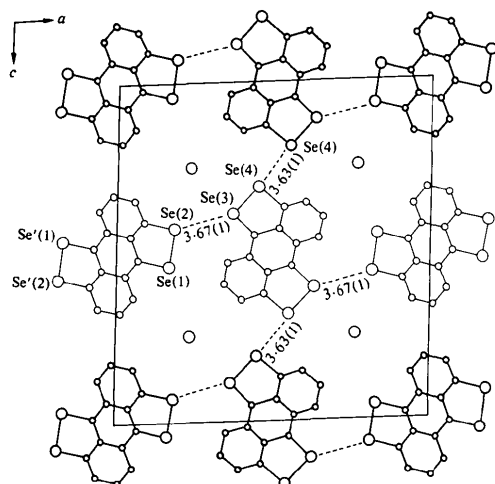

Fig. 9. TSA $I_{1.2}$: projection of the structure onto the ac plane.

Fig. 10. Temperature dependence of the d.c. conductivity of TSA $I_{1.2}$.

angle between molecules I and II is 11·7 (5)°. The two overlap patterns in the two stacks are practically identical (Fig. 8). One sees that the pattern differs in some respects from the overlap in the unoxidized species, Fig. 5. The mutual arrangement of the stacks is evident from Fig. 9, a projection onto the ac plane. There are no intermolecular Se–Se contacts as short as in the unoxidized species; notable contacts are between Se(2) and Se(3), 3·669 (9) Å, and Se(4) and Se'(4), 3·633 (9) Å.

Conclusions

As expected on the basis of the *molecular* structure short intermolecular Se–Se contacts occur in solids made up of planar heterocycles with 'exocyclic' heteroatoms (Endres, Keller, Queckbörner, Veigel & Schweitzer, 1982). The intermolecular Se–Se distances between the stacks increase upon oxidation of these materials, but the interplanar distances within the stacks decrease. The broad maximum of the d.c. conductivity (instead of a sharp phase transition) in TSA $I_{1.2}$ (Fig. 10) suggests that more pronounced intermolecular contacts could actually wipe out the often observed metal–insulator transition at lower
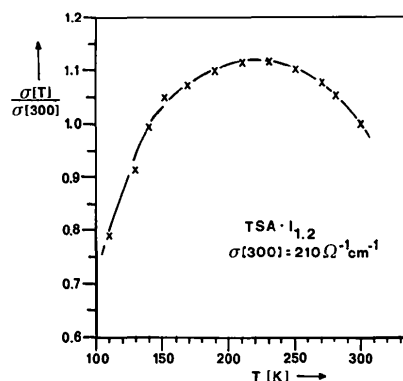
temperatures. These investigations indicate a route to the synthesis of organic materials which behave as metals even at very low temperatures.

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