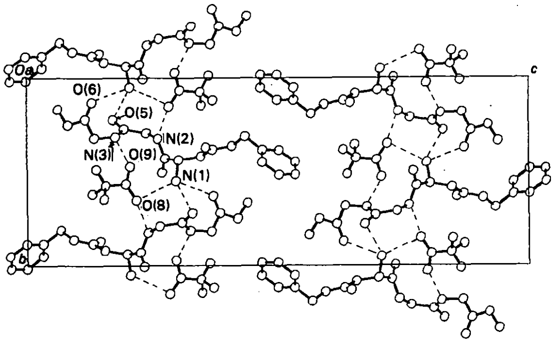


Fig. 2. The crystal structure of L-Asp(β-Bzl)-Gly-Gly-OMe.Tfa as viewed perpendicular to the *yz* plane. Contacts indicative of hydrogen bonding are shown by dashed lines.

2·80 (1) and 2·85 (1) Å respectively [symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, y, z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$]. The hydrogen-bonding network gives rise to layers normal to the *c* axis (Fig. 2). In each layer the hydrophilic cores of adjacent molecules are linked together, intercalating the trifluoroacetate anion, whereas the terminal benzyl and methyl hydrophobic groups protrude alternately from the surface of the layer. The layers are held together in the crystals only by van der Waals forces between hydrophobic groups.

References

ASWAD, D. W. (1984). *J. Biol. Chem.* **259**, 10714–10721.

BENEDETTI, E. (1977). In *Peptides. Proc. 5th American Peptide Symposium*, edited by M. GOODMAN & J. MEIENHOFER, pp. 257–273. New York: John Wiley.

BODANSKY, M. & KWEI, J. Z. (1978). *Int. J. Pept. Protein Res.* **12**, 69–74.

CAPASSO, S., MATTIA, C. A., MAZZARELLA, L. & ZAGARI, A. (1984*a*). *Int. J. Pept. Protein Res.* **23**, 248–255.

CAPASSO, S., MATTIA, C. A., MAZZARELLA, L. & ZAGARI, A. (1984*b*). *Int. J. Pept. Protein Res.* **24**, 85–95.

CAPASSO, S., MAZZARELLA, L., SICA, F. & ZAGARI, A. (1984). *Int. J. Pept. Protein Res.* **24**, 588–596.

EGGLESTON, D. S., VALENTE, E. J. & HODGSON, D. J. (1981). *Acta Cryst.* B**37**, 1428–1430.

Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1987). C**43**, 1108–1112

Structures of New Salts: *S*-Methylthiouronium–TCNQ (I) and *Se*-Methylselenouronium–TCNQ (II)*

BY G. G. ABASHEV, R. M. VLASOVA, N. F. KARTENKO, A. M. KUZMIN, I. V. ROZHDESTVENSKAYA, V. N. SEMKIN, O. A. USOV AND V. S. RUSSKIKH

A. F. Ioffe Physico-Technical Institute, Academy of Sciences of the USSR, Polytechnic str., 26, *Leningrad* 194021, *USSR*

(*Received* 21 *June* 1985; *accepted* 27 *November* 1986)

Abstract. Isostructural salts MT–TCNQ (I), $C_{14}H_{11}N_6S$, and MS–TCNQ (II), $C_{14}H_{11}N_6Se$, are monoclinic, $P2_1/c$, $Z = 4$. (I): $M_r = 295·35$, $a = 11·005\ (2)$, $b = 12·305\ (3)$, $c = 11·112\ (3)$ Å, $\beta = 100·98\ (2)°$, $V = 1477·2$ Å^3, $D_x = 1·33$ g cm^{-3}, μ(Mo $K\alpha$) = 1·7 cm^{-1}, $F(000) = 612$, $R = 0·042$ for 917 observed reflections. (II): $M_r = 342·24$, $a = 10·984\ (2)$, $b = 12·269\ (2)$, $c = 11·191\ (2)$ Å, $\beta = 100·90\ (1)°$, $V = 1480·9$ Å^3, $D_x = 1·54$ g cm^{-3}, μ(Mo $K\alpha$) = 18·7 cm^{-1}, $F(000) = 684$, $R = 0·049$ for 1349 observed reflections. Room temperature, λ(Mo $K\alpha$) = 0·71069 Å. Structures contain isolated pairs of planar TCNQ radical anions with mean interplanar distance 3·40 Å for both salts. Anions and cations lie in different layers parallel to the (100) plane. Hydrogen bonds are found between NH_2 groups of cations and nitrogen atoms of TCNQ anions.

Introduction. A considerable number of TCNQ salt structures have been reported elsewhere (Shibaeva, 1981). New salts of TCNQ with cations based on thio- and selenouronium [$NH_2C(=X)NH_2$, where X is S or Se] were prepared in the present work. Their synthesis, electrical properties at room temperature and structures are described below. The importance of these new salts lies in their practical use as materials for gas analysers.

---

* TCNQ = 2,2′-(2,5-Cyclohexadiene-1,4-diylidene)bispropanedinitrile.

0108-2701/87/061108-05$01.50

Experimental. Prismatic golden crystals of MT– and MS–TCNQ were obtained by the reaction of thiouronium and selenouronium iodides with neutral TCNQ solution in 1:1 molar ratio (Abashev, Batyaev, Zapolnov, Martsenyuk, Prosvirin & Russkikh, 1981). The composition was confirmed by spectral data. D_m was not determined. Electroconductivity was measured on pressed pellets at room temperature: 10^{-6} (I) and $10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (II).

Crystals 0·1 × 0·1 × 0·2 mm, Syntex $P2_1$ diffractometer, graphite- monochromatized Mo $K\alpha$ radiation, ω-scan technique, $2\theta_{\max} = 45°$, total intensity measurements up to $\sin\theta/\lambda = 0{\cdot}538$ Å^{-1}. Unit-cell dimensions were obtained from oscillation photographs and refined using setting angles of 22 reflections with $20 < 2\theta < 30°$. The space group $P2_1/c$ was unambiguously determined from systematic absences. Range of indices: (I) $0 \le h \le 6$, $0 \le k \le 13$, $-11 \le l \le 11$; (II) $0 \le h \le 11$, $0 \le k \le 13$, $-12 \le l \le 11$. For MT–TCNQ: 1209 reflections measured, 1130 unique, 917 observed with $I > 2\sigma(I)$. For MS–TCNQ: 1629 reflections measured, 1590 unique, 1349 observed with $I > 2\sigma(I)$. Intensity control showed no drift, Lorentz–polarization correction, no absorption correction.

The trial S and Se atomic coordinates were deduced from sharpened Patterson maps, C and N atoms were located from successive Fourier syntheses. Full-matrix least-squares (FMLS) refinement with anisotropic thermal parameters for only non-H atoms gave a residual $R = 0{\cdot}066$ (I) and $R = 0{\cdot}064$ (II). $\sum w(F_o - F_c)^2$ was minimized, $w = 1/\sigma^2(F_o)$. H atoms were located from difference Fourier syntheses. The final FMLS anisotropic refinements for non-H atoms and isotropic for H atoms gave $R = 0{\cdot}042$, $wR = 0{\cdot}036$, $S = 1{\cdot}94$, $(\Delta/\sigma)_{\max} = 0{\cdot}3$ (I) and $R = 0{\cdot}049$, $wR = 0{\cdot}046$, $S = 2{\cdot}55$, $(\Delta/\sigma)_{\max} = 0{\cdot}1$ (II). 234 parameters were refined. A final difference map showed no peaks or depressions $> 0{\cdot}3$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were performed with *XTL*-type program package (Usov, Kuzmin, Rozhdestvenskaya & Fundamenskii, 1980).

Discussion. Atomic positional and thermal parameters for both salts are listed in Table 1. Specific structure projections onto the (100) and (001) planes, interatomic distances and angles for the TCNQ molecule and MT and MS cations are shown in Figs. 1–4.*

The quinonoid ring of TCNQ molecules is planar, the maximal deviation from the least-squares plane (Table 2) is 0·011 (3) Å for C(20)–I. Cyanomethylene groups are also planar [the maximal deviation is 0·012 (6) Å for C(24)–II] and twisted from the quinonoid ring plane by the mean angle 5° in the same direction for both salts. The MT and MS moieties (without H atoms) are

Table 1. *Final fractional atomic positional and isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = (B_{11}B_{22}B_{33})^{1/3}.$$

	x	y	z	$B_{\rm eq}/B_{\rm iso}$(Å^2)
(I)				
MT$^+$				
S(1)	0·4466 (2)	0·4185 (1)	0·3131 (1)	4·95 (8)
N(2)	0·4093 (4)	0·1923 (3)	0·0120 (3)	3·9 (2)
N(3)	0·2862 (4)	0·4546 (3)	0·4525 (3)	4·5 (3)
C(4)	0·3778 (4)	0·3894 (4)	0·4371 (4)	3·4 (3)
C(5)	0·5705 (5)	0·3224 (5)	0·3281 (5)	4·8 (4)
H(6)	0·619 (4)	0·339 (3)	0·272 (4)	6·5 (12)
H(7)	0·626 (3)	0·325 (3)	0·412 (3)	3·5 (10)
H(8)	0·531 (5)	0·250 (4)	0·304 (4)	11·3 (17)
H(9)	0·382 (4)	0·194 (4)	0·086 (4)	8·0 (13)
H(10)	0·458 (3)	0·267 (3)	0·496 (3)	3·3 (9)
H(11)	0·246 (3)	0·056 (3)	0·016 (3)	5·0 (11)
H(12)	0·733 (4)	0·015 (4)	0·091 (4)	8·2 (13)
TCNQ$^-$				
N(13)	0·8797 (4)	0·4540 (4)	0·3940 (4)	5·0 (3)
N(14)	0·7735 (4)	0·1721 (3)	0·1593 (4)	4·8 (3)
N(15)	0·3045 (4)	0·1519 (3)	0·2350 (4)	5·1 (3)
N(16)	0·5841 (4)	0·3803 (3)	0·0196 (4)	4·5 (3)
C(17)	0·1800 (4)	0·0727 (3)	0·4932 (4)	2·4 (3)
C(18)	0·1578 (4)	0·4923 (4)	0·0924 (4)	3·0 (3)
C(19)	0·0730 (4)	0·4649 (4)	0·1605 (4)	2·9 (3)
C(20)	0·0018 (4)	0·3692 (4)	0·1357 (4)	2·8 (3)
C(21)	0·0244 (4)	0·3014 (4)	0·0384 (4)	3·1 (3)
C(22)	0·1090 (4)	0·1707 (4)	0·4690 (4)	3·0 (3)
C(23)	0·9111 (4)	0·3414 (3)	0·2062 (4)	2·9 (3)
C(24)	0·8929 (4)	0·4040 (4)	0·3098 (4)	2·5 (3)
C(25)	0·8353 (4)	0·2477 (4)	0·1812 (4)	3·5 (3)
C(26)	0·2697 (4)	0·0430 (3)	0·4229 (4)	2·9 (3)
C(27)	0·2902 (4)	0·1034 (4)	0·3187 (4)	3·1 (3)
C(28)	0·6496 (4)	0·4535 (4)	0·0449 (4)	3·3 (3)
H(29)	0·119 (3)	0·218 (3)	0·394 (3)	2·1 (8)
H(30)	0·981 (3)	0·269 (3)	0·522 (3)	3·7 (9)
H(31)	0·793 (3)	0·051 (2)	0·388 (3)	2·3 (8)
H(32)	0·937 (3)	0·011 (3)	0·274 (3)	1·7 (8)
(II)				
MS$^+$				
Se(1)	0·4451 (1)	0·4210 (1)	0·3041 (1)	4·69 (4)
N(2)	0·4055 (5)	0·1938 (5)	0·0104 (5)	3·6 (3)
N(3)	0·2808 (5)	0·4539 (5)	0·4549 (5)	4·2 (4)
C(4)	0·3696 (6)	0·3853 (6)	0·4391 (6)	3·3 (4)
C(5)	0·5778 (7)	0·3196 (7)	0·3290 (7)	5·0 (4)
H(6)	0·635 (6)	0·344 (5)	0·278 (5)	4·9 (17)
H(7)	0·643 (5)	0·319 (5)	0·420 (5)	4·5 (16)
H(8)	0·554 (5)	0·255 (5)	0·327 (5)	4·1 (15)
H(9)	0·384 (5)	0·215 (4)	0·064 (4)	2·0 (13)
H(10)	0·467 (6)	0·247 (6)	0·488 (6)	7·6 (21)
H(11)	0·225 (5)	0·058 (5)	0·012 (5)	5·1 (17)
H(12)	0·752 (6)	−0·009 (6)	0·102 (6)	5·9 (18)
TCNQ$^-$				
N(13)	0·8848 (6)	0·4535 (5)	0·3917 (5)	4·7 (4)
N(14)	0·7789 (5)	0·1721 (5)	0·1598 (5)	4·3 (4)
N(15)	0·3006 (6)	0·1515 (5)	0·2335 (5)	4·8 (4)
N(16)	0·5833 (5)	0·3792 (5)	0·0233 (5)	4·1 (3)
C(17)	0·1802 (5)	0·0737 (6)	0·4904 (5)	2·4 (3)
C(18)	0·1587 (6)	0·4939 (5)	0·0909 (6)	2·6 (4)
C(19)	0·0739 (6)	0·4654 (5)	0·1570 (5)	2·3 (3)
C(20)	0·0034 (6)	0·3694 (5)	0·1338 (6)	2·1 (3)
C(21)	0·0257 (6)	0·3009 (5)	0·0366 (6)	2·5 (4)
C(22)	0·1099 (6)	0·1701 (5)	0·4683 (6)	2·7 (4)
C(23)	0·9141 (6)	0·3386 (5)	0·2049 (6)	2·5 (4)
C(24)	0·8965 (6)	0·4028 (6)	0·3078 (6)	3·2 (4)
C(25)	0·8404 (6)	0·2461 (5)	0·1796 (6)	2·8 (4)
C(26)	0·2696 (6)	0·0405 (5)	0·4206 (5)	2·4 (3)
C(27)	0·2884 (6)	0·1024 (5)	0·3175 (6)	3·0 (4)
C(28)	0·6514 (6)	0·4531 (5)	0·0485 (6)	2·8 (4)
H(29)	0·125 (5)	0·224 (5)	0·403 (5)	4·4 (16)
H(30)	0·980 (4)	0·256 (4)	0·516 (4)	0·5 (10)
H(31)	0·799 (4)	0·048 (3)	0·395 (4)	−0·3 (9)
H(32)	0·941 (5)	0·022 (5)	0·286 (5)	3·4 (14)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43593 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

not strictly planar. S(1), Se(1), N(3) and C(5) deviate significantly from the mean plane, the maximal deviation being 0·066 (1) Å for Se(1). The dihedral angle between the mean planes through quinonoid ring and cation is 7 (I) and 8° (II).

The bond-length distribution in the TCNQ anion of both salts corresponds to the pseudo-aromatic type (Figs. 3, 4). A comparison with the TCNQ neutral molecule is shown in Table 3. The equality (in the limit range of e.s.d.'s) of *b*, *c* and *d* bond lengths in TCNQ anions confirms the completely ionic character of MT– and MS–TCNQ (Flandrois & Chasseau, 1977).

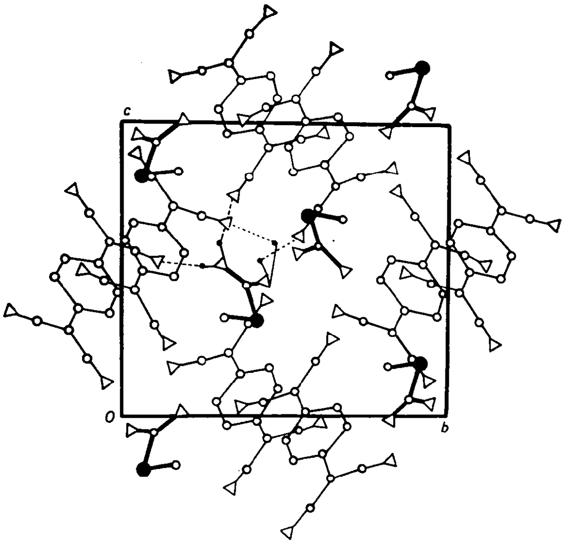


Fig. 1. Projection of the structure onto the (100) plane. The hydrogen bonds are represented by broken lines. Large filled circles: sulfur, selenium; open triangles: nitrogen; open circles: carbon; small filled circles: hydrogen.

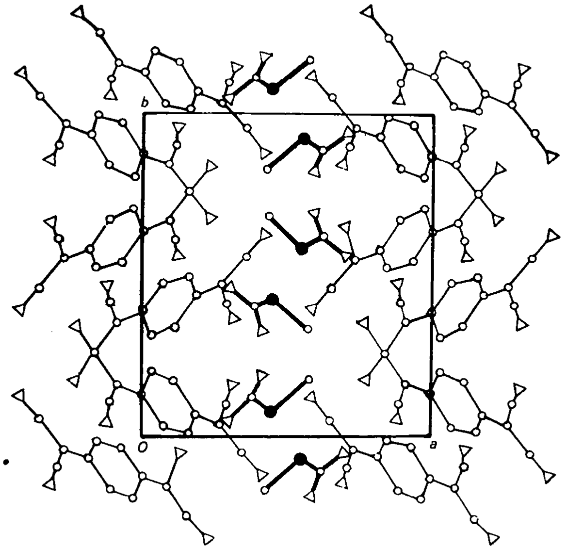


Fig. 2. Projection of the structure onto the (001) plane.

TCNQ anions are grouped into isolated pairs about inversion centres (Fig. 1). This overlapping is shown in Fig. 5. The mean interplanar spacing for TCNQ molecules is 3·40 Å for both salts. TCNQ anions and heavy atoms of the cations are positioned in different layers parallel to the (100) plane. S and Se atoms are located in the layer near $a/2$ (Fig. 2).

Hydrogen bonds are found between H atoms of the cation NH_2 groups and N atoms of TCNQ (Table 4). N···H bond lengths are in good agreement with the Hamilton & Ibers (1968) criterion: a hydrogen-bond length must be less than $r_H + r_N - 0{\cdot}2 = 2{\cdot}55$ Å, where r_H and r_N are van der Waals radii of H and N atoms ($r_H = 1{\cdot}20$, $r_N = 1{\cdot}55$ Å). The magnitudes of N—H···N angles (in the 135–165° range) do not contradict the presence of a hydrogen bond. The hydrogen bonds

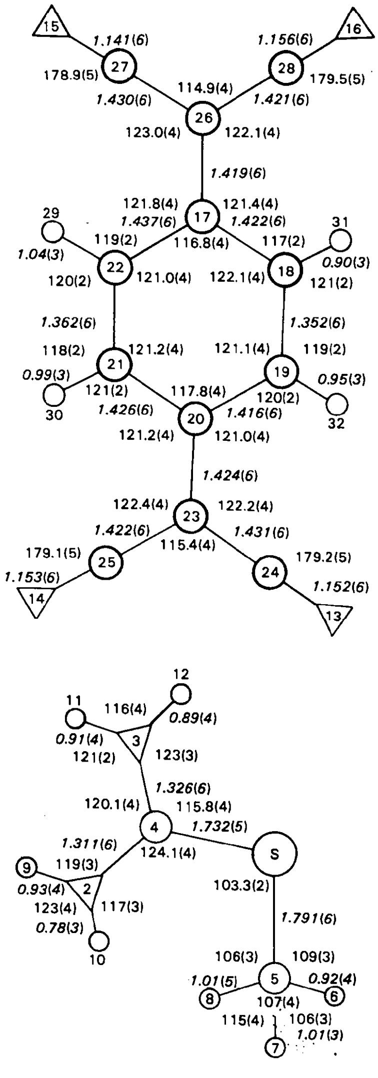


Fig. 3. Bond lengths (Å) and angles (°) in the TCNQ anion and MT cation (MT–TCNQ, e.s.d.'s in parentheses).

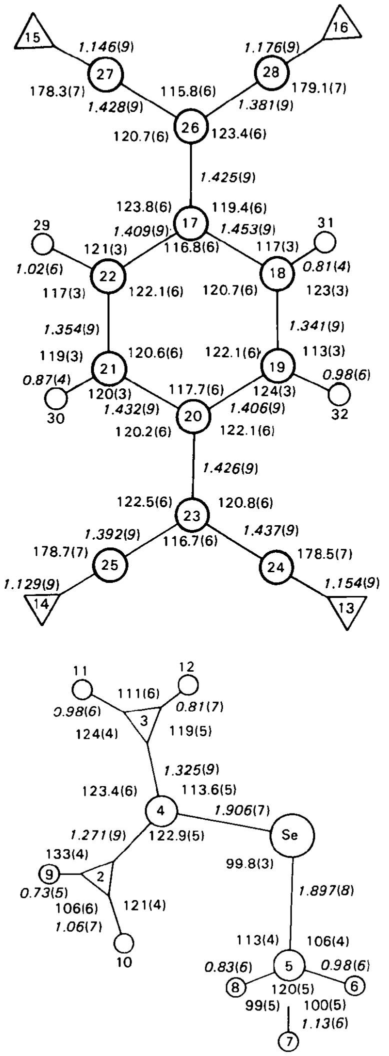


Fig. 4. Bond lengths (Å) and angles (°) in the TCNQ anion and MS cation (MS–TCNQ, e.s.d.'s in parentheses).

Table 2. *Least-squares planes and dihedral angles*

The equations of the planes are in the form: $Ax+By+Cz=D$, where x,y,z are coordinates in Å referred to the orthogonal axes $x\parallel a$, $y\parallel b$, $z\parallel c^*$ and D is origin-to-plane distance.

Plane	Plane-forming atoms	Deviations (Å, e.s.d.'s in parentheses) MT–TCNQ	MS–TCNQ	Coefficients MT–TCNQ	MS–TCNQ
Plane I	C(17)	0·007 (3)	0·006 (5)	A=0·5925	0·5966
	C(18)	−0·005 (4)	−0·008 (6)	B=0·5017	0·4985
	C(19)	−0·004 (4)	0·001 (6)	C=0·6303	0·6289
	C(20)	0·011 (3)	0·007 (6)	D=4·4021	4·4079
	C(21)	−0·010 (4)	−0·009 (7)		
	C(22)	0·001 (4)	0·003 (6)		
Plane II	C(23)	−0·001 (3)	−0·002 (6)	A=0·5966	0·5982
	C(24)	0·006 (4)	0·012 (6)	B=0·5471	0·5463
	C(25)	−0·005 (4)	−0·007 (6)	C=0·5871	0·5863
	N(13)	−0·004 (3)	−0·006 (5)	D=4·1142	4·1650
	N(14)	0·003 (4)	0·004 (5)		
Plane III	C(26)	0·003 (4)	0·004 (6)	A=0·5459	0·5459
	C(27)	−0·004 (4)	−0·011 (6)	B=0·5909	0·5943
	C(28)	−0·002 (4)	0·003 (6)	C=0·5940	0·5906
	N(15)	0·002 (4)	0·006 (5)	D=4·1874	4·1593
	N(16)	0·001 (3)	−0·001 (6)		
Plane IV	S(1),Se(1)	0·047 (1)	0·066 (1)	A=0·5290	0·5185
	N(2)	0·025 (4)	0·033 (6)	B=0·6062	0·6138
	N(3)	−0·034 (4)	−0·066 (7)	C=0·5939	0·5953
	C(4)	0·000 (4)	0·030 (7)	D=7·4466	7·4272
	C(5)	−0·039 (6)	−0·062 (9)		

Dihedral angles (°)		Mean		Mean
I–II	3·6 (2)	4·85	3·7 (3)	5·15
I–III	6·1 (2)		6·6 (3)	
I–IV	7·3 (3)		8·2 (4)	
II–III	3·9 (3)		4·1 (4)	

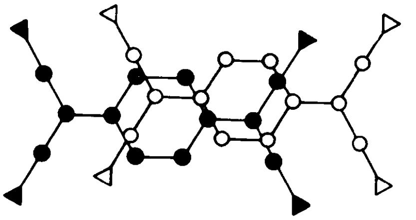
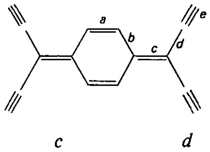


Fig. 5. Molecular overlap in the pair of TCNQ anions.

Table 3. *Comparison of the mean bond lengths* (Å) *in the TCNQ anion and in TCNQ*^{0}



	a	b	c	d	e	b–c	c–d
MT-TCNQ	1·357 (6)	1·425 (6)	1·422 (6)	1·426 (6)	1·151 (6)	0·003	−0·004
MS-TCNQ	1·348 (9)	1·425 (9)	1·425 (9)	1·412 (9)	1·151 (9)	0·000	−0·013
TCNQ^0*	1·344 (3)	1·442 (4)	1·373 (3)	1·435 (4)	1·138 (3)	0·069	−0·062

* Long, Sparks & Trueblood (1965).

Table 4. *Hydrogen-bond lengths* (Å) *and angles* (°)

	MT–TCNQ				MS–TCNQ			
X–H···Y	X–H	X–Y	H···Y	∠X–H···Y	X–H	X–Y	H···Y	∠X–H···Y
N(2)–H(9)···N(15)	0·93 (4)	2·967 (6)	2·07 (4)	163 (4)	0·73 (5)	2·986 (8)	2·39 (5)	140 (5)
N(2)–H(10)···N(16)	0·78 (3)	3·006 (6)	2·27 (3)	157 (3)	1·06 (7)	2·983 (8)	1·99 (7)	154 (6)
N(3)–H(11)···N(13)	0·91 (4)	2·951 (6)	2·24 (4)	135 (3)	0·98 (6)	2·954 (9)	2·17 (6)	136 (5)
N(3)–H(12)···N(14)	0·89 (4)	2·978 (5)	2·10 (5)	169 (4)	0·81 (7)	2·987 (8)	2·31 (7)	141 (6)

connect each cation with all anions in the unit cell (Fig. 1). These bonds promote the localization of charges and, perhaps, account for the low electroconductivity of MT– and MS–TCNQ.

References

ABASHEV, G. G., BATYAEV, I. M., ZAPOLNOV, M. K., MARTSENYUK, M. A., PROSVIRIN, V. S. & RUSSKIKH, V. S. (1981). SSSR Patent No. 802859: *Material for gas-analyser detectors*.

FLANDROIS, S. & CHASSEAU, D. (1977). *Acta Cryst.* B**33**, 2744–2750.

HAMILTON, W. C. & IBERS, I. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932–939.

SHIBAEVA, R. P. (1981). *Science and Technique Results,* Ser. *Crystal Chemistry,* Vol. 15, pp. 189–264, edited by V. V. BONDAR. Moscow: Soviet Institute of Scientific and Technique Information.

USOV, O. A., KUZMIN, A. M., ROZHDESTVENSKAYA, I. V. & FUNDAMENSKII, V. S. (1980). *Abstr. VIth Eur. Crystallogr. Meet.*, Aug. 1980, Spain, Barcelona, p. 150.

Acta Cryst. (1987). C**43**, 1112–1114

Structure of (1*S**,5*S**,*SR**)-1-(3-*p*-Toluenesulfinyl-2-propenyl)-2-methylene-7,7-dimethylbicyclo[3.3.0]octan-3-one

BY DUY H. HUA,† IBRAHEEM BADEJO AND PEGGY J. MCCANN

Department of Chemistry, Kansas State University, Manhattan, KS 66506, *USA*

AND FUSAO TAKUSAGAWA†

Department of Chemistry, University of Kansas, Lawrence, KS 66045, *USA*

(*Received* 4 *August* 1986; *accepted* 13 *January* 1987)

Abstract. $C_{21}H_{26}O_2S$, $M_r = 342{\cdot}50$, monoclinic, $C2/c$, $a = 28{\cdot}345$ (5), $b = 12{\cdot}303$ (2), $c = 11{\cdot}638$ (2) Å, $\beta = 103{\cdot}75$ (2)°, $V = 3942$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}154$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}738$ cm^{-1}, $F(000) = 1472$, room temperature, final $R = 0{\cdot}044$ for all 2594 reflections. The calculated molecular structure discloses the stereochemistry of the title compound to be 1*S**, 5*S** and *SR**. The five-membered rings forming the bicyclo[3.3.0]-octanone moiety deviate from the geometry of cyclopentane [C(1)—C(2) = 1·5254, C(1)—C(8) = 1·515 (4), C(4)—C(5) = 1·512 (3) Å; the bridging bond C(1)—C(5) = 1·561 (3) Å]. Angle C(11)—S(12)—C(13) = 96·16 (11)°.

Introduction. As part of our continuing study of stereospecific addition reactions of sulfinylallyl anions with ambident electrophiles (Hua, Sinai-Zingde & Venkataraman, 1985; Hua, 1986) and their application in the asymmetric total synthesis of antibiotic pentalenolactone (Duchamp & Chidester, 1972) (an agent which is active against Gram-positive/negative baceteria and fungi and which inhibits the enzyme glyceraldehyde-3-phosphate dehydrogenase), 2-[(*tert*-butyldimethylsilyloxy)methyl]-7,7-dimethylbicyclo-[3.3.0]-$\Delta^{1,2}$-octen-3-one (2) was treated with 1 equiv. of the anion derived from racemic *p*-tolyl allyl sulfoxide (1) and lithium diisopropylamide (LDA) in THF at 195 K for 30 min to provide the 1,4-adduct, 1-(3-*p*-toluenesulfinyl-2-propenyl)-2-methylene-7,7-dimethylbicyclo-[3.3.0]octan-3-one, (3), in 85% yield (m.p. 371–372 K). This product resulted from the rapid elimination of *tert*-butyldimethylsilyloxy ion from the initially formed enolate ion adduct. Together with sharp m.p., ^{1}H and ^{13}C NMR spectra support a single diastereomeric structure of (3). The relative stereochemistry at the S atom, C(1) and C(5) of (3) was proven by X-ray study. This proof, in turn, provides firm evidence of the stereochemical course followed in asymmetric addition reactions of chiral sulfinylallyl anions with cyclopentenones. Several reports on the X-ray crystallography of sulfoxides have previously been reported (Bandoli, Panattoni, Clemente, Tondello, Dondoni & Mangini, 1971; Hine, 1962; Thorup, 1971; Watkin & Hamor, 1971).

Experimental. A colorless prism, 0·41 × 0·39 × 0·22 mm, obtained by recrystallization from ether, was mounted on a glass fiber oriented approximately along [110]. Cell constants determined using 15 centered

---

† Authors to whom correspondence should be addressed.