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Structure of *p*-Phenylenedimethylenebis(dimethylsulfonium) 7,7,8,8-Tetracyano-*p*-quinodimethanide (1/3)

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Abstract. $C_{12}H_{20}S_2.3C_{12}H_4N_4$, $M_r = 842{\cdot}04$, triclinic, $P\bar{1}$, $a = 8{\cdot}013\,(3)$, $b = 10{\cdot}418\,(3)$, $c = 14{\cdot}090\,(4)$ Å, $\alpha = 91{\cdot}54\,(5)$, $\beta = 97{\cdot}57\,(5)$, $\gamma = 112{\cdot}78\,(5)^\circ$, $V = 1071{\cdot}12$ Å^3, $Z = 1$, $D_m = 1{\cdot}309$, $D_x = 1{\cdot}305$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 14{\cdot}26$ cm^{-1}, $F(000) = 436$, $T = 293$ K, $R = 0{\cdot}043$ for 3206 observed reflections. The complex is arranged in stacks of tetracyanoquinodimethane (TCNQ) species along the *y* axis and *p*-phenylenedimethylenebis(dimethylsulfonium) (Ps|Ar|) cations in channels between the stacks. Estimation of charge at the TCNQ species yields −0·66 and −0·79 e respectively for two independent TCNQ species, in acceptable agreement with the Flandrois–Chasseau model (−0·60 and −0·66 e). Geometry of the ring in the Ps|Ar| cation follows the Walsh-rule substituent effect.

Introduction. One of the most important pieces of information on the components of TCNQ complexes is the estimation of the charge transferred from donor to acceptor species. In principle it may be calculated by *ab initio* techniques, but practically the systems under study are too large, and usually less sophisticated methods are used (Coppens & Guru Row, 1978). Most often an approximate estimation of charge at the TCNQ species is carried out directly from the geometry parameters (Flandrois & Chasseau, 1977; Coppens & Guru Row, 1978; Kistenmacher, Emge, Bloch & Cowan, 1982; Krygowski & Anulewicz, 1984). The aim of this paper is to determine the crystal and molecular structure of the TCNQ complex with the *p*-phenylenedimethylenebis(dimethylsulfonium) cation (Ps|Ar|.3TCNQ), then to estimate the charge at the TCNQ species by use of the Flandrois & Chasseau (1977) method as well as the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983).

The complex (Pęçherz, Kryszewski, Pryzybylski & Karolak-Wojciechowska, 1984) under study has a particular importance because it is a full crystalline model of a new class of polymeric TCNQ complexes with polycations containing ionized S atoms in the main chain. These polymeric complexes have been recently synthetized and investigated (Pęçherz, Ciesielski & Kryszewski, 1981; Pęçherz & Kryszewski, 1982, 1983*a*,*b*). They exhibit higher electrical conductivities than well known ions (Rembaum, 1969; Hadek, Noguchi & Rembaum, 1976; Ciesielski & Kryszewski, 1976) with N^+ atoms in the main chain of the polycation. These polymeric TCNQ complexes with S^+-containing polycations cannot be obtained as single crystals suitable for crystal and molecular structure determination. Thus, the estimation of charge transfer between the compounds of the complex cannot be made directly. This parameter is of basic importance for elucidation of electrical properties, thus the estimation of the charge at the TCNQ species using the investigated model system might also throw light on the matter.

Experimental. The compound crystallizes in dark-violet triclinic form. Density measured by flotation. Preliminary data obtained from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation) and the latter adjusted by a least-squares fit of the optimized diffractometer setting angles ($20 \leq \theta \leq 30^\circ$) of 15 selected reflections; Syntex $P\bar{1}$ diffractometer, no absorption correction applied, $\theta \leq 60^\circ$, θ–2θ scan technique, Cu $K\alpha$ radiation at room temperature; intensities of two ($21\bar{1}$, 021) standard reflections monitored at frequent intervals showed no significant fluctuations during data collection; single crystal of dimensions 0·4 × 0·3 × 0·8 mm used; of 3752 reflections measured after data reduction 3586 independent, using criterion $|F_o| \geq 4\sigma|F_o|$ 3215 observed reflections

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used for solving structure; refinement performed with 3206 reflections (nine reflections affected by extinction); $h_{\min} = -9$, $h_{\max} = 9$, $k_{\min} = -12$, $k_{\max} = 12$, $l_{\min} = 0$, $l_{\max} = 16$.

Table 1. *Positional parameters* (×10⁴) *and equivalent U values* (×10³) *for the non*-H *atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å²)
S	812 (1)	1579 (1)	−785 (0·4)	51 (0·4)
C(41)	94 (3)	3705 (2)	115 (2)	45 (1)
C(42)	1620 (4)	4931 (3)	395 (2)	64 (1)
C(45)	−1521 (4)	3790 (3)	−273 (2)	62 (1)
C(47)	176 (4)	2302 (2)	232 (2)	51 (1)
C(48)	3156 (4)	2711 (3)	−766 (2)	75 (1)
C(49)	−265 (4)	2065 (3)	−1828 (2)	67 (1)
C(31)	5490 (3)	1365 (2)	3204 (2)	41 (1)
C(32)	3685 (3)	1293 (2)	3208 (2)	43 (1)
C(33)	3071 (3)	1456 (2)	4037 (2)	41 (1)
C(34)	4243 (3)	1733 (2)	4942 (1)	38 (1)
C(35)	6068 (3)	1839 (2)	4942 (2)	42 (1)
C(36)	6672 (3)	1658 (2)	4105 (2)	43 (1)
C(37)	3591 (3)	1890 (2)	5789 (2)	42 (1)
C(38)	4710 (3)	2173 (2)	6711 (2)	49 (1)
C(39)	1754 (3)	1751 (2)	5792 (2)	47 (1)
N(31)	275 (3)	1649 (2)	5795 (2)	65 (1)
N(32)	5563 (3)	2379 (3)	7455 (2)	70 (1)
C(310)	6061 (3)	1090 (2)	2346 (2)	47 (1)
C(311)	4839 (4)	744 (3)	1460 (2)	56 (1)
C(312)	7784 (4)	1016 (3)	2334 (2)	56 (1)
N(33)	3795 (4)	499 (3)	765 (2)	79 (1)
N(34)	9156 (4)	912 (3)	2324 (2)	81 (1)
C(21)	5747 (3)	4831 (2)	4165 (1)	35 (1)
C(22)	3881 (3)	4677 (2)	4106 (2)	37 (1)
C(23)	3171 (3)	4841 (2)	4901 (1)	37 (1)
C(27)	6485 (3)	4638 (2)	3351 (1)	38 (1)
C(28)	5457 (3)	4276 (2)	2410 (2)	44 (1)
C(29)	8348 (3)	4820 (3)	3383 (2)	48 (1)
N(21)	4701 (3)	3971 (2)	1636 (1)	66 (1)
N(22)	9828 (3)	4953 (3)	3368 (2)	76 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(47)–S	1·821 (3)	C(48)–S	1·786 (3)
C(49)–S	1·791 (3)	C(42)–C(41)	1·385 (3)
C(45)–C(41)	1·373 (4)	C(47)–C(41)	1·501 (4)
C(32)–C(31)	1·420 (4)	C(36)–C(31)	1·428 (3)
C(310)–C(31)	1·408 (3)	C(33)–C(32)	1·356 (3)
C(34)–C(33)	1·430 (3)	C(35)–C(34)	1·423 (3)
C(37)–C(34)	1·395 (3)	C(36)–C(35)	1·368 (3)
C(38)–C(37)	1·430 (3)	C(39)–C(37)	1·423 (4)
N(32)–C(38)	1·139 (3)	N(31)–C(39)	1·149 (4)
C(311)–C(310)	1·424 (3)	C(312)–C(310)	1·414 (4)
N(33)–C(311)	1·150 (3)	N(34)–C(312)	1·148 (5)
C(22)–C(21)	1·431 (3)	C(27)–C(21)	1·401 (3)
C(23)–C(22)	1·357 (3)	C(28)–C(27)	1·423 (3)
C(29)–C(27)	1·425 (3)	N(21)–C(28)	1·147 (3)
N(22)–C(29)	1·143 (4)	C(21)–C(25′)	1·430 (3)
		C(45)–C(42′)	1·379 (3)
C(48)–S–C(47)	103·2 (1)	C(49)–S–C(47)	105·3 (1)
C(49)–S–C(48)	101·2 (1)	C(45)–C(41)–C(42)	118·7 (3)
C(47)–C(41)–C(42)	121·4 (2)	C(47)–C(41)–C(45)	119·9 (2)
C(41)–C(47)–S	115·0 (2)	C(36)–C(31)–C(32)	117·7 (2)
C(310)–C(31)–C(32)	120·9 (2)	C(310)–C(31)–C(36)	121·3 (2)
C(33)–C(32)–C(31)	121·7 (2)	C(34)–C(33)–C(32)	120·7 (2)
C(35)–C(34)–C(33)	117·9 (2)	C(37)–C(34)–C(33)	120·2 (2)
C(37)–C(34)–C(35)	121·9 (2)	C(36)–C(35)–C(34)	121·0 (2)
C(35)–C(36)–C(31)	120·9 (2)	C(38)–C(37)–C(34)	122·3 (2)
C(39)–C(37)–C(34)	122·0 (2)	C(39)–C(37)–C(38)	115·7 (2)
N(32)–C(38)–C(37)	178·3 (3)	N(31)–C(39)–C(37)	179·5 (2)
C(311)–C(310)–C(31)	120·5 (2)	C(312)–C(310)–C(31)	122·2 (2)
C(312)–C(310)–C(311)	117·1 (2)	N(33)–C(311)–C(310)	177·3 (3)
N(34)–C(312)–C(310)	177·8 (3)	C(27)–C(21)–C(22)	121·9 (2)
C(23)–C(22)–C(21)	121·4 (2)	C(28)–C(27)–C(21)	123·2 (2)
C(29)–C(27)–C(31)	123·2 (2)	C(29)–C(27)–C(28)	113·5 (2)
N(21)–C(28)–C(27)	176·5 (3)	N(22)–C(29)–C(27)	177·1 (2)

Structure solved by direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). A difference Fourier synthesis, phased by the partial structure from an *E* map, provided positions for the remaining non-H atoms. A further difference map showed the positions of the H atoms. Isotropic thermal parameters of H atoms taken initially as 1·5 times the temperature factors of their parent C atoms. The parameters for CH_2 and both CH_3 groups of the cation were refined in the riding model. Refinement by blocked least squares with anisotropic temperature factors for all non-H atoms and unit weights converged to $R = 0{\cdot}043$, changes in all parameters became less than $\frac{1}{20}$ of their respective e.s.d.'s, on the final difference map no density > 0·4 e Å^{-3}; atomic scattering factors from *SHELX*76 (Sheldrick, 1976). All calculations performed using *SHELX*76 system of programs on the ODRA-1305 computer.

The atomic parameters for non-H atoms are given in Table 1.* Table 2 contains the bond distances and angles.

Discussion. The structure of Ps I Ar I.3TCNQ with the appropriate molecular atom numbering is shown in Fig. 1. As can be seen from Fig. 1, two crystallographically independent TCNQ (*A* and *B*) moieties are arranged in stacks along the *y* axis with interplanar separation *AB* about 3·14 Å. It is worth noting that the analogous distance for *BB′* TCNQ moieties is 3·51 Å. Ps I Ar I cations are located in channels between the stacks of TCNQ species. The values of the non-bonded interatomic distances (Fig. 1) clearly show that there are no strong cation–anion interactions in the crystal. The shortest ones were found for N(34)–S and N(33)–S, 3·347 (2) and 3·578 (2) Å respectively. Of these two values only the former is close to the sum of van der

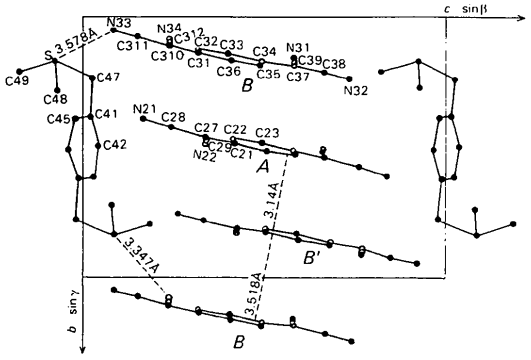

Fig. 1. The projection of the structure along |100|.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42531 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Waals radii for S and N atoms (3·35 Å) (Bondi, 1964). Probably due to this shorter contact the PsIArI cation is well anchored in the crystal. Consequently, the accuracy of bond-length estimations for this fragment is on the same level as for TCNQ (Table 2).

Fig. 1 presents the mutual positions of *A*, *B* and *B'* TCNQ species in the stack. One TCNQ ring (*A*) lies on a centre of symmetry, whereas the other two (*B* and *B'*) are related by it. The atom deviating most from the TCNQ plane is N(34) in the *B* species, 0·258 (3) Å. As mentioned above, this atom is closest to the S atom. It should be noted that TCNQ (*B*) deviates much more from planarity than TCNQ (*A*).

The PsIArI cation belongs to the symmetrically *p*-disubstituted benzenes and may be analysed in terms of the Walsh rule (Walsh, 1948; Coulson, Domenicano & Vaciago, 1975; Krygowski, 1984). When the difference of the bonds C(45)—C(42)—C(41)—C(45) $= b - a = \Delta = 0{\cdot}004$ Å is plotted against α which is the angle O(45)—C(41)—O(42) = 118·7 (3)° the point lies very well on the line Δ *vs* α proposed by Krygowski (1984), slightly pushed towards greater Δ and α values. This effect may be interpreted as a result of positive charge at the cation species.

Application of the HOSE model (Krygowski *et al.*, 1983) allows estimation of the percentage of quinoid-form contribution, and in consequence the charge at the TCNQ species, with an accuracy of 0·18 e (Krygowski & Anulewicz, 1984). Thus in our study we have estimated *q* at *A* and *B* molecules of TCNQ by use of this model and that proposed by Flandrois & Chasseau (1977). The results are $q(A) = -0{\cdot}66$ e and $q(B) = -0{\cdot}79$ e in comparison with values −0·60 and −0·66 e respectively from the Flandrois & Chasseau (1977) model. The rather comparable charges at TCNQ *A* and *B* molecules in the PsIArI.3TCNQ complex explain its high electrical conductivity (Pęcherz *et al.*, 1984).

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Structure of Benoxaprofen, 2-[2-(4-Chlorophenyl)-1,3-benzoxazol-5-yl]propionic Acid

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Abstract. $C_{16}H_{12}ClNO_3$, $M_r = 301{\cdot}7$, monoclinic, $A2/a$, $a = 12{\cdot}557$ (8), $b = 4{\cdot}941$ (11), $c = 48{\cdot}478$ (32) Å, $\beta = 101{\cdot}5$ (1)°, $U = 2947{\cdot}4$ Å^3, $Z = 8$, $D_m = 1{\cdot}36$, $D_x = 1{\cdot}36$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}72$ cm^{-1}, $F(000) = 1248$, room temperature, final $R = 0{\cdot}072$ for 1303 independent observed reflections.

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