Both *A* and *B* conformations of the SOaz(*W*) molecule can be directly compared with the previous one (Galy *et al.*, 1981). Fig. 4 summarizes the extraordinary versatility of this molecule in the setting of its aziridinyl wings.

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Structure of the 1/1·5 Complex Formed between the Bis(triphenylphosphoranediyl)ammonium cation (R^+) and 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ), $C_{36}H_{30}NP_2^+.C_{12}H_{12}N_4^-.0\cdot5C_{12}H_{12}N_4.C_2H_3N$

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Abstract. $R^+(\mathrm{TCNQ})^-(\mathrm{TCNQ})_{0\cdot5}.\mathrm{CH_3CN}$, $M_r = 885$, triclinic, $P\bar{1}$, $a = 8\cdot84\ (1)$, $b = 16\cdot70\ (1)$, $c = 17\cdot16\ (1)$ Å, $\alpha = 69\cdot85\ (7)$, $\beta = 84\cdot11\ (9)$, $\gamma = 85\cdot26\ (9)°$, $V = 2365\ (6)$ Å^3, $Z = 2$, $D_m = 1\cdot24$, $D_x = 1\cdot24$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot105$ mm^{-1}, $F(000) = 966$, room temperature, $R = 0\cdot0625$, $R_w = 0\cdot056$ for 2833 diffractometer-measured intensities with $I > 3\sigma(I)$. The cation has the expected non-linear structure. The structural unit contains 1·5 TCNQ molecules, TCNQ(*B*) being at a centre of symmetry while TCNQ(*A*) is in a general position. The TCNQ molecules are stacked in groups of three, *ABA*. Within the triad the molecules are displaced so that there is overlap between the quinonoid double bond and the ring of the adjacent molecule. Individual triads are well separated without overlap. A molecule of solvent, methyl cyanide, is included in the structural unit.

Introduction. The compound was prepared as part of an investigation into the preparation of conducting and semi-conducting complexes of TCNQ with various cations (Ahmad, Bryce, Halfpenny & Weiler, 1984). Its conductivity is that of a typical semi-conductor. The compound was considered worthy of structure determination owing to the large size of the cation, which is by far the most complex in a TCNQ compound studied by X-ray diffraction.

Experimental. Initially composition of compound unknown. Accurate cell dimensions from least-squares refinement of 12 strong reflections (Mo $K\alpha$ θmin. 5, max. 17°), Enraf–Nonius CAD-4 4-circle diffractometer. Density by flotation indicated $Z = 2$. 7604 reflections measured, Stoe Stadi-2 2-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; crystal 0·4 × 0·5 × 0·05 mm, layers $h = 0$–8, $k \pm 18$, $l \pm 19$, max. $\sin\theta/\lambda = 0\cdot595$ Å^{-1}, separate standard for each layer measured every 10 reflections (intensity variation < 2%). 7009 unique reflections ($R_{\rm int} = 0\cdot019$), 2833 with $I > 3\sigma(I)$ used for refinement. No absorption correction. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined using *SHELX*76 (Sheldrick, 1976) full-matrix least squares on *F* magnitudes. Phenyl groups treated as rigid hexagons with C—C = 1·395 Å. Difference map showed one molecule of methyl cyanide in asymmetric unit. Hydrogen atoms, including those of methyl cyanide, introduced at calculated positions (C—H = 1·08 Å) and all H within each molecule or phenyl group given same isotropic *U* value. All non-H atoms except C(1), C(2), C(3), C(7), C(8), C(13), C(14), C(19), C(20), C(25), C(26), C(31) and C(32) given anisotropic U_{ij}. These exceptions were necessary on account of limited capacity of *SHELX* program [2*N*(anis.) + *N*(iso.) ≤ 160], the basis for exception

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being lowest and least anisotropic U values. At a later stage individual scale factors for data-collection layers were introduced. Final weighting scheme $w = \{3{\cdot}739/[\sigma(F)^2 + 0{\cdot}00012(F)^2]\}$, parameters in equation refined in each cycle. Max. Δ/σ 0·05, $R = 0{\cdot}0625$, $R_w = 0{\cdot}056$; largest features on final difference map $\pm 0{\cdot}3$ e Å^{-3}. Atomic scattering factors from *SHELX*. Final atomic positions and U_{eq} values are given in Table 1,* bond distances and angles in Table 2, and the atom numbering scheme in Fig. 1.

Discussion. The structure determination shows that the cation has the expected non-linear structure with P—N—P 137·6 (4)°. The structural unit contains one and a half TCNQ molecules, the half arising from the molecule TCNQ(*B*) sited on a centre of symmetry, TCNQ(*A*) being in a general position. The TCNQ molecules are therefore stacked in groups of three, *ABA*, the mean molecular planes within which are inclined at 1·3 (3)°. There are 15 interatomic contacts within the range 3·30–3·47 Å; the distance between mean molecular planes of the triads is 3·30 (2) Å. Within the triads the TCNQ molecules are displaced lengthways so that there is overlap of the quinonoid double bond and the ring of the neighbouring molecule. Adjacent triads are well separated without overlap. The packing is shown in Fig. 2.

Although 109 determinations of structures of TCNQ complexes have been reported, the present one shows a unique combination of unusual features. The most noteworthy ones are:

(*a*) The cation is by far the largest and most complex in a TCNQ compound that has been studied by X-ray diffraction.

(*b*) The stoichiometry of the complex is unusual; although there are numerous examples in which the unit of structure contains charged and uncharged TCNQ species, only one other having this stoichiometry and symmetry has been reported (Ashwell, Eley, Wallwork, Willis, Peachey & Wilkes, 1977). In that structure the centrosymmetric cation is doubly charged but the anion is a similar triad of TCNQ molecules grouped on a centre of symmetry with no overlap between triads. The overlap within the triads (mean molecular planes 3·15 Å apart) is slightly more effective than in the present structure.

Ashwell *et al.* have made a detailed comparison of the TCNQ bond distances in the 1,1′-(*p*-phenylenedimethylene)diquinolinium complex with those in neutral TCNQ^0 (Long, Sparks & Trueblood, 1965) and the average for the TCNQ$^-$ anion obtained from a number of structures. Their values are quoted in Table 3(*a*). Following the procedure of Ashwell *et al.*, the mean distances in the present structure are listed in Table 3(*b*). Bearing in mind the limited accuracy, the weight of the evidence appears to relate TCNQ(*A*) to the anion.

(*c*) Only two TCNQ structures involving methyl cyanide as included solvent have so far been reported (Chasseau, Gaultier, Hauw & Jaud, 1973*a*,*b*). In the

Table 1. *Final atomic parameters* (×10^4) *and temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	*U* or U_{eq}†
P(1)	9094 (2)	3868 (1)	2566 (1)	37 (1)†
P(2)	8361 (2)	2078 (1)	3521 (1)	34 (1)†
N(1)	8355 (5)	2971 (3)	2789 (3)	36 (3)†
N(2)	11400 (8)	2904 (5)	5771 (5)	90 (6)†
N(3)	7222 (9)	3877 (5)	6799 (5)	96 (6)†
N(4)	9510 (9)	−2041 (4)	8927 (5)	90 (6)†
N(5)	5302 (9)	−1002 (5)	9878 (5)	100 (6)†
N(6)	3229 (9)	1840 (5)	7939 (5)	96 (6)†
N(7)	−900 (9)	2980 (5)	8767 (5)	100 (7)†
N(8)	4297 (14)	7163 (7)	−482 (6)	144 (8)†
C(1)	7549 (5)	1331 (2)	3160 (3)	38 (2)
C(2)	7103 (5)	1595 (2)	2349 (3)	47 (2)
C(3)	6454 (5)	1021 (2)	2068 (3)	53 (2)
C(4)	6252 (5)	184 (2)	2598 (3)	62 (5)†
C(5)	6698 (5)	−79 (2)	3408 (3)	59 (5)†
C(6)	7346 (5)	494 (2)	3689 (3)	49 (4)†
C(7)	10211 (5)	1640 (3)	3825 (3)	34 (2)
C(8)	10919 (5)	1924 (3)	4365 (3)	46 (2)
C(9)	12439 (5)	1681 (3)	4513 (3)	66 (6)†
C(10)	13252 (5)	1154 (3)	4122 (3)	79 (6)†
C(11)	12544 (5)	870 (3)	3582 (3)	68 (6)†
C(12)	11024 (5)	1113 (3)	3434 (3)	53 (4)†
C(13)	7266 (5)	2102 (2)	4452 (3)	35 (2)
C(14)	6158 (5)	2762 (2)	4386 (3)	45 (2)
C(15)	5266 (5)	2799 (2)	5093 (3)	71 (6)†
C(16)	5483 (5)	2177 (2)	5866 (3)	71 (6)†
C(17)	6591 (5)	1517 (2)	5932 (3)	66 (6)†
C(18)	7483 (5)	1480 (2)	5225 (3)	49 (4)†
C(19)	8617 (5)	4518 (3)	1546 (3)	42 (2)
C(20)	7752 (5)	4213 (3)	1082 (3)	60 (2)
C(21)	7403 (5)	4734 (3)	285 (3)	93 (7)†
C(22)	7919 (5)	5560 (3)	−48 (3)	83 (7)†
C(23)	8785 (5)	5865 (3)	415 (3)	79 (6)†
C(24)	9134 (5)	5344 (3)	1212 (3)	64 (5)†
C(25)	8439 (5)	4427 (3)	3269 (3)	41 (2)
C(26)	7205 (5)	5019 (3)	3090 (3)	62 (2)
C(27)	6583 (5)	5381 (3)	3680 (3)	93 (7)†
C(28)	7194 (5)	5150 (3)	4449 (3)	90 (7)†
C(29)	8428 (5)	4557 (3)	4628 (3)	75 (6)†
C(30)	9051 (5)	4196 (3)	4038 (3)	57 (5)†
C(31)	11099 (5)	3786 (3)	2527 (3)	37 (2)
C(32)	11856 (5)	3155 (3)	2151 (3)	45 (2)
C(33)	13443 (5)	3085 (3)	2184 (3)	63 (5)†
C(34)	14274 (5)	3646 (3)	2393 (3)	89 (7)†
C(35)	13517 (5)	4277 (3)	2669 (3)	92 (8)†
C(36)	11930 (5)	4347 (3)	2736 (3)	65 (5)†
C(37)	10355 (10)	2788 (5)	6233 (5)	57 (5)†
C(38)	9049 (8)	2604 (5)	6813 (5)	50 (5)†
C(39)	8061 (10)	3313 (6)	6801 (5)	66 (6)†
C(40)	8733 (8)	1784 (5)	7349 (5)	49 (5)†
C(41)	9762 (8)	1068 (5)	7352 (4)	47 (4)†
C(42)	9436 (8)	259 (5)	7867 (4)	50 (5)†
C(43)	8091 (9)	102 (5)	8387 (5)	50 (5)†
C(44)	7087 (8)	809 (5)	8394 (5)	51 (5)†
C(45)	7398 (8)	1607 (5)	7890 (5)	52 (5)†
C(46)	7735 (9)	−730 (5)	8920 (5)	54 (5)†
C(47)	8718 (10)	−1467 (6)	8933 (5)	61 (6)†
C(48)	6380 (10)	−894 (5)	9461 (5)	64 (6)†
C(49)	2135 (11)	1732 (5)	8385 (6)	70 (6)†
C(50)	763 (9)	1621 (5)	8914 (5)	51 (5)†
C(51)	−151 (10)	2382 (6)	8839 (5)	70 (7)†
C(52)	1357 (8)	69 (5)	9505 (5)	55 (5)†
C(53)	419 (9)	816 (5)	9455 (5)	52 (6)†
C(54)	−974 (9)	719 (5)	9971 (5)	52 (6)†
C(55)	4535 (13)	6948 (7)	198 (9)	106 (9)†
C(56)	4841 (12)	6676 (7)	1064 (7)	137 (10)†

† $U_{eq} = \frac{1}{3}(\sum_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j)$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39760 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°)

N(1)–P(1)	1·593 (5)	C(43)–C(44)	1·421 (11)
N(1)–P(2)	1·586 (4)	C(43)–C(46)	1·415 (10)
C(1)–P(2)	1·796 (5)	C(44)–C(45)	1·349 (10)
C(7)–P(2)	1·788 (5)	C(46)–C(47)	1·443 (12)
C(13)–P(2)	1·792 (5)	C(46)–C(48)	1·442 (11)
C(19)–P(1)	1·786 (5)	N(4)–C(47)	1·147 (12)
C(25)–P(1)	1·790 (6)	N(5)–C(48)	1·121 (11)
C(31)–P(1)	1·763 (5)	N(6)–C(49)	1·155 (12)
N(2)–C(37)	1·138 (11)	C(49)–C(50)	1·424 (12)
C(37)–C(38)	1·425 (11)	C(50)–C(51)	1·422 (13)
C(38)–C(39)	1·408 (12)	C(50)–C(53)	1·383 (10)
C(38)–C(40)	1·395 (10)	N(7)–C(51)	1·121 (12)
N(3)–C(39)	1·149 (12)	C(52)–C(53)	1·422 (12)
C(40)–C(41)	1·441 (11)	C(54)–C(53)	1·429 (11)
C(40)–C(45)	1·408 (10)	C(55)–C(56)	1·444 (18)
C(42)–C(41)	1·371 (10)	N(8)–C(55)	1·134 (17)
C(42)–C(43)	1·399 (10)		

All C—C (ring) 1·395, all C—H 1·080 Å, constrained

C(40)···C(50^{i})	3·305	C(43)···C(54^{i})	3·414
C(40)···C(51^{i})	3·310	C(44)···C(54^{i})	3·304
C(41)···C(49^{i})	3·358	C(45)···C(51^{i})	3·416
C(41)···C(50^{i})	3·340	C(39)···N(7^{i})	3·345
C(42)···C(52^{i})	3·343	C(52^{ii})···C(46^{iii})	3·437
C(3^{iv})···N(8^{ii})	3·377	C(53^{ii})···C(47^{iii})	3·473
C(42)···C(53^{i})	3·380	C(53^{ii})···C(46^{iii})	3·328
C(43)···C(53^{i})	3·420	C(54^{ii})···C(47^{iii})	3·446

P(2)–N(1)–P(1)	137·6 (4)	C(7)–P(2)–C(13)	106·3 (2)
C(19)–P(1)–N(1)	108·0 (3)	N(2)–C(37)–C(38)	177·4 (9)
C(25)–P(1)–N(1)	113·6 (3)	C(37)–C(38)–C(39)	115·2 (6)
C(31)–P(1)–N(1)	113·0 (2)	C(38)–C(39)–N(3)	178·1 (9)
C(19)–P(1)–C(25)	108·2 (2)	C(37)–C(38)–C(40)	123·3 (7)
C(25)–P(1)–C(31)	107·5 (3)	C(39)–C(38)–C(40)	121·4 (7)
C(1)–P(2)–N(1)	107·4 (3)	C(41)–C(40)–C(45)	116·9 (6)
C(7)–P(2)–N(1)	114·6 (2)	C(40)–C(41)–C(42)	120·5 (6)
C(13)–P(2)–N(1)	113·5 (2)	C(41)–C(42)–C(43)	121·3 (7)
C(1)–P(2)–C(7)	106·7 (2)	C(42)–C(43)–C(44)	118·2 (6)
C(43)–C(44)–C(45)	120·8 (6)	N(6)–C(49)–C(50)	178·1 (9)
C(44)–C(45)–C(40)	122·2 (7)	N(7)–C(51)–C(50)	178·2 (12)
C(42)–C(43)–C(46)	122·0 (7)	C(49)–C(50)–C(51)	115·1 (7)
C(44)–C(43)–C(46)	119·8 (7)	C(49)–C(50)–C(53)	119·7 (8)
C(43)–C(46)–C(47)	121·7 (6)	C(51)–C(50)–C(53)	125·2 (7)
C(43)–C(46)–C(48)	122·4 (7)	C(50)–C(53)–C(54)	118·7 (7)
C(47)–C(46)–C(48)	115·9 (7)	C(50)–C(53)–C(52)	123·4 (7)
N(4)–C(47)–C(46)	178·5 (8)	C(52)–C(53)–C(54)	117·9 (7)
N(5)–C(48)–C(46)	178·3 (9)	N(8)–C(55)–C(56)	179·9 (3)

All C—C—C (ring) 120·0°, constrained

Symmetry code: (i) $-1+x, y, z$; (ii) $1-x, -y, 2-z$; (iii) $-x, -y, -z$; (iv) $1-x, 1-y, -z$.

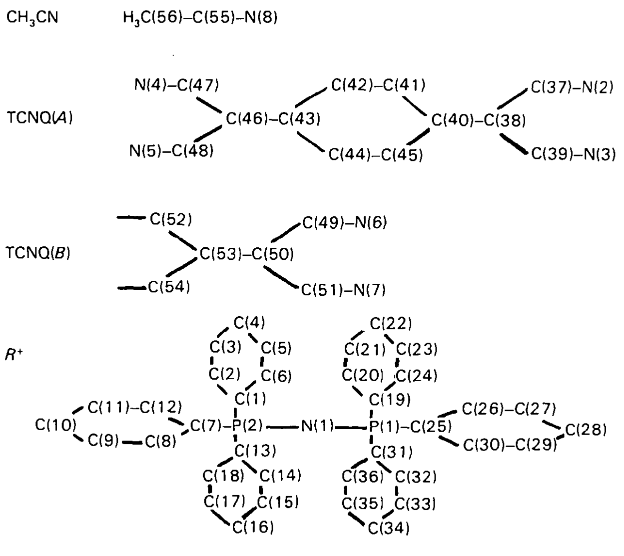


Fig. 1. Atom numbering scheme.

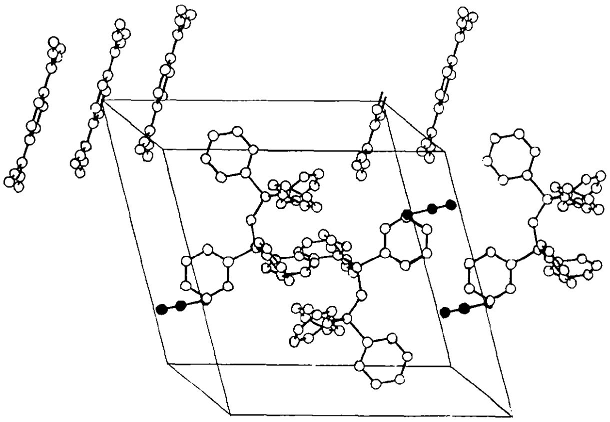
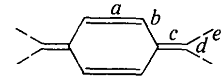


Fig. 2. View of the unit cell of the complex showing three units of structure. Molecules of methyl cyanide are shown in black for clarity.

Table 3. *Comparison of bond lengths in TCNQ* (Å)



(*a*) Neutral and charged TCNQ

	a	*b*	*c*	*d*	*e*
TCNQ^0	1·345	1·448	1·374	1·440	1·138
TCNQ$^-$	1·362	1·424	1·413	1·417	1·149

(*b*) TCNQ in present structure

	a	*b*	*c*	*d*	*e*
TCNQ(*A*)	1·360	1·417	1·406	1·424	1·138
TCNQ(*B*)	1·359	1·426	1·382	1·422	1·142

present structure, C—C—N is linear with the C—C bond (1·44 Å) predictably shortened by hyperconjugation. There is a relatively close contact of N(8) with C(3) of a phenyl group [3·38 (1) Å]. A close contact between the methyl C and a TCNQ N is reported by Chasseau *et al* (1973*a*), while in Chasseau *et al.* (1973*b*) contacts involving methyl cyanide are reported as being van der Waals values.

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