Crystal and Molecular Structure of the 2:3 Complex of *N*-Methylphenazinium with ααα′α′-Tetracyanoquinodimethane, $[(nmp)_2]^{2+}[(tcnq)_3]^{2-}$

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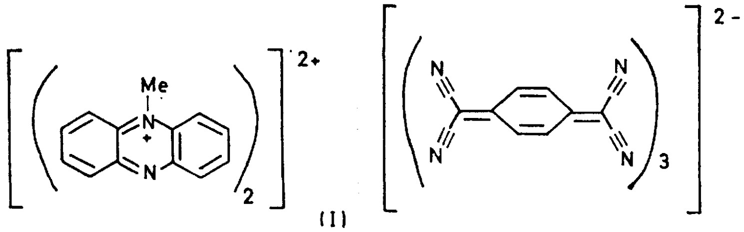
Crystals of the title compound(I) are triclinic with reduced cell dimensions a = 17.360(15), b = 7.695(6), c = 9.858 Å, α = 71.65(7), β = 76.08(8), γ = 86.92(8)°, Z = 1. The structure was solved from a three-dimensional Patterson function and refined in space group $P\bar{1}$ to 0.105, by use of 2 346 diffractometer data. The tcnq units form triads with the central planar unit on a centre of symmetry. No distinction, based on bond lengths, can be made between charged and neutral molecules. The non-planar nmp$^+$ ion retains an approximate mirror plane through the two nitrogen atoms and there are two different C–N bond lengths (1.335 and 1.371 Å) in the central ring. The crystal structure is built up of tcnq triads which repeat along the c axis while the holes are filled with centrosymmetrically related pairs of nmp$^+$ ions. Within the triads the separation between consecutive units is *ca.* 3.15 Å and two consecutive triads are separated by *ca.* 3.26 Å.

It is well known that some molecular complexes of the tcnq$^-$ ion radical are among those organic materials with the highest values for electrical conductivity. Correlation between the electrical properties and the crystal structures have shown a close relation between this desirable property and the arrangement of the molecules in solid state.[1] Between the organic electrical conductors, which crystallize in infinite, parallel, segregated stacks of anions exhibiting high values of conductivity, and the charge–transfer complexes, which crystallize in mixed stacks of alternating anions and cations, and in general exhibits low conductivity, there is a wide range of compounds with medium values of conductivity. We have determined the structure of (I) which belongs to a fairly large class of compounds which, in compaction at room temperature, exhibits modest values of conductivity.



(I)

EXPERIMENTAL

The only available crystal of (I) was very dark and prismatic, with cross-section *ca.* 0.24 × 0.4 mm².

Crystal Data.—$(C_{13}N_2H_{11})_2(C_{12}N_4H_4)_3$, M = 1 003.7. Triclinic, with reduced cell: a = 17.360(15), b = 7.695(6), c = 9.858(7) Å, α = 71.65(7), β = 76.08(8), γ = 86.92(8)°, U = 1 212.9 Å³, Z = 1, D_c = 1 373 kg m^{-3}. Mo-K_α radiation, λ = 0.710 69 Å; μ(Mo-K_α) = 0.5 cm^{-1}. Space group $P\bar{1}$ assumed.

Cell dimensions were obtained from precession photographs by a least-squares process. Intensities with $\theta \leqslant 25°$ were collected round b on a Hilger and Watts linear diffractometer equipped with a graphite monochromator. 2 346 reflexions whose intensities were $> 2\sigma$ were accepted and used throughout the analysis. No correction was made for absorption.

Structure Determination.—The structure was solved from a three-dimensional Patterson function. The trial structure was then refined by least-squares isotropically and anisotropically. When R was 0.12, a difference synthesis was calculated, and showed maxima of residual electron density at the positions calculated for hydrogen atoms. No sign of disorder was observed. Hydrogen atoms positions were included and refinement continued till a final R of 0.105. One of the factors which could have influenced the relatively high final value of R is that the crystal had cross-section only a little bigger than the diameter of the X-ray beam; this meant that the volume of the crystal bathed by the X-rays was only approximately constant during data collection.

RESULTS AND DISCUSSION

Table 1 shows the final co-ordinates, Table 2 temperature factors, Tables 3 and 4 bond lengths and angles of tcnq and nmp, and Table 5 the equations of some important planes in the structure and distances of relevant atoms from them. Figure 1 shows the projection of the structure down the b axis, and Figures 2—5 the modes of overlap between consecutives molecules. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP **21311** (16 pp., 1 microfiche).§

There are two independent tcnq units in the cell, one of which (A in Figure 1) lies on the centre of symmetry at the origin. This centrosymmetric tcnq is essentially

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§ For details see Notice to Authors No. 7 in *J.C.S. Perkins II*, 1974, Index issue.

[1] R. P. Shibaeva and L. O. Atovmyan, *Zhur. Strukt. Khim.*, 1972, **13**, 546; J. Gaultier, C. Hauw, J. Jaud, P. Dupoid, and J. Neel, First European Crystallographic Meeting, Bordeaux, 1973, Group C3; R. P. Shibaeva, L. O. Atovmyan, and V. F. Kaminskii, *ibid.*

planar: only the carbon atom which links the two cyano-groups to the quinoid ring is slightly out of the plane of the ring by 0.021 Å or *ca.* 4 σ (Table 5). The other (B in Figure 1) is not planar, small but significant deviations from the plane of the quinoid ring being found in the cyanomethylene groups (Table 5). The distortion, which gives the molecule a bow form, is very similar to that of tcnq in the structure of the 1 : 1 complex dmph–tcnq [2] (dmph = *NN′*-dimethyldihydrophenazine).

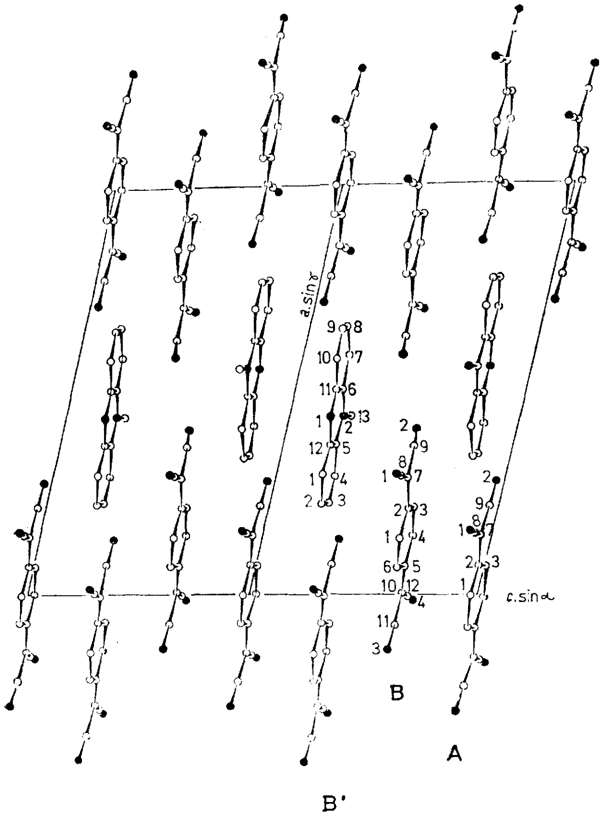

FIGURE 1 Projection of the structure down *b* showing the labelling of the atoms. Two consecutive cells are represented (open circles are carbon, closed circles nitrogen)

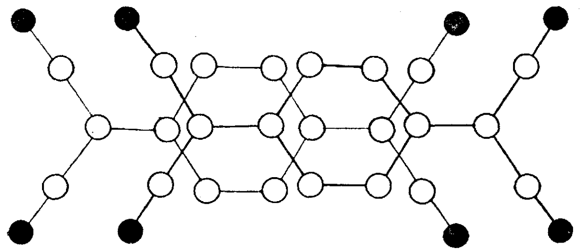

FIGURE 2 Projection of tcnq molecules A and B on the plane of the quinoid ring of molecule B

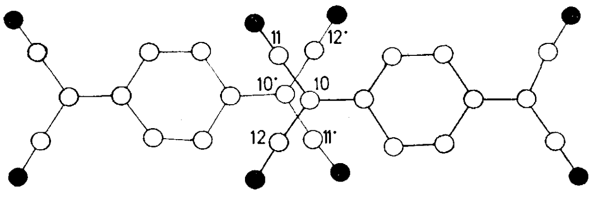

FIGURE 3 Projection of the tcnq molecules B and B′ on the plane of the quinoid ring of molecule B

TABLE 1

Atomic co-ordinates (Å), with standard deviations in parentheses

	X	*Y*	*Z*
(*a*) tcnq, Molecule A			
N(1)	2.684(5)	4.133(5)	−0.943(6)
N(2)	4.834(5)	0.269(5)	−0.378(6)
C(1)	−0.012(5)	1.461(5)	−0.273(6)
C(2)	1.254(5)	0.740(5)	−0.216(5)
C(3)	1.210(5)	−0.763(6)	0.053(5)
C(7)	2.504(5)	1.458(5)	−0.460(6)
C(8)	2.559(5)	2.942(6)	−0.713(6)
C(9)	3.780(5)	0.773(5)	−0.405(6)
H(1)	0.07(6)	2.30(6)	−0.41(7)
H(3)	2.08(7)	−1.35(7)	0.08(7)
(*b*) tcnq, Molecule B			
N(1)	5.081(5)	5.611(5)	−4.702(7)
N(2)	7.260(5)	1.683(6)	−4.313(6)
N(3)	−2.349(5)	1.223(6)	−3.343(6)
N(4)	−0.213(5)	−2.679(6)	−2.778(6)
C(1)	2.415(5)	2.910(5)	−3.913(6)
C(2)	3.680(5)	2.198(6)	−3.878(6)
C(3)	3.653(5)	0.700(6)	−3.600(6)
C(4)	2.470(5)	−0.006(6)	−3.391(6)
C(5)	1.195(5)	0.710(6)	−3.440(6)
C(6)	1.218(5)	2.220(6)	−3.709(6)
C(7)	4.927(5)	2.934(6)	−4.159(6)
C(8)	5.005(5)	4.428(6)	−4.466(6)
C(9)	6.216(5)	2.247(6)	−4.213(6)
C(10)	−0.031(5)	−0.006(5)	−3.244(6)
C(11)	−1.308(5)	0.687(5)	−3.300(6)
C(12)	−0.097(5)	−1.488(6)	−2.989(6)
H(1)	2.47(7)	3.79(7)	−4.08(7)
H(3)	4.46(7)	0.28(7)	−3.57(7)
H(4)	2.43(7)	−0.92(7)	−3.21(7)
H(6)	0.36(7)	2.83(7)	−3.77(7)
(*c*) nmp			
N(1)	7.440(5)	4.499(5)	−8.084(5)
N(2)	7.496(5)	1.582(5)	−7.547(5)
C(1)	5.016(6)	4.487(6)	−7.859(7)
C(2)	3.842(6)	3.776(7)	−7.645(7)
C(3)	3.847(6)	2.296(7)	−7.363(7)
C(4)	5.003(6)	1.540(7)	−7.309(7)
C(5)	6.264(5)	2.256(6)	−7.559(6)
C(6)	8.697(5)	2.319(6)	−7.820(6)
C(7)	9.998(6)	1.670(6)	−7.884(7)
C(8)	11.146(6)	2.489(7)	−8.171(7)
C(9)	11.084(6)	3.937(7)	−8.441(7)
C(10)	9.863(6)	4.610(7)	−8.386(7)
C(11)	8.616(5)	3.803(6)	−8.092(6)
C(12)	6.287(5)	3.755(6)	−7.840(6)
C(13)	7.506(6)	0.027(7)	−7.202(10)
H(1)	5.09(7)	5.46(7)	−8.02(8)
H(2)	2.98(7)	4.34(8)	−7.55(8)
H(3)	3.00(7)	1.92(8)	−7.27(8)
H(4)	4.96(7)	0.66(7)	−6.96(8)
H(7)	10.04(7)	0.69(7)	−7.69(8)
H(8)	12.07(7)	1.94(8)	−8.22(8)
H(9)	11.79(7)	4.42(7)	−8.48(8)
H(10)	9.75(7)	5.58(7)	−8.54(8)
H(13) 1	6.71(8)	−0.33(9)	−6.39(9)
H(13) 2	7.85(9)	−0.09(9)	−7.90(9)
H(13) 3	8.25(8)	−0.35(8)	−6.46(9)

The bond lengths and angles (Table 3) show that both A and B have an approximate *mmm* (D_{2h}) symmetry. The mean values of the chemically equivalent bond lengths (Table 3) are in excellent agreement between the two molecules and it is not possible in this case to

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[2] I. Goldberg and U. Shmueli, *Acta Cryst.*, 1973, **B29**, 421.

TABLE 2

Thermal parameters (Å² × 10³) in the form: exp $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$

(*a*) tcnq, Molecule A

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$U2_{13}$	$2U_{23}$	U_{iso}
N(1)	38(3)	44(3)	84(4)	−10(5)	−20(6)	−29(5)	
N(2)	30(3)	56(3)	78(4)	17(5)	−19(6)	−27(5)	
C(1)	20(2)	36(3)	35(3)	−7(4)	4(5)	−5(4)	
C(2)	19(2)	33(3)	35(3)	−7(4)	8(5)	−0(4)	
C(3)	17(2)	45(3)	32(3)	−5(4)	1(5)	−10(4)	
C(7)	18(2)	37(3)	41(3)	−6(4)	1(5)	−15(4)	
C(8)	15(2)	57(4)	44(3)	−12(5)	−11(5)	−8(4)	
C(9)	25(3)	32(3)	46(3)	−11(4)	−2(5)	−9(5)	
H(1) *	41						
H(3)	40						

(*b*) tcnq, Molecule B

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$U2_{13}$	$2U_{23}$	U_{iso}
N(1)	44(3)	47(3)	79(4)	−21(5)	−16(6)	−18(5)	
N(2)	27(3)	71(4)	65(4)	3(5)	−5(6)	−13(5)	
N(3)	31(3)	63(4)	81(4)	15(5)	−17(6)	−35(5)	
N(4)	36(3)	55(3)	74(4)	−15(5)	−17(6)	−22(5)	
C(1)	27(3)	34(3)	44(3)	−5(5)	1(5)	−10(5)	
C(2)	26(3)	43(3)	34(3)	−3(5)	−1(5)	−8(4)	
C(3)	20(3)	45(3)	44(3)	−8(4)	3(5)	−16(5)	
C(4)	34(3)	40(3)	36(3)	0(5)	−10(5)	−15(5)	
C(5)	20(2)	43(3)	38(3)	−6(4)	−3(5)	−13(4)	
C(6)	20(2)	42(3)	36(3)	3(4)	−2(5)	−10(4)	
C(7)	24(3)	50(3)	36(3)	−10(5)	−2(5)	−10(5)	
C(8)	20(3)	54(4)	48(3)	−21(5)	−5(6)	−14(5)	
C(9)	31(3)	44(3)	45(3)	−23(5)	−1(5)	−14(5)	
C(10)	21(2)	35(3)	42(3)	−2(4)	−8(5)	−17(4)	
C(11)	25(3)	35(3)	47(3)	−8(5)	−2(5)	−13(5)	
C(12)	16(2)	57(4)	42(3)	−22(5)	−2(5)	−18(4)	
H(1)	47						47
H(3)	51						51
H(4)	46						46
H(6)	45						45

(*c*) nmp

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$U2_{13}$	$2U_{23}$
N(1)	32(3)	45(3)	49(3)	−5(4)	−5(5)	−21(4)
N(2)	25(2)	36(3)	52(3)	−5(4)	−1(4)	−11(4)
C(1)	38(3)	53(4)	51(4)	21(5)	−12(6)	−30(5)
C(2)	29(3)	72(5)	61(4)	14(6)	−18(7)	−32(6)
C(3)	29(3)	68(4)	56(4)	−17(6)	−10(7)	−19(5)
C(4)	31(3)	56(4)	55(4)	−26(5)	−0(6)	−14(5)
C(5)	28(3)	48(3)	39(3)	−7(5)	−5(5)	−12(5)
C(6)	25(3)	39(3)	39(3)	−4(4)	2(5)	−10(4)
C(7)	28(3)	47(4)	66(4)	9(5)	−1(6)	−18(5)
C(8)	24(3)	74(5)	55(4)	−6(6)	−14(7)	−16(5)
C(9)	33(3)	66(4)	56(4)	−25(6)	−18(7)	−20(5)
C(10)	29(3)	59(4)	54(4)	−25(5)	−11(6)	−10(5)
C(11)	28(3)	50(3)	35(3)	3(5)	−3(5)	−16(5)
C(12)	31(3)	52(4)	33(3)	−4(5)	−6(5)	−21(5)
C(13)	33(3)	37(4)	134(7)	3(6)	−9(8)	−20(8)

H(1) *	57	H(9)	63
H(2)	66	H(10)	60
H(3)	64	H(13,1)	70
H(4)	57	H(13,2)	70
H(7)	58	H(13,3)	70
H(8)	62		

* U_{iso} for H atoms.

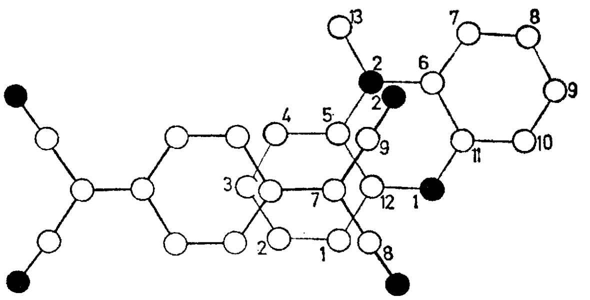
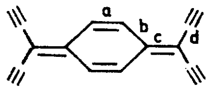


FIGURE 4 Projection of the tcnq molecule B and **nmp on the** plane of ring I of nmp

establish distinctions between neutral and charged molecules. Comparison with the Sunderesan and Wallwork[3] compilation of these averaged bond lengths in tcnq ^{0}, tcnq$^-$, and tcnq $^{1/2-}$ species shows that the values found here are in best agreement with those reported for tcnq $^{1/2-}$. However the differences, in terms of the standard deviations, between molecule A and neutral tcnq (centrosymmetric tcnq molecules are found to be neutral in similar structures[4,5] of 2 : 3 tcnq complexes in which triads are also observed) and between molecule

TABLE 3

Bond lengths (Å) and angles (°) in tcnq; means are given for assumed *mmm* (D_{2h}) symmetry. Standard deviations are in parentheses



Bond lengths

(*a*) tcnq, Molecule A

C(1)–C(3′)	1.356(7)	(a)
C(1)–C(2)	1.427(7)	
C(2)–C(3)	1.442(7)	
Mean	1.435	(b)
C(2)–C(7)	1.406(7)	(c)
C(7)–C(8)	1.427(8)	
C(7)–C(9)	1.420(8)	
Mean	1.424	(d)
N(1)–C(8)	1.147(8)	
N(2)–C(9)	1.146(8)	
Mean	1.147	
Mean C–H	0.92	

Bond angles

C(3′)–C(1)–C(2)	121.6(5)
C(2)–C(3)–C(1′)	121.3(5)
C(1)–C(2)–C(3)	117.1(5)
C(1)–C(2)–C(7)	121.9(5)
C(3)–C(2)–C(7)	121.0(5)
C(2)–C(7)–C(8)	121.5(5)
C(2)–C(7)–C(9)	123.4(5)
C(8)–C(7)–C(9)	115.0(5)
C(7)–C(8)–N(1)	176.1(6)
C(7)–C(9)–N(2)	177.4(6)

(*b*) tcnq, Molecule B

C(1)–C(6)	1.354(8)	
C(3)–C(4)	1.349(8)	
Mean	1.352	(a)
C(1)–C(2)	1.420(8)	
C(2)–C(3)	1.435(8)	
C(4)–C(5)	1.432(8)	
C(5)–C(6)	1.448(8)	
Mean	1.434	(b)
C(2)–C(7)	1.406(8)	
C(5)–C(10)	1.395(8)	
Mean	1.401	(c)
C(7)–C(8)	1.425(8)	
C(7)–C(9)	1.430(8)	
C(10)–C(11)	1.424(8)	
C(10)–C(12)	1.425(8)	
Mean	1.426	(d)
C(8)–N(1)	1.134(8)	
C(9)–N(2)	1.157(8)	
C(11)–N(3)	1.150(8)	
C(12)–N(4)	1.149(8)	
Mean	1.148	
Mean C–H	0.91	

C(1)–C(6)–C(5)	120.3(5)
C(6)–C(1)–C(2)	122.0(5)
C(2)–C(3)–C(4)	121.2(5)
C(3)–C(4)–C(5)	121.3(5)
C(1)–C(2)–C(3)	117.7(5)
C(4)–C(5)–C(6)	117.6(5)
C(1)–C(2)–C(7)	121.4(5)
C(3)–C(2)–C(7)	120.8(5)
C(6)–C(5)–C(10)	120.6(5)
C(4)–C(5)–C(10)	121.7(5)
C(2)–C(7)–C(8)	122.7(5)
C(2)–C(7)–C(9)	122.2(5)
C(5)–C(10)–C(11)	122.7(5)
C(5)–C(10)–C(12)	122.4(5)
C(8)–C(7)–C(9)	115.1(5)
C(11)–C(10)–C(12)	114.9(5)
C(7)–C(8)–N(1)	179.1(6)
C(7)–C(9)–N(2)	177.0(6)
C(10)–C(11)–N(3)	178,7(6)
C(10)–C(12)–N(4)	176.9(6)

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[3] T. Sundaresan and S. C. Wallwork, *Acta Cryst.*, 1972, **B28**, 2474.

[4] C. J. Fritchie, jun., and P. Arthur, jun., *Acta Cryst.*, 1966, **21**, 139.

[5] T. Sundaresan and S. C. Wallwork, *Acta Cryst.*, 1972, **B28**, 491.

TABLE 4

Bond lengths (Å) and bond angles (°) in nmp; means are for an assumed plane of symmetry. Standard deviations are in parentheses

Bond lengths	
N(1)–C(12)	1.336(8)
N(1)–C(11)	1.333(7)
Mean	1.335
N(2)–C(5)	1.373(7)
N(2)–C(6)	1.368(7)
Mean	1.371
C(5)–C(12)	1.436(8)
C(6)–C(11)	1.424(8)
Mean	1.430
C(1)–C(12)	1.433(8)
C(10)–C(11)	1.441(9)
Mean	1.437
C(4)–C(5)	1.413(9)
C(6)–C(7)	1.419(8)
Mean	1.416
C(1)–C(2)	1.342(9)
C(9)–C(10)	1.359(9)
Mean	1.351
C(3)–C(4)	1.349(9)
C(7)–C(8)	1.366(9)
Mean	1.358
C(2)–C(3)	1.416(9)
C(8)–C(9)	1.388(9)
Mean	1.402
N(2)–C(14)	1.483(9)
Mean C–H	0.94

Bond angles	
Ring I	
C(1)–C(2)–C(3)	120.2(6)
C(2)–C(3)–C(4)	122.7(6)
C(3)–C(4)–C(5)	118.7(6)
C(4)–C(5)–C(12)	119.8(5)
C(5)–C(12)–C(1)	118.5(5)
C(12)–C(1)–C(2)	120.1(6)
Ring II	
C(10)–C(9)–C(8)	121.5(6)
C(9)–C(8)–C(7)	122.1(6)
C(8)–C(7)–C(6)	118.8(6)
C(7)–C(6)–C(11)	119.8(5)
C(6)–C(11)–C(10)	118.9(5)
C(11)–C(10)–C(9)	119.0(6)
Ring II	
C(11)–N(1)–C(12)	117.6(5)
C(5)–N(2)–C(6)	121.3(5)
N(1)–C(12)–C(5)	123.0(5)
N(1)–C(11)–C(6)	123.6(5)
N(2)–C(5)–C(12)	117.5(5)
N(2)–C(6)–C(11)	123.6(6)
C(5)–N(2)–C(14)	118.9(5)
C(6)–N(2)–C(14)	120.1(5)

TABLE 5

Equations of some important planes in the structure and (in square brackets) distances (Å) of relevant atoms from them. Equations refer to an orthogonal X', Y', Z' system, calculated by:

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Plane (1): C(1)—(3), Molecule A

$$0.056\,56X' + 0.179\,28Y' + 0.982\,17Z' = 0$$

[C(1) −0.005, C(2) 0.005, C(3) −0.005, N(1) −0.001, N(2) −0.001, C(7) 0.022, C(8) 0.002, C(9) −0.006]

Plane (2): C(1)—(6), Molecule B

$$-0.057\,11X' - 0.176\,00Y' - 0.982\,72Z' = 3.144\,15$$

[C(1) −0.003, C(2) 0.004, C(3) −0.001, C(4) −0.003, C(5) 0.004, C(6) −0.001, N(1) 0.113, N(2) 0.280, N(3) 0.054, N(4) 0.049, C(7) 0.065, C(8) 0.153, C(9) 0.096, C(10) 0.021, C(11) 0.038, C(12) 0.037]

Plane (3): C(1)—(5), C(12) (Ring I)

$$-0.071\,52X' - 0.182\,91Y' - 0.980\,52Z' = 6.466\,96$$

[C(1) −0.009, C(2) 0.007, C(3) 0.001, C(4) −0.007, C(5) 0.004, C(12) 0.003]

Plane (4): C(6)—(11) (Ring II)

$$-0.119\,47X' - 0.178\,65Y' - 0.976\,65Z' = 6.164\,02$$

[C(6) −0.005, C(7) 0.005, C(8) −0.007, C(9) 0.009, C(10) −0.009, C(11) 0.007]

Plane (5): N(1), N(2), C(5), C(6), C(11), C(12) (Ring III)

$$-0.091\,67X' - 0.182\,96Y' - 0.978\,84Z' = 6.362\,62$$

[N(1) −0.010, N(2) −0.009, C(5) 0.005, C(6) 0.003, C(11) 0.006, C(12) 0.004]

B and tcnq$^-$ are not large, so we cannot be certain whether tcnq molecules in this compound are in fact all partially charged or whether tcnq^0 and tcnq$^-$ units are present.

The N-methylphenazinium ion [nmp]$^+$ is not planar, small but significant deviations are found from the least-squares plane calculated from the co-ordinates of the component atoms. However the three six-membered rings (I, II, and III in Figure 3) which can be considered in this molecule are planar (Table 5). The planes of the rings I and II form small angles of 1.6 and 1.2° with the heterocyclic ring III, so that the nmp$^+$ ion has a boat-like shape. The nmp$^+$ ion was found to be planar in the 1 : 1 complex with tcnq;[6] α-phenazine itself is planar[7] and in the 1 : 1 complex it forms with tcnq.[8] The NN'-dimethylphenazinium ion is not planar in the structure of the 1 : 1 complex of dmph–tcnq.[2] Departures from planarity are not quite the same in both cases and can probably be ascribed to intermolecular forces.

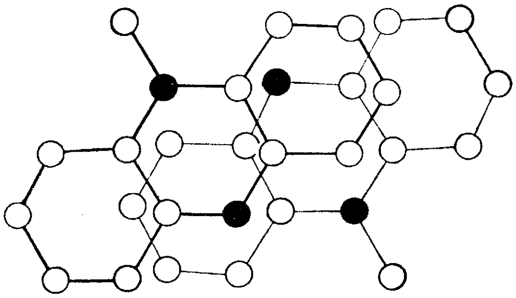

FIGURE 5 Projection of the nmp and nmp′ molecules on the plane of ring III of nmp (nmp′ is the molecule related to nmp through the centre of symmetry at ½, ½, − 1)

The nmp$^+$ ion has an approximate plane of symmetry which passes through the nitrogen atoms and the carbon atom of the methyl group. In Table 4 the bond lengths are averaged according to the approximate symmetry C_s (m); those in benzene rings I and II show no significant discrepancies from values for α-phenazine[7] and are similar to those found previously.[2,6,8] In heterocyclic ring III there are two different average values for the C–N bond length (**1.335** and **1.371** Å), corresponding to two different bonding situations. The first is comparable with the C–N bond (**1.345** Å) in phenazine[7] and in **1 : 1** phenazine–tcnq[8] (**1.344** Å). The second is comparable with the C–N bond (**1.386** Å) in 1 : 1 dmph–tcnq.[2] The values of **1.356** and **1.366** Å in [nmp]$^+$-[tcnq]$^-$,[6] which are between those found here, may be influenced by the disorder of the methyl group in the structure.

The methyl group is slightly (**0.06** Å) out of the plane of ring III. The N–C(M) bond length [**1.483**(9) Å] is in good agreement with literature values.[2,9] In the present complex, disorder in the methyl group between the two equivalent positions, as in 1 : 1 [nmp]$^+$[tcnq]$^-$, is

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unlikely since, if the material is completely pure, a short van der Waals contact of 2.37 Å between the disordered atoms would result. But, as in 1 : 1 [nmp]$^+$ [tcnq]$^-$, there is relatively large out-of-plane thermal motion in the methyl group; Fritchie gave two hypotheses [6] to explain this phenomenon, genuine thermal motion or a small (masked) disorder in the methyl group, and both apply here.

The projection of the structure down *b* (Figure 1) shows it to be composed of tcnq anions forming triads which repeat along the *c* axis; centrosymmetrically related pairs of cations fill the free space between the triads. In Figure 1 two neighbouring cells have been represented to show this arrangement more clearly.

The central tcnq of each triad is located on a crystallographic centre of symmetry. The planes of the quinoid rings of the tcnq units are essentially parallel. Within the triads two consecutive tcnq units overlap in the ring to external bond mode (Figure 2). Because of the nonplanarity of molecule B the separation distance between consecutive tcnq molecules is not well defined: within the triads the average value in the zone of overlap is *ca.* 3.15 Å. The interplanar distance between quinoid rings is 3.14 Å, the shortest found in complexes in which tcnq units form triads; it is a little longer than that [10] (3.07 Å) for [*NN'*-dimethylbenzimidazolium]$^+$[tcnq]$^-$ in which the tcnq units are arranged in isolated pairs, and slightly shorter [11] than (3.17 Å) in [ttf]$^+$[tcnq]$^-$ which crystallizes [12] with infinite stacks of tcnq. A similar distance (3.159 Å) with a different type of overlap has been found in the structure of Rb$^+$(tcnq)$^-$.[13]

The shortest C · · · C van der Waals contact between the units shown in Figure 3 is 3.35 Å, slightly shorter than the sum (3.40 Å) of the van der Waals radii.[14] The mean distance of C(10), C(11), and C(12) of molecule B from the plane defined by their symmetry-related atoms in B' is 3.26 Å.

In Figure 4 the distance from the plane of ring I to the C(2) and C(7) atoms of tcnq (B) are 3.38 and 3.34 Å and the distances of N(2) and C(9) from the plane of ring III are 3.18 and 3.27 Å, respectively. The type of overlap observed between the donor nmp and the acceptor tcnq, as well as the short distances, are common features in a variety of π–π charge-transfer molecular complexes.[15,16]

In Figure 5 the interplanar distance between rings III and III' is 3.42 Å. The distances of some of the carbon atoms of one of the molecules from the closest plane in the symmetry-related molecule are, in fact, rather small because of the folding of rings I and II with respect to ring III; the shortest distance is 3.36 Å.

The overlap situation as a whole is similar to that found in the structure of bis-(8-hydroxyquinolato)-copper(II)–tcnq molecular complex [17] in which overlap between donor–acceptor, donor–donor, and acceptor–acceptor components have been recognised [16] with the distinction that while in this compound the greatest interaction is observed between the donor and acceptor components, in our case it is between acceptor–acceptor tcnq molecules where the minimum distances and maximum overlap occur.

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