

## Crystal and Molecular Structure of the 1 : 2 Complex of Methyltriphenylphosphonium with $\alpha\alpha'\alpha'\alpha'$ -Tetracyano-3,7-naphthoquinodimethane, $(\text{Ph}_3\text{PMe})^+[(\text{tnap})_2]^-$

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Crystals of the title compound are triclinic with a non-reduced cell of  $a = 9.415(8)$ ,  $b = 14.606(12)$ , and  $c = 18.893(15)$  Å,  $\alpha = 68.07(7)$ ,  $\beta = 116.58(8)$ , and  $\gamma = 117.36(8)^\circ$ ,  $Z = 2$ . The structure was solved from a three-dimensional Patterson function and refined in space group  $P\bar{1}$ . The final  $R$  factor is 0.12 for 2 514 reflexions. The tnap molecules are arranged in groups of four (tetrads) almost parallel and equally spaced (3.30 Å). Two consecutive tetrads are 3.46 Å apart. The crystal structure is built up from thick layers parallel to the  $ab$  plane containing the tnap tetrads and separated from one another by the cations. Within the layers the tetrads of tnap are disposed in columns parallel to the  $b$  axis. In the cation the phosphorus atom is tetrahedrally co-ordinated with a  $\text{P}-\text{C}(sp^3)$  1.825 and mean  $\text{P}-\text{C}(sp^2)$  1.789 Å.

THE electrical and magnetic properties of some organo- and organometallic molecular complexes have been widely investigated, and it has been established that there is a close relation between the physical properties and the arrangement of the molecules of the compound in the solid state.<sup>1</sup>

Among molecular ion salts which crystallize in columns of infinite, flat, delocalised, ions are found the materials which show the lowest values of electrical resistivity. In this connection we have determined

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the crystal and molecular structure of the  $[\text{Ph}_3\text{PMe}]^+[(\text{tnap})_2]^-$  molecular complex which shows similar structural features to the related,<sup>2</sup>  $[\text{Ph}_3\text{PMe}]^+(\text{tcnq})_2^-$  ( $\text{tcnq} = \text{tetracyanoquinodimethane}$ ).

### EXPERIMENTAL

The crystals used, opaque to the visible light, did not show extinctions between crossed Nichols.

*Crystal Data.*— $\text{C}_{51}\text{H}_{30}\text{N}_8\text{P}$ ,  $M = 785.8$ . Triclinic,  $a =$

<sup>1</sup> R. P. Shibaeva and L. O. Atovmyan, *Zhur. Strukt. Khim.*, 1972, **13**, 546; J. Gaultier, C. Hauw, J. Jaud, P. Dupois, and J. Neel, First European Crystallographic Meeting, Bordeaux, 1973, Group C3; R. P. Shibaeva, L. O. Atovmyan, and V. F. Kaminski, *ibid.*

<sup>2</sup> A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc. (A)*, 1971, 2174.

9.415(8),  $b = 14.606(12)$ ,  $c = 18.893(15)$  Å,  $\alpha = 68.07(7)$ ,  $\beta = 116.58(8)$ ,  $\gamma = 117.36(8)^\circ$ ,  $U = 2017.0$ ,  $D_c = 1293$ ,  $Z = 2$ ,  $D_m = 1317$  kg m $^{-3}$ . Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å;  $\mu(\text{Mo-}K_\alpha) = 1.25$  cm $^{-1}$ . Space group  $P\bar{1}$  assumed.

Cell dimensions were obtained from zero-layer precession photographs and refined by a least-squares process. The reduced cell may be obtained by the transformation:

$$\begin{bmatrix} a_r \\ b_r \\ c_r \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} \text{ where } r \text{ means reduced.}$$

The intensities were collected round  $b$  on a Hilger and Watts linear diffractometer equipped with a graphite

vector between two molecules of tnap which, in the structure, are repeating in groups of four at the same distance and mutually parallel.

The structure was refined by a block-diagonal least-squares process until  $R$  was 0.12 and  $R'$  ( $= \Sigma w\Delta^2/\Sigma wF_o^2$ ) 0.02. Planes with  $|F_o| < 3|F_c|$  were omitted in the least squares and in the  $R'$  calculations. In the last cycle 34 reflexions were subject to this restriction. The weighting scheme used was:  $|F_o| \geq F_m$ ,  $w = 8/(F_m + |F_o| + C|F_o|^2)$ , and  $|F_o| < F_m$ ,  $w = [8/(F_m + |F_o| + C|F_o|^2)](F_o/F_m)^2$ , with  $C = 0.74$  and  $F_m = 8$ . Atomic scattering factors were taken from ref. 3.

Because of the relatively high value of  $R$ , a final difference synthesis was calculated when  $R$  was 0.13. This

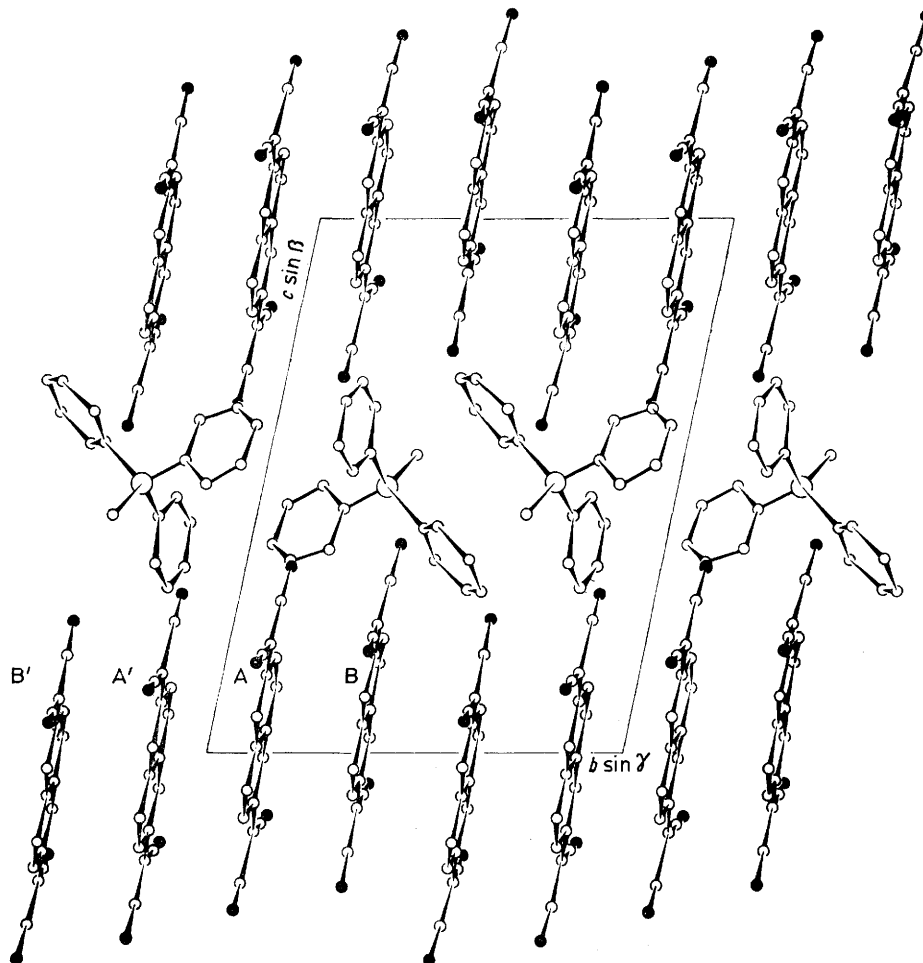


FIGURE 1 Projection of the structure down  $a$ , showing the relative positions in the cell of the molecules A and B, tnap molecules

monochromator, the crystal used had a cross-section of ca.  $0.35 \times 0.15$  mm $^2$ . 2514 reflexions whose intensities were  $>2\sigma$  were accepted and used throughout the analysis. No correction for absorption was applied.

**Structure Determination and Refinement.**—The structure was completely solved from a three-dimensional Patterson function after a failure of direct methods whose  $E$  map showed the largest peak in a position that would represent the location of one atom with the  $(2x, 2y, 2z)$  vector in correspondence with the largest peak of the Patterson synthesis, but this peak is, in fact, the intermolecular

showed peaks in the calculated positions of 27 hydrogen atoms but no sign of disorder in the structure was observed. The hydrogen atom positions were not used in further calculations.

#### RESULTS AND DISCUSSION

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21312

<sup>3</sup> 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, p. 202.

(18 pp., 1 microfiche).<sup>\*</sup> Tables 1 and 2 give final co-ordinates and thermal parameters, with their standard deviations, Tables 3 and 4, bond lengths and angles

TABLE 1

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

	X	Y	Z
P	6.148(4)	4.388(3)	9.377(3)
N(1A)	4.227(13)	2.567(14)	-2.288(14)
N(2A)	-0.434(15)	2.065(15)	-5.638(13)
N(3A)	0.439(14)	1.598(15)	6.586(12)
N(4A)	-4.186(13)	1.089(14)	3.157(14)
N(1B)	-4.134(14)	4.984(14)	3.582(13)
N(2B)	0.305(16)	5.267(17)	7.353(12)
N(3B)	-0.133(15)	5.698(14)	-4.819(12)
N(4B)	4.332(12)	5.850(13)	-1.108(13)
C(1A)	1.630(19)	2.024(13)	-0.242(14)
C(2A)	0.805(14)	1.851(13)	0.801(13)
C(3A)	1.740(17)	1.886(14)	2.336(15)
C(4A)	0.991(16)	1.713(15)	3.294(16)
C(5A)	-0.677(15)	1.559(13)	2.729(12)
C(6A)	-1.629(19)	1.492(15)	1.209(14)
C(7A)	-0.848(13)	1.664(13)	0.175(12)
C(8A)	-1.766(18)	1.626(15)	-1.358(15)
C(9A)	-1.015(16)	1.810(15)	-2.319(16)
C(10A)	0.679(15)	1.987(12)	-1.793(13)
C(11A)	1.350(13)	2.182(13)	-2.867(11)
C(12A)	2.949(13)	2.404(13)	-2.522(12)
C(13A)	0.330(14)	2.095(15)	-4.382(13)
C(14A)	-1.329(13)	1.407(12)	3.806(12)
C(15A)	-0.346(14)	1.491(14)	5.358(13)
C(16A)	-2.886(13)	1.246(13)	3.459(12)
C(1B)	-1.481(15)	5.122(13)	1.969(12)
C(2B)	-0.732(13)	5.253(12)	0.992(12)
C(3B)	-1.641(16)	5.254(13)	-0.626(13)
C(4B)	-0.916(15)	5.411(13)	-1.534(13)
C(5B)	0.761(13)	5.530(12)	-0.976(13)
C(6B)	1.674(15)	5.550(13)	0.566(12)
C(7B)	0.912(13)	5.378(12)	1.569(12)
C(8B)	1.821(15)	5.412(14)	3.147(13)
C(9B)	1.108(15)	5.292(15)	4.083(14)
C(10B)	-0.570(14)	5.173(12)	3.525(12)
C(11B)	-1.277(15)	5.054(14)	4.516(13)
C(12B)	-2.845(15)	5.010(15)	4.034(13)
C(13B)	-0.344(15)	5.156(17)	6.126(15)
C(14B)	1.442(13)	5.674(12)	-1.962(12)
C(15B)	0.552(13)	5.674(14)	-3.551(13)
C(16B)	3.069(13)	5.795(13)	-1.487(12)
C(1)	8.249(14)	5.219(15)	10.483(14)
C(2)	5.932(13)	2.989(12)	8.563(12)
C(3)	4.847(19)	2.765(19)	7.109(18)
C(4)	4.710(23)	1.559(20)	6.591(19)
C(5)	5.668(13)	0.741(15)	7.356(15)
C(6)	6.695(19)	0.973(22)	8.748(20)
C(7)	6.860(19)	2.094(19)	9.382(18)
C(8)	4.897(14)	3.545(12)	10.543(12)
C(9)	5.586(15)	3.411(13)	12.141(12)
C(10)	4.607(17)	2.730(15)	13.016(14)
C(11)	2.994(17)	2.277(16)	12.373(15)
C(12)	2.280(17)	2.395(17)	10.785(18)
C(13)	3.277(15)	3.024(16)	9.858(15)
C(14)	5.625(14)	5.958(13)	7.900(12)
C(15)	4.506(17)	6.464(16)	7.889(15)
C(16)	4.199(19)	7.768(16)	6.735(16)
C(17)	4.913(18)	8.437(16)	5.611(15)
C(18)	5.931(17)	7.915(13)	5.636(15)
C(19)	6.259(17)	6.611(17)	6.721(14)

with standard deviations, and Table 5 the equations of some important planes in the molecule and the deviations of relevant atoms from them. Figure 1 shows the projection of the structure down *a*, Figures 2—4, the types of overlap between pairs of tnap molecules, and Figure 5 the cation with the labelling of the atoms.

The tnap molecules are not planar, significant devi-

ations from the least-squares planes of the naphthoquinone ring within each molecule being found for

TABLE 2

Thermal parameters ( $\text{\AA}^2 \times 10^3$ ) used in the form:  $\exp -2\pi^2(h^2a^{*2}U_{11} + K^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hKa^*b^*U_{12} + 2Klb^*c^*U_{23} + 2hla^*c^*U_{13})$

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
P	59(2)	44(2)	38(2)	29(3)	-23(3)	-2(3)
N(1A)	77(8)	107(9)	109(9)	63(14)	-108(15)	-2(14)
N(2A)	105(9)	117(10)	78(8)	107(16)	-51(14)	-35(14)
N(3A)	93(9)	124(10)	65(7)	75(16)	-48(14)	-17(13)
N(4A)	73(7)	105(9)	106(9)	64(14)	-101(15)	-7(13)
N(1B)	90(8)	100(9)	97(8)	99(14)	-55(14)	23(13)
N(2B)	131(11)	169(13)	58(7)	146(20)	-54(16)	4(15)
N(3B)	122(10)	99(9)	64(7)	60(16)	-47(13)	5(14)
N(4B)	66(7)	89(8)	101(8)	53(13)	-52(13)	28(12)
C(1A)	153(13)	46(7)	60(8)	102(16)	-9(12)	63(16)
C(2A)	72(8)	47(7)	57(7)	47(13)	-14(12)	-30(12)
C(3A)	91(11)	55(8)	83(9)	59(15)	-36(14)	-34(16)
C(4A)	98(10)	71(9)	101(11)	68(16)	-14(15)	116(18)
C(5A)	85(9)	49(7)	54(7)	59(14)	-9(11)	36(13)
C(6A)	151(13)	54(8)	54(8)	101(17)	1(12)	51(16)
C(7A)	61(8)	47(7)	58(7)	55(13)	2(12)	-18(12)
C(8A)	114(12)	53(8)	78(9)	70(16)	-32(14)	-37(16)
C(9A)	93(10)	69(9)	96(10)	32(15)	-32(15)	104(16)
C(10A)	87(9)	34(7)	65(8)	45(13)	-5(11)	16(13)
C(11A)	73(8)	56(7)	33(6)	33(12)	-19(10)	35(11)
C(12A)	63(7)	67(8)	43(6)	71(13)	-36(11)	-19(11)
C(13A)	51(8)	79(9)	59(8)	58(14)	-23(13)	-16(12)
C(14A)	52(7)	48(7)	45(6)	33(11)	-28(10)	-9(11)
C(15A)	56(8)	72(8)	66(8)	61(13)	-25(13)	-2(12)
C(16A)	58(7)	61(8)	47(7)	37(12)	-38(12)	-18(11)
C(1B)	82(9)	49(7)	47(7)	41(13)	-15(11)	15(12)
C(2B)	64(8)	46(7)	44(6)	37(12)	-10(11)	2(11)
C(3B)	91(10)	47(7)	54(7)	31(14)	-13(12)	28(14)
C(4B)	76(9)	52(8)	60(8)	54(14)	-6(12)	36(13)
C(5B)	57(8)	42(7)	62(7)	28(12)	-8(11)	17(12)
C(6B)	86(9)	55(8)	49(7)	54(14)	-26(12)	15(13)
C(7B)	66(8)	33(6)	59(7)	36(12)	-31(11)	-39(12)
C(8B)	79(9)	59(8)	63(8)	45(14)	-36(13)	11(13)
C(9B)	76(9)	73(9)	66(8)	67(15)	-18(13)	27(14)
C(10B)	72(8)	44(7)	56(7)	27(12)	-12(11)	36(12)
C(11B)	76(9)	65(8)	51(7)	50(14)	-16(12)	17(13)
C(12B)	86(9)	74(9)	58(7)	73(15)	-38(13)	25(13)
C(13B)	67(9)	110(11)	66(9)	78(17)	-25(16)	22(14)
C(14B)	65(8)	44(7)	47(6)	25(12)	-24(11)	16(11)
C(15B)	57(8)	68(8)	52(7)	37(13)	-23(12)	-6(12)
C(16B)	58(7)	52(7)	45(6)	53(12)	-22(11)	-6(11)
C(1)	66(8)	70(9)	63(8)	1(14)	-60(13)	2(13)
C(2)	65(8)	48(6)	45(6)	60(12)	-17(11)	-14(11)
C(3)	113(12)	117(13)	111(12)	117(21)	-141(21)	-53(19)
C(4)	180(17)	131(14)	108(12)	206(27)	-176(22)	-110(23)
C(5)	131(12)	71(9)	77(9)	133(18)	-39(14)	27(17)
C(6)	106(12)	149(16)	135(14)	143(24)	-160(25)	-23(21)
C(7)	120(13)	115(13)	125(13)	147(22)	-178(21)	-68(20)
C(8)	70(8)	34(6)	62(7)	33(12)	-24(11)	12(12)
C(9)	98(9)	58(8)	42(6)	68(14)	-17(11)	26(13)
C(10)	112(11)	63(9)	72(8)	89(16)	-14(13)	57(16)
C(11)	83(10)	91(10)	78(9)	70(17)	10(16)	49(16)
C(12)	88(10)	86(11)	105(12)	66(17)	-19(18)	62(18)
C(13)	54(8)	83(10)	88(9)	37(14)	-35(15)	33(14)
C(14)	75(8)	48(7)	52(7)	78(13)	3(11)	7(12)
C(15)	109(11)	75(10)	77(9)	86(17)	-20(15)	29(16)
C(16)	127(12)	68(9)	88(10)	116(18)	14(15)	40(18)
C(17)	108(11)	72(10)	70(9)	66(17)	26(15)	40(16)
C(18)	92(11)	116(12)	59(9)	97(19)	55(16)	33(15)
C(19)	104(11)	92(10)	58(8)	91(18)	2(14)	47(15)

atoms N(3) (0.129 Å) in molecule A, and N(1) and N(2) in molecule B (0.192 and 0.219 Å). The departures

\* For details see Notice to Authors No. 7 in *J.C.S. Perkins II*, 1974, Index issue. This Supplementary Publication also contains the complete list of bond lengths and angles involving phosphorus in the cation, and mean values for the phenyl groups. The most important are listed in Table 4.

from planarity may be described (with one exception) as a small rotation of the cyano-groups about the C=C

TABLE 3

Bond lengths (Å) and bond angles (°) within the tnap molecules; means are given for an assumed  $2/m$  ( $C_{2h}$ ) symmetry. Standard deviations are in parentheses

(a) Bond lengths:	Molecule A	Mean	Molecule B	Mean
N(2)-C(12)	1.13(2)	1.14	1.15(2)	1.14
N(4)-C(16)	1.14(2)	1.14	1.13(2)	1.14
N(2)-C(13)	1.14(2)	1.14	1.12(2)	1.13
N(3)-C(15)	1.14(2)	1.14	1.14(2)	1.13
C(1)-C(2)	1.52(2)	1.50	1.42(2)	1.43
C(6)-C(7)	1.48(2)	1.50	1.43(2)	1.43
C(2)-C(3)	1.40(2)	1.40	1.46(2)	1.45
C(7)-C(8)	1.39(2)	1.40	1.43(2)	1.45
C(3)-C(4)	1.38(2)	1.38	1.33(2)	1.34
C(8)-C(9)	1.38(2)	1.38	1.35(2)	1.34
C(4)-C(5)	1.45(2)	1.46	1.47(2)	1.47
C(9)-C(10)	1.47(2)	1.46	1.47(2)	1.47
C(5)-C(14)	1.42(2)	1.42	1.36(2)	1.38
C(10)-C(11)	1.42(2)	1.42	1.40(2)	1.38
C(14)-C(15)	1.43(2)	1.42	1.43(2)	1.45
C(11)-C(13)	1.41(2)	1.42	1.47(2)	1.45
C(14)-C(16)	1.38(2)	1.39	1.43(2)	1.42
C(11)-C(12)	1.40(2)	1.39	1.40(2)	1.42
C(2)-C(7)	1.43(2)	1.39	1.44(2)	1.42

(b) Bond angles	Molecule A	Mean	Molecule B	Mean
C(1)-C(2)-C(7)	120(1)	119	121(1)	121
C(2)-C(7)-C(6)	118(1)	119	121(1)	121
C(2)-C(7)-C(8)	124(1)	124	120(1)	120
C(3)-C(2)-C(7)	124(1)	124	119(1)	120
C(7)-C(8)-C(9)	118(1)	118	119(1)	119
C(2)-C(3)-C(4)	117(1)	118	119(1)	119
C(8)-C(9)-C(10)	123(1)	123	122(1)	123
C(3)-C(4)-C(5)	122(1)	123	123(1)	123
C(9)-C(10)-C(11)	120(1)	121	119(1)	120
C(4)-C(5)-C(6)	122(1)	121	120(1)	120
C(10)-C(11)-C(12)	117(1)	117	119(1)	119
C(5)-C(6)-C(7)	117(1)	117	118(1)	119
C(9)-C(10)-C(11)	119(1)	118	121(1)	122
C(9)-C(10)-C(14)	117(1)	118	122(1)	122
C(1)-C(10)-C(11)	121(1)	121	120(1)	120
C(6)-C(5)-C(14)	121(1)	121	120(1)	120
C(10)-C(11)-C(12)	125(1)	125	124(1)	124
C(5)-C(14)-C(16)	124(1)	124	123(1)	124
C(10)-C(11)-C(13)	118(1)	120	121(1)	122
C(5)-C(14)-C(15)	121(1)	121	122(1)	122
C(12)-C(11)-C(13)	117(1)	116	115(1)	115
C(15)-C(14)-C(16)	115(1)	116	115(1)	115
N(1)-C(12)-C(11)	178(2)	179	177(2)	178
N(4)-C(16)-C(15)	179(2)	179	178(2)	178
N(2)-C(13)-C(11)	177(2)	178	176(2)	178
N(3)-C(15)-C(14)	178(2)	178	179(2)	178

TABLE 4

Bond lengths (Å) and bond angles (°) involving P in the cation  $[\text{Ph}_3\text{PMe}]^+$ , and mean values for the phenyl groups; standard deviations are in parentheses

(a) P-C( $sp^3$ )			
P-C(1)	1.825(15)	C(1)-P-C(2)	109.0(6)
(b) P-C( $sp^2$ )			
P-C(2)	1.755(13)	C(1)-P-C(8)	111.6(6)
P-C(8)	1.800(13)	C(1)-P-C(14)	106.0(6)
P-C(14)	1.804(13)	C(2)-P-C(8)	110.1(6)
Mean	1.786	C(2)-P-C(14)	110.4(6)
(c) Phenyl groups (mean values)			
C( $sp^2$ )-C( $sp^2$ )	1.387		
P-C-C	120.0		
C-C-C	119.9		

bonds which link these groups to the naphthoquinone ring as can be seen from the torsion angles around these C=C bonds (Table 6).

TABLE 5

Some important planes in the molecule, and (in square brackets) distances (Å) of relevant atoms from them. The planes are referred to an orthogonal system,  $X', Y', Z'$  where  $X' = X \sin \gamma + Z (\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$ ,  $Y' = Y + X \cos \gamma + Z \cos \alpha$ , and  $Z' = Z \{\sin^2 \alpha - [(\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma]^2\}^{1/2}$

Plane (1): C(1A)-(10A)	$0.336\ 85X' + 0.917\ 87Y' - 0.209\ 87Z' = 1.644\ 74$
	[C(1A) -0.000 16, C(2A) -0.000 41, C(3A) 0.000 81, C(4A) -0.008 47, C(5A) 0.019 02, C(6A) -0.008 87, C(7A) -0.004 00, C(8A) -0.010 38, C(9A) 0.014 27, C(10A) -0.002 15, N(1A) 0.067 70, N(2A) -0.004 78, N(3A) 0.129 11, N(4A) 0.041 06]
Plane (2): C(1B)-(10B)	$0.364\ 35X' + 0.909\ 11Y' - 0.201\ 93Z' = 4.907\ 06$
	[C(1B) -0.012 77, C(2B) -0.013 23, C(3B) -0.007 36, C(4B) 0.021 98, C(5B) -0.000 56, C(6B) 0.009 26, C(7B) -0.025 11, C(8B) -0.001 06, C(9B) 0.003 18, C(10B) 0.025 45, N(1B) 0.191 82, N(2B) 0.219 18, N(3B) 0.045 36, N(4B) -0.051 64]
Plane (3): C(2)-(7)	$-0.883\ 69X' - 0.209\ 60Y' + 0.418\ 52Z' = 0.100\ 27$
	[C(2) 0.00094, C(3) -0.022 13, C(4) 0.034 42, C(5) -0.023 65, C(6) 0.001 26, C(7) 0.009 38, P 0.016 48]
Plane (4): C(8)-(13)	$0.050\ 77X' + 0.993\ 15Y' - 0.105\ 25Z' = 4.270\ 96$
	[C(8) 0.010 52, C(9) 0.145 50, C(10) -0.028 20, C(11) 0.015 89, C(12) 0.008 70, C(13) -0.021 42, P 0.026 10]
Plane (5): C(14)-(19)	$0.609\ 35X' + 0.545\ 13Y' + 0.575\ 78Z' = 8.937\ 01$
	[C(14) 0.035 28, C(15) -0.019 51, C(16) 0.004 81, C(17) -0.005 16, C(18) 0.019 46, C(19) -0.034 83, P 0.095 74]

TABLE 6

Torsion angles (deg.)

Molecule A	Molecule B
C(1)-C(10)-C(11)-C(12)	-1(1)
C(9)-C(10)-C(11)-C(13)	4(1)
C(4)-C(5)-C(14)-C(15)	-3(1)
C(6)-C(5)-C(14)-C(16)	3(1)
C(1)-C(10)-C(11)-C(12)	5(1)
C(9)-C(10)-C(11)-C(13)	-5(1)
C(4)-C(5)-C(14)-C(15)	2(1)
C(6)-C(5)-C(14)-C(16)	-2(1)

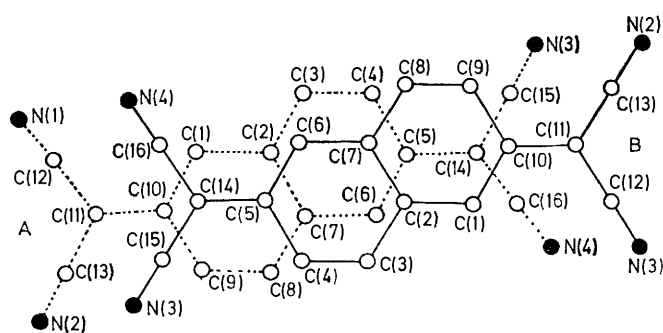


FIGURE 2 Projection of the tnap molecule B on the plane of molecule A showing the overlap between the two, and the labelling of the atoms

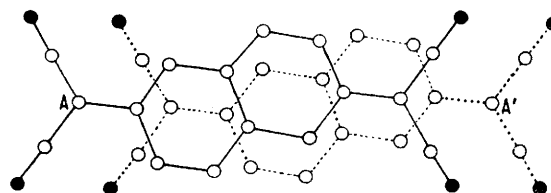


FIGURE 3 Projection of the tnap molecule A' on the plane of molecule A showing the overlap between the two

The least-squares planes of the naphthoquinone rings of molecules A and B form a small dihedral angle of  $1.7^\circ$ . Interplanar distances between molecules A and A'; and B and B' (Figure 1) are 3.29 and 3.46 Å. The distances from the ring atoms of one molecule of A to

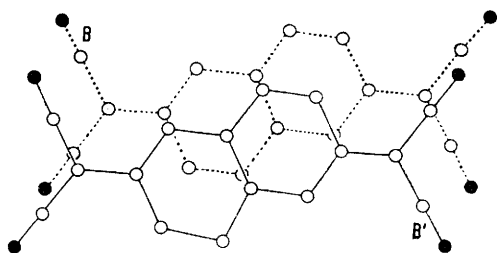


FIGURE 4 Projection of the tnap molecule B' on the plane of molecule B showing the overlap between the two

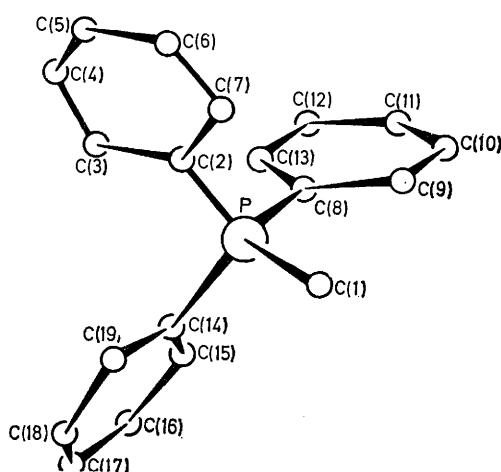


FIGURE 5 The cation  $[\text{Ph}_3\text{PMe}]^+$ , showing the labelling of the atoms

the plane of the B molecule vary from 3.23 to 3.37 Å; mean for all atoms 3.30 Å.

The tnap molecules are arranged in groups of four, almost parallel to each other and equally spaced. The straight line which would pass through their centres lies in the *bc* plane and forms an angle of *ca.*  $11^\circ$  with the *b* axis. The centre of gravity of each tetrad coincides with the origin of one cell. The smallest distance (B to B') between two consecutive tetrads is 3.46 Å.

Within the tetrads the ring to external bond type of overlap occurs between any two consecutive tnap molecules. The last molecule of one tetrad with the first of the next overlaps exclusively in the ring-to-ring manner (Figures 2–4).

<sup>4</sup> R. P. Shibaeva, L. O. Atovmyan, and L. P. Rozenberg, *Tetrahedron Letters*, 1971, 3303; H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *Acta Cryst.*, 1970, **B26**, 459; T. Sundaresan and J. C. Wallwork, *ibid.*, 1972, **B28**, pp. 2474, 1163.

<sup>5</sup> C. J. Fritchie, jun., *Acta Cryst.*, 1966, **20**, 107.

The crystal structure is built up of thick layers parallel to the *ab* plane containing the tnap tetrads and mutually separated by the cations. However, portions of the phenyl groups of the  $[\text{Ph}_3\text{PMe}]^+$  ions do penetrate into the idealized layers. Within the layers the tetrads are disposed in columns parallel to the *b* axis. Two neighbouring columns are related by the *a* translation.

Similar arrangements in tetrads have been found in several structures containing tcnq ions<sup>2,4</sup> in which the two different modes of overlap reported here also occur and in which the interplanar distances between the tcnq units within the tetrads vary from 3.16 to 3.45 Å, and the separation length between two consecutive tetrads is in the range from 3.30 to 3.62 Å.

From the bond lengths and angles in tnap (Table 3), and despite the non-planarity of the molecules, an approximate  $2/m$  ( $C_{2h}$ ) symmetry can be assigned to them, and in Table 3, means are given assuming such symmetry. Mean C=N bond lengths are 1.139 and 1.134 Å in molecules A and B, within the range reported for tcnq molecular complex structures.

The mean values of the equivalent carbon-carbon bond lengths in Table 3 for molecule B are somewhat closer to those which might be expected for 'neutral' tnap than are those of molecule A. However the differences between molecule A and 'neutral' tnap in terms of the standard deviations, are too small to be considered as significant.

In the cation the P-C(*sp*<sup>3</sup>) bond length [1.825(15) Å] is slightly, but not significantly longer than found<sup>5</sup> [1.786(8) Å] in  $[\text{MePh}_3\text{P}]^+\text{Ni}[\text{S}_2\text{C}_2(\text{CN})_2]^-$  and is comparable to that [1.800(4) Å] reported for  $[\text{MePh}_3\text{P}]^+[\text{tcnq}]^-$ .<sup>2</sup> Values of 1.81 and 1.80 Å for this bond have also been found in the structures of  $[\text{Ph}_3\text{PNEtPEtPh}_2]^+\text{I}^-$  (ref. 6) and  $[\text{Et}_3\text{P}]^+(\text{CS}_2)^-$  (ref. 7). The mean of the P-C(*sp*<sup>2</sup>) bond lengths (1.789 Å) does not differ significantly from those (1.799 and 1.792 Å) found for the structures with  $[\text{MePh}_3\text{P}]^+$  ion mentioned above.

The C-P-C bond angles are close to the tetrahedral value (mean  $109.45^\circ$ ) in agreement with that found in the structures of phosphonium ions.<sup>8</sup> The mean C-C bond length in the phenyl rings is 1.387 Å and mean C-C-C bond angle  $119.94^\circ$ .

The shortest contact between the tnap molecules and the phenyl groups is  $\text{N} \cdots \text{C}(\text{Ph})$  3.420 Å, which is 0.17 Å longer than the sum of the van der Waals radii.<sup>9</sup>

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<sup>6</sup> D. S. Payne, J. A. A. Mokuolu, and J. C. Speakman, *Chem. Comm.*, 1965, 599.

<sup>7</sup> T. N. Margulis and D. H. Templeton, *J. Chem. Phys.*, 1962, **36**, 2311.

<sup>8</sup> J. J. Daly, *Perspectives in Structural Chem.*, 1970, **3**, 165.

<sup>9</sup> A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.