phosphorus (Cruickshank, 1961) makes it difficult to compare the observed values with the P–O bond lengths in other compounds. For phosphorus–oxygen compounds P–O bond lengths ranging from 1·40 to 1·69 Å have been observed; the P–O bonds of the PO_2^- groups in $RbPO_3$, $Na_5P_3O_{10}$ and in $Na_4P_4O_{12} \cdot 4H_2O$ have a length of 1·49 Å (Cruickshank, 1961).

Inspection of Table 6 shows that the values of the valence angles in the metaphosphimates are closely related to the π character of the bonds. Relatively large values for O–P–O, N–P–N and P–N–P are found between relatively short bonds with large π character.

Calculations were carried out on the digital computer ZEBRA with programs devised by Dr D. W. Smits, Dr J. C. Schoone and Dr D. Rogers; the least-squares analysis was carried out by Dr J. S. Rollett on the Mercury Computer at Oxford. We wish to thank Professor E. H. Wiebenga for his interest throughout the course of this investigation and Professor N. L. Paddock for some interesting discussions. The work was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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The Crystal Structure of the 1:1 Complex of 7,7,8,8-Tetracyanoquinodimethan, and *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine

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The crystal is monoclinic, probably $C2/m$, with $a = 9 \cdot 88$, $b = 12 \cdot 71$, $c = 7 \cdot 72$ Å, $\beta = 97 \cdot 34°$, $Z = 2$.

The structure was deduced from a three-dimensional Patterson synthesis, and refined by block-diagonal least squares. The constituent molecules partially overlap each other with an interplanar spacing of 3·27 Å. Other intermolecular distances are consistent with van der Waals interaction.

Introduction

Many molecular complexes involving 7,7,8,8-tetracyanoquinodimethan (TCNQ) have been described by Melby, Harder, Hertler, Mahler, Benson & Mochel (1962). The crystal-structure analysis of the 1:1 complex with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was undertaken to assist further investigation (in the Division of Pure Chemistry) of its paramagnetic properties.

Experimental

Crystal data

Monoclinic

$a = 9 \cdot 88 \pm 0 \cdot 03$ Å

$b = 12 \cdot 71 \pm 0 \cdot 04$

$c = 97 \cdot 34 \pm 0 \cdot 05°$

$\beta = 7 \cdot 72 \pm 0 \cdot 03$

$V = 961 \cdot 5$ Å^3

Formula $C_{12}H_4N_4,C_{10}H_{16}N_2$; F.W. = 368·4
D_x (calculated density) = 1·27 ± 0·01 g.cm^{-3}
D_m(measured density) = 1·25 ± 0·02 g.cm^{-3}
$Z = 2$
$\mu = 7{\cdot}5$ cm^{-1} (Cu $K\alpha$)

Space group $C2$, Cm, or $C2/m$ (from precession and Weissenberg photographs. Systematic absences hkl for $h+k$ odd). $C2/m$ is consistent with the deduced structure. Molecular symmetry $2/m$

The black opaque crystals were grown in acetic acid solution. The predominant form was the prism {110}, elongated in the **c** direction. Crystals were frequently twinned on (100).

The specimen used, a regular solid of extreme dimensions 0·15 and 0·3 mm, was mounted about **b**. The unit-cell constants and the relative intensities were measured with the General Electric XRD 5 spectrogoniometer and goniostat, using a scintillation counter. Copper $K\alpha$ radiation was used, and reasonable monochromatization was achieved by means of a $K\beta$ filter and a reverter (pulse-height analyser). The moving-crystal moving-counter method of Furnas (1957) was used. Goniostat settings were precomputed. Of the 1122 accessible reflexions (those for which $2\theta \leq 165°$) significant counts were recorded for only 588. This low yield appears to be due to intense thermal motion in the structure, as very few reflexions were observed for which 2θ exceeded 100°. The range of observed intensities was about 1 to 10,000.

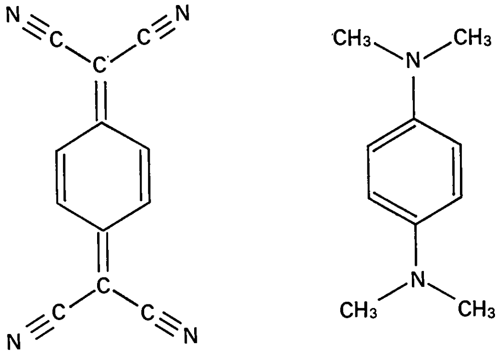

Fig. 1. 7,7,8,8-Tetracyanoquinodimethan (TCNQ) and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD).

Structure determination

Assuming the space group to be $C2/m$, the structural possibilities are very limited, and the trial structure was easily deduced from the three-dimensional Patterson synthesis. Refinement of the structure was accomplished by means of least-squares procedures, with the program of Mair (1963). This program uses the block-diagonal approximation with a 3 × 3 matrix for the position parameters, and a 6 × 6 matrix for the thermal parameters of each atom. The scale factor of observed structure amplitudes and the overall isotropic temperature factor are refined in a 2 × 2 matrix (Cruickshank, 1961). Schomaker's correction (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The weighting scheme used was $1/w = 1 + \{(F_o - 20)/32\}^2$. (Values of F_o range from 2·4 to 163·3). The scattering factor curves of Freeman (1959) were used throughout. No convergence acceleration factors were applied.

The thermal motion was assumed to be anisotropic for carbon and nitrogen atoms. Hydrogen atoms bonded to the respective rings were assigned reasonable positions and isotropic temperature factors, and their contributions were included in the structure-factor calculations. Attempts to locate and refine the parameters of the methyl hydrogen atoms were unsuccessful, however, perhaps because of some rotation of the group. At any rate these hydrogen atoms play no part in the refinement.

Table 1. *Final parameters*

$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0) \pm |x,y,z;\ x,\bar{y},z|$
Temperature factor $= \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$
B_i are the principal radii of the vibration ellipsoids

Atom	x × 10^4	y × 10^4	z × 10^4	β_{11} × 10^5	β_{22} × 10^5	β_{33} × 10^5	β_{12} × 10^5	β_{13} × 10^5	β_{23} × 10^5	B_1 Å^2	B_2 Å^2	B_3 Å^2
						TCNQ						
C(1)	0590	0952	−0383	1049	408	1611	−88	1219	50	2·23	2·77	5·10
C(2)	1224	0	−0779	934	483	1378	0	887	0	2·37	3·12	4·22
C(3)	2448	0	−1529	967	465	2037	0	1297	0	2·54	3·01	5·60
C(4)	3118	0941	−1890	915	643	1900	61	1236	−243	2·27	4·18	5·34
N(5)	3683	1705	−2199	1409	690	3657	−443	2224	−5	3·00	5·12	9·66
H(1)*	1012	1642	−0650	—	—	—	—	—	—	1·70	—	—
						TMPD						
C(6)	0593	0951	4622	1017	486	1737	−130	1014	51	2·62	3·34	4·90
C(7)	1229	0	4214	809	577	1300	0	868	0	2·04	3·73	3·88
N(8)	2407	0	3463	775	854	1629	0	988	0	2·12	4·42	5·52
C(9)	3127	0987	3168	1081	1043	2480	−963	1366	180	1·94	6·22	8·20
H(6)*	1028	1612	4354	—	—	—	—	—	—	2·00	—	—

* Parameters not refined.

A weakness of the analysis is of course the relatively low yield of observed reflexions, and it was felt that the unobserved reflexions ought also to play a part in the refinement. At a late stage, therefore, the structure factors for these reflexions were computed. Any reflexion for which F_c appreciably exceeded the estimated threshold value (there were, at most, 32 of these) was arbitrarily assigned a value for F_o of 60% of threshold, and included in the refinement. After 8 cycles the indicated coordinate shifts were reasonably small ($0{\cdot}5\sigma$ maximum, $0{\cdot}2\sigma$ average) and refinement was deemed to be complete. The final parameters are given in Table 1.

Assessment of results

A three-dimensional difference synthesis reveals no detail inconsistent with the proposed structure. Peaks as high as 0·4 e.Å^{-3} appear in the region of the methyl hydrogen atoms (not considered in the analysis), but elsewhere the residual density ranges from $-0{\cdot}21$ to 0·23 e.Å^{-3}. The estimated standard deviation of electron density is about 0·1 e.Å^{-3}.

The agreement between F_o and F_c is summarized in Table 2. Some of the more serious discrepancies result from failure to consider the inadequately resolved methyl hydrogen atoms. For example, the reflexion noted in category 4 is $11\bar{1}$, for which $F_o=6{\cdot}2$, and $F_c=-17{\cdot}9$. If the methyl hydrogen atoms are assumed to occupy the same space as the parent carbon atom (not a bad assumption for such a low-angle reflexion) F_c becomes $-1{\cdot}2$. More realistic assumptions regarding the distribution of these atoms (including that of free rotation about the N–CH$_3$ bond) can have only moderate effect on their contribution to this reflexion. The discrepancies (in category 3) for 111 and 001 can be rationalized in the same way. The agreement in general is reasonable, and there can be no doubt of the essential correctness of the proposed structure. The final agree-

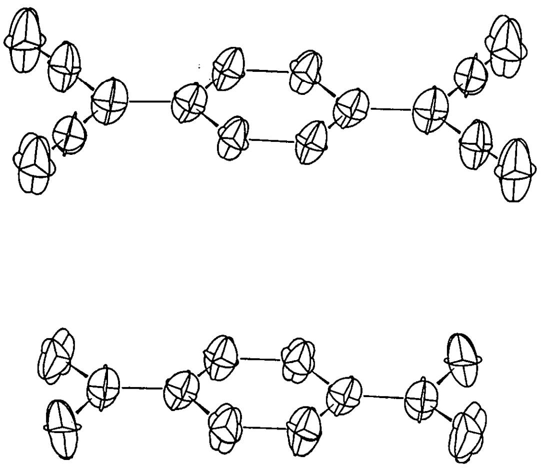
Fig. 2. The thermal motion ellipsoids.

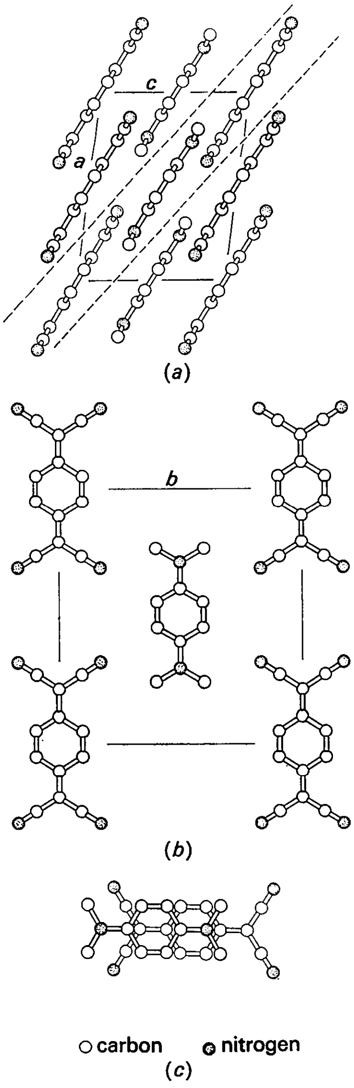

Fig. 3. (*a*) The structure, viewed along **b**. The heavily outlined molecules lie at $y=\frac{1}{2}$, and the rest at $y=0$. The dotted lines define a sheet of molecules. (*b*) A sheet of molecules in plan. (*c*) Overlapping molecules, viewed normal to their plane.

Table 2. *Agreement summary*

	Category	Number of reflexions Observed	Number of reflexions Unobserved
1	($\lvert\Delta F\rvert \le F_T$ or $\lvert\Delta F\rvert \le 0{\cdot}2F_o$)	575	495
2	($F_T < \lvert\Delta F\rvert \le 2F_T$ or $0{\cdot}2F_o < \lvert\Delta F\rvert \le 0{\cdot}4F_o$)	10	38
3	($2F_T < \lvert\Delta F\rvert \le 3F_T$)	2	1
4	($3F_T < \lvert\Delta F\rvert$) (see text)	1	

$\Delta F = \lvert F_o\rvert - \lvert F_c\rvert$
F_T = estimated minimum observable structure amplitude for reflexion concerned.

ment residual ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) is 0·083, for observed reflexions only. Copies of the table of F_o and F_c may be obtained by writing to the National Science Library, National Research Council, Ottawa, Canada, giving adequate reference to this paper.

The accuracy of the analysis is limited by intense thermal motion, resulting in a low yield of observed reflexions. The e.s.d.'s of coordinates range from 0·004 to 0·007 Å, and those of bonds from 0·006 to 0·010 Å.

The thermal motion ellipsoids are illustrated in Fig. 2. The most obvious mode of vibration is a rigid-body translation along a direction which makes an angle of about 70° with the molecular plane, and which is approximately normal to (101). Rigid-body libration does not appear to be important but there is certainly some non-rigid motion of the substituent groups in both molecules, resulting in intense thermal motion for N(5) and C(9). This behaviour obviously affects the apparent bond lengths in the groups. For example, if N(5) and C(9) are assumed to ride [in the nomenclature of Busing & Levy (1964)] on C(4) and N(8) respectively, the appropriate bond-length corrections are 0.037 and 0·023 Å. These corrections are probably overestimated, as the substituent groups undoubtedly have some rigidity. Nevertheless, they give a measure of the errors which can be expected in certain bond lengths.

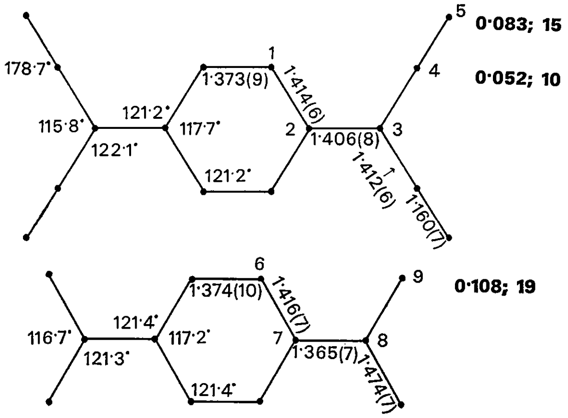

Fig. 4. Bond lengths and their e.s.d.'s (Å), and bond angles. Bold figures are the distances of certain atoms from the molecular planes, in Å, and in multiples of the corresponding e.s.d. of coordinates.

Discussion

Details of the crystal structure are illustrated in Fig. 3. The structure can be considered to consist of sheets of molecules as defined in Fig. 3(*a*, *b*). Adjacent sheets are held together by the interaction of unlike molecules which overlap each other as shown in Fig. 3(*c*), with an interplanar spacing of 3·27 Å. There are no significantly short contacts between non-overlapping molecules. The shortest such intermolecular distances are 3·45 and 3·47 Å, both for CH_3–N.

The structures of the constituent molecules are illustrated in Fig. 4. Both are essentially planar, although certain atoms [C(4) and N(5) in TCNQ; C(9) in TMPD] lie significantly out of the plane defined by the remaining atoms. It must be emphasized that the bond lengths in Fig. 4 have not been corrected for thermal motion, and that some of them [notably C(4)–N(5) and N(8)–C(9)] may be significantly underestimated. It is interesting that all the carbon–carbon distances in both molecules approach the aromatic value of 1·395 Å; it is clear that the nominal distribution of double and single bonds in TCNQ (Fig. 1) can be misleading.

The specimen material was prepared by Mr I. E. Scheffler of the Division of Pure Chemistry. Computations were performed on the IBM 1620 computer under the supervision of Dr F. R. Ahmed, using his programs and those of Dr G. A. Mair, and Mrs M. E. Pippy. Their assistance, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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