# Structure of $N,N,N',N'$-Tetramethyl-$p$-phenylenediamine

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**Abstract.** $C_{10}H_{16}N_2$, orthorhombic, $P2_12_12_1$, $a = 7\cdot947$ (5), $b = 20\cdot521$ (6), $c = 6\cdot136$ (2) Å, $Z = 4$, $D_c = 1\cdot09$, $D_m = 1\cdot08$ Mg m$^{-3}$. Diffraction data were obtained at 298 K. The structure was refined to $R = 0\cdot091$ for 783 reflections. The thermal motion was considerable as the temperature of measurement was rather close to the melting point of 324 K. The N atoms and the methyl C atoms deviate appreciably from the plane of the six-membered ring. No intermolecular distance shorter than a van der Waals contact was observed.

**Introduction.** We found that the photoconductivity of a $N,N,N',N'$-tetramethyl-$p$-phenylenediamine (TMPD) crystal exhibited significant magnetic-field dependence and are now carrying out a detailed investigation of the magnetic-field effects on photoconduction as well as those on delayed fluorescence. In connection with these studies, it was necessary to determine the crystal structure. The crystals of TMPD were obtained by sublimation in vacuum. A crystal was sealed in a thin-walled glass capillary for data collection since it is unstable in air. The space group was determined from Weissenberg photographs. The precise cell constants and intensity data were obtained with a Rigaku four-circle automatic diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation. 783 reflections with reliable intensities $[|F_o| \geq 3\sigma(F_o)]$ were obtained by measuring all reflections in the range $2\theta \leq 55°$. No absorption correction was made ($\mu = 0\cdot069$ mm$^{-1}$).

The structure was solved by the Patterson method, and refined by the full-matrix least-squares method. The final $R$ value was $0\cdot091$ for all observed reflections. The weighting scheme adopted was $w = 1/[\sigma^2(F_o) + (0\cdot10F_o)^2]^{1/2}$. The atomic scattering factors for C and N were taken from *International Tables for X-ray Crystallography* (1962), and that of H from Stewart, Davidson & Simpson (1965). Atomic coordinates are listed in Table 1.* Although the parameters for the H atoms were included in the above analysis, their refinement was not successful.

**Discussion.** Fig. 1 shows the arrangement of molecules in the crystal. TMPD molecules are closely packed to form a molecular layer parallel to the (010) plane. We can regard the crystal to be constructed by the stacking of these molecular layers. Although the intermolecular distances within the layer are shorter than those between neighboring layers, there is no intermolecular distance shorter than a usual van der Waals contact.

The equation of the plane of the six-membered ring of a TMPD molecule is $0\cdot7711x + 0\cdot2979y - 0\cdot5628z$

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34485 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters* ($\times 10^4$)

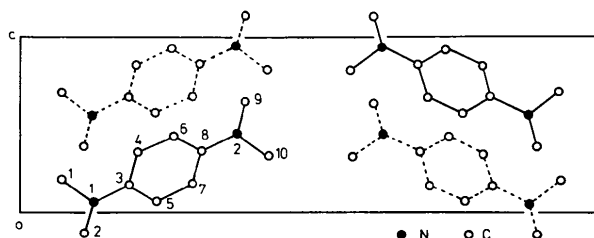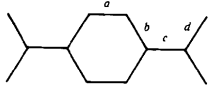| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(1) | 2555 (17) | 722 (5) | 1878 (24) |
| C(2) | 894 (15) | 1109 (4) | −1251 (18) |
| N(1) | 2030 (9) | 1266 (3) | 546 (13) |
| C(3) | 1888 (9) | 1886 (3) | 1555 (15) |
| C(4) | 2784 (10) | 2026 (4) | 3447 (14) |
| C(5) | 909 (9) | 2375 (4) | 612 (14) |
| C(6) | 2741 (9) | 2652 (3) | 4345 (15) |
| C(7) | 801 (10) | 2978 (3) | 1605 (16) |
| C(8) | 1713 (9) | 3143 (3) | 3477 (15) |
| N(2) | 1556 (9) | 3751 (3) | 4513 (14) |
| C(9) | 2633 (15) | 3898 (6) | 6275 (25) |
| C(10) | 1048 (24) | 4292 (4) | 3184 (21) |



Fig. 1. A projection of the molecular arrangement along the $a$ axis.

$= 1 \cdot 775$ (where $x$, $y$ and $z$ are in Å). The deviations of the atoms from this plane are: C(3) $-0 \cdot 002$, C(4) $-0 \cdot 021$, C(5) $0 \cdot 022$, C(6) $0 \cdot 025$, C(7) $-0 \cdot 018$, C(8) $-0 \cdot 005$, C(1) $-0 \cdot 417$, C(2) $-0 \cdot 117$, N(1) $0 \cdot 054$, N(2) $-0 \cdot 088$, C(9) $0 \cdot 054$, C(10) $0 \cdot 039$ Å. Molecular dimensions are shown in Fig. 2. TMPD is a strong electron donor and forms charge-transfer or ionic complexes with various electron acceptors. The bond lengths in the TMPD moiety in these complexes are compared in Table 2 with the bond lengths of the TMPD molecule determined by the present study. In all cases, we have averaged the observed bond distances, assuming $D_{2h}$ symmetry for the molecular geometry of TMPD. The bond lengths in TMPD and TMPD–TCNB (group $A$) are very similar except for the $N-CH_3$ bond length. This is expected since TMPD–TCNB is a charge-transfer complex with an essentially non-ionic ground state. The reason for the significant difference in $N-CH_3$ distances is not clear. It may be due to the large thermal motion of the methyl group in the TMPD crystal. The bond distances in ionic complexes (group $B$) are appreciably different from those in the TMPD crystal and the TMPD–TCNB complex, clearly indicating the quinoid character of the $TMPD^+$ ion. This change of molecular geometry on going from the TMPD neutral molecule to the $TMPD^+$ ion is consistent with the results of theoretical predictions (de Boer & Vos, 1972a).
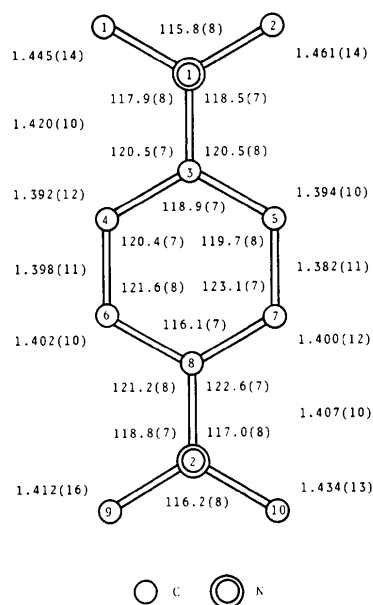


Fig. 2. Bond lengths (Å) and angles (°) in TMPD.

The computer used was a HITAC 8700/8800 at the Computer Center, University of Tokyo, with the UNICS (1967) system of programs.

Table 2. *Bond lengths* (Å) *of TMPD and TMPD moieties in various complexes* (*TCNB: tetracyano-benzene*; *TCNQ: tetracyano-p-quinodimethane*)



| | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|
| **Group A** | | | | |
| TMPD[1] | 1·390 | 1·397 | 1·414 | 1·438 |
| TMPD–TCNB[2] | 1·377 | 1·380 | 1·430 | 1·488 |
| **Group B** | | | | |
| TMPD$^+$ClO$_4^-$ (room temperature)[3] | 1·361 | 1·415 | 1·355 | 1·452 |
| TMPD$^+$ClO$_4^-$ (low temperature)[4] | 1·365 | 1·428 | 1·345 | 1·464 |
| TMPD$^+$TCNQ$^-$ [5] | 1·374 | 1·416 | 1·365 | 1·474 |
| TMPD$^+$TCNQ$_2^-$ [6] | 1·367 | 1·418 | 1·373 | 1·459 |
| TMPD$^+$I$^-$ [7] | 1·361 | 1·422 | 1·344 | 1·454 |
| TMPD$^+$chloranil$^-$ [8] | 1·374 | 1·403 | 1·357 | 1·465 |

References: (1) This work, (2) Ohashi, Iwasaki & Saito (1967), (3) de Boer & Vos (1972a), (4) de Boer & Vos (1972b), (5) Hanson (1965), (6) Hanson (1968), (7) de Boer & Vos (1968a), (8) de Boer & Vos (1968b).

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