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***N,N,N',N'*-Tetramethylbenzidine–Chloranil (1:1)**

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Abstract. Triclinic, $P\bar{1}$, $a=8.427$ (5), $b=8.938$ (3), $c=7.932$ (5) Å, $\alpha=93.36$ (4), $\beta=109.60$ (4), $\gamma=72.22$ (4)°, $C_{16}H_{20}N_2 \cdot C_6Cl_4O_2$, $Z=1$, $D_x=1.51$, $D_m=1.51$ g cm⁻³. Crystals were grown in cyclohexane solution. The TMBD molecule in this complex has a planar structure. TMBD and chloranil are stacked alternately along the c axis, making their molecular planes almost parallel to each other. The mean separation of the molecular plane is 3.29 Å.

Introduction. The (1:1) complex gives purple-black, needle-shaped crystals. The crystal chosen was less than 0.5 mm across, $\mu=5.94$ cm⁻¹ (Mo $K\alpha$). The cell

constants were determined by least-squares calculation based on 13 diffraction lines measured with a Geiger-flex diffractometer. Quartz powder was used as the internal standard. Since no systematic absences were observed, the space group is either $P\bar{1}$ or $P1$. The intensities were measured on a Rigaku-Denki computer-controlled four-circle automatic single-crystal diffractometer, with Mo $K\alpha$ radiation and a crystal monochromator. The intensities were corrected for background, Lorentz and polarization effects. All reflexions with $2\theta \leq 50$ were measured. 973 independent reflexions for which $|F_o| \leq 3\sigma(F_o)$ were obtained. The space group $P\bar{1}$ was tentatively assumed and this was later verified by structure-factor calculations. The

Table 1. Atomic coordinates and thermal parameters

(a) Atomic coordinates in fractions of cell edges and their standard deviations (10^{-3} Å).

Chloranil	X	Y	Z
Cl(1)	0.3379 (3)	0.1069 (3)	0.0887 (4)
Cl(2)	-0.0109 (3)	-0.3122 (3)	-0.1988 (3)
C(1)	0.1515 (10)	0.0522 (10)	0.0458 (11)
C(2)	-0.0141 (11)	-0.1396 (10)	-0.0915 (11)
C(3)	0.1485 (10)	-0.0944 (10)	-0.0478 (11)
O(1)	0.2795 (7)	-0.1765 (8)	-0.0813 (8)
TMBD	X	Y	Z
C(4)	0.0653 (10)	-0.0562 (10)	0.4696 (10)
C(5)	0.2338 (10)	-0.0447 (11)	0.5036 (11)
C(6)	0.3621 (12)	-0.1502 (11)	0.4473 (12)
C(7)	0.3306 (11)	-0.2831 (10)	0.3530 (11)
C(8)	0.1631 (10)	-0.2998 (10)	0.3235 (11)
C(9)	0.0382 (9)	-0.1903 (10)	0.3798 (11)
C(10)	0.6245 (13)	-0.3631 (12)	0.3162 (13)
C(11)	0.4211 (13)	-0.5270 (11)	0.2064 (14)
N(1)	0.4575 (9)	-0.3899 (8)	0.2978 (9)

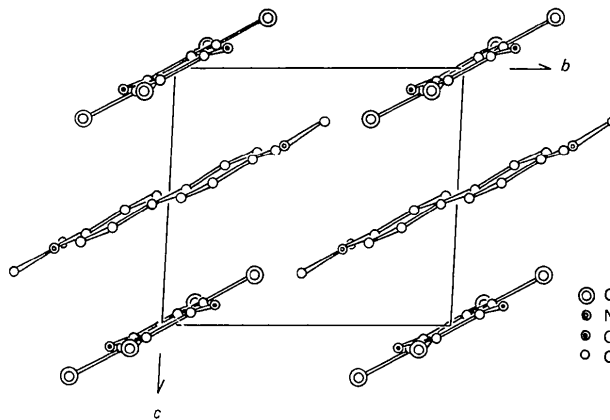


Fig. 1. Projection of the molecular arrangement onto the (100) plane.

Table 1 (cont.)

(b) Thermal parameters. The β 's are those used in the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

Chloranil	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0.01705	0.02057	0.03622	-0.01839	0.02600	-0.01736
Cl(2)	0.02173	0.01396	0.03244	-0.01348	0.02221	-0.02190
C(1)	0.01375	0.01369	0.02175	-0.01368	0.01349	-0.00721
C(2)	0.01736	0.00876	0.02411	-0.00593	0.02112	-0.01229
C(3)	0.01143	0.01219	0.02585	-0.00149	0.01685	-0.01150
O(1)	0.01319	0.02103	0.03094	-0.00386	0.02362	-0.02201
TMBD	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(4)	0.01452	0.01258	0.01561	-0.00587	0.01521	-0.00284
C(5)	0.01063	0.01420	0.02289	-0.01039	0.01030	-0.01487
C(6)	0.01801	0.01551	0.02940	-0.01415	0.02381	-0.01491
C(7)	0.01921	0.01148	0.02031	-0.00942	0.02537	-0.00693
C(8)	0.01224	0.00917	0.02765	-0.00917	0.01352	-0.00884
C(9)	0.00624	0.01431	0.02883	-0.00572	0.01646	-0.01290
C(10)	0.02031	0.02175	0.02878	-0.01197	0.02693	-0.01776
C(11)	0.02423	0.01402	0.03830	-0.00737	0.03840	-0.02520
N(1)	0.01445	0.01341	0.03024	-0.00496	0.02832	-0.01689

structure was solved by the Patterson method and was refined by block-diagonal least squares to give a conventional R index of 0.093. The weighting scheme was as follows: $w = 1/[\sigma^2(F_o) + (cF_o)^2]^{1/2}$, where σ is the standard deviation estimated from the counting statistics and c is the parameter which accounts for other types of error (Grant, Killean & Lawrence, 1969). After a few least-squares calculations, the value of c was determined as 0.075. At the same time least-squares calculations with space group $P1$ were carried out. The R value became 0.11. The atomic coordinates did not

change significantly, but the standard deviations in the atomic parameters increased. The usual $(F_o - F_c)$ synthesis with space group $P1$, including hydrogen atoms, did not show any anomalous peaks. The space group $P1$ was therefore adopted.*

Final parameters with their standard deviations are given in Table 1. Although the values of the C-H bond lengths are in a reasonable range, 0.84–1.18 Å (mean value 0.97 Å), we have omitted the hydrogen atoms from Table 1 because of the considerably large standard deviations in their positional parameters. Fig. 1 shows the arrangement of the molecules in the crystal. The equations of the molecular planes of TMBD and chloranil were calculated by the least-squares method. The equations are

$$-0.1009X - 0.4905Y + 0.8302Z = 3.293$$

for TMBD (without the methyl groups) and

$$-0.0634X - 0.4603Y + 0.8318Z = 0.0$$

for chloranil, where X , Y and Z are coordinates in Å with respect to the crystal axes a , b and c . The planes of TMBD and chloranil make an angle of about 2.6° . The relative orientation of TMBD and chloranil is shown in Fig. 2, with the bond lengths and angles.

Discussion. We have already reported the structure of the TMBD-chloranil (2:1) complex (Yakushi, Ikemoto & Kuroda, 1971). We determined the crystal structure of the (1:1) complex in order to compare, in particular, the relative orientations of the donor and acceptor molecules in the (2:1) and (1:1) complexes. In the polarized absorption spectra of this complex, it has been found that the direction of the transition moment of the second charge-transfer band is nearly perpendicular to that of the first. We have carried out a theoretical investigation of the electronic transitions of the TMBD-chloranil (2:1) and (1:1) complexes, and have found that the difference in the polarizations of the second charge-transfer bands can be understood on the basis of these molecular arrangements.

The HITAC 5020E computer at the Computer Centre, University of Tokyo, was used with the UNICS (1967) programs.

* A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30190 (6 pp.). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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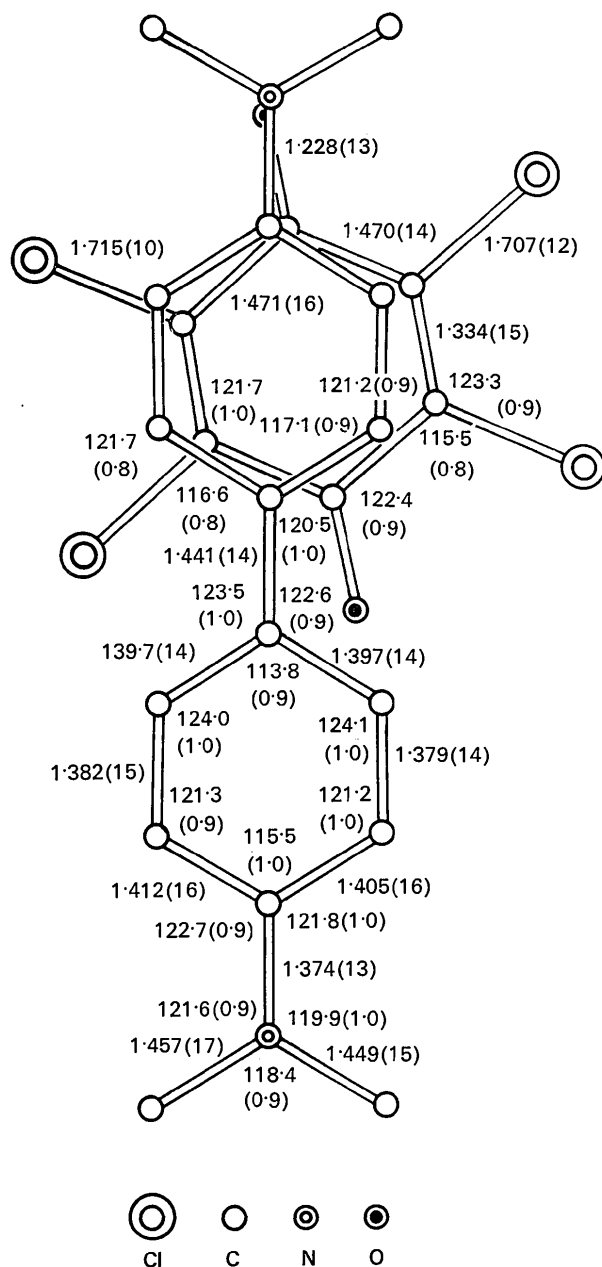


Fig. 2. Bond lengths (Å), bond angles ($^\circ$) and their e.s.d.'s, and relative orientation of TMBD with respect to chloranil found in the crystal.