

was 1.520 ± 0.0034 Å and for α -D-glucose monohydrate (Rogers & Haugh, 1968) 1.524 ± 0.0034 Å.

On the basis of the *t* test (Fisher & Yates, 1953), it can be seen that the C(4)–C(5) and C(5)–C(6) bond lengths are significantly different from each other and from all the other C–C bond lengths. In α -D-glucose monohydrate and in β -D-glucose, the C(5)–C(6) bond length is probably significantly smaller than the other C–C bond lengths but C(4)–C(5) is not.

The average C–O bond length, excluding the carbon atoms bonded to the oxygen atom in the ring and C(1)–O(1), is 1.424 ± 0.003 Å compared with 1.425 ± 0.003 Å for both β -D-glucose and α -D-glucose monohydrate. As with these two sugars, the C(1)–O(1) bond length in α -rhamnose monohydrate, 1.401 ± 0.003 Å, was significantly different from the other C–O bond lengths.

The C(5)–O(5) bond length differs significantly from all other C–O bond lengths while C(1)–O(5) does not. It has been noted by Snyder, Rosenstein, Kim & Jeffrey (1970) that in sugars where an oxygen atom is bonded to the C(6) atom in a direction parallel to the C(4)–C(5) bond as in α -D-glucose (Brown & Levy, 1965), no significant difference exists between bond lengths C(5)–O(5) and C(1)–O(5) but when the oxygen atom is bonded in a direction anti-parallel to the C(5)–H(5) bond, as in α -D-glucose monohydrate, a significant difference does exist. This difference can now be seen to exist when only hydrogen atoms are bonded to C(6).

The bond lengths and angles differ insignificantly from those quoted by McGeachin & Beevers, the largest discrepancy being 0.049 Å in the C(2)–O(2) bond which cannot now be considered significantly different from C(3)–O(3) and C(4)–O(4). The positions of the hydrogen atoms are close to those given by McGeachin & Bee-

vers with the exception of H(6) in the methyl group. The average C–H bond length for the carbon atoms in the ring was 0.96 Å and for the methyl group was 1.06 Å. The hydrogen bond distances are listed in Table 5 along with the O–H–O bond angles.

Table 5. *Hydrogen bond lengths and angles*

| Symmetry code | | | | | | |
|---------------|---------------|-----------------------------|------------------------|------------------------|-----------|------------|
| <i>a</i> | <i>x</i> , | <i>y</i> , | <i>z</i> +1 | | | |
| <i>b</i> | 1– <i>x</i> , | $\frac{1}{2}$ + <i>y</i> , | 1– <i>z</i> | | | |
| <i>c</i> | – <i>x</i> , | $-\frac{1}{2}$ + <i>y</i> , | – <i>z</i> | | | |
| <i>d</i> | <i>x</i> , | 1+ <i>y</i> , | <i>z</i> | | | |
| <i>e</i> | – <i>x</i> , | $-\frac{1}{2}$ + <i>y</i> , | – <i>z</i> +1 | | | |
| <i>i</i> | <i>j</i> | <i>k</i> | <i>D</i> (<i>ij</i>) | <i>D</i> (<i>jk</i>) | <i>ik</i> | <i>ijk</i> |
| O(3) | H(9) | O(5 <i>a</i>) | 0.91 Å | 2.07 Å | 2.81 Å | 138 |
| O(4) | H(10) | O(6) | 0.85 | 1.94 | 2.78 | 167 |
| O(6) | H(11) | O(4 <i>b</i>) | 0.83 | 1.93 | 2.74 | 168 |
| O(1) | H(12) | O(2 <i>c</i>) | 0.89 | 1.84 | 2.71 | 163 |
| O(6) | H(13) | O(1 <i>d</i>) | 0.87 | 2.10 | 2.91 | 157 |
| O(2) | H(14) | O(6 <i>e</i>) | 0.89 | 1.89 | 2.78 | 174 |

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The Crystal and Molecular Structure of the *N,N,N',N'*-Tetramethylbenzidine–Chloranil (2:1) Molecular Complex

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Crystals of the (2:1) complex of *N,N,N',N'*-tetramethylbenzidine (TMBD) and chloranil are monoclinic, space group *P2₁/a*, with *a* = 16.498, *b* = 8.413, *c* = 14.149 Å, β = 117.42°, *Z* = 2. The structure was solved directly by the symbolic-addition procedure, and was refined by the block-diagonal least-squares method. In this complex, the crystal structure comprises distinct molecular groups where one chloranil molecule is sandwiched between two TMBD molecules. The chloranil molecule is situated on one of the two benzene rings of TMBD; the other benzene ring is appreciably twisted around the bond connecting the two benzene rings. The dihedral angle between the two benzene rings in TMBD is 30.8°.

Introduction

The electronic spectra of single-crystals of molecular complexes that involve *N,N,N',N'*-tetramethylben-

zidine (TMBD) or benzidine (BD) as electron donor have been studied in our laboratory (Amano, Kuroda & Akamoto, 1969). Results showed that these molecular complexes take a non-ionic structure in the ground

state, although both TMBD and BD have a considerably low ionization potential; also their spectra comprise absorption bands associated with intramolecular transitions in the constituent neutral molecules and absorption bands associated with the charge transfer from the donor to the acceptor. We have found that TMBD and chloranil form a (2:1) complex as well as a (1:1) complex. In the (1:1) complex, the second charge transfer band is polarized almost perpendicular to the first one, although both are usually expected to be polarized in the same direction. In the (2:1) complex, the first and second charge transfer bands are found to have the same polarization direction. Accordingly, we attempted to determine the crystal structure of these (2:1) and (1:1) complexes. This paper reports on the crystal structure of the (2:1) complex. The structure of the (1:1) complex will be reported in a subsequent paper.

Experimental

Purple-black, needle-shaped crystals were obtained by slowly evaporating the solvent from acetone solution. The crystals are very stable and can be kept in air for a long period without any decomposition. The mole ratio of TMBD and chloranil in the crystals was 2:1, determined by chemical analysis. Crystals were elongated along the *b* axis.

The cell dimensions were obtained from zero-layer Weissenberg photographs (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) about the *b* and *c* axes. Powder diffraction lines of copper were superposed on the films for calibration purposes.

Crystal data

$$a = 16.498 \pm 0.012 \text{ \AA}$$

$$b = 8.413 \pm 0.003$$

$$c = 14.149 \pm 0.012$$

$$\beta = 117.42 \pm 0.06^\circ$$

$$V = 1743.2 \pm 1.8 \text{ \AA}^3$$

Formula $2(\text{C}_{16}\text{H}_{20}\text{N}_2) \cdot \text{C}_6\text{Cl}_4\text{O}_2$; F.W. 726

D_x (calculated density) = 1.38 g.cm^{-3}

D_m (measured density) = 1.37 g.cm^{-3}

$Z = 2$

$\mu = 36.0 \text{ cm}^{-1}$ (Cu $K\alpha$)

Space group $P2_1/a$ (from Weissenberg photographs)
(Absent spectra $h0l$ when h is odd, $0k0$ when k is odd)

A set of intensity data was obtained up to the 6th layer around the *b* axis and to the 10th layer around the *c* axis. The intensities were measured visually from multi-film Weissenberg photographs. Ni-filtered Cu $K\alpha$ radiation was used. No correction was made for absorption. Corrections for the Lorentz and polarization factors were made in the usual way.

The data were placed on the same relative scale by the method of Rollett & Sparks (1960). In all, 1886 non-zero independent reflexions from 4145 possible reflexions were obtained.

Structure determination and refinement

The structure was solved by the symbolic-addition procedure (Karle & Karle, 1963, 1966).

An absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's statistical method. The normalized structure factors, E_h 's, were computed by the equation

$$E_h^2 = F_h^2 / \varepsilon \sum_{j=1}^N f_{jh}^2,$$

where ε is unity for all reflexions other than $h0l$ and $0k0$ for which $\varepsilon = 2.0$. N is the number of atoms in the unit cell and F_h 's are on an absolute scale and corrected for thermal motion. Only normalized structure factors greater than 1.5 were used in the phase determination.

A program originally written by Bednowitz (1965) and modified by Iitaka facilitated the determination of signs and the application of the \sum_2 relationship. Reflexions 942, $\bar{2}13$ and $\bar{3}58$ were chosen to define the origin. Symbols were assigned to the phases of three additional reflexions as shown in Table 1. These form the basic set for applying the \sum_2 formula. From inspection of the interactions among the signs and symbols, it was decided that symbol *a* was probably minus and symbols *b* and *c* were probably both plus. With this assignment, the signs of 195 reflexions with $E \geq 1.51$ were determined. The component molecules were readily found from the E map computed with these phases.

Table 1. Starting reflexions for the phase calculation

| <i>h</i> | <i>k</i> | <i>l</i> | <i>E</i> | Sign |
|------------------|----------|----------|----------|----------|
| 9 | 4 | 2 | 3.88 | + |
| $\bar{2}$ | 1 | 3 | 3.60 | + |
| $\bar{3}$ | 5 | 8 | 3.61 | + |
| 2 | 7 | 0 | 2.96 | <i>a</i> |
| $\bar{1}\bar{1}$ | 3 | 2 | 2.93 | <i>b</i> |
| $\bar{6}$ | 2 | 8 | 2.83 | <i>c</i> |

A structure-factor calculation using atomic parameters obtained from the E map, gave an R value of 0.52. After calculating the Fourier synthesis, individual isotropic temperature factors were corrected. This reduced the R value to 0.34. The R value decreased to 0.14 after five cycles of block-diagonal least-squares refinement with isotropic temperature factors. Then anisotropic temperature factors were introduced, and the R value decreased to 0.100 after five cycles. The positions of the 8 hydrogen atoms attached to the benzene rings in TMBD were determined by the usual ($F_o - F_c$) synthesis, but the positions of the 12 hydrogen atoms in the methyl groups could not be determined. Possibly, the methyl groups rotate about C-N bonds. The eight hydrogen atoms were then included in the subsequent refinements, assuming isotropic temperature factors for them. Finally the R value reduced to 0.091, excluding non-observable reflexions. Atomic

Table 2. *Final parameters*(a) Atomic coordinates in fractions of cell edges and their standard deviations in 10^{-3} Å.

| | <i>X</i> | $\sigma(X)$ | <i>Y</i> | $\sigma(Y)$ | <i>Z</i> | $\sigma(Z)$ |
|------------------|----------|-------------|----------|-------------|----------|-------------|
| Chloranil | | | | | | |
| Cl(1) | 0.0929 | 3 | 0.3204 | 2 | -0.0076 | 3 |
| Cl(2) | 0.1188 | 3 | -0.2698 | 2 | 0.1535 | 3 |
| C(1) | 0.0387 | 8 | 0.1485 | 7 | -0.0059 | 9 |
| C(2) | 0.0500 | 8 | -0.1260 | 8 | 0.0687 | 8 |
| C(3) | 0.0981 | 8 | 0.0235 | 8 | 0.0662 | 9 |
| O(1) | 0.1793 | 6 | 0.0414 | 6 | 0.1205 | 7 |
| TMBD | | | | | | |
| C(4) | 0.4727 | 9 | 0.1993 | 8 | 0.5554 | 9 |
| C(5) | 0.4325 | 10 | 0.2794 | 9 | 0.4570 | 10 |
| C(6) | 0.3388 | 9 | 0.2671 | 9 | 0.3905 | 9 |
| C(7) | 0.2810 | 9 | 0.1828 | 8 | 0.4202 | 8 |
| C(8) | 0.1813 | 9 | 0.1717 | 8 | 0.3480 | 8 |
| C(9) | 0.1330 | 9 | 0.2925 | 8 | 0.2767 | 8 |
| C(10) | 0.0408 | 9 | 0.2793 | 8 | 0.2073 | 9 |
| C(11) | -0.0076 | 9 | 0.1427 | 8 | 0.2069 | 8 |
| C(12) | 0.0401 | 9 | 0.0229 | 8 | 0.2783 | 9 |
| C(13) | 0.1315 | 9 | 0.0375 | 8 | 0.3468 | 9 |
| C(14) | 0.3211 | 9 | 0.1095 | 8 | 0.5191 | 9 |
| C(15) | 0.4144 | 9 | 0.1151 | 8 | 0.5840 | 9 |
| C(16) | 0.6264 | 10 | 0.2716 | 11 | 0.5794 | 12 |
| C(17) | 0.6066 | 10 | 0.0982 | 11 | 0.7122 | 11 |
| C(18) | -0.1551 | 10 | 0.2669 | 10 | 0.0810 | 12 |
| C(19) | -0.1540 | 10 | -0.0020 | 10 | 0.1469 | 11 |
| N(1) | 0.5665 | 8 | 0.2084 | 8 | 0.6217 | 8 |
| N(2) | -0.1007 | 7 | 0.1266 | 7 | 0.1322 | 8 |

(b) Thermal parameters. The β 's are those used in the expression:

$$\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$$

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Chloranil | | | | | | |
| Cl(1) | 0.00547 | 0.01311 | 0.00909 | -0.00427 | 0.00620 | 0.00130 |
| Cl(2) | 0.00528 | 0.01515 | 0.00804 | 0.00483 | 0.00297 | 0.00577 |
| C(1) | 0.00340 | 0.00969 | 0.00717 | -0.00189 | 0.00433 | 0.00059 |
| C(2) | 0.00451 | 0.01197 | 0.00479 | 0.00380 | 0.00354 | 0.00328 |
| C(3) | 0.00371 | 0.01285 | 0.00661 | 0.00079 | 0.00379 | 0.00247 |
| O(1) | 0.00318 | 0.01815 | 0.00834 | -0.00034 | 0.00197 | 0.00024 |
| TMBD | | | | | | |
| C(4) | 0.00426 | 0.01268 | 0.00601 | -0.00005 | 0.00435 | -0.00119 |
| C(5) | 0.00526 | 0.01850 | 0.00670 | -0.00331 | 0.00528 | -0.00182 |
| C(6) | 0.00512 | 0.01734 | 0.00558 | -0.00062 | 0.00426 | 0.00214 |
| C(7) | 0.00445 | 0.01358 | 0.00504 | -0.00037 | 0.00418 | -0.00095 |
| C(8) | 0.00480 | 0.01154 | 0.00489 | 0.00074 | 0.00395 | -0.00029 |
| C(9) | 0.00449 | 0.01304 | 0.00440 | 0.00132 | 0.00306 | 0.00003 |
| C(10) | 0.00476 | 0.01232 | 0.00582 | 0.00100 | 0.00304 | -0.00136 |
| C(11) | 0.00408 | 0.01492 | 0.00511 | -0.00016 | 0.00343 | -0.00377 |
| C(12) | 0.00540 | 0.01326 | 0.00613 | -0.00062 | 0.00463 | 0.00075 |
| C(13) | 0.00517 | 0.01296 | 0.00487 | 0.00209 | 0.00205 | 0.00230 |
| C(14) | 0.00519 | 0.01489 | 0.00530 | -0.00042 | 0.00438 | 0.00178 |
| C(15) | 0.00438 | 0.01434 | 0.00567 | 0.00080 | 0.00228 | 0.00231 |
| C(16) | 0.00453 | 0.02628 | 0.01144 | -0.00222 | 0.00844 | 0.00226 |
| C(17) | 0.00558 | 0.02146 | 0.00827 | 0.00267 | 0.00166 | 0.00419 |
| C(18) | 0.00441 | 0.01655 | 0.01218 | 0.00540 | 0.00429 | 0.00081 |
| C(19) | 0.00521 | 0.01766 | 0.01071 | -0.00432 | 0.00663 | -0.00297 |
| N(1) | 0.00433 | 0.01947 | 0.00735 | 0.00090 | 0.00218 | 0.00080 |
| N(2) | 0.00399 | 0.01376 | 0.00758 | -0.00030 | 0.00347 | -0.00055 |

scattering factors for carbon, nitrogen, oxygen, chlorine and hydrogen were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme for the least-squares calculations was $w = (36.9/F_o)^2$ for $F_o > 36.9$ and $w = 1.0$ for $F_o \leq 36.9$.

Final parameters with their standard deviations are given in Table 2. Since the positions of some hydrogen atoms are not certain, hydrogen atoms are omitted from Table 2. A comparison of the observed and calculated structure factors is given in Table 3.

Table 3 (cont.)

| L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | L | FO | FC | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|----|----|---|----|----|---|----|----|---|----|----|---|----|----|------|----|----|------|----|----|---|----|----|----|----|----|----|------|----|---|----|----|---|----|----|---|----|----|----|---|---|---|------|---|---|---|---|---|------|---|---|---|---|----|---|---|---|------|---|----|---|---|----|------|---|----|---|---|----|------|---|----|---|---|----|------|---|----|---|---|----|------|---|---|----|
| 3 | 3 | 3 | 7 | 6 | -4 | 1 | 4 | -5 | 7 | 7 | -6 | 6 | 3 | -5 | H,K# | 4 | 9 | H,K# | 8 | 4 | 4 | 4 | 4 | -3 | 3 | 4 | -5 | H,K# | -9 | 9 | 8 | 9 | 7 | 3 | 6 | 8 | 8 | 5 | -4 | 8 | 4 | 3 | H,K# | 2 | 9 | 4 | 4 | 6 | H,K# | 5 | 9 | 1 | 6 | -6 | 3 | 4 | 2 | H,K# | 6 | 10 | 1 | 4 | -4 | H,K# | 7 | 10 | 1 | 4 | -6 | H,K# | 0 | 10 | 1 | 4 | -4 | H,K# | 7 | 10 | 1 | 4 | -6 | H,K# | 0 | 9 | 11 |

molecules, and deviations of the atoms from these planes, are presented in Table 4. The mean separation between plane 1 (chloranil) and plane 3 (one of the TMBD benzene rings) which are practically parallel to each other, is 3.162 Å; this is appreciably smaller than the usual van der Waals separation.

Fig. 2 and Table 5 show the intermolecular distances less than 3.5 Å found between the atoms of the nearest

neighbour TMBD and chloranil molecules, as well as the intermolecular distances less than 4.0 Å found between non-nearest molecules. The shortest one is C(3')-N(2)=3.097 Å. Such a close contact between the donor and the acceptor molecules indicates strong intermolecular interaction. The relative orientation of TMBD to chloranil found in the crystal is shown in Fig. 3.

Table 4. Least-squares planes and interplanar angles

(a) Direction cosines (*A, B, C*) with respect to crystallographic axes

| | Plane 1 | Plane 2 | Plane 3 | Plane 4 | Plane 5 |
|----------|---------|---------|---------|---------|---------|
| <i>A</i> | -0.5769 | -0.5103 | -0.5996 | -0.3722 | -0.2721 |
| <i>B</i> | 0.3694 | 0.3762 | 0.4151 | 0.8217 | 0.8119 |
| <i>C</i> | 0.9123 | 0.9215 | 0.8835 | 0.5545 | 0.5838 |

(b) Deviation of atoms which constitute the plane from the least-squares plane (Å × 10⁻³).

| Plane 1 | Plane 2 | Plane 3 | Plane 4 | Plane 5 | |
|---------|---------|---------|---------|---------|-----|
| Cl(1) | 14 | C(8) | -5 | C(4) | -49 |
| Cl(2) | 13 | C(9) | 3 | C(5) | -46 |
| C(1) | 17 | C(10) | 1 | C(6) | -45 |
| C(2) | 19 | C(11) | -3 | C(7) | -6 |
| C(3) | -6 | C(12) | 0 | C(14) | 17 |
| O(1) | -22 | C(13) | 4 | C(15) | -9 |
| | | | | N(1) | 140 |

(c) Interplanar angles

| 1-3 | 2-3 | 3-4 | 4-5 |
|------|------|-------|------|
| 3.9° | 8.3° | 30.8° | 7.5° |

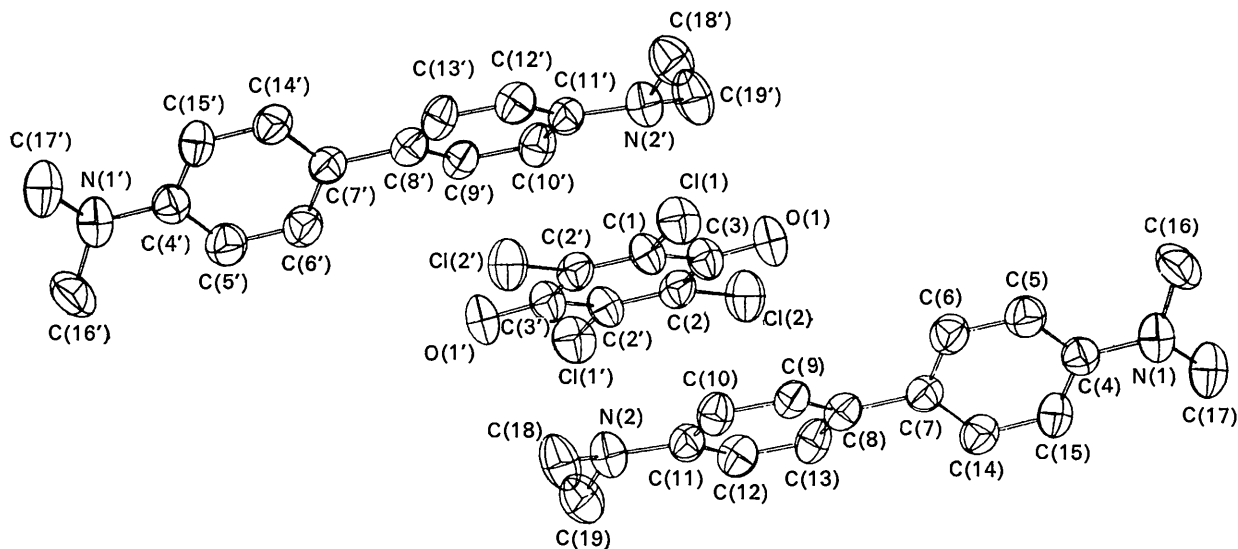


Fig. 1. Atomic numbering of the molecules. Ellipsoids represent anisotropic thermal parameters.

Table 5. Distances less than 3.5 Å between atoms of the nearest neighbour and distances less than 4.0 Å between atoms of the non-nearest neighbour, and their standard deviations (Å)

Symbols are shown in Fig. 2.

| | | |
|---|-------|---------|
| A | 3.492 | (0.010) |
| B | 3.097 | (0.013) |
| C | 3.312 | (0.013) |
| D | 3.359 | (0.013) |
| E | 3.430 | (0.014) |
| F | 3.398 | (0.013) |
| G | 3.347 | (0.015) |
| H | 3.353 | (0.014) |
| I | 3.292 | (0.014) |

Table 5 (cont.)

| | | |
|---|-------|---------|
| J | 3.195 | (0.014) |
| K | 3.389 | (0.011) |
| L | 3.386 | (0.012) |
| M | 3.967 | (0.016) |
| N | 3.684 | (0.015) |
| O | 3.754 | (0.015) |
| P | 3.867 | (0.014) |
| Q | 3.849 | (0.014) |
| R | 3.976 | (0.017) |
| S | 3.754 | (0.015) |
| T | 3.808 | (0.017) |
| U | 3.817 | (0.016) |
| V | 3.821 | (0.011) |
| W | 3.433 | (0.014) |
| X | 3.428 | (0.010) |

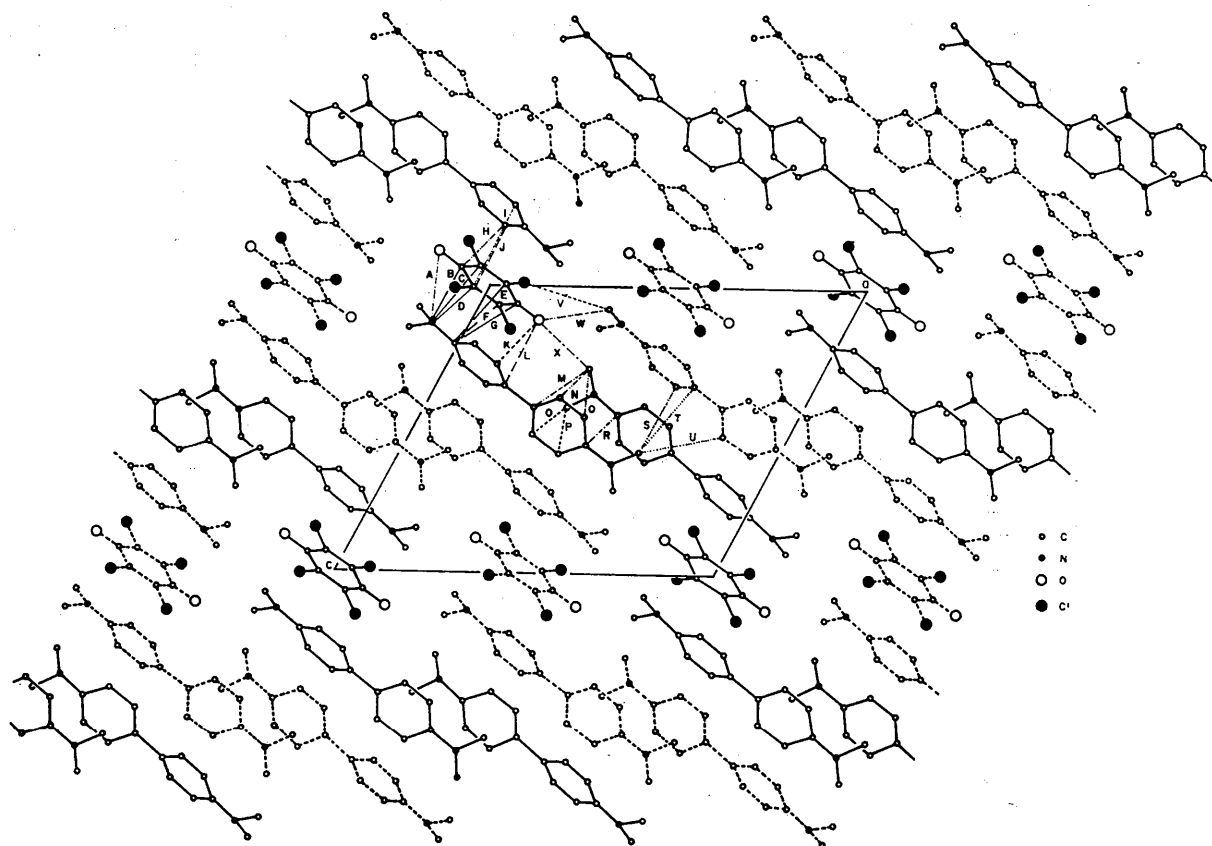


Fig. 2. Projection of the molecular arrangement onto the (010) plane. Symbols A, B, C...X, represent the intermolecular distances given in Table 5.

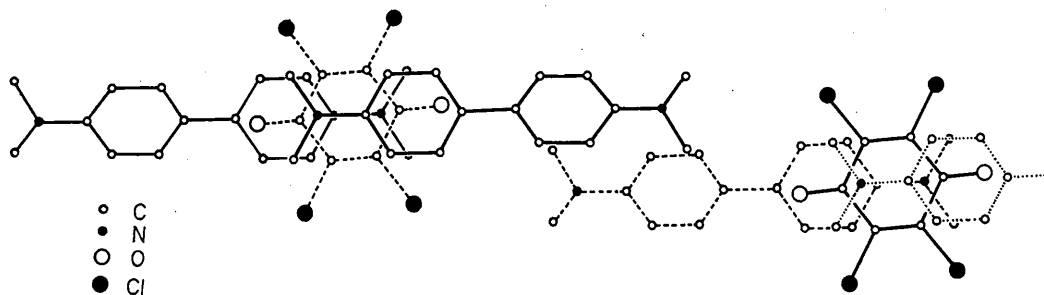


Fig. 3. Relative orientation of TMBD with respect to chloranil found in the crystal.

Molecular structures of the constituent molecules are illustrated in Fig. 4. Bond lengths given here have not been corrected for thermal motions.

Average standard deviations for chloranil, as calculated from the standard deviations in the coordinates of Table 2, are 0.009 Å for the C–Cl bonds, and 0.011 Å for the remaining bonds. The estimated standard deviations in the angles C–C–Cl are 0.6°; those of the remaining angles average 0.7°. The molecular structure has been reported for the chloranil molecule in the chloranil crystal (Chu, Jeffrey & Sakurai, 1962), in the 8-hydroxyquinoline-chloranil (2:1) complex (Prout & Wheeler, 1967) and in the TMPD–chloranil complex (Boer & Vos, 1968). These three sets of molecular dimensions and the present results are listed in Table 6, where *a* is the length of C(3)–O(1), *b* is that of C(1)–C(2'), *c* is the average length of C(1)–C(3) and C(2)–C(3), and *d* is that of C(1)–Cl(1) and C(2)–Cl(2). The data shown in Table 6 indicate that the molecular dimensions of chloranil in different crystals almost equal each other if the standard deviations are taken into account, and that the chloranil molecule always assumes quinoid structure.

Table 6. Bond lengths of chloranil*

| | TMBD–chloranil | 8-Hydroxyquinoline-chloranil | TMPD–chloranil | Chloranil |
|----------|----------------|------------------------------|----------------|--------------|
| <i>a</i> | 1.209 (11) Å | 1.20 (2) Å | 1.230 (10) Å | 1.195 (11) Å |
| <i>b</i> | 1.331 (10) | 1.30 (3) | 1.350 (10) | 1.342 (11) |
| <i>c</i> | 1.487 (12) | 1.49 (2) | 1.463 (10) | 1.477 (11) |
| <i>d</i> | 1.710 (9) | 1.703 (15) | 1.716 (7) | 1.714 (8) |

* Values for chloranil itself are corrected for thermal vibration; the others are not.

Average standard deviations for the TMBD are 0.013 Å (bond length) and 0.8° (bond angle). The C–C bonds in the benzene rings have an almost equal length; the average length of C–C bonds is 1.388 Å in plane 3, and 1.394 Å in plane 4. These values almost equal the length of the C–C bond in the free benzene molecule. The length of the C(7)–C(8) bond, connecting two benzene rings, is much longer than the other C–C bond lengths in the TMBD molecule. The bond length of C(11)–N(2) is 1.414 Å and that of C(4)–N(1) is 1.394 Å. Both are notably shorter than the lengths of N–CH₃ bonds. The lengths of the four N–CH₃ bonds are equal within experimental error (1.468 Å average). This average value equals the sum of the single-bond covalent radii, 1.47 Å. The non-planarity between the two benzene rings is probably due to the manner of packing. Data suggest that the quinoid structure contributes little to the TMBD molecule in this complex. In this respect, it is interesting to note that the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) molecule possesses a structure that indicates strong quinoid characteristics in TMPD–chloranil (Boer & Vos, 1968), TMPD–iodide (Boer, Vos, & Huml, 1968), TMPD–TCNQ (1:1) (Han-

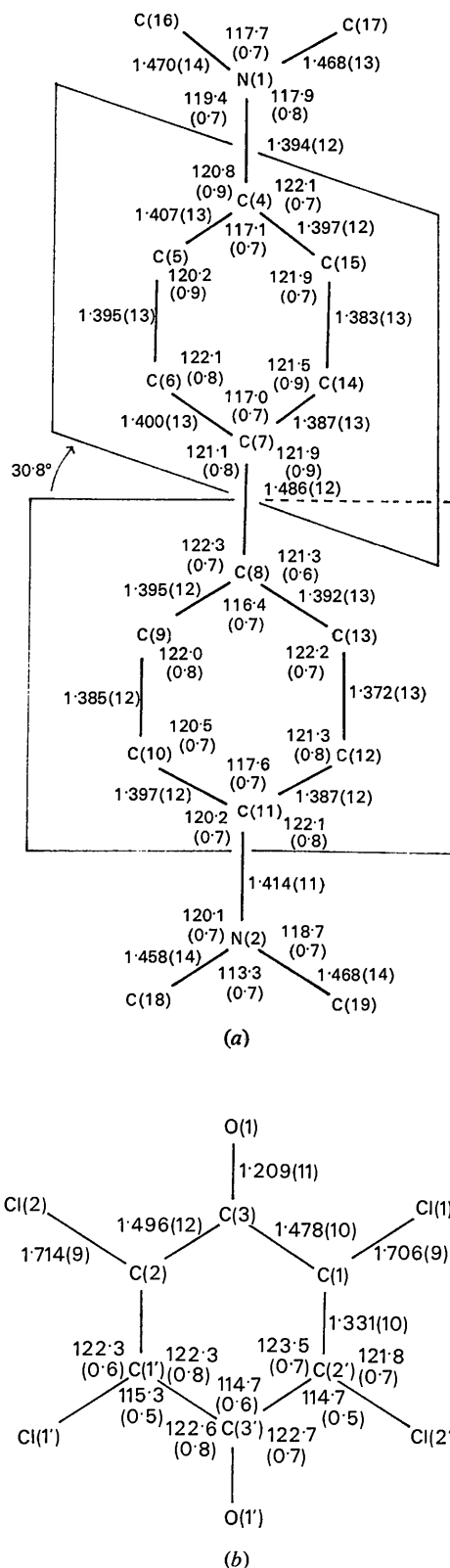


Fig. 4. Bond lengths (Å), bond angles (°) and their e.s.d.'s. (a) TMBD, (b) Chloranil.

son, 1965) and TMPD-TCNQ (1:2) (Hanson, 1968), in all of which the TMPD molecule is in the state of a monopositive ion.

Crystal-structure analyses of the TMPD-chloranil (1:1) complex and BD-TCNQ (1:1) complex are now in progress.

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Röntgenstrukturanalysen von Neophorbol, $C_{31}H_{35}O_9Br$, und Phorbol, $C_{20}H_{28}O_6$

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The crystal structures of neophorbol, $C_{31}H_{35}O_9Br$, and phorbol, $C_{20}H_{28}O_6$, have been determined from three-dimensional X-ray diffraction data, using an automatic diffractometer and $Cu K\alpha$ radiation. Neophorbol: The crystals are monoclinic, space group $P2_1$ with 2 molecules in a unit cell of dimensions $a=12.31$, $b=12.91$, $c=9.87$ Å, $\gamma=111.29^\circ$. The structure was solved by the convolution molecule method and successive Fourier syntheses. It was refined by least-squares methods to an R index of 0.064 for 1972 reflexions. The tetracyclic diterpene molecule neophorbol consists of a cyclopentene ring in envelope form, a cycloheptene ring in boat form, a cyclohexanone ring in envelope form and a cyclopropane ring. The absolute configuration was determined by measuring 131 Bijvoet pairs. Phorbol: The crystals are orthorhombic, space group $P2_12_12_1$; the unit cell has dimensions $a=18.575$, $b=12.777$, $c=9.611$ Å and contains 4 molecules. The structure was solved by the direct method. The final $R=0.054$ for 1916 reflexions. The configuration of the tetracyclic diterpene phorbol is similar to that of neophorbol. In both neophorbol and phorbol the molecules are held together in chains by hydrogen bonds.

Einleitung

Für Phorbol $C_{20}H_{28}O_6$, den Grundalkohol cocarcinogener Wirkstoffe aus Crotonöl, wurde von E. Hecker und Mitarbeitern mit chemischen und physikalischen Methoden die Struktur eines 4,9,12,13,20-Pentahydroxy-6-tigliadien-3-ons abgeleitet (Hecker, Kubinyi, Szczepanski, Härle & Brescky, 1965; Hecker, Bresch, Gschwendt, Härle, Kreibich, Kubinyi, Schairer, Szczepanski & Thielmann, 1966; Hecker, 1967). Den Strukturvorschlag zeigt Fig. 1.

Versuche an unserem Institut, die Struktur des Phorbols röntgenographisch nach der Faltmolekülmethode

unter Verwendung eines Dreiring-Sechsring-Skelettes aufzuklären, schlugen fehl. Deshalb wurde eine Lösung der Struktur über die Analyse eines Schweratomderivates angestrebt. Durch Veresterung mit brom- oder jodhaltigen Säuren bzw. Hydrazonbildung mit Hydrazinabkömmlingen wurden von der Gruppe E. Hecker insgesamt 9 Schweratomderivate von Phorbol dargestellt. Wegen Zwillingsbildung waren nur zwei Derivate für eine Kristallstrukturuntersuchung verwendbar. Von einem dieser beiden Derivate, dem Neophorbol-13,20-diacetat-3-*p*-brombenzoat, kurz Neophorbol genannt, wurde eine Röntgenstrukturanalyse durchgeführt. (Amit, Brandl, Brodherr, Gieren, Hädicke, Hoppe,