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The Crystal Structures of the Molecular Complexes between Benzidine and 7,7,8,8-Tetracyano-*p*-quinodimethane. III.* Benzidine–TCNQ Complex Containing Benzene

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(*Received* 5 *February* 1974; *accepted* 20 *February* 1974)

Crystals of the (1:1) complex of benzidine and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), containing benzene in the crystal lattice, are monoclinic, space group $P2_1/m$, with $a=17\cdot184$, $b=9\cdot852$, $c=7\cdot680$ Å, $\beta=100\cdot03°$, $Z=2$. The structure was refined by the method of constrained least-squares. The benzidine and the TCNQ molecules form alternately stacked molecular columns along the *c* axis. Benzidine and TCNQ in the nearest-neighbour columns are connected by hydrogen bonds to form infinite net planes parallel to the ($\bar{2}01$) plane. Between the columns there are channels running along the *c* axis in which benzene molecules are accommodated.

Introduction

Benzidine (BD) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) have been found to form, in addition to the solvent-free complex, solid molecular complexes which contain solvent molecules (Ohmasa, Kinoshita & Akamatu, 1969). The crystal structures of these complexes can be classified into three types. Type I is that found for the solvent-free complex, and type II, that for the dichloromethane-containing complex. The complexes which contain acetone, acetonitrile and 1,2-dichloroethane give X-ray powder diffraction patterns very similar to that of the dichloromethane-containing complex, and seem to have a type II structure. Type III comprises the complexes containing benzene, toluene, chlorobenzene, bromobenzene, nitrobenzene and benzonitrile.

We have already reported the crystal structure of the BD–TCNQ solvent-free complex (Yakushi, Ikemoto & Kuroda, 1974) and that of the dichloromethane-containing complex (Ikemoto, Chikaishi, Yakushi & Kuroda, 1972). In the present paper, we report the crystal structure of the benzene-containing complex, as a typical example of a type III complex.

Experimental

Dark purple crystals of the complex were obtained from a benzene solution. They grow, with slow cooling of the solution, into thick needle-like crystals elongated along the *c* axis. Chemical analysis of these crystals indicated that the molecular ratio of the components, BD: TCNQ: benzene, was 1:1:1·1 ± 0·15. Considering the crystal structure and the standard deviation of the chemical analysis, we decided that the molecular ratio was 1:1:1.

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* Part II: *Acta Cryst.* (1974). B**30**, 835–837.

From Weissenberg and precession photographs the approximate lattice constants and space group were determined. The accurate lattice parameters and the intensity data were obtained with the Rigaku four-circle automatic diffractometer employing Mo $K\alpha$ radiation monochromatized with a graphite crystal.

Crystal data

$a=17{\cdot}184$ (7), $b=9{\cdot}852$ (2), $c=7{\cdot}680$ (1) Å
$\beta=100{\cdot}03$ (1)°, $V=1280{\cdot}4$ Å^3
Formula: $C_{12}H_{12}N_2.C_{12}H_4N_4.C_6H_6$; F.W. 466
$D_c=1{\cdot}21$, $D_m=1{\cdot}25$ g cm^{-3} (by flotation)
$Z=2$
$\mu=0{\cdot}92$ cm^{-1} (Mo $K\alpha$)
Space group $P2_1/m$ (absent spectra: $0k0$ when k is odd).

Since the crystal gradually loses benzene molecules under atmospheric conditions, it was sealed in a thin-wall glass capillary to avoid decomposition. 1325 reflexions with reliable intensities $[F_o \geq 3\sigma(F_o)]$ were obtained by measuring all reflexions with $2\theta \leq 55°$. The reproducibility of the measurements and the stability of the crystal were checked by measuring the $80\bar{4}$, 080 and 102 reflexions once every 50 reflexions. Consequently, these standard reflexions were measured 67 times. The maximum deviations of the structure factors from the average values were 0·6, 0·6 and 0·8% for $80\bar{4}$, 080 and 102, respectively. No absorption correction was made, since the linear absorption coefficient is small.

Structure determination and refinement

From systematically absent reflexions, the space group is determined to be $P2_1/m$ or $P2_1$. The space group $P2_1/m$ was assumed tentatively, and was verified at a later stage by the calculation of structure factors. The positions and the orientations of the BD and TCNQ molecules were deduced from Patterson and R-value maps. The approximate positions of the atoms were refined by the block-diagonal least-squares method with isotropic temperature factors. The benzene molecules appeared in the difference synthesis. Although block-diagonal least-squares refinement reduced the R value to 13·5%, the geometries of the BD, TCNQ and benzene molecules were appreciably distorted. This was considered to be due to the presence of disorder in the position of the benzene molecules. The distortion of the molecular geometry of benzene is associated with large correlations between the positional parameters and the thermal parameters. In order to avoid the correlation problem, the constrained least-squares method was adopted (Scheringer, 1963; Pawley, 1972). The UNICS full matrix least-squares program (1967) was modified for this purpose. The refined parameters

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters* (*all* × 10^4)

The temperature factor expression used was $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. The estimated standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BD									
N(1)	−415 (5)	2500 (0)	−3110 (11)	35 (3)	81 (11)	260 (20)	0	−25 (6)	0
C(1)	233 (5)	2500 (0)	−1779 (11)	21 (3)	128 (14)	151 (16)	0	1 (6)	0
C(2)	559 (3)	1288 (7)	−1087 (7)	23 (2)	91 (8)	144 (11)	−6 (3)	1 (4)	5 (8)
C(3)	1229 (3)	1296 (7)	206 (7)	26 (2)	62 (6)	116 (10)	−10 (3)	4 (4)	24 (7)
C(4)	1608 (5)	2500 (0)	905 (9)	27 (3)	48 (10)	111 (14)	0	11 (5)	0
C(5)	2334 (5)	2500 (0)	2257 (10)	26 (3)	131 (15)	93 (14)	0	−2 (6)	0
C(6)	2679 (3)	1283 (8)	2900 (7)	26 (2)	87 (9)	129 (11)	2 (4)	−4 (4)	13 (8)
C(7)	3361 (3)	1294 (7)	4142 (7)	29 (2)	64 (7)	131 (11)	18 (4)	13 (4)	20 (8)
C(8)	3745 (4)	2500 (0)	4813 (9)	24 (3)	40 (9)	95 (13)	0	10 (5)	0
N(2)	4419 (4)	2500 (0)	6027 (10)	29 (3)	113 (14)	173 (17)	0	−27 (5)	0
TCNQ									
N(3)	1007 (3)	283 (7)	−5334 (7)	41 (3)	145 (9)	222 (12)	−21 (4)	4 (4)	−37 (9)
C(9)	1262 (3)	1283 (8)	−4697 (7)	24 (2)	113 (8)	133 (10)	−9 (4)	−4 (4)	−9 (8)
C(10)	1617 (4)	2500 (0)	−3982 (10)	19 (3)	69 (10)	141 (15)	0	0 (5)	0
C(11)	2291 (4)	2500 (0)	−2702 (10)	23 (3)	95 (11)	110 (14)	0	7 (5)	0
C(12)	2656 (3)	1246 (7)	−2004 (6)	26 (2)	54 (6)	100 (9)	0 (3)	13 (4)	−4 (7)
C(13)	3325 (3)	1255 (6)	−781 (7)	23 (2)	52 (7)	137 (11)	0 (3)	−1 (4)	4 (7)
C(14)	3691 (4)	2500 (0)	−139 (10)	18 (3)	69 (10)	149 (16)	0	2 (5)	0
C(15)	4375 (4)	2500 (0)	1161 (9)	19 (3)	103 (11)	96 (13)	0	9 (5)	0
C(16)	4754 (3)	1262 (7)	1830 (7)	22 (2)	127 (8)	139 (10)	11 (4)	−3 (4)	7 (9)
N(4)	5066 (3)	299 (6)	2321 (7)	41 (3)	145 (8)	205 (11)	32 (4)	−1 (4)	40 (8)
Benzene									
C(17)	3355	7500	−296	117	107	990	0	222	0
C(18)	3039	7500	1262	149	112	1344	0	264	0
C(19)	2220	7500	1180	132	141	1258	0	242	0
C(20)	1718	7500	−4600	162	113	1063	0	170	0
C(21)	2034	7500	−2017	182	92	1094	0	51	0
C(22)	2853	7500	−1935	148	96	987	0	126	0

Table 1 (*cont.*)

Hydrogen atomic coordinates are × 10³.

	x	y	z	B
HN(1)	−59 (4)	162 (7)	−347 (8)	6·6 (1·7)
H(2)	41 (3)	27 (7)	−165 (8)	4·6 (1·5)
H(3)	141 (3)	37 (7)	72 (8)	4·5 (1·5)
H(6)	248 (3)	38 (6)	241 (7)	2·7 (1·3)
H(7)	362 (3)	58 (6)	436 (7)	3·0 (1·4)
HN(2)	454 (4)	166 (7)	639 (8)	4·5 (1·9)
H(12)	246 (3)	37 (6)	−240 (7)	2·6 (1·2)
H(13)	359 (3)	41 (6)	−31 (6)	2·5 (1·2)

Table 2. *Atomic deviations* (Å) *from the least-squares planes of the* BD *and* TCNQ *molecules*

BD		TCNQ	
N(1)	−0·130	N(3)	−0·158
C(1)	−0·054	C(9)	−0·054
C(2)	−0·002	C(10)	−0·017
C(3)	0·024	C(11)	0·002
C(4)	0·018	C(12)	0·014
C(5)	0·015	C(13)	0·004
C(6)	0·014	C(14)	−0·020
C(7)	−0·007	C(15)	−0·001
C(8)	−0·037	C(16)	−0·022
N(2)	−0·067	N(4)	−0·079

of the benzene molecule were the position of the origin of the molecular axes fixed in the molecule, the Eulerian angles between crystal rectangular axes and molecular axes, and the common isotropic thermal parameters. The benzene molecule was assumed to have the C_{6h} point symmetry with C–C bond lengths of 1·396 Å. The atoms of the BD and TCNQ molecules, except hydrogen, were independently refined with anisotropic temperature factors. All the parameters were refined simultaneously and the R value decreased to 0·14.

At this stage the molecular structures of BD and TCNQ became reasonable. The hydrogen atoms of BD and TCNQ appeared clearly in an (F_o-F_c) synthesis. Full-matrix least-squares refinement with anisotropic temperature factors reduced the R value to 0·094 (model 1), where the positional parameters of benzene molecules were then fixed and the temperature factors of hydrogen atoms were taken as isotropic. From this model full-matrix least-squares refinements without restriction were started. The final R value became 0·085 (model 2), but the molecular structure of benzene was extremely distorted in this case. There is no significant difference in the position and geometries of BD and TCNQ molecules between model 1 and model 2. Although the structure analysis in space group $P2_1$ was also carried out, the distortion of the molecular dimensions of BD and TCNQ was more pronounced. We therefore adopted model 1 as the final structure.*

The weighting scheme was as follows: $w=1/[\sigma^2(F_o)+(0{\cdot}08F_o)^2]^{1/2}$. Atomic scattering factors for carbon and nitrogen were taken from *International Tables for X-ray Crystallography* (1962) and those for hydrogen from Stewart, Davidson & Simpson (1965).

Results and discussion

The final atomic parameters with their standard deviations are given in Table 1. The BD and the TCNQ molecules can be considered to be approximately planar. The equations of the molecular planes, calculated by the least-squares method, are:

$$-0{\cdot}6936X+0{\cdot}0Y+0{\cdot}8301Z=-1{\cdot}358$$

for BD (without amino groups and hydrogen atoms) and

$$-0{\cdot}6903X+0{\cdot}0Y+0{\cdot}8326Z=-4{\cdot}447$$

for TCNQ (without cyano groups and hydrogen atoms), where X, Y and Z are coordinates with respect to the crystal axes a, b and c (in Å). These planes make an angle of 0·3° with each other. The deviations of atoms from the least-squares planes are listed in Table 2. The bond lengths, bond angles and their standard deviations in each molecule are given in Fig. 1. As shown in Table 2 the TCNQ molecule has a shallow boat structure. A similar molecular structure of TCNQ is observed in the crystals of acenaphthene–TCNQ (Tickle & Prout, 1973), N,N'-dimethylhydrophenazine–TCNQ (Goldberg & Shmueli, 1973), (tetraphenylphosphonium)$^+$(TCNQ)$_2^-$ (Goldstein, Seff & Trueblood, 1968), (N,N'-dibenzyl-4,4′-bipyridy-

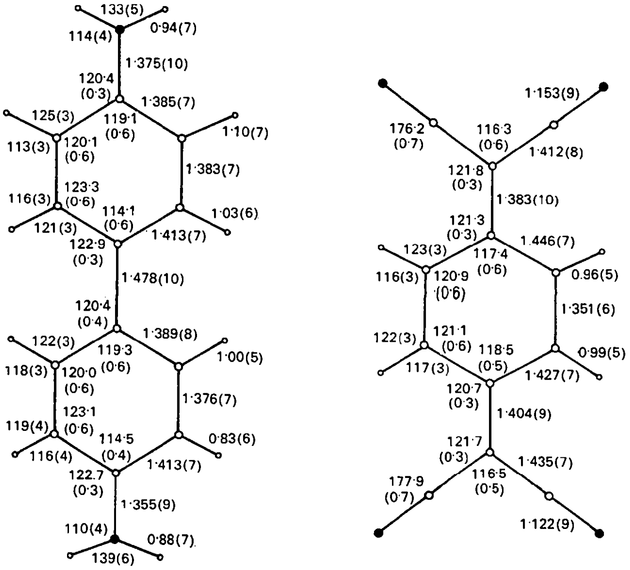

Fig. 1. Bond lengths and their e.s.d.'s (Å) and bond angles and their e.s.d.'s (°) in BD and TCNQ.

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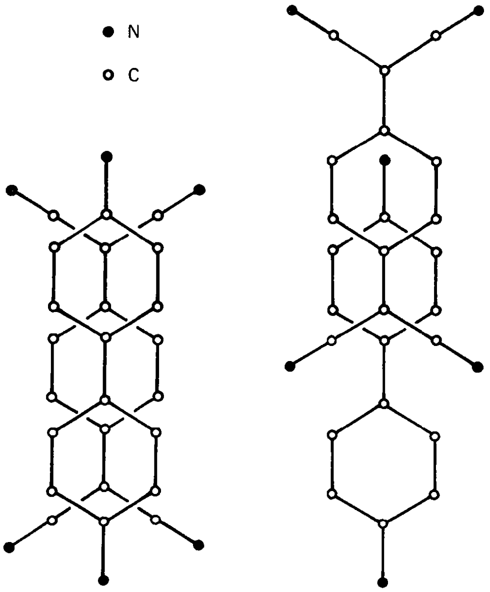
* A table of F_o and F_c has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30401 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

lium)$^{2+}$(TCNQ)$_4^{2-}$ (Sundaresan & Wallwork, 1972*a*), (1,1′-ethylene-2,2′-bipyridylium)$^{2+}$(TCNQ)$^{2-}$ (Sundaresan & Wallwork, 1972*b*) and rubidium$^+$TCNQ$^-$ (Hoekstra, Spoelder & Vos, 1972).

There are two kinds of relative orientation between BD and neighbouring TCNQ within the same molecular columns. The mean separation between the molecular planes of BD and those of TCNQ are 3·09 Å (type *A*) and 3·29 Å (type *B*); the former value is remarkably short. These relative orientations of BD and TCNQ are shown in Fig. 2. The overlap of type *A* is same as that in the BD–TCNQ solvent-free complex crystal (Yakushi, Ikemoto & Kuroda, 1974), and that in the BD–TCNQ dichloromethane-containing crystal (Ikemoto, Chikaishi, Yakushi & Kuroda, 1972). The overlap of type *B* is similar to that between *N,N,N′,N′*-tetramethylbenzidine and chloranil in their (2:1) molecular-complex crystal (Yakushi, Ikemoto & Kuroda, 1971). The distances between the atoms of the neighbouring BD and TCNQ molecules are listed in Table 3.



(*a*) (*b*)

Fig. 2. Relative orientations of BD with respect to TCNQ found in the crystal. (*a*) Type *A*, (*b*) type *B*.

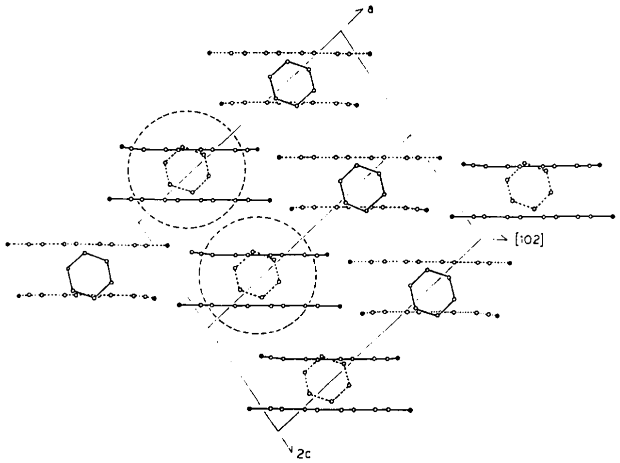


Fig. 3. Projection of molecular arrangement onto the (010) plane.

Table 3. *Distances less than* 3·4 Å *between atoms of the nearest-neighbour* BD *and* TCNQ *molecules and their e.s.d.'s* (Å)

BD···TCNQ (type *A*)			
C(1)···C(9)	3·312 (10)	C(5)···C(13)	3·351 (10)
C(1)···C(10)	3·149 (12)	C(5)···C(14)	3·212 (12)
C(2)···C(9)	3·211 (8)	C(6)···C(13)	3·212 (8)
C(2)···C(10)	3·328 (10)	C(6)···C(14)	3·365 (10)
C(3)···C(11)	3·337 (9)	C(7)···C(15)	3·329 (9)
C(3)···C(12)	3·216 (8)	C(7)···C(16)	3·219 (8)
C(4)···C(11)	3·190 (11)	C(8)···C(15)	3·177 (10)
C(4)···C(12)	3·341 (9)	C(8)···C(16)	3·335 (9)
BD···TCNQ (type *B*)			
C(5)···C(10)	3·332 (12)	C(8)···C(11)	3·399 (11)
C(6)···C(9)	3·300 (8)	N(2)···C(14)	3·394 (11)
C(7)···C(12)	3·388 (8)		

The projection of the crystal structure along the *b* axis is illustrated in Fig. 3. The BD–TCNQ pairs of type *A* are stacked along the *c* axis to form columns. The neighbouring molecular columns are connected by hydrogen bonds between the cyano groups of TCNQ and the amino groups of BD. The distances between an N atom of a benzidine molecule and the nearest N atoms of a TCNQ molecule in the neighbouring molecular column are 3·091 (7) and 3·099 (7) Å, as shown in Fig. 4. Thus there are infinite hydrogen-bonded sheets formed by the BD–TCNQ pairs of type *A* almost parallel to the ($\bar{2}$01) plane.

The projection of these sheets onto the ($\bar{2}$01) plane is drawn in Fig. 4. The arrangement of BD and TCNQ in these sheets is similar to that in the dichloromethane-containing crystal. The [102] and [010] directions in this crystal correspond, respectively, to the [100] and [010] in the latter. The lengths of these axes are [102] = 20·964, [010] = 9·852 Å in this crystal and [100] = 20·982, [010] = 9·950 Å in the latter. Furthermore, the angles between the least-squares plane of BD and the ($\bar{2}$01) plane is 3·0° in this crystal, while the corresponding angle in the latter is 2·2°. These values show that the structure of the hydrogen-bonded sheet in the benzene-containing crystal is almost the same as that in the dichloromethane-containing crystal, although their mode of stacking is a little different. In the latter crystal the sheets are stacked without any displacement in the direction parallel to the sheet plane. In this crystal, however, nearest-neighbour sheets are shifted by 4·7 Å along the [102] direction, and the channels in

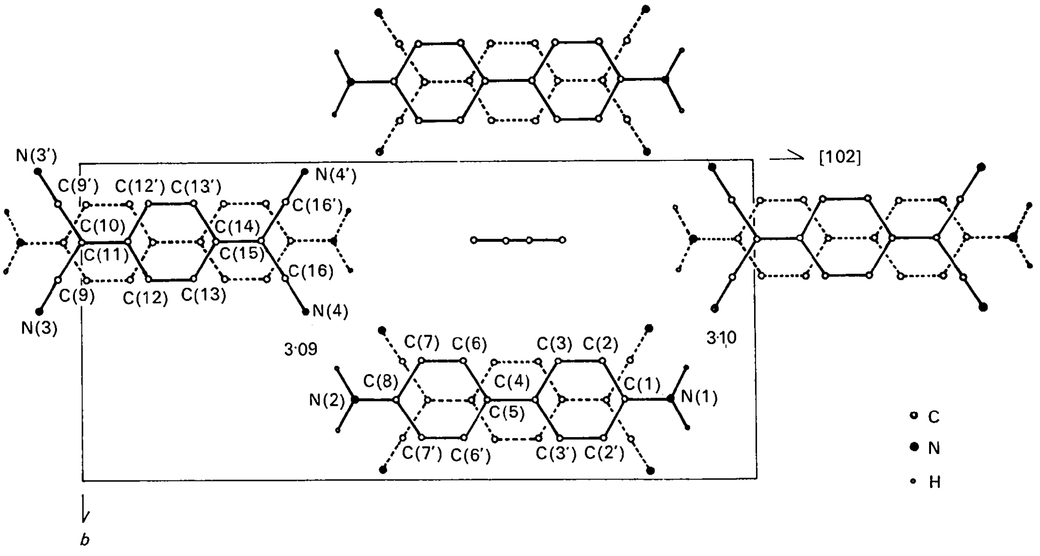


Fig. 4. Projection of molecular arrangement onto the $(20\bar{1})$ plane.

which the benzene molecules are located do not run perpendicular to the molecular planes but along the *c* axis. This structural difference seems to be caused by the difference in molecular shape between benzene and dichloromethane. The territory occupied by a benzene molecule, estimated from the bond lengths and van der Waals radii, is shown by the broken circles (radius 3·6 Å) in Fig. 3. These territories would overlap if the hydrogen-bonded sheets were stacked in the manner found in the dichloromethane-containing crystals.

The directions of the principal axes and the root-mean-square amplitudes of the atomic thermal motions were calculated from the atomic thermal parameters. In the benzene molecule the root-mean-square amplitudes along the principal axes parallel to the *b* axis are smaller than along the other principal axes on the (010) plane. The latter are considerably larger than those usually found for carbon atoms. The thermal motions of the atoms in the benzene molecule were analysed in terms of the rigid-body modes of translation and libration, but they could not be interpreted by rigid-body motion. These facts indicate disordered locations of the benzene molecule rather than large thermal motion. Seemingly there is a random disorder, since diffuse reflexions were not observed and the benzene molecules are loosely packed in the channels.

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

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