

# The Crystal Structure of Benzidine-*s*-Trinitrobenzene 1:1 Molecular Complex Benzene Solvate

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Crystals of the 1:1 complex of benzidine and *s*-trinitrobenzene, containing benzene in the crystal lattice, are monoclinic, space group  $P2_1/a$ , with  $a=15.605$  (6),  $b=19.598$  (5),  $c=6.850$  (2) Å,  $\beta=99.88$  (2)°,  $Z=4$ . The structure was solved by the direct method and was refined by the block-diagonal least-squares method. The benzidine and *s*-trinitrobenzene molecules form alternately stacked molecular columns along the  $c$  axis. Between these columns there are constricted channels running along the  $c$  axis, in which benzene molecules are located. The two benzene rings of benzidine are mutually twisted around the C-C bond between them.

## Introduction

We found that crystals of the molecular complex between benzidine (BD) and *s*-trinitrobenzene (TNB) contain benzene molecules in the crystal lattice when grown in a benzene solution, whereas the solvent-free crystals are grown in a chloroform solution. The X-ray powder-diffraction patterns indicate that the benzene-containing crystals easily lose benzene molecules to become the solvent-free crystals when kept in vacuum, and that the reverse process takes place when the solvent-free crystals are exposed to benzene vapour.

This phenomenon appears to be similar to that observed in the molecular complex between benzidine and tetracyanoquinodimethane (TCNQ) (Yakushi, Ikemoto & Kuroda, 1974). But we found that, although dichloromethane and toluene also enter the crystal lattice of the BD-TCNQ complex, they do not in the case of the BD-TNB complex. We noted also that the molecular geometry of TNB is not suited to the formation of such a hydrogen-bonded network as is formed in the solvent-containing crystals of the BD-TCNQ complex.

These facts aroused our interest in the crystal structure of the benzene-containing crystal of the BD-TNB complex.

We have already reported the structure of the solvent-free crystal of the BD-TNB complex (Tachikawa, Yakushi & Kuroda, 1974). We will report in this paper the structure of the benzene-containing crystal, BD-TNB-Bz.

## Experimental

Dark red acicular crystals of the BD-TNB-Bz complex were grown by slowly cooling a hot benzene solution. The molecular ratio of the components, BD:TNB:

Bz, was determined to be 2:2:1 by chemical analysis of these crystals. Since the crystals gradually lose benzene molecules when kept in air, those for the diffraction experiment were sealed in thin-walled glass tubes.

From Weissenberg photographs the space group was determined to be  $P2_1/a$ , since the following systematic absences were observed:  $h0l$  when  $h=2n+1$  and  $0k0$  when  $k=2n+1$ . The lattice parameters and the intensity data were obtained with a Rigaku four-circle automatic diffractometer employing Mo  $K\alpha$  radiation monochromatized with a graphite plate. The dimensions of the single crystal used for the intensity collection were  $0.45 \times 0.35 \times 0.50$  mm.

## Crystal data

$a=15.605$  (6),  $b=19.598$  (5),  $c=6.850$  (2) Å,  $\beta=99.88$  (2)°,  $V=2063.9$  Å<sup>3</sup>.

Formula:  $C_{12}H_{12}N_2 \cdot C_6H_3N_3O_6 \cdot (C_6H_6)_{0.5}$ .  $D_c=1.42$ ,  $D_m=1.40$  g cm<sup>-3</sup> (by flotation).  $Z=4$ ,  $\mu=1.30$  cm<sup>-1</sup> (Mo  $K\alpha$ ).

We obtained 2478 independent reflexions with  $|F_o| \geq 3\sigma(F_o)$  by measuring all reflexions with  $2\theta < 55^\circ$ . There were 14 non-zero reflexions which disagreed with the systematic absence  $h0l$  when  $h=2n+1$ . If they are taken into account, the space group should be  $P2_1$  or  $P2_1/m$ . However, we assumed the space group  $P2_1/a$ , neglecting the above reflexions, and solved the crystal structure, because their intensity is very weak ( $|F_o| \leq 4.4$  in absolute scale) and all other reflexions obey the systematic absence rules characteristic of this space group. No correction was applied for absorption or extinction.

## Structure determination and refinement

The structure was solved by the direct method. Among 360 reflexions with  $E \geq 2.00$ , the signs of 200 reflexions were determined manually, by choosing the reflexions  $11,8,2$ ,  $1,15,\bar{4}$ ,  $11,8,\bar{1}$  to define the origin. In the  $E$  map all atoms in BD and TNB except the hydrogen atoms appeared together with many ghost peaks, but

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the carbon atoms of benzene could not be found. A structure-factor calculation using atomic parameters obtained from the  $E$  map, neglecting the benzene molecule, gave an  $R$  value of 0.46. The benzene molecule, however, appeared in the Fourier map. The parameters were subsequently refined by the block-diagonal least-squares method. It was observed that the  $|F_o|$ 's of some of the strong reflexions were significantly smaller than the corresponding  $|F_c|$ 's. Since the absorption coefficient is small, these disagreements seem to originate from the extinction effect. Therefore, we also carried out a least-squares calculation eliminating the four reflexions of particularly high intensity. The final  $R$  value was 0.050 and 0.054, on excluding and including these reflexions, respectively.\* In the difference synthesis no anomalous peak was observed. Since the residual electron densities fell in the range  $+0.2$  to  $-0.3$  e Å<sup>-3</sup>, it was found that the assumption of the space group  $P2_1/a$  was a good approximation. The value of

$[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$  was 0.982 in the weighting scheme  $w = [\sigma^2(F_o) + (0.08 F_o)^2]^{-1}$ , where  $n$  and  $m$

Table 2. Atomic parameters of hydrogen

The values of fractional coordinates and their standard deviations in parentheses are multiplied by 10<sup>3</sup>.

Benzidine	$x$	$y$	$z$	$B$
HN(1)	339 (7)	104 (5)	343 (14)	11.6 (2.6)
HN(2)	423 (7)	152 (5)	372 (14)	12.6 (2.8)
H(2)	210 (5)	167 (4)	210 (10)	8.3 (1.9)
H(3)	433 (5)	274 (4)	447 (10)	7.7 (1.7)
H(4)	133 (4)	273 (3)	183 (10)	6.5 (1.5)
H(5)	356 (4)	377 (3)	422 (9)	7.0 (1.6)
H(8)	70 (4)	361 (3)	278 (9)	6.8 (1.5)
H(9)	289 (5)	466 (4)	259 (11)	8.8 (2.0)
H(10)	-9 (5)	460 (4)	231 (10)	8.6 (1.8)
H(11)	218 (5)	563 (4)	265 (11)	8.2 (1.8)
HN(3)	-4 (6)	580 (4)	158 (12)	9.8 (2.1)
HN(4)	76 (5)	617 (4)	173 (11)	8.7 (1.9)
<i>s</i> -Trinitrobenzene				
H(14)	314 (5)	218 (3)	852 (10)	7.4 (1.7)
H(16)	138 (5)	373 (4)	720 (10)	7.7 (1.7)
H(18)	393 (4)	417 (3)	935 (9)	6.3 (1.5)
Benzene				
H(19)	22 (5)	32 (4)	163 (11)	8.7 (1.9)
H(20)	79 (5)	97 (4)	438 (11)	8.7 (1.9)
H(21)	63 (5)	70 (4)	760 (11)	8.7 (1.9)

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30738 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters of carbon, nitrogen and oxygen

The values of the fractional coordinates, thermal parameters and their standard deviations in parentheses are multiplied by 10<sup>4</sup>. The temperature factor has the form  $\exp[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})]$ .

Benzidine	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
N(1)	3740 (4)	1478 (3)	3431 (11)	82 (4)	39 (2)	638 (26)	22 (2)	75 (8)	40 (6)
C(1)	3283 (4)	2095 (3)	3353 (9)	59 (3)	35 (2)	283 (15)	14 (2)	38 (5)	25 (4)
C(2)	2399 (4)	2119 (3)	2612 (9)	60 (3)	29 (2)	270 (14)	2 (2)	31 (5)	7 (4)
C(3)	3709 (3)	2703 (3)	3918 (8)	39 (2)	46 (2)	240 (14)	10 (2)	12 (4)	18 (4)
C(4)	1961 (3)	2737 (3)	2445 (8)	40 (2)	29 (2)	245 (13)	0 (2)	13 (4)	4 (4)
C(5)	3272 (3)	3318 (3)	3757 (7)	37 (2)	38 (2)	195 (11)	0 (2)	11 (4)	-1 (4)
C(6)	2374 (3)	3353 (3)	3012 (7)	36 (2)	29 (1)	178 (10)	0 (1)	11 (4)	3 (3)
C(7)	1891 (3)	4008 (3)	2843 (7)	37 (2)	29 (2)	179 (11)	-2 (1)	10 (4)	-3 (3)
C(8)	991 (3)	4025 (3)	2701 (9)	40 (2)	28 (2)	319 (15)	-3 (2)	8 (5)	3 (4)
C(9)	2302 (4)	4636 (3)	2815 (3)	48 (3)	29 (2)	302 (15)	-6 (2)	28 (5)	-10 (4)
C(10)	533 (4)	4627 (3)	2506 (10)	41 (2)	33 (2)	391 (19)	4 (2)	8 (5)	0 (5)
C(11)	1833 (4)	5239 (3)	2611 (10)	67 (3)	27 (2)	366 (18)	-10 (2)	34 (6)	-10 (4)
C(12)	939 (4)	5246 (3)	2425 (9)	62 (3)	27 (2)	297 (16)	4 (2)	9 (5)	-7 (4)
N(2)	463 (4)	5854 (3)	2254 (10)	81 (3)	31 (2)	536 (22)	9 (2)	-3 (7)	-4 (5)
<i>s</i> -Trinitrobenzene									
C(13)	3649 (3)	3163 (3)	8991 (7)	40 (2)	31 (2)	203 (12)	1 (2)	15 (4)	-2 (3)
C(14)	3041 (4)	2663 (3)	8424 (8)	46 (2)	32 (2)	226 (13)	1 (2)	24 (4)	-2 (4)
C(15)	2206 (4)	2877 (3)	7716 (8)	44 (2)	39 (2)	208 (12)	-3 (2)	21 (4)	-4 (4)
C(16)	1971 (3)	3553 (4)	7579 (8)	37 (2)	51 (2)	188 (12)	5 (2)	12 (4)	3 (4)
C(17)	2606 (4)	4026 (3)	8179 (8)	47 (2)	34 (2)	211 (13)	10 (2)	22 (4)	7 (4)
C(18)	3462 (3)	3851 (3)	8893 (8)	43 (2)	29 (2)	240 (13)	3 (2)	10 (4)	0 (4)
N(3)	4549 (3)	2949 (3)	9760 (7)	41 (2)	34 (2)	300 (13)	6 (1)	5 (4)	-1 (3)
N(4)	1539 (3)	2346 (3)	7102 (8)	48 (2)	59 (2)	299 (14)	-15 (2)	14 (5)	-18 (4)
N(5)	2381 (4)	4754 (3)	8046 (8)	64 (3)	40 (2)	291 (13)	17 (2)	38 (5)	15 (4)
O(1)	5078 (3)	3387 (2)	10326 (8)	44 (2)	40 (2)	510 (16)	0 (1)	17 (4)	-9 (4)
O(2)	4708 (3)	2341 (2)	9781 (8)	55 (2)	32 (1)	538 (18)	12 (1)	2 (5)	-1 (4)
O(3)	1761 (4)	1753 (3)	7336 (10)	84 (3)	44 (2)	635 (22)	-19 (2)	14 (7)	-29 (5)
O(4)	819 (3)	2543 (4)	6409 (10)	45 (2)	84 (3)	549 (20)	-15 (2)	2 (5)	-11 (6)
O(5)	1609 (3)	4898 (3)	7554 (8)	71 (3)	53 (2)	441 (16)	31 (2)	2 (5)	5 (4)
O(6)	2954 (3)	5170 (2)	8453 (9)	82 (3)	32 (1)	612 (20)	8 (2)	72 (6)	19 (4)
Benzene									
C(19)	104 (4)	154 (4)	3111 (10)	62 (3)	45 (2)	351 (19)	7 (2)	22 (6)	-2 (5)
C(20)	469 (5)	568 (4)	4654 (12)	63 (3)	36 (2)	464 (23)	-1 (2)	33 (7)	0 (5)
C(21)	366 (5)	411 (4)	6539 (11)	63 (3)	43 (2)	388 (21)	1 (2)	-1 (7)	-33 (6)

are, respectively, the numbers of reflexions and parameters. Atomic scattering factors for carbon, nitrogen and oxygen atoms were taken from *International Tables for X-ray Crystallography* (1962) and those for hydrogen from Stewart, Davidson & Simpson (1965).

### Results and discussion

#### (a) Arrangement of the molecules

Atomic parameters are given in Tables 1 and 2. Projections of the crystal structure along the *c* and *a* axes are illustrated in Figs. 1 and 2. The intermolecular atomic distances shorter than 3.6 Å are also shown in Fig. 1. The BD and TNB molecules, which are on the

general positions in an asymmetric unit, are alternately stacked along the *c* axis to form molecular columns. The four columns in the unit cell are related by the screw axes and the glide planes. This arrangement of columns leaves channels parallel to the *c* axis around the centre of symmetry, on which the benzene molecules lie with the molecular planes almost perpendicular to those of TNB or BD. This arrangement is consistent with the molecular ratio of the components found by chemical analysis. We have found similar structures for crystals of the BD-TCNQ complexes containing other solvent molecules (dichloromethane: Ikemoto, Chikaishi, Yakushi & Kuroda, 1972; benzene: Yakushi, Ikemoto & Kuroda, 1974). In crystals

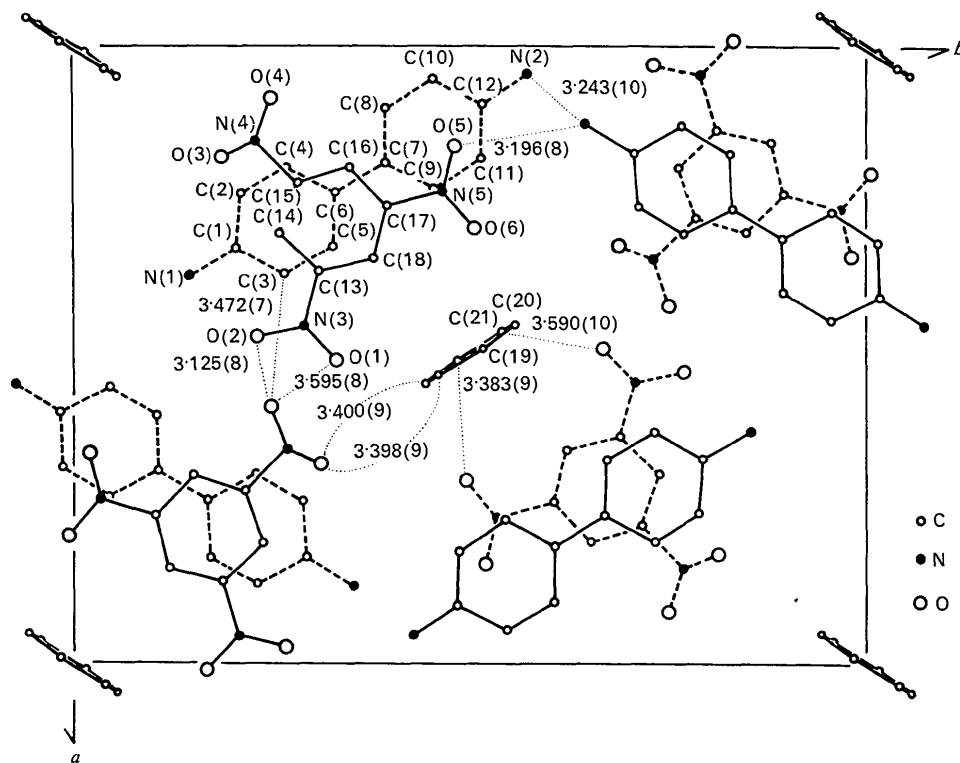


Fig. 1. A projection of the molecular arrangement along the *c* axis.

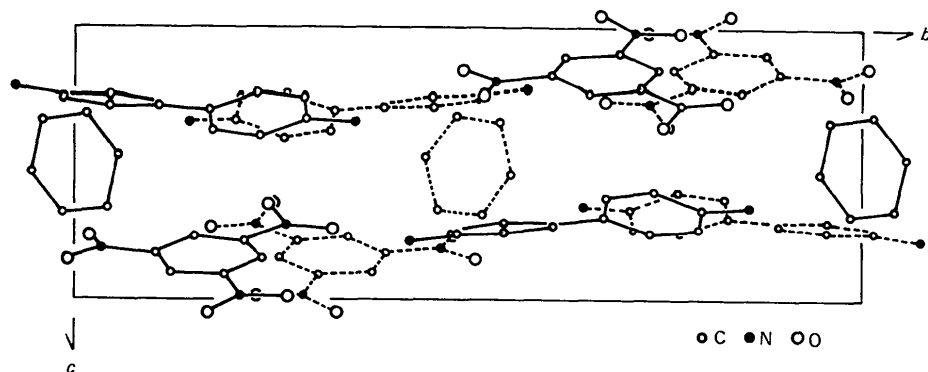


Fig. 2. A projection of the molecular arrangement along the *a* axis.

of BD–TCNQ complexes the arrangement of columns changes so that the channeled structure is stabilized by hydrogen bonds between the neighbouring columns when solvent molecules are accommodated, and the solvent molecules are loosely bound in the lattice as is indicated by their unusually large thermal param-

eters. In the case of the BD–TNB–Bz complex, no indication can be found for any specific interaction between columns or between column and benzene, and benzene molecules seem to be rather tightly bound. Presumably these structural differences are due to the molecular shape of TNB. Possibly the size of channel is determined in such a way that the benzene molecules are closely packed in the channel.

The relative orientation of BD and TNB in this crystal is different from that in the solvent-free crystal (Tachikawa, Yakushi & Kuroda, 1974) as is shown in Fig. 3. The average distance and dihedral angle between the molecular planes of BD and TNB are 3.848 Å and 5.4°, whereas the corresponding values in the solvent-free crystal are 4.004 Å and 7.3°. These differences are likely to be caused by the manner of packing.

The shortest contact between BD and TNB less than 3.4 Å are 3.319 (7) Å for C(6)–C(16) and 3.346 (7) Å for C(7)–C(16).

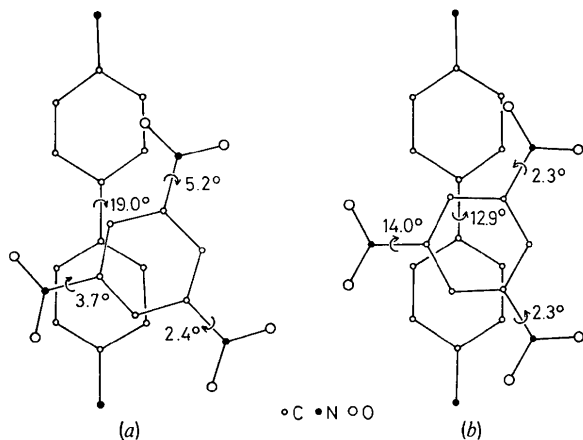


Fig. 3. Relative orientations of BD with respect to TNB. (a) Benzene-containing crystal. (b) Solvent-free crystal.

#### (b) Molecular structures

The geometries of BD, TNB and benzene are given in Figs. 4, 5 and 6. No systematic differences are observed in the bond lengths and bond angles of the BD and TNB molecules between the solvent-free and ben-

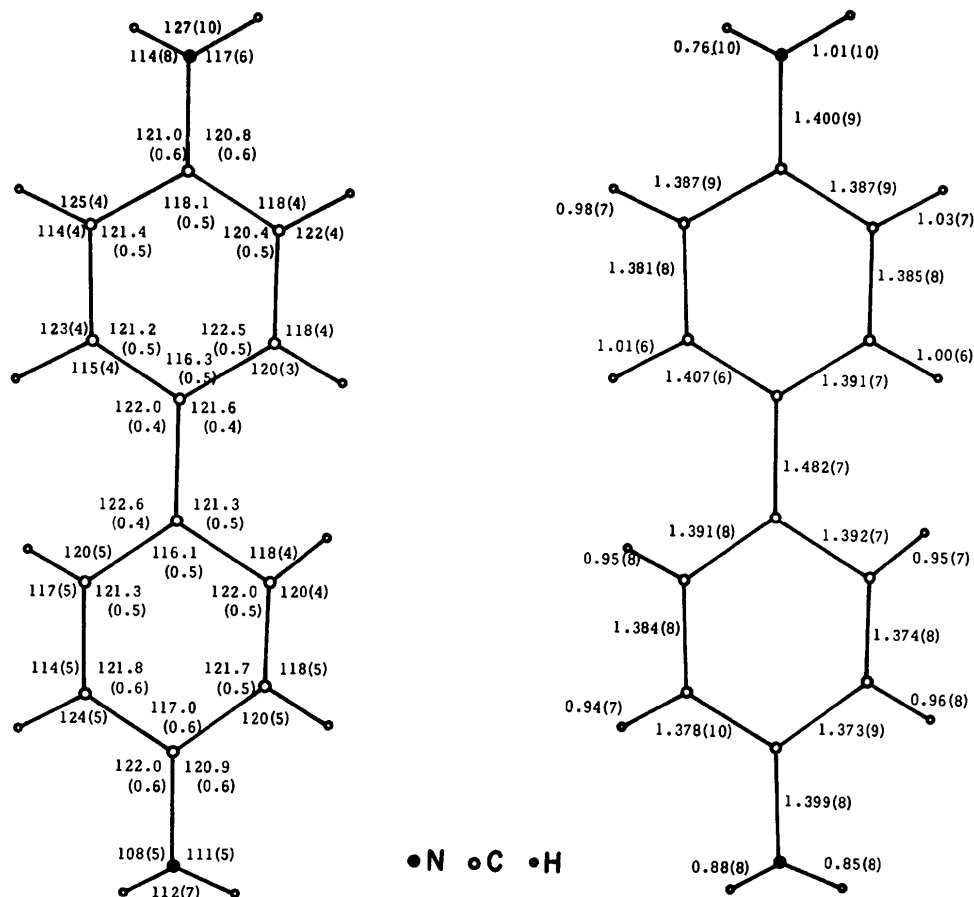


Fig. 4. Bond lengths (Å) and angles (°) of BD.

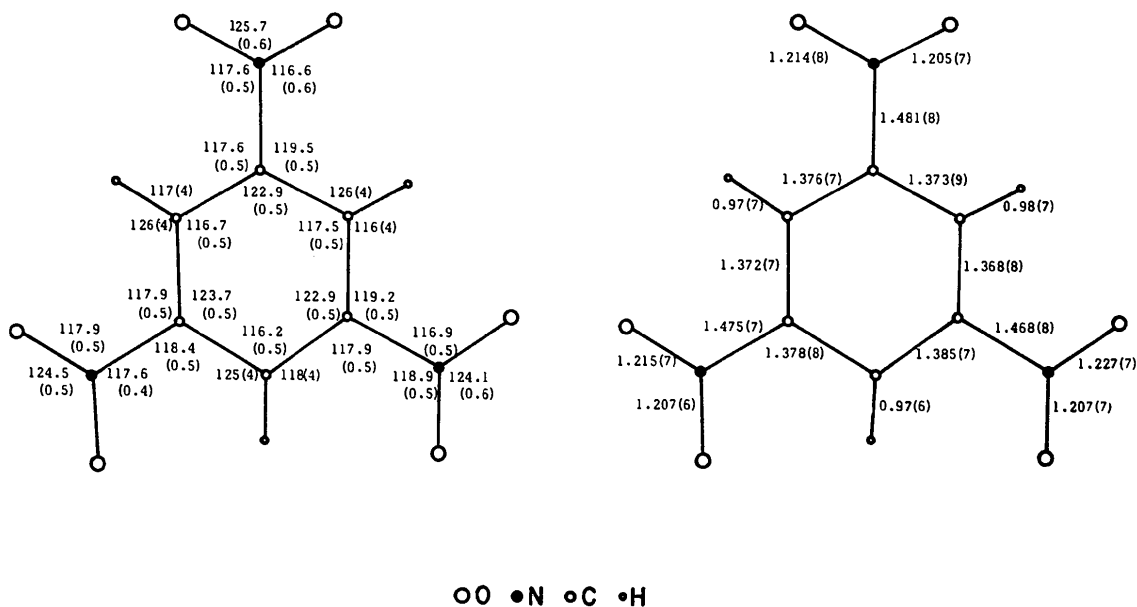


Fig. 5. Bond lengths (Å) and angles (°) of TNB.

zene-containing crystals. The benzene rings of BD are twisted by  $19.0^\circ$  around the C–C bond between them. The nitro groups in TNB are slightly twisted around the N–C bonds; the dihedral angles between the nitro groups and the benzene ring are  $2.4$ ,  $3.7$  and  $5.2^\circ$ . These dihedral angles in BD and TNB are different from those in the solvent-free crystal.

The average length of the C–C bonds in the benzene molecules, without correction for thermal motion, is  $1.371$  Å in this crystal. The corresponding value was reported to be  $1.377$  Å in the benzene crystal at  $-3^\circ\text{C}$  (Cox, Cruickshank & Smith, 1958). If we take into account the situation that the mean-square amplitudes of each carbon atom are slightly larger in the present complex than in the benzene crystal, the bond length of benzene found in the present study seems to be quite reasonable.

The principal root-mean-square amplitudes of the carbon atoms of benzene are  $0.26$ ,  $0.28$ ,  $0.31$  Å for C(19),  $0.26$ ,  $0.27$ ,  $0.33$  Å for C(20) and  $0.25$ ,  $0.28$ ,  $0.34$  Å for C(21). These values are significantly smaller than those of the benzene molecule in the BD–TCNQ–Bz complex and correspond to those of the nitrogen atoms of the nitro groups in this complex. This indicates that the benzene molecules are rather tightly bound 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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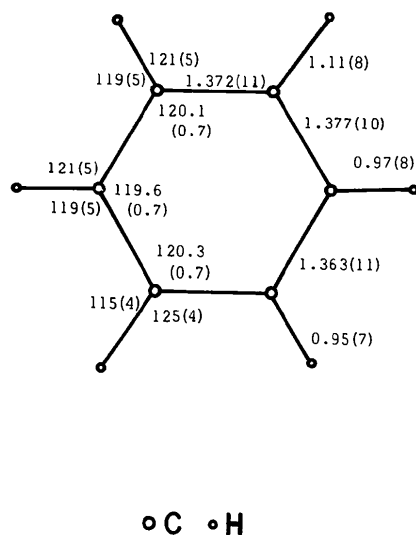


Fig. 6. Bond lengths (Å) and angles (°) of benzene.

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