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The Crystal Structure of the 1:1 Complex of *s*-Trinitrobenzene and *s*-Triaminobenzene

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The crystals of the 1:1 complex formed between *s*-trinitrobenzene and *s*-triaminobenzene are purple-black needles and monoclinic, space group $P2_1/a$ with cell dimensions: $a=14{\cdot}063$, $b=15{\cdot}079$, $c=6{\cdot}982$ Å $\beta=103{\cdot}5°$ and $Z=4$. The structure has been determined by a three-dimensional X-ray analysis using visually estimated Cu $K\alpha$ data. Phases were found for 110 reflexions by the symbolic addition procedure and the subsequent refinement was carried out by block-diagonal least-squares with anisotropic temperature factors, to an R value of 0·082. The component molecules are stacked alternately in infinite columns parallel to the c axis. The mean molecular planes are inclined at 69·3° to the stacking axis. The average spacings between overlapping molecules are 3·24 and 3·29 Å respectively. Bond lengths and angles in the *s*-trinitrobenzene molecule are in reasonable agreement with the corresponding values for the same molecule in other *s*-trinitrobenzene complexes. For the *s*-triaminobenzene molecule the average values are found to be: C–C = 1·400, C–N = 1·398 Å, ∠CCC = 120·0° and ∠CCN = 119·8°. Nitrogen atoms of amino groups are slightly out of the plane of the benzene ring.

Introduction

Crystal structures of the charge-transfer complexes formed by *s*-trinitrobenzene (TNB) as an acceptor have been reported by several authors (Brown, Wallwork & Wilson, 1964; Williams & Wallwork, 1966; Hanson, 1964, 1965, 1966). The result obtained for the series was that the charge-transfer forces of these complexes are fairly weak. The 1:1 molecular complex between TNB and *s*-triaminobenzene (TAB) is, however, one of the more highly coloured among the complexes of TNB and this fact suggests that there is a certain amount of charge-transfer in this complex. Moreover, the molecule TAB is considered to have an appreciable electron-donating power in view of the molecular form and fairly low values of the ionization potential (Nogami, Yoshihara, Nagakura & Yamaoka, 1969). However, no crystal structure of the complex formed by TAB as a donor has yet been reported. The crystal structure analysis of the charge transfer complex between TNB and TAB was undertaken in order to investigate the intermolecular relationships of the complex and to determine the molecular geometry of TAB.

Experimental

A sample of the complex was kindly supplied by Drs H. Hosoya and S. Iwata. Specimens for X-ray work were selected from the original samples without further treatment. The crystals were purple-black c-axis needles and very stable in air. The cell dimensions were obtained from zero level Weissenberg photographs (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å) about the b and c axes. Powder diffraction lines of copper were superposed on the films for calibration purposes.

Crystal data

$C_6H_3N_3O_6{\cdot}C_6H_9N_3$
F.W. = 336·27

Monoclinic

a	$=14{\cdot}063\pm0{\cdot}008$ Å	
b	$=15{\cdot}079\pm0{\cdot}008$	
c	$=6{\cdot}982\pm0{\cdot}008$	
β	$=103{\cdot}5\pm0{\cdot}2°$	
Z	$=4$	
V	$=1439{\cdot}8$ Å^3	
$D_x=1{\cdot}551$ g.cm^{-3}		$D_m=1{\cdot}55$ g.cm^{-3}
Systematic absences	$h0l$	$h=2n+1$
	$0k0$	$k=2n+1$
Space group	$P2_1/a$	(No. 14, C_{2h}^5)

Intensity data were collected for five layers $hk0$–$hk4$ about the c axis and ten layers $h0l$–$h9l$ about the b axis. The multiple-film equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a standard scale. 1833 non-zero reflexions were observed. The usual Lorentz, polarization and spot shape corrections were applied, but no absorption correction was made. During the refinement extinction corrections were found to be necessary for strong reflexions. They were corrected according to the formula $I_o=I_{\rm corr}\exp(-gI_{\rm corr})$. The constant g was estimated graphically. The structure factors obtained from various sets

of layer line photographs were put on the same scale by the least-squares method.

Structure determination

The structure was solved by obtaining the signs directly by means of the symbolic addition procedure (Karle & Karle, 1963). The program *SIGMA* written by Ashida was utilized to list the Σ_2 relationships for each reflexion and to calculate the associated probabilities. The reflexions $\bar{3}\,1\,2$, $\bar{2}\,1\,2$, $11\,4\,1$ were chosen to define the origin. Symbols were assigned to the phases of three additional reflexions. These six assignments, which form the basic set for applying the Σ_2 formula, are shown in Table 1. Through the application of the Σ_2 formula it was found from the relationships among the symbols that b and c were positive and a was negative. Signs of 110 reflexions out of 175 with $|E| \geq 1{\cdot}5$ were determined. After the refinement none of these signs were found to be incorrect. The component molecules

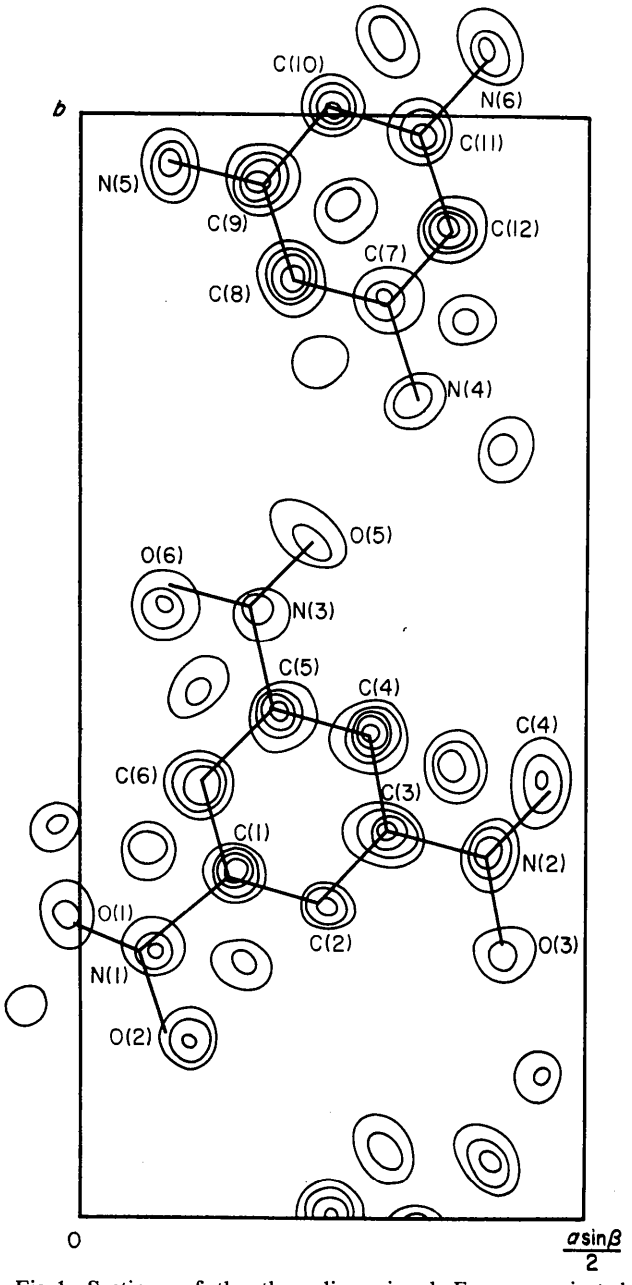


Fig. 1. Sections of the three-dimensional E map projected along the c axis. The contours are at equal intervals on an arbitrary scale.

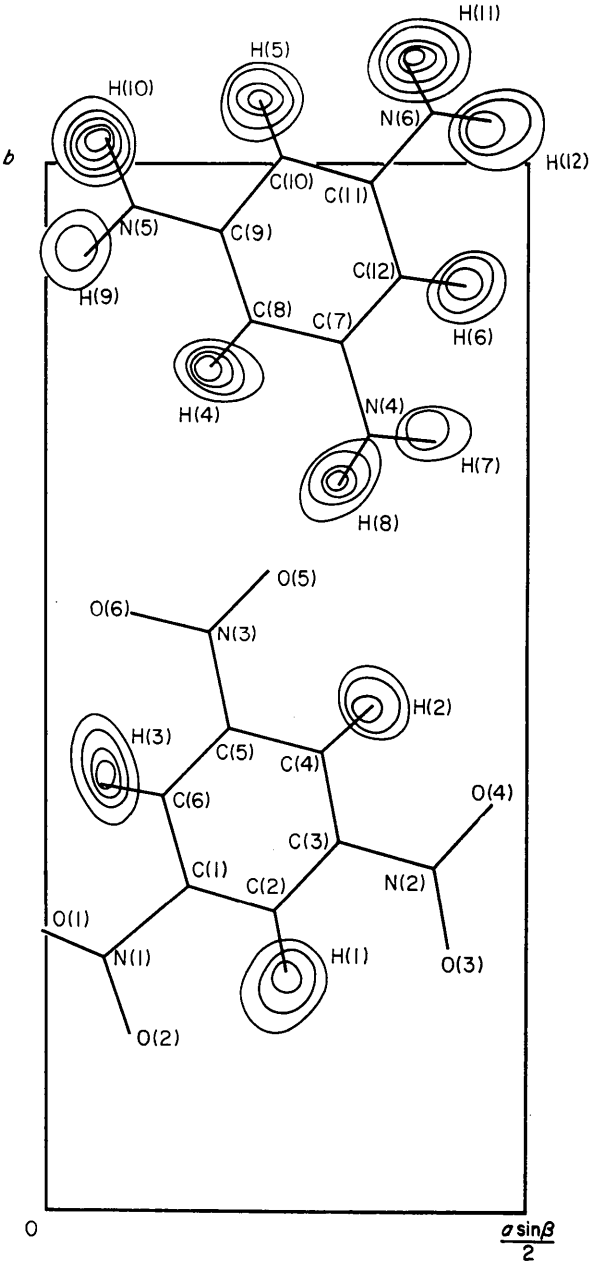


Fig. 2. Sections of the three-dimensional difference Fourier synthesis through the atomic centres parallel to (001). The contours are at intervals of 0·1 e.Å^{-3}, starting with 0·1 e.Å^{-3}.

were readily found from the E map (Fig. 1) computed with these phases.

Table 1. *Initial phase assignments*

h	k	l	$\|E_h\|$	Sign	No. of Σ_2 relations for the reflexion
$\bar{3}$	1	2	4·21	+	62
$\bar{2}$	1	2	3·09	+	45
11	4	1	3·20	+	35
4	10	4	3·39	*a*	28
12	4	0	3·15	*b*	22
$\bar{7}$	2	6	3·25	*c*	23

A structure factor calculation using 400 reflexions ($\sin\theta \leq 0{\cdot}35$) gave an R value of 0·34. The full set of data and individual isotropic temperature factors were then used in five cycles of block-diagonal least-squares refinement. The R value reduced to 0·177. Anisotropic thermal factors were introduced and the R value dropped to 0·123 after three cycles. Hydrogen atoms were located from a difference Fourier syntheses (Fig. 2) and were included in the least-squares refinement with isotropic temperature factors. After extinction corrections for 17 reflexions four more cycles of least-squares refinement were carried out with anisotropic temperature factors for carbon, nitrogen and oxygen atoms and with isotropic temperature factors for hydrogen atoms. The R factor dropped to 0·082 for all the observed reflexions. The atomic scattering factors for carbon, nitrogen and oxygen were taken from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The quantity $\Sigma w(kF_o - F_c)^2$ was minimized where w is the weight function and k is the scale factor. At the final stage of the refinement the following weighting scheme was employed: $w = (4F_{\min}/|F_o|)^2$ if $|F_o| > 4F_{\min}$, $w = 1$ if $4F_{\min} \geq |F_o| \geq F_{\min}$ and $w = 0{\cdot}2$ if $|F_o| < F_{\min}$, where $F_{\min} = 2{\cdot}0$.

The final atomic parameters are listed in Tables 2 and 3. Standard deviations in positional coordinates were: C = 0·004, N = 0·005, O = 0·005 and H = 0·05 Å. A comparison of the observed and calculated structure factors is given in Table 4.

Table 3. *Fractional coordinates* ($\times 10^3$) *and thermal parameters of hydrogen atoms*

	x	y	z	B
TNB				
H(1)	249 (3)	239 (3)	207 (6)	5·2 (0·8) Å^2
H(2)	336 (4)	491 (4)	199 (8)	2·9 (1·2)
H(3)	069 (3)	416 (3)	−058 (6)	2·3 (0·9)
TAB				
H(4)	328 (3)	307 (3)	769 (7)	3·1 (0·9)
H(5)	279 (3)	567 (3)	607 (7)	5·6 (0·9)
H(6)	069 (4)	385 (4)	428 (9)	3·1 (1·3)
H(7)	103 (5)	228 (5)	526 (10)	6·7 (1·6)
H(8)	199 (3)	197 (3)	652 (7)	3·9 (1·0)
H(9)	457 (5)	416 (5)	842 (10)	7·5 (1·7)
H(10)	442 (4)	517 (3)	803 (7)	4·7 (1·1)
H(11)	125 (3)	598 (3)	455 (6)	2·2 (0·7)
H(12)	035 (4)	540 (4)	380 (9)	6·5 (1·5)

Table 2. *The final atomic parameters of non-hydrogen atoms and their estimated standard deviations* (*all quantities* $\times 10^4$)

The anisotropic temperature factors are of the form:

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
TNB									
C(1)	1472 (3)	3144 (3)	0541 (6)	48 (2)	32 (2)	151 (9)	−7 (2)	28 (3)	−5 (3)
C(2)	2376 (3)	2898 (3)	1642 (6)	51 (2)	33 (2)	149 (9)	4 (2)	22 (3)	3 (3)
C(3)	3057 (3)	3549 (3)	2220 (6)	42 (2)	42 (2)	156 (9)	4 (2)	14 (3)	−3 (4)
C(4)	2872 (3)	4434 (3)	1734 (6)	40 (2)	41 (2)	164 (9)	−6 (2)	16 (3)	−11 (4)
C(5)	1947 (3)	4643 (3)	0618 (6)	49 (2)	29 (2)	141 (9)	1 (2)	28 (3)	−1 (3)
C(6)	1242 (3)	4009 (3)	−0005 (6)	42 (2)	42 (2)	148 (9)	3 (2)	13 (3)	−1 (4)
N(1)	0723 (3)	2463 (3)	−0073 (7)	52 (2)	49 (2)	274 (11)	−16 (2)	35 (4)	−31 (4)
N(2)	4035 (3)	3308 (3)	3356 (6)	47 (2)	63 (2)	187 (9)	10 (2)	13 (3)	−6 (4)
N(3)	1699 (3)	5572 (2)	0072 (6)	70 (3)	34 (2)	181 (9)	2 (2)	40 (4)	10 (3)
O(1)	−0028 (3)	2683 (3)	−1276 (8)	54 (2)	79 (3)	540 (18)	−24 (2)	−23 (5)	−38 (6)
O(2)	0872 (4)	1727 (3)	0610 (8)	108 (4)	45 (2)	503 (17)	−29 (2)	27 (6)	15 (5)
O(3)	4203 (3)	2530 (3)	3798 (7)	75 (2)	67 (2)	382 (14)	36 (2)	−27 (5)	−1 (4)
O(4)	4646 (3)	3904 (3)	3875 (7)	40 (2)	90 (3)	353 (12)	−4 (2)	−7 (4)	−5 (5)
O(5)	2309 (3)	6129 (2)	0776 (7)	97 (3)	36 (2)	339 (12)	−13 (2)	29 (5)	3 (3)
O(6)	0914 (3)	5728 (2)	−1032 (6)	79 (3)	51 (2)	262 (10)	26 (2)	27 (4)	35 (4)
TAB									
C(7)	1945 (3)	3294 (3)	5967 (6)	40 (2)	39 (2)	158 (9)	−3 (2)	21 (3)	−5 (3)
C(8)	2882 (3)	3506 (3)	6988 (6)	41 (2)	40 (2)	157 (9)	10 (2)	10 (3)	1 (4)
C(9)	3197 (3)	4390 (3)	7142 (6)	36 (2)	47 (2)	149 (9)	1 (2)	12 (3)	−7 (4)
C(10)	2566 (3)	5062 (3)	6186 (6)	48 (2)	36 (2)	174 (9)	2 (2)	16 (4)	−4 (4)
C(11)	1630 (3)	4834 (3)	5138 (6)	45 (2)	46 (2)	152 (9)	13 (2)	26 (3)	15 (4)
C(12)	1309 (3)	3965 (3)	5039 (6)	33 (2)	51 (2)	154 (9)	3 (2)	1 (3)	0 (4)
N(4)	1648 (3)	2413 (3)	5781 (7)	57 (2)	46 (2)	303 (12)	−10 (2)	7 (4)	−3 (4)
N(5)	4115 (3)	4606 (3)	8282 (7)	42 (2)	53 (2)	260 (11)	−7 (2)	6 (4)	−11 (4)
N(6)	1004 (3)	5483 (3)	4059 (7)	60 (2)	49 (2)	244 (11)	18 (2)	19 (4)	16 (4)

Results and discussion

Thermal motion

The thermal motion ellipsoids of the individual atoms are illustrated in Fig. 3. The molecular motion has been analysed in terms of the rigid body vibrations of translation (T) and libration (ω), using the approach described by Cruickshank (1956). Rigid body thermal parameters are given in Table 5. The bond lengths and angles were corrected for the effect of thermal motion indicated by the above rigid body analysis (Cruickshank, 1956, 1961). Nitro groups of TNB are considered to librate about the C–N bond. The N–O bond distances were corrected by the method of Busing & Levy (1964), assuming riding motion. Bond lengths and angles are given in Tables 6 and 7.

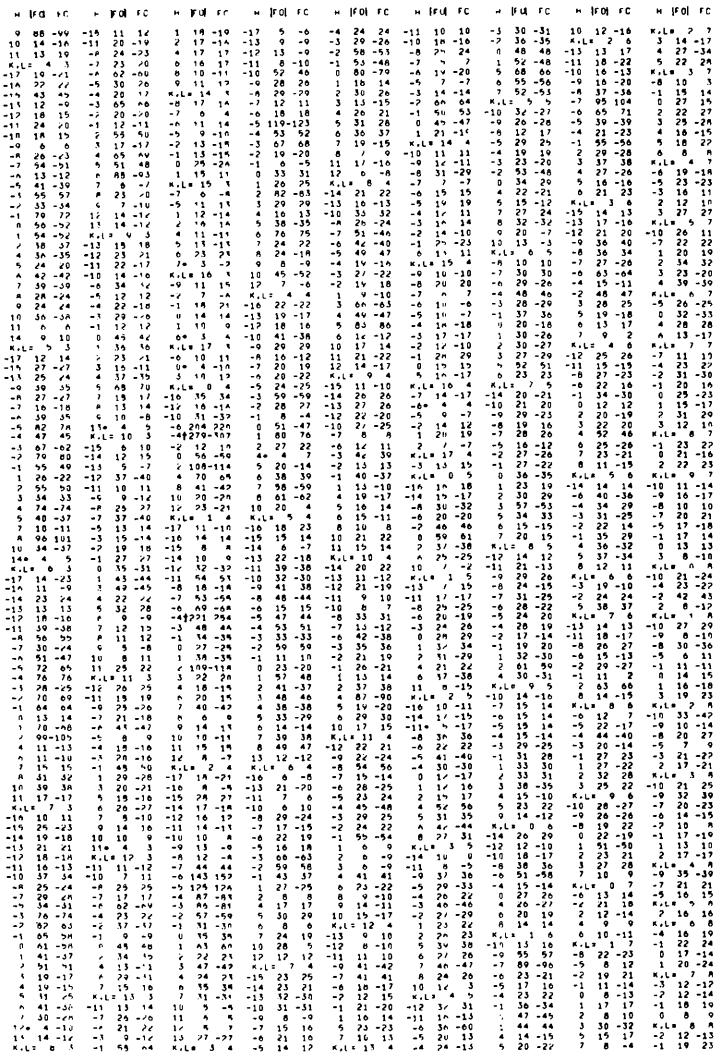
Crystal structure

The arrangement of the molecules in the crystal is shown in Figs. 4 and 5. The structure consists of infi-

Table 4. *Observed and calculated structure factors* ($\times 3$)

* Indicates reflexions for which $|F_o| < F_{min}$.
† Denotes the seventeen reflexions corrected for extinction.

Table 4 (*cont.*)



nite columns of alternate TNB and TAB molecules. The columns are parallel to the *c* axis. The planes of the aromatic rings of TNB and TAB molecules make angles of 69·6 and 69·0° with the *c* axis respectively. It is interesting that one constituent molecule is attracted unequally to its nearest neighbours. The average interplanar spacing between TAB and TNB(I) with the coordinates given in Table 2 is 3·24 Å and that between TNB(II) displaced one unit cell along the *c* axis and TAB is 3·29 Å. These are considerably less than the van der Waals distances for aromatic molecules (3·40 Å) and indicate the effect of the charge transfer force. Intermolecular distances between overlapping molecules are given in Fig. 6. The shortest intermolecular distances are C(2)···C(7), 3·271; C(5)···C(11), 3·301; C(5)···N(6), 3·259; N(3)···N(6), 3·161 Å. The overlapping of the constituent molecules is shown in Fig. 7.

Table 8 gives the intermolecular contacts between adjacent columns of molecules. A few rather short distances are found between the TNB molecule (1) and TAB (6) (Table 8, Fig. 5). The O(5) atom of TNB is connected to N(4) of TAB through H(8) by a weak hydrogen bond N–H···O (3·168 Å). The distance O(5)···H(8) is 2·3 Å, which is shorter than the van der Waals contact. There are no other unusual intermolecular contacts among the molecular stacks. The other relevant intermolecular distances are 3·074 Å for O···O, 3·242 Å for C···O, both between adjacent TNB molecules and 3·251 Å for N···N between TAB molecules. They are of the same order as generally accepted van der Waals distances.

Molecular structure

Details of the molecular structure are shown in Fig. 8. The average values in the TNB molecule (C–C=

1·384, C–N = 1·468, N–O = 1·233 Å, ∠CCC = 122·5 at $C(NO_2)$, 117·2 at CH, ∠CCN = 118·7, ∠CNO = 118·0 and ∠ONO = 123·9°) are in reasonable agreement with the corresponding values for the same molecule in other TNB complexes (Brown *et al.*, 1964; Williams *et al.*, 1966; Hanson, 1964, 1965, 1966). The C–N bond lengths in TNB molecule are near the average of 1·48 Å found for a number of nitro-aromatic hydrocarbons (Trotter, 1960). In the TAB molecule the average bond lengths and angles are: C–C = 1·400, C–N = 1·398 Å, ∠CCC = 120·0 and ∠CCN = 119·8°. The C–C bond of 1·400 Å is slightly longer than that of the TNB molecule. The C–N bond in TAB, 1·398 Å, is significantly shorter than the sum of the single-bond covalent radii, 1·47 Å, in contrast to the results found for nitrobenzene and some other nitro derivatives. The short C–N bonds are also found in other aniline derivatives such as *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961) and 2,5-dichloroaniline (Sakurai, Sundaralingam & Jeffrey, 1963). However, this value is significantly greater than those reported for the polynitro aromatic amines 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965) and 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Holden, 1966) in which average values of the C–N bond of amino groups is 1.32 Å.

The benzene rings of TNB and TAB molecules are planar. The equations of the least-squares planes of the benzene rings of TNB and TAB and $C–NO_2$ groups in TNB are presented in Table 9. The angle between the planes of two aromatic rings of TNB and TAB is 1°. Nitro groups are twisted from the benzene ring. The angles between the plane of $C–NO_2$ groups and the benzene ring are 9·9°, 0·9° and 5·9°, respectively. Nonplanarity appears to be a characteristic of the manner of packing. Nitrogen atoms of TAB deviate considerably from the mean plane of the benzene ring as shown in Fig. 8.

It is thought that the hydrogen atom coordinates are not determined with sufficient accuracy for discussion of the hydrogen atom positions to be meaningful. However, it seems likely that the nitrogen atoms of TAB exhibit some tetrahedral character in view of the direction of the displacements of the hydrogen atoms of the amino groups from the mean plane of TAB. The lone-pair orbital at N(6) is oriented with respect to the TNB(I) molecule at 3·24 Å, and the short distances between N(6)···N(3) (3·161 Å) and N(6)···C(5) (3·259 Å) (Fig. 6) may imply the existence of some interaction, through the nitrogen atoms of the amino group, between the overlapping molecules. The fact that the bond length C(11)–N(6) (1·412 Å) is longer than the other two C–N lengths of amino groups supports the above evidence of molecular interaction.

Computation

The main part of the calculations was performed on the HITAC 5020E computer of the Computer Centre of the University of Tokyo. The reduction of the original data was made with the program *FFLP* written by one of the authors (F.I.) and a computer search for the Σ_2 relations was carried out by the use of the program *SIGMA* written by T. Ashida The remaining calculations were made using the program *UNICS* (Crystallographic Society of Japan, 1967). The block-diagonal least-squares refinement was carried out by the use of the program *HBLS*-4 written by T. Ashida. Fig. 6 was drawn with a plotter from the direct output of the CDC 3600 computer at C. Ito Electronic Computing Service Co., Ltd. using *ORTEP* (Johnson, 1965).

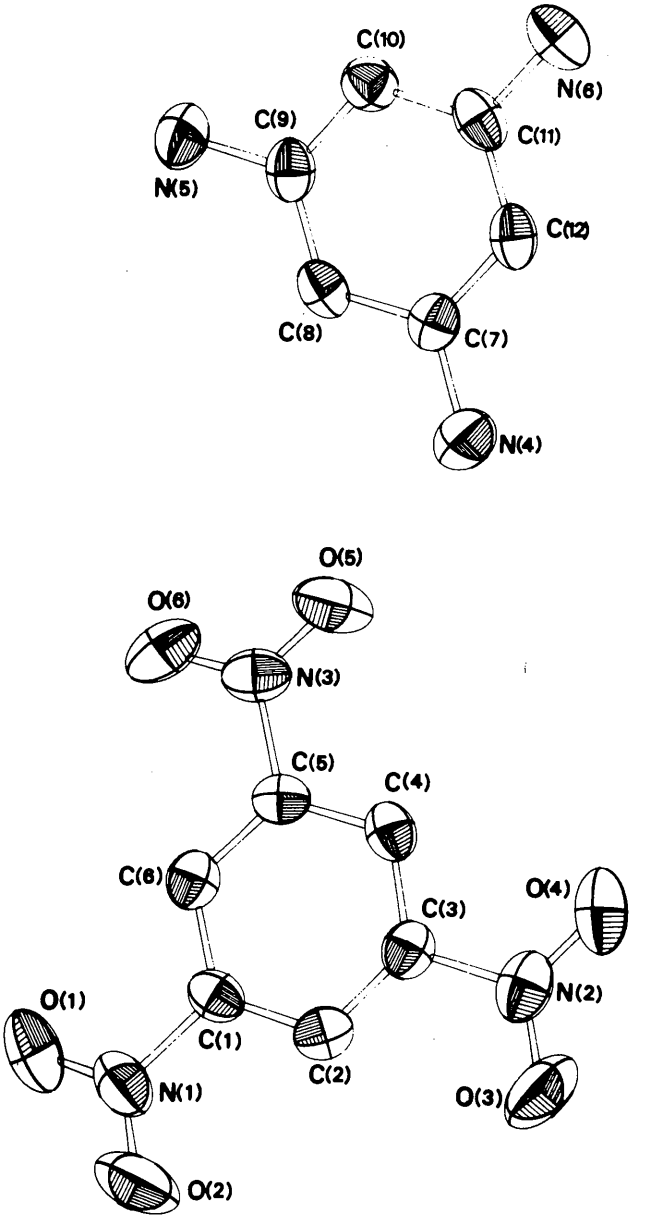


Fig. 3. A perspective drawing of the TNB and TAB molecules showing the ellipsoids of thermal motion with a probability of 50%.

Table 5. *Rigid-body thermal parameters*

TNB				TAB			
Principal axes of the molecule relative to the orthogonal crystal axes (a^*, b, c)							
Moment of inertia (Atomic weight × Å²)	Direction cosines			Moment of inertia (Atomic weight × Å²)	Direction cosines		
839·8	0·879	−0·385	0·348	231·8	0·902	−0·286	0·386
854·2	−0·420	−0·913	−0·007	234·8	−0·321	−0·950	0·005
1690·8	0·330	−0·136	−0·937	466·3	0·375	−0·125	−0·923
Molecular vibrational tensors							
Translation T(× 10^{-2} Å²)				Translation T(× 10^{-2} Å²)			
3·59 0·19 0·02 / 3·66 0·16 / 1·79				3·36 0·09 −0·02 / 4·66 −0·10 / 2·88			
σ(T) (× 10^{-2} Å²)				σ(T) (× 10^{-2} Å²)			
0·26 0·22 0·28 / 0·26 0·28 / 0·43				0·16 0·14 0·17 / 0·16 0·17 / 0·25			
Rotation ω(deg²)				Rotation ω(deg²)			
24·8 6·0 −0·9 / 18·4 3·8 / 16·6				21·6 1·1 −0·6 / 12·4 0·9 / 10·7			
σ(ω)				σ(ω)			
1·9 1·1 1·4 / 1·9 1·4 / 1·1				2·1 1·3 1·6 / 2·1 1·6 / 1·3			
Principal axes of the T and ω tensors relative to the molecular axes							
R.m.s. amplitude	Direction cosines			R.m.s. amplitude	Direction cosines		
0·133 Å	−0·002	−0·086	0·996	0·170 Å	0·042	0·054	0·998
0·185	−0·779	0·624	0·052	0·183	−0·997	0·073	0·038
0·195	0·626	0·776	0·068	0·216	0·071	0·996	−0·057
3·44°	−0·362	0·694	−0·623	3·20°	0·087	−0·414	0·906
4·41	0·406	−0·484	−0·775	3·57	0·087	−0·903	−0·421
5·34	0·839	0·533	0·107	4·66	0·992	0·116	−0·043

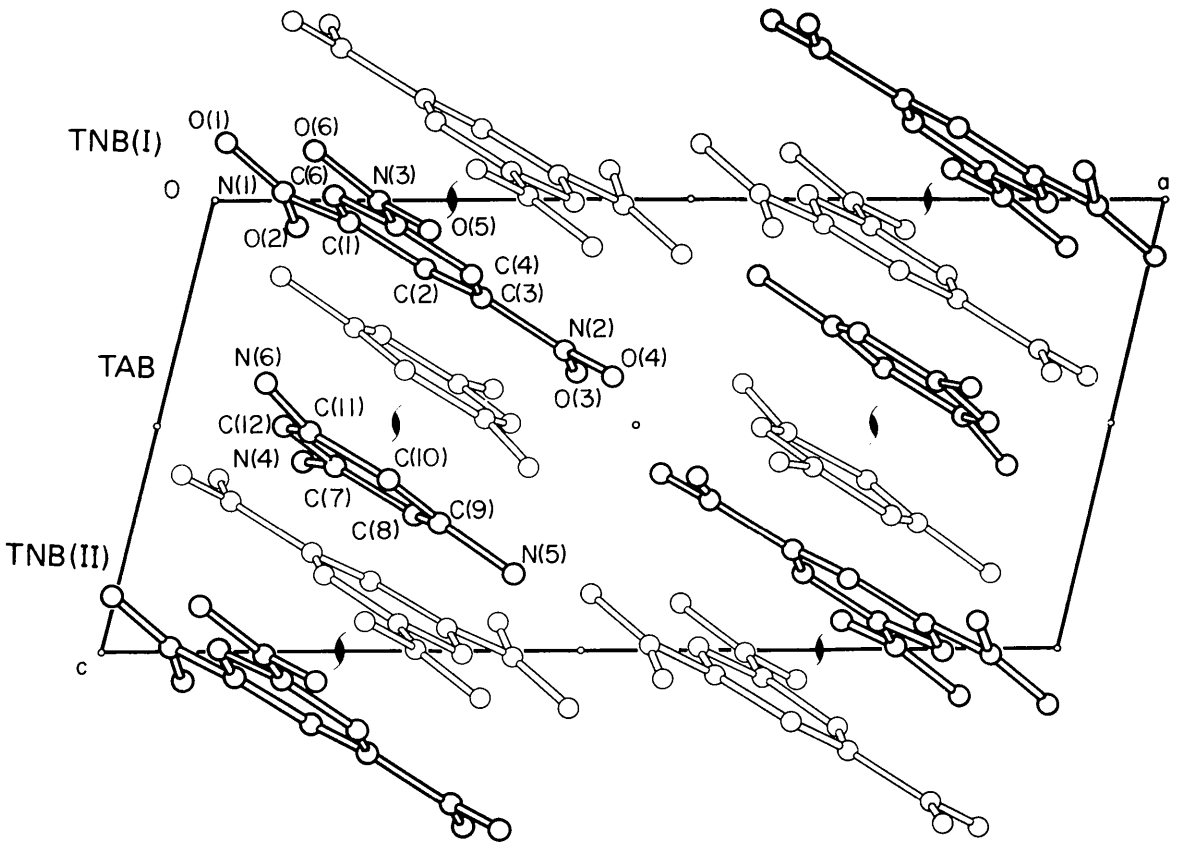


Fig. 4. Projection of the structure along the *b* axis.

Table 6. *Bond lengths with their estimated standard deviation* (Å)

TNB	Uncorrected	Corrected	TAB	Uncorrected	Corrected
C(1)–C(2)	1·375 (5)	1·381	C(7)—C(8)	1·381 (5)	1·386
C(2)–C(3)	1·364 (6)	1·372	C(8)—C(9)	1·401 (6)	1·407
C(3)–C(4)	1·386 (6)	1·392	C(9)—C(10)	1·409 (6)	1·413
C(4)–C(5)	1·389 (5)	1·395	C(10)–C(11)	1·391 (6)	1·396
C(5)–C(6)	1·373 (6)	1·380	C(11)–C(12)	1·383 (6)	1·389
C(6)–C(1)	1·375 (6)	1·381	C(12)–C(7)	1·403 (6)	1·407
C(1)–N(1)	1·462 (6)	1·463	C(7)—N(4)	1·390 (6)	1·392
C(3)–N(2)	1·464 (5)	1·466	C(9)—N(5)	1·389 (5)	1·391
C(5)–N(3)	1·472 (5)	1·474	C(11)–N(6)	1·411 (6)	1·412
N(1)–O(1)	1·232 (6)	1·247	C(8)—H(4)	0·92 (4)	
N(1)–O(2)	1·207 (6)	1·222	C(10)–H(5)	0·98 (6)	
N(2)–O(3)	1·222 (6)	1·233	C(12)–H(6)	0·93 (4)	
N(2)–O(4)	1·238 (6)	1·247	N(4)—H(7)	0·88 (6)	
N(3)–O(5)	1·219 (5)	1·228	N(4)—H(8)	0·90 (5)	
N(3)–O(6)	1·213 (5)	1·220	N(5)—H(9)	0·92 (7)	
C(2)–H(1)	0·83 (4)		N(5)—H(10)	0·98 (5)	
C(4)–H(2)	0·98 (6)		N(6)—H(11)	0·86 (4)	
C(6)–H(3)	0·81 (4)		N(6)—H(12)	0·90 (6)	

Table 7. *Bond angles with their estimated standard deviations*

TNB		TAB	
C(2)–C(1)–C(6)	122·6 (4)°	C(8)—C(7)—C(12)	120·0 (4)°
C(1)–C(2)–C(3)	117·7 (4)	C(7)—C(8)—C(9)	120·4 (4)
C(2)–C(3)–C(4)	122·8 (4)	C(8)—C(9)—C(10)	119·7 (4)
C(3)–C(4)–C(5)	116·9 (4)	C(9)—C(10)–C(11)	119·0 (4)
C(4)–C(5)–C(6)	122·2 (4)	C(10)–C(11)–C(12)	121·2 (4)
C(1)–C(6)–C(5)	117·8 (4)	C(7)—C(12)–C(11)	119·6 (4)
C(2)–C(1)–N(1)	118·9 (4)	C(8)—C(7)—N(4)	119·9 (4)
C(6)–C(1)–N(1)	118·5 (3)	C(12)–C(7)—N(4)	120·0 (4)
C(2)–C(3)–N(2)	119·2 (4)	C(8)—C(9)—N(5)	120·2 (4)
C(4)–C(3)–N(2)	118·0 (4)	C(10)–C(9)—N(5)	120·1 (4)
C(4)–C(5)–N(3)	119·7 (4)	C(10)–C(11)–N(6)	120·3 (4)
C(6)–C(5)–N(3)	118·0 (3)	C(12)–C(11)–N(6)	118·3 (4)
C(1)–N(1)–O(1)	117·1 (4)	C(7)—N(4)—H(7)	120 (4)
C(1)–N(1)–O(2)	118·9 (4)	C(7)—N(4)—H(8)	123 (3)
O(1)–N(1)–O(2)	124·0 (5)	H(7)—N(4)—H(8)	114 (5)
C(3)–N(2)–O(3)	118·5 (4)	C(9)—N(5)—H(9)	114 (4)
C(3)–N(2)–O(4)	118·6 (4)	C(9)—N(5)—H(10)	119 (3)
O(3)–N(2)–O(4)	122·9 (4)	H(9)—N(5)—H(10)	110 (6)
C(5)–N(3)–O(5)	116·7 (4)	C(11)–N(6)—H(11)	104 (2)
C(5)–N(3)–O(6)	118·4 (4)	C(11)–N(6)—H(12)	119 (4)
O(5)–N(3)–O(6)	124·9 (4)	H(11)–N(6)—H(12)	120 (5)
C(1)–C(2)–H(1)	122 (3)	C(7)—C(8)—H(4)	120 (3)
C(3)–C(2)–H(1)	120 (3)	C(9)—C(8)—H(4)	120 (3)
C(3)–C(4)–H(2)	125 (2)	C(9)—C(10)–H(5)	123 (3)
C(5)–C(4)–H(2)	118 (2)	C(11)–C(10)–H(5)	118 (3)
C(1)–C(6)–H(3)	122 (3)	C(7)—C(12)–H(6)	123 (3)
C(5)–C(6)–H(3)	120 (3)	C(11)–C(12)–H(6)	118 (3)

Table 8. *Intermolecular distances less than* 3·6 Å *between non-overlapping molecules*

1	x	y	z	6	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$
2	$-x$	$1-y$	$-z$	7	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-z$
3	$-x$	$1-y$	$1-z$	8	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
4	$1-x$	$1-y$	$1-z$	9	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1+z$
5	$1-x$	$1-y$	$2-z$	10	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	z

Atom (in molecule 1)	To atom	In molecule	d
C(6)	O(6)	2	3·300 (7) Å
O(1)	O(6)	2	3·290 (7)
N(6)	O(1)	2	3·474 (7)
N(6)	O(6)	2	3·523 (6)
C(12)	N(6)	3	3·554 (7)
N(5)	O(4)	4	3·401 (7)

Table 8 (*cont.*)

N(5)	N(5)	5	3·251 (6)
O(5)	N(4)	6	3·168 (6)
N(5)	O(2)	6	3·289 (6)
N(6)	O(3)	6	3·472 (7)
C(2)	O(5)	7	3·242 (6)
N(1)	O(5)	7	3·548 (6)
O(2)	O(5)	7	3·074 (8)
O(3)	O(6)	7	3·316 (6)
O(3)	N(4)	8	3·395 (6)
O(4)	N(4)	8	3·448 (6)
O(3)	O(1)	9	3·371 (8)
C(8)	O(1)	9	3·414 (6)
N(5)	O(2)	9	3·304 (6)
O(2)	N(2)	10	3·559 (8)
O(2)	O(4)	10	3·301 (8)

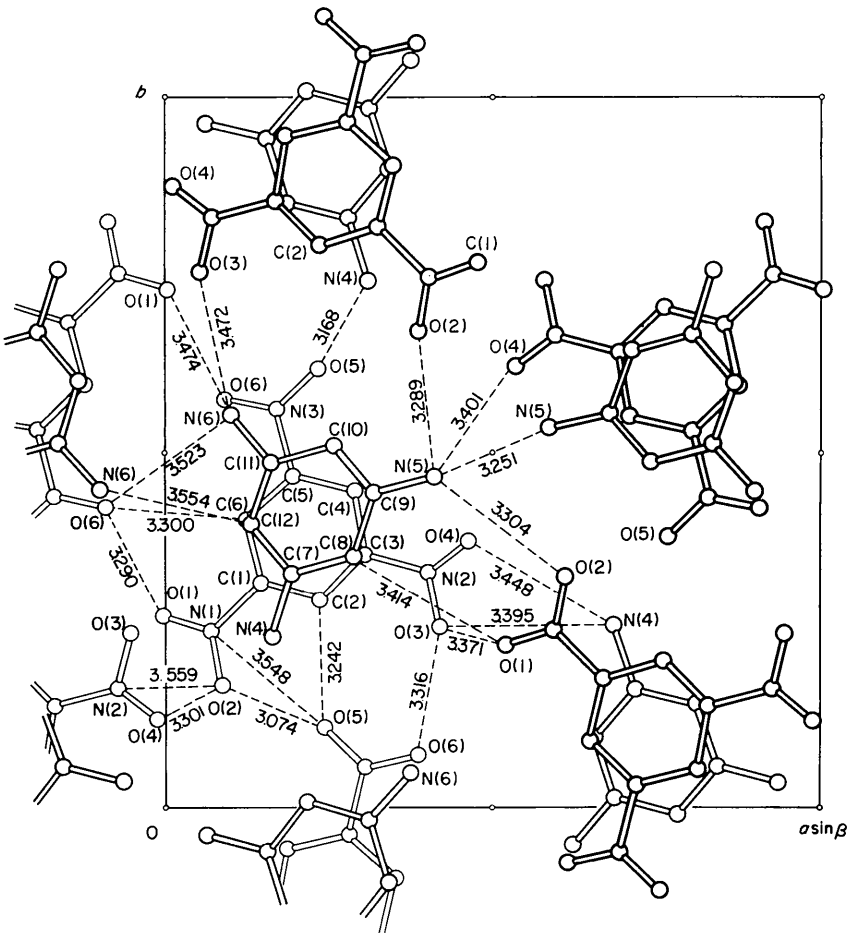


Fig. 5. The molecular arrangement viewed along the *c* axis. Intermolecular distances less than 3·6 Å are shown.

Table 9. *Least-squares planes*

Equation of the plane: $AX+BY+CZ=D$, where X, Y and Z are the coordinates in Å referred to the crystal axes a, b and c. D is the plane-to-origin distance in Å.

		A	*B*	*C*	*D*
1	Benzene ring of TNB	−0·5318	0·1345	0·9372	−0·1136
2	Benzene ring of TAB	−0·5451	0·1240	0·9335	3·0126
3	Nitro group C(1)–NO_2	−0·6094	0·2604	0·8705	0·3024
4	Nitro group C(3)–NO_2	−0·5184	0·1316	0·9426	−0·0661
5	Nitro group C(5)–NO_2	−0·6120	0·0945	0·9064	−0·6227

The displacements (Å) of atoms from the mean planes of the nitro groups

	Plane 3		Plane 4		Plane 5
C(1)	−0·0004	C(3)	0·0030	C(5)	−0·0002
N(1)	0·0014	N(2)	−0·0105	N(3)	0·0006
O(1)	−0·0005	O(3)	0·0038	O(5)	−0·0002
O(2)	−0·0005	O(4)	0·0038	O(6)	−0·0002

References

BROWN, D. S., WALLWORK, S. C. & WILSON, A. (1964.) *Acta Cryst.* **17**, 168.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

CADY, H. H. & LARSON, A. C. (1965). *Acta Cryst.* **18**, 485.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747, 754.

CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.

Crystallographic Society of Japan (1967). 5020 *UNICS*, The Universal Crystallographic Computation Program System.

DICKINSON, C., STEWART, J. M. & HOLDEN, J. R. (1966). *Acta Cryst.* **21**, 663.

HANSON, A. W. (1964). *Acta Cryst.* **17**, 559.

HANSON, A. W. (1965). *Acta Cryst.* **19**, 19.

HANSON, A. W. (1966). *Acta Cryst.* **21**, 97.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

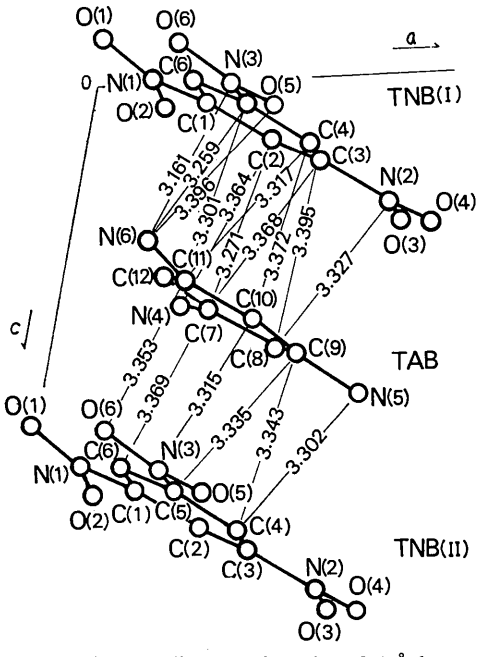


Fig. 6. Intermolecular distances less than 3·4 Å between overlapping molecules. The coordinates of TNB(II) are displaced along the *c* axis from those of TNB(I) which are shown in Table 2. The average interplanar spacings are 3·24 Å between TNB(I) and TAB and 3·29 Å between TAB and TNB(II).

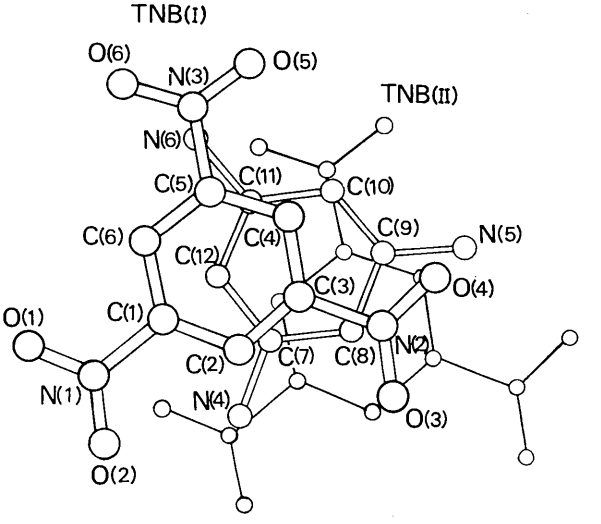


Fig. 7. Diagrammatic representation of the molecular overlap as seen perpendicular to the mean molecular planes.

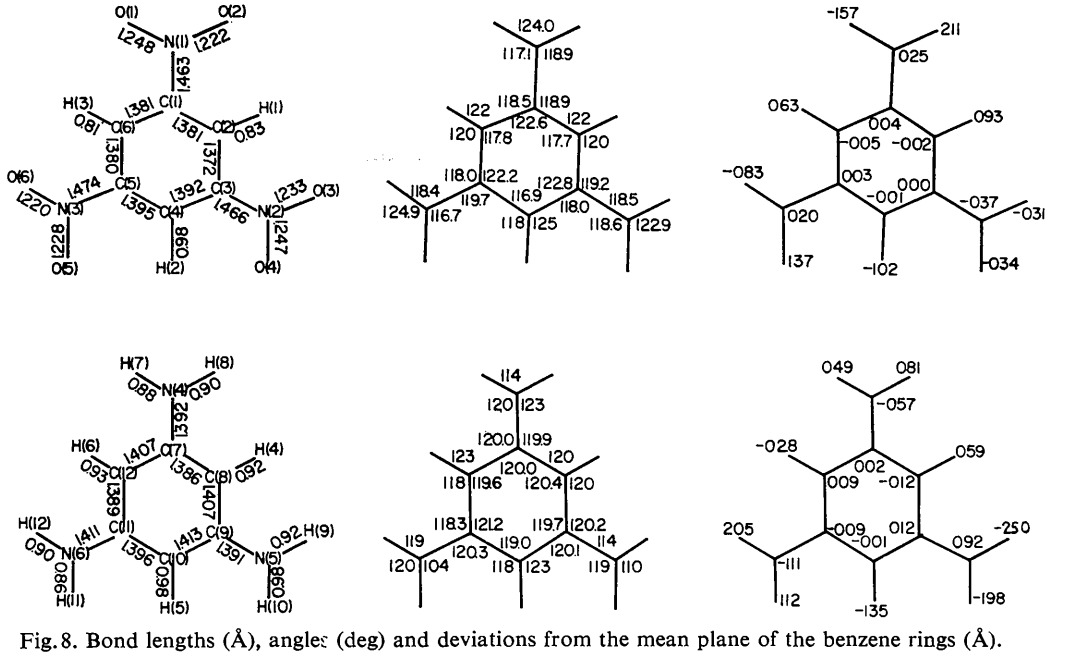


Fig. 8. Bond lengths (Å), angles (deg) and deviations from the mean plane of the benzene rings (Å).

JOHNSON, C. K. (1965). *ORTEP*. Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.

NOGAMI, T., YOSHIHARA, K., NAGAKURA, S. & YAMAOKA, A. (1969). Private communication.

SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

TROTTER, J. (1960). *Tetrahedron*, **8**, 13.

TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.

WILLIAMS, R. M. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 406.