

## The Crystal Structure of 1,3,5-Trinitrobenzene by Neutron Diffraction

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The crystal of 1,3,5-trinitrobenzene (*s*-TNB),  $C_6H_3N_3O_6$ , is orthorhombic *Pbca* with 16 molecules per unit cell ( $a=9.78$  (1),  $b=26.94$  (1),  $c=12.82$  (1) Å). The crystal structure has been determined by analysis of three-dimensional neutron diffraction data. The structure was solved by combination of Patterson and Fourier synthesis and the subsequent least-squares refinement of all positional and anisotropic thermal parameters with 1096 non-zero reflections yielded a final weighted *R* index of 0.046 ( $R=0.056$ ). There are two molecules in an asymmetric unit, one with a non-planar and the other with an essentially planar benzene ring. The  $NO_2$  groups are either twisted or bent out of the benzene ring plane. The oxygen atoms of the  $NO_2$  groups have unusually large vibration amplitudes at room temperature, yet maintain very close approach to the neighboring molecules. Several short  $O\cdots H$  distances (intra-molecular or intermolecular) were found, which appear to indicate  $C-H\cdots O$  type hydrogen bonding.

### Introduction

In recent years, the crystal structures of various 1,3,5-trinitrobenzene (*s*-TNB) complexes, which are known as charge transfer complexes, have been studied by many investigators as described in the later section. However, the complete crystallographic structure of the *s*-TNB crystal is not yet known. The crystal structure of *s*-TNB was investigated by Hertel & Römer (1930). They reported that *s*-TNB possesses an orthorhombic symmetry with 16 molecules per unit cell. Later, Chorghade (1939) has reinvestigated the crystal structure and found that *s*-TNB crystallizes in *Pcab* space group, which is in agreement with the results obtained by Gol'der, Zhdanov, Umanskiy & Glushkova (1952).

In the present study, X-ray diffraction with  $Cu K\alpha$  radiation was used initially but failed to collect enough number of reflection data for the structure determination mainly because of the large thermal vibrations of *s*-TNB at room temperature. Subsequently, this neutron diffraction measurement was performed to accomplish the structure analysis. The space group *Pcab* used by Chorghade (1939) and Gol'der *et al.* (1952) was transformed to the standard orientation *Pbca* in the present study.

### Experimental

The crystal used for the X-ray investigations was grown from the melt by Dr H. D. Fair in our laboratory. It was cleaved into a small needle shape with the diameter less than 0.2 mm. The unit-cell dimensions determined from rotation, Weissenburg and Buerger precession data with the  $Cu K\alpha$  radiation were  $a=9.78$ ,  $b=26.94$ ,  $c=12.82$  Å with the estimated standard deviations of 0.01 Å. The following extinctions were

established:  $hkl$  shows no systematic absences,  $0kl$  present only for  $k=2n$ ,  $h0l$  for  $l=2n$ ,  $hk0$  for  $h=2n$ , which gives us the unique choice of space group, *Pbca*, in the orthorhombic system, and confirms the findings of Chorghade (1939) and Gol'der *et al.* (1952). Three-dimensional diffraction intensities for  $Cu K\alpha$  X-rays were collected by a diffractometer out to a  $2\theta$  of  $80^\circ$ , but the intensities decreased so rapidly with increasing scattering angle that no measurable intensity reflections were found beyond  $60^\circ$  scattering angle. This fact suggests that the *s*-TNB crystal possesses unusually large thermal vibrations at room temperature. Using a total of 496 reflections observed within the reciprocal sphere of  $0.6 \text{ \AA}^{-1}$ , an attempt was made to determine the crystal structure by both Patterson synthesis and the symbolic addition procedure but this failed. A part of the reason for the failure may be attributable to the insufficiency of the number of reflection data, especially those reflections with larger  $\sin \theta/\lambda$ .

Subsequently, the neutron diffraction technique was employed to determine the crystal structure of *s*-TNB at room temperature, using  $0.985 \text{ \AA}$  wavelength neutrons. A cylindrical shaped crystal, approximately 4 mm in diameter and 6 mm long along the crystallographic *a* axis, was kindly supplied for this study by Dr W. J. Fisco from our laboratory. The crystal was mounted on the goniometer cradle with the *a* axis parallel to the goniometer rotation axis. The diffraction intensities were measured by  $\omega$ - $2\theta$  step scanning with  $0.1^\circ$  step intervals in  $2\theta$  over the entire range of each reflection peak. A low efficiency transmission type monitor counter was used in the incident beam, and diffraction intensities were measured for a preset number of incident neutrons. A complete set of three-dimensional reflection data (non-overlapping) was collected within the range of  $60^\circ$  in  $2\theta$ . Among the 1845 reflections investigated, 1098 reflections showed measurable intensity (the reflection

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intensity larger than 2-5σ in terms of counting statistics). The reflection intensities, in general, weakened so rapidly with increasing scattering angle that only

approximately 30% of the reflections showed measurable intensity in the higher scattering angle between 55 and 60°. This is the same phenomenon as that

Table 1. Observed and calculated structure factors

Table with 12 columns: h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc, h, k, l, Fobs, Fcalc. It contains a large grid of numerical data representing observed and calculated structure factors for various reflections.

observed in our X-ray diffraction data, and must be attributed to the fact that the *s*-TNB crystal possesses intense thermal lattice vibrations at room temperature. The systematic absences also agreed with the X-ray investigations.

The observed intensity data were corrected by the Lorentz factor but not corrected for absorption because its effect is small. The linear absorption coefficient for *s*-TNB is about  $0.6 \text{ cm}^{-1}$  (or  $\mu R = 0.12$ ), assuming an incoherent hydrogen cross-section of 40 barns (Rush, 1962). Assuming the crystal is ideally cylindrical, the absorption correction factors for this crystal are estimated to range from 1.23 to 1.27. As an initial attempt, a three-dimensional Patterson function was calculated without sharpening by the temperature factor. The vector peaks thus obtained were rather broad and overlapped. In particular, the short vector peaks, which arise from a pair of bonded atoms, merged together to form a circular band around the origin. Subsequently the Patterson function was sharpened by the temperature factor with  $B = 6.0 \text{ \AA}^2$ , which resolved the circular band into four peaks without

appreciable shift of positions. The Patterson function was analyzed under the assumption that the ring atoms of the *s*-TNB molecule possess approximately hexagonal symmetry within the resolution of the Patterson map. There are two molecules in an asymmetric unit, and one of the two molecules is oriented with the plane of the benzene ring inclined from the unit-cell axes, that is, the symmetry axes of the hexagonal benzene ring was neither parallel nor perpendicular to the symmetry axes of the unit cell. Under this circumstance, only the inversion symmetry operation of the *Pbca* space group could generate a pair of molecules whose intermolecular vectors overlap each other in a regular manner. The vector set formed by two such hexagons shows a readily distinguishable feature, oriented on a plane parallel to the original hexagons. Thus, six carbon atoms of the molecule (*A*), as designated in Table 2, were located from the Patterson synthesis. Then a series of Fourier synthesis using the observed structure factors, with the signs determined by the known atomic positions, were followed to locate the rest of the heavy atoms of both molecules. Hydrogen atom positions

Table 2. Final least-squares parameters of *s*-trinitrobenzene with standard deviations

The values of fractional coordinates and the temperature factors are multiplied by  $10^4$  and  $10^5$  respectively.

The temperature factor is of the form:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

Mol. ( <i>A</i> )	<i>X</i>	<i>Y</i>	<i>Z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	730 (6)	1053 (2)	1711 (4)	1078 (80)	120 (9)	534 (43)	144 (26)	-283 (50)	-37 (17)
C(2)	1770 (6)	1003 (2)	986 (4)	1129 (80)	123 (9)	587 (43)	-33 (22)	-131 (52)	29 (18)
C(3)	2029 (6)	529 (2)	643 (4)	877 (74)	142 (10)	473 (36)	32 (22)	-9 (47)	7 (17)
C(4)	1323 (5)	116 (2)	996 (4)	731 (72)	137 (10)	573 (41)	-18 (21)	-22 (47)	-21 (17)
C(5)	361 (5)	198 (2)	1765 (4)	779 (69)	134 (10)	622 (45)	-14 (22)	31 (51)	6 (18)
C(6)	4 (6)	663 (2)	2125 (5)	995 (88)	129 (10)	642 (44)	86 (22)	-74 (48)	-23 (17)
N(1)	357 (5)	1562 (2)	2073 (4)	1937 (75)	168 (8)	819 (35)	194 (20)	-293 (47)	8 (14)
N(2)	3125 (5)	452 (2)	-131 (4)	1474 (68)	189 (7)	810 (35)	-44 (20)	208 (46)	-5 (14)
N(3)	-337 (5)	-234 (2)	2221 (4)	1221 (64)	190 (8)	965 (43)	-55 (20)	285 (44)	-39 (15)
O(1)	-601 (9)	1605 (3)	2701 (6)	2151 (149)	249 (16)	865 (68)	300 (38)	-248 (81)	-14 (27)
O(2)	1068 (11)	1891 (3)	1726 (7)	2869 (181)	191 (15)	1420 (97)	154 (42)	-181 (109)	-52 (33)
O(3)	4057 (9)	751 (3)	-143 (8)	1655 (128)	244 (16)	1522 (93)	-95 (39)	540 (95)	-27 (34)
O(4)	3033 (10)	108 (3)	-695 (6)	2418 (166)	335 (20)	898 (67)	-155 (47)	884 (88)	-183 (33)
O(5)	34 (11)	-636 (3)	1926 (8)	2945 (188)	188 (14)	1522 (92)	-297 (42)	1273 (113)	-116 (32)
O(6)	-1168 (9)	-161 (3)	2886 (8)	1463 (125)	303 (18)	1371 (86)	-32 (38)	910 (87)	-2 (33)
H(1)	2288 (14)	1333 (4)	675 (10)	2357 (224)	149 (17)	1126 (99)	-104 (53)	421 (134)	133 (37)
H(2)	1572 (13)	-248 (4)	737 (10)	1933 (197)	144 (17)	1239 (111)	-31 (49)	506 (128)	-109 (40)
H(3)	-721 (15)	712 (5)	2722 (11)	2087 (222)	253 (24)	1070 (122)	126 (57)	622 (134)	-69 (44)
Mol. ( <i>B</i> )									
C(7)	1486 (5)	3482 (2)	514 (4)	799 (70)	83 (8)	493 (41)	59 (20)	-49 (43)	-27 (16)
C(8)	1768 (6)	3545 (2)	1569 (4)	1068 (77)	136 (9)	496 (42)	52 (23)	-23 (50)	-33 (17)
C(9)	927 (6)	3278 (2)	2241 (4)	1407 (90)	148 (10)	458 (46)	201 (25)	64 (54)	58 (17)
C(10)	-103 (6)	2962 (2)	1912 (5)	951 (86)	121 (9)	896 (56)	-14 (22)	100 (55)	84 (19)
C(11)	-312 (6)	2924 (2)	855 (4)	794 (74)	125 (9)	694 (48)	-15 (21)	-183 (55)	22 (17)
C(12)	473 (5)	3179 (2)	156 (4)	912 (70)	107 (8)	444 (36)	5 (21)	-110 (47)	-58 (15)
N(4)	2337 (4)	3762 (1)	-238 (3)	1352 (65)	148 (7)	607 (30)	-27 (18)	30 (39)	-18 (13)
N(5)	1189 (5)	3347 (2)	3385 (3)	1769 (85)	237 (10)	617 (38)	154 (23)	30 (46)	55 (16)
N(6)	-1381 (5)	2596 (2)	502 (4)	1348 (70)	163 (9)	1132 (45)	-75 (19)	-317 (50)	54 (17)
O(7)	2008 (9)	3758 (3)	-1139 (6)	2345 (147)	252 (15)	654 (54)	-275 (41)	28 (78)	51 (26)
O(8)	3356 (7)	3976 (3)	99 (6)	1206 (104)	299 (17)	821 (59)	-331 (34)	115 (68)	-20 (28)
O(9)	2231 (8)	3573 (3)	3634 (5)	1485 (119)	322 (18)	605 (51)	74 (38)	-139 (64)	-65 (27)
O(10)	354 (11)	3175 (4)	3954 (7)	2808 (185)	505 (28)	677 (61)	-76 (63)	-30 (96)	138 (35)
O(11)	-2038 (10)	2363 (4)	1129 (8)	2553 (166)	313 (21)	1598 (99)	-486 (50)	-755 (116)	343 (39)
O(12)	-1648 (9)	2591 (4)	-403 (9)	1543 (127)	313 (20)	1636 (103)	-392 (42)	-192 (99)	-131 (38)
H(4)	2535 (13)	3783 (4)	1830 (9)	1707 (175)	197 (20)	916 (85)	-53 (51)	-468 (119)	-70 (37)
H(5)	-723 (14)	2743 (5)	2506 (11)	1705 (202)	271 (22)	1111 (104)	-78 (56)	320 (124)	274 (47)
H(6)	268 (13)	3142 (4)	-736 (7)	2004 (188)	244 (22)	263 (65)	-42 (56)	-202 (98)	-119 (34)

were determined by the difference Fourier synthesis. The position parameters were further refined by the full-matrix least-squares method. In the initial stage of the refinement, an isotropic temperature factor was used for each individual atom. The weighted  $R$  index ( $wR = (\sum w(|F_o| - s|F_c|)^2 / wF_o^2)^{1/2}$ ) after the last cycle of the refinement with the isotropic temperature factor was 10%. The isotropic temperature factors were approximately  $3 \text{ \AA}^2$  for C atoms,  $5 \text{ \AA}^2$  for N and H atoms and 5 to  $8 \text{ \AA}^2$  for the O atoms. The difference Fourier map taken at this stage revealed considerable anisotropic thermal vibration for most of the atoms. Then the refinement was continued with an anisotropic temperature factor for each atom. The final discrepancy factor was  $R=0.059$ ,  $wR=0.046$  for 1096 observed reflections. The parameter shift in the last cycle was negligibly small. The observed and calculated structure factors are given in Table 1 and the final least-squares parameters, with the estimated standard deviations in parentheses, in Table 2.

The weighting scheme based on counting statistics (Evans, 1961) was used:  $\sigma = C \cdot (T+B)/(T-B)L$ , where  $\sigma$ ,  $T$ ,  $B$ ,  $C$ ,  $L$  are the standard deviations of the observed structure factor, total observed intensity, background, secondary extinction correction factor [ $F_c/F_o = \exp(gQ)$ ] and Lorentz factor respectively. The secondary extinction corrections were applied for the 6 most intense reflections, using the linear absorption analogy of the type  $\exp(-gQ)$ . However, the two strongest reflections, 202 and 062, were deleted from the refinement because the extinction was too severe to apply the single parameter empirical correction (Hamilton, 1957). The refinement was based on the structure factors. The quantity minimized was  $\sum w(|F_o|$

$-s|F_c|)^2$ . A set of crystallographic programs, re-edited by Gvildys (1965), was used for the Fourier summation, the least-squares refinement, and the calculation of the interatomic distances and angles and atomic thermal vibrations. The program *ORTEP* (Johnson, 1965) was used for the thermal ellipsoid representations.

### Crystal structure

There are two molecules in an asymmetric unit of the unit cell of the *s*-TNB crystal, designated molecule (*A*) and molecule (*B*). All atoms of each molecule occupy the general positions of the *Pbca* space group, and the mean plane of each molecule is inclined from the crystallographic axes. The least-squares best plane for the benzene ring of molecule (*A*) is oriented almost parallel to the (101) crystallographic plane. The angle between the normal for the plane of molecule (*A*) and the crystallographic *b* axis is approximately  $84^\circ$ . Among the type (*A*) molecules, any adjacent two related by the *a* glide-mirror reflection symmetry are oriented almost perpendicular to each other, and form a continuous zigzag chain stacking along the *a* axis. This resembles the molecular packing in the benzene crystal. A diagonal axis through carbon atoms C(9) and C(12) of molecule (*B*) is nearly parallel to the *c* axis. The normal for the molecular plane of molecule (*B*) is inclined to the *a* and *b* axes by  $40^\circ$  and  $50^\circ$  respectively. Consequently, the pair of molecules (*B*) related by the *a* glide-mirror reflection are roughly parallel to each other, and those related by the other glide-mirror symmetry are almost perpendicular to each other with the inclination angle of approximately  $80^\circ$ .

The least-squares best plane through the benzene

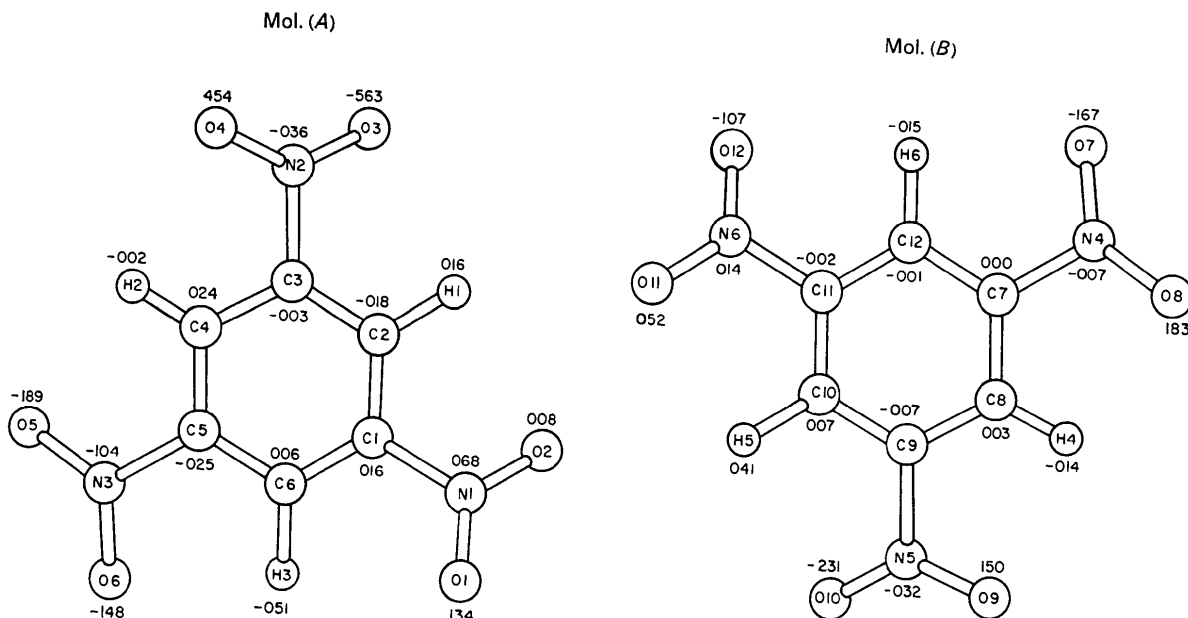


Fig. 1. Deviation of atoms from the mean plane of the benzene ring ( $\text{\AA} \times 10^{-3}$ ).

ring of each molecule is given by:

$-0.6801x + 0.1026y - 0.7259z + 1.7997 = 0$  for molecule (A), and

$0.6451x - 0.7633y - 0.0337z + 6.2590 = 0$  for molecule (B).

The distance of the atoms from each corresponding plane in ångström units are shown in Fig. 1, where the estimated standard deviations are approximately 0.005 Å for C and N atoms, 0.010 Å for O atoms and 0.013 Å for H atoms. The benzene ring of the molecule (A) is not quite planar. The largest deviation from the mean plane occurs at the C(4)-C(5) bond which makes an angle of approximately 88° to the normal to the least-squares plane. The C atom and its attached nitro-group atoms are essentially coplanar in both molecules. The mean plane of each nitro-group is generally inclined from the mean plane of the

benzene ring by either twisting around the C-N bond or simple bending at the attached C atom, or both. The dihedral angles between the least-squares best plane of a nitro-group and that of the benzene ring of molecule (A) are approximately 3° for the N(1) nitro-group achieved by both twisting and bending, 28° for the N(2) nitro-group mostly by twisting, and 8° for the N(3) nitro-group mostly by simple bending. H(1) and H(2) are essentially on the mean plane of the benzene ring but H(3) is slightly out of the plane. The benzene ring of molecule (B) is essentially planar and H(4) and H(6) are on the same plane but H(5) is slightly off from the plane. The mean planes of the N(4) and N(5) nitro-groups are both inclined to the benzene ring plane by approximately 10° twisting around their C-N bond and the N(6) nitro-group is twisted by approximately 5°.

The bond lengths and the unbonded intramolecular

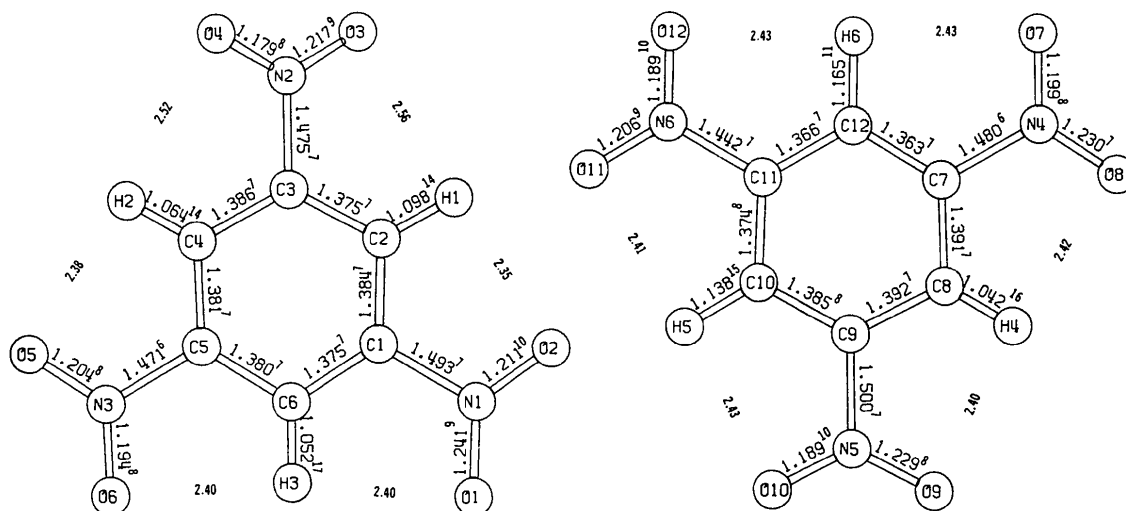


Fig. 2. Bond lengths (Å) of the molecule (A) and the molecule (B). The superscripts are e.s.d.'s (Å × 10<sup>-3</sup>).

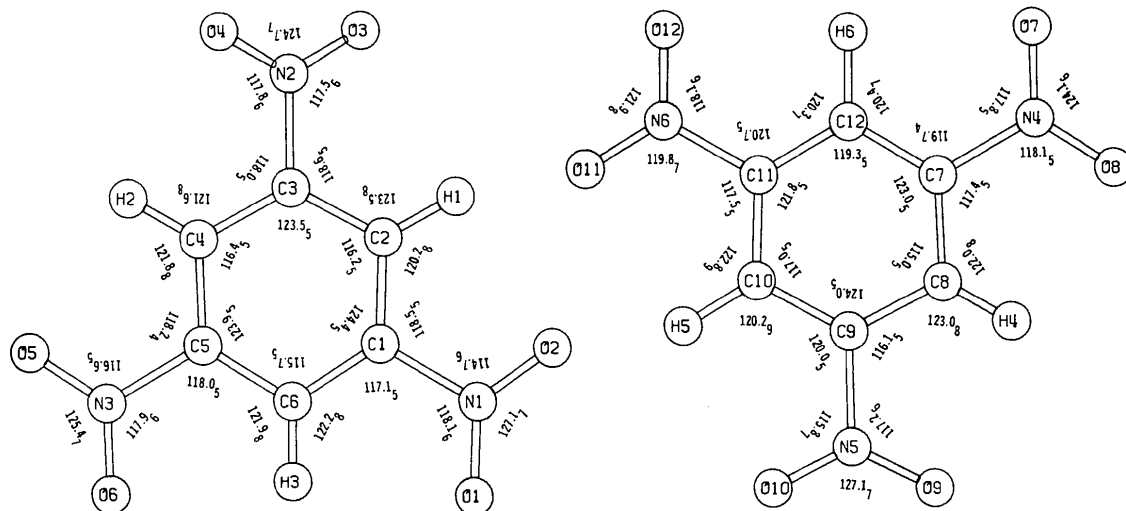


Fig. 3. Bond angles (°) of the molecule (A) and the molecule (B).

atomic distances between H and adjacent O atoms are given in Fig. 2. The C–C distances of molecule (*A*) are 1.38 Å within the estimated standard deviations and those of molecule (*B*) range from 1.37 to 1.39 Å, averaged to 1.38 Å. The C–N bonds of both molecules range from 1.47 to 1.50 Å, except the very short C(11)–N(6) bond of molecule (*B*) which is measured as  $1.443 \pm 0.007$  Å. One of the N–O bonds in each nitro-group is almost always shorter than the other. The difference of the two N–O bond lengths in a nitro-group is approximately 0.03 Å, except for the N(3) and N(6) nitro-group. Two exceptionally long C–H bonds were found; C(12)–H(6) ( $1.165 \pm 0.011$  Å) and C(10)–H(5) ( $1.138 \pm 0.015$  Å). Here, the longest bond C(12)–H(6) is involved in intermolecular hydrogen bonding but C(10)–H(5) is not. The non-bonded intramolecular distances between the H atoms and the adjacent O atoms range from 2.35 to 2.56 Å in molecule (*A*) and from 2.40 to 2.43 Å in molecule (*B*). Assuming the van der Waals radii of the O and H atoms are 1.40 and 1.20 Å respectively, all these distances are shorter than their van der Waals contact distance, particularly the H(1)···O(2) distance which is shorter by approximately 0.25 Å, an indication of an intramolecular hydrogen bond.

The bond angles of both molecules are summarized in Fig. 3, with the estimated standard deviations by subscripts. The C–C–C angles of molecule (*A*) are approximately  $124^\circ$  for the nitro-group substituted C atoms and  $116^\circ$  for the non-substituted C atoms. The corresponding angles of molecule (*B*) are not unique;

122 to  $124^\circ$  for the substituted C atoms and from 114 to  $119^\circ$  for the non-substituted C atoms. The two N–C–C angles from each carbon atom are almost the same with an average angle of  $118^\circ$  in molecule (*A*) but they are different by approximately  $3^\circ$  in molecule (*B*). The O–N–O angles range from  $125$  to  $127^\circ$  in molecule (*A*) and from  $122$  to  $127^\circ$  in molecule (*B*).

In general molecule (*B*), compared to molecule (*A*), exhibits better planarity but is distorted more severely to give widely spread values among the equivalent bond lengths and bond angles. The variation of the bond length of C–N (or C–H) for molecule (*B*) appears to be correlated to its bond angles C–C–C and O–N–O as compared in the following table (the e.s.d.'s are given in parenthesis):

Bond	C(9)–N(5)	C(7)–N(4)	C(11)–N(6)
C–N (Å)	1.500 (7)	1.480 (6)	1.443 (7)
O–N–O ( $^\circ$ )	127.1 (7)	124.1 (6)	121.9 (8)
C–C–C ( $^\circ$ )	124.0 (5)	122.9 (5)	121.8 (5)
Bond	C(12)–H(6)	C(10)–H(5)	C(8)–H(4)
C–H (Å)	1.165 (11)	1.138 (15)	1.042 (16)
C–C–C ( $^\circ$ )	119.3 (5)	117.0 (5)	115.0 (5)

The indications are that the decrease in bond length always accompanies the decrease in its bond angles for both C–N and C–H bonds of *s*-TNB. The correlation between the C–N bond length and the O–N–O angle has been found earlier in other aromatic nitrocompounds and explained on the basis of a hard sphere model (Coppens, 1962).

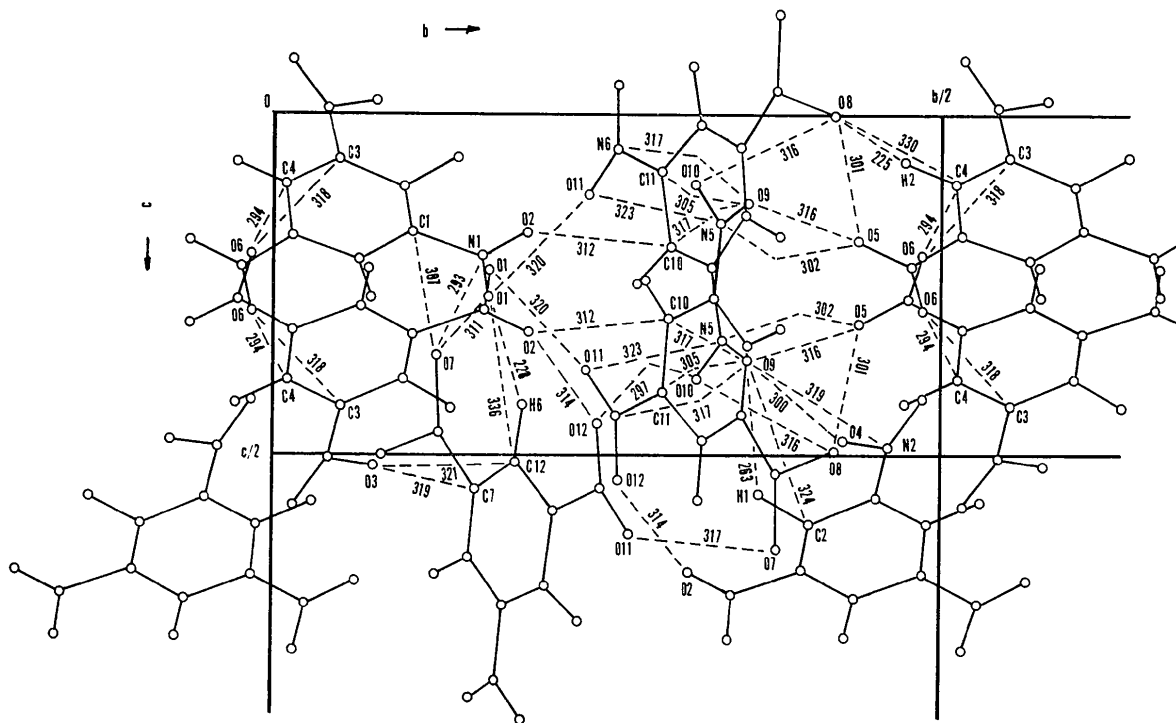


Fig. 4. The molecular arrangement viewed along the *a* axis. Short intermolecular distances are shown in Å × 10<sup>-2</sup>.

There are several reports for the structure of *s*-TNB molecules in a complex compound form; anthracene-*s*-TNB complex (at  $-150^{\circ}\text{C}$ ) by Brown, Wallwork & Wilson (1964); skatole and indole complexes ( $-140^{\circ}\text{C}$ ) by Hanson (1964); azulene complex ( $-95^{\circ}\text{C}$ ) by Hanson (1965); acepleiadylene complex ( $-150^{\circ}\text{C}$ ) by Hanson (1966); tricarbonylchromiumanisole complex by Carter, McPhail & Sim (1966); 2,4,6-tri(dimethylamino)-1,3,5-triazine complex by Williams & Wallwork (1966); *s*-triaminobenzene complex by Iwasaki & Saito (1970). The molecular structures of the *s*-TNB in the above complexes are not unique but distorted from the ideal planar molecule in a different way by each crystal, presumably because of the different intramolecular steric effects and intermolecular packing strains. The two component molecules of the above complexes are always stacked alternately in parallel layers keeping the intermolecular distances as  $3.3 \text{ \AA}$  or greater. Consequently, it is conceivable that the molecules in the *s*-TNB crystal suffer heavier packing strain than those in the charge-transfer complexes, and indeed they are distorted more than any individual *s*-TNB molecule in the complexes. Nevertheless, the bond lengths and angles of the *s*-TNB in the present study agree with those found in the complexes.

Many short intermolecular interatomic distances were found in the *s*-TNB crystal, among which only the distances less than  $3.25 \text{ \AA}$  between the heavy atoms and those less than  $2.6 \text{ \AA}$  between the hydrogens and the heavy atoms are presented in Fig. 4. The e.s.d.'s of the distances are an average  $0.009 \text{ \AA}$  for  $\text{O}\cdots\text{C}$ ,  $0.011 \text{ \AA}$  for  $\text{O}\cdots\text{N}$ ,  $0.013 \text{ \AA}$  for  $\text{O}\cdots\text{O}$ , and  $0.014 \text{ \AA}$  for  $\text{O}\cdots\text{H}$  distances. All these short distances occur between the oxygen atoms which occupy the periphery

of the molecule and the atoms of the neighboring molecules. The closest approaches are  $2.94 \text{ \AA}$  for  $\text{C}(4)\cdots\text{O}(6)$ ,  $2.93 \text{ \AA}$  for  $\text{N}(1)\cdots\text{O}(7)$ ,  $3.05 \text{ \AA}$  for  $\text{C}(11)\cdots\text{O}(9)$ , and  $3.07 \text{ \AA}$  for  $\text{C}(1)\cdots\text{O}(7)$ . Assuming van der Waals radii of  $1.57$ ,  $1.50$ , and  $1.40 \text{ \AA}$  for carbon, nitrogen and oxygen atoms respectively, these intermolecular distances appear to be the limit of the van der Waals contact. There are two short intermolecular distances between oxygen and hydrogen atoms, which are likely to form the  $\text{C-H}\cdots\text{O}$  type hydrogen bond. The  $\text{O}\cdots\text{H}$  distance, the  $\text{O}\cdots\text{C}$  distance, and the angle  $\text{C-H}\cdots\text{O}$  are  $2.25 \text{ \AA}$ ,  $3.30 \text{ \AA}$ , and  $168 \pm 1^{\circ}$  respectively for  $\text{C}(4)\text{-H}(2)\cdots\text{O}(8)$ , and  $2.28$ ,  $3.37 \text{ \AA}$  and  $154 \pm 1^{\circ}$  respectively for  $\text{C}(12)\text{-H}(6)\cdots\text{O}(1)$ . Fig. 5 is a schematic illustration of these configurations, including the intermolecular hydrogen bonds, viewed along the normal direction of each molecular plane. The bending (or non-planarity) of the benzene ring of molecule (A) could be explained by the very tight contacts of  $\text{O}(6)$  to  $\text{C}(4)$  and  $\text{O}(7)$  to  $\text{C}(1)$ . It is also interesting to notice that both oxygen atoms of (N4) nitro-group interact strongly by either van der Waals contacts or hydrogen bonds with neighbors. This tight contact of the (N4) nitro-group oxygens appears to influence strongly the thermal vibrations of molecule (B), not only the librations of the (N4) nitro-group but also those of the entire molecule, as will be discussed in the following section.

### Thermal vibrations

One of the most interesting features of the *s*-TNB is the large amplitude of the thermal vibrations at room temperature. The thermal ellipsoids of the *s*-TNB

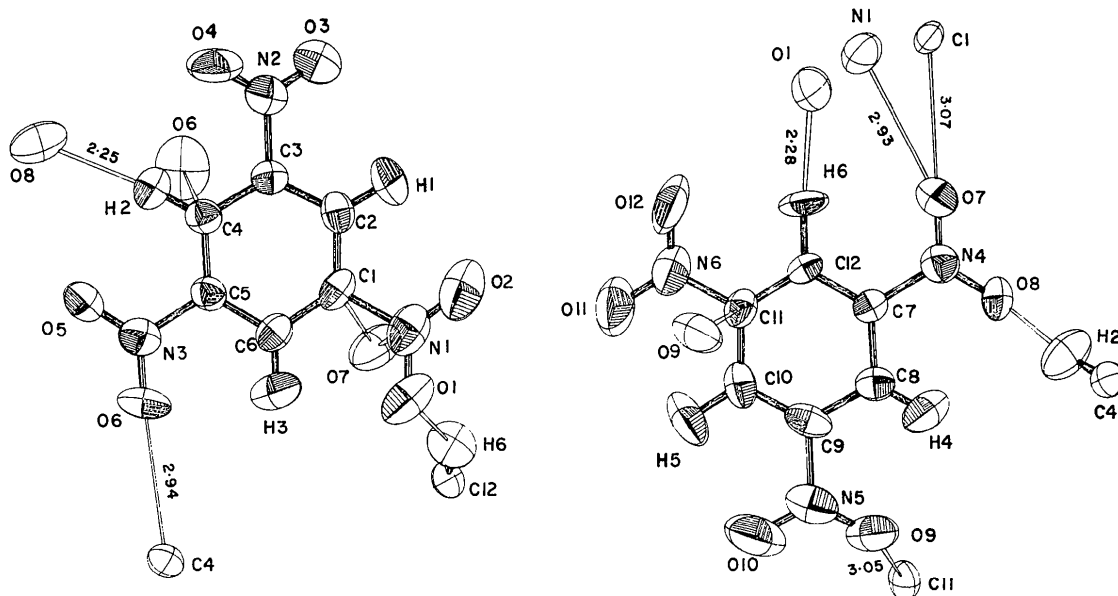


Fig. 5. Thermal ellipsoid representation viewed along the direction perpendicular to each molecular plane. Among the short contact neighbors, only those considered to be significantly short (less than  $3.07 \text{ \AA}$  for  $\text{C}\cdots\text{O}$ ,  $3.0 \text{ \AA}$  for  $\text{N}\cdots\text{O}$  contacts or  $2.3 \text{ \AA}$  for  $\text{O}\cdots\text{H}$  hydrogen bond) are shown without octant shading.

molecules scaled to include a 50% probability distribution are presented in Fig. 5, viewed along the normal direction of each molecule. The anisotropic thermal motions of the heavy atoms were examined by converting the thermal parameters in Table 2 into the three principal components of root-mean-square displacement from the equilibrium position. The results are presented in Table 3. The isotropic temperature factors equivalent to the anisotropic components ( $B = \frac{4}{3}(\beta_{11}^2 a^2 + \beta_{22}^2 b^2 + \beta_{33}^2 c^2)$ ; Hamilton, 1959) are also included in the Table. In the molecule (A), the isotropic  $B$ 's are in the ranges of  $3.7 \pm 0.2 \text{ \AA}^2$  for C atoms,  $5.7 \pm 0.2 \text{ \AA}^2$  for N atoms,  $7.0 \pm 0.5 \text{ \AA}^2$  for H atoms and  $8 \pm 1 \text{ \AA}^2$  for O atoms. This distribution of the isotropic  $B$ 's in molecule (A) appears to suggest that the molecule librates as a rigid body, so that the vibration amplitude of each atom is approximately proportional to its distance from the libration center located at the center of the benzene ring. Similar distribution of the isotropic  $B$ 's occur in molecule (B), e.g. the lowest vibration amplitude for the benzene ring atoms, and the highest for the oxygens. However, the magnitudes of the  $B$ 's are spread in wide ranges within a given atom group in a systematic way, which appears to indicate that the molecular libration center is shifted from the center of the benzene ring toward a position between the C(7) and C(12) atoms. Further investigations of the thermal ellipsoids suggest that each nitro-group executes additional twisting and bending motions in addition to the rigid body libration of the molecule. In Table 3, the cartesian coordinate axes (radial, normal, and tangential) which determine the direction of the largest r.m.s. displacement  $R_3$  are defined differently for each atom. For a C atom 'X', the radial axis is directed from the opposite atom in the benzene ring toward the 'X' atom, and the normal axis is in the direction perpendicular to both the radial direction and the vector between the two C atoms adjacent to the 'X' atom. For any atom 'Y' of an NO<sub>2</sub> group, the radial axis is directed from the C atom attached to the NO<sub>2</sub> group toward the atom 'Y', and the normal direction is perpendicular to both the radial axis and the direction defined by the two O atoms of the NO<sub>2</sub> group. The directions of the  $R_3$ 's appear to indicate that most of the benzene atoms and the N(1) nitro-group in the molecule (A) librate in the mean plane of the benzene ring about an axis near the center of the ring, with the exception of atoms C(4) and C(5) which are dislocated from the mean plane approximately by 0.025 Å toward opposite directions of each other. The ring atoms of molecule (B) are also dominated by the in-plane libration about an axis located somewhere between C(7) and C(12). The  $R_3$  direction of the atoms of the nitro-groups is always nearly perpendicular to the radial axis. This could be the indication that the nitro-groups vibrate as an independent rigid group with the libration center at the attached C atom, and exhibit motions quite different from those of the benzene ring. The dominant libra-

tions of the N(2) and N(2) nitro-group occur toward the direction normal to each nitro-group plane (normal bending). The nitro-groups of molecule (B) are affected by the off-centered in-plane oscillation of the benzene ring. The other motions superimposed on this are a combination of the normal bending and the oscillation about the C-N axis for the N(4) nitro-group, and the oscillations about the C-N axis for the N(5) and N(6) nitro-group. The large differences in the r.m.s. displacements of the two oxygens in each N(5) and N(6) nitro-group indicate that the oscillation axis is shifted from the C-N direction toward the C(9)···O(9) direction for the N(5) nitro-group and toward the C(11)···O(12) direction for the N(6) nitro-group. Similar type of nitro-group librations have been reported in the other nitro-compounds, for example, acepleiadylene-*s*-trinitrobenzene (Hanson, 1966), and tetryl (Cady, 1967).

Table 3. *Magnitudes of the principal axes of the thermal vibration ellipsoids and direction angles, relative to the three orthonormal vectors (radial, normal, and tangential, as defined in the text), of the longest principal axis of heavy atoms*

The isotropic temperature factors equivalent to the anisotropic temperature factors given in Table 2 are included.

	r.m.s. components ( $\text{\AA} \times 10^3$ )			$R_3$ directions ( $^\circ$ )			$B(\text{\AA}^2)$
	$R_1$	$R_2$	$R_3$	rad.	norm.	tan.	
Mol. (A)							
C(1)	161	193	279	81	86	10	3.71
C(2)	202	211	251	72	82	19	3.92
C(3)	196	204	231	85	80	11	3.54
C(4)	187	214	232	53	58	53	3.52
C(5)	194	218	229	87	45	45	3.66
C(6)	190	224	252	43	89	47	3.93
N(1)	208	261	337	86	76	15	5.90
O(1)	227	260	386	80	84	11	7.06
O(2)	253	336	388	67	76	27	8.63
N(2)	236	262	291	79	20	74	5.47
O(3)	245	299	383	90	25	65	7.81
O(4)	184	323	424	80	12	83	8.31
N(3)	221	258	306	68	22	88	5.50
O(5)	212	259	478	78	14	84	8.92
O(6)	175	333	393	81	10	87	7.81
H(1)	193	306	365	—	—	—	6.92
H(2)	210	264	367	—	—	—	6.58
H(3)	215	316	369	—	—	—	7.47
Mol. (B)							
C(7)	156	192	219	5	86	88	2.91
C(8)	198	215	244	35	86	55	3.77
C(9)	172	203	302	69	89	21	4.24
C(10)	193	217	285	71	78	23	4.35
C(11)	182	217	253	83	61	30	3.75
C(12)	162	207	228	63	90	27	3.18
N(4)	221	235	260	75	42	52	4.49
O(7)	223	264	376	89	20	70	6.88
O(8)	181	261	370	83	15	77	6.24
N(5)	222	261	329	70	74	26	5.91
O(9)	214	269	350	72	44	52	6.35
O(10)	228	367	441	85	23	68	9.98
N(6)	224	246	328	85	54	37	5.78
O(11)	225	285	489	83	29	62	9.80
O(12)	183	365	398	72	40	55	8.59
H(4)	209	282	332	—	—	—	6.10
H(5)	194	306	379	—	—	—	7.79
H(6)	144	308	316	—	—	—	5.73



The vibration amplitudes of oxygen atoms, in general, are closely related to their contact distances with the neighbors in such a way that the atoms with shorter contacts exhibit smaller amplitudes. For example, the O(9) of the N(5) nitro-group which shows a short contact distance with its neighbor [O(9)···C(11)=3.05 Å] shows much less vibration amplitude than the O(10) of the nitro-group. The same explanation could be given to the asymmetric libration of N(6) nitro-group, in which O(12) is involved to the short contact with its neighbor [O(12)···O(10)=2.97 Å]. In the case of the N(4) nitro-group, both oxygens are involved in the tight packing, O(7) by short van der Waals contact and O(8) by intermolecular hydrogen bonding as shown in Fig. 5. As a result, the vibration amplitudes of the entire nitro-group including the attached C(7) atom are reduced considerably when compared to the other equivalent atoms in the molecule. Perhaps, the apparent shift of the libration center in the molecule (*B*), as discussed earlier, may be attributed partly to this tight packing of the N(4) nitro-group oxygens.

An attempt to analyze quantitatively the thermal motions of the *s*-TNB molecule by a rigid body approximation may not be worthwhile because of the complicated internal motions discussed above. Nevertheless, analysis by the method of Schomaker & Trueblood (1968) was made for a segment of the molecule containing C and N atoms. This yields the result that the segment of molecule (*A*) oscillates about an axis approximately parallel to the C(1)–C(5) direction with an amplitude of 5.2°; in the case of molecule (*B*) the amplitude is 4.5° with oscillation about an axis approximately parallel to the C(9)–C(12) direction. The r.m.s. deviations of the observed  $U_{ij}$ 's from those calculated with the rigid body parameters,  $[\sum(\Delta U_{ij})^2/(\eta-s)]^{1/2}$ , were rather large, 0.0035 for the segment of molecule (*A*) and 0.0055 for that of molecule (*B*).

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## La Structure Cristalline du Tétramétaphosphate de Cuivre, $\text{Cu}_2\text{P}_4\text{O}_{12}$

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Copper tetrametaphosphate,  $\text{Cu}_2\text{P}_4\text{O}_{12}$ , crystallizes in the monoclinic system, space group  $C2/c$ . Unit-cell parameters are  $a = 12.552$  (8),  $b = 8.083$  (3),  $c = 9.573$  (3) Å;  $\beta = 118.66$  (1)°;  $Z = 4$ . The crystal structure has been determined and refined. Intensities were measured on a single-crystal diffractometer using Mo  $K\alpha$  radiation. The final  $R$  value is 0.058. Atomic coordinates, bond lengths and valency angles are given.

### 1. Préparation

Le tétramétaphosphate de cuivre, objet de cette étude, a été préparé suivant une méthode décrite par Warshauer (1903) et reprise plus tard par Thilo & Grunze

(1957). Cette même méthode a été suivie également par Beucher & Grenier (1968) pour la préparation de tous les métaphosphates de cations bivalents.

Dans le cas du cuivre, les cristaux obtenus sont de formes extrêmement variées. Les plus fréquentes sont