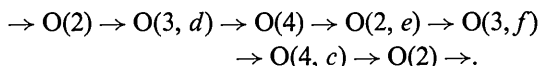


The hydrogen bonding in the DL structure is extensive and involves all the oxygen atoms. The distances and angles are shown in Table 7. The left and right handed molecules are linked in pairs across centers of symmetry by a hydrogen bond from O(1) to O(5), the ring oxygen atom, as shown in Figs. 3 and 4. These DL pairs are then linked into a three-dimensional network by a donor/acceptor chain of hydrogen bonds which interconnect molecules of the same sense through the sequence



These hydrogen bonded chains linking a sequence of D or of L molecules are therefore also centrosymmetrically related. There are two non-bonded O...O distances which are 3.16 and 3.30 Å and these are also shown in Table 7.

This research has been supported by the U.S. Public Health Service, National Institutes of Health, through Grant no. GM 11293. We wish to thank Dr R. D. Rosenstein for his valuable suggestions concerning this work and Mr G. L. Gartland for the visual measurement of intensities.

#### References

- BERGHUIS, J., HAANAPPEL, I. J. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BEURSKENS, P. T. (1963). *Sign Correlation by the Sayre Equation*. Technical Report, The Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pa. 15213.
- BROWN, G. M. & LEVY, H. A. (1963). *Science*, **141**, 921.
- BROWN, G. M. & LEVY, H. A. (1965). *Science*, **147**, 1038, and private communication.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *Fortran Crystallographic Least Squares Program*, ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
- COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.
- CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
- CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. New York: Pergamon Press.
- FERRIER, W. G. (1963). *Acta Cryst.* **16**, 1023.
- GURR, G. E. (1963). *Acta Cryst.* **16**, 690.
- HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph no. 3. Ann Arbor, Mich.: Edwards Bros. Inc.
- HORDVIK, A. (1961). *Acta Chem. Scand.* **15**, 16.
- JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.
- JEFFREY, G. A. & ROSENSTEIN, R. D. (1964). *Advances in Carbohydrate Chemistry*. Vol. 19. Edit. Wolfrom, M. E. New York: Academic Press.
- KARLE, I. L., HAUPTMAN, H., KARLE, J. & WING, A. B. (1958). *Acta Cryst.* **11**, 257.
- KIM, S. H. & ROSENSTEIN, R. D. (1967). To be published.
- LOMER, T. R., MILLER, A. & BEEVERS, C. A. (1963). *Acta Cryst.* **16**, 264.
- MCDONALD, T. R. R. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 654.
- MCGEACHIN, H. MCD. & BEEVERS, C. A. (1957). *Acta Cryst.* **10**, 227.
- RABINOWITZ, I. N. & KRAUT, J. (1964). *Acta Cryst.* **17**, 159.
- ROBERTSON, J. H. & SHELDRIK, B. (1965). *Acta Cryst.* **19**, 820.
- SAYRE, D. (1952). *Acta Cryst.* **5**, 60.
- SHIONO, R. (1966). *Data Reduction and Scaling Fortran Program*. The Crystallography Laboratory, Univ. of Pittsburgh, Pittsburgh, Pa. 15213.
- SUNDARALINGAM, M. (1965). *J. Amer. Chem. Soc.* **87**, 599.

*Acta Cryst.* (1967). **22**, 545

## The Structure of 1,3-Diamino-2,4,6-trinitrobenzene, Form I.

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(Received 16 March 1966 and in revised form 6 July 1966)

The crystal structure of 1,3-diamino-2,4,6-trinitrobenzene, form I, has been determined by X-ray diffraction. The dimensions of the monoclinic unit cell are:  $a_0 = 7.30$ ,  $b_0 = 5.20$ ,  $c_0 = 11.63$  Å,  $\beta = 95.9^\circ$ . The space group is *Pc* with two molecules per cell. The molecule is approximately planar with apparent intramolecular hydrogen bonds between adjacent amino and nitro groups. The benzene ring is distorted so as to relieve the overcrowding of the planar configuration. The molecules are linked by intermolecular hydrogen bonds into continuous chains.

#### Introduction

Two crystalline polymorphs of 1,3-diamino-2,4,6-trinitrobenzene have been identified by X-ray powder dif-

fraction. Form I is stable from room temperature to 217°C and form II from 217°C to its melting point, 286°C. The solid-solid transition is rapid on heating, and the transition temperature was determined by

microscopic observation. In the absence of solvent, form II can be supercooled to room temperature and stored indefinitely.

The crystal structure of form I has been determined by single-crystal X-ray diffraction procedures as part of a study of the molecular configurations and hydrogen bond networks present in nitroaromatic compounds.

Two different types of intermolecular hydrogen bonding have been reported for nitroaromatic amines. In *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), the amino group is bonded to oxygen atoms of nitro groups of two separate molecules; whereas in 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965)\*, each amino group is bonded to both oxygen atoms of one nitro group.

When a nitro group and an amino group are attached to adjacent carbon atoms of a benzene ring, there is also the possibility of intramolecular hydrogen bonding. Such bonding is observed in triaminotrinitrobenzene. A similar atomic configuration exists in the nitroguanidine molecule for which an intramolecular hydrogen bond 2.57 Å in length has been reported (Bryden, Burkhardt, Hughes & Donohue, 1956).

### Experimental

A sample of diaminotrinitrobenzene was obtained from the Organic Chemistry Division of the U. S. Naval Ordnance Laboratory. Satisfactory crystals of form I were grown by allowing form II to transform at room temperature under a saturated  $\gamma$ -butyrolactone solution which had been seeded with form I. The crystal used for the determination of unit-cell dimensions and for the collection of intensity data was of irregular shape and approximately 0.7 mm in its largest dimension (parallel to the *b* axis). All data were obtained at room temperature with a non-integrating Weissenberg camera using Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) filtered through nickel foil. The unit-cell dimensions are:

$$a_0 = 7.30 \pm 0.01, \quad b_0 = 5.20 \pm 0.01, \quad c_0 = 11.63 \pm 0.02 \text{ \AA}, \\ \beta = 95.9 \pm 0.3^\circ.$$

These values give a calculated volume of 439.3 Å<sup>3</sup> and a calculated density of 1.838 g.cm<sup>-3</sup> with two molecules per unit cell. The observed density, determined by flotation in an aqueous lead perchlorate solution, is 1.837 g.cm<sup>-3</sup>.

The following absences were observed on Weissenberg films taken about the *b* axis:  $h0l, l = 2n + 1$ . An  $hk0$  precession film showed no periodic absences in the  $0k0$  reflections; thus, the space group was shown to be *Pc* or *P2/c*. The known configuration of the molecule and the length of the *b* axis rule out *P2/c*; therefore, the space group is *Pc*.

Intensities of the  $h0l, h1l, h2l, h3l$  and  $h4l$  reflections were estimated visually by means of the multiple film technique using an intensity scale prepared from graduated exposures of the  $\bar{2}08$  reflection. Of the 736 reflections in the region of reciprocal space measured, 612 had measurable intensity. No cross-reference intensity exposures were taken. The five layer scale factors were assumed to be equal during the determination of the rough structure and were subsequently refined by least squares.

### The determination of atomic parameters

The intensity estimates were averaged giving greater weight to measurements in the mid-region of the intensity range, Lorentz and polarization corrections were applied and a three-dimensional Patterson calculation was performed with the crystallographic computing system, X-ray 63 (Stewart, 1964). The Patterson vector array was successfully interpreted by searching for the known planar distributions of vectors produced by the two benzene rings in the unit cell. This was done by plotting the value of the Patterson function on spheres 1.4, 2.4 and 2.8 Å from the origin, which contain the interatomic vectors between adjacent, alternate and opposite carbon atoms respectively. The angular orientation of the benzene ring planes was obvious from these plots, and an estimate was obtained of the orientation of the rings within the planes.

The *x* and *z* coordinates of one molecule were chosen arbitrarily so that the center of the ring was on the *b* axis. The *y* coordinate was estimated from intermolecular vectors of the Patterson function and adjusted by trial and error. The entire molecule was assumed to be planar and the correct distribution of the amino and nitro groups around the ring was determined by trial and error.

After four cycles of three-dimensional Fourier refinement and two cycles of full-matrix least-squares refinement including the scale factors and an overall temperature factor, the *R* value (including only observed reflections) was 0.151. Six more cycles of least-squares refinement including the scale factors and isotropic atomic temperature factors lowered *R* to 0.142.

A three-dimensional difference Fourier syntheses did not indicate positions for the hydrogen atoms but did indicate significant anisotropic thermal motion by some of the atoms, especially the oxygen atoms. Further least-squares refinement with the introduction of anisotropic temperature factors for all of the atoms lowered the *R* value to 0.096 but failed to converge properly. That is, even after eight cycles of full-matrix refinement, the shift/error ratio for some of the parameters was still about 0.5. The scale factors were not included in this full anisotropic refinement because of the degeneracy with the  $B_{22}$  temperature factors pointed out by Lingafelter & Donohue (1966).

With isotropic temperature parameters, the structure contains 71 independent parameters. Considering only

\* This structure determination of diaminotrinitrobenzene is referenced by Cady & Larson as Naval Ordnance Laboratory Technical Report 62-46.

observed reflection intensities, the overdetermination ratio is 8.6 (612/71). The introduction of anisotropic temperature factors for all atoms lowers this ratio to 3.9. This probably constitutes an over-extension of eye estimated data and may explain the lack of convergence observed in the full anisotropic refinement. Therefore, the final refinement was carried out with anisotropic temperature factors for the oxygen atoms and isotropic temperature factors for the carbon and nitrogen atoms. This compromise leaves the overdetermination ratio at 6.0. The scale factors were included in this mixed refinement.

Six cycles, starting with the parameters from the isotropic refinement, gave a final *R* value of 0.103. The average shift/error ratio for the parameters in the last cycle was 0.04; the maximum ratio was 0.15. The atomic scattering factors used in all calculations were those tabulated by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The weighting scheme used was similar to that recommended by Hughes (1941). Observed reflections were given weight 1.0 if *F<sub>o</sub>* was less than 10 and 10.0/(0.5*F<sub>o</sub>* + 5.0) if *F<sub>o</sub>* was greater than 10. The smallest weight given to an observed reflection was 0.23. Unobserved reflections were given weight 1.0 when *F<sub>c</sub>* was greater than *F<sub>min</sub>* and 0.0 when *F<sub>c</sub>* was less than *F<sub>min</sub>*, where *F<sub>min</sub>* is the observed structure factor calculated from the minimum observable intensity. After the last least-squares cycle, 27 of the 124 unobserved reflections calculated greater than their estimated threshold values. The maximum deviation from zero in a final difference Fourier synthesis was ±0.5 e.Å<sup>-3</sup>.

The quantity minimized during all least-squares cycles was  $\sum w(F_o - F_c)^2$  where *w* is the weight factor defined above. The anisotropic temperature factors used for the oxygen atoms were of the form:

$$\exp \left[ -\frac{1}{4}(h^2a^*2B_{11} + k^2b^*2B_{22} + l^2c^*2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23}) \right]$$

These *B<sub>ij</sub>* values are on the same scale as the isotropic *B* values used for the carbon and nitrogen atoms.

Calculations were performed on an IBM 7090 computer using codes from the X-ray 63 system (Stewart, 1964).

### Discussion

The final atomic parameters are given in Table 1. The numbers in parentheses are the errors in the last two digits as indicated by the inverse matrix from the final least-squares cycle. No errors are given for the *x* and *z* parameters of C(1) because these values were arbitrarily fixed to determine the origin of the unit cell.

The determination of layer scale factors by least-squares refinement rather than by direct measurement reduces the significance which can be placed on the temperature factors owing to the high correlations which exist between the scale and temperature factors. As pointed out by Lingafelter & Donohue (1966), when all of the atoms are given anisotropic temperature factors, the problem becomes degenerate. For this reason, the scale factors were not included in the attempted full anisotropic refinement. However, they were included in the final mixed refinement. Although the inverse matrix indicates correlation values as high as 0.39 between the scale factors and *B<sub>22</sub>* temperature factors of the oxygen atoms, the procedure seems justified by the fact that normal convergence was obtained.

The covalent bond lengths found for the 1,3-diamino-2,4,6-trinitrobenzene molecule are given in Fig. 1 and the bond angles are given in Fig. 2. The estimated standard deviations in the bond lengths range from 0.019 to 0.023 Å; those in the bond angles range from 1.3 to 1.6°.

Within the limits of error of the determination, the benzene ring is planar, and the nitrogen and oxygen atoms lie close to this plane. The equation of the best plane through the six carbon atoms, as determined by

Table 1. Atomic parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or <i>B<sub>11</sub></i>	<i>B<sub>22</sub></i>	<i>B<sub>33</sub></i>	<i>B<sub>12</sub></i>	<i>B<sub>13</sub></i>	<i>B<sub>23</sub></i>
C(1)	0.1760	0.7060 (27)	0.0015	3.91 (24)					
C(2)	0.0168 (21)	0.6447 (28)	-0.0814 (14)	3.47 (22)					
C(3)	-0.1520 (25)	0.8007 (29)	-0.0860 (15)	3.99 (24)					
C(4)	-0.1533 (21)	0.9932 (27)	-0.0029 (14)	3.89 (24)					
C(5)	-0.0046 (24)	1.0516 (27)	0.0756 (14)	3.78 (23)					
C(6)	0.1529 (23)	0.9062 (25)	0.0773 (14)	3.64 (23)					
N(1)	0.3279 (21)	0.5667 (24)	0.0030 (14)	4.37 (23)					
N(2)	0.0276 (22)	0.4379 (24)	-0.1595 (15)	4.35 (23)					
N(3)	-0.2922 (22)	0.7495 (26)	-0.1632 (14)	4.70 (25)					
N(4)	-0.3080 (22)	1.1599 (24)	0.0041 (14)	4.20 (22)					
N(5)	0.3080 (22)	0.9981 (25)	0.1640 (14)	4.19 (21)					
O(1)	0.1680 (21)	0.2956 (22)	-0.1566 (14)	4.80 (43)	5.42 (63)	6.32 (53)	2.81 (44)	-0.51 (37)	-1.47 (47)
O(2)	-0.1050 (21)	0.3830 (25)	-0.2309 (14)	5.26 (48)	8.31 (79)	6.33 (53)	3.43 (49)	-2.46 (43)	-3.61 (51)
O(3)	-0.4556 (20)	1.1120 (22)	-0.0581 (14)	3.03 (33)	6.60 (69)	5.44 (44)	1.23 (37)	-1.53 (30)	-1.48 (43)
O(4)	-0.3013 (20)	1.3385 (20)	0.0728 (13)	4.11 (37)	4.95 (58)	4.93 (43)	2.06 (37)	-0.42 (32)	-1.06 (42)
O(5)	0.2824 (21)	1.1835 (22)	0.2182 (13)	4.03 (37)	5.52 (61)	4.94 (46)	-0.56 (41)	-0.80 (32)	-1.08 (44)
O(6)	0.4483 (21)	0.8637 (24)	0.1724 (14)	3.30 (36)	7.28 (74)	5.30 (48)	1.70 (41)	-1.07 (32)	-0.79 (43)



the method of Schomaker, Waser, Marsh & Bergman (1959) is:

$$-3.062x - 3.305y + 8.000z = -2.850$$

where  $x$ ,  $y$  and  $z$  are fractional coordinates of the monoclinic cell. The distances of the atoms from this plane in Å are as follows:

C(1) through C(6);

$$0.01, -0.02, 0.02, -0.01, 0.01, -0.01$$

N(1) through N(5);

$$0.00, -0.04, 0.04, 0.01, 0.08$$

O(1) through O(6);

$$-0.11, -0.06, -0.11, 0.07, 0.18, -0.00.$$

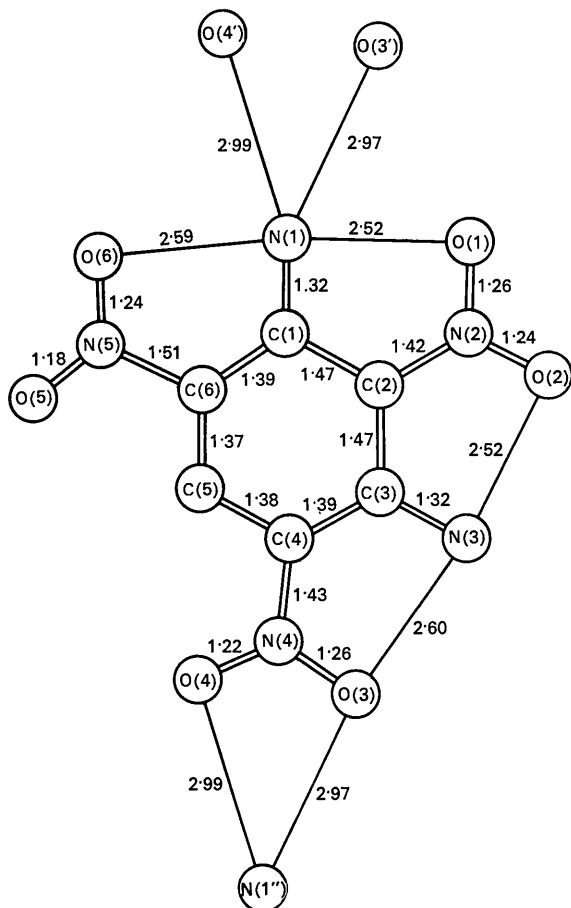


Fig. 1. Bond lengths.

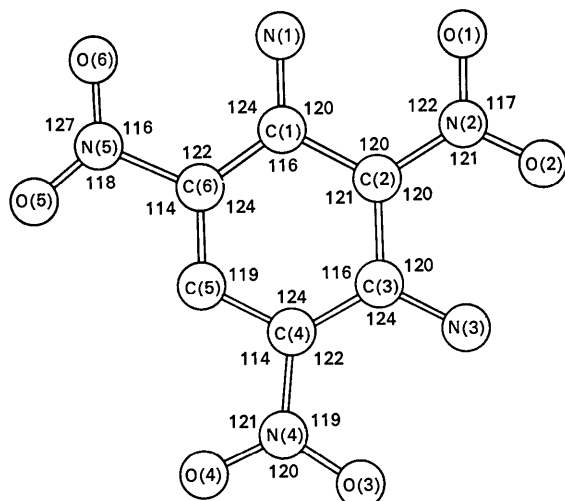


Fig. 2. Bond angles.

Unhindered nitro groups attached to an aromatic ring have been found to lie approximately in the plane of the ring, probably because the resonance stabilization energy is largest for a planar configuration. For example, in nitrobenzene (Trotter, 1959*a*), *p*-dinitrobenzene (Trotter, 1961*a*), *m*-dinitrobenzene (Trotter, 1961*b*) and *p*-nitroaniline (Trueblood *et al.*, 1961) the angles between the benzene and nitro group planes are all reported to be less than 12°. When carbon atoms are attached to the adjacent ring positions, the nitro group is rotated out of the plane. Examples of the angle between the nitro group plane and the ring plane for this arrangement are: nitromesitylene, 66.4° (Trotter, 1959*b*); 9-nitroanthracene, 84.7° (Trotter, 1959*c*); and 9,10-dinitroanthracene, 63.7° (Trotter, 1959*d*).

The steric effect of amino groups on adjacent ring positions should be similar to that of the corresponding carbon atoms in the anthracene structures. However, amino groups are known to form hydrogen bonds with nitro group oxygen atoms. Such intramolecular hydrogen bonding could allow closer approach of the oxygen atoms to the plane of the aromatic nucleus. All three nitro groups in 1,3,5-triamino-2,4,6-trinitrobenzene were found to be essentially coplanar with the ring (Cady & Larson, 1965).

A comparable configuration is present in the nitroguanidine molecule. In this case, the nitro group was also found to be coplanar with the rest of the molecule with an amine nitrogen-oxygen distance of 2.57 Å (Bryden *et al.*, 1956). If all the bond angles in nitroguanidine had their normal values, this distance would be impossibly short. The strain is relieved by expansion of two of the bond angles rather than by rotation of the nitro group out of the plane of the other atoms of the molecule. In diaminotrinitrobenzene, the nitro groups also lie approximately in the plane of the rest of the molecule, and the nitrogen-oxygen distances are 2.59, 2.52, 2.52 and 2.60 Å. The strain is similarly relieved by considerable distortion of the bond lengths and angles within the molecular plane rather than by rotation of the nitro groups out of this plane. The carbon-carbon distances on either side of the unoccupied ring position were found to be 1.38 and 1.37 Å; whereas both distances on the crowded side were found to be 1.47 Å (Fig. 1). The difference between the average lengths of the short and long bonds is four times the maximum standard error of an individual bond length. Therefore, the benzene ring distortion is significant.

The differences found between other chemically equivalent bond lengths and angles also appear to be

related to the crowding of the planar configuration. That is, the molecule contains an approximate twofold axis through N(2), C(2) and C(5) (Figs. 1 and 2). The one significant exception to this steric symmetry is the position found for N(5), which places it 1.51 Å from C(6). The oxygen atoms of the N(5) nitro group are not further from the ring than those of the other nitro groups. O(5) and O(6) lie 2.31 and 2.33 Å from C(6). The corresponding distances of O(1), O(2), O(3) and O(4) from C(2) and C(4) are 2.34, 2.31, 2.32 and 2.32 Å.

The triaminotrinitrobenzene molecule was also found to be planar. In this case, since all of the ring positions are occupied, the ring distortion consists of a symmetrical expansion. That is, the carbon-carbon bond lengths range from 1.435 to 1.450 Å (Cady & Larson, 1965). The normal value reported for benzene is 1.397 Å (Langseth & Stoicheff, 1956).

There appear to be two possible configurations for crowded nitro-aromatic amines; either the nitro groups are twisted out of the plane of the ring or the nitro groups lie in the plane and the ring is distorted. The fact that in diaminotrinitrobenzene the molecule assumes the planar configuration may indicate that any loss of resonance energy caused by distortion of the benzene ring is more than compensated by formation of intramolecular hydrogen bonds and resonance interaction between the nitro groups and the benzene ring.

The diaminotrinitrobenzene molecules are packed into the crystal lattice so that each molecule forms one link in a hydrogen-bonded chain in which the N(1) amino group is attached to O(3') and O(4') of the molecule located at  $(1+x, y-1, z)$ . The nitrogen-oxygen distances in the bonds of this chain are 2.97 and 2.99 Å (Fig. 1). The molecules of the chain are approximately coplanar; O(3') and O(4') lie only -0.35 and -0.17 Å from the plane of the benzene ring of the adjacent molecule. Therefore, the hydrogen atoms of the N(1) amino group can be in proper location for both the intramolecular and intermolecular hydrogen bonds in which they are apparently involved.

Since the N(1) amino group is in a hydrogen bonding environment almost identical with that reported for all three amino groups of triaminotrinitrobenzene (Cady & Larson, 1965), it is interesting to note that no such environment exists around N(3). The closest oxy-

gen atom is O(4'') of the symmetrically related molecule located at  $(x, 2-y, -\frac{1}{2}+z)$ . This atom is 3.10 Å away and lies 1.83 Å above the benzene ring plane. If this is a hydrogen bond at all, it is considerably weaker than those in the chains described above.

The only non-bonded intermolecular distance within 0.1 Å of van der Waals contact, using the atomic radii listed by Pauling (1960), is 2.86 Å between N(5) and O(1<sup>v</sup>) of the molecule located at  $(x, 1-y, \frac{1}{2}+z)$ . The observed displacement of N(5) from the position indicated by the approximate symmetry of the rest of the molecule may be caused by the influence of this neighboring molecule.

The author gratefully acknowledges the Foundational Research Fund of the U. S. Naval Ordnance Laboratory, Task FR-44, for financial support of this work and Dr J.M. Rosen and Mr H.T. Simmons of this laboratory for determinations of the phase transition temperature and density.

#### References

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BRYDEN, J. H., BURKARDT, L. A., HUGHES, E. W. & DONOHUE, J. (1956). *Acta Cryst.* **9**, 573.
- CADY, H. H. & LARSON, A. C. (1965). *Acta Cryst.* **18**, 485.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- LANGSETH, A. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 350.
- LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.
- PAULING, L. (1960). *Nature of the Chemical Bond*. 3rd edn. Ithaca; Cornell Univ. Press.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
- STEWART, J. M. (1964). Technical Report TR 64-6, NsG-398. Computer Science Center of the University of Maryland, College Park.
- TROTTER, J. (1959a). *Acta Cryst.* **12**, 884.
- TROTTER, J. (1959b). *Acta Cryst.* **12**, 605.
- TROTTER, J. (1959c). *Acta Cryst.* **12**, 237.
- TROTTER, J. (1959d). *Acta Cryst.* **12**, 232.
- TROTTER, J. (1961a). *Canad. J. Chem.* **39**, 1638.
- TROTTER, J. (1961b). *Acta Cryst.* **14**, 244.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.