

## Structure of 2,4-Dinitroaniline\*

BY L. PRASAD, E. J. GABE AND Y. LE PAGE

National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

(Received 28 May 1981; accepted 17 August 1981)

**Abstract.**  $C_6H_5N_2O_4$ ,  $P2_1/c$ ,  $a = 8.171(1)$ ,  $b = 12.863(1)$ ,  $c = 7.513(2)$  Å,  $\beta = 108.84(1)^\circ$ ,  $Z = 4$ ,  $D_c = 1.63$  Mg  $m^{-3}$ . The final residual  $R_F = 0.063$  for 785 observed reflections. The structure consists of planar molecules with both inter- and intramolecular hydrogen bonds.

**Introduction.** The nitro aromatic amines crystallize as planar molecules, joined by intermolecular hydrogen bonds between an amine group and the O atoms of the nitro group. The structures of *p*-nitroaniline ( $\gamma$  form) (Dhaneshwar, Tavale & Pant, 1978), 2,4,6-trinitroaniline (Holden, Dickinson & Bock, 1972) and 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Holden, 1966) have been solved along with the structure of 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965). The structure analysis of 2,4-dinitroaniline was undertaken to complete the study of the nitro aromatic amines. Preliminary X-ray data have been reported for 2,4-dinitroaniline (Mannan, Hossain & Shamsuzzoha, 1973); however, the reported cell [ $a = 7.603(1)$ ,  $b = 12.914(5)$ ,  $c = 9.146(2)$  Å and  $\beta = 122.09(1)^\circ$ ] was not made up of the three shortest translations and a different cell with dimensions  $a = 8.171(1)$ ,  $b = 12.863(1)$ ,  $c = 7.513(2)$  Å,  $\beta = 108.84(1)^\circ$ , was chosen. The transformation matrix from the old cell to the new cell is

$$\begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}.$$

Approximately 500 mg of 2,4-dinitroaniline powder of laboratory BDH was dissolved in acetone and pale-yellow plate-like crystals were obtained by slow evaporation.

The diffraction intensities of a  $0.25 \times 0.25 \times 0.25$  mm crystal of the title compound were measured at room temperature. Graphite-monochromatized Cu  $K\alpha$  radiation generated at 40 kV and 20 mA was used in a  $\theta/2\theta$  scan with line profile analysis (Grant & Gabe, 1978). A total of 1998 measurements were made up to  $2\theta = 110^\circ$ , giving 940 valid unique reflections of which 785 had a net intensity larger than  $3\sigma(I)$ , based on

counting statistics, and were considered to be observed. From the systematic absences the space group was determined as  $P2_1/c$ . The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979), but not for absorption ( $\mu = 1.166$   $mm^{-1}$ ). The cell parameters were obtained by least-squares refinement of the setting angles of 28 reflections with  $2\theta$  greater than  $60^\circ$  [ $\lambda(\text{Cu } K\alpha_1) = 1.5406$  Å].

The structure was solved by application of *MULTAN* (Germain, Main & Woolfson, 1971) to the 160 largest  $E$  values. The resulting  $E$  map revealed all the non-H atoms. Isotropic refinement followed by several anisotropic refinement cycles lowered the residual to  $R_F = 0.10$ . The H atoms were then located on a difference map and their positional and isotropic thermal parameters were refined while the other atoms were refined anisotropically by block-diagonal least squares with weights based on counting statistics. An extinction correction was included (Larson, 1970). One of the H atoms [NH(2)] refined to an unreasonable position. It was returned to the calculated position and not refined any further. The scattering curves for

Table 1. Atomic positional parameters and equivalent isotropic Debye–Waller parameters with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}$ (Å <sup>2</sup> )*
N(1)	0.5364 (5)	0.6410 (3)	0.2537 (5)	5.08 (19)
N(2)	0.3775 (5)	0.4350 (3)	0.1668 (5)	4.81 (19)
N(3)	−0.0639 (5)	0.5884 (3)	−0.3619 (5)	5.94 (22)
C(1)	0.3895 (5)	0.6241 (3)	0.1090 (6)	3.44 (20)
C(2)	0.3090 (5)	0.5271 (3)	0.0592 (6)	3.24 (19)
C(3)	0.1617 (5)	0.5147 (4)	−0.0952 (6)	3.64 (20)
C(4)	0.0927 (5)	0.6012 (4)	−0.1957 (6)	3.93 (21)
C(5)	0.1647 (6)	0.6988 (4)	−0.1487 (6)	4.45 (23)
C(6)	0.3116 (6)	0.7110 (3)	0.0016 (6)	4.02 (22)
O(1)	0.5144 (4)	0.4404 (3)	−0.3029 (5)	6.38 (18)
O(2)	0.2981 (4)	0.35308 (25)	0.1240 (5)	6.53 (18)
O(3)	−0.1118 (4)	0.6652 (3)	−0.4585 (5)	9.30 (23)
O(4)	−0.1326 (4)	0.5031 (3)	−0.3885 (4)	7.17 (19)
H(3)	0.111 (4)	0.4432 (25)	−0.129 (4)	4.0 (9)
H(5)	0.119 (4)	0.755 (3)	−0.206 (5)	4.4 (10)
H(6)	0.368 (4)	0.7962 (24)	0.043 (4)	3.7 (9)
NH(1)	0.566 (4)	0.583 (3)	0.310 (5)	5.6 (11)
NH(2)	0.601	0.716	0.290	4.65

\*  $B_{iso}$  is the arithmetic mean of the principal axes of the thermal ellipsoid.

\* NRCC No. 18939.

0567-7408/82/020674-02\$01.00

© 1982 International Union of Crystallography

neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final residuals are  $R_F = 0.063$  and  $R_W = 0.053$ . The atomic positional and equivalent isotropic temperature parameters are listed in Table 1.\*

All calculations were performed using the NRC PDP8-E system of programs (Larson & Gabe, 1978).

**Discussion.** The atom names, distances and angles are indicated in Fig. 1.

The calculated  $\chi^2$  value for the least-squares plane of the benzene ring is 10.19. The value of  $\chi^2$  at the 95% significance level is 12.84, showing that the benzene ring is planar within experimental error. The maximum deviation from the plane is 0.014 Å for C(2). The two nitro groups and the amino group are slightly twisted from the benzene plane. The dihedral angle between the amino group and the benzene plane is  $2.7 (0.5)^\circ$  while those between the benzene plane and the nitro groups [N(2),O(1),O(2)] and [N(3),O(3),O(4)] are  $4.3 (0.4)$  and  $6.6 (0.4)^\circ$  respectively. There is an intramolecular hydrogen bond between N(1) and O(1) and an intermolecular hydrogen bond between O(2) and N(1) of a neighbouring molecule at  $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ . The distances and angles involved are shown in Fig. 2. The nitro group consisting of N(3), O(3) and O(4) is not involved in hydrogen bonding and this probably accounts for the large thermal motion exhibited by O(3) and O(4).

\* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36364 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

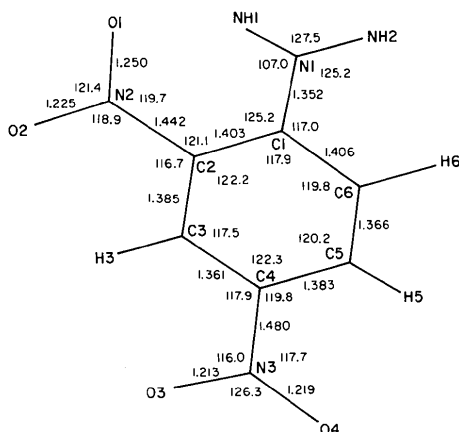


Fig. 1. Atom names, bond distances (Å) and angles ( $^\circ$ ) in the molecule. The e.s.d.'s on the bond distances are: C-C = 0.006 Å, C-N = 0.005 Å and N-O = 0.006 Å. E.s.d.'s on the angles are 0.4 $^\circ$ .

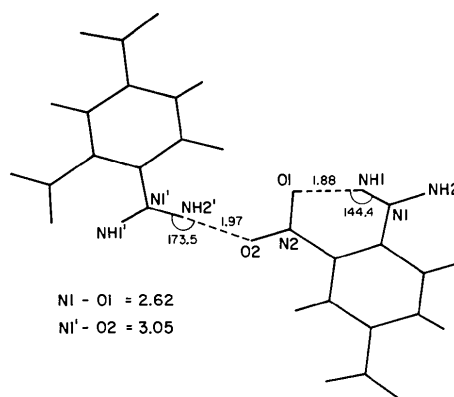


Fig. 2. Hydrogen-bonding scheme showing bond distances (Å) and angles ( $^\circ$ ). E.s.d.'s are 0.01 Å and 0.8 $^\circ$ .

The bond lengths and angles in 2,4-dinitroaniline are similar to those found in other nitro aromatic amines. The elongation of the C-C bonds on either side of the amino group with respect to the other bonds in the ring is observed, as in 2,3,4,6-tetranitroaniline (Dickinson *et al.*, 1966), 4-nitroaniline (Trueblood, Goldish & Donohue, 1961) and 2,4,6-trinitroaniline (Holden *et al.*, 1972).

One of the authors (LP) thanks the Natural Sciences and Engineering Research Council Canada for the award of a Visiting Fellowship.

## References

- CADY, H. H. & LARSON, A. C. (1965). *Acta Cryst.* **18**, 485-496.
- DHANESHWAR, N. N., TAVALE, S. S. & PANT, L. M. (1978). *Acta Cryst.* **B34**, 2507-2509.
- DICKINSON, C., STEWART, J. M. & HOLDEN, J. R. (1966). *Acta Cryst.* **21**, 663-670.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368-376.
- GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114-120.
- HOLDEN, J. R., DICKINSON, C. & BOCK, C. M. (1972). *J. Phys. Chem.* **76**, 3597-3602.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291-294. Copenhagen: Munksgaard.
- LARSON, A. C. & GABE, E. J. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOFF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 81-89. Delft Univ. Press.
- LE PAGE, Y., GABE, E. J. & CALVERT, L. D. (1979). *J. Appl. Cryst.* **12**, 25-26.
- MANNAN, KH. M., HOSSAIN, M. B. & SHAMSUZZOHA, MD. (1973). *Acta Cryst.* **B29**, 2315-2316.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009-1017.