

The Crystal and Molecular Structure of 2,7-Diazanaphthalene

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$C_8H_6N_2$ is monoclinic, $P2_1/n$ (systematic absences $h0l$ with $h + l$ odd and $0k0$ with k odd), with one molecule in the asymmetric unit and $a = 13.208$ (8), $b = 9.585$ (1), $c = 5.2063$ (5) Å, $\beta = 99.28$ (1)°, $Z = 4$, $V = 650.5$ (4) Å³, $D_c = 1.329$ g cm⁻³. X-ray diffraction data were collected at 20°C on a computer-controlled Philips diffractometer (PW 1100). The structure was solved by direct methods and refined by the full-matrix least-squares method to an R of 0.065 (weighted R 0.046). The molecule in the crystal is of lower symmetry than C_{2v} . The geometry of the molecule has been compared with NMR results obtained by Danieli, Lunazzi & Veracini [*J. Chem. Soc. Perkin II*, (1976), pp. 19–20]. As a result a C–H bond-length correction of 0.09 (2) Å was found.

Introduction

In our laboratory, chemical and physical properties of the diazanaphthalenes are studied. The crystal structures of diazanaphthalenes that have been solved so far, by workers in this and other laboratories, are listed in Table 1. The ratios of the interprotonic distances in the title compound have been obtained recently by Danieli, Lunazzi & Veracini (1976) from an NMR experiment. Comparison of their data with the present X-ray data has led to a C–H bond-length correction of 0.09 (2) Å.

Table 1. *Diazanaphthalenes of which the crystal structures have been solved*

Diazanaphthalene	Reference
1,5 (dihydrate)	Brufani, Duranti, Giacomello & Zambonelli (1961)
2,6 (dihydrate)	Brufani, Fedeli, Giacomello, Ricciari & Vaciago (1966)
1,8 (anhydrous)	Clearfield, Sims & Singh (1972)
2,3 (anhydrous)	Huiszoon, van de Waal, van Egmond & Harkema (1972)
1,3 (anhydrous)	Huiszoon (1976)

Experimental

2,7-Diazanaphthalene was prepared following the instructions of Danieli & Ricci (1973). The crude product was dissolved in diethyl ether and this solution was purified by passing it through a column packed with basic alumina. After thorough drying over molecular sieves, the solvent was evaporated and the residual 2,7-diazanaphthalene sublimed at 30°C and 0.5 torr. From

the product thus obtained, crystals were grown by slow sublimation at 20–22°C and 0.1 torr.

A crystal of cylindrical shape, length 0.7 mm and diameter 0.3 mm, was mounted in a Lindemann glass capillary and used for the experiments.

Cell constants (Table 2) and intensity data were obtained at 20°C with graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 0.90$ cm⁻¹. The θ - 2θ scan mode was applied. The scan speed was 0.04° s⁻¹, scan width 2°. θ values ranged from 3° to 30°. The stationary background was counted during half the scan time multiplied by a factor equal to $(I_{\text{bck}}/I_{\text{int}})^{1/2}$, on both sides of the peak, the factor $I_{\text{bck}}/I_{\text{int}}$ being estimated from a quick scan through the peak (I_{bck} background intensity, I_{int} integrated peak intensity). This rather special scan mode is a feature of the diffractometer; it reduces the measuring time without significant loss of accuracy. The data set contained 1985 reflexions of which 1526 have been used for the refinement (reflexions having intensities less than their standard deviation based on counting statistics have not been used in the refinement).

Table 2. *Crystal data for 2,7-diazanaphthalene at 20°C*

Space group*	$P2_1/n$ (monoclinic)
$a = 13.208$ (8), $b = 9.585$ (1), $c = 5.2063$ (5) Å	
$\beta = 99.28$ (1)°	
$V = 650.5$ (4) Å ³	
$D_c = 1.329$ g cm ⁻³	
$Z = 4$	
$\mu(\text{Mo } K\alpha) = 0.90$ cm ⁻¹	

* Reflexions $h0l$ with $h + l$ odd and $0k0$ with k odd are systematically absent in the data set.

Structure determination and refinement

The structure was solved with the aid of the multi-solution program *MULTAN* of Germain, Main & Woolfson (1971). The *E* map showed the positions of all the non-H atoms. The refinement was carried out with a local version of the program *ORFLS* of Busing, Martin & Levy (1962). The function minimized was $\sum w(|F_o| - s|F_c|)^2$, where the summation extends over all reflexions with intensity greater than the standard deviation as estimated from counting statistics. *s* is the scaling factor, $|F_o|$ and F_c are observed and calculated structure factors respectively. The weight, *w*, for each reflexion was taken to be $w = \sigma^{-2}$ with $\sigma = S + 0.01|F_o|$ where *S* is the standard deviation in $|F_o|$ based on counting statistics.

Atomic scattering-factor tables for C and N, calculated with the aid of relativistic Hartree-Fock-type wave functions, were taken from *International Tables for X-ray Crystallography* (1974). The scattering-factor table for bonded H was taken from Stewart, Davidson & Simpson (1965). After several cycles of refinement with non-H atomic parameters and the scaling factor only, all the H atoms were located by a difference Fourier map. The parameters in the last cycle of refinement were: positional parameters of all atoms, anisotropic thermal parameters of the non-H atoms, isotropic thermal parameters of the H atoms, an isotropic extinction factor (Larson, 1969) and a scaling factor. The final *R* was 0.056 (weighted *R* 0.046).*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32327 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Structural results

There is one crystallographically independent molecule in the unit cell. The final atomic positional and thermal parameters are given in Table 3. Bond lengths, bond angles and the numbering of the atoms are shown in Fig. 1. Standard deviations in the bond lengths and angles have been calculated with the program *ORFFE* of Busing, Martin & Levy (1964).

From Fig. 1 it is seen that the angles C(8)–C(9)–C(10) and C(9)–C(10)–C(5) of the left ring of the molecule differ from the corresponding angles of the right ring. In each case the difference is 0.5 (2)°. This means that, at least in the crystal, the molecule has a symmetry lower than C_{2v} . The smallest bond angles are found at the N atoms. This is also found in the other

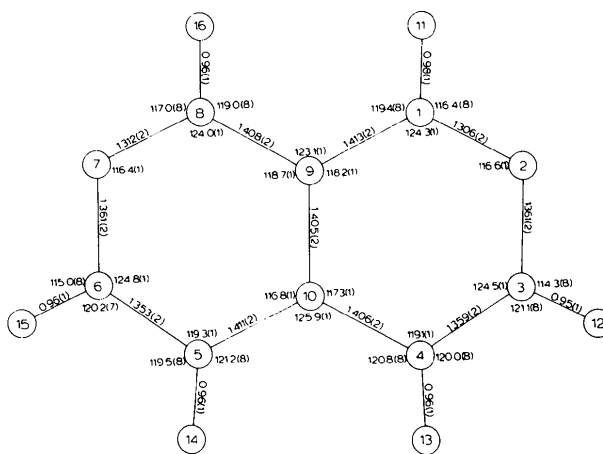


Fig. 1. Bond lengths and bond angles. Standard deviations are shown in parentheses and refer to the last digits.

Table 3. Atomic positional and thermal parameters ($\times 10^4$; for H $\times 10^3$)

The anisotropic temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ and the isotropic temperature factor $\exp(-8\pi^2U \sin^2 \theta/\lambda^2)$. The thermal parameters are in Å^2 . Standard deviations are shown in parentheses and refer to the last digits.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	4865 (1)	7591 (2)	605 (3)	363 (7)	633 (9)	61 (1)†	-50 (7)	114 (7)	-121 (8)
N(2)	4930 (1)	8548 (1)	2409 (3)	460 (7)	693 (9)	626 (8)	5 (6)	177 (6)	-163 (7)
C(3)	5870 (1)	9130 (2)	3170 (3)	546 (9)	553 (8)	511 (9)	-4 (7)	116 (7)	-151 (8)
C(4)	6729 (1)	8776 (1)	2194 (3)	414 (7)	473 (7)	468 (8)	-49 (6)	43 (6)	-69 (7)
C(5)	7485 (1)	7252 (1)	-928 (3)	338 (7)	506 (8)	507 (8)	-21 (6)	88 (6)	-4 (7)
C(6)	7307 (1)	6242 (2)	-2760 (3)	436 (8)	539 (8)	549 (9)	56 (6)	145 (7)	-62 (7)
N(7)	6378 (1)	5644 (1)	-3589 (3)	507 (7)	537 (7)	579 (8)	6 (6)	97 (6)	-150 (7)
C(8)	5610 (1)	6093 (2)	-2500 (3)	419 (7)	548 (8)	573 (9)	-59 (6)	59 (7)	-125 (8)
C(9)	5700 (1)	7132 (1)	-562 (2)	360 (6)	434 (7)	426 (7)	-5 (5)	62 (6)	-23 (6)
C(10)	6666 (1)	7741 (1)	261 (2)	360 (6)	388 (6)	377 (7)	5 (5)	56 (5)	35 (6)
H(11)	419 (1)	717 (2)	7 (3)	61 (4)					
H(12)	589 (1)	984 (2)	446 (2)	59 (4)					
H(13)	737 (1)	924 (1)	281 (3)	55 (4)					
H(14)	816 (1)	764 (1)	-49 (3)	58 (4)					
H(15)	785 (1)	591 (1)	-360 (3)	57 (4)					
H(16)	495 (1)	569 (1)	-308 (3)	62 (4)					

† $\times 10^3$.

Table 4. Atomic deviations (\AA) from the best plane through the heavy atoms

The equation of the best plane is given as $n_x x + n_y y + n_z z = d$, where n_x , n_y , and n_z are the direction cosines of the normal to the plane with respect to an orthogonal system of axes according to Williams (1959). d is the distance of the plane to the origin. The components of the normal to the plane, with respect to the monoclinic cell, are also given. The numbering of the atoms is in accordance with Fig. 1. A plus sign means a deviation towards the reader, a minus sign represents a deviation away from the reader.

Equation of plane

$$-0.0917x + 0.7012y - 0.7070z = 4.2989 \text{ \AA}$$

Components of normal in fractional coordinates

$$-0.01569, 0.07316, -0.1376$$

C(1)	-0.001 (1)	N(7)	-0.001 (1)	H(13)	+0.02 (1)
N(2)	-0.007 (1)	C(8)	+0.006 (3)	H(14)	+0.02 (1)
C(3)	-0.001 (1)	C(9)	+0.004 (2)	H(15)	+0.00 (1)
C(4)	+0.004 (1)	C(10)	+0.004 (2)	H(16)	+0.02 (1)
C(5)	-0.001 (1)	H(11)	-0.01 (1)		
C(6)	-0.007 (1)	H(12)	+0.01 (1)		

anhydrous diazaphthalenes of which structures are known (Table 1).

The equation of the best plane through the non-H atoms and the atomic deviations from this plane are given in Table 4. There are small deviations from planarity.

It is interesting to compare the present X-ray results with structural data obtained from other techniques. In a recent paper, Danieli, Lunazzi & Veracini (1976) reported the 100 MHz proton NMR spectrum of 2,7-diazaphthalene, partially oriented in the nematic phase of a liquid crystalline solvent. From the direct dipolar couplings these authors obtained the ratios of the interprotonic distances in the molecule. These ratios have been collected in Table 5, column 3. Danieli *et al.* (1976) gauged the interprotonic distances on the H(12)—H(13) distance which they assumed to be equal to the corresponding interprotonic distance in pyridine. Of the latter molecule, accurate bond lengths and inter-

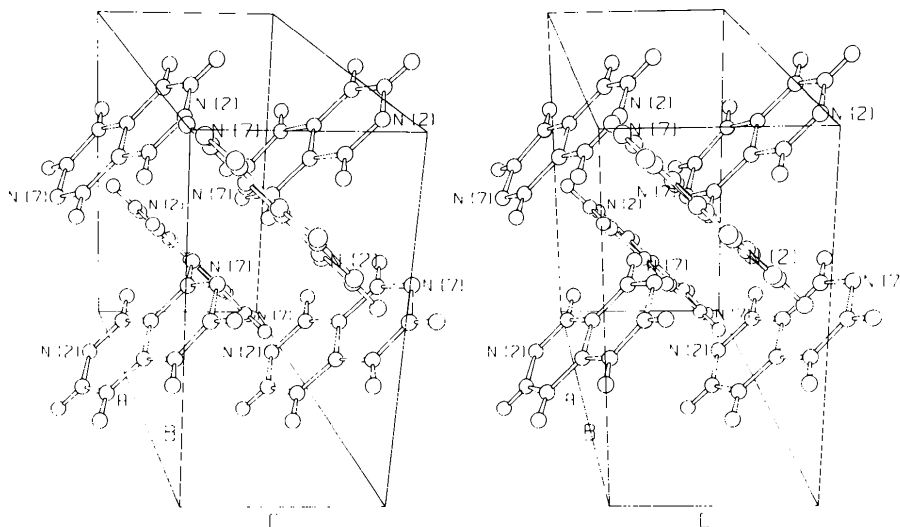


Fig. 2. Stereoscopic pair showing the molecular packing.

Table 5. The CH bond-length correction from a comparison of X-ray data and NMR results

Distances are in \AA .

	X-ray distances	NMR ratios of interprotonic distances	Distances calculated from the NMR ratios on basis of the X-ray distance H(11)—H(16)	Bond-length correction as calculated from the data of columns 2 and 4 and the molecular structure
H(11)—H(12)	3.89 (2)	1.641 (6)	4.03 (3)	0.08 (2)
H(11)—H(13)	4.65 (2)	1.963 (10)	4.82 (4)	0.09 (2)
H(11)—H(14)	5.32 (2)	2.223 (10)	5.46 (5)	0.08 (3)
H(11)—H(15)	5.62 (2)	2.339 (5)	5.75 (5)	0.08 (3)
H(11)—H(16)	2.51 (2)	1.020 (3)	2.51 (2)	—
H(12)—H(13)	2.33 (2)	1.0	2.46 (2)	0.13 (3)
H(12)—H(14)	4.75 (2)	1.975 (3)	4.85 (4)	0.09 (4)
H(12)—H(15)	6.49 (2)	2.723 (9)	6.69 (6)	0.11 (3)
H(13)—H(14)	2.64 (2)	1.065 (4)	2.62 (2)	—

protonic distances are known from microwave experiments done by Bak, Hansen-Nygaard & Rastrup-Andersen (1958).

The results of the X-ray experiment, however, permit the choice of an internal standard. From Fig. 1 it can be seen that the C(1)–H(11) and the C(8)–H(16) bonds are practically parallel. This implies that the X-ray H(11)–H(16) distance equals the interprotonic H(11)–H(16) distance. From this internal standard and the ratios of Table 5, column 3, corrections for the X-ray C–H bond lengths have been calculated. The results are given in Table 5, column 5. The mean value of these bond-length corrections is 0.09 (2) Å. If one adds this bond-length correction, 0.09 Å, to the X-ray C–H distances of 2,7-diazanaphthalene, a mean C–H distance of 1.05 (2) Å is found. This is, within the limits of accuracy, the same as the mean C–H distance for pyridine, 1.081 (3) Å (Bak *et al.*, 1958).

Table 6. *Intermolecular contacts (Å) within 0.1 Å greater than the sum of the relevant van der Waals radii (Kitaigorodsky, 1973)*

The atoms of the symmetry-related molecules are listed second. The symbol *Iuvw* indicates the operation to obtain the positions of the second atoms. *I* = 1 represents the identity operation, *I* = 2 the operation 0.5 – *x*, 0.5 + *y*, 0.5 – *z*. *u*, *v*, *w* are the fractional translations along the cell axes.

N(2)–H(12); H(12)–N(2)	$\bar{1}121$	2.60 (1)
N(2)–H(15)	$\bar{2}021$	2.76 (1)
N(2)–C(6)	$\bar{2}021$	3.457 (3)
C(3)–C(3)	$\bar{1}121$	3.621 (3)
C(3)–H(12); H(12)–C(3)	$\bar{1}121$	2.97 (1)
C(4)–C(6)	1/001	3.569 (2)
C(4)–C(6)	2/10 $\bar{1}$	3.672 (2)
C(4)–H(15)	2/10 $\bar{1}$	2.88 (1)
C(6)–N(2)	$\bar{2}120$	3.457 (3)
C(6)–C(4)	1/00 $\bar{1}$	3.569 (2)
C(6)–C(4)	2/1 $\bar{1}\bar{1}$	3.672 (2)
C(6)–H(12)	2/1 $\bar{1}0$	3.02 (1)
N(7)–C(8); C(8)–N(7)	$\bar{1}11\bar{1}$	3.478 (2)
N(7)–H(16); H(16)–N(7)	1/11 $\bar{1}$	2.59 (1)
C(8)–H(16); H(16)–C(8)	$\bar{1}11\bar{1}$	2.86 (1)
H(12)–C(6)	2/100	3.02 (1)
H(15)–N(2)	$\bar{2}120$	2.76 (1)
H(15)–C(4)	2/1 $\bar{1}\bar{1}$	2.88 (1)
H(16)–H(16)	$\bar{1}11\bar{1}$	2.41 (3)

Fig. 2 is an *ORTEP* (Johnson, 1965) stereo view showing the molecular packing. Owing to space-group symmetry, two sets of parallel molecules can be distinguished. The planes of the non-parallel molecules are nearly perpendicular to each other. The angle between these planes is 89.05°. The molecular planes of molecules belonging to both sets, are nearly parallel to the *a* crystallographic axis. The angles of the molecular planes with respectively the *a*, *b*, and *c* crystallographic axes are 5.26, 44.52 and 46.92°. The intermolecular close contacts are listed in Table 6.

A qualitative consideration of the molecular packing did not yield arguments that can explain the lack of a twofold molecular axis.

References

- BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.
- BRUFANI, M., DURANTI, D., GIACOMELLO, G. & ZAMBONELLI, L. (1961). *Gazz. Chim. Ital.* **91**, 287–298.
- BRUFANI, M., FEDELI, W., GIACOMELLO, G., RICCIERI, F. M. & VACIAGO, A. (1966). *Atti Acad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.* **40**, 187–193.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- CLEARFIELD, A., SIMS, M. J. & SINGH, P. (1972). *Acta Cryst.* **B28**, 350–355.
- DANIELI, R., LUNAZZI, L. & VERACINI, C. A. (1976). *J. Chem. Soc. Perkin II*, pp. 19–20.
- DANIELI, R. & RICCI, A. (1973). *Synthesis*, pp. 46–47.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HUISZON, C. (1976). *Acta Cryst.* **B32**, 998–1003.
- HUISZON, C., VAN DE WAAL, B. W., VAN EGMOND, A. B. & HARKEMA, S. (1972). *Acta Cryst.* **B28**, 3415–3419.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York, London: Academic Press.
- LARSON, A. C. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WILLIAMS, D. E. (1959). *Acta Cryst.* **A25**, 464–470.