

## 1,3,4,6-Tetraazacycl[3.3.3]azine: Crystal and Molecular Structure

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(Received 21 October 1977; accepted 24 November 1977)

$C_8H_5N_5$  (1,3,4,6-tetraazacycl[3.3.3]azine or 1,3,4,6,9b-pentaazaphenalene),  $M_r = 171.13$ , orthorhombic,  $P2_1cn$ ,  $a = 3.778$  (1),  $b = 13.63$  (1),  $c = 14.32$  (1) Å,  $V = 737.6$  (5) Å<sup>3</sup>,  $D_c = 1.54$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Cu K}\alpha) = 8.7$  cm<sup>-1</sup>. A Syntex  $P2_1$  diffractometer was used to collect 731 reflections and 138 parameters were refined to an  $R$  of 0.038. The molecule is planar and has aromatic bond distances; the central N atom is situated 0.033 Å from the molecular plane.

### Introduction

1,3,4,6-Tetraazacycl[3.3.3]azine (I), first reported by Shaw, Westler & Stefanko (1972), belongs to the class of cyclazines.† These are tricyclic systems containing a completely conjugated perimeter of  $sp^2$ -hybridized C or N atoms held planar by a centrally lying N atom (Windgassen, Saunders & Boekelheide, 1959; Gerson, Heilbronner, Joop & Zimmermann, 1963). In a more general sense, the cyclazines are bridged annulenes (Haddon, Haddon & Jackman, 1971) in which the bridging group, the non-basic N atom, does not participate with the peripheral  $\pi$  electrons to form a  $4n + 2$  or  $4n$  system. This has been demonstrated by chemical and spectral studies and by molecular-orbital calculations (Windgassen, Saunders & Boekelheide, 1959; Boekelheide & Small, 1961; Dewar & Trinajstić, 1969; Farquhar & Leaver, 1969; Farquhar, Gough & Leaver, 1976; Gerson, Heilbronner, Joop & Zimmermann, 1963; Boekelheide, Gerson, Heilbronner & Meuche, 1963).



The bridging by the trigonal N atom allows the [2.2.3]- and [3.3.3]cyclazines to assume planarity, which a non-bridged [10]- or [12]annulene cannot since the H atoms on the inside of the periphery point into the

center of the ring. For the same reason the [14]- and [16]annulenes are not completely planar (Bregman, 1962; Johnson, Paul & King, 1970).

In accordance with the Hückel rule, cycl[2.2.3]azine, a bridged [10]annulene, is aromatic (Windgassen, Saunders & Boekelheide, 1959), while cycl[3.3.3]azine, a bridged [12]annulene, is antiaromatic (Farquhar & Leaver, 1969; Dewar & Trinajstić, 1969). From a theoretical point of view, the azacyclazines are more complicated since the peripheral N atoms could contribute their non-bonding electrons to the conjugated  $\pi$  system.

The azacycl[3.3.3]azines, which are  $12\pi$  systems, have, with three, four and five N atoms present in the ring, been found to display a considerable degree of both physical and chemical aromaticity (Ceder & Andersson, 1972; Ceder, Andersson & Johansson, 1972; Ceder & Samuelsson, 1973; Ceder & Vernmark, 1977; Ginzel & Kuffner, 1970; Ceder & Witte, 1972; Shaw, Westler & Stefanko, 1972; Ceder & Rosén, 1973a,b; Shaw, O'Connor, Allen, Westler & Stefanko, 1974). They are far more stable than the carbocyclic analogue (Farquhar & Leaver, 1969).

Several criteria have been proposed to decide if a compound is aromatic or not (Labarre & Crasnier, 1971; Cook, Katritzky & Linda, 1974; Lewis & Peters, 1975). Some of them are based on chemical reactivity and thus refer to excited or transition states; others on physical properties, such as bond lengths and angles, NMR chemical shifts, resonance and stabilization energies, which refer to the ground state. Of these, the geometry of a molecule seems to be a useful criterion for a discussion of ground-state aromaticity.

The title compound undergoes electrophilic substitution reactions (Shaw, Balik, Holodnak & Prem,

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† For a discussion of the nomenclature, see Ceder & Beijer (1976), and for a review, Flitsch & Krämer (1977).

1976), but also reacts with dienophiles (Ceder & Andréasson, 1978), and possesses  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts and coupling constants which are similar to those of classical heteroaromatics. It therefore seemed of interest to determine the exact geometry of (I), including the position of the central N-atom relative to the plane of the ring.

### Experimental

1,3,4,6-Tetraazacycl[3.3.3]azine was synthesized as described by Shaw, Westler & Stefanko (1972) and was purified by column chromatography on silica gel. Crystals were obtained from a solution in  $\text{CH}_2\text{Cl}_2$ . The crystal used for data collection was  $0.15 \times 0.04 \times 0.04$  mm along *a*, *b* and *c* respectively. The crystal was mounted on a Syntex P2<sub>1</sub> diffractometer (Cu  $K\alpha$  radiation, monochromated with a graphite crystal). The cell dimensions were obtained by least squares from the Bragg angles of 10 low-order reflections. Intensities were collected in the range  $2\theta < 115^\circ$ ; 911 symmetry-related *hkl* and *hk $\bar{l}$*  reflections were measured. The  $\omega$ - $2\theta$  scan technique was used with scans ( $\Delta\omega$ ) of  $1.2^\circ$  (plus a correction for the  $\alpha_1$ - $\alpha_2$  separation). The typical rocking angle for the reflections was  $0.6^\circ$  in  $\omega$ . The background and integrated intensities were evaluated with a local version (Lindqvist & Ljungström, 1978) of the Larsen & Lehmann (1974) method for reflection profile analysis. The  $\omega$ -scan speed was varied from  $0.5^\circ \text{ min}^{-1}$  for the weakest reflections up to  $3.0^\circ \text{ min}^{-1}$  for the strongest reflections, thus improving the counting statistics for the weak intensities. Those 731 reflections having  $I > 2\sigma(I)$  were regarded as significant and used in subsequent calculations. The intensity of a standard reflection was monitored after every 15

reflections; only statistical variations were observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The positions of the H atoms were obtained from geometrical calculations. The refinement was carried out by block-diagonal least squares (*BLOCK*; Lindgren, 1977), and all positional and thermal (anisotropic for the C and N atoms, isotropic for H) parameters were varied. The final *R* was 0.038 and the corresponding parameters are listed in Table 1.\* The observed structure factors were weighted according to  $w = (10.0 + |F_o| + 0.03|F_o|^2)^{-1}$ . The O and C scattering factors were obtained from Doyle & Turner (1968), those for H from Stewart, Davidson & Simpson (1965).

### Discussion

The bond distances and angles are given in Figs. 1 and 2.

The lengths of the C—C bonds, all in ring C,  $1.375 \pm 0.005$  Å, vary very little and are close to the values expected for an aromatic C—C bond {1.395 Å in benzene; 1.38 Å for the inner bonds in the aromatic but not completely planar, deviation 0.085 Å, [18]annulene (Hirshfeld & Rabinovich, 1965; Bregman, Hirshfeld, Rabinovich & Schmidt, 1965); 1.38 Å for the C(3)—C(4) and C(4)—C(5) bonds in 2-(2',4'-dinitrobenzyl)pyridine (Seff & Trueblood, 1968); and 1.37 Å for C(4)—C(5) and C(5)—C(6) in pyrimidine

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33276 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters*

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.4479 (10)	0.4102 (2)	0.9182 (2)
N(3)	0.7119 (11)	0.2886 (2)	0.0161 (2)
N(4)	0.7155 (11)	0.1259 (2)	0.9726 (2)
N(6)	0.4485 (11)	0.0739 (2)	0.8294 (2)
N(9b)	0.4380*	0.2423 (2)	0.8727 (2)
C(2)	0.6175 (14)	0.3801 (3)	0.9932 (3)
C(3a)	0.6240 (11)	0.2186 (2)	0.9554 (3)
C(5)	0.6189 (13)	0.0600 (2)	0.9070 (3)
C(6a)	0.3573 (11)	0.1681 (2)	0.8094 (2)
C(7)	0.1858 (14)	0.1928 (3)	0.7279 (2)
C(8)	0.1017 (12)	0.2895 (3)	0.7101 (3)
C(9)	0.1878 (14)	0.3619 (2)	0.7732 (2)
C(9a)	0.3573 (11)	0.3402 (2)	0.8550 (2)
H(2)	0.722 (18)	0.433 (3)	0.043 (3)
H(5)	0.674 (15)	0.988 (2)	0.920 (2)
H(7)	0.116 (13)	0.136 (2)	0.687 (2)
H(8)	0.971 (16)	0.307 (3)	0.648 (2)
H(9)	0.127 (11)	0.426 (2)	0.763 (2)

\* Fixed to specify origin.

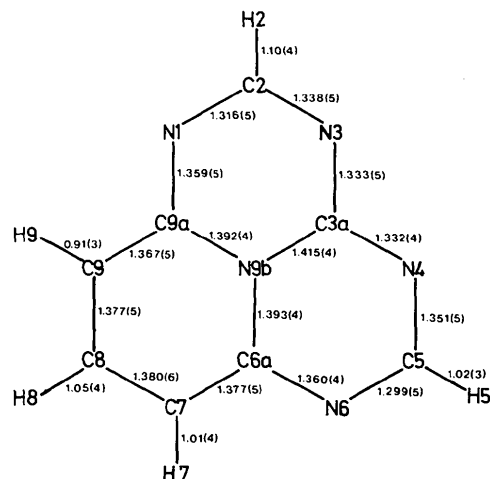


Fig. 1. Bond distances (Å).

(Wheatley, 1960)}. The distances indicate almost no bond alternation in ring *C* and these electrons are thus completely delocalized.

In rings *A* and *B* there are four types of peripheral C–N bonds [(a) C(2)–N(1) and C(5)–N(6) with an average length of 1.307 Å, (b) C(2)–N(3) and C(5)–N(4) with an average length of 1.345 Å, (c) C(3a)–N(3) and C(3a)–N(4) with a length of 1.333 Å, and (d) C(6a)–N(6) and C(9a)–N(1) with a length of 1.360 Å] in which the bond distances compare favourably with those in pyrimidine [C(2)–N(1) and C(2)–N(3) 1.315 ± 0.002 Å and C(4)–N(3) and C(6)–N(1) 1.338 ± 0.006 Å; Wheatley, 1960].

Obviously, the bonds under (a) possess more double-bond character than those under (d) while those under (b) and (c) occupy an intermediate position (Donohue, Lavine & Rollett, 1956). (I) has a plane of symmetry and a  $C_2$  axis through C(8)–N(9b)–C(3a) and the parameters for rings *A* and *B* should be the same. The greatest deviations in the observed bond distances and angles occur around C(2) and C(5), but these do not exceed the  $3\sigma$  level (Figs. 1 and 2). Rings *A* and *B* may thus be considered to be identical within experimental error.

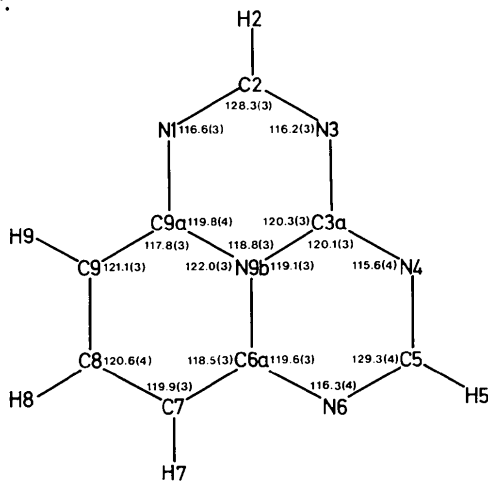


Fig. 2. Bond angles ( $^{\circ}$ ).

Table 2. Planarity of the molecule

Deviations are given from the best least-squares plane through the non-hydrogen atoms (Cartesian coordinates in Å).

Equation of the plane

$$0.8765X + 0.1305Y - 0.4633Z = -3.8758$$

Deviations

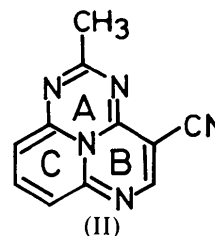
N(1)	-0.003 Å	C(2)	0.007 Å
N(3)	0.006	C(3a)	-0.008
N(4)	0.016	C(5)	0.014
N(6)	-0.010	C(6a)	-0.012
N(9b)	-0.033	C(7)	0.004
H(2)	0.12	C(8)	0.016
H(5)	-0.02	C(9)	0.011
H(7)	-0.06	C(9a)	-0.009
H(8)	0.03		
H(9)	-0.01		

The bond distances to the central N atom are distinctly longer than the peripheral ones. The mean value 1.400 Å is close to  $N(sp^3)$ – $C(sp^2)$  observed in 2,4,6-trinitrodiphenylamine [1.43 (2) Å is the bond distance between the amine N and C(1') in the unsubstituted ring; Divjaković, Nowacki, Edenharter, Engel, Ribár & Halasi, 1973] indicating no interaction between the central and peripheral electrons.

An interesting point is whether (I) is completely planar or not. Our measurements show that the N atom is located 0.033 Å from the peripheral plane (Table 2). It is reasonable to assume, however, that this deviation corresponds to a shift of the gravity center of the N(9b) electron density due to the asymmetric distribution of its non-bonding electron pair.

A comparison of our values with those of Hanson (1961) for the aromatic cycl[3.2.2]azine would be interesting. Unfortunately, the accuracy of his analysis on the dibromo derivative is less satisfactory because the scattering power of the Br atoms exceeds that of the lighter atoms.

At present, (I) is the only unsubstituted azacycl[3.3.3]azine for which an X-ray analysis has been reported. The results of a triaza system, (II), which carries a cyano group, are, however, available (Chiang, 1975).



A comparison between bond distances and bond angles in (I) and (II) shows that the geometries of the *A* and *C* rings are almost the same in the two compounds, while the geometries of the *B* rings are different. The electron-attracting CN group therefore affects the electron distribution only in the two peripheral bonds adjacent to C(4). These results are in agreement with

Table 3. Short intermolecular atomic distances (Å)

N(1)–C(2)	3.341 (7)	C(9)–N(1)	3.544 (6)
N(1)–N(3)	3.527 (5)	C(9)–C(9a)	3.362 (7)
C(9a)–C(2)	3.468 (6)	C(9)–N(9b)	3.565 (5)
C(9a)–N(3)	3.429 (5)	C(8)–C(9a)	3.562 (6)
C(9a)–C(3a)	3.534 (6)	C(8)–N(9b)	3.482 (5)
N(9b)–N(3)	3.483 (4)	C(8)–C(6a)	3.560 (6)
N(9b)–C(3a)	3.311 (5)	C(7)–N(9b)	3.569 (5)
N(9b)–C(6a)	3.466 (4)	C(7)–C(6a)	3.357 (7)
N(6)–N(4)	3.519 (5)	C(7)–N(6)	3.535 (6)
N(6)–C(5)	3.331 (6)		
C(6a)–C(3a)	3.538 (6)		
C(6a)–N(2)	3.416 (5)		
C(6a)–C(5)	3.450 (6)		

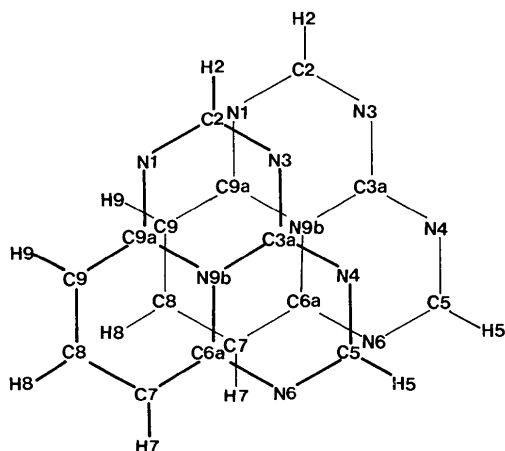


Fig. 3. The mutual orientation of two molecules in adjacent cells in the *a* direction, projected perpendicular to the molecular plane.

HMO calculations (Ceder & Andersson, 1972) and with experimental findings that such a group does not affect the directing effect in electrophilic substitution reactions (Ceder, Andersson & Johansson, 1972; Ceder & Samuelsson, 1973).

The results of the present investigation thus support the conclusion that the ground state of (I) is aromatic, since the bond lengths are close to what is expected for heterocycles usually classified as such and since very slight bond alternation is present.

The shortest intermolecular atomic distances are listed in Table 3, and the stacking perpendicular to the molecular plane is shown in Fig. 3. The deviation of N(9b) out of the molecular plane (Table 2) indicates that its non-bonding electron pair is directed towards C(3a).

The authors thank Dr Susan Jagner for revising the English text. Financial support has been obtained from the Swedish Natural Science Research Council (NFR).

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