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Phenazine-2,3-diamine

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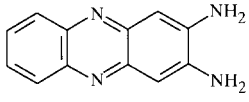
The planar electron-rich heterocyclic diamine 2,3-diaminophenazine (DAP), $C_{12}H_{10}N_4$, is of particular interest to both chemists and biochemists because of its rich organic chemistry and intense luminescence. In this paper, we report the first structure of DAP in its non-protonated form and describe the intriguing crystal packing, which features π–π, hydrogen- and T-bonded interactions.

Comment

The planar electron-rich heterocyclic diamine 2,3-diaminophenazine (DAP) is a compound which has long been of interest, initially because of its chemical and physical properties and more recently because of its mutagenic and genotoxic behaviour. The fact that DAP has a rich and varied chemistry is demonstrated by the vast number of organic transformations that have been published in the literature. In addition, the compound has been well characterized spectroscopically by NMR, absorption and most notably by emission techniques, where the remarkable luminescence of DAP has been intensively studied and exploited in analytical and biochemical applications.



DAP

DAP is known to luminesce strongly both in polar organic solvents (Zheng *et al.*, 1997) and in aqueous buffer solutions, especially when embedded within a micelle structure (Mekler & Bystryak, 1992). Indeed, it is the luminescence of DAP that sparked our interest in the molecule, especially as probes containing phenazine have shown potential in the exploration of nucleic acid structure. Further, DAP has been shown to damage DNA (Watanabe *et al.*, 1996) and so may have some role to play as a chemotherapeutic agent. The compound has found useful application in analytical chemistry as a catalymetric analyte, where it is used as a marker in fluorimetric determinations of laccase activity (Huang *et al.*, 1998) and in immunoassay determination of enzyme-catalysed reactions such as the oxidation of 1,2-phenylenediamine (*o*-PD) by horseradish peroxidase (Jiao *et al.*, 1998).

Synthetically, DAP is prepared by the catalysed autosensitized or photochemical oxidation cyclization of *o*-PD. The oxidation has been catalysed by various oxidants, including silver oxide, lead(IV) oxide, ferric chloride, cupric chloride and perchlorate and by cobalt perchlorate (Crank & Makin, 1989). The oxidation takes place in two one-electron transfer steps, a mechanism which may have relevance when studying the biological functions of metal-containing proteins (Loveless *et al.*, 1981). The fact that the heterocycle is produced in high yield in neutral or acid conditions, but not under basic conditions, perhaps explains why only structures of the protonated molecule (as its chloride or perchlorate salts) have been published previously (Brownstein & Enright, 1995; Peng & Liaw, 1986). These studies have shown that the heterocycle is protonated at the phenazine nitrogen although spectroscopic evidence suggests that the more basic amine N atoms are protonated in solution. When one of the phenazine N atoms is protonated the cation may exist in six resonance forms which, when the individual π bond strengths are considered, explains the lack of symmetry of the bond lengths in the structures of protonated DAP. In contrast, the structure of DAP (Fig. 1) shows a high degree of symmetry both in bond lengths and angles on each side of the molecular C_2 axis (Table 1). In the solid state, the structure of DAP is essentially planar, however a small degree of bending is discernible. This curvature may be attributed to the geometry of the central pyrazine ring which displays some distortions from that of an ideal aromatic ring (Table 1).

The crystal packing of DAP (Fig. 2) is particularly interesting and as the molecule is replete with numerous π-bonding and hydrogen-bond donor and acceptor sites it may be expected that it can act as a particularly versatile supramolecular tecton. Indeed, it is found that DAP forms infinite π–π stacks in the *x* and *z* directions, a feature which is a consequence of the orthorhombic crystal system. The average arene–arene non-bonded distance is 3.64 Å. The infinite π stacks are connected in three dimensions by way of intermolecular hydrogen bonds (Table 2). The hydrogen bonds connect the amine H1*A* and H16*A* and the aromatic H3 and H14 atoms of one molecule and the pyrazine N atoms (N5 and N12) of its nearest neighbour. In addition, there are T-bonded interactions which feature the terminal benzene ring

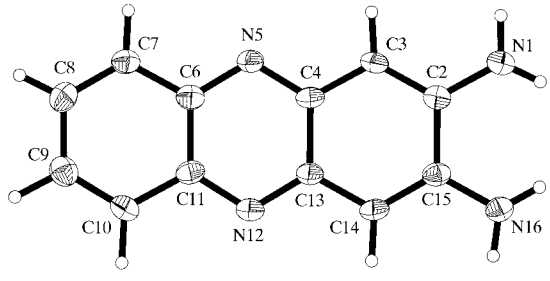


Figure 1
The molecular structure of DAP showing 50% probability displacement ellipsoids.

(C6–C11) of one molecule and the amine H atoms (H1*B* and H16*B*) of its nearest neighbour. The typical NH–π distance is 2.71 Å. The cumulative effect of these intermolecular interactions is to create a particularly attractive three-dimensional supramolecular network.

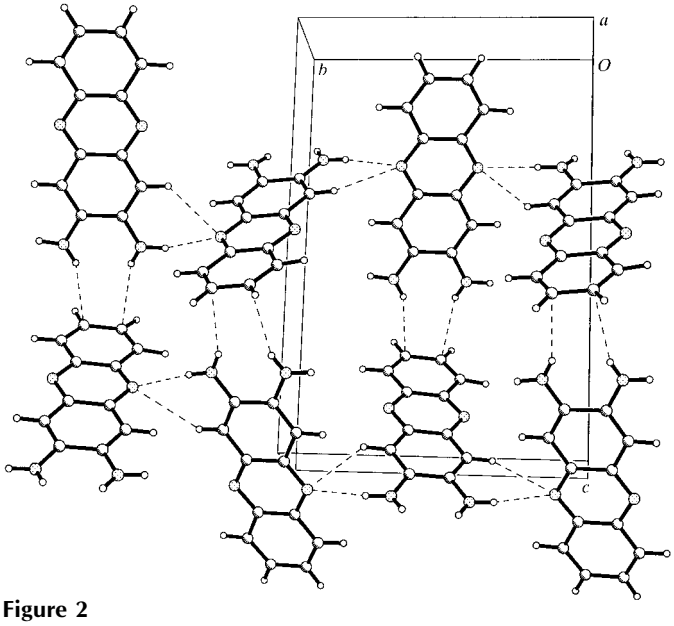


Figure 2
Diagram demonstrating the hydrogen- and T-bonding interactions within the crystal packing of DAP.

Experimental

2,3-Diaminophenazine was prepared by addition of a stoichiometric quantity of copper(II) hydroxide to an aqueous suspension of 1,2-phenylenediamine. The resultant brown precipitate was collected by filtration and subsequently crystallized by slow diffusion of acetonitrile vapour into a methanolic solution of the title compound.

Crystal data

$C_{12}H_{10}N_4$
M_r = 210.24
Orthorhombic, $P2_12_12_1$
a = 4.8355 (8) Å
b = 11.583 (2) Å
c = 17.304 (3) Å
V = 969.2 (3) Å^3
Z = 4
D_x = 1.442 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1452 reflections
θ = 2.12–26.35°
μ = 0.092 mm^{-1}
T = 293 (2) K
Trigonal prism, brown
0.30 × 0.25 × 0.20 mm

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.372 (3)	C11—N12	1.357 (3)
C4—N5	1.342 (3)	N12—C13	1.335 (3)
N5—C6	1.352 (3)	C15—N16	1.371 (3)
C3—C2—N1	122.0 (2)	C13—N12—C11	117.37 (19)
N1—C2—C15	118.9 (2)	C14—C15—N16	121.7 (2)
C4—N5—C6	117.59 (18)	N16—C15—C2	118.7 (2)

Data collection

Bruker AXS SMART CCD area-detector diffractometer
ω–2θ scans
3272 measured reflections
1182 independent reflections
985 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.37°
$h = -4 \rightarrow 6$
$k = -14 \rightarrow 13$
$l = -21 \rightarrow 8$
Intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.041
$wR(F^2)$ = 0.115
S = 1.046
1182 reflections
145 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 0.0252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N5^{i}	0.86	2.39	3.154 (3)	148
N1—H1B···C9^{ii}	0.86	2.79	3.586 (3)	154
N16—H16A···N12^{iii}	0.86	2.29	3.119 (3)	163
N16—H16B···C8^{ii}	0.86	2.68	3.474 (3)	154
C3—H3···N5^{i}	0.93	2.63	3.371 (3)	137
C14—H14···N12^{iii}	0.93	2.82	3.578 (3)	139

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (ii) $-\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$.

H atoms were placed geometrically with C—H and N—H distances of 0.93 and 0.86 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C, N)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1429). Services for accessing these data are described at the back of the journal.

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