Structure of 2-Amino-1,3-diazaazulene Hydrobromide Monohydrate

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Abstract. $C_8H_8N_3^+ \cdot Br^- \cdot H_2O$, $M_r = 244 \cdot 09$, monoclinic, orange prisms, $P2_1/a$, $a = 25 \cdot 436$ (6), $b = 7 \cdot 484$ (2), $c = 10 \cdot 798$ (2) Å, $\beta = 101 \cdot 61$ (2)°; $D_x = 1 \cdot 610$ Mg m^{-3} for $Z = 8$. The crystal contains two crystallographically independent molecules protonated at a ring N atom. They form a pseudocentrosymmetric dimer with two NH$\cdots$N hydrogen bonds. A significant difference between the two independent molecules concerns the second hydrogen-bonding scheme; one links to a bromide anion and the other to water.

Introduction. The present work was undertaken to reveal the site of protonation in 2-amino-1,3-diaza-azulene (Nozoe, Mukai, Takase, Murata & Matsumoto, 1953) and the effect of protonation on the molecular geometry.

Intensity data were collected with graphite-monochromated Mo $K\alpha$ radiation on a Rigaku four-circle automatic diffractometer using a crystal 0·6 × 0·6 × 0·4 mm. The θ–2θ scan was used for a range of $(1 \cdot 5 + 0 \cdot 35 \tan \theta)°$, the scan speed being 4° min^{-1} in 2θ. Four standard reflexions showed only statistical fluctuations throughout data collection. The intensities were corrected for Lorentz–polarization effects, but not for absorption, μ(Mo $K\alpha$) = 4·29 mm^{-1}. 4389 independent reflexions with $2\theta < 54 \cdot 0°$ were measured; 2627 with $|F_o| \geq 3\sigma(F_o)$ were used as observed.

The structure was determined by the heavy-atom method and refined by a block-diagonal-matrix least-

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Table 1. *Final atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

	x	*y*	*z*		*x*	*y*	*z*
Br(1)	2688 (1)	3071 (2)	6810 (1)	H(*W*11)	658 (6)	885 (22)	306 (14)
Br(2)	4082 (1)	6739 (2)	8843 (1)	H(*W*12)	616 (6)	1059 (22)	247 (14)
O(*W*1)	6271 (4)	9609 (18)	3027 (12)	H(*W*21)	544 (6)	598 (23)	106 (14)
O(*W*2)	5229 (5)	7124 (18)	1055 (11)	H(*W*22)	490 (6)	696 (21)	42 (14)
Molecule 1							
N(1)	3839 (4)	5363 (15)	3542 (9)	H(21)	427 (6)	642 (22)	579 (15)
C(2)	3661 (5)	5185 (17)	4629 (12)	H(22)	379 (6)	563 (22)	650 (14)
N(2)	3926 (5)	5791 (18)	5731 (10)	H(3)	300 (6)	395 (22)	511 (14)
N(3)	3183 (4)	4298 (14)	4436 (10)	H(4)	233 (6)	258 (22)	321 (14)
C(4)	2560 (6)	2992 (20)	2652 (15)	H(5)	207 (6)	188 (21)	117 (14)
C(5)	2406 (6)	2566 (20)	1414 (15)	H(6)	247 (7)	231 (22)	−41 (14)
C(6)	2655 (6)	2847 (18)	417 (15)	H(7)	324 (6)	378 (22)	−44 (14)
C(7)	3137 (6)	3715 (20)	386 (13)	H(8)	384 (6)	507 (22)	111 (14)
C(8)	3493 (5)	4504 (17)	1348 (11)				
C(9)	3459 (4)	4607 (17)	2624 (11)				
C(10)	3028 (5)	3918 (17)	3204 (12)				
Molecule 2							
N(1)	4984 (4)	7479 (15)	5537 (10)	H(21)	454 (6)	640 (22)	332 (14)
C(2)	5151 (5)	7593 (18)	4440 (11)	H(22)	503 (6)	704 (22)	259 (14)
N(2)	4893 (4)	6983 (15)	3368 (10)	H(3)	582 (6)	885 (22)	392 (14)
N(3)	5640 (4)	8524 (13)	4601 (10)	H(4)	647 (6)	1025 (22)	570 (14)
C(4)	6243 (5)	9916 (16)	6303 (13)	H(5)	675 (6)	1112 (23)	775 (14)
C(5)	6407 (5)	10467 (17)	7555 (13)	H(6)	637 (6)	1085 (22)	941 (14)
C(6)	6173 (5)	10220 (21)	8590 (14)	H(7)	560 (6)	939 (22)	948 (14)
C(7)	5681 (6)	9366 (22)	8638 (14)	H(8)	501 (6)	802 (22)	794 (14)
C(8)	5323 (5)	8533 (18)	7691 (12)				
C(9)	5359 (4)	8351 (16)	6416 (11)				
C(10)	5784 (5)	9002 (18)	5824 (12)				

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squares method. The positions of the H atoms were first estimated from geometrical considerations involving the possible hydrogen-bonding scheme, and then confirmed in the final difference Fourier map; their positional parameters were refined with the temperature factors kept constant at 4 Å^2. The final R was 0·105 for the observed reflexions and 0·225 for all reflexions. The weighting scheme used for minimizing $\sum w(|F_o| - |F_c|)^2$ was $w = 1/[\sigma^2(F_o) + 0·04217|F_o| - 0·00132|F_o|^2]$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic parameters obtained are given in Table 1.*

Discussion. The asymmetric unit consists of two formula units. Molecules 1 and 2 are connected by two NH···N hydrogen bonds, forming a pseudocentrosymmetric dimer (Fig. 1). A significant difference between the two independent molecules concerns the second hydrogen-bonding scheme. While molecule 1 is directly hydrogen-bonded to Br(1) and Br(2) anions,

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* Lists of structure factors, thermal parameters and bond angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34609 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
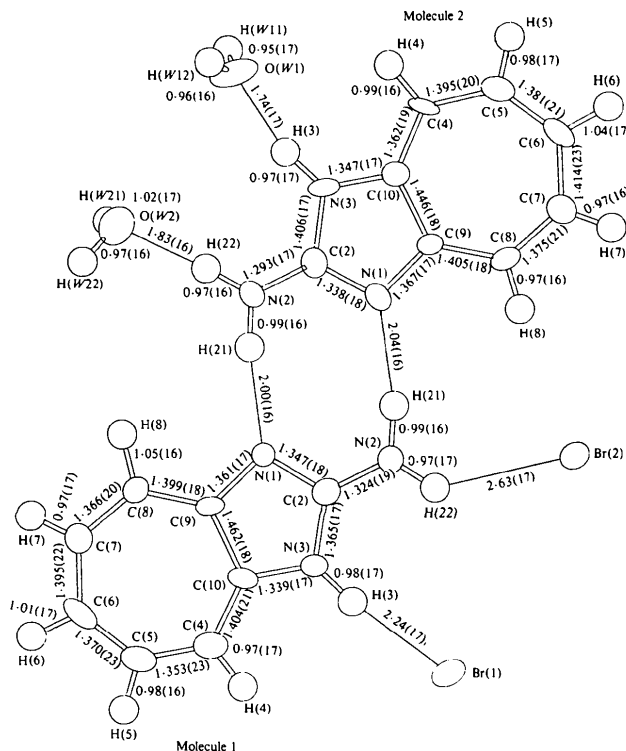
molecule 2 is indirectly linked to anions through O(W1) and O(W2). As shown in Fig. 2, in the crystal structure all H atoms attached to O or N participate in hydrogen bonding (Table 2).

Although the estimated standard deviations are rather large and a detailed discussion of bond lengths and angles is questionable, it should be noted that corresponding bond lengths and angles in molecules 1 and 2 appear to agree fairly well, especially in the seven-membered ring (Fig. 1 and Table 3).

Inspection of the bond lengths and angles suggests that the π electrons are delocalized over the whole molecule; in particular, the rather short C(2)—N(2) bond indicates conjugation of the amino group with the ring system.

C(9)—C(10) is longer than the other C—C bonds, but is somewhat shorter than the corresponding bonds in azulene-1,3-dipropionic acid (Ammon & Sundaralingam, 1966), *cis,cis*-1,3-bis(styryl)azulene (Fallon, Ammon, Anderson, Currie & LaBar, 1974), and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (Goldstein & Trueblood, 1967). This feature suggests some contribution from the canonical formulae where positive charge is on the seven-membered ring.
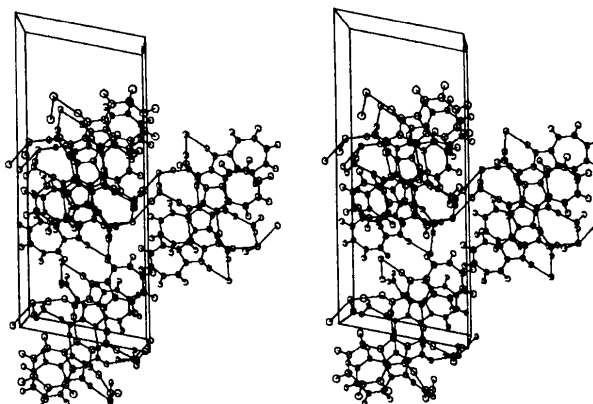

Fig. 2. Stereoscopic view of the crystal structure.

Fig. 1. Bond lengths (Å) with their e.s.d.'s in parentheses, and thermal ellipsoids at the 30% probability level.

Table 2. *Geometry of the hydrogen bonds*

The numbers 1 and 2 following the atomic number designate molecules 1 and 2 respectively.

Donor	Acceptor					
N(3)1	Br(1)	3·21 (1) Å	C(10)1	N(3)1	Br(1)	130 (1)°
N(2)1	Br(2)	3·38 (1)	C(2)1	N(2)1	Br(2)	155 (1)
O(W1)	Br(1)^i	3·30 (1)	Br(1)^i	O(W1)	Br(2)^{ii}	129·2 (4)
O(W1)	Br(2)^{ii}	3·41 (1)				
O(W2)	Br(2)^i	3·37 (1)	Br(2)^i	O(W2)	Br(2)^{iii}	108·6 (4)
O(W2)	Br(2)^{iii}	3·39 (1)				
N(3)2	O(W1)	2·69 (2)	C(10)2	N(3)2	O(W1)	118 (1)
N(2)2	O(W2)	2·80 (2)	C(2)2	N(2)2	O(W2)	127 (1)
N(2)1	N(1)2	3·02 (2)	C(2)1	N(2)1	N(1)2	112 (1)
N(2)2	N(1)1	2·98 (2)	C(2)2	N(2)2	N(1)1	113 (1)

Symmetry code
(i) $1 - x, 1 - y, 1 - z$ (iii) $x, y, -1 + z$
(ii) $1 - x, 2 - y, 1 - z$

Table 3. *Bond angles* (°) *and their e.s.d.'s in parentheses*

	Molecule 1	Molecule 2
C(2)–N(1)–C(9)	106·2 (1·1)	106·5 (1·1)
N(1)–C(2)–N(2)	123·4 (1·3)	125·2 (1·2)
N(1)–C(2)–N(3)	111·2 (1·1)	110·6 (1·1)
N(2)–C(2)–N(3)	125·4 (1·3)	124·1 (1·2)
C(2)–N(3)–C(10)	109·2 (1·1)	108·1 (1·1)
C(5)–C(4)–C(10)	126·0 (1·5)	125·6 (1·3)
C(4)–C(5)–C(6)	130·8 (1·6)	130·6 (1·4)
C(5)–C(6)–C(7)	129·7 (1·5)	128·3 (1·5)
C(6)–C(7)–C(8)	129·3 (1·4)	129·5 (1·5)
C(7)–C(8)–C(9)	127·6 (1·3)	127·5 (1·3)
N(1)–C(9)–C(8)	124·4 (1·2)	123·6 (1·2)
N(1)–C(9)–C(10)	108·6 (1·1)	109·4 (1·1)
C(8)–C(9)–C(10)	127·0 (1·2)	127·1 (1·2)
N(3)–C(10)–C(4)	125·5 (1·3)	123·2 (1·2)
N(3)–C(10)–C(9)	104·8 (1·1)	105·4 (1·1)
C(4)–C(10)–C(9)	129·6 (1·3)	131·4 (1·3)

The C(10)–N(3)–C(2) angle is larger than C(2)–N(1)–C(9). This difference may be mainly attributable to the protonation on N(3), as noticed by Singh (1965).

It has been established that in the present crystals protonation occurs at one ring N atom as formulated in (I) and therefore formula (II) proposed by Nozoe *et al.* (1953) is rejected.
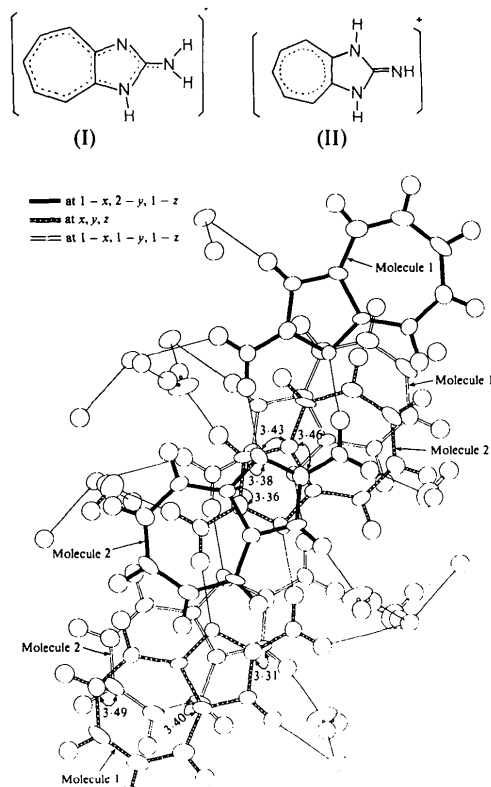

(I)   (II)

Fig. 3. Stacking of the molecular planes and interatomic contact distances (Å).

Table 4. *Deviations* (Å) *of atoms from the least-squares planes*

Asterisks denote atoms used to calculate the planes.

	Plane (I)		Plane (II)	
	Molecule 1	Molecule 2	Molecule 2	Molecule 1
N(1)	0·008*	0·122	0·014*	−0·205
C(2)	0·007*	0·151	−0·001*	−0·163
N(3)	0·014*	0·125	−0·010*	−0·174
C(4)	−0·004*	0·057	0·006*	−0·279
C(5)	−0·006*	−0·009	−0·003*	−0·336
C(6)	0·018*	−0·035	0·010*	−0·350
C(7)	0·009*	−0·046	−0·008*	−0·350
C(8)	−0·014*	0·004	−0·006*	−0·326
C(9)	−0·015*	0·060	−0·003*	−0·273
C(10)	−0·019*	0·081	0·001*	−0·261
N(2)	0·009	0·162	−0·040	−0·110
Br(1)	0·435		0·333	
Br(2)	−0·173		−0·155	
O(W1)	0·021		−0·167	
O(W2)	0·271		−0·024	

Equations of the planes are of the form $AX + BY + CZ + D = 0$, in which X, Y and Z are Cartesian coordinates in Å referred to the a, b and c^* axes respectively.

Plane	A	B	C	D
(I)	0·4572 (36)	−0·8727 (17)	0·1715 (29)	−1·245 (30)
(II)	0·4595 (33)	−0·8627 (16)	0·2110 (30)	−1·666 (50)

Each azulene ring is planar (Table 4), and the interplanar angle between molecules 1 and 2 is 2·3 (2)°. As shown in Fig. 3, considerable overlapping of atoms is observed between the molecules at x,y,z and those at $1 − x$, $1 − y$, $1 − z$. Contact distances between atoms are equal to or slightly longer than the sum of their van der Waals radii.

References

AMMON, H. L. & SUNDARALINGAM, M. (1966). *J. Am. Chem. Soc.* **88**, 4794–4799.

FALLON, L. III, AMMON, H. L., ANDERSON, A. G. JR, CURRIE, J. O. JR & LABAR, R. A. (1974). *Acta Cryst.* B30, 531–533.

GOLDSTEIN, P. & TRUEBLOOD, K. N. (1967). *Acta Cryst.* **23**, 148–156.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.

NOZOE, T., MUKAI, T., TAKASE, K., MURATA, I. & MATSUMOTO, K. (1953). *Proc. Jpn Acad.* **29**, 452–456.

SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.