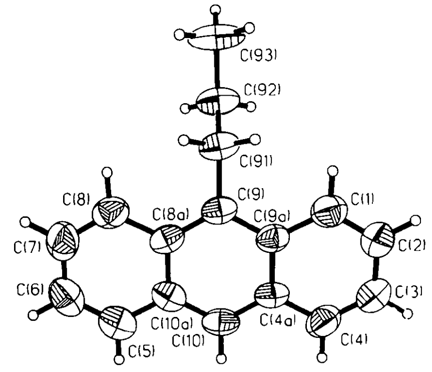

Fig. 1. Thermal-ellipsoid plot (50% level) of the title compound, showing the atom-numbering scheme. H-atom radii are arbitrary.

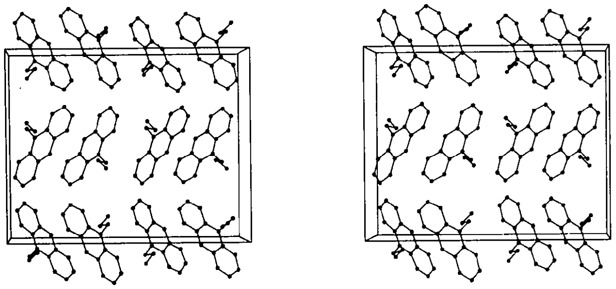

Fig. 2. Stereographic packing diagram of the title compound. View direction along x, y horizontal, z vertical. H atoms are omitted for clarity.

average of the bond distances C(8a)—C(9) and C(9)—C(9a) [1·407 (5) Å] is marginally larger than in anthracene [1·396 (3) Å], but substantially larger than the average of C(4a)—C(10) and C(10)—C(10a) [1·386 (6) Å]. The bond angles show this effect even more clearly. The bond angles C(1)—C(9a)—C(9) [123·8 (5)°] and C(8)—C(8a)—C(9) [123·3 (5)°] are larger than C(4)—C(4a)—C(10) [120·3 (5)°] and C(5)—C(10a)—C(10) [121·1 (5)°]. The in-plane bend of the linear anthracene skeleton [about an axis in the midpoint of C(9)—C(10) and perpendicular to the molecular plane] can also be described in terms of the diagonals of the peripheral rings, C(1)—C(4) and C(5)—C(8), which are parallel in anthracene, but make an angle of 2·4 (5)° in the title molecule.

We also observe a slight folding of the molecule along the axis C(9)—C(10). The angle between the two outer aromatic ring planes is 3·6 (5)°. A similar effect is noted in the 9-methylanthracene molecule.

The deviations of the aromatic C atoms from coplanarity, which are less than 0·01 Å in anthracene and 9,10-dimethylanthracene (Iball & Low, 1974), increase to 0·06 Å in the present case (r.m.s. 0·038 Å). This is similar to the distortion from planarity in 9-methylanthracene (0·01–0·08 Å).

The bond lengths are largely normal compared with anthracene. The exocyclic bond C(9)—C(91) is somewhat larger (2–3σ) than in 9-methylanthracene, but compares well with the corresponding value in another *n*-propyl-substituted aromatic compound that we have studied recently (Schrumpf & Jones, 1988).

The packing of 9-propylanthracene (Fig. 2) is different from that in 9-methyl-, 9,10-dimethyl- and unsubstituted anthracene. There are no unusually close intermolecular contacts in the present structure.

We thank the Fonds der Chemischen Industrie for financial assistance.

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Inside-Protonated 1,8-Diazabicyclo[6.4.3]pentadecane Picrate

By R. W. Alder, A. G. Orpen and J. M. White

*Departments of Inorganic and Organic Chemistry, The University, Bristol BS*8 1*TS, England*

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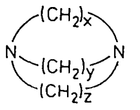
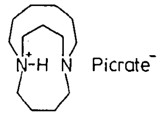
Abstract. $C_{13}H_{27}N_2^+.C_6H_2N_3O_7^-$, $M_r = 439{\cdot}56$, monoclinic, $P2_1/c$, $a = 11{\cdot}946$ (3), $b = 22{\cdot}900$ (8), $c = 7{\cdot}754$ (2) Å, $\beta = 102{\cdot}98$ (2)°, $V = 2067$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}02$ cm^{-1}, $F(000) = 936$, $T = 196$ K, $R = 0{\cdot}043$ for 3084 unique observed reflections. The title compound

has an intrabridgehead N(1)···N(8) distance of 2·663 (4) Å; the inside proton, which is crystallographically well located, is localized near N(8) [N(8)—H 0·950 (19), N(1)···H 1·772 (21) Å]. The bicyclic structure exhibits strain shown by the close intramolecular H···H contacts between methylene C—H groups and an average C—C—C angle of above ideal value. The geometry of the picrate anion is not unusual.

Introduction. Medium-ring bridgehead bicyclic diamines (1) display an interesting chemistry (Alder, 1983) as a result of the many possible interactions involving the bridgehead N atoms. The structure determination of the title compound, (2), is one of a series of structural studies on the inside-protonated salts of these bicyclic diamines. The geometry of the N···H—N hydrogen bond in these compounds is expected to be influenced to a large extent by the conformational preferences of the oligomethylene bridges. It is hoped that by studying the structural properties of a number of these compounds correlations between structure and properties of N···H—N bonds can be established and also that some insight can be gained into the preferred conformation in the parent diamines (1), and other medium-ring bicyclic species, for use as starting points for molecular-mechanics calculations.



(1)



(2)

$7 \leq x+y+2, x+z+2, y+z+2 \leq 12$

Experimental. Yellow rod (0·7 × 0·3 × 0·3 mm), from solvent diffusion using CH_2Cl_2 and diethyl ether; Nicolet *P*3*m* diffractometer, 15 reflections centred ($14 < \theta < 15°$), graphite-monochromated Mo *K*α; for data collection $2 < \theta < 27·5°$, temperature 196 K by Nicolet LT-1 N_2 gas flow. ω–2θ scans in 96 steps, ω-scan width $(1·0 + 0·35\tan\theta)°$; one quadrant of data (*hkl* and $-hkl$, 4381 reflections) measured over 63 X-ray hours with no detectable decay or movement; systematic absences ($h0l$: $l = 2n + 1$, $0k0$: $k = 2n + 1$) uniquely define space group. 3818 unique data, $R_{\text{int}} = 0·014$, used for structure solution and refinement, 3084 reflections with $F > 3\sigma(F)$ retained ($-16 < h < 16$, $0 < k < 30$, $0 < l < 10$). Direct methods and difference-Fourier methods, blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0·00063(F^2)]^{-1}$, anisotropic thermal parameters for all non-H atoms, methylene and phenyl H atoms were refined in idealized positions (C—H 0·96 Å), all other atoms were refined without constraint. $R = 0·0433$, $wR = 0·0545$, $S = 1·377$, data:variable ratio 10·8:1, max. peak and min. trough in final ΔF synthesis 0·29 and 0·22 e Å^{-3} respectively, max. shift/e.s.d. in final cycle 0·007; complex neutral-atom scattering factors for C,H,N,O from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

Table 1. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*/U_{iso}
N(1)	6981 (1)	1049 (1)	6315 (2)	28 (1)
C(2)	7159 (2)	1682 (1)	6046 (3)	38 (1)
C(3)	7337 (2)	2048 (1)	7735 (3)	42 (1)
C(4)	8582 (2)	2082 (1)	8781 (3)	44 (1)
C(5)	9122 (2)	1500 (1)	9442 (3)	36 (1)
C(6)	8629 (2)	1216 (1)	10902 (3)	36 (1)
C(7)	8564 (2)	556 (1)	10735 (3)	33 (1)
N(8)	7684 (1)	370 (1)	9140 (2)	25 (1)
C(9)	7949 (2)	−212 (1)	8412 (3)	29 (1)
C(10)	8351 (2)	−138 (1)	6703 (2)	31 (1)
C(11)	7423 (2)	56 (1)	5111 (3)	35 (1)
C(12)	7278 (2)	715 (1)	4840 (3)	34 (1)
C(13)	5779 (2)	945 (1)	6487 (3)	36 (1)
C(14)	5623 (2)	422 (1)	7633 (3)	35 (1)
C(15)	6476 (2)	405 (1)	9409 (3)	31 (1)
C(16)	2819 (2)	1344 (1)	8547 (2)	26 (1)
C(17)	1819 (1)	1663 (1)	7541 (2)	26 (1)
C(18)	1730 (2)	2258 (1)	7468 (2)	28 (1)
C(19)	2609 (2)	2598 (1)	8467 (3)	28 (1)
C(20)	3571 (2)	2343 (1)	9542 (3)	29 (1)
C(21)	3651 (1)	1747 (1)	9600 (2)	27 (1)
N(17)	863 (1)	1333 (1)	6493 (2)	34 (1)
N(19)	2512 (1)	3224 (1)	8377 (2)	35 (1)
N(21)	4670 (1)	1497 (1)	10763 (2)	33 (1)
O(16)	2972 (1)	815 (1)	8457 (2)	35 (1)
O(171)	724 (1)	826 (1)	6874 (2)	46 (1)
O(172)	207 (1)	1588 (1)	5275 (2)	60 (1)
O(191)	1714 (1)	3439 (1)	7279 (2)	52 (1)
O(192)	3238 (1)	3519 (1)	9385 (2)	50 (1)
O(211)	4606 (1)	1021 (1)	11447 (2)	45 (1)
O(212)	5573 (1)	1780 (1)	11014 (2)	54 (1)
H	7662 (15)	634 (8)	8185 (24)	32 (5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion. Atomic coordinates are presented in Table 1* for all non-H atoms; a perspective view of the structure is presented in Fig. 1, and a view of the cation with the methylene H atoms included is given in Fig. 2. Selected bond lengths, bond angles and torsion angles together with important non-bonded distances are listed in Table 2. The bicyclic structure exhibits strain; this is demonstrated by the close intramolecular H···H contacts [see Table 2(*d*)] between methylene C—H groups, and the average C—C—C bond angle of 114·5° compared with the idealized angle of 109·5°. The oligomethylene-bridge conformations are defined by the torsion angles listed in Table 2(*c*). The four-carbon bridge has a $g^+g^-g^+$ sequence of torsion angles and is comparable to the conformations observed in 1,6-diazabicyclo[4.4.4]tetradecane, its inside-protonated

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44442 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

salt (Alder, Orpen & Sessions, 1983) and its oxidized salt (Alder, Orpen & White, 1985). The three-carbon bridge has a conformation similar to that observed in the hydrochloride salt of manxine (1-azabicyclo[3.3.3]undecane) (Paul, Wang, Missavage & Byrn, 1972) and the ordered molecule of manxanediol (bicyclo[3.3.3]undecane-1,5-diol) (Murray-Rust, Murray-Rust & Watt, 1980). The inside proton is 0·950 (19) Å from N(8) and 1·772 (21) Å from N(1), the $N\cdots H-N$ angle is 154·8 (13)° and the $N(1)\cdots N(8)$ distance is 2·663 (4) Å. This is in contrast to the inside-protonated salt of the [4.4.4] diamine (Alder, Orpen & Sessions, 1983) which has an $N\cdots N$ distance of 2·526 Å and a linear hydrogen bond with the inside proton equidistant from both N atoms. The geometry of the picrate anion is not unusual. The closest intermolecular contacts occur between the cation and the picrate anion [Table 2(*d*)]. The distances quoted in Table 2(*d*) are based on hydrogen positions adjusted so that all C–H bonds are 1·08 Å.

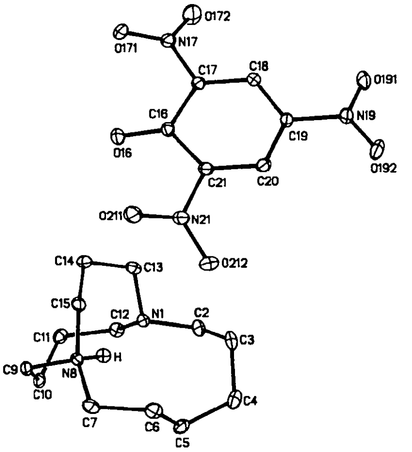

Fig. 1. A perspective view of the structure.

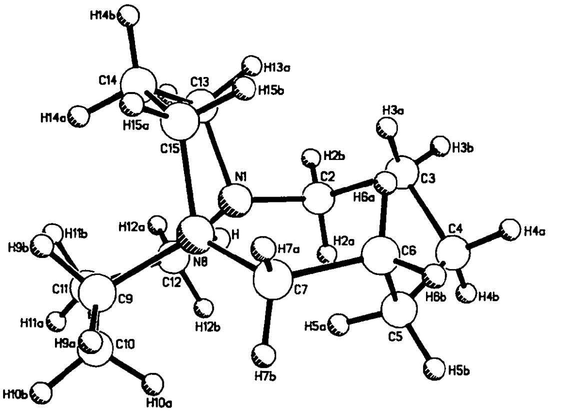

Fig. 2. A view of the cation with the methylene H atoms included.

Table 2. *Selected bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and non-bonded contacts* (Å)

(*a*) Bond lengths

N(1)–C(2)	1·486 (3)	N(1)–C(12)	1·484 (3)
N(1)–C(13)	1·491 (3)	C(2)–C(3)	1·529 (3)
C(3)–C(4)	1·527 (3)	C(4)–C(5)	1·518 (3)
C(5)–C(6)	1·534 (3)	C(6)–C(7)	1·517 (3)
C(7)–N(8)	1·493 (2)	N(8)–C(9)	1·509 (2)
N(8)–C(15)	1·506 (3)	N(8)–H	0·950 (19)
C(9)–C(10)	1·516 (3)	C(10)–C(11)	1·627 (3)
C(11)–C(12)	1·528 (3)	C(13)–C(14)	1·527 (3)
C(14)–C(15)	1·519 (3)		

(*b*) Bond angles

C(2)–N(1)–C(12)	109·2 (2)	C(2)–N(1)–C(13)	109·8 (2)
C(12)–N(1)–C(13)	112·8 (1)	N(1)–C(2)–C(3)	114·3 (2)
C(2)–C(3)–C(4)	114·5 (2)	C(3)–C(4)–C(5)	115·1 (2)
C(4)–C(5)–C(6)	114·6 (2)	C(5)–C(6)–C(7)	112·4 (2)
C(6)–C(7)–N(8)	111·5 (1)	C(7)–N(8)–C(9)	113·2 (1)
C(7)–N(8)–C(15)	112·9 (1)	C(9)–N(8)–C(15)	112·7 (1)
C(7)–N(8)–H	110·8 (11)	C(9)–N(8)–H	103·9 (12)
C(15)–N(8)–H	102·4 (11)	N(8)–C(9)–C(10)	111·3 (1)
C(9)–C(10)–C(11)	115·1 (2)	C(10)–C(11)–C(12)	116·0 (2)
N(1)–C(12)–C(11)	116·3 (2)	N(1)–C(13)–C(14)	115·1 (1)
C(13)–C(14)–C(15)	113·8 (2)	N(8)–C(15)–C(14)	110·2 (2)

(*c*) Torsion angles

Three-carbon bridge

N(1)–C(13)–C(14)–C(15)	48·5 (2)	C(13)–C(14)–C(15)–N(8)	−60·3 (2)

Four-carbon bridge

N(1)–C(12)–C(11)–C(10)	−59·3 (2)	C(12)–C(11)–C(10)–C(9)	89·7 (2)
C(11)–C(10)–C(9)–N(8)	−70·3 (2)		

Six-carbon bridge

N(1)–C(2)–C(3)–C(4)	87·1 (2)	C(2)–C(3)–C(4)–C(5)	−60·9 (3)
C(3)–C(4)–C(5)–C(6)	−68·9 (2)	C(4)–C(5)–C(6)–C(7)	143·6 (2)
C(5)–C(6)–C(7)–N(8)	−68·6 (2)		

(*d*) Selected non-bonded contacts (Å) [C–H bond lengths extended to 1·08 (Å)]

Intramolecular

H(2*a*)···H(12*b*)	2·073	H(2*b*)···H(3*b*)	2·274
H(3*a*)···H(6*a*)	2·145	H(3*a*)···H(13*a*)	2·136
H(5*b*)···H(6*b*)	2·261	H(6*a*)···H(15*b*)	2·111
H(7*a*)···H(11*a*)	2·266	H(7*b*)···H(9*a*)	2·212
H(9*b*)···H(14*a*)	2·136	H(10*b*)···H(11*a*)	2·251
H(11*b*)···H(14*a*)	1·871	H(12*a*)···H(13*b*)	2·202

Intermolecular

O(16)···H(14*b*)	2·445	O(16)···H(11*a*)	2·418
O(16)···H(15*a*)	2·283	O(191)···H(5*b*)	2·381

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