sequence of torsion angles (see Table 2) having an approximate local axis of symmetry (Alder *et al.*, 1983, 1985, 1988; White *et al.*, 1988*a,b,c*). The five-carbon bridges are interesting; the $g^+g^-g^-g^+$ sequence of torsion angles in both imply an approximate local axis of symmetry, in contrast to those observed in the inside-protonated salts of the [5.4.3]diamine, [5.5.2]-diamine and [6.5.3]diamine (White *et al.*, 1988*a,b,c*) and the inside-diprotonated [1.1.1]cryptand (Knochel, Brugge, Carboo, von Deuten, Kopf & Dreissig, 1986) which have conformations displaying a local plane of symmetry. The inside proton in (1) is localized near N(1) [N(1)—H 1·096 (33), N(7)···H 1·601 (33) Å], the N—H—N angle is 171·7 (17)°. The N(1)···N(7) distance is 2·690 (4) Å which represents the longest N···N distance observed for the inside-protonated salts of our series of bicyclic diamines. The *p*-nitrobenzoate anion is strongly hydrogen bonded to a molecule of *p*-nitrobenzoic acid (Emsley, 1980); the O(1)···O(5) distance is 2·460 (4) Å. The hydrogen is located near O(5) [O(5)—H(2) 1·04 (4); O(1)···H(2) 1·42 (4) Å], the O—H—O angle is 173 (4)°, and the dihedral angle between the planes of the two phenyl groups is 72·6°.

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Acta Cryst. (1988). C**44**, 1467–1469

Inside-Protonated 1,7-Diazabicyclo[5.4.2]tetradecane Picrate

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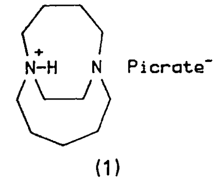
Abstract. $C_{11}H_{23}N_2^+.C_6H_2N_3O_7^-$, $M_r = 411·41$, monoclinic, $P2_1/c$, $a = 7·557\ (1)$, $b = 12·244\ (6)$, $c = 20·419\ (5)$ Å, $\beta = 91·34\ (2)°$, $V = 1889\ (1)$ Å^3, $Z = 4$, $D_x = 1·45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·01$ cm^{-1}, $F(000) = 904$, $T = 196$ K, $R = 0·077$ for 1695 unique observed reflections. The title compound has a short intrabridgehead N(1)···N(7) distance of 2·474 (7) Å; the inside proton is essentially equidistant from both bridgehead nitrogen atoms [N(1)—H 1·37 (7), N(7)···H 1·34 (7) Å, with N—H—N 132 (6)°].

Introduction. The structure analysis of the title compound (1) is one of a series of studies on medium-ring bicyclic diamines, and their oxidized and protonated ions (Alder, Orpen & Sessions, 1983; Alder, Orpen & White, 1985, 1988; White, Alder & Orpen, 1988*a,b,c,d*). The properties of the N—H—N hydrogen bond in these compounds are influenced to a large extent by the conformational requirements of the oligomethylene bridges connecting the bridgehead N atoms (Alder *et al.*, 1983). These compounds therefore provide an ideal means to study N—H—N hydrogen bonds of various geometries.



(1)

Experimental. Yellow block (0·6 × 0·6 × 0·6 mm) from solvent diffusion using CH_2Cl_2 and diethyl ether; Nicolet *P3m* diffractometer, refined cell parameters from angle data for 20 centred reflections ($13·5 < \theta < 14·0°$), graphite-monochromated Mo $K\alpha$ for data collection, $2 < \theta < 25°$, temperature 196 K by Nicolet LT1 N_2 flow. Wyckoff ω scans, one quadrant of data collected (hkl and $hk\bar{l}$) measured over 63 X-ray h with no detectable decay or movement; systematic absences ($h0l$ $l = 2n + 1$, $0k0$ $k = 2n + 1$) uniquely define the

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Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

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

	x	y	z	U_{eq}
N(1)	1775 (6)	10445 (4)	2148 (2)	65 (2)
C(2)	1921 (10)	11540 (6)	2414 (3)	83 (3)
C(3)	3632 (10)	12056 (6)	2311 (3)	85 (3)
C(4)	4328 (9)	12126 (5)	1635 (4)	73 (3)
C(5)	5527 (9)	11246 (5)	1402 (3)	71 (3)
C(6)	4791 (10)	10416 (6)	900 (3)	79 (3)
N(7)	3349 (6)	9823 (4)	1167 (2)	54 (2)
C(8)	2122 (8)	9284 (5)	686 (3)	64 (2)
C(9)	284 (8)	9356 (6)	901 (3)	73 (3)
C(10)	−292 (9)	9186 (6)	1570 (3)	84 (3)
C(11)	−46 (8)	9962 (7)	2095 (3)	81 (3)
C(12)	3136 (7)	9590 (5)	2355 (3)	56 (2)
C(13)	3873 (8)	9120 (5)	1723 (3)	63 (2)
C(14)	6934 (6)	5580 (4)	−422 (2)	38 (2)
C(15)	7101 (7)	5782 (4)	233 (2)	39 (2)
C(16)	7878 (8)	5034 (4)	709 (2)	51 (2)
C(17)	8448 (7)	4023 (4)	401 (2)	38 (2)
C(18)	8329 (7)	3832 (4)	−265 (2)	39 (2)
C(19)	7558 (6)	4602 (4)	−672 (2)	36 (2)
O(14)	8096 (10)	5220 (4)	1290 (2)	123 (3)
O(151)*	5304 (15)	7238 (10)	131 (8)	45 (4)
O(152)*	7314 (15)	7280 (9)	902 (5)	51 (4)
O(171)†	8941 (52)	3082 (26)	1395 (5)	62 (6)
O(172)†	10231 (36)	2485 (17)	525 (12)	56 (5)
O(191)	7901 (5)	3519 (3)	−1585 (2)	57 (1)
O(192)	6802 (5)	5130 (3)	−1725 (2)	53 (1)
N(15)	6481 (6)	6837 (4)	467 (2)	50 (2)
N(17)	9251 (6)	3165 (4)	796 (2)	49 (2)
N(19)	7417 (5)	4406 (3)	−1371 (2)	40 (1)
O(15*A*)‡	6248 (13)	6967 (7)	1045 (3)	90 (4)
O(15*B*)‡	6026 (23)	7553 (7)	106 (4)	150 (6)
O(17*B*)§	9603 (29)	2300 (8)	556 (4)	83 (5)
O(17*A*)§	9578 (20)	3403 (10)	1356 (3)	69 (4)
H(1)	2231 (96)	10443 (62)	1504 (33)	125 (25)¶

* Occupancy 0·42 (1).
† Occupancy 0·54 (2).
‡ Occupancy 0·58 (1).
§ Occupancy 0·46 (2).
¶ U_{iso}.

Table 2. *Selected bond lengths, bond angles, torsion angles and non-bonded contacts*

(*a*) Bond lengths

N(1)—C(2)	1·450 (9)	N(1)—C(11)	1·499 (8)
N(1)—C(12)	1·520 (8)	N(1)—H(1)	1·367 (69)
C(2)—C(3)	1·458 (11)	C(3)—C(4)	1·490 (10)
C(4)—C(5)	1·493 (9)	C(5)—C(6)	1·538 (9)
C(6)—N(7)	1·428 (8)	N(7)—C(8)	1·489 (7)
N(7)—C(13)	1·472 (7)	N(7)—H(1)	1·339 (72)
C(8)—C(9)	1·469 (9)	C(9)—C(10)	1·459 (9)
C(10)—C(11)	1·442 (10)	C(12)—C(13)	1·530 (8)

(*b*) Bond angles (°)

C(2)—N(1)—C(11)	117·0 (5)	C(2)—N(1)—C(12)	119·2 (5)
C(11)—N(1)—C(12)	111·2 (5)	C(2)—N(1)—H(1)	110·0 (32)
C(11)—N(1)—H(1)	100·5 (31)	C(12)—N(1)—H(1)	94·8 (31)
N(1)—C(2)—C(3)	113·9 (6)	C(2)—C(3)—C(4)	119·5 (6)
C(3)—C(4)—C(5)	118·9 (6)	C(4)—C(5)—C(6)	118·4 (6)
C(5)—C(6)—N(7)	110·5 (5)	C(6)—N(7)—C(8)	116·3 (4)
C(6)—N(7)—C(13)	113·4 (5)	C(8)—N(7)—C(13)	113·7 (4)
C(6)—N(7)—H(1)	113·8 (33)	C(8)—N(7)—H(1)	101·5 (30)
C(13)—N(7)—H(1)	95·5 (31)	N(7)—C(8)—C(9)	110·8 (5)
C(8)—C(9)—C(10)	125·2 (5)	C(9)—C(10)—C(11)	124·5 (7)
N(1)—C(11)—C(10)	114·6 (5)	N(1)—C(12)—C(13)	106·3 (4)
N(7)—C(13)—C(12)	109·6 (5)	N(1)—H(1)—N(7)	132·2 (56)

(*c*) Torsion angles (°)

Five-carbon bridge			
N(1)—C(2)—C(3)—C(4)	54·0 (8)	C(2)—C(3)—C(4)—C(5)	−93·2 (8)
C(3)—C(4)—C(5)—C(6)	106·5 (7)	C(4)—C(5)—C(6)—N(7)	−61·4 (7)
Four-carbon bridge			
N(7)—C(8)—C(9)—C(10)	−42·5 (9)	C(8)—C(9)—C(10)—C(11)	75 (1)
C(9)—C(10)—C(11)—N(1)	−46·3 (9)		
Two-carbon bridge			
N(1)—C(12)—C(13)—N(7)	13·5 (6)		

(*d*) Non-bonded contacts (Å) [C—H bond lengths extended to 1·08 (Å)]

Intramolecular			
H(2*b*)···H(3*b*)	2·305	H(3*a*)···H(4*b*)	2·164
H(3*b*)···H(5*b*)	2·157	H(3*b*)···H(12*a*)	2·042
H(4*b*)···H(5*a*)	2·139	H(5*b*)···H(13*b*)	2·152
H(6*a*)···H(13*b*)	2·273	H(6*b*)···H(8*b*)	2·189
H(8*a*)···H(9*a*)	2·249	H(8*a*)···H(13*a*)	2·144
H(8*b*)···H(9*b*)	2·228	H(9*a*)···H(10*b*)	2·160
H(10*a*)···H(11*b*)	2·215	H(10*a*)···H(13*a*)	2·280
H(10*b*)···H(11*a*)	2·230	H(11*b*)···H(12*b*)	2·266
H(12*a*)···H(13*b*)	2·277	H(12*b*)···H(13*a*)	2·275
Intermolecular			
H(2*b*)···O(14^{i})	2·231	H(5*b*)···H(11*a*^{ii})	2·338
H(6*b*)···O(15*b*^{iii})	2·295	H(8*a*)···H(18^{iv})	2·134

Symmetry code: (i) $1-x$, $y-0·5$, $0·5-z$; (ii) $x-1$, y, z; (iii) $1-x$, $2-y$, $-z$; (iv) $1-x$, $1-y$, $-z$.

space group. 2470 unique data ($0 \le h \le 8$, $0 \le k \le 14$, $0 \le l \le 24$), R_{int} = 0·029, 1695 reflections with $F > 3\sigma(F)$ retained and used for structure solution and refinement. Direct and difference Fourier methods, blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0·00126(F^2)]^{-1}$, anisotropic thermal parameters for all non-H atoms, methylene and phenyl hydrogens were refined in idealized positions (C—H 0·96 Å), all other atoms were refined without constraint. Two of the nitro groups in the picrate anion show resolvable disorder; site occupancy for O(151), O(152) refined to 0·42 (1) and that for O(15*A*), O(15*B*) to 0·58 (1), while the site occupancy for O(171), O(172) refined to 0·54 (2) and that for O(17*A*), O(17*B*) to 0·46 (2). While other atoms [especially O(14)] of the picrate anion showed signs of less severe disorder no resolution of these into distinct sites was possible. R = 0·077, wR = 0·104, S = 1·846, data:variable ratio 5·56:1, max. peak and min. trough in final ΔF synthesis 0·6 and 0·49 e Å^{-3} respectively, max. Δ/σ in final cycle 0·15; complex neutral scattering factors for C,H,N,O from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

Discussion. Atomic coordinates for all unconstrained atoms are presented in Table 1,* selected bond lengths, bond angles, torsion angles and important non-bonded contacts are given in Table 2; a perspective view of the structure is presented in Fig. 1 and a view of the cation with methylene hydrogens included in Fig. 2. The cation has a number of close intramolecular H···H non-bonded contacts (see Table 2*d*), these result in the bond angles of the framework atoms opening out; the average C—C—C angle is 121·3° compared with the idealized value of 109·5°. However, some of the

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* Lists of structure factors, anisotropic thermal parameters, complete bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44908 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

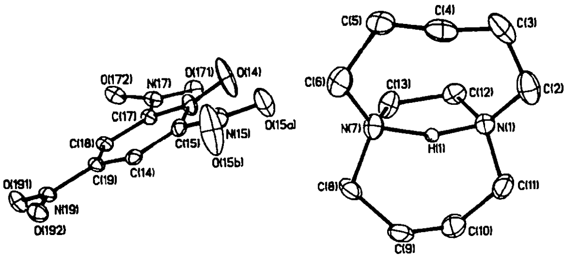

Fig. 1. A perspective view of the cation and anion of (1). H atoms, except for H(1), are omitted for clarity.

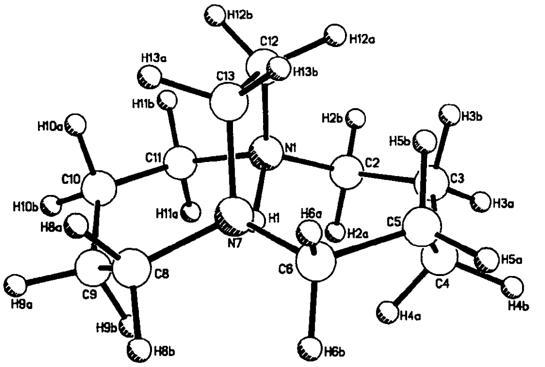

Fig. 2. Molecular structure of the cation of (1) showing methylene hydrogens.

observed increase in the C—C—C bond angles is probably related to the large anisotropic displacement parameters observed for the C atoms (average isotropic $U = 0{\cdot}074$ Å^2; see Table 1) indicating slight disorder or high thermal motion. The conformation of the five-carbon bridge is characterized by the $g^+g^-g^+g^-$ sequence of torsion angles, and has an approximate local plane of symmetry; this is similar to the five-carbon bridge conformations observed in the inside-diprotonated [1.1.1]cryptand (Knochel, Brugge, Carboo, von Deuten, Kopf & Dreissig, 1986) and the inside-protonated salts of the [5.4.3]-, [5.5.2]- and [6.5.3]diamines (White *et al.*, 1988*a*,*b*,*c*), but contrasts with the bridge conformations observed in the inside-protonated [5.5.4]diamine (White *et al.*, 1988*d*) which display a local axis of symmetry.

The four-carbon bridge has the typical sequence of torsion angles having an approximate local axis of symmetry (Alder *et al.*, 1983, 1985, 1988; White *et al.*, 1988*a*,*b*). The two-carbon bridge is slightly twisted away from an eclipsed geometry [torsion angle = 13·5 (6)°]. The inside proton is essentially equidistant from the two bridgehead nitrogens [N(1)—H(1) 1·37 (7), N(7)—H(1) 1·47 (7) Å], the N—H—N angle is 132 (6)° and the N···N distance is 2·474 (7) Å. This N···N distance is the shortest observed in our series of inside-protonated ions.

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Conformation of 1,3,5-Tricyclohexyl-1,3,5-triazacyclohexane

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Abstract. $C_{21}H_{39}N_3$, $M_r = 333{\cdot}6$, triclinic, $P\bar{1}$, $a = 19{\cdot}322\,(3)$, $b = 10{\cdot}076\,(2)$, $c = 5{\cdot}291\,(2)$ Å, $\alpha = 77{\cdot}81\,(2)$, $\beta = 84{\cdot}48\,(2)$, $\gamma = 85{\cdot}69\,(2)°$, $V = 1001\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}11$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}07$ mm^{-1}, $F(000) = 372$, $T = 293$ K, $R = 0{\cdot}058$ for 3641 independent observed reflections. The triazacyclohexane ring adopts a chair conformation with diequatorial–axial orientation of the cyclohexyl groups. The torsion angles around the N—C bonds in the triazacyclohexane ring are 55·8–61·4 (2),

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