

White, 1985, 1988). The five-carbon bridge has a  $g^-g^+g^-g^+$  sequence of torsion angles and has an approximate local plane of symmetry. This is similar to the conformation of the  $(CH_2)_2O(CH_2)_2$  bridges in the inside-diprotonated [1.1.1]cryptand (a [5.5.5] bicycle) (Knochel, Brugge, Carboo, von Deuten, Kopf & Dreissig, 1986). However, the absolute magnitudes of the central torsion angles in the cryptand are larger. This is a result of the oxygen atom tipping into the cavity towards the protons.

The inside proton is essentially equidistant from both bridgehead nitrogen atoms [N(1)—H 1.293 (25), N(7)—H 1.302 (24) Å], the N—H—N angle is 160.0 (26)° and the N(1)···N(7) distance is 2.555 (3) Å. This can be contrasted with the structure of the inside-protonated [6.4.3] diamine (Alder *et al.*, 1988) which has a significantly longer N···N distance [2.663 (4) Å] with the inside proton localized near one of the N atoms, and also with that of the inside-

protonated [4.4.4] diamine (Alder *et al.*, 1983) which has N···N 2.526 (3) Å and an apparently symmetrical N—H—N system. Close intermolecular contacts occur between the cation and anion, and between adjacent cations (see Table 2).

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### Inside-Protonated 1,7-Diazabicyclo[5.5.2]tetradecane Picrate

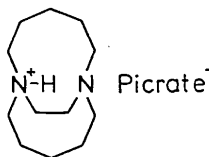
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**Abstract.**  $C_{12}H_{25}N_2^+ \cdot C_6H_5O_7^-$ ,  $M_r = 425.44$ , monoclinic,  $P2_1/c$ ,  $a = 7.834$  (3),  $b = 12.549$  (3),  $c = 20.750$  (5) Å,  $\beta = 93.52$  (2)°,  $V = 2036$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.01$  cm<sup>-1</sup>,  $F(000) = 904$ ,  $T = 293$  K,  $R = 0.064$  for 1623 unique observed reflections. The title compound has an intrabridgehead N(1)···N(7) distance of 2.555 (7) Å; the inside proton is localized near N(1) [N(1)—H 1.09 (5), N(7)···H 1.67 (5) Å].

**Introduction.** The structure study of the title compound (1) is one of a series of studies on the oxidized and protonated ions of medium-ring bicyclic diamines (Alder, 1983; Alder, Orpen & Sessions, 1983; Alder, Orpen & White, 1985, 1988; White, Alder & Orpen, 1988). The geometry of the N—H—N hydrogen bond in the inside-protonated species is influenced to a large extent by the conformational preferences of the oligomethylene bridges.



(1)

**Experimental.** Yellow rod (0.6 × 0.25 × 0.3 mm) from solvent diffusion using CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether; Nicolet P3m diffractometer, unit cell from least squares based on 15 centred reflections (12.5 < θ < 14°), graphite-monochromated Mo Kα; for data collection 2 < θ < 25°, room temperature, ω–2θ scans in 96 steps, ω-scan width (1.0 + 0.35 tan θ)°, one quadrant of data (hkl and hkl) measured over 62 X-ray hours with no detectable decay or movement; high-angle reflections (20 < θ < 25°) with count rate less than 13 counts s<sup>-1</sup> were not collected; systematic absences (h0l l = 2n + 1, 0k0 k = 2n + 1) uniquely define the space group. 2294 unique data,  $R_{\text{merge}} = 0.0131$ , 1623 reflections with  $F > 3\sigma(F)$  used for structure solution and refinement (0 < h < 8, 0 < k < 13, -21 < l < 21). Direct methods and difference-Fourier methods, blocked-cascade least-squares refinement on  $F$ ,  $w = [\sigma^2(F) + 0.00055(F^2)]^{-1}$ , anisotropic thermal parameters for all non-H atoms, methylene and phenyl protons were refined in idealized positions (C—H 0.96 Å), all other atoms were refined without constraint.  $R = 0.0637$ ,  $wR = 0.0846$ ,  $S = 2.048$ , data:variable ratio 5.85, max. peak and min. trough in final  $\Delta F$  synthesis 0.29 and -0.27 e Å<sup>-3</sup> respectively, max. shift/e.s.d. in final cycle 0.009; complex neutral-atom scattering factors for C, H, N, O from *Inter-*

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}$
N(1)	18244 (5)	14292 (3)	12857 (2)	57 (1)
C(2)	20039 (7)	14565 (5)	12750 (2)	81 (2)
C(3)	20698 (7)	15518 (5)	13114 (3)	89 (2)
C(4)	20793 (7)	15448 (5)	13849 (3)	87 (2)
C(5)	19592 (8)	16148 (5)	14192 (3)	98 (3)
C(6)	17943 (8)	15680 (4)	14370 (2)	82 (2)
C(8)	15565 (7)	14552 (5)	14120 (3)	95 (2)
C(9)	14605 (8)	13778 (5)	13663 (3)	96 (3)
C(10)	15557 (8)	12826 (4)	13440 (3)	90 (3)
C(11)	16022 (9)	12791 (4)	12738 (3)	99 (3)
C(12)	17790 (8)	13213 (4)	12580 (2)	86 (2)
C(13)	16991 (6)	15164 (4)	12669 (2)	63 (2)
N(7)	16980 (5)	15086 (3)	13856 (2)	65 (1)
C(14)	16494 (7)	15726 (4)	13286 (2)	75 (2)
O(21)	10927 (9)	13324 (4)	8569 (2)	176 (3)
C(20)	12914 (6)	15804 (3)	9740 (2)	55 (2)
O(15)	11810 (7)	15326 (3)	8692 (2)	132 (2)
N(2)	10822 (6)	13271 (4)	9129 (2)	72 (2)
C(19)	13114 (6)	15578 (4)	10379 (2)	57 (2)
C(15)	12097 (7)	15092 (4)	9265 (2)	69 (2)
O(41)	12323 (5)	13497 (3)	11484 (2)	91 (2)
N(4)	12729 (5)	14376 (4)	11295 (2)	70 (2)
C(18)	12538 (6)	14611 (3)	10610 (2)	53 (2)
C(16)	11586 (6)	14094 (3)	9546 (2)	54 (2)
C(17)	11780 (5)	13868 (4)	10192 (2)	56 (2)
O(42)	13312 (5)	15059 (3)	11660 (1)	91 (2)
N(6)	13511 (6)	16838 (3)	9536 (2)	77 (2)
O(22)	10124 (8)	12540 (4)	9349 (2)	133 (2)
O(61)	14273 (9)	17399 (4)	9907 (2)	175 (3)
O(62)	13404 (10)	17108 (4)	9000 (2)	192 (3)
H(1)	18105 (57)	14320 (38)	13378 (23)	89 (15)*

\*  $U_{iso}$ .

*national 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 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  $H \cdots H$  non-bonded contacts (see Table 2, where  $C-H$  distances are normalized to 1.08  $\text{\AA}$ ), these result in the bond angles of the framework atoms opening out; the average  $C-C-C$  bond angle is  $117.5^\circ$  compared with the idealized value of  $109.5^\circ$ . However, the real  $C-C-C$  bond angles are probably slightly less than those observed, owing to the large anisotropic thermal motions of the carbon atoms (average isotropic  $U = 0.086 \text{\AA}^2$ ; see Table 1). The two five-carbon bridges

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44589 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ), torsion angles ( $^\circ$ ) and non-bonded contacts ( $\text{\AA}$ )

N(1)—C(2)	1.477 (7)	N(1)—C(12)	1.505 (7)
N(1)—C(13)	1.505 (6)	N(1)—H(1)	1.095 (49)
C(2)—C(3)	1.489 (8)	C(3)—C(4)	1.525 (8)
C(4)—C(5)	1.500 (9)	C(5)—C(6)	1.486 (9)
C(6)—N(7)	1.470 (6)	C(8)—C(9)	1.523 (8)
C(8)—N(7)	1.432 (7)	C(9)—C(10)	1.496 (8)
C(10)—C(11)	1.522 (9)	C(11)—C(12)	1.537 (9)
C(13)—C(14)	1.533 (7)	N(7)—C(14)	1.461 (6)
C(2)—N(1)—C(12)	110.9 (4)	C(2)—N(1)—C(13)	113.9 (4)
C(12)—N(1)—C(13)	114.9 (4)	C(2)—N(1)—H(1)	107.1 (23)
C(12)—N(1)—H(1)	111.8 (25)	C(13)—N(1)—H(1)	97.4 (24)
N(1)—C(2)—C(3)	114.5 (4)	C(2)—C(3)—C(4)	117.0 (5)
C(3)—C(4)—C(5)	116.6 (5)	C(4)—C(5)—C(6)	117.8 (5)
C(5)—C(6)—N(7)	115.9 (4)	C(9)—C(8)—N(7)	115.2 (5)
C(8)—C(9)—C(10)	117.7 (5)	C(9)—C(10)—C(11)	118.2 (5)
C(10)—C(11)—C(12)	117.8 (5)	N(1)—C(12)—C(11)	115.0 (5)
N(1)—C(13)—C(14)	108.3 (3)	C(6)—N(7)—C(8)	109.6 (4)
C(6)—N(7)—C(14)	113.9 (4)	C(8)—N(7)—C(14)	113.4 (4)
C(13)—C(14)—N(7)	110.9 (4)		
<b>2-Carbon bridge</b>			
N(1)—C(13)—C(14)—N(7)	−15.7 (5)		
<b>5-Carbon bridges</b>			
N(1)—C(2)—C(3)—C(4)	63.4 (6)	C(2)—C(3)—C(4)—C(5)	−112.1 (6)
C(3)—C(4)—C(5)—C(6)	95.2 (6)	C(4)—C(5)—C(6)—N(7)	−47.6 (7)
N(7)—C(8)—C(9)—C(10)	63.7 (7)	C(8)—C(9)—C(10)—C(11)	−109.1 (6)
C(9)—C(10)—C(11)—C(12)	93.3 (6)	C(10)—C(11)—C(12)—N(1)	−49.3 (7)
<b>Intramolecular</b>			
H(2a)···H(12b)	2.263	H(3a)···H(4a)	2.181
H(3b)···H(5a)	2.126	H(3b)···H(13a)	2.222
H(3b)···H(14b)	2.337	H(4a)···H(5b)	2.187
H(5a)···H(6a)	2.293	H(5b)···H(6b)	2.296
H(6b)···H(8a)	2.165	H(8b)···H(9b)	2.373
H(8b)···H(14a)	2.304	H(9a)···H(11b)	2.175
H(9a)···H(13b)	2.346	H(9a)···H(14a)	2.178
H(9b)···H(10b)	2.144	H(10b)···H(11a)	2.208
H(11a)···H(12b)	2.358	H(11b)···H(12a)	2.353
H(11b)···H(13b)	2.071	H(13a)···H(14b)	2.268
H(13b)···H(14a)	2.270		
<b>Intermolecular</b>			
H(4a)···H(8b <sup>i</sup> )	2.156	H(5a)···H(17 <sup>ii</sup> )	2.311
H(12a)···O(15)	2.393	H(12a)···O(62)	2.394
H(14a)···H(11a <sup>ii</sup> )	2.362	H(19)···H(10a <sup>ii</sup> )	2.381
H(19)···H(10b <sup>ii</sup> )	2.288		

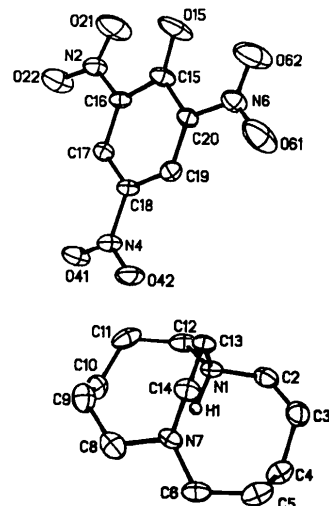
Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $3-x, y-0.5, 2.5-z$ .

Fig. 1. View of the structure showing thermal ellipsoids.

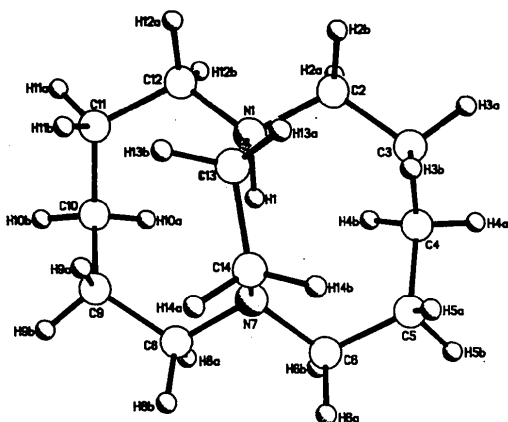


Fig. 2. View of the cation with methylene protons included.

2.555 (7) Å. This can be contrasted with the inside-protonated [5.4.3] diamine (White *et al.*, 1988) which has an N...N distance of 2.555 (3) Å, and an N—H—N angle of 160 (3)° with the inside proton essentially equidistant from both bridgehead nitrogens, the inside-protonated [6.4.3] diamine which has an N...N distance of 2.663 (4) Å (Alder, Orpen & White, 1988) with the inside proton localized near one of the bridgehead nitrogens, and the inside-protonated [4.4.4] diamine which has an intrabridgehead N...N distance of 2.526 Å and an apparently symmetrical N—H—N system (Alder, Orpen & Sessions, 1983). Close intermolecular contacts occur between the cation and anion, and between adjacent cations (see Table 2).

have similar conformations with  $g^+g^-g^+g^-$  sequences of torsion angles (see Table 2) and with an approximate local plane of symmetry. This is similar to the conformation of the five-carbon bridge in the inside-protonated [5.4.3] diamine (White, Alder & Orpen, 1988). The two-carbon bridge is slightly twisted away from an eclipsed geometry [torsion angle = 15.7 (5)°]. The cation has an approximate twofold rotation axis bisecting the two-carbon bridge and the intrabridgehead N...N vector. The inside proton is localized near N(1) [N(1)—H = 1.09 (5), N(8)—H = 1.67 (5) Å], the N—H—N angle is 134 (5)° and the N...N distance is

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### (+)-7,9-O,O-(3,3-Dimethylglutaryl)heliotridine,\* a Pyrrolizidine Alkaloid Analogue

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**Abstract.**  $C_{15}H_{21}NO_4$ ,  $M_r = 279.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.115$  (1),  $b = 7.989$  (1),  $c = 29.986$  (2) Å,  $V = 1465.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.26$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 7.14$  cm<sup>-1</sup>,  $F(000) = 600$ ,  $T = 291$  K, final  $R = 0.056$  for 936 unique observed [ $I \geq 3.0\sigma(I)$ ] reflections. The pyrrolizidine nucleus adopts an *exo-endo* conformation and the conformation of the ester carbonyl groups of the 11-membered macro-ring is antiparallel. The ester carbonyl group C(11)=O(11) is orientated in the same direction as C(8)—H.

\* Heliotridine is (1*S*-*cis*)-2,3,5,7a-tetrahydro-1-hydroxy-1*H*-pyrrolizine-7-methanol (*Chemical Abstracts* name).

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**Introduction.** Pyrrolizidine alkaloids continue to attract much attention because of their widespread occurrence and hepatotoxicity (Mattocks, 1986). The most toxic alkaloids are macrocyclic diesters of (+)-retronecine (3). Although many examples of monoesters and diesters of the epimeric base (+)-heliotridine (2) have been isolated, macrocyclic diesters of heliotridine have not yet been found to occur naturally (Robins, 1982). Recently, we reported the first synthesis of 11-membered macrocyclic diesters of heliotridine (Hagan & Robins, 1987). These pyrrolizidine alkaloid analogues were prepared from heliotridine and glutaric anhydride derivatives in readiness for a study of their toxicity. In order to gain more information about structure–biological–activity relationships in this area,