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## Inside-Protonated 1,7-Diazabicyclo[5.4.3]tetradecane Trifluoromethanesulfonate

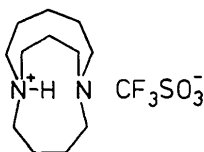
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**Abstract.** C<sub>12</sub>H<sub>25</sub>N<sub>2</sub><sup>+</sup>.CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, *M<sub>r</sub>* = 346.42, triclinic, *P* $\bar{1}$ , *a* = 12.616 (3), *b* = 7.876 (2), *c* = 8.590 (2) Å,  $\alpha$  = 75.72 (2),  $\beta$  = 85.23 (2),  $\gamma$  = 74.64 (2)°, *V* = 797.5 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.44 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 2.37 cm<sup>-1</sup>, *F*(000) = 368, *T* = 182 K, *R* = 0.037 for 2904 unique observed reflections. The title compound has an intrabridgehead N(1)··N(7) distance of 2.555 (3) Å; the inside proton is essentially equidistant from both bridgehead nitrogen atoms [N(1)–H 1.293 (25), N(7)–H 1.302 (24) Å].

**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). The interesting physical properties of these compounds are dependent to a large extent on the conformations of the oligomethylene bridges (Alder, 1983), and they also provide a convenient means to study N–H–N hydrogen bonds of various geometries (see Alder *et al.*, 1988).



(1)

**Experimental.** Colourless diamond (0.5 × 0.3 × 0.3 mm) from solvent diffusion using isopropyl alcohol and diethyl ether; Nicolet *P3m* diffractometer, unit cell by least squares based on 23 centred reflec-

tions (12.5 <  $\theta$  < 22.50°), graphite-monochromated Mo *K*α; for data collection 2 <  $\theta$  < 27.50°, temperature 182 K by Nicolet LT-1 N<sub>2</sub> gas flow. Wyckoff  $\omega$  scans, 3645 reflections measured over 60 X-ray hours with no detectable decay or movement. 3448 unique data, *R<sub>merge</sub>* = 0.0121, 2908 reflections with *F* > 3σ(*F*) used for structure solution and refinement (−16 < *h* < 16, 0 < *k* < 11, −12 < *l* < 12). Direct methods and difference-Fourier methods, blocked-cascade least-squares refinement on *F*, *w* = [σ<sup>2</sup>(*F*) + 0.0003(*F*<sup>2</sup>)]<sup>-1</sup>; anisotropic thermal parameters for all non-H atoms, methylene hydrogens were refined in idealized positions (C–H 0.96 Å), all other atoms were refined without constraint. *R* = 0.0374, *wR* = 0.052, *S* = 1.6, data:variable ratio 14.25, max. peak and min. trough in final Δ*F* synthesis 0.43 and 0.21 e Å<sup>-3</sup> respectively, max. shift/e.s.d. in final cycle 0.033; complex neutral-atom scattering factors for C, H, N, O, F, S from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

**Discussion.** Atomic coordinates for all non-hydrogen atoms are presented in Table 1,\* selected bond lengths, bond angles, torsion angles and important non-bonded contacts 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 bicyclic

\* 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 44587 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cation has a number of close intramolecular H...H contacts (calculated on the basis of C—H = 1.08 Å; see Table 2) both within the bridges and between the bridges. The strain imposed by these close contacts is taken up to a degree by opening out of the bond angles of the framework atoms; the average C—C—C angle is 115.2° compared with the idealized value of 109.5°. The conformations of the bridges are defined by the torsion angles listed in Table 2. The three-carbon bridge has an 'envelope'-like conformation similar to that observed in the inside-protonated salt of 1,8-diazabicyclo[6.4.3]pentadecane (Alder *et al.*, 1988). The four-carbon bridge has a  $g^+g^-g^+$  sequence of torsion angles and is similar to the conformation of a number of four-carbon bridges observed in other bicyclic structures (Alder, Orpen & Sessions, 1983; Alder, Orpen &

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.

	$x$	$y$	$z$	$U_{eq}$
S(1)	7492 (1)	1425 (1)	2816 (1)	22 (1)
O(1)	7104 (1)	420 (2)	1891 (2)	34 (1)
O(2)	7273 (1)	960 (2)	4521 (2)	34 (1)
O(3)	7297 (1)	3337 (2)	2121 (2)	34 (1)
C	8992 (1)	629 (2)	2668 (2)	27 (1)
F(1)	9490 (1)	1476 (2)	3425 (2)	45 (1)
F(2)	9343 (1)	928 (2)	1140 (1)	47 (1)
F(3)	9344 (1)	-1134 (2)	3305 (2)	50 (1)
N(1)	3887 (1)	3123 (2)	2957 (2)	21 (1)
C(2)	4157 (1)	1641 (3)	2084 (2)	29 (1)
C(3)	3377 (1)	2001 (3)	706 (2)	28 (1)
C(4)	2191 (1)	1915 (2)	1225 (2)	27 (1)
C(5)	1301 (1)	3728 (2)	961 (2)	28 (1)
C(6)	1010 (1)	4597 (3)	2397 (2)	29 (1)
N(7)	1929 (1)	5126 (2)	2962 (2)	20 (1)
C(8)	1730 (1)	5439 (2)	4621 (2)	26 (1)
C(9)	2390 (2)	3867 (3)	5866 (2)	28 (1)
C(10)	3637 (2)	3643 (3)	5774 (2)	27 (1)
C(11)	4261 (1)	2474 (3)	4649 (2)	28 (1)
C(12)	4260 (1)	4746 (3)	2028 (2)	30 (1)
C(13)	3468 (2)	6557 (3)	2161 (2)	30 (1)
C(14)	2289 (2)	6639 (2)	1815 (2)	29 (1)
H	2846 (22)	3872 (36)	3036 (33)	69 (8)*

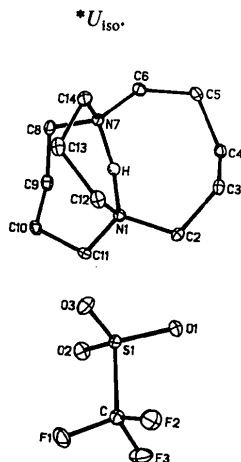


Fig. 1. View of the structure showing thermal ellipsoids.

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

N(1)—C(2)	1.490 (3)	N(1)—C(11)	1.488 (2)
N(1)—C(12)	1.498 (2)	N(1)—H	1.293 (25)
C(2)—C(3)	1.527 (3)	C(3)—C(4)	1.539 (3)
C(4)—C(5)	1.544 (2)	C(5)—C(6)	1.527 (3)
C(6)—N(7)	1.484 (3)	N(7)—C(8)	1.496 (2)
N(7)—C(14)	1.493 (2)	N(7)—H	1.302 (24)
C(8)—C(9)	1.523 (2)	C(9)—C(10)	1.534 (3)
C(10)—C(11)	1.526 (3)	C(12)—C(13)	1.534 (3)
C(13)—C(14)	1.523 (3)		
C(2)—N(1)—C(11)	112.2 (1)	C(2)—N(1)—C(12)	111.6 (1)
C(11)—N(1)—C(12)	114.1 (2)	C(2)—N(1)—H	113.6 (15)
C(11)—N(1)—H	105.8 (12)	C(12)—N(1)—H	98.7 (12)
N(1)—C(2)—C(3)	112.4 (1)	C(2)—C(3)—C(4)	115.0 (1)
C(3)—C(4)—C(5)	117.1 (2)	C(4)—C(5)—C(6)	116.6 (1)
C(5)—C(6)—N(7)	114.5 (1)	C(6)—N(7)—C(8)	112.6 (1)
C(6)—N(7)—C(14)	114.7 (1)	C(8)—N(7)—C(14)	112.2 (1)
C(6)—N(7)—H	112.1 (15)	C(8)—N(7)—H	105.2 (13)
C(14)—N(7)—H	98.9 (12)	N(7)—C(8)—C(9)	112.0 (1)
C(8)—C(9)—C(10)	115.4 (1)	C(9)—C(10)—C(11)	114.9 (2)
N(1)—C(11)—C(10)	114.3 (1)	N(1)—C(12)—C(13)	113.8 (1)
C(12)—C(13)—C(14)	111.9 (2)	N(7)—C(14)—C(13)	109.5 (1)
N(1)—H—N(7)	160.0 (26)		

2-Carbon bridge  
N(1)—C(12)—C(13)—C(14) -50.2 (2) C(12)—C(13)—C(14)—N(7) 58.4 (2)

4-Carbon bridge  
N(7)—C(8)—C(9)—C(10) 69.1 (2) C(8)—C(9)—C(10)—C(11) -88.1 (2)  
C(9)—C(10)—C(11)—N(1) 57.1 (2)

5-Carbon bridge  
N(1)—C(2)—C(3)—C(4) -69.0 (2) C(2)—C(3)—C(4)—C(5) 107.2 (2)  
C(3)—C(4)—C(5)—C(6) -96.0 (2) C(4)—C(5)—C(6)—N(7) 63.0 (2)

Intramolecular  
H(2a)...H(3b) 2.371 H(2a)...H(12b) 2.367  
H(2b)...H(4b) 2.359 H(2b)...H(11a) 2.100  
H(3a)...H(5b) 2.198 H(3a)...H(12b) 2.106  
H(3b)...H(4a) 2.208 H(4a)...H(5a) 2.231  
H(5a)...H(6b) 2.390 H(5b)...H(14a) 2.030  
H(6a)...H(8b) 2.312 H(8a)...H(10b) 2.379  
H(8a)...H(13b) 2.157 H(8a)...H(14b) 2.288  
H(8b)...H(9a) 2.367 H(9a)...H(10a) 2.267  
H(10b)...H(13b) 1.917 H(11b)...H(12a) 2.222  
H(12a)...H(13b) 2.389 H(12b)...H(13a) 2.386

Intermolecular  
O(3)...H(14a') 2.454 H(11a)...H(11a') 2.397  
H(12b)...H(12b'') 2.118

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

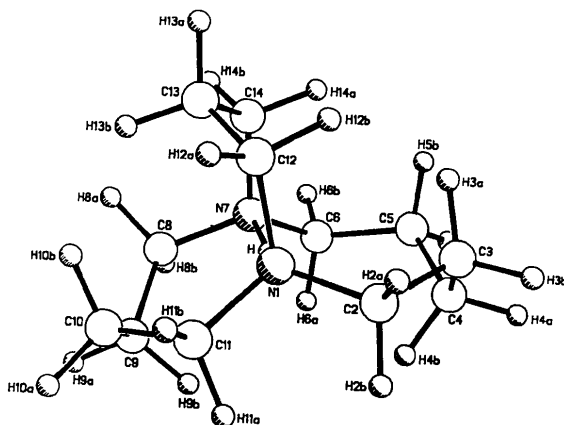


Fig. 2. View of the cation with methylene protons included.

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

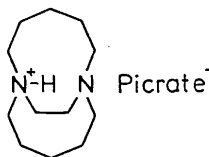
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**Abstract.**  $C_{12}H_{25}N_2^+ \cdot C_6H_5O_7^-$ ,  $M_r = 425.44$ , monoclinic,  $P2_1/c$ ,  $a = 7.834$  (3),  $b = 12.549$  (3),  $c = 20.750$  (5) Å,  $\beta = 93.52$  (2)°,  $V = 2036$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  g cm<sup>-3</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 <  $\theta$  < 14°), graphite-monochromated Mo  $K\alpha$ ; for data collection 2 <  $\theta$  < 25°, room temperature,  $\omega$ -2 $\theta$  scans in 96 steps,  $\omega$ -scan width (1.0 + 0.35 tan  $\theta$ )°, one quadrant of data ( $hkl$  and  $h\bar{k}l$ ) measured over 62 X-ray hours with no detectable decay or movement; high-angle reflections (20 <  $\theta$  < 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-*