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Inside-Protonated 1,7-Diazabicyclo[5.5.4]hexadecane *p*-Nitrobenzoate *p*-Nitrobenzoic Acid Solvate

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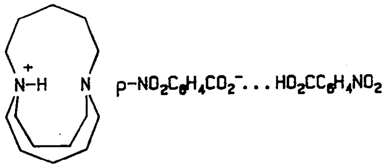
Abstract. $C_{14}H_{29}N_2^+.C_7H_4NO_4^-.C_7H_5NO_4$, $M_r = 558.63$, orthorhombic, *Pbca*, $a = 13.567$ (3), $b = 25.314$ (5), $c = 16.801$ (2) Å, $V = 5769.5$ (18) Å^3, $Z = 8$, $D_x = 1.29$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.89$ cm^{-1}, $F(000) = 2384$, $T = 293$ K, $R = 0.052$ for 2480 unique observed reflections. The title compound has an intrabridgehead N(1)···N(7) distance of 2.690 (4) Å. The inside proton is localized near N(1) [N(1)—H(1) 1.096 (33), N(7)···H(1) 1.601 (33) Å]. The *p*-nitrobenzoate anion is strongly hydrogen bonded to a *p*-nitrobenzoic acid molecule of crystallization; O(1)···O(5) = 2.460 (4) Å. The proton is localized near O(5) [O(5)—H(2) 1.04 (4); O(1)···H(2) 1.42 (4) Å; O(5)—H(2)···O(1) = 173 (4)°].

Introduction. The structural 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, Orpen & Sessions, 1983; Alder, Orpen & White, 1985, 1988; White, Alder & Orpen, 1988*a,b,c*). The properties of the N—H—N hydrogen bond in the inside-protonated species are influenced to a large extent by the conformational requirements of the oligomethylene bridges. These compounds therefore provide an ideal opportunity to study N—H—N hydrogen bonds of various geometries.



(1)

Experimental. Colourless block (0.6 × 0.7 × 0.5 mm) from solvent diffusion using CH_2Cl_2 and diethyl ether; Nicolet *P*3*m* diffractometer, refined cell parameters from angle data for 15 centred reflections ($14 < \theta < 15°$), graphite-monochromated Mo $K\alpha$ for data collection, $2 < \theta < 25°$, room temperature, ω–2θ scans in 96 steps, ω-scan width $(1.0 + 0.35\tan\theta)°$, data measured over 120 h with no detectable decay or movement; high-angle reflections ($20 < \theta < 25°$) with count rate less than 12 counts s^{-1} were not collected; systematic absences ($0kl$ $k = 2n+1$, $h0l$ $l = 2n+1$, $hk0$ $h = 2n+1$, $h00$ $h = 2n+1$, $0k0$ $k = 2n+1$, $00l$ $l = 2n+1$). Of 3572 unique data ($R_{\rm int} = 0.0072$), 2480 reflections with $F > 3\sigma(F)$ were retained ($0 \le h \le 17$, $0 \le k \le 31$, $0 \le l \le 20$) for structure solution and refinement. Direct methods and difference Fourier methods, blocked cascade least-squares refinement on F, $w = [\sigma^2(F) + 0.00063(F^2)]^{-1}$, anisotropic temperature factors 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. $R = 0.0519$, $wR = 0.0617$, $S = 1.323$, data:variable ratio 6.71, max. peak and min. trough in final ΔF synthesis = 0.19 and -0.18 e Å^{-3} respectively, max. shift/e.s.d. in final cycle = 0.026; complex neutral scattering factors for C,H,N,O from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

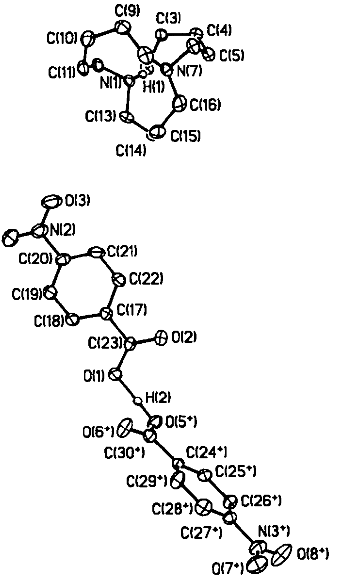


Fig. 1. Molecular structure of the cation of (1) and complex hydrogen-bonded anion. Atoms labelled with (+) have been generated from the coordinates in Table 1 by the symmetry operation (x, $1.5 - y$, $0.5 + z$). Methylene and phenyl hydrogens have been omitted for clarity.

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Table 1. *Atomic coordinates* (× 10^4) *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}
C(2)	1113 (3)	2623 (1)	516 (2)	63 (1)
C(3)	881 (3)	2666 (1)	−377 (2)	60 (1)
C(4)	1556 (3)	3021 (1)	−860 (2)	70 (1)
C(5)	1674 (3)	3589 (1)	−596 (2)	75 (1)
C(6)	734 (3)	3903 (2)	−540 (2)	79 (2)
C(8)	−710 (3)	4090 (2)	268 (3)	88 (2)
C(9)	−1415 (3)	3659 (2)	12 (2)	86 (2)
C(10)	−1927 (3)	3372 (2)	686 (3)	93 (2)
C(11)	−1320 (3)	3139 (2)	1349 (2)	79 (2)
C(12)	−548 (3)	2741 (1)	1108 (2)	72 (1)
C(13)	911 (3)	3093 (1)	1808 (2)	69 (1)
C(14)	1561 (3)	3580 (2)	1799 (2)	82 (2)
C(15)	1011 (3)	4101 (2)	1656 (2)	86 (2)
C(16)	947 (3)	4278 (1)	790 (2)	86 (2)
C(17)	274 (2)	6293 (1)	5626 (2)	51 (1)
C(18)	−276 (3)	6026 (1)	6175 (2)	81 (2)
C(19)	−907 (3)	5621 (2)	5959 (2)	86 (2)
C(20)	−973 (3)	5489 (1)	5185 (2)	63 (1)
C(21)	−422 (3)	5732 (2)	4620 (2)	85 (2)
C(22)	207 (3)	6137 (2)	4840 (2)	77 (2)
C(23)	926 (2)	6747 (1)	5861 (2)	52 (1)
C(24)	2016 (2)	6429 (1)	2216 (2)	46 (1)
C(25)	3027 (2)	6459 (1)	2202 (2)	52 (1)
C(26)	3593 (2)	6016 (1)	2336 (2)	58 (1)
C(27)	3134 (3)	5543 (1)	2468 (2)	52 (1)
C(28)	2138 (3)	5501 (1)	2482 (2)	69 (1)
C(29)	1582 (3)	5945 (1)	2351 (2)	71 (1)
C(30)	1382 (2)	6910 (1)	2093 (2)	58 (1)
O(1)	882 (2)	6880 (1)	6599 (1)	70 (1)
O(2)	1428 (2)	6968 (1)	5357 (1)	72 (1)
O(3)	−1696 (3)	4946 (1)	4250 (2)	126 (2)
O(4)	−2136 (3)	4853 (1)	5462 (2)	138 (2)
O(5)	1853 (2)	7328 (1)	1928 (2)	74 (1)
O(6)	488 (2)	6876 (1)	2164 (2)	90 (1)
O(7)	3318 (2)	4656 (1)	2763 (2)	104 (1)
O(8)	4624 (2)	5113 (1)	2563 (2)	124 (1)
N(1)	442 (2)	2978 (1)	1014 (1)	53 (1)
N(2)	−1668 (2)	5069 (1)	4949 (2)	89 (1)
N(3)	3734 (2)	5068 (1)	2613 (2)	77 (1)
N(7)	342 (2)	3920 (1)	278 (2)	63 (1)
H(1)	338 (24)	3351 (13)	695 (19)	85 (11)*
H(2)	1404 (27)	7355 (14)	6768 (21)	118 (13)*

* U_{iso}.

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

(*a*) Bond lengths (Å)

C(2)—C(3)	1·536 (4)	C(2)—N(1)	1·528 (4)
C(3)—C(4)	1·519 (5)	C(4)—C(5)	1·513 (5)
C(5)—C(6)	1·507 (5)	C(6)—N(7)	1·474 (5)
C(8)—C(9)	1·514 (6)	C(8)—N(7)	1·491 (5)
C(9)—C(10)	1·514 (6)	C(10)—C(11)	1·505 (6)
C(11)—C(12)	1·508 (5)	C(12)—N(1)	1·480 (4)
C(13)—C(14)	1·517 (5)	C(13)—N(1)	1·506 (4)
C(14)—C(15)	1·534 (6)	C(15)—C(16)	1·526 (6)
C(16)—N(7)	1·496 (5)	C(17)—C(18)	1·365 (5)
C(23)—O(1)	1·286 (4)	C(23)—O(2)	1·221 (4)
C(30)—O(5)	1·269 (4)	C(30)—O(6)	1·221 (4)
O(1)—H(2)	1·423 (35)	O(5)—H(2^{i})	1·042 (36)
N(1)—H(1)	1·096 (33)		

(*b*) Bond angles (°)

C(3)—C(2)—N(1)	111·8 (3)	C(2)—C(3)—C(4)	116·0 (3)
C(3)—C(4)—C(5)	118·0 (3)	C(4)—C(5)—C(6)	115·5 (3)
C(5)—C(6)—N(7)	112·2 (3)	C(9)—C(8)—N(7)	113·5 (3)
C(8)—C(9)—C(10)	115·0 (3)	C(9)—C(10)—C(11)	119·4 (3)
C(10)—C(11)—C(12)	116·3 (3)	C(11)—C(12)—N(1)	112·8 (3)
C(14)—C(13)—N(1)	113·2 (3)	C(13)—C(14)—C(15)	114·7 (3)
C(14)—C(15)—C(16)	115·5 (3)	C(15)—C(16)—N(7)	113·7 (3)
O(1)—C(23)—O(2)	125·0 (3)	O(5)—C(30)—O(6)	125·4 (3)
C(23)—O(1)—H(2)	113·0 (14)	C(30)—O(5)—H(2^{i})	113·9 (19)
C(2)—N(1)—C(12)	111·2 (2)	C(2)—N(1)—C(13)	110·3 (2)
C(12)—N(1)—C(13)	111·6 (2)	C(2)—N(1)—H(1)	108·3 (17)
C(12)—N(1)—H(1)	106·6 (17)	C(13)—N(1)—H(1)	108·7 (17)
C(6)—N(7)—C(8)	110·1 (3)	C(6)—N(7)—C(16)	110·8 (3)
C(8)—N(7)—C(16)	110·8 (3)	O(1)—H(2)—O(5A)	172·7 (37)

(*c*) Torsion angles (°)

Four-carbon bridge			
N(1)—C(13)—C(14)—C(15)	65·7 (4)	C(13)—C(14)—C(15)—C(16)	−92·5 (4)
C(14)—C(15)—C(16)—N(7)	65·9 (4)		
Five-carbon bridges			
N(1)—C(2)—C(3)—C(4)	99·7 (3)	C(2)—C(3)—C(4)—C(5)	−55·6 (4)
C(3)—C(4)—C(5)—C(6)	−57·1 (4)	C(4)—C(5)—C(6)—N(7)	96·8 (4)
N(7)—C(8)—C(9)—C(10)	98·6 (4)	C(8)—C(9)—C(10)—C(11)	−52·5 (5)
C(9)—C(10)—C(11)—C(12)	−57·9 (5)	C(10)—C(11)—C(12)—N(1)	96·1 (4)

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

Intramolecular			
H(3*a*)···H(9*a*)	2·103	H(3*a*)···H(12*a*)	2·152
H(5*a*)···H(6*b*)	2·221	H(5*b*)···H(14*b*)	2·270
H(5*b*)···H(16*a*)	2·073	H(6*a*)···H(9*a*)	2·104
H(8*a*)···H(11*a*)	2·327	H(9*a*)···H(10*a*)	2·352
H(9*b*)···H(10*b*)	2·344	H(11*a*)···H(13*a*)	2·154
H(11*a*)···H(15*b*)	2·271	H(11*b*)···H(12*b*)	2·217
H(14*a*)···H(15*a*)	2·250		
Intermolecular			
H(15*a*)···H(28)	2·153	H(15*b*)···H(18^{ii})	2·281
H(19)···H(28^{ii})	2·256	H(19)···O(4)	2·384

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

Discussion. Atomic coordinates for all unconstrained 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 molecular structure is presented in Fig. 1 and a view of the cation with methylene hydrogens included in Fig. 2. The cation exhibits strain which is demonstrated by an average C—C—C bond angle of 116·3° compared with the idealized value of 109·5°; this strain is caused to a large extent by close intramolecular H···H non-bonded contacts (see Table 2*d*). The framework atoms of the cation have an approximate twofold axis of symmetry bisecting the C(14)—C(15) bond in the four-carbon bridge and the midpoint between the bridgehead N atoms. The four-carbon bridge has the typical $g^+g^-g^+$

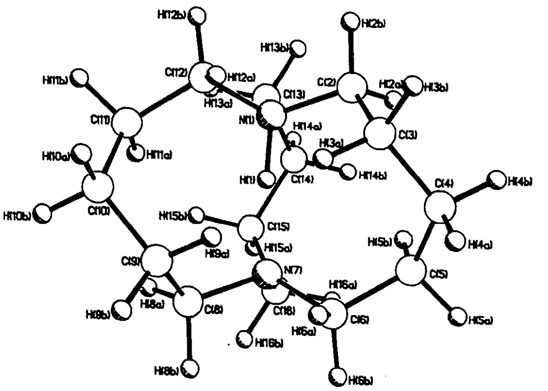

Fig. 2. Molecular structure of the cation of (1) showing the methylene hydrogens.

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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 44907 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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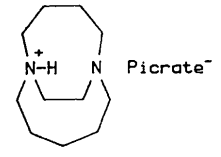
(*Received* 27 *February* 1988; *accepted* 5 *April* 1988)

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 *P*3*m* 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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