References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 148–153.

Behe, M. & Felsenfeld, G. (1981). *Proc. Natl Acad. Sci. USA*, **77**, 6468–6472.

Birnbaum, G. I. & Gentry, G. A. (1983). *J. Am. Chem. Soc.* **105**, 5398–5402.

Ehrlich, M. & Wang, R. Y.-H. (1981). *Science*, **212**, 1350–1357.

Hall, S. R. & Stewart, J. M. (1987). (Editors). *XTAL*2.2 *User's Manual*. Univs. of Western Australia and Maryland.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Radin, A. & Riggs, A. D. (1980). *Science*, **210**, 604–610.

Sato, T. (1983). *Nucleic Acids Res.* **11**, 4933–4938.

Takenaka, A., Kato, M. & Sasada, Y. (1980). *Bull. Chem. Soc. Jpn*, **53**, 383–387.

Taylor, R. & Kennard, O. (1982*a*). *J. Am. Chem. Soc.* **104**, 3209–3212.

Taylor, R. & Kennard, O. (1982*b*). *J. Mol. Struct.* **78**, 1–28.

Acta Cryst. (1988). C**44**, 872–874

Inside-Protonated 1,8-Diazabicyclo[6.5.3]hexadecane Picrate

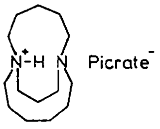
By J. M. White, R. W. Alder and A. G. Orpen

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

(*Received* 27 *November* 1987; *accepted* 19 *January* 1988)

Abstract. $C_{14}H_{29}N_2^+.C_6H_2N_3O_7^-$, $M_r = 453{\cdot}54$, triclinic, $P\bar{1}$, $a = 8{\cdot}435\,(2)$, $b = 12{\cdot}036\,(2)$, $c = 12{\cdot}630\,(2)$ Å, $\alpha = 62{\cdot}78\,(2)$, $\beta = 86{\cdot}45\,(2)$, $\gamma = 73{\cdot}77\,(2)^\circ$, $V = 1091{\cdot}5\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}38$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}99$ cm^{-1}, $F(000) = 484$, $T = 293$ K, $R = 0{\cdot}051$ for 1867 unique observed reflections. The title compound has an intrabridgehead N(1)···N(8) distance of 2·610 (5) Å, the inside proton is localized near N(8) with N(8)—H = 1·19 (3), N(1)···H = 1·49 (3) Å and N—H···N = 154 (3)°. The strain imposed by a number of short intramolecular non-bonded H···H contacts is relieved by an expansion in C—C—C angles to a mean value of 116·7 (7)°.

Introduction. Medium-ring bicyclic compounds exhibit many interesting structural and chemical properties (Alder, 1983). 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*). These compounds provide an ideal opportunity to study N—H—N hydrogen bonds of various geometries.



(1)

Experimental. Yellow rod (0·9 × 0·20 × 0·05 mm) from solvent diffusion using CH_2Cl_2 and diethyl ether; Nicolet *P*3*m* diffractometer, 22 reflections centred (12 < θ < 13°), graphite-monochromated Mo *K*α for data collection, 2 < θ < 25°, room temperature, ω–2θ scans in 96 steps, ω scan width 1·0 + 0·35tanθ°, data measured over 127 X-ray hours with no detectable

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

	x	*y*	*z*	U_{eq}*/*U*
C(17)	1977 (4)	3819 (3)	9425 (3)	52 (2)
C(18)	1626 (4)	3363 (3)	10669 (3)	47 (1)
C(19)	1844 (4)	3956 (3)	11337 (3)	51 (2)
C(20)	2428 (4)	5029 (3)	10836 (3)	49 (2)
C(21)	2776 (4)	5543 (3)	9649 (3)	51 (2)
C(22)	2511 (4)	4976 (3)	8984 (3)	49 (2)
O(1)	1875 (4)	3288 (3)	8809 (2)	86 (2)
O(21)	529 (5)	1826 (3)	10681 (3)	123 (2)
O(22)	822 (5)	1809 (3)	12298 (3)	126 (2)
O(41)	2271 (3)	5213 (3)	12575 (2)	88 (2)
O(42)	3080 (4)	6648 (3)	11044 (3)	99 (2)
O(61)	1737 (4)	5768 (3)	7002 (2)	107 (2)
O(62)	3976 (4)	6006 (3)	7417 (2)	109 (2)
N(2)	966 (4)	2261 (3)	11255 (3)	65 (2)
N(4)	2598 (4)	5671 (3)	11533 (3)	69 (2)
N(6)	2770 (4)	5618 (3)	7707 (2)	67 (2)
N(1)	3485 (3)	248 (3)	7948 (2)	61 (1)
C(2)	5181 (5)	255 (4)	8222 (4)	97 (3)
C(3)	5377 (5)	1588 (4)	7823 (4)	91 (3)
C(4)†	5714 (13)	2482 (11)	6525 (12)	86 (6)
C(5)†	4466 (8)	2838 (6)	5596 (5)	76 (3)
C(6)	2823 (5)	3744 (4)	5651 (4)	89 (2)
C(7)	1562 (7)	3320 (4)	5268 (4)	112 (3)
N(8)	1320 (4)	2081 (3)	6216 (2)	68 (2)
C(9)	593 (6)	1414 (4)	5681 (4)	94 (3)
C(10)	1866 (7)	694 (5)	5142 (4)	107 (3)
C(11)	2739 (6)	−717 (4)	5929 (4)	91 (3)
C(12)	4101 (5)	−1069 (4)	6835 (4)	96 (3)
C(13)	3542 (5)	−997 (4)	7974 (4)	88 (2)
C(14)	2290 (5)	494 (4)	8804 (3)	82 (2)
C(15)	547 (5)	1059 (4)	8265 (4)	86 (3)
C(16)	284 (5)	2298 (4)	7135 (4)	86 (3)
C(5′)‡	4884 (25)	3436 (19)	5764 (15)	113 (11)
C(4′)‡	5558 (25)	1865 (18)	6552 (19)	80 (9)
H(1)	2540 (45)	1313 (36)	6818 (32)	112 (12)

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

† Occupancy 0·658 (5).

‡ Occupancy 0·342 (5).

0108-2701/88/050872-03$03.00

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

(*a*) Bond lengths

N(1)–C(2)	1·495 (6)	N(1)–C(13)	1·472 (6)
N(1)–C(14)	1·504 (5)	N(1)–H(1)	1·487 (30)
C(2)–C(3)	1·501 (7)	C(3)–C(4)	1·558 (12)
C(3)–C(4′)	1·490 (25)	C(4)–C(5)	1·452 (15)
C(5)–C(6)	1·526 (7)	C(6)–C(7)	1·489 (8)
C(6)–C(5′)	1·674 (21)	C(7)–N(8)	1·486 (5)
N(8)–C(9)	1·516 (7)	N(8)–C(16)	1·485 (6)
N(8)–H(1)	1·188 (31)	C(9)–C(10)	1·515 (7)
C(10)–C(11)	1·504 (6)	C(11)–C(12)	1·502 (7)
C(12)–C(13)	1·518 (8)	C(14)–C(15)	1·494 (6)
C(15)–C(16)	1·489 (5)	C(5′)–C(4′)	1·624 (25)

(*b*) Bond angles

C(2)–N(1)–C(13)	110·3 (3)	C(14)–C(15)–C(16)	113·5 (4)
C(2)–N(1)–C(14)	111·5 (4)	C(13)–N(1)–C(14)	110·3 (3)
C(2)–N(1)–H(1)	118·5 (16)	C(13)–N(1)–H(1)	107·6 (20)
C(14)–N(1)–H(1)	98·0 (15)	N(1)–C(2)–C(3)	114·4 (3)
C(2)–C(3)–C(4)	123·8 (7)	C(2)–C(3)–C(4′)	94·6 (10)
C(3)–C(4)–C(5)	115·9 (9)	C(4)–C(5)–C(6)	113·5 (8)
C(5)–C(6)–C(7)	103·7 (5)	C(7)–C(6)–C(5′)	138·9 (10)
C(6)–C(7)–N(8)	112·6 (3)	C(7)–N(8)–C(9)	110·8 (3)
C(7)–N(8)–C(16)	111·2 (3)	C(9)–N(8)–C(16)	111·4 (3)
C(7)–N(8)–H(1)	115·0 (19)	C(9)–N(8)–H(1)	107·5 (25)
C(16)–N(8)–H(1)	100·6 (20)	N(8)–C(9)–C(10)	113·1 (4)
C(9)–C(10)–C(11)	118·0 (3)	C(10)–C(11)–C(12)	119·5 (5)
C(11)–C(12)–C(13)	115·7 (4)	N(1)–C(13)–C(12)	113·5 (3)
N(8)–C(16)–C(15)	110·4 (4)	C(6)–C(5′)–C(4′)	104·3 (15)
C(3)–C(4′)–C(5′)	106·3 (17)		

(*c*) Torsion angles

Three-carbon bridge			
N(1)–C(14)–C(15)–C(16)	−57·6 (6)	C(14)–C(15)–C(16)–N(8)	61·2 (6)
Five-carbon bridge			
N(1)–C(13)–C(12)–C(11)	−95·1 (5)	C(13)–C(12)–C(11)–C(10)	78·7 (7)
C(12)–C(11)–C(10)–C(9)	−76·7 (6)	C(11)–C(10)–C(9)–N(8)	91·1 (6)
Six-carbon bridge major			
N(1)–C(2)–C(3)–C(4)	−82·5 (7)	C(2)–C(3)–C(4)–C(5)	59·9 (11)
C(3)–C(4)–C(5)–C(6)	68·5 (11)	C(4)–C(5)–C(6)–C(7)	−144·8 (7)
C(5)–C(6)–C(7)–N(8)	75·6 (5)		
Six-carbon bridge minor			
N(1)–C(2)–C(3)–C(4′)	−79·6 (9)	C(2)–C(3)–C(4′)–C(5′)	152·1 (14)
C(3)–C(4′)–C(5′)–C(6)	−81·2 (17)	C(4′)–C(5′)–C(6)–C(7)	−53·5 (18)
C(5′)–C(6)–C(7)–N(8)	81·9 (10)		

(*d*) Selected non-bonded contacts (Å) for the major conformer [s.o.f. = 0·658 (5)] [C—H bond lengths extended to 1·08 (Å)]

Intramolecular			
H(2*a*)···H(3*b*)	2·220	H(2*b*)···H(12*b*)	2·183
H(3*a*)···H(6*b*)	2·083	H(3*a*)···H(14*a*)	2·064
H(4*a*)···H(5*a*)	2·295	H(5*a*)···H(6*a*)	2·294
H(5*b*)···H(7*a*)	2·213	H(5*b*)···H(10*a*)	2·271
H(6*a*)···H(7*b*)	2·353	H(6*a*)···H(16*a*)	2·076
H(7*a*)···H(10*a*)	2·135	H(9*a*)···H(10*b*)	2·233
H(9*b*)···H(11*b*)	2·330	H(9*b*)···H(15*b*)	1·995
H(10*b*)···H(11*a*)	2·257	H(11*a*)···H(12*a*)	2·256
H(11*b*)···H(13*b*)	2·237	H(12*a*)···H(13*a*)	2·231
H(13*a*)···H(15*b*)	2·124	H(14*b*)···H(15*b*)	2·397
Intermolecular			
H(7*a*)···H(7*a*$^{\text{i}}$)	2·107	H(10*b*)···O(22$^{\text{ii}}$)	2·351
H(12*a*)···O(62$^{\text{iii}}$)	2·480	H(14*a*)···O(1)	2·334
H(16*a*···O(1)	2·424		

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

decay or movement; high-angle reflections ($20 < \theta < 25°$) with count rate less than 8 counts s^{-1} were not collected; 3179 unique data, $R_{\text{merge}} = 0{\cdot}018$, used for structure solution, and refinement of 1867 reflections with $F > 3\sigma(F)$ retained ($0 < h < 11$, $-15 < k < 15$, $-16 < l < 16$). Direct methods and difference Fourier methods, blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0{\cdot}00046(F^2)]^{-1}$, anisotropic thermal parameters for all non-H atoms, methylene and phenyl protons were refined in idealized positions (C—H 0·96 Å), H atoms on the disordered methylene carbons were fixed in idealized positions, $R = 0{\cdot}0510$, $wR = 0{\cdot}0625$, $S = 1{\cdot}56$ data:variable ratio 5·96:1, max. peak and min. trough in final ΔF synthesis 0·27 and $-0{\cdot}19$ e Å^{-3} respectively, max. shift/e.s.d. in final cycle 0·102; 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 and torsion angles in Table 2(*a*)–(*c*) and important non-bonded contacts in Table 2(*d*). A perspective view of the molecular structure of

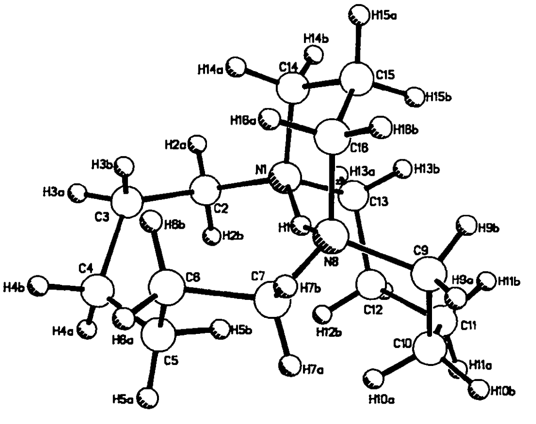


Fig. 1. Molecular structure of the cation of (1). The major (0·658) conformer of the cation is shown.

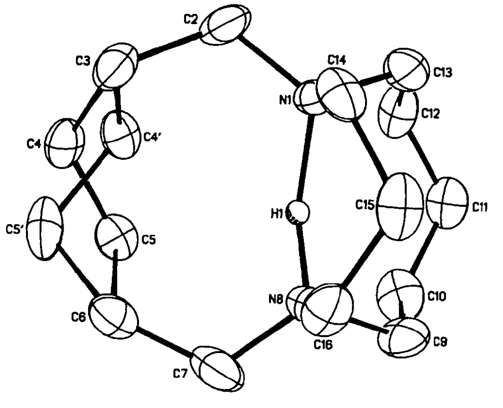


Fig. 2. Molecular geometry of the cation of (1) with both orientations of the disordered $(CH_2)_6$ chain shown.

---

* 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 44699 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the major conformer of the cation is represented in Fig. 1, and a view of the cation showing both conformations is given in Fig. 2. Atoms C(4) and C(5) in the six-carbon bridge are disordered. This disorder is effectively a racemization and results in an approximate mirror plane of symmetry for the cation perpendicular to and bisecting the N(1)···N(8) vectors. Site occupancy for C(4), C(5) refined to 0·658 (5) and for C(4′), C(5′) to 0·342 (5). The two conformations for the six-carbon bridge which result (see Table 2) are both similar to that observed in the inside-protonated [6.4.3]diamine (Alder *et al.*, 1988). The conformation of the five-carbon bridge is similar to those observed in the inside-protonated [5.4.3]diamine and [5.5.2]diamine (White *et al.*, 1988*a*,*b*), having an approximate plane of symmetry; the three-carbon bridge has the typical envelope-like conformation (Alder *et al.*, 1988; White *et al.*, 1988*a*). The bicyclic cation has a number of close intramolecular H···H contacts (see Table 2*d*). The strain imposed by these close contacts is taken up to some degree by an opening of the C—C—C angles; the average C—C—C angle is 116·7 (7)° compared with the idealized value of 109·5° (this average does not include those angles from the six-carbon bridge which are disordered). The inside proton is localized towards N(8) [N(8)—H = 1·19 (3), N(1)···H 1·49 (3) Å], the N—H—N angle is 154 (3)° and the N···N distance is 2·610 (5) Å. This can be contrasted with a number of inside-protonated bicyclic diamines; for [6.4.3]diamines [N···N = 2·663 (4), N—H 0·95 (2), 1·77 (2) Å (Alder *et al.*, 1988)], for [5.4.3]diamine [N···N 2·555 (3), N—H 1·30 (3), 1·30 (2) Å (White *et al.*, 1988*a*)], for [5.5.2]diamine [N···N = 2·555 (7), N—H 1·09 (5), 1·67 (5) Å (White *et al.*, 1988*b*)] and for the [4.4.4]diamine [N···N = 2·526 (3) Å] and an apparently symmetrical linear N—H—N system (Alder *et al.*, 1983).

References

Alder, R. W. (1983). *Acc. Chem. Res.* **16**, 321–327.

Alder, R. W., Orpen, A. G. & Sessions, R. B. (1983). *J. Chem. Soc. Chem. Commun.* pp. 999–1000.

Alder, R. W., Orpen, A. G. & White, J. M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 949–950.

Alder, R. W., Orpen, A. G. & White, J. M. (1988). *Acta Cryst.* C**44**, 287–289.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Sheldrick, G. M. (1985). *SHELXTL*, revision 5.1. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

White, J. M., Alder, R. W. & Orpen, A. G. (1988*a*). *Acta Cryst.* C**44**, 662–664.

White, J. M., Alder, R. W. & Orpen, A. G. (1988*b*). *Acta Cryst.* C**44**, 664–666.

Acta Cryst. (1988). C**44**, 874–878

Crystal Structure and Photochemistry of Two α-Cycloalkyl-4-carboxyacetophenones

By Stephen V. Evans and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

(*Received* 9 *October* 1987; *accepted* 15 *January* 1988)

Abstract. The photochemical behaviour of two α-cycloalkylacetophenones has been correlated with the crystal and molecular structural data. In both cases Mo $K\alpha_1$ radiation was used, $\lambda = 0{\cdot}70930$ Å, $T = 295$ K. α-Cyclopentyl-4-carboxyacetophenone,* $C_{14}H_{16}O_3$, $M_r = 232{\cdot}28$, triclinic, $P\bar{1}$, $a = 10{\cdot}809$ (2), $b = 22{\cdot}683$ (4), $c = 5{\cdot}091$ (1) Å, $\alpha = 94{\cdot}68$ (1), $\beta = 92{\cdot}74$ (1), $\gamma = 77{\cdot}97$ (2)°, $V = 1216{\cdot}1$ (4) Å^3, $Z = 4$ (2 molecules per asymmetric unit), $D_x = 1{\cdot}268$ g cm^{-3}, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 496$, $R = 0{\cdot}056$ for 2129 reflections. α-Cyclooctyl-4-carboxyacetophenone,† $C_{17}H_{22}O_3$, $M_r = 274{\cdot}36$, triclinic, $P\bar{1}$, $a = 6{\cdot}6335$ (6), $b = 9{\cdot}7489$ (12), $c = 11{\cdot}5888$ (14) Å, $\alpha = 80{\cdot}658$ (10), $\beta = 88{\cdot}449$ (8), $\gamma = 88{\cdot}344$ (10)°, $V = 739{\cdot}0$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}233$ g cm^{-3}, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 296$, $R = 0{\cdot}042$ for 2135 reflections. The molecular conformations and geometries are very similar to those of related chloro derivatives, except that one of the independent molecules of the cyclopentyl compound has a conformation which involves a 100° rotation about the C(carbonyl)—C_α bond from that observed in all the other molecules. All the molecules have geometries which are favourable for photochemical reaction *via* hydrogen abstraction processes, and increasing amounts of cyclization products with increasing cycloalkyl ring size can be correlated with changing angles between biradical *p* orbitals.

---

* 1-(4-Carboxyphenyl)-2-cyclopentylethanone; 4-cyclopentylmethylcarbonylbenzoic acid.

† 1-(4-Carboxyphenyl)-2-cyclooctylethanone; 4-cyclooctylmethylcarbonylbenzoic acid.

0108-2701/88/050874-05$03.00