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The Structure of 1,8-Octanediamine Dihydrobromide, $C_8H_{20}N_2.2HBr$

BY JOSÉE BRISSON AND FRANÇOIS BRISSE

Département de Chimie, Université de Montréal, CP 6210, *Succ. A, Montréal, Québec, Canada H3C* 3*V*1

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Abstract. $M_r = 306{\cdot}08$, orthorhombic, $Pba2$, $a = 18{\cdot}396\,(5)$, $b = 15{\cdot}792\,(4)$, $c = 4{\cdot}588\,(2)$ Å, $V = 1332{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}49$, $D_x = 1{\cdot}485$ Mg m^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}49$ mm^{-1}, $F(000) = 616$, $T = 293$ K, final $R = 0{\cdot}037$ for 1305 observed reflections. The structure consists of layers of approximately planar diammonium cations in a fully-extended conformation sandwiched between layers of bromide ions. One ammonium group forms hydrogen bonds with three bromide ions while the other ammonium group is connected to four bromide ions. The Br$\cdots$N hydrogen-bond distances range from 3·29 (1) to 3·43 (1) Å.

Introduction. Continuing our study of the geometry and conformation of compounds with a linear aliphatic sequence, we have undertaken to examine the structures of oligomethylenediamine dihydrohalides of the type $^+H_3N-(CH_2)_x-NH_3^+.2X^-$. The structure of 1,8-octanediamine dihydrobromide presented here will be compared with that of *N,N'*-octamethylenedibenzamide as well as with those of other oligomethylenediamine dihydrohalides.

Experimental. Synthesis similar to that of 1,7-heptanediamine dihydrobromide (Brisson & Brisse, 1984; preceding paper). Needle-like crystals, 0·08 × 0·09 × 0·27 mm, from glacial acetic acid, density by flotation in bromoform/bromobenzene. A second crystalline form was isolated from ethanol; this structure will be investigated at a later date. Crystals obtained from acetic acid solution undergo a phase change at 234 K resulting in the destruction of the crystal. This prevented low-temperature data collection as was done for 1,7-heptanediamine dihydrobromide to minimize thermal vibrations in aliphatic chain. Unit-cell dimensions from 25 centered reflections, $10 < \theta < 25°$. Data collection: Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\bar{\alpha}$ radiation, ω–2θ scan mode, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14\tan\theta)°$, orientation verified every 100 reflections, intensity monitored every hour on three reference reflections, max. fluctuation of standard intensities 1·2%, $2\theta_{\max} = 150°$ ($0 \le h \le 23$, $0 \le k \le 19$, $0 \le l \le 5$). 1546 reflections measured of which 1305 satisfy $I > 1{\cdot}96\sigma(I)$, 241 unobserved, Lp and absorption corrections applied, transmission factor 0·32 to 0·62. Structure solved by Patterson method, least-squares refinement by block-diagonal approximation based on *F*'s, anisotropic for Br, N and C, H atoms located on difference Fourier syntheses isotropically refined, final $R = R_w = 0{\cdot}037$, w derived from counting statistics, $S = 1{\cdot}24$; mean $(\Delta/\sigma) = 0{\cdot}45$, $(\Delta/\sigma)_{\max} = 0{\cdot}70$, residual electron density in final difference Fourier synthesis −0·30, 0·46 e Å^{-3}. Scattering factors for Br, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), real and imaginary parts of anomalous dispersion of Br from Cromer & Liberman (1970). Computer programs as described in preceding paper.

Discussion. The observed systematic absences are compatible with either the *Pbam* or *Pba*2 space group. The refinement carried out in *Pbam* converged when R_w reached 0·047. However, in the *Pba*2 space group, R_w could be lowered to 0·037. The latter space group proved to be correct on the basis of Hamilton's test.

The list of refined atomic coordinates is given in Table 1,* and the bond distances, angles and torsion angles appear in Table 2.

The 1,8-octanediamine cation, shown in Fig. 1, is in the extended conformation. There is a significant departure from planarity, since some of the torsion angles, given in Table 2, deviate by as much as 20° from the *trans* value of 180°. However, the methylene chain does not show the marked curvature that was reported for the 1,6-hexanediamine cation (Borkakoti, Lindley, Moss & Palmer, 1978) or the 1,7-heptanediamine cation (Brisson & Brisse, 1984). Although not planar, the chain is nearly centrosymmetric.

In contrast to the 1,7-heptanediamine cation, the average C—C bond distance, 1·497 (7) Å, is quite short, while the C—C—C angles have an average of 114·8 (10)°. These quantities are clearly different from the corresponding values in *N,N'*-octamethylenedibenzamide (Pineault & Brisse, 1983), where ⟨C—C⟩ is 1·519 (4) Å and ⟨C—C—C⟩ is 112·6 (3)°. Here, again, one should not compare these values individually

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* Lists of structure factors, anisotropic thermal parameters and details of the hydrogen-bonding scheme have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39408 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates for* 1,8-*octanediamine dihydrobromide* ($\times 10^5$ *for* Br, $\times 10^4$ *for* N *and* C, $\times 10^3$ *for* H), U_{eq} (Å^2 $\times 10^4$ *for* Br, $\times 10^3$ *for* N *and* C), U_{iso} (Å^2 $\times 10^2$ *for* H)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Br(1)	21721 (3)	20238 (3)	100	530 (1)
Br(2)	87513 (2)	6167 (2)	−299 (56)	463 (1)
N(1)	6196 (2)	4039 (2)	5170 (39)	46 (1)
N(2)	2331 (2)	−1510 (2)	5166 (44)	45 (1)
C(1)	5441 (2)	3751 (3)	5211 (47)	57 (2)
C(2)	5368 (3)	2819 (3)	5397 (35)	51 (3)
C(3)	4621 (3)	2472 (3)	4894 (55)	60 (2)
C(4)	4572 (3)	1519 (3)	4871 (44)	62 (2)
C(5)	3826 (3)	1152 (3)	5253 (52)	61 (3)
C(6)	3791 (3)	217 (3)	5380 (41)	61 (3)
C(7)	3045 (3)	−167 (3)	4791 (42)	52 (2)
C(8)	3054 (3)	−1102 (3)	5191 (52)	68 (3)
H(11)	522 (3)	408 (3)	667 (12)	4 (1)
H(12)	529 (3)	392 (3)	314 (14)	7 (2)
H(21)	572 (3)	254 (3)	389 (13)	8 (2)
H(22)	556 (3)	264 (3)	740 (15)	7 (2)
H(31)	433 (3)	271 (3)	643 (11)	5 (2)
H(32)	448 (3)	267 (3)	264 (15)	8 (2)
H(41)	476 (3)	127 (3)	289 (16)	9 (2)
H(42)	492 (3)	130 (3)	654 (11)	4 (1)
H(51)	362 (3)	137 (4)	762 (15)	7 (2)
H(52)	349 (4)	140 (4)	362 (15)	9 (2)
H(61)	412 (3)	3 (4)	355 (11)	6 (2)
H(62)	398 (3)	4 (3)	742 (11)	5 (1)
H(71)	268 (3)	13 (4)	631 (12)	7 (2)
H(72)	285 (2)	3 (3)	279 (12)	4 (2)
H(81)	341 (3)	−134 (3)	351 (13)	7 (2)
H(82)	325 (4)	−110 (4)	749 (16)	10 (2)
H(N11)	638 (3)	394 (3)	332 (12)	5 (2)
H(N12)	649 (3)	363 (3)	700 (14)	6 (2)
H(N13)	623 (3)	449 (3)	591 (15)	6 (2)
H(N21)	203 (2)	−129 (3)	356 (11)	3 (1)
H(N22)	224 (3)	−163 (4)	695 (16)	10 (3)
H(N23)	236 (3)	−201 (3)	413 (13)	6 (2)

Table 2. *Bond distances* (Å), *bond angles and torsion angles* (°) *in* 1,8-*octanediamine dihydrobromide*

N(1)–C(1)	1·462 (6)	N(1)–C(1)–C(2)	113 (1)
C(1)–C(2)	1·481 (7)	C(1)–C(2)–C(3)	116 (1)
C(2)–C(3)	1·498 (8)	C(2)–C(3)–C(4)	115 (1)
C(3)–C(4)	1·508 (7)	C(3)–C(4)–C(5)	116 (1)
C(4)–C(5)	1·501 (8)	N(2)–C(8)–C(7)	115 (1)
C(5)–C(6)	1·479 (7)	C(8)–C(7)–C(6)	111 (1)
C(6)–C(7)	1·525 (9)	C(7)–C(6)–C(5)	115 (1)
C(7)–C(8)	1·488 (8)	C(6)–C(5)–C(4)	116 (1)
C(8)–N(2)	1·478 (6)		
N(1)–C(1)–C(2)–C(3)	−169 (1)	C(6)–C(7)–C(8)–N(2)	170 (1)
C(1)–C(2)–C(3)–C(4)	176 (1)	C(5)–C(6)–C(7)–C(8)	−176 (1)
C(2)–C(3)–C(4)–C(5)	163 (1)	C(4)–C(5)–C(6)–C(7)	−161 (1)
C(3)–C(4)–C(5)–C(6)	−177 (1)		

but in a combined manner such as in the advance per CH_2 group. This is the distance between consecutive CH_2 groups in a direction parallel to the chain axis. In the 1,8-octanediamine cation the advance per CH_2 is 1·261 (8) Å similar to 1·264 (4) Å in *N*,*N*′-octamethylenedibenzamide. This corroborates a similar observation in aliphatic chains with seven CH_2 groups (Brisson & Brisse, 1984).

The molecular structure of 1,8-octanediamine dihydrobromide is represented by the stereoscopic pair in Fig. 2. The structure consists of almost planar 1,8-octanediamine cations and bromide anions, placed in alternate layers **c**/2 apart from each other. The packing is similar to that of 1,6-hexanediamine dihydrochloride (Borkakoti *et al.*, 1978) and 1,7-heptanediamine dihydrobromide (Brisson & Brisse, 1984); the differences occur in the H-bonding scheme. In 1,6-hexanediamine, one NH_3^+ is H bonded to two Cl^- ions and the other NH_3^+ is bonded to three Cl^- ions. In the case of 1,7-heptanediamine, both NH_3^+ are H bonded to three bromide ions. In the present case, N(1) is hydrogen bonded to three Br atoms with Br···N(1) distances ranging from 3·315 (13) to 3·415 (12) Å. A fourth bromine is at 3·329 (12) Å, but since the Br···H(N12) distance is 3·45 (5) Å and Br···H(N12)–N(1) is 74 (3)°, this contact is not considered as a hydrogen bond. N(2) is in turn H bonded to four Br atoms. The Br···N(2) distances vary between 3·291 (14) and 3·436 (14) Å. In this case H(N22) participates in a bifurcated hydrogen bond.

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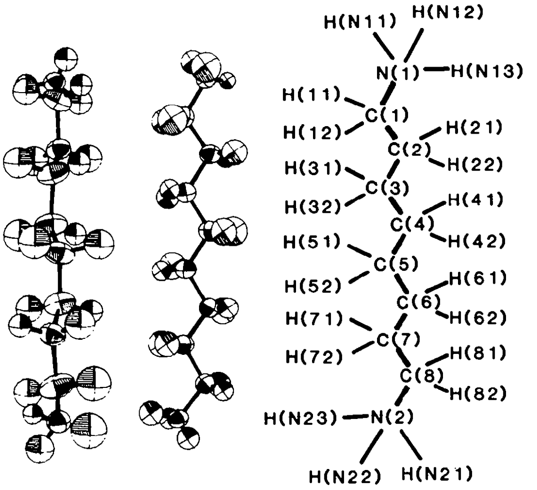

Fig. 1. Numbering scheme and front and side views of the 1,8-octanediamine cation.

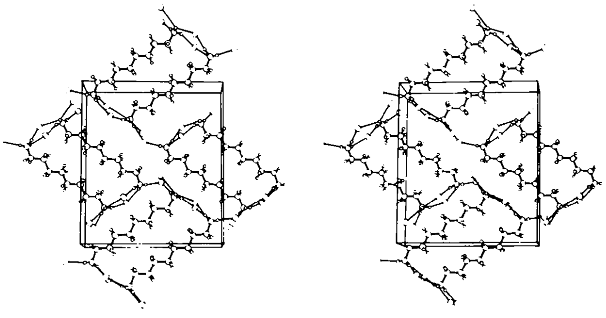

Fig. 2. Stereoview of the unit-cell contents of 1,8-octanediamine dihydrobromide. The *a* and *b* axes are vertical and horizontal, respectively.

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Structure of 1,1,1′,1′,3,3,3′,3′-Octamethyl-2,2′-biindanylidene, $C_{26}H_{32}$

By Tullio Pilati and Massimo Simonetta

Dipartimento di Chimica-Fisica ed Elettrochimica dell'Università e Centro del CNR, Via Golgi 19, 20133 *Milano, Italy*

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Abstract. $M_r = 344{\cdot}5$, orthorhombic, $Pbca$, $a = 21{\cdot}093\,(3)$, $b = 11{\cdot}495\,(2)$, $c = 8{\cdot}235\,(1)$ Å, $V = 1996{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}131$, $D_x = 1{\cdot}146$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 752$, room temperature, $R = 0{\cdot}045$ for 1592 ($I > 1\sigma$) reflections. Steric hindrance reflects little on the ethylenic bond length [1·350 (2) Å], but more on the adjacent single bonds [mean 1·584 (1) Å] and on the angles involving methyl groups, which range between 105·6 (1) and 118·2 (1)°. The five-membered ring has an envelope conformation to minimize the steric hindrance of the methyl groups. There is no twisting around the central C–C bond which maintains its double-bond character. The molecule is at a crystallographic centre of symmetry, but has approximate $2/m$ symmetry.

Introduction. The conformation of overcrowded ethylenes has been a subject of interest in our laboratory for a long time, from both experimental and theoretical points of view (Favini, Simonetta, Sottocornola & Todeschini, 1982, and references therein). The present study is in line with our previous work. The interaction between the substituents can act on the ethylenic system in two ways: by twisting around the double bond or by distorting the geometry of the neighbouring groups.

The most evident example of the first type is diisopropyl 9,9′-bifluorenylidene-1,1′-dicarboxylate (Bayley & Hull, 1978). In this molecule the dihedral angle between the fluorene mean planes is 50–54°; the consequent π-overlap reduction that lengthens the double bond to 1·391 (11)–1·395 (11) Å is clear evidence of a partial diradical situation. On the other hand, the C(ethyl)–C(phenyl) bond lengths are unaffected or shortened: 1·458 (12)–1·489 (14) *versus* 1·483 (5)–1·488 (5) Å in fluorenone (Luss & Smith, 1972).

syn-2,2′-Bifenchylidene(E) (Pilati & Simonetta, 1977) is an example of the second type: here the distortion of the tetrasubstituted ethylenic plane is quite small [maximum deviation 0·106 (4) Å] and the double bond is only 1·347 (3) Å, but the mean value of the C_{sp^2}–C_{sp^3} bond distance is 1·565 (7) Å and the range of the C_{sp^2}–C_{sp^3}–C_{sp^3} angles is 99·4 (2)–122·4 (2)°.

Experimental. D_m by flotation in dilute K_2HgI_4 solution; colourless prism 0·25 × 0·20 × 0·18 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω-scan technique. Cell constants from setting angles of 25 reflections with $9 < \theta < 14°$; correction for Lorentz and polarization but not for absorption. No significant variation of intensity in 3 standard reflections. 4540 reflections measured with $\theta < 27{\cdot}5°$, range of hkl: 0 to 27, 0 to 14, −10 to 10, 2273 independent, 1592 with $I > \sigma(I)$, agreement factor on observed intensity 0·026. All carbon atoms from *MULTAN* (Germain, Main & Woolfson, 1971), H atoms from Fourier synthesis. Anisotropic carbon, isotropic H atoms, final secondary extinction parameter $g = 3{\cdot}5\,(2) \times 10^{-5}$ (Larson, 1967, equation 3); full-matrix least-squares refinement on F, $w = 4F_o^2/\{\sigma^2(F_o^2) + 0{\cdot}0009(F_o^4)\}$; final $R = 0{\cdot}045$, $R_w = 0{\cdot}041$, $S = 1{\cdot}63$, $\Delta_{\max}/\sigma = 0{\cdot}05$, $\Delta\rho = 0{\cdot}15$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used include Enraf–Nonius (1979) *SDP, ORTEP* (Johnson, 1965) and various in-house programs for data reduction and geometrical analysis running on a Gould SEL 32/7780 computer. The final positional parameters and their e.s.d.'s are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39368 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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