The title compounds differ from one compound already analysed (Bocelli & Grenier-Loustalot, 1982*a*) only by the two chlorine atoms on the rings, but the conformations of the tetramethylene segments are strikingly different. In fact a *gauche–trans–gauche* conformation characterizes the chains of HDM and the unchlorinated derivative, while HDP shows a significant displacement from an all-*trans* arrangement [C(8)–C(10)–C(11)–C(12) = 167·8 (7)]. The conformation of the rest of the chain of HDP and HDM remains quite similar to that in the unchlorinated derivative, which is in all three cases significantly shifted away from a *trans* arrangement by the conformation around C(7)–O(1)–C(8)–C(10) and C(11)–C(12)–O(3)–C(14). Further differences between the unchlorinated and chlorinated compounds occur in the orientation of the C(9) and C(13) methyl groups which are *trans* each to other and axial with respect to the chain in the first case and in HDM. In HDP they lie on the same side with respect to the C(8)–C(10)–C(11)–C(12) sequence [1·00 (8) and 1·05 (9) Å out of plane]. Moreover, in HDP, the dihedral angles [43·5 (7) and 41·2 (7)°] formed by the bond direction with the normal to the least-squares plane force the methyls to occupy a position intermediate between axial and equatorial.

It may be interesting to compare the chain conformation of the present structures with those of 1,4-butanediyl dibenzoate (Bocelli & Grenier-Loustalot, 1982*b*) and 1,4-butanediyl bis(*p*-chlorobenzoate) (Bocelli & Grenier-Loustalot, 1984*a*) which are *gauche–trans–trans* and all-*trans*, respectively.

These conformational changes of the aliphatic chain reflect on the length (distance between the centre of the rings) of the molecules which is 9·53 (4) Å in the derivative with no substituent, 11·51 (6) Å in that with only the methyls, 13·06 (6) Å in that with only the chlorines and 12·71 (9), 11·54 (2) Å in HDP and HDM, respectively.

The geometry of the benzene rings is normal [1·380 (4), 1·385 (8) and 1·386 (3) Å, 119·9 (4), 119·8 (7) and 120·1 (4)° – average distances and internal angles] and their planes form a dihedral angle of 1·4 (1)° in HDP and are parallel by geometry requirements in HDM. In agreement with the results of Domenicano, Vaciago & Coulson (1975), Domenicano, Mazzeo & Vaciago (1976), and Domenicano & Murray-Rust (1979), the internal angles at the chlorine atoms are larger than the adjacent ones.

The carboxylic moieties are tilted by 0·4 (2), 2·3 (2) and 6·0 (1)° with respect to their aromatic rings. The angles opposite the C=O bonds show the usual narrowing with respect to the adjacent ones.

The packing of the molecules in the unit cell is determined by van der Waals interactions and no significant intermolecular contacts are observed.

This work was supported by CNR (Rome) and by CNRS (Paris) through an International Scientific Project (ERA 895).

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The Structure of 1,7-Heptanediamine Dihydrobromide at 173 K, $C_7H_{18}N_2.2HBr$

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(*Received* 12 *January* 1984; *accepted* 16 *April* 1984)

Abstract. $M_r = 292\cdot06$, m.p. = 531 K, monoclinic, $P2_1/c$, $a = 4\cdot766\ (5)$, $b = 16\cdot915\ (10)$, $c = 14\cdot856\ (14)$ Å, $\beta = 97\cdot54\ (8)°$, $V = 1187\cdot4$ Å^3, $Z = 4$, $D_m = 1\cdot53$, $D_x = 1\cdot593$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71069$ Å, $\mu = 6\cdot55$ mm^{-1}, $F(000) = 584$, $T = 173$ K, final $R = 0\cdot043$ for 1310 observed reflections. The

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aliphatic chain is in the all-*trans* conformation with normal bonds and angles. However, a marked curvature of the chain is noted. Each hydrogen atom of each NH_3^+ group is hydrogen-bonded to a bromide ion. $Br\cdots N$ hydrogen-bond distances range from 3·28 (1) to 3·38 (1) Å.

Introduction. In the course of our study of compounds containing an aliphatic chain, we have undertaken to look at the structures and conformations of the series of oligomethylene diammonium salts. These compounds provide information on the possible conformations of chains terminated by H-bonded nitrogen atoms. First, the structure of 1,3-propanediamine dihydrochloride was reinvestigated (Brisson & Brisse, 1982*a*). We then concentrated on larger counterions, such as bromide and iodide, especially since 1,6-hexanediamine dihydroiodide (Han, 1963) presented an unusual conformation in the aliphatic portion of the chain, g^-ttg^+, where $g \simeq 60°$ and $t \simeq 180°$.

Experimental. Synthesis similar to that of 1,3-propanediamine dihydrochloride. Crystals isolated from ethanol, 0·12 × 0·12 × 0·26 mm, density by flotation in bromoform/bromobenzene, Enraf–Nonius CAD-4 diffractometer, unit-cell dimensions from 25 centered reflections with $10 < \theta < 25°$, data collected at 173 K using Mo $K\bar{\alpha}$ graphite-monochromated radiation, $2\theta_{\max} = 50{\cdot}0°$, $0 \le h \le 5$, $0 \le k \le 20$, $-17 \le l \le 17$; orientation monitored every 100 reflections, intensity checked every hour with three standard reflections, max. fluctuation of the standard intensities 2·4%, 2094 measured reflections of which 1310 had $I \ge 1{\cdot}96\sigma(I)$. Lp and absorption corrections applied,* transmission factor in range 0·43–0·50. Structure solved by Patterson procedure, refinement on *F*'s by block-diagonal approximation least-squares method. H atoms found on difference Fourier syntheses, isotropically refined. Final $R = 0{\cdot}043$, $R_w = 0{\cdot}044$ with weighting scheme based on counting statistics, $S = 1{\cdot}35$ (5 reflections omitted from last cycles of refinement), mean $(\Delta/\sigma) = 0{\cdot}04$, $(\Delta/\sigma)_{\max} = 0{\cdot}35$. Extreme fluctuations of electron density on final difference Fourier synthesis −0·65, 0·97 e Å^{-3}. The three highest peaks are all within 1·00 to 1·20 Å of Br(1). The possibility of disorder of Br(1) was investigated. The highest residual peaks were identified as Br atoms each with an initial occupancy factor of 0·1. Upon refinement these parameters tended towards zero and there was no significant improvement in either *R* or *S*. 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 for Br from Cromer & Liberman (1970).

Discussion. The atomic numbering is given in Fig. 1. The final atomic coordinates are listed in Table 1.* The bond distances, bond angles and torsion angles are given in Table 2.

The low-temperature data collection was made because of problems with the thermal vibrations encountered previously with structures of compounds with long aliphatic chains. As can be seen in Fig. 1, the aliphatic chain is entirely in the *trans* conformation. However, the atoms depart from coplanarity. The chain presents a very marked curvature such as the one reported for 1,6-hexanediamine dihydrochloride (Borkakoti, Lindley, Moss & Palmer, 1978).

There is nothing unusual about the $C(sp^3)$—$C(sp^3)$ bond distances or the $C(sp^3)$—$C(sp^3)$—$C(sp^3)$ bond angles in the diammonium cation which average 1·516 (12) Å and 112·4 (7)°, respectively. These values are, however, significantly different from their counterparts in *N*,*N'*-heptamethylenedibenzamide [1·490 (5) Å, 115·2 (4)°] (Brisson & Brisse, 1982*b*) or in piperazinium bis(*n*-heptanoate) [1·507 (5) Å, 114·0 (4)°] (Sangin & Brisse, 1984). However, the advance per methylenic group along the chain direction is nearly constant no matter what the extremities of the chain are. This value is 1·258 (5), 1·264 (5),

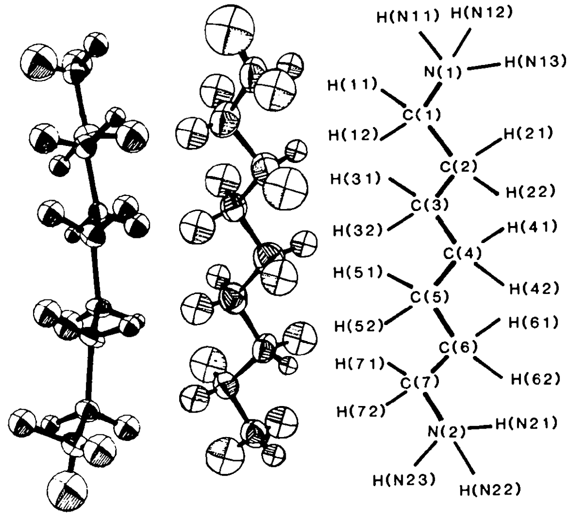

Fig. 1. Atomic numbering and perpendicular views of the diammonium chain.

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* The programs used here are modified versions of *NRC*-2 data reduction, *NRC*-10 bond distances and angles, *NRC*-22 mean planes (Ahmed, Hall, Pippy & Huber, 1973); *FORDAP* Fourier and Patterson maps (Zalkin); *NUCLS* least-squares refinement (Doedens & Ibers, 1967); *ORTEP* stereoviews (Johnson, 1965).

* Lists of structure factors, anisotropic thermal parameters and details of the hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39407 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates for* 1,7-*heptanediamine dihydrobromide* (×10^5 *for* Br, ×10^4 *for* N *and* C, ×10^3 *for* H), U_{eq} (Å^2, ×10^4 *for* Br, ×10^3 *for* N *and* C), $U_{\rm iso}$ (Å^2, ×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)	10327 (17)	10591 (5)	−5322 (5)	230 (2)
Br(2)	2082 (18)	−22605 (5)	−20825 (6)	276 (3)
N(1)	3489 (14)	5732 (4)	3930 (4)	26 (2)
N(2)	5342 (14)	2290 (4)	−1463 (5)	27 (2)
C(1)	5257 (17)	5435 (5)	3244 (5)	24 (3)
C(2)	3466 (18)	5044 (5)	2449 (5)	25 (3)
C(3)	5337 (17)	4694 (5)	1784 (5)	25 (3)
C(4)	3758 (17)	4179 (5)	1049 (6)	27 (3)
C(5)	5706 (17)	3829 (5)	422 (5)	24 (3)
C(6)	4319 (17)	3236 (5)	−265 (6)	27 (3)
C(7)	6506 (17)	2889 (5)	−783 (6)	28 (3)
H(N11)	474 (21)	591 (5)	444 (6)	7 (3)
H(N12)	247 (18)	609 (5)	391 (6)	4 (3)
H(N13)	229 (16)	518 (4)	417 (5)	3 (2)
H(N21)	400 (16)	241 (4)	−188 (5)	3 (2)
H(N22)	663 (19)	206 (5)	−184 (6)	5 (3)
H(N23)	485 (22)	186 (6)	−124 (7)	7 (3)
H(11)	654 (16)	585 (4)	303 (5)	3 (2)
H(12)	659 (14)	507 (4)	359 (4)	2 (2)
H(21)	197 (16)	457 (5)	265 (5)	3 (2)
H(22)	224 (15)	543 (4)	215 (5)	2 (2)
H(31)	628 (14)	511 (4)	154 (4)	1 (2)
H(32)	712 (17)	436 (5)	207 (5)	4 (3)
H(41)	213 (16)	444 (4)	61 (5)	3 (2)
H(42)	253 (16)	371 (5)	124 (5)	3 (2)
H(51)	734 (14)	359 (4)	74 (4)	1 (2)
H(52)	644 (17)	427 (4)	18 (5)	3 (2)
H(61)	285 (15)	345 (4)	−73 (5)	2 (2)
H(62)	345 (19)	284 (5)	9 (6)	4 (3)
H(71)	694 (18)	334 (5)	−122 (6)	6 (3)
H(72)	842 (17)	266 (4)	−34 (5)	3 (2)

Table 2. *Bond distances* (Å), *angles and torsion angles* (°) *in* 1,7-*heptanediamine dihydrobromide*

N(1)–C(1)	1·492 (10)	N(1)–C(1)–C(2)	111·6 (7)
C(1)–C(2)	1·515 (11)	C(1)–C(2)–C(3)	110·8 (7)
C(2)–C(3)	1·534 (12)	C(2)–C(3)–C(4)	114·2 (7)
C(3)–C(4)	1·517 (12)	C(3)–C(4)–C(5)	112·3 (7)
C(4)–C(5)	1·519 (12)	C(4)–C(5)–C(6)	115·0 (7)
C(5)–C(6)	1·519 (12)	C(5)–C(6)–C(7)	109·5 (7)
C(6)–C(7)	1·495 (12)	C(6)–C(7)–N(2)	113·2 (7)
C(7)–N(2)	1·486 (11)		
N(1)–C(1)–C(2)–C(3)	−176·2 (6)	C(3)–C(4)–C(5)–C(6)	173·6 (7)
C(1)–C(2)–C(3)–C(4)	170·7 (7)	C(4)–C(5)–C(6)–C(7)	175·3 (7)
C(2)–C(3)–C(4)–C(5)	−178·5 (7)	C(5)–C(6)–C(7)–N(2)	179·0 (7)

1·260 (12) Å for 1,7-heptanediamine dihydrobromide, *N,N'*-heptamethylenedibenzamide and piperazinium bis(*n*-heptanoate), respectively. Even the combination of the standard C(sp^3)—C(sp^3) distance of 1·535 Å and the tetrahedral angle, 109·45°, gives an advance per CH_2 of 1·253 Å. From this observation one may see a concomitant relationship between the C—C bond distance and the C—C—C bond angle.

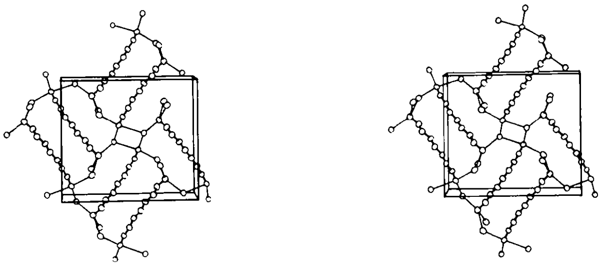

Fig. 2. Stereoscopic view of the packing in 1,7-heptanediamine dihydrobromide. The *b* and *c* axes are horizontal and vertical, respectively.

N—H···Br hydrogen bonds connect each diamine to three bromide ions.* Two aliphatic chains, forming a dimer, lie on a plane while the bromide ions are in a second plane parallel to the first one. This packing mode (Fig. 2) is similar to that reported by Borkakoti *et al.* (1978) for 1,6-hexanediamine dihydrochloride, although the two compounds have a slightly different hydrogen-bonding scheme. In the 1,6-hexanediamine salt, one NH_3^+ group is connected to only two chloride ions and the second NH_3^+ group to three chloride ions, whereas in the 1,7-heptanediamine cation both NH_3^+ groups are connected to three bromide ions.

We wish to thank the Natural Sciences and Engineering Research Council of Canada for its financial support (grant A5968). We also acknowledge the help of Mr M. Olivier during the data collection.

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* See deposition footnote.

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