The Crystal Structures of Hexamethyleneiminium *p*-Chlorobenzoate and Dimorphs of Hexamethyleneiminium *p*-Bromobenzoate

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The crystal structures of hexamethyleneiminium *p*-chlorobenzoate (**1**), and the monoclinic [**2**(**m**)] and orthorhombic [**2**(**o**)] forms of hexamethyleneiminium *p*-bromobenzoate have been determined from visually estimated Cu $K\alpha$ data. The crystal data are: $P2_1/c$, $a=10.10(2)$, $b=16.78(1)$, $c=9.01(2)$ Å, $\beta=118.4(2)°$, $Z=4$ for **1**; C2/c, $a=25.47(2)$, $b=7.01(1)$, $c=16.29(1)$ Å, $\beta=109.1(1)°$, $Z=8$ for **2**(**m**); and Pbca, $a=11.55(1)$, $b=27.40(1)$, $c=8.57(1)$ Å, $Z=8$ for **2**(**o**). The structures of **1**, **2**(**m**), and **2**(**o**) were refined to R values of 0.072, 0.100, and 0.083 for 1628, 1009, and 1013 non-zero reflections, respectively. In the crystals of **1**, the type of hydrogen bond and the molecular arrangement in (010) plane are the same as those in piperazinediylium terephthalate. In **2**(**m**), two pairs of the base and acid ions related by a twofold axis are linked together by N–H···O hydrogen bonds. The crystal structure of **2**(**o**) is very similar to that of piperidinium and pyrrolidinium *p*-substituted benzoates in Pbca, but there is a difference in the combination mode of the base and acid ions participating in the hydrogen bonds. In all the crystals, the hydrogen bond extending along the long axis of the acid ion is shorter than that nearly perpendicular to the axis. Hexamethyleneimine rings in **1**, **2**(**m**), and **2**(**o**) take a similar twist-chair conformation.

It has been found for crystals of piperidinium and pyrrolidinium *p*-substituted benzoates that the N–H···O hydrogen bonds linking together the base and acid ions are usually formed around a 2_1 axis.[1–3] The crystal structures of the title compounds have been examined in order to ascertain whether the type of hydrogen bonds is maintained or not by the enlargement of the ring size of the base, to see what types of hydrogen bonds other than the 2_1 type are possible in the crystals, if any, and to determine the conformation of hexamethyleneimine ring in the crystals.

Experimental

Equimolar amounts of the base and the acid were dissolved in dry benzene. The crystals of hexamethyleneiminium *p*-chlorobenzoate (**1**) and of monoclinic form of hexamethyleneiminium *p*-bromobenzoate [**2**(**m**)] were grown from the solutions by slow evaporation. The crystals of orthorhombic form of hexamethyleneiminium *p*-bromobenzoate [**2**(**o**)] were grown from the filtrate of **2**(**m**) by slow evaporation. Crystal data and experimental details are given in Table 1. The systematic absences for **2**(**m**) showed the possible space group to be C2/c or Cc, but the latter was ruled out by the structure analysis.

The specimens were sealed in glass capillaries, since the crystals of the compounds decompose gradually. The intensity data were collected on equi-inclination Weissenberg photographs using Cu $K\alpha$ radiation. Intensities were estimated visually and corrected for Lorentz and polarization factors and spot shape.

Table 1. Crystal data and experimental details

	Hexamethyleneiminium *p*-chlorobenzoate (**1**) $(C_6H_{12}NH_2)^+(ClC_6H_4CO_2)^-$ *F.W.*=255.7	Hexamethyleneiminium *p*-bromobenzoate $(C_6H_{12}NH_2)^+(BrC_6H_4CO_2)^-$, *F.W.*=300.2	
		Monoclinic form [**2**(**m**)]	Orthorhombic form [**2**(**o**)]
Mp/°C	131—133	141—143	118—120
Morphology	Plates developed {010}	Plates developed {100}	Plates developed {010}
Space group	$P2_1/c$	C2/c	Pbca
a/Å	10.10(2)	25.47(2)	11.55(1)
b/Å	16.78(1)	7.01(1)	27.40(1)
c/Å	9.01(2)	16.29(1)	8.57(1)
β/°	118.4(2)	109.1(1)	
V/Å^3	1342(3)	2751(3)	2713(4)
Z	4	8	8
D_m/g cm^{-3}	1.26	1.46	1.47
D_x/g cm^{-3}	1.265	1.450	1.469
μ(Cu $K\alpha$)/cm^{-1}	24.5	44.5	44.8
Dimensions of crystals used/mm	0.50×0.15×0.25 0.25×0.15×0.60	0.20×1.20×0.35 0.25×0.35×0.55	0.70×0.15×0.20 0.30×0.10×0.50
Layers photographed	0*kl* to 6*kl* *hk*0 to *hk*6	*h*0*l* to *h*5*l* *hk*0 to *hk*6	0*kl* to 8*kl* *hk*0 to *hk*6
Non-zero reflections	1628	1009	1013
Percentage accessible	53	32	33
B/Å^2 from Wilson's plot	5.2	11.8	5.7

TABLE 2. FINAL ATOMIC PARAMETERS OF THE NON-HYDROGEN ATOMS ($\times 10^4$, except B_{eq}) AND THOSE OF THE HYDROGEN ATOMS ($\times 10^3$, except B_{iso}) WITH VALUES OF e.s.d. IN PARENTHESES

	x	y	z	B_{eq} or B_{iso}/Å^2
(a) Hexamethyleneiminium *p*-chlorobenzoate (**1**)				
C(1)	1737(4)	1408(2)	4606(4)	4.4(1)
C(2)	912(4)	698(2)	4130(5)	5.2(2)
C(3)	−104(5)	553(2)	2450(5)	5.3(2)
C(4)	−289(4)	1115(2)	1239(5)	5.2(2)
C(5)	485(4)	1824(2)	1687(5)	5.6(2)
C(6)	1493(5)	1970(2)	3363(5)	5.4(2)
C(7)	2856(4)	1547(2)	6430(4)	4.8(2)
O(8)	3685(3)	2139(2)	6811(3)	5.8(1)
O(9)	2869(4)	1043(2)	7487(3)	6.5(1)
Cl(10)	−1533(1)	937(1)	−868(1)	6.5(1)
N(11)	4506(4)	1466(2)	10739(4)	5.0(1)
C(12)	3894(6)	849(3)	11445(6)	6.4(2)
C(13)	4829(6)	643(3)	13285(6)	7.4(3)
C(14)	5677(6)	1313(3)	14460(6)	7.4(3)
C(15)	7168(5)	1517(3)	14500(6)	6.6(2)
C(16)	7050(5)	1893(3)	12890(6)	6.3(2)
C(17)	6131(5)	1439(3)	11266(6)	6.2(2)
H(2)	111(5)	28(3)	502(6)	6(1)
H(3)	−59(5)	5(3)	214(6)	6(1)
H(5)	33(5)	225(3)	91(6)	6(1)
H(6)	202(5)	246(2)	366(5)	4(1)
H(11A)	421(4)	202(2)	1099(5)	4(1)
H(11B)	401(7)	137(4)	945(7)	9(2)
H(12A)	366(5)	34(3)	1081(5)	5(1)
H(12B)	277(6)	107(3)	1127(7)	7(1)
H(13A)	580(7)	32(4)	1347(7)	9(2)
H(13B)	404(5)	41(3)	1357(6)	6(1)
H(14A)	489(5)	191(3)	1394(5)	5(1)
H(14B)	591(6)	121(3)	1573(7)	8(1)
H(15A)	778(7)	197(4)	1546(8)	9(2)
H(15B)	770(5)	97(2)	1476(5)	5(1)
H(16A)	818(6)	192(3)	1305(7)	7(1)
H(16B)	659(5)	243(3)	1271(6)	5(1)
H(17A)	642(5)	81(2)	1157(5)	4(1)
H(17B)	624(7)	159(4)	1020(8)	9(2)
(b) Hexamethyleneiminium *p*-bromobenzoate, monoclinic form [**2**(**m**)]				
C(1)	846(5)	7856(15)	1320(7)	7.9(6)
C(2)	1420(5)	7505(15)	1620(8)	8.2(6)
C(3)	1790(5)	8800(23)	1550(8)	9.5(7)
C(4)	1617(4)	10615(15)	1230(6)	7.2(5)
C(5)	1067(4)	11067(16)	913(6)	7.2(6)
C(6)	684(4)	9722(15)	977(6)	7.1(5)
C(7)	418(5)	6428(18)	1401(7)	8.4(7)
O(8)	626(3)	4976(11)	1864(5)	9.7(5)
O(9)	−75(4)	6855(13)	1054(7)	9.9(5)
Br(10)	2151(1)	12471(2)	1186(1)	10.3(1)
N(11)	−736(3)	4301(12)	1419(5)	7.2(4)
C(12)	−1300(5)	4969(19)	953(10)	10.1(8)
C(13)	−1764(6)	3682(25)	743(9)	10.8(9)
C(14)	−1731(6)	2092(21)	1388(12)	11.3(10)
C(15)	−1387(5)	407(18)	1355(9)	10.3(8)
C(16)	−780(5)	792(16)	1675(8)	8.6(7)
C(17)	−577(6)	2369(15)	1201(8)	8.6(7)
H(2)	157(5)	613(20)	194(7)	10(4)
H(3)	225(5)	859(20)	183(8)	9(3)
H(5)	96(5)	1245(12)	69(7)	5(3)
H(6)	25(4)	1012(17)	71(7)	7(3)
H(11A)	−70(5)	436(22)	214(8)	11(4)
H(11B)	−49(5)	526(18)	137(8)	10(4)
H(12A)	−139(6)	608(23)	105(9)	12(4)
H(12B)	−120(5)	543(20)	45(8)	11(4)
H(13A)	−208(5)	447(20)	63(8)	10(4)
H(13B)	−176(7)	300(22)	34(10)	12(5)
H(14A)	−217(5)	180(21)	128(8)	9(4)
H(14B)	−166(7)	271(18)	210(9)	11(5)
H(15A)	−149(6)	−71(23)	159(9)	13(5)
H(15B)	−154(5)	24(19)	69(7)	9(4)
H(16A)	−66(6)	135(23)	233(9)	12(4)
H(16B)	−58(6)	−52(25)	180(11)	15(5)
H(17A)	−74(5)	231(15)	63(8)	8(4)
H(17B)	−21(6)	240(15)	122(9)	9(4)
(c) Hexamethyleneiminium *p*-bromobenzoate, orthorhombic form [**2**(**o**)]				
C(1)	4236(8)	1210(3)	8712(9)	2.3(4)
C(2)	3925(9)	1646(3)	9513(12)	3.3(4)
C(3)	4633(9)	2063(3)	9332(11)	3.4(4)
C(4)	5603(10)	2048(4)	8450(13)	4.4(5)
C(5)	5900(10)	1640(4)	7675(13)	4.1(5)
C(6)	5228(9)	1212(3)	7837(9)	2.8(5)
C(7)	3477(9)	763(3)	8822(12)	3.4(5)
O(8)	2703(7)	748(3)	9829(8)	4.2(4)
O(9)	3720(8)	414(3)	7904(9)	5.2(4)
Br(10)	6493(2)	2619(1)	8244(2)	7.5(1)
N(11)	2386(7)	−376(2)	7831(9)	3.0(4)
C(12)	1183(11)	−238(4)	8122(13)	4.1(5)
C(13)	408(9)	−601(4)	9032(14)	3.8(4)
C(14)	492(10)	−1129(3)	8482(12)	4.0(5)
C(15)	1503(10)	−1405(4)	9173(14)	4.3(5)
C(16)	2685(10)	−1239(3)	8636(12)	3.9(5)
C(17)	2969(9)	−713(3)	9009(13)	3.4(4)
H(2)	320(9)	164(4)	1003(16)	3(3)
H(3)	441(13)	238(5)	1000(17)	6(4)
H(5)	672(13)	161(6)	710(18)	7(5)
H(6)	550(11)	92(4)	743(14)	3(3)
H(11A)	246(14)	−56(6)	679(17)	7(4)
H(11B)	285(12)	−7(5)	768(19)	6(3)
H(12A)	91(8)	−13(4)	707(11)	1(2)
H(12B)	122(15)	7(7)	861(20)	8(5)
H(13A)	−51(9)	−44(3)	888(13)	2(2)
H(13B)	55(13)	−59(6)	1015(17)	7(4)
H(14A)	−32(11)	−132(4)	872(15)	4(3)
H(14B)	52(11)	−112(4)	730(14)	4(3)
H(15A)	148(8)	−182(4)	897(14)	2(3)
H(15B)	135(10)	−140(5)	1032(17)	5(4)
H(16A)	281(11)	−131(4)	769(16)	4(3)
H(16B)	319(9)	−142(4)	912(14)	3(3)
H(17A)	263(10)	−61(4)	991(16)	4(3)
H(17B)	379(9)	−69(4)	896(13)	2(2)

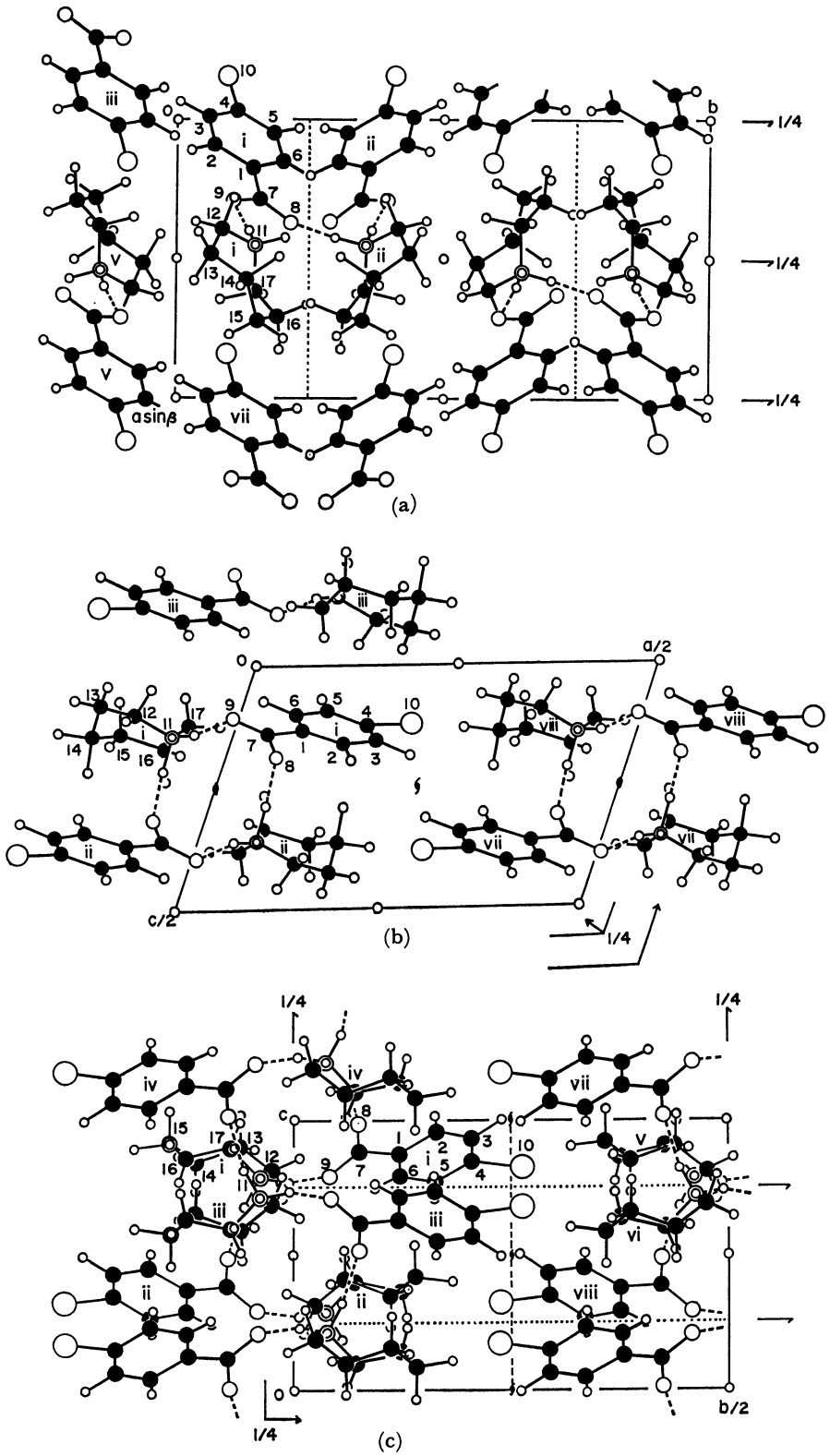

Fig. 1. Projections of the crystal structures and numbering of the non-hydrogen atoms. (a) **1** viewed along c, (b) **2**(**m**) viewed along b, and (c) **2**(**o**) viewed along a. Broken lines show hydrogen bonds.

Symmetry code: for **1**: (i) x, y, z; (ii) x, $1/2-y$, $1/2+z$; (iii) $-x$, $-y$, $-z$; (iv) $-x$, $-y$, $1-z$; (v) $1-x$, $-y$, $2-z$; (vi) $1-x$, $-y$, $3-z$; (vii) $1+x, y, 1+z$; (viii) $x, y, 1+z$; for **2**(**m**): (i) x, y, z; (ii) $-x, y$, $1/2-z$; (iii) $-x$, $2-y$, $-z$; (iv) $-x$, $1-y$. $-z$; (v) x, $1+y$, z; (vi) $-x$, $1+y$, $1/2-z$; (vii) $1/2-x$, $1/2+y$, $1/2-z$; (viii) $1/2+x$, $1/2+y$, z; for **2**(**o**): (i) x, y, z; (ii) $1/2-x$, $-y$, $-1/2+z$; (iii) $1/2+x$, y, $3/2-z$; (iv) $1-x$, $-y$, $2-z$; (v) $1/2-x$, $1/2+y$, z; (vi) $1-x$, $1/2+y$, $3/2-z$; (vii) $1/2+x$, $1/2-y$, $2-z$; (viii) x, $1/2-y$, $-1/2+z$.

Structure Determination and Refinement

The structure of **1** was solved by the symbolic addition procedure and the structures of **2(m)** and **2(o)** by the Patterson method. Refinement was made by block-diagonal least-squares calculations. For **1** all the H atoms were located from a difference Fourier synthesis. Further refinement was carried out including the parameters of the H atoms. The weighting scheme used was $w=1.0$ for $0<|F_o|\leq F_{max}$, and $w=(F_{max}/|F_o|)^2$ for $|F_o|>F_{max}$, where $F_{max}=6.5$.

For **2(m)** and **2(o)**, the coordinates of nine and thirteen H atoms were determined from difference Fourier syntheses at the stages of $R=0.124$ and 0.110, respectively. The positional parameters of the remaining H atoms were calculated by assuming the usual geometry, and were included in the subsequent refinement. The same weighting scheme was used with $F_{max}=16.0$ for **2(m)** and 14.0 for **2(o)**. The final R values for the non-zero reflections were 0.072 for **1**, 0.100 for **2(m)**, and 0.083 for **2(o)**. The final atomic parameters are given in Table 2.[4]

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[5] Computations were carried out at the Okayama University Computer Center. The programs used were SIGM, TANG, HBLS-V, and DAPH.[6]

Results and Discussion

The projections of the crystal structures and the numbering of the atoms are shown in Fig. 1. Geometry of the hydrogen bonds is summarized in Table 3. Bond lengths and angles are given in Table 4.

Crystal Structures. In the crystals of **1**, the base and acid ions are linked together by two kinds of N–H···O hydrogen bonds to form a ribbon along a c glide plane. The type of hydrogen bond is the same as that found in piperazinediylium terephthalate (**3**).[7] The ribbons are stacked along a in alternate succession of the base and acid ions to form a sheet parallel to (010). The molecular arrangement in the sheet is also the same as that in **3**. The doubling of b occurs in **1** because of the loss of molecular symmetry $\bar{1}$ in the base and acid ions.

Table 3. Geometry of hydrogen bonds
Lengths in Å and angles in degrees.

Crystals	**1**	**2(m)**	**2(o)**
Type of hydrogen bonds	Glide	2	2_1
a) Hydrogen bond between base (i) and acid (i)			
N(11)···O(9)	2 686(5)	2.655(14)	2.658(12)
H(11B)···O(9)	1.68(7)	1.73(13)	1.68(16)
N(11)–H(11B)···O(9)	163(6)	168(12)	165(15)
N(11)···O(9)–C(7)	115.1(3)	111 0(9)	120.0(8)
b) Hydrogen bond between base (i) and acid(ii)			
N(11)···O(8)	2.804(5)	2.759(12)	2.769(11)
H(11A)···O(8)	1.79(5)	1.63(15)	1.77(18)
N(11)–H(11A)···O(8)	167(4)	167(13)	163(15)
N(11)···O(8)–C(7)	147.8(3)	128.4(8)	133.1(7)

Table 4. Bond lengths (l/Å) and angles (ϕ/°) with values of e.s.d. in parentheses

	1 (X=Cl)	**2(m)** (X=Br)	**2(o)** (X=B)
C(1)–C(2)	1.400(6)	1.404(18)	1.423(14)
C(2)–C(3)	1.388(7)	1.341(20)	1.414(15)
C(3)–C(4)	1.386(7)	1.392(19)	1.353(16)
C(4)–C(5)	1.375(6)	1.361(16)	1.344(17)
C(5)–C(6)	1.384(7)	1.385(16)	1.413(15)
C(6)–C(1)	1.393(6)	1.430(17)	1.370(14)
C(1)–C(7)	1.505(6)	1.517(18)	1.510(14)
C(7)–O(8)	1.238(5)	1.275(16)	1.244(13)
C(7)–O(9)	1.269(6)	1.234(17)	1.269(14)
C(4)–X(10)	1.732(5)	1.901(11)	1.881(12)
N(11)–C(12)	1.493(7)	1.465(19)	1.462(15)
N(11)–C(17)	1.476(6)	1.489(17)	1.524(14)
C(12)–C(13)	1.507(8)	1.439(25)	1.547(17)
C(13)–C(14)	1.502(9)	1.516(26)	1.525(17)
C(14)–C(15)	1.528(8)	1.483(24)	1.512(16)
C(15)–C(16)	1.534(8)	1.486(20)	1.511(17)
C(16)–C(17)	1.514(7)	1.533(20)	1.514(16)
N(11)–H(11A)	1.03(5)	1.15(15)	1.03(18)
N(11)–H(11B)	1.04(7)	0.94(13)	0.99(16)
C(1)–C(2)–C(3)	120.4(4)	122.2(13)	118.6(9)
C(2)–C(3)–C(4)	119.6(4)	120.3(14)	121.1(10)
C(3)–C(4)–C(5)	120.8(4)	121.1(11)	120.9(11)
C(4)–C(5)–C(6)	119.6(4)	118.3(10)	120.1(11)
C(5)–C(6)–C(1)	121.0(4)	122.2(11)	121.1(10)
C(6)–C(1)–C(2)	118.5(4)	115.5(11)	118.2(9)
C(3)–C(4)–X(10)	120.1(4)	119.8(9)	118.7(9)
C(5)–C(4)–X(10)	119.1(3)	119.1(8)	120.4(9)
C(2)–C(1)–C(7)	119.7(4)	123.4(11)	120.3(9)
C(6)–C(1)–C(7)	121.8(4)	121.0(11)	121.5(9)
C(1)–C(7)–O(8)	119.0(4)	114.1(11)	119.1(9)
C(1)–C(7)–O(9)	116.8(4)	116.9(12)	116.4(9)
O(8)–C(7)–O(9)	124.2(4)	128.9(12)	124.4(10)
N(11)–C(12)–C(13)	117.3(5)	120.9(14)	118.1(10)
C(12)–C(13)–C(14)	116.9(5)	116.2(15)	114.6(10)
C(13)–C(14)–C(15)	114.2(5)	117.4(15)	113.8(10)
C(14)–C(15)–C(16)	115.9(5)	113.7(13)	115.3(10)
C(15)–C(16)–C(17)	116.3(4)	116.0(12)	114.7(10)
C(16)–C(17)–N(11)	111.9(4)	111.9(11)	109.9(9)
C(17)–N(11)–C(12)	117.6(4)	117.7(10)	117.6(8)
H(11A)–N(11)–C(12)	108(3)	105(8)	111(10)
H(11B)–N(11)–C(12)	107(4)	108(8)	109(9)
H(11A)–N(11)–C(17)	111(2)	110(8)	104(10)
H(11B)–N(11)–C(17)	103(4)	112(8)	111(9)

In the crystals of **2(m)**, two pairs of the base and acid ions related by a twofold axis are linked together by two kinds of N–H···O hydrogen bonds. The hydrogen-bonded units are stacked along b in alternate succession of the base and acid ions to form a ribbon. The ribbons related by $\bar{1}$ are held together by van der Waals interactions and dipole-dipole interactions between the acid ions to form a sheet parallel to (100). The sheets are stacked along a by weak interactions.

In **2(o)** all atoms of the acid ion and a center of the base ion occupy positions similar to those of piperidinium *p*-substituted benzoates[1,2] and of pyrrolidinium *p*-substituted benzoates[3] in Pbca, but the position of N

differs by about $c/4$. This difference causes a change in the combination mode of the base and acid ions participating in the hydrogen bonds. In **2**(**o**) base ion (i) donates the hydrogen bonds to acid ions (i) and (ii), while in the others it is base ion (ii) that doantes the hydrogen bonds to the corresponding acid ions, where the symmetry code follows that given in Fig. 1(c) for all the crystals.

For the crystals of **1**, **2**(**m**), and **2**(**o**), all the intermolecular contacts correspond to those expected for the usual van der Waals interactions. The shortest contacts are found between C(7^{i}) and H($11B^{i}$): 2.42(7) Å for **1**, 2.44(13) Å for **2**(**m**) and 2.59(16) Å for **2**(**o**).

Geometry of the Hydrogen Bonds. Irrespective of the type of hydrogen bond, the bond N(11^{i})···O(9^{i}) extending nearly parallel to the long axis of the acid ion is shorter than the other one N(11^{i})···O(8^{ii}) lying nearly perpendicular to the long axis. A notable difference between the two hydrogen bonds is that the former is associated with the nearly tetrahedral C–O···N angle, while in the latter the angle takes a significantly larger value, especially for the glide type.

TABLE 5. THE LEAST-SQUARES PLANES AND DISPLACEMENTS (l/Å) OF THE ATOMS FROM THE PLANES $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

	1 (X=Cl)	**2**(**m**) (X=Br)	**2**(**o**) (X=Br)
(I) Benzene ring			
1:	$0.898X-0.422Y-0.126Z+1.665=0$		
2(**m**):	$0.245X-0.335Y-0.910Z+3.343=0$		
2(**o**):	$-0.538X+0.285Y-0.793Z+7.620=0$		
C(1)[a]	0.011	0.007	0.008
C(2)[a]	−0.004	−0.013	−0.004
C(3)[a]	−0.008	0.021	0.005
C(4)[a]	0.013	−0.022	−0.010
C(5)[a]	−0.005	0.015	0.014
C(6)[a]	−0.007	−0.007	−0.012
C(7)	0.043	−0.049	0.056
O(8)	0.190	−0.288	−0.159
O(9)	−0.100	0.075	0.257
X(10)	0.032	−0.058	0.022
(II) Carboxylate group			
1:	$0.835X-0.538Y-0.111Z+1.860=0$		
2(**m**):	$0.305X-0.471Y-0.828Z+3.829=0$		
2(**o**):	$-0.636X+0.386Y-0.668Z+6.813=0$		
C(1)[a]	−0.001	−0.005	−0.005
C(7)[a]	0.004	0.018	0.017
O(8)[a]	−0.001	−0.006	−0.006
O(9)[a]	−0.001	−0.007	−0.006
(III) Hexamethyleneimine ring			
1:	$0.616X-0.762Y-0.201Z+3.560=0$		
2(**m**):	$0.404X-0.211Y-0.890Z+3.610=0$		
2(**o**):	$0.230X+0.294Y+0.928Z-6.571=0$		
N(11)[a]	−0.058	−0.034	−0.013
C(12)[a]	0.052	0.026	0.010
C(15)[a]	−0.059	−0.026	−0.009
C(16)[a]	0.068	0.035	0.012
C(13)	0.118	0.072	0.235
C(14)	−0.709	−0.682	−0.605
C(17)	0.765	0.762	0.808
Dihedral angle (ϕ/°) between planes (I) and (II)	7.6	9.8	10.9

a) Used for calculation of the planes.

Molecular Structures. *(a) Benzoate Ions*: The benzene rings and carboxylate groups are planar within experimental errors (Table 5). The C(1)–C(7)–O(9) angles remain constant in these crystals, the O(9) participating in shorter hydrogen bond. The corresponding angles in the related compounds also take a restricted range of values, 116.1—117.4°.[1-3,7] On the other hand, in **2**(**m**) the C(1)–C(7)–O(8) angle is smaller and the O(8)–C(7)–O(9) angle larger than the corresponding angles in **1** and **2**(**o**). A similar opening of the O–C–O angle has been observed in trifluoroacetic acid.[8] Shortening of the C(7)–O(9) bond in **2**(**m**) can be explained in terms of the *s*-character of the C(7) atom,[9] the C(7)–O(8) bond length in **2**(**m**) being unexpectedly large.

TABLE 6. THE TORSION ANGLES (ϕ/°) IN THE HEXAMETHYLENEIMINE RINGS

		1	**2**(**m**)	**2**(**o**)
χ_0	C(17)–N(11)–C(12)–C(13)	41.3	37.9	29.0
χ_1	N(11)–C(12)–C(13)–C(14)	36.4	33.2	46.3
χ_2	C(12)–C(13)–C(14)–C(15)	−81.8	−79.5	−83.4
χ_3	C(13)–C(14)–C(15)–C(16)	68.6	71.3	68.3
χ_4	C(14)–C(15)–C(16)–C(17)	−54.0	−58.3	−60.4
χ_5	C(15)–C(16)–C(17)–N(11)	70.8	72.7	79.3
χ_6	C(16)–C(17)–N(11)–C(12)	−86.7	−81.8	−84.4

(b) Hexamethyleneiminium Ions: Let $A(i)$ be the non-hydrogen atoms in the rings, where i is an integer from 11 to 17 and $A(i+7)=A(i)$ in the present numbering system. In each crystal of **1**, **2**(**m**) and **2**(**o**), the planarity through the four atoms $A(i)$, $A(i+1)$, $A(i+4)$, and $A(i+5)$ is the best when $i=11$ (Table 5). In each ring the C(14) and C(17) deviate from the plane in opposite directions. The torsion angles around each bond in the rings show the twist-chair conformation[10] (Table 6). The hexamethyleneimine rings in **1**, **2**(**m**), and **2**(**o**) take similar conformations irrespective of the crystallographic environment of the rings. For cycloheptane the conformation has been estimated to be more stable than the chair conformation by 5.9 kJ mol^{-1}.[10]

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