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Study of Short Hydrogen Bonds. I. Structures of 4-Methylpiperidinium Hydrogen Bis(*p*-methylbenzoate) and Piperidinium Hydrogen Bis(*p*-methylbenzoate)

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(Received October 17, 1985)

The crystal structures of 4-methylpiperidinium hydrogen bis(*p*-methylbenzoate) **1** and piperidinium hydrogen bis(*p*-methylbenzoate) **2** have been determined by X-ray diffraction method. Crystal data: **1**, monoclinic, $P2_1/n$ (No. 14), a=19.260(2), b=8.0061(5), c=14.065(1) Å, β=94.391(7)°, V=2162.5(3) Å^3, Z=4, D_x=1.141 g cm^{-3}; **2**, orthorhombic, $Pcan$ (No. 60), a=10.292(1), b=25.248(4), c=7.763(2) Å, V=2017.2(5) Å^3, Z=4, D_x=1.177 g cm^{-3}. Final R values for **1** and **2** are 0.088 and 0.065 for 3446 and 1510 unique reflections, respectively. In both crystals the piperidinium cations and the hydrogen bis(benzoate) anions are held together by two kinds of N-H···O hydrogen bonds. The structure of **2** is disordered around a two-fold axis. Two benzoate residues in the anions are linked by the very short O-H···O hydrogen bonds; in **1** asymmetric [O···O 2.505(3), O-H 1.07(5), H···O 1.48(5) Å, O-H···O 158(5)°]; in **2** crystallographically symmetric [O···O related by the two-fold axis 2.473(4), O···H 1.25(5) Å, O···H···O 163(5)°]. The short hydrogen bonds in hydrogen bis(carboxylate) anions are discussed with reference to the crystal structures of **1** and **2**.

Very short hydrogen bonds with O···O distances between 2.4 and 2.5 Å are of interest in connection with the nature of hydrogen bonding.[1] In general, hydrogen bis(carboxylate) anions tend to form the very short hydrogen bonds in the crystals.[1—29] In many cases the anions have crystallographic symmetry $\bar{1}$ or 2,[1—19] but it is difficult to determine whether the hydrogen atoms participating in the hydrogen bonds are situated at the midpoint of the two oxygen atoms or not, because either ordered or disordered structure involving the hydrogen atoms makes possible to account for the observations. The genuine symmetry has been proposed for some crystallographically symmetric hydrogen bonds,[7,9,13] but the range of the O···O distances can not be differentiated from those found in crystallographically asymmetric hydrogen bonds. Therefore, it is desirable to examine more throughly the geometric details of the symmetric hydrogen bonds and the asymmetric ones. In the present work crystals of **1** and **2**, which contain the same anions but have different symmetry, have been studied.

Experimental

Experimental details for **1** and **2** are listed in Table 1. The compounds were prepared by the same procedure as reported previously.[30] Systematic absences were determined from the Weissenberg photographs. The intensities were collected on a Rigaku AFC-5 four-circle diffractometer equipped with rotating anode using Ni filtered Cu $K\alpha$ (λ=1.5418 Å) with ω—2θ scan method [scan speed 4° min^{-1} in ω, scan range $\Delta 2\theta$=1.2°+0.15° tanθ]. Background was measured for 4 s on either side of peak. Three standard reflections were recorded after every 57 reflections; their fluctuation was within 3% in F. Lorentz and polarization correction were applied,

Table 1. Crystal Data and Experimental Details

	1	2
Chemical formula	$C_6H_{14}N^+\cdot C_{16}H_{15}O_4^-$	$C_5H_{12}N^+\cdot C_{16}H_{15}O_4^-$
Formula weight	371.48	357.45
Mp(θ_m/°C)	95—98 decomposed	111—113 decomposed
Morphology	Prismatic **b**	Prismatic **c**
Solvent for crystallization	Toluene	Benzene
Space group	$P2_1/n$ (No. 14)	$Pcan$ (No. 60)
Systematic absences	$h+l$ odd for $h0l$ k odd for $0k0$	l odd for $0kl$ h odd for $h0l$ $h+k$ odd for $hk0$
a/Å	19.260(2)	10.292(1)
b/Å	8.0061(5)	25.248(4)
c/Å	14.065(1)	7.763(2)
β/°	94.391(7)	
V/Å^3	2162.5(3)	2017.2(5)
Z	4	4
D_x/g cm^{-3}	1.141	1.177
F(000)	800	768
Size of specimen/mm	0.30×0.25×0.25	0.30×0.20×0.40
μ(Cu $K\alpha$)/mm^{-1}	0.59	0.62
$2\theta_{max}$/°	125	120
No. of unique reflections	3446	1510
No. of reflections with $\lvert F_o\rvert$>1.0$\sigma(F_o)$	3008	1387

but no absorption correction.

Structure Determination and Refinement

The structure of **1** was solved by *MULTAN* 78, and refined by block-diagonal least-squares method. All the unique reflections within $2\theta_{\max}$ were used for the refinement. The value minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1/[\sigma(F_o)^2+0.0006|F_o|+0.0040|F_o|^2]$ for $|F_o|>0$, and $w=0.608$ for $|F_o|=0$. All the hydrogen atoms were located on a difference Fourier map. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. Correction for the secondary extinction was applied for the strongest 26 reflections according to the equation: $I_{\mathrm{corr}}=I_o(1+gI_c)$, where $g=2.74\times10^{-5}$. Final R was 0.088 for 3446 unique reflections. In the final difference Fourier map $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ were +0.20 and −0.23 e Å^{-3}, respectively.

For **2**, orientation and position of the anion were found from a three-dimensional Patterson map. The non-hydrogen atoms of the cation were found by successive application of Fourier and difference Fourier syntheses. Since the space group is *Pcan* and $Z=4$, a twist form having a two-fold symmetry was assumed for the cation at first. After refinement by block-diagonal least-squares method, a difference Fourier map showed some peaks in the region of the cation, which could not be explained as those of the hydrogen atoms. Thus, the conformation of the cation was changed to a chair form, and a disordered structure around a two-fold axis was assumed. All the hydrogen atoms were located on a difference Fourier map. Full-matrix least-squares calculations were performed, the N-C, C-C, and N-H lengths of the cation being restrained to 1.51, 1.53, and 1.00 Å, respectively. The positional parameters of the hydrogen atoms attached to the carbon atoms of the cation were fixed. The other hydrogen atoms were refined isotropically and the non-hydrogen atoms anisotropically using 1428 non-zero reflections. The $\sum w(|F_o|-|F_c|)^2$ was minimized, where $w=1/\sigma(F_o)^2$. The extinction correction was applied with $g=2.49\times10^{-5}$ for the strongest 12 reflections. Final R was 0.065 for 1510 unique reflections. The $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ were +0.23 and −0.30, respectively.

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.31) Programs used were *MULTAN* 78,32) *RSSFR*-5,33) *HBLS*-V,34) *FMLS*,34) modified version of *CRLS*,35) *DAPH*,34) *MOLCON*,36) and *ORTEP*.37) Computations were carried out at Okayama University Computer Center.

Results and Discussion

The final atomic parameters for **1** and **2** are listed in Table 2.38) The thermal ellipsoids of the molecules are shown in Fig. 1 with numbering of the atoms, and the stereo views of the crystal structures in Fig. 2. Bond lengths and angles are listed in Table 3. The geometries of the hydrogen bonds are summarized in Table 4.

Crystal Structure. In the crystal of **1**, the O(10) and O(20) atoms of the hydrogen bis(carboxylate) anion are linked together by an asymmetric O-H···O hydrogen bond. The O(19) of the anion accepts two hydrogen bonds from N(21) and N(21$^{\mathrm{ii}}$) to form a

Table 2. Final Atomic Parameters (Positional ×10^4) of the Non-Hydrogen Atoms with e.s.d.'s in Parentheses

	x	y	z	B_{eq}/Å^2
4-Methylpiperidinium hydrogen bis(p-methylbenzoate) (**1**)				
C(1)	4857(1)	5571(4)	2856(2)	5.6(1)
C(2)	5386(1)	4970(5)	3501(2)	6.2(1)
C(3)	6024(1)	4594(6)	3173(3)	7.2(2)
C(4)	6164(2)	4808(6)	2242(3)	7.6(2)
C(5)	5636(2)	5409(6)	1607(3)	8.0(2)
C(6)	4986(2)	5779(5)	1920(3)	7.3(2)
C(7)	4159(1)	5995(4)	3172(2)	5.5(1)
C(8)	6863(2)	4377(8)	1899(4)	10.9(3)
O(9)	3686(1)	6484(4)	2616(2)	7.9(1)
O(10)	4090(1)	5812(3)	4080(1)	6.1(1)
C(11)	1836(1)	4762(4)	5008(2)	5.3(1)
C(12)	1809(2)	5608(5)	5854(2)	6.6(2)
C(13)	1246(2)	5393(5)	6417(2)	7.3(2)
C(14)	709(2)	4326(5)	6124(2)	6.5(2)
C(15)	741(2)	3501(5)	5267(2)	6.9(2)
C(16)	1295(2)	3706(5)	4707(2)	6.2(1)
C(17)	2436(1)	5016(4)	4404(2)	5.2(1)
C(18)	97(2)	4068(6)	6724(3)	8.8(2)
O(19)	2443(1)	4267(3)	3616(1)	5.75(9)
O(20)	2914(1)	5991(3)	4721(2)	6.7(1)
N(21)	2241(1)	6020(3)	1902(2)	5.8(1)
C(22)	2424(2)	4743(5)	1181(2)	6.5(2)
C(23)	2064(2)	5107(5)	232(2)	7.4(2)
C(24)	1285(2)	5229(5)	270(3)	7.2(2)
C(25)	1112(2)	6519(5)	1019(3)	7.5(2)
C(26)	1481(2)	6145(5)	1972(2)	6.6(2)
C(27)	911(3)	5609(8)	−717(4)	12.0(3)
Piperidinium hydrogen bis(*p*-methylbenzoate) (**2**)				
C(1)	1549(2)	1320.3(8)	2605(2)	4.67(9)
C(2)	2510(2)	1553.1(8)	3602(3)	5.4(1)
C(3)	2474(2)	2086.5(8)	3961(3)	5.8(1)
C(4)	1492(2)	2407.2(8)	3362(2)	5.5(1)
C(5)	525(2)	2174.5(9)	2372(3)	5.7(1)
C(6)	557(2)	1639.8(9)	1989(2)	5.3(1)
C(7)	1568(2)	745.7(9)	2182(3)	5.5(1)
C(8)	1473(3)	2992.6(9)	3741(4)	7.8(1)
O(9)	734(1)	550.7(6)	1237(2)	6.86(8)
O(10)	2503(1)	478.4(6)	2841(2)	7.34(9)
N(11)a)	−1536(3)	−4(3)	1941(4)	6.2(2)
C(12)b)	−2194(3)	−500(1)	2589(4)	8.4(2)
C(13)a)	−3635(5)	−509(2)	2103(8)	8.9(3)
C(14)a)	−4236(4)	−12(14)	2899(20)	8.7(6)
C(15)a)	−3563(5)	463(2)	2058(7)	7.7(3)
C(16)b)	−2194(3)	500(1)	2411(4)	8.4(2)

a) Occupancy factor was assumed to be 0.5. b) C(12) and C(16) were related with each other by the two-fold axis, and the refinement was made as a single atom at the position of C(12).

Table 3. Bond Lengths (*l*/Å) and Bond Angles (*ϕ*/°) with e.s.d.'s in Parentheses

4-Methylpiperidinium hydrogen bis(*p*-methylbenzoate) (**1**)			
C(1)–C(2)	1.397(5)	C(15)–C(16)	1.384(6)
C(2)–C(3)	1.378(6)	C(11)–C(16)	1.383(5)
C(3)–C(4)	1.368(6)	C(11)–C(17)	1.500(4)
C(4)–C(5)	1.387(6)	C(14)–C(18)	1.515(6)
C(5)–C(6)	1.390(6)	C(17)–O(19)	1.261(4)
C(1)–C(6)	1.368(5)	C(17)–O(20)	1.262(4)
C(1)–C(7)	1.487(4)	N(21)–C(22)	1.501(5)
C(4)–C(8)	1.505(8)	C(22)–C(23)	1.485(6)
C(7)–O(9)	1.219(4)	C(23)–C(24)	1.509(6)
C(7)–O(10)	1.302(4)	C(24)–C(25)	1.530(6)
C(11)–C(12)	1.374(5)	C(25)–C(26)	1.499(6)
C(12)–C(13)	1.401(6)	N(21)–C(26)	1.478(5)
C(13)–C(14)	1.380(6)	C(24)–C(27)	1.544(7)
C(14)–C(15)	1.380(6)		
C(6)–C(1)–C(2)	119.3(3)	C(14)–C(15)–C(16)	121.9(4)
C(1)–C(2)–C(3)	118.8(4)	C(11)–C(16)–C(15)	119.6(4)
C(2)–C(3)–C(4)	122.6(4)	C(12)–C(11)–C(17)	120.4(3)
C(3)–C(4)–C(5)	118.1(4)	C(16)–C(11)–C(17)	120.3(3)
C(4)–C(5)–C(6)	120.2(4)	C(13)–C(14)–C(18)	121.0(4)
C(1)–C(6)–C(5)	120.9(4)	C(15)–C(14)–C(18)	120.7(4)
C(2)–C(1)–C(7)	121.0(3)	C(11)–C(17)–O(19)	119.6(3)
C(6)–C(1)–C(7)	119.6(3)	C(11)–C(17)–O(20)	117.2(3)
C(3)–C(4)–C(8)	121.7(4)	O(19)–C(17)–O(20)	123.2(3)
C(5)–C(4)–C(8)	120.2(4)	C(26)–N(21)–C(22)	112.1(3)
C(1)–C(7)–O(9)	122.0(3)	N(21)–C(22)–C(23)	110.9(3)
C(1)–C(7)–O(10)	115.5(3)	C(22)–C(23)–C(24)	112.2(3)
O(9)–C(7)–O(10)	122.5(3)	C(23)–C(24)–C(25)	109.7(3)
C(16)–C(11)–C(12)	119.3(3)	C(24)–C(25)–C(26)	111.6(3)
C(11)–C(12)–C(13)	120.7(4)	N(21)–C(26)–C(25)	111.0(3)
C(12)–C(13)–C(14)	120.1(4)	C(23)–C(24)–C(27)	112.2(4)
C(13)–C(14)–C(15)	118.3(4)	C(25)–C(24)–C(27)	112.0(4)
Piperidinium hydrogen bis(*p*-methylbenzoate) (**2**)			
C(1)–C(2)	1.387(3)	C(7)–O(9)	1.232(3)
C(2)–C(3)	1.376(3)	C(7)–O(10)	1.282(3)
C(3)–C(4)	1.376(3)	N(11)–C(12)	1.510(8)
C(4)–C(5)	1.388(3)	C(12)–C(13)	1.530(7)
C(5)–C(6)	1.383(3)	C(13)–C(14)	1.53(4)
C(1)–C(6)	1.386(3)	C(14)–C(15)	1.53(4)
C(1)–C(7)	1.488(3)	C(15)–C(16)	1.438(6)
C(4)–C(8)	1.507(4)	N(11)–C(16)	1.487(8)
C(6)–C(1)–C(2)	118.1(2)	C(1)–C(7)–O(9)	120.8(2)
C(1)–C(2)–C(3)	120.6(2)	C(1)–C(7)–O(10)	115.8(2)
C(2)–C(3)–C(4)	121.8(2)	O(9)–C(7)–O(10)	123.4(2)
C(3)–C(4)–C(5)	117.7(2)	C(16)–N(11)–C(12)	115.1(5)
C(4)–C(5)–C(6)	121.0(2)	N(11)–C(12)–C(13)	111.4(4)
C(1)–C(6)–C(5)	120.8(2)	C(12)–C(13)–C(14)	106(2)
C(2)–C(1)–C(7)	121.8(2)	C(13)–C(14)–C(15)	107(2)
C(6)–C(1)–C(7)	120.1(2)	C(14)–C(15)–C(16)	114(2)
C(3)–C(4)–C(8)	121.4(2)	N(11)–C(16)–C(15)	110.1(4)
C(5)–C(4)–C(8)	120.9(2)		

Table 4. Geometries of Hydrogen Bonds in **1** and **2**[a] (*l*/Å, *ϕ*/°)

4-Methylpiperidinium hydrogen bis(*p*-methylbenzoate) (**1**)			Piperidinium hydrogen bis(*p*-methylbenzoate) (**2**)		
(I)	O(10)···O(20)	2.505(3)	(I)	O(10)···O(10$^{\mathrm{ii}}$)	2.473(4)
	O(10)–H(10)	1.07(5)		O(10)···H(10)	1.25(5)
	H(10)···O(20)	1.48(5)		O(10)···H(10)···O(10$^{\mathrm{ii}}$)	163(5)
	O(10)–H(10)···O(20)	158(5)			
(II)	N(21)···O(19)	2.791(4)	(II)	N(11)···O(9$^{\mathrm{ii}}$)	3.060(7)
	N(21)–H(21B)	1.13(4)		N(11)–H(11A)	1.00(6)
	H(21B)···O(19)	1.71(4)		H(11A)···O(9$^{\mathrm{ii}}$)	2.09(6)
	N(21)–H(21B)···O(19)	159(3)		N(11)–H(11A)···O(9$^{\mathrm{ii}}$)	162(5)
(III)	N(21$^{\mathrm{ii}}$)···O(19)	2.780(4)	(III)	N(11$^{\mathrm{iv}}$)···O(9)	2.945(7)
	N(21$^{\mathrm{ii}}$)–H(21A$^{\mathrm{ii}}$)	0.91(4)		N(11$^{\mathrm{iv}}$)–H(11B$^{\mathrm{iv}}$)	1.00(7)
	H(21A$^{\mathrm{ii}}$)···O(19)	1.88(4)		H(11B$^{\mathrm{iv}}$)···O(9)	2.19(7)
	N(21$^{\mathrm{ii}}$)–H(21A$^{\mathrm{ii}}$)···O(19)	174(4)		N(11$^{\mathrm{iv}}$)–H(11B$^{\mathrm{iv}}$)···O(9)	131(5)

a) Symmetry code: for **1**, (i) x, y, z; (ii) $1/2-x, -1/2+y, 1/2-z$; for **2**, (i) x, y, z; (ii) $x, -y, 1/2-z$; (iii) $-x, y, 1/2+z$; (iv) $-x, -y, -z$.

ribbon along a two-fold screw axis. The ribbons related by a center of symmetry form a sheet along the [101] by van der Waals interactions. The sheets related by an *n* glide plane are stacked along the [10$\bar{1}$] to form the $P2_1/n$ structure. Crystals of many acid salts[9,21,22,24,28] with the asymmetric hydrogen bond adopt this space group.

The structure of **2** is disordered around a two-fold axis. This disordered structure adopts the same space group as potassium hydrogen bis(*p*-methoxybenzoate)[5] [*Pcan*, $Z=4$, $a=7.05(7)$, $b=35.77(10)$, $c=6.16(6)$, O···O 2.48(2) Å]. The O···O distances in them are equal to within the experimental errors. The disordered structure may be split into two fundamental structures: types *A* and *B*, by eliminating the two-fold axis, resulting in two possible N–H···O hydrogen-bond systems as shown in Fig. 3. The center of symmetry is retained in the type *A*, while the *c* glide plane is retained in the type *B*. This means that the elimination of the two-fold axis gives rise to the descent of the space group to its maximal subgroups, $P2_1/a$ for the type *A* and $Pca2_1$ or $Pc2_1n$ for the type *B*. In both cases the environments of the O(9) and O(9$^{\mathrm{ii}}$) are different. For the type *A*, the O(9) and O(9$^{\mathrm{ii}}$) accept hydrogen bonds from N(11$^{\mathrm{iv}}$) and N(11), respectively, in the different way. For the type *B*, only the O(9$^{\mathrm{ii}}$) accepts two kinds of hydrogen bonds from N(11) and N(11$^{\mathrm{iii}}$). Thus, the hydrogen bond O(10)···H(10)···O(10$^{\mathrm{ii}}$) is not the "centered,"[1] but the disordered. In fact, though H(10) was found on the two-fold axis, the peak in the difference Fourier map was as low as 0.21 eÅ^{-3}. The O···O distance is significantly shorter than that in **1**, probably depending on their crystallographic symmetry, because the same trend is also seen in ammonium hydrogen bis(acetate)[6] [2.474(6) Å for $\bar{1}$, 2.517(4) Å for asymmetric] and in potassium hydrogen

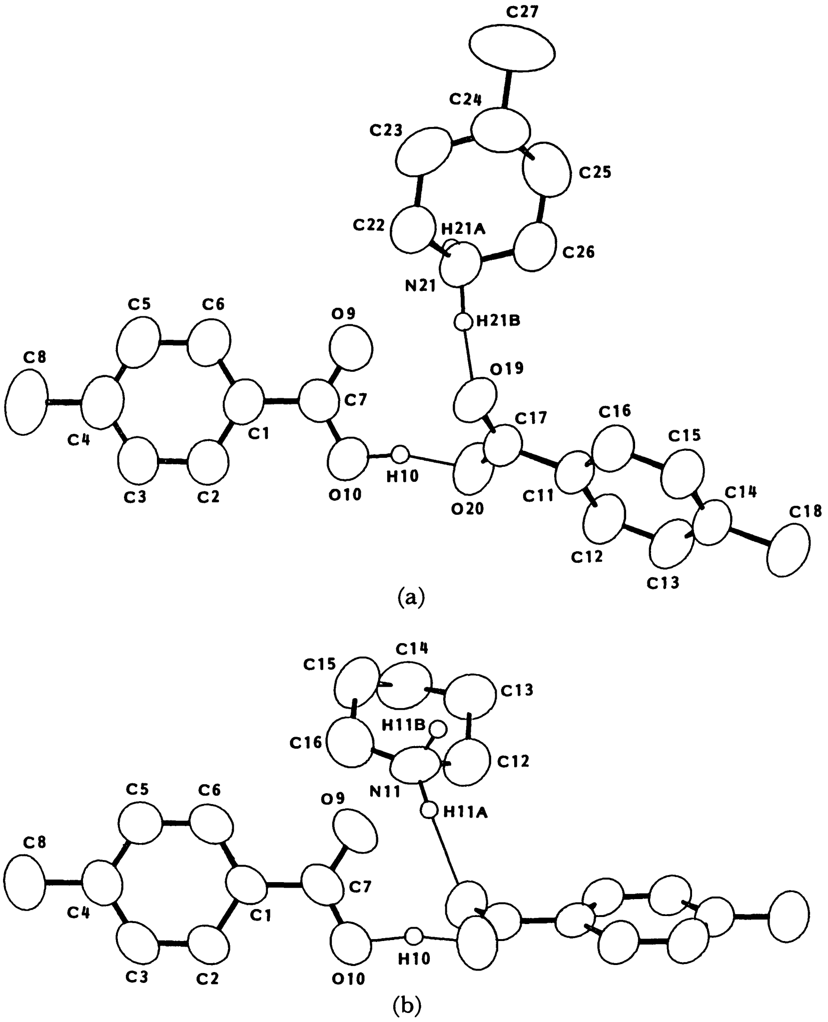


Fig. 1. Views of the molecules **1** (a) and **2** (b) with numbering of the atoms. The hydrogen atoms attached to the carbon atoms are omitted. Ellipsoids of 50% probability are used for the non-hydrogen atoms; the hydrogen atoms are represented as spheres equivalent to B=1.0 Å^2. The hydrogen bonds are shown by thin lines.

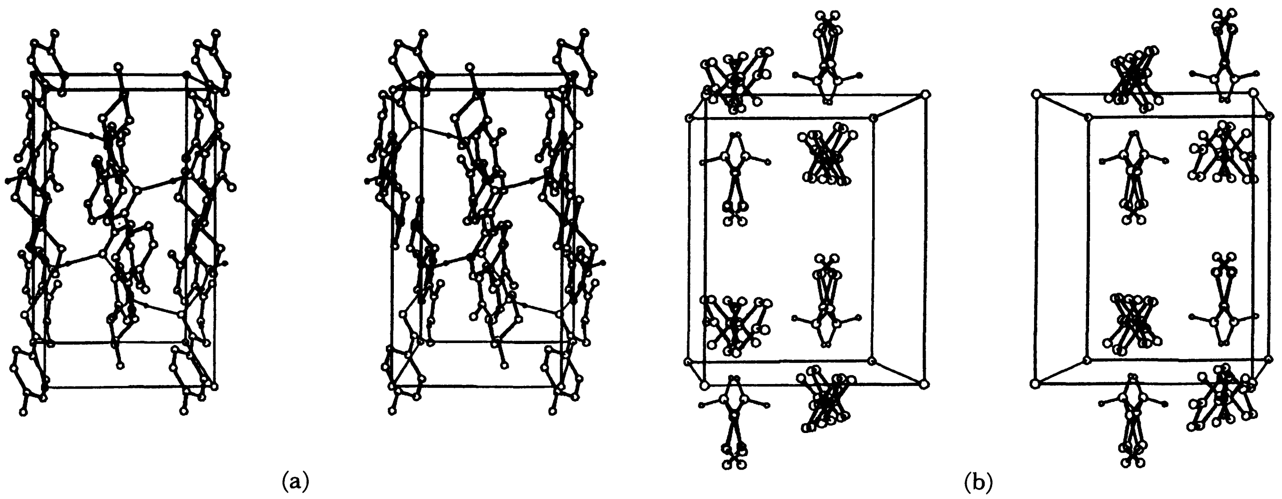
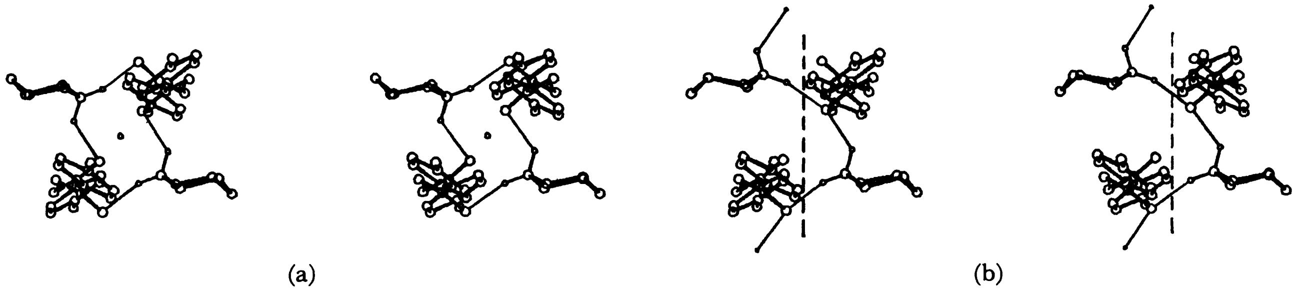


Fig. 2. Stereo views of molecular packing. (a) For **1**, the **a** axis points onto the plane of the paper, the **b** axis left to right, and the **c** axis upwards. The hydrogen bonds are shown by thin lines. (b) The disordered structure for **2**. The **a** axis points upwards, the **b** axis onto the plane of the paper, and the **c** axis left to right. Only the molecular arrangement around the two-fold axes at y=0 is shown. See Fig. 3 for the hydrogen bonds.



(a) (b)

Fig. 3. Two possible N-H···O hydrogen-bond systems in **2**. The hydrogen bonds are shown by thin lines. (a) Type *A* with the center of symmetry; (b) type *B* with the glide plane.

Table 5. The O···O Distances in Crystallographically Symmetric Hydrogen Bonds

Compound	Space group	Symmetry of anion	Radiation a)	O···O (l/Å)
$\mathrm{KH(C_6H_5COO)_2}$ 3)	$C2/c$	$\bar{1}$	X	2.51(4)
$\mathrm{NH_4H[CH_2(COO)_2]}$ 12)	$C2/c$	$\bar{1}$	X	2.488(3)
		2		2.476(3)
$\mathrm{KH(}p\mathrm{\text{-}MeOC_6H_4COO)_2}$ 5)	$Pbcn$	2	X	2.48(2)
$\mathrm{NaH(CH_3COO)_2}$ 11)	$Ia3$	2	N	2.48(1)
$\mathrm{NH_4H(CH_3COO)_2}$ 6)	$P\bar{1}$	$\bar{1}$	X	2.474(6)
$\mathrm{KH(CHOHCOO)_2}$ 13)	$P\bar{1}$	$\bar{1}$	N	2.474(8)
				2.440(8)
$\mathrm{C_5H_{10}NH_2H(}p\mathrm{\text{-}MeC_6H_4COO)_2}$ b)	$Pcan$	2	X	2.473(4)
$\mathrm{KHS(CH_3COO)_2}$ 15)	$P2/c$	$\bar{1}$	X	2.47(1)
$\mathrm{RbHS(CH_3COO)_2}$ 15)	$P2/c$	$\bar{1}$	X	2.46(2)
$\mathrm{KH(CCl_3COO)_2}$ 10)	$I\bar{4}2d$	2	X	2.46(2)
$\mathrm{NH_4H(C_6H_5COO)_2}$ 16)	$C2/c$	$\bar{1}$	X	2.46(1)
$\mathrm{KH(}p\mathrm{\text{-}FC_6H_4COO)_2}$ 19)	$C2/c$	$\bar{1}$	X	2.460(4)
$\mathrm{KH(}p\mathrm{\text{-}HOC_6H_4COO)_2}$ 4)	$P2/c$	$\bar{1}$	X	2.458(6)
$\mathrm{NH_4H(CCl_3COO)_2}$ 14)	$I\bar{4}2d$	2	X	2.454(6)
$\mathrm{RbHO(CH_2COO)_2}$ 9)	$I\bar{4}2d$	2	N	2.449(3)
$\mathrm{KH(CHBr_2COO)_2}$ 17)	$Pbcn$	$\bar{1}$	X	2.44(3)
$\mathrm{KH(CF_3COO)_2}$ 7)	$I2/a$	$\bar{1}$	N	2.437(4)
$\mathrm{KH(}m\mathrm{\text{-}ClC_6H_4COO)_2}$ 8)	$C2/c$	$\bar{1}$	X	2.437(6)
$\mathrm{RbH(CHBr_2COO)_2}$ 18)	$P2_1/n$	$\bar{1}$	X	2.43(2)

a) X denotes X-Ray and N neutron. b) This work.

meso-tartrate13) [2.440(8) and 2.474(8) Å for $\bar{1}$, 2.521(5) Å for asymmetric].

Molecular Structure. For **1** the anion is composed of ionized and neutral residues. The C-O and C=O bond lengths of the neutral residue are close to those in some benzoic acids,39,40) which display no disorder in the carboxyl groups. The C(17)-O(19) bond in the ionized residue is longer than 1.22—1.25 Å found in acidic salts of alkaline metals in which the corresponding O atoms accept no hydrogen bond. The piperidinium ring takes a chair conformation as in piperidinium benzoates:41,42) N(21) and C(24) deviate by −0.644 and 0.661 Å from the plane through C(22), C(23), C(25), and C(26). The methyl group is equatorially bonded to the ring: the torsion angle C(22)-C(23)-C(24)-C(27)=180.0 (4)° and C(26)-C(25)-C(24)-C(27)=−179.6(4)°.

For **2** the bond lengths of C(7)-O(9) and C(7)-O(10) correspond to the average for the ionized and neutral residues because of disordering. The piperidinium ring takes a chair conformation as in **1**.

The Short Hydrogen Bonds of Hydrogen Bis(carboxylate) Anions. The O···O distances for crystallographically symmetric hydrogen bonds are listed in Table 5, where the H···O distances and the O···H···O angles are not given, because the hydrogen atom is assumed to lie on $\bar{1}$ or 2 in most of the structure analyses. The geometries of the hydrogen bonds for some asymmetric hydrogen bonds are shown in Table 6. It is seen from Tables 5 and 6 that (i) the intermolecular O···O distances range from 2.51 to 2.43 Å and 2.57 to 2.44 Å for the symmetric and asymmetric hydrogen bonds, respectively, (ii) the lower limit of the O···O distances is expected to be about 2.4 Å for both the symmetric and asymmetric bonds as shown for general O-H···O hydrogen bonds,43) and (iii) for the ionized residues the C(17)-O(20) bond participating in the hydrogen bond is longer than C(17)-O(19). The effects of a decrease in the O···O distance can be confirmed from Table 6: (i) the O-H distance is increased, while the H···O distance is decreased,43,44) (ii) the C(7)-O(10) length in the neutral residue is decreased while the C(7)=O(9) length is increased, and (iii) difference in the bond lengths of C(7)-O(10) and C(17)-O(20) is

Table 6. Geometries of Asymmetric Hydrogen Bonds[a)] (l/Å, ϕ/°)

Compound	Space group	Radiation	O···O	O–H	H···O	O–H···O	C(7)=O(9)	C(7)–O(10)	C(17)–O(19)	C(17)–O(20)
(I)	$P\bar{1}$	N(295K)	2.571(1)	1.036(1)	1.537(1)	176.2(1)	1.210(1)	1.307(1)	1.245(1)	1.249(1)
		N(120K)	2.566(2)	1.036(2)	1.531(2)	176.8(2)	1.215(1)	1.308(1)	1.247(1)	1.253(1)
(II)	$P2_1/n$	X	2.563(2)	0.97(3)	1.61(3)	167(3)	1.203(2)	1.304(2)	1.237(2)	1.260(2)
(III)	$P\bar{1}$	N	2.521(5)	1.019(8)	1.514(8)	168.7(7)	1.206(5)	1.315(5)	1.256(5)	1.260(5)
(IV)	$P2_1/n$	X	2.505(3)	1.07(5)	1.48(5)	158(5)	1.219(4)	1.302(4)	1.261(4)	1.262(4)
(V)	$P2_1/c$	N	2.498(3)	1.107(4)	1.392(4)	177.6(3)	1.207(2)	1.291(2)	1.226(3)	1.275(3)
(VI)	$P2_1/c$	X	2.486(2)	1.04(3)	1.47(3)	166(3)	1.233(2)	1.290(2)	1.231(2)	1.289(2)
(VII)	Cc	X	2.482(2)	1.25(2)	1.31(2)	152(2)	1.220(2)	1.297(2)	1.219(2)	1.280(2)
(VIII)	$P2_1/c$	N	2.476(2)	1.152(3)	1.328(3)	174.2(3)	1.221(2)	1.294(2)	1.230(2)	1.275(2)
(IX)	$P2_1/c$	X	2.462(3)	1.01(5)	1.47(5)	165(5)	1.223(4)	1.286(4)	1.235(4)	1.277(4)
(X)	$I2/c$	X	2.450(2)	1.13(3)	1.33(3)	171(3)	1.226(2)	1.285(2)	1.217(2)	1.290(2)
(XI)	$Pbca$	N(295K)	2.444(2)	1.163(3)	1.281(3)	179.4(3)	1.217(1)	1.260(2)	1.229(1)	1.260(2)
		N(120K)	2.437(1)	1.167(1)	1.270(1)	179.3(1)	1.226(1)	1.276(1)	1.235(1)	1.276(1)

a) The numbering of the atoms corresponds to that of **1**. (I) $NaHC_2O_4 \cdot H_2O$.[23,29)] (II) $LiHO(CH_2COO)_2$.[22)] (III) $KH(CHOHCOO)_2$.[13)] (IV) $CH_3C_5H_9\ NH_2H(p\text{-}MeC_6H_4COO)_2$ (This work). (V) $KH(CHCl_2COO)_2$.[24)] (VI) $LiH[C_4H_8(COO)_2]$.[28)] (VII) $KH(OOCCH_2CHOHCOO) \cdot H_2O$[26)] (VIII) $KHO(CH_2COO)_2$.[9)] (IX) $NaHO(CH_2COO)_2$.[21)] (X) $NH_4HO(CH_2COO)_2$.[25)] (XI) $KH(HCOO)_2$.[27)]

decreased, as for the lengths of C(7)–O(9) and C(17)–O(19). These tendencies show that with a decrease in the O···O distance, the hydrogen atom comes closer to the midpoint.[43,44)] However, the "asymmetric-centered"[1)] hydrogen bond has never been reported. Even at the O···O distance of 2.388(4) Å the intramolecular hydrogen bond in lithium hydrogen phthalate is the "asymmetric-noncentered."[45)] Thus, the bond symmetry should be introduced by a crystallographic symmetry.[46)]

For the symmetric hydrogen bonds in the compounds with alkaline metals as cations, it has been impossible to distinguish the disordered symmetry from genuine one by diffraction methods, but the present study of **2** with the piperidinium cation makes it possible to conclude that the hydrogen bond in the crystals of **2** is disordered and still not the "symmetric-centered."[1)]

The authors thank the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the diffractometer.

References

1) I. Olovsson and P.-G. Jönsson, "X-Ray and Neutron Diffraction Studies of Hydrogen Bonded Systems," in "The Hydrogen Bond, Recent Developments in Theory and Experiments," ed by P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, New York, Oxford (1976). Vol. II, Part B, Chap. 8, pp. 426—433.

2) J. C. Speakman, *Nature* (*London*), **162**, 695 (1948).

3) J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, *J. Chem. Soc.*, **1954**, 180.

4) L. Manojlović, *Acta Crystallogr., Sect. B*, **24**, 326 (1968).

5) D. R. McGregor and J. C. Speakman, *J. Chem. Soc.* (*A*), **1968**, 2106.

6) I. Nahringbauer, *Acta Chem. Scand.*, **23**, 1653 (1969).

7) A. L. Macdonald, J. C. Speakman, and D. Hadži, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 825.

8) A. L. Macdonald and J. C. Speakman, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1564.

9) J. Albertsson and I. Grenthe, *Acta Crystallogr., Sect. B*, **29**, 2751 (1973).

10) L. Golič and F. Lazarini, *Cryst. Struct. Commun.*, **3**, 645 (1974).

11) M. J. Barrow, M. Currie, K. W. Muir, J. C. Speakman, and D. N. J. White, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 15.

12) G. Chapuis, A. Zalkin, and D. H. Templeton, *J. Chem. Phys.*, **62**, 4919 (1975).

13) M. Currie, J. C. Speakman, J. A. Kanters, and J. Kroon, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1549.

14) L. Golič and F. Lazarini, *Cryst. Struct. Commun.*, **4**, 487 (1975).

15) H. Herbertsson, *Acta Crystallogr., Sect. B*, **32**, 3107 (1976).

16) I. A. Oxton, T. S. Cameron, O. Knop, and A. W. McCulloch, *Can. J. Chem.*, **55**, 3831 (1977).

17) J. Baran, V. Videnova, T. Glowiak, and H. Ratajczak, *Acta Crystallogr., Sect. B*, **35**, 2722 (1979).

18) V. Videnova, J. Baran, T. Glowiak, and Ratajczak, *Acta Crystallogr., Sect. B*, **36**, 459 (1980).

19) J. Longo and M. F. Richardson, *Acta Crystallogr., Sect. B*, **38**, 2482 (1982).

20) M. Currie, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 832.

21) J. Albertsson, I. Grenthe, and H. Herbertsson, *Acta Crystallogr., Sect. B*, **29**, 1855 (1973).

22) H. Herbertsson, *Acta Crystallogr., Sect. B*, **32**, 2381 (1976).

23) R. Tellgren, J. O. Thomas, and I. Olovsson, *Acta Crystallogr., Sect. B*, **33**, 3500 (1977).

24) D. Hadži, I. Leban, B. Orel, M. Iwata, and J. M. Williams, *J. Cryst. Mol. Struct.*, **9**, 117 (1979).

25) H. Herbertsson and B. Hedman, *Acta Crystallogr., Sect. B*, **38**, 320 (1982).

26) H. J. Geise, J. F. J. Van Loock, and A. T. H. Lenstra, *Acta Crystallogr., Sect. C*, **39**, 69 (1983).

27) K. Hermansson, R. Tellgren, and M. S. Lehmann, *Acta Crystallogr., Sect. C*, **39**, 1507 (1983).

28) X. He and B. M. Craven, *Acta Crystallogr., Sect. C*, **40**, 1157 (1984).

29) R. G. Delaplane, R. Tellgren, and I. Olovsson, *Acta Crystallogr., Sect. C,* **40**, 1800 (1984).

30) S. Kashino, K. Kanei, and S. Hasegawa, *Bull. Chem. Soc. Jpn.,* **45**, 1247 (1972).

31) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72—98.

32) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, "*MULTAN* 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs. of York, England, and Louvain, Belgium (1978).

33) T. Sakurai, "*RSSFR*-5. The Universal Crystallographic Computing System (I)," The Crystallographic Society of Japan (1967).

34) T. Ashida, "*HBLS*-V, *FMLS* and *DAPH*. The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka Univ. (1973).

35) F. Takusagawa, "*CRLS*. Technical Report, ICR-1982-0001-0002-001," The Institute for Cancer Research, Philadelphia (1982).

36) S. Fujii, "*MOLCON*, The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka Univ. (1979).

37) C. K. Johnson, "*ORTEP*. Report ORNL-3794," Oak Ridge National Laboratory, Tennessee (1965).

38) Tables of anisotropic thermal parameters, atomic parameters for hydrogen atoms, bond lengths and angles involving hydrogen atoms, and structure factors have been deposited as Document No. 8625 at the Office of the Chemical Society of Japan.

39) K. Ohkura, S. Kashino, and M. Haisa, *Bull. Chem. Soc. Jpn.,* **45**, 2651 (1972).

40) M. Colapietro and A. Domenicano, *Acta Crystallogr., Sect. B,* **33**, 2240 (1977).

41) S. Kashino, Y. Sumida, and M. Haisa, *Acta Crystallogr., Sect. B,* **28**, 1374 (1972).

42) S. Kashino, *Acta Crystallogr., Sect. B,* **29**, 1836 (1973).

43) M. Ichikawa, *Acta Crystallogr., Sect. B,* **34**, 2074 (1978).

44) W. Joswig and H. Fuess, *Acta Crystallogr., Sect. B,* **38**, 2798 (1982).

45) H. Küppers, Å. Kvick, and I. Olovsson, *Acta Crystallogr., Sect. B,* **37**, 1203 (1981).

46) M. Catti and G. Ferraris, *Acta Crystallogr., Sect. B,* **32**, 2754 (1976).