

pattern of shortened and lengthened ether bonds. As is evident from Fig. 1, the pyranose ring adopts the expected ⁴C₁ conformation. The ring torsion angles, from 52 to 65° (Table 6 of the deposited data) lie within the range for strain-free pyranose rings (Jeffrey, 1973).

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Study of Short Hydrogen Bonds. II.* Structure of Piperidinium Hydrogen Bis(*p*-bromobenzoate)

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Abstract. C₅H₁₂N⁺.C₁₄H₉Br₂O₄⁻, *M_r* = 487.19, triclinic, *P* $\bar{1}$, *a* = 12.264 (3), *b* = 12.252 (3), *c* = 7.367 (1) Å, α = 106.78 (2), β = 93.71 (2), γ = 67.67 (2)°, *V* = 979.1 (4) Å³, *Z* = 2, *D_x* = 1.653 Mg m⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.5418 Å, μ = 5.5 mm⁻¹, *F*(000) = 488, *T* = 291 K, final *R* = 0.048 for 3112 unique reflections. In the crystal there are two kinds of hydrogen bis(*p*-bromobenzoate) anions having $\bar{1}$ symmetry. Two benzoate residues in each are linked by short O...H...O hydrogen bonds with O...O 2.451 (6) and 2.460 (8) Å, respectively. The KKM effect was clearly observed in the former hydrogen bond. The center of gravity of the piperidinium cation lies nearly on ($\frac{1}{4}, 0, \frac{1}{2}$). The cations and anions related by a pseudo glide plane parallel to (012) are linked by two kinds of N—H...O hydrogen bonds to form a ribbon along *a*.

Introduction. In the present work the structure of the title compound has been determined in order to see the effect of the *p*-bromo substituent on the mode of the hydrogen bonds and the crystal structure compared with piperidinium hydrogen bis(*p*-methylbenzoate) (Misaki, Kashino & Haisa, 1986).

Experimental. The compound was prepared by a procedure reported previously (Kashino, Kanei & Hasegawa, 1972). Crystals grown by slow evaporation from benzene solution were plates developed along {010}. Twinned crystals grew frequently as hexagonal prisms elongated along an axis corresponding to the *a* axis of the single crystal. A specimen, 0.20 × 0.18 × 0.23 mm, was cut from a large single crystal. Lattice parameters were determined with 20 reflections in the range 16 < 2θ < 39°. The intensities were collected on a Rigaku AFC-5 four-circle diffractometer equipped with a rotating anode using Ni-filtered Cu *K*α (λ = 1.5418 Å) with ω–2θ scan method (scan speed 6° min⁻¹ in ω, scan range 1.2° + 0.15° tanθ in ω, 2θ_{max} = 125°). Background was measured for 4 s on either side of peak. Three standard reflections were recorded after every 57 reflections; their fluctuation was within 2.5% in *F*. Lorentz and polarization corrections were applied, but no absorption correction. Number of unique reflections 3112, of which 3019 were > 1.0σ(*F*_o); *R*_{int} = 0.014 for 165 *h*0*l* reflections. All the unique reflections (ranging over *h* = –14 to 14, *k* = 0 to 14, *l* = –8 to 8) were used for the refinement. The structure was solved by the Patterson heavy-atom method, and refined by full-matrix least squares. The non-H atoms were refined anisotropically and the H atoms iso-

* Part I: Misaki, Kashino & Haisa (1986).

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tropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)^2 + 0.0030|F_o| + 0.0013|F_o|^2]$ for $|F_o| > 0$, and $w = 0.6217$ for $|F_o| = 0$. All the H atoms were located on a difference Fourier map, and two H atoms involving the O...H...O hydrogen bonds were fixed at $\bar{1}$. A correction for secondary extinction was applied for the strongest 20 reflections [$I_{\text{corr}} = I_0(1 + 1.0 \times 10^{-5} I_0)$]. Final R was 0.048 for 3112 unique reflections ($wR = 0.070$, $S = 1.49$). $(\Delta/\sigma)_{\text{max}}$ in the final refinement cycle was 0.06 for non-H atoms and 1.1 for H atoms. Max. and min. $\Delta\rho$ in the final difference Fourier map were 0.40 and $-0.70 \text{ e } \text{\AA}^{-3}$; the high and low regions in $\Delta\rho$ were located near the Br atoms. A difference Fourier map calculated by excluding the H atoms at $\bar{1}$ clearly showed the KKM effect (Kroon & Kanters, 1972) for one of the O...H...O hydrogen bonds (Fig. 1). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Programs used: *RSSF5*-5 (Sakurai, 1967), *FMLS* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971). Computations were carried out at Okayama University Computer Center.

Discussion. The final atomic parameters are listed in Table 1.* The thermal ellipsoids of the molecules are shown in Fig. 2 with atomic numbering. Bond lengths and angles are listed in Table 2. A stereoview of the crystal structure is shown in Fig. 3.

In the crystal there are two kinds of hydrogen bis(p-bromobenzoate) anions, *A* and *B*. The benzoate residues in the anions are approximately planar, the dihedral angle between the planes of the benzene ring and the O—C—O group being $10.3(3)^\circ$ for *A* and $4.4(6)^\circ$ for *B*. The residues in each anion are linked by crystallographically centrosymmetric O...H...O hydrogen bonds [$\text{O}(A10)\dots\text{O}(A10')$ $2.451(6)$; $\text{O}(B10)\dots\text{O}(B10')$ $2.460(8) \text{ \AA}$]. The KKM effect was clearly observed for the former hydrogen bond. The effect was not so noticeable for the latter, but the region of $\Delta\rho$ higher than $0.2 \text{ e } \text{\AA}^{-3}$ spread by 0.7 \AA from the center of the hydrogen bond along the line connecting $\text{O}(B10)$ and $\text{O}(B10')$. The spacing between the planes of O—C—O groups participating in the hydrogen bond is $0.321(7) \text{ \AA}$ for the former, and $0.188(7) \text{ \AA}$ for the latter. For other compounds in which the KKM effect is found the spacing is also large [0.37 \AA for potassium hydrogen meso-tartrate (Kroon & Kanters, 1972), 0.17 \AA for hydrazinium hydrogen oxalate (Thomas, 1973)], while the spacing is around 0.06 \AA for many

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with British Library Document Supply Centre as Supplementary Publication No. SUP 51301 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum \beta_{ii} / a_i^2.$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C(A1)	1446 (3)	-3036 (4)	-2564 (5)	3.2 (2)
C(A2)	1184 (4)	-4083 (4)	-3326 (6)	3.9 (2)
C(A3)	2077 (4)	-5240 (4)	-3942 (6)	3.9 (2)
C(A4)	3228 (4)	-5317 (4)	-3863 (5)	3.3 (2)
C(A5)	3503 (4)	-4288 (4)	-3220 (6)	3.8 (2)
C(A6)	2607 (4)	-3157 (4)	-2557 (6)	3.6 (2)
C(A7)	463 (4)	-1827 (4)	-1801 (6)	3.7 (2)
Br(A8)	4472.1 (4)	-6891.4 (4)	-4641.7 (7)	4.60 (3)
O(A9)	-565 (3)	-1737 (3)	-2003 (5)	4.8 (2)
O(A10)	785 (3)	-949 (3)	-893 (5)	4.3 (1)
C(B1)	-6510 (3)	3109 (4)	590 (5)	3.2 (2)
C(B2)	-6256 (4)	4155 (4)	760 (6)	3.8 (2)
C(B3)	-7158 (4)	5321 (4)	1227 (6)	3.8 (2)
C(B4)	-8288 (4)	5423 (4)	1460 (5)	3.2 (2)
C(B5)	-8565 (4)	4396 (4)	1215 (6)	3.9 (2)
C(B6)	-7673 (4)	3256 (4)	800 (6)	3.7 (2)
C(B7)	-5532 (4)	1891 (4)	218 (6)	3.4 (2)
Br(B8)	-9506.4 (4)	7003.3 (4)	2165.6 (7)	4.56 (3)
O(B9)	-4500 (3)	1811 (3)	64 (5)	4.7 (2)
O(B10)	-5833 (3)	982 (3)	127 (5)	4.6 (1)
N(11)	-2660 (3)	116 (4)	-2390 (5)	3.6 (2)
C(12)	-3296 (5)	-514 (5)	-3855 (7)	5.7 (3)
C(13)	-2629 (6)	-1089 (6)	-5715 (8)	6.1 (3)
C(14)	-2367 (6)	-127 (6)	-6403 (8)	6.5 (3)
C(15)	-1732 (6)	503 (6)	-4871 (8)	6.6 (3)
C(16)	-2416 (5)	1065 (5)	-2971 (8)	5.6 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Anions	<i>A</i>	<i>B</i>	
C(1)—C(2)	1.392 (6)	1.400 (6)	
C(2)—C(3)	1.389 (7)	1.396 (7)	
C(3)—C(4)	1.377 (7)	1.361 (7)	
C(4)—C(5)	1.373 (7)	1.385 (7)	
C(5)—C(6)	1.374 (7)	1.370 (7)	
C(1)—C(6)	1.374 (6)	1.381 (6)	
C(1)—C(7)	1.488 (6)	1.479 (6)	
C(4)—Br(8)	1.902 (5)	1.890 (5)	
C(7)—O(9)	1.226 (6)	1.242 (6)	
C(7)—O(10)	1.278 (6)	1.283 (6)	
Cation			
N(11)—C(12)	1.496 (8)	C(14)—C(15)	1.52 (1)
C(12)—C(13)	1.48 (1)	C(15)—C(16)	1.514 (9)
C(13)—C(14)	1.55 (1)	N(11)—C(16)	1.481 (7)
Anions	<i>A</i>	<i>B</i>	
C(6)—C(1)—C(2)	118.6 (4)	118.5 (4)	
C(1)—C(2)—C(3)	120.9 (5)	120.2 (4)	
C(2)—C(3)—C(4)	118.2 (5)	119.2 (5)	
C(3)—C(4)—C(5)	121.8 (5)	121.5 (5)	
C(4)—C(5)—C(6)	119.0 (5)	119.0 (5)	
C(1)—C(6)—C(5)	121.3 (5)	121.5 (5)	
C(2)—C(1)—C(7)	119.0 (4)	119.3 (4)	
C(6)—C(1)—C(7)	122.3 (4)	122.2 (4)	
C(3)—C(4)—Br(8)	119.2 (4)	119.3 (4)	
C(5)—C(4)—Br(8)	119.0 (4)	119.1 (4)	
C(1)—C(7)—O(9)	120.3 (4)	119.6 (4)	
C(1)—C(7)—O(10)	114.9 (4)	115.6 (4)	
O(9)—C(7)—O(10)	124.8 (5)	124.7 (5)	
Cation			
C(12)—N(11)—C(16)	112.2 (4)	C(13)—C(14)—C(15)	108.8 (6)
N(11)—C(12)—C(13)	111.6 (5)	C(14)—C(15)—C(16)	112.2 (6)
C(12)—C(13)—C(14)	111.1 (6)	N(11)—C(16)—C(15)	110.3 (5)

cases in which the KKM effect is not observed. Thus, the KKM effect tends to be observed when the spacing is comparatively large.

The center of gravity of the piperidinium cation lies nearly on $(\frac{1}{2}, 0, \frac{1}{2})$. The piperidinium ring takes a chair conformation: N(11) and C(14) deviate by $-0.647(8)$ and $0.68(1)$ Å, respectively, from the plane through C(12), C(13), C(15) and C(16). The cation and anions are linked by two kinds of N—H...O hydrogen bonds to form a ribbon along *a* [N(11)...O(A9) 2.772(6), H(111)...O(A9) 1.94(5) Å, N(11)—H(111)...O(A9) 172(5)°; N(11)...O(B9) 2.734(6), H(112)...O(B9) 2.02(5) Å, N(11)—H(112)...O(B9) 154(5)°]. In the ribbon the anions *A* and *B* are related by a pseudo glide plane parallel to (01 $\bar{2}$). The ribbons are stacked along *c* by van der Waals interactions between the benzene rings of the anions *A* (*x*, *y*, *z*) and *B* ($1+x$, $-1+y$, *z*). The dihedral angle between the benzene rings is 14.7(2)°, the distance between these rings being about 3.61 Å.

In piperidinium hydrogen bis(*p*-methylbenzoate) (*Pcan*, *Z* = 4) the cation has 2 symmetry by disordering and the anion also has 2 symmetry (Misaki, Kashino & Haisa, 1986). The arrangement of the cations and the anions in the ribbon is similar to that in the present crystal, but the anions are related by a *c*-glide plane in place of the pseudo glide plane. The contact between the methyl group and piperidinium ring in the ribbons related by a 2₁ screw along *b* and thus a

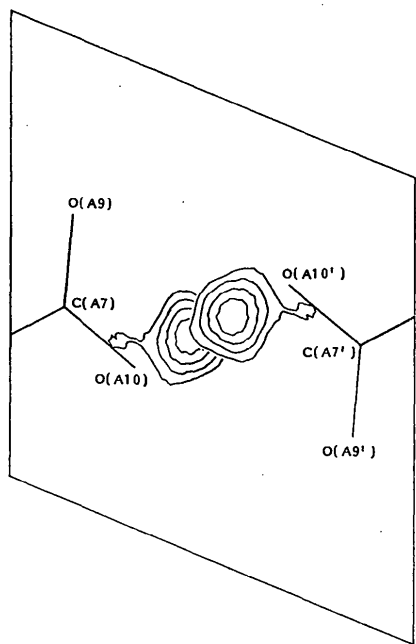


Fig. 1. Difference Fourier map viewed down the *c* axis in the region of the O...H...O hydrogen bond in the anion *A* showing the KKM effect. The origin lies at the center of the figure; the *a* axis points downward and the *b* axis left to right. Contours are drawn from 0.20 to 0.35 e Å⁻³ with intervals of 0.05 e Å⁻³.

2₁ along *c* would be lengthened by the bromo substitution to cause a loose packing between the ribbons. Hence, in the crystal of the *p*-bromo compound the ribbons are related by $\bar{1}$ instead of 2₁, and the symmetry of the anions is $\bar{1}$ in place of 2. The elimination of the 2₁ axes along *b* and *c* from the *Pcan* structure would result in a *P2/c* structure. In fact, the structure of the *p*-bromo compound has the pseudo glide plane perpendicular to a pseudo 2 along *c* at $(\frac{1}{2}, 0, \frac{1}{2})$. The present result gives an indication of the symmetry exchange of the short hydrogen bonds between 2 and $\bar{1}$ by the change of surroundings in the crystals.

The *p*-bromo compound has a tendency to form the twinned crystals with (01 $\bar{2}$) as a boundary plane, with a pseudo monoclinic cell. The relationship between the reciprocal lattices of the pseudo monoclinic cell and the triclinic cell of the single crystal is expressed as: $a_m^* = -b_t^*/2$, $b_m^* = c_t^* - b_t^*/2$ and $c_m^* = (a_t^* - b_t^*)/3$, where *m* stands for the pseudo monoclinic lattice and *t* the triclinic lattice.

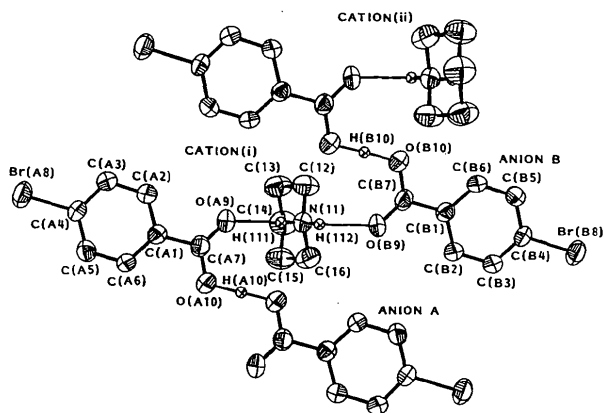


Fig. 2. Thermal ellipsoids (50% probability) with atomic numbering. The H atoms attached to the O and N atoms are represented as spheres equivalent to $B = 1.0$ Å². Two crystallographically independent hydrogen bis(*p*-bromobenzoate) anions *A* and *B*, and the piperidinium cations at (i) *x*, *y*, *z* and (ii) $-1-x$, $-y$, $-z$, are shown.

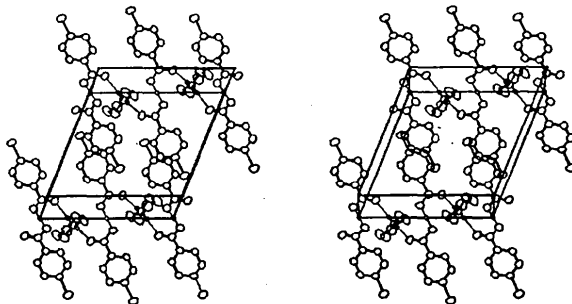


Fig. 3. Stereoscopic view of the crystal structure. The *a* axis points from left to right, the *b* axis upwards, and the *c* axis into the plane of the paper; the H atoms attached to the C atoms are omitted.

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Structure of 4-[(2-Benzoyl-1-methyl)vinyleneimino]butyric Acid

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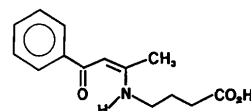
Abstract. $C_{14}H_{17}NO_3$, $M_r = 247.29$, monoclinic, $P2_1/n$, $a = 12.109$ (5), $b = 10.907$ (3), $c = 10.846$ (3) Å, $\beta = 113.06$ (2)°, $V = 1318.0$ (8) Å³, $Z = 4$, $D_x = 1.246$, $D_m = 1.25$ g cm⁻³ (by flotation), $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 6.781$ cm⁻¹, $F(000) = 528$, $T = 298$ K, $R = 0.0525$ for 1425 observed reflections. The enamino system in the title compound is very nearly planar and has a *cis-s-cis* conformation. The resulting six-membered ring involves a hydrogen bond between the NH and the ketonic carbonyl. The conformation of the carboxypropyl fragment enables molecules related by a centre of symmetry to organize in dimeric structures characterized by hydrogen bonding between the two enaminone heteroatoms of one molecule and the carboxylic oxygens of the other.

Introduction. As part of a programme of synthesis of potential γ -aminobutyric acid (GABA) receptor agonists (Bartholini, 1985; Krogsgaard-Larsen, Falch & Hjedts, 1985) to be tested for central nervous system activity, we have prepared a series of imines of GABA with 1,3-dicarbonyl derivatives (Merlini & Arnoldi, 1988). The structure of the products, although sup-

ported by analytical and spectroscopic data, is open to the possibility of regioisomerism, geometrical isomerism and tautomerism.

Although examples of regioselective attack of amines onto aromatic 1,3-diones have been known for a long time (Beyer & Claisen, 1887), and tautomerism has been studied with the aid of NMR (Dudek & Holm, 1961, 1962) and UV spectroscopy (Ostercamp, 1970), the results are not completely unambiguous. Moreover, information about the conformation of the carboxypropylimino side chain would be useful for structure-activity studies.

Therefore we report here the crystal and molecular structure of the title compound (1), prepared from GABA and benzoylacetone. X-ray analysis of this kind of compound has been performed, to our knowledge, only on metal complexes (Iida, Yuasa, Kibayashi & Iitaka, 1981).



(1)

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