

of block-diagonal least squares gave  $R = 0.061$ ,  $wR = 0.072$ ,  $S = 1.18$ , for 2393 reflections with  $|F_o| > 2\sigma(F_o)$  and 344 variables. The tetrafluoroborate anion is disordered, two possible orientations for the anion being found on a difference Fourier map. No evidence for extinction.  $(\Delta/\sigma)_{\min} = 0.001$ . Final difference map contained no peak higher than  $0.5 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic coordinates with their estimated standard deviations are given in Table 1.\* The numbering scheme is presented in Fig. 1. The bond distances and angles are shown in Table 2.

This compound is a racemate in solution (from circular dichroism) but the single crystal is polar.

The length of the S<sup>1</sup>–N( $sp^2$ ) bond is 1.589 (6), 1.597 (6) Å, which is in good agreement with that of the S–N bond from other experimental data (Yokomori *et al.*, 1985; Eliopoulos, Sheldrick & Hamodrakas, 1983; Cameron, Hair & Morris, 1973, 1974; Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Jordan, Smith, Lohr & Lipscomb, 1963). The S<sup>1</sup>–C( $sp^3$ ) bond length is also in good agreement with those of other compounds (Yokomori *et al.*, 1985; Wheatley, 1954; Bullough & Wheatley, 1957; Truter, 1962).

The authors wish to thank Dr. Kiyotane Sekido for helping with the operation of the diffractometer.

\* Lists of structure amplitudes, H-atom positional parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51681 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- ASHIDA, T. (1981). *HBLSVI. The Universal Computing System—Nagoya*, pp. 65–70. Nagoya Univ., Japan.
- BULLOUGH, P. K. & WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 233–237.
- CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1973). *J. Chem. Soc. Perkin Trans. 2*, pp. 1951–1954.
- CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1974). *Acta Cryst.* **B30**, 221–225.
- CHALKLEY, G. R., SNODIN, D. J., STEVENS, G. & WHITING, M. C. (1978). *J. Chem. Soc. Perkin Trans. 1*, pp. 1580–1587.
- COREY, E. J. & CHAYKOVSKY, M. (1965). *J. Am. Chem. Soc.* **87**, 1353–1364.
- ELIOPOULOS, E., SHELDRIK, B. & HAMODRAKAS, S. (1983). *Acta Cryst.* **C39**, 1693–1695.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 202–207. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- JORDAN, T., SMITH, H. W., LOHR, L. L. JR & LIPSCOMB, W. N. (1963). *J. Am. Chem. Soc.* **85**, 846–851.
- KÁLMÁN, A. (1967). *Acta Cryst.* **22**, 501–507.
- KÁLMÁN, A., DUFFIN, B. & KUCSMAN, A. (1971). *Acta Cryst.* **B27**, 586–594.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- OKUMA, K., NAKANISHI, K., HONDA, T., OHTA, H., YOKOMORI, Y. & SEKIDO, K. (1985). *Chem. Lett.* pp. 333–336.
- OKUMA, K., NAKANISHI, K. & OHTA, H. (1984). *J. Org. Chem.* **49**, 1402–1407.
- SHIMAGAKI, M., TSUCHIYA, H., BAN, Y. & OISHI, T. (1978). *Tetrahedron Lett.* pp. 3435–3438.
- TROST, B. M. & MELVIN, L. S. JR. (1975). *Sulfur Ylides*. New York: Academic Press.
- TRUTER, M. R. (1962). *J. Chem. Soc.* pp. 3393–3399.
- WHEATLEY, P. J. (1954). *Acta Cryst.* **7**, 68–72.
- YOKOMORI, Y., SEKIDO, K., HIROKAWA, S., OKUMA, K. & OHTA, H. (1985). *Acta Cryst.* **C41**, 461–463.

*Acta Cryst.* (1989). **C45**, 917–921

## Study of Short Hydrogen Bonds. III.\* Structures of Pyrrolidinium Hydrogen Bis(*p*-methylbenzoate) and Hexamethyleneiminium<sup>†</sup> Hydrogen Bis(*p*-methylbenzoate)

BY SHINTARO MISAKI, SETSUO KASHINO<sup>‡</sup> AND MASAO HAISA

*Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan*

(Received 17 October 1988; accepted 6 December 1988)

**Abstract.** Pyrrolidinium hydrogen bis(*p*-methylbenzoate) (1), C<sub>4</sub>H<sub>10</sub>N<sup>+</sup>.C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>,  $M_r = 343.42$ , ortho-

rhombic, space group *Pcan*,  $a = 9.835$  (1),  $b = 25.143$  (2),  $c = 7.6448$  (4) Å,  $V = 1890.4$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.207 \text{ Mg m}^{-3}$ ,  $\mu = 0.64 \text{ mm}^{-1}$ ,  $F(000) = 736$ , final  $R = 0.089$  for 1515 unique reflections. Hexamethyleneiminium hydrogen bis(*p*-methylbenzoate) (2), C<sub>6</sub>H<sub>14</sub>N<sup>+</sup>.C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>,  $M_r = 371.48$ ,

\* Part II: Misaki, Kashino & Haisa (1989).

† Alternative name: perhydroazepinium.

‡ To whom correspondence should be addressed.

monoclinic, space group  $P2_1/n$ ,  $a=24.740(2)$ ,  $b=10.9005(7)$ ,  $c=7.8488(5)$  Å,  $\beta=93.893(6)^\circ$ ,  $V=2111.7(2)$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=1.168$  Mg m<sup>-3</sup>,  $\mu=0.61$  mm<sup>-1</sup>,  $F(000)=800$ , final  $R=0.055$  for 3125 unique reflections.  $\lambda(\text{Cu } K\alpha)=1.54178$  Å,  $T=295$  K. The crystal structure of (1) is isotypic with that of piperidinium hydrogen bis(*p*-methylbenzoate) and the pyrrolidinium cation is disordered around a twofold axis. Two benzoate residues in the anion are linked by the crystallographically symmetric O...H...O hydrogen bond with O...O 2.445(4) Å. In the hydrogen bis(*p*-methylbenzoate) anion of (2) neutral and ionized benzoate residues are linked by the asymmetric O—H...O hydrogen bond with O...O 2.538(2) Å. In (2), the two anions and two cations which are related are held together by two kinds of N—H...O hydrogen bond around a  $\bar{1}$ . The effect of the environment on the symmetry and the O...O distance of the short hydrogen bonds is discussed for the same anion in different crystals.

**Introduction.** From the previous study of the short hydrogen bonds in the crystals of piperidinium hydrogen bis(*p*-methylbenzoate) and 4-methylpiperidinium hydrogen bis(*p*-methylbenzoate) it was found that the O...O distance is shorter in the symmetric hydrogen bond than in the asymmetric one for the same anion (Misaki, Kashino & Haisa, 1986). It was also found that exchange of the *p*-methyl substituent of the anion for the *p*-bromo substituent causes a symmetry change in the short hydrogen bond (Misaki, Kashino & Haisa, 1989). In the present work the effect of the ring-size of cations on the symmetry and the geometry of the hydrogen bond has been studied with the same hydrogen bis(*p*-methylbenzoate) anion.

**Experimental.** Experimental details are listed in Table 1. Compounds (1) and (2) were prepared by the procedure reported previously (Kashino, Kanei & Hasegawa, 1972). The crystals were grown by slow evaporation from benzene solutions. The lattice parameters were determined with 20 reflections by least squares. The intensities for (1) and (2) were collected on a Rigaku AFC-5 four-circle diffractometer equipped with a rotating anode ( $\omega-2\theta$  scan method, scan speed 4° min<sup>-1</sup> in  $\omega$ , scan range 1.2° + 0.15° tan $\theta$  in  $\omega$ , Ni-filtered Cu  $K\alpha$  at 40 kV, 200 mA). Background was measured for 4 s on either side of the peak. Three standard reflections were recorded after every 97 reflections. Lorentz and polarization corrections were applied, but no absorption correction. All the unique reflections within  $2\theta_{\text{max}}$  were used for the refinement.

For (1), orientation and position of the anion were found from a three-dimensional Patterson map. The non-H atoms of the cation were found by successive Fourier and difference syntheses. The cation was disordered around a twofold axis. The parameters of all

Table 1. *Experimental details*

	(1)	(2)
Morphology	Prismatic c	Prismatic c
Size of specimen (mm)	0.25 × 0.13 × 0.30	0.33 × 0.20 × 0.38
Range of $2\theta$ for lattice parameters (°)	35 to 41	44 to 46
Systematic absences	$l$ odd for $0kl$ $h$ odd for $h0l$ $h+k$ odd for $hkl$	$h+l$ odd for $h0l$ $k$ odd for $0k0$
$2\theta_{\text{max}} [(\sin\theta/\lambda)_{\text{max}}]$ ( $\theta$ in °, $\lambda$ in Å)	125 [0.5753]	120 [0.5617]
$h$ range	0 to 11	-27 to 27
$k$ range	0 to 28	0 to 12
$l$ range	0 to 8	0 to 8
Fluctuation of standard reflections (%)	1.0	1.6
Number of unique reflections	1515	3125
Number of reflections with $ F_o  > \sigma(F_o)$	1390	3012
$R$	0.089	0.055
$wR$	0.059	0.058
$S$	1.30	2.16
$(\Delta/\sigma)_{\text{max}}$ for non-H/H atoms	0.06/0.38	0.13/1.43
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.20/-0.19	0.21/-0.21

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{1}{3} \sum_i \beta_{ii} / a_i^{*2}$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Pyrrolidinium hydrogen bis( <i>p</i> -methylbenzoate) (1)				
C(1)	0.1569 (2)	0.13145 (9)	0.2107 (3)	3.8 (1)
C(2)	0.2554 (2)	0.1568 (1)	0.3110 (3)	4.4 (1)
C(3)	0.2497 (3)	0.2108 (1)	0.3389 (4)	4.6 (1)
C(4)	0.1461 (3)	0.2420 (1)	0.2715 (3)	4.3 (1)
C(5)	0.0457 (3)	0.2163 (1)	0.1741 (3)	4.5 (1)
C(6)	0.0519 (2)	0.1620 (1)	0.1429 (3)	4.2 (1)
C(7)	0.1610 (3)	0.07284 (9)	0.1795 (3)	4.3 (1)
C(8)	0.1421 (5)	0.3007 (1)	0.3042 (5)	6.0 (2)
O(9)	0.0781 (2)	0.05142 (6)	0.0827 (2)	5.19 (9)
O(10)	0.2600 (2)	0.04855 (7)	0.2582 (2)	5.7 (1)
N(11)†	-0.1518 (4)	0.001 (1)	0.226 (3)	4.0 (4)
C(12)	-0.2396 (3)	0.0466 (1)	0.2119 (4)	6.8 (2)
C(13)	-0.3774 (4)	0.0283 (2)	0.2474 (9)	13.2 (3)
Hexamethyleneiminium hydrogen bis( <i>p</i> -methylbenzoate) (2)				
C(1)	0.66352 (6)	0.1313 (1)	0.7295 (2)	4.24 (7)
C(2)	0.67969 (6)	0.0413 (2)	0.6199 (2)	5.04 (8)
C(3)	0.73315 (7)	0.0284 (2)	0.5905 (3)	6.2 (1)
C(4)	0.77299 (7)	0.1023 (2)	0.6670 (3)	6.2 (1)
C(5)	0.75680 (7)	0.1915 (2)	0.7753 (3)	6.5 (1)
C(6)	0.70318 (7)	0.2070 (2)	0.8061 (2)	5.9 (1)
C(7)	0.60635 (7)	0.1479 (2)	0.7694 (2)	4.73 (8)
C(8)	0.83205 (8)	0.0861 (3)	0.6357 (4)	9.9 (2)
O(9)	0.59273 (6)	0.2169 (2)	0.8788 (2)	8.39 (9)
O(10)	0.57189 (4)	0.0813 (1)	0.6743 (2)	5.30 (6)
C(11)	0.38429 (6)	0.1620 (1)	0.7328 (2)	3.70 (7)
C(12)	0.36670 (6)	0.0736 (2)	0.8428 (2)	4.77 (8)
C(13)	0.31379 (7)	0.0736 (2)	0.8880 (2)	5.86 (9)
C(14)	0.27679 (6)	0.1601 (2)	0.8271 (2)	5.74 (9)
C(15)	0.29492 (7)	0.2501 (2)	0.7218 (3)	6.1 (1)
C(16)	0.34809 (7)	0.2518 (2)	0.6740 (2)	4.82 (8)
C(17)	0.44038 (6)	0.1588 (1)	0.6716 (2)	3.76 (7)
C(18)	0.21832 (7)	0.1546 (3)	0.8676 (4)	9.0 (1)
O(19)	0.45256 (4)	0.2329 (1)	0.5612 (2)	5.36 (6)
O(20)	0.47264 (4)	0.0780 (1)	0.7374 (2)	4.69 (5)
N(21)	0.51961 (5)	0.1741 (1)	0.3075 (2)	4.09 (6)
C(22)	0.57239 (6)	0.2403 (2)	0.3128 (2)	4.54 (8)
C(23)	0.56807 (6)	0.3654 (2)	0.3932 (2)	5.06 (8)
C(24)	0.53759 (7)	0.4608 (2)	0.2847 (3)	5.47 (9)
C(25)	0.48068 (6)	0.4242 (2)	0.2201 (2)	4.94 (8)
C(26)	0.47876 (6)	0.3229 (2)	0.0882 (2)	4.88 (8)
C(27)	0.48054 (7)	0.1940 (2)	0.1556 (2)	4.84 (8)

† N(11) is disordered around the twofold axis, the occupancy factor being 0.5.

the non-H atoms were refined anisotropically by the full-matrix least-squares method. The H atoms of the anion were located on a difference Fourier map. The H-atom positions of the cation were calculated by assuming usual geometry. The positional parameters of the H atoms of the cation were fixed and their thermal parameters were assumed to be identical to  $B_{Cq}$  of the non-H atoms to which they were attached. The value minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/[\sigma(F_o)^2 - 0.0304|F_o| + 0.0018|F_o|^2]$  for  $|F_o| > 0$ , and  $w = 0.5141$  for  $|F_o| = 0$ . The extinction correction was applied for the strongest 10 reflections, according to  $I_{corr} = I_o(1 + gI_c)$ , where  $g = 1.29 \times 10^{-5}$ .

The structure of (2) was solved by the direct method and refined by the block-diagonal least-squares method. The value minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/[\sigma(F_o)^2 - 0.2491|F_o| + 0.0125|F_o|^2]$  for  $|F_o| > 0$ , and  $w = 1.9063$  for  $|F_o| = 0$ . All the H atoms were located on a difference Fourier map. The non-H atoms were refined anisotropically and the H atoms isotropically. The extinction correction was applied with  $g = 0.59 \times 10^{-5}$  for the strongest 11 reflections.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Programs used: *MULTAN84* (Main, Germain & Woolfson, 1984), *RSSFR-5* (Sakurai, 1967), *HBL5*, *FMLS* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979), and *ORTEP* (Johnson, 1971). Computations

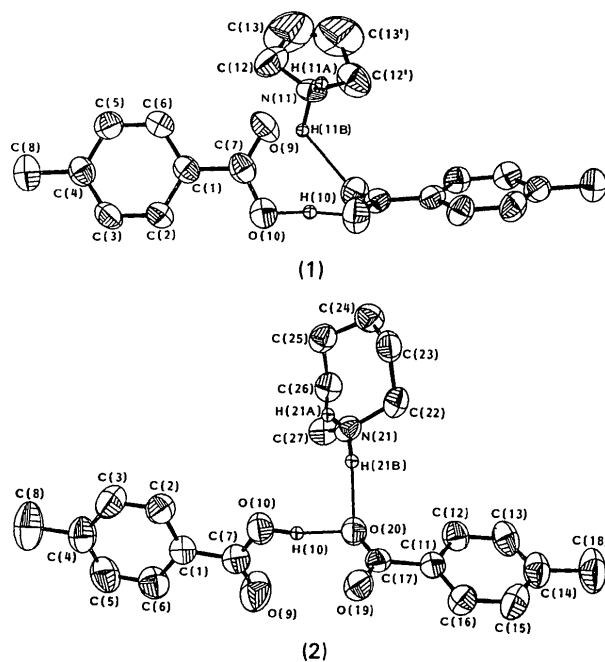


Fig. 1. The thermal ellipsoids (50% probability) with atomic numbering. The H atoms attached to the O and N atoms are represented as spheres equivalent to  $B = 1.0 \text{ \AA}^2$ . (1) Pyrrolidinium hydrogen bis(*p*-methylbenzoate). Disordered N atom is omitted. (2) Hexamethyleneiminium hydrogen bis(*p*-methylbenzoate).

Table 3. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

The atoms related by the twofold axis are denoted with primes.

Pyrrolidinium hydrogen bis( <i>p</i> -methylbenzoate) (1)				
C(1)	C(2)	1.390 (4)	C(1) C(7)	1.493 (4)
C(2)	C(3)	1.376 (4)	C(7) O(9)	1.226 (3)
C(3)	C(4)	1.385 (4)	C(7)-O(10)	1.297 (3)
C(4)	C(5)	1.395 (4)	N(11)-C(12)	1.44 (3)
C(5)	C(6)	1.387 (4)	C(12)-C(13)	1.457 (8)
C(6)	C(1)	1.387 (3)	C(13) C(13')	1.42 (1)
C(4)	C(8)	1.497 (5)	C(12') N(11)	1.55 (3)

C(6)	C(1)	C(2)	118.1 (2)	C(6)-C(1)-C(7)	120.4 (2)
C(1)	C(2)	C(3)	120.6 (2)	C(1)-C(7)-O(9)	120.8 (2)
C(2)	C(3)	C(4)	122.1 (3)	C(1)-C(7)-O(10)	114.3 (2)
C(3)	C(4)	C(5)	117.2 (2)	O(9)-C(7)-O(10)	124.9 (3)
C(4)	C(5)	C(6)	121.1 (2)	C(12')-N(11)-C(12)	108 (2)
C(5)	C(6)	C(1)	120.9 (2)	N(11)-C(12)-C(13)	107 (1)
C(3)	C(4)	C(8)	121.0 (3)	C(12)-C(13)-C(13')	108.7 (6)
C(5)	C(4)	C(8)	121.8 (3)	C(13')-C(12')-N(11)	103 (1)
C(2)	C(1)	C(7)	121.4 (2)		

Hexamethyleneiminium hydrogen bis( <i>p</i> -methylbenzoate) (2)				
C(1)	C(2)	1.382 (2)	C(15)-C(16)	1.392 (3)
C(2)	C(3)	1.365 (3)	C(16)-C(11)	1.385 (2)
C(3)	C(4)	1.379 (3)	C(14)-C(18)	1.503 (3)
C(4)	C(5)	1.369 (3)	C(11)-C(17)	1.499 (2)
C(5)	C(6)	1.375 (3)	C(17)-O(19)	1.237 (2)
C(6)	C(1)	1.387 (3)	C(17)-O(20)	1.274 (2)
C(4)	C(8)	1.508 (4)	N(21)-C(22)	1.490 (2)
C(1)	C(7)	1.480 (2)	C(22)-C(23)	1.509 (3)
C(7)	O(9)	1.207 (2)	C(23)-C(24)	1.513 (3)
C(7)-O(10)	1.313 (2)	C(24)-C(25)	1.517 (3)	
C(11)-C(12)	1.384 (2)	C(25)-C(26)	1.512 (3)	
C(12)-C(13)	1.379 (3)	C(26)-C(27)	1.501 (2)	
C(13)-C(14)	1.377 (3)	C(27)-N(21)	1.499 (2)	
C(14)-C(15)	1.377 (3)			

C(6)-C(1)-C(2)	117.8 (2)	C(14)-C(15)-C(16)	121.6 (2)
C(1)-C(2)-C(3)	120.2 (2)	C(15)-C(16)-C(11)	120.2 (2)
C(2)-C(3)-C(4)	122.6 (2)	C(13)-C(14)-C(18)	121.7 (2)
C(3)-C(4)-C(5)	117.0 (2)	C(15)-C(14)-C(18)	120.8 (2)
C(4)-C(5)-C(6)	121.5 (2)	C(12)-C(11)-C(17)	121.4 (1)
C(5)-C(6)-C(1)	120.9 (2)	C(16)-C(11)-C(17)	120.1 (1)
C(3)-C(4)-C(8)	122.2 (2)	O(19)-C(17)-O(20)	124.0 (1)
C(5)-C(4)-C(8)	120.8 (2)	C(27)-N(21)-C(22)	118.0 (1)
C(2)-C(1)-C(7)	122.7 (2)	N(21)-C(22)-C(23)	111.3 (1)
C(6)-C(1)-C(7)	119.6 (2)	C(22)-C(23)-C(24)	115.6 (2)
O(9)-C(7)-O(10)	123.2 (2)	C(23)-C(24)-C(25)	115.0 (2)
C(16)-C(11)-C(12)	118.5 (2)	C(24)-C(25)-C(26)	114.0 (2)
C(11)-C(12)-C(13)	120.3 (2)	C(25)-C(26)-C(27)	116.3 (2)
C(12)-C(13)-C(14)	122.1 (2)	C(26)-C(27)-N(21)	114.7 (1)
C(13)-C(14)-C(15)	117.4 (2)		

were carried out at Okayama University Computer Center.

**Discussion.** The final atomic parameters for (1) and (2) are listed in Table 2.\* The thermal ellipsoids of the molecules are shown in Fig. 1, with atomic numbering. Bond lengths and angles are listed in Table 3. The stereoviews of the crystal structures are shown in Fig. 2.

The structure of (1) is isotypic with that of piperidinium hydrogen bis(*p*-methylbenzoate) (Misaki, Kashino & Haisa, 1986). The pyrrolidinium cation is disordered around a twofold axis (the atoms related by

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, and torsion angles of the hexamethyleneiminium ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51672 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the twofold axis in the cation are denoted with primes hereafter). The cation can take one of two orientations with equal probability. C(12) and C(13) can be treated as one site though  $B_{eq}$  of C(13) is rather large. The position of the N atom is split into two sites around the twofold axis, the separation between the sites being 0.37 (7) Å. Thus, there are two possible sets of N—H...O hydrogen bonding between the cation and anion, and the disordering extends over whole crystals as discussed previously (Misaki, Kashino & Haisa, 1986). There are two kinds of N—H...O hydrogen bonds for each set: for the first set (i) N(11)—H(11B)...O(9) ( $x, -y, \frac{1}{2}-z$ ) and (ii) N(11)—H(11A)...O(9) ( $-x, -y, -z$ ) [N...O 3.00 (3), H...O 2.25 Å, N—H...O 123° for (i); N...O 2.80 (3), H...O 1.85 Å, N—H...O 150° for (ii)]. The other possible set is related to the first by the twofold axis. The anion O...H...O hydrogen bond of 2.445 (4) Å has twofold

symmetry in the crystal, but it is not 'centered' (Misaki, Kashino & Haisa, 1986). The pyrrolidinium ring takes an envelope conformation: C(13') deviates by 0.31 (1) Å from the plane through N(11), C(12), C(13) and C(12').

In (2), O(10) and O(20) in the anion are linked by an asymmetric O—H...O hydrogen bond [O(10)...O(20) 2.538 (2), H(10)...O(20) 1.54 (2) Å, O(10)—H(10)...O(20) 171 (2)°]. O(20) accepts an additional hydrogen bond from N(21) ( $1-x, -y, 1-z$ ) [N...O 2.779 (2), H...O 1.89 (2) Å, N—H...O 167 (2)°], and O(19) accepts a hydrogen bond from N(21) [N...O 2.752 (2), H...O 1.92 (2) Å, N—H...O 164 (2)°]. The two anions and two cations related by a  $\bar{1}$  form a hydrogen-bonded unit. The units are stacked along  $c$  by van der Waals interactions to form a column. The columns related by an  $n$  glide plane form a sheet parallel to (040). The sheets related by a twofold screw axis are stacked along  $b$  to complete the whole structure. The hexamethyleneiminium ring takes a twist-chair conformation (Moritani, Sasahara, Kashino & Haisa, 1987).

The cell dimensions  $a$ ,  $b$  and  $c$  of (1) are similar to  $b$ ,  $a$  and  $c$  respectively, of (2). The elimination of the twofold axis and the twofold screw axis along  $b$  from the disordered structure of (1) gives rise to a fundamental structure  $P112_1/n$ , which is similar to the structure of (2). The similarity in the arrangement of the cations and anions around  $\bar{1}$  is remarkable. In the fundamental structure of (1) the hydrogen-bonded units are stacked along  $c$  by van der Waals interactions to form a column as in (2). The columns are related by a twofold screw axis instead of the  $n$  glide plane of (2) to form a sheet parallel to (400). The sheets related by an  $n$  glide plane are stacked along  $c$ . This difference in the symmetry operation for sheet formation is caused by the difference in size of the cation. That is, the contact between the methyl group and the cation ring [H(8C)...H(15A) ( $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$ ) 2.60 Å in (1)] would become too small if the cation were exchanged for the larger hexamethyleniminium ion.

The O...O distance in the short hydrogen bonds differs significantly from crystal to crystal even if the anion is the same: 2.445 (4) Å for (1), 2.473 (4) Å for piperidinium hydrogen bis(*p*-methylbenzoate), 2.505 (3) Å for 4-methylpiperidinium hydrogen bis(*p*-methylbenzoate) and 2.538 (2) Å for (2). In piperidinium hydrogen bis(*p*-methylbenzoate) there is a short contact of 2.60 Å between O(10) and an H atom attached to the C atom of the 4-position of the piperidinium ring, but in (1) there is no short contact which prevents an approach of the O atoms. In (2) short contacts O(9)...H(22B) ( $x, y, 1+z$ ) 2.57 (2) Å and C(17)...H(21A) 2.77 (2) Å prevent the O...O distance from being short. The O—H...O angle for (2) is close to 180° but in 4-methylpiperidinium hydrogen bis(*p*-methylbenzoate) the angle is decreased to 158° by a packing effect, so that the O...O distance is shorter

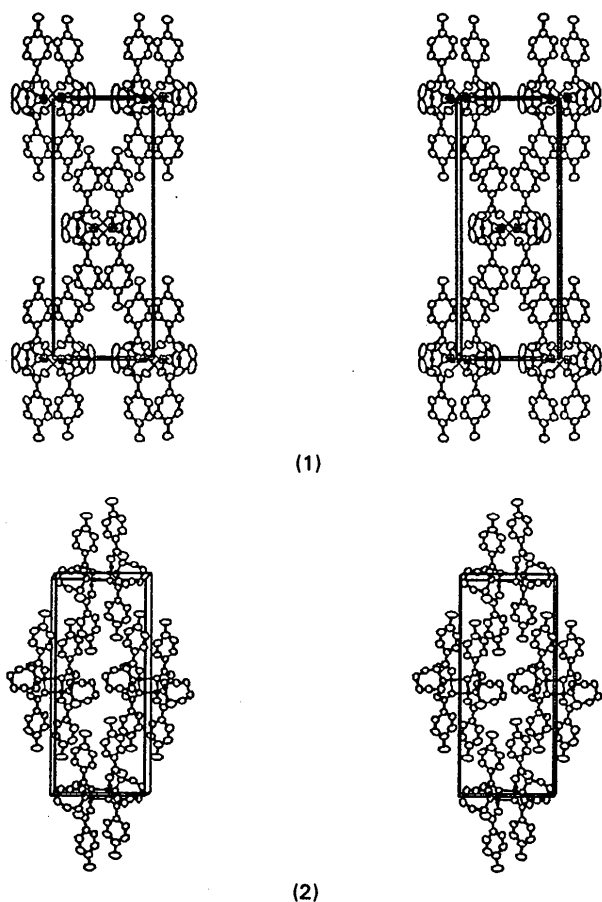


Fig. 2. Stereoscopic views of the crystal structures. The H atoms attached to the C atoms are omitted. (1) Pyrrolidinium hydrogen bis(*p*-methylbenzoate). The  $a$  axis points from left to right, the  $b$  axis upwards and the  $c$  axis onto the plane of the paper. (2) Hexamethyleniminium hydrogen bis(*p*-methylbenzoate). The  $a$  axis points downwards, the  $b$  axis from left to right and the  $c$  axis onto the plane of the paper.

than that for (2). The results of this study clearly show that the symmetry and O...O distances of the short hydrogen bonds depend on the crystallographic environment.

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

#### References

- ASHIDA, T. (1973). *HBL5, FMLS and DAPH. The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- FUJII, S. (1979). *MOLCON. The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- KASHINO, S., KANEI, K. & HASEGAWA, S. (1972). *Bull. Chem. Soc. Jpn*, **45**, 1247–1248.
- MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MISAKI, S., KASHINO, S. & HAISA, M. (1986). *Bull. Chem. Soc. Jpn*, **59**, 1059–1065.
- MISAKI, S., KASHINO, S. & HAISA, M. (1989). *Acta Cryst.* **C45**, 62–65.
- MORITANI, Y., SASAHARA, N., KASHINO, S. & HAISA, M. (1987). *Acta Cryst.* **C43**, 154–158.
- SAKURAI, T. (1967). *RSSF5-5. The Universal Crystallographic Computing System (I)*. The Crystallographic Society of Japan.

*Acta Cryst.* (1989). **C45**, 921–923

## Structure of 28-Hydroxyfriedelan-3-one

BY K. SUBRAMANIAN,\* S. SELLADURAI AND K. SIVAKUMAR

*Department of Physics, Anna University, Madras-600 025, India*

M. N. PONNUSWAMY

*Department of Crystallography and Biophysics, University of Madras, Madras-600 025, India*

AND E. SUKUMAR

*Captain Srinivasamurthy Drug Research Institute, Madras-600 106, India*

(Received 20 September 1988; accepted 28 November 1988)

**Abstract.**  $C_{30}H_{50}O_2$ ,  $M_r = 442.7$ , orthorhombic,  $P2_12_12_1$ ,  $a = 14.017$  (5),  $b = 28.671$  (11),  $c = 6.428$  (2) Å,  $V = 2583.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.132$  cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 4.866$  cm<sup>-1</sup>,  $F(000) = 984$ ,  $T = 296$  K,  $R = 0.075$  for 2430 observed reflections. The compound was isolated from the plant *Pristimera grahamii*. The molecule consists of five fused six-membered rings *A*, *B*, *C*, *D* and *E*. The ring junctions *A/B*, *B/C*, *C/D* and *D/E* are, respectively, *cis*, *trans*, *gauche*. Rings *A*, *B*, *C* are in a chair conformation. Rings *D* and *E* are, respectively, in twist-boat and distorted chair conformations. The packing of the molecules is due to van der Waals forces and there are no intermolecular hydrogen bonds.

**Introduction.** The title compound was isolated for the first time from the plant *Pristimera grahamii*. The plant is said to be used as an anti-cancer drug and also for protection in repelling insect and microbial attack, as an

indigenous medicine in India. This structure investigation has been undertaken to interpret the spectral data.

**Experimental.** Transparent, colourless crystals were grown from benzene solution. Crystal dimensions 0.5 × 0.4 × 0.45 mm, CAD-4 diffractometer, graphite-monochromated Cu *K*α radiation. Cell dimensions were determined by least-squares refinement using  $2\theta$  values of 25 medium-angle reflections ( $25^\circ < \theta < 35^\circ$ ). Intensity data were collected at room temperature by  $\omega/2\theta$  scan technique up to  $2\theta \simeq 170^\circ$  with  $h$  0–16,  $k$  0–34 and  $l$  0–7. Two standard reflections monitored every 100 measurements, variation less than 2%; 2648 unique reflections measured of which 2430 intensities observed  $|I| > 3\sigma(I)$ . The intensities were corrected for  $L_p$  effects; no absorption corrections. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Hydrogen atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-hydrogen atoms refined by full-matrix least-squares

\* To whom correspondence should be addressed.