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Structures of Dimorphs of Hexamethyleneiminium* p-Hydroxybenzoate and Pyrrolidinium p-Hydroxybenzoate

BY YOSHIMITSU MORITANI, NORIMITSU SASAHARA, SETSUO KASHINO† AND MASAO HAISA

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

Abstract. Cu $K\alpha$, $\lambda = 1.5418$ Å, $T = 295$ K. Hexamethyleneiminium p-hydroxybenzoate, $C_6H_{14}N^+.C_7H_5O_3^-$, $M_r = 237.30$; orthorhombic form: $P2_12_12_1$, $a = 11.984$ (2), $b = 14.326$ (1), $c = 7.612$ (1) Å, $V = 1306.9$ (3) Å^3, $Z = 4$, $D_m = 1.20$, $D_x = 1.206$ Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 512$, $R = 0.047$ for 1127 non-zero reflections; monoclinic form: $P2_1/n$, $a = 14.816$ (2), $b = 14.719$ (2), $c = 6.0611$ (7) Å, $\beta = 93.768$ (9)°, $V = 1318.9$ (3) Å^3, $Z = 4$, $D_m = 1.20$, $D_x = 1.195$ Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 512$, $R = 0.061$ for 2006 non-zero reflections. Pyrrolidinium p-hydroxybenzoate, $C_4H_{10}N^+.C_7H_5O_3^-$, $M_r = 209.25$, monoclinic, Cc, $a = 5.93$ (2), $b = 17.97$ (2), $c = 10.26$ (2) Å, $\beta = 96.0$ (2)°, $V = 1088$ (4) Å^3, $Z = 4$, $D_m = 1.27$, $D_x = 1.278$ Mg m^{-3}, $\mu = 0.78$ mm^{-1}, $F(000) = 448$, $R = 0.066$ for 734 non-zero reflections. In dimorphs of hexamethyleneiminium p-hydroxybenzoate, the benzoate ions related by a twofold screw axis are held together by an O—H···O hydrogen bond between the p-hydroxyl group and the carboxylate group to form a ribbon of benzoate ions, while in pyrrolidinium p-hydroxybenzoate a similar ribbon is formed by the benzoate ions related by an n-glide plane. This difference can be attributed to the size of the cations. In all these crystals, the ribbons are held together by the cations through two kinds of N—H···O hydrogen bonds between the iminium N and the carboxylate O atoms. The hexamethyleneimine rings take twist-chair conformations disordered between two

conformers. The pyrrolidine ring takes an approximate C_s conformation.

Introduction. Many salts of p-substituted benzoic acids with cyclic secondary amines crystallize in *Pbca* or its maximal subgroup $P2_1/c$ (Kashino, Sumida & Haisa, 1972; Kashino, 1973; Kashino, Kataoka & Haisa, 1978; Kashino, Sasahara, Kataoka & Haisa, 1981), while piperidinium p-hydroxybenzoate (PIH) crystallizes in *Cc* (Fukuyama, Kashino & Haisa, 1973). In the present work, the study has been extended to the crystal structures of dimorphs of hexamethyleneiminium p-hydroxybenzoate (HMI) and pyrrolidinium p-hydroxybenzoate (PYH), and it has been ascertained that the intermolecular O—H···O hydrogen bonding involving the p-hydroxyl and carboxyl groups plays an important role in the crystal structures.

Experimental. Experimental details are listed in Table 1. All the crystals obtained from ethanol solutions by slow evaporation at room temperature. Monoclinic crystals of HMI grown at first, then orthorhombic crystals from the same batch. D_m by flotation in benzene–CCl$_4$.

For HMI weak diffuse scattering evident in Weissenberg photographs (211 and 121 for orthorhombic form; $\bar{1}01$, $\bar{1}11$, 401 and 411 for monoclinic form), but no attempt made to analyze it. Intensity data, Rigaku AFC-5 four-circle diffractometer equipped with rotating anode, ω–2θ scan method [scan speed 4° min^{-1} in ω, scan range (2θ): $1.2° + 0.15°\tan\theta$], Ni-filtered Cu $K\alpha$ at 40 kV, 200 mA, background measured for 4 s on either side of the peak; three standard reflections

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Table 1. *Experimental details*

	HMI Orthorhombic form	HMI Monoclinic form	PYH
M.p. (decomposed) (K)	413–415	426–431	407–408
Crystal habit	Prismatic c	Prismatic c	Plates developed {010}
Crystal size (mm)	0·10×0·03×0·20	0·10×0·05×0·25	0·50×0·10×0·30 for a-axis photographs 0·21×0·19×0·75 for {101}-axis photographs
Refinements for lattice parameters			
Number	23	20	48
2θ range (°)	18–99	13–37	58–96
Systematic absences	h00, h odd 0k0, k odd 00l, l odd	0k0, k odd h0l, h+l odd	h0l, l odd hkl, h+k odd
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0·5617	0·5753	0·6486
Range of h, k, l	$0 \le h \le 13$ $0 \le k \le 16$ $0 \le l \le 8$	$0 \le h \le 16$ $0 \le k \le 16$ $-6 \le l \le 6$	$0 \le h \le 6$ $0 \le k \le 22$ $-11 \le l \le 12$
Fluctuation of standard reflections			
$\Sigma(|F_o|/|F_o|_{initial})/3$	0·996–1·008	0·988–1·022	–
Number of			
unique reflections	1144	2089	1271
non-zero reflections	1127	2006	734
reflections with $|F_o| > \sigma(|F_o|)$	1114	1946	–
R for non-zero reflections	0·047	0·061	0·066
wR	0·063	0·064	0·080
S	1·11	0·84	0·74
$(\Delta/\sigma)_{max}$	1·00	0·89	1·00
$\Delta\rho$ max. (min.) (e Å⁻³)	+0·14 (−0·17)	+0·32 (−0·32)	+0·28 (−0·22)

recorded every 57 reflections. Lorentz and polarization corrections; no absorption correction. Non-zero reflections within $(\sin\theta/\lambda)_{max}$ used in structure analysis and refinement. Structures solved by *MULTAN*78. Fourier and difference Fourier maps showed disordering in the hexamethyleneiminium rings [C(13), C(14), C(15) and C(16) in orthorhombic form; C(14) and C(15) in monoclinic form]. Structures refined (non-H atoms anisotropically) by full-matrix least-squares method, C—C, C—N and C—H lengths in the cation rings restrained to 1·52, 1·49 and 1·00 Å, respectively, occupancy factors of 0·5 assumed for the disordered atoms, $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1·0/\sigma(|F_o|)^2$. The positions of non-disordered H atoms determined from difference Fourier maps and refined isotropically; the disordered H atoms fixed in geometrically idealized positions, their thermal parameters assumed to be equal to B_{eq} of the C atoms to which they are attached. Correction for secondary extinction with $I_{corr} = I_o(1+gI_c)$ (orthorhombic form: $g = 3·75 \times 10^{-6}$ for 200, 121, 002, 012 and 122; monoclinic form: $g = 4·00 \times 10^{-6}$ for 10$\bar{1}$, 220, 301 and 311).

Intensity data for PYH collected on equi-inclination Weissenberg photographs for the zeroth to fourth layers about a axis, and the zeroth to eighth layers about [101] axis, 734 independent non-zero reflections (57% of the accessible reflections) estimated visually. Lorentz and polarization corrections and spot-shape correction; no absorption correction. The structure solved by Patterson method, refined by block-diagonal least-squares method (non-H atoms anisotropically). A difference Fourier synthesis revealed the H atoms

except for four in the pyrrolidine ring. The positional parameters of the remaining H atoms calculated by assuming usual geometry. All the H atoms refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1·0$ for $|F_o| \le 10·0$ and $w = (10·0/|F_o|)^2$ for $|F_o| > 10·0$. Correction for secondary extinction for 022, 023, 11$\bar{1}$, 130 and 131 with $g = 2·10 \times 10^{-5}$.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), modified version of *CRLS* (Takusagawa, 1982), *HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1965). Computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Discussion. The final atomic parameters are listed in Table 2.* Thermal ellipsoids of the molecules are shown in Fig. 1 with the atomic numbering. Bond lengths and angles are listed in Table 3, where the bond lengths for the hexamethyleneimine rings are omitted, because the values are in agreement with the constrained values within 1·0σ. Projections of the crystal structures are shown in Fig. 2. Geometries of the hydrogen bonds are summarized in Table 4.

The hexamethyleneimine rings in both orthorhombic (O) and monoclinic (M) forms of HMI are disordered between conformers A and B, so that detailed discussion of the molecular structures is not possible. However, inspection of the endocyclic torsion angles χ_i of the conformers [O(A), O(B), M(A) and M(B)] shows that χ_i (mod 7) in M(A) corresponds to $-\chi_{i+3}$ in M(B), $-\chi_{7-i}$ in O(A) and χ_{4-i} in O(B) (Table 5). All the conformers take twist-chair conformations, as found in some hexamethyleneimine rings (Kashino et al., 1981) and cycloheptane rings (de Kok & Romers, 1980), in agreement with theoretical expectation for the cycloheptane ring (Bocian & Strauss, 1977). It can be shown that if the atomic positions of the non-disordered part were fixed at the observed positions, no other twist-chair conformations could satisfy the packing requirement.

The pyrrolidine ring in PYH takes approximate C_s symmetry; C(14) deviates by 0·28 (2) Å from the plane through the other four non-hydrogen atoms in the ring. The C(14)—C(15) bond is shortened by the violent vibrational motion of C(14) (Ashida & Kakudo, 1974; Kashino et al., 1978).

In both forms of HMI, the benzoate ions related by the twofold screw axis along **b** are held together by an intermolecular O—H···O hydrogen bond between the p-hydroxyl and carboxylate groups to form a ribbon of benzoate ions. The ribbons are held together by the cations through two kinds of N—H···O hydrogen bonds. That is, in the orthorhombic form, the ribbons related by twofold screw axes along **a** and **c** are held together to form a three-dimensional network. In the

monoclinic form, the ribbons related by a **c** translation are held together to form a sheet parallel to (100). The sheets are stacked along **a** to complete the structure.

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

Disordered atoms are denoted by A or B, their occupancy factors being 0·5.

$$B_{eq} = \tfrac{4}{3}\sum_i\beta_{ii}/a_i^{*2}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Orthorhombic form of HMI				
C(1)	0·9532 (3)	0·3033 (2)	0·8390 (4)	3·2 (1)
C(2)	1·0673 (3)	0·3135 (2)	0·8754 (5)	3·9 (1)
C(3)	1·1418 (3)	0·2448 (2)	0·8330 (5)	4·3 (2)
C(4)	1·1072 (3)	0·1631 (2)	0·7522 (5)	3·7 (1)
C(5)	0·9936 (3)	0·1515 (2)	0·7184 (5)	4·0 (1)
C(6)	0·9194 (3)	0·2218 (2)	0·7620 (5)	3·6 (1)
C(7)	0·8721 (3)	0·3803 (2)	0·8761 (4)	3·5 (1)
O(8)	0·9099 (2)	0·4552 (2)	0·9461 (3)	4·2 (1)
O(9)	0·7742 (2)	0·3698 (2)	0·8264 (4)	4·9 (1)
O(10)	1·1839 (2)	0·0986 (2)	0·7098 (4)	5·1 (1)
N(11)	0·5944 (2)	0·4796 (2)	0·7969 (4)	3·7 (1)
C(12)	0·5118 (4)	0·4027 (3)	0·7753 (6)	5·3 (2)
C(13A)	0·3990 (5)	0·4390 (4)	0·7146 (8)	3·4 (3)
C(13B)	0·389 (1)	0·421 (1)	0·813 (3)	13 (1)
C(14A)	0·3326 (6)	0·4820 (7)	0·864 (1)	5·1 (3)
C(14B)	0·348 (1)	0·518 (2)	0·764 (4)	18 (2)
C(15A)	0·3563 (9)	0·581 (1)	0·923 (2)	10·4 (8)
C(15B)	0·3764 (6)	0·6062 (7)	0·866 (1)	5·8 (4)
C(16A)	0·4752 (8)	0·6122 (5)	0·884 (1)	5·1 (3)
C(16B)	0·4994 (8)	0·6307 (6)	0·879 (1)	5·8 (4)
C(17)	0·5714 (3)	0·5491 (3)	0·9380 (5)	4·4 (2)
Monoclinic form of HMI				
C(1)	0·7110 (1)	0·5735 (2)	0·2751 (4)	3·26 (9)
C(2)	0·7502 (2)	0·5818 (2)	0·0747 (4)	3·9 (1)
C(3)	0·8024 (2)	0·5132 (2)	−0·0040 (4)	4·3 (1)
C(4)	0·8161 (2)	0·4339 (2)	0·1160 (4)	3·9 (1)
C(5)	0·7778 (2)	0·4243 (2)	0·3172 (4)	4·0 (1)
C(6)	0·7256 (2)	0·4940 (2)	0·3945 (4)	3·7 (1)
C(7)	0·6571 (2)	0·6494 (2)	0·3657 (4)	3·7 (1)
O(8)	0·6412 (1)	0·7185 (1)	0·2429 (3)	4·25 (8)
O(9)	0·6315 (2)	0·6414 (2)	0·5551 (3)	6·0 (1)
O(10)	0·8678 (1)	0·3683 (1)	0·0298 (3)	5·5 (1)
N(11)	0·5310 (1)	0·7155 (2)	0·8585 (4)	4·2 (1)
C(12)	0·4681 (2)	0·6365 (2)	0·8612 (6)	5·7 (2)
C(13)	0·4278 (2)	0·6214 (3)	1·0824 (7)	6·4 (2)
C(14A)	0·3963 (5)	0·7004 (5)	1·220 (1)	6·0 (3)
C(14B)	0·3608 (6)	0·6963 (7)	1·127 (1)	8·2 (5)
C(15A)	0·3643 (4)	0·7810 (5)	1·0788 (9)	5·6 (3)
C(15B)	0·4033 (7)	0·7864 (6)	1·196 (1)	7·9 (4)
C(16)	0·4404 (2)	0·8427 (2)	1·0126 (6)	6·2 (2)
C(17)	0·4855 (2)	0·8045 (2)	0·8145 (6)	6·0 (2)
PYH				
C(1)	0·855 (1)	0·8296 (3)	0·6705 (5)	3·8 (2)
C(2)	1·050 (1)	0·8146 (3)	0·6101 (6)	4·2 (3)
C(3)	1·198 (1)	0·7594 (4)	0·6551 (6)	4·5 (3)
C(4)	1·155 (1)	0·7159 (3)	0·7613 (6)	4·0 (2)
C(5)	0·960 (1)	0·7297 (3)	0·8212 (6)	4·6 (3)
C(6)	0·812 (1)	0·7863 (3)	0·7771 (6)	4·6 (3)
C(7)	0·697 (1)	0·8916 (3)	0·6229 (5)	3·9 (2)
O(8)	0·6970 (9)	0·9114 (2)	0·5045 (5)	5·3 (2)
O(9)	0·571 (1)	0·9194 (3)	0·6968 (5)	6·0 (2)
O(10)	1·3047 (8)	0·6606 (3)	0·7992 (4)	5·3 (2)
N(11)	0·438 (1)	1·0317 (3)	0·4257 (5)	4·4 (2)
C(12)	0·196 (2)	1·0118 (5)	0·399 (1)	7·2 (4)
C(13)	0·071 (2)	1·0552 (7)	0·488 (1)	9·0 (6)
C(14)	0·230 (2)	1·1127 (8)	0·542 (2)	12·2 (8)
C(15)	0·455 (1)	1·0907 (4)	0·5280 (8)	5·9 (4)

Table 3. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

	HMI Orthorhombic form	Monoclinic form	PYH
C(1)—C(2)	1·403 (5)	1·386 (4)	1·394 (8)
C(2)—C(3)	1·367 (6)	1·376 (4)	1·372 (9)
C(3)—C(4)	1·386 (6)	1·383 (4)	1·386 (9)
C(4)—C(5)	1·395 (6)	1·386 (4)	1·387 (9)
C(5)—C(6)	1·384 (6)	1·385 (4)	1·39 (1)
C(6)—C(1)	1·368 (5)	1·385 (4)	1·387 (9)
C(1)—C(7)	1·497 (4)	1·498 (4)	1·504 (8)
C(7)—O(8)	1·281 (4)	1·273 (4)	1·266 (8)
C(7)—O(9)	1·242 (4)	1·238 (4)	1·225 (8)
C(4)—O(10)	1·343 (5)	1·358 (4)	1·362 (8)
N(11)—C(12)			1·48 (1)
C(12)—C(13)			1·46 (1)
C(13)—C(14)			1·47 (2)
C(14)—C(15)			1·41 (2)
C(15)—N(11)			1·49 (1)
C(6)—C(1)—C(2)	117·5 (3)	118·2 (2)	118·1 (6)
C(1)—C(2)—C(3)	121·0 (4)	121·1 (3)	121·4 (6)
C(2)—C(3)—C(4)	121·2 (4)	120·2 (3)	120·6 (6)
C(3)—C(4)—C(5)	118·3 (4)	119·6 (3)	118·5 (6)
C(4)—C(5)—C(6)	119·7 (4)	119·5 (3)	121·0 (6)
C(5)—C(6)—C(1)	122·3 (4)	121·4 (3)	120·4 (6)
C(6)—C(1)—C(7)	121·2 (3)	120·5 (2)	120·8 (6)
C(2)—C(1)—C(7)	121·3 (3)	121·3 (2)	121·1 (5)
C(1)—C(7)—O(8)	117·8 (3)	117·6 (2)	117·2 (6)
C(1)—C(7)—O(9)	117·8 (3)	118·2 (3)	120·0 (6)
O(8)—C(7)—O(9)	124·2 (3)	124·2 (3)	122·7 (6)
C(3)—C(4)—O(10)	118·9 (4)	117·7 (3)	117·9 (6)
C(5)—C(4)—O(10)	122·8 (4)	122·7 (3)	123·5 (6)
C(15)—N(11)—C(12)			107·3 (6)
C(17)—N(11)—C(12)	116·8 (3)	114·3 (3)	
N(11)—C(12)—C(13/13A)	111·8 (4)	114·0 (3)	107·6 (8)
N(11)—C(12)—C(13B)	119·6 (8)		
C(12)—C(13/13A)—C(14/14A)	112·2 (6)	121·6 (4)	105 (1)
C(12)—C(13/13B)—C(14B)	115 (2)	110·5 (5)	
C(13/13A)—C(14/14A)—C(15/15A)	120 (1)	112·5 (6)	110 (1)
C(13/13B)—C(14B)—C(15B)	124 (2)	114·8 (8)	
C(14A)—C(15A)—C(16/16A)	113 (1)	113·9 (6)	
C(14B)—C(15B)—C(16/16B)	116 (1)	116·1 (8)	
C(15A)—C(16/16A)—C(17)	119 (1)	111·1 (4)	
C(15B)—C(16/16B)—C(17)	113·1 (8)	125·1 (5)	
C(14)—C(15)—N(11)			106 (1)
C(16/16A)—C(17)—N(11)	110·0 (5)	113·7 (3)	
C(16B)—C(17)—N(11)	113·9 (5)		

Table 4. *Geometries of hydrogen bonds; lengths in Å and angles in degrees*

Symmetry code: (i) x, y, z; (ii) ¾−x, 1−y, ½+z; (iii) 2−x, ½+y, ½−z for orthorhombic form of HMI. (i) x, y, z; (ii) x, y, −1+z; (iii) ½−x, ½+y, ½−z for monoclinic form of HMI. (i) x, y, z; (ii) x, 2−y, −½+z; (iii) −½+x, ¾−y, −½+z for PYH.

		HMI Orthorhombic form	Monoclinic form	PYH
(1)	O(9ⁱ)···N(11ⁱ)	2·677 (4)	2·674 (3)	2·702 (8)
	O···H	1·86 (4)	1·74 (4)	1·9 (1)
	H—N	0·82 (4)	0·97 (4)	0·84 (9)
	O···H—N	172 (4)	161 (4)	170 (10)
(2)	O(8ⁱ)···N(11ⁱⁱ)	2·829 (4)	2·756 (3)	2·725 (8)
	O···H	1·86 (4)	1·74 (4)	1·70 (9)
	H—N	0·99 (5)	1·01 (4)	1·0 (1)
	O···H—N	166 (4)	179 (4)	176 (8)
(3)	O(8ⁱ)···O(10ⁱⁱⁱ)	2·625 (4)	2·608 (4)	2·608 (8)
	O···H	1·94 (5)	1·72 (4)	1·74 (8)
	H—O	0·69 (5)	0·89 (4)	0·91 (8)
	O···H—O	174 (6)	178 (4)	160 (8)

Table 5. *Endocyclic torsion angles* (°) *of four confor-*
mers of the hexamethyleneimine rings

	Orthorhombic form		Monoclinic form	
	$O(A)$	$O(B)$	$M(A)$	$M(B)$
χ_1 C(17)–N(11)–C(12)–C(13)	65·7 (5)	33 (1)	−84·5 (4)	−84·5 (4)
χ_2 N(11)–C(12)–C(13)–C(14)	−78·3 (7)	35 (2)	40·9 (6)	70·2 (6)
χ_3 C(12)–C(13)–C(14)–C(15)	81 (1)	−73 (3)	29·4 (8)	−75·6 (8)
χ_4 C(13)–C(14)–C(15)–C(16)	−26 (2)	60 (3)	−83·0 (7)	76 (1)
χ_5 C(14)–C(15)–C(16)–C(17)	−50 (2)	−50 (2)	81·5 (6)	−35 (1)
χ_6 C(15)–C(16)–C(17)–N(11)	87 (1)	77·6 (8)	−63·5 (5)	−28·1 (7)
χ_7 C(16)–C(17)–N(11)–C(12)	−72·8 (6)	−88·3 (6)	76·6 (4)	76·6 (4)

The *b* dimensions of the dimorphic forms are close to each other, indicating that these are mainly determined by the mode of the O—H···O hydrogen bond. Since the unit-cell volumes are approximately the same, this means that the areas of *ac* planes in the unit cells or the cross sections per ribbon perpendicular to **b**, and thus the vacant space among the ribbons, are also close for the dimorphic forms, irrespective of the difference in the
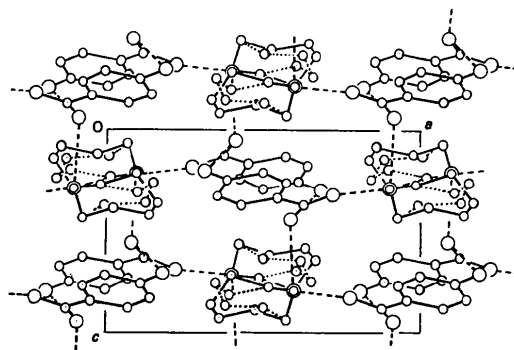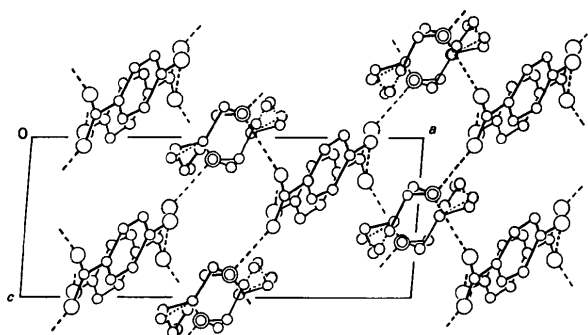

(a)

(b)

(c)

Fig. 1. The thermal ellipsoids of the molecules with atomic numbering. Ellipsoids of 50% probability are used for the non-H atoms; the H atoms attached to the N and O atoms are represented as spheres equivalent to $B = 1 \cdot 0 \, \text{Å}^2$, the other H atoms are omitted; (a) orthorhombic and (b) monoclinic forms of HMI. In the hexamethyleneimine rings the black and white bonds correspond to the A and B conformers, respectively. (c) PYH.
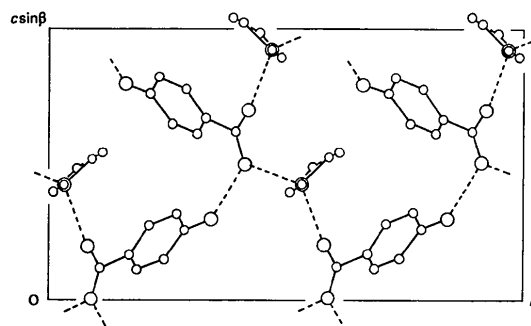

(a)

(b)

(c)

Fig. 2. Projections of the crystal structures (○: O, ◎: N, ○: C). Hydrogen bonds are shown by broken lines. (a) Orthorhombic and (b) monoclinic forms of HMI viewed along **b**; the disordered conformers B of the hexamethyleneiminium ions are shown by dotted bonds. (c) PYH viewed along **a**.

symmetry operations relating the ribbons. This vacant space is just enough for the hexamethyleneimine ring, but too wide for the pyrrolidine or piperidine ring. Thus, the ribbons for the five- or six-membered ring, if any, should be formed by a different mode of O—H···O hydrogen bonding.

The crystal of PYH is isostructural with that of PIH (Fukuyama *et al.*, 1973). The benzoate ions related by an *n*-glide plane perpendicular to **b** are held together by an intermolecular O—H···O hydrogen bond to form a ribbon along [101]. The ribbons related by a *c*-glide plane are held together by the cations through two kinds of N—H···O hydrogen bonds, resulting in a three-dimensional network.

A common feature of the four crystals is the formation of the ribbons of benzoate ions *via* O—H···O hydrogen bonds. However, for PYH and PIH the benzoate ions in the ribbons are related by the glide plane in place of the twofold screw axis. The repetition period of the ribbons in PYH and PIH is the length of the [101] axis. The period is 11·30 (2) Å for PYH and 11·59 (1) Å for PIH. The values are almost equal irrespective of the difference in the size of pyrrolidine and piperidine rings, and smaller by a factor of about 0·78 than the values of *b* for the dimorphic forms of HMI. Thus, the glide operation results in ribbons with smaller period and larger cross section compared to the 2_1 operation. The vacant space among the ribbons thus formed is suitable for the packing of the smaller size ring such as the piperidine or pyrrolidine ring.

The dihedral angle between the planes of the benzene ring and the carboxylate group is 23·7 (3)° in PYH and 16·6 (2)° in PIH, and 4·9 (1) and 6·0 (1)° in the orthorhombic and monoclinic forms of HMI, respectively, reflecting the difference in the mode of O—H···O hydrogen bonding. However, the O···O distances in the four crystals remain in a smaller range of values, 2·60

to 2·63 Å, than the N···O distances, 2·67 to 2·83 Å. For all these crystals the C(7)—O(9) bond is shorter than C(7)—O(8), probably because O(8) accepts N—H and O—H hydrogen bonds, while O(9) accepts only one N—H hydrogen bond.

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Structure of 2',4'-Dihydroxychalcone

BY FRANK R. FRONCZEK, NESRIN TANRISEVER AND NIKOLAUS H. FISCHER

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA

Abstract. 1-(2,4-Dihydroxyphenyl)-3-phenyl-2-propen-1-one, $C_{15}H_{12}O_3$, $M_r = 240·3$, orthorhombic, *Pbca*, $a = 7·3653$ (6), $b = 23·667$ (2), $c = 14·054$ (2) Å, $V = 2449·8$ (8) Å^3, $Z = 8$, $D_x = 1·303$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 0·85$ cm^{-1}, $F(000) = 1008$, $T = $ 297 K, $R = 0·035$ for 1385 observations (of 2153 unique data). The compound was isolated from Florida false rosemary (*Ceratiola ericoides*; Empetraceae). The carbonyl function is oriented *s-cis* to the *trans* C=C double bond and *syn* to a phenolic OH group, forming