The results of our structural analysis confirm the indications of ^{14}N NQR measurements, thus explaining the anomalies in the quadrupole parameters $|e^2qQ|$ and η in *m*-cyanoaniline and *p*-cyanoaniline.

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The Structures of 2-Hydroxy-5-methylbenzoic Acid and Dimorphs of 2,5-Dihydroxybenzoic Acid

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Abstract

The crystal structures of 2-hydroxy-5-methylbenzoic acid (1), $C_8H_8O_3$, and the ordered [2(*o*)] and disordered [2(*d*)] forms of 2,5-dihydroxybenzoic acid, $C_7H_6O_4$, have been determined. The crystal data are: $P2_1/a$, $a = 21{\cdot}24$ (2), $b = 5{\cdot}114$ (7), $c = 3{\cdot}307$ (9) Å, $\beta = 103{\cdot}76$ (8)°, $Z = 4$, $D_x = 1{\cdot}311$, $D_m = 1{\cdot}31$ Mg m^{-3}, m.p. 424–425·5 K for 1; $P2_1/a$, $a = 23{\cdot}945$ (2), $b = 4{\cdot}908$ (1), $c = 5{\cdot}621$ (1) Å, $\beta = 100{\cdot}981$ (8)°, $Z = 4$, $D_x = 1{\cdot}578$, $D_m = 1{\cdot}57$ Mg m^{-3}, m.p. 481–483 K for 2(*o*); and Pa, $a = 11{\cdot}229$ (2), $b = 11{\cdot}830$ (3), $c = 4{\cdot}966$ (4) Å, $\beta = 90{\cdot}50$ (3)°, $Z = 4$, $D_x = 1{\cdot}552$, $D_m = 1{\cdot}55$ Mg m^{-3}, m.p. 488–490 K for 2(*d*). The final R values for 1, 2(*o*) and 2(*d*) were 0·073, 0·035 and 0·039 for 904, 961 and 960 non-zero reflexions, respectively. Molecules of 2 show a quinonoid structure as found in salicylic acid. The crystal structures of 1 and 2(*o*) are of the benzoic acid type, and that of 2(*d*) is of the salicylic acid type. The crystal structures of 1, 2(*o*) and 2(*d*) are mainly determined by van der Waals interactions between the acid dimers, and the hydrogen bonding of the phenolic hydroxylic groups plays only an additional role. The morphotropism of benzoic acids is discussed.

Introduction

The present work on benzoic acids forms part of a systematization of the crystal structures of aromatic compounds (Haisa, 1978). The crystal structures of monocarboxylic acids have recently been discussed on the basis of morphotropism (Kashino & Haisa, 1980). The crystal structures of the title compounds have been examined in order to see the effects on them of the phenolic hydroxylic groups.

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Table 1. *Experimental details*

Crystal	1	2(*o*)	2(*d*)
Morphology	Prisms elongated along **b**, bounded by {001}, {100}, {20$\bar{1}$} and {010}	Plates developed {100}, elongated along **b**	Prisms elongated along **c**, bounded by {100} and {010}
μ(Cu $K\alpha$) (mm^{-1})	0·86	1·15	1·13
Dimensions of crystals used (mm)	0·23 × 0·70 × 0·11 0·20 × 0·40 × 0·15	0·13 × 0·23 × 0·13	0·08 × 0·10 × 0·19
Reflexions to be measured	1674	968	998
Non-zero reflexions	904	961	960

Experimental

Crystals of 1 and 2(*o*) were grown from aqueous solutions by slow evaporation. Crystals of 2(*d*) were obtained from a mixed solution of chloroform and acetone (3:1 in volume). The morphology of the crystals and the experimental details are given in Table 1.

Intensity data of 1 were collected on equi-inclination Weissenberg photographs for the layers *h*0*l* to *h*4*l* and *hk*0 to *hk*3 using Cu $K\alpha$ radiation (λ = 1·5418 Å), and visually estimated.

The data of 2(*o*) and 2(*d*) were collected on a Rigaku four-circle diffractometer. The intensities were measured up to $2\theta = 120°$ with the ω–2θ scan method (scan speed 4° min^{-1} in 2θ; scan range in 2θ: 1·2° + 0·15° tan θ) using Ni-filtered Cu radiation at 40 kV and 200 mA. Background was measured for 5 s on either side of the peak. Three reference reflexions showed no intensity deterioration. Reflexions larger than $\sigma(F)$ were used in the refinement as non-zero reflexions.

The intensities were corrected for Lorentz and polarization factors (and spot shape for visual data), but not for absorption.

Structure determination and refinement

The structures were solved by the Patterson method. The locations of the H atoms were determined from the difference syntheses. The refinements were made by block-diagonal least-squares calculations.

For 1 and 2(*o*), an extinction correction was applied at the stages of R = 0·091 and 0·043 respectively for the five strongest reflexions according to the formula $I_{\rm corr} = I_{\rm obs}/(1 - gI_{\rm obs})$, where g was $4\cdot75 \times 10^{-5}$ for 1 and $3\cdot50 \times 10^{-5}$ for 2(*o*). Subsequent refinements reduced R for the non-zero reflexions to 0·073 for 1, and 0·035 for 2(*o*). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1\cdot0$ for $|F_o| \le F_{\rm max}$ and $(F_{\rm max}/|F_o|)^2$ for $|F_o| > F_{\rm max}$, where $F_{\rm max}$ was 8·0 for both 1 and 2(*o*).

For 2(*d*), the systematic absence was *h*0*l* for *h* odd. The 0*k*0 reflexions with *k* odd were very weak, but significant (Table 2). Based on this fact, $Z = 4$ and the Patterson map, the structure was pseudo-$P2_1/a$. A difference Fourier map at R = 0·073 showed disordering of the H atoms of the 5-hydroxyl groups (Fig. 1). After an extinction correction with $g = 2\cdot30 \times 10^{-5}$ for the five strongest reflexions, the least-squares refinement ($F_{\rm max}$ = 12·0), including the H atoms with the occupancy factor of 0·5, gave a final R = 0·039. Refinement of the occupancy factor was not carried out. The refinement assuming $P2_1/a$ increased R to 0·048.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The computations were carried out at the Okayama University Computer Center, and at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The programs used were *SIGM*, *HBLS*-V and *DAPH* (Ashida, 1973) and

Table 2. *Observed and calculated structure factors* (×10) *for* 0*k*0 *reflexions of* 2(*d*)

k	$\|F_o\|(\sigma)$	$\|F_c\|$	*k*	$\|F_o\|(\sigma)$	$\|F_c\|$
1	17 (2)	13	8	68 (2)	70
2	91 (1)	96	9	0	15
3	11 (4)	9	10	79 (2)	79
4	13 (4)	12	11	9 (8)	9
5	13 (4)	13	12	49 (2)	55
6	413 (5)	412	13	0	6
7	12 (12)	15			

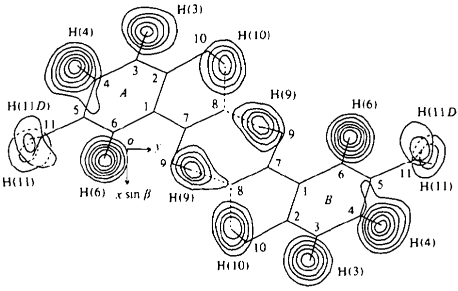

Fig. 1. Difference Fourier map for 2(*d*) at the stage of R = 0·073, showing the disorder at H(11). Contours are at intervals of 0·1 e Å^{-3} starting at 0·1 e Å^{-3}. The molecular frames are based on the final positional parameters.

Table 3. *Final atomic parameters* (*positional* $\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}/B_{iso} (Å^2)
(*a*) 2-Hydroxy-5-methylbenzoic acid (1)				
C(1)	1030 (2)	5003 (8)	1897 (5)	4·0 (2)
C(2)	1531 (2)	5688 (8)	1048 (6)	4·3 (2)
C(3)	1957 (2)	7729 (8)	1856 (6)	4·5 (2)
C(4)	1883 (2)	8983 (9)	3426 (6)	4·9 (2)
C(5)	1390 (2)	8348 (9)	4318 (7)	4·8 (2)
C(6)	964 (2)	6339 (8)	3495 (6)	4·2 (2)
C(7)	572 (2)	2869 (8)	1076 (6)	4·1 (2)
O(8)	623 (1)	1635 (6)	−321 (4)	4·8 (1)
O(9)	113 (1)	2381 (6)	1939 (4)	5·0 (1)
O(10)	1627 (1)	4495 (7)	−504 (7)	6·0 (2)
C(11)	1302 (3)	9818 (12)	6032 (7)	7·0 (3)
H(3)	228 (2)	798 (10)	132 (6)	4 (1)
H(4)	224 (2)	1027 (8)	410 (6)	3 (1)
H(6)	62 (2)	585 (9)	402 (6)	3 (1)
H(9)	−17 (3)	75 (12)	132 (7)	7 (2)
H(10)	125 (3)	278 (12)	−83 (9)	8 (2)
H(11*A*)	172 (4)	1081 (18)	661 (10)	12 (3)
H(11*B*)	85 (4)	974 (18)	605 (10)	11 (2)
H(11*C*)	140 (3)	902 (12)	681 (8)	7 (2)
(*b*) 2,5-Dihydroxybenzoic acid, ordered form [2(*o*)]				
C(1)	3955·3 (6)	5219 (3)	4811 (2)	2·44 (6)
C(2)	3989·0 (6)	3567 (3)	6859 (3)	2·74 (6)
C(3)	3570·9 (7)	1617 (3)	6929 (3)	3·06 (7)
C(4)	3123·2 (6)	1334 (3)	5012 (3)	2·85 (6)
C(5)	3085·7 (6)	2988 (3)	2979 (3)	2·33 (5)
C(6)	3499·2 (6)	4896 (3)	2854 (3)	2·39 (6)
C(7)	4397·3 (6)	7276 (3)	4736 (3)	2·65 (6)
O(8)	4794·3 (5)	7623 (3)	6451 (2)	3·64 (5)
O(9)	4337·1 (4)	8728 (2)	2740 (2)	3·23 (5)
O(10)	4416·3 (5)	3763 (3)	8816 (2)	3·97 (5)
O(11)	2620·5 (4)	2614 (2)	1119 (2)	2·96 (5)
H(3)	358·4 (8)	50 (4)	838 (3)	2·5 (4)
H(4)	281·4 (7)	−3 (4)	505 (3)	1·3 (3)
H(6)	348·3 (7)	606 (3)	146 (3)	1·0 (3)
H(9)	464·4 (9)	1008 (5)	295 (4)	3·6 (5)
H(10)	465·3 (9)	522 (5)	847 (4)	3·8 (5)
H(11)	256·3 (9)	415 (5)	26 (4)	3·4 (5)
(*c*) 2,5-Dihydroxybenzoic acid, disordered form [2(*d*)]				
C(1*A*)	−974 (3)	698 (3)	4914 (8)	2·8 (2)
C(2*A*)	−1946 (4)	1011 (3)	6517 (8)	3·4 (2)
C(3*A*)	−2323 (4)	259 (3)	8470 (8)	3·6 (2)
C(4*A*)	−1794 (4)	−755 (3)	8834 (8)	3·5 (2)
C(5*A*)	−837 (4)	−1068 (3)	7247 (7)	3·2 (2)
C(6*A*)	−431 (4)	−335 (3)	5294 (8)	3·2 (2)
C(7*A*)	−529 (3)	1466 (3)	2897 (7)	2·6 (2)
O(8*A*)	−978 (3)	2416 (2)	2400 (6)	3·5 (1)
O(9*A*)	392 (2)	1122 (2)	1465 (6)	3·6 (1)
O(10*A*)	−2505 (3)	2020 (3)	6255 (6)	4·7 (2)
O(11*A*)	−324 (3)	−2118 (2)	7527 (6)	4·4 (1)
C(1*B*)	955 (3)	4266 (3)	−4920 (7)	2·5 (2)
C(2*B*)	1912 (3)	3962 (3)	−6543 (8)	2·9 (2)
C(3*B*)	2343 (3)	4702 (4)	−8514 (8)	3·4 (2)
C(4*B*)	1807 (4)	5763 (3)	−8813 (8)	3·4 (2)
C(5*B*)	847 (4)	6066 (3)	−7206 (8)	3·0 (2)
C(6*B*)	420 (3)	5352 (3)	−5299 (7)	2·8 (2)
C(7*B*)	529 (3)	3501 (3)	−2795 (8)	3·0 (2)
O(8*B*)	984 (2)	2578 (2)	−2393 (6)	3·6 (1)
O(9*B*)	−391 (3)	3880 (2)	−1461 (6)	3·4 (1)

Table 3 (*cont.*)

	x	y	z	B_{eq}/B_{iso} (Å^2)
O(10*B*)	2484 (3)	2945 (3)	−6360 (6)	4·3 (1)
O(11*B*)	352 (3)	7129 (2)	−7511 (7)	4·9 (2)
H(3*A*)	−303 (4)	54 (4)	954 (9)	2·2 (10)
H(4*A*)	−215 (3)	−124 (3)	1024 (8)	1·0 (8)
H(6*A*)	25 (4)	−59 (3)	416 (8)	1·0 (8)
H(9*A*)	59 (4)	159 (3)	23 (9)	1·8 (9)
H(10*A*)	−221 (5)	243 (4)	489 (11)	3·9 (12)
H(11*A*)*	23 (10)	−232 (9)	599 (21)	3·7 (24)
H(11*DA*)*	−23 (12)	−243 (11)	925 (27)	5·9 (32)
H(3*B*)	295 (4)	448 (4)	−971 (9)	2·4 (10)
H(4*B*)	207 (4)	632 (3)	−1025 (8)	1·4 (9)
H(6*B*)	−25 (3)	553 (3)	−412 (8)	0·9 (8)
H(9*B*)	−55 (5)	321 (4)	14 (11)	4·2 (12)
H(10*B*)	211 (4)	257 (4)	−495 (10)	2·7 (11)
H(11*B*)*	51 (9)	758 (8)	−907 (21)	3·2 (24)
H(11*DB*)*	11 (12)	734 (10)	−588 (24)	5·4 (31)

* Occupancy factor = 0·5.

MOLCON (Fujii, 1979). The final atomic parameters are listed in Table 3.*

Description and discussion of the structures

The projections of the crystal structures and the numbering of the non-H atoms are shown in Fig. 2.

Table 4. *Geometry of the hydrogen bonds* (*lengths in* Å *and angles in degrees*)

	1	2(*o*)	2(*d*)	
(I) Intramolecular				
			A	*B*
O(10)···O(8)	2·615 (4)	2·576 (1)	2·623 (4)	2·639 (4)
H(10)···O(8)	1·58 (7)	1·72 (2)	1·86 (5)	1·80 (5)
O(10)–H(10)···O(8)	143 (6)	148 (2)	141 (4)	148 (5)
(II) Intermolecular				
(*a*) Between carboxylic groups of				
	i and ii	i and ii	*A* and *B*	*B* and *A*
O(9)···O(8)	2·680 (4)	2·717 (1)	2·665 (4)	2·670 (4)
H(9)···O(8)	1·62 (6)	1·74 (2)	1·81 (4)	1·55 (6)
O(9)–H(9)···O(8)	177 (5)	176 (2)	179 (4)	170 (5)
(*b*) Between 5-hydroxylic groups of				
		i and iv	B^{iv} and A^{i}	A^{i} and B^{iii}
O(11)···O(11)		2·768 (2)	2·722 (6)	2·768 (6)
H(11)···O(11)		1·89 (2)	1·96 (11)	1·86 (11)
O(11)···H(11*D*)		–	1·81 (14)	1·88 (13)
O(11)–H(11)···O(11)		170 (2)	135 (9)	146 (9)
O(11)···H(11*D*)–O(11)		–	164 (13)	176 (12)

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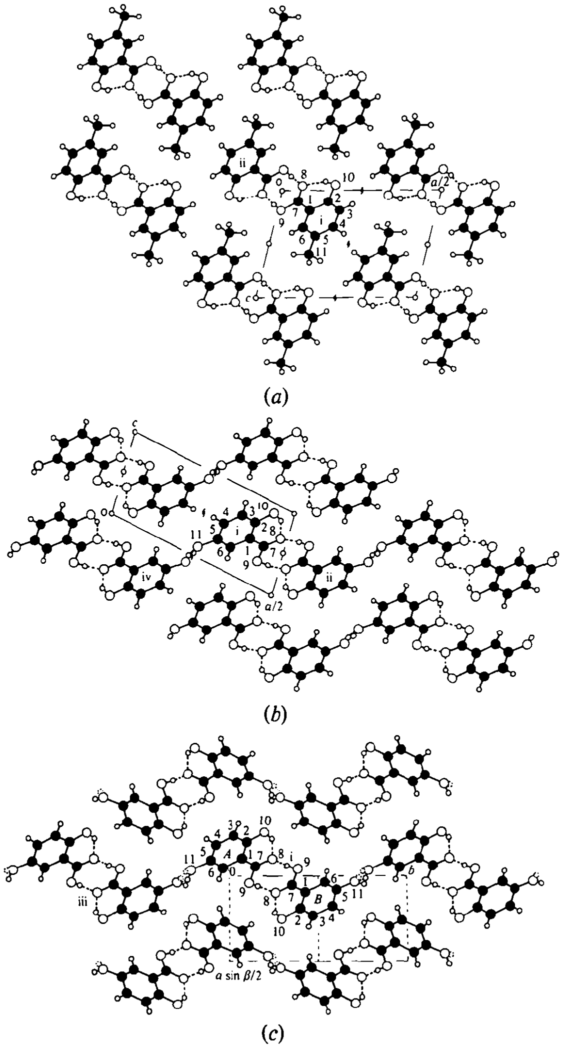
* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and least-squares planes of benzene rings for 1, 2(*o*) and 2(*d*), and bond lengths and angles of respective molecules of 2(*d*) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36568 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a)

(b)

(c)

Fig. 2. Projections of the crystal structures, showing the hexagonal arrangements of the dimers, and numbering of the non-H atoms. (*a*) 1 viewed along **b**; (*b*) 2(*o*) viewed along **b**; and (*c*) 2(*d*) viewed along **c**. Broken lines show hydrogen bonds. Symmetry code: for 1 (i) *x*,*y*,*z*; (ii) −*x*,−*y*,−*z*; (iii) *x*, 1 + *y*, *z*; (iv) −*x*, 1 − *y*, −*z*; for 2(*o*) (i) *x*,*y*,*z*; (ii) 1 − *x*, 2 − *y*, 1 − *z*; (iii) *x*, −1 + *y*, *z*; (iv) ½ − *x*, ½ + *y*, −*z*; for 2(*d*) (i) *x*,*y*,*z*; (ii) *x*, *y*, 1 + *z*; (iii) *x*, −1 + *y*, 1 + *z*; (iv) *x*, −1 + *y*, 2 + *z*.

The geometry of the hydrogen bonds is summarized in Table 4.

Table 5. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	1 (X = C)	2(*o*) (X = O)	2(*d*)* (X = O)
C(1)–C(2)	1·398 (6)	1·398 (2)	1·401 (6)
C(2)–C(3)	1·415 (6)	1·391 (3)	1·394 (6)
C(3)–C(4)	1·356 (7)	1·375 (3)	1·375 (6)
C(4)–C(5)	1·397 (7)	1·391 (2)	1·391 (6)
C(5)–C(6)	1·406 (6)	1·374 (1)	1·370 (6)
C(6)–C(1)	1·388 (6)	1·404 (1)	1·404 (6)
C(1)–C(7)	1·490 (6)	1·469 (2)	1·459 (6)
C(7)–O(8)	1·227 (5)	1·230 (2)	1·238 (5)
C(7)–O(9)	1·305 (5)	1·314 (2)	1·318 (5)
C(2)–O(10)	1·345 (5)	1·356 (2)	1·360 (5)
C(5)–X(11)	1·510 (8)	1·387 (1)	1·380 (6)
C(2)–C(1)–C(6)	119·3 (4)	119·6 (1)	119·4 (4)
C(1)–C(2)–C(3)	118·6 (4)	119·6 (2)	119·5 (4)
C(2)–C(3)–C(4)	120·7 (5)	120·4 (2)	120·4 (4)
C(3)–C(4)–C(5)	122·4 (5)	120·3 (2)	120·3 (4)
C(4)–C(5)–C(6)	116·6 (4)	120·4 (1)	120·4 (4)
C(5)–C(6)–C(1)	122·4 (4)	119·8 (1)	120·2 (4)
C(2)–C(1)–C(7)	119·9 (4)	119·6 (1)	120·5 (4)
C(6)–C(1)–C(7)	120·8 (4)	120·8 (1)	120·2 (4)
C(1)–C(7)–O(8)	122·2 (4)	121·7 (2)	123·0 (4)
C(1)–C(7)–O(9)	115·9 (4)	115·8 (2)	115·8 (4)
O(8)–C(7)–O(9)	121·9 (4)	122·5 (2)	121·3 (4)
C(1)–C(2)–O(10)	123·0 (4)	122·9 (2)	123·1 (4)
C(3)–C(2)–O(10)	118·4 (4)	117·5 (2)	117·4 (4)
C(4)–C(5)–X(11)	121·7 (5)	117·3 (1)	119·8 (4)
C(6)–C(5)–X(11)	121·6 (4)	122·3 (1)	119·8 (4)

* Average of the values in molecules *A* and *B*. The respective values are deposited.

Molecular structures

Bond lengths and angles are given in Table 5. Though molecular dimensions in 2(*d*) have some inaccuracy because of the disordering and pseudo-symmetry, the average values of equivalent bond lengths and angles of the independent molecules are in agreement with the corresponding values of 2(*o*) except the angle involving the O(11) atom (Table 5). In 2(*o*), the C(4)–C(5)–O(11) angle is smaller than C(6)–C(5)–O(11) as usually found in phenols (Fukuyama, Ohkura, Kashino & Haisa, 1973), but these angles in 2(*d*) are equal to each other as an effect of the disordering. In fact, the anisotropic thermal parameter B_{11} of O(11) in 2(*d*) is unusually large [7·0 Å^2 for O(11*A*) and 7·6 Å^2 for O(11*B*)].

In the molecules of 1 and 2 an intramolecular hydrogen bond is formed between O(8) and the 2-hydroxy group (Table 4). O(8) lies closely in the plane of the benzene ring. The dihedral angle between the benzene ring and the carboxylic group is 1·1° for 1 and 1·3° for 2(*o*). The geometry of the hydrogen bond is close to that found in salicylic acid (Bacon & Jude, 1973) and *o*-nitrophenols (Kagawa, Kawai, Kashino & Haisa, 1976).

In the molecule of 1, the inner angle at C(5) is smaller than the sp^2 angle as found in other methyl-substituted benzene derivatives (Domenicano, Vaciago & Coulson, 1975).

In the molecule of 2, the C(3)–C(4) and C(5)–C(6) bonds are significantly shorter than the other C–C bonds in the benzene ring, and the C(2)–O(10) bond is shorter than C(5)–O(11). This fact shows the predominant contribution of a quinonoid structure such as that suggested for salicylic acid (Cochran, 1953; Sundaralingam & Jensen, 1965; Bacon & Jude, 1973).

Crystal structures

In the crystals of 1 and 2(*o*), the structures consist of centrosymmetric dimers linked by hydrogen bonds between the carboxylic groups. The [100] and [001] of 1 correspond to [102] and [00$\bar{1}$] of 2(*o*) respectively (Fig. 2). The dimers are stacked along **b**, with a spacing of 3·42 Å in 1 and 3·31 Å in 2(*o*), by van der Waals interactions to form a column, in which the shortest contact is 3·363 (8) Å for $C(7^{i})\cdots C(7^{iv})$ in 1 and 3·302 (3) Å for $C(3^{i})\cdots C(7^{iii})$ in 2(*o*). The columns, related by a **c** translation and 2_1 axis, are packed into a distorted hexagonal array, in which the long axes of the dimers viewed along **b** are arranged in parallel. In 1, the columns are held together by van der Waals interactions. In 2(*o*), in addition to these interactions, there is an $O-H\cdots OH$ hydrogen bond between molecules i and iv related by the 2_1 axis at $x = \frac{1}{4}$ and $z = 0$. The dihedral angle between the benzene rings related by the 2_1 axis is 83·8° in 1 and 84·9° in 2(*o*), being close to 85·0° in benzene (Cox, Cruickshank & Smith, 1958).

In the crystals of 2(*d*), the structure consists of pseudo-centrosymmetric dimers linked by hydrogen bonds between the carboxylic groups. The dimers are stacked along **c**, with a spacing of 3·29 Å, by van der Waals interactions to form a column, in which the shortest contacts are 3·258 (6) Å for $C(7B^{i})\cdots C(3B^{ii})$ and 3·294 (6) Å for $C(3A^{i})\cdots C(7A^{ii})$. The columns related by a **b** translation are held together by hydrogen bonds between the 5-hydroxylic groups to form a sheet in (100).

Two modes of hydrogen bonding are possible here (Fig. 3):

(1) $\cdots O(11B^{iv})-H(11B^{iv})\cdots O(11A^{i})-H(11A^{i})\cdots O(11B^{iii})-H(11B^{iii})\cdots$

and

(2) $\cdots H(11DB^{iv})-O(11B^{iv})\cdots H(11DA^{i})-O(11A^{i})\cdots H(11DB^{iii})-O(11B^{iii})\cdots$.

The disordering may occur between these two. The sheets are stacked along **a**. Diffuse scattering and doubling of the cell dimension of *a* or *b* have not been observed.

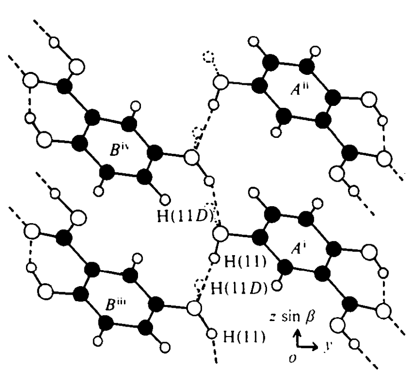


Fig. 3. The hydrogen-bond system between 5-hydroxylic groups of 2(*d*) viewed along **a**. Symmetry code as in Fig. 2.

The dimers viewed along **c** are packed in a hexagonal arrangement, and the long axes are arranged in an alternate way. However, the relative arrangements of the centers of the molecules are almost the same as 2(*o*). As a glide plane in 2(*o*) is replaced by a translation along [120] in 2(*d*), and a **c** translation in 2(*o*) by an *a* glide plane in 2(*d*), **a**, **b** and **c** of 2(*o*) correspond to (**a** + 2**b**), −**c** and −**a**/2 of 2(*d*), respectively.

Morphotropism

Formation of a column by parallel stacking of the hydrogen-bonded dimers is widely observed in the structures of benzoic acids. The modes of packing of the columns are divided into two types, parallel and alternate. Benzoic acid (Bruno & Randaccio, 1980), 1, 2(*o*) and some 3- or 2-halogenobenzoic acids (Tanaka, Ashida, Sasada & Kakudo, 1967; Ferguson & Islam, 1975; Ferguson & Sim, 1962, 1961) belong to the former, and salicylic acid, 2(*d*), 2-methyl, 4-methoxy and 4-bromobenzoic acids (Katayama, Furusaki & Nitta, 1967; Bryan, 1967; Ohkura, Kashino & Haisa, 1972) to the latter. The two types are closely related to each other as shown by the occurrence of the dimorphs and the correspondence of the crystallographic axes between 2(*o*) and 2(*d*).

The remarkable similarity of the crystal structures of benzoic acid, 1 and 2(*o*), and salicylic acid and 2(*d*) shows that the hydrogen bonding of the phenolic hydroxylic groups plays only an additional role in determining the structure.

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The Structure of Benzyl 4-*O*-(2,3-Dideoxy-α-L-pent-2-enopyranos-4-ulosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside

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Abstract

$C_{21}H_{26}O_7$, m.p. 376 K, M_r = 390·42, is monoclinic, space group $P2_1$, with a = 9·797 (2), b = 8·739 (2), c = 12·141 (3) Å, β = 91·90 (2)°, Z = 2, d_m = 1·19, d_c = 1·25 Mg m^{-3}. The structure was solved by direct methods and refined by the full-matrix least-squares procedure to R = 0·043 (R_w = 0·039, $w = 1/\sigma_I^2$) for 1281 independent reflections with $I > 2\sigma_I$. The unsaturated dihydropyranone ring was found to have the $^{O}H_5$ half-chair conformation. The rhamnopyranose ring exhibits the $^{1}C_4(L)$ chair conformation strongly deformed due to fusion with the non-planar dioxolane ring. The interglycosidic φ and ψ angles are 29 (4) and 27 (2)° respectively.

Introduction

The stannic-chloride-catalyzed reaction between benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside and 1-*O*-benzoyl-2,3-dideoxy-DL-pent-2-enopyranos-4-ulose yields a mixture of two diastereoisomeric benzyl 4-*O*-(2,3-dideoxy-α-L-pent-2-enopyranos-4-ulosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranosides (Grynkiewicz, 1980). These compounds are the precursors of disaccharides belonging to the 4-*O*-pentopyranosyl-L-rhamnose family; the disaccharides can be obtained by proper chemical modifications of the dihydropyranone moiety.

From the mixture of two diastereoisomeric products the less polar one (Fig. 1), melting at 376 K, was separated by column chromatography and its molecular structure determined. The reasons for undertaking the present study were to determine: (*a*) the

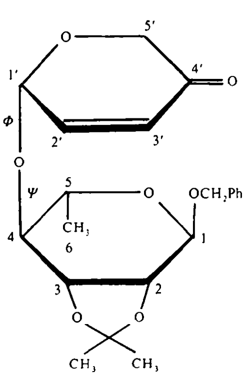

Fig. 1. Haworth formula of the title compound with the systematic atom numbering.

0567-7408/82/051485-05$01.00