

Crystal Structures of D-(+)- and *meso*-Hydrobenzoin. Absolute Direction of the Dipole Moment of D- and L-Hydrobenzoin in the Crystal and Correlation with Crystal Morphology, Pyroelectric Effect, and Absolute Configuration

William T. Pennington, Sumita Chakraborty, I. C. Paul,* and D. Y. Curtin*

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801.
Received December 22, 1987

Abstract: Polar crystals of racemic hydrobenzoin have been shown to react to give benzaldehyde at different rates along the two directions of the polar axis when suspended in aqueous potassium periodate. The Kundt-Bürker pyroelectric test shows well-developed electrical polarity. A crystal structure determination permits correlation of these phenomena with the internal structure of the crystal. The crystals are monoclinic, $a = 5.8372$ (9) Å, $b = 7.904$ (1) Å, $c = 12.405$ (2) Å, $\beta = 93.04$ (1)°, the space group is $P2_1$, and the structure has been refined to an R factor of 0.033 on 1154 nonzero reflections. The structure of *meso*-hydrobenzoin shows the molecules to exist in the centrosymmetric anti conformation. Crystals are monoclinic, $a = 12.542$ (2) Å, $b = 5.084$ (1) Å, $c = 9.305$ (1) Å, $\beta = 106.67$ (2)°, the space group is $P2_1/c$. Refinement resulted in $R = 0.045$ based on 748 nonzero reflections.

Racemic (threo) hydrobenzoin holds an important place in the history of stereochemistry; it was one of the few compounds whose crystal morphologies were early recognized¹ to permit optical resolution by hand-separation of the two enantiomers, the method Pasteur had employed with sodium ammonium tartrate tetrahydrate.² The preparation of crystals of the enantiomers of hydrobenzoin and their resolution by mechanical separation have even been made the basis of an experiment in an introductory laboratory course in organic chemistry.³ In addition the crystals of *threo*-hydrobenzoin were reported, on the basis of morphological examination, to have a polar structure, suggesting that they should possess properties of particular interest.⁴ Nevertheless there appears to have been no determination of a structure of either this substance or the diastereomer, *meso*-hydrobenzoin. In the present paper we report the crystal structure of *D*-(+)-hydrobenzoin (or 1(*R*),2(*R*)-diphenylethane-1,2-diol) by X-ray methods and discuss the relationship between the morphology, absolute configuration, and electric dipole of the enantiomeric hydrobenzoin⁵ and the pyroelectric effect.⁶ In addition the oxidation reaction of single crystals suspended in aqueous periodic acid solution has been found to be anisotropic, and a correlation of the preferred reaction direction with crystal structure is reported.

meso-Diols, also, have been of special interest to chemists; although often described as being "optically inactive because of internal compensation", some of them, particularly tartaric acid and a few of its close relatives,⁷ exist in the crystalline state as

Table I. X-ray Structural Information for D-(+)- and *meso*-Hydrobenzoin

	D-(+)- hydrobenzoin	<i>meso</i> - hydrobenzoin
formula	$C_{14}H_{14}O_2$	
mol wt	214.26	
system	monoclinic	monoclinic
a (Å)	5.8372 (9)	12.542 (2)
b (Å)	7.904 (1)	5.084 (1)
c (Å)	12.405 (2)	9.305 (1)
β (deg)	93.04 (1)	106.67 (2)
V ($\times 10^{-24}$ cm ³)	571.5	568.4
Z	2	2
D_{calcd} (g/cm ³)	1.25	1.25
radiation	Cu K α	Mo K α
λ (Å)	1.54178	0.71073
μ (cm ⁻¹)	6.20	0.77
space group	$P2_1$	$P2_1/c$
diffractometer	Syntex $P2_1$	Nonius CAD-4
cell dimensions	15 r ($85^\circ < 2\theta < 96^\circ$)	25 r ($26^\circ < 2\theta < 36^\circ$)
total unique data	2471	1514
data ($> 3\sigma$)	1154	748
mode data collection	θ -2 θ scan	θ -2 θ scan
speed data collection (deg/min)	2-19.5	2-16.5
analytical absorption correction	yes	yes
transmission range	0.63-0.95	0.97-0.99
hydrogen location	difference maps	
weighting scheme	$w = [1.00/(\sigma^2(F) + 0.001F^2)]$	
no. of variables	201	101
final R (nonzero data)	0.033	0.045
final R_w	0.051	0.056

racemates containing pairs of molecules in chiral conformations. The crystal structure of *meso*-hydrobenzoin is reported here.

Experimental Section

Microanalyses were carried out by J. Nemeth and his associates. Fourier transform infrared spectra were obtained in Nujol mull with a Nicolet 7000 FTIR spectrophotometer or IBM IR/32 FTIR spectrophotometer. Optical goniometric data were measured on a Tecom two-circle optical goniometer. Optical rotations were measured with a Rudolph Research Autopol III automatic polarimeter. DSC studies were carried out with a Du Pont Model 900 thermal analyzer. Photographs were taken with a Beseler Topcon Super D camera mounted on a Bausch and Lomb Model LS dynoptic polarizing microscope with 160 ASA Ektachrome film.

Sources of *meso*- and *dl*-Hydrobenzoin. *meso*-Hydrobenzoin was prepared in 92% yield by the procedure of ref 3. From ethyl acetate there were obtained crystals: mp 135 °C; ¹H NMR (CHCl₃) δ (benzylic protons) 4.81.

(1) (a) Forst, C.; Zincke, Th. *Liebigs Ann.* **1876**, *182*, 279-293. (b) Erlenmeyer, E., Jr. *Chem. Ber.* **1887**, *30*, 1531. (c) Groth, P. *Chemische Kristallographie*: Verlag von Wilhelm Engelmann: Leipzig, 1919; Vol. 5, pp 195-196. (d) Read, J.; Campbell, I. G. M.; Barker, T. V. *J. Chem. Soc.* **1929**, 2305-2318.

(2) (a) Pasteur, L. *Ann. Chim. Phys.* **1848**, *24*[3], 442. (b) Groth, P. *Chemische Kristallographie*: Verlag von Wilhelm Engelmann: Leipzig, 1910; Vol. 3, p 333.

(3) Fieser, L. F. *Experiments in Organic Chemistry*: D. C. Heath, Lexington, MA, 1960; pp 188-190.

(4) See: (a) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525-541. (b) Paul, I. C.; Curtin, D. Y. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987. (c) *threo*-Hydrobenzoin crystals were reported by Ostromyslenski to be triboluminescent [Beilstein's Handbook, [1], VI, 491]. (d) Hall, R. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 2848-2854.

(5) See: Lang, S. B. *Sourcebook of Pyroelectricity*: Gordon and Breach: New York, 1974.

(6) For examples of the application of the three-powder pyroelectric method to the determination of absolute configuration, see: (a) Patil, A. A.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1985**, *107*, 726-727. (b) Patil, A. O.; Pennington, W. T.; Paul, I. C.; Curtin, D. Y.; Dykstra, C. E. *Ibid.* **1987**, *109*, 1529-1535.

(7) See Duesler, E. N.; Mondragon, M.; Tapscott, R. E. *Acta Crystallogr.* **1984**, *C40*, 1286-1288 for references.

Table II. Final Atomic Coordinates for D-(+)-Hydrobenzoin

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O1	1.0765 (3)	-0.4527	0.3588 (1)
O2	1.0512 (3)	-0.1694 (3)	0.4787 (1)
C1	0.9006 (3)	-0.3350 (3)	0.3276 (1)
C2	0.8473 (3)	-0.3407 (3)	0.2065 (1)
C3	1.0067 (3)	-0.4047 (3)	0.1379 (2)
C4	0.9547 (4)	-0.4139 (5)	0.0272 (2)
C5	0.7462 (4)	-0.3567 (5)	-0.0157 (2)
C6	0.5882 (4)	-0.2901 (4)	0.0517 (2)
C7	0.6379 (3)	-0.2836 (3)	0.1626 (2)
C8	0.9897 (3)	-0.1605 (3)	0.3653 (1)
C9	0.8207 (3)	-0.0185 (3)	0.3466 (1)
C10	0.6254 (3)	-0.0075 (3)	0.4065 (1)
C11	0.4681 (3)	0.1226 (3)	0.3872 (2)
C12	0.5028 (4)	0.2419 (3)	0.3077 (2)
C13	0.6956 (4)	0.2307 (3)	0.2475 (2)
C14	0.8536 (3)	0.1018 (3)	0.2673 (1)
H1A	1.024 (4)	-0.525 (5)	0.404 (2)
H2	1.124 (5)	-0.266 (5)	0.490 (3)
H1B	0.769 (4)	-0.356 (3)	0.363 (2)
H3	1.165 (5)	-0.440 (4)	0.168 (2)
H4	1.068 (5)	-0.460 (4)	-0.018 (3)
H5	0.701 (5)	-0.371 (6)	-0.089 (3)
H6	0.435 (6)	-0.264 (5)	0.028 (3)
H7	0.527 (5)	-0.236 (5)	0.206 (2)
H8	1.134 (3)	-0.135 (3)	0.325 (2)
H10	0.600 (4)	-0.092 (4)	0.462 (2)
H11	0.327 (4)	0.133 (4)	0.429 (2)
H12	0.400 (6)	0.329 (6)	0.292 (3)
H13	0.723 (6)	0.322 (6)	0.191 (3)
H14	0.992 (5)	0.096 (4)	0.228 (2)

Isomerization of *meso*-hydrobenzoin to the *dl* form was accomplished in 83% yield by heating with potassium hydroxide at 160 °C under reduced pressure as reported earlier by Collet.⁸ Purification by crystallization from ethyl acetate gave crystals: mp 120–121 °C (lit.⁸ mp 121 °C); ¹H NMR δ (benzylic protons) 4.69.

D-(+)-Hydrobenzoin "99% optically pure" was obtained from the Aldrich Chemical Co. and after further purification by crystallization from ethanol had mp 144.5–146.5 °C and $[\alpha]_D^{22} +118^\circ$ (c 0.5 g/100 mL in benzene). The specific rotation is quite solvent-dependent; the generally accepted literature value^{9,10} for the specific rotation in benzene is $[\alpha]_D^{19} +122^\circ$. A differential thermal analysis scan of the recrystallized sample showed no evidence of the presence of the L(-) enantiomer.¹¹

X-ray Structure Analyses of D-(+)- and *meso*-Hydrobenzoin. A thin colorless plate obtained from the crystallization of a sample of racemic hydrobenzoin synthesized by Dr. Robert C. Hall was employed for the X-ray structure determination, and as described below was shown to correspond to the D-(+) enantiomer. The crystal of *meso*-hydrobenzoin was also a thin colorless plate. The crystal data and the details of the data collection, structure solution, and refinement for both D-(+)- and *meso*-hydrobenzoin are summarized in Table I. For both determinations, the structure solution was carried out with MULTAN80.¹² The atomic scattering factors were those of Cromer and Waber¹³ for neutral atoms, and all computations, other than structure solution, were performed with the SHELX76 package of computer programs.¹⁴ Atomic

(8) Collet, A. *Synthesis* 1973, 664–665.

(9) Eisenlohr, F.; Hill, L. *Chem. Ber.* 1937, 70, 942–947.

(10) Read, Campbell, and Barker¹⁴ measured optical rotations of single crystals obtained by crystallization of racemic hydrobenzoin from ethyl acetate and found specific rotations of +92.0, +90.1, and +98.3° (mp 146 °C in each case). These rotations approximate that of the completely resolved sample. It was subsequently shown by Fieser (ref 3) that single crystals obtained from a solution of racemic hydrobenzoin had $[\alpha]_D$ in chloroform of -97.0 and +97.6°. The specific rotation in chloroform of resolved material given in ref 1d was -99°. Other "single" crystals were found by Read, Campbell, and Barker to contain substantially more of the enantiomeric hydrobenzoin with rotations from 44 to 77°. It is not clear how the minor enantiomer is incorporated in such crystals but in our X-ray work there was no indication of the second enantiomer.

(11) See: Fouquey, C.; Jacques, J. *Tetrahedron* 1967, 23, 4009–4019.

(12) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN80, a system of computer programs for the automatic solution of crystal structures from X-ray data. University of York, England, and University of Louvain, Belgium, 1980.

(13) Cromer, D. T.; Waber, J. T. *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2 B.

(14) Sheldrick, G. M. SHELX76, a program for crystal structure determination; University of Cambridge: England, 1976.

Table III. Final Atomic Coordinates for *meso*-Hydrobenzoin

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O1	0.4975 (1)	0.4087 (3)	-0.1878 (2)
C1	0.4647 (2)	0.3982 (4)	-0.0530 (2)
C2	0.3410 (2)	0.4442 (4)	-0.0829 (2)
C3	0.2879 (2)	0.6414 (5)	-0.1788 (3)
C4	0.1752 (2)	0.6853 (6)	-0.2043 (4)
C5	0.1150 (2)	0.5336 (7)	-0.1344 (3)
C6	0.1662 (2)	0.3396 (7)	-0.0385 (3)
C7	0.2795 (2)	0.2932 (6)	-0.0131 (3)
H1A	0.494 (2)	0.250 (6)	-0.224 (3)
H1B	0.482 (1)	0.227 (4)	-0.006 (2)
H3	0.329 (2)	0.743 (6)	-0.234 (3)
H4	0.144 (2)	0.819 (6)	-0.266 (3)
H5	0.039 (3)	0.578 (7)	-0.157 (3)
H6	0.129 (2)	0.229 (7)	0.012 (3)
H7	0.314 (2)	0.151 (6)	0.048 (3)

coordinates for D-(+)- and *meso*-hydrobenzoin are given in Tables II and III, respectively. Lists of observed and calculated structure factors and the final values of the anisotropic thermal parameters for both compounds have been deposited (supplementary material).

Absolute Configuration of the Crystal from Racemic Hydrobenzoin. On the crystal used for the X-ray determination, particular care was taken to assign the direction of the crystallographic axes and index the major faces. X-ray diffraction measurements were made to attempt to assign the absolute configuration by using Cu K α radiation. By the application of criteria proposed by Hope and de la Camp,¹⁵ a group of 30 reflections was chosen that should be particularly sensitive to the anomalous scattering effect for oxygen. Each of these reflections and its symmetry-related reflection were measured on the upper and lower hemispheres of the χ circle of the diffractometer, and the results were compared with corresponding values for the Friedel-related reflections. Absorption corrections were applied, and the reflections were measured at very slow scan speeds. The agreement factor, R_{disp} ,¹⁶ was 0.34. Of the 30 reflections, 24 were in agreement with an assignment of the D-(+) configuration to the molecules in this crystal.

The same crystal as was used for these X-ray measurements, with the faces defining the direction of the polar axis noted, was subjected to the Kundt-Bürker pyroelectric test. There was a clear separation of the powders indicating the direction of polarity of the *b* axis.

Periodic Acid Oxidation of D-(+)-Hydrobenzoin. A small crystal of hydrobenzoin whose orientation could be identified by its morphology was held between two glass slides, and a solution of 1.13 g of H₂IO₆ in 2 mL of water was injected into the space between the slides so that it surrounded the crystal. Progress of the reaction was followed by microscopic observation and photography. Formation of the oily product was apparent after 1 min. Reaction was found to occur preferentially next to the (011) and (0 $\bar{1}$ 1) faces at the -*b* side of the crystal as shown by the gradual etching away of that side of the crystal and accumulation of an oily layer of benzaldehyde just outside the crystal. As the reaction progressed, other faces began to react but more slowly. The (100) and (100) faces were least reactive and, in fact, although the crystal gradually became thinner, its length (along *a*) did not change perceptively. The crystal had completely dissolved after 1 h.

In a control experiment in which a similar crystal was placed between two microscope slides and surrounded by water without periodic acid, there was no evidence of significant dissolution of the crystal after 7 days at ambient temperature.

Various attempts to anchor the crystal in the surrounding solution by gluing one surface to a glass slide gave similar results, but there was more difficulty in seeing clearly the effects of the reaction and the glue tended to dissolve before the crystal had reacted fully.

Application of the Kundt-Bürker Three-Powder Pyroelectric Test to D-(+)-Hydrobenzoin Single Crystals. A single crystal of D-(+)-hydrobenzoin was heated on a glass microscope slide to 100–110 °C and immediately sprayed with a mixture of yellow flowers of sulfur, carmine, and lycopodium powder dyed with methylene blue as described earlier.⁶ The side of the crystal identified morphologically as the +*b* side of the

(15) Hope, H.; de la Camp, U. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallog.* 1972, A28, 201–207.

(16) Note the following

$$R_{\text{disp}} = \sum (|\Delta F_{\text{obsd}}| - |\Delta F_{\text{calcd}}|) / \sum (|\Delta F_{\text{obsd}}|)$$

$$\Delta F_{\text{obsd}} = (|F_{\text{obsd}}(hkl)| - |F_{\text{obsd}}(h\bar{k}l)|)$$

$$\Delta F_{\text{calcd}} = (|F_{\text{calcd}}(hkl)| - |F_{\text{calcd}}(h\bar{k}l)|)$$

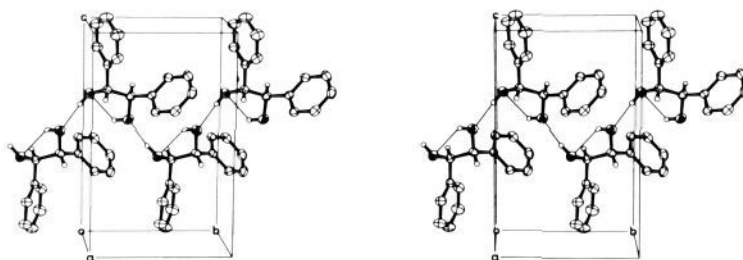


Figure 1. Crystal structure of D-(+)-hydrobenzoin as determined with a single crystal separated from a crystallization of the racemic compound. One hydroxyl group of each molecule is intramolecularly hydrogen bonded to the adjacent hydroxyl, which, in turn, forms an intermolecular hydrogen bond to an adjacent molecule related by the 2_1 -axis. Hydrogen bonded chains thus run through the crystal parallel to the b axis.

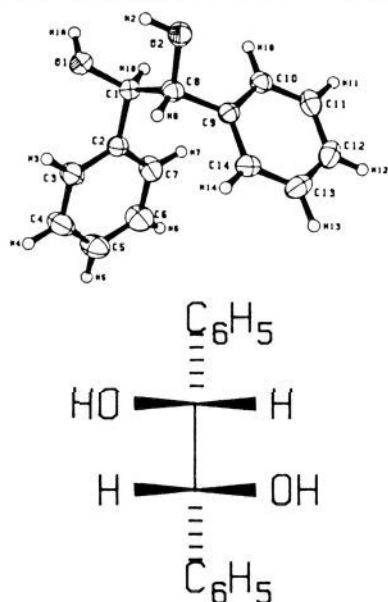


Figure 2. Top, the conformation of the D-(+)-hydrobenzoin molecule as it occurs in the crystal together with the numbering system employed in discussing the X-ray structural results. Bottom, the Fischer projection formula of the same molecule.

crystal attracted the blue powder and the $-b$, the red-yellow.

As a check on reliability, variations of the test were applied to crystals of hydrobenzoin and several other substances, the absolute direction of whose polar axes had been reported in Groth's survey.^{2b} Crystals of hydrobenzoin (110–120 °C), picric acid (90 °C), resorcinol (68 °C), *p*-chloroacetanilide (130 °C), and sucrose (90 °C) were heated for 30 min to the temperature given in parentheses, and the test, applied by each of the three methods below, showed good separation of the positively and negatively charged powder; the indication of the direction of the crystal dipole was independent of the method used in all cases. Conditions employed for these tests were as follows. (1) The crystal was heated and then sprayed immediately while still hot. (2) The crystal was heated on a glass slide and then allowed to cool for 5 min by placing the slide on a metal surface acting as a heat sink. (3) After heating, the crystal was cooled for 15 min as in (2). If, however, after heating the crystal was allowed to cool for 1 h at ambient temperature, none of the substances above showed any separation of the positively and negatively charged powder. An experiment with hydrobenzoin showed that crystals heated for 20 min (80 °C) and cooled for 1 h lost their polarity; however, when heated as before but cooled *under vacuum* (3 mm), they still showed some separation of positive and negative powders in the test.

A test for second harmonic generation^{4d} gave a signal that was somewhat more intense than that obtained with urea.

Results and Discussion

Crystal Structure of D-(+)-Hydrobenzoin. The crystal structure of D-(+)-hydrobenzoin is shown in Figure 1.¹⁷ The hydrobenzoin molecule has a *gauche* conformation, its hydroxyl groups having a torsion angle of 54.8° about the central C(1)–C(8) bond. Such a conformation is stabilized by internal hydrogen bonding of one

(17) Assignment of the D-(+) configuration is based on the anomalous scattering of oxygen described in the experimental section and is consistent with the other results reported here.

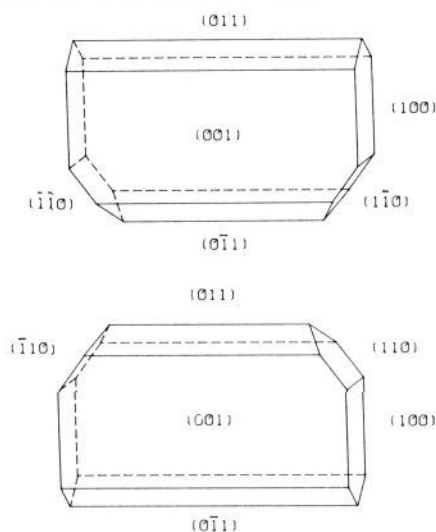


Figure 3. Drawings of crystals of D-(+) (upper drawing) and L(-) hydrobenzoin (lower drawing) as obtained from ethanol solvent showing the most common faces. The view is down c^* with a to the right in the page. The major face in each crystal is (001). The (100) face slants upward on the right end of each crystal forming an angle of 93° with (001). The hemihedral (corner) faces, $(\bar{1}\bar{1}0)$ and (110) in the D-(+) crystal or (110) and $(\bar{1}\bar{1}0)$ in the L(-) distinguish the two enantiomeric configurations. Figure 32.1 of ref 3 shows photographs of such crystals nearly 1 cm in length obtained from crystallization of racemic hydrobenzoin from ether solution. Specific rotations reported for those crystals were -97.0 and $+97.6^\circ$.

hydroxyl group to the other; the phenyl groups are thus adjacent but staggered with respect to one another, each phenyl group lying between the phenyl group and hydrogen atom on the neighboring tetrahedral carbon atom. (The C(phenyl)–C(1)–C(8)–C'(phenyl) torsion angle is 62.9°.)

Absolute Configuration. It had been determined previously¹⁸ by a series of chemical interrelations that the dextrorotatory (+) enantiomer of hydrobenzoin has the D configuration as shown in Figure 2.

The crystal morphologies of enantiomeric crystals of hydrobenzoin of known optical rotation (grown from ethyl acetate) had been reported^{1,19} without knowledge of either the absolute configuration or the crystal structure. The subsequent determination of the absolute configuration^{17,18} allows assignment of absolute configurations to crystals of known morphology.²⁰ These as-

(18) Berti, G.; Bottari, F. *J. Org. Chem.* **1960**, *25*, 1286–1292.

(19) (a) Note that assignment of the a and c axes is the reverse in the present paper from that employed by Groth in ref 1c.

(20) A crystal with (001), (100), (00 $\bar{1}$), $(\bar{1}00)$, (011), (01 $\bar{1}$), and (010) faces developed was examined on an X-ray diffractometer, and a number of measurements were carried out on 30 reflections especially sensitive to the anomalous scattering of oxygen. That same crystal was submitted to the pyroelectric test to identify the electrically positive end of the b axis. The results of the pyroelectric test and of the X-ray study each indicated that the crystal had the D-(+) configuration, consistent with our other work. It can be concluded that determination of the absolute configuration of hydrobenzoin by anomalous dispersion gives results in agreement with the determination by chemical methods as previously reported.

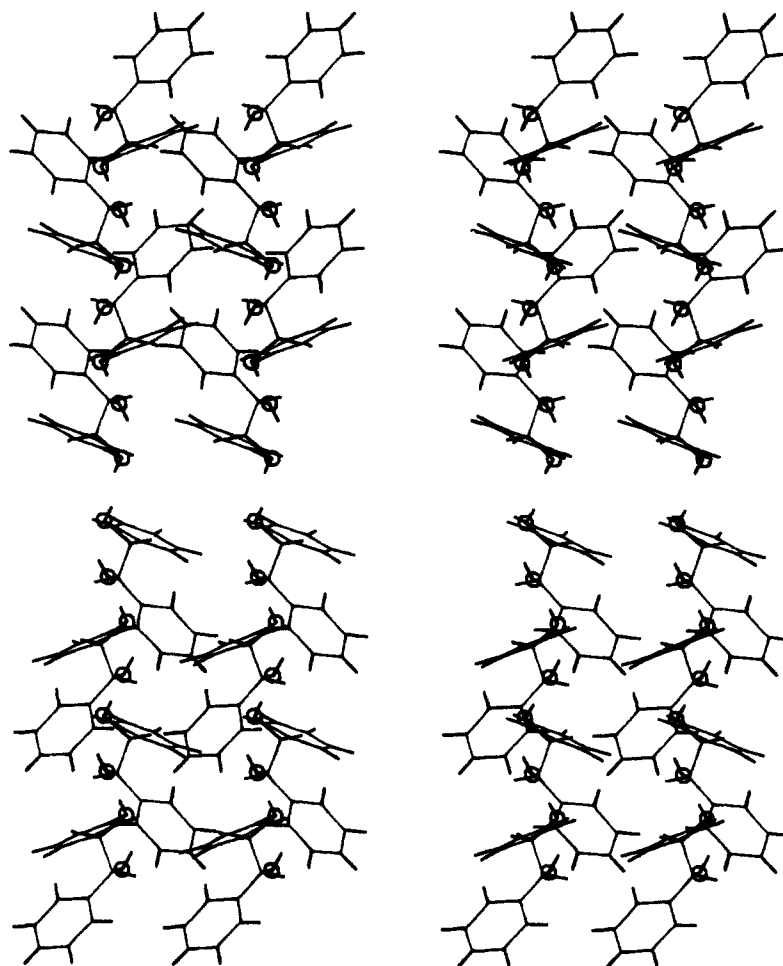


Figure 4. Stereopair drawings of D-(+)- (upper drawing) and L-(-)-hydrobenzoin oriented as in the crystal drawings of Figure 3 (view down c^* with a to the right and b up in the plane of the page). Note that the structures are layered along the c axis, each layer containing either molecules of orientation A (coordinates x, y, z) or orientation B ($-x, \frac{1}{2} + y, -z$). We have selected the B molecules as forming the more stable (001) face since this permits the hydrogen bonded chains to proceed uninterrupted whereas a surface formed by A molecules would have interrupted chains.

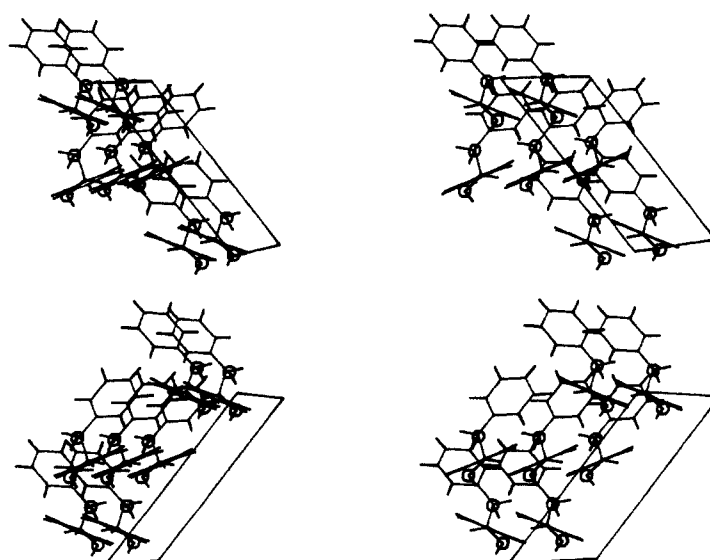


Figure 5. Stereopair views showing the structures at the observed hemihedral ($1\bar{1}0$) face (lower drawing) and the (110) plane (upper drawing), its structural opposite not required by symmetry and not observed in crystals of D-(+)-hydrobenzoin. The axial orientation is the same as in Figure 3.

signments are shown in Figure 3. Our X-ray structure determination thus allows the internal structures of the D and L enantiomers to be fitted to the corresponding crystals as shown by comparison of Figures 3 and 4.

The Hemihedral Faces of D-(+)-Hydrobenzoin. Figure 3 shows that ($1\bar{1}0$) and ($\bar{1}\bar{1}0$) faces in the D-(+) isomer or the (110) and

($\bar{1}10$) faces in the L(-) isomer are unaccompanied by their centrosymmetrically related counterparts and provide a means of distinguishing between the two enantiomeric crystals. In Figure 5 is shown the crystal structure at the ($1\bar{1}0$) face found in the D-(+) crystal and also the structure that would be found at the (110) plane that is not a developed face in this enantiomer. A group

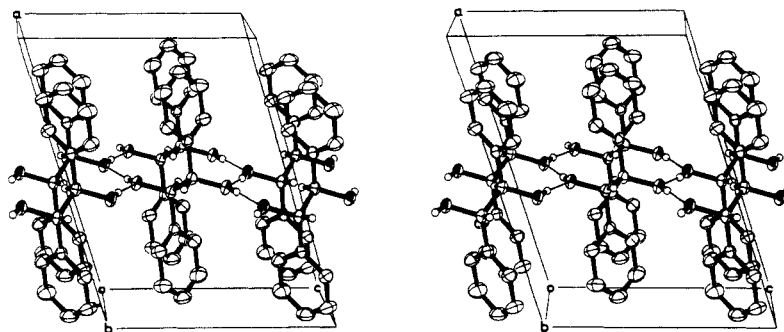


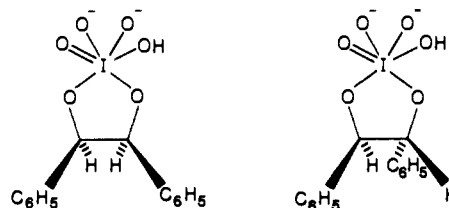
Figure 6. Stereopair drawing of *meso*-hydrobenzoin. The conformation is that most stable in solution with hydroxyl groups and phenyl groups anti to each other. Since internal hydrogen bonding is impossible, all hydroxyl groups take part in intermolecular hydrogen bonds, in this case forming a two dimensional network in the *bc* plane.

at the Weizmann Institute has made much progress in explaining and even controlling crystal morphology of organic crystals by systematically changing the crystallization medium to alter the relative rate of crystal growth at various faces.²¹ They have demonstrated the dramatic effects of small amounts of additives on crystal growth of a number of substances. It would be unwise to attempt to explain the shapes of chiral hydrobenzoin crystals without more information; in particular, knowledge of the effect of solvents (and additives) on the relative rates of crystal growth in directions normal to the faces of interest is desirable.^{22,23}

Structure of *meso*-Hydrobenzoin. This structure, shown in Figure 6, is made up of centrosymmetric molecules lying at crystallographic centers. The hydroxyl groups are thus anti to one another and are involved in intermolecular hydrogen-bonded chains. The molecular conformation can be seen in Figure 6. Were the molecule to adopt a conformation with internal hydrogen bonding like that in the racemic structure, the phenyl groups would be staggered between C-O and C-phenyl bonds on the neighboring tetrahedral carbon atom with resulting increased steric strain. It seems likely, then, that in spite of differences in packing forces and hydrogen-bonding geometry the conformations of the two stereoisomeric hydrobenzoin in the crystal approximate those in solution. Studies²⁴ in solution of the infrared spectra of 1,2-dialkylethanedioles have provided evidence that with large alkyl groups such as *tert*-butyl the chiral isomers have one of the two hydroxyl groups involved in intramolecular hydrogen bonding in the major conformation in solution as is the case in the structure of (+)- or (-)-hydrobenzoin. However, the *meso* isomer is prevented by unfavorable steric interaction of the substituents from forming the conformer with internal hydrogen bonding and thus exists in solution in the all-anti conformer analogous to that in the crystal structure of the *meso* isomer reported here.^{25,26}

Reaction of Single Crystals of Hydrobenzoin with Periodic Acid.

The anisotropy of hydrobenzoin crystals and, in particular, the difference in structure at faces {011} and {0 $\bar{1}$ 1} at the opposite ends of the polar *b* axis suggested the possibility of finding preferential reaction at one end of the crystal with an appropriate reagent as had been found with the reaction of ammonia gas with polar *p*-bromobenzoic anhydride crystals.²⁷ A particularly attractive reaction, characteristic of 1,2-dihydroxy compounds, was the oxidative cleavage with periodic acid.²⁸ This reaction has been extensively studied in solution²⁹ and found to occur by way of a cyclic iodate ester of the type whose hydrate dianion is illustrated below for *meso*- and D-(+)-hydrobenzoin.^{29d} In many cases



equilibration of the periodate ester with starting glycol is sufficiently rapid to allow an equilibrium to be maintained throughout reaction. Early evidence for the importance of an intermediate cyclic 5-membered iodate ester of this sort was provided by the observation³⁰ that *cis*-diols underwent periodate oxidation in solution more rapidly than did *trans*-diols. In an extension of the argument, threo acyclic diols were more reactive³¹ than erythro, and, by extension to the hydrobenzoin, the racemic isomers were found to react with a *k* 4 times that of the *meso* isomer.³² As shown in the structures of the intermediate cyclic iodate esters above, that from the *meso*-diol has an energetically unfavorable *cis* phenyl-phenyl interaction, which is absent in the *trans* D-(+) ester shown.

(21) For an excellent review, see: Addadi, L.; Berkovitch-Yellin, Z.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. *Topics in Stereochemistry*; Eliel, E. L.; Wilen, S. H., Allinger, N. L., Eds.; Interscience: New York, 1986; Vol. 16, Chapter 1.

(22) The literature is somewhat confusing as to the effect of solvent on crystal growth of racemic hydrobenzoin. Thus ether was employed by Erlenmeyer (ref 1b) and Fieser (ref 3) to give crystals with hemihedral faces. On the other hand Reis and Schneider (ref 23a) reported that crystals from ether showed no hemihedral faces although they were still polar since they were shown to give a pyroelectric effect. In ether there is agreement that crystals tend to be twinned (ref 3c and 23b). We found that faces of form {110} are poorly developed when the crystal is grown from this solvent. In our work with chloroform, crystals were poorly developed, and many crystals were twinned. In ethyl acetate the oblique faces ({110} and {1 $\bar{1}$ 0}) in the D enantiomer were very highly developed and {100} was missing or very small. Read, Campbell, and Barker (ref 1d) found that in chloroform there was again formation of a conglomerate (shown by polarimetric examination) but without the development of hemihedral faces. They further note that the shape of a crystal of one enantiomer of hydrobenzoin is influenced by whether or not the other enantiomer is present in the solution.

(23) (a) Reis, A.; Schneider, W. *Z. Krist.* **1928**, *69*, 62-76. (b) Bodewig, *Liebigs Ann.* **1876**, *182*, 279-295.

(24) Kuhn, L. P. *J. Am. Chem. Soc.* **1958**, *80*, 5950-5954.

(25) Early attempts (ref 26) to use dipole moment measurements to establish configuration were disappointing. The dipole moment in benzene of racemic hydrobenzoin was 2.7 D as was expected, but the moment of the *meso* isomer was almost as large, 2.1 D. It was recognized that the moment of the *meso* isomer could not be used to draw conclusions about the conformation of the molecule around the central C-C bond since the hydroxyl groups make a major contribution to the moment and can exist in a variety of conformations around their O-C single bonds with a substantial net moment even if the arrangement around the central C-C bond is anti.

(26) (a) Weissberger, A.; Sängewald, R. *Z. Phys. Chem.* **1931**, *12*[B], 399-406. (b) Hassel, O.; Naeshagen, E. *Ibid.* **1931**, *14*, 232-236. (c) Eisenlohr, F.; Hill, L. *Z. Phys. Chem.* **1937**, *36*[B], 30-44.

(27) Duesler, E. N.; Kress, R. B.; Lin, C.-T.; Shiao, W.-I.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1981**, *103*, 875-879.

(28) Jackson, E. L. *Organic Reactions*; Wiley: New York, 1944; Vol. 2, pp 341-375.

(29) See particularly these studies of the reaction mechanism: (a) Price, C. C.; Kneil, M. *J. Am. Chem. Soc.* **1942**, *64*, 552-554. (b) Buist, G. J.; Bunton, C. A.; Miles, J. H. *J. Chem. Soc. B* **1959**, 743-748. (c) Buist, G. J.; Bunton, C. A. *J. Chem. Soc. B* **1971**, 2117-2128. (d) Buist, G. J.; Bunton, C. A.; Hipperson, W. C. P. *Ibid.* **1971**, 2128-2142. Other references are cited in these papers.

(30) R. Criegee, quoted in ref 29a.

(31) See ref 29b.

(32) Zuman, P.; Sicher, J.; Krupicka, J.; Svoboda, M. *Collect. Czech. Chem. Commun.* **1958**, *23*, 1237-1215.

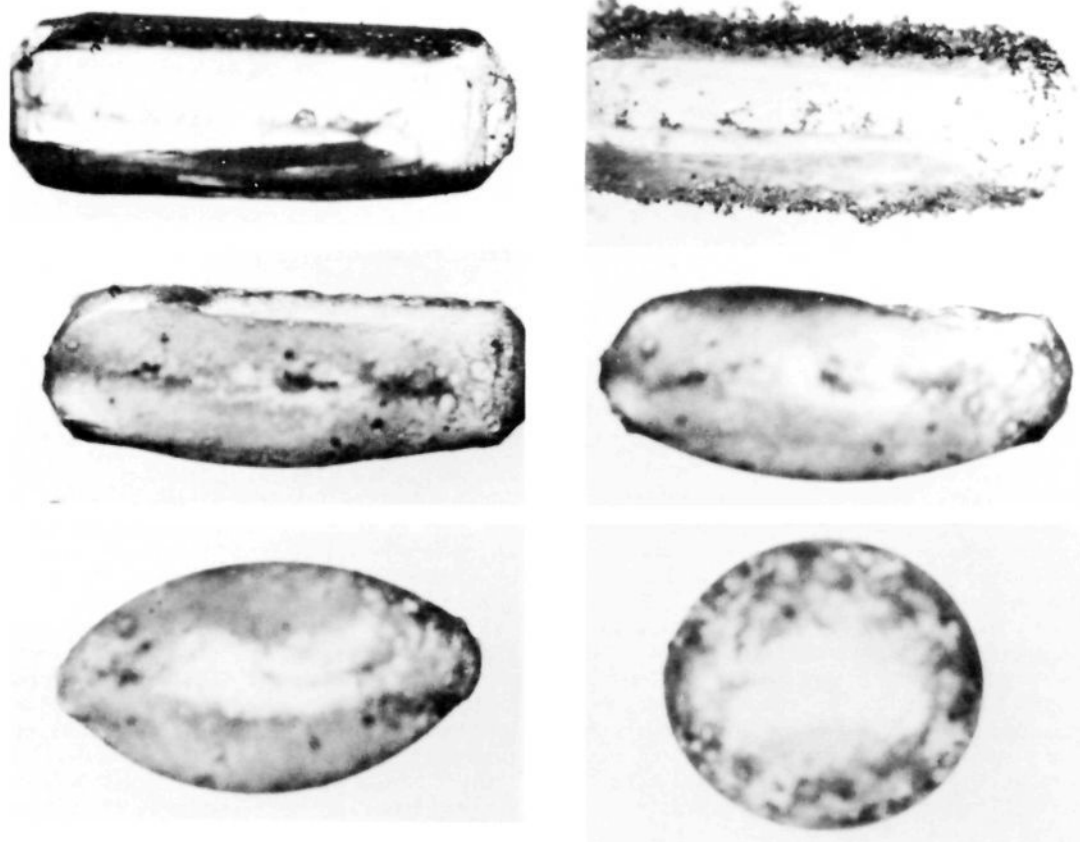


Figure 7. A series of photographs taken after successive intervals of reaction of a single crystal of D-(+)-hydrobenzoin held between microscope slides and bathed with an aqueous solution of periodic acid. The orientation is that of Figure 3 (view down c^* with a to the right and b up to the plane of the page). Note the build up of an oily benzaldehyde layer only at one side (at the $-b$ end) of the crystal. (a) The crystal before reaction. (b) The same crystal sprayed in the Kundt-Bürker pyroelectric test. The powder on the upper side of the crystal appears blue, that on the lower side, orange. (c) Reaction after 3 min. (d) After 24 min. (e) After 50 min. (f) After 75 min.

In a periodate reaction of a *threo*-hydrobenzoin crystal at a crystal surface, those faces at which the hydroxyl groups are exposed and in an orientation suitable for formation of the requisite cyclic periodate ester, might be expected to be more reactive than the others. Ideally such a reaction should be carried out as a solid-gas reaction in order to avoid the possibility of reaction by dissolution followed by reaction in a layer of solution near the crystal surface rather than at the solid surface. Our previous attempts to carry out such reactions with crystals suspended in solvent had not been encouraging because organic crystals often have a rate of solution that is rapid compared to the rate of reaction at the solid-solution interface.³³ However, a study by Holland, Richardson, and their collaborators³⁴ of the stereospecific oxidation by osmium tetroxide of tiglic acid crystals suspended in an aqueous medium provided encouragement.

A single crystal of D- or L-hydrobenzoin was held between two microscope slides immersed in a bath of periodic acid solution. As reaction occurred there was a change in the dimensions of the crystal. The reaction product is benzaldehyde, which separates as an oil that can be seen to form specifically at the end of the crystal's $-b$ axis. (If the crystal is the L(-) enantiomer, reaction would occur preferentially at $+b$.) In Figure 7 photographs of a single D-(+) crystal undergoing reaction are shown. It can be seen that reaction occurs initially at the $(0\bar{1}1)$ [and $(0\bar{1}\bar{1})$] faces at the $-b$ end of the polar axis. In Figure 8 is a stereo pair drawing

viewed normal to (001) showing the uppermost faces, (011) and $(0\bar{1}1)$ sloping to the top and bottom, and with (100) shown to the right of the drawing (the twofold screw axis produces an equivalent set of faces on the underside of the crystal). It will be seen that those faces that are most reactive contain exposed hydroxyl groups accessible for formation of the requisite cyclic periodate ester.

To test for the possibility that reaction occurs by initial dissolution of the hydrobenzoin molecules at the surface and reaction in the adjacent liquid layer, control experiments were carried out in which the crystal was suspended in water without periodic acid; there was no measurable change in the dimensions of the crystal during the time that had been required for complete reaction in the original experiment.

It follows that the heterogeneous periodate oxidation reaction can, in principle, be used to establish the absolute direction of the polar axis of a crystal when the internal structure (without the absolute orientation) is known or to establish the absolute configuration of a crystal whose morphology and structure (without the absolute configuration) are known.

meso-Hydrobenzoin crystals reacted much more slowly. As discussed above, molecules in the crystal have a conformation such that formation of a cyclic periodate ester intermediate is impossible without a major conformational change. The time required for reaction of a crystal of *meso*-hydrobenzoin was 3.5 h under conditions in which a crystal of a D crystal had disappeared in 1 h. It seems very likely that in this case reaction proceeds by a breakdown of the crystal structure at the reacting surface to allow intramolecular rotation and formation of the usual cyclic intermediate.

Pyroelectric Effect and Calculation of the Direction of the Molecular Dipole Moment. The chiral hydrobenzoin provide a test of the use of the three-powder pyroelectric method for

(33) (a) See ref 4a, note 41. (b) Curtin, D. Y.; Stein, A. R. *Can. J. Chem.* **1969**, 3637-3639.

(34) (a) Holland, H. L.; Richardson, M. F. *Mol. Cryst. Liq. Cryst.* **1980**, 58, 311-314. (b) Chenchaiyah, P. C.; Holland, H. L.; Richardson, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 436-437. (c) Chenchaiyah, P. C.; Holland, H. L.; Munoz, B.; Richardson, M. F. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1775-1778.

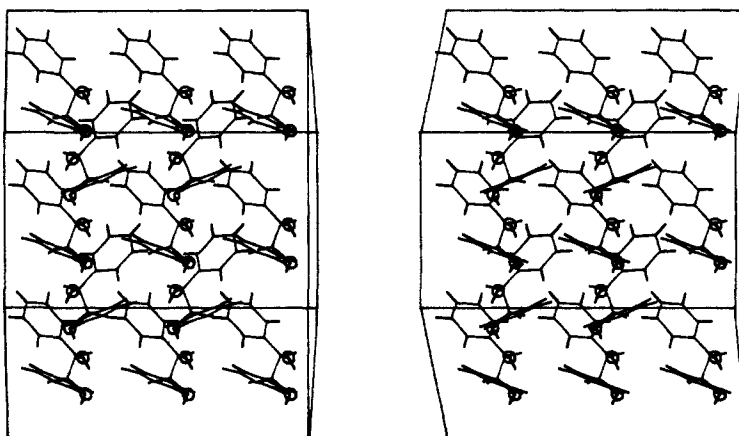


Figure 8. A drawing of the structure of D-(+)-hydrobenzoin in the orientation of Figures 3 (view down c^* with a to the right and b up in the plane of the page) and of the photographs of the reacting crystal in Figure 7. The major (001) face as well as the bounding (011), (0 $\bar{1}$ 1), and (100) faces are outlined.

measuring absolute configurations of single crystals.⁶ When a single crystal of D-(+)-hydrobenzoin was heated and sprayed with lycopodium powder, carmine, and sulfur, the blue lycopodium powder adhered to the (011) face at the $+b$ side of the crystal and the red-yellow carmine and sulfur to the $-b$ face, indicating that the (+) end of the polar b axis was negatively charged when the crystal was heated and the (-) end positive (Figure 7). In the same way the three-powder test indicated that L-(-)-hydrobenzoin has a positive charge at the (+) end of the b axis and a minus charge at the (-) end. A calculation with MNDO, of the MOPAC set of programs,³⁵ of the direction of the dipole moment of an isolated molecule of D-(+)-hydrobenzoin with the geometry found in the crystal structure determination above indicated that the component of the electric dipole parallel to the polar axis b is 1.0 D, the negative end of the dipole pointing toward $+b$. In the same way the L enantiomer would have the positive end of the dipole pointing toward $+b$. This is in agreement with the results found by the pyroelectric test (Figure 7), indicating that the side of the crystal at the (+) end of the polar b axis of D-(+)-hydrobenzoin is electrically negative.

It follows that, as was discussed in previous examples,⁶ we can deduce the absolute orientation of the enantiomeric molecules of *threo*-hydrobenzoin and thus the direction of the crystal dipole moment from the molecular absolute configuration. On the other hand we could equally well have determined the absolute configuration of the molecules from the crystal structure determination (without the use of anomalous scattering) together with the results of the pyroelectric test and knowledge of the direction of the dipole induced by heating the crystal.

Since the major part of the molecular dipole moment is due to the moment of the hydroxyl group, it is of interest to compare an estimation of the direction of the electric moment of hydrobenzoin by vector addition of the moments of its two independent hydroxyl groups. These can be approximated from the dipole moment of the simplest alcohol, methanol.^{36,37} When this dipole moment is used to approximate the moments of the hydroxyl groups in the hydrobenzoin structure, the estimated value of the component of the resultant moment along b is 1.2 D and in the same direction as the result obtained with MNDO. In these

calculations we have made no allowance for hydrogen bonding and other intermolecular interactions in the crystal, but the agreement with the pyroelectric results suggests that these effects are not large enough to alter the calculated direction of the crystal dipole moment.

The extent to which this approach can be extended remains to be seen. It depends on two assumptions: first, that the direction of the electric dipole produced by heating the crystal can be predicted from the crystal dipole moment^{38,39} and, second, that the direction of the crystal dipole can be estimated with sufficient reliability from crystal structure data by calculation with readily available programs like MNDO or, in favorable cases, even by vector addition of group dipole moments estimated from simple structures in the various functional group classes. It should then be possible to test further the utility of the Kundt-Bürker pyroelectric test as a simple method of determining the direction of the polar axis of a polar crystal or interpreting the preferred direction of reaction along the polar axis of such a crystal. Such a development, in addition to providing a potentially useful method of assigning absolute configuration, should provide further insight into the mechanistic details of reactions occurring at crystal surfaces when there is a difference in reactivity at the two ends of a polar direction in a crystal.

Acknowledgment. This material is based on research activity supported by the National Science Foundation under Grant CHE 82-09393. We are indebted to Dr. Robert C. Hall for the crystals of racemic and *meso*-hydrobenzoin employed for the two crystal structure determinations reported here. We also thank Dr. George Mahler, Andy Burke, and Professor William Pirkle for helpful advice and assistance and for making a polarimeter available.

Registry No. D-(+)-Hydrobenzoin, 52340-78-0; *meso*-hydrobenzoin, 579-43-1; *dl*-hydrobenzoin, 655-48-1; benzaldehyde, 100-52-7.

Supplementary Material Available: Tables of thermal parameters for D-(+)-hydrobenzoin and *meso*-hydrobenzoin, tables of intramolecular distances and angles for D-(+)-hydrobenzoin and *meso*-hydrobenzoin (8 pages); listings of observed and calculated structure factors for D-(+)-hydrobenzoin and *meso*-hydrobenzoin (14 pages). Ordering information is given on any current masthead page.

(35) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285-1293.

(36) We are indebted to Professor Scott Kahn for making available results of ab initio calculations carried out at Cambridge University for the series of alcohols methanol, ethanol, propanol, 2-propanol, and *tert*-butyl alcohol using CADPAC (ref 37). In each case the dipole, with the negative end placed at the oxygen atom, points away from the unshared electron pair on oxygen and approximately bisects the C-O-H angle.

(37) Amos, R. D. *CADPAC: The Cambridge Analytical Derivatives Package*; S. E. R. C. Publication No. CCP1/84/4, Computational Science Group, Science and Engineering Research Council, Daresbury Laboratory, Warrington, WA4 4AD, England, 1984. See Amos, R. D. *Chem. Phys. Lett.* **1984**, *108*, 185-190.

(38) In our previous studies of *p*-bromobenzoic anhydride and mandelic acid (ref 6) as well as in the present work, the electric dipole moment induced by heating the crystal has been found to have the same absolute orientation as the inherent electric moment of the crystal estimated from the crystal structure. There is little information correlating the change in structure with the electric dipole induced when a molecular crystal is heated. However, careful work on a few inorganic salts such as lithium iodate has been reported (see ref 39). We are indebted to Professor S. Lang for calling this work to our attention.

(39) See: Abrahams, S. C. *Aust. J. Phys.* **1985**, *38*, 289-298 and references cited there.