The X-Ray Crystal Structures of the Yellow and White Forms of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate and a Study of the Conversion of the Yellow Form to the White Form in the Solid State†[1,2]

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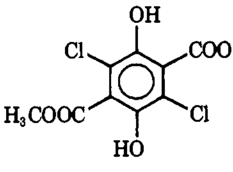
Abstract: The rearrangement in the solid state of the yellow form (**Y-1**) to the white form (**W-1**) of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate has been investigated. Crystal structures of **Y-1** and **W-1** have been determined by X-ray diffraction. The crystals of **Y-1** are triclinic, $a = 9.595$ (1), $b = 4.301$ (1), and $c = 7.970$ (1) Å, α = 114°19′ (1′), β = 94°58′ (1′), γ = 106°9′ (1′), and there is one molecule of $C_{10}H_8O_6Cl_2$ ($M = 295.0$) in the unit cell; the space group is $P\bar{1}$. The structure has been refined to an R factor of 0.074 on 906 independent nonzero structure amplitudes. The molecule of **Y-1** sits on a center of symmetry and the nonhydrogen atoms in the molecule are almost coplanar. There is a short intramolecular –O—H---O hydrogen bond (2.532 (6) Å) and there are significant exocyclic bond angle distortions resulting from intramolecular overcrowding. The principal intermolecular forces are van der Waals interactions. The crystals of **W-1** are triclinic, $a = 9.842$ (4), $b = 7.841$ (3), and $c = 10.576$ (5) Å, α = 116°23′ (2′), β = 124°10′ (2′), γ = 88°59′ (2′), and there are two molecules of $C_{10}H_8O_6Cl_2$ ($M = 295.0$) in the unit cell; the space group is $P\bar{1}$. The structure has been refined to an R factor of 0.060 on 1733 independent nonzero structure amplitudes. There are two crystallographically independent molecules of **W-1**, each sitting on the centers of symmetry at 0, 0, 0 and 0, $^1/_2$, 0. The structure of **W-1** is made up of stacks of nearly coplanar molecules along the b axis with intermolecular –O—H---O═C(OCH_3) hydrogen bonding within the stack. There is crystallographic and nuclear quadrupole resonance evidence for a bifurcated hydrogen bonding arrangement (I). The major difference in the molecular conformation from that in **Y-1** is the rotation of the carbomethoxyl groups out of the plane of the benzene rings by 86°28′ and 72°38′ in the two molecules. From the X-ray results it follows that the change from **Y-1** to **W-1** involves not only a change in hydrogen bonding but also the flipping of every other aromatic ring 180°. This process has been shown to involve nucleation followed by a highly anisotropic migration of the reaction front through the crystal. Optical goniometry in conjunction with the X-ray results shows that the migration of the front is rapid in directions normal to [1 1 0], the long axis of the crystal, and slow in the [1 1 0] direction. This observation is explained by consideration of the crystal structures of **Y-1** and **W-1**. Attempts to influence the nucleation process have been unsuccessful. Differential scanning calorimetry has shown the change of **Y-1** to **W-1** to be endothermic with a ΔH of 0.6 kcal/mol; the endotherm associated with the melting of **W-1** is 10 kcal/mol. **W-1** reverts to **Y-1** when allowed to stand in contact with a solvent saturated with **1**.



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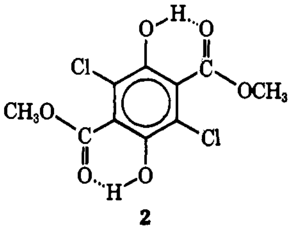

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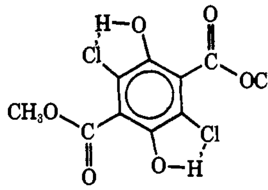

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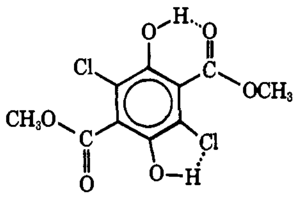

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It was reported by Hantszch[5] that dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (**1**) exists in a yellow and a white crystalline form; the yellow form (**Y-1**) was reported to be converted to the white (**W-1**) when heated at 140°, well below the melting point of the latter. In solvents such as chloroform or methanol, the two types of crystals gave solutions with identical uv spectra. However, the methanol solutions were white while the chloroform solutions were yellow. A further investigation of the solution chemistry of these substances[6] has provided evidence that these solutions contain a solvent-dependent rapidly established equilibrium mixture of a yellow compound doubly hydrogen bonded internally to the ester carbonyl groups (**2**), a white species, doubly hydrogen bonded internally to chlorine (**3**), and a hybrid species **4** with an internal hydrogen bond to oxygen at one end and chlorine at the other. A study of the nqr and ir spectra of the two solids **Y-1** and **W-1** led to the proposal[7] that they differed in their hydrogen bonding in the same way as **2** and **3** in solution.

Studies of intramolecular rearrangements of organic molecules in the solid state have shown them to have unusual features not found in solution chemistry.[8]

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† Figure 2 of this paper appears on p 880.

(1) Taken from the Ph.D. Thesis of Stephen R. Byrn, submitted to the University of Illinois, 1971. This work was presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

(2) We are indebted to the Advanced Research Projects Agency of the Department of Defense (Contract No. HC 15-67-C-0221) for partial support of this work.

(3) Sinclair Oil Company Fellow, 1967–1968; National Science Foundation Fellow, 1968–1970.

(4) Alfred P. Sloan Research Fellow, 1968–1970.

(5) A. Hantszch, *Chem. Ber.*, 48, 797 (1915).

(6) D. Y. Curtin and S. R. Byrn, *J. Amer. Chem. Soc.*, 91, 6102 (1969).

(7) D. Y. Curtin and S. R. Byrn, *ibid.*, 91, 1865 (1969).

Table I. Final Positional[a,b] and Thermal Parameters[c,d] for Y-1

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−0.0849 (5)	0.1578 (12)	0.1283 (7)	2.2 (2)	2.3 (2)	2.5 (2)	0.9 (1)	0.9 (2)	0.7 (2)
C(2)	0.0665 (6)	0.3566 (12)	0.1473 (7)	2.3 (2)	2.0 (2)	2.5 (2)	0.6 (1)	0.6 (2)	0.6 (2)
C(3)	0.1469 (5)	0.1964 (13)	0.0219 (7)	1.6 (2)	2.4 (2)	2.8 (2)	0.5 (1)	0.8 (2)	0.9 (2)
C(7)	−0.1621 (5)	0.3473 (13)	0.2676 (7)	2.5 (2)	2.7 (2)	2.8 (2)	1.1 (2)	1.0 (2)	0.9 (2)
C(8)	−0.3777 (7)	0.3464 (20)	0.3870 (11)	2.9 (3)	4.1 (3)	4.7 (3)	1.3 (3)	2.0 (2)	0.5 (3)
O(1)	0.1378 (4)	0.6978 (10)	0.2824 (5)	2.6 (2)	2.3 (2)	3.2 (2)	0.6 (1)	0.9 (1)	−0.1 (2)
O(2)	−0.1062 (4)	0.6626 (11)	0.3851 (6)	3.4 (2)	3.5 (2)	5.1 (2)	0.5 (1)	2.3 (2)	−0.7 (2)
O(3)	−0.2984 (4)	0.1552 (10)	0.2587 (6)	2.7 (2)	3.3 (2)	4.5 (2)	0.8 (1)	1.9 (1)	0.5 (2)
Cl(1)	0.3302 (1)	0.4682 (4)	0.0640 (2)	1.9 (1)	3.4 (1)	3.9 (1)	0.0 (1)	1.0 (1)	0.3 (1)
				B_θ, Å^2					
H(1)	0.100 (9)	0.816 (24)	0.333 (12)	5 (2)					
H(2)	−0.470 (10)	0.179 (23)	0.349 (11)	3 (2)					
H(3)	−0.379 (8)	0.554 (21)	0.378 (10)	5 (3)					
H(4)	−0.326 (10)	0.457 (25)	0.512 (14)	2 (3)					

[a] Expressed in fractions of the unit cell edge with estimated standard deviations in parentheses. [b] For atom numbering, see Figure 3. [c] Anisotropic thermal parameters (Å^2) expressed as $\exp[-\frac{1}{4}(\beta_{11}h^2a^{*2} + \beta_{22}k^2b^{*2} + \beta_{33}l^2c^{*2} + 2\beta_{12}hka^*b^* + 2\beta_{13}hla^*c^* + 2\beta_{23}klb^*c^*)]$. [d] Isotropic thermal parameters expressed as $\exp[-B_\theta \sin^2 \theta/\lambda^2]$.

Most of the reactions previously studied have involved rather extensive intramolecular changes. It was of interest, therefore, to examine a rearrangement which appeared to involve nothing more complex than a reordering of hydrogen bonds. This paper reports the X-ray crystal-structure determinations of the yellow (Y-**1**) and white (W-**1**) solids, and then examines in some detail the solid-state conversion of the yellow form Y-**1** to the white form W-**1**.

Experimental Section

Crystallographic Examination and Data Collection for Y-1. The yellow form (Y-**1**) of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate[5,6] crystallized in thin plates from ethanol. The crystal data are: $C_{10}H_8O_6Cl_2$, $M = 295.0$, triclinic, $a = 9.595$ (1), $b = 4.301$ (1), and $c = 7.970$ (1) Å, $\alpha = 114°19'$ (1′), $\beta = 94°58'$ (1′), $\gamma = 106°9'$ (1′), $V = 280.2 \times 10^{-24}$ cm^3, $\rho_{\text{measd}} = 1.75$ g cm^{-3}, $Z = 1$, $\rho_{\text{calcd}} = 1.75$ g cm^{-3}, $F(0\,0\,0) = 150$, $\mu = 54.2$ cm^{-1} (Cu Kα), no systematic absences, space group $P1$ or $P\bar{1}$.

The cell data were obtained from a least-squares refinement of the settings for the four angles for 12 reflections centered manually on a four-circle diffractometer (Cu Kα, $\lambda = 1.54184$ Å). The density was measured by flotation in a mixture of methylene dibromide and carbon tetrachloride. A crystalline plate of dimensions 0.075 × 0.25 × 0.25 mm was mounted about the c axis (0.25 mm) and placed on a Picker FACS-1 diffractometer. Data were collected using the θ–2θ scan technique, and a scan rate of 1 deg min^{-1}, and a base scan width of 2°; the width of the scan range was increased at higher 2θ angles. Backgrounds at both limits of the scan range were measured for 10 sec. The take-off angle was 4°. Reflections were measured using a scintillation counter with attenuators being inserted when the count rate exceeded 10,000 counts sec^{-1}. Pulse height analysis and a nickel filter were used to obtain monochromatic radiation. A total of 906 reflections out of a possible 948 in the 2θ range 0–130° was considered to be significantly above zero, *i.e.*, with the threshold count greater than 0.07 times the total background count and also greater than 50 counts. The intensity of a standard reflection, measured after every 25 reflections, did not vary by more than ±1% during the period of data collection. No absorption or extinction corrections were applied. The appearance of the crystal did not change during the period of data collection.

Structure Determination of Y-1. The structural solution was based on a set of previously collected film data.[9] Statistical tests based on the distribution of normalized structure amplitudes (E's) suggested that the space group was $P\bar{1}$. With one molecule in the unit cell, the space group $P\bar{1}$ would require that the molecule occupy a crystallographic center of symmetry. The structure was solved by Patterson and heavy atom methods based on the chlorine atom.

Full-matrix least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atoms using unit weights for the data and minimizing $\Sigma w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2$ gave an R factor[10] of 0.088. A difference map to locate the four hydrogen atoms contained seven positive peaks with heights greater than 0.40 e/Å^3. Four of these peaks were in chemically reasonable positions for hydrogen atoms. A cycle of full-matrix least-squares refinement upon a model including the hydrogen atoms with isotropic temperature factors gave R of 0.085. However, the resulting dimensions of the bonds and angles involving the hydrogen atoms were somewhat unreasonable and one temperature factor became quite large. The observed structure amplitude of the $\bar{1}\,1\,\bar{2}$ reflection which had a value for $|F_{\text{obsd}}| - |F_{\text{calcd}}|$ of −22.9 was assumed to suffer from extinction and absorption and was omitted from the least-squares refinement. The refinement converged after three full-matrix least-squares cycles, to give an R factor of 0.074 on all nonzero reflections. The refined thermal parameters for the hydrogen atoms were quite reasonable. Apart from some peaks very near the position of the chlorine atom, there were only two positive peaks greater than 0.3 e/Å^3 in a final difference map. These were located near the oxygen atoms of the carbomethoxyl group but were in positions that could not reasonably correspond to real structural detail.

Calculation of the amplitudes for the "unobserved" reflections did not indicate any anomalies. The atomic scattering curves used in the analysis were those for neutral atoms in the compilation by Ibers,[11a] that for Cl being corrected for the effects of anomalous dispersion.[11b] The final atomic coordinates and thermal parameters are given in Table I.[12]

Crystallographic Examination and Data Collection for W-1. Needles of W-**1** suitable for X-ray analysis were obtained from ether. Crystal data are: $C_{10}H_8O_6Cl_2$, $M = 295.0$, triclinic, $a = 9.842$ (4), $b = 7.841$ (3), and $c = 10.576$ (5) Å, $\alpha = 116°23'$ (2′), $\beta = 124°10'$ (2′), $\gamma = 88°59'$ (2′), $V = 574.6 \times 10^{-24}$ cm^3, $\rho_{\text{measd}} = 1.71$ g cm^{-3}, $Z = 2$, $\rho_{\text{calcd}} = 1.71$ g cm^{-3}, $F(0\,0\,0) = 300$, $\mu = 52.8$ cm^{-1} (Cu Kα), no systematic absences, space group either $P1$ or $P\bar{1}$.

The cell data and density were obtained as described for Y-**1**. A needle (0.05 × 0.75 × 0.075 mm), elongated along the b axis, was used to obtain the intensity data on a Picker FACS-1 diffractometer (Cu Kα radiation). The data were collected as described for Y-**1**. A total of 1776 symmetry nonequivalent reflections in the 2θ range 0–130° was scanned. The intensity of a standard reflection, determined after every 25 measurements, did not vary by more than ±2% during the period of data collection.

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(8) See J. D. McCullough, Jr., D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 874 (1971), and references cited therein.

(9) S. R. Byrn, Ph.D. Thesis, University of Illinois, 1971.

(10) $R = \Sigma||F_{\text{obsd}}| - |F_{\text{calcd}}||/\Sigma|F_{\text{obsd}}|$.

(11) (a) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209; (b) D. H. Templeton, ref 11a, pp 213–216.

(12) The final list of h, k, l, $|F_{\text{obsd}}|$, and F_{calcd}, and intermolecular contacts <3.70 Å for both Y-1 and W-1 will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

Table II. Final Positional[a,b] and Thermal Parameters[c,d] for W-1

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1A)	−0.0332 (6)	0.0488 (6)	0.1217 (6)	2.3 (2)	1.7 (2)	2.0 (2)	0.7 (1)	1.6 (2)	1.0 (2)
C(2A)	−0.1612 (6)	0.0224 (7)	−0.0473 (6)	2.0 (2)	1.7 (2)	2.3 (2)	0.6 (1)	1.5 (2)	1.1 (2)
C(3A)	−0.1257 (6)	−0.0276 (7)	−0.1659 (6)	2.0 (2)	1.8 (2)	1.4 (2)	0.4 (1)	0.8 (2)	0.9 (2)
C(7A)	−0.0707 (6)	0.1133 (7)	0.2514 (6)	2.0 (2)	2.2 (2)	2.2 (2)	0.7 (2)	1.3 (2)	1.3 (2)
C(8A)	−0.1978 (8)	−0.0012 (11)	0.3453 (10)	4.2 (3)	4.4 (3)	4.2 (3)	1.2 (3)	3.3 (3)	2.6 (3)
O(1A)	−0.3156 (4)	0.0406 (5)	−0.0845 (5)	2.0 (1)	3.1 (2)	3.1 (2)	1.1 (1)	1.8 (1)	2.0 (1)
O(2A)	−0.0516 (6)	0.2841 (5)	0.3461 (5)	5.8 (2)	2.3 (2)	4.1 (2)	1.2 (1)	4.1 (2)	1.4 (2)
O(3A)	−0.1348 (5)	−0.0421 (6)	0.2425 (5)	4.0 (2)	2.5 (1)	2.9 (2)	0.8 (1)	2.8 (1)	1.5 (1)
Cl(1A)	−0.2841 (2)	−0.0633 (2)	−0.3757 (2)	2.5 (1)	3.6 (1)	1.9 (1)	1.0 (1)	1.0 (1)	1.6 (1)
				B_θ, Å^2					
H(1A)	−0.334 (11)	0.109 (13)	−0.135 (12)	6 (2)					
H(2A)	−0.286 (9)	0.040 (10)	0.300 (9)	2 (2)					
H(3A)	−0.107 (9)	0.104 (10)	0.467 (10)	2 (2)					
H(4A)	−0.204 (9)	−0.119 (12)	0.355 (10)	4 (2)					
				β_{11}					
C(1B)	0.1694 (6)	0.5154 (7)	0.0647 (6)	1.5 (2)	2.0 (2)	2.2 (2)	0.6 (1)	1.2 (2)	1.2 (2)
C(2B)	0.0488 (6)	0.4900 (7)	−0.1049 (7)	1.7 (2)	1.6 (2)	2.2 (2)	0.5 (1)	1.4 (2)	1.0 (2)
C(3B)	−0.1208 (6)	0.4738 (7)	−0.1665 (6)	1.5 (2)	2.0 (2)	1.6 (2)	0.4 (2)	0.6 (1)	1.0 (2)
C(7B)	0.3540 (6)	0.5437 (7)	0.1361 (6)	1.7 (2)	2.4 (2)	1.8 (2)	0.7 (2)	1.1 (2)	1.1 (2)
C(8B)	0.5768 (8)	0.3934 (11)	0.1993 (10)	2.3 (2)	4.9 (4)	4.9 (4)	2.3 (2)	2.5 (3)	3.1 (3)
O(1B)	0.1034 (5)	0.4733 (6)	−0.2011 (5)	2.2 (2)	3.3 (2)	2.6 (2)	1.0 (1)	1.8 (1)	1.9 (1)
O(2B)	0.4472 (4)	0.6942 (6)	0.1855 (5)	1.7 (2)	3.1 (2)	4.5 (2)	0.7 (1)	1.7 (1)	2.6 (2)
O(3B)	0.4013 (4)	0.3871 (5)	0.1388 (5)	2.0 (2)	2.8 (2)	4.0 (2)	1.4 (1)	1.9 (1)	2.3 (2)
Cl(1B)	−0.2720 (2)	0.4363 (2)	−0.3780 (2)	2.1 (1)	3.9 (1)	2.1 (1)	0.8 (1)	1.0 (1)	1.9 (1)
				B_θ, Å^2					
H(1B)	0.039 (9)	0.526 (11)	−0.263 (10)	2 (2)					
H(2B)	0.599 (11)	0.249 (13)	0.168 (11)	5 (2)					
H(3B)	0.605 (10)	0.427 (12)	0.117 (11)	4 (2)					
H(4B)	0.642 (11)	0.500 (13)	0.308 (12)	3 (2)					

[a] Expressed as fractions of the unit cell edge with estimated standard deviations in parentheses. [b] The atoms in the two independent molecules are designated A and B (see text). [c] Anisotropic thermal parameters (Å^2) expressed as $\exp[-{}^1/_4(\beta_{11}h^2a^{*2} + \beta_{22}k^2b^{*2} + \beta_{33}l^2c^{*2} + 2\beta_{12}hka^*b^* + 2\beta_{13}hla^*c^* + 2\beta_{23}klb^*c^*)]$. [d] Isotropic thermal parameters expressed as $\exp[-B_\theta \sin^2 \theta/\lambda^2]$.

Using the criteria that the threshold count must be greater than 0.07 × total background count and also greater than 50 counts, 1733 reflections were judged to have intensity significantly above background. No absorption or extinction corrections were applied.

Structure Determination of W-1. The distribution of normalized structure amplitudes (E's) suggested that the space group was the centrosymmetric $P\bar{1}$. The very weak intensities for reflections with $k = 2n + 1$ and the presence in the Patterson map of a peak at 0, $^1/_2$, 0 with a height comparable to 62% of the height of the origin peak led to the belief that there were two crystallographically independent molecules each sitting on centers of symmetry separated by $b/2$. Therefore, there are two "half-molecules" in the crystal asymmetric unit. The structure was solved by location of the chlorine atoms and the use of these atoms to phase an electron density map. It became apparent that the atoms of the benzene rings and the bonded substituent atoms were almost exactly related by the pseudorepeat. However, the two molecules were rotated with respect to each other such that the *same* substituents are not always related by pseudosymmetry and this rotation and the position of the carbomethoxyl groups are the major factors preventing complete repeat at $b/2$. Once the nature of the pseudosymmetry was recognized, the positions of all the nonhydrogen atoms were readily determined and full-matrix least-squares refinement of the positional and isotropic thermal parameters using all observed data gave an R factor of 0.13. All intensities were given unit weight and the quantity minimized was $\Sigma w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2$. Refinement of positional and anisotropic thermal parameters for the nonhydrogen atoms reduced R to 0.079.

A difference Fourier map revealed seven peaks in reasonable positions for hydrogen atoms with heights greater than 0.45 e/Å^3. A peak of 0.34 e/Å^3, about 1.0 Å from one of the hydroxyl oxygen atoms, was assigned to the remaining hydrogen atom. Refinement of the eight hydrogen positions required division of the atoms in the asymmetric unit into two groups. All atoms of molecule A (located on the center at 0, 0, 0) formed the first group and those of molecule B (located on the center at 0, $^1/_2$, 0) formed the second group. Three cycles of full-matrix least-squares refinement varying the thermal parameters of the hydrogen atoms isotropically were performed on molecule A and two cycles on molecule B. The R factor was reduced to 0.071. The temperature factor of the hydrogen H(1A) attributed to the peak of 0.34 e/Å^3 became unreasonably large. A difference Fourier map leaving this atom out of the structure factor calculation showed three peaks in the range 0.3–0.4 e/Å^3; one of these peaks was that previously ascribed to the hydrogen atom. At least 50% of the height of the two other peaks could be accounted for by the large negative $|F_{\text{obsd}}| - |F_{\text{calcd}}|$ values for the 0 2 0, $\bar{1}$ 2 0, and 1 2 $\bar{1}$ reflections. Thus, refinement was attempted eliminating these reflections. Three cycles of full-matrix least-squares refinement on molecule A and two cycles on molecule B gave an R of 0.056, a converged model, and quite reasonable thermal parameters for all the hydrogen atoms (B_θ = 1.8–6.1 Å^2). The largest peak on a final difference map was 0.30 e/Å^3, and the closest heavy atom to this peak was C(8A). The largest negative peak in this map had an intensity of −0.51 e/Å^3 and was very close to Cl(1A).

One final complete cycle of full-matrix least-squares using all nonzero data gave a final R of 0.060. Calculation of the structure amplitudes for the "unobserved" reflections did not reveal any anomalies. The atomic scattering curves were those described earlier.[11] The final values of the positional and thermal parameters are given in Table II.[12]

Preparation of Crystalline Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate (Y-1) Employed for Studies of the Solid State Rearrangement to W-1. About 15 g of 1[5,6] was purified by sublimation at 120° (1 mm) over a period of 7 days. Recrystallization from absolute ethanol and a further sublimation gave 6.7 g of 1, mp 181–183°. (This was chiefly the white crystalline form W-1). Recrystallization from doubly distilled ethanol in glass tubes which had been degassed and sealed under argon and cooled to −18° gave crystals of Y-1 which showed at least two habits. (Each habit gave identical X-ray precession photographs.) Attempts to obtain crystals of Y-1 by sublimation onto a cold finger at Dry Ice temperatures failed. However, when a few sublimed crystals of Y-1 were placed in a closed vial and the bottom of the vial heated in an oil bath at 135° for a few days a mixture of crystals of Y-1 and W-1 collected in the upper part of the vial. Precession photographs of the 0 k l net of crystals of Y-1 so obtained indicated that they had the same structure as crystals grown in solution. Interfacial angles of crystals of two habits of Y-1 were measured with a Techne two-circle goniometer and compared with the angles cal-

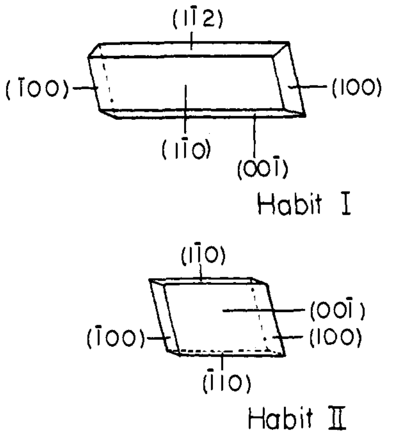

Figure 1. Schematic drawings of crystals of **Y-1** of habit I and habit II.

culated from the unit cell dimensions for all faces having Miller indices between (and including) +1 and −1. If the comparison was made between the measured interfacial angles assuming an error of ±3° and calculated angles between faces, there was a unique set of assignments; the correctness of these assignments was confirmed by the fact that all faces so assigned to crystals of habit II were also found in crystals of habit I and a comparison of the extinction between crossed polaroids of crystals with the two habits was consistent. It was noted further that the 0 *k l* net was in approximately the reflecting position when a crystal of habit II was oriented in a precession camera with the face assigned indices (1 0 0) approximately normal to the X-ray beam. Drawings of the two habits are shown in Figure 1 and calculated and observed interfacial angles are given in Table III.

Table III. Goniometric Results

Angle between faces	Calcd, deg	Obsd (habit I), deg	Obsd (habit II), deg
(1 $\bar{1}$ 0)–(0 0 $\bar{1}$)	67.4	67.8	65.2
(1 $\bar{1}$ 0)–(1 0 0)	86.1	86.6	89.0
(1 $\bar{1}$ 0)–(1 $\bar{1}$ 2)	60.6	59.9	
(0 0 $\bar{1}$)–(1 0 0)	103.3	102.6	101.4
(0 0 $\bar{1}$)–(1 $\bar{1}$ 2)	128.0	127.7	
(1 0 0)–(1 $\bar{1}$ 2)	74.0	75.1	
(1 0 0)–($\bar{1}$ 0 0)	180.0	177.4	
(0 0 $\bar{1}$)–(0 0 1)	180.0		178.2
(1 $\bar{1}$ 0)–($\bar{1}$ 1 0)	180.0		179.0

Thermal Rearrangement of Single Crystals of Y-1 to W-1. Crystals of **Y-1** were heated in a Mettler FP-2 stage and observed with a Bausch and Lomb polarizing microscope equipped with a Bessler Topcon camera. Two different crops of crystals gave identical results.

When a crystal of habit I sitting on (1 $\bar{1}$ 0) was heated above 110° the transformation of **Y-1** to **W-1** began at some point on the crystal, spread rapidly in directions normal to the long axis [1 1 0] of the crystal, and the front which had formed then proceeded more slowly in the long direction of the crystal (Figure 2).† In agreement with this conclusion, a crystal of habit II sitting on (1 0 0) showed no frontal movement when viewed from the top but simply became uniformly cloudy as would be expected if the front moved vertically through the crystal. Crystals which had been prepared by sublimation had less well-formed faces and none of the small number carefully examined belonged either to habit I or habit II. Rearrangement began at 140° and a poorly defined reaction front moved through the crystal to give an opaque product which became somewhat more transparent after 5–10 min at 140°.

Examination under crossed polarizing filters of product "crystals" formed from rearrangement of habit I showed that substantial regions of the crystals still transmitted light, different regions of the crystal transmitting at different angles of rotation. A transformed "crystal" mounted intact on an X-ray powder camera gave arc-like or blotchy powder rings indicating that the product was polycrystalline but that the crystallites had some preferred orientation.[13] Similarly, a crystal of **Y-1** was aligned with the *h k* 0 net in the reflecting position on a precession camera equipped with a heater.[8] After 0.5 hr at 135° a second precession photograph showed arc-like powder lines and no discernible spots, thus indicating no relationship between the orientation of the product and the *h k* 0 net of the starting material. A powder photograph of the product either before or after grinding showed the same lines as a powder photograph of **W-1** purified by crystallization and ground. The onset temperature was quite unpredictable and ranged from 110 to 140°. Once initiated, however, the rate at which reaction spread through the crystal varied in a regular way with temperature. Thus, if initiation occurred at 115°, reaction of a typical crystal (0.6 × 0.3 × 0.1 mm) required 5 min, but when it was not initiated until the temperature had reached 140° passage of the reaction front through the crystal required only 5 sec (see Figure 2e). As can be seen in Figure 2, there were no signs of softening of the crystal and the product "crystal" still retained the same shape and even showed defects which had been present in the starting crystal.

A number of experiments were carried out in an attempt to learn more about factors influencing the initiation of reaction. A crystal

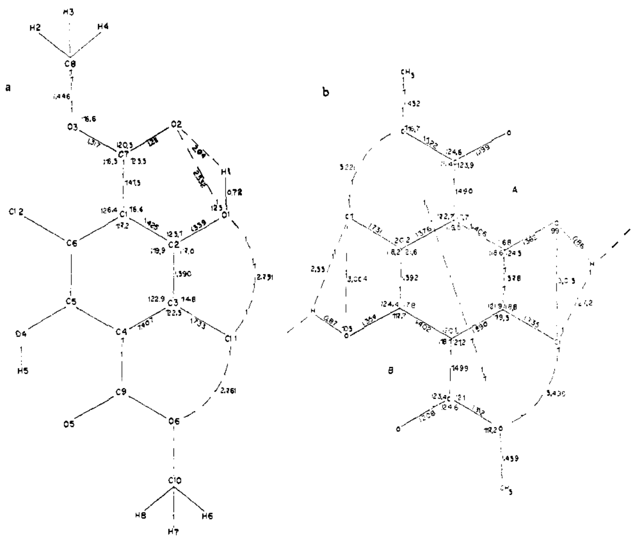

Figure 3. The atom numbering, and in particular, the numbers of the atoms related by the crystallographic centers of symmetry, and the bond lengths and angles in **Y-1** are shown in a, while those for the two independent half-molecules of **W-1** (separated by the line) are shown in b. The estimated standard deviations for C–Cl, C–C, and C–O bonds range from 0.006 to 0.009 Å for **Y-1** and 0.007–0.011 Å for **W-1**, the estimated standard deviations for C–C–C, C–C–Cl, and C–C–O angles are from 0.3 to 0.5° for **Y-1** and 0.4 to 0.6 for **W-1**.

Lengths and Angles Not Shown in Figure 3

Y-1

C(8)–H(2)	0.91 (12) Å	O(3)–C(8)–H(4)	112 (6)°
C(8)–H(3)	0.93 (9) Å	H(2)–C(8)–H(3)	112 (8)°
C(8)–H(4)	0.93 (14) Å	H(2)–C(8)–H(4)	120 (9)°
O(3)–C(8)–H(2)	103 (6)°	H(3)–C(8)–H(4)	98 (8)°
O(3)–C(8)–H(3)	112 (5)°		

W-1

	Molecule A	Molecule B
C(8)–H(2)	0.86 (10) Å	1.08 (11) Å
C(8)–H(3)	0.96 (16) Å	1.15 (10) Å
C(8)–H(4)	0.98 (9) Å	0.88 (19) Å
O(3)–C(8)–H(2)	108 (6)°	114 (6)°
O(3)–C(8)–H(3)	108 (5)°	112 (5)°
O(3)–C(8)–H(4)	105 (6)°	104 (8)°
H(2)–C(8)–H(3)	109 (8)°	99 (8)°
H(2)–C(8)–H(4)	123 (8)°	123 (9)°
H(3)–C(8)–H(4)	103 (8)°	105 (9)°

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(13) H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures," Wiley, New York, N. Y., 1962, pp 384 and 555.

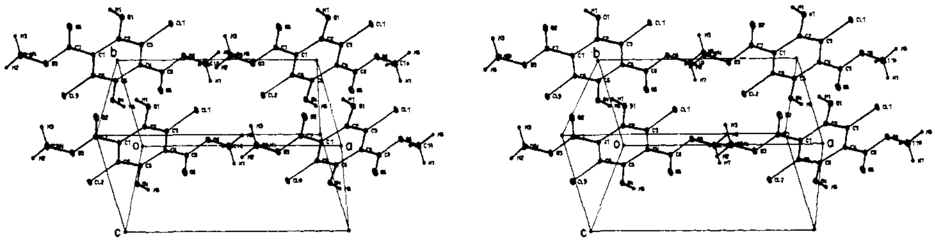

Figure 4. Stereoscopic view of the packing in **Y-1**, showing the relationship of molecules arranged within the stacks in the *b* direction and between the stacks in the *a* direction.

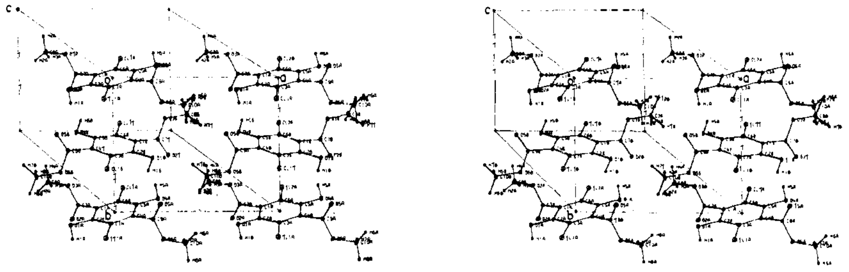

Figure 5. Stereoscopic view of the packing of **W-1**, showing particularly the arrangement of molecules in the *b* direction and in the *a* direction.

which had been heated until reaction had proceeded half-way was cooled rapidly and cleaved with a razor blade to separate the yellow from the white part. A precession photograph of the *h k* 0 net of the yellow part showed no evidence that **Y-1** had undergone any change before rearrangement. Attempts to nucleate the reaction were carried out by pricking a crystal with a pin, fusing a small amount of **W-1** to one end of the crystal of **Y-1** by allowing a tiny amount of saturated **1** in ethanol to evaporate, covering the crystal with mineral oil, partially coating it with stopcock grease, exposing one end of the crystal to direct sunlight, or spotting a part of the crystal with concentrated hydrochloric acid solution. In no case did a treated crystal show any indication that reaction was initiated in the treated region or at a temperature lower than the normal range.

Equilibrium Studies. In an effort to cause the product **W-1** to revert to **Y-1**, a crystal of **Y-1** was heated at 0.2°/min to 113° where reaction was initiated. The temperature was quickly lowered to 40° at which point the crystal was approximately one-half yellow and one-half white. After 1 hr there was no change so the temperature was raised to 85°. After 30 min there was no visible change. The temperature was then raised to 100° at a rate of 0.2°/min. At 100° the front began to move sporadically as the transformation of **Y-1** to **W-1** resumed. At no time during these operations was there any sign of reversal of the front as might have been expected if the change of **W-1** to **Y-1** had occurred. It was noted further that both **Y-1** and **W-1** were stable and underwent no observable change after standing for over a year at ambient temperature. In consideration of the known[14] acceleration of polymorphic transformations by wetting with a solvent, a crystal of **W-1** (0.76 mg) and a crystal of **Y-1** (1.52 mg) were allowed to sit together in a saturated solution of **1** in spectral grade hexane at room temperature. After 9 days the crystal of **W-1** had become opaque and yellow (weight 0.70 mg) whereas the yellow crystal had remained clear (weight 1.36 mg). These results suggest that there is a transition temperature (or region) between 25 and 100° below which **Y-1** is the more stable form and above which **W-1** is the more stable form of **1**. The slow rate of transformation of the solids in this temperature range has prevented further study of the equilibration process.

Differential Scanning Calorimetry. The behavior of **Y-1** and **W-1** on heating at 10°/min was examined with the aid of a Du Pont Model 900 Thermal Analyzer equipped with a differential scanning calorimeter (dsc) cell. Runs in triplicate of **Y-1** showed an endotherm corresponding to rearrangement to **W-1** with an extrapolated onset of 132° and a subsequent endotherm corresponding to the melting of the product (**W-1**) with an extrapolated onset of 188°. Calibration of the instrument with standard samples of naphthalene, benzoic acid, *trans*-cinnamic acid, and indium was carried out using the equation[15] $E = a\Delta HM/T_s\Delta T_s A$ to determine E, the calibration coefficient of the instrument. Here a is the heating rate (degrees per minute), A is the area of the peak (square inches), ΔH is the heat of melting (millicalories/milligram), M is the mass of the sample (milligrams), T_s is the X axis sensitivity (10°/in.) and ΔT_s is the Y axis sensitivity (1.0°/in.). The value of E (and standard deviation) of 153.68 (7.88) obtained was used to convert the areas corresponding to the endotherms of **Y-1** to ΔH. The ΔH for the conversion of **Y-1** to **W-1** was 0.612 (0.060) kcal/mol and that associated with the melting of **W-1** was 10.09 (0.561). A dsc of **W-1** showed only a melting endotherm (ΔH 10.65 (0.318)) with an extrapolated onset of 186°. In addition, the following mixtures of **Y-1** and **W-1** were examined with a heating rate of 40°/min: 100% **Y-1**, 74.6% **Y-1**, 52.7% **Y-1**, and 27% **Y-1**. All showed the same extrapolated onset of 119 ± 1° for the rearrangement of **Y-1** to **W-1** and of 187 ± 1° for the melting of the **W-1**.

Results and Discussion

X-Ray Structural Results. The atom numbering (including that of atoms related by a center of symmetry), bond lengths, and angles in the half-molecule of **Y-1** and in the two independent half-molecules of **W-1** are shown in Figure 3. Stereoscopic views of the packing of the molecules of **Y-1** and **W-1** in the crystal are shown in Figure 4 and 5. The results of some best plane calculations in both structures are given in Table IV.

Structure of Y-1. The molecule of **Y-1** sits on the center of symmetry at the origin. To a first approximation, the entire molecule (with the exception of the methyl hydrogen atoms) is planar. There is an intramolecular hydrogen bond between the phenolic proton and the carbonyl group of the adjacent carbomethoxyl group as was anticipated by the infrared study reported previously.[7]

In **Y-1**, the six atoms of the benzene ring are planar within the accuracy of the analysis while Cl(1), O(1), and C(7) are −0.014, 0.019, and 0.000 Å from this plane. The best plane through the heavy atoms of the carbo-

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[14] W. C. McCrone, "Physics and Chemistry of the Organic Solid State," Vol. 2, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience, New York, N. Y., 1965, Chapter 8.

[15] "Instruction Manual, 900 Thermal Analyzer and Modules," E. I. du Pont de Nemours, Instrument and Equipment Division, Wilmington, Del., 1968, Sect. 8.

Table IV. Details of Best Planes for **Y-1** and **W-1**[a]

	Y-1				**W-1**			
					Molecule A		Molecule B	
C(1)	**−0.004**	**0.000**	**−0.005**	**−0.013**	**0.004**	**0.004**	**0.003**	**−0.001**
C(2)	**0.004**	−0.107	**0.009**	**0.001**	**−0.004**		**−0.003**	
C(3)	**−0.004**		**0.002**	**0.002**	**0.004**		**0.003**	
C(4)	**0.004**		**0.005**	**0.013**	**−0.004**		**−0.003**	
C(5)	**−0.004**		**−0.009**	**−0.001**	**0.004**		**0.003**	
C(6)	**0.004**	0.115	**−0.002**	**−0.002**	**−0.004**		**−0.003**	
Cl(1)	−0.014		**0.000**	**−0.002**	0.015		0.037	
C(12)			**0.000**	**0.002**				
O(1)	0.019		0.028	**0.014**	0.035		0.051	
C(7)	0.000	**−0.001**	**−0.002**	**−0.018**	−0.078	**−0.015**	−0.076	**0.001**
C(9)			**0.002**	**0.018**				
O(2)	0.097	**0.001**		0.077	−1.105	**0.006**	−1.073	**−0.001**
O(3)	−0.105	**0.000**		−0.129	1.123	**0.005**	1.056	**−0.001**
O(4)			−0.028	**−0.014**				
C(8)	−0.016	0.085		−0.048	1.188	0.165	1.120	0.053
χ^2	3.21	0.07	7.98	49.94	2.88	9.33	1.42	0.11
P	>0.05	>0.05	>0.05	<0.005	>0.05	<0.01	>0.10	>0.50

[a] The distances from the plane (in Ångströms) of atoms included in the plane calculation are given in bold type. The results of a χ^2 significance test are also shown with the probability (*P*) of a planar set of atoms having such a χ^2 value.

methoxyl group makes an angle of 5°18′ with the plane of the benzene ring. The exocyclic angles at C(1) [here described in terms of the symmetry-equivalent C(4)], C(2), and C(3) bespeak of significant intramolecular overcrowding apparently mainly involving the chlorine atom. The Cl(1)---O(1) and Cl(1)---O(6) distances are 2.751 (4) and 2.761 (5) Å, respectively, whereas the sum of the van der Waals radii for Cl and O is 3.20 Å.[16] If a planar model of the structure was constructed with 120° exocyclic angles at C(2), C(3), and C(4), the greatest overcrowding would be between Cl(1) and O(6).

This strain is relieved by an increase of the C(4)–C(3)–Cl(1) angle (122.3 (4)°) at the expense of the C(2)–C(3)–Cl(1) angle (114.8 (4)°), a very large increase of the C(3)–C(4)–C(9) angle (126.4 (3)°) at the expense of the C(5)–C(4)–C(9) angle (116.4 (5)°), and an increase of the C(4)–C(9)–O(6) angle to 116.5 (5)°, mainly at the expense of the O(5)–C(9)–O(6) angle (120.3 (4)°).[17] With the increase in the C(6)–C(1)–C(7) angle, it is not surprising that the C(1)–C(2)–O(1) angle is 123.1 (5)° whereas the C(3)–C(2)–O(1) angle is 117.0 (5)°. The corresponding angles in salicylic acid (**5**)[18] are 122.7 (3) and 117.6 (3)°. The O(1)---O(2) distance of 2.532 (6) Å is indicative of a fairly strong O–H---O hydrogen bond; the corresponding length in salicylic acid (**5**) is 2.620 (3) Å.[18] There is both spectral[19] and X-ray structural evidence[20] that bulky substituents at the 3 and 6 positions in salicylic acids increase the strength of the intramolecular hydrogen bond. It is somewhat surprising that the alleviation of the intramolecular steric strain in **Y-1** takes the form of bond angle deformation rather than a greater out-of-plane bending or greater rotation of the carbomethoxyl group.[21]

The dimensions involving H(1) differ considerably from those found in salicylic acid.[18] The O(1)–H(1), H(1)---O(2) lengths, and the C(2)–O(1)–H(1) and O(1)–H(1)---O(2) angles are 0.72 (10) and 2.04 (10) Å, and 123 (8) and 127 (7)° in **Y-1** compared to 1.03 (4) and 1.70 (4) Å, and 106 (2) and 146 (2)° in salicylic acid. There is a contact of 3.046 (6) Å between O(1) and O(5) [symmetry-related to O(2)] in the molecule at *x*, 2 + *y*, 1 + *z*. The possibility exists that there is a weak attractive interaction between these atoms forming a very unsymmetrical bifurcated hydrogen bond; the H(1)---O(5) distance is 2.41 (13) Å, while the C(2)–O(1)---O(5) and O(1)–H(1)---O(5) angles are 144.8 (3) and 148 (10)°. A length of 2.41 Å would correspond to a very long H---O distance for hydrogen bonding, but, in view of the low accuracy of the location of the hydrogen atom, it is doubtful if any definite conclusion can be drawn. In any event, such an interaction would not have been detected in the spectroscopic study[7] and could have little effect on the strong intramolecular hydrogen bond.

The molecules of **Y-1** arrange themselves in stacks or columns along the *b* axis.[12] Each molecule within a stack is displaced such that the center of one ring lies almost over the hydroxyl oxygen atom of the adjacent molecule in the stack. The perpendicular distance between molecules in the stack is 3.38 Å with the shortest interatom distance being 3.38 Å between C(2) and C(5). The O(1)---O(5) distance referred to above is the shortest contact (not involving hydrogen atoms) between stacks. There are also close contacts between the basic molecule and one at *x*, 1 + *y*, 1 + *z*; the shortest contact (3.45 Å) involves the phenolic oxygen atom O(1) in the basic molecule and the methyl carbon atom C(10) in the other molecule. The corresponding O(1)---H(8) distance is 2.73 Å. There is a fairly short contact, 3.47 Å, between a chlorine atom in the basic molecule and the centrosymmetrically related chlorine atom in the molecule at 1 + *x*, 1 + *y*, *z*; this distance is 0.13 Å shorter than twice the van der Waals radius for chlorine.[16]

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(16) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed, 1960, pp 257–264.

(17) In unstrained esters, the C–C–O (R) and O=C–O (R) angles are typically 112–114° and 124–126°, respectively; see, for example, W-1 and J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, **90**, 2144 (1968).

(18) M. Sundaralingam and L. H. Jensen, *Acta Crystallogr.*, **18**, 1053 (1965).

(19) C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 661 (1961).

(20) S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *J. Amer. Chem. Soc.*, **92**, 4428 (1970).

(21) For example, in *o*-chlorobenzoic acid, the chlorine atom and the carbon atom of the carboxyl group are displaced 0.036 and 0.058 Å on *opposite* sides of the plane of the benzene ring and the carboxyl group is rotated 13.7° out of the plane of the ring in addition to bond angle deformation: G. Ferguson and G. A. Sim, *Acta Crystallogr.*, **14**, 1262 (1961).

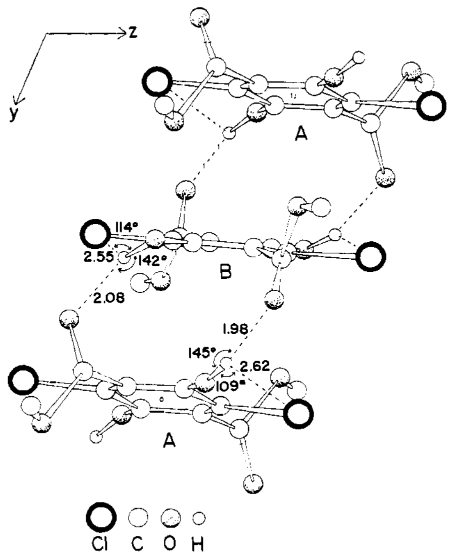
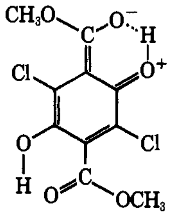


Figure 6. View of the molecular arrangement within a stack of W-**1** molecules showing the dimensions of the hydrogen bonding system. For clarity, the hydrogen atoms on the methyl groups are omitted.

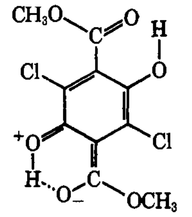
Structure of W-1. The two crystallographically independent molecules of W-**1** sit about the centers of symmetry at 0, 0, 0 (molecule A) and 0, $^1/_2$, 0 (molecule B) (Figure 5). The planes of the benzene rings in the two molecules are inclined at an angle of 12°4′ to each other. The relative tilting of the two molecules is undoubtedly due to the existence of two intermolecular hydrogen bonds, —O—H---O═C(OCH$_3$), on one side of the intramolecular Cl–Cl vector (Figure 6).

The steric overcrowding present in Y-**1** does not appear to be manifested in W-**1** on the basis of the observed bond angles. The atoms Cl, O(1), and C(7) are all displaced from the plane of the benzene ring; in molecule A, the displacements are 0.015, 0.035, and −0.078 Å, while in molecule B, they are 0.037, 0.051, and −0.076 Å. The carbomethoxyl groups are rotated out of the planes of the benzene rings by 86°28′ and 72°38′ in molecules A and B, respectively.

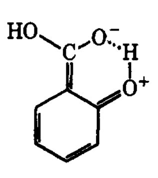
The corresponding bond lengths (excluding those involving hydrogen atoms) in the two molecules of W-**1** agree within twice the estimated standard deviations. A comparison of the distances and angles between the two forms of **1** reveals differences in the directions to be expected for the presence of a strong intramolecular O—H---O hydrogen bond and intramolecular overcrowding in the molecule Y-**1**. There are significant differences in the C(1)–C(2), C(2)–O(1), C(1)–C(7), and C(1)–C(6) lengths between the two forms. In particular, the short C(2)–O(1) length (1.339 (7) Å), the long C(1)–C(2) length (1.425 (7) Å), and the comparatively short C(1)–C(7) length (1.475 (8) Å) when compared to those in the molecules of W-**1** and the generally accepted values[22] lead to the conclusion that **1a** and **1b** are important contributors to the resonance hybrid structure for Y-**1**. Sundaralingam and Jensen[18] had previously noted a long C(1)–C(2) bond in salicylic acid (**5**) where there is also an intramolecular O-H---O hydrogen bond and had suggested that **5a** would be an important contributor to that resonance hybrid. The apparently stronger hydrogen bond (as inferred from the corresponding O---O distances) and the symmetrical nature of the Y-**1** molecule would suggest that the lengthening of the C(1)–C(2) bond would be even more significant in this molecule as C(1)–C(2) is a single bond in both **1a** and **1b**. In salicylic acid, the C–C (ring), C–O (phenol), and C–C (carboxy) distances are 1.404 (4), 1.358 (4), and 1.457 (4).[18] The bond lengths and angles in the benzene ring are slightly more uniform in the molecules of W-**1** than in Y-**1**, with the C(1)–C(2) being the longest bond in all three molecules although strikingly so in Y-**1**. In W-**1** the ring-hydroxyl oxygen distances of 1.354 (8) and 1.362 (7) Å agree with that found in salicylic acid[18] and also that in tetrachlorohydroquinone (1.349 Å),[23] while the C–Cl lengths (1.731 (9) and 1.735 (9) Å) agree well with those lengths found for C (aromatic)–Cl lengths in molecules without an ortho chlorine atom.[24,25]



1a



1b



5a

As shown in Figures 5 and 6, the molecules of W-**1** are arranged in stacks along the *b* axis. The principal intermolecular interactions within the stacks are two O—H---O═C(OCH$_3$) hydrogen bonds between pairs of adjacent molecules. The O---O distances are 2.733 (6) and 2.813 (7) Å, while the H---O distances are 1.98 (11) and 2.08 (8) Å; the C–O(1)–H(1) angles are 99 (7) and 103 (6)° and the O(1)–H(1)---O (carbonyl) angles are 145 (5) and 142 (8)°. The O---O distances fall well within the range of O---O distances in O—H---O hydrogen bonds as determined by neutron diffraction and compiled by Hamilton and Ibers,[26] although the H---O distances and the O—H---O angles lie near the respective upper and lower limits contained in that listing.

The relatively long H---O distances and the small O—H---O angles are among several pieces of evidence which suggest that the hydroxyl hydrogen atoms are involved in a bifurcated hydrogen bond to the ortho chlorine atoms. The O---Cl distances are 3.013 (6) and 3.004 (6) Å, while the H---Cl distances are 2.62 (13) and 2.55 (12) Å; the O—H---Cl angles are 109 (8) and 114 (4)°. Although the O---Cl distances in W-**1** are longer than that in Y-**1** and the H---Cl distances are only two standard deviations less than the upper limit (2.8 Å) suggested by Hamilton and Ibers[27] for hydrogen bonding, the positions of the hydrogen atoms indicate an attractive H---Cl interaction. H(5A) [symmetry equivalent to H(1A)] is 0.19 (9) Å out of the plane of the atoms C(5A), O(4A), and O(2B), and H(5B) is 0.31 (8) Å out of the plane of C(5B), O(4B), and O(2A) (Figure 5); in each case the deviation is *in*

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(22) L. E. Sutton, Ed., *Chem. Soc. Spec. Publ.*, No. 11, 512 (1958).

(23) T. Sakurai, *Acta Crystallogr.*, **15**, 443 (1962).

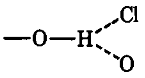
(24) R. Rudman, *Chem. Commun.*, 536 (1970); *Acta Crystallogr., Sect. B*, **27**, 262 (1971).

(25) H. Hope, *ibid.*, *Sect. B*, **25**, 78 (1969).

(26) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 259–265.

(27) Reference 26, pp 14–16.

the direction of the chlorine atom. If only the —O—H---O interaction were involved, one would expect the hydrogen atoms to lie in these planes. While a double intramolecular O—H---Cl hydrogen bound white species **3** has been demonstrated to exist in solution,[6] the principal evidence for involving the chlorine atom in hydrogen bonding in the crystal of **W-1** came from ^{35}Cl nuclear quadrupole resonance studies of **Y-1** and **W-1**.[7] The nqr spectra of **Y-1** had a single resonance at 36.650 MHz while that of **W-1** had resonances at 35.290 and 35.360 MHz. A difference of 1.3 MHz in the nqr is usually associated with major changes in the substituents on a benzene ring. On the basis of the theory of Townes and Dailey,[28] hydrogen bonding to a chlorine atom should lower its ^{35}Cl nqr frequency relative to the nonhydrogen bonded chlorine atom. In 2,6-dichlorophenol, there were two nuclear quadrupole resonances at 35.304 and 35.856, while in the corresponding methoxy compound the absorptions were at 35.586 and 35.826 MHz. The 35.856- and 35.826-MHz absorptions were assigned to the corresponding trans chlorines and the lower ^{35}Cl resonance in the *cis*-phenol was explained by hydrogen bonding to chlorine.[29] It is very likely, however, that some of the differences in the nqr spectra between **Y-1** and **W-1** arise from the severe steric overcrowding for the chlorine atom in **Y-1**. The relative magnitude of the effects of the hydrogen bonding and of the overcrowding cannot readily be assessed. It should be further emphasized that the H---Cl interaction represents a fairly minor perturbation to the O—H---O hydrogen bond and that consequently there is clearly a significant difference in the **W-1** species in the crystal and species **3** in solution. Intermolecular bifurcated hydrogen bonds



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have been proposed in the tetrachlorohydroquinone[23] and pentachlorophenol[30] structures.

In the crystal of **W-1**, the intermolecular contacts between atoms in the molecules arranged in stacks range from 3.30 to 3.68 Å, except for lengths (not considering hydrogen bonds) of 3.02, 3.18, and 3.24 involving phenolic oxygen atoms and oxygen atoms of ester groups.[12] Neighboring stacks of molecules are held together by van der Waals forces. Some contacts important in this packing are: a distance of 3.11 Å between ester carbonyl atoms of molecules related by a unit cell translation in y and z; contacts in the range 3.29–3.35 Å between the methyl carbon atoms and the carbomethoxyl or phenolic oxygen atom of molecules related by a unit cell translation in x; contacts of 3.27 and 3.68 Å between the chlorine atom and the carbomethoxyl oxygen and methyl carbon atoms, respectively, of molecules related by a unit cell translation in both x and z. There are no intermolecular contacts involving the phenolic hydrogen atoms sufficiently short to influence their positions relative to the C—O---O plane.

Solid State Rearrangement. It will be seen (Figure 4) that molecules of **Y-1** are arranged in stacks along the b axis and that when viewed down the axis through the ring centers all molecules in a stack have the same order of attachment of substituents (chloro, hydroxyl, carbomethoxyl) proceeding clockwise around the ring. In the case of **W-1** (Figure 5) a given order of attachment of groups which is clockwise in one ring is counterclockwise in the rings above and below it in the same stack. It is clear then that although the transformation of **Y-1** to **W-1** seems superficially to involve only the change of a hydrogen position there is the more serious requirement that every other ring be flipped upside down before the new structure can pack in its preferred state.

The greater stability of **W-1** at higher temperatures is understandable in terms of the crystal structures of **Y-1** and **W-1**. The intramolecular overcrowding in **Y-1** (a part of the price in energy which must be paid for the strong internal O—H---O=C hydrogen bond) becomes progressively less tolerable as thermal vibrations increase with a rising temperature.

Without implying a specific sequence of events, the change from **Y-1** to **W-1** involves a large rotation of the carbomethoxyl groups out of the plane of the benzene rings; in this way intramolecular strain will be reduced. In order to reduce interference between carbomethoxyl groups in adjacent molecules and to maximize the possibilities for intermolecular O—H---O=C (carbomethoxyl) hydrogen bonding with such a molecular conformation, half of the molecules in a stack must rotate almost 180° about the Cl–Cl intramolecular axis (see Figure 4). Such a rotation must necessarily disrupt the molecular arrangement within a stack and will also affect the adjacent stacks in the c direction. However, the adjacent stacks in the a direction will be less affected by rotation of a molecule about the Cl–Cl vector.

These structural relationships are fully consistent with the observation that the rearrangement proceeds rapidly *normal* to the long [1 1 0] axis of the crystal and much more slowly *in* the [1 1 0] direction. In the stereopair drawing (Figure 7) of the structure of **Y-1** are indicated two lines parallel to [1 1 0] which lie in the $(1\ \bar{1}\ 0)$ plane and thus define the most prominent ("top") face of the crystal as well as the long macroscopic crystal axis. The two-dimensional *layer* of stacks of molecules lying in the bc plane that will be affected by the crystal rearrangement is shown in Figure 7 and is almost normal to [1 1 0]. The angle between [1 1 0] and the best plane of the aromatic ring is only 1.4°. As there will be relatively little influence upon the layer of molecules adjacent in the [1 1 0] direction due to rotations about the Cl–Cl axis, it is not surprising that the intralayer rearrangement is fast and the interlayer rearrangement is slow. Figure 8 is a view of the crystal structure of **Y-1** in which the orientation has been changed so that the view is nearly normal to the $(1\ \bar{1}\ 0)$ face which is shown bounded by the four lines. The [1 1 0] direction is from left to right. From this figure it can be seen that rotation of the molecules of **Y-1** around the Cl–Cl vector should disrupt the molecules within the stack and in adjacent stacks in the c direction (*i.e.*, in the approximately vertical direction in Figure 8) but have little effect on neighboring stacks in the [1 1 0] direction.

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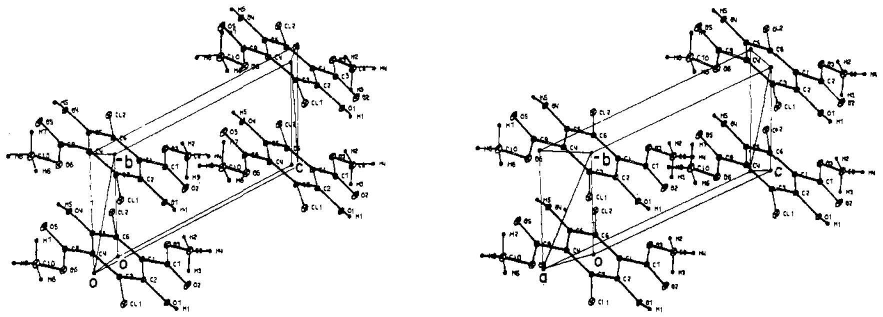

Figure 7. Stereoscopic view of the crystal structure of Y-**1**. The centers of the aromatic rings lie in the (1 0 0) plane. The *b* axis is vertical and the *a* axis is the one most nearly toward the viewer. The diagonal lines are parallel to the long axis of the crystal [1 1 0].

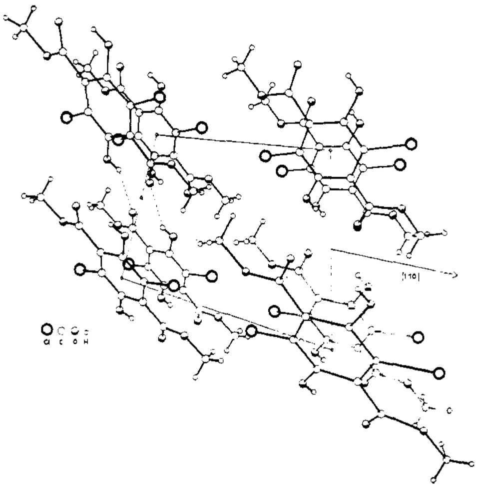

Figure 8. A view of the crystal structure of Y-**1** along a direction almost normal to [1 1 0]. The outline of the (1 $\bar{1}$ 0) plane is indicated. The possible weak O—H---O intermolecular interaction between the basic molecule and one at *x*, 2 + *y*, 1 + *z* is shown by a dashed line.

The conversion of Y-**1** to W-**1** presents a problem in classification: should this change be considered as a solid state reaction ("dynamic isomerism")[14] or as a polymorphic transformation? Application of the criterion of McCrone[14] that "two polymorphs will be different in crystal structure but identical in the liquid and vapor states" cannot be applied in a completely straightforward way. There are, however, species in solutions of **1**[6] which although differing in detailed structure from their counterparts in crystalline Y- and W-**1** can be considered to correspond roughly to these two species in terms of their hydrogen bonding; on this basis Y-**1** and W-**1** can be classified as isomeric chemical species rather than polymorphs. There is recognized the possible existence of a third crystalline solid with the hydrogen bonding of Y-**1** at one end of the molecule and of W-**1** at the other (corresponding to the substance **4** found in solution[6]) but no indication of it has been detected. Regardless of the formal classification of the change of Y-**1** to W-**1**, the small ΔH of 0.62 kcal/mol and the rather low degree of molecular reorganization are reminiscent of certain polymorphic transformations[31-35] between molecular crystals whose structures have been determined. Rearrangement of α- to β-resorcinol[31] is particularly pertinent to the present discussion since it, like the rearrangement of Y-**1** to W-**1**, involves breaking and re-forming of hydrogen bonds. The change in molar volume (an increase of 2.5%) in the change from Y-**1** to W-**1** is somewhat less in absolute magnitude and opposite in sign to that observed[31] for the change from α- to β-resorcinol which underwent a 3.7% decrease in volume. In each case substantial disorder was introduced into the product but a crystal of α-resorcinol which had undergone the transition showed rotation photographs which had streaks indicating that crystallites of product had been formed with preferential orientation in certain directions; similar results were obtained in the present study of the rearrangement of W-**1** to Y-**1**. There seems to have been no detailed microscopic observation of oriented single crystals of α-resorcinol as they underwent polymorphic transformation.

Although a few monocrystal–monocrystal polymorphic transformations of molecular crystals have been reported[35] to lead to product with a particular orientation of the crystallographic axes relative to the axes of the starting crystal, the case of the rearrangement of β- to α-*p*-nitrophenol is especially noteworthy by way of contrast. This change involves a negligible change in molecular volume, no change in crystal symmetry, no alteration in the order of attachment of hydrogen bonds, and a seemingly relatively minor alteration in the arrangement in the chains of intermolecularly hydrogen-bonded nitrophenol molecules. Nevertheless, the relative orientation of the mother and daughter phases is random and it has been suggested that the transformation possibly goes through an intermediate amorphous state.[34] Certainly a more detailed understanding of such transformations will be of great help in studies of molecular rearrangements in the solid state.

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