chloride in dry acetonitrile (1.0 ml) was added 2,3-dimethylbutane (0.1 ml). These solutions, which were used as controls, were degassed, sealed, and heated to 98° for 1 hr. Recovery of the hydrocarbon by preparative glpc (Ucon Polar, 70°) showed that no incorporation of deuterium had taken place. Two similar solutions were prepared, but to each of these was added benzoyl peroxide (0.70 mmole). They were degassed, sealed, and heated to 98° for 1 hr. The results of analyses for both deuterium incorporated into the unreacted hydrocarbon (mass spectrometry) and for alkyl chloride produced (glpc, SE30, 85°) are to be found in Table III.

Reaction of Deuterium Chloride with Benzoyl Peroxide and Cyclohexane. To duplicate 0.60 *M* solutions of deuterium chloride in dry acetonitrile (1.0 ml) were added cyclohexane (0.1 ml) and benzoyl peroxide (0.58 mmole). The sealed, degassed ampoules were heated to 98° for 1 hr. Analysis for deuterium incorporation into the unreacted cyclohexane, and for formation of cyclohexyl chloride, gave the results shown in Table III. Control experiments in which the benzoyl peroxide was omitted gave no incorporation of deuterium.

Acknowledgments. The authors are pleased to acknowledge the generous financial support of this work by the National Research Council and the University of Alberta.

Structures in Solution of the Yellow and White Forms of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate[1]

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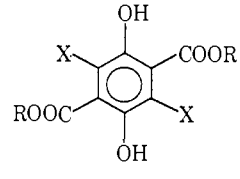
Abstract: The puzzling dependence of the color (and spectra) of solutions of dimethyl 2,5-dihydroxy-3,6-dichloroterephthalate (I) on the nature of the solvent has now been found to be due to the presence of three species in a solvent-dependent equilibrium. One (Y-I) has intramolecular hydrogen bonds to the carbonyl oxygen atoms at each end of the molecule; the second (W-I) has two intramolecular hydrogen bonds to the chlorine atoms; and the third (H-I) is a hybrid with one hydrogen bond to a carbonyl group and the other to a chlorine atom. Application of a statistical treatment of the uv spectra of solutions in cyclohexane, carbon tetrachloride, chloroform, and mixtures of these with ethanol gives ratios of these three species which are in agreement with results from infrared studies. Replacement of the hydroxyl protons by deuterons is shown to shift the hydrogen-bonded carbonyl stretching vibration (in chloroform solution) to lower frequency but not the unbonded carbonyl vibration.

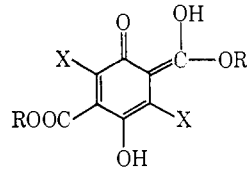
Dimethyl sulfoxide has been found to be unusually effective at breaking up hydrogen bonds to the carbonyl oxygen atoms, and the same behavior is observed when it is employed as a solvent for ir spectra of other hydroxy esters such as methyl salicylate.

In the years between 1882 and 1915, studies[3] of 2,5-dihydroxyterephthalic acid, its 3,6-dihalo derivatives, and their esters A showed that they frequently could be isolated in a yellow or green and a white modification and gave solutions whose uv-visible spectra depended on the nature of the solvent. The structural basis of these observations was a matter of considerable controversy; it was proposed by Hantzsch[3b] that the colored species were enols with the structure B and the white species the dihydroxy diesters A. It was striking that the half-substituted halo acid and its esters C have shown no evidence of the existence of such binate members. In a previous communication[4] we have reported that the two crystalline forms of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (I) were each true dihydroxy diesters but differed in the nature of their hydrogen bonding, the yellow isomer having strongly hydrogen-bonded carbonyl groups and the white having hydrogen-bonded chlorine atoms. We now present evidence that primary species present in dilute carbon tetrachloride or chloroform solutions of I are the yellow substance Y-I with intramolecular hydrogen bonds to the carbonyl oxygen atoms, the colorless substance (W-I) with the intramolecular hydrogen bonds directed to the chlorine atoms, and the hybrid compound H-I.

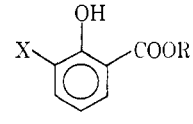


A

I, R = CH_3; X = Cl



B



C

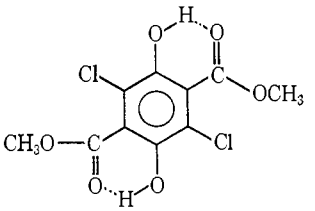
A 2% solution in chloroform of either crystalline solid Y-I or W-I shows two well-defined absorption maxima in the carbonyl stretching region at 1742 and at 1679 cm^{-1} corresponding to the absorptions at 1700 cm^{-1} in the spectrum of the white crystalline form and 1666 cm^{-1} in that of the yellow solid. As was observed with the spectra of the solids[4] exchange of the hydroxylic protons for deuterium shifted the lower frequency absorption in chloroform solution from 1679 to 1666 cm^{-1}

(1) We are indebted to the National Science Foundation for a grant providing partial support of this work.

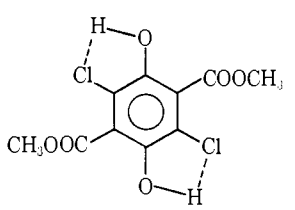
(2) Sinclair Oil Co. Fellow, 1966–1967. National Science Foundation Fellow, 1967–1968.

(3) See (a) A. Hantzsch, *Chem. Ber.*, **48**, 797 (1915); (b) *ibid.*, **48**, 785 (1915).

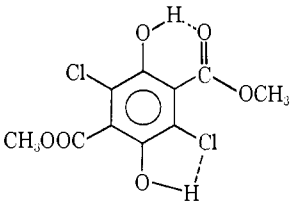
(4) D. Y. Curtin and S. R. Byrn, *J. Am. Chem. Soc.*, **91**, 1865 (1969).



Y–I

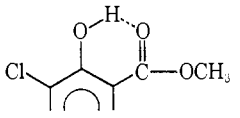


W–I

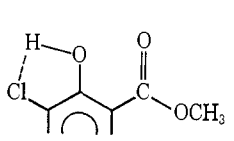


H–I

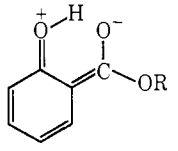
(in this case) but left the higher frequency absorption unchanged. Since a molecular weight determination in chloroform showed no indication of association,[5] we conclude that the lower-frequency absorption is due to the functional group assembly shown in the half-molecule D. Both ir[6] and nmr[7] evidence have shown that



D



E



F

the closely related substance, methyl salicylate, is essentially completely internally hydrogen bonded in the same medium and with the carbonyl stretching frequency in chloroform at 1679 cm^{-1} in excellent agreement with the value found for the lower frequency absorption of I.

Evidence that the second functional group assembly present in dilute chloroform and responsible for the higher frequency carbonyl absorption is that shown in the half-molecule E is provided in part by the example of *o*-chlorophenol which has been shown[8,9] in comparable media to exist very largely as the species with an intramolecular hydrogen bond to chlorine and with an enthalpy of about 1.4 kcal/mole associated with the intramolecular oxygen–hydrogen–chlorine bond. If the absorption coefficients of the two carbonyl functional groups are assumed to be approximately equal,[10] then

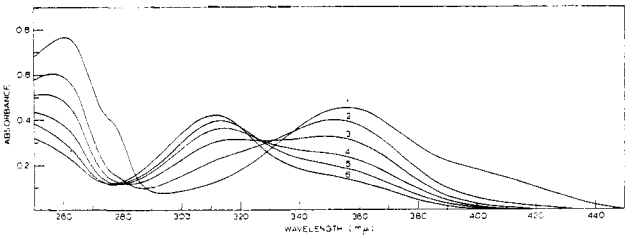


Figure 1. Ultraviolet spectra of I in chloroform–ethanol mixtures. The solvents corresponding to spectra 1–6 were as follows: 1, $CHCl_3$; 2, 20% C_2H_5OH–80% $CHCl_3$; 3, 40% C_2H_5OH–60% $CHCl_3$; 4, 60% C_2H_5OH–40% $CHCl_3$; 5, 80% C_2H_5OH–20% $CHCl_3$; 6, C_2H_5OH. The concentration of I in curves 1–5 is the same (within the error of dilution of a stock solution of I in chloroform). The concentration of I in curve 6 is not precisely the same although both concentrations were about 9×10^{-5} *M*.

there are nearly equal concentrations of the two functional group assemblies D and E in these solutions.

Further information about the nature of this equilibrium has come from repetition and extension of the observations reported in 1915 by Hantzsch[3b] on the dramatic change of the uv spectrum with a change of solvent. Hantzsch had observed what looked like a change of a single uv maximum from 308 mμ in ethanol to 348 mμ (with a shoulder at about 400 mμ) in chloroform. We have now measured the uv spectrum in a number of solvent mixtures covering the range from pure chloroform to pure ethanol. Some of the results are shown in Figure 1. It will be seen that the shoulder above 400 mμ in chloroform solution disappears rapidly as the solution is made richer in ethanol; at the same time the maximum at 356 mμ in chloroform decreases more gradually and a maximum not evident in chloroform solution appears at 315 mμ as the mole fraction of ethanol is increased.[11] There are two regions at about 330 and 280 mμ which approximate isosbestic points. These curves provide striking evidence for the conclusion, not evident from Hantzsch's more limited data, that we are dealing with an equilibration between what may be considered in the first approximation as three species; the absorption at 315 mμ is due to W-I, that at 356 mμ to H-I, and that above 400 mμ to Y-I. The correctness of this interpretation is supported strongly by a more detailed analysis of the spectral data. If it is assumed that the two functional group assemblies at the opposite ends of the molecule I act independently of one

$$\text{W-I} \overset{K_{W}^{H}}{\rightleftharpoons} \text{H-I} \overset{K_{H}^{Y}}{\rightleftharpoons} \text{Y-I}$$

another in their solvent-dependent equilibria, then it is appropriate to consider an equilibrium constant for an equilibrium between the hydrogen-bonded chlorine and the hydrogen-bonded carbonyl functional group assemblies as shown. Application of statistics[12] gives the

$$\text{E} \overset{K_{fg}}{\rightleftharpoons} \text{D}$$

(5) Results in agreement with the present work were obtained by A. Hantzsch (*Ann.*, **384**, 135 (1911)), who found the related diethyl ester had mol wt 310 in methanol and 341 in benzene (boiling point elevation) (calcd 323).

(6) (a) G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and W. Liddel, *J. Am. Chem. Soc.*, **58**, 548 (1936); (b) estimates of the hydrogen bond strength have been as high as 6.9 kcal/mole [B. A. Zudorozhnyi and I. K. Ishchenko, *Opt. Spektrosk.*, **19**, 551 (1965)]; (c) C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 661 (1961).

(7) A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **82**, 5057 (1960); L. W. Reeves, E. A. Allan, and K. O. Strømme, *Can. J. Chem.*, **38**, 1249 (1960).

(8) See A. W. Baker and A. T. Shulgin, *Can. J. Chem.*, **43**, 650 (1965).

(9) E. A. Allan and L. W. Reeves, *ibid.*, **66**, 613 (1962); **67**, 591 (1963).

(10) Support for this approximation comes from a comparison of the relative integrated absorption intensities in the crystalline isomers W-I and Y-I[4] which are approximately equal when compared by relating them through the carbon–hydrogen bending absorption at 1400–1465 cm^{-1}. See J. L. Mateos, R. Cetina, E. Olivera, and S. Meza [*J. Org. Chem.*, **26**, 2494 (1961)] for a study of methyl *p*-hydroxybenzoate and its cyclic hydrogen-bonded dimer which have comparable integrated intensities of the carbonyl stretching absorptions.

(11) Although the spectra obtained in the present work agree well in general with those reported by Hantszch,[3b] there are, in some cases, differences of as much as 7–8 mμ in the positions of the maxima.

(12) L. L. Smail, "College Algebra," McGraw-Hill Book Co., Inc., New York, N. Y., 1931, p 297 ff.

Table I. Solvent Dependence of the Spectra of the Dimethyl Ester (I)

Solvent	Dielectric constant	Ultraviolet spectrum, λ_{max}, mμ (ϵ)	Infrared spectrum, $\nu_{C=O}$, cm^{-1}	Nuclear magnetic resonance spectrum position of O*H* and OC*H*$_3$ (τ)	
C_6H_{14}	1.9[a]	400 sh 364 (*ca.* 2600) 275 sh 264 (*ca.* 6360)		*b*	*b*
CCl_4	2.2[a]	400 sh 361 (4440) 278 sh	1750 } (0.0011 *M* or 1678[c] } 0.00056 *M*)	*b*	*b*
$CHCl_3$	4.8[a]	400 sh 356 (4900) 276 sh 261 (7540)	1742 } (0.075 *M*, 1679[c] } 2.2%)	0.82	5.94
THF	7.4[d]	350 (2820) 313 (3720)	1746[c] (5%) 1671	0.80	6.05
C_2H_5OH	24.3[a]	313 (3570)	1745[c] } (0.075 *M*, 1725 } 2.2%) 1670	*e*	6.07
DMSO	45[d]	313 (5600)	1735 (8%)	0.00	6.11

[a] Values at 25°: see A. A. Maryott and E. A. Smith, "Tables of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, Aug 10, 1951. [b] Not sufficiently soluble. [c] This is the more intense of the carbonyl absorptions. [d] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966). [e] Fast exchange with the ethanol protons.

following relationship between the equilibrium constants for the equilibria between Y-I, H-I, and W-I and the equilibrium constant K_{fg} for the equilibrium between the two functional group assemblies E and D. From these relationships the following equations can be derived giving the mole

$$K_H^Y = K_{fg}/2 \qquad K_W^H = 2K_{fg}$$

fractions f_Y, f_H, and f_W, of the three compounds Y-I, H-I, and W-I in terms of the functional group equilibrium constant K_{fg}. Finally, if the assumptions are

$$f_Y = K_{fg}^2/(K_{fg} + 1)^2$$
$$f_H = 2K_{fg}/(K_{fg} + 1)^2$$
$$f_W = 1/(K_{fg} + 1)^2$$

made that the absorption at 410 mμ is due only to Y-I, that at 365 mμ only to H-I, and that at 300 mμ only to W-I and that the values of ϵ in the range of solvents being considered are constant for each of the three species then from the curves in medium 1 and medium 2 the value for K_{fg} in each medium can be calculated from the absorptions at 410 mμ and at 365 mμ in each medium or completely independently from the absorptions at 365 and 300 mμ in each medium by use of the equations

$$K_{fg^1} = A_{21}[(A_{12}A_{11})^{1/2} - A_{12}]/[A_{22}A_{11} - A_{21}(A_{12}A_{11})^{1/2}]$$

and

$$K_{fg^2} = (K_{fg} + 1)(A_{11})^{1/2} - (A_{12})^{1/2}$$

where K_{fg^1} and K_{fg^2} are the functional group constants in media 1 and 2, A_{11} and A_{12} are the absorbances in medium 1 at λ_1 and λ_2, and A_{21} and A_{22} are the absorbances in medium 2 at λ_1 and λ_2. In Table I are summarized the spectral data for I in several solvents and in Table II are values of K_{fg} in several solvents calculated by the method just discussed from pairs of uv spectra and also from the relative intensities of the high and low frequency carbonyl stretching absorptions in the infrared spectra (assuming the intensities of the carbonyl absorptions to be approximately equal).

Table II. The Ratio of Carbonyl Hydrogen Bonded to Chlorine Hydrogen Bonded Functional Groups (D/E) in Solutions of I

Solvent	Method of measurement: Carbonyl absorption (ir)	Ultraviolet spectrum λ_1 410 mμ λ_2 365 mμ	Ultraviolet spectrum λ_1 300 mμ λ_2 365 mμ
C_6H_{14}		3.4	3.2
20% C_2H_5OH in C_6H_{14}		0.21	0.22
CCl_4	1.9	2.1	2.2
20% C_2H_5OH in CCl_4		0.26	0.25
$CHCl_3$	1.0	1.3	1.3
20% C_2H_5OH in $CHCl_3$		0.34	0.33

It can be seen that the internal consistency is excellent—in fact so good that the agreement appears to be partially fortuitous. The results strongly support the over-all picture of an equilibrium involving three primary absorbing species, Y-I, H-I, and W-I. It is seen further that the carbonyl hydrogen bonded compound Y-I is favored in the equilibrium in cyclohexane (60% Y-I, 35% H-I, and 5% W-I) but progressively less so as the solvent is changed to carbon tetrachloride and then to chloroform. When any of these solvents is made 20% in ethanol K_{fg} is reduced to about 0.3 where the composition of the mixture is 5% Y-I, 35% H-I, and 60% W-I. As the solvent becomes richer in ethanol it is clear that the equilibrium is shifted still further toward W-I.

The nmr spectrum of I in deuteriochloroform showed a single hydroxyl proton absorption at τ 0.82 and a single methyl absorption at τ 5.94. Comparison with the values for the hydroxyl proton of methyl salicylate[7] (τ −0.6) and *cis-o*-chlorophenol (τ 4.4) is consistent with the proposed rapid equilibrium between the three species.[13]

(13) If the values for the hydroxyl proton of methyl salicylate and *cis-o*-chlorophenol are used together with the equilibrium constant of 1.3 measured in this work to estimate the position to be expected for the hydroxyl proton resonance of I a value of τ 1.0 is obtained. This is in reasonable agreement with the value of 0.82 obtained here; the model compounds are less than ideal because of the anticipated electronic

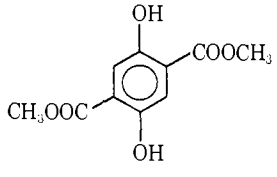
Table III. Spectra of Model Compounds in Various Solvents

Compound	Type of spectra[a]	DMSO	C_2H_5OH	$CHCl_3$	C_6H_{12}	CCl_4
Dimethyl terephthalate (II)[b]	Uv	365 (4,400)	252 (15,900) 378 (6,200)	255 (15,500) 382 (5,690)		
	Ir	1728 1679		3220 1680		
	Nmr			0.0		
Methyl salicylate	Uv		306 (4,370)[c]		308 (4,270)[c]	
	Ir	1720[b] 1674		1679[d]		3210[d] 1684
	Nmr	−0.51[b,e]		−0.64[b]		−0.56[f]
Methyl benzoate	Uv		227 (12,300)[g]		227 (12,400)[g]	
	Ir	1719[b]	1721[h] 1704	1720[d]		1729
o-Chlorophenol	Uv		216 (6,400)[i] 275 (2,350)			212 (6,450)[i] 271 (2,350) 278 (2,450)
	Ir					3603.2[j] 3547.1
	Nmr	0.0[b,e]		4.4		4.5[k]

[a] Ultraviolet, λ_{max} in mμ and ε (in parentheses). Infrared, carbonyl stretching frequencies in cm^{-1}. Nmr, hydroxyl proton positions relative to tetramethylsilane in τ units. [b] Present work. [c] E. D. Bergmann, Y. Hirshberg, and S. Pinchas, *J. Chem. Soc.*, 2351 (1950). The λ_{max} listed under cyclohexane was actually measured in isooctane. [d] See ref 6c. [e] Our results are in substantial agreement with those reported by Tribble and Traynham[14] since the completion of this work. [f] See ref 7. [g] W. F. Forbes and J. F. Templeton, *Can. J. Chem.*, **36**, 180 (1959). [h] Methyl benzoate has been found to show two carbonyl stretching frequencies in methanol by H. Minato, *Bull. Chem. Soc. Japan*, **36**, 1020 (1963). [i] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1294 (1959). [j] See ref 8. [k] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, **60**, 1314 (1956).

As shown by the data in Table I, tetrahydrofuran was less effective than ethanol in shifting the equilibrium toward W-I. Dimethyl sulfoxide was most effective in this respect; the only carbonyl stretching absorption evident in the ir spectrum in this solvent was that of the nonhydrogen-bonded ester at 1735 cm^{-1}.

The behavior of dimethyl 2,6-dihydroxyterephthalate (II) is in striking contrast to that of I. As was noted by



II

Hantszch,[3b] its spectrum changes only slightly when the solvent is changed from chloroform to ethanol and the maximum is at a very different position from that of its dimethyl ether. The predominant existence of only intramolecularly hydrogen-bonded ester groups is substantiated by the observation that there is only a single carbonyl stretching absorption at 1680 cm^{-1} in the ir spectrum in chloroform; this peak shifted to 1673 cm^{-1} on deuteration. Spectral data are summarized in Table III. Since dimethyl sulfoxide was so effective at shifting the equilibrium in the case of I, it was of interest to examine the ir spectrum of II in this solvent. There was indeed a carbonyl absorption at 1728 cm^{-1} as well as one at 1672 cm^{-1}, the ratio of intensities being approximately 5:6. A further compound examined in this solvent was methyl salicylate which again showed two carbonyl absorptions, at 1720 and 1672 cm^{-1}, but in a ratio of less than 1:2.[15]

It is apparent that in carbon tetrachloride- or chloroform–ethanol mixtures a significant shift of the equilibrium away from species with an intramolecularly hydrogen-bonded ester carbonyl group requires the presence both of the ethanol solvent and the chlorine atoms on the aromatic ring. This confirms the earlier proposal that ethanol is acting to stabilize (relatively) the species W-I and H-I. A hint that at least part of this effect is due to external hydrogen bonding of the ethanol to the ester carbonyl is provided by the appearance of a third carbonyl absorption at 1720 cm^{-1} in the spectrum of I in that solvent.[16] It seems likely that the unusual effectiveness of dimethyl sulfoxide in destablizing Y-I relative to W-I is due to at least two factors. Interaction of dimethyl sulfoxide with the ester carbonyl can help replace the loss of the chelate ring[17a] in the transformation of Y-I to W-I and may show preferential assistance to W-I by forming bifurcated hydrogen bonds.[17b]

The assignment of structures Y-I, H-I, and W-I to the three species in the equilibrium discussed earlier requires further consideration of the question of whether the uv maxima are reasonable. A satisfactory model for W-I (λ_{max} 308) would seem to be the dimethyl ether, dimethyl 3,6-dichloro-2,5-dimethoxyterephthalate, shown by Hantszch[3b] to have a similar spectrum (λ_{max} 305 mμ) in ethanol. The most reasonable model for the doubly chelate compound Y-I (λ_{max} 400 mμ) is the corresponding ester II lacking the chlorine atoms and just shown to be in the doubly chelate form (λ_{max} 382 mμ). The degree of correction for the two chlorine atoms required for the estimation of the position of the long wavelength maximum of Y-I from that of II is not easy to determine[18]

interaction of the two sets of substituents in the doubly substituted compound I.[14]

(14) M. T. Tribble and J. G. Traynham, *J. Am. Chem. Soc.*, **91**, 379 (1969).

(15) This is not in complete agreement with Tribble and Traynham's conclusion[14] that there is no intramolecular hydrogen bonding in methyl salicylate in dimethyl sulfoxide.

(16) See Table III, footnote *h*.

(17) (a) A substantial interaction of DMSO with the ester grouping is suggested by the ir data in Table III. Thus methyl benzoate shows a shift of its carbonyl stretching frequency from 1727 cm^{-1} in carbon tetrachloride to 1719 cm^{-1} in DMSO. (b) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, p 166.

(18) See A. I. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964, Chapter 3.

but there is reason to suppose that the correction should be positive and could easily be as large as 18 mμ.[19]

It is perhaps surprising that an equilibrium between a species with hydrogen bonding to a carbomethoxyl group on the one hand and to a chlorine atom on the other should fail to lie well toward the carbonyl-bonded side; in fact the half-substituted molecule methyl 3-chlorosalicylate (C, X = Cl, R = CH_3) was studied by Hoyer[20] who found in CCl_4 evidence for the carbonyl-bonded species alone. One possibility is that in the fully substituted compound I there is steric interference with coplanarity of the carbomethoxy groups with the ring with consequent destabilization of the intramolecular hydrogen bond to the carbonyl oxygen atoms. Although a contribution of this factor cannot be ruled out, it is relevant that a 6-methyl group introduced into the ring of methyl salicylate has no such deleterious effect on the chelate ring.[6c] A second factor which appears likely to be important is steric inhibition of resonance. A careful X-ray crystal structure[21] of salicylic acid has shown that formation of the OHO=C hydrogen bond is accompanied by distortion of the carbon–carbon bond distances of the aromatic ring in a way which suggests that the dipolar resonance structure F is a significant contributor. In the molecule Y-I the analogous distortion required for the chelate ring at one end of the molecule is directly opposed to that required for stabilization of the chelate ring at the other. Evidence for this effect is provided by the ir data in Table III showing that DMSO is more effective in opening the chelate rings of the doubly substituted molecule II than that of methyl salicylate itself.

In conclusion it may be noted that not only does this investigation solve a vexing structural problem that has persisted for many years, but it points to a set of compounds which could be uniquely valuable in studying details of hydrogen bonding. The three isomeric forms of I are unusual both because of the balanced equilibrium of their interconversion and because of the large differences between their spectra.

(19) It may be noted that the first chlorine introduced is *ortho* to a carbomethoxyl and to a chlorine atom and *meta* to a second of each of these substituents and the second chlorine introduces a similar set of relationships and is in addition *para* to the first chlorine. Estimation of the increments involved by comparing the maxima of pairs of compounds, *i.e.*, *o*-chlorophenol and phenol, methyl *o*-chlorobenzoate and methyl benzoate, etc., shows that if strict additivity were observed the total difference would be 43 mμ. The actual difference should be less than that.[18]

(20) H. Hoyer, *Z. Elect.*, **63**, 313 (1957).

(21) M. Sundaratingham and L. H. Jensen, *Acta Cryst.*, **18**, 1053 (1965).

Experimental Section

All melting points were measured on a Kofler hot stage. Ir spectra were measured on a Perkin-Elmer Model 521 spectrophotometer and in every case were calibrated with the 1601 cm^{-1} absorption of polystyrene. Nmr spectra were measured in part by Mr. R. Thrift and his associates on a Varian Associates Model A-60A or A-56-60 spectrometer. Uv spectra were determined on a Bausch and Lomb Model 505 or a Cary Model 14M spectrophotometer.

Reaction of Chlorine with 2,5-Dicarbomethoxy-1,4-cyclohexanedione (III). 2,5-Dichloro-3,6-dicarbomethoxybenzoquinone (IV). A solution of 20 g of chlorine in 20 ml of glacial acetic acid was added dropwise over 1 hr at 65° to 1.5 g (0.0066 mole) of III[22] prepared by a modification of the method[23] previously employed for the diethyl ester. After 24 hr, removal of 10 ml of acetic acid under reduced pressure precipitated 1.0 g (51%) of a mixture, mp 172–210°, of the yellow quinone IV with hydroquinone I. The progress of the reaction could be followed conveniently by tlc on silica (benzene eluent) since the dione III showed blue fluorescence, the quinone IV no fluorescence, and a second product shown below to be the hydroquinone I green fluorescence. The quinone IV after purification by chromatography on silica gel (benzene eluent) and by crystallization from benzene and sublimation, 140° (0.2 mm), had mp 240°. Its nmr spectrum ($CDCl_3$) showed a singlet at τ 6.02. Its ir spectrum showed strong carbonyl absorptions at 1682 and 1744 cm^{-1}.

Anal. Calcd for $C_{10}H_6Cl_2O_6$: C, 41.1; H, 2.1; Cl, 24.2. Found: C, 41.2; H, 1.9; Cl, 26.7.

Dimethyl 2,5-Dichloro-3,6-dihydroxyterephthalates (Y- and W-I). A second fraction obtained in the purification of the quinone IV above by chromatography amounted to about 14% of the theoretical amount of Y-I, mp 177–179° (transition to white at 140°). Recrystallization from ethanol gave yellow plates of I which turned white at about 140° and melted at 177–179° (lit.[3b] mp 177–179°). The hydroquinone I was also synthesized (yield 50%) by reduction of 1.8 g of a mixture of the quinone IV and I with zinc (0.2 g) in acetic acid at 100°, mol wt (chloroform) 260 (calcd 295).

Spectral Studies. Chloroform was purified by the method of Fieser.[24] Tetrahydrofuran was distilled from lithium aluminum hydride. Dimethyl sulfoxide was purified by the method of Smith, Fainberg, and Winstein.[25]

The deuteration of I or II was carried out by saturating the chloroform solution with D_2O and measuring the spectrum of the resulting solution in calcium fluoride cells. Nmr spectra of the resulting solutions showed that exchange had been complete.

Dimethyl 2,5-dihydroxyterephthalate (II) was prepared in 80% yield by reaction of the corresponding dicarboxylic acid[26] with diazomethane.[27] Recrystallization from methanol and sublimation at 120° (0.01 mm) gave II, mp 177–178°.

Anal. Calcd for $C_{10}H_{10}O_6$: C, 53.1; H, 4.5. Found: C, 53.4; H, 4.6.

(22) H. Ebert, *Ann.*, **229**, 52 (1885).

(23) A. T. Nielsen and W. R. Carpenter, *Org. Syn.*, **45**, 25 (1965).

(24) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p 283.

(25) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(26) F. Hemmelmayr, *Monatsh. Chem.*, **38**, 82 (1917).

(27) F. Arndt, "Organic Syntheses," Coll. Vol. II, Ed. H. Blatt, John Wiley & Sons, Inc., New York, N. Y., 1943, p 165.