ENTHALPIES OF INTRAMOLECULAR HALOGEN-HYDROXYL INTERACTIONS

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ABSTRACT

Enthalpies of halogen-hydroxyl interactions have been evaluated for the 2-halophenols in carbon tetrachloride. These values, in -kcal/mole, corrected for the temperature dependence of absorptivity coefficients, are Cl = 1.44, Br = 1.21, and I = 1.08. From enthalpy differences measured in unsymmetrical 2,6-dihalophenols, it is shown that the interaction in 2-fluorophenol lies between those in 2-bromophenol and 2-iodophenol, thus reaffirming the order Cl > Br > F > I.

The nature of halogen-hydroxy interactions is still open to conjecture despite intensive investigations (1-21) during the past several years. The investigations have been pursued by the use of several different techniques and have encompassed both intra- and intermolecular interactions of various phenols and alcohols. However, despite this attention, many aspects of the interactions are inadequately understood. For example, there has been no general agreement as to accepted values of these energies of interaction, nor has the relative order of energies within the halogen series been unambiguously determined.

For both 2-haloethanols and 2-halophenols, it is generally agreed that in "inert" solvents, 1, the difference $(\Delta \nu_{OH})$ between the frequencies of the free and bonded O—H configurations increases in the order F < Cl < Br < I, and 2, the proportion of the compound existing in the free (or *trans*) form increases in the same order. In addition, for the 2-halophenols, it is accepted that the O—H group is constrained to two coplanar positions by resonance interaction with the aromatic π -system and that it spends negligible time in residence between them. On the other hand, there is disagreement over the following points concerning these interactions. 1. Can these interactions be considered to be hydrogen bonds in the usual sense? 2. If we consider that these interactions embrace all contributions, such as from orbital basicity, atomic diameter, polarizability, and dipole moment, which halogen admits of the largest energy of interaction? 3. What is the relative order within the halogen series of the energies of interaction? 4. Does the Badger-Bauer rule (3), which states that the enthalpy of interaction (ΔH) is proportional to $\Delta \nu_{OH}$, apply to this interaction in which the O—H ···· X is highly bent away from the preferred rectilinear orientation?

Disagreement on question 1 stems from the fact that half-band widths and absorptivities of the O—H bands of 2-halophenols are only slightly larger than those of phenoland alkyl-substituted phenols. In analogy with intermolecular hydrogen bonding, it would have been expected that both should show marked increases (9, 22). Explanations for this unexpected behavior have been offered previously (13, 15) and shall be the subject of subsequent discussions. However, this paper will deal only with the remaining three questions by the critical evaluation of enthalpies of these interactions, specifically, in the 2-halophenols in the single solvent, carbon tetrachloride.

Since 2-fluorophenol and 2-fluoroethanol each exhibit but a single O—H band, the enthalpy of interaction cannot be evaluated directly by these spectroscopic techniques. These bands are grossly unsymmetric, indicating that the two components occur so close

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together that they contribute to a single band envelope. It has been observed previously (13), however, that unsymmetrical 2,4,6-trihalophenols exhibit two bands, each displaying a frequency characteristically assignable to the appropriate ortho-halide, regardless of the combination specifically represented. In the three possible unsymmetric 2-fluoro-6-halophenols (with or without a 4-halogen substituent), the O—H · · · · F band has the higher frequency in each case and is much broader than any of those involving the other halogens. Enthalpy differences can be measured accurately, thus allowing the relative strengths of the interactions to be determined. These data, combined with the measured enthalpies for 2-chloro-, 2-bromo-, and 2-iodo-phenol, determine the enthalpy of the fluorine-hydroxyl interaction to within perhaps a tenth of a kcal per mole. Obviously, the solvent is participating in these interactions and the *cis* and *trans* forms might be solvated or stabilized by different amounts. Therefore, enthalpies determined for one solvent system need not necessarily apply to a second, nor need the relative order established in one solvent system be the same as in a second. This is a moot question and will be investigated later in detail.

EXPERIMENTAL

The enthalpy calculations in this study required that the experimental data be obtained from compounds of high purity. If an ortho-halophenol displaying a *cis* to *trans* absorbance ratio¹ of 40 were contaminated by as little as $2\frac{1}{2}\%$ of non-ortho-halopenated phenol (which would absorb at approximately the same frequency as the *trans*-isomer) the apparent ratio would be halved. Consequently, an undetermined but relatively large error would be embodied in any calculation involving that ratio. The same problem exists in the corresponding unsymmetrical dihalophenols but to a smaller degree since the absorbance ratios are more nearly unity. To meet the demands of purity, frequent use was made of gas-liquid chromatography (g.l.c.) in the course of synthesis, isolation, and purification of all compounds.

The separations were performed on a Wilkins Aerograph A-700 Autoprep, using helium as a carrier gas. Three 5 ft, 3/8 in. diameter columns were necessary: Apiezon L (7% on 50–60 mesh Anakrom), ethylene glycol succinate (5% on 60–80 mesh acid-washed Chromosorb W), and 20 *M* Carbowax (10% on the Chromosorb support). These columns are abbreviated in the following discussion as A-L, EGS, and 20 *M*, respectively.

The four monohalophenols were obtained from commercial sources. 2-Fluoro-(Aldrich Chemical Company), 2-chloro-, and 2-iodo-phenols (Eastman Kodak) were purified by preparative separation on the 20 M column. Analyses by reinjection verified the absence of both free phenol and the para-isomer. 2-Bromophenol (Dow Chemical Company) required the Apiezon L column. A small phenolic contaminant, although well separated at 112 °C and 300 ml/min gas flow (phenol at 2.3 min, 2-bromophenol at 5.0 min, and air at 0.5 min) was still present in the purified sample. The residual impurity (0.05%) was undoubtedly due to unsuspected tailing either from the column or from the collection technique. A second pass reduced this to an acceptable level. For the other monohalophenols, a single separation achieved adequate purity.

None of the unsymmetrical 2,6-dihalophenols have heretofore been described in the literature. They were synthesized by the halogenation of an appropriate, purified monohalo compound, and separated from the congeneric para- and di-substitution products as described in Table I. The corresponding trihalophenols also investigated have been described earlier (13). (See below.)

The solvent employed in these studies, carbon tetrachloride, was dried by suspended P_2O_5 , and filtered directly into the sample cell in which the desired phenol had previously been captured from the Autoprep. This technique was employed when weighed samples were not required, as it effectively precluded the absorption of water. It has been observed here, as previously (23), that when small amounts of liquid phenols are weighed for dissolution, water pickup appears severe despite the employment of an acceptably dry solvent and an inert atmosphere. It must be concluded that the initial absorption of water by certain phenols, when dry, is extremely rapid.

The spectra were recorded directly in absorbance on a Beckman IR-7 prism-grating spectrophotometer at an effective resolution of 1.8 cm⁻¹. The absorbance potentiometer was calibrated by a set of linearity discs over the optical density (o.d.) range of 0.05 to 0.91, and found, after a zero adjustment, to be linear to within ± 0.005 o.d. units. The temperature runs were obtained in 1 cm cells at phenol concentrations of approximately $5 \times 10^{-3} M$. The temperature of both sample and reference cells was controlled and measured by thermistors. The read-out thermistor was in contact with the solution inside the cell; we believe the temperature to be accurate to within 0.1 °C, described previously (23).

¹The cis and trans names apply to the two coplanar conformers in which the hydroxyl group is directed toward, and away from, respectively, the halide.



				Time of emergence, min			Melting
А, В	Agent	III/II	Column†	I	11	III	of II
F, Cl F, Br F, I Cl, Br	$Cl_{2}(CCl_{4})$ $Br_{2}(CCl_{4})$ $ICl(HOAc)$ $Br_{2}(CCl_{4})$	$1.4 \\ 26 \\ 11 \\ 14 \\ 2.2 \\ 2.2 \\ 3$	$\begin{array}{c} 20 \ M \ (180^\circ) \\ EGS \ (110^\circ) \\ 20 \ M \ (180^\circ) \\ 20 \ M \ (175^\circ) \\ EGS \ (140^\circ) \end{array}$	$2.2 \\ 2.3 \\ 2.2 \\ 3.0 \\ 2.6$	4.4 9.0 12.9 10.2 5.9	$6.4 \\ 12.8 \\ 18.6 \\ 13.4 \\ 6.0 \\$	6364° 47-48° Oil 55-56°
I, CI I, Br	$Cl_2(CCl_4)$ Br ₂ (CCl ₄)	3.3 4.9	EGS (140°) EGS (155°)	$\begin{array}{c} 2.6\\ 2.3\end{array}$	$egin{array}{c} 5.2 \ 7.2 \end{array}$	6.9 10.8	38–39° 60–61°

*Determined by planimetry of the appropriate chromatographic scan. †All were adjusted to a carrier gas flow of about 300 ml/min at the oven temperatures indicated. In the chlorination of o-iodophenol, there was generation of free iodine. The 5.2 min peak proved, however, to be the desired chloroiodo isomer and its homogeneity was established by rechromatography on the 20 M column (emergence at 17.2 min, 180° 300 cc He/min of the injected sample; it was observed as a single peak of unchanged infrared spectrum).

TABLE II

 ν_{OH} frequencies and half-band widths, cm⁻¹

		ν _{OH}	$\frac{1}{2}\Delta\nu_{OH}$	
	1	2	1	2
2-Fluorophenol		3 591.0		22.0
2-Chlorophenol	3603.2	$3 \ 547.1$	~ 23	18.4
2-Bromophenel	3 602.7	3 527.8	~ 23	18.5
2-Iodophenol	3600.0	3 505.1	19.0	20.0
2-Fluoro-6-chlorophenol	3 580.5	3 543.8	28.4	20.5
2-Fluoro-6-bromophenol	3 578.6	3 524.9	28.5	20.0
2-Fluoro-6-iodophenol	3 578.7	3 501.9	32.0	25.1
2-Chloro-6-bromophenol	3 535.1	3 521.6		
2-Chloro-6-iodophenol	3 532.9	$3 \ 494.8$	19.1	
2-Bromo-6-iodophenol	$3 \ 513.4$	$\sim 3 490$		

The voH band referred to as 1 is the band due to the O—H group oriented *trans* or, for the dihalo-phenols, toward the 2-position substituent. The half-band widths lined out could not be determined accurately because of inadequate band separation.

The spectra were obtained at temperatures ranging from 25 to 75 °C; in order to assure the necessary accuracy, a minimum of three repeat runs at the temperature extremes and two at intermediate points were taken. Band areas were measured repeatedly with a rolling disc planimeter until it was felt that the areas of these somewhat arbitrarily divided bands had been established to within 0.3%. The spectral data are given in Table II.

DISCUSSION

The energy of intramolecular halogen-hydroxyl interactions has always been considered to be less than that of intermolecular hydrogen bonds. Early attempts to evaluate this energy employed qualitative arguments (24), based either on measured free energies (2) and estimated entropies (25) or on relative peak heights of competitive halogens (13). The former arguments indicated that the bond strengths increased parallel to the increase in frequency shift in going from fluorine to iodine. This established the order I > Br> Cl > F. In contrast, the latter arguments (13), employing peak heights, indicated

that the order was Cl > Br > F > I. The early direct measurements of enthalpies of halophenols in the vapor state (6, 26) tended to support the latter order although the quantitative results were questioned (26) because of impure samples. More recent quantitative work is in general agreement that iodine forms the weakest bond of any halogen, but there is yet uncertainty concerning the strengths of interactions to the remaining halogens. Regarding intermolecular effects, there is now apparent agreement that the order of decreasing strength is F > Cl > Br > I. All of these data are summarized in Table III.

TABLE III	
Literature enthalpies of halogen-hydroxyl interaction	
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			Halide				
environment	Compound	Technique	F	Cl	Br	I	Ref.
Vapor state	2-Chlorophenol	Infrared		3.9			6
	2-Iodophenol	Infrared				3.2	26
Intramolecular,	∠2-Halophenols	Infrared		1.27	1.86	1.00	27
liquid	2-Halophenols	Nuclear magnetic resonance		2.3	2.0	1.5	28
	2-Haloethanols	Infrared	2.1	1.2	1.2	0.8	17
Intermolecular, liquid	Phenol vs. aliphatic halides	Infrared	3.1	2.2	2.0	1.7	20
	Phenol vs. cyclohexyl halides	Infrared	2.6	2.4	1.8	2.0	19

Other techniques have also been used but, unfortunately, have added further disagreement over the relative order of the halogens. The nuclear magnetic resonance (n.m.r.) values quoted in Table III are larger than those obtained from infrared, but nonetheless, maintain the order most generally accepted for the three heavier halogens, namely, Cl > Br > I. However, no interaction at all involving fluorine could be detected and it was assumed to be zero. This assumption was modified in a subsequent paper wherein the authors inferred that there was indeed interaction, but weaker than that involving iodine. Qualitative arguments employing dipole moment measurements of these phenols have led to conflicting assignments for fluorine. One report (29) attributes to fluorine the strongest interaction of any halogen; another (14) places it between bromine and iodine as suggested in the work below. Finally a qualitative infrared investigation of competitive hydrogen bonding (16) concluded that fluorine does indeed enter into an interaction in 2-fluorophenol but that its energy of interaction is the smallest of any halogen.

Enthalpies of 2-Halophenols

The enthalpies reported in this study have been obtained from area measurements of the two competitive hydroxyl bands displayed by each halophenol. These bands are shown in Fig. 1 for the 2-halophenols and in Fig. 2 for the unsymmetrical 2,6-dihalophenols. Enthalpy values derived in this way are based upon the assumption that the ratio of the band absorptivity coefficients is temperature independent. This assumption is inherent in all of the infrared data quoted above. We have examined this premise in a previous publication (30) and have found that corrections amounting to several percent of the measured enthalpies must be applied to obtain more accurate values.

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FIG. 2. von bands of the unsymmetrical 2,6-dihalophenols. Solvent CCl₄.

These corrections are obtained from the absorptivities of phenol and of symmetrical 2,6-dihalophenols measured at 25 and 75 °C. For these compounds, only a single O-H band exists; the temperature dependency of phenol should parallel that of the transcomponent of the 2-halophenols and the temperature dependency of the dihalophenols that of the *cis*-component. This assumption appears to be reasonable and it is consistent with the behavior of the other band parameters such as the temperature shifts of frequencies and of half-band widths. The temperature corrections were calculated by the relationship

$$\Delta H_{\rm c} = -4.571 \frac{\partial \log \frac{\alpha_1}{\alpha_2}}{\partial 1/T},$$

where α_1 and α_2 are the absorptivity coefficients of the two bands in each compound. As shown previously (30), this can be put into the form

$$\Delta H_{\rm c} = -4.571 \left[\frac{\log \frac{\alpha_1^{25}}{\alpha_1^{75}} - \log \frac{\alpha_2^{25}}{\alpha_2^{75}}}{0.483 \times 10^{-3}} \right] {\rm cal/mole}$$

for temperature limits of 25 and 75 °C. The ratios, α^{25}/α^{75} for phenol, dichloro-, dibromo-, and diiodo-phenols were found (30) to be 1.075, 1.056, 1.055, and 1.053, respectively. The value of this ratio for the fluoro group, measured here from 2,6-difluorophenol, is 1.066. Since the enthalpy for *o*-fluorophenol must be derived indirectly, this ratio can be utilized only in obtaining corrections for the enthalpy differences in the mixed fluorohalophenols. The corrections for the other 2-halophenols are, in kcal/mole, -0.07, Cl; -0.08, Br; and -0.09, I. The addition of these corrections to the measured enthalpies of the 2-halophenols results in an increase of absolute magnitude in each case.

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Enthalpy values of h	halophenols,	kcal/mole	(solutions i	n carbon	tetrachloride)
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				Area			Peak height	
			Correction	$-\Delta H$ measured	$-\Delta H$ corrected	Correction	−∆H measured	$-\Delta H$ corrected
2-Hal	ophen	ols						
F	•				1.19*			
Cl			0.07	1.37	1.44	0.39	1.24	1.63
Br			0.08	1.13	1.21	0.52	1.10	1.62
I			0.09	0.99	1.08	0.50	0.94	1.44
Polyh	aloph	enols†						
(2)	(4)	(6)						
F	Н	Ci	0.04(+)	0.14	0.18	0.24	0.03	0.27
F	Η	Br‡	0.04(+)	0.06	0.10	0.36	-0.03	0.33
F	Н	I	0.05(-)	0.41	0.36	0.35	0.58	0.93
Ēι	Η	Br		§		0.12	0.06	0.18
ΓĪ	I-I	I	0.01(-)	0.56	0.55	0.11	0.66	0.77
Br	Н	I		ş		0.00	0.33	0.33
F	Br	Br‡	0.04(+)	0.04	0.08	0.36	0.14	0.50
F	I	I	0.05(-)	0.38	0.33	0.35	0.70	1.05
Ē	Cl	I	0.01(-)	0.57	0.56	0.11	0.61	0.72

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*Derived value, not directly measurable. †Favored halide is underlined. ‡Bromo group favored by area, fluoro by peak height. \$Not measurable with accuracy.

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A summary of these corrections, together with the measured and corrected enthalpies, is given in Table IV. Also listed are the corresponding values for the unsymmetrical diand tri-halophenols. Results obtained by the use of optical densities are included for comparison. It can be seen that these values are much less consistent than those from band areas and that the corrections are so large as to have little meaning. This behavior indicates that temperature dependencies of optical densities cannot be transferred from one molecular system to another and that enthalpies based upon peak heights are not as reliable as those from band areas. Therefore, only the latter values will be considered in the following discussion. The enthalpies and ranking of the 2-halophenols that admit of direct measurement are, from Table IV, Cl (1.44) > Br (1.21) > I (1.08). A value can now be obtained for 2-fluorophenol by considering the following data from the mixed dihalophenols.

Unsymmetrical Di- and Tri-halophenols

All of the 2-halophenols except 2-fluorophenol have two well-resolved bands, thereby permitting enthalpies to be determined directly. However, due to the occurrence of only a single band in 2-fluorophenol, the enthalpy of interaction must be evaluated indirectly, i.e., by use of the unsymmetrical 2-fluoro-6-halophenols. The two bands in each of these three compounds are resolved adequately to permit the determination of relative band areas.

The bands were separated into the respective areas by arbitrary graphical techniques. Fortunately, as shown previously (31), the calculated enthalpy is virtually insensitive to the way the bands are separated (within reasonable limits) as long as any assumptions are applied consistently throughout a temperature run. Results corresponding to those discussed above for 2-halophenols are also listed in Table IV. Since the absorptivity temperature ratios are in the order F > Cl > Br > I, the pairing of the halogens acts to increase the enthalpy correction of the heavier with respect to the lighter. In the case of $F \leftrightarrow Cl$ and $F \leftrightarrow Br$, the numerical value of the observed enthalpy difference is increased in each case because the interaction energy is larger for the heavier two halogens. However, in the remaining four comparisons ($F \leftrightarrow I$, $Cl \leftrightarrow Br$, $Cl \leftrightarrow I$, and $Br \leftrightarrow I$), the reverse occurs because the lighter atom dominates the interaction.

These relationships are diagrammed for clarity in Fig. 3 and are shown for both area and optical density measurements. The arrows point to the halogen forming the stronger



FIG. 3. Enthalpy differences, in kcal/mole, of the halogen-hydroxyl interaction as determined (A) from corrected area measurements, and (B) from uncorrected optical density values. Arrow points in direction of stronger association. Compounds examined OH

X, Y = F, Cl, B, I; X \neq Y.

interaction (with the O—H group), and the enthalpy differences in kcal/mole are recorded on each arrow. The values missing from the diagram, for 2-bromo-6-iodophenol and for 2-bromo-6-chlorophenol, were not obtained due to inadequate band separation. This prevented accurate assignment of areas to the appropriate bands.

For the area diagram (Fig. 3) there is remarkable good internal agreement in the ΔH difference between chlorine and iodine by the two different routes. The direct value is 0.55 kcal/mole, and the value obtained by adding I \rightarrow F and F \rightarrow Cl is 0.54 kcal/mole. For the trihalophenols, the corresponding direct value is 0.56 kcal/mole. The two-step value is not available since the F \rightarrow Cl compound was not run; however, the I \rightarrow F value is 0.33 kcal/mole compared to 0.36 kcal/mole found for the dihalophenol. Due to the internal consistency of these results and to the reproducibility of the values obtained in duplicate runs, we believe the accuracy of these data to be better than ± 0.05 kcal/mole.

Direct comparisons of energies obtained from the mixed dihalophenols give the following order for the decreasing enthalpy of the halogen-hydroxyl interaction: Cl > Br > F> I. Fluorine is definitely placed to the right of bromine by area measurements, although by only a small amount. It is placed to the left of bromine by use of peak height calculations, but not when the corrections are added. Such values that are obtained through the employment of peak heights become yet less reliable as the band separations become very small. Under these conditions, the temperature dependence of each band is diluted by the temperature dependence of the other, and as $\Delta \nu$ approaches zero, the enthalpy measured by peak heights will also approach zero. This effect is observed in the optical density diagram for the compounds 2-bromo-6-iodophenol and 2-bromo-6-chlorophenol, the two specific compounds not amenable to area measurement. The band separations are approximately 17 cm⁻¹ and 14 cm⁻¹, respectively; in the former case, the band shows only an inflection point but no double maximum. The sum I \rightarrow Br and Br \rightarrow Cl is 0.39 kcal/mole, only two-thirds of the well-resolved I \rightarrow Cl value of 0.66 kcal/mole.

From the excellent agreement in the enthalpy differences between the di- and trihalphenols, one must conclude that the presence of the additional halogen in the 4-position has no effect on these values. However, as correctly pointed out by the referee, there could conceivably be an appreciable difference in solvent effects for the 2-halo- and 2,6-dihalo-phenols. In the former compounds, the *trans*-conformer affords greater opportunity for solvent interaction, whereas in the latter compounds, the hydroxyl group in either conformer should be shielded from the solvent by approximately equal amounts. This could result in an internal inconsistency in transferring data between the monoand di-substituted phenols. For this reason, the direct comparison of the interaction to fluorine and to bromine in 2-bromo-6-fluorophenol is given first preference. Thus, since this comparison shows that the ΔH to bromine is unequivocally larger than to fluorine, the enthalpy value for the fluorine–hydroxyl interaction is taken as 1.19 kcal/mole, slightly lower than that of O—H \cdots Br.

Analogous Interactions in the 2-Haloethanols

Some intersting comparisons can be made between the data given here for the 2-halophenols and those recently published for the 2-haloethanols (17). Although these families are chemically dissimilar, the many spectral features they display in common strongly suggest that the actual physical interactions between the —OH and halo groups are qualitatively similar in both. Since band separations are small in these latter compounds, the use of peak heights for enthalpy evaluations was mandatory; therefore, it was necessary for the previous authors to accept the concomitant inaccuracies discussed above.

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The enthalpies found (Table III) for the $O - H \cdots I$ and $O - H \cdots Br$ interactions were -0.8 and -1.2 kcal/mole, values surprisingly close to those given here for the 2-halophenols. The value for the $O-H \cdots Cl$ interaction was considered to be equal to, or slightly less than, that of the O-H \cdots Br interaction. This is at variance with the increase found in the 2-halophenols and can readily be explained by the inherent decrease in measured ΔH as $\Delta \nu$ approaches zero. More disturbing is the placement of the O—H · · · F interaction as the largest of the four. This is based on the premise that the very unsymmetrical band shown by 2-fluoroethanol can be graphically resolved into two separate components and that the individual temperature dependency of each band can be determined. The procedure is, at best, questionable since many infrared bands are unsymmetric in compounds where only a single conformer can exist.

Compounds demonstrating this type of band dissymmetry are the unsymmetrical 2,6-dihalophenols. As discussed above, two ν_{OH} bands occur due to interactions with the two proximal halogens. Each band can be produced by only a single conformer; rotation around the C—O bond is restricted by at least 4 kcal/mole so that the O—H group is constrained to an in-plane residence. In the two compounds 2-fluoro-6-iodophenol and 2-fluoro-4,6-diiodophenol, the band due to the O-H \cdots F interaction is grossly unsymmetric, as is readily observed for the former compound in Fig. 2. In order to assess the extent of this dissymmetry, two parameters are evaluated. These are defined as follows: the band is divided left and right by a vertical line drawn through the band maximum. The high-frequency part of the half-band width lying to the left of this line is divided by that to the right. This ratio is a measure of band dissymmetry and is unity for a symmetric band.

Values of this ratio found at 25 and 75° for the above two compounds are



In the first compound, the symmetry of the band increases with temperature. In the second, however, the dissymmetry increases in a manner similar to that observed in the single band in 2-fluoroethanol, and from which an apparent ΔH had been calculated (17). Despite this difference in temperature behavior of band shape, the ΔH 's (F \leftrightarrow I) measured in the two phenols are identical. This supports the obvious conclusions that the $O-H\cdots$ F bands in these phenols consist of only one conformer and that the dissymmetry is due to other factors. Calculated ΔH values predicated upon assumed symmetry must therefore be discounted.

ACKNOWLEDGMENT

We thank Dr. Finger of Illinois State Geological Survey for a generous sample of the 2,6-difluorophenol employed in this study.

REFERENCES

- O. R. WULF and U. LIDDEL. J. Am. Chem. Soc. 57, 1464 (1935).
 L. PAULING. J. Am. Chem. Soc. 58, 94 (1936).
 R. M. BADGER and S. H. BAUER. J. Chem. Phys. 5, 839 (1937).
 M. M. DAVIES. Trans. Faraday Soc. 34, 1427 (1938).

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- M. M. DAVIES. Trans. Faraday Soc. 36, 333 (1940).
 L. R. ZUMWALT and R. M. BADGER. J. Am. Chem. Soc. 62, 305 (1940).
 R. MECKE. Z. Elektrochem. 52, 107 (1948).
 A. W. BAKER and A. T. SHULGIN. J. Am. Chem. Soc. 80, 5358 (1958).
 M. KUHN, W. LÜTTKE, and R. MECKE. Z. Anal. Chem. 170, 106 (1959).
 M. OKI and H. IWAMURA. Bull. Chem. Soc. Japan, 33, 717 (1960).
 L. W. REEVES, E. A. ALLEN, and K. O. STRØMME. Can. J. Chem. 38, 1249 (1960).
 A. W. PROSS and F. VAN ZEGGEREN. Spectrochim. Acta, 16, 563 (1960).
 A. W. BAKER and W. W. KAEDING. J. Am. Chem. Soc. 51, 5904 (1959).
 H. RICHARDS and S. WALKER. Trans. Faraday Soc. 57, 412 (1961).
 E. A. CUTMORE and H. E. HALLAM. Trans. Faraday Soc. 58, 40 (1962).
 H. BOURASSA-BATAILLE, P. SAVAGEAU, and C. SANDORFY. Can. J. Chem. 41, 2240 (1963).
 P. J. KRUEGER and H. D. METTEE. Can. J. Chem. 42, 326 (1964).
 L. J. BELLAMY and H. E. HALLAM. Trans. Faraday Soc. 55, 220 (1959).
 MARIE-LOUISE JOSIEN. Pure Appl. Chem. 4, 33 (1962).
 R. WEST, D. L. POWELL, L. S. WHATLEY, M. K. T. LEE, and P. VON SCHLEYER. J. Am. Chem. Soc. 84, 3221 (1962). 21 (1962).
 21. C. G. CANNON. Mikrochim. Acta, 555 (1955).
 22. M. ST. C. FLETT. Spectrochim. Acta, 10, 21 (1957).
 23. A. W. BAKER, H. O. KERLINGER, and A. T. SHULGIN. Spectrochim. Acta, 20, 1477 (1964).
 24. L. PAULING. The nature of the chemical bond. 2nd ed. Cornell University Press, Ithaca, N.Y. 1948.

- L. PAULING. The nature of the chemical bond. 2nd ed. Cornen Oniversity Frees, reason, -Chap. 9.
 H. H. JAFFE. J. Am. Chem. Soc. 79, 2373 (1957).
 G. ROSSMY, W. LÜTTKE, and R. MECKE. J. Chem. Phys. 21, 1606 (1953).
 D. A. K. JONES and J. G. WATKINSON. Chem. Ind. London, 661 (1960).
 E. A. ALLAN and L. W. REEVES. J. Phys. Chem. 66, 613 (1962); 67, 591 (1963).
 W. F. ANZILLOTI and B. C. CURRAN. J. Am. Chem. Soc. 65, 607 (1943).
 A. W. BAKER, H. O. KERLINGER, and A. T. SHULGIN. Spectrochim. Acta, 20, 1467 (1964).
 A. W. BAKER and A. T. SHULGIN. Spectrochim. Acta, 19, 1611 (1963).

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- 1. Shota Nanbu, Masahiko Sekine, Munetaka Nakata. 2012. Intramolecular hydrogen-atom tunneling and photoreaction mechanism of 4-bromo-2-chloro-6-fluorophenol in low-temperature argon matrices. *Journal of Molecular Structure* 1025, 69-73. [CrossRef]
- Shota Nanbu, Masahiko Sekine, Munetaka Nakata. 2011. Hydrogen-Atom Tunneling in Isomerization Around the C–O Bond of 2-Chloro-6-Fluorophenol in Low-Temperature Argon Matrixes. The Journal of Physical Chemistry A 115, 9911-9918. [CrossRef]
- 3. Usha John, Sunny Kuriakose, K.P.R. Nair. 2007. Vibrational overtone spectra of o-fluorophenol and the "anomalous" order of intramolecular hydrogen bonding strengths. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **68**, 331-336. [CrossRef]
- Igor M. Skvortsov, Oleg E. Makarov, Evgenii E. Fedorov. 2006. Further consideration of the gas–liquid chromatographic method for determining the intramolecular hydrogen bond energies with the example of 2-substituted phenols. *Journal of Chromatography* A 1132, 248-255. [CrossRef]
- 5. Giuseppe Buemi. 2004. Basis set effects on the energy of intramolecular O-H#halogen hydrogen bridges in ortho-halophenols and 2,4-dihalo-malonaldehyde. *Chemical Physics* **300**, 107-117. [CrossRef]
- 6. Oksana Tishchenko, Eugene S. Kryachko, Minh Tho Nguyen. 2002. Theoretical vibrational analysis of monohalogenated phenols. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 58, 1951-1969. [CrossRef]
- 7. Matthias Kauch, Dieter Hoppe. 2001. Synthesis of substituted phenols by directed ortho-lithiation of in situ N-silyl-protected O-aryl N-monoalkylcarbamates. *Canadian Journal of Chemistry* **79**:11, 1736-1746. [Abstract] [PDF] [PDF Plus]
- 8. B. Czarni??-Matusewicz, Th. Zeegers-Huyskens. 2000. Mid- and near-infrared study of the hydrogenbonded complexes between pentachlorophenol and proton acceptors. *Journal of Physical Organic Chemistry* 13:10.1002/1099-1395(200005)13:5<>1.0.CO;2-0, 237-243. [CrossRef]
- Boguska Czarnik-Matusewicz, Asit K. Chandra, Minh Tho Nguyen, Thérèse Zeegers-Huyskens. 1999. Theoretical and Experimental (400–10000 cm–1) Study of the Vibrational Spectrum of Pentachlorophenol. *Journal of Molecular Spectroscopy* 195, 308-316. [CrossRef]
- 10. Giovanni Nicolisi, Mario Piattelli, Claudia Sanfilippo. 1993. Lipase-catalyzed regioselective protection of hydroxyl groups in aromatic dihydroxyaldehydes and ketones. *Tetrahedron* 49, 3143-3148. [CrossRef]
- 11. M.A. Broda, J.P. Hawranek. 1990. Vibrational dephasing of vs (OH) in 2,4-dichlorophenol. *Journal of Molecular Structure* 219, 215-220. [CrossRef]
- Salman R. Salman, A.R. Kudier. 1990. 1H NMR study of dilution and complex formation of o-halophenols. Spectrochimica Acta Part A: Molecular Spectroscopy 46, 1147-1152. [CrossRef]
- 13. Muhammad Entazul Huque, Stanley Walker. 1989. Dielectric relaxation processes of symmetrically substituted phenols in a few glassy media. *Chemical Physics* 130, 345-351. [CrossRef]
- M.A. Broda, J.P. Hawranek. 1988. Vibrational dephasing of vs(OH) in 2,6-dichloro-4-nitrophenol. *Journal of Molecular Structure* 177, 351-358. [CrossRef]
- 15. H. Abramczyk, D. Samios, Th. Dorfmüller. 1987. Vibrational relaxation of proton acceptor in H-bonded complexes. *Journal of Molecular Liquids* 36, 277-292. [CrossRef]
- Ernst Schmitz, Ingeborg Pagenkopf. 1985. ortho-Spezifische Bromierung von Phenolen. Journal fr Praktische Chemie 327:10.1002/prac.v327:6, 998-1006. [CrossRef]
- Thomas E. Boothe, Ronald D. Finn, Manhar M. Vora, Ali M. Emran, Paresh J. Kothari. 1984. Radioisotopic labelling by surface catalysis—II. Mechanism of radioiodinations on chromatographic surfaces. *The International Journal of Applied Radiation and Isotopes* 35, 1138-1143. [CrossRef]
- Henrik Tylli, Henrik Konschin. 1979. A raman spectroscopic study of the OH and OD torsion in 1,2-dihydroxybenzene. *Journal of Molecular Structure* 57, 13-19. [CrossRef]
- 19. S. Geresh, O. Levy, Y. Markovits, A. Shani. 1975. On the mechanism of intramolecular photocycloaddition of substituted oallylphenols to cyclic ethers. *Tetrahedron* **31**, 2803-2807. [CrossRef]
- 20. M. Simonyi, F. Tüdős The Hydrogen Atom Abstraction Reaction from O-H Bonds 127-183. [CrossRef]
- 21. E. Fishman, Tun Li Chen. 1969. An investigation of the hydrogen bonding characteristics of butanediols. *Spectrochimica Acta Part A: Molecular Spectroscopy* 25, 1231-1242. [CrossRef]
- 22. Tien-sung Lin, E. Fishman. 1967. Enthalpies of intramolecular hydrogen bonds of orthohalophenols and deuterated orthohalophenols in the vapor phase. *Spectrochimica Acta Part A: Molecular Spectroscopy* 23, 491-500. [CrossRef]

- 23. M. Simonyi, F. Tüd"s, J. Pospiŝil. 1967. Kinetics of radical polymerization—XIX. study of the reactivities of phenols towards polyvinyl acetate radicals. *European Polymer Journal* **3**, 101-115. [CrossRef]
- 24. A.W. Baker, M.D. Yeaman. 1966. Arbitrary techniques of band resolution—application to enthalpy calculations. *Spectrochimica Acta* 22, 1773-1785. [CrossRef]
- 25. A.W. Baker, D.E. Bublitz. 1966. Enthalpies of intramolecular interactions in ferrocenyl alcohols. *Spectrochimica Acta* 22, 1787-1799. [CrossRef]
- 26. A.W. Baker, T. Shulgin. 1966. Solvent stabilization of conformers in o-iodophenol. Spectrochimica Acta 22, 95-105. [CrossRef]