

## Far-Infrared Studies of Hydrogen Bonding

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**Abstract:** Direct spectroscopic observations of the hydrogen-bond stretching frequencies ( $\nu_\sigma$ ) in pure cresols and chlorophenols have been obtained in the far-infrared. Previous difficulties in making assignments have been obviated by the use of the following criteria, which provide confident identification of  $\nu_\sigma$ : (1) disappearance of the absorption when  $\text{OCH}_3$  is substituted for  $\text{OH}$ ; (2) absence of the band in the Raman spectrum; (3) observation of a broad asymmetric band contour. Although no generalizations may yet be drawn, there is no simple correlation between  $\nu_\sigma$  and mid-infrared bonded O-H frequency shifts ( $\Delta\nu_s$ ) for these compounds. The stretching frequency of the intramolecular H bond in *o*-chlorophenol is lower than those of the intermolecular hydrogen bonds in the other examples.

Infrared investigations of hydrogen bonding have been primarily concerned with the shift ( $\Delta\nu_s$ ) in the "free" or nonbonded A-H stretching frequency ( $\nu_s$ ) occurring when a proton donor is placed in a hydrogen-bonding environment. Various properties of the weak, intermolecular hydrogen-bonding interaction are inferred from this perturbation of a fairly localized intramolecular vibration.<sup>1</sup> It is also important, and perhaps more pertinent, to observe the stretching ( $\nu_\sigma$ ) and bending ( $\nu_\beta$ ) frequencies of hydrogen bonds themselves directly. These modes may be illustrated as follows.



As Pimentel and McClellan<sup>1</sup> have stated, "Of all the vibrational degrees of freedom of hydrogen bonded polymers,  $\nu_\sigma$  and  $\nu_\beta$  are the most interesting." The force constants obtained from these frequencies provide information about the hydrogen-bonding potential function as well as being a measure of the bond strength. The extent to which these low-energy vibrations affect the band shape and intensity of the bonded A-H stretch ( $\nu_s'$ ) may be determined, and their very important contribution to thermodynamic functions calculated.

Since the hydrogen-bond frequencies lie in the far-infrared, where instrumentation has been a problem, few direct observations of these vibrations have been made, and these primarily by Raman spectroscopy.<sup>4,2</sup> Even in the Raman investigations, as exemplified by the work of Gross and Valkov,<sup>3</sup> extremely long exposure times (50–100 hr) are required. Owing to recent advances in far-infrared technology, renewed interest in infrared studies has been generated, as evidenced by scattered reports in the literature. Among the hydrogen-bonding molecules observed in the far-infrared are formic and acetic acids,<sup>4–6</sup> other carboxylic acids,<sup>7–9</sup>

phenol, and various derivatives,<sup>10–12</sup> and methanol-amine and phenol-amine complexes.<sup>13</sup>

Unambiguous assignment of the hydrogen-bond frequencies has provided a major difficulty in far-infrared investigations. Present instrumental limitations preclude the usual dilution techniques used in the mid-infrared. Furthermore, the low-frequency spectrum is surprisingly rich. Even for light molecules, low-energy intramolecular vibrations such as torsions<sup>14</sup> and certain skeletal motions of aromatic rings fall in the far-infrared. The frequencies of many of the latter modes are dependent on the nature of the ring substituents, which move with appreciable amplitude during the vibration. These bands are designated as X-sensitive vibrations.<sup>15</sup> Difference combinations of higher frequency bands also complicate this region, and although they are generally weak, so are the hydrogen-bond vibrations. Other sources of low-frequency absorption are dipole-dipole transitions (translational modes),<sup>16</sup> molecular rotation,<sup>17,18</sup> and lattice vibrations in solids.<sup>19</sup>

Unfortunately, since in effect the entire masses of both molecules involved in a hydrogen bond move during the  $\nu_\sigma$  and  $\nu_\beta$  vibrations, conventional isotopic substitution is of little value in confirming the assignments. For example, deuteration generally causes frequency shifts of only 2–3  $\text{cm}^{-1}$ ,<sup>12,13</sup> which is within the experimental uncertainty of the location of the rather broad band centers. We have initiated a program of direct spectroscopic observation of hydrogen bonds and have established certain criteria for making more positive assignments. We report here the examples of

(1) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(2) E. F. Gross in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, Inc., New York, N. Y., 1959.

(3) E. F. Gross and V. I. Valkov, *Dokl. Akad. Nauk SSSR*, **67**, 919 (1949); **74**, 453 (1950).

(4) R. C. Millikan and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 3515 (1958).

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(6) Y. Nakai and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **81**, 881 (1960).

(7) V. Lorenzelli, *Compt. Rend.*, **255**, 274 (1962).

(8) V. Lorenzelli and A. Alemagna, *ibid.*, **256**, 3626 (1963).

(9) A. E. Stanevich, *Opt. Spectry. (USSR)*, **16**, 243 (1964).

(10) V. Lorenzelli, G. Randi, and F. Gesmundo, *Ann. Chim. (Rome)*, **53**, 213 (1963).

(11) A. E. Stanevich, *Opt. Spectry. (USSR)*, **16**, 425, 539 (1964).

(12) R. J. Jakobsen and J. W. Brasch, *Spectrochim. Acta*, **21**, 1753 (1965).

(13) S. G. W. Ginn and J. L. Wood, *Nature*, **220**, 467 (1963); *Proc. Chem. Soc. (London)*, 370 (1964); *Chem. Commun.*, 628 (1965).

(14) W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **17**, 857 (1961); **18**, 977 (1962); **19**, 611 (1963).

(15) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

(16) R. J. Jakobsen and J. W. Brasch, *J. Am. Chem. Soc.*, **86**, 3571 (1964).

(17) W. J. Lafferty, D. W. Robinson, R. V. St. Louis, J. W. Russell, and H. L. Strauss, *J. Chem. Phys.*, **42**, 2915 (1965).

(18) G. M. Barrow and P. Datta, *ibid.*, **43**, 2137 (1965).

(19) D. A. Dows in "Physics and Chemistry of the Organic Solid State," Vol. I, D. Fox, Ed., Interscience Publishers, Inc., New York, N. Y., 1961.

Table I. Low-Frequency Vibrations of Cresols, Chlorophenols, and the Corresponding Anisoles

	Spectra, cm <sup>-1</sup>		Assignment	Spectra, cm <sup>-1</sup>		
	Infrared	Raman		Infrared	Raman	
<i>o</i> -Cresol	...	...	$\tau(\text{OCH}_3)$	108 s,b	...	<i>o</i> -Methylanisole
	124 s,b	...	$\nu_\sigma$	...	...	
	190 s	190 vs	X-sensitive	178 s	179 vs	
	...	...	X-sensitive	245 m	241 s	
<i>m</i> -Cresol	...	...	$\tau(\text{OCH}_3)$	106 s,b	...	<i>m</i> -Methylanisole
	146 s,b	...	$\nu_\sigma$	...	...	
	214 s	216 s	X-sensitive	222 vs	224 vs	
	246 m	245 s	X-sensitive	...	...	
<i>p</i> -Cresol	...	...	$\tau(\text{OCH}_3)$	98 s,b	...	<i>p</i> -Methylanisole
	124 s,b	...	$\nu_\sigma$	...	...	
	178 s	...	X-sensitive	158 sh	...	
	...	...	X-sensitive (?)	240 s	238 m	
<i>o</i> -Chlorophenol	84 s,b	...	$\nu_\sigma$	...	...	<i>o</i> -Chloroanisole
	...	...	$\tau(\text{OCH}_3)$	110 s,b	...	
	176 s	175 vs	X-sensitive	160 s	162 vs	
	254 m	252 sh	X-sensitive <sup>a</sup>	196 s	203 m	
<i>m</i> -Chlorophenol	...	...	$\tau(\text{OCH}_3)$	108 vs,b	...	<i>m</i> -Chloroanisole
	130 s, b	...	$\nu_\sigma$	...	...	
	192 m	194 s	X-sensitive	188 s	194 s	
	...	...	X-sensitive	...	207 sh	
<i>p</i> -Chlorophenol	...	...	$\tau(\text{OCH}_3)$	94 s,b	...	<i>p</i> -Chloroanisole
	122 m,b	...	$\nu_\sigma$	...	...	
	160 s	...	X-sensitive	144 vs	...	
	...	...	X-sensitive	212 s	214 w	

<sup>a</sup> We believe that this mode involves out-of-plane bending of the Cl (see Table II) and has been shifted to a higher frequency in *o*-chlorophenol because of the intramolecular hydrogen bond.

the cresols and chlorophenols, where these criteria have enabled us to make assignments of  $\nu_\sigma$  and to clarify some of the problems raised by previous work.

### Experimental Section

Far-infrared spectra were obtained at room temperature using the techniques of Fourier transform spectroscopy which have been fully described elsewhere.<sup>20,21</sup> A RIIC FS-520 Michelson interferometer with a 0.0005-in. Mylar beam splitter and a Golay detector was used, and high-frequency radiation ( $>600\text{ cm}^{-1}$ ) was removed by filtration with black polyethylene. The single-beam interferograms were cosine transformed using an IBM 7094 computer, and the resulting spectra could be averaged and/or ratioed against background to effectively give a double-beam spectrum. Calibration of the instrument was periodically checked using water vapor, and the frequencies were found to be accurate to  $\pm 2\text{ cm}^{-1}$ .

All chemicals were commercially available and were redistilled *in vacuo* before each use. Far-infrared spectra of the neat liquids were obtained at path lengths between 0.15 and 0.25 mm using cells with high-density polyethylene windows. Atmospheric water absorptions were eliminated by evacuating the main chamber of the interferometer and by purging the sample compartment with dry, high-purity nitrogen.

A Beckman IR-12 spectrophotometer was used to record the spectra of liquid samples compressed between NaCl windows between 3650 and 3000  $\text{cm}^{-1}$ . The bonded O-H frequencies ( $\nu_{\text{s}'}$ ) are very broad, and band centers can only be approximated. Raman scattering by the pure liquids was recorded on a Cary Model 81 spectrophotometer using 7-mm diameter cells.

### Results and Discussion

Three criteria for making more positive identification of the hydrogen-bond frequencies, in order of importance, are as follows.

(1) The bands associated with hydrogen-bond stretches or bends should disappear *completely* when

(20) L. Mertz, "Transformations in Optics," John Wiley and Sons, Inc., New York, N. Y., 1965.

(21) P. L. Richards, *J. Opt. Soc. Am.*, **54**, 1474 (1964); W. J. Hurley, *J. Chem. Educ.*, **43**, 236 (1966).

a group incapable of hydrogen bonding is substituted for the H atom. In the present examples we have substituted the methoxy ( $\text{OCH}_3$ ) group for the hydroxyl (OH). The bands assigned as  $\nu_\sigma$  are completely absent in the corresponding anisole spectra, whereas the only effect of substitution on the remaining far-infrared absorptions is a minor shift in frequency.

(2) The hydrogen-bond frequencies should be extremely weak in the Raman spectrum. These vibrations involve the relatively weak intermolecular bond, where the electron density is low. Consequently, the polarizability change during these motions will be small, and the corresponding Raman shifts, although allowed by selection rules, will have little intensity. The long exposure times required in the early photographic Raman studies of hydrogen bonding<sup>2,3</sup> lend experimental support to this criterion. Even with modern photoelectric detectors,  $\nu_\sigma$  is observed only with difficulty for liquid water,<sup>22</sup> and using identical techniques we have been unable to detect the corresponding bands in the simple alcohols or acetic acid. The infrared absorptions assigned as  $\nu_\sigma$  for the cresols and chlorophenols are absent in our Raman spectra. Since there are, of course, many other reasons why an infrared band might have little or no Raman intensity, this criterion *must not* be regarded as a sufficient condition for proof of hydrogen bonding.

(3) The far-infrared absorptions due to hydrogen bonding should be broad and asymmetric. The bonded A-H stretch ( $\nu_{\text{s}'}$ ) in the mid-infrared is usually extremely broad ( $\Delta\nu_{1/2} \approx 200\text{ cm}^{-1}$ ) and often quite asymmetric<sup>1</sup> due at least in part to the contributions of polymers with varying degrees of association, which have different band centers and intensities. This

(22) G. E. Walrafen, *J. Chem. Phys.*, **40**, 3249 (1964).

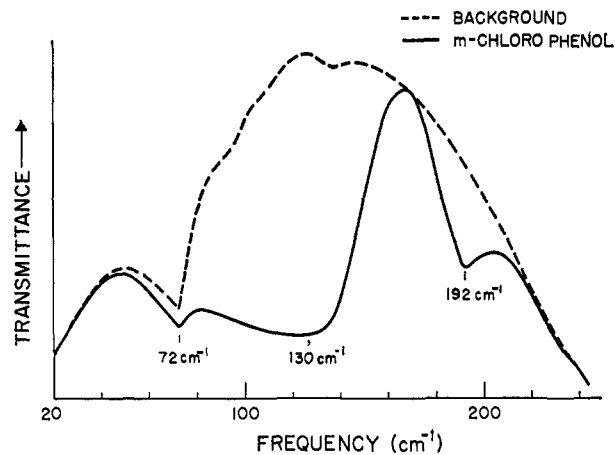


Figure 1. Single-beam spectrum for *m*-chlorophenol (0.20 mm, neat liquid).

should also be true of  $\nu_\sigma$  and  $\nu_\beta$  of neat liquids. In addition, the contours of the low-frequency bands will reflect the anharmonicity of the vibration. At room temperature there is significant population of upper vibrational states, and transitions originating from these excited states will occur at different energies from the  $0 \rightarrow 1$  absorption. The bands assigned as  $\nu_\sigma$  in our examples are broad and generally asymmetric toward lower frequencies. Once again, this must *not* be regarded as a unique characteristic of hydrogen-bond vibrations.

The infrared and Raman spectra observed below  $255 \text{ cm}^{-1}$  for the cresols, chlorophenols, and the corresponding anisoles are given in Table I. For comparison, data for the parent compounds are presented in Table II. Excellent agreement in frequency may be noted wherever the same band is observed in both the infrared and Raman spectrum. Several of the compounds listed in Tables I and II have been examined previously by other workers; agreement between the corresponding frequencies is generally satisfactory. The bands other than  $\nu_\sigma$  given in the tables are not the principal concern of this paper, and some of their assignments must be regarded as only probable. It will be recalled that X-sensitive vibrations are those modes in which substituent groups X move with appreciable amplitude. Normal coordinate analysis is difficult for these vibrations since the normal modes cannot be simply described as motions of either the ring or the substituents. Assignments of X-sensitive bands are therefore based on empirical observations of substituent shifts and by analogy to previous studies.<sup>16, 23, 24</sup>

Each of the bands assigned as  $\nu_\sigma$ <sup>25</sup> satisfies *all* of the criteria mentioned above. Typical background and sample spectra are shown in Figure 1. The ratioed spectrum (*m*-chlorophenol *vs.* background) is shown as curve A in Figure 2 and the ratioed spectrum of *m*-chloroanisole (also *vs.* background) is shown as curve B. The asymmetric band at  $130 \text{ cm}^{-1}$  in *m*-chlorophenol, assigned as  $\nu_\sigma$ , is absent from the spectrum of *m*-chloroanisole. Bands due to pure anisole and chlorobenzene are indicated above the *m*-chloroanisole spectrum to

(23) R. J. Jakobsen and E. J. Brewer, *Appl. Spectry.*, **16**, 32 (1962).

(24) R. J. Jakobsen and F. F. Bentley, *ibid.*, **18**, 88 (1964).

(25) The hydrogen-bond absorptions are assigned as  $\nu_\sigma$  since  $\nu_\beta$  is expected to lie at lower frequencies.

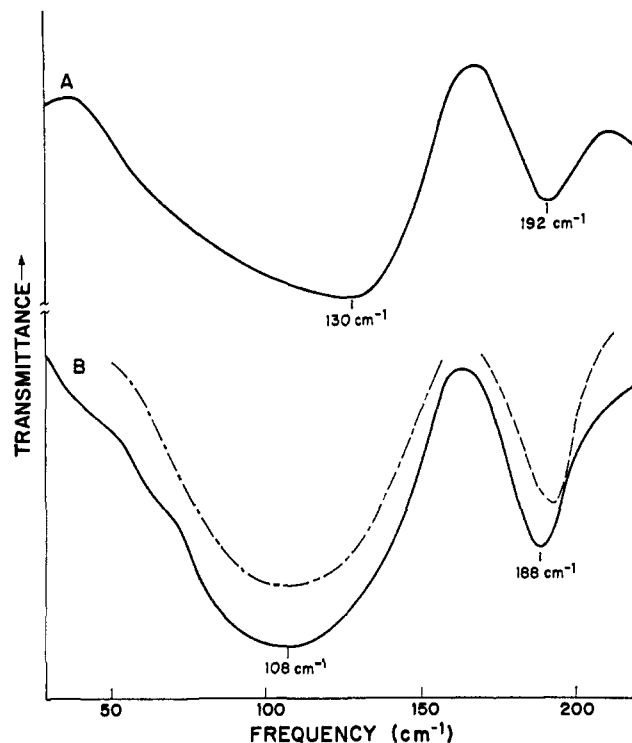


Figure 2. Ratioed spectra for *m*-chlorophenol (A) and *m*-chloroanisole (B) *vs.* cell background. The curves superimposed on spectrum B show the bands due to anisole (— — — —) and chlorobenzene (— — —).

show that this spectrum is, in fact, simply a combination of the frequencies of the two pure parent compounds. Thus the absorptions near  $190 \text{ cm}^{-1}$  in both spectra of Figure 2 may be correlated with the band at  $194 \text{ cm}^{-1}$  in pure chlorobenzene, and the absorption at  $108 \text{ cm}^{-1}$  in *m*-chloroanisole corresponds to the band at  $106 \text{ cm}^{-1}$  in pure anisole.

Table II. Low-Frequency Vibrations of Parent Compounds<sup>a</sup>

	Infrared, $\text{cm}^{-1}$	Raman, $\text{cm}^{-1}$	Assignment
Toluene	214 s	221 vs	X-sensitive <sup>b</sup> [ $\gamma(\text{CH}_3)$ ]
Anisole	106 vs,b	...	$\tau(\text{OCH}_3)$
	216 vw	211 m	X-sensitive [ $\gamma(\text{OCH}_3)$ ]
Chlorobenzene	194 m	196 s	X-sensitive <sup>b</sup> [ $\gamma(\text{Cl})$ ]
Phenol (melt)	177 <sup>c</sup> vs,b	...	
	247 <sup>c</sup> s	242 <sup>d</sup> s	X-sensitive <sup>d</sup> [ $\gamma(\text{OH})$ ]

<sup>a</sup> The assignments given in brackets should only be taken as approximate descriptions of the vibrations. Key to tables: vs = very strong; s = strong; sh = shoulder; m = medium; w = weak; vw = very weak; b = broad. <sup>b</sup> Assignments taken from R. R. Randle and D. H. Whiffen in "Molecular Spectroscopy," G. Sell, Ed., The Institute of Petroleum, London, 1955. <sup>c</sup> J. H. S. Green, W. Kynaston, and H. A. Gebbie, *Nature*, **195**, 595 (1962). <sup>d</sup> J. C. Evans, *Spectrochim. Acta*, **16**, 1382 (1960).

For *o*-, *m*-, and *p*-cresol the  $\nu_\sigma$  frequencies are 124, 146, and  $124 \text{ cm}^{-1}$ , respectively, which closely match the bands at 126, 148, and  $130 \text{ cm}^{-1}$  assigned as  $\nu_\sigma$  by Jakobsen and Brasch.<sup>12</sup> However, on the basis of its temperature-dependent behavior in a polyethylene matrix, these authors also tentatively assigned a band in *o*-cresol at  $187 \text{ cm}^{-1}$  as a hydrogen-bond vibration. This is undoubtedly the same band as our absorption at  $190 \text{ cm}^{-1}$ , which not only has a strong Raman

counterpart, but appears also in both the infrared and Raman spectra of *o*-methylanisole. Its assignment as an X-sensitive vibration confirms an earlier identification by Green.<sup>26</sup> We feel that the infrared absorption in *p*-cresol at 179 cm<sup>-1</sup>, also tentatively assigned as  $\nu_\sigma$  in ref 12, is due to an X-sensitive vibration as well. Although no corresponding Raman shift is observed for *p*-cresol, an analogous infrared absorption is found at 158 cm<sup>-1</sup> in *o*-methylanisole. Our assignments are in agreement with approximate calculations by Davydova, *et al.*,<sup>27</sup> which predict nonplanar vibrations near 184, 179, and 149 cm<sup>-1</sup> for *o*-, *m*-, and *p*-cresol, respectively. Somewhat low frequencies are also observed for X-sensitive vibrations in *p*-chlorophenol and *p*-chloroanisole (Table I), and indeed seem to be characteristic of *para*-disubstituted benzenes in general.<sup>11,23</sup>

The bands assigned as  $\nu_\sigma$  in *o*-, *m*-, and *p*-chlorophenol occur at 84, 130, and 122 cm<sup>-1</sup>. The unusually low value for *o*-chlorophenol is undoubtedly due to the large amount of *intramolecular* hydrogen bonding present. Mecke and co-workers<sup>28</sup> have found that the *cis* form of the *o*-halophenols is energetically more stable than the *trans* form, and both mid-infrared<sup>29</sup> and nmr<sup>30</sup> investigations have shown that a significant concentration of monomeric *o*-chlorophenol exists in the pure liquid. This is also consistent with the low boiling point of *o*-chlorophenol relative to the *meta* and *para* isomers. *o*-Nitrophenol also forms an intramolecular hydrogen bond, which would be expected to be stronger than that of *o*-chlorophenol due to resonance stabilization. The hydrogen-bond stretching frequencies are in accord with this expectation, being respectively 95<sup>11</sup> and 84 cm<sup>-1</sup>.

### Conclusions

Table III lists the values of  $\nu_\sigma$  and  $\Delta\nu$  for the cresols and chlorophenols. Certainly solvent effects can alter

(26) J. H. S. Green, *Chem. Ind. (London)*, 1575 (1962).

(27) N. I. Davydova, I. A. Zhigunova, L. A. Ignatyeva, and M. A. Kovner, *Opt. Spectry. (USSR)*, **18**, 605 (1965).

(28) G. Rossmly, W. Lüttke, and R. Mecke, *J. Chem. Phys.*, **21**, 1606 (1963).

(29) J. N. Finch and E. R. Lippincott, *J. Phys. Chem.*, **61**, 894 (1957).

(30) G. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *ibid.*, **60**, 1311 (1956).

the frequencies  $\nu_s$  and  $\nu_s'$  in the mid-infrared<sup>31</sup> and  $\nu_\sigma$  in the far-infrared, in a manner as yet undetermined. Nevertheless, with this reservation it will be noted that there is no simple relationship between  $\nu_\sigma$  and  $\Delta\nu_s$ . Even the ordering of the frequencies is different. However, it must be stressed that no general conclusions should be drawn from these extremely limited data. The values of  $\nu_\sigma$  so far reported in the literature fall in a rather limited spectral range, 75–225 cm<sup>-1</sup>. Except for the observation that the vibrations of intramolecular hydrogen bonds lie at lower energies than those of intermolecular H bonds, little may be said at this time. We are extending our far-infrared study to include a much wider range of hydrogen bonding compounds, from which we hope to obtain a more significant correlation between the vibrational frequencies of hydrogen bonds and the more traditional parameters used to describe hydrogen bonding.

**Table III.** Comparison of  $\nu_\sigma$  and  $\Delta\nu_s$  Frequencies for Neat Cresols and Chlorophenols

		$\nu_\sigma$ , cm <sup>-1</sup>	$\Delta\nu_s^a$ ± 10 cm <sup>-1</sup>
Cresols	<i>ortho</i>	124	187
	<i>meta</i>	146	267
	<i>para</i>	124	267
Chlorophenols	<i>ortho</i> (intra)	84	83
	<i>ortho</i> (inter)	?	148
	<i>meta</i>	130	208
	<i>para</i>	122	263

<sup>a</sup> Positions for the "free" O–H band,  $\nu_s$ , were obtained from dilute solution studies. The values were 3612 and 3608 cm<sup>-1</sup> for the cresols and chlorophenols, respectively; P. von R. Schleyer, private communication.

**Acknowledgment.** This work was supported in part by the Office of Naval Research. Computer facilities were in part supported by National Science Foundation Grant NSF-GP579.

(31) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 3718 (1963).