

The Infrared Spectra of Substituted Aromatic Compounds in Relation to the Chemical Reactivities of Their Substituents.

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The frequency of the out-of-plane CH deformation absorption of most 1 : 3- and 1 : 3 : 5-substituted aromatic compounds is a linear function of the reactivities of the substituents as determined by Hammett's σ values but halogens are exceptional in behaving as though they had zero σ values. 1 : 4-Substituted aromatic compounds follow a similar relation in those cases in which at least one substituent contains a double bond in conjugation with the ring. The reasons for this are discussed.

CHANGES in the polar environment of a particular grouping within a molecule are reflected in changes in the infrared absorption bands originating in that group. In many cases this is best shown by studies of intensity and a number of important advances have recently thus been made (Mecke, *J. Chem. Phys.*, 1952, **20**, 1935; Barrow, *ibid.*; 1953, **21**, 2008; Jones, Ramsey, Keir, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 80; Thompson, Institute of Petroleum Conference on Molecular Spectroscopy, London, 1954). However, in some cases changes in the frequency can also be correlated with the polarity of substituent groups and this then offers a convenient approach, as the measurement of absolute extinction coefficients is attended by considerable instrumental difficulties.

Goulden (*Spectrochim. Acta*, 1954, **6**, 129) has shown that there is a linear relation between the OH stretching frequencies of monomeric aliphatic acids and their pK_a values, whilst similar but different relations hold for aromatic acids and for phenols. Flett (*Trans. Faraday Soc.*, 1948, **44**, 767) has pointed out that the characteristic frequencies of acid, aldehyde, and amino-groups in aromatic compounds can be correlated with Hammett's

σ functions (Hammett, "Physical-Organic Chemistry," McGraw Hill, New York, 1940, p. 188), and similar relations have been reported by Ingraham, Corse, Bailey, and Stitt (*J. Amer. Chem. Soc.*, 1952, **74**, 2297) for substituted phenols and catechols, and by Fuson, Josien, and Shelton (*ibid.*, 1954, **76**, 2526) for an extensive series of substituted aromatic carbonyl compounds.

Basically, Hammett's σ values measure changes in the electron density of a carbonyl group attached to an aromatic ring. They can therefore be regarded as being a measure of the overall effect of the substituted ring rather than of the localised effect of the substituent. This is supported by the additivity of the effects of two or more substituents which appear to be without effect upon each other. The use of different values for the same group in the *meta*- and *para*-positions arises from the conjugation of the latter with the carbonyl group which results in a difference in the overall effects of the substituted rings.

It was thought therefore of interest to see whether a relation could be found between σ values and some general vibrational mode of the ring itself. For this purpose we studied the out-of-plane CH deformations of 1:3-, 1:4-, and 1:3:5-substituted aromatic compounds, as we had previously noted regularities in this series. These deformation modes give rise to what are normally the strongest bands in the low-frequency region of the spectrum, and are therefore usually easy to identify. They occur in the regions of 775, 810, and 850 cm^{-1} and can be regarded as being derived respectively from motions involving three adjacent ring-hydrogen atoms, two adjacent ring-hydrogen atoms, and of an isolated ring-hydrogen atom situated between two substituents (Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397). 1:3-Disubstituted compounds therefore show the first and the last of these absorptions. Aromatic compounds with two or more adjacent substituents have not been considered as steric effects often cause the substituents to lie out of the plane of the ring. In consequence, σ values derived from kinetic studies do not in these cases provide a true measure of the polar effects of the substituents.

Experimental.—The spectra were obtained with a Perkin-Elmer 21 recording spectrometer with a rock-salt prism. Samples were determined as solids dispersed in liquid paraffin and/or in solution in suitable solvents. For the particular frequencies studied very little difference is found between the solid and the solution spectra. The observed CH out-of-plane deformation absorptions are listed in Tables 1 and 3 (below) and are discussed below. The bands have been identified as being the strongest in the appropriate spectral regions after allowance for any bands due to particular substituents known to absorb in the same region. A few 1:3-disubstituted materials show a number of strong bands in the expected regions, and identification of the two δCH absorptions was then based on the expectation that any polar effects would affect them both to approximately the same extent so that they would retain their usual spacing of about 75 cm^{-1} apart.

RESULTS AND DISCUSSION

(a) 1:3- and 1:3:5-Substituted Compounds.—The observed frequencies of the out-of-plane CH deformations of the compounds studied are listed in Table 1, together with some of Cole and Thompson's values (*Trans. Faraday Soc.*, 1950, **46**, 103). They are plotted in

TABLE 1. Out-of-plane ring CH deformation frequencies (cm^{-1}).

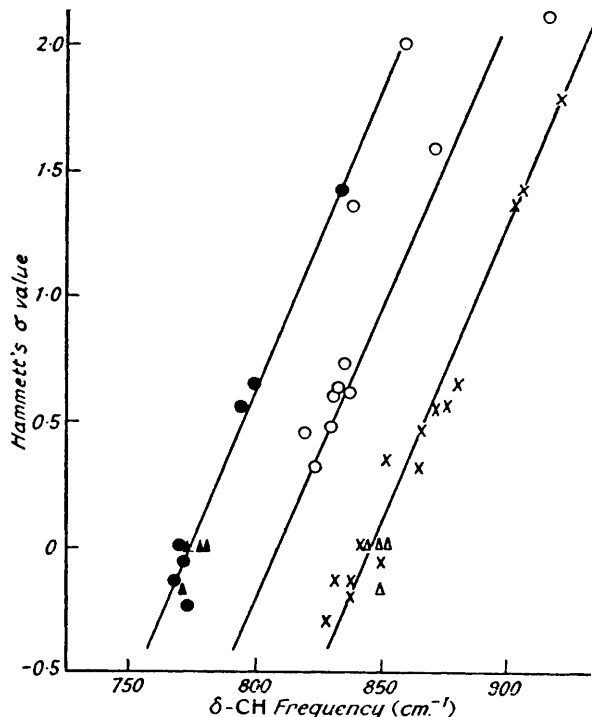
1:3-Substituted compounds				1:3:5-Substituted compounds					
Me ₂	769	838	* (Cl) ₂	780	—	Me ₃	838	(OEt) ₃	866
Me, NO ₂	801	880	* Cl, I	773	—	Me ₂ , NO ₂	872	Me ₂ , NH ₂	828
(NO ₂) ₂	835	906	* Br, Me	773	—	Me, (NO ₂) ₂	903	CO ₂ H, (NO ₂) ₂	921
OH, Me	772	850	* F, CH ₃	778	—	(NO ₂) ₃	917	* (Cl) ₃	853
(OH) ₂	772	842	NH ₂ , Cl	771	849	Me ₂ , OH	832	* (Br) ₃	850
NH ₂ , NO ₂	795	866				OH, (OEt) ₂	865	† (F) ₃	854
						(OMe) ₃	852		

* Cole and Thompson (*loc. cit.*). † Nielsen, Liang, and Smith, *Discuss. Faraday Soc.*, 1950, **9**, 177.

the Figure directly against the sum of Hammett's *meta*- σ values for the substituents. It will be seen that, with the exception of the halogen derivatives (which have not been plotted

on this basis), the points lie reasonably close to one or other of two parallel straight lines. The first of these connects points involving the vibration of 3 adjacent hydrogen atoms, and the second connects points involving the vibration of a lone hydrogen atom with substituents on either side. It will be seen also that a similar line derived from those 1 : 4-substituted materials in which such a plot is considered to be appropriate (see below) appears to be roughly parallel with the other two, and midway between them.

When plotted on the same basis, the halogen derivatives show a wide scatter but it is significant that they all fall very close to these lines if the halogens are assumed to have zero σ values (see Fig.). The numbers involved are thought to be too great for this to be coincidental but no satisfactory explanation can be offered yet.



δ -CH vibrations of: ● 3 adjacent ring hydrogen atoms.
 ▲ 2 " " " (halogen-substituted).
 ○ 2 " " " " "
 × An isolated ring hydrogen atom
 △ " " " (halogen-substituted).

Hammett's σ values are not readily available for a number of substituents—particularly the larger alkyl groups—which it would have been interesting to plot in this way. However, an alternative check on the validity of this relation can be obtained by deriving σ values from the observed frequencies of a few simple alkylbenzenes and employing these in the prediction of the frequencies of other compounds. Thus the 1 : 3 : 5-derivatives of triethyl-, triisopropyl-, and tri-*tert.*-butyl-benzene absorb respectively at 865, 870, and 874 cm^{-1} , corresponding to σ values of +0.14, +0.18, and +0.21 for the ethyl, isopropyl, and *tert.*-butyl group (McCaulay, Lien, and Launer, *J. Amer. Chem. Soc.*, 1954, **76**, 2554). The use of these values in the prediction of the CH deformation frequencies of other alkylbenzenes gives the results shown in Table 2, in which they are compared with observed values. The agreement for the principal bands is good, despite the fact that the positive σ values imply that relative to the methyl group, there is an electron withdrawal from the ring

rather than an electron donation which would be expected from the theory of hyperconjugation. The agreement in respect of the second CH deformation absorption of 1:3-substituted compounds near 840 cm^{-1} does not appear to be good, but this band is relatively weak in hydrocarbons and it is correspondingly less easy to identify.

TABLE 2. *Out-of-plane ring CH deformation frequencies of alkylbenzenes.*

Substituents	ν , calc. (cm^{-1})	ν , found (cm^{-1})	Substituents	ν , calc. (cm^{-1})	ν , found (cm^{-1})
1 : 3 : 5-Me ₂ , Et *	842	845	1 : 3-Me, Et † ...	778	781
Me ₂ , Pr ⁱ *	848	846	Et ₂ †	787	792
Me ₂ , Bu ^t *	850	847	Pr ⁱ ₂ †	793	793
Me, Et ₂ *	856	855	Me, Bu ^t †	781	781
Me, Pr ⁱ ₂ *	858	858	Et, Bu ^t †	791	794
Me, Bu ^t ₂ *	862	859			

* McCaulay *et al.* (*loc. cit.*). † A.P.I. Spectra. ‡ Schlatter and Clark, *J. Amer. Chem. Soc.*, 1953, 75, 361.

1:4-Substituted Compounds.—Hammett's σ values for *para*-substituents differ from the corresponding *meta*-values, as additional mesomeric effects are called into play by the direct conjugation of the substituents, through the ring, with the carboxyl group. These *para*- σ values will therefore be appropriate only to those compounds which contain a similar conjugated substituent. In other cases the polar effects of the substituents will often be in direct opposition to one another and the overall effects upon the δCH ring vibrations will be relatively small.

It is therefore to be expected that any relation which may exist between Hammett's *para*- σ values and δCH ring frequencies will be confined to compounds containing an unsaturated group in conjugation with the ring. In other compounds these frequencies will tend to group themselves about the points corresponding to a zero σ value. This appears to be essentially what is found. The results are given in Table 2 and it will be seen from these and from the Figure that the compounds studied which contain a conjugated group follow a roughly linear relation with Hammett's σ values, whilst the remainder group themselves about 810 cm^{-1} . In plotting the Figure, Hammett's *para*- σ values have been used throughout with the exception of that for the *p*-dimethylamino-group. This has been found to be unsatisfactory in previous cases (Flett, *loc. cit.*) and is based on limited data. Instead, we have used a value calculated directly from the pK_a value of *p*-dimethylaminobenzoic acid.

TABLE 3. *Out-of-plane ring CH deformation frequencies of 1:4-substituted compounds (cm^{-1}).*

Substituents	ν	Substituents	ν	Substituents	ν	Substituents	ν
Cl ₂	818	Me, NH ₂	814	NMe ₂ , CHO	824	Me, NO ₂	834
(OH) ₂	826	Me, NMe ₂	806	Cl, CHO	839	(NO ₂) ₂	872
(NH ₂) ₂	826	Me, OH	815	NO ₂ , NH ₂	838	NO ₂ , NMe ₂	820
Cl, NH ₂	819	* F, Me	817	NO ₂ , CHO	850	* Br, I	807
Cl, OH	822	* Cl, Me	809	OH, CHO	836	* Cl, I	811
Br ₂	806	* Br, Me	803	OH, COMe	830	* F ₂	805
Me ₂	798	* Br, Cl	816	OMe, COMe	833	* Me, I	800

* Cole and Thompson (*loc. cit.*).

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