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THE INFRARED SPECTRA OF AROMATIC COMPOUNDS. III THE
1045 - 1185 cm^{-1} VIBRATION IN MONOSUBSTITUED BENZENES.

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Abstract

In monosubstituted benzenes of the type $(\text{phenyl})_n\text{M}$, where n is the valence of the substituent element M, the frequency of the 1045-1185 cm^{-1} vibration is directly related to the partial ionic character of the $\text{C}_{\text{ar}}\text{-M}$ bond. Using the square of the electronegativity of the substituent as a measure of the bond polarity, a plot is presented which relates this parameter to the corresponding frequency. From the four straight-line curves obtained for group IVB, VB, VIB and VIIB elements, an expression is derived equating electronegativity with the observed frequency. Electronegativity values calculated from this equation compare favorably with accepted values.

One of the frequencies of monosubstituted benzenes in the region 1045-1185 cm^{-1} is found to be sensitive to the nature of the substituent element. The literature contains conflicting evidence concerning the nature of the modes giving rise to this band. Cole and Thompson,¹ using a simplified potential function

and assuming a substituent of infinite mass, calculated that the band in the region of 1065 cm^{-1} for monosubstituted benzenes is a C-H out-of-plane bending vibration. On the other hand, Randle and Whiffen,² through both calculation and analogy with $\text{C}_6\text{H}_5\text{D}$, find bands in this area which correspond to a C-H in-plane bending vibration and a planar ring vibration. The latter is labeled an "X-sensitive vibration", its frequency being sensitive to the nature of the substituent. For chloro-, bromo-, and iodobenzene, those authors cite the planar ring vibrational frequencies 1083 , 1072 , and 1061 cm^{-1} , respectively, which can be seen from Table I to correspond to the band studied in this investigation. However, the frequency which they list for fluorobenzene is 1217 cm^{-1} , while the band chosen in this study falls at 1159 cm^{-1} .

It is not the intent of this note to decide the correct assignment, but rather to present some observations which may be useful in determining the true vibrational mode. These observations were made on a series of compounds of the type $(\text{phenyl})_n\text{M}$, where n is the valence of the substituent atom M.

Experimental

The spectra were obtained under the same experimental conditions outlined in paper I³ of this series.

Results

The frequencies for the investigated vibration for group IVB, VB, VIB, and VIIB substituent elements are presented in Table I. Although there is a general tendency toward an inverse

Table I.

Characteristic Frequencies for Various Substituent Atoms in Mono-substituted Benzene

Compound	Substituent Element	Frequency (cm ⁻¹)
Fluorobenzene(1)	F	1159
Chlorobenzene(1)	Cl	1082
Bromobenzene(1)	Br	1070
Iodobenzene(1)	I	1066
Diphenylether(s)	O	1175
Diphenylsulfide(1)	S	1080
Diphenylselenide(1)	Se	1064
Triphenylamine(s)	N	1182
Triphenylphosphine(s)	P	1088
Triphenylarsine(s)	As	1075
Triphenylstibine(s)	Sb	1065
Triphenylbismuthine(s)	Bi	1056
Tetraphenylmethane(m)	C	1188
Tetraphenylsilane(s)	Si	1106
Tetraphenylgermane(s)	Ge	1089
Tetraphenylstannane(s)	Sn	1075
Tetraphenyllead(s)	Pb	1060

l = spectra obtained from liquid sample

m = spectra obtained from Nujol mull

s = spectra obtained from CS₂ solution

frequency-mass relationship, it is apparent that this is not a consistent behavior. Thus, within experimental error, the vibration frequency for each of the pairs of elements phosphorus-germanium, arsenic-tin, and selenium-lead is the same. The consistent decrease in frequency with increasing atomic number within each periodic group and the large difference in frequencies between the second and third period elements within each group

is significant, since this behavior parallels the electronegativity values for the substituent elements. Or, stated another way, the observed frequencies appear to be related to the partial ionic character of the carbon-substituent element bonds.

The partial ionic character of a bond is usually expressed in terms of the bond's extra ionic energy, or the difference between the bond's observed energy and its theoretical covalent energy.⁴ Unfortunately extra ionic energies are known for only a few types of carbon-M bonds. These data are available for carbon-halogen bonds, and Figure 1 shows that a linear relationship does exist between the extra ionic energy of the bond and the frequency of the 1045-1185 cm^{-1} vibration. Pauling⁴ has shown that the electronegativities of the elements are proportional to the square roots of the extra ionic energy of the bond formed with other elements. The linear plot of Figure 1 suggests that a plot of vibration frequency versus the square of electronegativity of the substituent element should likewise produce linear curves. This deduction is verified by the curves plotted in Figure 2. An interesting feature of the plot is its common intercept, which indicates that any number of phenyl groups attached to a central atom of theoretically zero electronegativity will have common vibrations at 984 cm^{-1} .

Some comment should be made concerning the deviation of the points for iodine and selenium in the figure. Electronegativity data are available to only the first decimal place (see Table II), hence any error in that figure is squared in obtaining the abscissa values. Iodine shows the largest deviation, but since

Fig. 1 - Vibration frequency vs extra ionic energy of carbon-halogen bond.

Fig. 2 - Relation between vibration frequency and electronegativity of substituent element.

Table II
Electronegativity Values

Element	Calculated	Pauling	Others
F	4.00	4.0	
Cl	3.00	3.0	
Br	2.75	2.8	
I	2.65	2.5	2.6 ⁵
O	3.42	3.5	
S	2.48	2.5	
Se	2.26	2.4	
N	2.96	3.0	
P	2.14	2.1	
As	2.00	2.0	
Sb	1.89	1.8	
Bi	1.79	---	1.8 ⁵ 1.8 ⁶
C	2.51	2.5	
Si	1.93	1.8	
Ge	1.79	1.7	
Sn	1.66	1.7	
Pb	1.52	---	1.5 ⁶

the iodine point falls on the curve in Figure 1, this suggests that the published electronegativity value for iodine may be slightly erroneous.

An equation relating the slopes of all of the four lines in Figure 2 in terms of the valence of the substituent is as follows:

$$\text{Slope} = 2^{n/2} [7.70 + (n-1)0.15] \quad (1)$$

Incorporating this expression into the general equation for a straight line involving slope and intercept, an equation was obtained which yields electronegativity values directly from knowledge of the corresponding frequency and the valence of the substituent. It is (for the B group elements investigated)

$$E = 2^{-n/4} \left(\frac{\nu - 984}{7.70 + (n-1)0.15} \right)^{1/2} \quad (2)$$

Table II shows the good correspondence of electronegativity values obtained from the above equation with those listed by Pauling and others. It should be noted that Haissinsky's value for the electronegativity of iodine is more in agreement with the value obtained in this research, and is probably more correct. The values obtained for germanium and tin also appear more accurate than those of Pauling, since in his table both elements have the same values, which is somewhat unlikely.

An interesting application of equation 2 arises in the case of deuterium. In view of the simple electronic configuration of the hydrogen isotopes, deuterium can be considered as either a group 1 or group 7 element. Since the A and B subdivisions of the groups begin in the fourth period, deuterium can be thought

of as the highest member of the halogen series, and thus equation 2 should apply to its phenyl compound, monodeutero benzene. Comparison of the spectrum of that compound⁷ with the spectra of the other monosubstituted benzenes indicates that the monodeutero benzene band at 1030 cm^{-1} is the appropriate one to use in equation 2. The calculation leads to an electronegativity of 2.06 for deuterium, which is close to the 2.13 value listed⁶ for hydrogen. It should be noted that the 1030 cm^{-1} band has been assigned fairly conclusively to a C-H planar bending vibration,⁷ and since this band varies in position depending on the substituent, the evidence points to the fact that the "X-sensitive vibration" arises from a C-H planar mode.

References

1. A. R. H. Cole and H. W. Thompson, Trans. Farad. Soc., 46, 103 (1950).
2. R. R. Randle and D. H. Whiffen, Preprint of paper presented at Conference on Molecular Spectroscopy, Institute of Petroleum, October 28-29, 1954.
3. M. Margoshes and V. A. Fassel, Spectrochim. Acta, 7, 14 (1955).
4. L. Pauling, Nature of the Chemical Bond, Cornell Univ. Press, Second Ed., 1948, p. 59.
5. M. Haissinsky, J. Phys. Radium, 7, 7 (1946); J. Chem. Phys., 15, 152 (1947).
6. W. Gordy, J. Chem. Phys., 14, 305 (1946).
7. C. R. Bailey, R. R. Gordon, J. B. Hale, N. Herzfeld, C. K. Ingold, and H. G. Poole, J. Chem. Soc. 1946, 299.