Substituent Effect on the Infrared C–H Frequencies of 1, 3, 5-Trisubstituted Benzenes

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Several investigations have been reported on the substituent effect of the C–H absorptions of aromatic compounds. Katritzky and coworkers¹⁾ investigated extensively the infrared spectra of aromatic compounds in the frequency range between 2000—650 cm^{-1}, while Bellamy²⁾ has pointed out the existence of the linear relation between the out of plane deformational frequencies of aromatic compounds and Hammett σ_m constants of the substituents. On the other hand, Raman spectra of some 1, 3, 5-trisubstituted benzenes were reported by Kohlrausch³⁾ and complete assignment of the vibrational frequencies of 1, 3, 5-trichlorobenzene was carried out by Scherer and three others.⁴⁾ In the present paper, the infrared absorptions of 1, 3, 5-trisubstituted benzenes are reported, and the C–H absorption frequencies

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1) A. R. Katritzky and P. Simmons, *J. Chem. Soc.*, **1959**, 2051, 2058; A. R. Katritzky and R. A. Jones, *ibid.*, **1959**, 3670.

2) L. J. Bellamy, *ibid.*, **1955**, 2818, 4221.

3) K. W. Kohlrausch, *Monatsh.*, **76**, 215, 231 (1947).

4) J. R. Scherer, J. C. Evans, W. W. Muelder and J. Overend, *Spectrochim. Acta*, **18**, 57 (1962).

TABLE 1. INFRARED C–H ABSORPTIONS OF 1, 3, 5-TRISUBSTITUTED BENZENES
(Potassium bromide pellet)

Substituent	Hammett σ-value	NMR Chemical shift*1	C–H Absorption, cm^{-1}		
			Stretching (weighted mean)	Out of plane deformation	In plane bend region
OCH_3	−0.268	4.03 (4.01)	3003	825	987, 1036
OH	−0.37	3.80*2 (—)	—	813	1007
CH_3	−0.170	3.30 (3.32)	3016	836	1036
H	0.00	2.73	(3047)	(850)	(1035)
Cl	+0.227	2.72 (2.79)	3085	851	1098
Br	+0.232	2.35 (2.42)	3076	849	1097
I	+0.276	1.90 (—)	3069	846	1099
CO_2CH_3	+0.45	1.23 (—)	3095	875, 882	1107
NO_2	+0.778	0.62*3 (0.96)	3106	920	1077

*1 These NMR data are in accordance with the previous report by Yukawa and coworkers (shown in parentheses) [Y. Yukawa, M. Sakai, K. Kabazawa and T. Tsuno, *Mem. Inst. Sci. Ind. Research Osaka Univ.*, **17**, 185 (1960)] and the authenticity of the materials being checked.

*2 in deuterium oxide.

*3 in chloroform-*d*.

are correlated with some parameters which stand for the electronic effect of substituents.

Experimental

Materials. 1, 3, 5-Trisubstituted benzenes used were known compounds and prepared by the usual procedure, their purity being checked by comparison of the physical constants. Their NMR spectra also support their constitution and purity.

Spectral Measurement. Infrared spectra were determined using a Hitachi Model EPI-2 infrared spectrophotometer in the frequency range between 4000 and 650 cm^{-1}. To determine the C–H stretching frequencies more exactly, a Perkin-Elmer 112G grating infrared spectrophotometer was employed. Proton magnetic resonance spectra were determined with a JNM C-60 or a Varian A-60 high resolution nuclear magnetic resonance spectrometer in carbon tetrachloride, chloroform-*d* and other solvents.

Results and Discussion

Infrared C–H stretching, C–H in plane deformation and C–H out of plane deformation frequencies of 1, 3, 5-trisubstituted benzenes are shown in Table 1 and Fig. 1. The assignment of C–H deformation bands is, though tentative, rather straightforward because there are relatively few other absorptions in the region from 900 cm^{-1} to 800 cm^{-1} (out of plane deformation region) and from 1200 cm^{-1} to 1000 cm^{-1} (in plane deformation region). Assignment of the bands in C–H in plane bending region is ambiguous and different assignments were reported.5) But, in most instances, there appear only one or two absorption bands of considerable intensities in this region. Always an absorption band appears in the region between 1100 cm^{-1} and 1000 cm^{-1} throughout the series of 1, 3, 5-trisubstituted benzenes. But the locations of the bands in this region cannot be correlated with any substituent parameters employed in the following discussion. In some cases, there appear several absorptions in the C–H stretching region, and in case when more

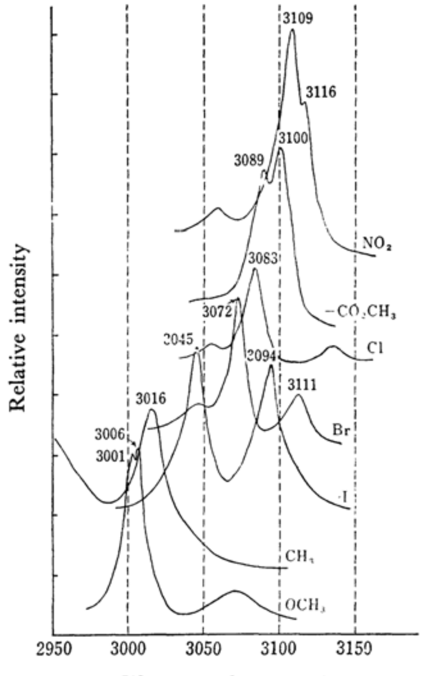

Fig. 1. C–H Stretching absorptions of 1, 3, 5-trisubstituted benzenes (1, 3, 5-$C_6H_3X_3$). Only the kind of substituent (X) is indicated in the figure to distinguish the compound.

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5) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed., Methuen & Co. Ltd., London (1958), p. 64.

than one absorption bands are observed, the mean frequencies weighted by their extinction coefficients are employed to correlate with substituent parameters.

To investigate the effect of substituent on these frequencies, several parameters to account for the electronic effect of substituent, such as σ_p,[6] σ_o^*[7] and NMR chemical shifts of aromatic protons of these compounds, were chosen and tested whether any correlation between the frequencies and parameters exists or not by plotting the C-H frequencies *versus* the parameters above. In order to estimate the electronic effect of the 1, 3, 5-substituents, it is reasonable to employ a substituent constant, $\sigma_p+2\sigma_o^*=\sigma_\Sigma$, but the Hammett σ_p constant itself will also be suitable to estimate the effect of the substituents, since the σ_o^* constant varies approximately proportionally with the change in σ_p constants.

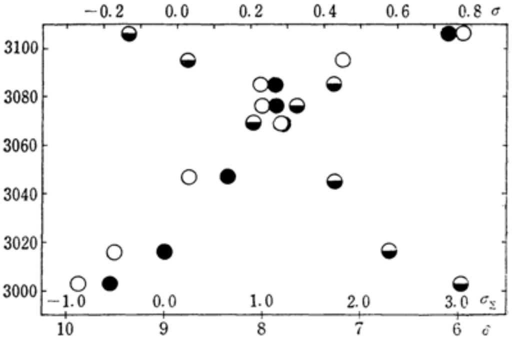

Fig. 2. C-H Stretching frequency *vs.* substituent constant plot.

○ Hammett σ-constant, ● $\sigma_\Sigma(=2\sigma_o^*+\sigma_p)$, and ◒ NMR chemical shift.

The C-H stretching frequency *vs.* σ_p, $\sigma_p+2\sigma_o^*$ and NMR plot were shown in Fig. 2 and fairly good linear relations were observed between these quantities. The C-H out of plane deformation frequencies of these compounds also vary linearly with such parameters. The linear relations may be explained in terms of the electron density effect leading to the C-H bond contraction when the substituent is electron attracting.

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[6] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[7] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons Inc., New York (1956), p. 556.