

ELECTRICAL EFFECTS IN THE INFRARED AND THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF ORGANIC ISOTHIOCYANATES

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THE important purpose of correlating the frequency shifts and intensity changes in absorption spectra is to get a better understanding as to how different electronic interactions affect any particular absorption band. Consideration of the infrared absorption spectra together with the ultraviolet absorption spectra would, therefore, provide interesting information concerning both the ground and excited states. Since the quantum mechanical calculations of electron distribution around linkages are not sufficiently accurate, it is considered important to study the effect of structural changes on the band positions and intensities of a series of related molecules in the infrared and ultraviolet regions.

As a result of a number of investigations,¹⁻⁴ it has been possible to conclude that the wavelength changes in the B-band of the ultraviolet absorption spectra of benzene derivatives are mainly caused by resonance and steric interactions. Consequently, the position of the B-band in the ultraviolet absorption spectra for *para*-disubstituted benzenes appears to be a good measure of the resonance effects. It has also been possible to conclude that the infrared fre-

quency shifts in *meta*- and *para*-disubstituted benzene derivatives are determined by the same factors that decide the chemical reactivity.⁵ In this paper we have reported on the electrical effects in the infrared and the near ultraviolet absorption spectra of organic isothiocyanates.

There have been no reports of the ultraviolet absorption spectra of organic isothiocyanates in the literature.⁶ We have now studied the near ultraviolet absorption spectra of a number of alkyl and aryl isothiocyanates. Recently, Lieber, Rao and Ramachandran⁷ have made extensive studies on the infrared spectra of organic isothiocyanates and have assigned the characteristic isothiocyanate vibration frequency between 2060 and 2105 cm.⁻¹ We have now studied the substituent effects on this vibration frequency in *para*-substituted phenyl isothiocyanates.

The ultraviolet absorption spectra were recorded in purified cyclohexane using a Cary recording spectrophotometer and also a Beckman model DU spectrophotometer. The wavelengths (λ_{\max}) in m μ and the molar extinction coefficients (ϵ_{\max}) corresponding to the absorp-

TABLE I
Infrared and ultraviolet absorption spectra of organic isothiocyanates (R-NCS)

R	ν , cm. ⁻¹	λ_{\max}	log ϵ_{\max}	λ_{\max}	log ϵ_{\max}
CH ₃	..	249	3.34
C ₂ H ₅	..	249	3.41
<i>n</i> -C ₄ H ₉	..	249	3.50
<i>n</i> -C ₇ H ₁₅	..	249	3.50
C ₆ H ₅	..	270.5	4.11	281	4.12
4-CH ₃ C ₆ H ₄	..	272	4.20	283.5	4.19
4-ClC ₆ H ₄	..	276	4.20	287.5	4.19
4-CH ₃ OC ₆ H ₄	..	275.5	4.19	286.5	4.16
4-N(CH ₃) ₂ C ₆ H ₄	..	297.5	4.58	310	4.54
4-CH ₃ COC ₆ H ₄ *	..	292	4.37	305	4.40
4-NO ₂ C ₆ H ₄ †	..	312.5	4.24	323	4.15
2-ClC ₆ H ₄	..	276.5	4.09	286	4.08

* This compound has an additional peak around 240 m μ . † This compound also has an additional peak around 250 m μ and the 323 m μ band appears as a shoulder.

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tion maxima are summarized in Table I. The infrared spectra were recorded in carbon tetrachloride solutions using a Perkin Elmer, Model 21, spectrophotometer. The -NCS vibration frequencies are listed in Table I.

All the *n*-alkyl derivatives show a band at 249 $m\mu$, characteristic of the isothiocyanate group. The intensity of this band appears to increase with the chain-length of the alkyl group. The phenyl derivatives exhibit two absorption bands at wavelengths considerably higher than the alkyl derivatives. The intensities of these bands are also much greater than those of the alkyl derivatives.

The λ_{\max} values of the *para*-substituted phenyl isothiocyanates can be correlated with the Taft resonance parameters⁸ and the Hammett σ -values⁹ of the substituents and they approximately follow Rao's correlations.^{3,4} The approximately linear relations seem to hold as long as the *para*-substituent is an electron-donating group, indicating that the isothiocyanate group is electron-withdrawing in nature. The large wavelength shifts in the *p*-acetyl and the *p*-nitro derivatives are probably due to the absorption of these groups themselves. It is interesting to note that the *p*-acetyl derivative shows an absorption band around 240 $m\mu$, corresponding to the B-band of acetophenone indicating that there is negligible interaction between the isothiocyanate and the acetyl groups. This is understandable since both the groups are electron-withdrawing in nature.^{3,4} The *p*-nitro derivative similarly shows an absorption band around 250 $m\mu$ probably due to the absorption of the nitro group. The intensities of the ultraviolet bands of these phenyl derivatives seem to increase with the electron-contributing power of the *para*-substituent. This is consistent with the general trends proposed by Rao and Silverman.¹⁰ The *ortho*-chloro derivative absorbs at about the same λ_{\max} as the *para*-chloro derivative; however, there is considerable decrease in the intensity of the bands. Such intensity changes indicate small steric influence of the *ortho*-substituent.^{11,12}

The isothiocyanate vibration frequencies in the *para*-substituted phenyl derivatives show a nice trend with the reactivities of the groups. The plots of the frequency ν , against Hammett σ or Brown σ^+ values^{9,13} are found to be excellently linear. However, the ν - σ^+ plot (cf. Fig. 1) seems to show lesser deviations from linearity just as the many other systems investigated earlier by Rao and Silverman.⁵ The slope of this plot is about -30. The σ^+ value of the

acetyl group was assumed to be about the same as the σ value for the group since the group is *meta*-directing in nature.¹⁴

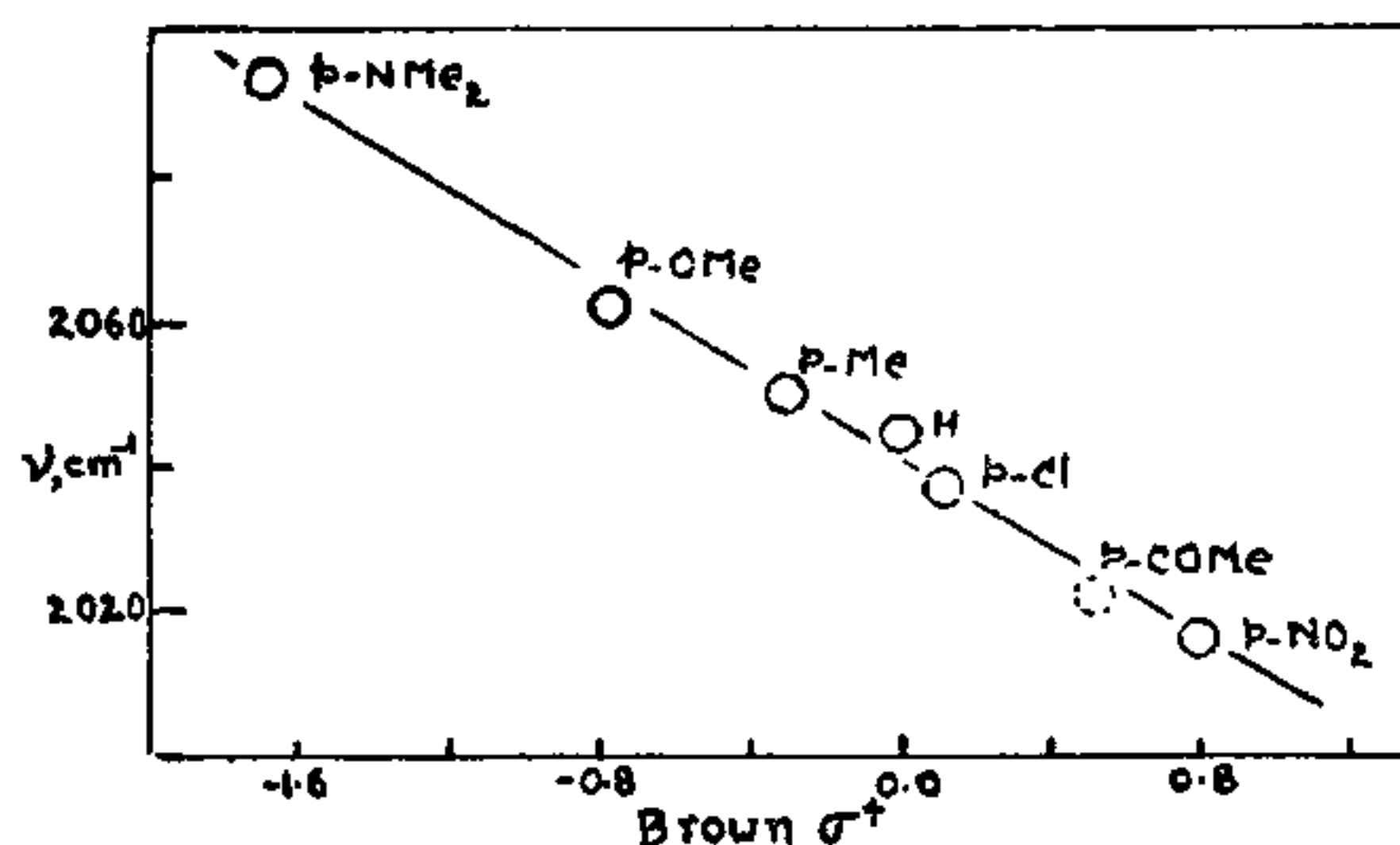


FIG. 1. Correlation of the isothiocyanate vibration frequencies in *para*-substituted phenyl isothiocyanates with the electrophilic substituent constants

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