

SUBSTITUTION EFFECTS IN *o*-NITROPHENOLS

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PMR chemical shifts and wave numbers of out-of-plane deformation vibrations of OH groups and ionization constants of 4- and 5-substituted 2-nitrophenols have been correlated with the respective substituent constants using two- and four-parameter equations.

In our paper¹ dealing with the influence of substituents on PMR chemical shifts of the protons bonded by an intramolecular hydrogen bond we tested the validity of the proposed Eq. (1) using, besides others, also a set of eight 4- and 5-substituted

$$\delta = \delta_0 + a\sigma_1 + b\sigma_2 \quad (1)$$

2-nitrophenols. This set was not sufficient, the number of the derivatives used being too small. Eq. (1) proved applicable also for evaluation of substituent effects on the wave numbers of the stretching² and deformation³ vibrations of the groups bonded

TABLE I

PMR Chemical Shifts and Wave Numbers of Out-of-Plane Deformation Vibrations of Hydroxyl Group of 4- and 5-Substituted 2-Nitrophenols

| Substituent | $\delta(\text{OH})$ p.p.m. | $\gamma(\text{OH})$ cm^{-1} | Substituent | $\delta(\text{OH})$ p.p.m. | $\gamma(\text{OH})$ cm^{-1} |
|------------------------------------|-------------------------------|---|--|-------------------------------|---|
| 4-NH ₂ | 10.12 | 649 | 4-Br | 10.52 | 666 |
| 4-OCH ₃ | 10.29 | 659 | 4-I | 10.55 | — |
| 4-C(CH ₃) ₃ | 10.45 | 666 | 5-Br | — | 668 |
| 4-CH ₃ | 10.41 | 666 | 4-COOCH ₃ | 10.84 | 681 |
| 5-CH ₃ | 10.61 | 679 | 5-NO ₂ | 10.69 | 661 |
| —H | 10.59 | 669 | 4-SO ₂ CH ₃ | 10.95 | 681 |
| 4-C ₆ H ₅ | 10.59 | 673 | 4-SO ₂ N(CH ₃) ₂ | — | 681 |
| 4-F | 10.35 | 662 | 4,5-Cl ₂ | — | 664 |
| 5-OCH ₃ | 11.01 | 682 | 4-NO ₂ | 11.08 | 680 |
| 4-Cl | 10.49 | 664 | | | |

by intramolecular hydrogen bond. Problematic, too, was the choice of dual substituent constants for characterization of influence of $-M$ type substituents at *para* position to OH group.

Now we have measured the $^1\text{H-NMR}$ chemical shifts of hydroxyl protons and wave numbers of out-of-plane deformation vibrations of OH bond in a series of substituted 2-nitrophenols, and we have tested their ability of correlation with substituent constants.

EXPERIMENTAL

The PMR spectra were measured with the use of a 60 MHz spectrometer Jeol in deuteriochloroform with tetramethylsilane as internal standard at 25°C . IR spectra were measured with a UR-20 apparatus (Zeiss, Jena) in carbon disulphide. The used *o*-nitrophenols were either commercial products or were prepared in our laboratory by known methods; their purity was checked by melting points and PMR spectra. Correlation analysis was carried out with the use of computer Odra.

RESULTS AND DISCUSSION

The measured chemical shifts in PMR spectra (δ) and wave numbers (γ) of out-of-plane deformation vibrations of hydroxyl group of sixteen 4- and 5-substituted 2-nitrophenols are given in Table I along with the data of Nyquist⁴. Eq. (1) was used for correlation of δ and γ with the substituent constants. The problem of applicability of dual constants was approached by using a set of 22 published^{5,6} ionization constants of 2-nitrophenols in water and extending Eq. (1) to the form of Yukawa-Tsuno equation⁷ (Eq. (2))

$$pK = pK_0 + a(\sigma_{01} + r_1 \Delta\sigma_1^-) + b(\sigma_{02} + r_2 \Delta\sigma_2^+), \quad (2)$$

where a , b , r_1 and r_2 are constants, $\Delta\sigma^- = \sigma^- - \sigma_0$, and $\Delta\sigma^+ = \sigma^+ - \sigma_0$, and σ_0 are Taft's substituent constants⁸. The Eqs (1) and (2) had the following form for the values studied:

$$\delta(\text{OH}) = 10.57 + 0.82\sigma_1^- - 0.73\sigma_2, \quad R = 0.992, \quad s = 0.06 \text{ p.p.m.}$$

$$\gamma(\text{OH}) = 669.2 + 31.6\sigma_1 - 36.4\sigma_2, \quad R = 0.920, \quad s = 3.7 \text{ cm}^{-1}$$

$$pK = 7.04 - 1.91(\sigma_{01} + 1.03\Delta\sigma_1^-) - 0.72(\sigma_{02} + 0.32\Delta\sigma_2^+).$$

In the case of IR and NMR data the influence of substituents was characterized by using the substituent constants $\sigma_{m,p}$ of Jaffé and σ^- . It can be stated that the correlations obtained were very good and satisfactory with NMR and IR data, respectively. The correlation of pK_a according to Eq. (2) was found to be significant at 95%

probability level. The applicability of dual constants can be estimated from the value r_1 and r_2 (1.03 and 0.32, respectively) of Yukawa–Tsuno equation. The fact that the value of r_1 is close to unity and that of r_2 approaches 0.27 (which is the value found for ionization of substituted benzoic acids in water) indicates that σ^- and Jaffé's $\sigma_{m,p}$ constants can be used for characterization of $-M$ and $+M$ type substituents in the case of substituted *o*-nitrophenols. Besides a rather labourious calculation, the Eq. (2) presents some difficulties in that there are considerable differences between the values of some “normal” substituent constants given in different reports^{7,8,10}.

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