CHEMISTRY LETTERS, pp.765-768, 1974. Published by the Chemical Society of Japan

SUBSTITUENT EFFECTS ON ^{13}C CHEMICAL SHIFTS OF CARBOXYL CARBONS IN SUBSTITUTED BENZOIC ACIDS

Jun NIWA and Mitsuru YAMAZAKI*

Department of General Education, Nagoya University, Chikusa, Nagoya 464

*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464

The ^{13}C chemical shifts of carboxyl carbons of substituted benzoic acids in dimethyl sulfoxide-d_6 show a linear relationship with pK_a-values for m- and electron-withdrawing p-substituents, whereas for electron-donating p-substituents they show upfield deviations from the regression line. The chemical shifts are determined by Yukawa-Tsuno's equation with a negative r-value.

In order to examine the substituent effect on carboxyl carbons (C_1) of m- and p-substituted benzoic acids in dimethyl sulfoxide-d_6 (DMSO), proton-decoupled natural abundance ^{13}C FT NMR spectra were obtained at 25.2 MHz on a Varian XL-100-15 with a VFT-100X at 27°C. The concentration of samples was maintained at 10.5±0.5 Mol%, because the chemical shifts were independent of a change in the concentration within ±0.5 Mol%. The chemical shifts were reproduced within ±0.04 ppm.*1)

As Fig. 1 shows, there exists an excellently linear relationship of a positive slope between the chemical shifts of C_1 and the pK_a-values[1] in DMSO for m- and electron-withdrawing p-substituents, which is expressed by Eq. (1), whereas electron-donating p-substituents show upfield deviations from the regression line:

$$\delta(C_1) = 0.81pK_a - 8.87 \qquad (1)$$

where r= 0.997 and s= 0.07.*2)

We have found that the chemical shifts of C_1 show a roughly linear relationship of a negative slope with pi-electron densities on C_1, while there exists a linear relationship of a positive slope between the pi-electron densities and the σ-values.

Table. Chemical Shifts of Carboxyl Carbons (C_1) in m- and p-Substituted Benzoic Acids.

Subst.	$\delta(C_1)$ [a]	$q^{\pi}(C_1)$ [b]	P_{1z2z} [b]	pK_a [d]
1. p-NH_2	0.20	—	—	12.7
2. m-NH_2	0.56	—	—	11.6
3. p-NMe_2	0.16	—	—	—
4. m-NMe_2	0.56	—	—	—
5. p-OH	-0.12	0.7908	0.2850	11.8
6. m-OH	0.08	0.7946	0.2746	11.1
7. p-MeO	-0.24	0.7913	0.2842	—
8. p-Me	0.00	0.7925	0.2802	—
9. m-Me	0.08	0.7933	0.2763	11.0
10. p-Cl [c]	-0.79	0.7993	0.2797	10.1
11. m-Cl [c]	-1.19	0.8011	0.2760	—
12. p-CN [e]	-1.84	0.7957	0.2774	—
13. m-CN	-1.70	0.7951	0.2751	—
14. p-NO_2	-1.62	0.7996	0.2727	8.9
15. m-NO_2	-1.70	0.7976	0.2739	—
16. p-CO_2H	-0.59	—	—	—
17. m-CO_2H	-0.63	—	—	—
18. H	0.00	0.7932	0.2772	11.0
19. H [c]	0.00	0.7974	0.2777	11.0

a) All values listed are relative to benzoic acid, in which $\delta(C_1)$= 167.18 ppm from TMS. b) All values were calculated by INDO method, except for chloro-derivatives. Values of bond lengths and bond angles of substituted benzoic acids were chosen from Ref. 3). c) For chloro-derivatives CNDO/2 method was used. In Fig. 2 plots for chloro-derivatives are relative to the pi-bond order in benzoic acid which was calculated by CNDO/2 method. d) Cited from Ref. 1). e) This compound showed a somewhat broadened signal.

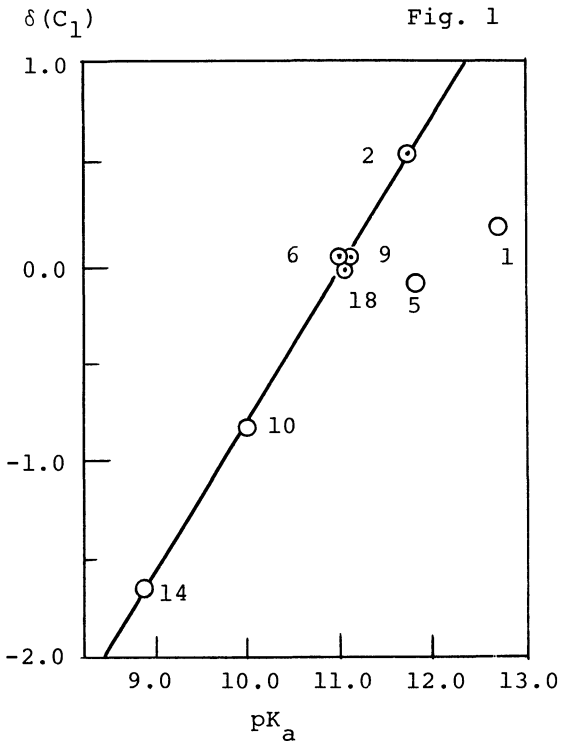

Fig. 1

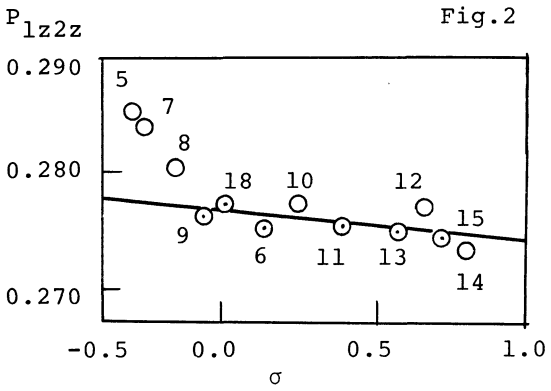

Fig.2

Fig. 1. Correlation between $\delta(C_1)$ and pK_a-values in DMSO.

Fig. 2. Plots of pi-bond orders, P_{1z2z}, against the σ-values.

*Numbered points correspond to entries in the Table. ⊙: m-substituent, ○: p-substituent.

Therefore, the whole trend of the chemical shifts of C_1 can empirically be correlated with Hammett's σ. In addition, ^{13}C chemical shifts of C_1 of carbonyl groups in aldehyde and ketone are known to exhibit upfield shifts in a conjugative system.[2] Accordingly, in the present case, the upfield deviations of plots for electron-donating p-substituents may be interpreted as showing the presence of the extra-conjugation between the aryl ring and the carboxyl group. The degree of the conjugation may be reflected in the change in the pi-bond order between C_1 and the ring carbon (C_2) bonded to the carboxyl group. Figure 2 shows a plot of pi-bond orders, P_{1z2z}, against the σ-values. In Fig. 2, plots for electron-donating p-substituents show considerable deviations up from the regression line. This result means that the degree of conjugation caused by such substituents exceeds that caused by the other substituents, which is determined by the σ-values. This extra-conjugative interaction between electron-donating p-substituent and the carboxyl group may cause the upfield shift from the regression line. Therefore, it is reasonable to apply Yukawa-Tsuno's equation[4] to the present case (see Fig. 3); the relationship is expressed as:

$$\delta(C_1) + 0.05 = -2.65(\sigma - 0.71\Delta\sigma_R^+) \qquad (2)$$

where $\Delta\sigma_R^+ \equiv \sigma^+ - \sigma$, and r= 0.989 and s= 0.13.*[2] This result provides us with an example of the application of Yukawa-Tsuno's equation with a negative r-value. In

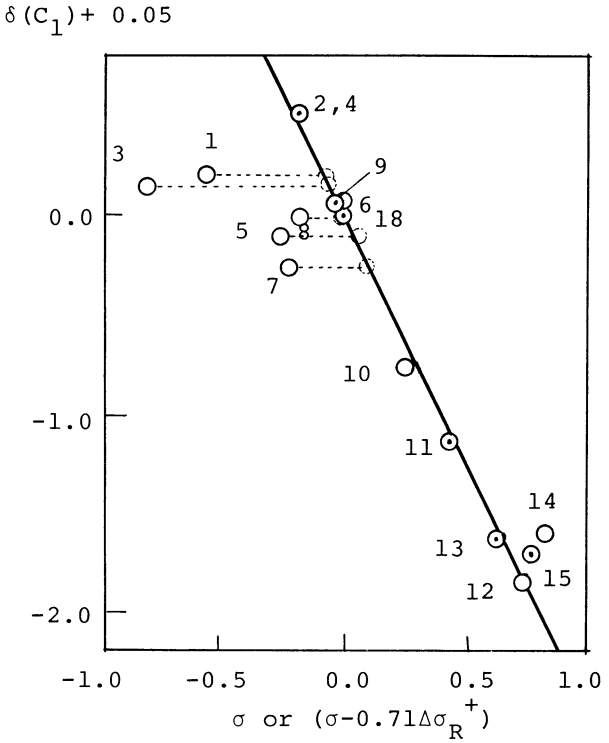

Fig. 3. Correlation between $\delta(C_1)$ and σ-value or $(\sigma - 0.71\Delta\sigma_R^+)$. Numbered points correspond to entries in the Table. Dotted circles are plotted against the corrected substituent constant $(\sigma - 0.71\Delta\sigma_R^+)$. ⊙: m-substituent, ○: p-substituent.

this correlation, the values of σ_{DMSO} for NH_2- and OH-groups obtained by using the correlation line between the pK_a-values[1] in DMSO and the σ-values of the other substituents were employed; σ(m-NH_2): -0.22, σ(p-NH_2): -0.62, σ(m-OH): -0.04 and σ(p-OH): -0.29. In Fig. 3, the downfield deviation of the plot for p-NO_2 may be attributed to the contribution of the inverse conjugation in contrast with the case of electron-donating p-substituents. Such a situation is more clearly observed in the case of ring substituted methyl benzoates.[5]

References

1) C. D. Ritchie and E. Uschold, J. Amer. Chem. Soc., 90, 2821 (1968).
2) J. B. Stothers, "Carbon-13 NMR Spectroscopy", (Organic Chemistry, Vol. 24, A Series of Monographs. ed. by A. T. Blomquist and H. Wasserman), Academic Press, New York and London (1972), p. 279.
3) Tables of Interatomic Distance and Configuration in Molecules and Ions, Chem. Soc. London, Spec. Publ. 11 (1958).
4) Y. Yukawa and Y. Tsuno, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.) 86, 873 (1965); Y. Yukawa, Y. Tsuno, and M. Sawada, Bull. Chem. Soc. Japan, 39, 2274 (1966).
5) Unpublished data.
*1) Measurement conditions: spectral width, 5000 Hz; aquisition time, 0.4 sec; data points, 4096; pulse width, 70 μsec.
*2) r: correlation coefficient; s: standard deviation.

(Received April 9, 1974)