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A SUCCESSFUL SEPARATION OF POSITION-DEPENDENT INDUCTIVE EFFECTS FOR THE BASICITIES OF QUINOLINES[1)]

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abstract: The substituent effects on the basicities of 3-, 4-, 5-, 6-, and 7-substituted quinolines were separated into inductive($\rho_i\sigma_i$) and pi-electronic($\rho_\pi\sigma_\pi$) components for each position by means of the LSFE equation, whose C_{ij} ($=\rho_i/\rho_{i,4\alpha}$) set derived was essentially equal to that for the solvolysis of 1-(1-naphthyl)ethyl chlorides.

The utility of Taft's DSP eq 1 concerning separation of substituent effects into polar and resonance contributions has been widely studied for various chemical reactivities and physical properties.[2,3)] There is, however, controversy between the merits of the DSP eq 1 and the LSFE eq 2, which, we believe, is a more precise expression of actual substituent effects. Recently, important differences have been pointed out and discussed.[1,4-6)] To assess the relative merits of the equations, it is important to analyse substituent effects in the naphthalene or naphthalene-like pi-systems, especially for a variety of substituent positions beyond ordinary meta and para ones.[2,5)]

$$\log k/k_o = \rho_I\sigma_I + \rho_R\bar{\sigma}_R \qquad (1)$$

$$\log k/k_o = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^- \qquad (2)$$

Since quinoline may be considered as an aza analogue of the pi-electron system of naphthalene, substituent effects in the quinoline system may reasonably be compared with the effects in the 1-naphthyl systems.[2,5)] Here, we wish to report that there exist position-dependent constants in the inductive effect component for basicities of quinolines and for various reactions of 1-naphthyl derivatives. Such constancy, covering greatly different reactivities, has not previously been clearly found by using Taft's DSP treatment. The results of applying the LSFE eq 2 to ΔpK 's of a series of substituted quinolines in water are summarized in Table 1.[7)]

Figure 1 shows the linear ρ_i-ρ_i relations found between the ρ_i values for the quinoline basicities and those for 1-naphthyl reactivities for the corresponding positions of substituents. The results are of interest because the good linearity for each line through the origin shows that the ratios of the ρ_i in a given set of reactivities remain constant for other sets, obviously independent of types of reactions.

The figure consists of several reactions; (*A*) the present basicities of quinolines, (*B*) solvolysis of 1-(1-naphthyl)ethyl chlorides,[5)] (*C*) detritiation of 1-tritionaphthalenes,[8)] (*D*) basicities of 1-naphthylamines,[9)] and (*E*) acidities of 1-naphthalenecarboxylic acids.[10)] According to our knowledge of substituent effects on benzene reactivities at the para position, these five sets belong to different classes of reactivity with respect to the behavior of resonance exaltation. The reaction *B* [11)] and *C* (*E*) [12)] correspond to strongly (weakly) electrophilic resonance exaltation by pi-donor substituents, while *D* [13)] and *A* [1)] correspond to strongly and to very weakly nucleophilic resonance exaltation by pi-acceptor substituents, respectively.

The linearity between the ρ_i's in any two reactions means that the ratio of ρ_i in a given reaction set ($\rho_i/\rho_{i,4\alpha} = C_{ij}$) [15)] is dependent solely on position and is independent of reaction. Based on the quinoline basicities, the following positional inductive constants were obtained; $C_{3\alpha}$=1.23, $C_{4\alpha}$=1.00, $C_{5\alpha}$=0.76, $C_{6\alpha}$=0.58, and $C_{7\alpha}$=0.70. The set of C_{ij} values, indeed, is essentially identical with the set derived from the solvolysis of 1-(1-naphthyl)ethyl chlorides reported before (1.37, 1.00, 0.75, 0.57, and 0.72, respectively);[5b)] the discrepancy of $C_{3\alpha}$ values might be ascribed to larger errors involved in the ρ_i values due to the very limited number of substituents analyzed. The result is equivalent to our previous observation that the ρ_i ratio ($\rho_{i,meta}/\rho_{i,para}$ = 1.18) for pyridine basicities is essentially equal to the ratio obtained from general benzene reactivities (1.17).[1)]

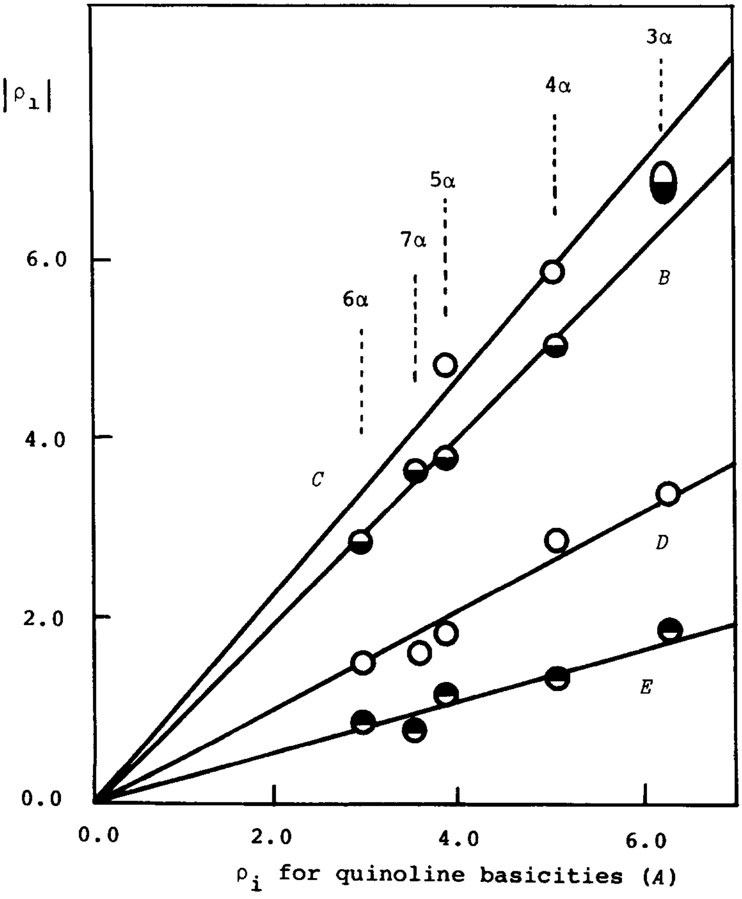
Table 1. Correlation Results for Basicities of Quinolines[a)] by means of the LSFE eq 2

Subst position[b)]	ρ_i	ρ_π^+	ρ_π^-	n[c)]
3α	6.28	1.29		6 : 0
4α	5.11	10.01		4 : 0
5α	3.89	3.32	(2.1)	5 : 2[d)]
6α	2.96	2.08	2.45	7 : 2
7α	3.56	4.15	2.66	6 : 2

a) Data of ΔpK_a were taken from Ref. 2a. The substituent constants were taken from Ref. 1. b) α refers to the position of nitrogen in quinoline. c) Number of substituents except H for pi-Donors : pi-acceptors. d) For the twisted NO_2 substituent, σ_π^-=0.20 was used.

Thus, the relative inductive effects are apparently insensitive to variation of electronic demand or supply in the reaction center. The absence of any reaction-dependent effects implies that the pi-inductive effect is, if detectable, not reflected in the ρ_i values, but in the remaining ρ_π values. This conflicts with the separation by means of DSP eq 1 that the inductive effect ρ_I includes the pi-inductive effect and, therefore, that the relative ρ_I values may depend on the specific pi-systems or the reactions concerned.[2,16)]

The contribution of pi-donor resonance effects (ρ_π^+) separated in the quinoline basicities reasonably show the sequence of magnitude, 4α>7α>5α>6α>3α, which is quite similar to that of the transmissibility of charge in the naphthalene pi-network.[5)] Generally, in the DSP approach, there is no definite rule to choose the most proper resonance constants among the four (σ_R^o, σ_R(BA), σ_R^+, and σ_R^-) and a best-fit correlation is taken as the criterion.[2)] It is, therefore, difficult to determine which parameter to use in an intermediate reactivity class, for example, between σ_R(BA) and σ_R^+. As the $\bar{\sigma}_R$ value used



ρ_i for quinoline basicities (*A*)

Fig. 1 The ρ_i-ρ_i plots for the reactions *B*,*C*,*D*,*E* vs *A* changes, the resulting $\bar{\rho}_I$ (and the relative $\bar{\rho}_I$) value must also change. Contrarily, the ρ_i (and the relative ρ_i) derived from the LSFE approach is unequivocally determined in any kind of reactivity class, because a single set of resonance constant (σ_π^+ or σ_π^-) is utilized consistently. Thus, the same position-dependent C_{ij} values in the quinoline and the relevant 1-naphthyl systems provide evidence for the validity of the general LSFE treatment.

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14) Note that pi-donor substituents show weak resonance exaltations in the basicities of pyridines.[1)]
15) The subscripts i and j in C_{ij} represent the respective naphthalene carbon positions to which a substituent(i) and a reaction side chain (j=α in the quinoline) are attached.
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