

Polar Substituents and the Luminescence of Organic Compounds

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An hypothesis is presented in which the interaction of inductive effects on the π -electron system of a complex molecule is interpreted as a shift in the potential energy of the ground and excited states. The model allows the effect of polar substituents on various luminescence processes to be described. It is predicted that the rate constant and the activation energy of radiationless deactivation of the first excited singlet state, as well as the energy of the $O-O$ phosphorescence band, will be correlated by Taft σ^* substituent constants.

THE Hammett equation has found considerable success in correlating numerous spectroscopic phenomena (see ref. 1 for a recent review). The first reported extension of the equation to the properties of excited states was made by Ziffer and Sharpless² who showed that the quantum yields of photolysis of diazoacetophenones were related to the substituent constant, σ . The success of this correlation was attributed to the involvement of a triplet in the reaction. As is well known, the electronic distribution in the lowest triplet state, T_1 , is generally closer to that of the ground state than is the first excited singlet state, S_1 . The latter authors² therefore expected reactions proceeding *via* S_1 to be less well correlated by ground-state substituent constants. Later studies^{3,4} showed that the dissociation constants of a wide range of aromatic acids and bases in both excited singlet and triplet states could be related to σ constants.

The recent finding that the relative fluorescence quantum yields of 5,5-disubstituted oxybarbituric acids⁵ are correlated by Taft⁶ polar substituent constants (σ^*) is further evidence of the useful application of so-called free-energy relationships to processes involving the excited singlet state. Whereas photochemical quantum yields are analogous to rate constants of normal chemical reactions, the physical basis for a correlation between fluorescence quantum yields and σ^* is not immediately apparent.

Previous discussions (*e.g.* ref. 7) of substituent effects on the luminescence of organic compounds have been almost entirely concerned with those substituents which show resonance interactions with the π -electron system of the fluorophore; the relevance of inductive effects in luminescence spectroscopy has hitherto received little attention. The following paper proposes a theoretical basis for the effect of polar groups on the photophysics of organic molecules.

Inductive Effects and Potential Energy Curves.—Consider two molecules Ar-X and Ar-Y where X is an electron donating substituent and Y is an electron-withdrawing group. If no resonance occurs between X or Y and the π -electrons of the chromophore Ar, then following Taft's convention,⁶ X and Y are designated as polar groups. It is now generally accepted that inductive

effects alone are of minor significance in u.v. and visible absorption spectroscopy; attempts to associate Hammett or Taft constants with wavelength maxima or absorption intensities have, with a few notable exceptions, met with failure.^{1,8} It is often assumed from such results that polar groups have no influence on electronic energy levels. A more correct conclusion would be that the energy difference between the ground state and the first excited singlet state, $\Delta E(S_1 - S_0)$, is approximately constant or at least shows no trend with σ in an homologous series.

The potential-energy surface of a complex molecule cannot readily be obtained by direct experimentation or molecular orbital calculations. However, a schematic representation is adequate for the purposes of the following discussion. Figure 1a depicts a two-dimensional

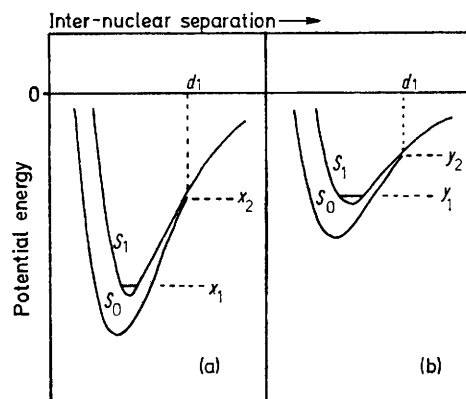


FIGURE 1 Potential-energy curves of S_0 and S_1 in (a) Ar-X and (b) Ar-Y. Higher singlets and all triplets are omitted for clarity

projection of the n -dimensional potential well of the conjugated π -electron system in compound Ar-X based on a generalised internuclear co-ordinate, d . The corresponding curves for the ground state, S_0 , and the first excited singlet state, S_1 , of Ar-Y are shown in Figure 1b. The potential energy (P.E.) of a covalent bond is determined by the charge density within that bond. In Ar-Y, electrons are withdrawn from the π -orbitals, and

¹ A. R. Katritzky and R. D. Topsom, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972.

² H. Ziffer and N. E. Sharpless, *J. Org. Chem.*, 1962, **27**, 1944.

³ H. H. Jaffé and H. Lloyd Jones, *J. Org. Chem.*, 1965, **30**, 964.

⁴ E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234.

⁵ L. A. King, *J.C.S. Perkin II*, 1976, 844.

⁶ R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, J. Wiley, New York, 1956.

⁷ S. G. Schulman and W. L. Paul, *Fluorescence News*, 1973, **7**, 25.

⁸ H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' J. Wiley, New York, 1962.

thus the potential energy of S_0 is lower, *i.e.* less negative, than that in Ar-X. In both derivatives, $\Delta E(S_1 - S_0)$ is assumed to be constant as discussed above. The lowest vibrational levels of S_1 in Ar-Y and Ar-X are denoted y_1 and x_1 respectively (see Figure 1).

At some 'bond length', d_1 , the curves of S_0 and S_1 will approach sufficiently closely for quantum mechanical tunnelling⁹ to occur from S_1 to S_0 . This point, often called a cross-over point, is shown for Ar-Y and Ar-X by y_2 and x_2 respectively. Assuming that the relative potential energies of the cross-over points and the minima of S_1 are proportionately related, then it follows that

$$[\text{P.E.}(y_2) - \text{P.E.}(y_1)] < [\text{P.E.}(x_2) - \text{P.E.}(x_1)]$$

Substituent Constants and Non-radiative Processes.—The energy difference between the cross-over point and the lowest vibrational level of S_1 can be described as the activation energy, E_a , for radiationless deactivation of S_1 . It is now seen that E_a is partly determined by the inductive effect of the substituents. The relationship is of the type,

$$E_a = f(1/\sigma^*) \quad (1)$$

where σ^* is the Taft polar substituent constant. The rate constant of radiationless deactivation, k_1 , is related to E_a by the Arrhenius equation,

$$k_1 = A[\exp(-E_a/RT)] \quad (2)$$

The quantum yield of fluorescence, ϕ_f , is given by

$$k_1 = (1/\phi_f - 1)\tau_0 \quad (3)$$

The Taft polar energy equation may be written

$$\log(k/k_0) = \rho^*\Sigma\sigma^* \quad (4)$$

When τ_0 , the natural lifetime of S_1 , is approximately constant within a series (as occurs in the 5,5-disubstituted oxybarbiturates⁵), then from equations (1)–(3) it follows that, at a given temperature, the fluorescence quantum yield decreases as σ^* assumes larger positive values. For series where τ_0 is not constant, the expected relation is between k_1 and σ^* . Such behaviour is encountered in substituted benzenes, for example, where neither ϕ_f nor τ_0 is individually correlated with substituent constants. Using data from Berlman,¹⁰ k_1 has been calculated, using equation (3), for 21 mono-, di-, and tri-substituted benzenes. (Derivatives where resonance can take place with the substituent, *e.g.* phenol, biphenyl, have been excluded.) Figure 2 shows the distribution of $\log k_1$ as a function of $\Sigma\sigma^*$, the sum of all six substituent constants, including hydrogen, in the aromatic ring. The correlation coefficient ($r = 0.86$) is statistically significant ($P \ll 0.001$). This correlation is surprisingly good when it is realised that k_1 is subject to experimental error in both ϕ_f (estimated by Berlman¹⁰ as $\pm 10\%$) and τ_0 (obtained from the integrated absorption spectrum). The

anomalously high value of k_1 for phenyl ether (compound t in Figure 2) may result from an interaction (*e.g.* energy transfer) between the two phenyl groups.

In the Taft equation (4), the susceptibility of a reaction to a given set of substituents is measured by the reaction constant, ρ^* . In a similar manner, the variation in potential energy of the ground and excited states of a chromophore could, in principle, be described by an analogous 'sensitivity' constant. The slope of the curve in Figure 2 ($\rho^* = 0.38$) is apparently characteristic of

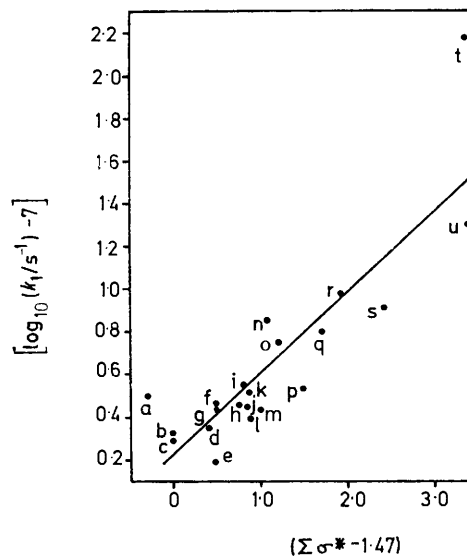


FIGURE 2 Relationship between the non-radiative decay constant, k_1 , and the sum of Taft substituent constants, $\Sigma\sigma^*$, in substituted benzenes ($1.47 = 3\sigma^*_{\text{H}}$). The straight line represents the least-squares fit. Data (ref. 10) determined at room temperature in cyclohexane: a = 1,3,5-triethyl-; b = 1,3,5-trimethyl-; c = 1,2,4-trimethyl-; d = 4-ethyl-1-methyl-; e = 1,4-dimethyl-; f = 1,3-dimethyl-; g = 1,2-dimethyl-; h = s-butyl-; i = isopropyl-; j = cyclohexyl-; k = n-propyl-; l = ethyl-; m = methyl-; n = bibenzyl-; o = diphenylmethane; p = benzene; q = benzyl acetate; r = 4-methoxy-1-methyl-; s = methoxy-; t = phenyl ether; u = 1,4-dimethoxy. For compounds q–u, substituent constants were unavailable and $\Sigma\sigma^*$ values have been calculated from homologous substituents on the basis of an enhancement factor of 2.8 for removal of an α -methylene group (see ref. 6)

the benzene ring and may provide a basis for comparing the influence of inductive factors on the excited states of different chromophores. Since non-radiative decay constants are predicted to increase with $\Sigma\sigma^*$, then $\rho^* \geq 0$.

Temperature Effects.—From equations (1)–(3) it can also be seen that the temperature coefficient of fluorescence is related to the substituent constant. For a given chromophore, temperature quenching of fluorescence will become less pronounced as $\Sigma\sigma^*$ increases. This effect is illustrated by the oxybarbiturates (Table). (Only relative fluorescence quantum yields were determined for these compounds and the temperature coefficient of fluorescence is more conveniently expressed¹¹ as $\Delta \log I_f/\Delta T$.)

⁹ G. W. Robinson, *J. Mol. Spectroscopy*, 1961, **6**, 58.

¹⁰ I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1971.

¹¹ L. A. King, J. N. Miller, D. T. Burns, and J. W. Bridges, *Analyt. Chim. Acta*, 1974, **68**, 205.

In that study,¹¹ amylobarbitone, pentobarbitone, butobarbitone, and barbitone could not be differentiated from each other in terms of $\Delta \log I_t/\Delta T$. As expected, the relative quantum yields of the above four oxybarbiturates are also broadly similar^{5,12} and clearly distinguishable from seconal and phenobarbitone (see Table).

Relative quantum yields, temperature coefficients of fluorescence, and substituent constants of selected oxybarbituric acids

Compound	$\Sigma\sigma^*$	$\Delta \log I_t/\Delta T^*$	rel. ϕ_t
Barbitone	-0.20	-2.5×10^{-2}	0.55
Seconal	-0.08	-1.6×10^{-2}	0.13
Phenobarbitone	+0.50	-8.3×10^{-3}	0.05

* Ref. 11. [†] Ref. 12. Data obtained at room temperature in ethanolic alkaline solution. Quantum yields are relative to an arbitrary standard (butobarbitone) for which rel. $\phi_t = 1.00$.

In principle, fluorescence quantum yields at very low temperatures can be calculated from room temperature data. In practice, such an analysis would not prove particularly useful. At temperatures below the glass point of the solvent, reorientation within the solvation sphere of the solute does not occur during the lifetime of the first excited singlet state and the fluorescence transition arises from the so-called 'frozen-in Franck-Condon state'. It is for this reason that 77 K fluorescence spectra are blue-shifted relative to spectra recorded in fluid solution. The available data indicate that within an homologous series, the apparent decrease in the potential energy of S_1 at 77 K is approximately constant. Thus, although the activation energy is decreased at low temperatures, the ratio E_a (minimum) : E_a (maximum) for a given range of σ^* values is higher than at room temperature. It is, therefore, concluded that the relative effect of polar substituents will be more marked at 77 K than at 293 K. Such an effect has been found in the 5,5-disubstituted oxybarbituric acids^{12,13} where only those members with saturated groups at the C-5 position show measurable fluorescence at 77 K.

Fluorescence Quenching.—Under normal circumstances, the activation energy, E_a , is supplied by collisions of the excited molecule with solvent molecules. Fluorescence quenching is facilitated by certain added solutes (quenchers). Provided that fluorescence quenching occurs by a bimolecular kinetic route, then regardless of the nature of the quencher, fluorescent species with low activation energies will be more effectively quenched than those where E_a is higher. Marcondes *et al.*¹⁴ have demonstrated that the fluorescence quenching of *meso*-substituted anthracenes by triphenylphosphine is well correlated by Hammett σ constants for the anthracene substituents. Within an homologous series and under standard conditions, the degree of fluorescence quenching of an indi-

vidual member of that series is thus directly related to its absolute fluorescence efficiency.

Phosphorescence and Substituent Effects.—The discussion of the radiationless deactivation of the excited singlet state has so far ignored the possibility of $S_1 \rightarrow T_1$ intersystem crossing. The term k_1 as defined in equations (2) and (3) should properly contain a component $k_{i.s.}$, the rate constant of intersystem crossing. However, there is no reason for believing that $k_{i.s.}$ is sensitive to inductive effects. Similarly, the lifetime of T_1 would also not be expected to be influenced by polar groups.

Nevertheless, a substituent effect should be present in the energy of the $O-O$ band of the phosphorescence transition. The lowest triplet state of a molecule is always situated at a less negative potential energy than the ground state. If the inductive effect operating on P.E.(S_0) has a proportionate effect on P.E.(T_1), then as P.E.(S_0) becomes less negative (*i.e.* increasing σ^*), $\Delta E(T_1 - S_0)$ will also decrease. The data of Zimmerman *et al.*¹⁵ support this deduction. Figure 3 shows the

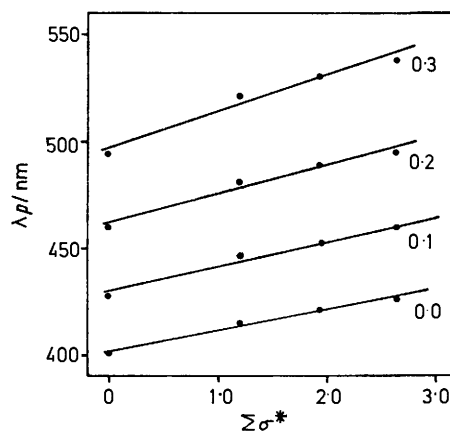


FIGURE 3 Inductive effect of substituents on the principal wavelength maxima (λ_p) in the phosphorescence spectrum of disubstituted cyclohexanedienones. Compounds in order of increasing $\Sigma\sigma^*$: 4,4-dimethyl-; 4,4-diphenyl-; 4-dichloromethyl-4-methyl-; 4-methyl-4-trichloromethyl- (data from ref. 15)

polar substituent effect on the phosphorescence wavelength maxima of 4,4-disubstituted cyclohexanedienones. A similar trend is anticipated in singlet triplet ($S_0 \rightarrow T_1$) absorption spectra.

Conclusion.—The model presented above consolidates many otherwise unrelated phenomena in the luminescence of organic compounds. Relatively few large-scale systematic studies have been made of the fluorescence and phosphorescence of homologous series and considerable scope exists for testing the hypothesis. Provided that sufficiently precise determinations of fluorescence quantum yields and lifetimes can be made, empirical

¹² L. A. Gifford, W. P. Hayes, L. A. King, J. N. Miller, D. T. Burns, and J. W. Bridges, *Analyt. Chem.*, 1974, **46**, 94.

¹³ L. A. Gifford, W. P. Hayes, L. A. King, J. N. Miller, D. T. Burns, and J. W. Bridges, *Analyt. Chim. Acta*, 1972, **62**, 214.

¹⁴ M. E. R. Marcondes, V. G. Toscano, and R. G. Weiss, *Tetrahedron Letters*, 1974, **46**, 4053.

¹⁵ H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, 1967, **89**, 6589.

relationships between k_1 and σ^* could be used to predict excited-state properties of novel members of a series.

The effects of polar substituents on molecular luminescence are summarised below.

(1) The activation energy, E_a , for radiationless deactivation of S_1 decreases, and the rate constant, k_1 , increases as $\Sigma\sigma^*$ becomes more positive. At 77 K, the relative effect of substituents will be more pronounced than at room temperature. (2) When the natural

lifetime, τ_0 , of S_1 does not vary appreciably across a series, then ϕ_f will decrease as $\Sigma\sigma^*$ increases. (3) A positive correlation exists between the energy of the $O-O$ phosphorescence band and $\Sigma\sigma^*$.

The following parameters will be independent of inductive effects: (1) the wavelength of maximum fluorescence, (2) the intersystem crossing rate constant, and (3) the lifetime of the lowest triplet state.

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