Polar Substituents and the Luminescence of Organic Compounds. Part 3.[1] Structural Determinants

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Further data are presented to illustrate the relationship of the $S_1 \rightarrow S_0$ non-radiative rate constant and the triplet energy of homologous series with Taft polar substituent constants. The magnitude of the inductive effect exerted by a given substituent depends on the site of substitution and the number of π electrons in the chromophore.

LINEAR free energy relationships (l.f.e.r.s) have three uses in organic chemistry. First, a body of data may be summarised by relatively few parameters. Secondly, the behaviour of untested members of a series may be interpolated or extrapolated, and finally, the reaction constant (ρ) provides insight into the mechansim.

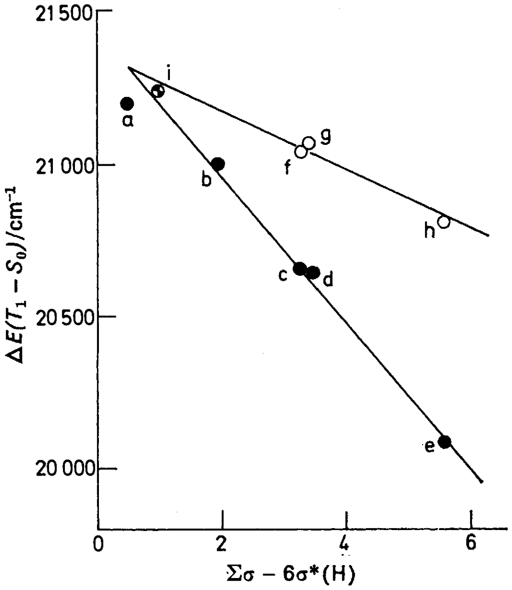

FIGURE 1 Inductive effect of α- and β-substituents on the triplet energy, $\Delta E(T_1 - S_0)$, of naphthalene. $\Sigma\sigma^*$ refers to all substituents including hydrogen. The straight lines represent the least-squares fits. a, 1-Methyl; b, 1-methoxy; c, 1-chloro; d, 1-bromo; e, 1,5-dibromo; f, 2-chloro; g, 2-bromo; h, 2,6-dibromo; i, naphthalene. Data for compounds a and b from ref. 4, remainder from ref. 3, determined at 77 K

The extension of l.f.e.r.s to the physical properties of molecular excited states[1,2] has similar objectives, although ρ now has a different interpretation and is more conveniently described by two new sensitivity constants, ε_f and ε_p.[1] This paper presents further correlations of the $S_1 \longrightarrow S_0$ non-radiative rate constant (k_1) and the triplet energy, $\Delta E(T_1 - S_0)$ of homologous series with Taft polar substituent constants, and identifies those features of the substituted molecule which determine the magnitude of the inductive effect.

Naphthalenes.—Figure 1 shows the effect of substitution on the 0—0 phosphorescence band of naphthalene.[3,4] α-Substitution produces a more marked effect (ε_p 0.67 kcal mol^{-1}; r 0.99, $P \ll 0.001$) than β-substitution (ε_p 0.27 kcal mol^{-1}; r 0.99, $P \ll 0.001$). These data exclude fluoronaphthalene.†

Biphenyls.—The relationship between $\log_{10} k_1$ and $\Sigma\sigma^*$ for 4-substituted biphenyls is illustrated by Figure 2. The non-radiative rate constant has been calculated from the equation $k_1 = (1 - \theta_f)/\tau_f$ by using the fluorescence quantum yields (θ_f) and fluorescence decay times (τ_f) given by Berlman.[6] Substitution of a phenoxy-group in biphenyl (compound g in Figure 2) leads to an anomalously high value of k_1. Diphenyl ether behaves

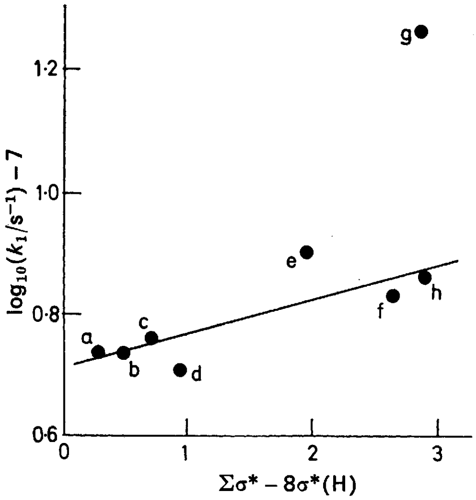

FIGURE 2 Relationship between the non-radiative decay constant k_1 and Taft polar substituent constants in 4-biphenyls. $\Sigma\sigma^*$ refers to all substituents including hydrogen. The straight line is the least-squares fit (compound g excluded). a, 4-Isopropyl; b, 4-methyl; c, 4-benzyl; d, biphenyl; e, 4-methoxy; f, 4,4′-di-isobutoxy; g, 4-phenoxy; h, 4,4′-dimethoxy. Data from ref. 6 determined at room temperature

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† The Taft σ^* scale of ground state polar substituent constants appears to be equally suitable for describing excited state processes. However, fluorine and groups containing fluorine are exceptions to this rule. Although $\sigma^*(\mathrm{Cl}) \simeq \sigma^*(\mathrm{F}) = 3.08$, fluorobenzene is considerably more fluorescent than chlorobenzene.[5] In the correlation of substituted benzenes,[2] 1,4-bis(trifluoromethyl)benzene was omitted. The calculated value of $\Sigma\sigma^* - 3\sigma^*(\mathrm{H})$ for this derivative is 5.64 whereas the non-radiative rate constant ($\log_{10} k_1/\mathrm{s}^{-1}$ 7.70) suggests that $\Sigma\sigma^* - 3\sigma^*(\mathrm{H})$ is close to 1.5. With α- and β-fluoronaphthalenes[3] the energy of the 0–0 phosphorescence band is much greater than expected. It is therefore concluded that fluorine has a relatively low electronegativity in the excited state. The above data are consistent with $\sigma^*(\mathrm{F}) = \sigma^*(\mathrm{CF_3}) \simeq 0.5$.

[1] Part 2, L. A. King, *J.C.S. Perkin II*, 1977, 919.

[2] L. A. King, *J.C.S. Perkin II*, 1976, 1725.

[3] J. Ferguson, T. Iredale, and J. A. Taylor, *J. Chem. Soc.*, 1954, 3160.

[4] C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, London, 1968.

[5] R. T. Williams and J. W. Bridges, *J. Clin. Path.*, 1964, **17**, 371.

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

similarly,[2] and in both cases intramolecular energy transfer may make an important contribution to the

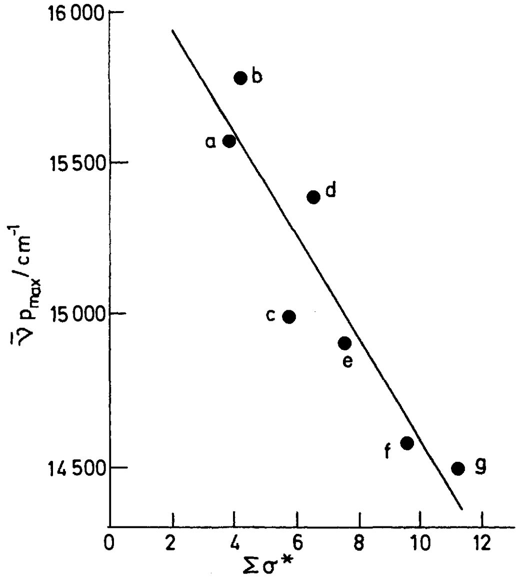

FIGURE 3 Polar substituent effect on the phosphorescence maximum ($\tilde{\nu}_{p,max.}$) of substituted fluorescein dianions. The straight line is the least-squares fit. $\Sigma\sigma^*$ refers to four replaceable hydrogen atoms in the xanthenone ring system. a, Iodo; b, bromo; c, di-iodo; d, dibromo; e, tri-iodo; f, tetraiodo; g, tetrabromo. Data from ref. 7 determined at 90 K

overall non-radiative decay of S_1. The regression line in Figure 2 excludes 4-phenoxybiphenyl (ε_f 0.074 kcal mol^{-1}; r 0.81, $P < 0.05$).

Fluoresceins.—The correlation of the phosphorescence maxima of bromo- and iodo-substituted fluorescein dianions with $\Sigma\sigma^*$ is shown in Figure 3 (ε_p 0.48 kcal mol^{-1}; r 0.92, $P < 0.01$). Although such substitution is primarily in the xanthenone ring system, geometric isomers have not been separated.[7] Furthermore, these data are based on peak maxima rather than the 0–0 bands, and hence the value of ε_p should be taken as an approximation.

ε_f, ε_p, *and Molecular Structure.*—In a symmetrical molecule, it has been predicted that the inductive effect of a given substituent, as measured by ε_f or ε_p, will be inversely related to d, the distance of the substituted ring atom from the centre of symmetry.[1] Figure 1 demonstrates this effect in substituted naphthalenes. If a uniform bond length is assumed, then the ratio $\varepsilon_p(\alpha) : \varepsilon_p(\beta)$ of 2.5 is very close to that expected from an interaction having a distance dependence proportional to $1/d^3$.

The sensitivity constants, ε_f and ε_p, will also be determined by the size of the chromophore, or, more precisely, the number of conjugated π-electrons. The polar effect of a substituent modifies the potential energy of the π-electrons.[2] This perturbation will decrease as the number of π-electrons (n) in the chromophore increases. Clearly n is related to d in so far as when n is small, d must also be small. The relationship between ε_f, ε_p, and molecular structure may be visualised by assuming that the inductive effect has a limited range. In large molecules, the majority of π-electrons will not experience the electrostatic field of a given substituent. The Table provides a summary of the available sensitivity constants together with values of d based on a standard bond length of 1.39 Å. Figure 4 shows the relationship between ε_f, ε_p, and the reciprocal of nd^3, an empirical measure of molecular size and site of substitution.

Summary of sensitivity constants

Series	ε_f/kcal mol^{-1}	ε_p/kcal mol^{-1}	d/Å [a]	Solvent
Benzene [b]	0.51		1.39	Cyclohexane
4-Cyclohexadienone [b]		1.57	1.39	EPA [e]
α-Naphthalene [d]		0.67	1.84	Petroleum
β-Naphthalene [d]		0.27	2.51	Petroleum
4-Biphenyl [d]	0.074		3.48	Cyclohexane
α-Anthracene [c]		0.22	2.78	EPA
meso-Anthracene [c]	0.34		1.39	Ethanol
Fluorescein dianion [d]		0.48		EPA

[a] Distance from substituted ring atom to centre of symmetry. For 4-cyclohexadienones, d 1.39 Å is an estimate. In the fluorescein dianions, the sites of substitution and the extent of the chromophore are uncertain. [b] Ref. 2. [c] Ref. 1. [d] This work. [e] EPA = ethanol–isopentane–ether.

When used in conjunction with a table of Taft σ^* constants, Figure 4 enables predictions to be made for certain excited state properties of symmetrical organic molecules.

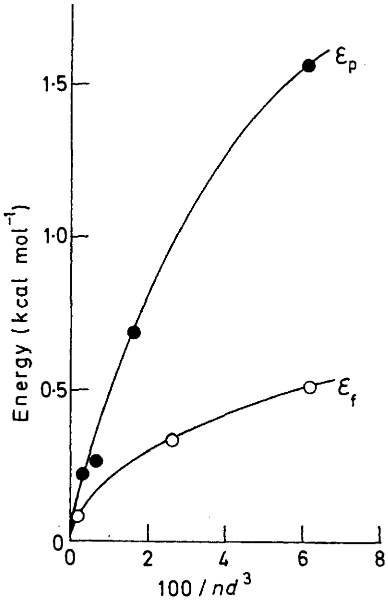

FIGURE 4 Relationship between sensitivity constants and molecular structure where n is the number of π-electrons in the chromophore

With asymmetrical molecules, variously positioned substituents could be used to probe the distribution of π-electron density in the chromophore.

[7/1375 *Received, 28th July,* 1977]

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