Polar Substituents and the Luminescence of Organic Compounds. Part 2.[1] Anthracene Derivatives

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A well defined inductive effect is present in the fluorescence and phosphorescence of substituted anthracenes. The rate of non-radiative decay of the first excited singlet state and the energy of the triplet state are correlated by Taft polar substituent constants in agreement with theoretical predictions.

A PREVIOUS paper[1] described how the inductive effect of substituents could interact with the potential energy surfaces of a chromophore and modify certain properties of the excited states. The major consequences of this theory are that the activation energy, E_a, for radiationless deactivation of S_1, the first excited singlet state, and the energy of the *0–0* phosphorescence transition will show a negative correlation with the sum of Taft[2] substituent constants ($\Sigma\sigma^*$). By applying the Arrhenius equation to the thermal activation of the excited state quantum in S_1, it was shown that k_1, the rate constant for internal conversion from S_1, will increase with $\Sigma\sigma^*$.

Derivatives of anthracene have considerable importance as scintillators and fluorescence standards. An understanding of substituent effects could be used, for example, in predicting fluorescence quantum yields of new members of the series.

The presence of a polar substituent effect in *meso*-substituted anthracenes has already been indicated by fluorescence quenching studies.[1,3] In the following treatment, polar effects are shown to be an important determinant of the luminescence properties of this family of compounds.

Luminescence of Substituted Anthracenes.—Figure 1 shows the relationship between log k_1 and $\Sigma\sigma^*$ for anthracene and sixteen *meso*-substituted derivatives. The non-radiative rate constant has been calculated from equation (i) by using the fluorescence quantum

$$k_1 = (1/\Theta_f - 1)/\tau_0 \qquad \text{(i)}$$

yields (Θ_f) and natural lifetimes (τ_0) compiled by Birks.[4] As before, $\Sigma\sigma^*$ applies to all ring substituents (including hydrogen). Derivatives such as 9-phenylanthracene and anthracene-9-carboxylic acid, where the substituent may show some resonance interaction with the π-electrons of the ring, as well as those compounds such as 9-bromoanthracene where a heavy-atom effect is expected to increase the non-radiative decay of S_1, have been excluded from this analysis.

meso-Substituted anthracenes where $R^1 = R^2$ (see Figure 1) are centrosymmetric and will have zero dipole moments. Therefore, the probability of vibrational transitions within S_1 will be less than in those compounds where $R^1 \neq R^2$. In the transition state theory, the Arrhenius constant, A, is expressed as $(RT/Nh)\exp(\Delta S^{\ddagger}/R)$. The entropy of activation, $\Delta S^{\ddagger}$, may be directly associated with the vibrational transition probability. It follows that centrosymmetric derivatives will have lower values of $\Delta S^{\ddagger}$ and A, and therefore k_1, than their asymmetric homologues. The effect of this selection rule is demonstrated in Figure 1.

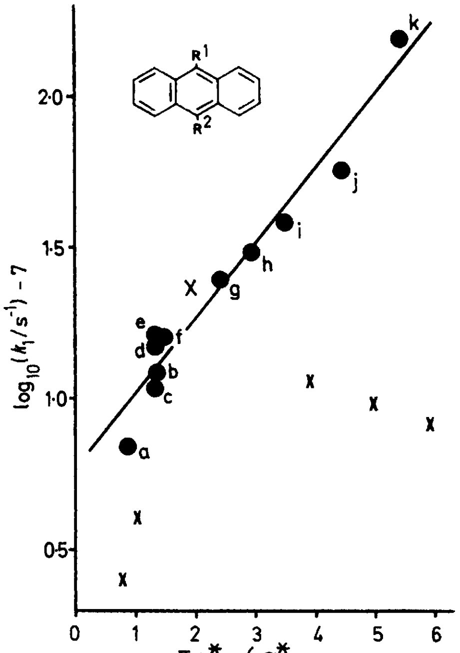

FIGURE 1 Relationship between the non-radiative decay constant, k_1, and the sum of Taft substituent constants, $\Sigma\sigma^*$, in *meso*-substituted anthracenes; data (ref. 4) determined at room temperature in alcohol. Asymmetric series (●): a, 9-ethyl-10-methyl-; b, 9-n-butyl-; c, 9-isobutyl-; d, 9-n-propyl-; e, 9-ethyl-; f, 9-methyl-; g, 9-methoxy-10-methyl-; h, 9-methoxy; i, 9-acetoxy-; j, 9-chloro-; k, 9-chloro-10-methoxy-. Centrosymmetric series (×) in order of increasing $\Sigma\sigma^*$: 9,10-di-n-propyl-; 9,10-dimethyl-; anthracene; 9,10-dimethoxy-; 9,10-diacetoxy-; 9,10-dichloro-. The straight line represents the least-squares fit for the asymmetric series

For asymmetric anthracenes, the high correlation between log k_1 and $\Sigma\sigma^*$ (r 0.97, $P \leqslant 0.001$) suggests that A is essentially constant, whereas in the centrosymmetric series A may be over ten times lower than would be expected on the basis of inductive effects alone.

Because the natural lifetimes of the first excited

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[1] Part 1, L. A. King, *J.C.S. Perkin II*, 1976, 1725.

[2] R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956.

[3] M. E. R. Marcondes, V. G. Toscano, and R. G. Weiss, *Tetrahedron Letters*, 1974, 4053.

[4] J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley, New York, 1970, p. 121.

singlet states of the anthracene derivatives considered here are approximately constant, centrosymmetric members will have higher fluorescence quantum yields.

The energy of the *O–O* phosphorescence transition, $\Delta E(T_1 - S_0)$, of α-chloroanthracenes [5] decreases regularly as $\Sigma\sigma^*$ increases (r 0.999, $P \leqslant 0.001$) (see Figure 2). Limited data [5] for the phosphorescence of *meso*-substituted anthracenes suggest that the substituent effect is greater than in the α-series.

Generalisation of ρ^*. The slope of the least-squares line in Figure 1 (0.25) is an estimate of ρ^*, the sensitivity constant for polar effects on k_1 under the conditions used. For comparison, $\rho^* = 0.38$ for substituted benzenes [1] in cyclohexane solution at room temperature. An analogous value of ρ^* cannot be obtained directly from a plot of $\Sigma\sigma^*$ against triplet energies such as is shown in Figure 2. To maintain dimensional consistency, it is proposed to introduce two new constants, ε_f and ε_p which are defined in equations (ii) and (iii).

$$\begin{aligned}\varepsilon_f &= \Delta E_a/\Delta\Sigma\sigma^* \\ &= (2.3 \times 10^{-3})\, RT\, \Delta\log k_1/\Delta\Sigma\sigma^* \text{ kcal mol}^{-1} \qquad \text{(ii)}\end{aligned}$$

$$\begin{aligned}\varepsilon_p &= \Delta\Delta E(T_1 - S_0)/\Delta\Sigma\sigma^* \\ &= (2.86 \times 10^{-3})\Delta\bar{\nu}\ (\text{cm}^{-1})/\Delta\Sigma\sigma^* \text{ kcal mol}^{-1} \qquad \text{(iii)}\end{aligned}$$

The expression in (ii) is derived from the Arrhenius equation. In (iii), $\Delta\Delta E(T_1 - S_0)/\Delta\Sigma\sigma^*$ represents the change in energy of the *O–O* phosphorescence band for unit change in the sum of σ^*. A further disadvantage of using ρ^* is that this constant is predicted to be inversely related to T, the absolute temperature. Indeed, such a relationship has been found in the oxybarbiturates.[6] However, both ε_f and ε_p are essentially temperature-independent.

The effect of polar substituents on anthracene luminescence may now be summarised as:

ε_f 0.34 kcal mol^{-1} (asymmetric *meso*-substitution)
ε_p 0.22 kcal mol^{-1} (α-substitution)

At present, insufficient data are available to relate ε_f and ε_p to features in the molecular structure of the chromophore. However, the site of substitution in an aromatic system appears to be one such factor. In a symmetrical molecule like anthracene, the centre of symmetry coincides with the centre of the potential well associated with the π-electrons. Because inductive effects diminish rapidly with distance, substituents at ring positions close to the centre of the potential well should exert a greater inductive effect than those more distant. Thus, in the anthracenes, both ε_f and ε_p should increase in the order $\beta < \alpha <$ *meso*. The possibility then exists of using these constants as 'spectroscopic rulers.' The significance of the difference in ε_f between *meso*-substituted anthracenes and substituted benzenes [1] (ε_f 0.51 kcal mol^{-1}) cannot be assessed because the effect of different solvents on ε_f is at present unknown.

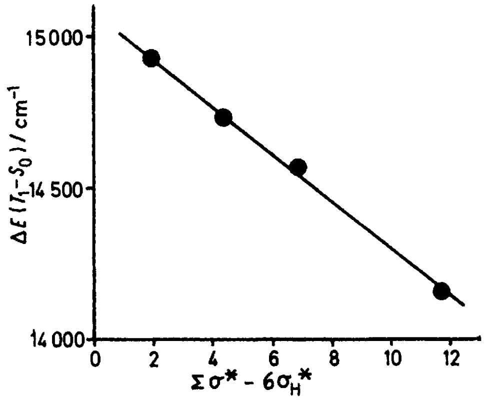

FIGURE 2 Inductive effect of α-substituted chlorine atoms on the triplet energy, $\Delta E(T_1 - S_0)$, of anthracene. Compounds in order of increasing $\Sigma\sigma^*$: anthracene; 1-chloroanthracene; 1,5-dichloroanthracene; 1,4,5,8-tetrachloroanthracene (data from ref. 5). The substituent constant for a chlorine atom is taken as $\sigma^*(\text{ClCH}_2) \times 2.8$. The least-squares line is shown

In conclusion, the data presented here further support the theory of inductive effects on molecular excited states.

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[5] M. Zander, 'Phosphorimetry,' Academic Press, London, 1968.

[6] L. A. King, *J.C.S. Perkin II*, 1976, 844.