Inductive Effect in the Relative Fluorescence Quantum Yields of Oxybarbiturates

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In 5,5-disubstituted oxybarbituric acids, a high correlation exists between the inductive contribution of the C-5 substituents, as measured by Taft polar constants, and the fluorescence quantum yield at room temperature.

DURING studies of the fluorescence properties of 5,5-disubstituted derivatives of oxybarbituric acid (pyrimidine-2,4,6-trione), it was found that compounds with unsaturated groups in the 5-position showed a weaker fluorescence than those with alkyl substituents.[1,2] However, variations in the C-5 side-chains had no effect on the molar absorptivity (a finding confirmed by Miles and Schenk [3]), the fluorescence Stokes shift, or the shape of the excitation and fluorescence spectra. At 77 K, the effect was even more pronounced. Here, only oxybarbiturates with saturated substituents exhibited significant fluorescence.

No conjugation can exist between the heterocyclic chromophore in oxybarbiturates and unsaturated groups in the C-5 side-chains. It was therefore suspected that inductive effects were responsible for the large variation in the fluorescence quantum yields. However, such electrostatic effects generally have only a feeble influence on fluorescence characteristics. Furthermore, the weak fluorescence of 5-phenyl-substituted oxybarbiturates (*e.g.* phenobarbitone) could be due to intramolecular energy transfer from the heterocyclic singlet state to the phenyl triplet state.[4] A further study has now been carried out using a wider range of 5,5-disubstituted oxybarbiturates to investigate these effects.

EXPERIMENTAL

The oxybarbituric acids examined (Table) were obtained from various commercial sources. 5-Ethyl-5-(*p*-nitrophenyl)oxybarbituric acid was synthesised by Dr. L. A. Gifford. Each compound was dissolved in 0.1M aqueous potassium hydroxide to give a solution of *ca.* 4×10^{-5}M. The absorbance (A) of each solution was measured at 265 nm. Fluorescence intensities (I_f) were determined using an excitation wavelength of 265 nm, an emission wavelength of 410 nm, and an overall resolution of 6 nm. All measurements were made at 20°. The relative quantum yield $(\phi_f)_r$ of each compound was defined as (I_f/A) and related to 5-ethyl-5-(s-butyl)oxybarbituric acid (butabarbitone), the quantum yield of which was arbitrarily assigned as unity (Table). (The relative quantum yields derived here clearly have no absolute significance. However, because the spectral characteristics of 5,5-disubstituted oxybarbituric acids are similar, it follows that relative quantum yields bear a fixed relationship to the true fluorescence quantum yields in each case.)

RESULTS

The inductive contribution of the C-5 substituents may be quantitatively expressed [5] by Taft polar constants (σ^*).

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[1] 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.

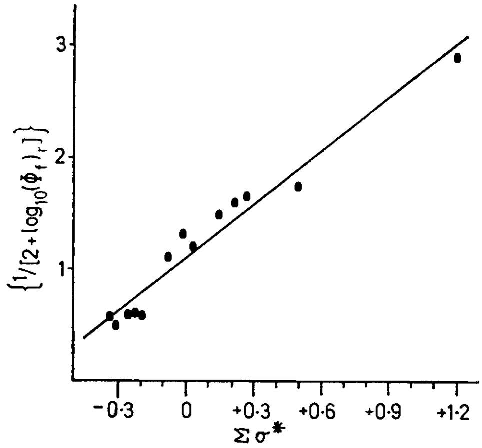
[2] L. A. Gifford, W. P. Hayes, L. A. King, J. N. Miller, D. T. Burns, and J. W. Bridges, *Analyt. Chem.*, 1974, **46**, 94.

[3] C. I. Miles and G. H. Schenk, *Analyt. Chem.*, 1973, **45**, 130.

[4] L. A. King, *Spectrochim. Acta*, 1975, **31A**, 1933.

[5] R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 619.

In the Table, the term $\Sigma\sigma^*$ represents the sum of the two substituent constants at the 5-position of the heterocyclic ring (the C-5 atom is not included). In those cases where the polar constants for particular groups were not listed by Taft,[5] an estimate has been made on the basis of the linear additivity of such constants. For example, the difference in σ^* between the n-propyl and n-butyl groups (-0.02) represents the effect of adding an ω-carbon atom to a three carbon chain. It follows that for 1-methylbutyl, $\sigma^*_{\text{calc.}} = -0.02 + \sigma^*$ (s-butyl). No attempt has been made to derive constants for the 3-hydroxybutyl or *p*-nitrophenyl groups although in the latter case it is expected that $\sigma^* \gg 0.6$.



Correlation of the room temperature fluorescence quantum yields of 5,5-disubstituted oxybarbituric acids in aqueous 0.1M-potassium hydroxide, and the sum of Taft polar substituent constants at the 5-position. The straight line represents the best fit by least squares analysis

Compounds examined

Oxybarbituric acid	$\Sigma\sigma^*$	$(\phi_f)_r$
5-Ethyl-5-(1-methylbutyl)	-0.33	0.57
5-Ethyl-5-s-butyl	-0.31	1.00
5-Ethyl-5-isoamyl	-0.25	0.51
5-Ethyl-5-n-butyl	-0.23	0.46
5,5-Diethyl	-0.20	0.51
5-Allyl-5-(1-methylbutyl)	-0.08	0.079
5-Allyl-5-neopentyl	-0.02	0.057
5-Allyl-5-isobutyl	$+0.03$	0.067
5-Ethyl-5-(1-methylbut-1-enyl)	$+0.15$	0.049
5-Ethyl-5-cyclohex-1-enyl	$+0.22$	0.042
5-Ethyl-5-cyclohept-1-enyl	$+0.27$	0.040
5-Ethyl-5-phenyl	$+0.50$	0.037
5,5-Diphenyl	$+1.20$	0.022
5-Ethyl-5-(*p*-nitrophenyl)		0
5-Ethyl-5-(3-hydroxybutyl)		0.61

From the Table, it will be seen that a rank correlation is present between $\Sigma\sigma^*$ and $(\phi_f)_r$. The Figure shows the almost linear relationship between $\Sigma\sigma^*$ and an empirical function of the relative quantum yield. The correlation (r 0.98) is highly significant ($P \leqslant 0.001$). The limited range of fluorescence quantum yields of oxybarbiturates determined in ethanolic alkali[2] may also be fitted to a similar curve with equally good precision.

DISCUSSION

No previous reports have appeared linking quantum yields of luminescence with the Hammett equation although Ziffer and Sharpless[6] successfully correlated certain photochemical quantum yields.

The data presented here show that differences in the fluorescence quantum yields of oxybarbiturates can be adequately interpreted in terms of the inductive effect operating at the 5-position by using ground-state values of σ^*. The fluorescence quantum yield is increased by electron-donating alkyl groups and decreased by the more electronegative alkenyl and aryl groups. Since compounds with phenyl substituents follow the same relationship as other oxybarbiturates, it is concluded that intramolecular energy transfer, which can be clearly demonstrated[4] at liquid nitrogen temperatures, is not an important route for deactivating the excited state of phenobarbitone and its congeners at room temperature.

The non-fluorescence of 5-ethyl-5-(*p*-nitrophenyl)oxybarbituric acid is consistent with the expected high value of $\Sigma\sigma^*$ for this compound. On the other hand, insertion of an hydroxy-group at the 3′-position in 5-ethyl-5-n-butyloxybarbituric acid has little effect on the quantum yield. Although less data are available, 5,5-disubstituted thiobarbiturates show the opposite effect, *i.e.* quantum yields are increased by electron-withdrawing groups at C-5.[7]

Since the molar absorptivities and the shape of the absorption spectra of 5,5-disubstituted oxybarbituric acids are essentially constant, it follows that the natural lifetime τ_0 of the first excited singlet state of the series is also constant. Absolute fluorescence quantum yields ϕ are related to τ_0 by equation (1) where k_1 is the rate constant for internal conversion.

$$(1/\phi - 1) = k_1\tau_0 \qquad (1)$$

In terms of relative quantum yields, this leads to (2)

$$k_1 = [(1/\phi_f)_r - \phi_0]/\tau_0\phi_0 \qquad (2)$$

where ϕ_0 is the absolute quantum yield of the arbitrary standard. However, no *a priori* relationship exists between k_1 and free-energy changes. For the compounds studied here, it is found that a plot of $1/(\phi_f)_r$ against $\exp(\Sigma\sigma^*)$ is non-linear. Insertion of the data into the empirical equation (3) is also unsuccessful in producing

$$\log\,(\phi_f)_r = \rho^*\Sigma\sigma^* + \text{constant} \qquad (3)$$

a linear relationship, *i.e.* ρ^*, the 'reaction' constant is a function of $\Sigma\sigma^*$. However, if ρ^* is assumed constant over a small range of $\Sigma\sigma^*$ values, then it may be shown from the temperature dependence[8] of the fluorescence intensities of barbitone, quinalbarbitone (seconal), and phenobarbitone that, at least between 278 and 350 K, equation (4) applies where a and b are constants and T

$$\rho^* = -a/T + b \qquad (4)$$

is the absolute temperature. A similar equation applies to many organic reaction series.[9]

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