# The Quenching of Singlet Excited Azo-compounds by Conjugated Dienes

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QUENCHING by piperylene has generally been taken to indicate that a photochemical reaction involves triplet species.[1] However, we now show that piperylene quenches the $n–\pi^*$ *singlet* excited state of certain cyclic azo-compounds, (I) and (II).

(I)   (II)
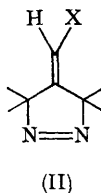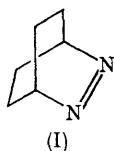
Steel and Thomas[1] recently reported that 2,3-diazabicyclo[2,2,2]oct-2-ene (I) fluoresces strongly ($\Phi_f = 0.20 \pm 0.04$ in iso-octane at 25°). This and the much more weakly fluorescent 2,3-diazabicyclo[2,2,1]hept-2-ene are apparently the only aliphatic azo-compounds which have previously been observed to fluoresce;[1] but we now find that several compounds of the type (II) are fluorescent. For example, the chloro-compound (II; X = Cl)[3] fluoresces rather weakly in hexane solution, the emission spectrum (λ_{max} 450 mμ) bearing an approximate mirror-image relationship to the $n–\pi^*$ absorption band. Overlap of the emission and absorption spectra indicates that the (0–0) transition occurs at 362 mμ (27,600 cm.$^{-1}$), but the absence of fine structure makes this estimate rather rough.
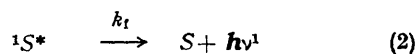
Fluorescence spectra of the azo-compounds were determined for dilute, deoxygenated, hexane solutions containing various amounts of piperylene. Curve A in the Figure shows the relative fluorescence intensity:
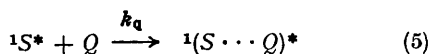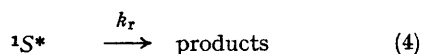
$$\frac{\Phi}{\Phi_0} =$$

$$\frac{\text{fluorescence intensity in presence of piperylene}}{\text{fluorescence intensity in hexane alone}}$$

for 2,3-diazabicyclo[2,2,2]oct-2-ene (1) as a function of diene concentration. A plot of the reciprocal of the relative fluorescence intensity (Φ_0/Φ) *versus* diene concentration (line B) was linear up to at least 2M-diene, giving the least-squares line:

$$\Phi_0/\Phi = 0.998 + 3.34 \text{ [piperylene]}$$

There was no observable overlap between the absorption spectrum of piperylene and the fluorescence spectrum of the azo-compound, so that, even if the (0–0) band of the diene occurs at as long a wavelength as 320 mμ,[4] quenching by direct singlet–singlet energy transfer cannot be significant. The simplest scheme consistent with our results therefore involves quenching *via* an excited complex of the $n–\pi^*$ azo-singlet $^1S^*$ and the diene Q (*cf.*, refs. 5 and 6):

$$S \xrightarrow{h\nu} {}^1S^* \qquad (1)$$

$$^1S^* \xrightarrow{k_f} S + h\nu^1 \qquad (2)$$

$$^1S^* \xrightarrow{k_d} S \tag{3}$$

$$^1S^* \xrightarrow{k_r} \text{products} \tag{4}$$

$$^1S^* + Q \xrightarrow{k_q} {}^1(S \cdots Q)^* \tag{5}$$

Step (1) is excitation, (2) fluorescence; (3) includes all radiationless deactivation processes except quenching by diene [Step (5)],[†] and (4) allows for photolytic decomposition.[7] The scheme leads to a fluorescence quenching relationship of the Stern–Volmer type:

$$\Phi_0/\Phi = 1 + k_q[Q]/(k_d + k_r + k_f) \tag{6}$$

which may be rewritten as

$$\Phi_0/\Phi = 1 + \tau_0\Phi_0 k_q[Q]$$

since the quantum yield of fluorescence in absence of quencher $(\Phi_0) = k_f/(k_d + k_r + k_f)$, and the natural radiative lifetime of the excited singlet $(\tau_0) = 1/k_f$. With the values of τ_0 and Φ_q given by Steel and Thomas[2] for compound (I) and the empirical gradient of our Stern–Volmer plot, k_q (the rate constant for quenching of the excited singlet diazabicyclo-octene) becomes $1 \cdot 01 \times 10^7$ l. mole^{-1} sec.$^{-1}$, or approximately 1/2000 of the bimolecular, diffusion-controlled rate constant in hexane at 25°.

Very similar results were obtained for the azo-compounds (II), e.g., for (II; X = Cl), the Stern–Volmer gradient $(\tau_0\Phi_0 k_q)$ was 3·51; but until values of τ_0 and Φ_0 become available for these compounds, no estimate of k_q can be given. In the case of the chloro-compound (II; X = Cl) it is also of interest that the dependence of the initial rate of photolysis (to give methylenecyclopropanes[3]) on piperylene concentration was almost exactly identical with the fluorescence quenching curve.
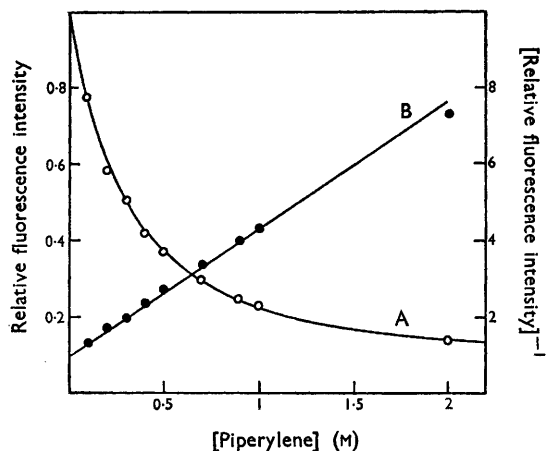

FIGURE. Quenching of fluorescence of 2,3-diazabicyclo-[2,2,2]oct-2-ene by piperylene. A (open circles): relative fluorescence intensity versus piperylene concentration. B (full circles): reciprocal of relative fluorescence intensity versus piperylene concentration

Other points of relevance to this study, which will be discussed in full elsewhere, are that (a) the absorption and fluorescence spectra of the azo-compounds were not shifted by piperylene, and (b) qualitatively similar results were obtained with cyclohexa-1,3-diene as quencher.

Hammond and his co-workers have recently observed the quenching of excited singlets of aromatic hydrocarbons by dienes.[5] With piperylene as quencher, they found that k_q for naphthalene was $1 \cdot 2 \times 10^8$, and for 1-methylnaphthalene $5 \cdot 1 \times 10^7$ l. mole^{-1} sec.$^{-1}$. Piperylene quenching of singlets is evidently a rather inefficient process for both naphthalenes and azo-compounds: but caution in the interpretation of quenching experiments in general is none the less to be recommended.

† Inclusion of an intersystem crossing step $^1S^* \to {}^3S^*$ would affect the kinetic treatment only to the extent that an extra rate constant k_{1c} must then be added to the factor $(k_3 + k_f + k_1)$ in equation (6). However, k_{1c} is probably very small (cf. ref. 3).

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[3] S. D. Andrews and A. C. Day, Chem. Comm., 1966, 667.
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[6] L. A. Singer and G. A. Davis, J. Amer. Chem. Soc., 1967, 89, 158.
[7] C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, J. Amer. Chem. Soc., 1964, 86, 679.