Photoreduction of the n,π^* Singlet of 9,10-Diazaphenanthrene by Triethylamine

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Summary The photoreduction of 9,10-diazaphenanthrene by triethylamine in benzene has a limiting quantum yield of *ca.* 0·8, occurs substantially from the n,π^* singlet state, and gives 9,10-dihydro-9,10-diazaphenanthrene.

TRIETHYLAMINE, TEA, is an efficient photoreducing agent for the n,π^*, π,π^* and charge-transfer triplets respectively of benzophenone,[1] fluorenone[2,3] and *p*-aminobenzophenone.[4] TEA may quench the singlets of fluorenone,[3] and *p*-aminobenzophenone,[4] while it is a photoreducing agent for the n,π^* singlet of the nitrogen heterocycle phenazine.[5,6] We now report the quenching and photoreduction of 9,10-diazaphenanthrene, DAP, by triethylamine.

The low energy n,π^* singlet transition of DAP (400 nm; $\epsilon \sim 400$) in benzene is blue-shifted in alcohol. The first π,π^* singlet transition is at 365 nm in benzene. Fluorescence is observed from the n,π^* singlet,[7] and low temperature phosphorescence is observed from the π,π^* triplet,[7a] 770 nm, 38 kcal mol^{-1}.

In the preparative experiment recrystallized DAP (0·25 g, Aldrich) was irradiated (GE-H-85-A3 lamp) in Pyrex under nitrogen for 12 h in 250 ml of 5% TEA in benzene. Acetylation and work-up gave 9,10-diacetyl-9,10-dihydro-9,10-diazaphenanthrene, m.p. 170—172° (lit.,[8] 170°), indicating that 9,10-dihydro-DAP is produced in the photoreduction. Irradiation at 366 nm of $4 \cdot 26 \times 10^{-4}$M DAP and 0·10M TEA in benzene gives a regular increase in absorption at wavelengths below 400 nm, and subsequent brief exposure to air oxidises the dihydro-compound and almost fully restores the original spectrum. This sensitivity to oxidation by air has been noted previously.[9]

Fluorescence intensities and quantum yields of photoreduction were determined as affected by concentration of TEA in benzene (see Table).

The ratio $\phi_0/\phi(\text{fl})$, is described by the Stern–Volmer relationship, equation (1). The slope, determined graphically or by least-squares analysis, 14M^{-1}, is k_q/k_d, the ratio

$$\phi_0/\phi(\text{fl}) = 1 + k_q[\text{TEA}]/k_d \qquad (1)$$

of rate constant for quenching of singlet by the amine to that for self and solvent induced deactivation.

TABLE

Effect of TEA on fluorescence and photoreduction of DAP in benzene

TEA(M)	$\phi_0/\phi(\text{fl})^a$	$\phi(\text{red})^b$
0·000	1·00	—
0·0304	1·44	—
0·0608	1·87	—
0·122	2·76	—
0·182	3·54	—
0·0046	—	0·07
0·0076	—	0·12
0·046	—	0·41
0·152	—	0·51

[a] Solutions of 10^{-3}M DAP in spectrograde benzene were irradiated at 409 nm in a Farrand spectrophosphorimeter; fluorescence emission was recorded from 400 to 620 nm. $\phi_0/\phi(\text{fl})$ is the ratio of peak heights at 497 nm without and with added quencher, TEA.

[b] Degassed solutions of $8 \cdot 5 \times 10^{-4}$M DAP in 0·004—0·16M TEA in benzene were irradiated at 366 nm on a Bausch and Lomb 38-86-01 monochromator, and spectra were determined after timed intervals on a Cary 14 spectrometer. Rates of photoreduction of DAP were determined from the increase in absorbance at 384 nm. Corrections were applied for light absorption by the product and quantum yields were determined by ferrioxalate actinometry.[10] Quantum yields, $\phi(\text{red})$, were the same under irradiation at 405 nm in the n,π^* band.

The inverse plot of $\phi(\text{red})$ *vs.* TEA is linear, consistent with equation (2), in which k_d is as before, k_r is the rate constant for interaction of the excited compound with TEA, and f is the fraction of these interactions which lead to

$$1/\phi(\mathrm{red}) = 1/\mathrm{f} + k_\mathrm{d}/\mathrm{f}k_\mathrm{r}[\mathrm{TEA}] \qquad (2)$$

reduction. Least-squares analysis gives an intercept, 1·27 ± 0·25, indicating a limiting quantum yield of *ca.* 0·8, a slope of 0·057 ± 0·002 M, and a ratio of slope to intercept, $k_\mathrm{d}/k_\mathrm{r} = 0{\cdot}045\mathrm{M}$, $k_\mathrm{r}/k_\mathrm{d} \simeq 22\mathrm{M}^{-1}$. It appears that k_r for interaction in the reduction process has about the same value as k_q for fluorescence quenching. The observed quantum yield is 0·51 in 0·15M TEA, and fluorescence quenching indicates that 69% of the n,π^* singlet is quenched by TEA at this concentration. Thus photoreduction appears to occur substantially, if not solely, from the n,π^* singlet of DAP. The π,π^* triplet has low energy and may be unreactive.

The theoretical radiative lifetime for DAP, τ_0, may be calculated[11] approximately [equation (3)] in which ν_m is the

$$\tau_0 \approx 3{\cdot}5 \times 10^8/\nu_\mathrm{m}{}^{-2}\epsilon_\mathrm{m}\Delta\nu_{\frac{1}{2}} = 3{\cdot}5 \times 10^{-7}\,\mathrm{s} \qquad (3)$$

absorption frequency, $\simeq$ 25,000 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$ is the half-width of the absorption band $\simeq$ 5900 cm^{-1} and $\epsilon = 400$. The quantum yield of fluorescence, obtained by comparison with that of perylene, is about 0·01. This indicates that the lifetime is $\simeq 3{\cdot}5 \times 10^{-9}$ s, $k_\mathrm{d} \simeq 2{\cdot}8 \times 10^8\,\mathrm{s}^{-1}$, and k_r for the n,π^* singlet of DAP and TEA is *ca.* $6 \times 10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, approaching diffusion control. Similar high rate constants have been observed for photoreduction of phenazine by triethylamine and tri-n-butylstannane,[5,6] also largely *via* the n,π^* singlet. The high reactivity of the n,π^* singlet of DAP and the low reactivity of its π,π^* triplet may be compared to the quenching[3] of the π,π^* singlet and photoreduction of the π,π^* triplet[2] of fluorenone by TEA. Experiments now in progress indicate that dibenzoquinoxaline, which like fluorenone has low lying π,π^* singlet, behaves like fluorenone in that its singlet is quenched and its triplet is reduced by TEA.

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