The Fluorescence of Cyclic Azo-compounds: Determination of Singlet Lifetimes

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WE report recent fluorescence studies on two aliphatic azo-compounds, 2,3-diazabicyclo[2,2,1]-hept-2-ene (DBH) and 2,3-diazabicyclo[2,2,2]oct-2-ene (DBO),[1,2] and the direct determination of the singlet n–π^* lifetime of the latter.

Although n–π^* fluorescence, including fluorescence of nitrogen-containing compounds, is well known[3] aliphatic azo-compounds have not previously been observed to fluoresce. This is generally believed to be due to the fact that either azo-compounds have short photodissociative lifetimes relative to their natural radiative lifetimes, or that other radiationless processes are particularly efficient. However, we have recently observed emission from both DBH and DBO.

In the case of DBH the n–π^* absorption band exhibits one predominant vibrational progression with peaks at 29,530 ($0''$–$0'$ transition), 30,010, 30,480, and 30,970 cm.$^{-1}$. The fluorescence excitation maxima were observed at 29,540, 30,030, and 30,490 cm.$^{-1}$, with the same sequence of intensities as the absorption maxima. The band which should have occurred at 30,970 cm.$^{-1}$ was too weak to be seen on our apparatus. Since there is a relatively large uncertainty (approximately $\pm$ 50 cm.$^{-1}$) in our measurement of the excitation maxima, the excellent agreement is partly fortuitous. The emission spectrum exhibited an approximate mirror-image relationship to the absorption spectrum, maxima occurring at 29,550, 29,140, 28,680, and 28,240 cm.$^{-1}$. Because of the low quantum yield of fluorescence ($\phi_f = 0{\cdot}014 \pm 0{\cdot}0015$ at 1·9 torr and 27°c and for $\nu_{exc1t} = 30{,}770$ cm.$^{-1}$) and the low vapour pressure of DBH (s.v.p. = 2 torr at 25°c), the emission maxima at the longer wavelengths could not be determined with great precision. It is interesting to note, however, that the spacing between the two strongest emission bands (29,550 and 29,140) is 410 cm.$^{-1}$ and that we observed a strong direct absorption for DBH in a KBr disc at 403 $\pm$ 2 cm.$^{-1}$. This is in a region commonly ascribed to ring bending modes.[4]

In contrast to DBH, DBO exhibits a more complex absorption spectrum; in the gas phase more than one vibrational progression can be observed. And although the excitation spectrum is still in good agreement with the absorption spectrum, the

mirror-image relationship between absorption and emission appears to have been lost. These points are illustrated by the spectra shown in Figure 1. Because of the lack of mirror-image relationship we originally thought that the emission was from more than one state, possibly from both singlet and triplet. However, several experiments indicate that the spectrum does in fact correspond only to DBO fluorescence. (a) The shapes of the emission spectra in the gas phase and in solution are identical. (b) At different equilibrium vapour-pressures in the gas phase the shape of the emission is unchanged. (c) The (0″–0′) bands in emission and in absorption appear to coincide, as they very clearly do for DBH. (d) The emission can be quenched by O_2, but no part of the emission is quenched selectively. Results (a) and (b) make it extremely unlikely that the emission is due to the presence of an impurity, while from (c) and (d) it would appear doubtful that any state other than the DBO singlet is participating.[5] An additional reason for believing that only one state is involved is discussed below.

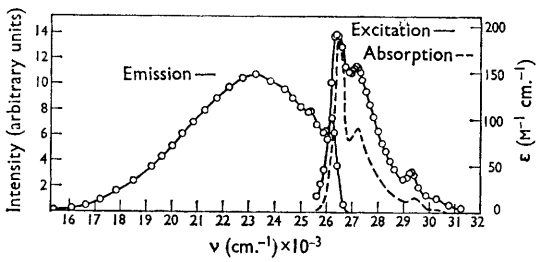

FIGURE 1. *Fluorescence, excitation, and absorption spectra of DBO in iso-octane at 25°. In emission spectrum: resolution = 180 cm.$^{-1}$ at 24·7 × 10^3 cm.$^{-1}$, and* ν *(excitation) = 27·0$_3$ × 10^3 cm.$^{-1}$. In excitation spectrum: resolution = 19 cm.$^{-1}$ at 28·6 × 10^3 cm.$^{-1}$, and* ν *(emission) = 22·2$_2$ × 10^3 cm.$^{-1}$. Absorption maxima are at 26·46, 27·21, and 29·41 × 10^3 cm.$^{-1}$.*

The high fluorescence quantum yield for DBO ($\phi_f = 0{\cdot}20 \pm 0{\cdot}04$ in iso-octane at 25°c) together with the large calculated[6] value of the natural radiative lifetime, τ_0(calc) = 2·9$_4$ × 10^{-6} sec., led us to hope we could determine the lifetime directly by a simple flash technique.[7] A degassed solution of DBO in iso-octane was irradiated by means of an air-spark flash, which decayed from its peak intensity to $1/e$ times that value in $0{\cdot}30 \pm 0{\cdot}04 \times 10^{-6}$ sec.; the emitted light was monitored by a photomultiplier, oscilloscope circuit. Typical traces, one of scattered light from the flash and one of light emitted by the DBO solution, are shown in Figures 2a and 2b, respectively. The exciting light was passed through a Corning 7–39 filter with maximum transmittance at 365 mμ. Various filters were placed between the photomultiplier and the emission port. These included a Corning 3–73 which passes wavelengths above 440 mμ, and interference filters with peak transmittances at 402, 436, 503, and 602 mμ and band passes of about 10 mμ. In no case did the measured emission lifetime depend upon the filter used. This is additional evidence that only one state is involved. The dashed curve in Figure 2b was computed by means of

$$I_{em}(t_1) = \alpha \sum_{j=0}^{i} I_{ex}(t_j)\exp - \frac{(t_1 - tj)}{\tau}$$

α is an arbitrary scaling factor which allows for the fact that the photomultiplier sees unknown and differing fractions of the incident and emitted light. It is chosen so as to make the maximum emission intensity match that for the experiment. The

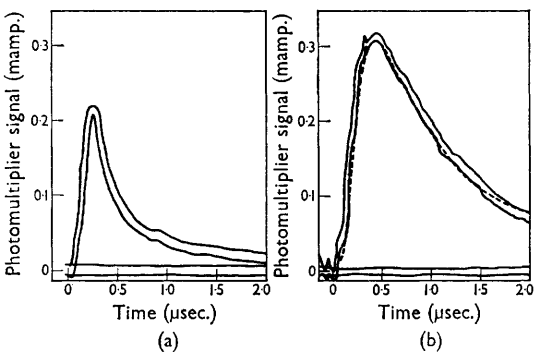

FIGURE 2. *Copies of oscilloscope traces.* (a) *Profile of scattered light from flash. Horizontal trace is for zero signal, recorded in same exposure.* (b) *Profile of emission by DBO in iso-octane. - - - - calculated profile for* $\tau = 0{\cdot}33$ *μsec. Corning filters and neutral density filters were used to eliminate scattered light from* 2b *and reduce photomultiplier current to level recorded in* 2a.

$I_{ex}(t_j)$ were taken from the flash profile of 2*a*, $t_{j+1} - t_j = 0{\cdot}05\mu$ sec., $\alpha = 0{\cdot}433$, and the "best fit" value of the actual fluorescence lifetime was found to be $\tau = 0{\cdot}33 \pm 0{\cdot}05 \times 10^{-6}$ sec. Thus, the experimental result for the natural radiative lifetime is $\tau_0(\text{exp}) = \tau/\phi_f = 1{\cdot}7 \pm 0{\cdot}4 \times 10^{-6}$ sec. This is surprisingly close to the calculated value, considering that Strickler and Berg's derivation of the lifetime formula assumed a strongly allowed transition, whereas the n–π^* transition is generally described as "forbidden." The fact that τ_0(exp) is somewhat smaller than τ_0(calc) suggests that higher order terms in the expansion of Strickler

and Berg's electronic transition moment integral cannot be entirely neglected.

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[4] A. R. Katritzky, "Physical Methods in Heterocyclic Chemistry," Volume II, Academic Press, New York, 1963, p. 173, *et seq.*
[5] Oxygen is thought to quench singlet and triplet states with similar efficiencies (R. Livingston and V. S. Rao, *J. Phys. Chem.*, 1959, **63**, 794.) Thus, unless a postulated triplet state had the same lifetime as singlet DBO, addition of oxygen would have distinguished between the two states.
[6] Using the modified formula of S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814.
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