# THE EFFECT OF DISSOLVED MOLECULAR OXYGEN ON THE FLUORESCENCE OF 9,10-DIMETHYLANTHRACENE AND 9,10-DIPHENYLANTHRACENE

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## Summary

The fluorescence yields of 9,10-dimethylanthracene (DMA) and 9,10-diphenylanthracene (DPA) were measured in degassed cyclohexane and found to be unity. The effect of dissolved oxygen was investigated and the quenching constants were calculated to be $2.3 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$. Particular attention was given to experimental details such as dissolution equilibrium, absorbed light, self-absorption and emission anisotropy.

## 1. Experimental details

9,10-diphenylanthracene (DPA) and 9,10-dimethylanthracene (DMA) were obtained from the Aldrich Chemical Company and were recrystallized three times from cyclohexane (Burdick and Jackson Laboratories; distilled in glass; spectrophotometry grade), the large crystals being again recrystallized and stored in closed vials in the dark. Quinine bisulfate (QBS), obtained from the Eastman Kodak Company, was recrystallized three times from an ethanol–water mixture and similarly preserved. Solutions of the anthracene derivatives in cyclohexane were prepared (using photographic red light in a dark room) at approximately $10^{-4}$ M, diluted by a factor of 10, and the optical densities were accurately measured in the neighborhood of 365 nm using a 10 cm cell in a Cary-14 spectrophotometer so that, at 365 nm, $\epsilon C(10) \approx 0.7 - 0.8$. The solutions were then volumetrically diluted by a factor of 5 to give an optical density of 0.015 in a 1 cm fluorescence cuvette. The two solutions were put into matched fluorescence cuvettes, degassed in vacuum by freeze–thaw cycles and sealed in glass under vacuum. These solutions had solute concentrations of approximately $2 \times 10^{-6}$ M. If the solutions were not kept in the dark prior to degassing, the absorption of fluorescent room light would cause the formation of dissolved singlet oxygen followed by the formation of transannular peroxides. After degassing, the solutions were not subject to this deterioration in the presence of light. It may be noted here that a non-degassed dilute solution of DPA in cyclohexane which had been on the shelf for a number of weeks gave

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only very weak fluorescence when irradiated with 365 nm light. A solution of QBS in 1 N aqueous $H_2SO_4$ was prepared at approximately $10^{-4}$ M, diluted by a factor of 10, and its optical density was measured in a 10 cm absorption cell ($\epsilon C(10) \approx 1.03$) in the neighborhood of 365 nm. This solution was then volumetrically diluted by a factor of 5 to give an optical density of 0.022 in a 1 cm fluorescence cuvette. This solution was approximately $10^{-6}$ M, and was not degassed. This method produced much more reliable data than were obtained by measuring the optical densities of the fluorescence samples in a 10 cm cell. This is important since errors introduced by inaccurate measurement of absorption have a considerable effect on the computed fluorescence yield.

The emission spectra were recorded using a Hitachi–Perkin–Elmer fluorescence spectrophotometer model MPF-2A in right-angle geometry, the excitation wavelength being 365 nm. The slits for the excitation monochromator and the emission spectrometer were set at 3 nm and 2 nm respectively. The spectra were corrected for the wavelength dependence of the emission spectrometer transmission and the photomultiplier sensitivity using a variation of the rhodamine-B method [1, 2]. The emission spectrum of QBS was measured using one of the matched cuvettes. In one set of experiments, after the spectra of the degassed solutions had been recorded, the seal was broken and air was allowed to enter while the fluorescence intensity at 430 nm was recorded as a function of time.

For experiments where pure oxygen was added to the samples, a bulb of oxygen was attached through a grease-free stopcock to the glass system containing the cuvette and the degassing bulb. After each addition of gas the whole apparatus could be removed, the solution poured back and forth between the cuvette and degassing bulb (so that saturation would obtain in the solution phase) and then replaced in position for another measurement of fluorescence intensity. Of course, these maneuvers were performed in the darkened room with the aid of photographer red lamps.

The mass spectra were recorded using a Hitachi–Perkin–Elmer RMU-6H spectrometer.

## 2. Results and discussion

The fluorescence yield calculations were performed as previously reported [1, 2]. These results are summarized in Table 1. It can be seen that the fluorescence yields of DMA and DPA are unity, within experimental error. The emission yield of QBS reported in Table 1 is taken from ref. 2, in which we reported the results of an absolute determination with an estimated error of 7%. The yields reported in this paper are yields relative to that standard, and the accuracy of our present results must derive primarily from that estimation and, in a secondary and less important way, from measurements of the volume, the optical density ratios and the relative emission intensity ratios, all of which we are able to measure to better than

TABLE 1

Fluorescence yields $\phi_f$ of 9,10-dimethylanthracene and 9,10-diphenylanthracene in degassed cyclohexane at 26 °C

| | *Emission* | *Absorption* | $\phi_f$ [a] |
|---|---|---|---|
| DMA in cyclohexane | $190.0_4$ | $44.9_5 \times 1/5$ | 1.00 |
| DPA in cyclohexane | $150.0_9$ | $35.3_9 \times 1/5$ | 1.00 |
| QBS in 1 N $H_2SO_4$ | $140.7_9$ | $51.4_7 \times 1/5$ | 0.56[b] |

Intensities (corrected and integrated) in arbitrary units.
[a]The refractive indices at 365 nm and 26 °C were determined using Cauchy's dispersion formula and the data listed in ref. 3. The values are $1.44_2$ for cyclohexane and $1.34_5$ for aqueous 1 N $H_2SO_4$. The "$n^2$ correction" was used.
[b]See ref. 2.

1%. Thus, we may consider the estimated error in yields to be about 8%, but the ratio of the yields (which is independent of the absolute value of $\phi_f$ for the QBS standard, as well as of all refractive index corrections) can be computed to be 1.00 with an error not exceeding 1%. Thus, any report suggesting a difference in fluorescence yields for DMA and DPA may be spurious and the difference may possibly be due to dissolved oxygen interference prior to, or during, the $\phi_f$ measurements. In addition, deviations of the yield of DPA from unity have been noted (see for example ref. 4, Table 1). We wish to suggest here that, on the basis of our observations, the presence of dissolved oxygen may be an important source of such discrepancies.

When the seal was broken and the fluorescent solution was brought into contact with the atmosphere no sudden decrease in fluorescence intensity at 430 nm was observed since time was required for the oxygen to reach the solution volume under observation. After 1 min the intensity began to decrease, and after 3 - 4 min the decrease stopped and an intensity plateau was reached.

Using $5 \times 10^{-5}$ cm$^2$ s$^{-1}$ for the diffusion coefficient of oxygen in cyclohexane and reasonable boundary conditions, it was not possible to describe the results in terms of a simple diffusion of oxygen to the volume under observation. The short times observed suggest that other mechanisms such as convection are required for the description. The concentration is given as $2.3 \times 10^{-3}$ M oxygen in solution compared with the fluorescing solute at about $5 \times 10^{-6}$ M. The decrease in fluorescence is attributed to quenching of excited singlet molecules (DMA or DPA) by ground state oxygen to produce triplet anthracene derivatives: a collision-induced intersystem crossing [5 - 7]. It should be noted that without oxygen no intersystem crossing occurs since the fluorescence yield is unity for the degassed solutions. Now, if the fully aerated system was continuously irradiated, the fluorescence intensity continued to decrease but much more slowly than before. Whereas previously the decrease was due to the increasing supply of oxygen to the fluorescing volume, here the decrease was due to a combination of three

effects: (i) quenching of excited singlets by ground state oxygen, (ii) a decrease in the concentration of absorbing molecules concomitant with the formation of a transannular peroxide of the anthracene derivatives, followed by replenishment of oxygen and ground state absorbers into the fluorescing volume and (iii) quenching of excited singlets by this peroxide. After a few hours of such irradiation the cuvettes were removed and left in the presence of room light. Subsequent measurements showed that the fluorescence intensity decreased, and the optical density at 365 nm decreased, while a new absorption band at 220 nm appeared. This is the region of peroxide absorption. Subsequently, the solvent was evaporated and the remaining crystals were examined by mass spectrometry. The presence of the peroxide was thus confirmed by mass spectrometry and UV absorption. These results were not observed with the original solutions which were kept in the dark, nor with crystals taken directly from a sample bottle.

Because of the small concentrations used in these experiments, self-absorption of the fluorescence was expected to be negligible, especially for QBS where the overlap of the long wavelength tail of the absorption spectrum and the short wavelength tail of the fluorescence spectrum is very small. However, for DMA and DPA the overlap is much larger. With the possibility of a required correction in mind we measured the fluorescence spectrum of each solution from solutions ranging in concentration from $10^{-5}$ to $10^{-7}$ M and compared the emission profiles at the different concentrations. For the concentrations reported in this paper the short wavelength side of the emission profile did not differ from those at the lowest concentrations investigated. In addition, the light emitted from the degassed solutions used in the yield experiments was passed through a 1 cm cuvette containing a sample of the fluorescence solution, and the concentration in this cuvette was varied. After passing through this cuvette, the light entered the spectrometer in the usual way. For QBS as well as the anthracene derivatives we found that we could accurately determine the optical density of the fluorescing solution in the long wavelength tail of the absorption band without having to take into account Rayleigh or Raman scattering. The optical densities determined in this way were compared with those obtained using concentrated solutions in the Cary-14 absorption spectrophotometer, with excellent agreement. Thus, we can say that for both QBS and the anthracene derivatives the passage of the fluorescence through about 0.5 cm of solution had a negligible effect on the light emerging from the solution–quartz interface, and no self-absorption correction was applied. Furthermore, although the scattered Raman band is under the short wavelength side of the fluorescence spectrum, its contribution to the emission profile was negligible at the light intensities used in these experiments.

We also considered the problem of the emission anisotropy of the fluorescing system. It is known that polarization of fluorescence is a source of systematic errors in the measurement of fluorescence intensity and that quantum yields of emission will be proportional to the light emitted into a

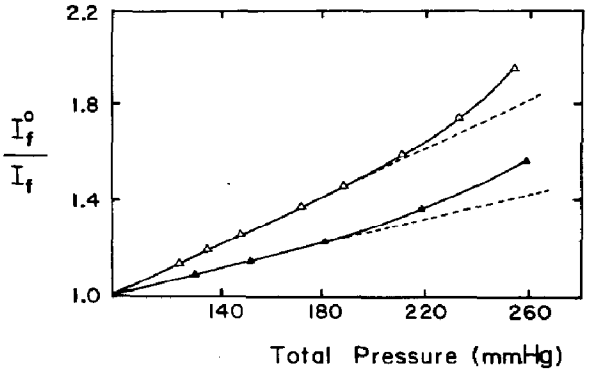


Fig. 1. Stern–Volmer plots of oxygen quenching of DMA (△) and DPA (▲).

given solid angle only under special circumstances, or if the emission anisotropy of the fluorescing system vanishes [1, 8 - 10]. However, the measured emission anisotropy $r$ was in all cases less than 0.04. In addition, the state of polarization of the exciting radiation as well as the polarization effects produced by the analyzing emission spectrometer were determined to be negligible. The corrections would be at least one order of magnitude less than what we conservatively estimate to be our overall experimental error. Figure 1 shows Stern–Volmer plots for DMA and DPA. The intensity ratios were computed by measuring the areas under the corrected emission spectra, and these were plotted against the total measured pressure over the solutions. The least-squares slopes (in linear regions) are 0.0052 $mmHg^{-1}$ for DMA and 0.0027 $mmHg^{-1}$ for DPA. Since the ratio of the oxygen concentration in cyclohexane to the partial pressure of oxygen above the solution is $2.08 \times 10^{-3}/159.6$ mol $l^{-1}$ $mmHg^{-1}$ [11, 12], the values of $k_Q/k_f$ for DMA and DPA are 349 l $mol^{-1}$ and 163.5 l $mol^{-1}$ respectively in the linear region of the plots. If the radiative lifetimes for DMA and DPA are taken to be 14.40 ns and 7.58 ns respectively [13] $k_Q$ is computed to be $2.3 \times 10^{10}$ l $mol^{-1}$ $s^{-1}$ for either substance, the difference in the quenching curves being due entirely to the difference in lifetimes. Now, if the quenching is diffusion controlled, and we take the viscosity of cyclohexane to be $9 \times 10^{-3}$ P at 26 °C, then on the assumption that the quenching diameters of DMA and DPA are the same the computed ratio of quenching diameters for either DMA or DPA to oxygen is about 10 [14].

Figure 1 shows that as the oxygen pressure is increased the curve eventually departs from a straight line. As stated previously, this effect occurs when the peroxide begins to be seen in the system. The steady state kinetics give rise to a description in terms of the following equation:

$$\frac{I_f^0}{I_f} = \frac{[M_0]}{[M]}\left(1 + \frac{k_Q}{k_f}[O_2] + \frac{k_Q'}{k_f}[MO_2]\right)$$

where $k_Q$ is the constant for quenching of singlet excited M by ground state oxygen to give triplet M and $k_Q'$ is the quenching constant for $MO_2$. $[M_0]$ is

TABLE 2

Comparison of experimentally measured and calculated values of radiative lifetimes

| *Solute–solvent* | $\phi_f$ | $\tau$ (ns) | $\tau/\phi_f$ (ns) | $\tau_0$(calc) [a] (ns) |
|---|---|---|---|---|
| DMA–cyclohexane | 1.00 | 14.40[b] | 14.40 | 14.3 |
| DPA–cyclohexane | 1.00 | 7.58[c] | 7.58 | 7.6 |
| DPA–benzene | 0.84 | 7.37[d] | 8.77 | 8.9 |
| | 0.85 | 7.30[e] | 8.60 | 8.5 |

[a]The calculations were done using the Strickler and Berg equation. (The indices of refraction used were $n_f = 1.434$ and $n_a = 1.442$.) (See ref. 15.)
[b]From ref. 16.
[c]From refs. 13 and 17.
[d]From ref. 18.
[e]From ref. 19.

the original concentration of DMA or DPA, prior to irradiation. The deviation from linearity is directly proportional to the $MO_2$ concentration.

Table 2 shows the comparison between experimental lifetimes $\tau$ and calculated radiative lifetimes $\tau_0$. The Strickler and Berg equation adequately describes the results in these cases. The calculated values of the Stern–Volmer constant for quenching of the lowest excited singlet state of DMA and DPA by dissolved oxygen are $2.4 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$ and $2.2 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$ respectively.

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## References

1 J. A. Poole and A. Findeisen, *J. Chem. Phys.*, *67* (1977) 5338.
2 B. Gelernt, A. Findeisen, A. Stein and J. A. Poole, *J. Chem. Soc., Faraday Trans. II*, *70* (1974) 939.
3 D. E. Gray (ed.), *American Institute of Physics Handbook*, McGraw-Hill, New York, 1973, Section 6, p. 3.
W. E. Forsythe (ed.), *Smithsonian Physical Tables*, Smithsonian Institution Press, Washington, DC, 9th edn., 1954, Table 552.
E. W. Washburn (ed.), *International Critical Tables*, Vol. 7, McGraw-Hill, New York, 1930, p. 40.
4 G. Heinrich, S. Schoof and H. Gusten, *J. Photochem.*, *3* (1975) 317.
K. P. Chakravorty, Photophysics and photochemistry of anthracene derivatives, *Ph.D. Dissertation*, Temple University, Philadelphia, PA, 1981.
5 R. Potashnik, C. R. Goldschmidt and M. Ottolenglir, *Chem. Phys. Lett.*, *9* (1971) 424.
O. L. J. Gijzman, *J. Chem. Soc., Faraday Trans. II*, *70* (1974) 1143.

6 G. Porter and M. R. Topp, *Proc. R. Soc. London, Ser. A, 315* (1970) 163.
7 J. T. Richards, G. West and J. K. Thomas, *J. Phys. Chem., 74* (1970) 4137.
8 E. D. Cehelnik, K. D. Mielenz and R. A. Velapoldi, *J. Res. Natl. Bur. Stand., Sect. A, 79* (1) (1975) 1.
9 K. D. Mielenz, E. D. Cehelnik and R. L. McKenzie, *J. Chem. Phys., 64* (1976) 370.
10 P. P. Feofilov, *The Physical Basis of Polarized Emission* (Engl. transl.), Consultants Bureau, New York, 1961, p. 40.
11 A. B. McKeon and R. R. Hibbard, *Anal. Chem., 9* (1956) 1490.
12 T. M. Vermer, L. A. Kiyanskaya and A. S. Cherkov, *J. Gen. Chem. U.S.S.R., 33* (1963) 2281.
13 J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem., 80* (1976) 969.
14 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966, p. 626.
15 S. J. Strickler and R. A. Berg, *J. Chem. Phys., 37* (1962) 814.
16 B. Stevens and B. E. Alger, *J. Phys. Chem., 72* (1968) 2582.
17 D. J. S. Birch and R. E. Imhof, *Chem. Phys. Lett., 32* (1975) 56.
18 W. R. Ware and B. A. Baldwin, *J. Chem. Phys., 40* (1964) 1703; *43* (1965) 1194.
19 J. B. Birks and D. J. Dyson, *Proc. R. Soc. London, Ser. A, 275* (1963) 135.