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Photoreactions and Fluorescence Ageing in Anthracene Single Crystals and Microcrystals at Room Temperature: Note II

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Photoreactions and Fluorescence Ageing in Anthracene Single Crystals and Microcrystals at Room Temperature

Note II†

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Wavelength and intensity changes of fluorescence as results of U.V. irradiation of anthracene single crystals and microcrystals photoexcited in O_2 or N_2 are reported. The hypothesis of formation of new emitters as result of photodimerization is supported by the spectral variations observed.

I INTRODUCTION

Following the early work by Luther and Weigert[1] on the photodimerization of anthracene crystals, recently this reaction has been reinvestigated.[2–4] It has been shown that U.V. irradiation of anthracene gives dimer,[5] photoperoxide[6,7] and anthraquinone[5] depending on the experimental conditions used.

We have already reported the effect of photoreactions on the intensity of anthracene fluorescence.[5] In the present paper we extend our interest to the general behaviour of anthracene fluorescence in relation to defect formations as a consequence of photoreactions in single crystals and microcrystals irradiated in O_2 or N_2. A correlation between the effects found on irradiated single crystals and microcrystals is sought.

† For Note I see Ref. 5.

Recently the change of emission intensity of other aromatic hydrocarbon crystals[8,9] was reported.

II FLUORESCENCE OF ANTHRACENE SINGLE CRYSTALS IN NITROGEN AND OXYGEN AT ROOM TEMPERATURE

The general change of λ_{max} of the fluorescence spectra polarized along (a) and (b) axes of irradiated anthracene under N_2 is shown in Figure 1. The trend of the bands is similar to the one previously reported.[5] That is an initial smooth decrease of intensity is followed by an increase and by a final decay.

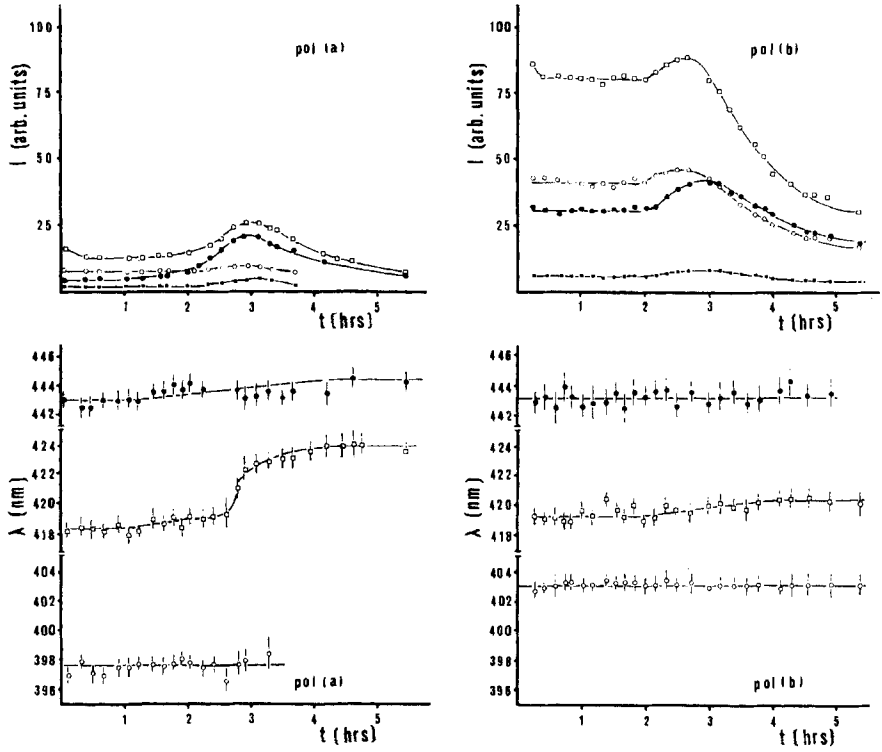

FIGURE 1 Anthracene single crystal irradiated in N_2. Top: variation of I (fluorescence intensity in arbitrary units) against t (hrs of irradiation). Bottom: variation of λ_{max} (nm) against t (hrs of irradiation).

○ band near 398/403 nm
□ band near 420 nm
● band near 443 nm
■ band near 474 nm

All data pertaining to this figure are referred to the same single crystal.

However an interesting feature to be taken into consideration is the variation of the intensity ratios among the bands. This is particularly evident for the band near 443 nm with respect to the 398 nm (a) and the 403 nm (b) bands. In some instances the 443 band, which at the beginning of the experiment is weaker than that at 403 nm, becomes stronger when the 420 nm band increases in intensity.

Following the results already reported[5] on the photodimerization of anthracene, we studied whether this photoreaction may have some effect on the wavelength of the reemission bands. For this purpose λ_{max} of each fluorescence band was measured and plotted vs. the irradiation time in Figure 1 (bottom); the initial and final λ_{max} values for both polarizations are collected in Table I.

TABLE I

Values of λ_{max} (nm) for (a) and (b) polarized fluorescence spectra of anthracene single crystals at the beginning and after long irradiation time.

	pol. (a)			pol. (b)		
Initial values	397.6 ± 0.7	418.3 ± 0.6	443.0 ± 0.7	403.0 ± 0.6	419.1 ± 0.6	443.2 ± 0.9
Final values	397.6 ± 0.8	423.6 ± 0.7	444.0 ± 0.8	403.0 ± 0.7	420.6 ± 0.7	443.2 ± 0.9

When anthracene is irradiated under N_2 a red-shift is found for both polarizations of the band near 420 nm. This behaviour becomes evident after 120 min. of irradiation and is related to the rise of the fluorescence intensity. Within the experimental errors also the 443 nm(a) polarized band shows a similar, smaller effect, whereas the 398 nm(a) and the 403 nm(b) bands were unaffected. The bands near 474 nm were too broad to detect any shift.

Figure 2 shows the general effect of photoreactions in O_2 on the fluorescence emission (the 474 nm band was not measured). As already mentioned,[5] after the initial decay there is a relative smooth increase and after long irradiation the fluorescence becomes undetectable. This behaviour is similar for both polarizations. Owing to the weaker increase compared with that in N_2, the wavelength red-shift of the 419 nm(a) polarized band is less pronounced ($\simeq 1$ nm).

III FLUORESCENCE OF ANTHRACENE MICROCRYSTALS

In order to clarify the effect of the photoreactions of anthracene on the fluorescence wavelengths, we extended our interest to microcrystals. For this

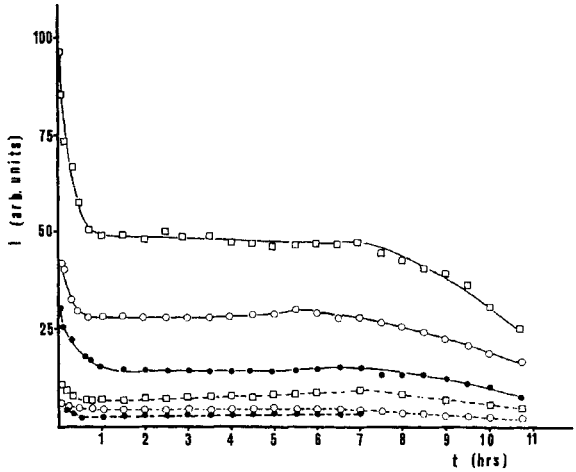

FIGURE 2 Anthracene single crystal irradiated in O_2. Variation of I (fluorescence intensity in arbitrary units) against t (hrs of irradiation).

..... pol. (a)
——— pol. (b)

For ○, □, ●, see Figure 1.

purpose we have studied the effect of long irradiation on the fluorescence of microcrystals (powders) in N_2 or O_2.

An important feature was obtained by plotting the intensity of each band vs. the irradiation time (Figures 3 and 4). During the photoreaction in O_2 there is a steep overall decrease of the intensity and the ratios of the intensity among the bands are changed (Figure 3 top). As a result of irradiation in O_2, microcrystals show a blue-shift of the 425 nm band to 422 nm (Figure 3 bottom), approaching the value reached by the corresponding band of anthracene single crystal in N_2 after long exposure. For comparison see Figure 1 pol. (b).

When anthracene microcrystals are irradiated in N_2 there is no evidence for band shift within the experimental errors even where a change in intensity is recorded (Figure 4).

IV DISCUSSION AND CONCLUSION

The above reported results may be correlated by considering that the photodimerization of anthracene in N_2 gives rise to new emitter centers formed as the reaction proceeds.[5] The variations reported for the intensities and wavelengths of fluorescence emission suggest that these new emitters

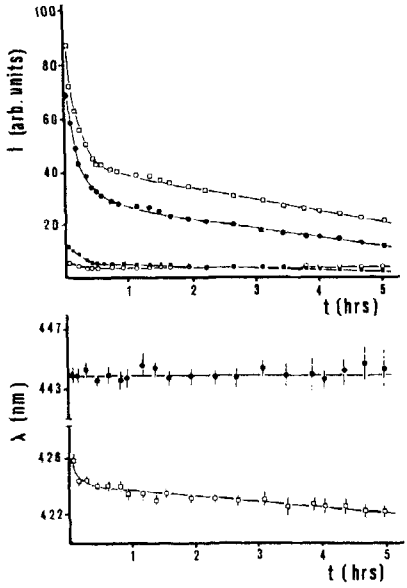

FIGURE 3 Anthracene microcrystals irradiated in O_2. Top: variation of I (fluorescence intensity in arbitrary units) against t (hrs of irradiation). Bottom: variation of λ_{max} (nm) against t (hrs of irradiation)

For ○, □, ●, ■, see Figure 1.

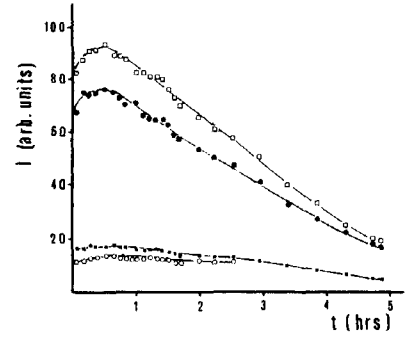

FIGURE 4 Anthracene microcrystals irradiated in N_2. Variation of I (fluorescence intensity in arbitrary units) against t (hrs of irradiation).

For ○, □, ●, ■, see Figure 1.

may have a characteristic unpolarized fluorescence spectrum which superimposes that of the bulk in the region 410–455 nm. In fact by subtracting the spectrum recorded for (b) polarization before the increase of fluorescence intensity ($\simeq$60 min.) from the one taken at the maximum of such increase ($\simeq$162 min.), a curve with maxima near 426 nm and 443 nm is obtained. By repeating this procedure for the (a) polarized spectra taken at $\simeq$54 min. and $\simeq$157 min. of irradiation the same curve was obtained (Figure 5).

Supposing that this curve is associated with the spectrum of these emitters, it is possible to explain the red-shift of the band near 420 nm of the irradiated single crystals—(418.3 → 423.6 nm) pol. (a) and (419.0 → 420.6 nm) pol. (b)—as caused by the superimposition of the above 426 nm band. The spectral variations due to the unpolarized fluorescence of new emitters are enhanced on the (a) polarization because of its lower intensity.

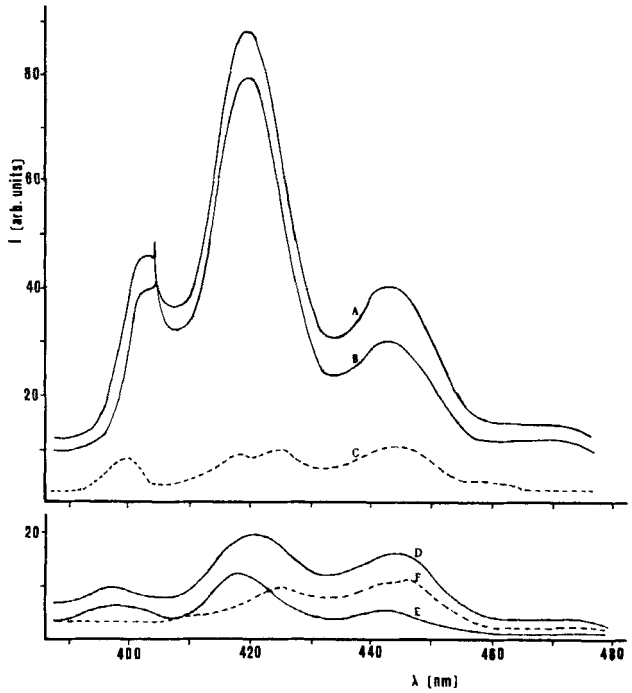

FIGURE 5 Anthracene single crystal irradiated in N_2. Top: pol. (b) A, B: fluorescence spectra recorded after $\simeq$162 min. and $\simeq$60 min. of irradiation.

C = A–B (see text).

Bottom: pol. (a) D, E: fluorescence spectra recorded after $\simeq$157 min. and $\simeq$54 min. of irradiation.

F = D–E (see text).

The above spectra refer to the same experiment as reported in Figure 1.

In order to explain why in O_2 the fluorescence intensity of single crystals increases after the initial steep decrease and why the shift of the bands is less pronounced, it is necessary to invoke that the new emitters are sites of high reactivity for the photooxidation. Therefore the above photoreaction is competitive with fluorescence and the general result is a smooth increase of intensity.

Following the above model it is possible to understand also the behaviour of microcrystals irradiated in N_2. Microcrystals have a high number of defects whose effect is supposed to be similar to that already described for the new emitter centers obtained by irradiation of single crystal in N_2. As the photodimerization proceeds in powders, new centers are formed having a spectrum similar to that of edges or cracks already present in high number. Under these conditions the fluorescence intensity may increase very little at the beginning of irradiation (Figure 4), and the wavelengths remain unchanged.

To find a correlation between the irradiation of microcrystals in O_2 and the blue shift recorded, we subtracted from the initial spectrum in O_2 those taken at increasing irradiation time (within 30 min.). The curves obtained (Figure 6) have the same maxima near 426 nm and 443 nm already found using this procedure for the intensity increase of single crystal in N_2. Therefore we assume that oxygen reacts preferentially at defects, like edges or

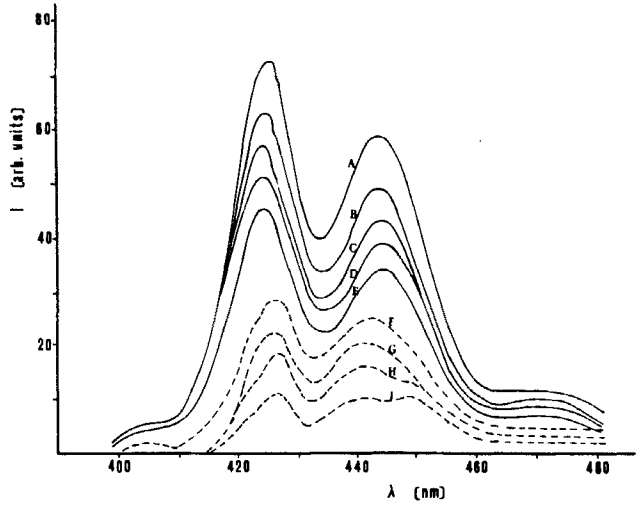

FIGURE 6 Anthracene microcrystals irradiated in O_2. A, B, C, D, E: fluorescence spectra recorded after ≃5 min., ≃9 min., ≃14 min., ≃18 min., ≃27 min. of irradiation.

I = A–B; H = A–C; G = A–D; F = A–E (see text).

The above spectra refer to the same experiment as reported in Figure 3.

cracks, quenching more effectively the emission from such defects than the emission from the bulk. As a result the spectrum of microcrystals in O_2 (Figure 6), which differs from the one of single crystals at the beginning of the photoreaction (Figure 5) approaches, by a blue-shift, the long exposure spectrum of single crystals in N_2.

The role of defects on the fluorescence emission has been recently reviewed.[10]

V EXPERIMENTAL

Anthracene was purified by zone refining (over 70 passes) and the absence of the usual impurities (e.g. carbazole) was tested by a Perkin–Elmer F 30 gas chromatograph equipped with an apiezon L column.

Microcrystals of anthracene, obtained by sublimation under CO_2, were collected and placed within two silica disks in an appropriate cell for gases.

All other experimental conditions were those reported in Ref. 5.

The reproducibility of the results collected was checked by taking over 15 runs for every kind of experience.

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