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The Effect of Long Irradiation on the Fluorescence Emission of Anthracene Crystals at Room Temperature

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The Effect of Long Irradiation on the Fluorescence Emission of Anthracene Crystals at Room Temperature

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Microphotographs showing the effect of increasing irradiation time of anthracene single crystals are reported and the surface effect correlated to the fluorescence emission changing.

The interest aroused in recent years in the photoreactivity of anthracene in the solid state[1] stimulated us to study anthracene fluorescence and its changes due to the photoreactions brought about by long exposure to U.V. radiations. Preliminary results[2a,b] already reported on the effect of photoreactions on fluorescence of anthracene at room temperature show spectral variations connected with the progress of the photoreactions (dimerization and photo-oxidation). Experiments carried out under N_2 gave evidence, besides an overall decrease of emission intensity, of a red shift of the 420 nm band particularly prominent for the *a* polarization.[2b] The latter behaviour was explained by assuming that new emitters appeared as the result of damage caused by the photodimerization. In fact an effect associated with the superimposition of an unpolarized spectrum on those taken for *a* and *b* polarizations was suggested. Recently the effect of long irradiation of anthracene at room temperature was studied with respect to the fluorescence emission at low temperatures.[3,4]

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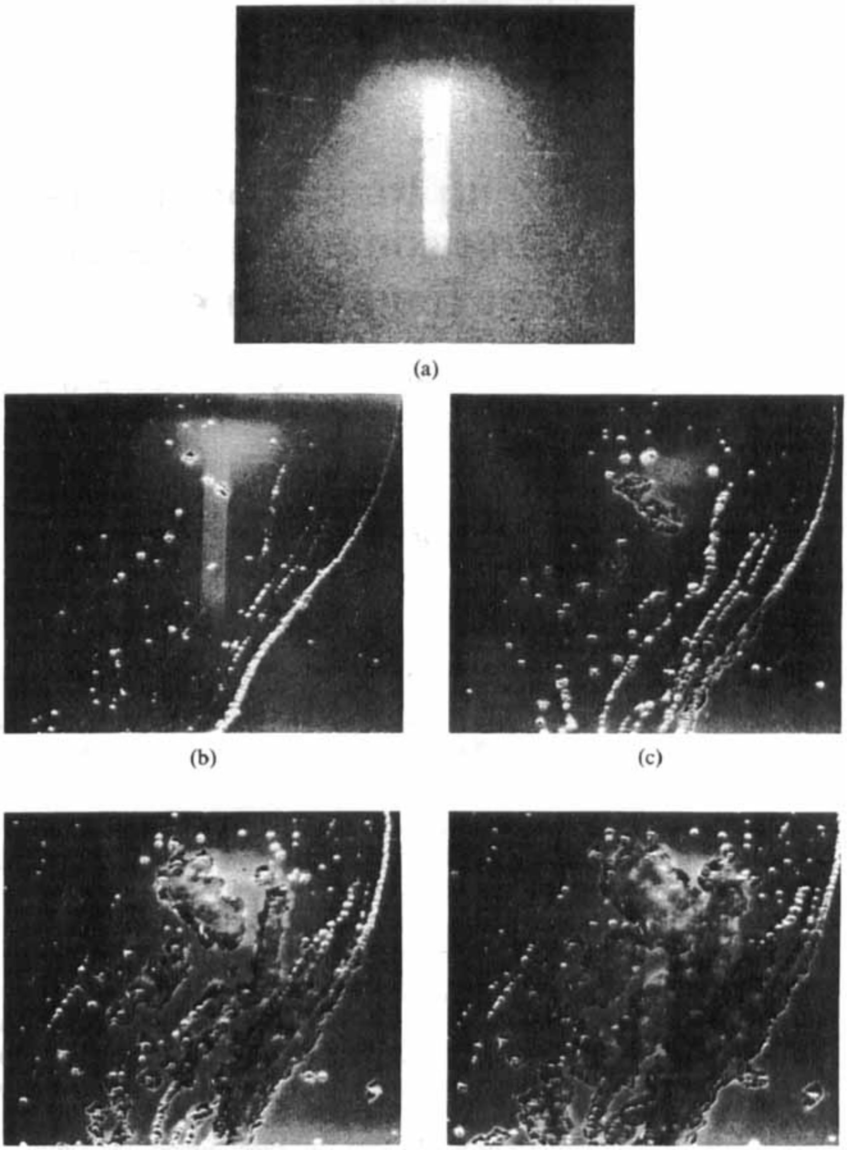

(a)

(b)

(c)

(d)

(e)

FIGURE 1 Microphotographs (magn. × 71) of a single crystal of anthracene at increasing irradiation time. (a = 31 min; b = 96 min; c = 173 min; d = 232 min; e = 300 min) showing the surface change and the image of the slit taken as reported in the text. Slit dimensions were $7.89 \cdot 10^{-2} \times 0.53$ mm.

New evidence supporting the above hypothesis is now added by taking into consideration the fluorescence spectra of anthracene single crystals during irradiation in N_2 in conjunction with detailed microscopic observations of the irradiated surface. For this purpose, anthracene single crystals prepared as previously reported[2a,b] were mounted in an optical cell flushed with N_2. The fluorescence emission obtained by exciting the sample with front face arrangement (G.E.C. Hg 250 W lamp, Chance Pilkington OX1 filter) was allowed to pass through a Wollaston prism and focused on the slit of a E 778 Hilger Spectrograph equipped with a 1P 28 phototube and a Perkin–Elmer 196 recorder. In order to ascertain which portion of the surface of the irradiated crystals was responsible for the recorded spectra, a microscope connected with an Exakta VX1000 camera (equipped with a green filter cutting out the exciting light at 365 nm), was mounted behind the irradiated thin crystal.

By this arrangement photographs of the fluorescing crystal during progressive irradiation were obtained. In addition the light of an external lamp, focused on the plane of spectrograph plate holder, was allowed to pass inside the instrument through a reverse path. An image of the slit was projected on the crystal surface. By this procedure photograms of both irradiated crystal surface and slit image could be taken and correlated with the fluorescence spectra recorded at the same irradiation time.

In Figure 1 a number of photographs obtained at increasing irradiation times are collected and the corresponding spectra (*a* polarization) are shown in Figure 2. While Figure 1a shows no surface damage, Figures 1b,c,d,e illustrate the progressive effect of irradiation on the surface of the crystal with particular evidence to the portion "seen" by the slit. The effect of long irradiation on the emission intensity is then correlated with the surface damage as evident from a comparison of Figure 1c and 1a (taken at 173 and 31 min of irradiation respectively). In fact Figure 1c corresponds to a spectrum which is more intense in the region 410–460 nm and red-shifted with respect to the spectrum recorded after 31 min (Figure 1a). Moreover the intensity decrease is seen to be connected with the progressive spreading of the non-fluorescing dimer on the area covered by the slit (cfr. Figure 1c, d, e, with Figure 2c, d, e). It is noteworthy that the zone of the crystal "seen" by the slit is the same as that on which the exciting light is focused.

The above results are of supporting evidence to the conclusions already given[2a] on the grounds of visual observations of the crystal. Now microscopic examination shows that at 173–232 min, the portion of surface "seen" by the slit has been progressively occupied by unemitting dimer and by zones of localized fluorescence emission (new emitters); however small portions of unreacted anthracene surface are still present. (A similar behaviour has also been reported by Craig and Rajikan[4] during a study of the influence of

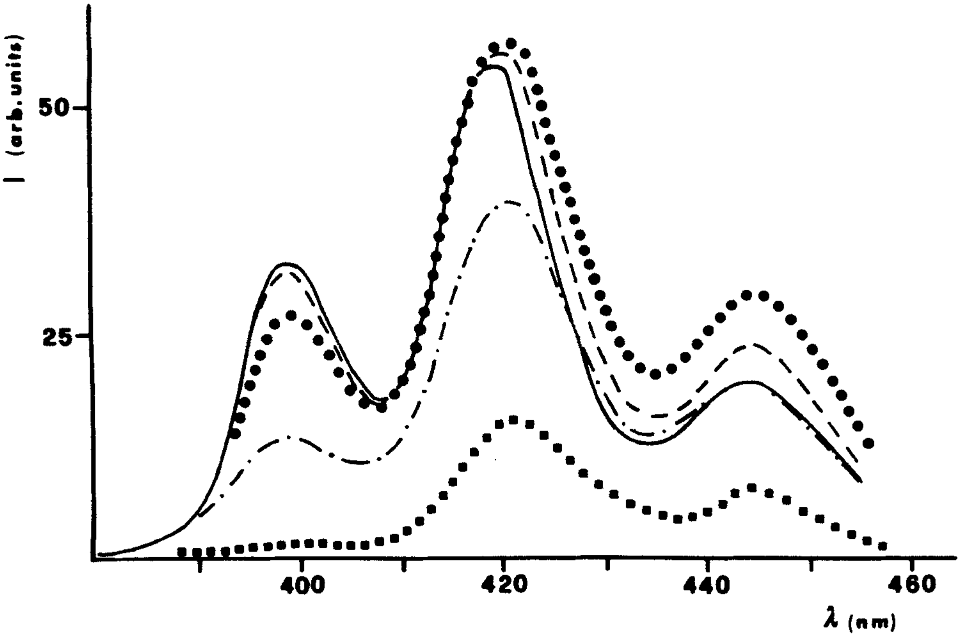

FIGURE 2 Fluorescence emission of anthracene single crystal (pol. *a*) after 31 min ——— a; 96 min - - - b; 173 min ● ● ● ● c; 232 min -·-·- d; 300 min ■ ■ ■ ■ e of irradiation. Surface changes are those reported in Figure 1.

radiation on anthracene crystals at room temperature.) A typical room temperature fluorescence spectrum taken at this stage is that reported in Figure 2d. The importance of the new emitters of the anthracene spectrum is shown mainly by the hyperchromic effect of the 446 nm band with respect to the 400 nm one.

Moreover an interesting feature is the spectrum recorded after long irradiation (~300 min). Even if characterized by a different intensity ratio, this spectrum has the same peak wavelengths as those found[2b] in the "difference" curve obtained by subtracting from the spectrum at the maximum of intensity that one recorded before the intensity increase. We have suggested[2b] that such "difference" curve may be correlated with the effect of the new emitters. In fact after long irradiation the reemitted light from the new emitters is prominent giving rise to a red-shifted spectrum which is of low intensity (because of progressive quenching).

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