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On the Fluorescence of 9-Cyanoanthracene

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On the Fluorescence of 9-Cyanoanthracene

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Abstract—The polarized green fluorescence of 9–cyanoanthracene crystals is reanalysed and found to be structured.

The green emission is progressively weakened by irradiation, and becomes replaced by a blue fluorescence.

Introduction

Solid state photoreactions have received a great deal of attention in the last years.[1] The irradiation of anthracene[2,3] and anthracene derivatives[3] was studied either for spectroscopic purpose[2] or to have more information on the products formed in the solid state.[3]

During the photochemical dimerization of 9–cyanoanthracene[3] under irradiation with the light of mercury lamp (filtered with an 0×1 Change Pilkington filter) a progressive change in the fluorescence was observed, in agreement with earlier work under different conditions.[4] The fluorescence spectrum is now remeasured and compared with that reported in the literature.[4] Important points of difference have stimulated us to reanalyse the fluorescence emission of 9–CNA in order to have additional information on the nature and properties of the solid state photoreaction involved.

Fluorescence emission of 9–CNA

Thin crystals ($\simeq 10\mu$) of 9–CNA prepared by sublimation were mounted on a pinhole drilled in a brass disk. This method of

mounting was found important to isolate a central portion of the crystal away from the edges which acted as emission sites, if irradiated, even at the very beginning of the exposure. In fact, under the microscope the major part of the green fluorescence from a free sample could be seen to be reemitted from edges or surface imperfection on the crystal.

From a masked crystal the green fluorescence was very weak at the beginning of the exposure to the mercury light and at first increased in intensity as new emitting centres appeared in the irradiated area. The green fluorescence recorded was different in detail from that reported in the literature.[4] The main feature was the presence of vibrational structure as shown in Fig. 1. After increasing in intensity to a maximum this green fluorescence emission decreased. At the same time, after 20–30 minutes exposure under our conditions, a blue emission appeared, and eventually (after $\simeq 100$ minutes) completely replaced the green. Figure 2 shows the two spectra together.

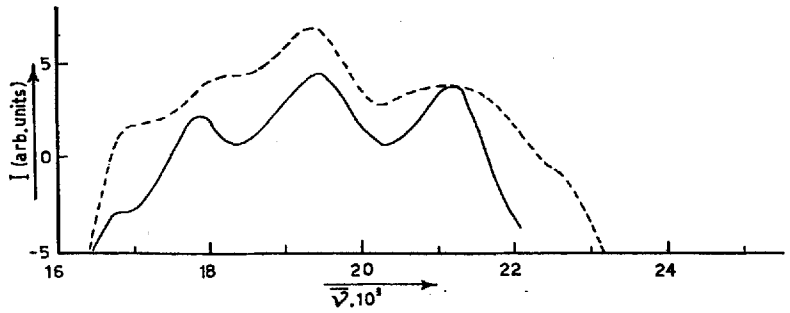

Figure 1. Fluorescence of 9-cyanoanthracene crystal at beginning of exposure to the mercury light.
– – – – emission parallel to the (*a*) axis
——— emission parallel to the (*c*) axis

The fluorescence was found to be polarized with the (*a*) polarization more intense for the green band but less intense for the blue. By irradiating a powder of 9-CNA (microcrystals) an intense green structured fluorescence is obtained from the beginning. This seems to be due to the large number of preformed traps

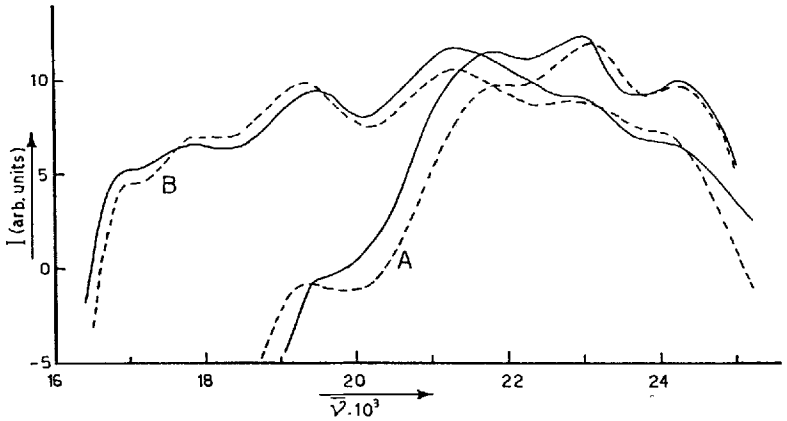

Figure 2. Fluorescence of 9–cyanoanthracene crystal: (A) after 100 minutes of exposure; (B) after 24 minutes of exposure.
– – – – emission parallel to the (*a*) axis
——— emission parallel to the (*c*) axis

(edges . . .) which act as reemitting sites whereas in well-formed crystals the emitting centres appear only in the course of irradiation.

Experimental

9–cyanoanthracene samples were prepared by sublimation in a metal crucible. The light of a mercury lamp (Mazda 250W) filtered with a Change Pilkington 0 × 1 filter was focused on the sample. The fluorescence light, passed through a Wollaston prism, was analysed with a E 742 Hilger-Watts spectrograph. The spectra were recorded on photographic plates and measured on a Hilger microphotometer. Iron arc spectrum was used for calibration.

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