Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Photoreactions and Fluorescence Ageing in Crystalline Anthracene

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Version of record first published: 21 Mar 2007.

To cite this article: D. Donati , G. G. T. Guarini & P. Sarti-fantoni (1973): Photoreactions and Fluorescence Ageing in Crystalline Anthracene, Molecular Crystals and Liquid Crystals, 21:3-4, 289-297

To link to this article: http://dx.doi.org/10.1080/15421407308083324

Molecular Crystals and Liquid Crystals. 1973. Vol. 21, pp. 289–297
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Printed in Great Britain

Photoreactions and Fluorescence Ageing in Crystalline Anthracene

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Received August 4, 1972

Abstract—Fluorescence changing of anthracene crystals in air, O_2, N_2, recorded at room temperature is reported. Two different products formed under irradiation of anthracene were isolated and recognized as anthracene dimer and anthraquinone. A correlation between the above fluorescence change and the photochemical behaviour of anthracene was found.

1. Introduction

In previous papers the ageing of green fluorescence of irradiated 9-CN, anthracene(1,2) together with the growth of surface defects(3) was reported. 9-CN, anthracene crystals are known to react, under irradiation with mercury light, to give the trans-dimer.(4) The thermal behaviour of anthracene and anthracene derivative photodimers was also studied.(5,6) Because of the importance of defects(3,7,8) with respect either to the solid state reactions or to the fluorescence,(9) we have now studied in this respect, the effect of irradiation on anthracene crystals and have searched for defects induced by the exciting light. The surface changes in irradiated anthracene crystals were followed microscopically and correlated with the photo-products formed. The fluorescence of anthracene is widely studied either at low temperatures(9,10) or at room temperature.(11) Craig and Akon(12) reported that irradiated anthracene crystals showed an ageing effect when exposed to exciting light even in the absence of oxygen. The literature refers also to other cases of fluorescence decay of irradiated anthracene.(13†,14,15)

Studies of photocurrents have shown the presence of photoperoxide and anthraquinone on irradiated anthracene.(16,17)

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† We could not examine the original manuscript.

2. Fluorescence of anthracene crystals in air, oxygen and nitrogen at room temperature

The change in intensity of the 421 mμ b-polarized band recorded during the irradiation of anthracene single crystals in air is reported in Fig. 1. The polarized emission along the a-axis behaved similarly.

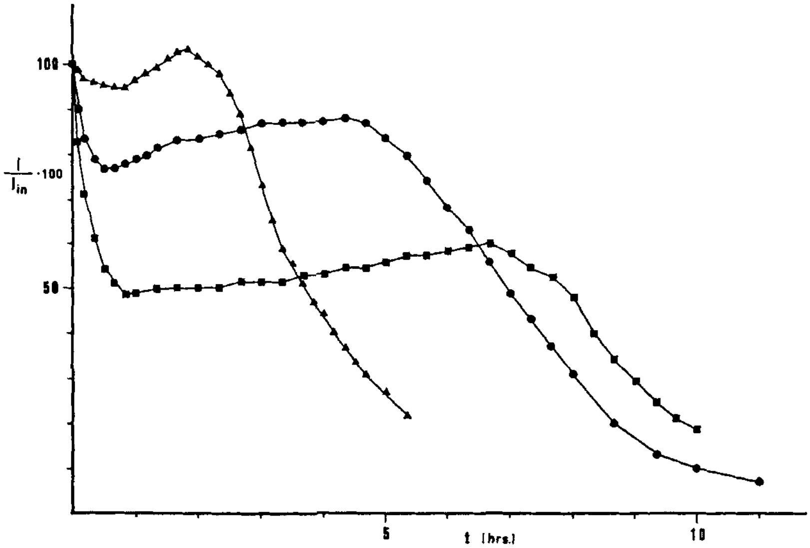

Figure 1. Percentual intensity variation of 421 mμ fluorescence peak of anthracene as a function of irradiation time respectively in: air, ●; nitrogen, ▲; oxygen, ■.

I = intensity at time t; I_{in} = initial intensity.

At the beginning of the experiments there was a decay of reemission ($\simeq$ 20–30%) in both polarizations within 20–30 min of exposure to the exciting light under our experimental conditions. Then the fluorescence smoothly increased for 6–7 h ($\simeq$ 10%); after that the reemitted light intensity decreased significantly to undetectable values for long exposures.

As anthracene crystals have been reported to give both photooxides(15,16,17) and the photodimer(4) under UV irradiation, we investigated whether the formation of the above photoproducts could be correlated with the observed fluorescence behaviour. For this purpose we examined the fluorescence of anthracene single crystals in dry oxygen and dry nitrogen respectively.

In O_2 the initial decrease is particularly steep: $\simeq$ 40–50% within 20–30 min. After that the fluorescence increased for $\simeq$ 6–7 h and then decreased to undetectable values (Fig. 1).

Anthracene had a different behaviour in N_2; in fact the fluorescence decrease of the first period was found to be very small (5–10%) or absent in some cases. After that the reemission increased to a maximum and then decreased (Fig. 1).

In all cases reported it was possible to define three regions of reemission, i.e.

(i) initial decrease (small for N_2)
(ii) smooth increase
(iii) final decrease to undetectable values

of which the relative importance† will be discussed later.

3. Microscopic examination of anthracene crystals in air, oxygen and nitrogen

Because we found it important to check whether there was a change on the surface of the crystal, we introduced from time to time, a right angle microscope between the sample and the spectrograph during the experiments reported in the previous section.

Under these conditions, during the first fluorescence decrease it was possible to notice that, in air, linear nuclei parallel to the a-axis appeared on the crystal surface within 1 min. By taking micrographs at successive irradiation times it was possible to follow the growth of these nuclei. This effect is shown in Fig. 2. Regions of crystal which received stronger irradiation showed a high number of shorter linear nuclei. The plot in Fig. 3 shows that the linear nuclei grew rapidly within 5–10 min and then maintained the same length. Typical dimensions were 50 μ × 2 μ.

Longer irradiation of anthracene crystals produced lance-shaped areas enclosing one or two linear nuclei (Fig. 4). The above areas were found to be elongated parallel to the a-direction of the crystal. The observations in crossed nicols showed that these areas differed in brightness from the unchanged crystal portions. Cracks mainly

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† The initial intensities of fluorescence and the extent of regions (i, ii, iii) are strongly dependent on several parameters (intensity of the irradiating light, crystal thickness . . .).

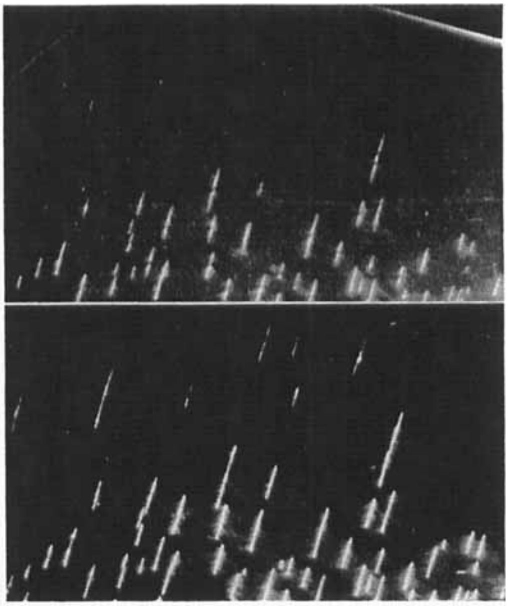

Figure 2. Growth of linear nuclei (needles) on irradiated anthracene surface (× 120).

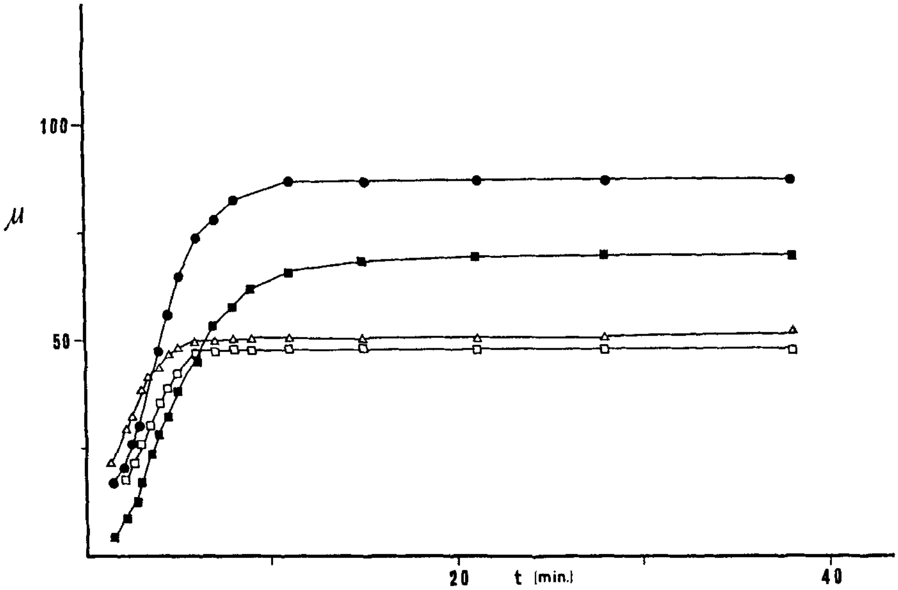

Figure 3. Plot of the length (μ) of 4 linear nuclei (needles), as grown on the same crystal surface, vs. time.

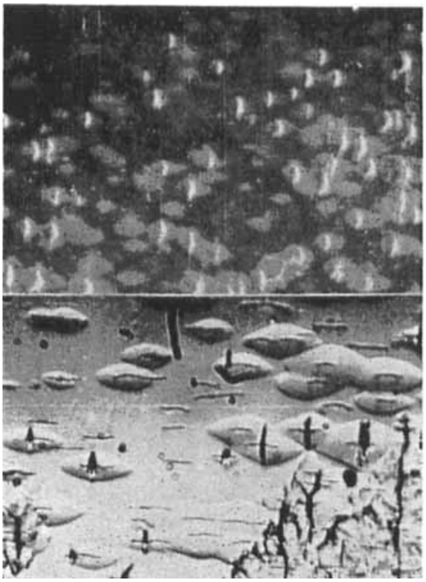

Figure 4. Irradiation of anthracene crystal in air: lance-shaped areas, linear nuclei (needles) and cracks are shown in fluorescence (top × 120) and in transparence (bottom × 170).

parallel to *b*-axis appear in the lance-shaped areas after prolonged irradiation (Fig. 4). Further exposure (7–9 h or more) gave rise to non fluorescing areas revealed as black spots which grew with the irradiation time and covered all the crystal after very long exposure (Fig. 5).

Water vapour was found to be very important for the growth of the linear nuclei. In fact when anthracene was irradiated in oxygen or dry air, linear nuclei were absent or very few in number, while the crystal appeared yellow after long irradiation. The absence of linear nuclei was also observed under nitrogen but in this case the crystal did not turn yellow even when the surface appeared damaged owing to the prolonged irradiation.

Following Russian authors,(13) we irradiated anthracene crystals dipped in water and found that the fluorescence decreased even in this case. This was in contrast with the findings of the above authors who reported no variation in the fluorescence yield when the sample was dipped in water. Microscopic examination of the crystal irradiated under water showed that most of the mentioned nuclei grew out of the sample surface (Fig. 6). This observation enabled us to consider the above surface nuclei as a new kind of the needle-shaped crystals which in some circumstances (wet air) grew epitaxially on the anthracene surface.

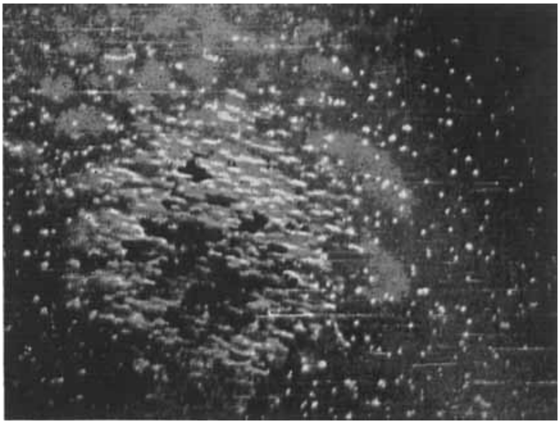

Figure 5. Irradiation of anthracene crystal in oxygen: bright emitters (cracks) and black spots are shown at the maximum of the emission (6–7 h.) × 95.

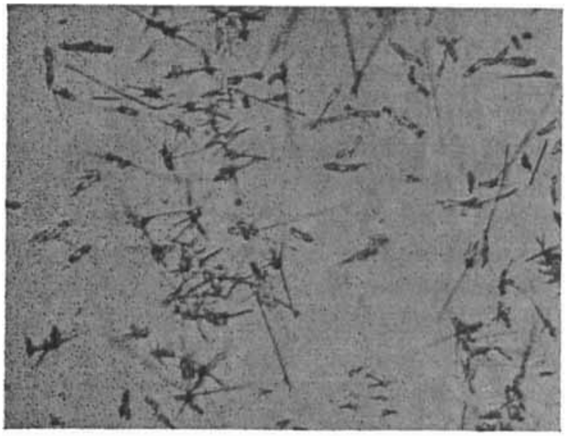

Figure 6. Anthraquinone needles emerging from the surface on anthracene crystal irradiated under water (× 375).

4. Detection of anthraquinone and anthracene dimer

The results reported in previous sections prompted us to investigate the chemical nature of the needles observed upon the irradiated anthracene surface and to search for the presence of anthraquinone whose photoformation has been reported.(16) Accordingly the new material (needles) was obtained by irradiating with low intensity UV light in presence of air and water vapour. Repeated treatment allowed us to collect enough product to record an IR spectrum. The unknown product was recognized as anthraquinone by comparison of the IR spectrum in KBr with that of an authentic sample.

The non fluorescing areas formed after long irradiation were identified as anthracene photodimer. In fact the IR spectrum of an anthracene crystal irradiated in N_2 atmosphere for 48 h was identical to that of a sample of pure anthracene dimer in KBr.

5. Conclusion

The microscopic examination and the fluorescence of anthracene crystals recorded in different conditions suggest that the first decay in air and oxygen is related to photooxidation leading to anthraquinone, which crystallizes epitaxially in presence of water vapour as long needles parallel to the *a*-axis of anthracene. The importance of the presence of water is not easy to explain, but it could be correlated to the photoelectret behaviour shown by anthracene.(18)

The initial decay is followed by a smooth increase in fluorescence within 1–7 h ($\simeq 10\%$). Microscopic examination showed that this effect was concomitant with the growing in number of the cracks parallel to the *b*-axis which appeared as brighter emitters than the bulk of the crystal (Fig. 4). This effect is associated with new emitters originating near the cracks.

The final decay is connected with a progressive spreading of the non reemitting areas (dimer) on the portion of the crystal surface which is focused on the slit.

In the anthracene crystals irradiated in a N_2 atmosphere, the initial decay of fluorescence, if present, is strongly reduced supporting the idea of photooxidation as the main cause of the decays reported for O_2, and air.

The above fluorescence decay in N_2 may be due to a very small oxygen amount present in spite of the N_2 flux or to any other different quenching mechanism. Again the progress of photodimerization causes lance-shaped areas and cracks which are responsible also in this case for the increase of the reemitted light ($\simeq 10\%$). The successive decay of fluorescence is due to the formation of black spots as in the cases previously described (O_2 and air).

6. Experimental

Anthracene previously zone refined (over 70 passes) was sublimed in a crucible to give single crystals in presence of air or CO_2. As far as the above reported results are concerned crystals grown under these two conditions were found to behave similarly. Samples used were 1.5–5 μ thick. In order to avoid strain effects,(9a) anthracene crystals were freely mounted by sticking, with stopcock grease, only one corner out of the irradiated portion of the crystal.

O_2, N_2 and dry air experiments were performed by using a cell in which the above gases were flowing during the whole experiment. In all cases special care was devoted to record the fluorescence only from well-formed portions of the crystal surface(3) by using the Hartmann diaphragm.

The anthraquinone needles were swept from anthracene by dropping methanol over the surface of the crystals.

The light of a Mazda lamp (250 w) filtered with a Chance Pilkington filter OX1 was focused on the sample with a front face assembly. The fluorescence emission passed through a Wollaston prism, was analysed with a Hilger–Watts E 778 spectrometer equipped with a RCA 1P 28 photomultiplier and registered with a Perkin Elmer 196 recorder.

All fluorescence experiments were carried out at room temperature.

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