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Fluorescence and Photoreactivity in Crystalline Anthracene and Some Related Derivatives

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Following fluorescence microscopical investigations a photochemical cycle is established to rationalise the behaviour of anthracene, anthracene 9,10 epiperoxide, anthraquinone, anthrone and di-*p*-anthracene when these compounds are exposed to u.v. irradiation under different environmental conditions. It is proposed that a green emitting intermediate, akin to an anthracenic excimer, is pivotal in this cycle and that the interconversions occur topotactically.

INTRODUCTION

In recent years there has been considerable interest in the solid-state photo-reactivity of anthracene(I) and its derivatives. The topochemical preformation theory of Cohen and Schmidt¹ may be applied in many cases when a parent molecule undergoes photo-dimerization to a daughter structure but the 9-substituted and 9,10 disubstituted anthracenes² yield centrosymmetric dimers instead of the mirror symmetrical units predicted by the theory. In several instances, notably in anthracene itself and its 9-CN derivative defects have been shown to exert a controlling influence on the reaction. However, the photo-reactivity of anthracene is very sensitive to the experimental conditions employed and the photodimer is but one of many products that can be formed by varying the atmosphere surrounding the crystals.³ Numerous photo-oxidation products can be formed and in several cases the full crystal structure

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data for these have been reported. One of these products, anthracene 9,10 epiperoxide(II), upon X-ray irradiation⁴ was found to undergo a single crystal \leftrightarrow single crystal transformation to a mixture of anthraquinone(III) and anthrone(IV). The space group remains invariant but the products are always twinned in a manner which is related to the unit cell of the parent.⁵ Since the structures of anthracene, anthracene 9,10 epiperoxide, anthraquinone and anthrone are closely inter-related (see Table I) it is not unreasonable to expect the interconversion of these compounds through a photochemical cycle. In this paper we establish, following fluorescence microscopical investigations, evidence for such photo-induced solid-state interconversion that also involves di-*p*-anthracene(V). The central pivotal role of an excimeric state in this cycle is also indicated.

TABLE I
Crystal data

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	(β)	<i>Z</i>	Space group
Anthracene	8.561	6.036	11.163	124	2	<i>P</i> 2 _{1/a}
Anthracene 9,10 epiperoxide	15.94	5.86	11.43	108.2	4	<i>P</i> 2 _{1/a}
Anthraquinone: Anthrone	15.8	4.0	7.9	102	2	<i>P</i> 2 _{1/a}
Di- <i>p</i> -anthracene	8.127	12.08	18.85		4	<i>Pbca</i>

EXPERIMENTAL

Anthracene was purified by zone refining and thin crystals (*ca* 1–100 μm) were grown from a benzene solution on microscope slides. Anthraquinone and anthrone (BDH) were recrystallised from ethanol and thin crystals were grown from ethanolic solutions. The anthracene 9,10 epiperoxide was prepared by the photo-oxidation of anthracene solution in carbon disulphide⁶ and purified by crystallisation from benzene. The product was characterised employing differential scanning calorimetry (DSC) and i.r. spectra. Di-*p*-anthracene was prepared by irradiation of anthracene solution in benzene contained in a pyrex vessel with light from a high pressure mercury arc. The photodimer crystals were washed with benzene and checked by a melting point determination and electron diffraction. Diels–Alder adducts of anthracene to 2-methyl butene and cyclo-pentadiene were prepared by u.v. irradiation of benzene solutions of anthracene containing the olefinic compound. No analysis is provided for these adducts.

All investigations were carried out on a fluorescence microscope [Reichert Zetopan] and irradiations were carried out in air using the filtered light

(<400 nm) from a high pressure mercury lamp. Fluorescence was observed from the same surface as that irradiated. To minimize interference in the fluorescence spectra and to achieve maximum resolution the spectra were recorded in four regions; blue, green, yellow and orange, employing cut-off filters at <460 nm, <490 nm, <560 nm, <600 nm respectively. All spectra were recorded according to the following sequence (a) non-polarised light (b) polarised light (c) crossed nicols.

RESULTS

a) Anthracene

The fluorescence spectra of anthracene are shown in Figure 1. There are three main peaks at 425 nm, 445 nm and 474 nm together with a minor peak at 545 nm. The same peaks are observed in polarised light (Figure 1b) and in crossed nicols (Figure 1c) with the exception that in crossed nicols a red shift occurs in the 474 nm peak to 482 nm. The first two peaks in the spectra of anthracene correspond to its characteristic blue fluorescence whilst the last two peaks correspond to green and yellow emissions respectively.

Blue and green areas in anthracene are observed upon fluorescence ageing for *ca.* 10^4 s (compare the reports of D. Donati, G. G. T. Guarini and P. Sarti-Fantoni, Ref. 3). The green fluorescing areas are normally associated with edges and cracks. With the aid of a diaphragm built into the microscope it is possible to record spectra from the blue and green areas separately (see Figures 1d and 1e). It can be seen that the positions of the three main peaks remain unchanged whereas the fourth minor peak is submerged in the case of the blue areas but is resolved and split into peaks at 520 nm and 545 nm in the green areas.

b) Anthracene 9,10 epiperoxide

The spectra of anthracene 9,10 epiperoxide (Figure 2) is very similar to that of anthracene (*cf.* Figure 1a) and its behaviour on fluorescence ageing also follows the anthracene pattern.

c) Anthraquinone

Anthraquinone fluoresces in the yellow region when irradiated with non-polarised u.v. radiation. The main peak is at 545 nm with a shoulder at 575 nm (see Figure 3a). Anthraquinone does not fluoresce when irradiated with polarised u.v. radiation. On prolonged irradiation of anthraquinone (*ca.* 5×10^3 s) green and blue fluorescence appears (see Figure 3b). Fluorescence

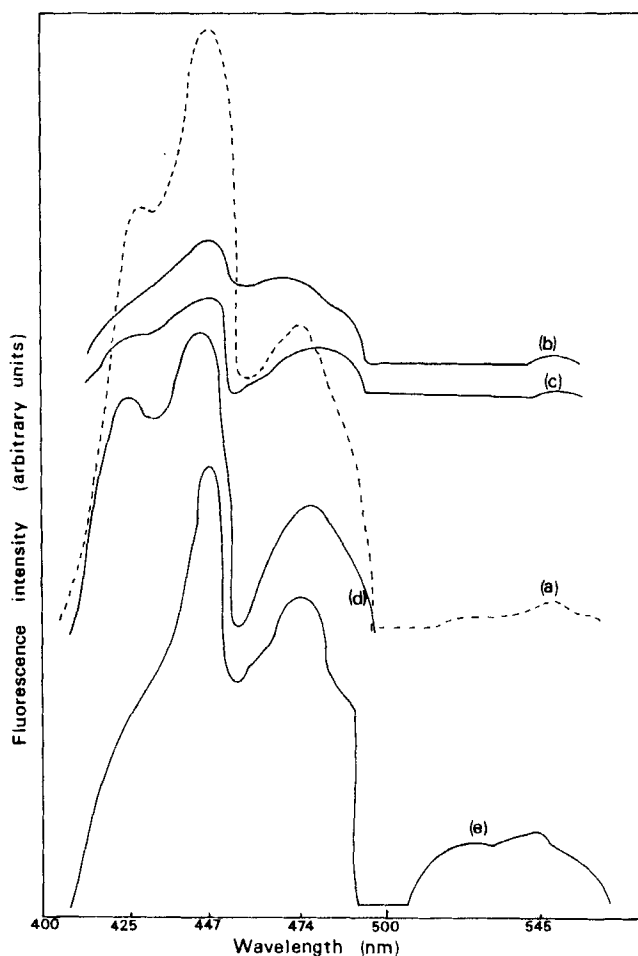


FIGURE 1 Fluorescence spectra of thin crystals of anthracene: (a) in non-polarised u.v. radiation; (b) in polarised u.v. radiation; (c) in crossed nicols; (d) spectra of a blue emitting region in an aged crystal, non-polarised radiation; (e) spectra of a green emitting region in an aged crystal, use of non-polarised radiation. Note the difference in blue and green emitting regions with respect to the existence of the yellow band.

aged crystals of anthraquinone have a polarised yellow band (see Figures 3c, e, f) whilst the blue and green bands are not polarised (Figures 3e and 3f).

d) Anthrone

The spectrum and general behaviour of anthrone (Figure 4) is very similar to that of anthraquinone and it shows yellow fluorescence at 545 nm with a

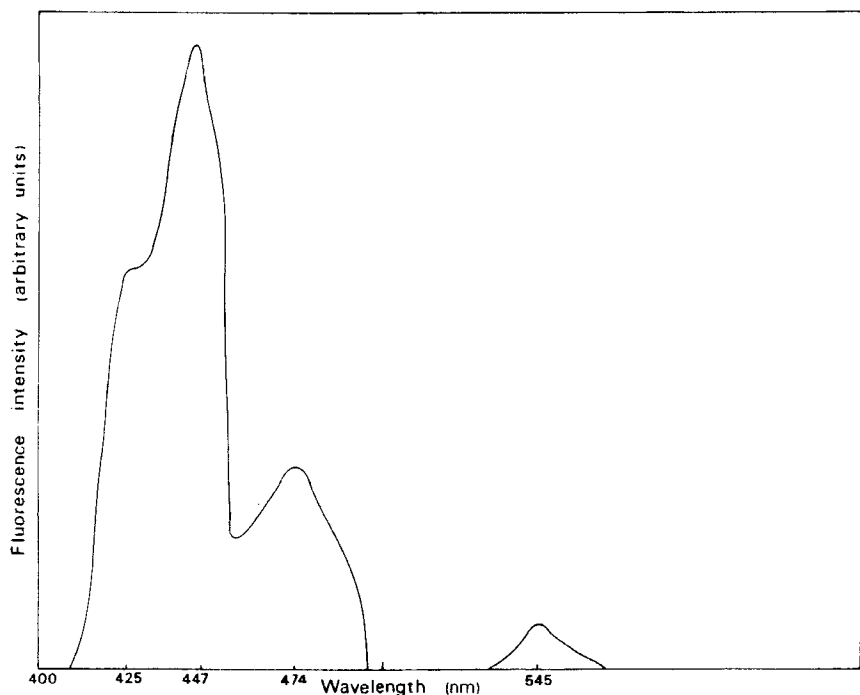


FIGURE 2 Fluorescence spectra of anthracene 9,10 epiperoxide thin crystals when irradiated with non-polarised u.v. radiation. Notice the correspondence between this spectrum and that of anthracene (Figure 1a).

shoulder at 573 nm in non-polarised u.v. radiation. After prolonged irradiation unpolarised blue and green areas are formed.

e) Di-*p*-anthracene

The anthracene photodimer does not fluoresce but on irradiation for *ca.* 5×10^3 s fluorescence appears with peaks at 440, 470 and 545 nm as shown in Figure 5a. The blue and green peaks are unpolarised initially but upon further ageing they become polarised.

f) Diels–Alder adducts to anthracene

Diels–Alder adducts of cyclo-pentadiene to anthracene fluoresce in the green region with some blue and yellow fluorescence (Figure 6a). Polarised fluorescence is not observed except after fluorescence ageing.

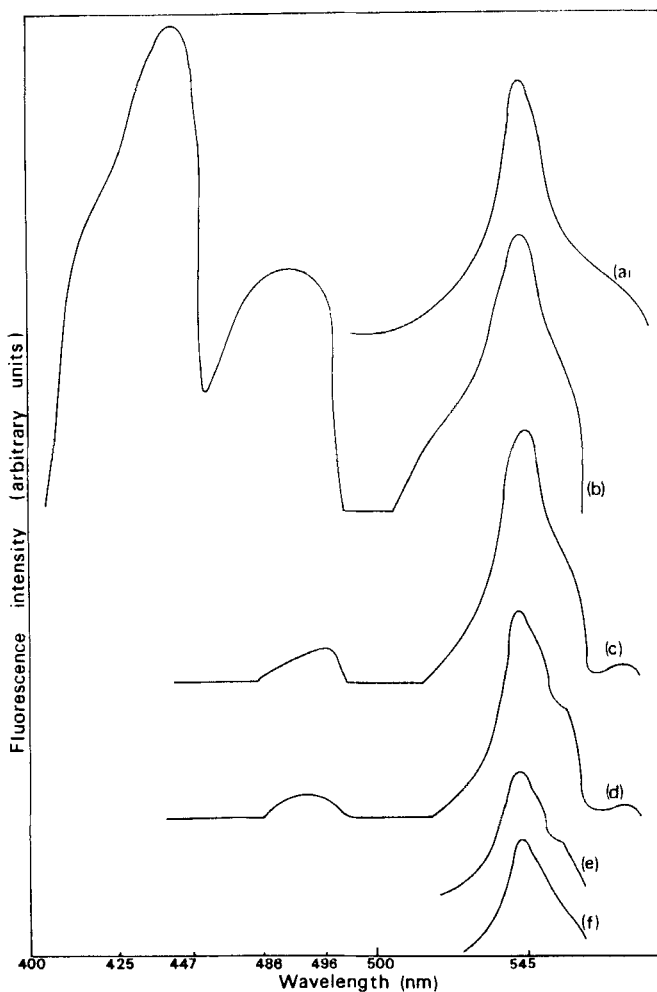


FIGURE 3 Fluorescence spectra of anthraquinone: (a) in non-polarised u.v. radiation. In polarised u.v. radiation this band disappears: (b) spectra of a blue emitting region in an aged crystal, use of non-polarised radiation; (c) spectra of a yellow emitting region in an aged crystal, use of non-polarised radiation; (d) spectra of a green fluorescing region in an aged crystal, use of non-polarised radiation; (e) spectra after ageing in polarised radiation; (f) spectra after ageing, crystal between crossed nicols. Note that the spectra (e) and (f) do not exist in fresh crystals.

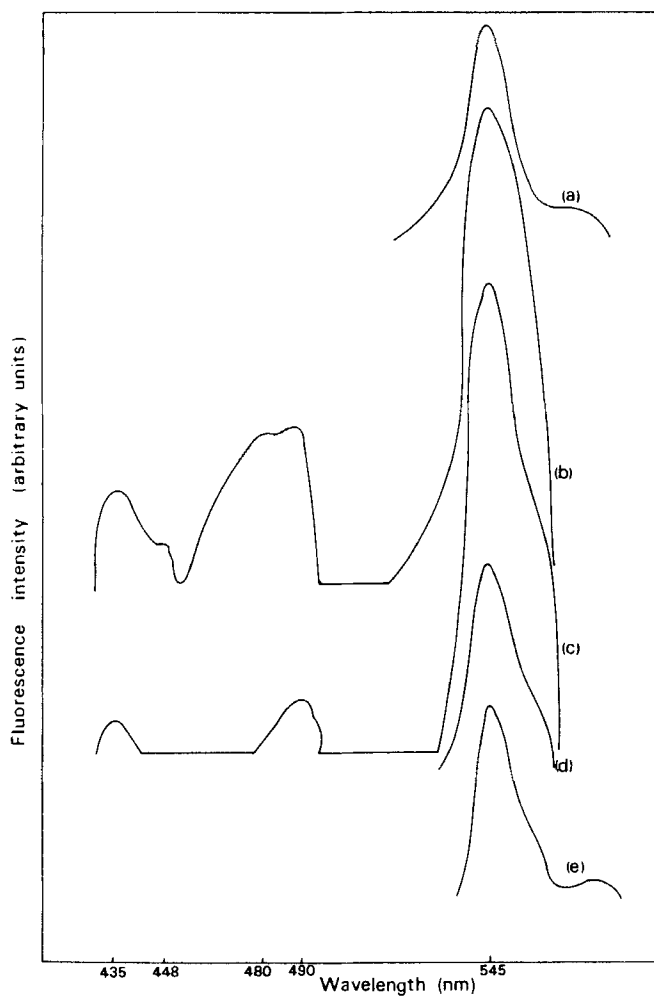


FIGURE 4 Fluorescence spectra of anthrone: (a) in non-polarised u.v. radiation (this band disappears in polarised u.v. radiation); (b) spectra of a yellow fluorescing region in an aged crystal, use of non-polarised radiation; (c) spectra of a blue fluorescing region in an aged crystal, use of non-polarised radiation; (d) and (e) spectra of an aged crystal in polarised radiation and crossed nicols respectively (note that as in (a) a fresh crystal does not fluoresce in polarised radiation).

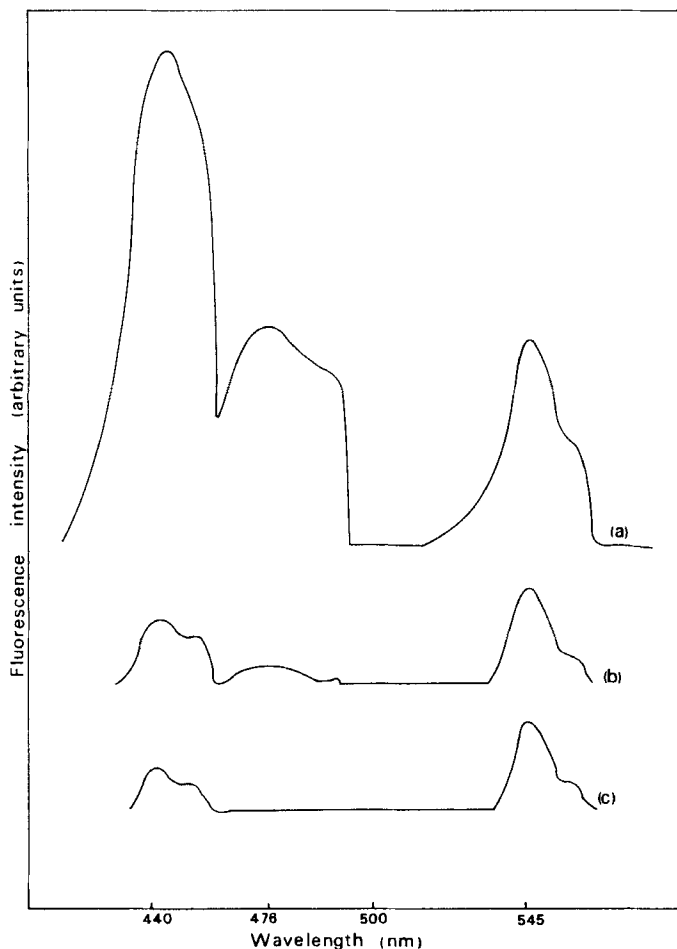


FIGURE 5 Fluorescence spectra of an aged di-*p*-anthracene crystal: (a) in non-polarised u.v. radiation; (b) and (c) in polarised radiation and crossed nicols respectively. Note that the polarised spectra in (b) and (c) do not occur except at later stages of ageing.

DISCUSSION

The spectra of the compounds studied can be classified into four groups.

- 1) anthracene and anthracene 9,10 epiperoxide
- 2) anthraquinone and anthrone
- 3) di-*p*-anthracene
- 4) Diels–Alder adducts.

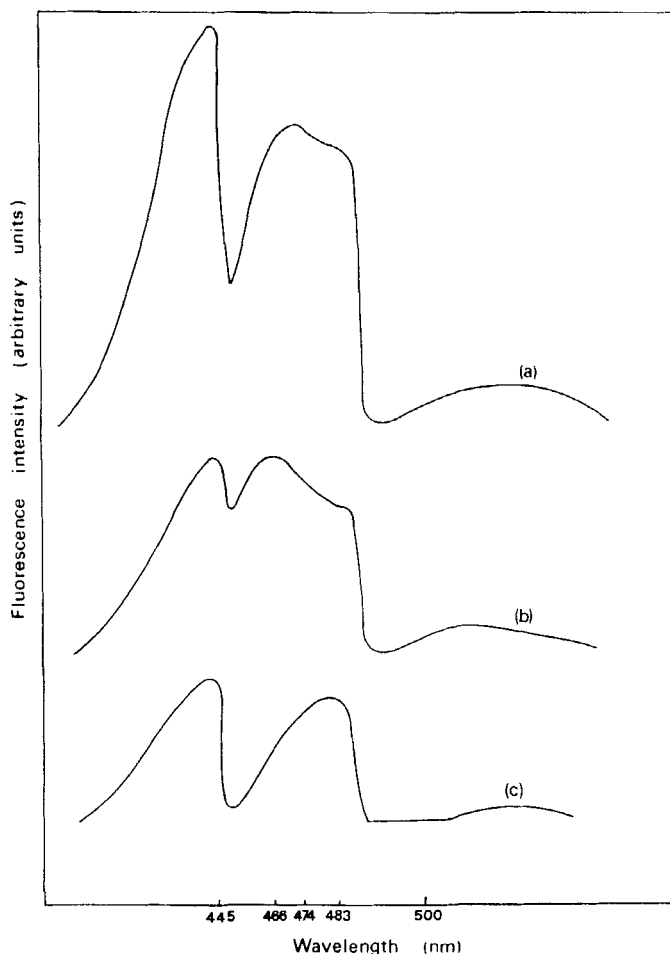
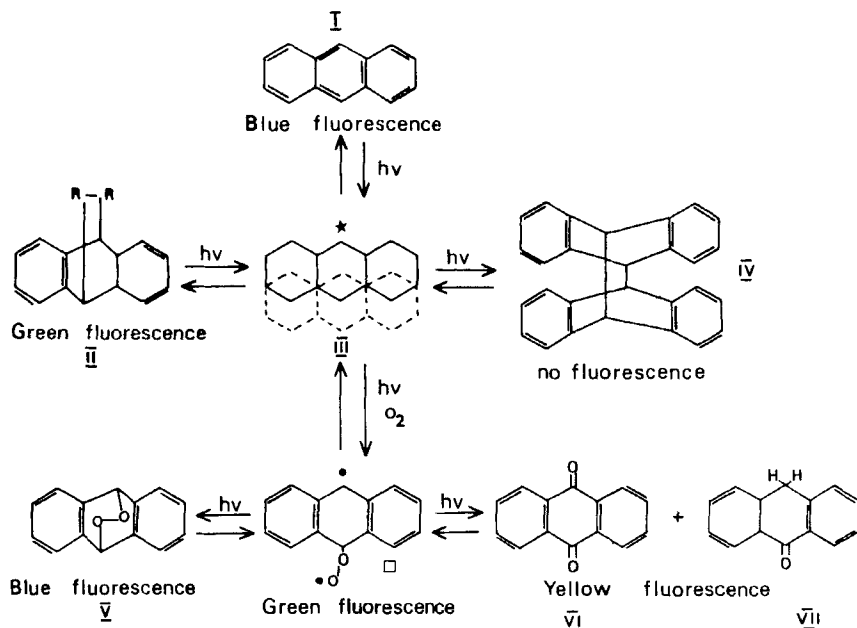


FIGURE 6 Spectra of Diels-Alder adduct of anthracene to cyclopentadiene: (a) in non-polarised radiation (note the major green band which leads to the green fluorescence of the adduct); (b) and (c) spectra in polarised radiation and in crossed nicols (note that the polarised bands do not appear except after fluorescence ageing).

The first three bands in group 1 spectra are inherent in the anthracenic structure and compare with the bands observed in solution fluorescence spectra. The yellow peak can be attributed to trace quantities of anthraquinone and/or anthrone and the green peak to an excimeric emission.⁷ Group 2 spectra show green and blue fluorescence upon ageing. This is attributed to photoreduction of anthraquinone and anthrone to anthracene 9,10 epiper-oxide, di-*p*-anthracene and anthracene. During such a photoreaction the anthraquinone/anthrone acquires the orientation of a mesomorphic phase

which, in all probability, has an orientation similar to the products. This follows from the observation that the polarised yellow fluorescence of anthraquinone/anthrone does not occur except after ageing. The nascently generated blue and green bands are not polarised suggesting the random arrangement of the products (probably close to structural imperfections).

The anthracene dimer (group 3) spectra show fluorescence in the blue, green and yellow regions after prolonged irradiation. This reveals the possibility of the photodecomposition of the dimer to the monomer and subsequently to its photo-oxidation products. The fact that nascently generated blue and green emissions are submerged in polarised emissions may be rationalised in terms of the association of such fluorescence with localised regions on the surface.



A scheme for the possible photoreactions in the anthracene cycle.

The spectra of Diels–Alder adducts (group 4) are related to the above spectra in that they possess a mainly green (excimer) emission but a prolonged irradiation show the presence of blue and yellow emissions attributable to photo-decomposition and subsequent photo-oxidation.

Scheme 1 suggests a mechanism for the photo-stimulated chemical inter-conversions of the above-mentioned four groups. The photodimerisation of anthracene occurs preferentially along several crystallographic directions

permitted in the anthracene crystal⁸ and the decomposition of anthracene 9,10 epiperoxide to a mixture of anthraquinone and anthrone⁴ was found to occur along [010] which remains an invariant direction during the transformation. The preferential orientation of anthracene 9,10 epiperoxide formed by irradiation of the underlying anthracene matrix in an air/CS₂ atmosphere⁹ is shown in Figure 7. The preferred orientation of anthraquinone/anthrone on an anthracene matrix is shown in Figure 8 which is taken following irradiation in an air/H₂O atmosphere.⁹ Consequently, one sees that in all the photo-induced reactions involving the anthracenic compounds considered the orientation of the products is controlled by the crystallographic structure of the reactant i.e. the reactions are topotactic.

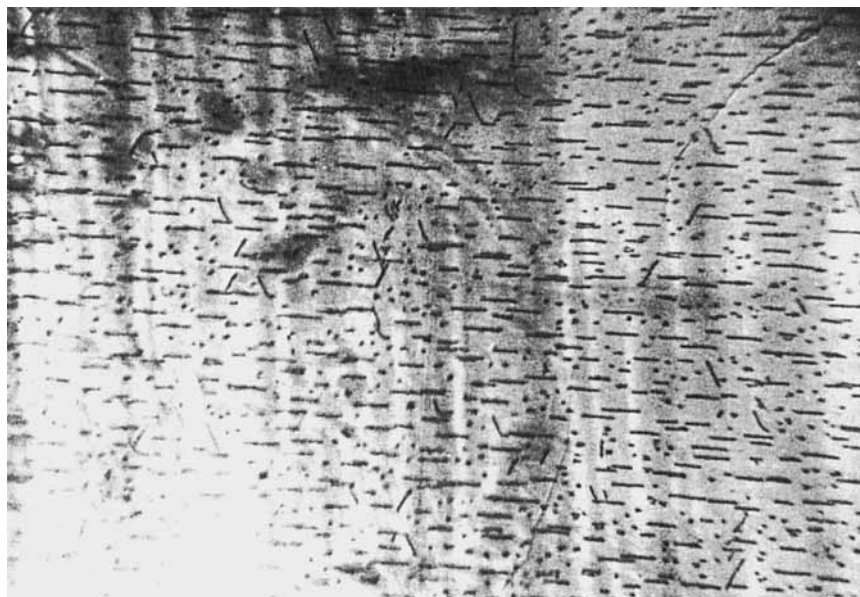


FIGURE 7 Cleavage surface of anthracene showing preferential growth of the 9,10 epiperoxide upon u.v. irradiation in air/CS₂ atmosphere for 2×10^3 s. ($\times 230$)

Finally we should like to emphasize here that the observations of the growth of product (daughter) phases on parent molecular phases in preferred crystallographic directions resemble similar behaviour during phase transformations in such materials¹⁰ and dismisses the generality of isotropic growth at an interface.¹¹



FIGURE 8 Cleavage surface of anthracene showing preferential growth of anthraquinone/anthrone on the peroxide matrix. Ultra-violet irradiation undertaken in air/H₂O atmosphere for 2×10^3 s. ($\times 465$)

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