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Annealing of the 6060 Å Color Center in Gamma-Irradiated Anthracene†

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Abstract—Anthracene crystals irradiated by γ-rays exhibit an absorption peak at 6060 Å. Upon annealing, this peak increases and then decreases. When this peak is examined with polarized light, the maximum in the *b* crystallographic direction is attained before the maximum in the *a* direction. This is believed to arise from the rotation of a defect. A kinetic scheme, written on this basis, is shown to match the data very well.

Introduction

Several investigators(1–4) have reported color-center formation in aromatic hydrocarbons exposed to ionizing radiation. The usually transparent materials become colored and absorption bands appear in the visible region of the spectrum. Color centers may result from a variety of lattice imperfections, and the defects responsible for absorption in most organic crystals are largely unidentified.(5)

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Of the aromatic hydrocarbons, anthracene, because of its large photo-response and use as a scintillation counter, has been the most widely investigated. In particular, Blum *et al.*(1) have shown that the magnitude of the 6060 Å absorption in irradiated anthracene, measured normal to the *ab* cleavage plane, increased and then decreased as a consequence of thermal annealing. Thermal bleaching of radiation-induced defects in organic materials is not unusual. However, the report of an optical absorbing species that increases with annealing indicates an uncommon behavior pattern for these materials.(5) In the present investigation, an analysis of the annealing kinetics of the 6060 Å center is given with a proposed reaction mechanism to explain the observed results.

Experimental Procedure

Synthetic anthracene (Eastman H–480) was purified by chromatography, vacuum sublimation, and zone refining.(6) No impurities were detected by gas chromatography, and it was concluded that the total impurity content was less than 1 ppm. The final purity and structural defect concentration of the material was checked by measuring the triplet exciton lifetime which was found to be between 20 and 25 msec. This lifetime is equivalent to that of the best material that has been reported.(7)

Single crystals were grown by the Bridgman method and oriented sections were cut from boules with a string saw. In the *ab* cleavage plane, the *a* and *b* axes can be distinguished by double refraction.(8) The c' direction is normal to the cleavage plane. The crystals were irradiated at the Brookhaven gamma facility for doses of $\sim 10^8 R$ and optical density measurements were made on a Cary 14 spectrophotometer with air in the reference compartment. In order to obtain a base line for the radiation-induced peaks, each run was started in the infra-red. Polarized filters, inserted between the light source and the crystal, served to polarize the beam.

For annealing, the crystals were placed in a Pyrex ampule and packed in a powder of anthracene to reduce surface sublimation. A copper-constantan thermocouple, situated near the crystal, monitored the temperature. All samples were annealed in air in a temperature-controlled furnace since a few selected samples annealed in vacuum were shown to give identical results for identical annealing schedules.

Results

The absorption spectrum of an irradiated anthracene crystal[1] is characterized by a resolvable peak at 6060 Å and a less definitive absorption at 5350 Å. These absorptions seem to grow in a similar manner with increasing temperature, although the lack of resolution of the 5350 Å peak hinders a quantitative analysis. The 6060 Å peak, however, is not obscured by the radiation-induced background, thus lending itself to a kinetic study. It should be noted that the spectrum of an unirradiated sample is characterized by a lack of structure in this region.

The polarized spectrum of anthracene, irradiated to a dose of $10^8 R$ and annealed for 630 minutes at 110 °C, is shown in Fig. 1. The *b* axis absorption exceeds that of the *a* axis and an additional center at ~4950 Å is noted. The magnitude of the *b* absorption at 6060 Å remains dominant in the early stages of annealing and reaches a maximum value while the *a* axis absorption is still increasing. As the *b* absorption diminishes, the *a* absorption reaches a maximum and becomes the major absorption constituent. This behavior is illustrated in Fig. 2.

These curves suggest that the absorptions are controlled by different rate mechanisms. It appears that the growth of the *a* absorption is possibly a response to the *b* absorption decay, i.e., a process which converts the *b* dominant absorption to an *a* dominant one, such as a rotation of a defect. On the basis of this assumption, the following kinetic scheme was found to be the simplest reaction which fit the data satisfactorily

$$\begin{tikzcd}
 & n_b \arrow[r, "k_3"] \arrow[dd, "k_5"] & N' \\
N \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & & \\
 & n_a \arrow[r, "k_4"'] & N'
\end{tikzcd}$$

where N and N' are non-absorbers at 6060 Å and n_b and n_a are the

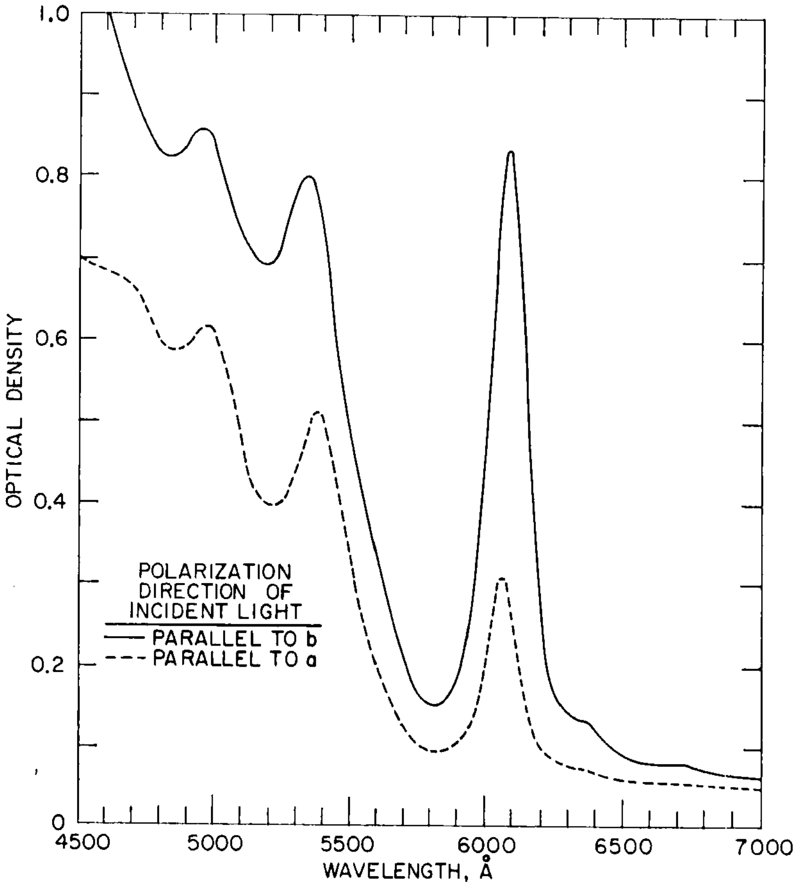

Figure 1. Polarized absorption spectrum of irradiated anthracene following annealing for 630 minutes at 110 °C.

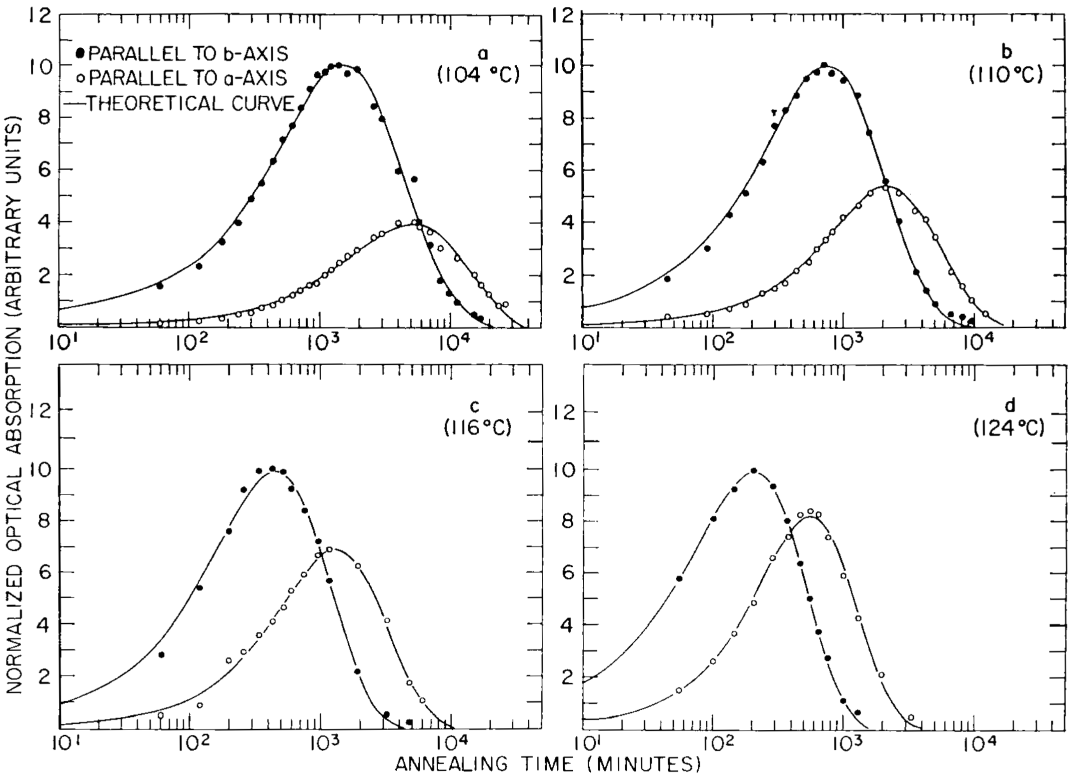

Figure 2. Isothermal annealing curves, taken at various temperatures, and illustrating that the *b* axis absorption maximum precedes that of the *a* axis. The solid curve, based upon the kinetic scheme described above, is a computer fit to the experimental data.

optical absorbers for the incident light parallel to the b and a axes respectively. The rate constant k_1 is responsible for the growth and the constants k_3 and k_5 are responsible for the decay of the b absorption. In a similar fashion, k_2 and k_5 govern growth and k_4 governs decay of the a absorption. The equations governing these reactions are:

$$\frac{\mathrm{d}n_b}{\mathrm{d}t} = k_1 N - (k_3 + k_5) n_b \tag{1}$$

$$\frac{\mathrm{d}n_a}{\mathrm{d}t} = k_2 N + k_5 n_b - k_4 n_a \tag{2}$$

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -(k_1 + k_2) N. \tag{3}$$

The solution of these equations gives:

$$n_b = n_{b0}\, e^{-kt} + \frac{k_1 N_0}{k - K}\left[e^{-Kt} - e^{-kt}\right] \tag{4}$$

and

$$\begin{aligned} n_a = {} & e^{-kt}\left[\frac{k_5 n_{b0}}{k_4 - k} - \frac{k_5 k_1 N_0}{(k - K)(k_4 - k)}\right] \\ & + e^{-Kt}\left[\frac{k_2 N_0}{k_4 - K} + \frac{k_5 k_1 N_0}{(k - K)(k_4 - K)}\right] \\ & + e^{-k_4 t}\left[n_{a0} - \frac{k_5 n_{b0}}{k_4 - k} + \frac{k_5 k_1 N_0}{(k_4 - k)(k_4 - K)} - \frac{k_2 N_0}{k_4 - K}\right]. \end{aligned} \tag{5}$$

here n_{b0} and n_{a0} are the values of n_b and n_a prior to annealing, $k = k_3 + k_5$, and $K = k_1 + k_2$.

The solid lines in Fig. 2 represent the computer-simulated curves obtained from a least-squares fit to the experimental data. The data for n_b were fitted using k, K and $k_1 N_0$ as adjustable parameters. The values for k_4, k_5 and $k_2 N_0$ were then obtained from the n_a data. The rate constants and activation energies for growth and decay are given in Table 1. The activation energies were evaluated by assuming that the rate constants can be expressed in the Arrhenius form, $k = ce^{-E/kT}$, where E is the activation energy and c is a constant.

TABLE 1 Rate Constants and Activation Energies for Irradiated Anthracene Using Polarized Light.

Temperature (°C)	k_1 (10^{-3} min^{-1})	k_2 (10^{-3} min^{-1})	k_3 (10^{-3} min^{-1})	k_4 (10^{-3} min^{-1})	k_5 (10^{-3} min^{-1})
104	1.16 ± .22	.14 ± .02	.16 ± .03	.12 ± .01	.10 ± .01
110	1.84 ± .15	.28 ± .02	.35 ± .03	.32 ± .01	.32 ± .01
116	2.65 ± .46	.50 ± .06	.75 ± .06	.49 ± .04	.67 ± .05
124	5.00 ± .86	.78 ± .09	1.65 ± .18	1.47 ± .05	2.23 ± .10
$\bar{E}$(ev)	1.0 ± 0.2	1.2 ± 0.2	1.6 ± 0.2	1.6 ± 0.3	2.1 ± 0.2

Discussion

During annealing, the *b* polarized absorption attains a maximum before the *a* absorption. Since both the *a* and the *b* polarization peaks have the same wavelength and since both grow and decay with the same energy, it seems unlikely that there are two independent species involved. It is more reasonable to suppose that a rotation is responsible for the observed shift in the absorption maxima. This apparent rotation of the absorbing center could be due to (1) a physical reorientation of the absorbing molecule, (2) a migration of a trapped carrier from traps of one orientation to others, or perhaps only, (3) a movement around the molecule of the active site. The second mechanism has been found to occur in alkali halides.(14,15) Since the activation energy for k_5 which corresponds to the apparent rotation is about 2.1 ev, comparable to that for self-diffusion in anthracene,(16) the first mechanism is also possible. The activation energy for the third process could be large or small, depending upon the nature of the defect.(17)

The defect responsible for the absorption peak at 6060 Å has not yet been identified. While it has been fairly well established that the radical which causes the EPR spectrum in γ-irradiated anthracene is that formed by hydrogen addition to an anthracene molecule,(4,9) the different annealing kinetics of the EPR signal(1,10) and the optical absorption spectrum indicate that the two signals have different origins. While a radical may indeed be responsible for the observed absorption, other viable interpretations include electrons or holes in deep traps or impurity molecules. There is ample evidence for the production of impurity molecules(11) and electron and hole traps(12,13) in γ-irradiated anthracene.

A more detailed analysis of the absorption spectrum in irradiated anthracene must await the identification of the absorbing centers. If trapped carriers are involved, the nature of the trap and sign of the carrier must be determined.

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