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Publisher: Taylor & Francis

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## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 28 Mar 2007.

To cite this article: Youici Akasaka, Kouichi Murakami, Kohzoh Masuda & Susumu Namba (1971): Optical Absorption Bands of the Radical in Irradiated Anthracene Single Crystals, *Molecular Crystals and Liquid Crystals*, 13:4, 377-380

To link to this article: <http://dx.doi.org/10.1080/15421407108083552>

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# Optical Absorption Bands of the Radical in Irradiated Anthracene Single Crystals

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Received November 13, 1970; in revised form December 7, 1970

**Abstract**—The correlation between the ESR spectrum and the optical absorption bands in the visible region has been studied in an anthracene single crystal irradiated with 1.5 MeV electron beam by the isochronal annealing method. The optical absorption bands are observed at 470, 500, 537, and 608 nm. Among these absorption bands, the band at 470 nm is found to be that of the radical produced by irradiation, which may be dibenzo-cyclohexadienyl radical.

The optical absorption spectrum of an anthracene single crystal irradiated with high energy radiation was studied by Damask *et al.*,<sup>(1)</sup> who reported the absorption bands at 495, 535, 606, and 632 nm. On the other hand, the dibenzo-cyclohexadienyl radical has also proposed by many workers<sup>(2-5)</sup> to be produced in the same crystal irradiated with high energy radiation. Damask *et al.*,<sup>(1)</sup> studied the possible correlation between the two strong optical absorption bands at 535 and 606 nm and the ESR signal by the isochronal annealing method, but an obvious correspondence between them was not observed.

In the present study, besides the optical absorption bands at 500, 537, and 608 nm, which are in agreement with those found by Damask,<sup>(1)</sup> the band at 470 nm was detected, and is shown to be due to the radical by the isochronal annealing.

Crystals obtained by Bridgeman technique from zone-refined anthracene were irradiated with 1.5 MeV electron beam at 77 °K and at room temperature to the dose of  $1 \times 10^8$  rad.

Figure 1 shows the optical absorption spectrum of an anthracene single crystal irradiated to  $10^8$  rad at room temperature. Optical

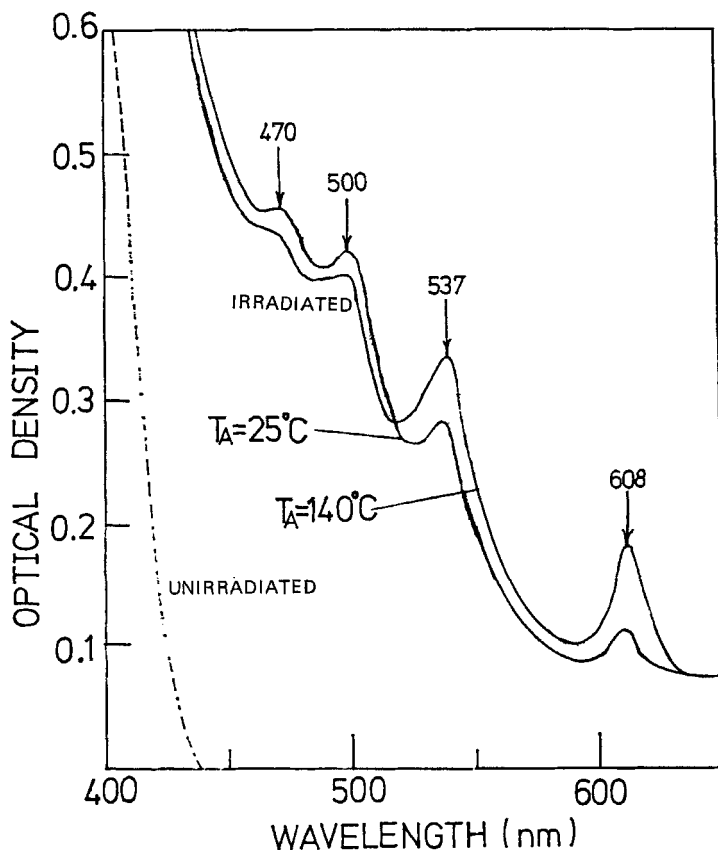


Figure 1. Optical absorption spectrum of an anthracene single crystal irradiated with 1.5 MeV electron beam at room temperature to the dose of  $10^8$  rad.

absorption bands appear at 470, 500, 537, and 608 nm. No essential difference in optical absorption was observed between samples irradiated at room temperature and at 77 °K. The ESR signal observed at room temperature was that of the radical showing 4 lines with the intensity ratio of 1:3:3:1,<sup>(1-5)</sup> for both samples irradiated at room temperature and at 77 °K. Isochronal annealing behaviors were studied with the annealing time of 30 minutes at each temperature, and the results are shown in Fig. 2. The annealing behavior of the optical absorption band at 470 nm was similar to that of the ESR signal. The bands at 537 nm and 608 nm<sup>(6)</sup> increase to maxima and

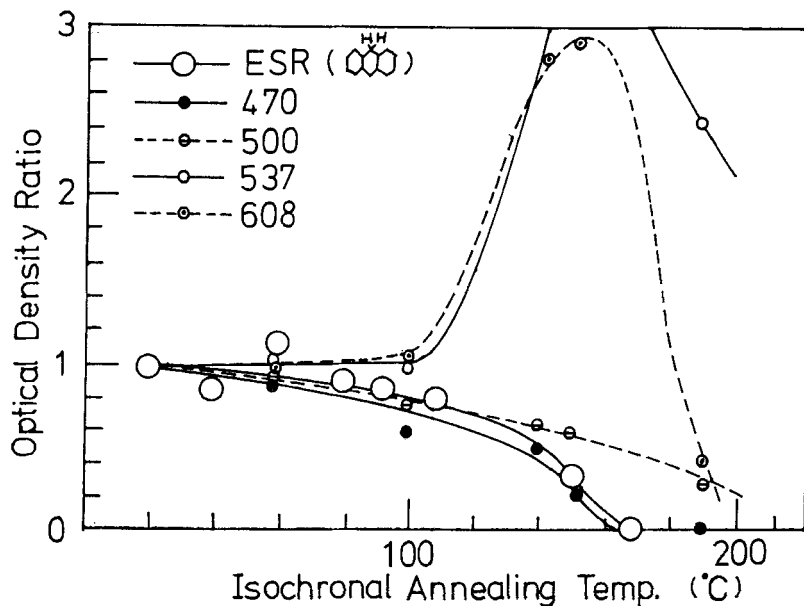


Figure 2. Isochronal annealing behaviors of the optical absorption bands and the ESR center induced by irradiation in an anthracene single crystal.

then decrease with the increase of annealing temperature. The absorption at 500 nm decays monotonously with temperature, and disappears thoroughly at about 200 °C. The results of the isothermal annealing at 105 °C indicate that the decays of the optical absorption bands at 470 nm and 500 nm are exponential with the lifetime of  $1200 \pm 250$  and  $4500 \pm 1000$  minutes, respectively. The activation energy required for the decay of the ESR signal was determined from Arrhenius plots of the isochronal annealing results to be  $0.22 \pm 0.01$  eV, as shown in Fig. 3. On the other hand,  $0.20 \pm 0.01$  eV was obtained for the activation energy for annealing the optical absorption band at 470 nm. Both activation energies are in agreement within experimental error. This agreement and the similar annealing behavior between the 470 nm absorption and the ESR signal suggest strongly that the absorption at 470 nm is caused by the radical, which has been proposed to be the dibenzo-cyclohexadienyl radical. The activation energy obtained here is significantly lower than that reported by McGhie *et al.*<sup>(7)</sup>

The activation energy for the quenching of the optical absorption

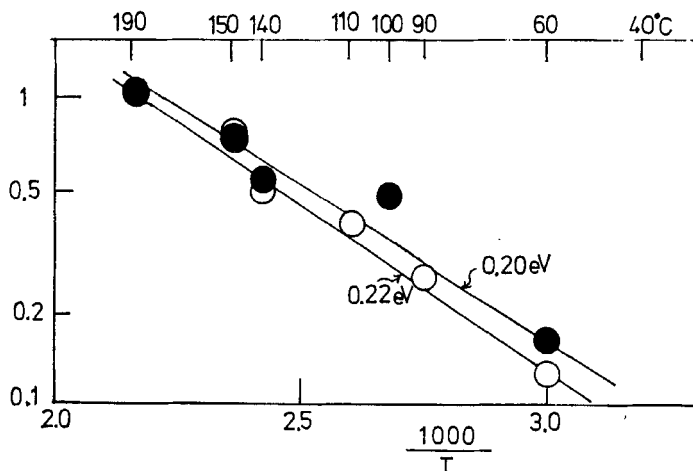


Figure 3. Arrhenius plots of the quenching of 470 nm band and the ESR center induced by irradiation in an anthracene single crystal.

● 470 nm band. ○ ESR center.

band at 500 nm was found to be  $0.10 \pm 0.02$  eV. The 500 nm absorption and the other absorption bands may correspond to some other defects than the radical.

### Acknowledgements

The authors would like to express their thanks to Prof. K. Sakaguchi of Osaka Institute of Technology for supplying samples and Dr Y. Nakai and Mr T. Takagaki of Osaka Laboratories for Radiation Chemistry of JAERI for the irradiation of 1.5 MeV electron beam of Van de Graaff accelerator.

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