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

Radiation-Induced Radicals in Anthracene Single Crystals

Taisu Chong [a] & Noriaki Itoh [a]
[a] Department of Nuclear Engineering, Nagoya University, Nagoya, Japan

Version of record first published: 29 Aug 2007.

To cite this article: Taisu Chong & Noriaki Itoh (1976): Radiation-Induced Radicals in Anthracene Single Crystals, Molecular Crystals and Liquid Crystals, 36:1-2, 99-113

To link to this article: http://dx.doi.org/10.1080/00268947608084834

Mol. Cryst. Liq. Cryst., 1976, Vol. 36, pp. 99–113

Printed in Holland

Radiation-Induced Radicals in Anthracene Single Crystals

TAISU CHONG and NORIAKI ITOH

Department of Nuclear Engineering, Nagoya University, Nagoya, Japan

(*Received Apirl 22, 1976*)

EPR and optical absorption studies have been made on anthracene single crystals irradiated with electrons at liquid nitrogen temperature. Studies of annealing of the EPR spectra induced by irradiation at liquid nitrogen temperature revealed that they consisted of a broad singlet and two sets of angular dependent lines. The angular dependence of the latter was studied and they were ascribed to the 9- and 1-dibenzo-cyclohexadienyl radicals. From comparison of the change in the EPR spectra with the change in the optical absorption spectra at room temperature, optical absorption bands at 535 and 675 nm were ascribed to 9- and 1-dibenzo-cyclohexadienyl radicals. An optical absorption band at 645 nm, which is created by irradiation at liquid nitrogen temperature and decays within two hours at room temperature was suggested to arise from the 2-dibenzo-cyclohexadienyl radical. The broad singlet, which is annealed below room temperature, was ascribed to the 9-anthracyl radical.

I INTRODUCTION

Studies of radiation-induced radicals in aromatic hydrocarbon single crystals, such as naphthalene and anthracene, have been reported by many workers.[1–16] Well-identified radicals produced by room temperature (referred to as RT) irradiation of naphthalene and anthracene single crystals are the 1-hydronaphthyl radical[12] (referred to as 1-HNR) and 9-dibenzo-cyclohexadienyl radical[3,5] (referred to as 9-DBCR), respectively. The structures of these radicals are shown in Figure 1. It has been suggested that during the irradiation of X or γ-rays a hydrogen atom is released from a parent molecule by an electronic encounter and that the released hydrogen atom may subsequently be attached to another parent molecule after migrating in the crystals, forming a cyclohexadienyl type radicals described above. ENDOR studies[7,13] of naphthalene and anthracene single crystals irradiated with X-rays at RT indicate clearly that 1-HNR and 9-DBCR are located at the lattice point parallel to the parent molecules. It has been also suggested that 2-HNR is produced by irradiation of naphthalene.[15]

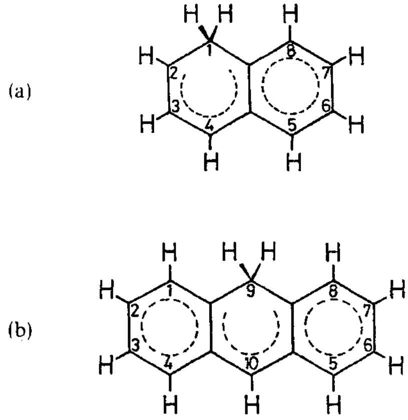


FIGURE 1 The 1-hydronaphthyl radical (a) and the 9-dibenzo-cyclohexadienyl radical (b).

The electronic properties of 1-HNR have been studied in most detail and it is known[17,18] that 1-HNR has optical transitions at 337, 380 and 539 nm and a prominent emission band at 541 nm: the 539 and 541 bands being accompanied with the vibrational structures. The decay of the emission intensity of 1-HNR, which is excited with pulsed electrons, indicates that the lifetime of the first excited state of 1-HNR is 80 nsec at liquid nitrogen temperature (referred to as LNT). The occurrence of luminescence has made it feasible to study the energy transfer from the excitons to the radical and the rate constants of the interaction of the singlet- and triplet-excitons with 1-HNR have been obtained.[19] An analysis of the structures of the transition at 539 nm has revealed the charge transfer transitions from the radical to the host molecules.[20] In view of these results, the radicals appear to be an important localized state which may be utilized for studies of the guest-host interaction and also the host properties of the crystal such as exciton and charge carrier transports. The photocurrent induced by the detrapping of charge carriers trapped by radicals in naphthalene has been observed recently.[21]

Radiation chemical processes in napththalene crystals are understood fairly well.[15] At low temperatures, the naphthyl radical, a radical with a missing hydrogen atom from a naphthalene molecule and 1- and 2-HNR are produced. The naphthyl radical (referred to as NR) is unstable at RT and is converted into a diamagnetic species, possibly a dimer molecule, in a first order reaction. 1-HNR is stable at RT and 2-HNR is less stable than 1-HNR but more stable than NR. It is also shown that a new radical, which has been assigned to be a dimer radical, a radical with an additional hydrogen atom to a dimer molecule, is produced by a prolonged annealing at RT.

For anthracene efforts have been made to assign optical absorption bands associated with 9-DBCR by Blum *et al.*[1] and by Akasaka *et al.*[10] From isochronal annealing experiments, Akasaka *et al.* found that the EPR signal for 9-DBCR is diminished around 410 K and ascribed an optical absorption band at 470 nm, which shows the same annealing curve, to 9-DBCR. They also reported anomalous increases of optical absorption bands at 535 and 606 nm when irradiated specimens were warmed above 410 K. Since their measurements of optical absorption were made at RT, the resolution of the absorption is not good enough to obtain annealing curves of each absorption band accurately. In anthracene cyclohexadienyl type radicals other than 9-DBCR have not been found and the thermal stability of various radicals has not been studied in detail.

In the present paper, we report the optical absorption and EPR spectra of anthracene single crystals irradiated with electrons at LNT. Careful comparison of the change of the optical absorption spectra with that of EPR spectra after the specimens were warmed to RT was made. It was concluded that 1-, 2- and 9-DBCR are produced by irradiation at LNT. Both the thermal stability of these radicals at RT and the optical absorption bands associated with them were presented. Annealing of anthracyl radical, a radical with a missing hydrogen atom from an anthracene molecule (referred to as AR) was also studied.

II EXPERIMENTAL TECHNIQUES

Highly purified anthracene powder from Tokyo Chemical Institute (A495) was further purified by distillation and zone-refining method. Anthracene single crystals were grown by the Bridgman technique. From an ingot of the single crystal, specimens of $2 \times 6 \times 10$ mm^3 and $3 \times 3 \times 10$ mm^3 were obtained for optical absorption and EPR measurements, respectively. Anthracene single crystals were irradiated with electrons (2 MeV, 10 μA) from a Van de Graaff accelerator at LNT. For irradiation, a conventional cryostat was used.

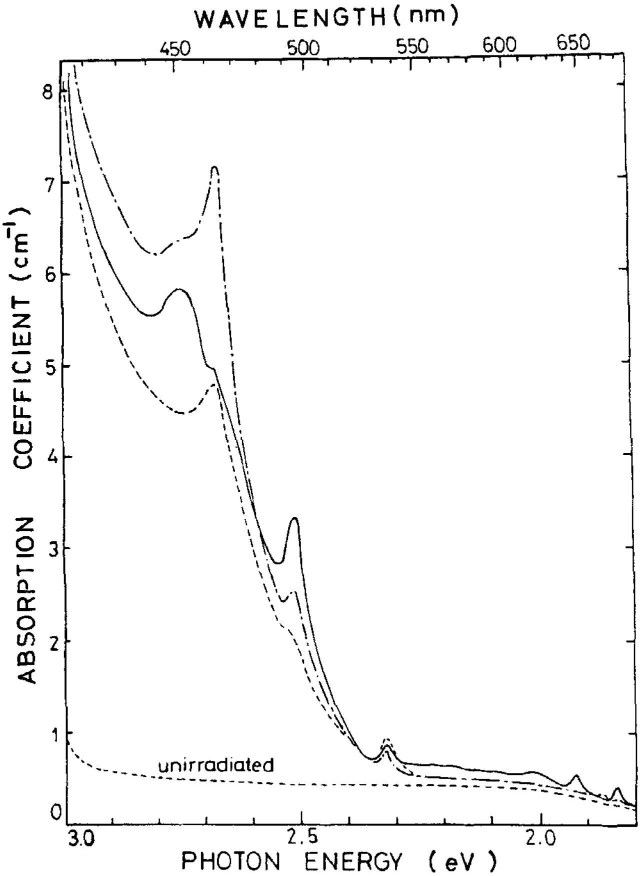
The measurements of the optical absorption spectra were made with a double beam spectrophotometer (Shimadzu MPS-50L) at LNT. The incident light was perpendicular to the crystalline a-b plane. In order to obtain the dichroic spectra, a Glan–Thompson prism was used.

For EPR measurements, a specimen of $3 \times 3 \times 10$ mm^3 was sealed off in an evacuated quartz tube. The tube was immersed in liquid nitrogen in a metal cryostat with aluminum windows, placed in a close vicinity of the window and irradiated with electrons. The measurements of the EPR spectra were made with an X-band spectrometer (Japan Electron Optics.

JES-ME) at temperatures between 77 and 300 K using variable-temperature accessories. Further details of the experimental techniques, have been described already.[15]

III EXPERIMENTAL RESULTS

Optical absorption spectra measured with light polarized along *a*- and *b*-axes of anthracene single crystals irradiated with the electrons at LNT are shown in Figures 2(a) and (b), respectively. The solid lines are spectra obtained just after irradiation at LNT. In the figures the spectra obtained after the specimen was kept for 2.5 and 51.5 hours at RT are also shown. Figure 3 shows the detail of the optical absorption spectra between 535 and 700 nm for heavily irradiated anthracene single crystals, measured at 30 K. The solid and dashed



(a)

lines were obtained with light polarized along *a*- and *b*-axes, respectively. The prominent band at 535 nm is nearly isotropic. At the long wavelength side of the 535 nm band, several less intense bands are observed. Among them, bands at 645 and 675 nm are most intense. As discussed later the lines with solid arrows are assigned to the vibrational structures of the 675 nm band and those with dashed arrows to the vibrational structures of the 645 nm band. Three bands at 535, 645 and 675 nm are of primary concern in the present paper.

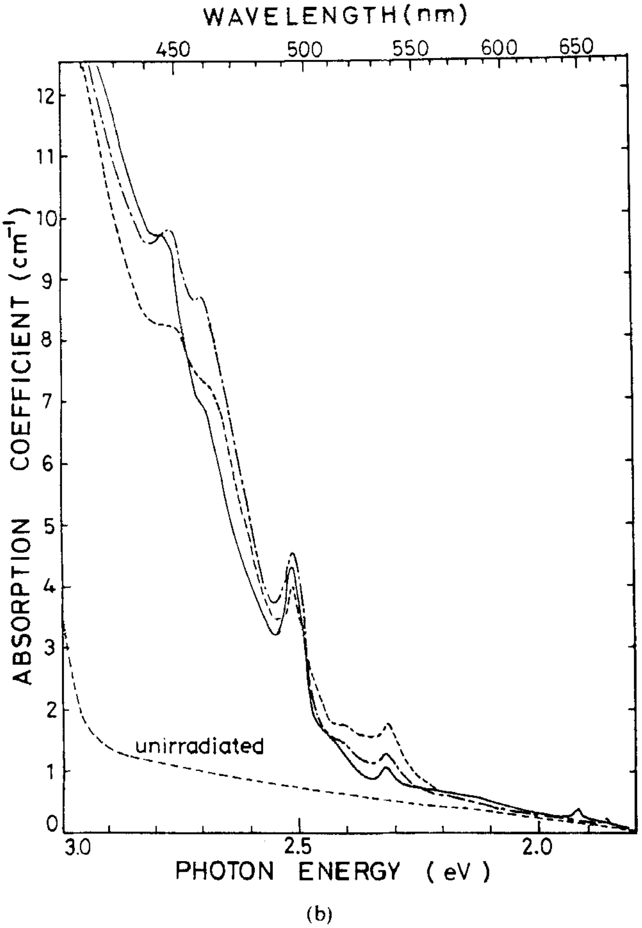


FIGURE 2 Optical absorption spectra of the anthracene single crystal irradiated with electrons at LNT. Measurements were made at LNT with light incident perpendicular to the *a*-*b* plane and polarized along the *a*-axis (a) and the *b*-axis (b). The solid lines are the spectra measured at LNT just after irradiation and the dot-dashed and dashed lines are the spectra measured at LNT after the specimen was kept for 2.5 and 51.5 hours at RT, respectively.

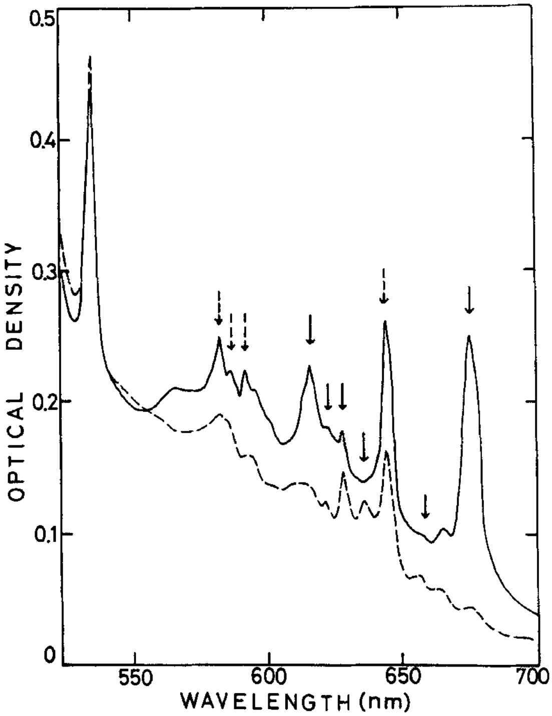


FIGURE 3 Details of the optical absorption spectra of the anthracene single crystal, irradiated at LNT, between 520 and 700 nm. The solid and dashed lines are the spectra measured with light polarized along *a*- and *b*-axes at 30 K, respectively. The solid and dashed arrows indicate the bands which show similar annealing behavior to those of the 675 and 645 nm bands at RT, respectively.

It is seen from Figure 2 that the bands at 465 and 665 nm are enhanced by warming to room temperature and they are gradually annihilated at RT. Bands at 645 and 675 nm are annealed after warming to RT. An increase in the optical density around 535 nm is observed by prolonged annealing at RT. This increase, however, takes place predominantly in the b-polarized spectrum. Since the 535 nm band observed in the specimen irradiated at LNT is non-polarized, a substantial part of the increase cannot be ascribed to the increase of the same species created at LNT. By annealing at higher temperatures it has been shown by Akasaka *et al.*[10] and by Blum *et al.*[1] that the 535 nm band is much enhanced. A similar measurement was made in the present study, where the optical absorption spectra were obtained at LNT not at RT as in the case of previous authors. The difference in the absorption spectra measured at LNT before and after annealing at 383 K for 50 min is shown in Figure 4. It is clear that the difference is composed of a broad b-polarized

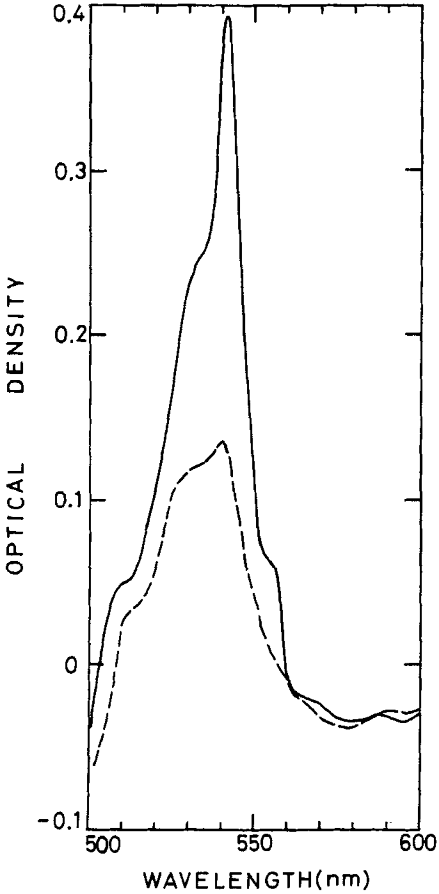


FIGURE 4 Difference between the optical absorption spectra before and after annealing for 50 minutes at 383 K. The specimen irradiated at LNT and kept for 20 days at RT was used. The dashed and solid lines are the difference measured with light polarized along *a*- and *b*-axes, respectively.

spectra. Therefore the former conclusion that the species for the 535 nm band is increased by a factor of 2 by annealing around 400 K is not correct. Since their measurements were made with unpolarized light at RT, the resolution was not apparently good enough.

The change of the heights of the optical absorption bands at 535, 645 and 675 nm while the specimen was kept at RT was measured and the result is shown in Figure 5. In order to determine the height of each band the optical absorption was measured at LNT. The height of the 535 nm band after annealing was determined from the a-polarized spectrum. The annealing

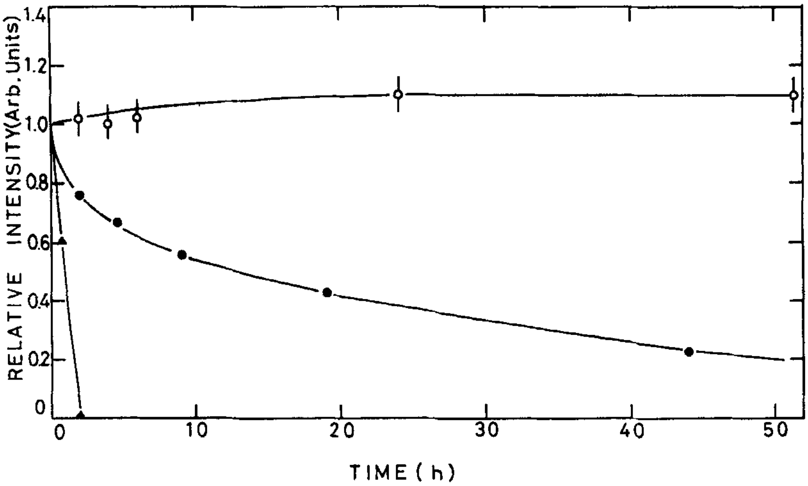


FIGURE 5 Change of the optical absorption peaks at 535 (○), 675 (●) and 645 (▲) nm bands at RT. The irradiation was made at LNT and the abscissa indicates the time while the specimen was kept at RT.

curve of the bands marked with solid and dashed arrows in Figure 3 are the same as those of 675 nm and 645 nm bands, respectively. It is seen that the 645 nm band disappears rapidly and the 675 nm band decreases slowly, while the 535 nm band remains constant in height. The properties of the prominent optical absorption bands studied in this paper are listed in Table I.

Angular dependence of the EPR spectra of anthracene single crystals irradiated at LNT was measured at LNT and also at the temperatures between 140 K and RT. Figures 6(a) and (b) show the EPR spectra measured at 140, 230 and 280 K and at angles $\theta = 0°$ and 100°, respectively, where θ is the angle between the a-axis and the direction of the magnetic field. The EPR

TABLE I

Prominent optical absorption bands in anthracene crystal irradiated at LNT

Wavelength (nm)	Polarization	Production by irradiation	Behaviour at RT	Assignment
465	a	no	grow	
535	isotropic	yes	stable	9-DBCR
645	a	yes	decay immediately	2-DBCR
665	isotropic	no	grow	
675	a	yes	decay gradually	1-DBCR

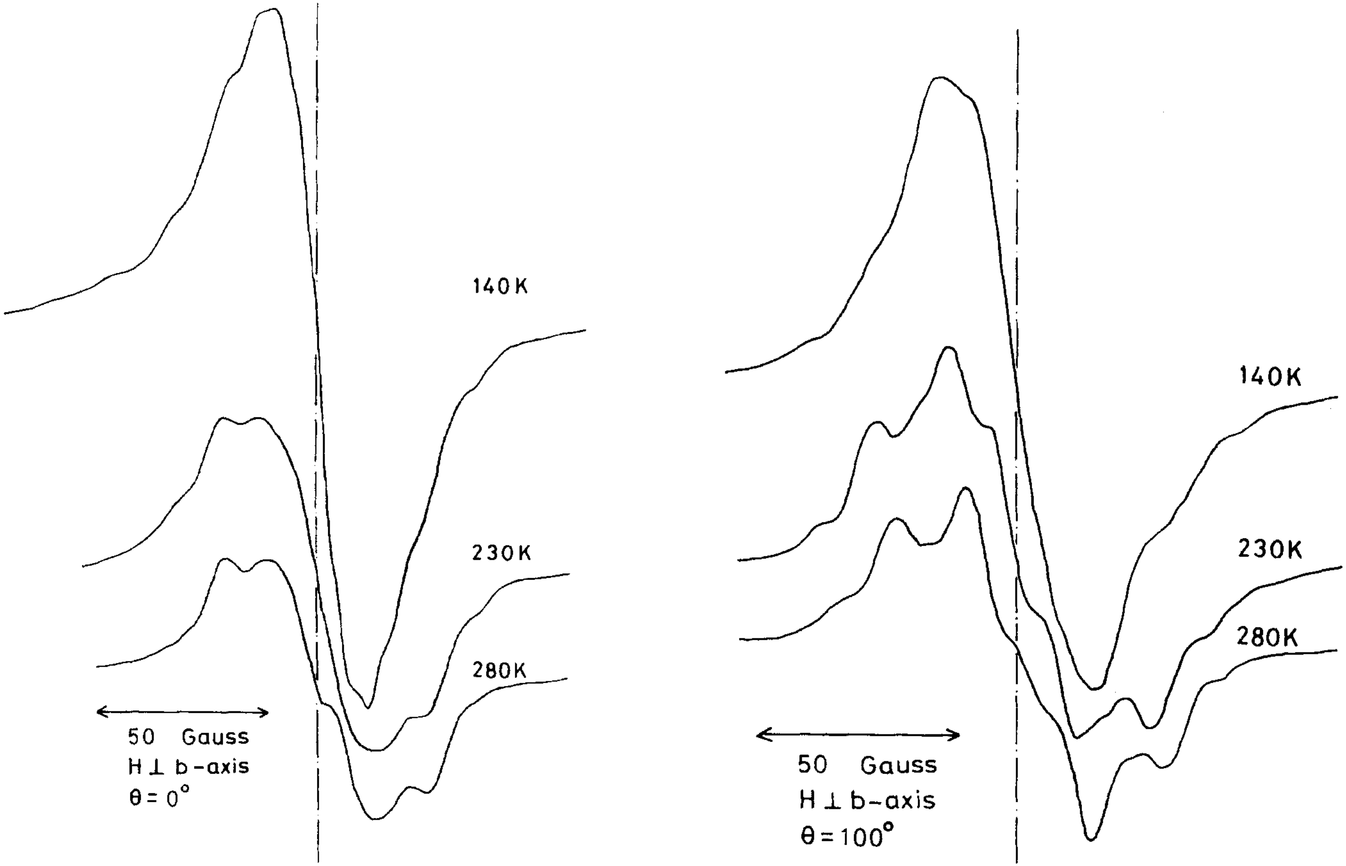


FIGURE 6 EPR spectra of the anthracene single crystal irradiated with electrons at LNT, measured at 140, 230 and 280 K. Measurements were made at $\theta = 0$ (a) and $\theta = 100$ (b), where θ is the angle between the a-axis and the direction of the magnetic field.

spectra observed at LNT were similar with those observed at 140 K. Subtraction of the EPR spectrum observed at 280 K from that observed at 140 K gives a singlet spectrum, with a peak-to-peak width of 27–30 Gauss, independent of the direction of the magnetic field within the experimental error. It was shown that the total area of EPR spectrum at 140 K is nearly twice of that at 280 K.

In order to analyze the EPR spectrum remaining at 280 K, subsequent change of the spectra at RT was measured at various directions of the magnetic field. Figures 7(a) and (b) show the EPR spectra of a specimen irradiated at LNT obtained immediately after warming to RT (solid line) and after keeping 51 hours at RT (dashed line) at angles $\theta = 0^\circ$ and 100°. It is clearly seen that the shape of the EPR spectra are considerably changed. This result indicates that at least two paramagnetic species are involved in the specimen immediately after warming to RT. It was found that the EPR spectrum observed after 51 hours' annealing at RT was the same as that observed after 100 hours' annealing within the experimental error. Four lines are resolved in this spectrum and the angular dependence of the position of the lines is shown in Figure 8 by open circles. The solid lines in the figure are the result of theoretical calculation. The change of the intensity of the EPR spectrum of a specimen irradiated at LNT while being kept at RT was investigated in detail and the result is shown by open circles in Figure 9. The curves in Figure 9 are discussed later.

IV DISCUSSION

The EPR spectrum of anthracene single crystals irradiated at LNT was found to be a superposition of a broad singlet spectrum with a width of 27 ~ 30 Gauss and the angular dependent spectra with structures. The former is annealed prominently between 140 K and 280 K and the latter is stable at 280 K. Both the absence of the angular independence and of the major hyperfine structures in the singlet spectrum clearly indicate that the singlet spectrum is due to the 9-anthracyl radical. The EPR spectrum of 9-AR has been studied by Kasai *et al.*[22] and Akasaka *et al.*,[11] respectively. Kasai *et al.*[22] measured the EPR spectrum of 9-AR trapped in an argon matrix at 4 K. They have shown that the EPR spectrum of 9-AR is a singlet with a width of 17 Gauss. The difference between the widths of the two spectra may be caused by the interaction of the radical wave function with the neighboring molecules and/or by the dipole interaction with other radicals in crystals. The presence of 1- and 2-AR may have made the apparent width larger. A similar observation has been made for naphthalene.[15]

The EPR spectra of a specimen irradiated at LNT and warmed to RT include at least two components. One which is stable at RT is essentially

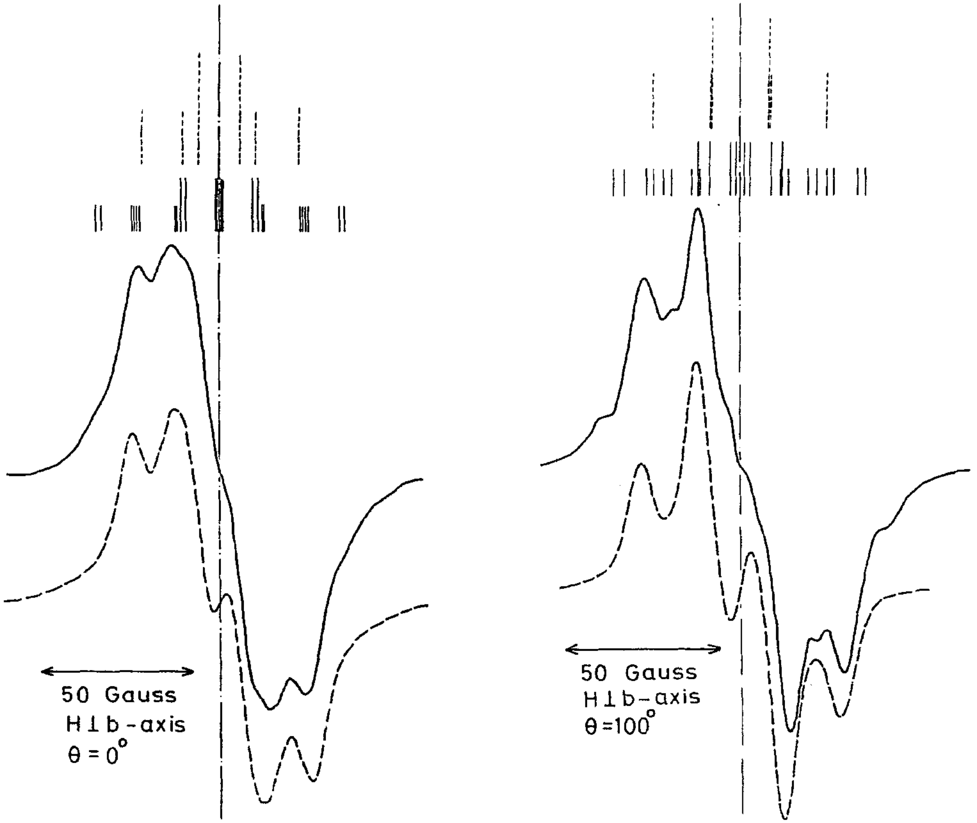


FIGURE 7 EPR spectra of the anthracene single crystal irradiated at LNT and then warmed to RT. Measurements were made at RT just after the specimen was warmed to RT and after annealed for 51 hours at RT at $\theta = 0$ (a) and $\theta = 100°$ (b), where θ is the angle between the a-axis and the direction of the magnetic field. Calculated EPR lines associated with 1- and 9-DBCR are shown at the top by the solid and dashed lines, respectively.

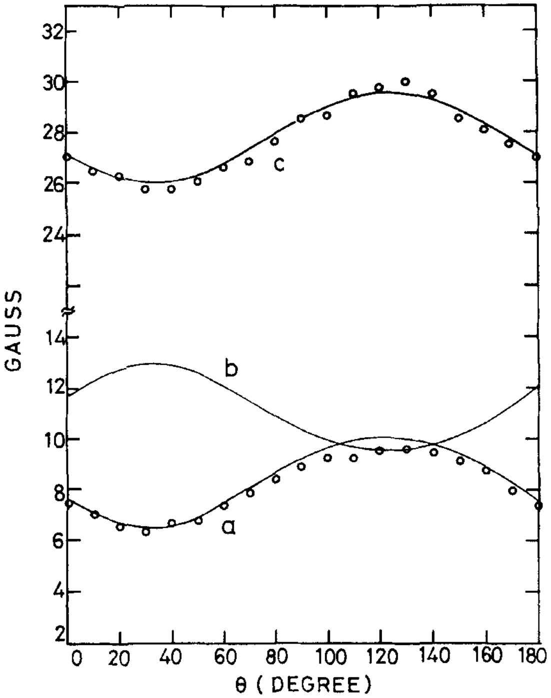


FIGURE 8 Angular dependence of the EPR lines of the anthracene single crystal irradiated at LNT and annealed for 51 hours at RT. The open circles represent the positions of the experimental EPR lines. The solid lines are the calculated results.

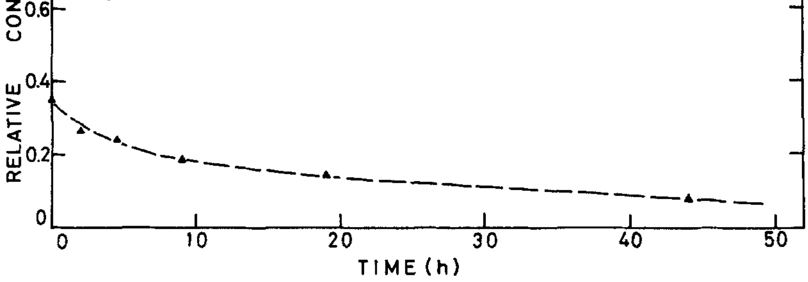


FIGURE 9 Change of the radical concentration at RT in anthracene single crystal irradiated at LNT. Open circles (○) show the EPR intensity and closed circles (●) and closed triangles (▲) connected with dashed lines show the annealing behaviour of the 535 and 675 nm optical absorption bands at RT, respectively. The sum of the concentration of the species for the 535 and 675 nm bands is shown by the solid line. The abscissa indicates the time while the specimen was kept at RT.

the same as that observed previously in specimens irradiated at RT.[3] Through the analysis of the angular dependence of the EPR spectra[5] and also of the ENDOR spectra,[7] it has been ascribed to 9-DBCR. The same method employed for the analysis of 1-HNR[12] and the values of the hyperfine tensor for C-H in 1-HNR were utilized and the solid lines a, b and c shown in Figure 8 were obtained. The spin densities obtained by Kinell[23] were used. The result of the calculation is also shown at the top of Figures 7(a) and (b) by the dashed lines. The intensity of the line b is the half of that of a and may not have been resolved experimentally. The good agreement between experimental and theoretical results ensures that the method of analysis may be used for similar radicals in anthracene.

One considers now the analysis of the other component of the EPR spectrum of a specimen just after warming to RT. Because of the low concentration of the radical annealed at RT and of the complexity of the EPR spectra, the subtraction of the spectrum after annealing from that before annealing can not lead to spectra clear enough to separate each lines contained in the spectrum annealed at RT. Inspection of the EPR spectra produced by irradiation at LNT at large splitting reveals that the radical is produced by irradiation at LNT. The fact that the radical is produced at LNT and that its EPR spectrum is angular dependent suggests that the radical has a simple structure and an additional hydrogen atom. The positions of the EPR lines due to 1- and 2-DBCR were calculated with a similar method employed for the calculation of the EPR lines due to 9-DBCR. The spin densities obtained by Kinell *et al.*[23] were used. The positions of the calculated lines for 1-DBCR were qualitatively in good agreement with the additional EPR lines present before annealing at all angles between $\theta = 0^\circ$ and 180°. On the upper side of Figure 7, the positions of the calculated EPR lines due to 1 and 9-DBCR for 0° and 100° are shown with solid and dashed lines, respectively. Even if 2-DBCR is present, their outer-most component of the EPR lines should appear at a larger magnetic field than the field where the experimental spectra are observed. Thus it is concluded that the solid EPR spectrum in Figure 7 consists of EPR signals of 1 and 9-DBCR.

Two cyclohexadienyl type radicals were found through the EPR analysis: both are produced by irradiation at LNT. Further, referring to Table I, optical absorption bands at 535, 645 and 675 nm are produced by irradiation at LNT. These have different thermal stabilities at RT: stable, decay gradually and decay in 2 hours at RT. It is known that a cyclohexadienyl radical has a sharp optical absorption band in the visible region.[24] By comparing with the results of EPR experiments that 9-DBCR is stable at RT and 1-DBCR is annealed gradually at RT, it is concluded that the 9-DBCR has an optical absorption band at 535 nm and the 1-DBCR at 675 nm. The change of the total concentration of 1- and 9-DBCR at RT was constructed from the relative change of the intensity of the optical absorption bands at 535 nm and 675 nm by choosing an appropriate ratio of the initial concentrations of the two radicals. In Figure 9, two dashed lines indicate the change of the concentration of 9- and 1-DBCR obtained from the optical absorption measurements (Figure 5) and the solid line is their sum. Good agreement with the total intensity of the EPR lines (open circles) substantiates the assignment of the 535 and 675 nm bands.

Blum *et al.*[1] and Akasaka *et al.*[10] investigated the effect of isochronal annealing on the optical absorption and EPR spectra of anthracene single crystals irradiated at RT. They reported an anomalous increase of the 535 nm band by annealing at 400 K, while the intensity of the EPR spectrum is almost unaltered. As shown in the present investigation, the annealing produces new broad b-polarized bands around 535 nm but does not enhance the sharp isotropic 535 nm band typical of the radical. Thus the conclusion by Akasaka *et al.* that the sharp isotropic 535 nm band is not associated with 9-DBCR is incorrect.

The 645 nm band appears to be also associated with a radical produced by irradiation at LNT. Since the main products of irradiation such as 9-AR and 9-DBCR are not reactive at LNT, the 645 nm band may be ascribed to one of the primary products of radiation. Thus it is suggested that the 645 nm band is due to 2-DBCR. In view of the strength of the C—H bonds at positions 9, 1 and 2, it is reasonable that DBCR with an additional hydrogen atom at positions 9, 1 and 2 are more stable in this order.

The EPR results indicate that the destruction of both 9-AR and 1-DBCR does not always produce new radicals. It was suggested that the naphthyl radical is converted to a naphthalene dimer at RT.[8] A similar reaction may occur in anthracene below RT. The subsequent conversion of 1-DBCR to a diamagnetic species may be ascribed to the formation of a hydrogen molecule.[15] Optical absorption bands, such as 525, 465 and 665 nm, which are not produced by irradiation at LNT but grow during or by warming to RT may be correlated with the anthracene dimer.

Acknowledgement

The authors express their gratitudes to M. Hattori and N. Nakazawa for cooperation in the early part of the investigation. They are grateful to T. Nakayama and K. Nakagawa for helpful discussion. Thanks are also due to the member of the Van de Graaff group for assistance.

References

1. H. Blum, P. L. Mattern, R. A. Arndt, and A. C. Damask, *Mol. Crystals*, **3**, 269 (1967).
2. G. A. Simpson, J. Castellanos, A. Cobas, and S. Z. Weisz, *Mol. Crystals*, **5**, 165 (1968).
3. L. A. Harrah and R. C. Hughes, *Mol. Crystals*, **5**, 141 (1968).

4. T. Okubo, N. Itoh, and T. Suita, *J. Phys. Soc. Japan*, **24**, 1179 (1968).
5. T. Inoue, *J. Phys. Soc. Japan*, **25**, 914 (1968).
6. T. Okubo, N. Itoh, and T. Suita, *Mol. Cryst. Liq. Cryst.*, **6**, 227 (1969).
7. U. R. Böhme and G. W. Jesse, *Chem. Phys. Letters*, **3**, 329 (1969).
8. T. Chong and N. Itoh, *Mol. Cryst. Liq. Cryst.*, **11**, 315 (1970).
9. H. Ringel, A. C. Damask, R. A. Arndt, and W. B. Whitten, *Mol. Cryst. Liq. Cryst.*, **14**, 63 (1971).
10. Y. Akasaka, K. Murakami, K. Masuda, and S. Namba, *Mol. Cryst. Liq. Cryst.*, **13**, 377 (1971).
11. Y. Akasaka, K. Masuda, and S. Namba, *J. Phys. Soc. Japan*, **30**, 1686 (1971).
12. N. Itoh and T. Okubo, *Mol. Cryst. Liq. Cryst.*, **17**, 303 (1972).
13. U. R. Böhme and H. C. Wolf, *Chem. Phys. Letters*, **17**, 582 (1972).
14. A. Piccini and W. B. Whitten, *Mol. Cryst. Liq. Cryst.*, **18**, 333 (1972).
15. T. Chong and N. Itoh, *J. Phys. Soc. Japan*, **35**, 518 (1973).
16. N. Itoh and T. Chong, *Energy and Charge Transfer* (ed. by K. Masuda and M. Silver), Plenum Press, New York, 1974, p. 45.
17. T. Chong, Y. Shibata, and N. Itoh, *Phys. Stat. Sol.* (**a**)**27**, 599 (1975).
18. V. A. Smirnov, O. M. Andreev, and M. V. Alfimov, *Chem. Phys. Letters*, **28**, 84 (1974).
19. T. Chong and N. Itoh, *Phys. Stat. Sol.* (b) (in print).
20. K. Nakagawa and N. Itoh, to be published.
21. T. Nakayama and N. Itoh, *Solid State Commu.*, **16**, 635 (1975).
22. P. H. Kasai, P. A. Clark, and E. B. Whipple, *J. American Chem. Soc.*, **92**, 2640 (1970).
23. P. Kinell, A. Lund, and A. Shimizu, *J. Phys. Chem.*, **73**, 4175 (1969).
24. T. Shida and I. Hanazaki, *Bull. Chem. Soc. Japan*, **43**, 646 (1970).