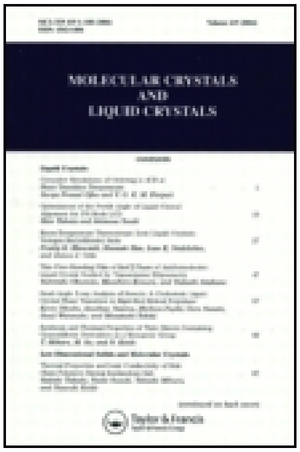

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Radiolysis in Naphthalene Single Crystals

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Abstract—Experimental studies of optical absorption and electron paramagnetic resonance of naphthalene single crystal irradiated at liquid nitrogen, dry ice and room temperatures have been made. It is found that the epr spectrum associated with the l-hydronaphthyl radical is produced at all temperatures studied. Optical absorption bands at 337, 395 and 530 nm are assigned to be associated with the l-hydronaphthyl radical. Irradiation at liquid nitrogen temperature produces a broad doublet epr spectrum as well as that associated with the l-hydronaphthyl radical; the former is considered to be caused by the naphthyl radical. Irradiation at dry ice and room temperatures produces optical absorption bands which are associated neither with the hydronaphthyl nor the naphthyl radical. It is suggested that the radiation products at higher temperature are the hydronaphthyl radical and the naphthalene dimer which is formed as the result of reaction of the naphthyl radical with a neighboring molecule.

1 Introduction

Little is known about radiation effects on single crystal of aromatic hydrocarbons. Some secondary radiation effects, such as effects on scintillation efficiency[1] and on electron mobilities[2] have been studied. These investigations, however, give little information about the nature of the radiation products which act as the

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recombination or trapping centers. Recently epr studies of the X-irradiation products in naphthalene[3] and anthracene[4–7] single crystals have been made and the species identified[3,6] as the radicals with a hydrogen atom added to the host molecules (hydronaphthyl radical‡ in the case of naphthalene). No other paramagnetic centers have been identified in these molecules irradiated at room temperature.

Studies of radiation effects in the polycrystalline benzene have been made by Onishi *et al.*[8] They showed that both the cyclohexadienyl radical (a hydrogen atom added to benzene molecule) and the phenyl radical (benzene molecule missing a hydrogen atom) are produced by X-irradiation at −196 °C, and suggested that a hydrogen atom is detached from a benzene molecule by irradiation and that the detached hydrogen atom is trapped by another benzene molecule. So far the existence of radicals with a missing hydrogen (naphthyl radical in the case of naphthalene) atom have not been reported in irradiated naphthalene and anthracene single crystals.

Recently Lloyd *et al.*[9] found that the naphthyl radical is produced in tritiated naphthalene crystals submitted to radioactive decay at liquid nitrogen temperature. They also observed that the hydronaphthyl radical is produced after the specimen is warmed to room temperature. They suggested that the naphthyl radical begins to react with a neighboring molecule as the temperature is increased producing a hydrogen atom and the naphthyl dimer: the former reacts with a naphthalene molecule to form the hydronaphthyl radical.

The present paper describes epr and optical absorption studies of the radiation products of naphthalene single crystals irradiated between liquid nitrogen and room temperatures. It is shown that irradiation at liquid nitrogen temperature produces 1-hydronaphthyl and naphthyl radicals. Only the 1-hydronaphthyl radical is identified by epr studies in the specimen X-irradiated at room temperature. It is suggested that the non-paramagnetic

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‡ In some papers the hydronaphthyl radical is referred simply as naphthyl radical.

center created in addition to the 1-hydronaphthyl radical by X-irradiation at room temperature is a kind of dimer molecule.

2 Experimental Techniques

Reagent grade naphthalene powder was purified by vaporization. Crystals were grown by the Bridgeman technique in an evacuated cell. The crystal orientation was determined with a polarizing microscope. For epr measurements specimens of $3 \times 3 \times 10\ mm^3$ in dimension were sealed off in an evacuated sample cell. Optical measurements were made with specimens of $10 \times 10 \times 2\ mm^3$ in dimensions in a conventional cryostat, in which the specimen was kept in vacuum. In order to avoid sublimation of the specimen for optical absorption measurements around 0 °C, the specimens were sandwiched between quartz plates.

For the optical measurements the specimens were irradiated with X-ray from an X-ray tube operated at 50 keV, 40 mA, through an aluminum window attached to the cryostat. Both X-irradiation and irradiation with electrons from a van de Graaff accelerator were employed for epr measurements. Most epr studies were made with electron-irradiated specimens since a higher concentration of radiation products is required to get a high signal to noise ratio. It is confirmed that the effect of X-irradiation and electron-irradiation is qualitatively the same. The sample cells containing the specimens for epr measurements were kept in liquid nitrogen or in alcohol dry ice mixture, and were transferred to the dewar for epr measurement after irradiation.

Optical measurements were made with a double beam spectrophotometer (Shimadzu MPS-50). To obtain the dichroic spectrum a Glan-Thompson prism was used. Epr measurements were made with an X-band spectrometer JES-ME. The microwave power used in these measurements was approximately 0.2 mW. Although the saturation behaviour was not studied in detail the microwave power used is considered low enough to avoid the saturation.

3 Experimental Results

Figures 1a and 1b show the epr spectrum of a specimen irradiated at room temperature and measured at the same temperature with the magnetic field perpendicular to the *b*-axis and at an angle ϕ to the a' axis. This spectrum is ascribed by the present authors to the hydronaphthyl radical.[3] The g value of the spectrum is 2.0016 and is almost independent of the direction of the magnetic field. The hyperfine splitting parameters depend on the direction

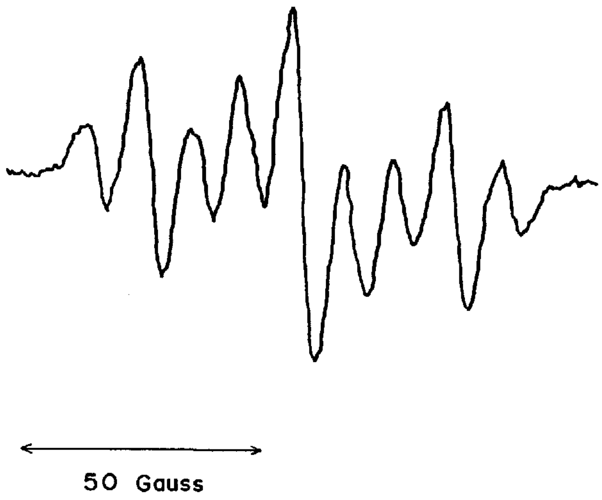

Figure 1a

Figure 1b

Figure 1. An X-band epr spectrum of naphthalene single crystal electron-irradiated at room temperature. The magnetic field is perpendicular to the *b*-axis and oriented to the a'-axis with (a) $\phi = 20°$ (b) $\phi = 95°$.

of the magnetic field very strongly as shown in Fig. 1. Detailed analysis of the angualr dependence will be published separately.[10] Apparently no other paramagnetic centers exist in the specimen irradiated at room temperature. The spectrum was obtained with the microwave power just above the detection limit. With increasing microwave power saturation takes place. Figure 2 shows the spectrum of a specimen irradiated at liquid nitrogen temperature and measured at the same temperature. It is clear that the spectrum is the superposition of that shown in Fig. 1 and a broad spectrum. Upon warming the specimen to room temperature

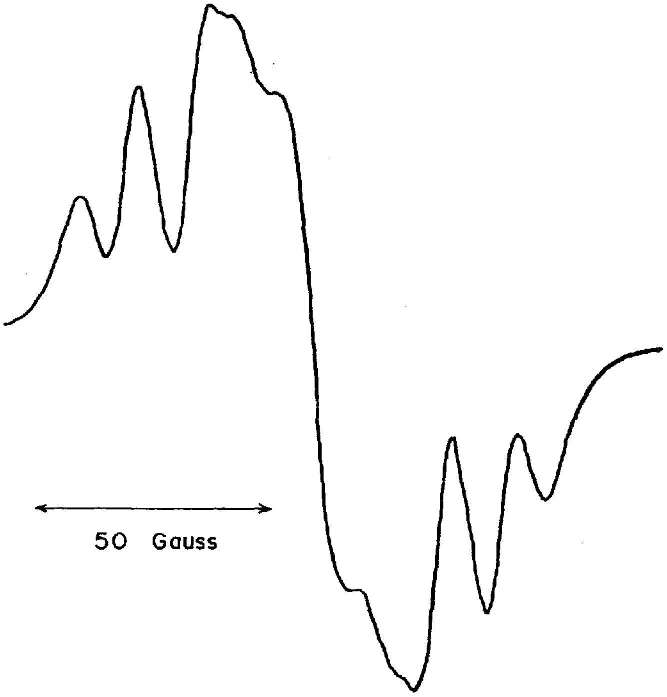

Figure 2. An X-band epr spectrum (measured at liquid nitrogen temperature) of naphthalene single crystal electron-irradiated at liquid nitrogen temperature. The magnetic field is perpendicular to the b-axis and oriented to the a'-axis with an angle $\phi = 20°$.

the intensity ratio of the broad spectrum to that due to the hydronaphthyl radical decreases and after the specimen is kept at room temperature for several hours the broad spectrum disappears completely, while the spectrum for the hydronaphthyl radical remain strong. The epr spectrum measured at room temperature immediately after the specimen is warmed to room temperature is shown in Fig. 3.

The results of the epr measurements indicate that the species produced by irradiation depends upon the irradiation temperature. This result is more clearly seen from the study of the optical

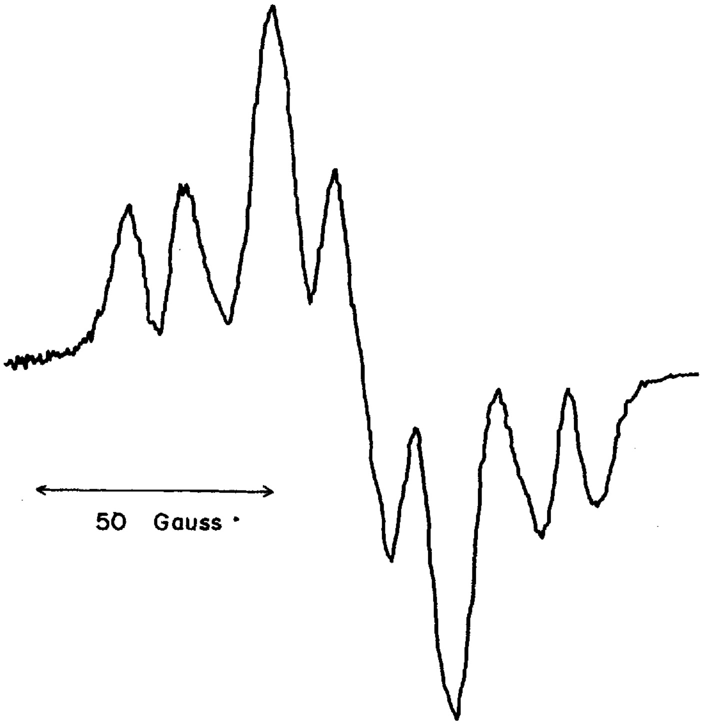

Figure 3a

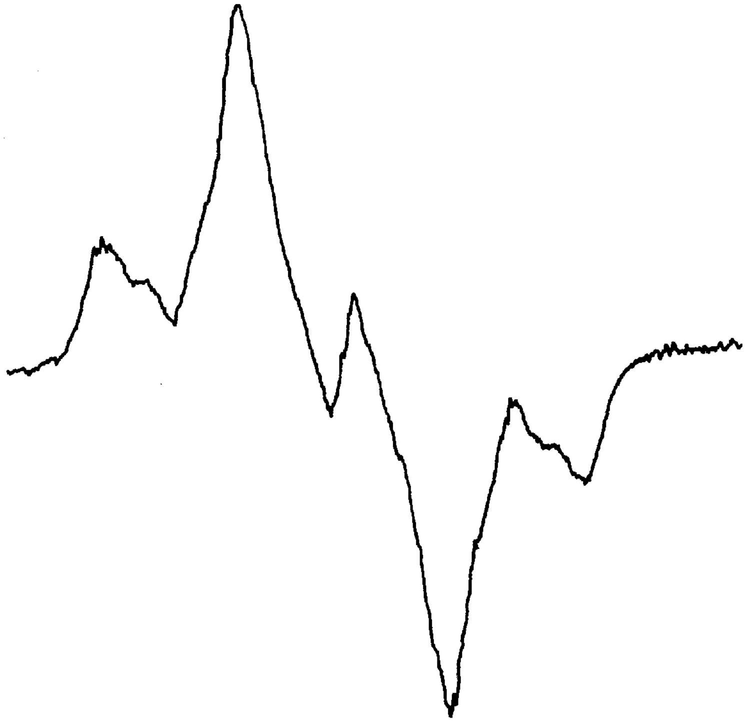

Figure 3b

Figure 3. An X-band epr spectrum of naphthalene single crystal electron-irradiated at liquid nitrogen temperature: The magnetic field is perpendicular to the b-axis and oriented to the a'-axis with an angle of (a) $\phi = 20°$, and (b) $\phi = 95°$. The measurement was made just after the temperature has reached room temperature.

absorption. Figure 4 shows the change in the optical absorption curves of a naphthalene single crystal upon X-irradiation at liquid nitrogen temperature, measured with the incident light beam perpendicular to the a–b plane and polarized along the a- and b-axes. It is seen that several optical absorption bands are created. Comparing the spectra measured with light polarized along a- and b-axes, it is clear that the band at 539 nm and some bands at its shorter wavelength side are almost isotropic. Other bands at 453, 395 and

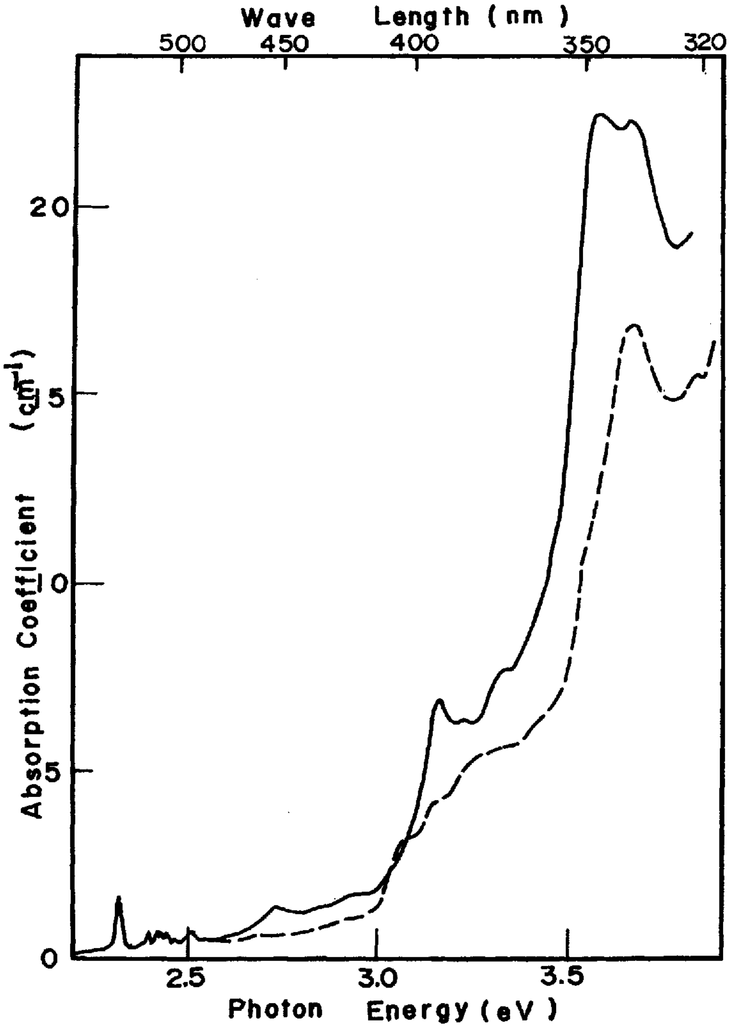

Figure 4. The change in optical absorption of naphthalene single crystal caused by X-irradiation for 20 hours at liquid nitrogen temperature. The measurement was made at liquid nitrogen temperature, with light incident along the *c*′-axis and polarized along the *a*-axis (dotted line) and along the *b*-axis (solid line).

350 nm show stronger absorption for light polarized along *b*-axis: this result indicates that the transition dipoles for these absorption bands are oriented along the short axis. There are some other less prominent bands whose transition dipoles are oriented along the long axis. The main optical absorption bands created by irradiation at liquid nitrogen temperature are summarized in Table 1. The detailed structure of the optical absorption bands around 500 nm is shown in Fig. 5. Figure 6 shows the optical absorption curves of a naphthalene single crystal irradiated at dry ice temperature. Comparing with the result of irradiation at liquid nitrogen temperature, it is clear that isotropic bands at 360 and 381 nm, bands polarized along the *b*-axis at 420 and 453 nm and a band polarized along the *a*-axis at 445 nm are created in addition to the bands created at liquid nitrogen temperature. As shown in Fig. 7, the irradiation at room temperature produces the same absorption bands that were produced at dry ice temperature: The intensity of the 445 and 453 nm bands relative to the intensity of the 337 nm band is higher in the specimen irradiated at room temperature than that irradiated at dry ice temperature. Table 2 shows the optical absorption bands which appear in the specimen irradiated above dry ice temperature.

TABLE 1 Main Optical Absorption Bands Created by Irradiation at Liquid Nitrogen Temperature

Wave Length (nm)	Photon Energy (eV)	Polarization	Comments
337	3.68	isotropic or *b*-axis	1-Hydronaphthyl radical
350	3.54	*b*-axis	
395	3.14	*b*-axis	1-Hydronaphthyl radical
405	3.06	*a*-axis	
453	2.74	*b*-axis	
539	2.30	isotropic or *a*-axis	1-Hydronaphthyl radical

Figure 8 shows the optical absorption band measured at liquid nitrogen temperature of a specimen irradiated at liquid nitrogen temperature and warmed to room temperature. It is clear that

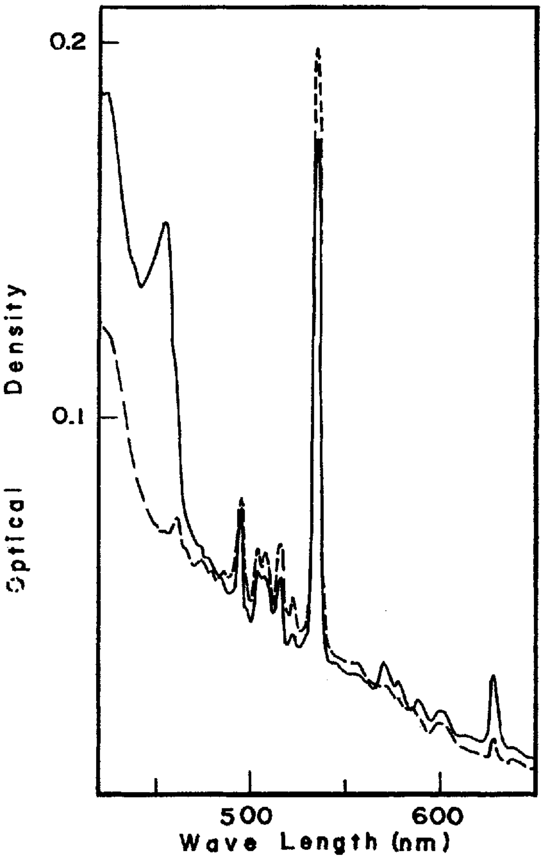

Figure 5. Details of the absorption spectrum shown in Fig. 4 in the wavelength region of 400–650 nm.

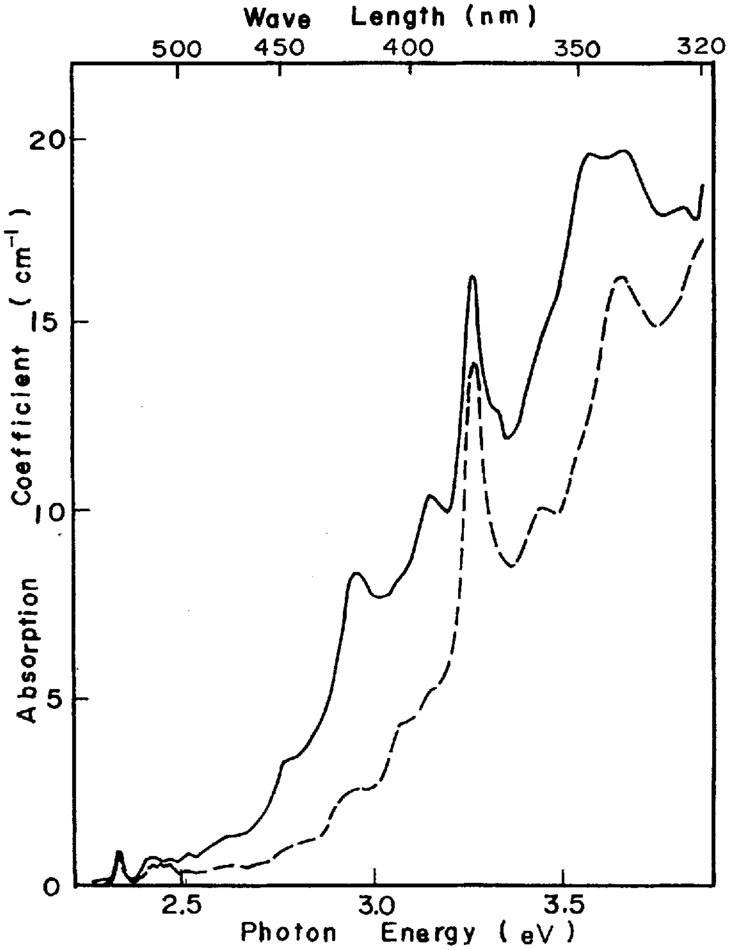

Figure 6. The change in optical absorption of naphthalene single crystal caused by X-irradiation for 20 hours at dry ice temperature. The measurement was made at dry ice temperature, with light incident along the c'-axis and polarized along the a-axis (dotted line) and along the b-axis (solid line).

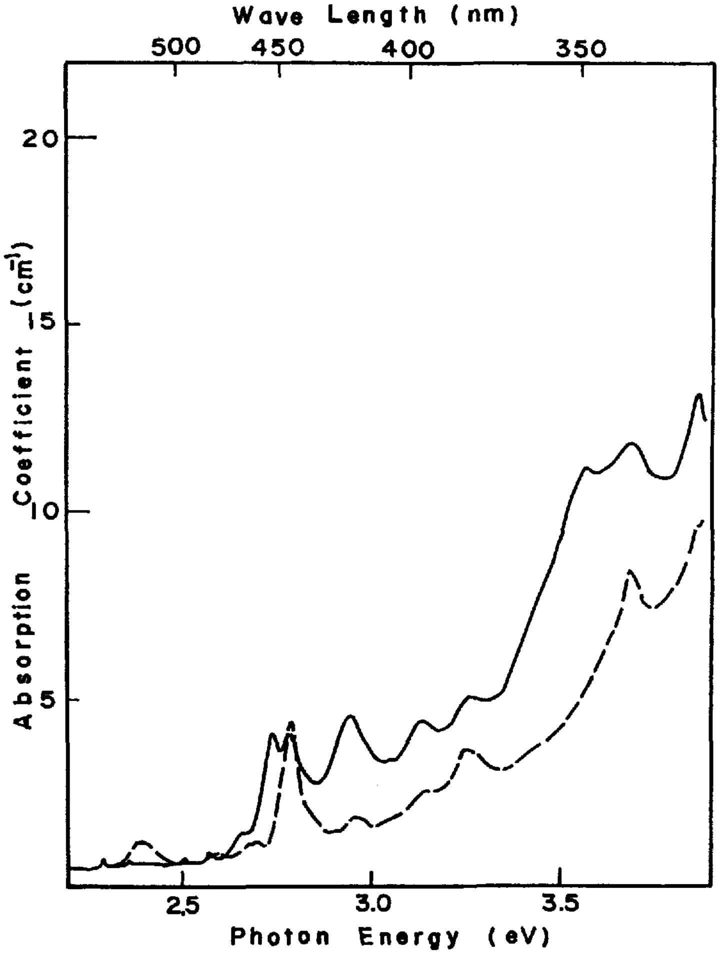

Figure 7. The change in optical absorption of naphthalene single crystal caused by X-irradiation for 20 hours at Room temperature. The measurement was made at Room temperature, with light incident along the c'-axis and polarized along the a-axis (dotted line) and along the b-axis (solid line).

TABLE 2 Main Optical Absorption Bands Created by Irradiation above Dry Ice Temperature

Wave Length (nm)	Photon Energy (eV)	Polarization	Comments
337	3.68	isotropic or *b*-axis	1-hydronaphthyl radical
350	3.54	*b*-axis	
360	3.44	isotropic	
381	3.25	isotropic	
395	3.14	*b*-axis	1-hydronaphthyl radical
405	3.06	*a*-axis	
420	2.95	*b*-axis	
445	2.79	*a*-axis	
453	2.74	*b*-axis	
539	2.30	isotropic or *a*-axis	1-hydronaphthyl radical

the optical absorption bands at 337, 350, 395 and 539 nm decreased in intensity. The band at 405 nm disappear completely and that at 453 nm retain the same intensity. It is also clear that the ratio of the height of the 337 nm band to that of the 350 nm band decreases.

4 Discussions

Both epr and optical experiments indicate that the radiation products at liquid nitrogen, dry ice and room temperatures are different. The epr spectrum of the specimen irradiated at room temperature is the most simple. This spectrum has been assigned to the 1-hydronaphthyl radical.[3] The angular dependence of the spectrum is in accordance with that predicted from the theory.[10] The examination of the spectrum indicates that there are very few (if any) paramagnetic species in the specimen irradiated at room temperature other than the hydronaphthyl radical. Since the spectrum is obtained with very low microwave power, it appears that the hydronaphthyl radical is the only paramagnetic center produced by irradiation at room temperature.

It is clear from Fig. 2 that irradiation at liquid nitrogen temperature produces new paramagnetic species as well as the hydro-

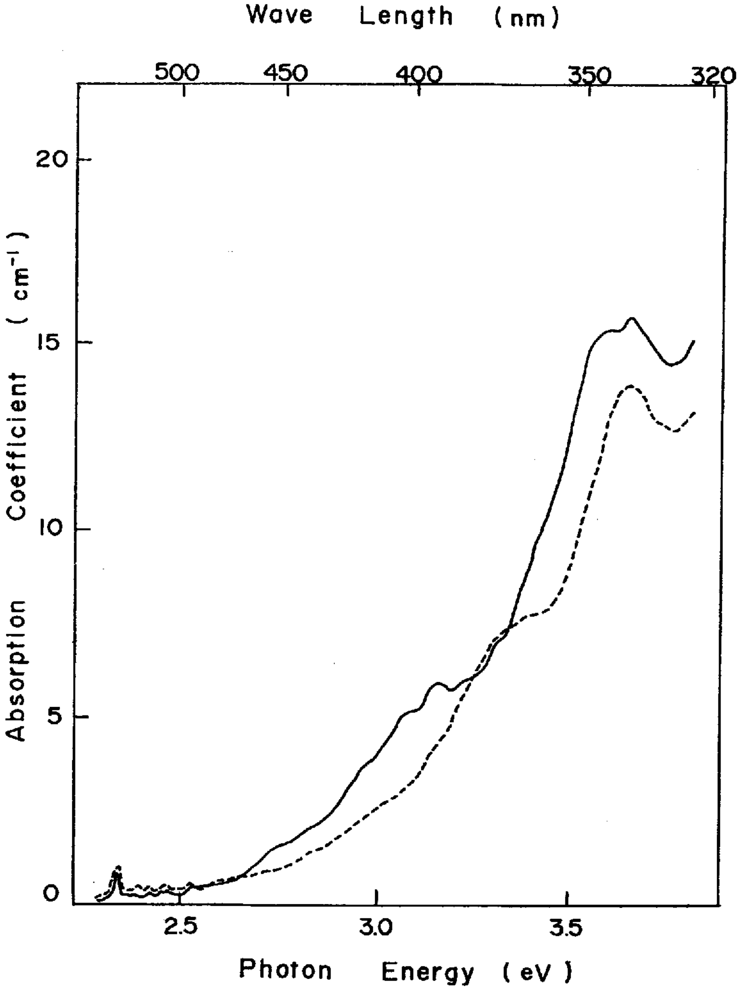

Figure 8. The change in optical absorption of naphthalene single crystal caused by irradiation at liquid nitrogen temperature for 20 hours and subsequent warming to room temperature. The measurement was made at liquid nitrogen temperature, with light incident along the c'-axis and polarized along the a-axis (dotted line) and along the b-axis (solid line).

naphthyl radical. Comparison of Fig. 2 and Fig. 3a indicates that the ratio of the intensity of the new spectrum to that for the hydronaphthyl radical decreases as the specimen is warmed to room temperature. The epr spectrum for the new species may be obtained by subtracting the epr spectrum shown in Fig. 1, from that shown in Fig. 2 or in Fig. 3. Subtraction of the curve of Fig. 1b from that of Fig. 3b shows that the spectrum consists of a doublet with a separation between 10 and 20 gauss. Inspection of the curves of Figs. 1a and 3a indicates that the same doublet exists as the difference of these two curves. We therefore conclude that the irradiation at liquid nitrogen temperature produces the hydronaphthyl radical and a new radical whose epr spectrum consists of a doublet and that the new radical is unstable around room temperature. It is also deduced from the curves of Figs. 1a and 2 that the concentrations of the hydronaphthyl radical and the new radical are of the same order of magnitude.

Since it is clear that the hydronaphthyl radical is produced by irradiation at liquid nitrogen temperature one may ask where the additional hydrogen comes from. It is reasonable to consider that the hydrogen atom originated from a naphthalene molecule and reacted with a naphthalene molecule to form a hydronaphthyl radical after diffusion in the crystal. If this is the case one expects a hydronaphthyl radical and a naphthyl radical were produced. The epr spectrum for the naphthyl radical has been studied by Lloyd *et al.*[9] in tritiated naphthalene at liquid nitrogen temperature. They found that the spectrum of the naphthyl radical is a doublet with a separation of 17 gauss. Although it is not very easy to obtain the accurate spectrum in the present case, it is reasonable to conclude that the epr doublet discussed in the last paragraph is associated with the naphthyl radical. We conclude, therefore, that irradiation at liquid nitrogen temperature produces a hydronaphthyl radical and a naphthyl radical in pair.

We discuss now the study of the optical absorption. There are a number of optical absorption bands created by irradiation. Since the hydronaphthyl radical has been identified it is of interest to find the optical absorption bands for this radical. There are two criteria for distinguishing the bands of this radical from the other optical absorption bands: (i) the hydronaphthyl radical is produced by irradiation at liquid nitrogen, dry ice and room temperatures, and (ii) the hydronaphthyl radical created at liquid nitrogen temperature remains stable when the temperature is raised to room temperature although its concentration may be reduced. The optical absorption bands produced at all these temperatures are those at 337, 350, 395, 405, 453 and 539 nm. Among them the 405 nm band disappears completely by warming the specimen to room temperature, and the 350 nm band is also reduced substantially while the height of 453 nm band is unaltered. Theoretical calculation by Hanazaki[11] suggests that there are four absorption bands associated with the hydronaphthyl radical in the uv and visible region. Thus, we conclude that the bands at 337, 395 and 530 nm are associated with the hydronaphthyl radical, since the intensity ratio of these three bands is nearly the same in every case.

The optical absorption bands for the hydronaphthyl radical found in the present study may be compared with the result of theoretical study.[11] The calculation is based on the semiempirical method developed by Praiser and Parr,[12] combined with the SCF method for an open shell developed by Lonquet-Higgines and Pople.[13] Ten $2p\pi$ AO's of the carbon ring and a pseudo π orbit formed by H_2 are taken into account to perform the SCF calculation with the hyper-conjugation between CH_2 group and the remaining[14] π electrons being included. The transitions whose energies are below that of the fundamental absorption of the naphthalene molecule are listed in Table 3. Comparing with the experimental transition energies listed in Table 1, it is reasonable to conclude that the three theoretical transitions at 2.31, 3.14, and 3.52 eV are indeed observed experimentally. The transition at 3.68 eV is probably hidden under the fundamental absorption of naphthalene single crystal. A few remarks should be made about this assignment. (1) The ratio of the theoretical oscillator strengths of the three bands, 1:5.1:11.5, may be compared with the experimental averaged apparent intensity

TABLE 3 Optical Transitions in the Hydronaphthyl Radical[11]

Transition Energy (eV)	Transition Moment‡ (Å) short axis	Transition Moment‡ (Å) long axis	oscillator strength
2.31	0.084	0.007	1.45×10^{-3}
3.14	0.082	0.141	7.34×10^{-3}
3.52	0.014	0.736	1.67×10^{-1}
3.68	0.152	0.599	1.23×10^{-1}

‡ absolute value.

ratio of the three bands, 1:5:17. The latter value may contain error due to the overlap of several bands. However, the qualitative agreement between the experimental and the theoretical ratios is reasonably good. (2) The transition with a strong dipole moment along the short axis may give the optical absorption polarized along the *b*-axis and the transition with a strong dipole along the long axis may give the optical absorption polarized along the *a*-axis. The agreement between the observed polarization and that predicted from the theory is not good. The reason why the theoretical dipole orientation is not in accord with the experimental orientation is not clear. It is noted here that there are some experimental problems, especially for the transition at 337 nm, that is, the overlap of the band with other bands may affect the apparent orientation dependence of the absorption coefficient.

We discuss now the radiation products produced above dry ice temperature. Epr studies indicate that the ratio of the amount of naphthyl radical to that of hydronaphthyl radical produced by irradiation at dry ice temperature is much lower than the ratio at liquid nitrogen temperature. On the other hand, it is clear from the result of the optical absorption study that another species has been created by irradiation at this temperature. Irradiation at room temperature produced apparently no paramagnetic species other than the hydronaphthyl radical, although the optical absorption study indicates that there are other species present. By comparing Fig. 6 with Fig. 7 it is clear that the most prominent radiation products at dry ice temperature and room temperature are not the same.

In discussing the nature of the radiation products produced only at high temperatures, it is again noted that stoichiometry predicts that there are molecules with less hydrogen in naphthalene crystal irradiated at these temperatures. Since the primary radiation products at these temperatures are the naphthyl and hydronaphthyl radicals, it is considered that the naphthyl radical is reactive under irradiation. In this connection it is interesting to remark on the reaction of the naphthyl radical in polycrystallene naphthalene studied by Lloyd.[9] They observed that the naphthyl radical is not stable around room temperature and that hydronaphthyl radical is produced when the naphthyl radical becomes unstable. They proposed the following reactions to explain their result.‡

$$C_{10}H_7^{\cdot} + C_{10}H_8 \rightarrow (C_{10}H_7)_2 + H^{\cdot}$$

$$C_{10}H_8 + H^{\cdot} \rightarrow C_{10}H_9^{\cdot}$$

If this reaction indeed takes place the radiation at these temperatures produces the naphthalene dimer and the hydronaphthyl radical. Since the former is diamagnetic, only the hydronaphthyl radical is observed by an epr measurement. The hydrogen vacancy may diffuse in the crystal to some extent. If this is the case, one would expect that two naphthyl radicals combine to form a naphthalene dimer. In any case, it appears most reasonable to assume that the naphthalene dimer is produced above dry ice temperature.

The above argument suggests that the optical absorption bands created most prominently at dry ice temperature and those produced most prominently at room temperature are associated with some kinds of naphthalene dimer. The optical absorption of

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‡ In the present study where both hydronaphthyl radical and the naphthyl radical are produced at liquid nitrogen temperature, the thermal instability of the naphthyl radical may result in the annihilation of the hydronaphthyl radical as well in the above reaction, when the specimen is warmed to room temperature.

the α-naphthalene dimer in solution is known to be at 300 nm which is at shorter wavelength than that of the spectrum produced at dry ice and room temperatures. The dimer molecule created in the crystal, however, may have a complex steric structure, which may affect the transition energies considerably. Among the optical absorption bands listed in Table 2, the bands at 360 and 381 nm are prominently produced at dry ice temperature, whereas the bands 445 and 453 nm are more intense than those at 360 and 381 nm in the specimen irradiated at room temperature. When the specimen irradiated at dry ice temperature is warmed to room temperature, the bands at 360 and 381 nm decrease and the bands at 445 and 453 nm increase. Thus it appears that these bands are all associated with naphthalene dimer and the difference in configuration results in different optical absorption bands.

On the reactivity of naphthyl radical it is noted that the height of 2.79 eV band, for example, in the specimen irradiated at liquid nitrogen temperature and warmed to room temperature is much smaller than that in the specimen irradiated at room temperature. This result may indicate that the reaction is stimulated by irradiation, that is, the radical is reactive when the radical or the neighboring molecule are in the excited state. Further studies are required for a more definite assignment of these bands.

The following are the conclusions which may be drawn from the present study.

(i) The hydronaphthyl radical is created by irradiation between liquid nitrogen and room temperature.

(ii) The naphthyl radical is the complementary pair to the hydronaphthyl radical in specimens irradiated at liquid nitrogen temperature.

(iii) The naphthyl radical in naphthalene single crystals is reactive during irradiation above dry ice temperature. Radiation products at room temperature are suggested to be the naphthalene dimer and the hydronaphthyl radical.

As indicated in this study, radiation damage introduces radicals in a single crystal of the aromatic hydrocarbons. We seem to have here a system in which one can study both the static and the dynamic interaction between these radicals and surrounding molecules, the position and the orientation of which are constrained.

Acknowledgements

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