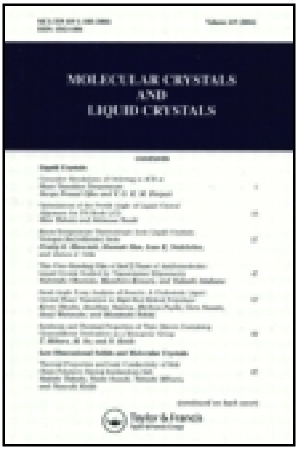

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Optical and EPR Studies of Radiation-Induced Radicals in Phenanthrene Single Crystals

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Optical and EPR Studies of Radiation-Induced Radicals in Phenanthrene Single Crystals

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Phenanthrene single crystals irradiated with γ rays at liquid nitrogen temperatures have been studied by electron paramagnetic resonance and optical absorption experiments. The optical absorption spectra at low temperature, obtained with the light polarized to the a-, b- and c'-axes of the crystals, showed five bands in the long wavelength region and seven bands in the shorter one. These bands were compared with the energies and polarizations of transitions calculated using SCF–CI molecular orbital theory for the five kinds of the hydrogen added phenanthrene radicals. From the annealing at room temperature the 373,377,383,558 and 611 nm bands were attributed to the absorptions of 9-hydro-phenanthryl radical which is most stable among the isomers of the hydrogen added radicals. Considering the energies and polarizations of the absorption bands, the other four bands in the long wavelength region of 638,643, 671 and 677 nm were assigned to the transitions of 1-, 4-, 3- and 2-hydro-phenanthryl radicals, respectively. The 450 and 467 nm bands which appeared upon the annealing at room temperature were ascribed to the transitions of 9-hydro-10,10'-diphenanthryl radical. EPR spectra at room temperature exhibit a triplet-doublet-triplet characteristic and from analysis of the spectra, these lines were identified as the signal of 9-hydro-phenanthryl radical.

1 INTRODUCTION

A number of experiments have been reported on the radicals produced by irradiation of ionizing radiation on the aromatic crystals, such as benzene, naphthalene and anthracene.[1] Recently Chong and Itoh[1] measured the optical absorption spectrum of radicals in anthracene crystals at low temperature successive to the low temperature irradiation. They detected five main absorption bands and assigned the lower three weak bands to be associated with 1-, 2- and 9-dibenzo-cyclohexadienyl radicals, respectively. The present author examined to assign the all seven bands including the other strong bands and the absorptions upon annealing comparing them with the

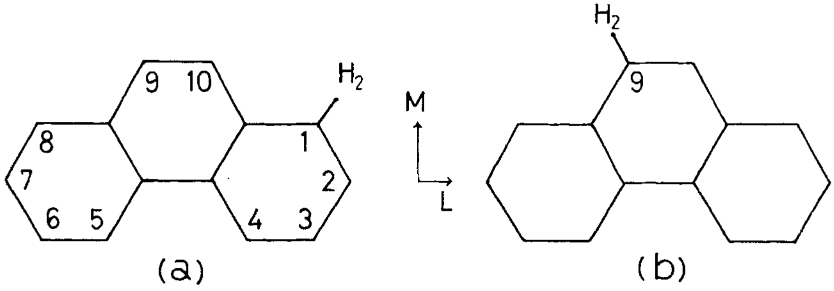


FIGURE 1 (a) 1-hydro-phenanthryl radical, (b) 9-hydro-phenanthryl radical. Similarly 2-, 3-, 4-hydro-phenanthryl radicals have an additional hydrogen atom at 2,3 and 4 carbon sites, respectively.

theoretically calculated transition energies and moments for these radicals, and obtained reasonable results.[2] In anthracene a molecule has three different carbon sites where an addition of hydrogen atom may occur. In the spectrum of radicals in anthracene crystals the lowest three weak bands correspond to the lowest transitions of three radicals in which an addition of hydrogen atom occurs on each site of the above different carbons. The other two bands correspond to the next lowest absorption of the above radicals of anthracene. A phenanthrene molecule has five different carbon sites. If additions of a hydrogen atom occur on all the different carbons and the absorption bands of radical do not overlap each other, five similar weak bands may stand side by side in the log wavelength region and strong bands follow in the shorter wavelength side of the spectrum. It is interesting to examine whether these bands expected will appear in the spectrum and that each band will be possible to assign to the transitions of each radical.

In this paper an observation and assignment of such absorption bands are described and also the EPR spectrum of the radicals is reported.

2 EXPERIMENTAL

Ultra pure grade (zone refined) phenanthrene was purchased from Tokyo Kasei Co. and was further zone refined by 100 passes. Single crystals were grown by the Bridgman method. Crystals of $3 \times 4 \times 8$ mm^3 cut parallel to the ab-plane for use in the EPR study and $6 \times 8 \times 2$ mm^3 cut parallel to the ab-plane or bc'-plane for the optical measurements were used. For unirradiated crystals weak absorptions at 367 and 383 nm (Figure 2a) were detected near the absorption edge of phenanthrene crystals. These two bands are considered to be ones of $^1A_{1g} \rightarrow {}^1B_{2u}$ 380 nm absorption system of anthracene.[3–5] From the intensity of the absorption bands the concentration

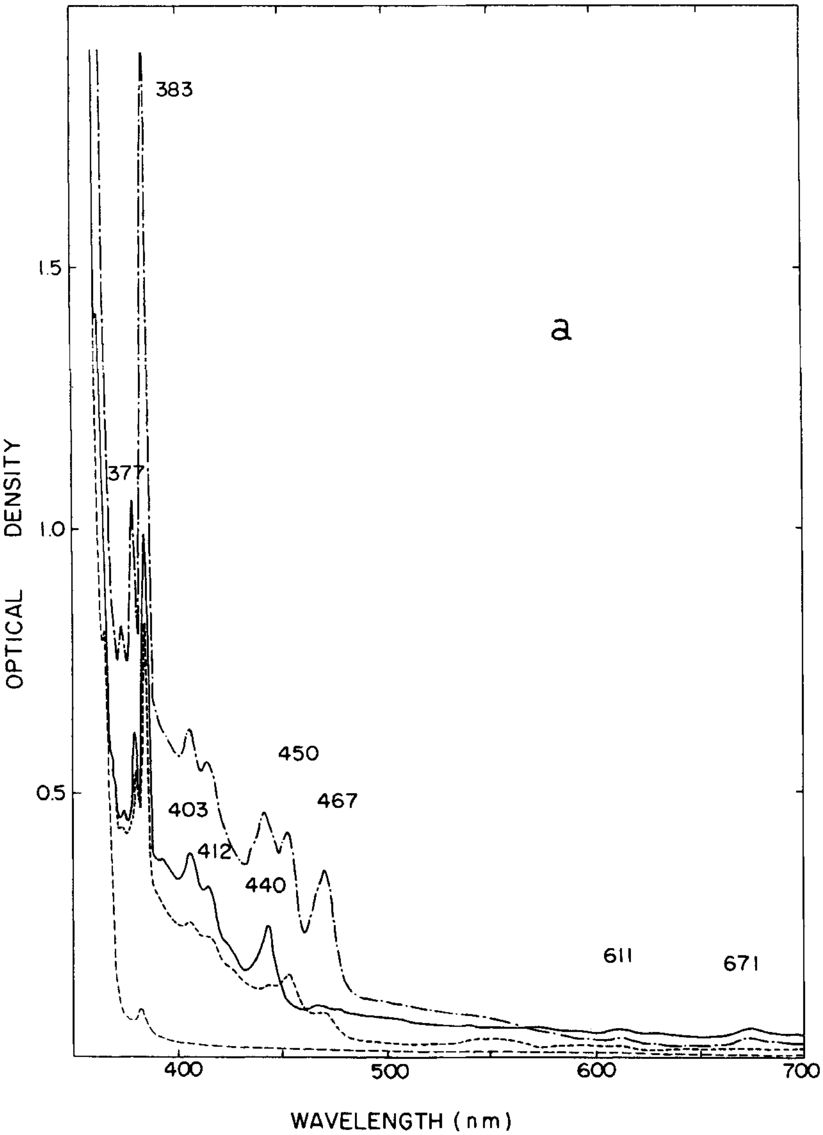


FIGURE 2 Optical absorption spectra at 77°K of phenathrene single crystals irradiated with γ rays at 77°K. Irradiation doses were 1.25×10^7 rad for the crystal to obtain (a) and (b) and 5×10^6 rad for (c). The incident light is perpendicular to the a-b plane and polarized along the a-axis (a) and the b-axis (b). Spectrum c was obtained using light incident perpendicular to the b-c' plane and polarized along the c'-axis. The solid line is the spectrum just after irradiation and the dot-dashed and dashed lines are the spectra at 77°K after the annealings for one hour and 50 hours, respectively. The fine dashed line is the spectrum of unirradiated crystals at room temperature.

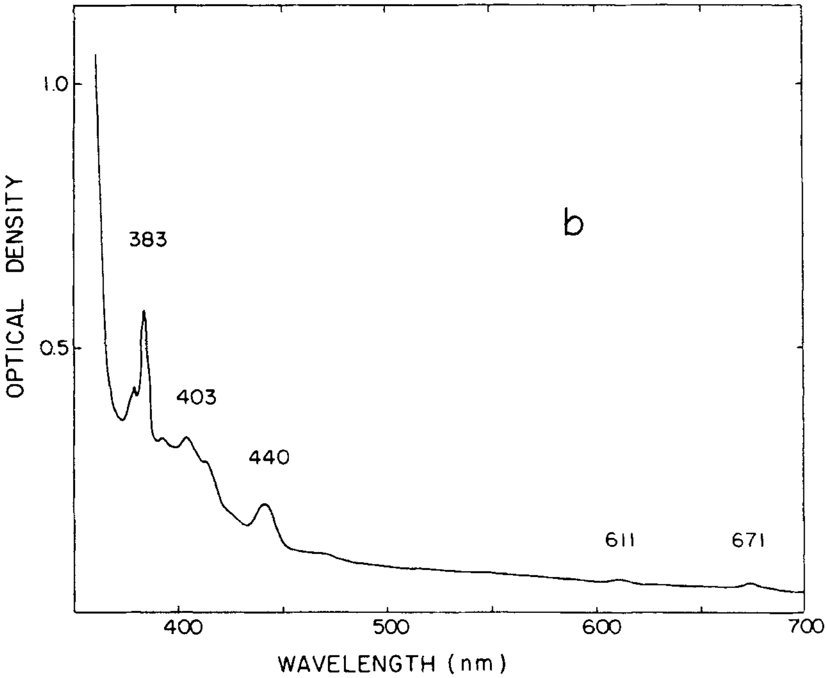


FIGURE 2b

of anthracene in the crystal was estimated to be 3 ppm. Since no absorption band associated with the radicals of anthracene was detected in the spectrum of irradiated crystals, this impurity was thought to not affect the results of this study. Crystals were iradiated at liquid nitrogen temperature with γ rays. Irradiation doses were $5 \times 10,^6$ 1.25×10^7 and 5×10^7 rad for optical studies and 5×10^7 rad for EPR measurements. Crystals were set in a magnetic field with b-axis perpendicular to the field and were rotated around the b-axis. EPR measurements were made at liquid nitrogen temperature and room temperature using a microwave frequency of approximately 9.5 GHz and a power of 0.2 mW. Optical measurements were made at liquid nitrogen temperature with a double beam spectrometer (Shimazu MPS-50).

3 RESULTS AND DISCUSSION

3.1 Optical absorption spectra

Figure 2(a), (b) and (c) show the optical absorption spectra of phenanthrene single crystals irradiated with γ-rays at 77°K and measured at the same temperature. The Figure 2(a) and (b) were obtained with a- and b-

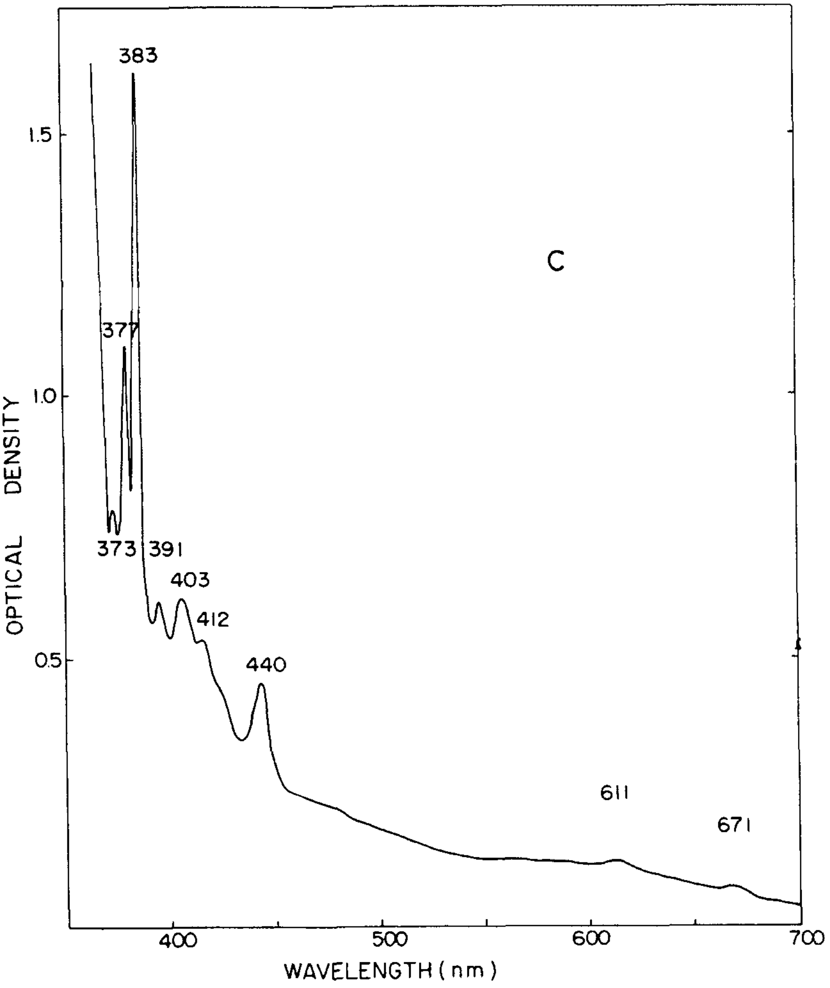


FIGURE 2c

polarized light incident along the c'-axis using a crystal cleavaged along the a–b plane and (c) was measured with c'-polarized light incident along the a-axis using a crystal cut parallel to the b–c' plane. The rate of irradiation doses of γ-rays for the crystals used to obtain Figure 2(a) and (b) to (c) was 2.5 : 1. The details of the absorption spectra in the long wavelength region are shown in Figure 3(a), (b) and (c). As the absorption intensities in these spectra are weak, the irradiation doses to obtain the spectra in Figure 3 were four times as much as that for Figure 2(a) and (b). Note that the scale of optical density for the spectrum (c) is large compared with that for the spectra (a) and (b). Main absorption bands at 373, 377, 383, 391, 403, 412 and 440 nm were detected in the shorter wavelength region and at 558, 611, 638, 643, 671 and 677 nm in the longer one, respectively. As is analogized from the case of naphthalene and anthracene, these bands are considered to be caused from the hydrogen added phenanthrene radicals. The expected hydrogen added phenanthrene radicals are 1-, 2-, 3-, 4- and 9-hydrophenanthryl radicals. In order to analyze the experimental spectra, the electronic transition energies and moments of these five kinds of radicals were calculated using the SCF molecular orbital theory. The method and parameters were the same as those in the case of anthracene[2]. The results are shown in Table I. The chemical reactivities for the five different carbons of a phenanthrene molecule are larger for 9, 1, 4, 3 and 2 carbons in this order according to the values of the delocalization energy and the free balance index.[7] Among the optical absorption bands the intensities of 373, 377 and 383 nm bands in the short wavelength region and 558 and 611 nm bands in the long wavelength one increase upon the annealing at room temperature for two hours.

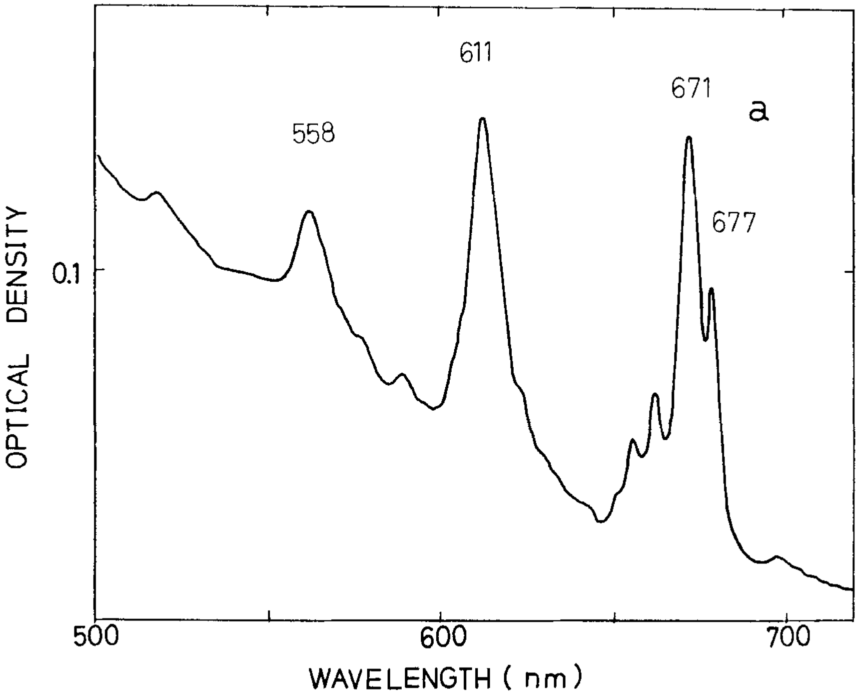


FIGURE 3 Details of the optical absorption spectra in the longer wavelength region. Figures a, b and c were measured using light polarized along the a-, b- and c'-axes, respectively. Irradiation doses were 5 × 10^7 rad. Note that the scale of optical density for c is larger than those for a and b.

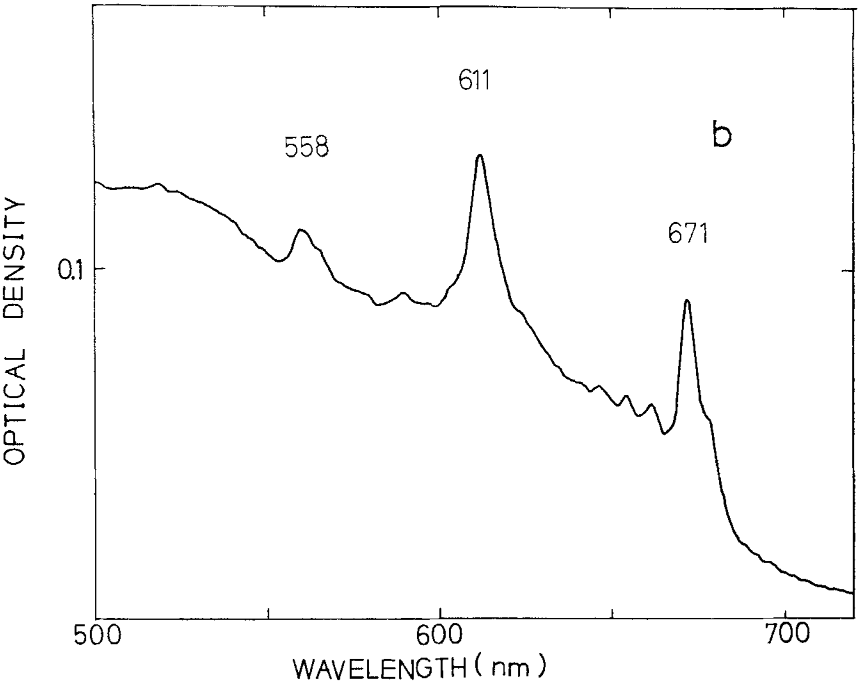


FIGURE 3b

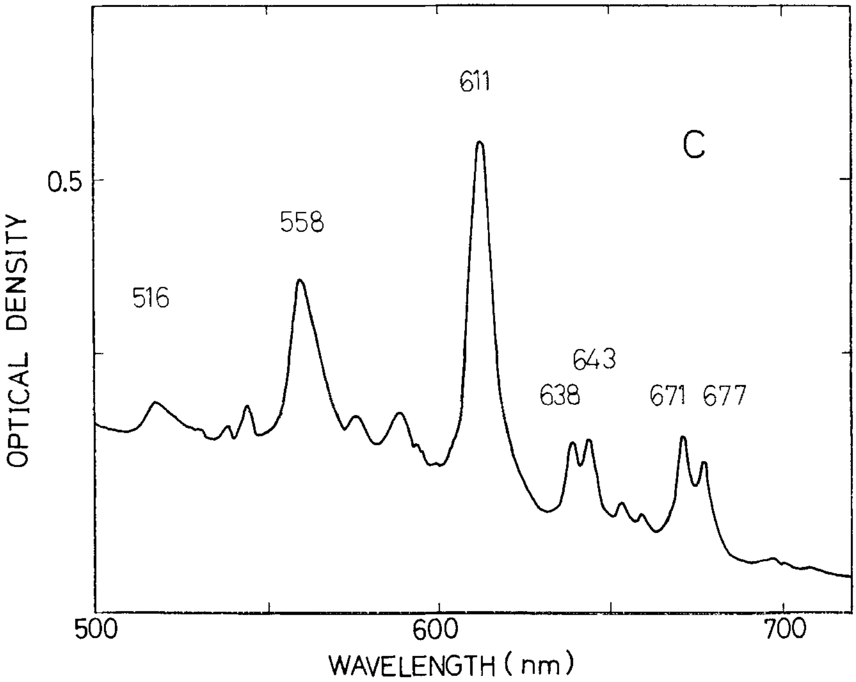


FIGURE 3c

TABLE I

Theoretical electronic transitions in 1,2,3,4 and 9-hydrophenanthryl radicals

		Transition moment (Å)		
	Energy (eV)	Long-axis (L)	Short-axis (M)	Oscillator strength
1-H_2-phenanthrene	2.00	0.084	0.058	1.83×10^{-3}
	2.86	0.147	0.099	7.80×10^{-3}
	3.10	0.932	0.569	3.22×10^{-1}
	3.54	1.196	0.098	4.44×10^{-1}
	3.95	0.134	0.311	3.95×10^{-2}
2-H_2-phenanthrene	1.75	0.031	0.177	4.93×10^{-3}
	2.69	0.116	0.866	1.79×10^{-1}
	3.46	0.026	0.009	2.31×10^{-4}
	3.87	0.040	0.050	1.37×10^{-3}
	3.97	0.345	0.419	1.02×10^{-1}
3-H_2-phenanthrene	2.06	0.100	0.121	4.30×10^{-3}
	2.22	0.046	0.081	1.67×10^{-3}
	2.85	0.734	0.385	1.71×10^{-1}
	3.63	1.202	0.553	5.54×10^{-1}
4-H_2-phenanthrene	1.91	0.144	0.079	4.49×10^{-3}
	2.95	0.782	0.227	1.71×10^{-1}
	3.13	0.050	0.059	1.61×10^{-3}
	3.65	0.576	0.636	2.34×10^{-1}
9-H_2-phenanthrene	2.46	0.152	0.101	7.15×10^{-3}
	2.94	0.442	0.167	5.72×10^{-2}
	3.11	0.920	0.200	2.55×10^{-1}
	3.72	0.076	0.157	9.86×10^{-3}

The strong 377 and 383 nm bands are observed as clear peaks even after the annealing at room temperature for three months. Therefore these five bands are supposed to be transitions of 9-hydro-phenanthryl radical (referred to as 9-H_2-phenanthrene) which is most stable among the five kinds of hydrogen added radicals. In the calculated transitions of 9-H_2-phenanthrene, strong 2.94 eV and weak 2.46 eV transitions are obtained. The strong 383 nm band in the experimental spectrum may be corresponded to the theoretical 2.94 eV transition and this band appears prominently in a- and c'-spectra. The 377 and 373 nm peaks may be ascribed to the vibrational structures of the 383 nm band. The 611 nm band which appears clearly in the long wavelength region is thought to correspond to the theoretical 2.46 eV transition. The 558 nm band may be regarded as a vibrational structure of the 611 nm band, since the annealing behavior is the same as that of 611 nm band. In the Figure 3(c), other than 611 and 558 nm bands, four peaks at 638, 643, 671 and 677 nm

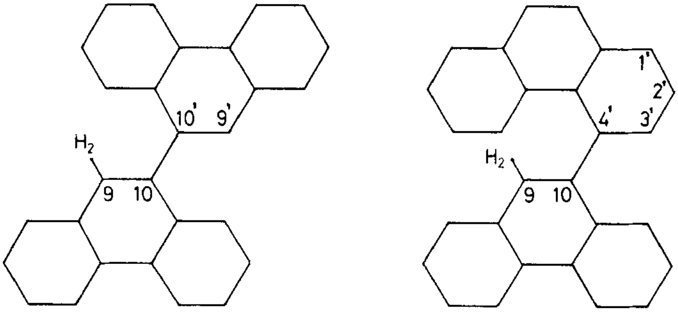
TABLE II

Direction cosines of the angles between the axes of a molecule in a unit cell of phenanthrene and the crystal axes (Ref. 6)

	Long-axis (L)	Short-axis (M)
a-axis	−0.2417	0.4601
b	−0.0668	0.8704
c'	−0.9680	−0.1750

are observed distinctly in the longer wavelength side than 611 nm. These four bands are likely to correspond to the transitions of the four kinds of hydrogen added phenanthrene radicals other than 9-H_2-phenanthrene. From the calculated results the weak bands of these radicals are expected to lie in the lower energy region than that of 9-H_2-phenanthrene. The peaks at 638 and 643 nm are not found in the a- and b- spectra, so these two bands are thought to correlate with transitions polarized along to the long axes L of radicals. On the other hand the 671 and 677 nm bands appear in the a-, b- and c'-spectra and the polarizations of the transitions may be isotropic or along the short axis M. In the calculated results for these four radicals, the polarizations of the lowest transitions of 1- and 4-H_2-phenanthrene are along L axes and those of 2- and 3-H_2-phenanthrene are along the short axes M of radicals. Therefore the 677 nm band may be identified with the 1.75 eV transition of 2-H_2-phenanthrene from the reasons of the energy and polarization. The other isotropic band at 671 nm may be associated with the other short axis polarized theoretical transition of 2.06 eV of 3-H_2-phenanthrene. On the other hand, two *c*-polarized 638 nm and 643 nm bands may be correlated with 1-H_2- or 4-H_2-phenathrene. The calculated energies of the lowest transition of these two radicals are higher for 1-H_2-phenanthrene, so we may assign the 638 nm band to 1-H_2-phenanthrene and the 643 nm band to 4-H_2-phenanthrene. Then according to our assignment the bands of the lowest transitions of the five kinds of radicals appear side by side from higher energy-side in the order of 9-, 1-, 4-, 3- and 2-H_2phenanthrene. In the shorter wavelength region, other than the bands for 9-H_2-phenanthrene, 440, 412, 403 and 391 nm bands exist. These bands are thought to be absorptions of the four kinds of hydrogen added radicals other than 9-H_2-phenanthrene. Among these four bands, decay of strong 440 nm band appears to be most rapid. Among the lowest four bands in the lower energy region, the 671 nm band which is assigned to the transition of 3-H_2-phenanthrene is most unstable upon annealing. From this decay behavior we may identify the 440 nm band with the 2.85 eV transition of 3-H_2-phenanthrene. Experimental polarization of the band is consistent with that of the calculated result. We could not assign in the present study the other three bands of 391, 403 and 412 nm.

Upon the annealing at room temperature for two hours two absorption bands at 467 nm and 450 nm appear. The 467 nm band is polarized along the a-axis and the 450 nm band is isotropic. Considering from the case of naphthalene and anthracene, these two bands seem to be ones caused from a dimer radical of phenanthrene.[1,2] We considered as dimer models 10,10'-diphenanthrene and 10,4'-diphenanthrene. Hydrogen added diphenanthrene radicals in which an additional hydrogen atom is attached to the most reactive carbon atom, were assumed. These radicals are 9-hydro-10,10'-diphenanthryl radical and 9-hydro-10,4'-diphenanthryl radical. We calculated the energies and transition moments of these radicals. In the case of 9-hydro-10,4'-diphenanthryl radical, our SCF calculation did not converge and only the result for 9-hydro-10,10'-diphenanthryl radical was obtained.



(a) (b)

FIGURE 4 (a) 9-hydro-10,10'-diphenanthryl radical, (b) 9-hydro-10,4'-diphenanthryl radical.

The calculated values are shown in Table III. This radical has two transitions of medium intensity in a little higher energy region than that of the lowest absorption bands of hydrogen added phenanthrene radicals. The oscillator strength of the 2.48 eV transition is larger than that of the 3.04 eV transition.

TABLE III

Theoretical electronic transitions in 9-hydro-10,10'-diphenanthryl radical

	Transition moment (Å)		
Energy (eV)	Long-axis (L)	Short-axis (M)	Oscillator strength
2.48	0.264	0.187	9.12×10^{-3}
3.04	0.132	0.116	2.69×10^{-3}
3.39	1.109	0.790	1.61×10^{-1}
4.06	1.100	0.879	1.73×10^{-1}

TABLE IV

Main optical absorption bands in phenanthrene crystals irradiated and measured at 77°K

Experimental				Theoretical		
Wavelength (nm)	Photon energy (eV)	Intensity	Polarization	Transition energy (eV)	Oscillator strength	Assignment
677	1.83	weak	a,b,c'	1.75	4.93×10^{-3}	2-H_2-phenanthrene
671	1.85	weak	a,b,c'	2.06	4.30×10^{-3}	3-H_2-phenanthrene
643	1.93	weak	c'	1.91	4.49×10^{-3}	4-H_2-phenanthrene
638	1.94	weak	c'	2.00	1.83×10^{-3}	1-H_2-phenanthrene
611	2.03	weak	a,b,c'	2.46	7.15×10^{-3}	9-H_2-phenanthrene
558	2.22	weak	a,b,c'			9-H_2-phenanthrene
467[a]	2.65	medium	a,c'	2.48		9-hydro-10,10'-diphenanthryl
450[a]	2.75	medium	a,b,c'	3.04		
440	2.82	medium	a,b,c'	2.85	1.71×10^{-1}	3-H_2-phenanthrene
412	3.01	weak	a,b,c'			
403	3.08	medium	a,b,c'			
391	3.17	weak	c'			
383	3.24	strong	a,c'	2.94	5.72×10^{-2}	9-H_2-phenanthrene
377	3.29	strong	a,c'			
373	3.32	medium	a,c'			

[a] Indicates the band which appears after annealing at room temperature.

This prediction is very similar to that of the experimental one. Then we may identify the theoretical 2.48 eV transition with the experimental 467 nm band and the 3.04 eV transition with the 450 nm band.

3.2 EPR spectra

EPR spectra of a phenanthrene single crystal which was irradiated and measured at 77°K are shown in Figure 5, where θ denotes the angle between the direction of the magnetic field and the a-axis of the crystal. Figure 6(a), (b) and (c) show the EPR spectra at room temperature of a phenanthrene

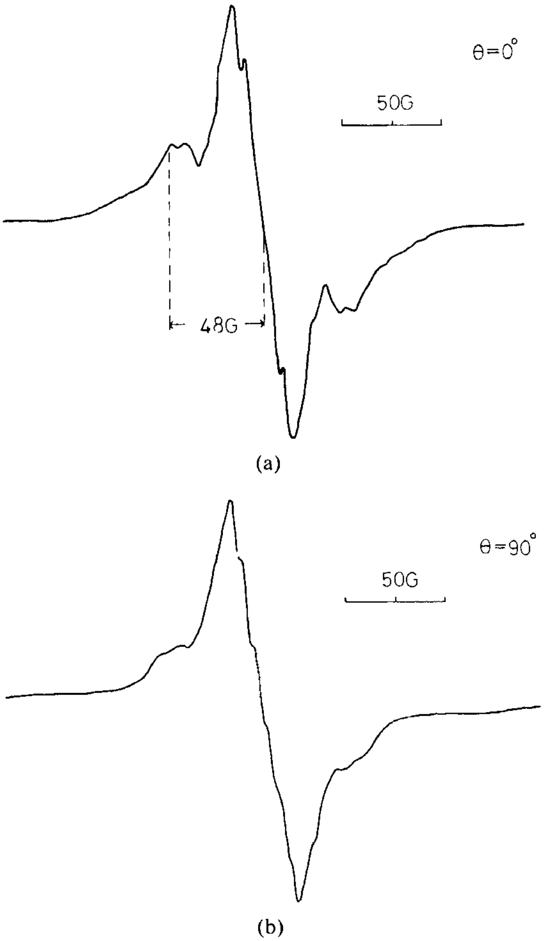


FIGURE 5 EPR spectra of a phenanthrene single crystal irradiated with γ rays at 77°K. Measurements were made at 77°K at $\theta = 0°$ (a) and $\theta = 90°$ (b).

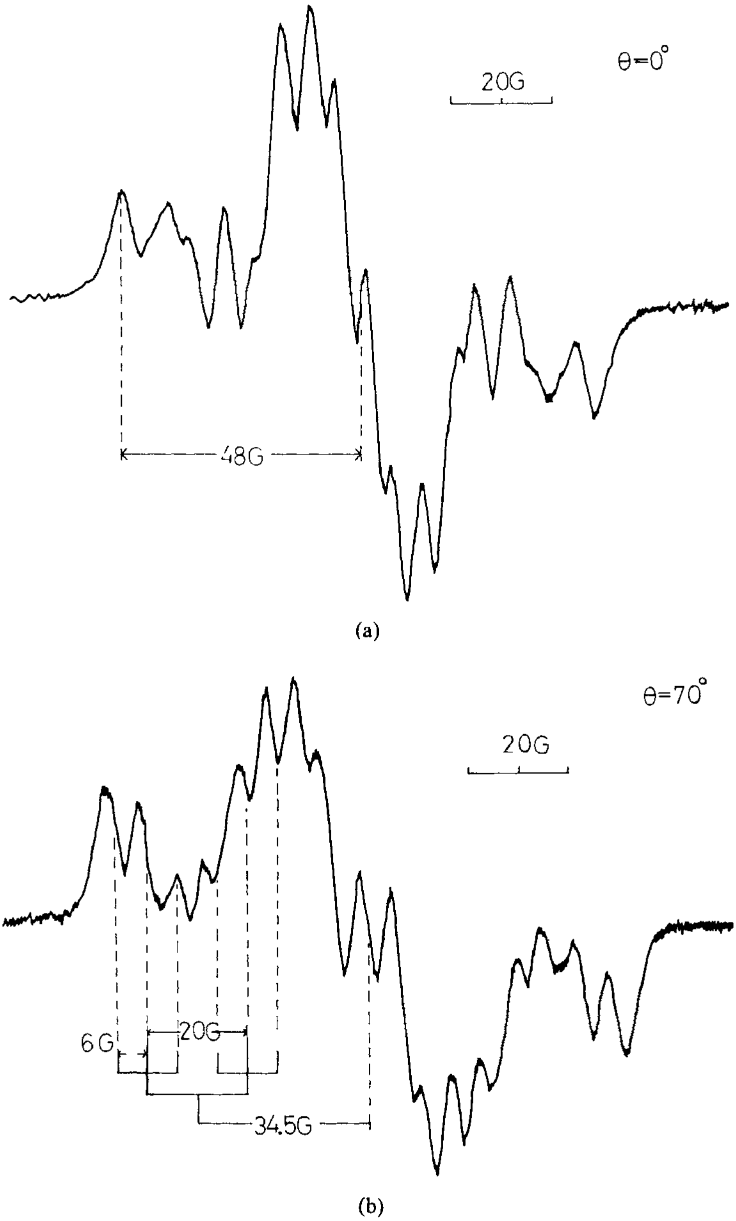


FIGURE 6 EPR spectra of a phenanthrene single crystal which was irradiated with γ rays at 77°K and annealed at room temperature for 50 hours. Measurements were made at room temperature at $\theta = 0°$ (a), $\theta = 70°$ (b) and $\theta = 165°$ (c).

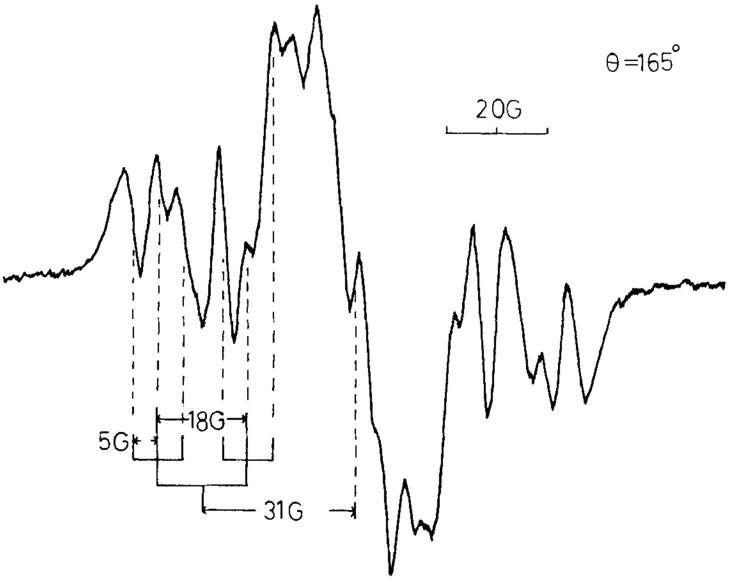


FIGURE 6c

crystal which was irradiated at 77°K and annealed at room temperature for 50 hours. The spectra of a sample which was irradiated at low temperature and not annealed, are broad and thought to be mixed with spectra of many kinds of species. So we begin to consider the spectra of an annealed sample shown in Figure 6. The spectra are composed from a broad triplet which further splits to the six lines. These spectra are in agreement with a previously reported spectra of phenanthrene crystals irradiated at room temperature.[9] The splittings of the main triplets are 34.5 gauss at $\theta = 70°$ and 31 gauss at $\theta = 165°$, respectively. These triplets are considered to be caused from hydrogen added phenanthrene radicals similarly to the case of other aromatics. In order to analize the spectra the spin densities of the five kinds of hydrogen added phenanthrene radicals were calculated using McLachlan's method. The parameters used were the same as those in the case of pyrene.[8] The calculated spin densities are shown in Table V. The predicted splittings due to the methylene protons are 37.4, 49.8, 44.1, 39.9 and 33.2 gauss for 1-, 2-, 3-, 4- and 9-hydro-phenanthryl radicals, respectively. The hyperfine splittings A, due to the α-proton were calculated in the same manner as in a previous paper.[8] In the optical absorption spectrum of a crystal annealed for 50 hours the strongest remaining absorption is the 383 nm band which has been assigned to 9-H_2-phenanthrene in the previous section. Therefore we

TABLE V

Calculated spin densities of 1-,2-,3-,4- and 9-hydrophenanthryl radicals

Number of carbons	1-H_2-phenanthrene	2-H_2-phenanthrene	3-H_2-phenanthrene	4-H_2-phenanthrene	9-H_2-phenanthrene
H_2 (methylene)	0.106	0.141	0.125	0.113	0.094
1	−0.009	0.519	−0.063	0.407	0.159
2	0.375	−0.013	0.173	−0.101	−0.053
3	−0.092	0.195	−0.010	0.415	0.139
4	0.367	−0.071	0.453	−0.011	−0.047
5	−0.024	0.054	−0.026	0.038	0.036
6	0.039	−0.024	0.049	−0.017	−0.014
7	−0.020	0.052	−0.024	0.038	0.027
8	0.040	−0.026	0.052	−0.021	−0.008
9	0.154	−0.047	0.193	−0.035	−0.013
10	−0.036	0.068	−0.050	0.057	0.628
11	0.142	−0.072	0.175	−0.057	−0.073
12	−0.063	0.197	−0.072	0.150	0.129
13	0.043	−0.025	0.052	−0.016	−0.025
14	−0.021	0.051	−0.027	0.040	0.022

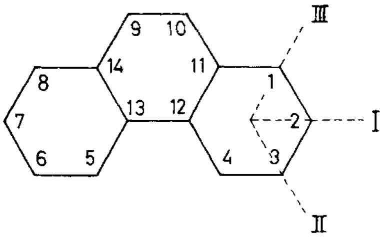


FIGURE 7 Site number and direction number.

first assume these spectra to be caused from 9-H_2-phenanthrene. The square of direction cosines of the angle between the direction II of a molecule (see Figure 7) and the direction of the magnetic field becomes equal to that for the direction III at $\theta = 70°$ and $\theta = 165°$. The values of the A/ρ (ρ: spin density) for the directions II and III are the same at these rotation angles and the spectra have relatively simple structures. The splittings for the directions I, II and III at $\theta = 70°$ are shown in Table VI for 9-H_2-phenanthrene. The theoretical spectrum consists of 33.2 gauss triplet due to the methylene proton, which splits further into 23.1 gauss doublets and 5.8 gauss triplets due to α-protons. This feature of the spectrum is in close agreement with the experimental spectrum which is composed from 34.5 gauss triplet, 20 gauss doublets and 6 gauss triplets. For $\theta = 165°$ the theoretical spectrum is constructed with a 33.2 gauss triplet, 17.9 gauss doublets and 4.5 gauss triplets. The experimental spectrum exhibits a 31 gauss triplet, 18 gauss doublets and 5 gauss triplets. As for the other four kinds of hydrogen added radicals, the splittings of the main triplets are calculated to be 37.4, 49.8 44.1 and 39.9 gauss and these values are too large compared with the observed splittings. Based on the close agreements between the experimental spectra and the calculated spectra of 9-H_2-phananthrene, we concluded that the EPR spectra of annealed crystals were ascribed to 9-H_2-phenanthrene.

TABLE VI

Calculated hyperfine splittings for the α-proton coupling in 9-hydro-phenanthryl radical at $\theta = 70°$ and $\theta = 165°$

		Position			
		I	II	III	Experimental
	A/ρ (gauss)	13.4	37.0	36.7	
$\theta = 70°$	Splitting (gauss)	0.7	5.1	23.1	20.0
				5.8	6.0
	A/ρ (gauss)	33.3	28.8	28.4	
$\theta = 165°$	Splitting (gauss)	1.8	4.0	17.9	18.0
				4.5	5.0

TABLE VII

Calculated proton hyperfine coupling constants (gauss) of 1- and 9-phenanthryl radicals. The coupling constants were obtained using the hyperfine splitting of 508 gauss for the hydrogen atom. Calculations were made with FACOM-M190 at the computer center of Kyoto University

Site number of hydrogen	1-phenanthryl	9-phenanthryl
2	17.2	
3	6.2	
4	4.6	
5		4.2
10		16.1
Line profile	doublet	doublet

The spectra of not annealed crystals are broad and poorly resolved. It seems to be a superposition of a broad singlet in the center and a triplet which appears in the both sides of the center line. In the spectrum at $\theta = 0°$ of annealed crystals the outer most peaks lie apart 48 gauss from the center. In the spectrum of not annealed crystals the outer most peaks are found at an interval of 48 gauss from the center. From this fact the broad triplet in the spectrum of not annealed crystals may be attributable to hydrogen added phenanthrene radicals. The large center line seems to involve both the center line of triplets due to hydrogen added phenanthrene radicals and lines due to hydrogen subtracted phenanthrene radicals. As an example we calculated the splittings of 1-phenanthryl radical, whose hydrogen atom at position 1 is subtracted, and of 9-phenanthryl radical using INDO approximation.[10] The results are shown in Table VII. The spectra are doublets of 17.2 and 16.1 gauss for 1- and 9-phenanthryl radicals, respectively. These lines enter in the width of the center line of spectrum.

4 CONCLUSIONS

The optical absorption spectra exhibit seven strong or medium bands in the shorter wavelength side and five weak bands in the longer one. Among the strong or medium bands, 373, 377, 383 nm bands which are stable at room temperature were assigned to 9-H_2-phenanthrene and 440 nm bands was attributed to the transition of 3-H_2-phenanthrene. The weak bands in the longer wavelength region were ascribed to the transitions of 9-, 1-, 4-, 3- and 2-H_2-phenanthrene from the shorter wavelength side in this order. Upon annealing two medium bands were observed in a little shorter wavelength region than that for the lowest absorption bands of hydrogen added radicals. These bands were assigned to 9-hydro-10,10'-diphenanthryl radical. The results of the observations and assignments are shown in Table IV. The EPR spectra of crystals as irradiated at low temperature are broad and supposed to be mixed with many kinds of hydrogen subtracted and added radicals. Upon annealing at room temperature for 50 hours the spectra change into triplet-doublet-triplet lines and this spectrum was attributed to 9-H_2-phenanthrene.

References

1. T. Chong and N. Itoh, *Mol. Cryst. Liq. Cryst.*, **36**, 99 (1976). Other works on this problem are summarized in this reference.
2. T. Kawakubo, *Mol. Cryst. Liq. Cryst.*, **53**, 1 (1979).
3. S. Matsumoto, *Bull. Chem. Soc. Japan*, **40**, 2749 (1967).
4. K. W. Benz and H. C. Wolf, *Z. Naturforschg.*, **19a**, 181 (1964).
5. R. M. Hochstrasser and G. J. Small, *J. Chem. Phys.*, **48**, 3612 (1968).
6. J. Trotter, *Acta Cryst.*, **16**, 605 (1963).
7. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, (John Wiley and Sons Inc., New York, 1961).
8. T. Kawakubo, *Mol. Cryst. Liq. Cryst.*, **46**, 11 (1978).
9. H. Blum, P. L. Mattern, R. A. Arndt, and A. C. Damask, *Mol. Cryst. Liq. Cryst.*, 3, 269 (1967).
10. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).