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On the Assignments of the Optical Absorption Bands of Radiation-Induced Radicals in Naphthalene and Anthracene Single Crystals

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Assignments of optical absorption bands of radiation-induced radicals in naphthalene and anthracene single crystals have been made using SCF-CI molecular orbital calculations. Electronic transition energies and moments of 11 kinds of radicals, which are supposed to be produced in the crystals, have been calculated. All seven main absorption bands measured hitherto in naphthalene crystal at 77°K have been assigned to α- and β-hydronaphthyl radicals. Five bands in naphthalene including the lowest 710 nm band and three adjoining strong and medium bands, which appear after annealing at room temperature, are found to correspond reasonably to the calculated transition of 1-hydro-4,1′-binaphthyl radical. The 675 nm and 645 nm bands of irradiated anthracene were assigned to 2- and 1-dibenzo-cyclohexadienyl radicals respectively. This assignment conflicts with that by Chong *et al.* All five absorption bands measured in anthracene at 77°K were ascribed to the absorptions of 1-, 2-, and 9-dibenzo-cyclohexadienyl radicals. The strong 465 nm band and weak 665 nm bands, which appear after annealing at room temperature, were explained as the spectrum of 9-hydro-10,9′-bianthryl radical.

1 INTRODUCTION

Optical and EPR investigations of radiation induced radicals in the aromatic hydrocarbons, such as benzene, naphthalene, and anthracene have been carried out by many workers.[1] Radicals in anthracene crystals have been studied from the early days. The 9-dibenzo-cyclohexadienyl radical is known to be stable at room temperature and has been studied in most detail.

Recently, Chong and Itoh[1] have reported the optical absorption spectrum of an anthracene single crystal which was irradiated at 77°K and annealed at room temperature. They have found six prominent bands in the absorption spectrum and assigned three weak bands in the long wavelength region

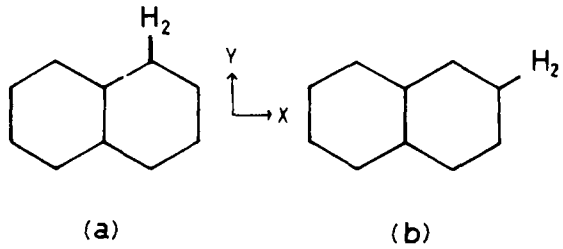

FIGURE 1 (a) α-hydronaphthyl radical. β-hydronaphthyl radical.

to 1-, 2-, and 9-dibenzo-cyclohexadienyl radicals (referred to as 1-H_2-A, 2-H_2-A, and 9-H_2-A), respectively. However the other three medium or strong bands have not been assigned. The optical absorption spectrum of radiation-induced radicals in naphthalene crystal[2,3] has been reported by the same authors. They observed seven prominent absorption bands[2] and then sorted them into three groups by the annealing experiments[3] for the crystal irradiated at 77°K. They assigned two groups among them to α- and β-hydronaphthyl radicals (referred to as α-H_2-N and β-H_2-N). The third group which grows at the later stage of annealing was considered to be associated with the radical produced by adding a hydrogen atom to a dimer molecule. On the other hand, theoretical calculations for the radicals produced in these crystals have not been carried out except for α-H_2-N.[4] The theoretically calculated transition energies and moments provide important information and are useful for a reasonable assignment of the absorption spectrum.

In this paper, theoretical calculations for the radicals produced in naphthalene and anthracene crystals are carried out with SCF-CI molecular orbital theory and the assignments of the absorption bands of the radicals in these crystals are performed.

2 NAPHTHALENE

2.1 Naphthalene radicals

It has been reported that the seven main absorption bands[2] are observed in naphthalene crystal irradiated at 77°K and during the annealing at room temperature four bands[3] grow gradually. The absorption bands are summarized in Table I and the spectrum is shown schematically in Figure 2. The 539 nm, 395 nm, and 337 nm bands are stable at room temperature and are assigned to α-H_2-N. On the other hand, the 632 nm and 350 nm bands decay rapidly at toom temperature and, therefore, these are considered to be associated with β-H_2-N. We begin by calculating the transition energies

TABLE I

Main optical absorption bands in naphthalene crystals irradiated at 77°K (a), and the bands which appear after annealing at room temperature (b) (Refs. 2, 3).

(a)

Wave length (nm)	Photon energy (eV)	Polarization	Assignment in Refs. 2, 3	Assignment in this paper
632	1.96	b	β-H_2-N	β-H_2-N
539	2.30	Iso.[a] or a	α-H_2-N	
453	2.74	b		β-H_2-N
405	3.06	a		β-H_2-N
395	3.14	b	α-H_2-N	
350	3.54	b	β-H_2-N	β-H_2-N
337	3.68	Iso. or b	α-H_2-N	

(b)

Wave length (nm)	Photon energy (eV)	Polarization	Assignment in this paper
710	1.75	Iso. or a	1-H_2-4,1′-BN
480	2.58	Iso. or b	1-H_2-4,1′-BN
453	2.74	b	1-H_2-4,1′-BN
445	2.79	Isotropic	1-H_2-4,1′-BN
420	2.95	Iso. or b	1-H_2-4,1′-BN

[a] iso. (isotropic)

of β-H_2-N. The method of calculation is the same as used for hydrogen added benzene and naphthalene radicals.[4] This method is based on the semi-empirical method developed by Praiser and Parr, combined with the SCF method for an open shell developed by Longuet-Higgins and Pople. The H_2 unit of CH_2 in the radical is regarded as a pseudo atom. The ionization potential and electron affinity of the H_2-atom are taken to be 9.4219 eV and -0.7007 eV. The overlap integral and the resonance integral between the pseudo π-orbital of the H_2-atom and the adjacent carbon $2p\pi$ atomic orbital are 0.613 and -5.90 eV, respectively. Using these values the SCF calculation was carried out for 11 electrons. Configuration interaction was considered among 19 lower energy configurations of radical doublet states. Results of the calculation are shown in Table II together with the experimental results. The calculated lowest transition of 1.85 eV may correspond to the 632 nm band in the experimental spectrum. Polarization rate of absorption intensity in the theoretical spectra is considered assuming the radical has the same orientation as the host molecule. The direction cosine of the angles between short or long axis of the radical and the *a*- or *b*-axis of the crystal are shown in Table III.[6] The transition with a strong dipole moment along the short axis may give the optical absorption polarized

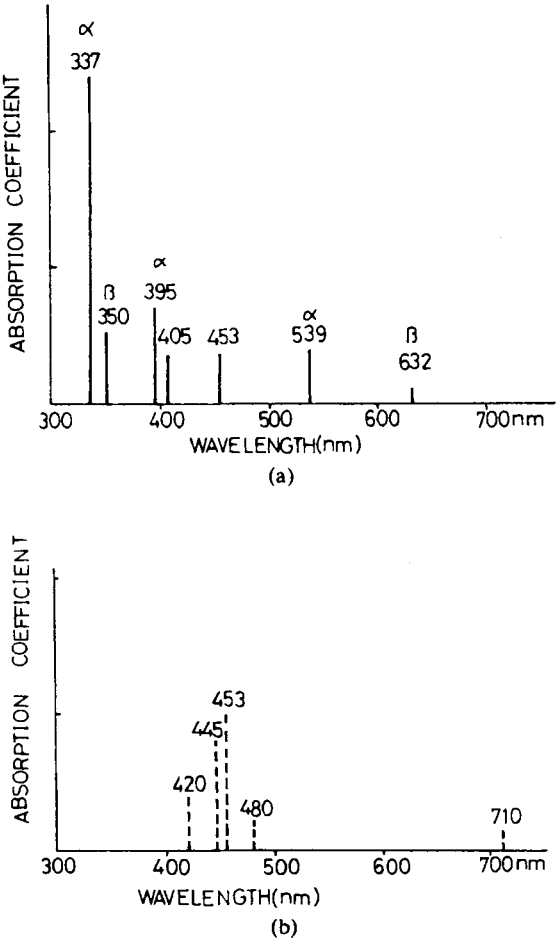

FIGURE 2 (a) Main optical absorption bands in naphthalene crystal irradiated at 77°K (Refs. 2, 3). α and β indicate the bands of α- and β-H_2-N, respectively. (b) The bands which appear after annealing at room temperature.

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 polarization of the lowest theoretical transition is consistent with the experimental results. The calculated next lowest transition is the strong 2.68 eV band polarized along *b*-axis. This transition may correspond to the experimental 453 nm band (2.74 eV). This band is observed clearly in Figure 5 of Ref. 2 together with the 632 nm band (β-H_2-N) and the 539 nm band (α-H_2-N). The theoretical 3.07 eV and 3.59 eV bands may be regarded to correspond to the experimental 405 nm (3.06 eV) and 350 nm (3.54 eV) bands, respectively.

TABLE II

Optical transitions in the β-hydronaphthyl radical

Theoretical				Experimental		
	Transition moment (Å)					
Energy (eV)	X	Y	Oscillator strength	Photon energy (eV)	Wave length (nm)	Polarization
1.85	0.022	0.067	8.01×10^{-4}	1.96	632	b
2.68	0.476	0.477	1.06×10^{-1}	2.74	453	b
3.07	0.424	0.395	8.96×10^{-2}	3.06	405	a
3.59	0.180	0.128	1.52×10^{-2}	3.54	350	b
4.21	0.494	0.144	9.70×10^{-2}			

TABLE III

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

	Long axis X	Short axis Y
a-axis	0.4379	0.3207
b	0.2103	0.8718
c′	−0.8741	0.3704

The theoretical polarization direction of the 3.59 eV transition is along b-axis and agrees with the experimental results. Though the 405 nm band does not exhibit a clear peak in the experimental spectrum due to the overlap with the other bands, this band is polarized along a-axis. The theoretical polarization direction is along the b-axis and so does not agree with the experimental results. However, the calculated transition moment for the X-axis is larger than that for the Y-axis and therefore this discrepancy is not important. Then we may be able to assign all the main absorption bands measured at 77°K to the α-H_2-N and β-H_2-N, respectively.

2.2 Naphthalene dimer radical

Our next step is to consider the absorption which appears after the annealing at room temperature. These bands are shown in Table I(b) and have been attributed by Chong *et al.* to the hydrogen added binaphthy radical.[3] Many structural isomers of hydro-binaphthyl radicals may be supposed. In

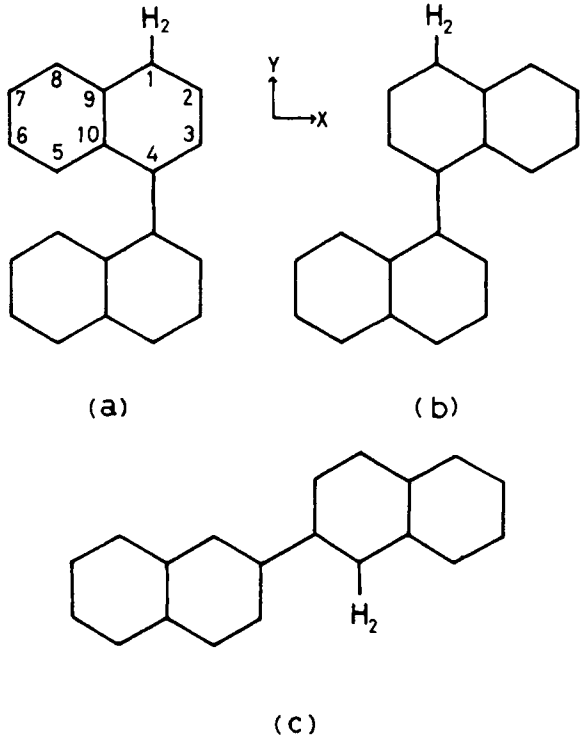

FIGURE 3 (a) 1-hydro-4,1′-binaphthyl radical. (b) 8-hydro-5,1′-binaphthyl radical. (c) 5-hydro-6,2′-binaphthyl radical.

this paper we consider three isomers of binaphthyl: 4,1′-, 5,1′-, and 6,2′-binaphthyl. The additional hydrogen atom is assumed to attach to the most chemically reactive carbon site from the calculations of the reactive indexes of the above three kinds of binaphthyl. The models of hydro-binaphthyl radicals for calculation are 1-hydro-4,1′-binaphthyl radical (referred to as 1-H_2-4,1′-BN), 8-H_2-5,1′-BN, and 5-H_2-6,2′-BN, respectively. These radicals are illustrated in Figure 3. The method of calculation of the transitions for these radicals is the same as that used for β-H_2-N. The length of the C—C bond combining the two naphthalene molecules is assumed to be 1.51 Å which is the same value as that of the similar bond in biphenyl. The results of the calculation are shown in Table IV. We compare these results with the experimental spectrum in Table I(b). The feature of the experimental spectrum is as follows; the lowest absorption is very weak and is located at 710 nm. Near 450 nm three adjoining strong or medium absorptions are observed. Among these three bonds the lowest one is the strongest and is polarized along *b*-axis and the other two are isotropic. The

TABLE IV

Optical transitions in hydro-binaphthyl radicals

	Theoretical				Experimental		
		Transition moment (Å)					
	Energy (eV)	X	Y	Oscillator strength	Photon energy (eV)	Wave length (nm)	Polarization
	1.96	0.066	0.082	1.88×10^{-3}	1.75	710	Iso. or a
	2.77	0.228	0.056	1.33×10^{-2}	2.58	480	Iso. or b
	3.39	0.055	1.572	7.31×10^{-1}	2.74	453	b
1-H_2-4,1′-BN	3.45	0.460	0.651	1.91×10^{-1}	2.79	445	Isotropic
	3.48	0.209	0.170	2.21×10^{-2}	2.95	420	Iso. or b
	3.81	0.711	0.032	1.68×10^{-1}			
	3.95	0.138	0.040	7.14×10^{-3}			
	2.02	0.027	0.064	8.38×10^{-4}			
	2.76	0.231	0.000	1.28×10^{-2}			
	3.47	0.198	0.951	2.85×10^{-1}			
8-H_2-5,1′-BN	3.50	0.195	0.278	3.52×10^{-2}			
	3.56	0.759	1.485	8.63×10^{-1}			
	3.82	0.665	0.308	1.79×10^{-1}			
	3.90	0.052	0.072	2.63×10^{-3}			
	2.12	0.345	0.088	2.34×10^{-2}			
	3.21	0.580	0.130	9.87×10^{-2}			
5-H_2-6,2′-BN	3.47	1.693	0.285	8.91×10^{-1}			
	3.67	0.535	0.090	9.39×10^{-2}			
	3.95	0.164	0.454	7.99×10^{-2}			

calculated energies of the lowest transition for the three radicals are smallest for 1-H_2-4,1′-BN. That is 1.96 eV and it is close to the experimental value of 1.75 eV. In the spectrum of 1-H_2-4,1′-BN three adjoining strong transition of 3.39 eV, 3.45 eV, and 3.48 eV are found and among these transitions the lowest one is the strongest and polarized clearly along the *Y*-axis and the other two are not strongly polarized. This feature is very similar to that of the experimental spectrum. In the spectrum of 8-H_2-5,1′-BN the strongest transition of 3.56 eV has the highest energy among the three adjoining transitions of 3.47 eV, 3.50 eV, and 3.56 eV. In the spectrum of 5-H_2-6,2′-BN the lower four transitions are all strongly polarized along one axis of the radical. These characteristics of the spectra are not consistent with the experimental results. Therefore, we may prefer 1-H_2-4,1′-BN among the three models. The theoretical spectrum of 1-H_2-4,1′-BN indicates the existence of the 2.77 eV band between the lowest transition and the three adjoining strong or medium transitions. This band may be found clearly as a peak near 2.58 eV in the experimental spectrum (Figure 1 of Ref. 1), whose intensity is consistent with the theoretical value. Then, we may take

the five theoretical transitions of 1-H_2-4,1'-BN to correspond to the experimental bands which appear after annealing. However the theoretical energies of the strong or medium adjoining three bands are considerably higher than those of the experimental values. This discrepancy may be partially attributable to the simple steric configuration of the model in which the two naphthalene molecules are located in a common plane. In the case that the overlap of π-electrons in the two naphthalene molecules occurs by an inclination of the two molecular planes, the lowering of the energies may be expected due to the charge transfer interaction of the two naphthalene molecules.

3 ANTHRACENE

3.1 Anthracene radicals

The weak 675 nm, 645 nm, and 535 nm bands and the medium intensity bands of 495 nm and 452 nm have been observed in anthracene crystal irradiated at 77°K.[1] After annealing at room temperature the strong 465 nm band and the weak 665 nm bands appear. These bands are summarized in Table V and illustrated schematically in Figure 5. The decay of the 675 nm band at room temperature is slow and that of the 645 nm band is very fast, while the intensity of the 535 nm band is constant. From these annealing behaviors Chong *et al.*[1] assigned the 675 nm, 645 nm, and 535 nm bands to 1-, 2-, and 9-H_2-A, respectively. Now we calculate theoretically the energies and transition moments of these radicals. The same method used in naphthalene is adopted to anthracene. The SCF calculation was carried out for 15 π-electrons which are the sum of 14 π-electrons of anthracene and that of H_2-atom. Configuration interaction was considered among

TABLE V

Main optical absorption bands in anthracene crystals irradiated at 77°K.

Wave length (nm)	Photon energy (eV)	Intensity	Polarization	Assignment in Ref. 1	Assignment in this paper
675	1.84	Weak	a	1-H_2-A	2-H_2-A
665[a]	1.86	Weak	—		9-H_2-10,9'-BA
645	1.92	Weak	a	2-H_2-A	1-H_2-A
535	2.32	Weak	Isotropic	9-H_2-A	9-H_2-A
495	2.50	Medium	Isotropic		2-H_2-A
465[a]	2.67	Strong	a		9-H_2-10,9'-BA
452	2.74	Medium	Isotropic		Mixed band 1-H_2-A and 2-H_2-A

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

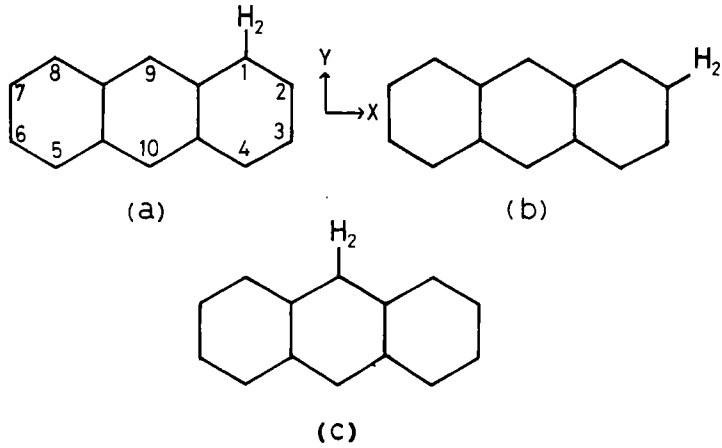

FIGURE 4 (a) 1-dibenzo-cyclohexadienyl radical. (b) 2-dibenzo-cyclohexadienyl radical. (c) 9-dibenzo-cyclohexadienyl radical.

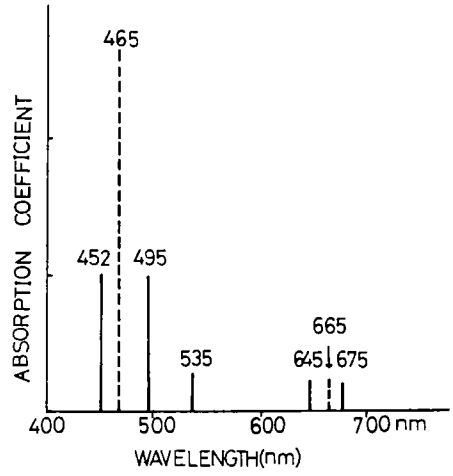

FIGURE 5 Main optical absorption bands in anthracene crystal irradicated at 77°K (Ref. 1). The dotted lines indicate the bands which appear after annealing at room temperature.

17 lower energy configurations of the radical doublet states. The results of the calculation are shown in Table VI. The lowest transitions of these radicals were obtained to be 1.91 eV, 1.61 eV, and 2.99 eV for 1-, 2-, and 9-H_2-A, respectively. Among these values the energy of 9-H_2-A is the highest. This fact is consistent with the experimental results. The calculated energy of the lowest transition in 1-H_2-A is higher than that of 2-H_2-A. This fact

TABLE VI

Optical transitions in dibenzocyclohexadieyl radicals

	Theoretical				Experimental		
		Transition					
	Energy (eV)	X	Y	Oscillator strength	Photon energy (eV)	Wave length (nm)	Polarization
1-H_2-A	1.91	0.177	0.085	6.39×10^{-3}	1.92	645	a
	2.99	0.804	0.556	2.49×10^{-1}	2.74	452	Isotropic
	3.07	0.065	0.081	2.87×10^{-3}			
	3.61	1.172	0.361	4.73×10^{-1}			
2-H_2-A	1.61	0.081	0.017	9.55×10^{-4}	1.84	675	a
	2.66	1.031	0.528	3.11×10^{-1}	2.50	495	Isotropic
	3.10	0.297	0.124	2.80×10^{-2}	2.74	452	Isotropic
	3.58	0.308	0.140	3.56×10^{-2}			
9-H_2-A	2.99	0.060	0.000	9.38×10^{-4}	2.32	535	Isotropic
	3.20	0.000	0.188	9.81×10^{-3}			
	3.52	0.014	0.000	5.84×10^{-5}			

conflicts with the Chong's assignment. As seen in the experimental spectrum (Figure 3 in Ref. 1) the 675 nm band is completely polarized along the *a*-axis, while the polarization ratio of the 645 nm band along the *a*-axis to the *b*-axis is about 1.5 : 1. The theoretical polarizations along the *a*-axis to the *b*-axis, calculated from the transition moments along the X- and Y-axis, are 4.9 : 1 for 2-H_2-A and 1.35 : 1 for 1-H_2-A, respectively. From these results we may assign the experimental 675 nm (1.84 eV) band to 2-H_2-A and 645 nm (1.92 eV) band to 1-H_2-A. Chong *et al.* assigned these bands for the reason that the strength of the C—H bond at position-1 is stronger than that at position-2. According to our assignment, the decay of 1-H_2-A, which is more stable as a radical than 2-H_2-A, turns out to be faster than that of 2-H_2-A. The reason for this fact may be explained by the consideration that in the crystal lattice 1-H_2-A may be more chemically reactive than

TABLE VII

Direction cosines of the angles between the axes of a molecule in a unit cell of anthracene and the crystal axes (Ref. 7).

	Long axis X	Short axis Y
a-axis	0.4950	0.3207
b	0.1222	0.8943
c'	−0.8602	0.3118

2-H_2-A for the reaction with the surrounding molecules due to the favorable position to react in three dimensions. The next lowest theoretical transitions of these three radicals are lowest in energy for 2-H_2-A. The experimental 495 nm band (2.50 eV) may be taken to correspond to the next lowest transition of 2-H_2-A judging from the energy (2.66 eV), intensity, the decay behavior, and the isotropic polarization of the transition. The width of the experimental 452 nm band is broader than the other bands, therefore it seems to be a band overlapped by more than two bands. The 2.99 eV and 3.07 eV bands of 1-H_2-A and the 3.10 eV band of 2-H_2-A may be associated with this band.

3.2 Anthracene dimer radicals

Now we consider the absorption bands of anthracene which appear after annealing. In the case of naphthalene the similar absorption bands could be reasonably explained by a model of hydrogen added binaphthyl radical. Then we adopt a similar model for anthracene. Three kinds of bianthracene were taken up: 10,9′-, 4,1′-, and 6,2′-bianthracene. The additional hydrogen atom was assumed to be attached to the chemically most reactive carbon atom. Then, the models for the calculation are the following three kinds of hydro-bianthryl radicals: 9-hydro-10, 9′-bianthryl radical (referred to as 9-H_2-10, 9′-BA), 9-H_2-4,1′-BA, and 10-H_2-6,2′-BA, respectively. The results of the calculations are shown in Table VIII. We compare these results with

TABLE VIII

Optical transitions in hydro-bianthryl radicals

	Theoretical				Experimental		
		Transition moment (Å)					
	Energy (eV)	X	Y	Oscillator strength	Photon energy (eV)	Wave length (nm)	Polarization
9-H_2-10,9′-BA	1.64	0.000	0.035	1.74×10^{-4}	1.86	665	—
	2.80	0.000	2.134	1.11	2.67	465	a
	3.15	0.351	0.000	3.38×10^{-2}			
	3.35	0.317	0.000	2.93×10^{-2}			
9-H_2-4,1′-BA	2.38	0.112	0.096	4.54×10^{-3}			
	2.78	0.443	1.337	4.81×10^{-1}			
	3.00	0.326	0.082	2.95×10^{-2}			
	3.47	0.113	0.162	1.17×10^{-2}			
10-H_2-6,2′-BA	3.05	0.093	0.101	4.99×10^{-3}			
	3.24	0.093	0.000	2.44×10^{-3}			
	3.51	0.045	0.175	1.00×10^{-2}			

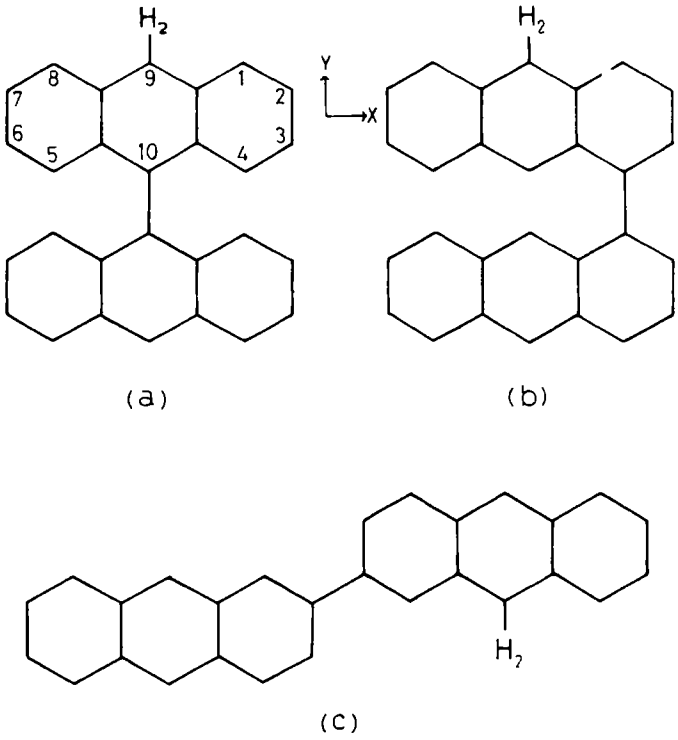

FIGURE 6 (a) 9-hydro-10,9′-bianthryl radical. (b) 9-hydro-4,1′-bianthryl radical. (c) 10-hydro-6,2′-bianthryl radical.

the experimental spectrum. Chong *et al.* observed clearly the increment of the absorption intensity of the 465 nm band. As for the growth of the 665 nm band they confined themselves to a qualitative result. Recently, Matsuyama *et al.*[5] reexamined the annealing behavior of anthracene crystal irradiated at low temperature and found that the increment of the 665 nm (666 nm as measured by Matsuyama) band is the same as that of the 465 nm (461 nm) band. Therefore we consider these two bands. The lowest and the next lowest transitions of 9-H_2-10,9′-BA are located at 1.64 eV and 2.80 eV, respectively and both transitions are strongly polarized along the *Y*-axis. These transition energies are close to the experimental values of 1.86 eV (665 nm) and 2.67 eV (465 nm). The transition energies of 9-H_2-4,1′-BA and 10-H_2-6.2′-BA are generally higher than that of 9-H_2-10,9′-BA and differ from the experimental values. Then we may take up 9-H_2-10,9′-BA. The polarization of the experimental 465 nm band is along the *a*-axis, so the *Y*- axis of the radical is supposed to tend towards the *a*-axis of crystal.

4 CONCLUSIONS

In order to assign the optical absorption bands of irradiated naphthalene and anthracene crystals, the electronic transition energies and moments of the radicals, which are supposed to be produced in the crystals, have been calculated theoretically and compared with the experimental results. The theoretically calculated values are not always very close to the experimental values, however they reproduce the characteristic features of the experimental spectra. Using these results, assignments of all the main absorption bands have been carried out for irradiated naphthalene and anthracene. The results are summarized in Tables I and V.

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