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

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(*Received May 14, 1979*)

Biphenyl single crystals irradiated with γ rays at liquid nitrogen temperature have been investigated by electron paramagnetic resonance and optical absorption experiments. EPR spectra at room temperature exhibit a triplet characteristic separated by 39 gauss and each line of the triplet further splits to a triplet. The main triplet has been interpreted as being caused by hydrogen added biphenyl radicals. The splitting of each line of the main triplet is consistent with the calculated splittings of 2-hydro-biphenyl radicals and 4-hydro-biphenyl radicals. The presence of 3-hydro-biphenyl radicals could not be judged from the EPR spectra due to the broadness of the lines. In the optical absorption spectra at low temperature, obtained with the light polarized to the a-, b- and c'-axes of the crystals, nine bands were detected. Transition energies were calculated using SCF-CI molecular orbital theory for the three kinds of the hydrogen added biphenyl radicals. By comparing the experimental spectra with the theoretical transitions of the three kinds of radicals, the bands at 666 nm and 424 nm have been assigned to the transitions of 2-hydro-biphenyl radicals, the 660 nm band to that of 3-hydro-biphenyl radicals, and the bands at 604 nm and 598 nm to the ones of 4-hydro-biphenyl radicals. The decays of these radicals at room temperature are very similar and upon annealing a new absorption band appears at 462 nm.

1 INTRODUCTION

Studies of the effects of ionizing radiation on the aromatic hydrocarbon crystals, such as benzene, naphthalene and anthracene have been reported by many workers.[1] It is known that both hydrogen subtracted and added radicals are produced in the crystals. However, detailed analysis of the spectrum of the radicals in single crystals at low temperature and studies of annealing effects have been made only in the case of naphthalene[2,3] and anthracene.[1] Biphenyl is one of the simple aromatics and its physical and chemical properties have been studied extensively. In this paper EPR and

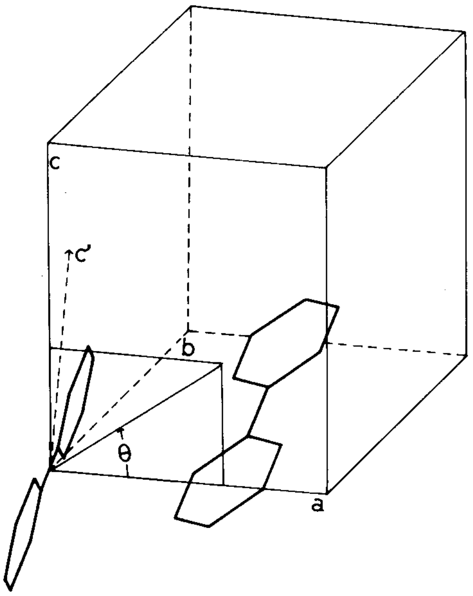


FIGURE 1 A unit cell of biphenyl crystals and the direction of the magnetic field.

optical absorption spectra of the radicals produced in biphenyl single crystals by irradiation with γ rays at low temperature and its annealing effects are reported.

2 EXPERIMENTAL

Biphenyl powder of pure grade was purified by zone refining and single crystals were grown by the Bridgman technique in an evacuated cell. Single crystals of 3 × 4 × 8 mm^3 cut parallel to the ab-plane for use in the EPR study and 6 × 8 × 2 mm^3 cut parallel to the ab-plane for the optical measurements were irradiated at liquid nitrogen temperature with γ rays up to a dose

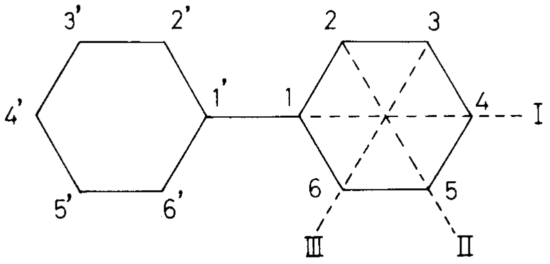
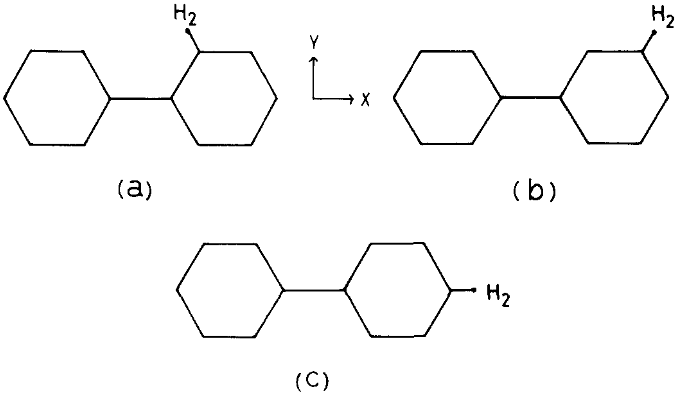


FIGURE 2 Site number and direction number.



(a) (b)

(C)

FIGURE 3 (a) 2-hydro-biphenyl radical; (b) 3-hydro-biphenyl radical; (c) 4-hydro-biphenyl radical.

of 5 × 10^7 rad. For the optical measurements other crystals cut parallel to the bc'-plane were irradiated up to a half dose of that for crystals cut parallel to the ab-plane. Crystals were set in a magnetic field with the 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 or 0.4 mW. Optical measurements were made at liquid nitrogen temperature with a double beam spectrometer (Shimadzu MPS–50).

3 RESULTS AND DISCUSSION

3.1 EPR spectra

Figure 4 shows typical EPR spectra at liquid nitrogen temperature of a biphenyl crystal irradiated at 77°K, where θ denotes the angle between the direction of the magnetic field and the a-axis. The spectra at room temperature of the above sample which was annealed for 45 hours at room temperature, are shown in Figure 5. First, we consider the spectra after the annealing at room temperature. The spectrum at each angle exhibits a broad triplet which splits further to triplet lines. The splittings of the main triplet are 39 gauss which are independent of the rotation angle of θ. This spectrum feature is similar to that of the radicals in other aromatics,[1] so this triplet is considered to be caused by the methylene protons of hydrogen added radicals. Three kinds of hydrogen added radicals of biphenyl are considered to be present. These radicals are 2-hydro-biphenyl radical which has an additional hydrogen atom at position 2 of the ring carbon, 3-hydro-biphenyl

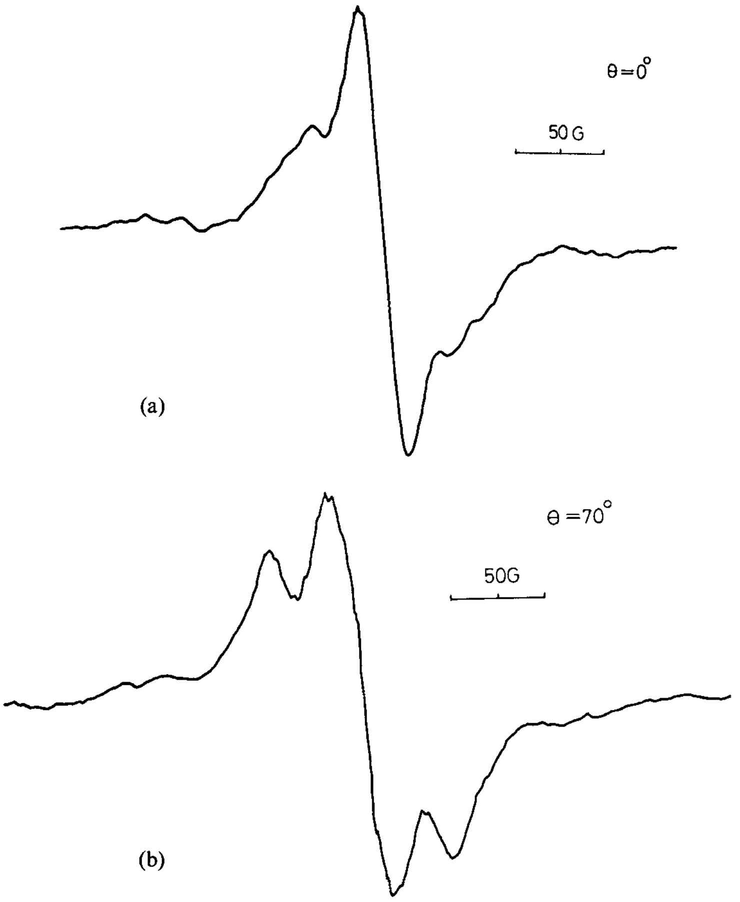


FIGURE 4 EPR spectra of a biphenyl single crystal which was irradiated with γ rays at 77°K. Measurements were made at 77°K just after irradiation at $\theta = 0°$ (a) and $\theta = 70°$ (b).

radical and 4-hydro-biphenyl radical, respectively (Figure 3). We calculated the spin densities of these radicals using McLachlan's method. The H_2 in the CH_2 group was treated as a hetero-atom with the parameters: $h_{H_2} = -1.0, h_c = 0.3, k_{c-H_2} = 2.6$.[5] The results are shown in Table I. The calculated splittings due to the methylene protons[6] are 45.9, 52.9 and 45.9 gauss for a 2-hydro-biphenyl (referred to as 2-H_2-biphenyl), 3-H_2-biphenyl and 4-H_2-biphenyl, respectively. These values are larger than the observed splitting of 39 gauss. The hyperfine splittings A, due to the α proton were calculated using the principal value of the hyperfine tensor for an α proton: $A_x = -13$, $A_y = -42$ and $A_z = -30$ gauss.[4] The value of A/ρ (ρ: spin density) and

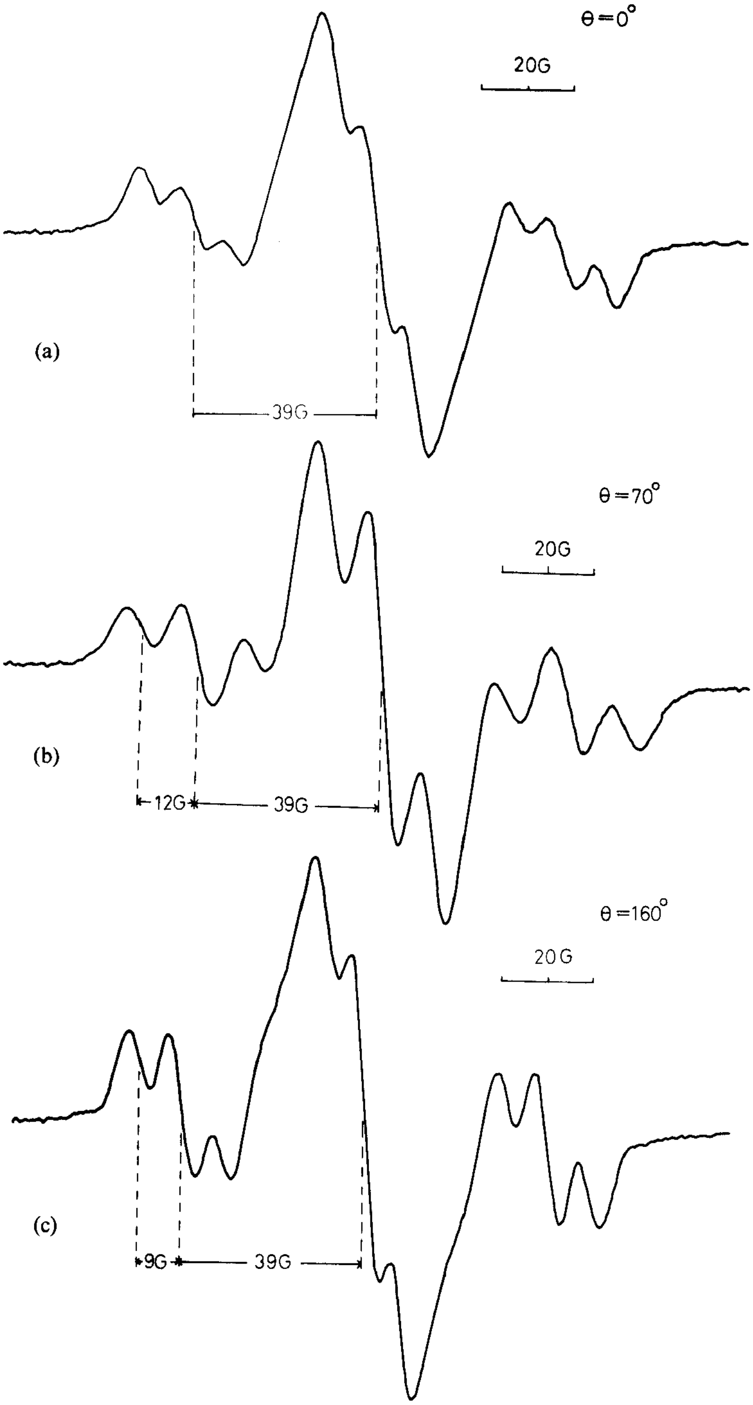


FIGURE 5 EPR spectra of a biphenyl single crystal which was irradiated with γ rays at 77°K and annealed at room temperature for 45 hours. Measurements were made at room

TABLE I

Calculated spin densities of 2-, 3- and 4-biphenyl radicals

Number of carbons	2-H_2-biphenyl	3-H_2-biphenyl	4-H_2-biphenyl
H_2 (methylene)	0.130	0.150	0.130
1	0.290	−0.093	0.288
2	−0.010	0.361	−0.084
3	0.307	−0.016	0.302
4	−0.084	0.369	−0.010
5	0.304	−0.107	0.302
6	−0.091	0.371	−0.084
1'	−0.027	0.007	−0.027
2'	0.077	−0.015	0.078
3'	−0.025	0.000	−0.025
4'	0.076	−0.012	0.077
5'	−0.025	0.000	−0.025
6'	0.077	−0.015	0.078

the splittings for the directions I, II and III (see Figure 2) are shown in Table II and Table III. The values of the A/ρ for the position II and III are the same at $\theta = 70°$ and 160°. The splittings for the direction II and III at $\theta = 70°$ are 11.2 and 11.4 gauss for a 2-H_2-biphenyl, and 11.1 and 11.2 gauss for a 4-H_2-biphenyl, respectively. These values are consistent with the observed value of 11.5 gauss. In the case of $\theta = 160°$ the calculated splittings lie between 8.3 gauss and 9.9 gauss for a 2-H_2-biphenyl and 4-H_2-biphenyl. These values are close to the observed splitting of 9.0 gauss. The calculated splittings for a 3-H_2-biphenyl are a little larger than the observed values for both $\theta = 70°$ and 160°, however, this fact may not mean the absence of 3-H_2-biphenyl radicals considering the broad line width of the spectrum. The spectra at 77°K of a biphenyl crystal as irradiated at low temperature are shown in Figure 4. The spectra are poorly resolved for all the rotation angles. In the spectrum at $\theta = 70°$, a peak is seen at 47 gauss apart from the center. This peak corresponds to the main triplet in the spectrum after the annealing

TABLE II

Calculated hyperfine splittings for the α-proton coupling at $\theta = 70°$.

		Position			Experimental
		I	II	III	
A/ρ (gauss)		13.1	36.8	37.1	
Splitting (gauss)	2-H_2-biphenyl	3.8	11.2	11.4	11.5
	3-H_2-biphenyl	4.8	13.3	13.8	
	4-H_2-biphenyl	3.8	11.1	11.2	

TABLE III

Calculated hyperfine splittings for the α-proton coupling at $\theta = 160°$.

		Position			Experimental
		I	II	III	
A/ρ (gauss)		34.3	28.8	27.5	
	2-H_2-biphenyl	9.9	8.8	8.4	
Splitting (gauss)	3-H_2-biphenyl	12.7	10.4	10.2	9.0
	4-H_2-biphenyl	9.9	8.7	8.3	

(see Figure 5) and so this peak is considered to be associated with the hydrogen added biphenyl radicals. The central line may be regarded as a line mixed with the hydrogen added radicals and hydrogen subtracted radicals. Corresponding to the hydrogen added radicals, three kinds of hydrogen subtracted radicals are thought to be present. These are 2-biphenyl radical whose hydrogen atom at position 2 is subtracted, 3-biphenyl radical and 4-biphenyl radical. The splittings of these radicals were calculated using the unrestricted self-consistent field method of INDO approximation[7] with FACOM–M190 at the computer center of Kyoto University. The results are shown in Table IV. The theoretical spectra are a doublet with a splitting of 17.4 gauss for the 2-biphenyl radical and triplets of 18 gauss for the 3- and 4-biphenyl radicals, respectively. These lines are all involved in the center line of the experimental spectrum and cannot be observed separately. Upon annealing at room temperature, the spectrum becomes more clearly resolved and after 20 or 45 hours the spectrum becomes identical to that of a sample irradiated at room temperature. It is considered that the hydrogen subtracted radicals diminish by the annealing and the lines from the stable hydrogen added radicals appear clearly.

TABLE IV

Predicted proton hyperfine coupling constants (gauss) of the three kinds of hydrogen subtracted radicals. Calculated coupling constants are obtained using the hyperfine splitting of 508 gauss for the hydrogen atom.

Site number of hydrogen	2-biphenyl	3-biphenyl	4-biphenyl
2		17.6	6.4
3	17.4		18.7
4	6.3	18.7	
5	4.0	5.7	18.7
6	5.5	4.1	6.4
Line profile	doublet	triplet	triplet

3.2 Optical absorption spectra

The optical absorption spectra of biphenyl single crystals irradiated with γ rays at 77°K, are shown in Figure 6. The Figures 6(a) and (b) are the absorption spectra obtained with a- and b-polarized light incident along the c'-axis and (c) is that obtained with c'-polarized light incident along the a-axis using a crystal cut parallel to the bc'-plane. Since the absorption intensity measured with the c'-polarized light is very strong compared with that of a crystal cut parallel to the ab-plane, the irradiation dose of γ rays for the bc'-plane crystals was one half for the ab-plane crystals. Main absorption bands are detected at 666, 660, 604, 598, 424, 406, 402, 394, 378 nm, respectively. The results obtained from the analysis of the EPR spectra indicate the presence of hydrogen subtracted radicals and hydrogen added radicals.

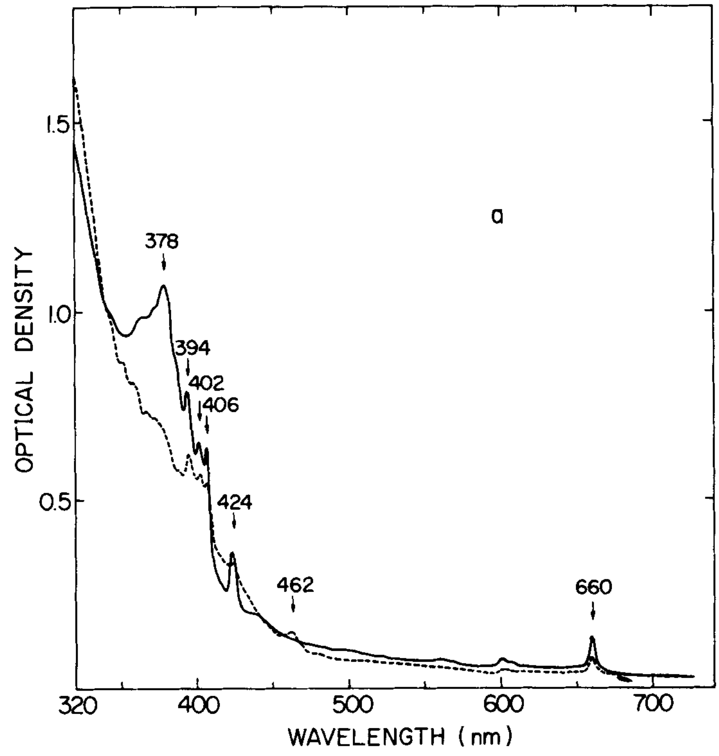
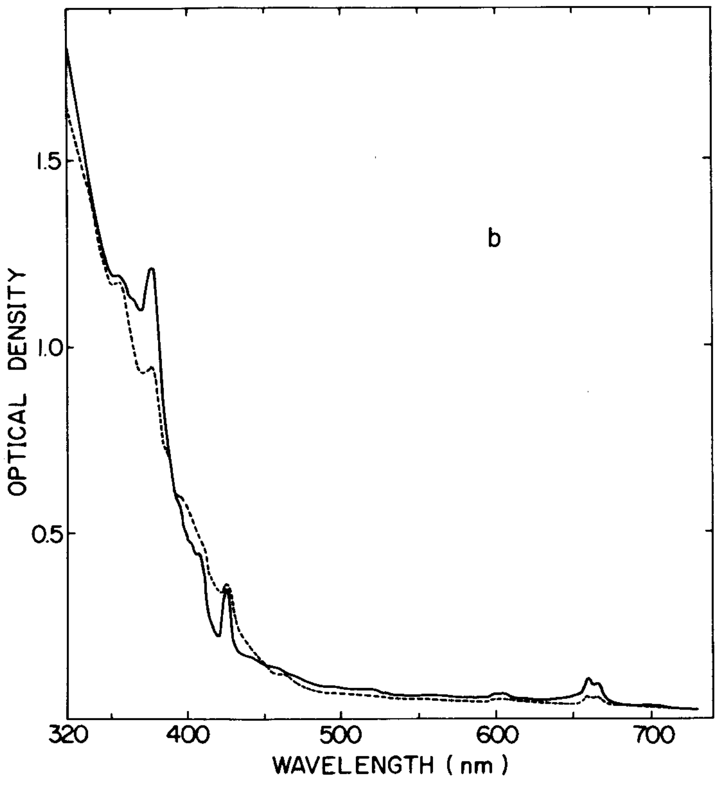
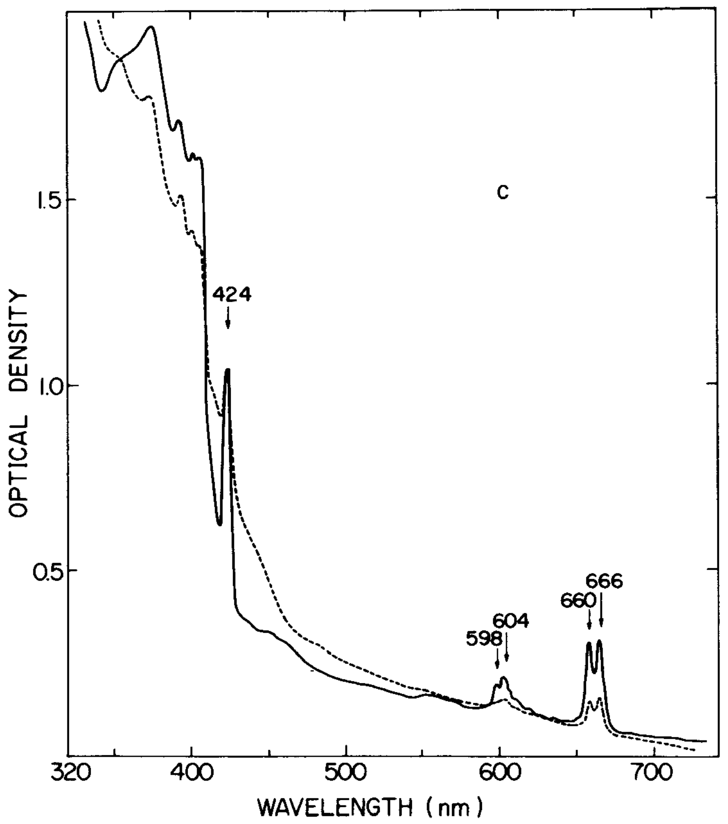


FIGURE 6 Optical absorption spectra at 77°K of biphenyl single crystals irradiated with γ rays at 77°K. The incident light is perpendicular to the a-b plane and polarized along the a-axis (a) and the b-axis (b). The solid line is the spectrum just after irradiation and the dotted line is that after annealing for 20 hours at room temperature. Spectrum c was obtained using light incident perpendicular to the b-c' plane and polarized along the c'-axis. Irradiation dose for a crystal to obtain the spectrum c is one half the dose of that to obtain the spectra a and b.


b
OPTICAL DENSITY
1.5
1.0
0.5
320
400
500
600
700
WAVELENGTH (nm)


c
OPTICAL DENSITY
1.5
1.0
0.5
424
598
604
660
666
320
400
500
600
700
WAVELENGTH (nm)

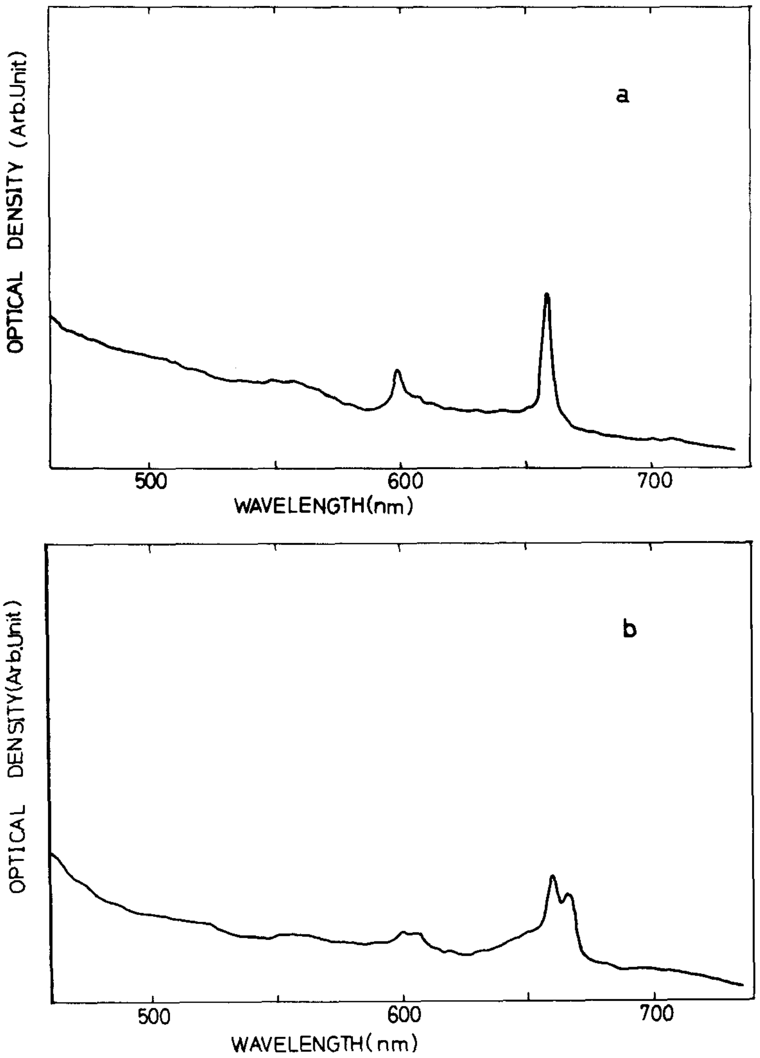
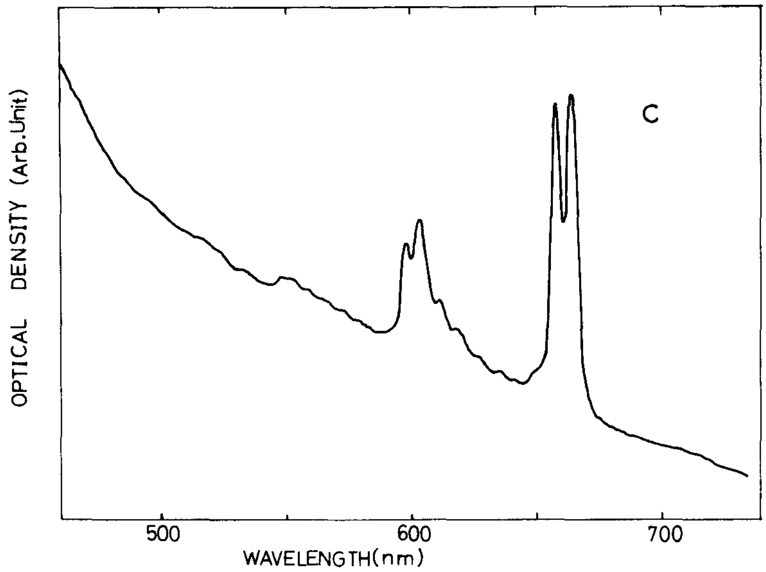


FIGURE 7 Details of the optical absorption spectra shown in Figure 6 in the longer wavelength region. Figures a, b, and c correspond to the a, b, and c in Figure 6.

Since the hydrogen subtracted radicals have no optical absorption far away from that of an undamaged molecule, we consider the three kinds of hydrogen added radicals, 2-H_2-biphenyl, 3-H_2-biphenyl and 4-H_2-biphenyl. Recently the present author examined the assignments of the optical absorption bands of radiation-induced radicals in naphthalene and anthracene crystals by comparing the observed spectrum with the theoretically calculated transition



energies of the hydrogen added radicals and obtained a reasonable result.[8] We adopted the same method for biphenyl and calculated the electronic transition energies and moments of the hydrogen added biphenyl radicals. The parameters used were the same as those of the previous paper.[8] The results of the calculations for 2-H_2-biphenyl, 3-H_2-biphenyl and 4-H_2-biphenyl are shown in Table V. The energies of the lowest transitions are lowest in 2-H_2-biphenyl among the three radicals. The lowest weak absorption band at 666 nm in the experimental spectrum may be assigned to this lowest transition of 2-H_2-biphenyl. A polarization rate of absorption in the theoretical spectra was considered assuming that the radical has the same orientation as the host molecule. The direction cosines of the angle between the short or long axis of the radical and the a-, b- and c'-axes of the crystal are shown in Table VI.[9] The transition with a strong dipole moment along the long axis may give the optical absorption polarized along the c'-axis, and the transition with a strong dipole along the short axis may give the optical absorption polarized along the b- and the a-axes. The polarization of the lowest absorption band at 666 nm is along the c'-axis. This fact is consistent with the theoretical indication, but no band appears at 666 nm in the experimental spectrum parallel to the a-axis. The next lowest absorption band in the experimental spectrum is the 660 nm band. This band may be assigned to the lowest transition of the 3-H_2-biphenyl judging from the order of the lowest transitions among the three kinds of radicals. The correspondence in the polarization rate of this band between the theoretical

TABLE V

Theoretical electronic transitions in 2-, 3-, and 4-hydro-biphenyl radicals

	Energy (eV)	Transition moment (Å)		Oscillator strength
		Long-axis (L)	Short-axis (M)	
2-H_2-biphenyl	1.92	0.086	0.042	1.54×10^{-3}
	3.14	1.149	0.383	4.01×10^{-1}
	3.60	0.449	0.090	6.57×10^{-2}
	3.90	0.164	0.151	1.68×10^{-2}
	4.00	0.501	0.184	9.94×10^{-2}
3-H_2-biphenyl	2.06	0.047	0.034	6.00×10^{-4}
	3.40	0.699	0.461	2.08×10^{-1}
	3.92	0.111	0.029	4.52×10^{-3}
	4.15	0.042	0.042	1.28×10^{-3}
4-H_2-biphenyl	2.24	0.003	0.079	1.22×10^{-3}
	2.56	0.220	0.002	1.08×10^{-2}
	3.34	0.021	0.622	1.13×10^{-1}
	3.71	0.032	0.494	7.92×10^{-2}
	3.96	0.144	0.206	2.19×10^{-2}
	4.13	1.618	0.025	9.42×10^{-1}

and the experimental results is good. Continued from the 666 nm and the 660 nm bands, the third and the fourth lower bands are the two neighbouring clear peaks at 604 nm (2.05 eV) and 598 nm (2.07 eV). The band at 604 nm does not appear in the spectrum parallel to the b-axis and both bands appear clearly in the c'-spectrum. The theoretical indication for the third and fourth lower transitions are the adjoining two bands of the 4-H_2-biphenyl at 2.24 eV and 2.56 eV. According to the calculation, the 2.24 eV transition should appear in the b-spectrum and the 2.56 eV transition is stronger parallel to the c'-axis. These predictions disagree with the experimental spectrum. This discrepancy may be partially attributable to the simple steric configuration of the model which is assumed to belong to the symmetry of C_{2y}. If we assume an appropriate asymmetric model, the configuration mixings among the differently excited electronic configuration states occur and then the energies and polarizations of the transitions to be calculated may be near to the experimental spectrum. This case in 4-H_2-biphenyl resembles to that in 9-dibenzo-cyclohexadienyl radical which is assumed to belong to a symmetry of C_{2v}. The consistency of the calculated transition energies and moments with the experimental ones in 9-dibenzo-cyclohexadienyl radical is not good contrast to the close agreements in 1- and 2-dibenzo-cyclohexadienyl radicals.[8] According to the above discussion we finally assigned the 604 nm and 598 nm bands to the transitions of 4-H_2-biphenyl. Now the next lower band is the

TABLE VI

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

	Long axis (L)	Short axis (M)
a-axis	0.2964	−0.5384
b	−0.0240	0.8215
c'	0.9548	0.1878

strong 424 nm band. The fifth lower transition in the theoretical spectrum is the 3.14 eV transition of 2-H_2-biphenyl. This transition is the lowest strong transition among those of the three radicals, with an oscillator strength of 4×10^{-1}, and the theoretical polarization is parallel to the c'-axis. In the experimental spectra the 424 nm (2.92 eV) band is the lowest strong band and polarized to the c'-axis. Hence the 424 nm band may be identified with the 3.14 eV transition of 2-H_2-biphenyl. We could not assign the bands which appear at wavelength shorter than 424 nm in the experimental spectra in the present study. The assignment of the absorption bands of radicals in biphenyl crystals is more difficult compared with that in naphthalene and anthracene for the following two reasons. In anthracene the three kinds of hydrogen added radicals exhibit clearly different decay behavior at room temperature, and so the absorption bands were separated into three groups by the annealing experiments. In the contrary, the annealing behavior of the three kinds of hydrogen added radicals of biphenyl are very similar in the present experiment, therefore these radicals can not be distinguished by annealing experiments. Secondly, the agreement of the calculated polarization ratio of an optical transition with the experimental one, especially a : b ratio, is not good compared to the cases in naphthalene and anthracene.[8] This fact suggests a rupture of co-planarity of the two benzene rings in the hydrogen added biphenyl radicals. This problem may be solved by an elaborate calculation adopting a model with a steric configuration.

The spectra after the annealing at room temperature for 20 hours are shown in Figure 6(a), (b) and (c) as the dotted lines. Upon annealing the absorption bands of the radicals decay and a new band appears at 462 nm. In naphthalene crystals four strong or medium bands around 450 nm and a band at 710 nm appear upon annealing and in anthracene a strong 465 nm band and a weak 665 nm band grow at room temperature. Supposing that the 462 nm band in biphenyl corresponds to the bands around 450 nm in naphthalene and the 465 nm band in anthracene, the 462 nm band seems to be a strong absorption in the shorter wavelength side of a hydrogen added dimer radical of biphenyl. A weak absorption band in the long wavelength region, which corresponds to the 710 nm band in naphthalene and the 665 nm band in anthracene, may become observable by prolonged irradiation.

4 CONCLUSIONS

The EPR spectra exhibit a triplet separated by 39 gauss and each line of the triplet further splits to a triplet. The main triplet was ascribed to hydrogen added biphenyl radicals. The analysis of the splitting due to an α-proton coupling shows the presence of 2-H_2-biphenyl and 4-H_2-biphenyl radicals. The presence of 3-H_2-biphenyl could not be judged due to the broadness of the lines. In the optical absorption spectra, nine bands were detected. Among these bands the lower five bands could be assigned to the transitions of 2, 3 or 4-H_2-biphenyl radicals by comparing with the theoretically calculated spectrum and the result is shown in Table VII. The decays of these hydrogen added radicals at room temperature are very similar to each other and the absorption bands could not be separated out by the annealing experiments in the present study.

TABLE VII

Main optical absorption bands in biphenyl crystals irradiated with γ rays at 77°K

Experimental				Theoretical		
Wave-length (nm)	Photon energy (eV)	Intensity	Polariza-tion	Transition energy (eV)	Oscillator strength	Assignment
666	1.86	weak	c', b	1.92	1.54×10^{-3}	2-H_2-biphenyl
660	1.88	weak	c', a, b	2.06	6.00×10^{-4}	3-H_2-biphenyl
604	2.05	weak	c', b	2.24	1.22×10^{-3}	4-H_2-biphenyl
598	2.07	weak	c', a, b	2.56	1.08×10^{-2}	4-H_2-biphenyl
424	2.92	strong	c', b, a	3.14	4.01×10^{-1}	2-H_2-biphenyl
406	3.05		a, c'			
402	3.08		a, c'			
394	3.15		a, c'			
378	3.28	strong	c', a, b			

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