UV-Irradiated Formation of Diradicals of Diphenylbutadiyne and Some of Its *p,p′*-Disubstituted Derivatives

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It was found for the first time that aromatic diacetylenes give strong ESR signals of stable carbon radical species in solution or in the solid state upon irradiation of UV light. The numbers of radicals reached to the order of 10^{20} radicals per mole of diacetylene, and the solution became red colored due to the formation of oligomers by their recombination. The radical species were stable almost indefinitely under an inert atmosphere. The unusual stability of these radicals is attributed to a resonance effect of aromatic rings linked to the butadiyne. Very slow quenching in the dark seems to be due to the recombination between them. Theoretical calculations indicated that monomeric diradicals on 1- and 4-carbons with the sp configuration, are formed, which combine to form dimeric or higher species detected by ESR spectroscopy.

The photo-polymerization of diacetylenes (DAs) in the solid state, which is often called topochemical polymerization, is well known, and the polymerization mechanism has been more or less established as dicarbene propagation in the crystal lattice.[1] It is said that the butatriene diradical is first formed on carbons 1 and 4 by irradiation or heat, which then adds to the adjacent DA molecules to form dimeric and oligomeric diradicals, which then transform to the more stable dicarbenes and continue further propagation. These intermediate diradicals, or dicarbenes, have been detected by ESR spectroscopy only for single crystals, or at low temperatures.[2,3] This is because the DAs studied by many researchers, were hexa-2,4-diyne derivatives, and their diradicals have no contribution to resonance stabilization by aromatic rings; also, they have labile propargyl hydrogen atoms, readily abstracted by diradicals or dicarbenes. There have only been a few studies[4,5] on the topochemical polymerization of aromatic DAs, probably because the majority of them do not undergo solid-state polymerization, and the product polymers are intractable and useless for any application. Iwase et al.[6] recently reported on the thermal polymerization of 1,4-bis(4-benzylpyridinium)butadiyne triflate, and detected ESR signals when its DMF solution was heated to 80 °C; they simply assumed that the signal was of the dicarbene species.

Apart from topochemical polymerization, aromatic DAs are very interesting compounds in various fields of chemistry. It was previously found that aromatic DAs, such as diphenylbutadiyne (DPB) and butadiynylene-*p,p′*-(*N,N*-di-*n*-butylbenzamide) (BBA), interact with transient free radicals, such as propagating methacrylate radicals, without forming a chemical bond, and intense ESR signals of the propagating methacrylate and acrylate radicals were observed at polymerization temperatures above 50 °C for systems containing small amounts of aromatic DAs.[7,8] The polymers obtained in the presence of DPB do not contain any fragment of DPB, according to the ultraviolet absorption spectra of the polymers, indicating that there is no bond between the DPB and the polymer radicals. It seems that aromatic DAs simply stabilize the propagating radicals by a certain interaction. When aromatic DAs, such as DPB and 4,4′-methoxycarbonyldiphenylbutadiyne, were heated, intense ESR signals were observed showing the presence of stable radicals, and the numbers of radicals increased in the presence of a stable radical such as diphenylpicrylhidrazyl (DPPH).[9] When DPB was added to a solution of DPPH, the yellow color of the solution disappeared, and the amount of DPPH consumed, increased with the temperature, however, upon cooling the yellow color reappeared, suggesting that the interaction is reversible. Such rather unusual behaviors of aromatic DAs are intriguing, and it seems that there are interesting undiscovered properties of aromatic DAs. When DPB was irradiated with UV light in the solid state or in solution, strong ESR signals were detected. Therefore, the UV-irradiated radical formation of some aromatic DAs in solution is reported in this paper.

Experimental

DAs. Aromatic DAs were synthesized by the usual oxidative coupling reaction of respective aromatic acetylenes. Dipheylbutadiyne, DPB was prepared from phenyl acetylene, supplied by Farchan (GFS Chemicals), [mp 82–84 °C, elemental analysis: Calcd: C, 95.05; H, 4.95%. Found: C, 95.20; H, 4.80%]. In the cases of *N,N′*-dimethyl-*N,N′*-di-*n*-butyl-*p,p′*-butadiynylenedibenzamide (MBA), [mp 92–94 °C, elemental analysis: Calcd: C, 78.50; H, 7.53; N, 6.54%. Found: C, 78.22; H, 7.61; N, 6.50%], and *N,N,N′,N′*-tetra-*n*-butyl-*p,p′*-butadiynylenedibenzamide (BBA),[8] [mp 112–113 °C, elemental analysis: Calcd: C,

79.65; H, 8.65; N, 5.46%. Found: C, 80.78; H, 8.49; N, 5.39%],
p-bromobenzoic acid (Aldrich) was converted to the respective
amides, which were then reacted with trimethylsilyl acetylene to
obtain *p*-ethynylbenzamides by the Sonogashira reaction.[10] The
ethynylbenzamides were then converted to the respective DAs
by the oxidative coupling reaction. Di(*p*,*p*′-methoxyphenyl)buta-
diyne (MPB) was prepared by an oxidative coupling reaction of
p-methoxyethynylbenzene, synthesized from iodoanisole and tri-
methylsilyl acetylene by the Sonogashira reaction[10] [mp 140–
141 °C, elemental analysis: Calcd: C, 82.42; H, 5.38%. Found:
C, 81.35; H, 5.11%]. *p*,*p*′-Dinitrodiphenyldiacetylene (DNP) was
prepared by an oxidative coupling reaction of *p*-ethynylnitroben-
zene [mp no melting, elemental analysis: Calcd: C, 65.76; H, 2.76;
N, 9.59%. Found: C, 65.56; H, 2.50; N, 9.39%]. An asymmetric
diacetylene, *p*-pentoxy-*p*′-nitrodiphenylbutadiyne (PNB) was syn-
thesized by an oxidative coupling reaction of *p*-pentoxyethynyl-
benzene and *p*-nitroethynylbenzene, instead of the usual Cadiot
coupling, and the three products were separated by extraction
and recrystallization using the difference in solubility [mp 145–
155 °C, elemental analysis: Calcd: C, 75.66; H, 5.74; N, 4.20%.
Found: C, 75.81; H, 5.63; N, 4.10%]. The yield was about 30%.
m,*m*′-Di(*N*-*n*-butylcarbonylamino)diphenylbutadiyne (CAB), was
synthesized by the reaction of *m*-ethynylaniline (Aldrich) with
valeryl chloride (Aldrich), followed by an oxidative coupling
reaction[5] [no mp, elemental analysis: Calcd: C, 77.97; H, 7.05;
N, 6.99%. Found: C, 77.78; H, 7.11; N, 6.87%]. Because PNB
is a new compound, its ^{1}H NMR spectrum is shown in Fig. 1. In-
tegration of the peaks exactly corresponded to the respective pro-
ton quantities (peak 1: 2.03, peak 2: 2.02, peak 3: 2.03, peak 4:
2.06, peak 5: 2.07, peak 6: 2.06, peak 7–8: 4.015, and peak 9:
3.00). The chemical structures of these aromatic diacetylenes
are shown in Scheme 1. Characterizations of some of the products
were made by FTIR (Nicolet 510 P) and NMR (Bruker Avance
400 MHz) spectroscopy.

ESR Measurement. ESR spectra were taken at room temper-

ature using a JEOL ESR spectrometer (Model RE3X). The sam-
ples were placed in quartz tubes with an inner diameter of 3
mm, supplied by Wilmad LabGlass, and after degassing the sys-
tem by a freeze-and-thaw process, the tubes were sealed off in a
vacuum. In the case of photoreaction, the tubes were irradiated
with a 450 W medium-pressure mercury lamp supplied by Ace
Glass, at a distance of 20 cm between the lamp and the tubes.
Of total energy radiated, approximately 40–48% was in the ultra-
violet portion of the spectrum, 40–43% in the visible, the balance
in the infrared, according the specification of the lamp.

The number of free radicals was calculated by double numeri-
cal integration of the first derivative of the resonance curve from
the equation[12]

$$A = \int_{H_A}^{H_B} dH \int_{H_A}^{H} dH' S(H'), \tag{1}$$

where H_A and H_B are the initial and final parts of the resonance
curve, respectively, and $S(H')$ is the value of the absorption at
field H'. The free radical concentrations were measured by a com-
parison with a NaCl:Mn^{++} crystal calibrated by atomic absorption
spectroscopy, taking both spectra under the same ESR spectrom-
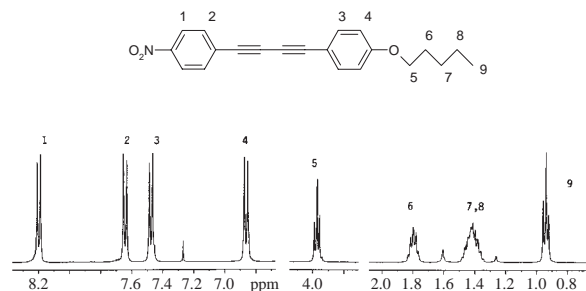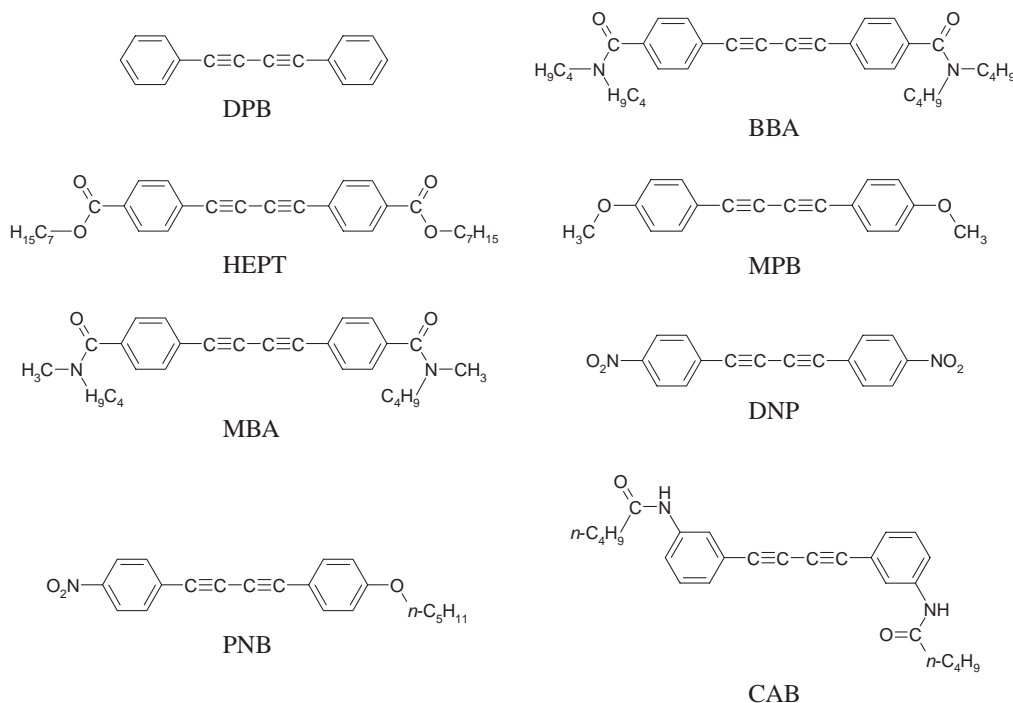eter conditions.

Fig. 1. ^{1}H NMR spectrum of *p*-pentoxy-*p*′-nitrodiphenyl-
butadiyne (PNB).

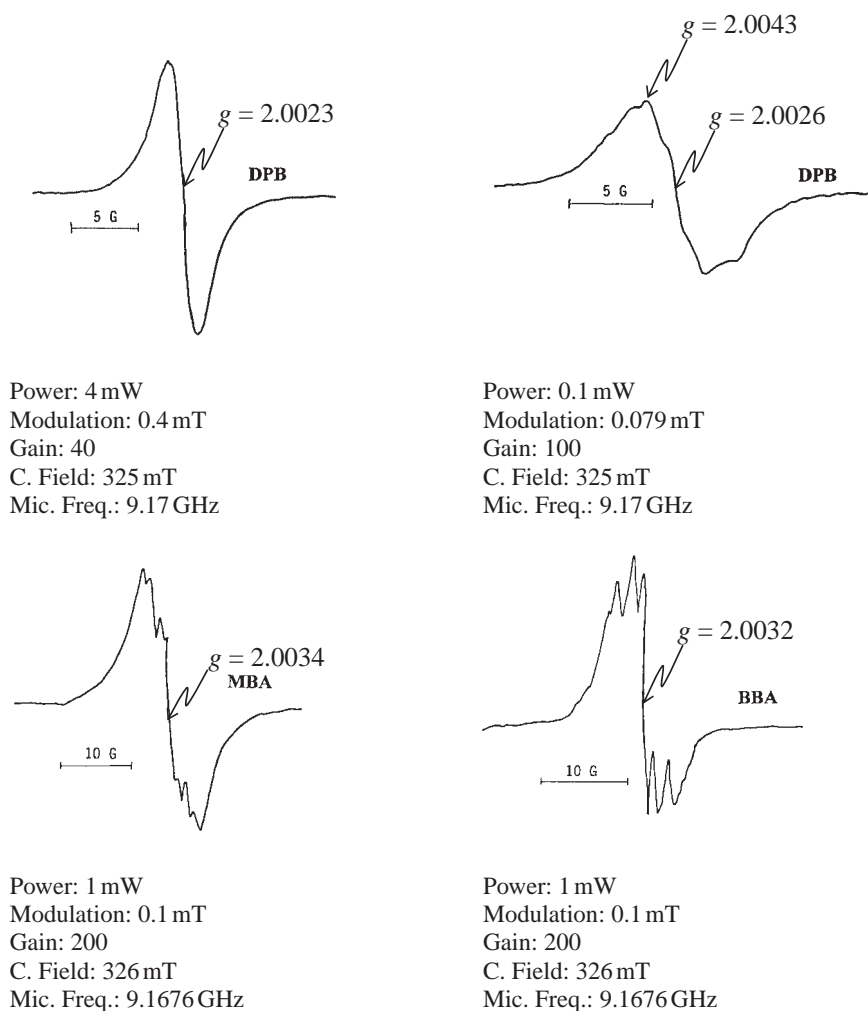Scheme 1. Chemical structures of aromatic diacetylenes which appear in this article.

$g = 2.0023$

DPB

5 G

Power: 4 mW
Modulation: 0.4 mT
Gain: 40
C. Field: 325 mT
Mic. Freq.: 9.17 GHz

$g = 2.0043$

$g = 2.0026$

DPB

5 G

Power: 0.1 mW
Modulation: 0.079 mT
Gain: 100
C. Field: 325 mT
Mic. Freq.: 9.17 GHz

$g = 2.0034$
MBA

10 G

Power: 1 mW
Modulation: 0.1 mT
Gain: 200
C. Field: 326 mT
Mic. Freq.: 9.1676 GHz

$g = 2.0032$

BBA

10 G

Power: 1 mW
Modulation: 0.1 mT
Gain: 200
C. Field: 326 mT
Mic. Freq.: 9.1676 GHz

Fig. 2. ESR spectra of THF solutions of DPB, BBA, and MBA irradiated with UV light.

Computational Details. All geometry optimizations were carried out with the Jaguar 5.0 suite of programs,[13] using the B3LYP hybrid functional with the 6-31(d,p) basis. An unrestricted method was used to treat open shell systems, while for closed systems a restricted formalism was applied. All geometry optimizations were carried out without symmetry restrictions. Time-dependent B3LYP in combination with the 6-31G(d,p) basis set (TD-B3LYP) implemented in the Gaussian 03 suite of programs was used to model the UV spectra.[14]

Results and Discussion

Diradical Formation. When these aromatic DAs were irradiated with UV light at room temperature in tetrahydrofuran (THF) or dioxane, colorless solutions gradually developed a reddish color; intense ESR signals (Fig. 2), appeared, and the signal intensity increased with the irradiation time. Such phenomenon had not been observed before, and aliphatic DAs did not show any ESR signal on irradiation in solution. The splitting in the spectra of BBA and MBA is due to the interaction of radicals with the nucleus of amide nitrogen. The UV spectra of some aromatic DAs in THF solution shown in Fig. 3. The π–π^* transitions of butadiyne groups lie in the range of 290–390 nm, and the substituted groups decrease the transition energy, showing red shift of the peaks. During irra-
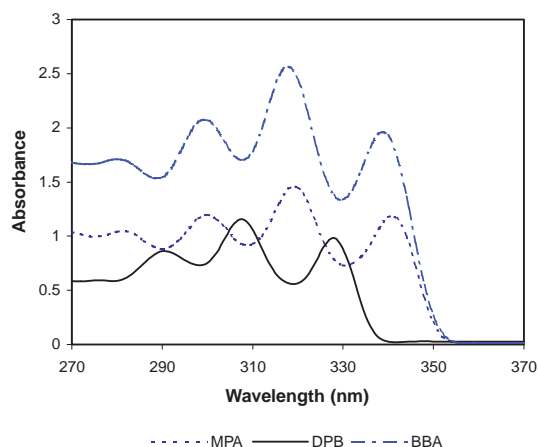
Fig. 3. UV absorption spectra of aromatic DAs in a THF solution. Concentrations: $\approx 10^{-5}$ M.

diation with UV light, the direct formation of a triplet state is forbidden. However, there is a possibility of spin inversion in the S1 state to produce T0, which corresponds to the energy of visible region. According to TD-B3LYP calculations, a vertical transition to the S1 state of the diphenyldiacetylenes is

highly allowed (oscillator strength 0.89), and lies 3.62 eV ($\lambda = 342$ nm) above the S0 state. The S0 $\rightarrow$ S1 transition has two main contributions, HOMO–LUMO and HOMO–1–LUMO+1 excitations, and this energy corresponds to the near-UV region. Since the T0 state of DPB lies below S1 (2.35 eV above S0 state), T0 can be formed. The theoretical structure of previously radicals was calculated by geometry optimizations (Fig. 4). According to a natural bond orbital analysis, four sp hybrid atoms of the DA unit in the S0 state remained as sp hybrids in the T0 state with a total spin density of 0.76 on the sp carbons linked to the benzene rings. The most appropriate valence structure for the description of the electronic state of the T0 state is butatriene structure with unpaired
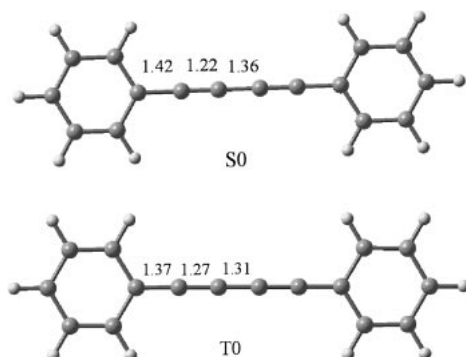

Fig. 4. B3LYP/6-31(d,p) optimized structure of DPB at the S0 and T0 states. The numbers are the bond lengths.

electrons on pure p orbitals. Therefore, the radical species are more likely the triplet sp diradicals, rather than the sp^2 diradicals, and they are not dicarbenes. Figure 5 shows the unpaired electron density distribution for triplet state of DPB diradicals. As can be seen the unpaired electrons are located mostly on Pz orbitals of the C1 and C4. The C2 and C3 carbons, ortho and para positions of phenyl rings (Pz orbitals), also present an unpaired electron density due to delocalization. Phenyl carbons linked to sp-carbons present a negative spin density due to spin polarization.

Stability of Diradicals. With respect to the stability of the diradicals, the monomeric diradicals may not be stable enough to be detected by ESR spectroscopy at room temperature or higher. Therefore, the ESR signals can be attributed to dimeric diradicals and oligomeric diradicals formed by the combination of monomeric diradicals. No emission was observed during irradiation, or when the irradiation was stopped. However, the nonradiative S1 $\rightarrow$ S0 and the slow T0 $\rightarrow$ S0 quenching processes are possible. Such coupling of monomeric diradicals
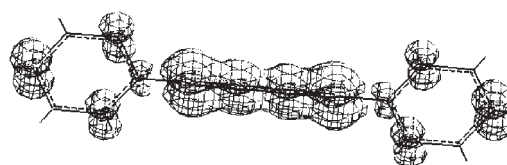

Fig. 5. Electron density distribution for the triplet state of DPB diradicals.

Table 1. Diradical Formation of Aromatic Diacetylenes in THF with UV Irradiation at Room Temperature

System	Irradiation time (min)	$[DA]_0$[b] (mol L^{-1})	No. of radicals /mol$_{DA}$ $\times 10^{19}$	[diradical] $\times 10^{-5}$ (mol L^{-1})	$g \pm 0.0006$
DPB-THF	0		—	—	—
	5		2.18	1.4	2.0023
	32		7.82	4.9	2.0023
	50	0.75	11.2	6.9	2.0023
	76		14.8	9.2	2.0023
	91		16.2	10.1	2.0023
	6 days[a]		11.8	7.3	
	16 days[a]		11.2	6.9	
BBA-THF	0		—	—	—
	7		no detectable	—	—
	35		12.2	2.7	2.0032
	49	0.27	17.8	4.0	2.0032
	76		29.8	6.7	2.0032
	85		40.8	9.1	2.0032
	6 days[a]		34.3	7.7	
	16 days[a]		11.6	2.6	
MBA-THF	0		0.41	0.1	2.0034
	11		24.7	8.4	2.0034
	16		44.5	15.1	2.0034
	33	0.41	71.2	24.2	2.0034
	59		91.9	31.3	2.0034
	74		101	34.4	2.0034
	6 days[a]		56.3	19.1	
	16 days[a]		57.0	19.4	

a) Without irradiation and kept in a dark place at room temperature. b) Initial concentration of DA in THF.
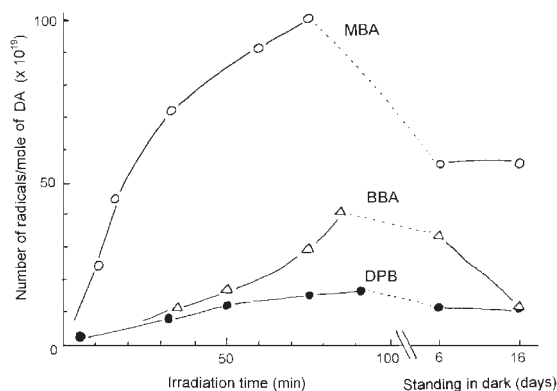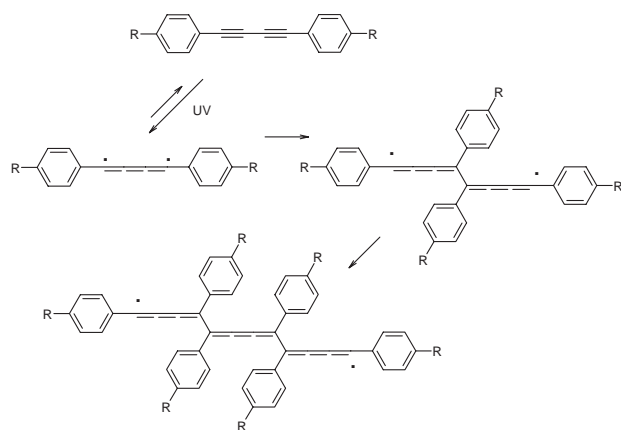
Fig. 6.   Relationships between the time and the numbers of radicals formed per mole of DA.

Scheme 2. Diradicals formed by the irradiation of UV light.

is evident from the fact that when solutions of linear polymers containing aromatic DA groups in their main chains were irradiated by UV light, the solutions became gel as cross-linking took place.[15] Coloring of the systems, due to an increase in conjugation, also indicates the formation of oligomeric species by recombination.

The changes in the numbers of diradicals with the irradiation time are shown in Table 1, and plots are shown in Fig. 6. The numbers of radicals increased with the irradiation time, and after about 90 min 1–10 diradicals are formed per 10^4 DA molecules, which was calculated ignoring the consumption by the coupling between them. The increase slowed down with lapse of time, indicating that slow recombination between the diradicals proceeds as their concentrations increases, as shown in Scheme 2. The numbers of radicals formed per mole of DA are greater for the substituted DAs than DPB, and this is probably because of the resonance contribution of the carbonyl groups. The diradicals of DPB, which are smaller than the others, can couple more efficiently, but the differences between MBA and the others are too large to be explained. The diradicals may undergo other reactions apart from the coupling, which is discussed in a later section. It is worth mentioning that the red color of the solutions, which developed rapidly when irradiated, did not change appreciably with the irradiation time, indicating that a high-molecular-weight species was not being formed. As can be seen in

Fig. 6, the radical concentration decreased when the irradiation was stopped, but after a certain time the radical concentration remained unchanged in the dark for 10 days, suggesting that no recombination took place. However, in the case of BBA, the concentration decreased upon standing in the dark; the difference may be due to the steric effect of the dibutylamino groups, which may decrease the rate of oligomerization. Thus continues the slow recombination in the dark. The others form oligomeric diradicals more rapidly than BBA.
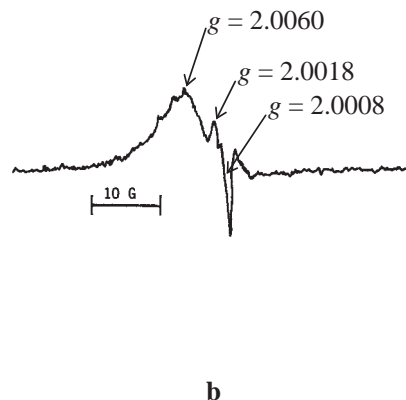
In the case of the solid-state polymerization of DAs, ESR signals of such diradicals or triplet dicarbenes in propagation have been investigated in detail for single crystals.[16,17] However, they never give ESR signals in solution. When a solution of topochemically polymerizable aliphatic DAs, such as 1,8-N,N′-dibutylaminocarboxyocta-3,5-diyne, was irradiated with UV light, nothing happened, and no ESR signals were observed. This is because the diradicals of aliphatic DA molecule are too labile to be detected by ESR spectroscopy; or more likely, they simply do not form diradicals as isolated molecules. The fact that those aliphatic DAs undergo polymerization in the solid state at moderate temperature, indicates that several molecules should be situated at a very close position, so that oligomers are formed in the beginning, and in a such manner that the energy required for the formation of diradicals is decreased. In contrast to these observations for topochemically polymerizable aliphatic DAs, the aromatic DAs in this work show their ESR signals even at elevated temperatures, because of the resonance stabilization by the aromatic groups and because there is no labile hydrogen adjacent to the radicals, such as propargyl hydrogen. On the other hand, butadiynylene dibenzamides,[5] which are topochemically polymerizable aromatic DAs, gave ESR signals at room temperature when irradiated in the solid state with UV light, suggesting that their propagating diradicals or dicarbenes are stable enough to be detected by ESR spectroscopy. Figure 7a shows ESR spectrum of another topochemically polymerizable aromatic DA (CAB) irradiated with UV light in the solid state for 170 min at room temperature. CAB rapidly polymerized to give deep-blue crystals of polydiacetylene, which is a totally intractable solid. According to an extensive work done by Sixl,[18] the propagating species of the solid-state topochemical polymerization of aliphatic DAs are dicarbenes. Therefore, although a detailed analysis of spectrum is difficult, the ESR signal of CAB, which undergoes solid-state polymerization, may be that of the dicarbenes in propagation according to Sixl. However, because CAB is an aromatic DA, the signal could be from diradicals. Figure 7b shows the ESR signal of CAB irradiated in THF solution, which is red colored due to much less conjugation than poly-CAB obtained in the solid state. The signal of the solution is thought to be that of the sp-diradicals of a mixture of oligomeric species. However, the signals of the two difference systems resemble each other, since both are highly conjugated species, and although it is difficult to determine whether they are dicarbenes or diradicals, it can be said that the signals in solution are likely to be those of the sp-diradicals.

Polymerization by Diradical Coupling.   It can be seen from the Table 1 that the concentration of the diradicals is in the order of 10^{-5--4} mol/L, which is considered to be high

a   b
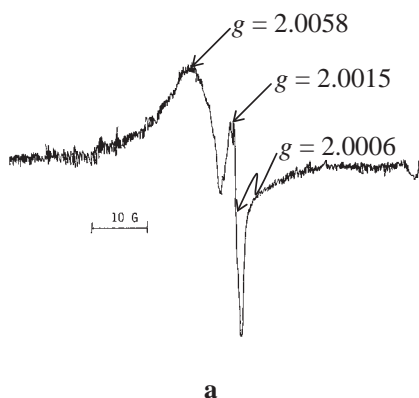
Microwave Frequency: 9.172 GHz   Microwave Frequency: 9.1614 GHz

Gain: 500, Modulation: 0.1 mT   Gain: 400, Modulation: 0.1 mT
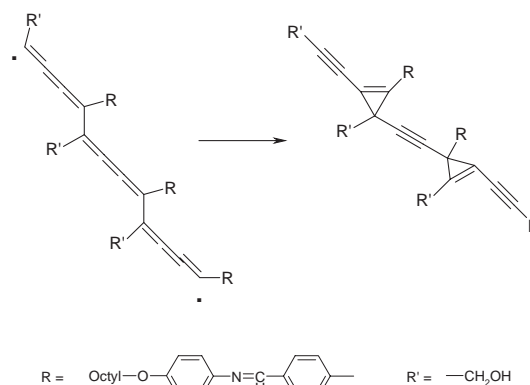
H_0: 325.0 mT, ΔH: ±10.0 mT H_0: 325.0 mT ΔH: ±10.0 mT

Fig. 7. ESR spectra of a topochemically polymerizable aromatic DA (CAB) in the solid state (a) and in THF solution (b) irradiated with UV light.
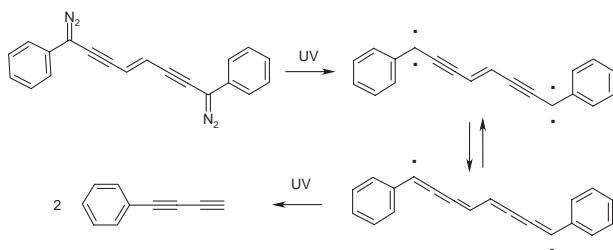
Scheme 3. Photo-dissociation of the dimeric dicarbene proposed by Iwamura et al.[20]

Scheme 4. Biscyclopropenyl compound from the trimeric diradical.[22]

for free radical reaction systems. In the free radical polymerization of vinyl monomers, the concentration of the propagating radicals in the steady state, is in the range of 10^{-7}–10^{-9} mol/L,[19] and termination takes place by the collision of two radicals. There is no doubt that these diradicals combine to form oligomers as the numbers of radicals decrease in the dark, as shown in Table 1. However, it can be concluded that these diradicals are rather too stable to combine with each other to form poly-DAs by recombination due to the steric hindrance of aromatic rings as well as their resonance stabilization. Iwamura and co-workers have reported dicarbenes of the phenyldiacetylene dimer,[20] in which they proposed photo-dissociation of the dimeric dicarbene to phenyldiacetylene (Scheme 3). They could not detect ESR spectra of either dicarbene or diradical, but obtained phenyldiacetylene in 70% yield. It seems that the supposed dicarbene rapidly changes to a more stable diradical, followed by rapid dissociation to form phenyldiacetylene, which is no longer a radical species, but a stable compound. The 1,4-diradicals of phenyldiacetylene will not be stable enough to be detected by ESR. In this work, however, if such photo-dissociation of dimeric or trimeric diradicals takes place, the products are also diradicals, but less stable due to less conjugation. They can couple to each other to return to a dimer or trimer again. Therefore, this is not the reason why no polymer can be obtained. In the case

of low temperature topochemical polymerization of aliphatic DAs, the terminal carbene is said to add to the adjacent monomer DA to form a cyclopropenyl chain end.[21] However, in this work the diradicals of aromatic DA are stable and in a dilute solution the probability of addition to monomer is unlikely. Sugawara and co-workers[22] heated a liquid crystalline-forming diacetylene at its nematic temperature (130 °C), and isolated a trimeric intermediate. They suggested that the trimer was a biscyclopropenyl compound, rather than a butatriene-type trimeric diradical, as shown in Scheme 4. In this work, the reaction conditions were somewhat different from those mentioned above (low temperature and dilute solution), but the formation of the cyclopropenyl compounds during the irradiation cannot be excluded. However, the cyclopropenyl derivatives do not give ESR signals.

In order to see if an electrostatic attraction between the diradicals with different electronic densities might accelerate the recombination, dioxane solutions of 4,4′-dimethoxydiphenylbutadiyne (MPB), 4,4′-dinitrodiphenylbutadiyne (DNP), and their mixture (MPB/DNP) were irradiated at room tempera-
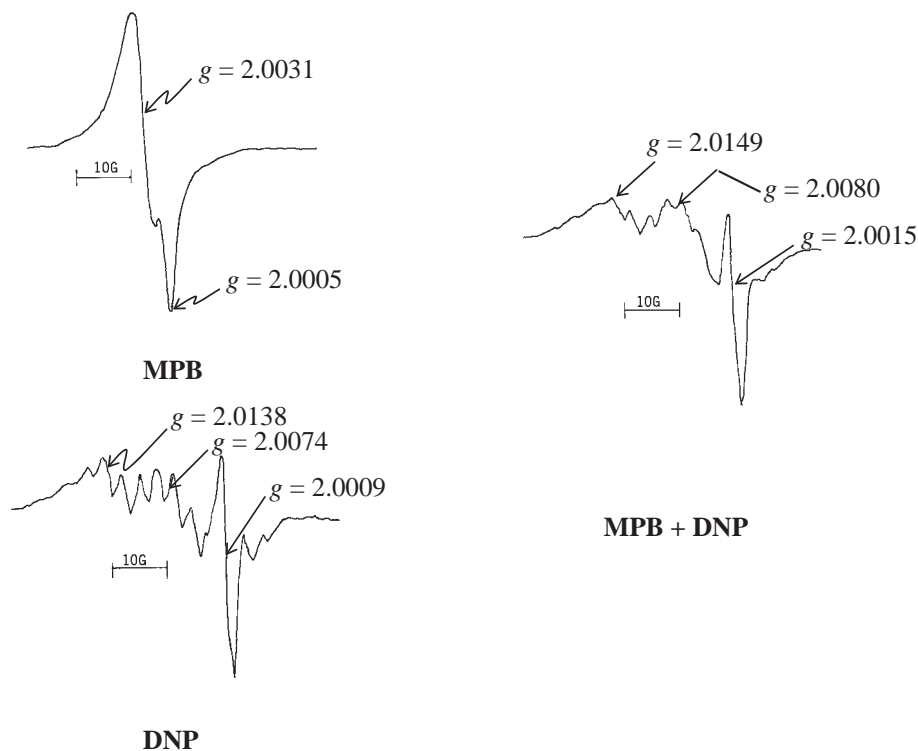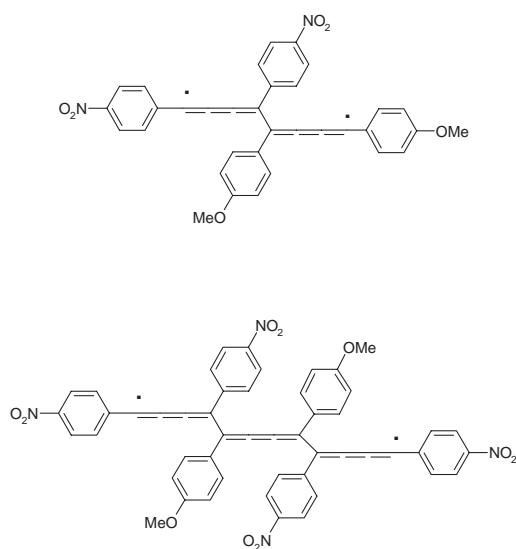
Fig. 8.   ESR spectra of 4,4′-dimethoxydiphenylbutadiyne (MPB), 4,4′-dinitrodiphenylbutadiyne (DNP), and their mixture (MPB + DNP). Power: 1 mW, Cent. Field: 336.2 mT, Mod. Freq.: 100 kHz, Mic. Freq.: 9.44 GHz.

Scheme 5. Possible products of co-coupling of diradicals.

Fig. 9.   ESR spectrum of asymmetric DA (PNB) irradiated for 275 min at room temperature. Concentration of PNB in THF = 0.138 M.

ture for 2 h; their ESR spectra are shown in Fig. 8. It is known that DNP and MPB form a charge-transfer complex and co-crystallize as a 1:1 adduct through their benzene rings.[11] The color of the solution of MPB is colorless, and that of DNP is pale yellowish brown. A solution containing the both DAs has a more intense color of pale brown. After irradiation, the colors intensified, suggesting that more extended conjugation systems were formed. The signal of the mixed system clearly shows that there are two types of radicals. The mixture of DNP and MPB is not equimolar due to the poor solubility of DNP in the solvent. The species shown in Scheme 5 is a possible struc-
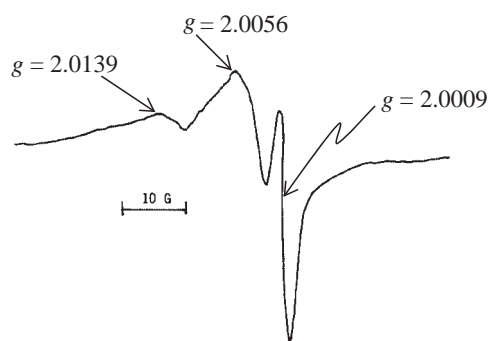
ture of the diradical. The isolation of the products seems to be technically impossible due to the low concentration of diradicals; approximately being only 1 radical per 1000 molecules. It is difficult to obtain a solution with high DNP concentration, because of its very poor solubility in most solvents. Therefore, an asymmetric DA (PNB) was irradiated in dioxane for 275 min; its ESR spectrum is shown in Fig. 9. The signal also indicates that there are two different types of radicals, one adjacent to the alkoxyphenyl and the other to the nitrophenyl groups, which greatly resembles that of the above mixed system. A small amount of solid particles precipitated in the system during irradiation in the ESR tube, and isolation of the product was attempted; this was not successful, due to the minute quantity of the product. It seems that even for the unsymmetrical systems, the formation of recombination product is

very slow, indicating that the steric hindrance overcomes the electrostatic attraction.

Conclusion

It was shown for the first time that aromatic DAs form stable diradicals by UV irradiation, of which intense ESR signals are observed at room temperature. Based on theoretical calculations, the radical species are considered to be sp-diradicals, rather than sp^2-diradicals or dicarbenes, but the observed ESR signals are thought to be those of dimeric or higher species formed by the recombination of the monomeric diradicals. An estimation of the numbers of unpaired electrons formed after 1 h of irradiation (Table 1) indicated that one out of 40000 molecules exists as diradicals, and its concentration in the systems of this work, was on the order of 10^{-4} mol/L. The diradicals were stable under an inert atmosphere. The coupling or oligomeric diradicals to form high molecular diradicals is extremely slow due to the steric hindrance, as well as to the high stability by the resonance stabilization by the aromatic rings. The formation of cyclopropenyl derivatives, or a cyclic trimer or a tetramer, is possible, which this could be another reason why a high polymer could not be obtained.

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