Dimerization of 1-Phenylcycloalkene Cation Radicals Dependent on Their Structure

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Received March 8, 1995⊗

Abstract: Irradiation of 1-phenylcyclopentene (**1a**) with 1,4-dicyanobenzene (DCNB) in acetonitrile gave [2 + 4] cycloadducts, tetralin-type dimers (**2**−**4**), together with a 2:1 adduct of **1a** with DCNB (**5**), through an electron transfer reaction. However, similar irradiation of 1-phenylcyclohexene (**1b**) gave 1-cyano-2-phenylcyclohexane (**7**) and 1:1 adducts of **1b** with DCNB (**8** and **9**), instead of yielding dimeric products. Transient absorption spectra obtained by pulse radiolysis and laser flash photolysis of **1a** showed simultaneous formation of a new absorption band with λ_{max} around 480 nm, attributable to dimer cation radicals, and decreasing absorption bands for monomer cation radicals (**1a**$^{\bullet+}$, λ_{max}: 400 and 670 nm). In the case of **1b**, by contrast, only absorption bands for monomer cation radicals **1b**$^{\bullet+}$ were observed in a region similar to those of **1a**$^{\bullet+}$. The optimized structure of the monomer olefin cation radicals, calculated by the PM3 method, suggested that, unlike the chairlike structure of **1b**$^{\bullet+}$, the fully planar structure of **1a**$^{\bullet+}$ would, on interacting with another neutral **1a**, promote the formation of dimer cation radicals.

It is well-known that on direct UV irradiation aromatic acyclic olefins like styrenes undergo [2 + 2] cycloaddition to give *cis*-cyclobutane-type dimers through the formation of their excimers,[1−3] while photoinduced electron-transfer dimerization of the olefins with cyanoaromatics as electron acceptors yields *trans*-cyclobutane-type and/or tetralin-type dimers through the cation radicals of the olefins.[2−7] Similarly, it has been reported that direct irradiation of 1-phenylcycloalkenes (**1**) also yields [2 + 2] cyclodimers.[8,9] However, there has so far been no investigation of photoinduced electron transfer (ET) dimerization of **1**. We now report that irradiation of 1-phenylcyclopentene (**1a**) in the presence of 1,4-dicyanobenzene (DCNB) gave four kinds of tetralin-type dimers, while similar irradiation of 1-phenylcyclohexene (**1b**) produced two kinds of 1:1 adducts of **1b** combined with DCNB. Secondly, it was found that the transient absorption spectra obtained by pulse radiolysis and laser flash photolysis of **1a** showed absorption bands attributable to monomer and dimer cation radicals; however, in the case of **1b**, only the monomer cation radical was observed. Thirdly, the experiment demonstrated that dimerization of the olefins depends on the structure of their monomer olefin cation radicals.

Experimental Section

^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer and a Bruker DRX-500 spectrometer. Mass spectra were determined with a Shimadzu GCMS-QP1000 gas chromatograph mass spectrometer and a JEOL JNX-DX303HF mass spectrometer. Gas chromatography was performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector. Irradiations were carried out with a 400-W high-pressure mercury lamp (Riko UVL-400HA).

Photoinduced Electron Transfer Dimerization of 1a. When **1a** (0.1 M) was irradiated with DCNB (0.1 M) in acetonitrile with a 400-W high-pressure mercury lamp through a Pyrex filter for 8 h, **1a** was almost consumed and three dimers (**2**−**4**) were produced with yields of 11, 23, and 7%, respectively, together with 2:1 and 1:1 adducts of **1a** with DCNB [**5** (31%) and **6** (∼1%), respectively]. One of the dimers was purified by column chromatography on silica gel using hexane as an eluent, and X-ray crystallographic analysis revealed the structure of the purified dimer to be that of a tetralin-type dimer **3**. The same method was used in the case of adduct **5**. On the basis of their MS and ^{13}C NMR spectra data, dimer **2** was identified as a stereoisomer of **3**, while dimer **4** was found to be the dehydro dimer of **2** and **3**.

Dimer **2**: ^{13}C NMR (CDCl$_3$) δ 151.36, 146.81, 140.12, 129.88, 127.77, 127.45, 126.09, 125.39, 125.24, 125.13, 57.81, 55.81, 47.58, 47.09, 39.17, 30.03, 29.39, 29.13, 23.13, 22.60; HRMS calcd for $C_{22}H_{24}$ *m/z* 288.1878, found 288.1883, major fragment (relative intensity) 288 (15%), 245 (46%), 210 (100%), 144 (41%), 129 (31%), 91 (37%), 44 (29%).

Dimer **3**: mp 83−84 °C from hexane; ^{13}C NMR (CDCl$_3$) δ 150.39, 143.95, 138.35, 130.21, 128.79, 127.85, 127.77, 125.66, 125.40, 125.16, 58.83, 48.92, 44.36, 39.41, 38.22, 35.08, 30.41, 27.79, 23.00, 21.76; HRMS calcd for $C_{22}H_{24}$ *m/z* 288.1878, found 288.1871, major fragment (relative intensity) 288 (46%), 246 (31%), 245 (100%), 220 (41%), 217 (38%), 91 (32%).

Dimer **4**: HRMS calcd for $C_{22}H_{22}$ *m/z* 286.1722, found 286.1708, major fragment (relative intensity) 286 (100%), 243 (87%), 209 (45%), 208 (43%), 167 (66%), 165 (48%), 142 (31%), 115 (36%), 91 (44%), 44 (44%).

Adduct **5**: mp 205−207 °C from dichloromethane; ^{13}C NMR (CDCl$_3$) δ 156.32, 149.83, 143.54, 141.92, 131.77, 130.24, 129.67, 128.74, 127.96, 127.81, 125.84, 125.74, 125.56, 119.07, 109.52, 56.27, 55.52, 49.57, 49.40, 38.38, 38.18, 27.94, 27.87, 21.58, 21.53; HRMS calcd for $C_{29}H_{27}N$ *m/z* 389.2144, found 389.2130, major fragment (relative intensity) 389 (100%), 346 (88%), 217 (36%), 91 (89%).

Adduct **6**: HRMS calcd for $C_{18}H_{17}N$ *m/z* 247.1362, found 247.1369, major fragment (relative intensity) 247 (28%), 218 (42%), 144 (100%), 129 (41%), 115 (44%).

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⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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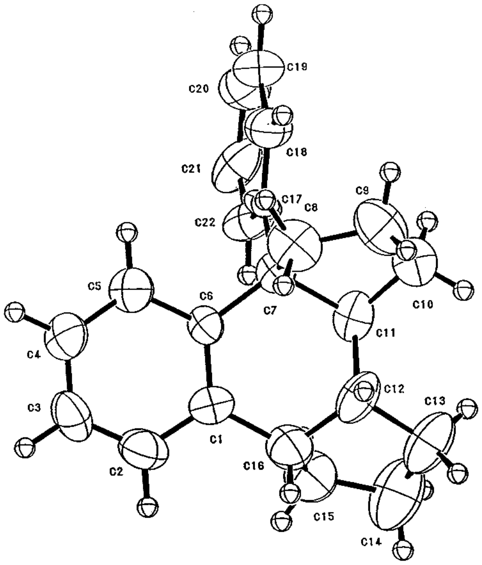


Figure 1. ORTEP drawing of dimer **3**.

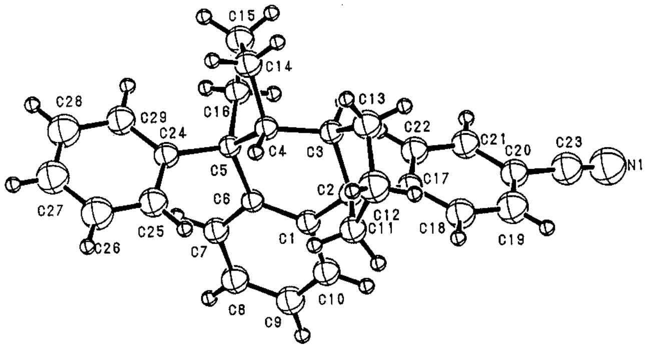


Figure 2. ORTEP drawing of adduct **5**.

Photoinduced Electron Transfer Reaction of 1b with DCNB. Olefin **1b** (0.1 M) with DCNB (0.1 M) was irradiated in acetonitrile under a nitrogen stream at room temperature using a 400-W high-pressure mercury lamp. The concentrated reaction mixtures were separated by column chromatography, on silica gel with hexane as an eluent, to give *cis*- and *trans*-1-cyano-2-phenylcyclohexane (**7**, 13%) and two kinds of 1:1 adducts of **1b** combined with DCNB (**8** and **9**; **8**/**9** = 1.6; 34%), without yielding dimeric products. The structures of the products were identified on the basis of the following spectra data.

Adduct **8**: ^{13}C NMR (CDCl$_3$) δ 152.23, 141.75, 139.02, 136.74, 132.22, 128.80, 128.66, 127.23, 126.71, 119.09, 109.90, 31.91, 27.25, 21.48; HRMS calcd for $C_{19}H_{17}N$ *m*/*z* 259.1362, found 259.1376, major fragment (relative intensity) 259 (27%), 130 (100%), 129 (35%), 115 (39%), 91 (23%).

Adduct **9**: ^{13}C NMR (CDCl$_3$) δ 151.00, 141.09, 136.74, 131.99, 129.24, 128.34, 128.22, 125.69, 125.15, 119.09, 109.60, 42.70, 32.41, 25.90, 17.50; HRMS calcd for $C_{19}H_{17}N$ *m*/*z* 259.1362, found 259.1349, major fragment (relative intensity) 259 (87%), 231 (57%), 230 (46%), 143 (44%), 129 (37%), 128 (49%), 116 (35%), 115 (92%), 91 (100%), 38 (78%).

Pulse Radiolysis. The L-band linear accelerator at Osaka University was used as the source of electron pulse, with an energy value of 28 MeV, pulse width of 8 ns, and dose of 0.7 kGy per pulse. The diameter of the electron beam spot on the surface of the cell was ca. 3 mm. A 450-W xenon lamp (Osram, XBO-450) was used as the analyzing light source. The light passing through the sample solution was monitored first by using a monochromator (CVI-Laser, DIGIKROM-240) and then by a photomultiplier (Hamamatsu Photonics, R-1477). The light signal was amplified on a transient digitizer (Tektronix, 7912AD).

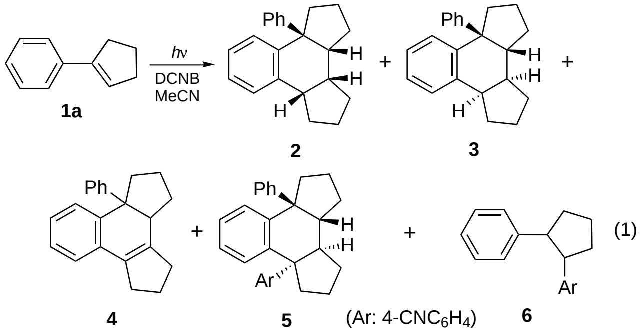
γ-Radiolysis. The γ-radiolysis of glassy rigid matrix of degassed chlorobutane solutions was carried out in 1.5-mm-thick Suprasil cells cooled in liquid nitrogen at 77 K by a ^{60}Co γ source (dose, 4.5 × 10^6 Gy). The optical absorption spectra of the 77 K matrix were measured with a spectrophotometer (Hitachi 323) and a multichannel photodetector (Otsuka Electronics, MCPD-100). After the irradiated sample at 77 K was placed in a precooled quartz Dewar vessel, the absorption spectra were determined as follows. Immediately after the liquid nitrogen was removed from the vessel, the sample was again placed in the vessel and the absorption spectra were measured with the MCPD every 3 s during an increase in temperature up to room temperature.

Laser Flash Photolysis. Laser flash photolysis was carried out with a XeCl (308 nm) excimer laser (Lambda Physik EMG-101) with a pulsed xenon arc (Wacom KXL-151, 150 W) as the monitoring light source. The monitoring light coming from a monochromator (JASCO CT-25C) was amplified by a photomultiplier (Hamamatsu Photonics R-928) and stored in a storage scope (Iwatsu TS-8123), and the signals were transferred to a personal computer (NEC PC-9801VX21) and accumulated 3−5 times in order to be averaged. The system was controlled by a computer, which was also used to analyze the decay curves. Sample solutions containing **1** (20 mM) and DCNB (150 mM) in acetonitrile were used under air.

Results and Discussion

Photoinduced Electron Transfer Dimerization of 1a with DCNB.

When **1a** (0.1 M) was irradiated with DCNB (0.1 M) in acetonitrile through a Pyrex filter for 8 h with a 400-W high-pressure mercury lamp, **1a** was almost consumed and three dimers (**2**−**4**) were produced with yields of 11, 23, and 7%, respectively (eq 1), together with 2:1 and 1:1 adducts of **1a** with DCNB [**5** (31%) and **6** (~1%), respectively]. The structures of dimer **3** and adduct **5** were determined by X-ray crystallographic analysis (Figures 1 and 2; Table 1), and other dimers were identified by their spectra data.



Although it has been reported, mainly on the basis of MS spectra, that direct UV irradiation of **1a** forms cyclobutane-type dimers, their structure has not been determined yet.[8] In the cases of acyclic olefins such as styrene, 4-methylstyrene, and 4-methoxystyrene, both [2 + 2] and [2 + 4] cyclodimers were formed through ET reaction, depending on the initial concentration and the substituents on the benzene rings.[2,3,10] Therefore, it is significant that **1a** produces [2 + 4] cyclodimers without yielding any [2 + 2] dimers through similar ET reactions.

Photoinduced Electron Transfer Reaction of 1b with DCNB. In the case of 1-phenylcyclohexene (**1b**), direct irradiation gives [2 + 2] cyclodimers at room temperature through an excimer and a [2 + 4] cyclodimer at −70 °C through its *trans* isomer.[9] By contrast, irradiation of **1b** with DCNB under conditions similar to those created in the case of **1a** gave no dimers but produced 1-cyano-2-phenylcyclohexane (**7**, 13% at 20% conversion of **1b**) and 1:1 adducts of **1b** combined with

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[10] Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895−6903.

Table 1. Crystal and Structure Analysis Data of Compounds **3** and **5**

formula	**3**: $C_{22}H_{24}$	**5**: $C_{29}H_{27}N$
formula weight	288.43	389.54
crystal system	triclinic	monoclinic
space group	$P1$; $Z = 2$	$P2_1/n$; $Z = 4$
lattice parameter		
a/Å	10.810(8)	10.936(2)
b/Å	12.587(5)	10.842(4)
c/C	6.212(2)	18.059(2)
α/deg	93.77(3)	90
β/deg	98.97(4)	96.43(1)
γ/deg	95.47(5)	90
V/Å^3	828.4(8)	2127.8(8)
D_{calcd}/g cm^{-3}	1.156	1.216
crystal size/mm^3	0.140 × 0.560 × 0.940	0.240 × 0.160 × 0.480
diffractometer	Rigaku AFC5S	Rigaku AFC5S
radiation	Mo Kα ($\lambda = 0.710$ 69 Å)	Mo Kα ($\lambda = 0.710$ 69 Å)
monochrometer	graphic	graphic
scan type	$\omega-2\theta$	$\omega-2\theta$
2θ max	55.1°	55.0°
computer program	TEXSAN system[a]	TEXSAN system[a]
structure solution	SIR88[b]	MITHRIL[c]
hydrogen atom treatment	calcd, not refined	calcd, not refined
refinement	full-matrix, anisotropic	full-matrix, anisotropic
least-squares weight	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
no. of measurement reflns	total 3991, unique 3792	total 5409, unique 5145
no. of obsns[d]	988	1718
no. of variables	199	121
residuals R; R_w	0.084; 0.096	0.083; 0.090
max shift/error	0.40	0.01
$\Delta\rho_{max}$/e$^-$ Å^3	0.25	0.49

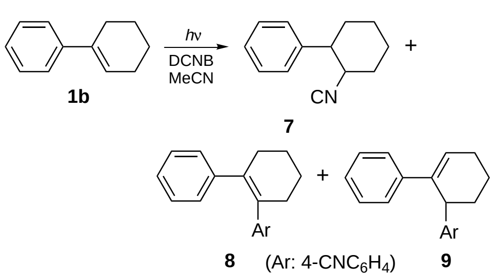
[a] See ref 26. [b] Direct method, see ref 27. [c] Direct method, see ref 28. [d] $I > 3.00\sigma(I)$.

Table 2. Oxidation Potentials (E_{ox}), Free Energy Change (ΔG), and Ionization Potentials (I), and Heat of Formation

1	E_{ox}/V[a] (vs Ag/AgCl)	I/eV[b]	ΔG/eV[c]	$H(n)$[d] (kcal/mol)	$H(\bullet+)$[e] (kcal/mol)	ΔH[f] (kcal/mol)
1a	1.60	8.90	−1.08	26.91	218.83	191.92
1b	1.64	9.11	−1.03	9.80	211.46	191.66

[a] Measured by cyclic voltammetry. [b] Calculated by the PM3 method. [c] See text. [d] Heat of formation for neutral **1**. [e] Heat of formation for $1^{\bullet+}$. [f] $\Delta H = H(\bullet+) - H(n)$.

DCNB (**8** and **9**, 34%; eq 2).[11,12] Olefins **1a**,**b** possess almost the same oxidation potentials (E_{ox} = 1.60 and 1.64 V vs Ag/AgCl, respectively) as well as similar ionization potentials (Table 2). The free energy change (ΔG) associated with the ET process from ground state **1** to excited DCNB ($E_{red} = -1.57$ V vs Ag/AgCl) was calculated using Weller's equation to be exothermic for both olefins.[13] Therefore, the remarkable difference in the products resulting from the photoinduced ET reactions of **1a**,**b** suggests that the reaction routes depend on the reactivity of the monomer cation radicals of the olefins generated ($1a^{\bullet+}$ and $1b^{\bullet+}$) but not on the initial ET process.



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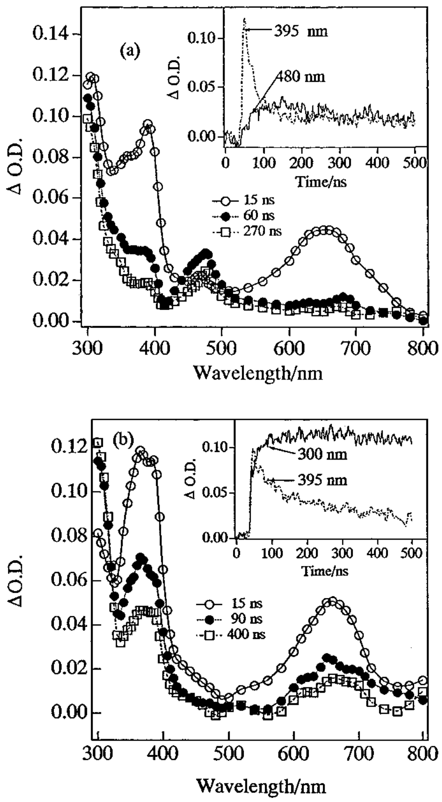

Figure 3. Transient absorption spectra obtained at various times after an 8-ns pulse irradiation of **1** (10 mM) in chlorobutane at room temperature: (a) **1a** and (b) **1b**.

Transient Absorption Spectra of $1^{\bullet+}$. Upon pulse radiolysis of **1a** (10 mM) in chlorobutane under argon at room temperature, simultaneous formation of a new transient absorption band with λ_{max} around 480 nm was observed after the decay around 400 and 670 nm of the initial absorption bands, due to the presence of monomer cation radical $1a^{\bullet+}$. An increase in the concentration of **1a** intensifies the 480-nm band: therefore, the 480-nm band is attributed to the resulting dimer cation radicals (Figure 3a). The transient absorption spectra obtained by γ-ray irradiation of **1a** (8 mM) in degassed chlorobutane at 77 K was confirmed to be consistent with those observed above (Figure 4a); in particular, we observed that the 480-nm transient band occurred on warming, but not at 77 K. However, in the case of **1b**, no transient absorption band attributable to the dimer cation radical of **1b** was observed by pulse radiolysis and γ-ray irradiation (Figures 3b and 4b). Laser (308 nm) flash photolysis of **1a** (20 mM) in acetonitrile with DCNB (150 mM) gave transient bands for monomer and dimer cation radicals of **1a**, similar to those observed through the techniques described above, while only transient bands attributable to monomer cation radical were observed in the case of **1b** (Figure 5). From these results, there is no doubt that $1b^{\bullet+}$ cannot react with another neutral **1b** to form the dimer cation radical.

Pulse Radiolysis of dimer 3. Figure 6 shows transient absorption spectra measured by pulse radiolysis of dimer **3** in 1,2-dichloroethane. The absorption bands were observed around 320, 440, 480−500, and 600 nm. It is interesting that the transient spectra obtained resemble those of **1a** at 60 and 270 ns after pulse (see Figure 3a).

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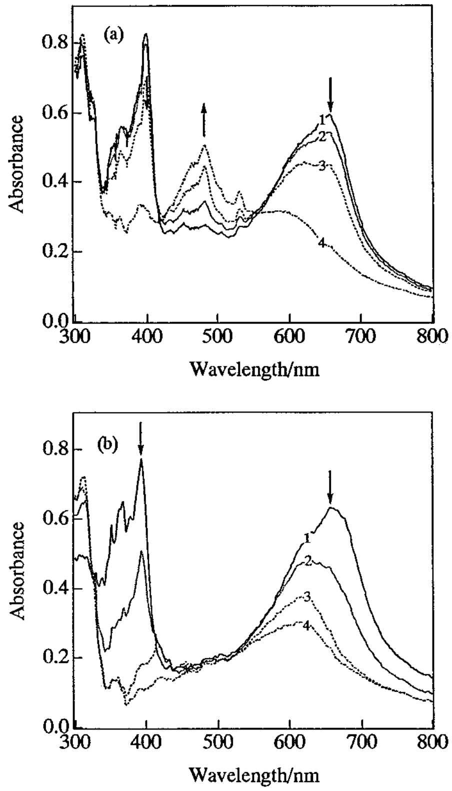

Figure 4. Transient absorption spectra obtained by γ-ray irradiation of **1** (8 mM) in chlorobutane (1 at 77 K; 2−4 on warming): (a) **1a** and (b) **1b**.

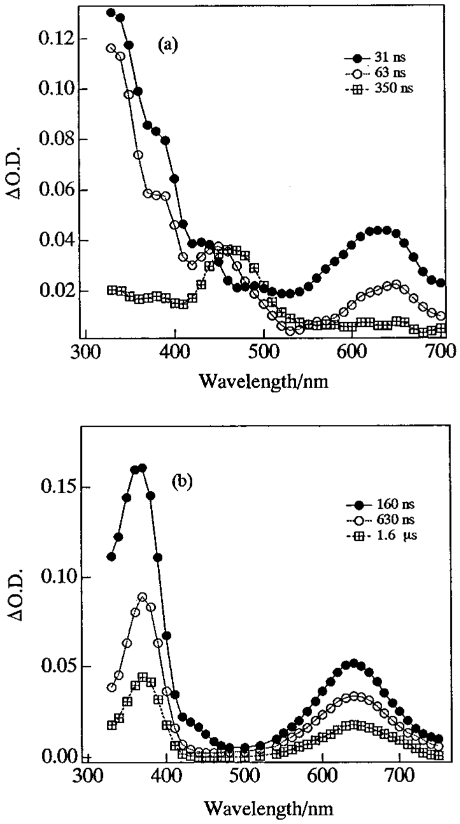

Figure 5. Transient absorption spectra obtained at various times after laser (308 nm) flash photolysis of **1** (20 mM) in acetonitrile under air in the presence of DCNB (150 mM): (a) **1a** and (b) **1b**.

Optimized Structure of $\mathbf{1}^{\bullet+}$. Using semiempirical molecular orbital calculation with the PM3 method,[14] $\mathbf{1a}^{\bullet+}$ was optimized to give a fully planar structure, although it was calculated that the optimized structure for neutral **1a** has a dihedral angle of 33.6° between the benzene and cyclopentene rings. On the other hand, the optimized $\mathbf{1b}^{\bullet+}$ does not have a planar but chairlike structure with a dihedral angle of 6.7° between the benzene ring and ethylene bond, while that of neutral **1b** was calculated to be 16.6°, smaller by 17° than that of **1a** (See Figure 7).

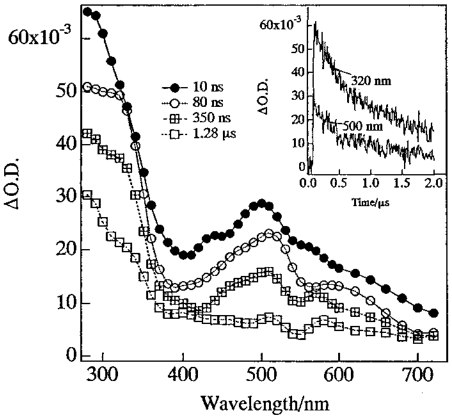

Figure 6. Transient absorption spectra obtained by pulse radiolysis of **3** (10 mM) in 1,2-dichloroethane at room temperature.

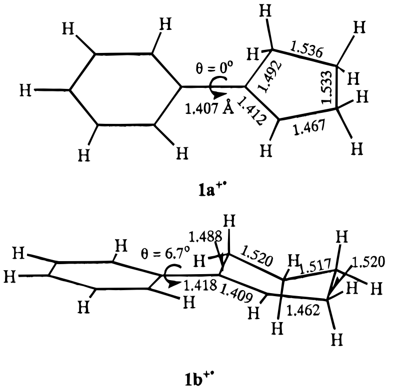

Figure 7. Optimized structure of monomer cation radicals of **1a**,**b** obtained by semiempirical molecular orbital calculation with the PM3 method.

Calculation of Heat of Formation. Using the PM3 method, the heat of formation of **3** was calculated to be 27.09 kcal/mol, which is lower by ca. 4.2 kcal/mol than that of **2**. This is one of the reasons why the formation of **3** is preferred to that of **2**.

Mechanism of Dimerization. Dimerization of **1a** through ET would be explained similarly by the mechanism proposed previously for the dimerization of acyclic olefins as shown in Scheme 1. When the monomer cation radical $\mathbf{1a}^{\bullet+}$ reacts with another neutral olefin **1a**, two probable π-complexes (**10** and **11**) are expected to be formed by their syn-head-to-head and anti-head-to-head interaction, finally to collapse into dimers **2** and **3**, respectively. On interacting with another neutral **1a**, the planer structure of $\mathbf{1a}^{\bullet+}$ would promote the formation of *cis*- and *trans*-cyclobutane dimer cation radicals (**12** and **13**) or acyclic 1,4-dimer cation radicals (**14** and **15**) as primary intermediates.[15−18] A 1,3-sigmatropic shift from **12** and **13** or 1,6-cyclization from **14** and **15** would give substituted hexatriene cation radicals (**16** and **17**).[6,16,19] ET followed by a proton shift gives dimers **2** and **3**, or deprotonation followed by loss of a hydrogen atom yields dehydrodimer **4**. In addition, formation

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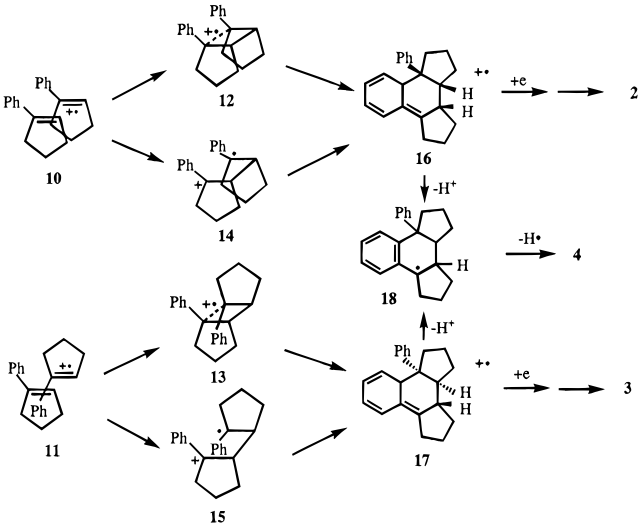
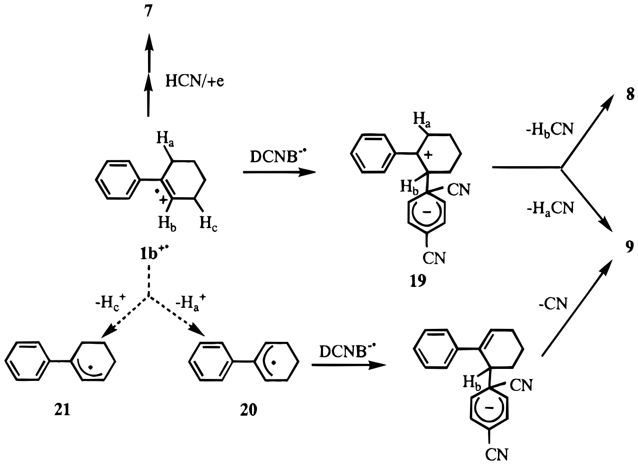
Scheme 1



Scheme 2



of adduct **5** suggests the trapping of the hexatriene cation radicals by neutral DCNB or its anion radical (DCNB$^{\bullet-}$).[3]

In dimerization of styrene, α-methylstyrene, and 4-methoxystyrene through their cation radicals, transient dimer species with absorption in the region of 450−500 nm have been observed,[20−23] and a mixture of [2 + 2] and [2 + 4] cyclodimers was produced.[2,3,7,10] Therefore, it should be noted that photoinduced ET dimerization of **1a** yields [2 + 4] dimers. The fact that the reaction produced only [2 + 4] dimers may be due to the large steric repulsion between the benzene and cyclopentene rings of the dimer cation radicals **12**−**15**, which makes the cyclobutane-type dimer cation radicals (**12** and **13**) unstable and accelerates the collapse to hexatriene-type dimer cation radicals (**16** and **17**).

480-nm Transient. The 480-nm transient in Figures 3a, 4a, and 5a is probably attributable to dimer cation radicals; however, there are several candidates for the transient, from **10** to **17**, as shown in Scheme 1. Under the conditions described above, no neutral [2 + 2] cyclodimers were produced at all; therefore, dimer cation radicals **12** and **13** can be excluded from the list of possible candidates. In the case of acyclic dimer cation radicals **14** and **15**, transient bands from both the benzyl radical site ($\lambda_{\max}$, ~300 nm)[24] and the benzyl cation site ($\lambda_{\max}$, ~320 nm)[25] are likely to be observed; however, **14** and **15** do not display an absorption band around 480 nm. Furthermore, it is not possible that the 480-nm transient is attributable to π-complexes **10** and **11** formed on initial interaction. Because the π-complexes undergo rapid σ-bond formation to give dimer cation radicals **12**−**15**, they cannot come into existence until ca. 300 ns after the pulse irradiation.

On the other hand, as in the pulse radiolysis of dimer **3**, the transient spectra obtained closely resemble those of the dimer cation radicals generated by pulse radiolysis, γ-radiolysis, and laser photolysis of **1a**. If π-complex **11** is generated upon the pulse radiolysis of **3**, decomposition from **3**$^{\bullet+}$ to **11** must proceed rapidly through several steps. For the reasons described above, and given that hexatriene-type dimer cation radicals **16** and **17** are the nearest intermediates that produce final neutral dimers **2**−**4**, **16** and **17** seem to be the most plausible candidates at the present stage. However, other possibilities for the 480-nm transient cannot be ruled out completely for lack of further evidence, for example distonic 1,4-dimer cation radicals, where π-electrons of two phenyl groups interact with each other as in charge transfer and/or charge resonance interactions.

Addition of 1b$^{\bullet+}$ to DCNB$^{\bullet-}$. The photoreaction of **1b** with DCNB is considered to be analogous to that of 2,3-dimethyl-2-butene (TME) with DCNB and 1,4-dicyanonaphthalene (DCN) reported by Arnold et al.,[11] who initially suggested that the photosubstitution reaction of DCNB and DCN with TME occurred via an electron transfer, proton transfer, radical coupling mechanism.[11a] However, according to a more recent study, addition of an allyl radical generated by deprotonation from the cation radical of TME (TME$^{\bullet+}$) to DCNB$^{\bullet-}$ or formation of a zwitterion by the combination of TME$^{\bullet+}$ and DCNB$^{\bullet-}$ can better account for the observed results.[11b] Deprotonation from **1b**$^{\bullet+}$ is expected to generate two kinds of neutral radicals **20** and **21** as shown in Scheme 2. Calculation of the heat of formation for **20** and **21** using PM3 suggests that radical **21** is more stable by ca. 4.3 kcal/mol than **20**, which is probably due to the resonance effect between the allyl radical and the phenyl group. However, the adducts between **21** and DCNB$^{\bullet-}$ were not observed although addition of **20** to DCNB$^{\bullet-}$ followed by loss of CN$^-$ would give adduct **9**. Furthermore, in the case of TME, the homocoupling of the allyl radical generated from deprotonation of TME$^{\bullet+}$ occurred to give several dimers of TME;[11a] by contrast, no dimer of **1b** was produced in the photoreaction of **1b** with DCNB. Formation of adducts **8** and **9**, therefore, is explained using Scheme 2, where combination of **1b**$^{\bullet+}$ and DCNB$^{\bullet-}$ gives a zwitterion intermediate (**19**) as a primary adduct, followed by loss of H$^+$ and CN$^-$ to yield the adducts. UV irradiation of **1b** and KCN in acetonitrile−2,2,2-trifluoroethanol solution with 1-cyanonaphthalene has been reported to give *cis*- and *trans*-2-cyano-1-phenylcyclohexane (**7**);[12] therefore, adduct **7**, produced by irradiation of **1b** with DCNB in acetonitrile, should result from the reaction between **1b**$^{\bullet+}$ and HCN produced under the reaction conditions.

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Conclusion

The reactivity of monomer cation radicals of 1-phenylcyclopentene (**1a**) and 1-phenylcyclohexene (**1b**) is determined by their structures. Calculation of their optimized structures shows that **1a**$^{\bullet+}$ is completely planar but **1b**$^{\bullet+}$ is distorted and nonplanar. Pulse radiolysis, γ-ray radiolysis, and laser flash photolysis of **1a** give transient absorption spectra which resemble each other, in that the $\lambda_{\max}$ occurs around 480 nm, a band attributable to dimer cation radicals of **1a**. The 480-nm transient can probably be ascribed to hexatriene dimer cation radicals **16** and **17**, although other possibilities cannot be entirely excluded. In the case of **1b**, however, no band attributable to its dimer cation appeared. Consistent with the direct observation of dimer cation radical species, irradiation of **1a** with DCNB in acetonitrile gives tetralin-type dimers **2**−**5** as major products, together with a minor 1:1 adduct of **1a** with DCNB (**6**). However, irradiation of **1b** under similar conditions yields 1:1 adducts (**8** and **9**) of **1b** combined with DCNB, without forming dimeric products. Furthermore, it is noteworthy that 1-phenylcyclopentene gives only [2 + 4] cycloadducts as dimers, while aromatic acyclic olefins like styrenes produce [2 + 2] and/or [2 + 4] dimers depending on the concentration of the olefins and the electron donating groups on the benzene rings.

JA950770O