

The Thermal and Photochemical Behavior of the Cyclomers Derived from 1,1′-(1,3-Propanediyl)bis(pyridinyl) Diradicals

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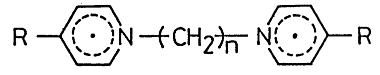
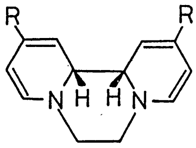
Reduction of 1,1′-(1,3-propanediyl)bis(pyridinium) dibromide (**5a**) with sodium amalgam afforded the *meso*- and *dl*-cyclomers formed by intramolecular cyclization of the diradical (**2a**). The *meso*-cyclomer (**6a**) was thermally converted into the *dl*-cyclomer (**7a**), while retroversion of **7a** into **6a** was achieved photochemically. Reduction of the 4,4′-dimethyl (**5b**) and 4,4′-di-*t*-butyl (**5c**) derivatives of **5a** similarly afforded the corresponding *meso*-(**6b** and **6c**) and *dl*-(**7b** and **7c**) cyclomers, which can be interconverted to each other. Using NMR spectroscopy to follow the reaction the energies for thermal conversion of *meso*- to *dl*- cyclomers were found to be 58.6, 74.5, and 84.5 kJ mol^{-1} for **6a**, **6b**, and **6c**, respectively. Photodissociation of the cyclomers at −196 °C gave the diradicals (**2a**—**2c**), which showed characteristic triplet ESR spectra. The ESR spectra for both **2a** and **2b** indicated that there were two conformations, each with different zero-field splitting parameters, in 2-methyltetrahydrofuran glass. In contrast, the ESR spectrum of **2c** indicated that it has only one conformation. The 4,4′-bis(methoxycarbonyl) derivative (**2d**) of **2a** also forms cyclomers which, upon photolysis, regenerate the diradical. It was concluded that 1,1′-(1,3-propanediyl)bis(pyridinyl) diradicals are substantially in thermal equilibrium with the cyclomers.

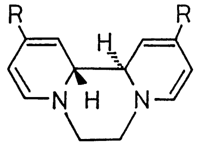
Molecules containing two chromophores connected through methylene bridges have attracted attention with respect to the intramolecular transannular interaction and orientations of the two chromophores with respect to each other. For example, the mechanism of exciplex or excimer formation for the type of A–$(CH_2)_n$–D, where A and D are electron acceptor and donor,[1] respectively, or A and D are same aromatic hydrocarbon moieties,[2] have been extensively studied by means of stationary and time-resolved fluorescence measurements. These studies showed that the interaction between the two chromophores depends on the number (n) of methylene groups in the bridge and the intramolecular interaction takes place most effectively when n=3 (so called, n=3 rule).[3]



1 n = 2
2 n = 3



3 (meso)

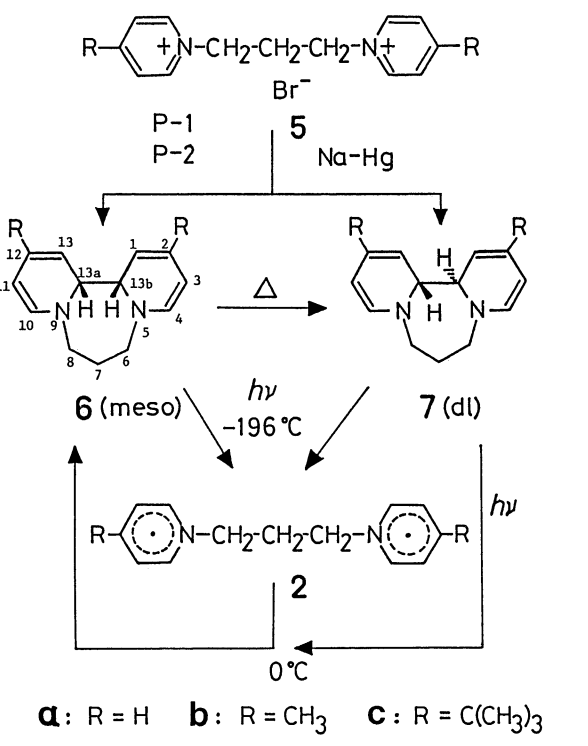


4 (dl)

a: R=H **b**: $R=CH_3$ **c**: $R=C(CH_3)_3$
d: $R=COOCH_3$

Pyridinyl diradicals of the type P˙y–$(CH_2)n$–P˙y (P˙y=4-(methoxycarbonyl)pyridinyl, n=2, 3, 4, 5), which possess two stable π-radicals connected by methylene chain, have been investigated in order to determine intramolecular radical–radical interactions and the conformation of the diradicals, since 1967.[4] For a series of these diradicals, the strongest visible absorption band was observed when n=3 (**2d**) and this band was attributed to an intramolecular charge-transfer complex with parallel sandwich structure composed of two monoradical moieties. However, the results obtained at that time involved some of unsolved problems mainly caused by the limited experimental techniques. Thereafter, the complex formation between 1-alkyl-4-(methoxycarbonyl)pyridinyl radicals and alkali halides was found[5] and, moreover, the complex formation with various metal halides was reported.[6] These complexes show strong absorption in the visible region. After the clarification on the existence of an equilibrium system between a pyridinyl radical and the dimer, a reinvestigation of the diradicals was carried out and, as one of the results, the cyclomer formation of **2d** was demonstrated in 1981.[7] We have elucidated the fact that **1d** is usually in the form of photosensitive cyclomers.[8] Cyclomer formation of the 1,1′-(1,2-ethanediyl)bis(pyridinyl) diradicals (**1a**—**1c**) without any electron-withdrawing and electron-delocalizing group in the pyridine rings was also established.[9,10]

These recent results suggested to us that the properties of **2d** and its homologues should be reexamined carefully. This paper reports that (1) 1,1′-(1,3-propanediyl)bis(pyridinyl) diradicals (**2a**—**2c**) are clearly in equilibrium with their cyclomers of *meso*- and *dl*-forms; (2) that the resulting *meso*- and *dl*-



Scheme 1.

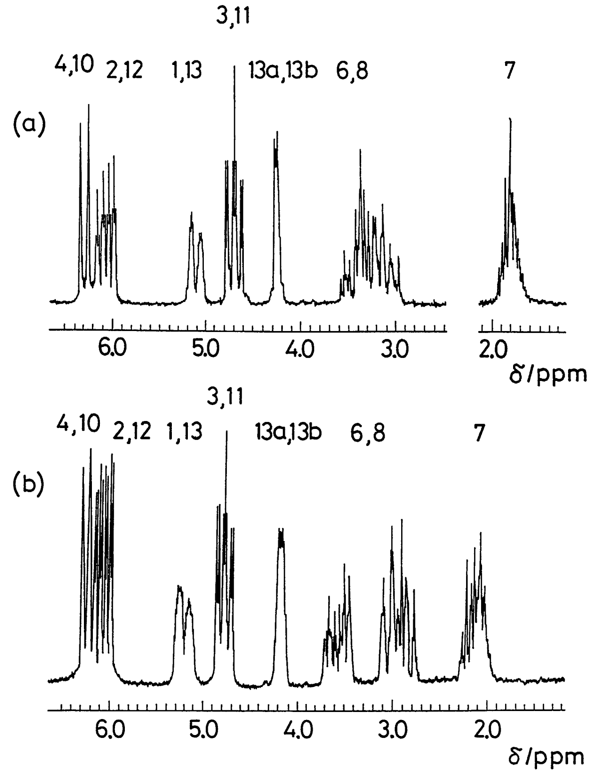


Fig. 1. ^{1}H NMR spectra of **6a** and **7a** in CD_3CN at room temperature. (a): **6a**, (b): **7a**.

isomers can interconvert into each other; and (3) that both cyclomers are photolized to yield the diradical. In addition, the cyclomer formation from **2d** is also presented though the isolation of the *meso*- and *dl*-forms was unsuccessful. The reactions of **2a**—**2c** are summarized in Scheme 1.

Results and Discussion

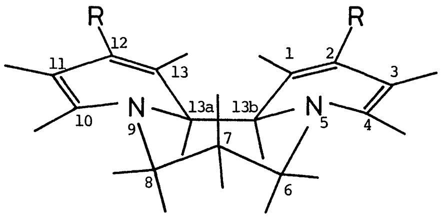
Reduction of Bispyridinium Salts and Structures of Reduction Products. Reduction of 1,1′-(1,3-propanediyl)bis(pyridinium) dibromide (**5a**) with sodium amalgam was carried out by two procedures: (P-1) Using standard vacuum line techniques, **5a** and 3% sodium amalgam in degassed CH_3CN were stirred in a flask at 0 °C for 75 min. After the amalgam changed to a liquid state, the solvent was removed, the residue was extracted with 2-methyltetrahydrofuran (MTHF), and then the solvent was replaced by CD_3CN or CH_3CN. (P-2) According to the method described in the preceding paper,[10] a solution of **5a** in water was added dropwise to a suspension of 3% sodium amalgam in cyclohexane or hexane with stirring for 30 min. After further stirring for 30 min, the organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was replaced by CD_3CN or CH_3CN using a vacuum line. Care was taken in handling the products in the tube to maintain the temperature lower than 25 °C in the dark. The solutions obtained by P-1[11] and P-2 procedures showed no ESR signal and exhibited well-resolved NMR spectra, indicating that the products are diamagnetic. The ^{1}H NMR spectrum of the product in P-2 (Fig. 1a) was simpler than that obtained in P-1. When both were warmed in CD_3CN at 80 °C, the spectra changed gradually, showing thermal conversion, and finally gave the spectrum shown in Fig. 1b. These results indicate that the product in P-2 was one isomer (**6a**) and that in P-1 a mixture of **6a** and its isomer (**7a**) was present.

In contrast to the thermal conversion, light irradiation caused conversion in the reverse direction. The solution of **7a** in CD_3CN was irradiated at 0 °C by using a high pressure Hg-lamp (500W) equipped with a UV-29 glass filter, which is transparent at wavelengths longer than 290 nm. After 25 min irradiation, the ^{1}H NMR spectrum showed the almost pure solution of **6a**. Analysis of the spectra in Fig. 1, ^{1}H NMR simulation (with the first-order approximation) and the comparison of them with the spectra of **3a** and **4a** substantiated that both **6a** and **7a** have a structure of 7,8,13a,13b-tetrahydro-6*H*-dipyrido[1,2-a:2′,1′-c][1,4]diazepine. This structural assignment was corroborated by the ^{13}C NMR and mass spectral (m/z=200, M$^+$) measurements of **6a** and **7a**. By reference to the lower stability of the *cis*-cyclomer of **2d** compared to the *trans*-cyclomer[8] and to the lower stability of *meso*-cyclomer (**3a**—**3c**) compared to the *dl*-cyclomer (**4a**—**4c**),[9,10] the stable isomer **7a** was assigned to the *dl*(*trans*)-form and the less stable isomer **6a** to the *meso*(*cis*)-form.

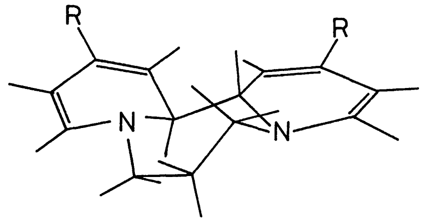
Table 1. ^{1}H NMR, ^{13}C NMR, and Absorption Spectral Data for **6a**, **7a**, **6b**, **7b**, **6c**, and **7c**

Cyclomer	**6a**		**7a**		**6b**		**7b**		**6c**		**7c**	
(1) ^{1}H NMR data in CD_3CN[a]												
Position	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)
1, 13	5.10(dddd)[b]	1.4, 1.1 3.2, 9.2	5.21(dddd)	1.3, 1.5 3.2, 9.5	4.83(qddd)	1.3, 0.7 2.0, 2.9	4.98(qddd)	0.8, 1.5 2.0, 2.8	4.94(ddd)	<1.0, 2.2 3.5	5.05(ddd)	<1.0, 2.2 3.0
2, 12	6.06(dddd)	0.9, 1.1 5.4, 9.2	6.06(ddd)	1.0, 5.5 9.5								
3, 11	4.68(ddd)	1.4, 5.4 6.8	4.76(ddd)	1.5, 5.5 7.0	4.58(dd)	2.0, 7.0	4.65(dd)	2.0, 7.0	4.70(dd)	2.2, 7.3	4.90(dd)	2.2, 7.4
4, 10	6.27(dddd)	0.5, 0.9 1.1, 6.8	6.23(dddd)	1.0, 1.0 1.3, 7.0	6.22(dd)	0.7, 7.0	6.19(dd)	0.8, 7.0	6.24(dd)	<1.0, 7.3	6.21(dd)	<1.0, 7.4
6, 8	2.95—3.60 (m)		2.75—3.15 (m) 3.45—3.75 (m)		2.96—3.55 (m)		2.75—3.11 (m) 3.43—3.70 (m)		2.78—3.62 (m)		2.76—3.12 (m) 3.40—3.70 (m)	
7	1.65—1.95 (m)		1.98—2.30 (m)		1.6 —1.9 (m)		1.7 —2.3 (m)		1.60—1.90 (m)		1.98—2.26 (m)	
13a, 13b	4.24(ddd)	0.5, 1.1	4.17(dd)	1.0, 3.2	4.18(qd)	0.9, 2.9	4.06(qd)	0.8, 2.8	4.17(d)	3.5	4.07(d)	3.0
CH_3					1.79(dd)	0.9, 1.3	1.81(dd)	0.8, 1.5				
$C(CH_3)_3$									1.14(s)		1.17(s)	
(2) ^{13}C NMR data in CD_3CN												
	δ(ppm)		δ(ppm)		δ(ppm)		δ(ppm)		δ(ppm)		δ(ppm)	
1, 13	93.1		93.3		96.4		96.2		93.2		93.4	
2, 12	125.1		124.4		132.9		132.3		145.1		144.9	
3, 11	109.2		109.6		105.7		106.0		102.7		102.6	
4, 10	137.9		134.8		137.6		134.4		137.5		134.4	
6, 8	53.0		49.2		52.8		49.2		52.4		49.0	
7	32.7		29.2		32.7		29.3		32.3		29.5	
13a, 13b	62.1		61.0		62.8		61.9		62.9		60.9	
CH_3					20.0		20.1					
$\underline{C}(CH_3)_3$									32.9		33.0	
$C(\underline{C}H_3)_3$									28.4		28.3	
(3) Absorption maximum in CH_3CN												
	$\lambda_{max}(\varepsilon)$		$\lambda_{max}(\varepsilon)$		$\lambda_{max}(\varepsilon)$		$\lambda_{max}(\varepsilon)$		$\lambda_{max}(\varepsilon)$		$\lambda_{max}(\varepsilon)$	
	330 (6000)		365 (3400)		328 (7000)		363 (3900)		325 (7400)		360 (5000)	

a) J Values were obtained by simulation. b) s=singlet, d=doublet, q=quartet, m=multiplet.



6 meso



7 dl

R = H, CH_3, $C(CH_3)_3$

Reduction of the 4,4′-dimethyl (**5b**) and 4,4′-di-*t*-butyl (**5c**) derivatives by the procedures of P-1 and P-2 usually afforded the mixture of isomers (**6b** and **7b** from **5b**; **6c** and **7c** from **5c**) even in the reduction in aqueous solution, though the product ratio varied with reaction conditions. The isomer composition was shifted towards **7b** and **7c** by warming and, conversely, toward **6b** and **6c** by light irradiation, the conversions being demonstrated by ^{1}H NMR, ^{13}C NMR, and absorption spectroscopy. The spectral data are summarized in Table 1.

The similar proton chemical shifts compared well with those of **3a**—**3c** and **4a**—**4c**, and the appearance of five ^{13}C chemical shifts for each compound (Table 1) could be interpreted as arising from a 1,2-dihydropyridine structure.[12,13] In the ^{1}H NMR spectra of **6a** and **7a** in CD_3CN at room temperature, the α-methylene protons of the *meso*-isomer appear as a multiplet (occurring at 2.95—3.60 ppm), while those of the *dl*-isomer appear as two distinct sets of multiplets (occurring at 2.75—3.15 ppm and 3.45—3.75 ppm). Similar features for the methylene protons were observed for the *meso*- and *dl*-cyclomers of the dimethyl and di-*t*-butyl derivatives. Since no modifications of these ^{1}H NMR spectra were observed upon heating the solution up to 130 °C in DMSO-d_6, the *meso*- and *dl*-cyclomers are concluded to be somewhat conformationally rigid on the NMR time scale. The nonequivalency of α-methylene protons for all *dl*-cyclomers is presumably due to one of the α-protons pointing toward the shielding region of the adjacent pyridine ring and hence appearing in the upfield region, as reported for annulated 2,2′-bipyridines.[14] Possible stable structures for the *meso*- and *dl*-cyclomers were readily assigned by reference to the structures of the corresponding cyclomers **3a**—**3c** and **4a**—**4c**, as **6** and **7**.

Thermal and Photochemical Conversions of *meso*- and *dl*-Cyclomers. The thermal and photochemical conversions mentioned above were also observed by change in the aborption spectra. The spectra of Fig. 2a changed gradually into that of Fig. 2b by warming at 80 °C. The resulting solution then changed to the spectrum of Fig. 2a on light irradiation. Similar spectral changes were observed for **6b** ⇌ **7b** and **6c** ⇌ **7c**. The concentration of each cyclomer was determined in CH_3CN by following spectroscopically the slow formation of methylviologen cation radical (ε=13000 at 605 nm)[15] from methylviologen dichloride. The thermal and photochemical conversions were completely reversible for the degassed solution in a sealed tube. The *meso*-*dl* conversion could be followed by NMR measurements for the sealed solution in CD_3CN. The rates of isomerization of **6a**—**6c** apparently obeyed a first-order kinetics.[16] The rate constants (k), A factors, and activation energies are summarized in Table 2. The activation energies are compared to those of σ-bond cleavages in which free radicals are formed in the transition state.[17] These values are much smaller than those for the isomerization of **3a**—**3c** (94.1, 112.5, and 120.5 kJ mol^{-1} for **3a**, **3b**, and **3c**, respectively).[10] This difference may be ascribed to the larger strain energies of **6a**—**6c**, because they have seven-membered rings containing a trimethylene bridge. In general, the activation energy decreases with an increase in strain energy.[18] Further,

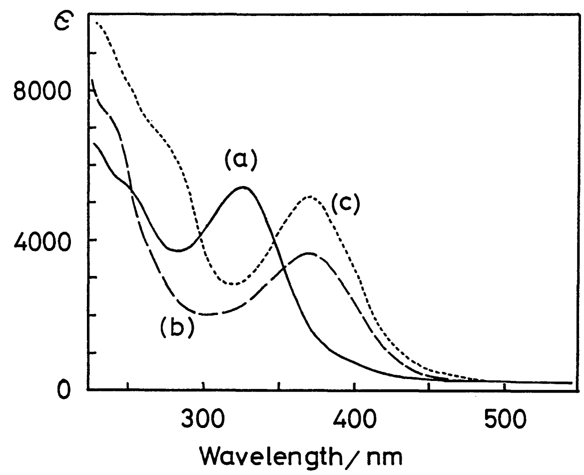


Fig. 2. Absorption spectra of **6a**, **7a**, and **2a** in MTHF. (a): **6a** at room temperature, (b): **7a** at room temperature, and (c): **2a** at −196 °C.

Table 2. First-order Rate Constants and Activation Parameters for Thermal Conversion of *meso*-Cyclomers

Conversion	Temp	$10^5 k$[a)]	A	E_a
	K	$mol^{-1}\,dm^3\,s^{-1}$	s^{-1}	$kJ\,mol^{-1}$
	333.5	32.5 ±1.3		
6a → **7a**	344.4	64.1 ±3.3	5.98×10^5	58.6±1.7
	354.7	113.3 ±4.8		
	334.5	1.58±0.10		
6b → **7b**	344.6	3.50±0.35	6.31×10^6	74.5±2.1
	354.8	7.25±0.44		
	334.0	4.75±0.23		
6c → **7c**	343.5	11.4 ±0.5	1.00×10^9	84.5±2.1
	355.3	34.5 ±0.9		

a) Rate constants (k) are apparent values.

the A values obtained are smaller than those for the isomerizations of **3a**—**3c** (1.00×10^{10}, 3.98×10^{11}, and 1.00×10^{12} for **3a**, **3b**, and **3c**, respectively). This difference may be caused by that the pyridinyl rings bonded by a trimethylene bridge are more restricted stereochemically in the transition state as compared to the isomerizations of **3a**—**3c**.

In contrast to the thermal conversion of *meso*-cyclomer, the photochemical conversion of *dl*-cyclomer into *meso*-cyclomer was very rapid at room temperature. Such a facile C–C bond cleavage on light irradiation is characteristic of pyridinyl radical dimers.[19,20]

The behaviors of thermal and photochemical conversions of the present cyclomers resemble those of **3** and **4**. The mechanism of these conversions is fundamentally similar. Since the formation of **7a**—**7c** from **2a**—**2c**, which were generated by photodissociation of **6a**—**6c** and **7a**—**7c** at low temperature, did not occur, the activation energies to form **7a**—**7c** from **2a**—**2c** must be considerably higher than those to form **6a**—**6c**.

Photolysis of *meso*- and *dl*-Cyclomers at Low Temperature. In the preceding paper,[10] we reported that **1a**—**1d** are readily generated by photolysis of the corresponding cyclomers. A similar photodissociation was observed for the present cyclomers. Light irradiation of the solution of **6a** and **7a** at −196 °C exhibited a spectrum identical to Fig. 2c. This species was stable for a long period at −196 °C, but a rise of temperature led to a spectral change into the spectrum of Fig. 2a. The spectral shape of Fig. 2c (λ_{max} 376 nm) is different from those of Fig. 2a and 2b and resembles that of 1,1′-(1,2-ethanediyl)bis(pyridinyl) diradical (λ_{max} 370 nm).[9] Hence, the spectrum of Fig. 2c is assigned to **2a**. The dimethyl (**6b** and **7b**) and di-*t*-butyl (**6c** and **7c**) derivatives showed similar evidence for diradical generation.

The generation of the diradicals clearly proven by ESR measurements. The solutions of **6a**—**6c** or **7a**—**7c** in MTHF showed no ESR signal at −196 °C. Irradiation of either solution of **6a** or **7a** with visible light shorter than 500 nm led to an appearance of strong ESR signal, as shown in Fig. 3a. The signal intensity increased with the time of irradiation, being accompanied by a change of the spectral shape into those of Figs. 3b and 3c. A similar spectrum and change were observed for the dimethyl derivative (Fig. 4a, 4b, and 4c). These spectra are certainly due to the triplet

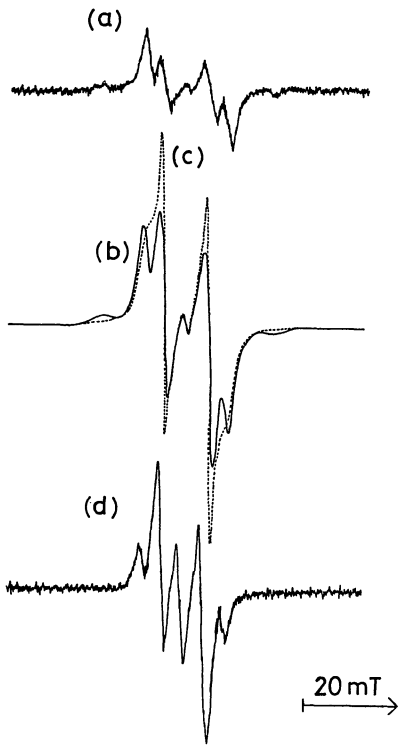


Fig. 3. Triplet ESR spectra of **2a** generated by photodissociation of **6a** or **7a** in MTHF. (a): Recorded after 0.5 min light irradiation at −196 °C; (b), (c): Recorded after 10 min, and 40 min light irradiation, respectively, at −196 °C; (d): Recorded after the rise of temperature to −145 °C.

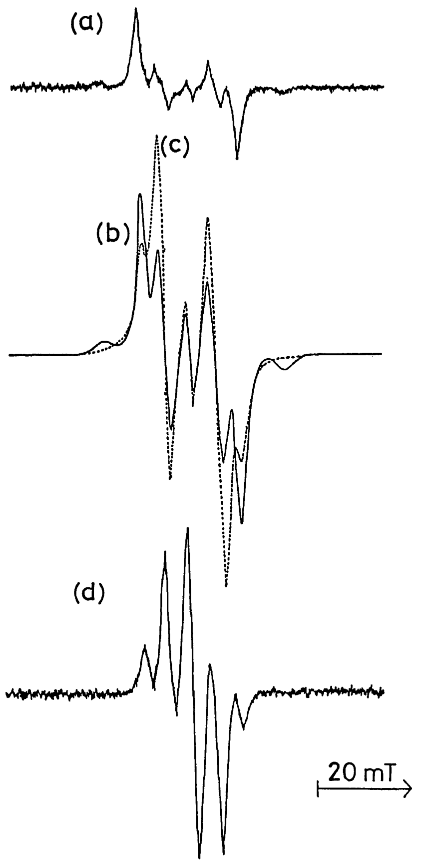


Fig. 4. Triplet ESR spectra of **2b** generated by photodissociation of **6b** or **7b** in MTHF. (a): Recorded after 0.5 min light irradiation at −196 °C; (b), (c): Recorded after 10 min, and 40 min light irradiation, respectively, at −196 °C; (d): Recorded after the rise of temperature to −145 °C.

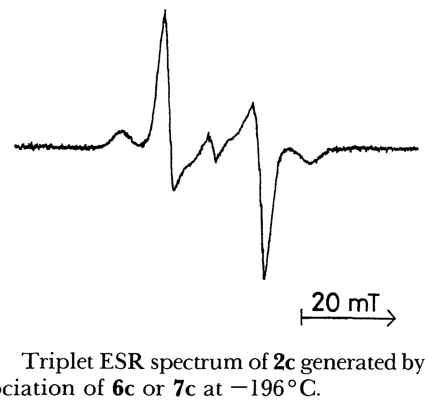


Fig. 5. Triplet ESR spectrum of **2c** generated by photodissociation of **6c** or **7c** at −196 °C.

transitions of two spin system of **2**, and are interpreted as arising from two triplet components, T(1) and T(2), both of which are stabilized in glassy matrix. For **2c**, a triplet ESR spectrum, which was consistent with only one component, was observed (Fig. 5). The zero-field parameters for the triplet spectra are listed in Table 3. The T(1) spectra of **2a** and **2b** appeared strongly in the early stage of irradiation, and the spectral intensity of the T(2) component increased with the irradiation time. Upon warming to −145 °C, only the T(2) spectra remained (Figs. 3d and 4d, respectively). The triplet ESR spectrum of **2c** was no longer observed at −145 °C, implying that **2c** is less stable than **2a** and **2b**. The E values for the observed triplet species are close to zero, in contrast to those for **1a—1d** ($|E|$=0.0012—0.0017 cm^{-1}).[8,10] The zero E value implies that the structures of the present diradicals are conformationally flexible compared with those of **1a—1d**. Change in the separation (Table 3) from metastable T(1) to stable T(2) is attributable to conformational stabilization in the solvent matrix at low temperature since the change occurs in the dark at −196 °C. The di-*t*-butyl derivative (2c) presumably is less mobile form in the glassy matrix at −196 °C.

Properties of 1,1′-(1,3-Propanediyl)bis[4-(methoxycarbonyl)pyridinyl] Diradical at Low Temperature. Reduction of the corresponding bis(pyridinium) dibromide with sodium amalgam affords the mixture of *cis*- and *trans*-cyclomers of **2d**, as reported by Hermolin and Kosower,[7] but the properties of the cyclomers are hitherto unknown. Therefore, we carefully examined the cyclomers in solution. However, the pure solution of each cyclomer could not be prepared, because the cyclomers are thermally unstable at the temperature above 70 °C. Conversions of the *meso*- and *dl*-cyclomers were not observed.

It is evident that **2d** exists as the cyclomers under usual conditions, since the reduction product showed no ESR signal due to diradical at low temperature and the following photodissociation is understood in analogy with those of **6a—6c** and **7a—7c**. Irradiation of the cyclomers of **2d** in solution with visible light shorter than 500 nm in MTHF at −196 °C gave the ESR spectrum of Fig. 6, in which the central strong line is due to the monoradical impurity produced in the preparation. This spectrum certainly displays the triplet transition of the two-spin system of **2d**. The

Table 3. Zero-Field Splitting Parameters for Diradicals

Diradicals	T(1)			T(2)		
	$\|D_1\|$/cm^{-1}	$\|E_1\|$/cm^{-1}	r/nm[a)]	$\|D_2\|$/cm^{-1}	$\|E_2\|$/cm^{-1}	r/nm[a)]
2a	0.0177	0	0.53	0.0121	0	0.60
2b	0.0191	0	0.51	0.0126	0	0.59
2c	0.0194	0	0.51			
2d	0.0154	0	0.55			

a) Average separation of two spins estimated from the relation $D=-(3/2)g^2\beta^2r^{-3}$.

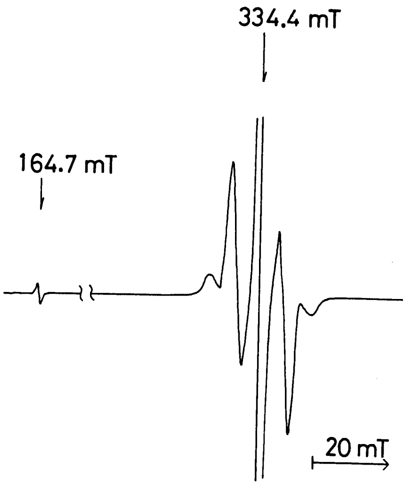


Fig. 6. Triplet ESR spectrum of **2d** generated by photodissociation of its cyclomers in MTHF at −196 °C.

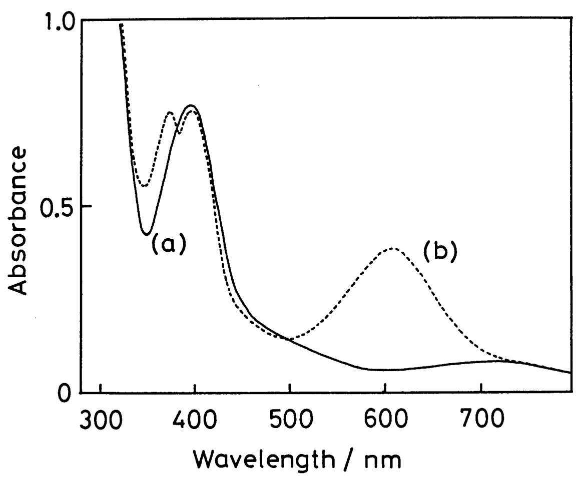


Fig. 7. Spectral change of the cyclomers of **2d** in MTHF on light irradiation at −150 °C. (a): Before irradiation (b): After irradiation.

zero-field parameter, $|D|=0.0154\ \mathrm{cm}^{-1}$ is consistent with a spin–spin dipolar interaction for an average separation of 0.55 nm of the two-spin system. This triplet signal remained unchanged for a long period at −196 °C. With the rise of temperature to −150 °C, the triplet signal gradually decreased, accompanied by the color change from colorless to a blue solution. The blue color with the absorption at 600 nm (Fig. 7) is characteristic of the intermolecular association of two pyridinyl rings,[21,22] as discussed for the association of **1d**. Further rising of the temperature led to the re-formation of cyclomers.

Conclusion

The present paper reports the cyclomer formation of 1,1′-(1,3-propanediyl)bis(pyridinyl) diradicals (**2**) and the thermal and photochemical behaviors of the cyclomers. The *meso*-cyclomer (**6a**—**6c**) is thermally converted into the *dl*-form (**7a**—**7c**) and, inversely, the *dl*-form is photochemically converted into the *meso*-form. The unstable diradical intermediates were detected spectroscopically at low temperature.

Radical–radical interaction between two pyridinyl radical moieties connected through two-to-five methylene chain has been a subject of investigation since 1967.[4,6,23,24] However, recent studies with careful handling of pyridinyl radicals revealed the facile cyclomer formation for 1,1′-(1,2-ethanediyl)bis(pyridinyl) diradicals,[8,10] the 1,1′-(1,3-propanediyl)bis[4-(methoxycarbonyl)pyridinyl] diradical,[7] and, in the present study, for 1,1′-(1,3-propanediyl)bis(pyridinyl) diradical derivatives. Based upon the results obtained so far, we make the following conclusions: (1) Pyridinyl diradicals of the type $\mathrm{P^{\bullet}y{-}(CH_2)_n{-}P^{\bullet}y}$ (n=2,3) are converted to the corresponding cyclomers (of *meso*- and *dl*-forms) under ambient conditions. (2) The *meso*- and *dl*-cyclomers are convertible to each other by going through the diradical intermediate. (3) The 4,4′-bis(methoxycarbonyl) derivatives can form the complex with metal halides;[7] in the absence of the halides the diradicals form cyclomers. (4) Radical–radical interaction can also occur intermolecularly, as observed for **1d** and **2d** in solution at low temperature.[8]

Experimental

Standard vacuum line techniques were used in the preparation and purification of the diradicals, cyclomers, and solvents. UV-vis spectra were measured on a Cary Model 14 spectrophotometer, ESR spectra were recorded on a Varian Model E-109E EPR spectrometer, and NMR spectra were recorded on a JEOL 90Q NMR spectrometer. Irradiation was carried out with a Ushio 500 W Hg lamp and Toshiba filters. Mass spectra were obtained by using a JEOL Model LMS-DX300 mass spectrometer.

Materials. 1,1′-(1,3-Propanediyl)bis(pyridinyl) dibromide (**5a**) was prepared by treating 1,3-dibromopropane with a large excess of pyridine without solvent in a sealed tube at 70 °C for about 6 h. A dark solid product was filtered off and recrystallized from methanol to yield colorless crystals, mp 242—243 °C. Found: C, 42.73; H, 4.21; N, 7.99%. Calcd for $C_{13}H_{16}N_2Br_2$: C, 43.36; H, 4.47; N, 7.77%. 1,1′-(1,3-Propanediyl)bis(4-methylpyridinium) dibromide (**5b**) and 1,1′-(1,3-propanediyl)bis(4-*t*-butylpyridinium) dibromide (**5c**) were prepared in a similar manner as above: **5b**, colorless, mp 245—246 °C. Found: C, 46.31; H, 5.40; N, 7.50%. Calcd for $C_{15}H_{20}N_2Br_2$: C, 46.41; H, 5.19; N, 7.21%. **5c**, colorless, mp 233—234 °C. Found: C, 53.10; H, 6.59; N, 5.98%. Calcd for $C_{21}H_{32}N_2Br_2$: C, 53.40; H, 6.83; N, 5.93%.

1,1′-(1,3-Propanediyl)bis[4-(methoxycarbonyl)pyridinium] dibromide (**5d**) was prepared by treating 1,3-dibromopropane with a large excess of methyl isonicotinate without solvent in a sealed tube at 70 °C for about 2 days. A dark solid produced was filtered off and recrystallized from methanol–water (1:1) to yield colorless crystals, mp 120—

123 °C. Found: C, 42.99; H, 4.51; N, 6.27%. Calcd for $C_{17}H_{20}N_2O_4Br_2$: C, 42.88; H, 4.23; N, 5.88%.

Solvents. Acetonitrile (Guaranteed Reagent) was passed through an alumina column and distilled. After degassing, the solvent was treated with 1-methyl-4-methoxycarbonylpyridinyl radical to remove radical-reactive impurities. The solvent was distilled again under vacuum at low temperature and stored over previously degassed molecular sieves 4A in a storage vessel. 2-Methyltetrahydrofuran (MTHF) was refluxed over sodium for 3 days, degassed, and then distilled onto sodium and anthracene in a storage vessel.

Reduction of Bispyridinium Salts. Reduction of **5a**, **5b**, and **5c** was each carried out by two procedures: (P-1) A dibromide (ca. 0.025 mmol), 3% sodium amalgam (0.15 mmol), and a Teflon-sealed stirring bar were placed in a reaction flask connected to a vacuum line. After 5 h of pumping at 10^{-6} Torr (1 Torr=133.322 Pa), degassed CH_3CN (5 cm^3) was distilled in, and the flask was sealed and stirred at 0 °C. The solution became yellowish and then almost colorless. After about 10 h, the solvent was removed and the residue was extracted with MTHF to obtain a colorless solution. The solvent was replaced by an appropriate one for spectral measurements. (P-2) According to the method described in the preceding paper,[10] the aqueous solution of a dibromide (ca. 0.3 mmol in 5 cm^3 of water) was added dropwise to a suspension of 3% sodium amalgam in cyclohexane with stirring. Reaction proceeded smoothly without any hazard and the cyclohexane layer gradually turned yellow. After stirring for about 30 min, the separated cyclohexane layer was dried over anhydrous magnesium sulfate, and then the solution was moved into a tube connected to a vacuum line. After degassing, the solvent was replaced for spectral measurement. The product from **5a** in P-2 was almost pure **6a**; MS (20 ev) m/z (rel intensity) for **6a**: 200 (M^+; 39), 121 (49), 120 (66), 106 (15), and 93 (100). Pure **7a** was obtained by heating the solution of **6a** in a degassed solution of **6a** in a sealed tube at 80 °C for 30 min in the dark. m/z for **7a**: 200 (M^+; 62), 121 (46), 120 (84), 106 (36), and 93 (100). The product from **5a** in P-1 was a mixture of **6a** and **7a** and the solution was heated at 80 °C to yield the solution of pure **7a**. The product from **5b** was usually a mixture of **6b** and **7b** in both P-1 and P-2. The pure **6b** was obtained by irradiation of the solution of the mixture with a 500 W Hg lamp equipped with a UV-29 glass filter for 20 min. m/z for **6b**: 228 (M^+; 29), 135 (42), 134 (81), 107 (100). Pure **7b** was obtained by heating the solution of **6b** in a degassed sealed tube at 80 °C for 1 h. m/z for **7b**: 228 (M^+; 38), 135 (39), 134 (82), 107 (100). The product from **5c** was also a mixture of **6c** and **7c**. The pure **6c** and **7c** were obtained in a similar manner as above. m/z for **6c**: 312 (M^+; 20), 177 (37), 176 (100), 149 (78), and m/z for **7c**: 312 (M^+; 19), 177(36), 176 (100), 149(100).

Reduction of 1,1′-(1,3-propanediyl)bis[4-(methoxycarbonyl)pyridinium] dibromide (**5d**) was carried out by the procedure P-1, because the reduction in the presence of water leads to hydrolysis of the methoxycarbonyl group. The bromide (ca. 0.027 mmol), 3% sodium amalgam (ca. 0.15 mmol), and CH_3CN (5 cm^3) were stirred in a degassed sealed flask at 0 °C. At the early stage of reduction, an ESR signal of the cation radical produced by one electron reduction of the dication appeared. This signal disappeared gradually, giving the cyclomer solution. After stirring for about 10 h, the solvent was removed, the residue was extracted with benzene, and then the solvent was replaced by MTHF for spectral measurements.

Kinetic Treatment of Thermal Conversion. The kinetics of thermal conversion of **6a**—**6c** into **7a**—**7c** were followed by measuring the change of an ^1H NMR spectrum with time at various temperatures. Change of the integrated signal intensities of H(13a) and H(13b) protons of the *meso*- and *dl*-cyclomers were analyzed as the first-order reaction. The sample was dissolved in CD_3CN, degassed, and then sealed in a sample tube.

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