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The 1,1'-Trimethylenebis(pyridinyl) Diradical and Its Photosensitive Cyclomers

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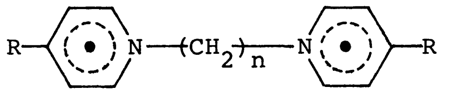
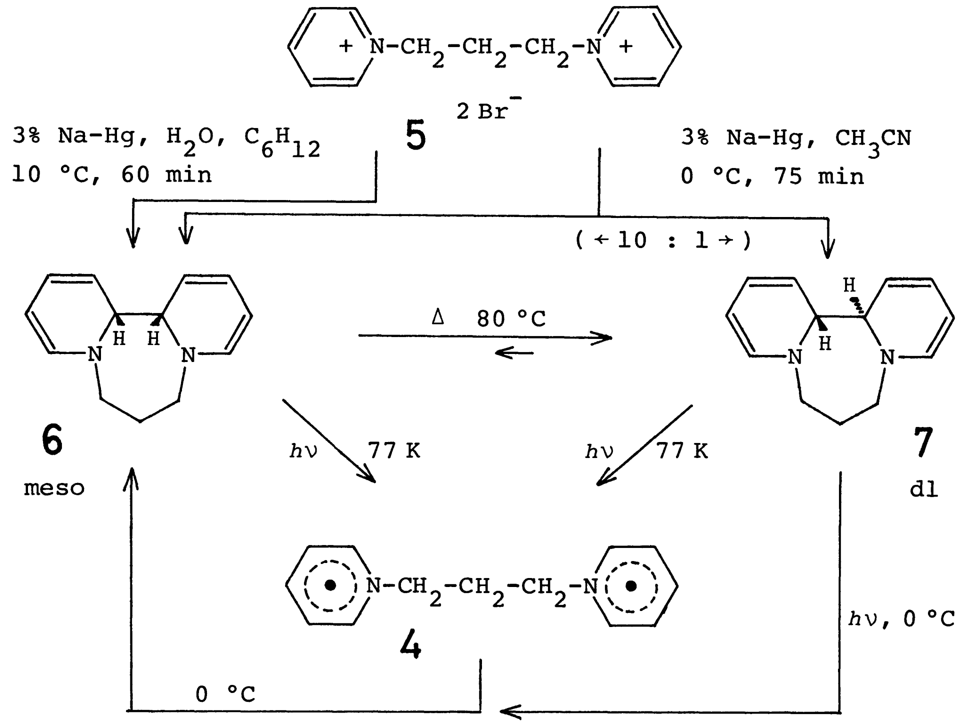
Reduction of 1,1'-trimethylenebis(pyridinium) dibromide with sodium amalgam produces the cyclomers of 1,1'-trimethylenebis(pyridinyl) diradical. Meso and dl forms of the cyclomers are convertible to each other. Two conformations of the diradical are observed in the triplet ESR spectrum at 77 K.

It has been demonstrated that 1,1'-ethylenebis[4-(methoxycarbonyl)pyridinyl] diradical (**1**) is essentially in equilibrium with the cyclomers formed by intramolecular cyclization and the cyclomers photodissociate to generate the diradical.¹⁾ Similar cyclomer formation has also been reported for the 1,1'-trimethylenebis[4-(methoxycarbonyl)pyridinyl] diradical (**2**).²⁾ Subsequently, we elucidated the cyclomer formation of 1,1'-ethylenebis(pyridinyl) diradical (**3**) without any electron withdrawing and delocalizing substituent in the pyridine rings.³⁾ The meso and dl cyclomer forms are convertible to each other and photolytically generate the diradical **3**. This paper reports that 1,1'-trimethylenebis(pyridinyl) diradical (**4**) also forms stable cyclomers with meso and dl structures, which are convertible to each other and photolytically generate the diradical. Mutual relation of the substances is summarized in Scheme 1.



1 : R = $COOCH_3$, n = 2
2 : R = $COOCH_3$, n = 3
3 : R = H, n = 2
4 : R = H, n = 3

Reduction of 1,1'-trimethylenebis(pyridinium) dibromide (**5**) with sodium amalgam was carried out by two procedures: (P-1) A solution of **5** (105 mg) in water (5 cm^3) was added dropwise to a suspension of 3% sodium amalgam (1.5 g) in cyclohexane (10 cm^3) with stirring at 10 °C 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. (P-2) Using standard vacuum line techniques, **5** (105 mg) and 3% sodium amalgam (450 mg) in degassed CH_3CN (30 cm^3) were stirred in a flask at 0 °C for 75 min. After the amalgam changed to a liquid state, the solvent was removed, residue was extracted with 2-methyltetrahydrofuran (MTHF), and then the solvent was replaced by CD_3CN or



Scheme 1.

CH_3CN. Care was taken in handling the products to maintain the temperature lower than 25 °C in the gloom.

The structures of the above products were determined as follows. The ^1H NMR spectrum of the product in P-1 (Fig. 1a) was simpler than that obtained in P-2. When both products were warmed in CH_3CN at about 80 °C, the spectra changed gradually, showing thermal conversion, and finally gave the spectrum shown in Fig. 1b after 20 min. These results indicate that the product in P-1 was one isomer (6) and that in P-2 was the mixture with another isomer (7). Analysis of these spectra by the aid of ^1H NMR simulation with the first-order approximation and by comparing them with the spectra of 1,2-dihydropyridine derivatives substantiated that both of 6 and 7 have a structure of 1,1'-trimethylene-1,1'2,2'-tetrahydro-2,2'-bipyridine. This structure was supported by the measurements of ^{13}C NMR and mass spectra (m/z = 200, M^+) of 6 and 7. Product ratio of 6 to 7 in P-2 was about 10/1. By reference to the less stability of cis cyclomer of 2 than the trans cyclomer[2)] and to the less stability of meso cyclomer of 3 than the dl cyclomer,[3)] the stable isomer 7 was assigned to the dl-form and the less stable isomer 6 to the meso-form.

In contrast with the thermal conversion, light irradiation caused the conversion of 7 to 6. When the solution of 7 in CD_3CN was irradiated by using a high pressure Hg-lamp (500 W) equipped with a UV-29 glass filter at 0 °C, the ^1H and ^{13}C NMR spectra changed gradually and finally exhibited those of the almost pure meso-form after 25 min. The above thermal and photochemical conversions were completely reversible for the degassed solution in a sealed tube.

These results were supported by the measurements of absorption spectra,

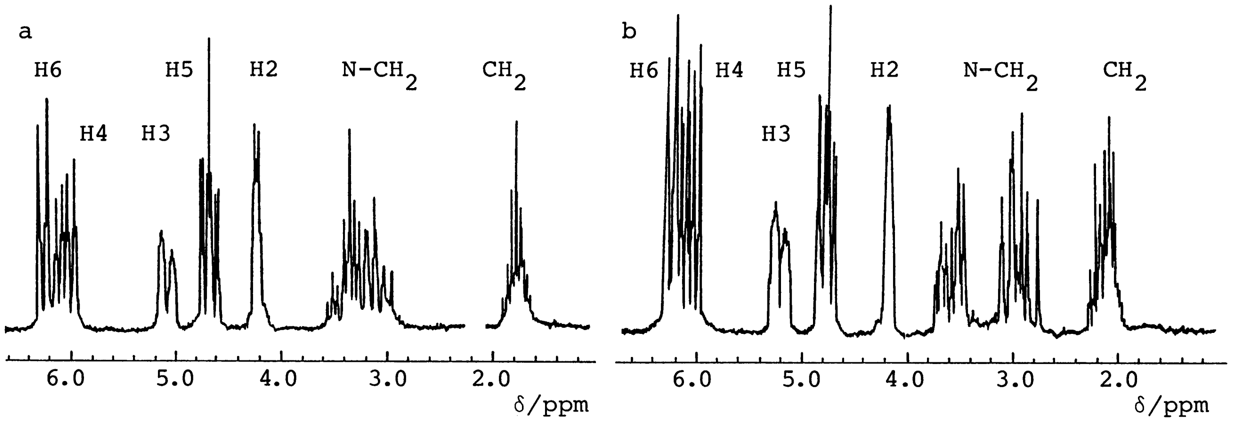


Fig. 1. ^{1}H NMR spectra of the meso (a) and dl (b) cyclomers in CD_3CN.

which are illustrated with Figs. 2 and 3. The concentration of each cyclomer solution was determined in CH_3CN by following spectroscopically the slow formation of methylviologen cation radical ($\varepsilon = 13000$ at 605 nm)4) from methylviologen dichloride. The spectrum of Fig. 3a changed on light irradiation into that of Fig. 3c, which is identical with Fig. 2a. The resulting solution showed the spectrum of Fig. 3a after warming at 80 °C. At 77 K, light irradiation of the solutions of **6** and **7** exhibited the identical spectra of Figs. 2c and 3b, which are readily assigned to the intermediate diradical **4** of the photochemical process. The diradical was observed in the measurements of the ESR spectra as follows.

The solutions of **6** and **7** in MTHF showed no ESR signal at 77 K. Irradiation of either solution of **6** or **7** with visible light shorter than 500 nm led to an appearance of strong ESR signal as shown in Fig. 4a. The signal intensity increased with further irradiation, being accompanied by a change of the spectral shape (Fig. 4, b and c). These spectra are certainly due to the triplet transitions of a two spin system of **4** and the change in the shape would be ascribed to

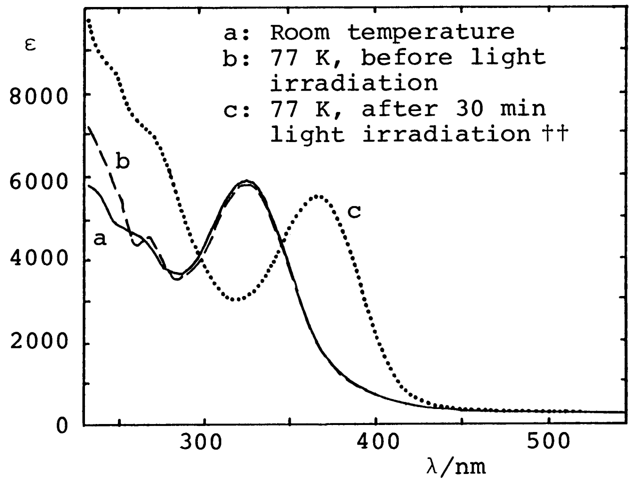


Fig. 2. Absorption spectrum of **6** and its change on light irradiation in MTHF. ††Intensity is inaccurate because of incomplete photolysis.

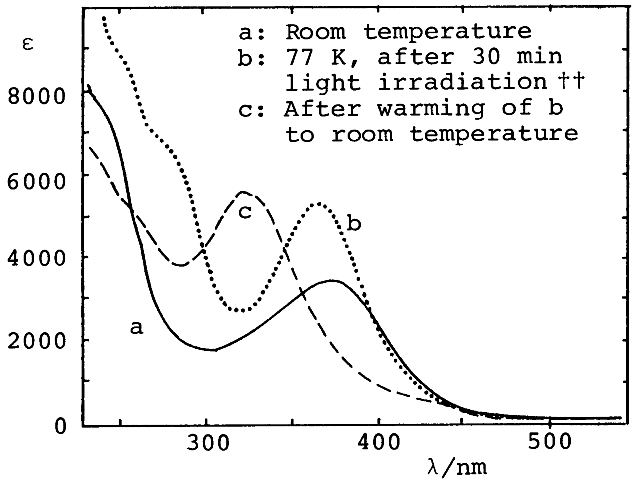


Fig. 3. Absorption spectrum of **7** and its change on light irradiation in MTHF. ††See the ††-note of Fig. 2.

a change of the diradical conformation with time. The signal is interpreted as arising from two triplet components, T(1) and T(2), with zero-field parameters: For T(1), $|D_1| = 0.0177$ and $|E_1| \approx 0$ cm^{-1} and for T(2), $|D_2| = 0.0121$ and $|E_2| \approx 0$ cm^{-1}. The T(1) spectrum appeared strongly in the early stage of irradiation, intensity of the T(2) spectrum increased with time, and finally only the T(2) spectrum remained after the rise of the solution temperature to 128 K (Fig. 4d). Zero E value of both triplet species implies that the interaction between the two pyridinyl rings in **4** is released, compared with those in **1** and **3** ($|E| = 0.0012 - 0.0017$ cm^{-1}).[1,3] The D_1 and D_2 values are consistent with the spin-spin average separations of 0.52 and 0.59 nm, respectively, using the relation of $D = -(3/2)g^2\beta^2r^{-3}$. Change in the separation is derived from a conformational change of the diradical.

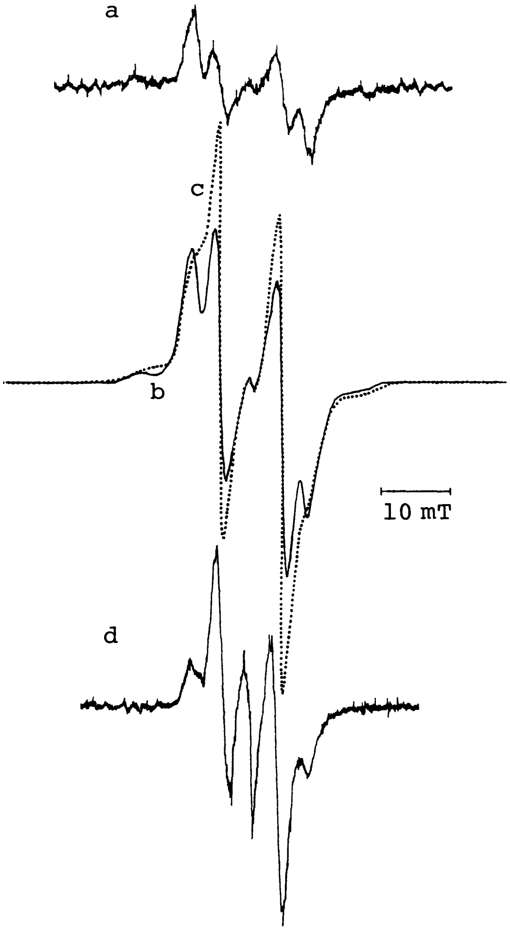


Fig. 4. Triplet ESR spectra of **4** generated in MTHF glass. a, b, and c were recorded after 0.5, 10, and 40 min light irradiations, respectively. d was recorded after a rise in temperature to 128 K.

The present results prove that **4** is essentially in equilibrium with **6** and **7**, while the equilibrium tends overwhelmingly toward the cyclomers in the dark. The cyclomers cleave thermally and photochemically to form **4**, which reforms cyclomers **6** and **7** according to the mechanistic conditions. Photodissociation of the cyclomers occurs from a $\pi\sigma^*$ state and involves rotation around the N-CH_2 bond followed by rotation around the CH_2-CH_2 bonds to the diradical, which stabilizes keeping the conformations possible in a solvent cage at low temperature.

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References

1) Y. Ikegami, T. Muramatsu, K. Hanaya, S. Onodera, N. Nakayama, and E. M. Kosower, J. Am. Chem. Soc., 109, 2876 (1987).
2) J. Hermolin and E. M. Kosower, J. Am. Chem. Soc., 103, 4813 (1981).
3) T. Muramatsu, K. Hanaya, and Y. Ikegami, Chem. Lett., 1986, 2139.
4) J. Hermolin, M. Levin, Y. Ikegami, M. Sawayanagi, and E. M. Kosower, J. Am. Chem. Soc., 103, 4795 (1981).

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