

The 1,1'-Ethylenebis[4-(methoxycarbonyl)pyridinyl] Diradical and Its Photosensitive Cyclomers

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Abstract: One electron reduction of 1,1'-ethylenebis[4-(methoxycarbonyl)pyridinium] ion (2^{2+}) first gives the cation radical (2^{2+}), which showed a well-resolved ESR spectrum, and further reduction affords cyclomers formed by intramolecular cyclization of the diradical ($2^{2\bullet}$). Photodissociation of the cyclomers give $2^{2\bullet}$, which was characterized by an ESR triplet spectrum with the zero field parameters, $|D| = 0.0178$ and $|E| = 0.0017 \text{ cm}^{-1}$, and also by absorption spectrum. Calculations of the D value suggest that the dihedral angle of the N-CH₂-CH₂-N group of $2^{2\bullet}$ in a rigid glass is about 75°. Photolysis of the cyclomer via the $\pi\sigma^*$ state leads to the diradical through rotation around the ring N-CH₂ bond followed by rotation around the CH₂-CH₂ bond. Association of $2^{2\bullet}$ to polydiradical π -complexes at low temperature is proposed on the basis of ESR data and confirmed spectroscopically.

Preparation of 1,1'-ethylenebis[4-(methoxycarbonyl)pyridinyl] diradical ($2^{2\bullet}$) was first reported in 1967 with a demonstration of the triplet transition of this two spin system.² The results at that time, however, were rather qualitative because the reduction of the bispyridinium salt, followed by extraction, gave the diradical species in low yield. The study of 1-alkyl-2-(methoxycarbonyl)pyridinyl radicals revealed that the radicals are in equilibrium with the covalently bonded 4,4'-dimer in solution and that the 4,4'-bond can be cleaved photochemically.³ Such equilibrium systems have been found for many pyridinyl radicals.⁴⁻¹⁰ Our deeper understanding of pyridinyl radical behavior led us to suspect that the low yield of the above diradical $2^{2\bullet}$ may be related to intramolecular covalent bond formation. We therefore undertook a reexamination of the diradical. In the present paper, we report the preparation, cyclomer formation, photochemical behavior, and spin-spin interaction of $2^{2\bullet}$.

Results and Discussion

Reduction of the Bispyridinium Salt. Reduction of 1,1'-ethylenebis[4-(methoxycarbonyl)pyridinium] (2^{2+}) dibromide with sodium amalgam in degassed acetonitrile was followed spectroscopically as shown in Figure 1. Figure 1 shows the spectral changes during the course of reduction of $2^{2+} \cdot 2\text{Br}^-$ (2.65×10^{-2} mmol) with a large excess of 3% sodium amalgam in acetonitrile (5 mL) at 0 °C. With progressive reduction, the solution showed the growth of a broad absorption band at 365 nm, which shifted at a certain stage to the shorter wavelength side and then to the longer side. The solution showing the absorption of Figure 1e had a green color and exhibited a strong ESR signal. Further reduction resulted gradually in the disappearance of the color with a change of the spectrum into that of curve 1f, Figure 1. An ESR signal appeared for the solution at the beginning of the reduction but

after showing no increase for a while increased abruptly at the time when the absorption maximum shifted from 360 to 378 nm (cf. Figure 1e) and then decreased rapidly as reduction progressed further.¹¹

An ESR spectrum of the solution having an absorption maximum at 378 nm exhibited a well-resolved hyperfine structure, which could be interpreted as arising from the cation radical, 2^{2+} (Figure 2). The hyperfine splitting constants shown with the structure were given by comparing them with those of 1-alkyl-4-(methoxycarbonyl)pyridinyl radicals.¹² Since 1-alkyl-4-(methoxycarbonyl)pyridinyl radicals usually show absorption bands in the range of 380-398 nm,¹³ the observed band at 378 nm is due to 2^{2+} . The broad absorption band in this region is presumed to be made up by the superposition of the bands due to 2^{2+} and diamagnetic species formed by the two-electron reduction of 2^{2+} .

The diamagnetic product extracted with 2-methyltetrahydrofuran (MTHF) from the reaction mixture showed the following properties. (1) The absorption spectrum shown in Figure 3a has a maximum at 377 nm, and the shape of the spectrum is different from those of 1-alkyl-4-(methoxycarbonyl)pyridinyl radicals.^{13,14} (2) No ESR signal was observed either at room temperature or -196 °C in the dark. (3) The ¹H and ¹³C NMR spectra measured in CD₃CN indicated that the product is composed mainly of two chemical structures, though the presence of several components made complete analysis difficult, as will be described later. These properties strongly support the conclusion that the product is composed of cyclomers formed by intramolecular coupling at 2 and 2' positions of $2^{2\bullet}$. The cyclomers are best represented by meso and *dl* forms depicted below for the relatively stable stereochemical structures. The absorption bands of pyridinyl radical dimers in the 350-nm region have been assigned to $\pi\sigma \rightarrow \pi\sigma^*$ transitions.^{4,5}

The ¹H and ¹³C chemical shifts observed for the cyclomer solution in CD₃CN are summarized in Table I, together with those of meso and *dl* cyclomers of 1,1'-ethylenebis[4-(methyl)pyridinyl] diradical and their assignments.¹⁵ The ¹H NMR spectra of the

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(2) Kosower, E. M.; Ikegami, Y. *J. Am. Chem. Soc.* **1967**, *89*, 461.

(3) Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4795.

(4) For a recent review, see: Kosower, E. M. *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer: Berlin, Heidelberg, 1983; Vol 112, pp 117-162.

(5) Ikegami, Y. *Rev. Chem. Intermed.* **1986**, *7*, 91.

(6) Akiyama, K.; Kubota, S.; Ikegami, Y. *Chem. Lett.* **1981**, 469.

(7) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y. *J. Am. Chem. Soc.* **1983**, *105*, 3601.

(8) Akiyama, K.; Tero-Kubota, S.; Ikenoue, T.; Ikegami, Y. *Chem. Lett.* **1984**, 903.

(9) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Ikenoue, T. *J. Phys. Chem.* **1985**, *89*, 339.

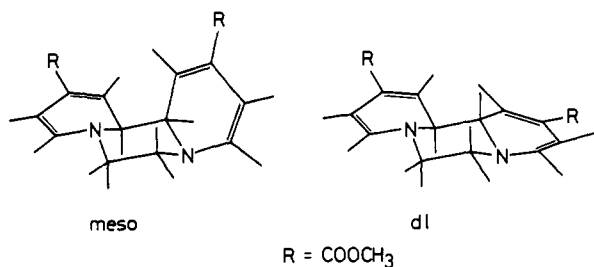
(10) Akiyama, K.; Ishii, T.; Tero-Kubota, S.; Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3535.

(11) Since the reduction proceeds as the reaction of a suspension of slightly soluble $2^{2+} \cdot 2\text{Br}^-$ in acetonitrile with solid sodium amalgam, the rate does not always go along with a function of time. The highest intensity of the ESR signal was observed after the substrate dissolved completely. The concentration of 2^{2+} is connected with $2 \cdot 2^{2+} \rightleftharpoons$ cyclomers (or $2^{2\bullet}$) + 2^{2+} and apparently affected by the components in the solution.

(12) Akiyama, K.; Kubota, S.; Ikegami, Y. *J. Phys. Chem.* **1981**, *85*, 120.

(13) Kosower, E. M. *Pyridinyl Radicals in Biology*; In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. II, pp 1-53.

(14) Ikegami, Y.; Seto, S. *J. Am. Chem. Soc.* **1974**, *96*, 7811.



4,4'-dimethyl cyclomers have been analyzed by the aid of NMR simulation with the first-order approximation, in analogy with the spectra of meso and *dl* cyclomers of 1,1'-ethylenebis(pyridinyl) diradical.¹⁶ The ¹H NMR spectrum of the present cyclomer solution consists of comparatively broad lines, though the peaks can be assigned as shown in Table I. The line-broadening is mainly caused by the coexistence of several cyclomers with different stereochemical structures, which would be the above meso and *dl* forms and the nitrogen-interconverted forms of them. The presence of several cyclomer structures are clearly recognized in the ¹³C NMR spectrum as an appearance of three or four lines with slightly different chemical shifts (Table I). Thus, the present diradical forms at least four cyclomer structures, while the diradical with the hydrogen or methyl group at 4 and 4' positions forms only two cyclomer structures.^{15,16}

A rise in temperature during the reduction of 2²⁺ frequently resulted in the formation of a green final solution. Such a color was also seen after heating the final reduction product in the presence of sodium bromide above 100 °C. The green solution showed absorption bands at 348 and 670 nm (715 nm at -196 °C) in MTHF. On the basis of the complex formation of 1-ethyl-4-(methoxycarbonyl)pyridinyl radical with sodium halides¹⁷ as well as that of polymethylenebis[4-(methoxycarbonyl)pyridinyl] diradicals with divalent metal halides,^{4,18} the green substance is presumed to be the complex of sodium bromide with the diradical 2²⁺ in equilibrium with the cyclomers. The complex is diamagnetic and insensitive to light. Details of the complex formation will be reported elsewhere. Reduction of 2²⁺·2I⁻ with 3% sodium amalgam proceeded in a manner similar to that of the bromide but very slowly, because the iodide is scarcely soluble in acetonitrile.

The concentration of the cyclomer solution in acetonitrile was determined by following spectroscopically the slow formation of methylviologen cation radical ($\epsilon = 13\,000$ at 605 nm)³ from methylviologen dichloride, giving $\epsilon = 3200$ at 377 nm for the cyclomer solution. The yield of cyclomers in the reduction of 2²⁺·2Br⁻, followed by the extraction with MTHF, was estimated to be 63%.

Photolytic Cleavage of Cyclomers. It has been made clear that some pyridinyl radical dimers are dissociated by light at the C-C bond formed in the dimerization, as demonstrated for the dimers of 1-methyl-2-(methoxycarbonyl)pyridinyl,^{3,19} 1-alkyl-4-phenylpyridinyl,^{6,7} and various alkylpyridinyl radicals.⁸⁻¹⁰ A similar photodissociation was observed for the present cyclomers. The solution of cyclomers in MTHF showed no ESR signal at -196 °C, except a weak line due to a radical impurity. Irradiation of the solution with visible light shorter than 500 nm led to a strong ESR signal as shown in Figure 4. This spectrum is certainly due to the triplet transition of a two-spin system generated by photodissociation. The zero field parameters are $D = 0.0178$ and $E = 0.0017$ cm⁻¹. In the photolytic generation of pyridinyl radical pairs from their dimers, the E value is usually close to zero. Therefore, the above E value strongly implies that the species is 2²⁺ in which two pyridinyl moieties are sterically restricted by

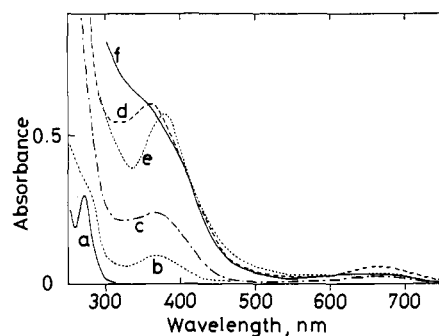


Figure 1. Spectral change during the course of reduction of 2²⁺·2Br⁻ (2.65×10^{-2} mmol) with 3% sodium amalgam in acetonitrile (5 mL) at 0 °C: (a) 2²⁺·2Br⁻ saturated in acetonitrile and (b, c, d, e, and f) spectra recorded after stirring for 1, 2, 4, 5, and 7 h, respectively.

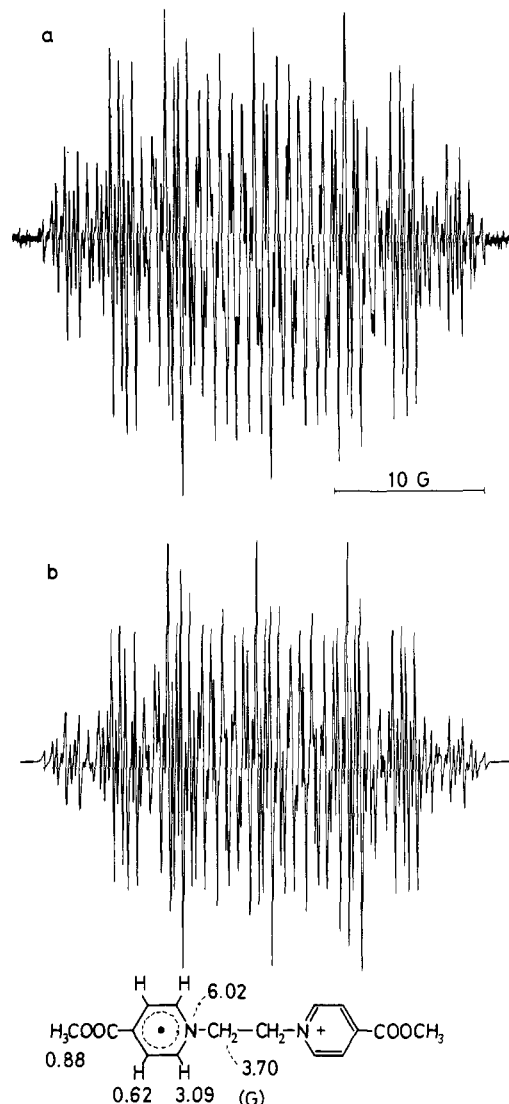


Figure 2. ESR spectrum of 2²⁺ in acetonitrile at room temperature (a) and the simulated one with the hyperfine splitting constants (b).

bonding of the ethylene bridge. The D value is consistent with a spin-spin dipolar interaction for an average separation of 5.4 Å, by using the relation $D = -(3/2)g^2\beta^2r^{-3}$.

The change of the absorption spectrum on irradiation at -196 °C is shown in Figure 3. Appearance of bands at 300 and 395 nm clearly demonstrates the photolytic formation of 2²⁺ from the cyclomers. Raising the temperature of the system after diradical formation through photodissociation led to reformation of the cyclomers. These steps could be repeated many times on a given sample.

(15) Muramatsu, T.; Hanaya, K.; Ikegami, Y., unpublished results.

(16) Muramatsu, T.; Hanaya, K.; Ikegami, Y. *Chem. Lett.* **1986**, 2139.

(17) Ikegami, Y.; Watanabe, H.; Seto, S. *J. Am. Chem. Soc.* **1972**, *94*, 3274.

(18) Kosower, E. M.; Hajdu, J.; Nagy, J. B. *J. Am. Chem. Soc.* **1978**, *100*, 1186.

(19) Ikegami, Y.; Sawayanagi, M.; Kubota, S. *Heterocycles* **1981**, *15*, 1027.

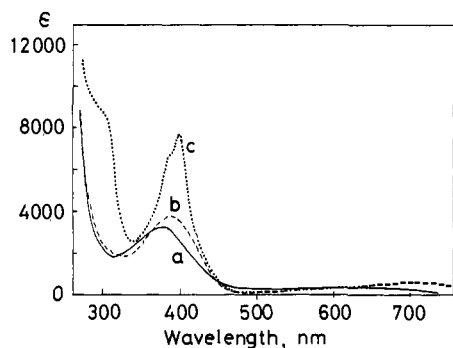


Figure 3. Spectral change of the cyclomer solution in MTHF on light irradiation, $c = 1.4 \times 10^{-3}$ M: (a) at room temperature, (b) at -196 °C before irradiation, and (c) at -196 °C after 15-min irradiation.

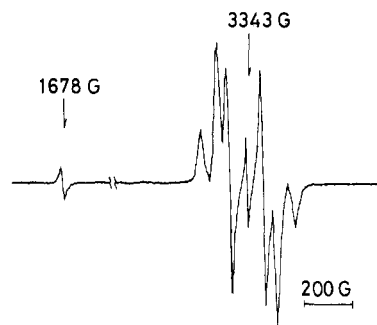


Figure 4. Triplet ESR spectrum of the diradical 2^{**} generated by the photodissociation of the cyclomers in MTHF at -196 °C, $c = 7.1 \times 10^{-3}$ M.

Table I. ^1H and ^{13}C Chemical Shifts (δ in ppm) for Cyclomers in CD_3CN^a

cyclomer		assignment
		meso dl
^1H NMR		
2.6 ~ 3.3	1.84 (dd)	1.74 (dd) CH_3
3.68, 3.73, 3.75	2.91 (s)	3.08 (s) $\text{N}-\text{CH}_2$
4.0 ~ 4.30, 4.40 ~ 4.70	4.02 (qd)	4.24 (qd) COOCH_3
	4.98 (dd)	4.63 (dd) H_2, H_2'
5.0 ~ 5.15, 5.20 ~ 5.38	5.09 (qddd)	4.90 (qddd) H_5, H_5'
5.80 ~ 6.25	6.12 (dd)	6.03 (dd) H_3, H_3'
		H_6, H_6'
^{13}C NMR		
24.4, 26.8, 27.8	19.3	19.7 CH_3
50.9, 51.0, 51.2	46.9	51.0 $\text{N}-\text{CH}_2$
55.0, 55.3, 55.7, 57.8	57.2	59.1 COOCH_3
92.0, 94.2, 95.3	103.2	97.8 C_2, C_2'
99.3, 99.4	108.8	106.6 C_3, C_3'
126.8	132.6	133.7 C_5, C_5'
136.0, 137.7, 137.9,	137.4	137.8 C_4, C_4'
139.1		C_6, C_6'
174.6		COOCH_3

^ad = doublet, s = singlet, and q = quartet.

Radical Association at Low Temperature. The ESR and absorption spectra characteristic of the diradical, shown in Figures 3 and 4, remained unchanged for a long period at -196 °C, indicating that the conformation of the diradical remained fixed in a solvent cage. Light irradiation of the cyclomer solution at -50 °C did not give rise to any ESR signal. At intermediate temperatures, the spectral changes indicated a variation arising from diradical association, as follows: Light irradiation of the

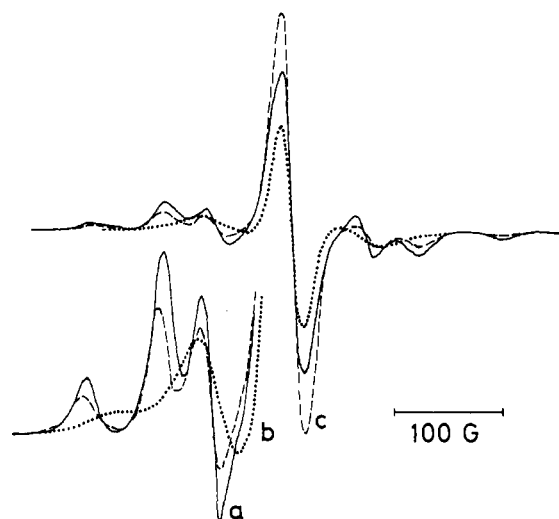


Figure 5. Temperature dependence of the triplet spectrum of 2^{**} generated by the photodissociation of the cyclomers in MTHF, $c = 1.2 \times 10^{-2}$ M: (a) recorded at -135 °C with continuous irradiation, (b) recorded at -100 °C with continuous irradiation, and (c) recorded after the solution of (b) was cooled down to -145 °C in the dark.

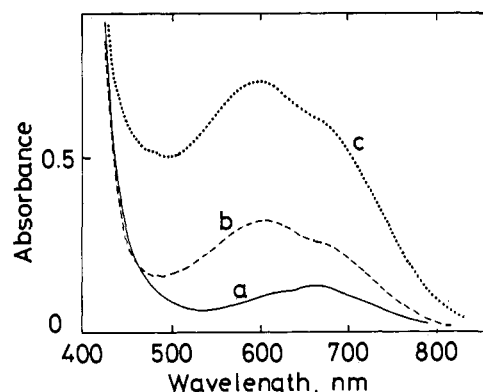
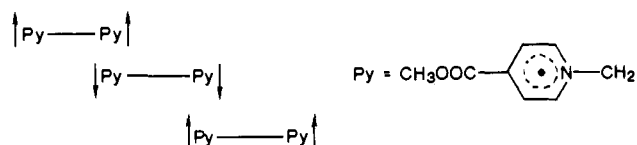


Figure 6. Spectral change in the visible region of the cyclomer solution in MTHF on light irradiation, $c = 7.8 \times 10^{-3}$ M: (a) before irradiation at -70 °C, (b) after irradiation at -70 °C, and (c) after irradiation at -100 °C.

cyclomer solution in MTHF at -135 °C (i.e., at the glass formation temperature) gave the ESR spectrum of Figure 5a, which has a strong central line due to the monoradical moiety, besides the triplet spectrum. In the spectrum obtained at -100 °C (Figure 5b), the triplet spectrum is deformed with a change of interspin distance caused by the restricted motion of the diradical. Cooling of this solution to -145 °C led to an increase of the monoradical signal as seen in Figure 5c. Intensity of the monoradical signal increased with the cyclomer concentration. Such a change in the ESR spectrum may be interpreted as due to association of the diradical producing a species, as shown below, which should have an ESR spectrum resembling that of the monoradical. The integrated signal intensity due to the monoradical significantly increased with lowering of the temperature.



Diradical association was parallel with the appearance of an absorption band at 600 nm (Figure 6) as well as a blue color of the solution. The intensity of the 600-nm band is dependent on the concentration and can be assigned to the charge-transfer transition characteristic of the intermolecular association of two pyridinyl rings.^{14,20}

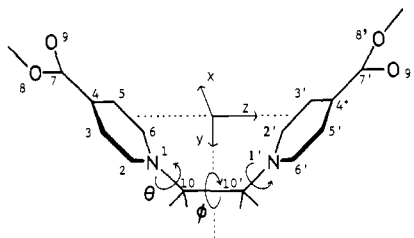


Figure 7. Structure of the diradical 2^{**} showing molecular axes, x , y , and z . $\phi = 0^\circ$ for the cis conformation, and $\theta = 0^\circ$ when the pyridinyl ring is perpendicular to the $C(10')-C(10)-N(1)$ plane.

Conformation of 2^{} at -196°C .** In order to clarify the molecular structure of 2^{**} generated in MTHF glass, calculations of the dipolar splitting tensors were performed for the assumed structure, by using McLachlan's spin densities of the pyridinyl radical (point-charge approximation). The following simplifying assumptions were made: (1) An isotropic g factor is applicable. (2) Each spin is delocalized within a pyridinyl moiety, and the electronic structure of each of the two pyridinyl rings is similar to that of the pyridinyl monoradical. (3) The diradical has a C_{2v} symmetric structure, and the methoxycarbonyl group is coplanar with the pyridinyl ring. The molecular axes are chosen as is shown in Figure 7. With these assumptions, the matrix of the D tensor can be diagonalized.

The D and E parameters of the dipolar splitting can be calculated with the aid of the following equations²¹⁻²³

$$D = \frac{3}{4}g^2\beta^2 \sum_{ij} \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5} \rho_i \rho_j$$

$$E = \frac{3}{4}g^2\beta^2 \sum_{ij} \frac{y_{ij}^2 - x_{ij}^2}{r_{ij}^5} \rho_i \rho_j$$

where r_{ij} is the distance between the i and j atoms, and where ρ_i and ρ_j are the π -spin densities on the i atom in one pyridinyl group and on the j atom in the other pyridinyl group in a diradical. Bond lengths in the pyridinyl ring, the methoxycarbonyl group, and the ethylene C-C group were taken as equal to those of pyridine, the methoxycarbonyl group in methyl benzoate, and ethane, respectively. The parameters in the Hückel and McLachlan's calculations were chosen by reference to those reported earlier,¹² except $\alpha_0 = \alpha + 1.2\beta$ for the carbonyl oxygen.

There are an infinite number of ways varying ϕ and θ independently. However, in the range $90^\circ > \phi > 270^\circ$, the rotation by θ is restricted by steric repulsion of 2 and 2' hydrogen atoms. The calculated D values for possible conformations are shown in Figure 8 as a function of ϕ , for three θ values. The largest D value is expected for a twisted cis structure ($\phi = 0^\circ$ and $\theta = 40^\circ$) and the smallest value for a trans structure ($\phi = 180^\circ$). By comparing the observed D parameter ($|D| = 190.4$ G) with the calculated ones, the agreement was best for the case $\phi = 70 \sim 80^\circ$. This angle is reasonable because it corresponds to that of a possible structure in which the two pyridinyl rings slightly rotated around the central C-C bond after the breakage of the C-C bond of the cyclomers in a solvent cage, regardless of the stereochemical structure of the cyclomers. Thus, we could estimate ϕ to be nearly 75° in MTHF. However, the dependence of D on θ was very small (Figure 8, in which three extreme D values for 0, 60, and 120° of θ are shown), so that the θ value could not be estimated. Moreover, the absolute values of calculated E parameter ($|E| < 3.5$ G) are smaller than the observed ones ($|E| = 18.8$ G). The discrepancy between the calculated and observed E values may

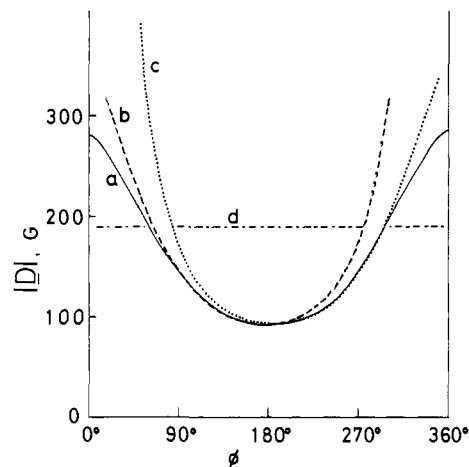


Figure 8. Calculated D values as a function of ϕ : (a) $\theta = 0^\circ$, (b) $\theta = 60^\circ$, and (c) $\theta = 120^\circ$, and (d) obsd D value.

be mainly caused by the point-charge approximation.

Conclusion

The deeper understanding of pyridinyl chemistry accumulated over the past few years had led us to reexamine the behavior of 2^{**} and 2^{*+} . The triplet spectrum of 2^{**} observed by employing a system of computer accumulation in 1967² was presumably detected as a result of the photodissociation of cyclomers, because the measurements had been carried out in a lighted room. Our new results show that the equilibrium between 2^{**} and the cyclomers tends overwhelmingly toward the cyclomers in the dark.

The present paper reports the cyclomer formation of 2^{**} and establishes the photolytic cleavage of the cyclomers to the diradical. Calculations for the diradical suggest a rather detailed structure at low temperature and give an indication of how diradical and covalent isomers may be interconverted. The first step is dissociation from a $\pi\sigma^*$ state involving rotation around the ring $N-CH_2$ bond followed by rotation around the CH_2-CH_2 bond to the diradical, which is stable at low temperature. At higher temperatures, the cyclomer reforms through rotation around the CH_2-CH_2 bond followed by bond formation by rotation around the ring $N-CH_2$ bonds. The stability of pyridinyl radicals is responsible for the approximate balance between the stability of the diradical and covalent forms. The results promise further development in the understanding of diradicals through studies on the equilibrium and kinetic physical and chemical properties of pyridinyl diradical systems.

Experimental Section

Standard vacuum line techniques were used in the preparation and purification of the diradical, cyclomers, and solvents.

Materials. 1,1'-Ethylenebis[4-(methoxycarbonyl)pyridinium] dibromide ($2^{2+} \cdot 2Br^-$) was prepared by treating 1,2-dibromoethane with a large excess of methyl isonicotinate without solvent in a sealed tube at 70°C for about 3 days. A dark solid produced was filtered off, washed with methanol, and then recrystallized from CH_3OH-H_2O (1:1) to yield colorless crystals, mp $203.5-205^\circ\text{C}$. Anal. Calcd for $C_{16}H_{18}N_2O_4Br_2$, found C, 41.54; H, 3.82; N, 6.37. The corresponding diiodide ($2^{2+} \cdot 2I^-$) was prepared as reported previously.¹⁸

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

Reduction of $2^{2+} \cdot 2Br^-$. The dibromide (12.26 mg, 0.0265 mmol), 3% sodium amalgam (120 mg, 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, degassed acetonitrile (5 mL) was distilled in, and the flask was sealed and stirred at 0°C . The solution became yellowish green and then almost colorless. After about 20 h, the solvent was removed, and the residue was extracted with MTHF to obtain a slightly

(20) Ito, M.; Nagakura, S. *J. Am. Chem. Soc.* **1967**, *89*, 3959.

(21) Wiersma, D. A.; Kommandeur, J. *Mol. Phys.* **1967**, *13*, 241.

(22) Mukai, K.; Tamaki, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1239.

(23) Mukai, K.; Sakamoto, J. *J. Chem. Phys.* **1978**, *68*, 1432.

colored (yellowish green) solution. Care was taken in handling the product to maintain the temperature lower than 25 °C.

To examine the course of reduction spectroscopically, the reaction flask was equipped with cells for ESR and absorption measurements connected with/through an intervening sintered glass filter. During the reduction, the ESR and absorption spectra were measured periodically after filtration.

Instrumentation. 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. The ^1H off-resonance decoupling and INEPT techniques were used to analyze ^{13}C NMR spectra. Irradiations were carried out with a Ushio 500-W xenon lamp and Toshiba filters.

Acknowledgment. We are grateful to Associate Professor Shozo Tero-Kubota for his helpful discussions. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 60430001 from the Ministry of Education, Science and Culture, Japan.

Structure of 3-Cyanocyclopropene by Microwave Spectroscopy and ab Initio Molecular Orbital Calculations. Evidence for Substituent-Ring Double-Bond Interactions

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Abstract: A high-quality least-squares molecular structure has been obtained for 3-cyanocyclopropene by microwave spectroscopy. Comparison of the experimental bond lengths ($r(\text{C}_1\text{C}_2) = 1.292 \text{ \AA}$; $r(\text{C}_1\text{C}_3) = 1.511 \text{ \AA}$; $r(\text{C}_3\text{C}_4) = 1.453 \text{ \AA}$) with those of the corresponding bonds in cyclopropene and cyanocyclopropane indicates that some factor is present in addition to the 3b₁ cyclopropyl (HOMO) $\rightarrow \pi^*$ cyano (LUMO) interaction believed to contribute to the latter compound. These differences are attributed to a decrease in four-electron repulsive interactions ($2b_2$ (cyclopropenyl π) $\leftrightarrow \sigma$ (C-CN)) and an increase in two-electron stabilizing interactions ($2b_2$ (cyclopropenyl) $\pi \rightarrow \sigma^*$ (C-CN)) relative to cyclopropene. Geometry-optimized ab initio molecular orbital calculations at the 6-31G* level support the experimental structural differences and the foregoing conclusions. In particular, the calculated molecular energies suggest that substitution of a cyano group at C₃ of cyclopropene is approximately 1 kcal/mol more stabilizing than substitution on cyclopropane.

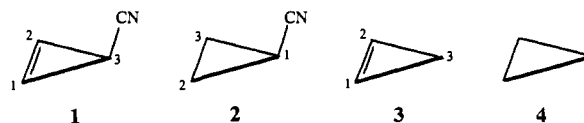
In contrast to the extensive and growing literature concerning the influence of substituents on the structure and stability of the cyclopropyl ring, relatively little is known about the corresponding effects on the cyclopropenyl ring. The latter is potentially a fascinating group. For example, Komendantov et al. have determined the Hammett σ_p constant for the 2,3-diphenylcycloprop-2-enyl group to be -0.52 , or over twice as large in an absolute sense as that for the *trans*-2,3-diphenylcyclopropyl group (-0.24).¹ As these authors pointed out, this means that the former group is one of the strongest known organic electron-donating groups. Similar, albeit smaller, relative donor effects have also been observed in kinetic studies of solvolysis reactions.²

The possibility of σ -electron withdrawal from the cyclopropenyl ring to generate cyclopropenyl cation character was proposed by Greenberg et al.³ on the basis of calculated relative heats of reaction and by Lien and Hopkinson⁴ on the basis of calculated relative strain energies. Although these are certainly reasonable suggestions, it can be extremely difficult to establish a contribution from specific orbitals (in this case, the double bond π orbitals) on the basis of relative total molecular energies. In contrast, high-quality structural studies can provide key information concerning the effects of specific orbitals.

A number of single-crystal X-ray molecular structures are available for highly substituted cyclopropenes, but only a few gas-phase microwave and electron diffraction structures have been reported for simple systems.⁵ Allen^{5a} has attributed the obser-

vation that geminate difluoro substitution shortens the adjacent single bond significantly more in cyclopropene than in cyclopropane to improved $\sigma(1,3)$ overlap in 3,3-difluorocyclopropene, while Domnin et al.⁶ have concluded that the available bond length data indicate that cyclopropenium ion character in substituted cyclopropenes appears to be of minor importance. Thus, recent conclusions regarding this problem are contradictory.

In a program to elucidate the precise nature of the effects of substituents upon the structure of the cyclopropyl ring, we have recently reported several microwave and ab initio computational studies of geometric and electronic structures for a variety of simple cyclopropyl species.⁷⁻¹⁰ As an aid to understanding the structural and electronic effects of substituents which serve as π -electron acceptors from the cyclopropane ring, and to begin extending our knowledge to the cyclopropene ring, we recently reported a microwave study of the normal isotopic species of 3-cyanocyclopropene (**1**).¹¹ This work provided dipole moment



(5) (a) Allen, F. H. *Tetrahedron* **1982**, *38*, 645. (b) Zinlin, V. N.; Il'yasov, A. V.; Nafikova, A. A.; Zuev, M. B.; Plemenkov, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim. (Engl. Transl.)* **1986**, 46.

(6) Domnin, I. N.; Kopf, J.; Keyanlyan, S.; de Meijere, A. *Tetrahedron* **1985**, *41*, 5377.

(7) Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961.

(8) Harmony, M. D.; Nandi, R. N.; Tietz, J. V.; Choe, J.-I.; Getty, S. J.; Staley, S. W. *J. Am. Chem. Soc.* **1983**, *105*, 3947.

(9) Taylor, W. H.; Harmony, M. D.; Cassada, D. A.; Staley, S. W. *J. Chem. Phys.* **1984**, *81*, 5379.

(10) Rall, M.; Harmony, M. D.; Cassada, D. A.; Staley, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 6184.

(1) Komendantov, M. I.; Fomina, T. B.; Kuzina, N. A.; Domnin, I. N. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 219.

(2) Breslow, R.; Lockhart, J.; Small, A. *J. Am. Chem. Soc.* **1962**, *84*, 2793.

(3) Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983**, *39*, 1533.

(4) Lien, M. H.; Hopkinson, A. C. *J. Mol. Struct. (THEOCHEM)* **1987**, *149*, 139. We thank Prof. Hopkinson for a preprint of this paper.