Intramolecular Association in Pyridinyl Cation Radicals

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Abstract: A series of pyridinyl cation radicals, $Py\cdot(CH_2)_nPy^+$ (in which $Py\cdot$ and Py^+ are $4\text{-}CH_3OOCC_5H_4N\cdot$ and $4\text{-}CH_3OOCC_5H_4N^+\text{–}$, respectively, and $n = 3$, 4, and 5), has been prepared from the corresponding diiodides. Epr and light absorption spectroscopy revealed that the intramolecular association of the pyridinyl and pyridinium ends in the cation radicals with $n = 3$ and 4 occurred even at room temperature. Solvent dependence of absorption and epr spectra suggested that the intramolecularly associated form amounts to ~90% in the cation radical, $n = 3$, and ~40%, $n = 4$, in MTHF. Importance and efficiency of the trimethylene group for electronic interaction between radical and parent ion were discussed.

A number of examples are known of the reversible dimerization of cation,[1,2] neutral,[1,3] or anion radical[4–6] to species which are not the result of covalent bond formation but of π–π interaction. However, most of the dimerization of the free radicals occurs in liquid or solid solution only at low temperature.

In a previous paper, Itoh and Nagakura[3] reported spectroscopic studies of the dimerization of substituted pyridinyl radicals at low temperature. Subsequently, Itoh and Kosower[7] demonstrated that a strong intramolecular association of two pyridinyl moieties occured in α,ω-dipyridinylalkanes, $Py\cdot(CH_2)_nPy\cdot$, $n = 3$ and 4, even at room temperature. Intramolecular association of two pyridinyl ends was demonstrated by the characteristic absorption spectrum and the loss of paramagnetism, which were parallel to those observed for the dimerization of pyridinyl radical in nonpolar solvents at low temperature.[3] Importance and efficiency of the trimethylene group for the intramolecular interaction of two pyridinyl radicals were emphasized. (The diradicals were abbreviated to **3**, **4**, and **5** for $n = 3$, 4, and 5.)

Hirayama[8] pointed out the intramolecular excimer formation of various α,ω-diphenylalkanes, $C_6H_5(CH_2)_n\text{-}C_6H_5$, occured only when $n = 3$. Recently, Chandross and Dempster[9] also observed fluorescence spectra due to the intramolecular excimers in the 1,3-dinaphthylpropanes. Leonard, *et al.*,[10] reported intramolecular energy transfer in the systems of various dinucleotides, where the chromophores were linked by a trimethylene chain.

A few spectroscopic studies of anion or cation dimer radicals (such as naphthalene dimer cation, $(C_{10}H_8)_2^+$) have been reported,[11–14] while various examples of the radical dimer have been reported in both liquid and solid states. Ishitani and Nagakura[15] demonstrated the electronic interaction between the two benzene rings of the paracyclophane monoanion radical as a model of the benzene dimer anion on the basis of both experimental and theoretical studies.

In this paper, preparation and separation of the pyridinyl cation radicals $Py\cdot(CH_2)_nPy^+$ obtained from α,ω-dipyridinium alkanes have been made, where $Py\cdot$ and Py^+ are 4-carbomethoxypyridinyl radical and the corresponding pyridinium cation, and $n = 3$, 4, and 5, respectively. The closed and open forms of pyridinyl cation radicals of both $n = 3$ and 4 were proposed in the solution at room temperature from the absorption and epr spectroscopies. The closed form cation radical is considered as the complex between radical and the parent molecule, *i.e.*, the dimer cation, of which the complex formation is unable to be accomplished from the pyridinyl and pyridinium salt without a linkage by tri- or tetramethylene chain even at 77°K.

Experimental Results

Preparation of Cation Radicals. The bis(4-carbomethoxypyridinium iodides) with tri-, tetra-, and pentamethylenes were reduced by contacting with 3% sodium amalgam in acetonitrile under high vacuum.[7] The reaction solution was kept at room temperature about 1 hr, the acetonitrile removed, and the diradical extracted with a small amount of 2-methyltetrahydrofuran (abbreviated to MTHF). The monocation radical was then extracted with MTHF from the reaction residue. Greenish yellow solutions of the cation radicals were obtained (abbreviated **3**$^+$ for trimethylene, **4**$^+$ for tetramethylene, and **5**$^+$ for pentamethylene chains, respectively). In the case of **3**$^+$, the cation radical was also prepared from the corresponding dibromide. These procedures were performed under high vacuum.

The concentration of the cation radical was determined by the electron transfer reaction with methylviologen dichloride in acetonitrile. The method and procedure were described in the previous paper, for determination of concentration of the diradicals.[7] Diradical content of the MTHF solution of cation radical was checked with visible absorption spectrum of diradical which shows considerable strong absorption at 6000–7000 Å, as reported in the previous paper.

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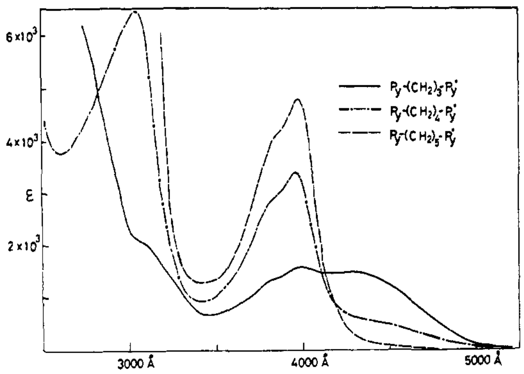

Figure 1. Ultraviolet and visible absorption spectra of the cation radical 3^+, 4^+, and 5^+ in MTHF at room temperature. The molar absorption coefficient (ε) was obtained from the spectra at a concentration of 1–3 × 10^{-4} *M* in MTHF solution.

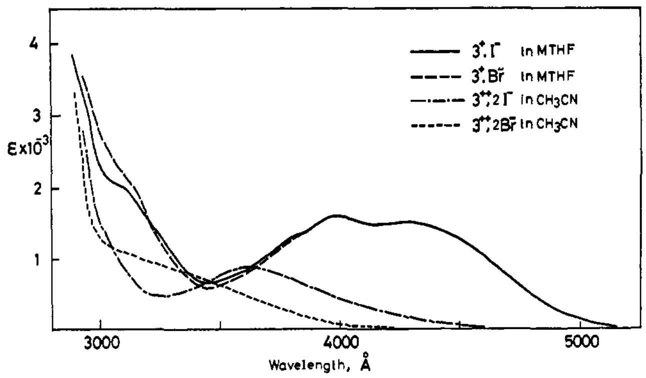

Figure 2. Ultraviolet absorption spectra of the cation radical 3^+ with counterions I^- and Br^- in MTHF, and of the parent molecules 1,1′-trimethylenebis(4-carbomethoxypyridinium iodide) and its bromide in acetonitrile.

Visible and Uv Absorption Spectra. The electronic absorption spectrum of the cation radical 5^+ is very similar to that of pyridinyl mono radical as shown in Table I. The uv spectrum of 3^+ in MTHF is remarkably different from that of 5^+. The intensity of absorption maximum (3990 Å) very much decreased and a new broad band appeared at ~4300 Å, while a uv absorption band at ~3000 Å seems to be shifted to shorter wavelength region. The cation radical 4^+ in MTHF showed a spectrum intermediate between that of 3^+ and 5^+. No appreciable difference in the uv and visible spectra of 3^+ was observed with the counterions, I^- and Br^-, though the absorption maximum at 3800–4000 Å in CH_3CN appeared at 3950 Å with the bromide and at 3800 Å with the iodide (Figures 2 and 3). The reason for the blue shift of this band is not obvious at this stage. Furthermore, no concentration dependence of uv and visible absorption spectra of 3^+ and 4^+ was observed at room temperature, respectively, by using 1 mm and 1 cm lightpath length cells (concentration range, 10^{-2}–5 × 10^{-4}).

Table I. Spectroscopic Data and Apparent Relative Spin Concentration of Cation Radical in MTHF at Room Temperature

Cation radical	Spin/radical,[a] %	Absorption maxima (Å) and absorption coefficients[b]
3^+	9	3100 s (~2000), 3800 s, 3990 (1560), 4300 (1500)
4^+	~60	3040 (6400), 3800 s, 3970 (3400), 4450 (500)
5^+	100	3040 (12,000), 3800 s, 3970 (4800)
1-CH_3[c]	100	2950 (11,000), 3750 s, 3920 (4500), 6400 (90)

[a] Spin concentration as measured by comparison of the epr signal strength with that of pyridinyl monoradical. [b] s = shoulder. [c] Data from 1-methyl-4-carbomethoxypyridinyl (monomer) in isopentane solution.

The absorption spectrum of 3^+ exhibited remarkable solvent dependence. The intensity of the new band (~4300 Å) considerably decreased with an increase of solvent polarity, while the intensity of the 3990-Å band increased, as shown in Figure 3. The new absorption at ~4300 Å of 4^+ in MTHF almost disappeared in CH_3CN, as shown in Figure 4. The spectrum of 4^+ in acetonitrile is very similar to those of the pyridinyl radical and 5^+ in absorption maxima and intensities. The absorption spectrum of 5^+ showed no appreciable solvent dependence.

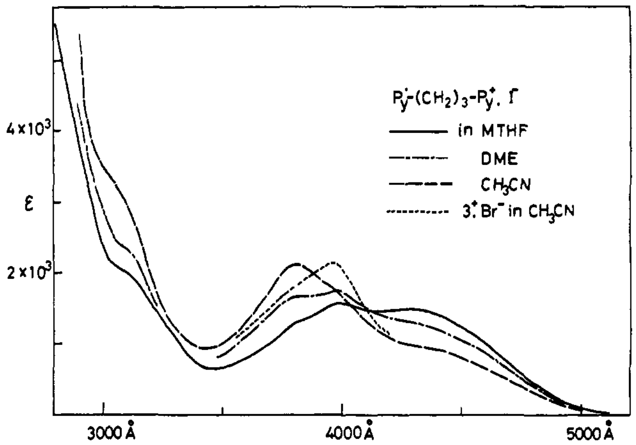

Figure 3. Solvent dependence of the pyridinyl cation radical 3^+ at room temperature (approximate concentrations are 5 × 10^{-4} *M*).

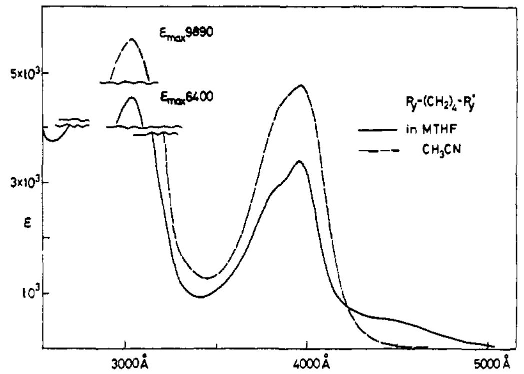

Figure 4. Solvent dependence of the cation radical 4^+ at room temperature (approximate concentrations are 2 × 10^{-4} *M*).

Uv and visible spectra of three cation radicals in MTHF were measured at 77°K. The intense visible band was observed in 5^+ at 77°K, and almost the same behavior was observed in the corresponding diradical.[7] This visible band at ~6300 Å is best ascribed to intermolecular interaction between pyridinyl moieties in 5^+. In the case of 3^+, a substantial red shift of the 4300-Å band was observed at 77°K, along with the appearance

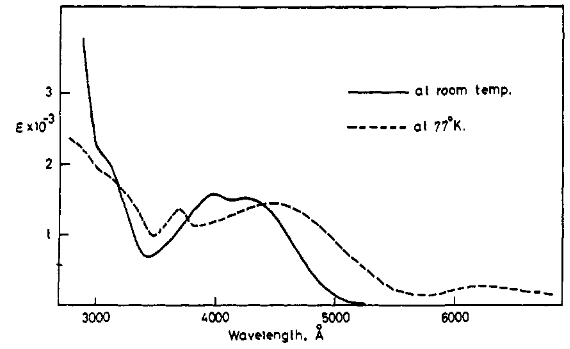

Figure 5. Ultraviolet and visible absorption spectra of the cation radical 3^+ at low and room temperatures in MTHF.

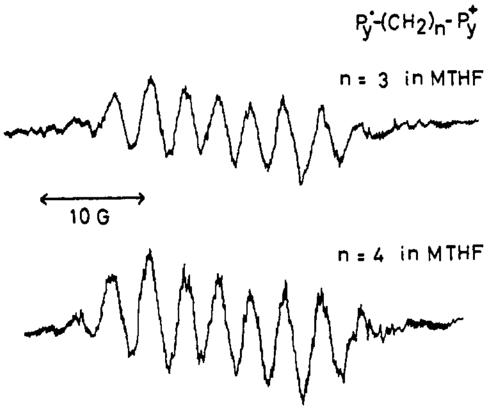

Figure 6. Epr spectra of the cation radical 3^+ and 4^+ in MTHF. Approximate concentrations are 3^+, 3×10^{-4} *M*; 4^+, 2×10^{-5} *M*.

of a visible band at 6400 Å and a blue shift of the ~3990-Å band. The longest wavelength band also seems to be intermolecular charge-transfer band between pyridinyl moieties of 3^+. The low-temperature spectrum of 3^+ is shown in Figure 5.

Epr Spectra. The epr spectra of the cation radicals 3^+, 4^+, and 5^+ were measured at room temperature in both MTHF and CH_3CN solutions. These spectra of 3^+, 4^+, and 5^+ are unexpectedly very similar to those of the corresponding diradicals reported in the previous paper,[7] respectively. A comparison of the epr spectrum of 3^+ with that of the corresponding diradical in both MTHF and CH_3CN solutions is made in Figure 7.

The strengths of the epr signals obtained for the cation radicals 3^+ and 4^+ were observed to fall considerably below that expected from the optical absorption spectroscopy. The apparent spin concentrations of 3^+ and 4^+ were determined by comparison of epr signal strengths obtained from the solutions of 3^+ and 4^+ with that from solution of 1-methyl-4-carbomethoxypyridinyl radical of known concentration. The procedure of determination of apparent spin concentration was reported in the previous paper. The results were 3^+ (~9%) and 4^+ (~60%) in comparison with the pyridinyl assumed at 100% in MTHF solutions at room temperature. Furthermore, solvent dependence of the apparent spin concentrations of 3^+ was determined to be ~9% in MTHF, ~12% in 1,2-dimethoxyethane (DME), and ~50% in CH_3CN. These results well correspond to the solvent dependence of absorption spectra, as summarized in Table II.

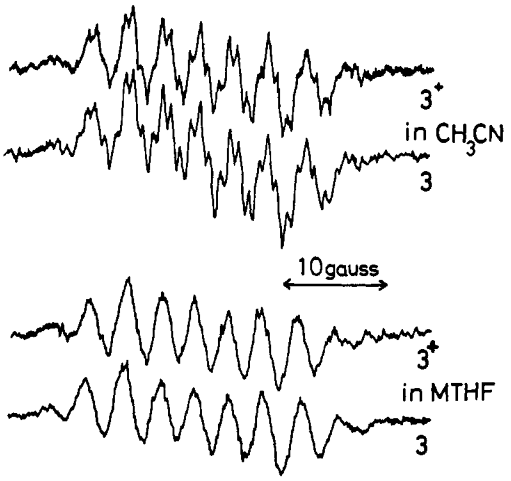

Figure 7. A comparison of the epr spectrum of 3^+ with that of the corresponding diradical 3 in MTHF and in acetonitrile. Approximate concentrations are 10^{-4}–10^{-5} *M*.

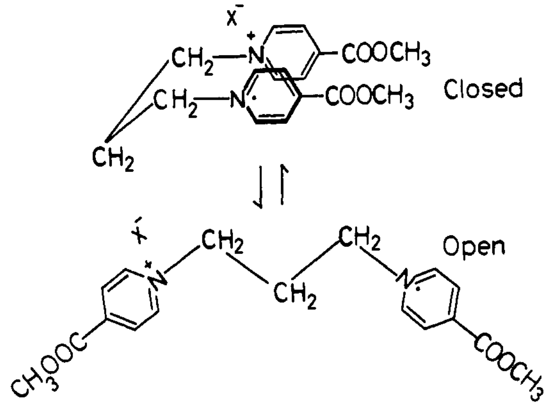

Figure 8. The assumed illustration of the closed and open form cation radicals, 3^+.

Discussion

Kosower reported that the charge-transfer band from a counterion to the 1-alkyl-4-carbomethoxypyridinium cation had a maximum and intensity much dependent on solvent polarity.[16] In this paper, since 1,1′-trimethylenebis(4-carbomethoxypyridinium iodide) showed a weak absorption (λ_{max} 3700 Å in CH_3CN), which seems to be charge-transfer band between the cation and anion, as shown in Figure 2, the pyridinium portion (Py^+, X^-) in the cation radical 3^+ may show the CT band at 3500–4000 Å. However, Figure 2 reveals that

Table II. Solvent Dependence of Spectroscopic Data and Apparent Relative Spin Concentration of 3^+, I^-

Solvent	Spin/radical %	Absorption maxima and coefficients
MTHF[a]	~9	3100 s (2000), 3800 s, 3990 (1560), 4300 (1560)
DME[b]	~12	3100 s (2250), 3800 s, 3990 (1750), 4350 s (1200)
CH_3CN	~50	3100 s (2900), 3800 (2100) 4400 s (850)

[a] 2-Methyltetrahydrofuran. [b] 1,2-Dimethoxyethane.

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(16) E. M. Kosower, *J. Amer. Chem. Soc.*, 80, 3253 (1958).

the concentration-independent absorption spectrum of **3**$^+$ at 3500–4500 Å is also independent of halogen anion (I^- and Br^-). It seems that the charge-transfer band between Py^+ and I^- arises from only ~9% of the cation radical **3**$^+$ (open form), and the resulting weak CT band in **3**$^+$ is covered by the absorption due to another ~90% of the cation radical (closed form), as will be mentioned later. Therefore, the new absorption band at ~4300 Å region can be attributed to an intramolecular interaction between $Py\cdot$ and Py^+ moieties of **3**$^+$. In the case of **4**$^+$, a weak absorption band was observed at ~4500 Å, and intensities of absorption maxima at 3100 and 3900 Å appreciably decreased in MTHF solution in comparison with that of the pyridinyl radical or cation radical **5**$^+$. Intramolecular association between $Py\cdot$ and Py^+ ends of the **4**$^+$ molecules seems to occur to some extent in MTHF but not in CH_2CN. These results are accommodated by postulating equilibrating open and closed forms analogous to those proposed for the diradicals.[7]

The absorption spectrum of the cation radical **3**$^+$ depends very much on the solvent. A broad absorption in the ~4300 Å region of the MTHF solution decreased with increasing solvent polarity, while uv absorption bands at 3900 and 3100 Å increased. These two uv bands are known to be associated with the isolated form of the pyridinyl radical. The solvent dependence of the absorption spectrum of **3**$^+$ is explained by considering a composition of the closed and open forms of the cation radical in equilibrium. The composition of closed and open forms is consistent with the result obtained by determination of spin concentration associated with the open form of the cation radical, as mentioned above.

In pyridinyl diradicals **4** and **5** reported previously,[7] epr hyperfine structures of the diradicals were attributed to a pyridinyl end of the open form diradical in which two ends of the diradicals show neither magnetic nor electronic interactions. Epr spectrum of the diradical **3** was also ascribed to the $Py\cdot$ end of the open form in medium or high concentration, although spin dipolar interaction between $Py\cdot$ moieties of the diradical **3** was observed in very dilute solution. In this paper, epr spectra of the cation radicals are very similar to those of the corresponding diradicals, as mentioned in the previous section. These results demonstrate that the epr spectra obtained in the cation radicals may be ascribed to the $Py\cdot$ end of the open form of the cation radicals, respectively. Apparent relative spin concentrations determined from the epr intensities of **3**$^+$, **4**$^+$, and **5**$^+$ seem to be regarded as the fractions of the open forms of the cation radicals, respectively. If the closed form of the cation radical shows an appropriate epr signal, the epr signal might arise from delocalization of an odd electron over two equivalent pyridinyl (or pyridinium) moieties of the closed form. Howarth and Fraenkel[12] reported the epr spectrum of naphthalene dimer cation $(C_{10}H_8)_2{}^+$ at low temperature and the equivalent delocalization of an odd electron over two naphthalenes.

Ishitani and Nagakura[15] reported electronic interaction between two benzene rings in the paracyclophane anion. They observed strong epr hyperfine structure associated with eight equivalent protons of two benzene rings and with eight methylene protons at low temperature. In this paper neither epr spectrum due to the closed form of cation radical at room temperature nor at low temperature was observed. The failure of the closed form of cation radical to show epr spectrum may be understood in terms of the motional broadening of pyridinyl–pyridinium system in the closed form. The closed form cation radical seems to take a number of energetically similar arrangements in equilibrium. Itoh and Kosower[7] reported that the closed form of the pyridinyl diradical was accompanied by the broad absorptions at ~3800 and ~6700 Å. The large half-width of the absorption spectra[17] of the diradical **3**, ~6000 cm^{-1}, and the cation radical **3**$^+$, ~3800 cm^{-1}, compared with that of the pyridinyl monomer, ~1800 cm^{-1}, may be attributed to a number of energetically similar conformations of the closed forms in both diradical and cation radical. An electron exchange between $Py\cdot$ and Py^+ in the closed form cation radical which may have a number of similar conformations in equilibrium results in undetectable broad epr spectrum.

Now we have to turn our attention to the property of the new absorption band at 4300–4500 Å of the closed form cation radical. As mentioned above, Ishitani and Nagakura reported a strong visible band at 7600 Å of the paracyclophane anion and attributed it to a resonance band between two benzene rings. If the closed form cation radical is assumed to be a paracyclophane-type conformation which was proposed for the pyridinyl diradical **3** in the previous paper, the charge resonance band due to the transition between the following two electronic states should be observed in visible or ir region, ($Py\cdot$, $Py^+ \pm Py^+$, $Py\cdot$) I, II, where $Py\cdot$ and Py^+ are pyridinyl and pyridinium moieties of the closed form cation radical **3**$^+$ or **4**$^+$, respectively. According to the theoretical consideration by Ishitani and Nagakura, the transition energies between two states I and II are mostly determined by an amount of overlap integral between half-occupied molecular orbital of $Py\cdot$ and the lowest vacant orbital of Py^+. However, average distance of $Py\cdot$ and Py^+ planes seems to be larger than that of the closed form of the corresponding diradical or that of the pyridinyl dimer, proposed in the previous papers.[3,7] The heat of the complex formation ($-\Delta H$) of the pyridinyl and pyridinium cation (undetected in the system of $Py\cdot$ and Py^+ without a tri- or tetramethylene chain in MTHF even at 77°K) seems to be much smaller than that of $Py\cdot$–$Py\cdot$ system in the radical dimer or in the closed form diradical. On the other hand, the theoretical consideration suggests the following relation between the heat of the complex formation ($-\Delta H$) and the transition energy of the charge resonance band (ΔE); $-\Delta H = -\Delta E/2$.[15] Since $-\Delta H$ can be expected to be <10 kcal,[18] the charge resonance band seems to be over 14,000 Å. Therefore, it is unlikely that the broad absorption at 4300–4500 Å in the closed form cation radical **3**$^+$ or **4**$^+$ is the charge resonance band, and more likely that the band may be ascribed to the transition from the I to the lower of the following two states III

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[17] The half-widths of the spectra were estimated from the 3820-Å band in the diradical **3**, the 4300-Å band in the cation radical **3**$^+$, and the 3920-Å band in the pyridinyl.

[18] The heat of the complex formation of the radical and parent cation was tentatively assumed to be <10 kcal, since the $-\Delta H$ of the radical dimer was reported to be 10 kcal for $(TCNQ^-)_2$[5] and 8 kcal for $(TCNE^-)_2$ [R. Chang, *J. Phys. Chem.*, 74, 2029 (1970)].

and IV, $(\mathrm{Py}\cdot{}^{*}\ \mathrm{Py}^{+} \pm \mathrm{Py}^{+}, \mathrm{Py}\cdot{}^{*})$, where $\mathrm{Py}\cdot{}^{*}$ is a locally excited state of pyridinyl radical end. Then, this absorption band may be regarded as the shifted local excitation of the pyridinyl at ~3900 Å. Furthermore, the shortest wavelength absorption of Py· at ~3100 Å seems to be shifted to shorter wavelength region in the closed form cation radical, as seen in Figure 1.

As mentioned in the introductory section, the trimethylene is most efficient for intramolecular electronic interactions in excimer[8,9] and also in energy transfer.[10] The results obtained in this paper give further evidence of the importance of the trimethylene chain for the interaction of the radical and parent molecule, *e.g.*, in one type of the dimer radical $(\mathrm{A})_2^{+}$ or $(\mathrm{A})_2^{-}$; the favorable length of the trimethylene for the intramolecular interaction in dipyridinylalkanes was demonstrated in the previous paper.

Experimental Section

Materials. Three bis(pyridinium iodides)[7] were prepared from 4-carbomethoxypyridine and three corresponding diiodoalkanes. 1,1′-Trimethylenebis(4-carbomethoxypyridinium bromide) was also obtained from 1,3-dibromopropane, mp 160–163° (*Anal.* Calcd for $\mathrm{C_{17}H_{20}O_4N_2Br_2}$: C, 42.85; H, 4.20; N, 5.88. Found: C, 42.49; H, 4.20; N, 5.42).

The acetonitrile was spectrograde. 2-Methyltetrahydrofuran and 1,2-dimethoxyethane were refluxed with potassium metal for several hours and distilled. Refluxing and distillation were repeated two or three times.

Absorption Spectra. A Cary Model 11 recording spectrophotometer was used. In the determination of low-temperature spectra, a quartz dewar was used.

Epr Spectra. Epr measurements were made with JEOLCO P-10 ESR spectrometer with 100-kc modulation.

Preparation of Cation Radicals. Bis(pyridinium iodide) (~0.1 g) and 3% sodium amalgam (~0.5 g) were sealed into the reaction tube. After evacuating to $\sim 10^{-5}$ mm, degassed acetonitrile (about 10 ml) was introduced by using a vacuum line. The reaction tube was shaken some time for about 0.5 hr at 5 to −20°. After connecting the reaction tube to the vacuum line, the solvent was removed and residue washed with a small amount of MTHF (~2 ml) in order to remove the diradical. After washing two times, the cation radical was extracted with MTHF (~10 ml). A slightly greenish yellow solution of the cation radical was obtained.

Determination of concentration of cation radical and of relative spin concentration was done using the same procedures as described in the previous paper.[7]

Acknowledgment. The author wishes to express his thanks to Professor S. Nagakura for reading the manuscript and discussions. Thanks are also due to Professor T. Okamoto for his encouragement.

Macro Rings. XLI. Preparation and Reactions of [2.2]Metaparacyclophane[1,2]

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Contribution No. 2744 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California. Received October 30, 1970

Abstract: Treatment of [2.2]paracyclophane (I) with aluminum chloride in dichloromethane saturated with hydrogen chloride at −10° gave [2.2]metaparacyclophane (II) in 46% yield and small amounts of 1,2,2a,3,4,5-hexahydropyrene. Compound II was characterized by its spectral properties, its tetracyanoethylene complex, by its oxidation to a mixture of isophthalic and terephthalic acids, and by its reductive cleavage with potassium to *p,m′*-dimethylbibenzyl. The pattern of products of rearrangement of 4-methyl[2.2]paracyclophane (III) and of 4-bromo[2.2]paracyclophane (IV) to the corresponding [2.2]metaparacyclophanes was examined. Solution of I or II in fluorosulfonic acid–sulfuryl chloride–dichloromethane at −80 to −98° gave nmr spectra of structures in which one proton had added to a bridgehead position of the para rings. These solutions with sodium methoxide–methanol gave back only starting material. At 100° in deuteriotrifluoroacetic acid, all positions of II underwent isotopic exchange at roughly the same rate except the most hindered 8 position. Acetylation of II gave a mixture of monoacetylated [2.2]metaparacyclophanes and 1-acetyl-5,7,12,14,16(4)-tetracyclo$[9.2.2.1^{4,11}.0^{8,16}]$hexadecapentaene (XVI), whose structures were demonstrated. Bromination of II gave a mixture of monobrominated [2.2]metaparacyclophanes, whose structures were demonstrated. The reactivities and spectral properties of II and its derivatives are discussed in terms of the crystal structure and strain energy of II.

Since the original description of the conversion of [2.2]paracyclophane (I) to [2.2]metaparacyclophane (II),[2a] several elegant syntheses of II[3a-d] have appeared, one of which involved tetradehydro[2.2]metaparacyclophane as an intermediate.[3b] Three reports of studies of ring inversion of II have also appeared,[2b,3c,3e] one of which[2b] demonstrated that at temperatures up to 200° only the meta ring underwent rotation.

Since the structures of I and II are central to this study, they are compared here. Combustion of II by Boyd, *et al.*, demonstrated the substance possessed a strain energy of 23 kcal mol^{-1} as compared to 31 kcal mol^{-1} for I.[4] A preliminary refinement in a single

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(1) The authors thank the National Science Foundation for a grant used in support of this research. D. T. H. also thanks the National Science Foundation for a Traineeship, 1965–1969.

(2) Preliminary accounts of parts of this work have already appeared: (a) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Amer. Chem. Soc.*, **88**, 1324 (1966); (b) D. T. Hefelfinger and D. J. Cram, *ibid.*, **92**, 1073 (1970).

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