Stable Free Radicals. IV. Intramolecular Association in Pyridinyl Diradicals[1,2]

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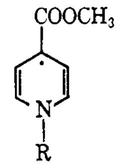
Abstract: A series of pyridinyl diradicals, $Py\cdot(CH_2)_nPy\cdot$ (in which $Py\cdot = 4\text{-}CH_3OOCC_5H_4N\text{-}$ and $n = 3$, 4, or 5), has been prepared by reduction of the corresponding diiodides. Examination of epr spectra over a range of concentrations and temperatures reveals that spin concentration (measured by comparison with standard) divided by the titrimetric radical concentration varies from 2% ($n = 3$) through 20% ($n = 4$) to 100% ($n = 5$). Low relative spin concentrations are accompanied by strong visible absorption bands. Relatively minor changes in the ultraviolet absorption spectra [judged by comparison to $PyR\cdot$ (R = alkyl)] are found, indicating that the chemical nature of the pyridinyl radical moiety has not been changed. These observations are best explained by *intramolecular association* of the $Py\cdot$ groups to yield singlet species analogous to the singlet pyridinyl radical dimers found previously.

The discovery that pyridinyl radicals (**1**) could be generated[6] and isolated[7] permitted physical and chemical studies[8] with these stable, yet reactive, free radicals.



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A number of examples are now known of the reversible dimerization of free radicals to species which are not the result of covalent bond formation. Dimer formation for N-ethylphenazyl and the radical cation derived from 1,4-bis(N,N-dimethylamino)benzene is characterized by the loss of paramagnetism and the appearance of a new long-wavelength absorption band (*ca.* 8000 Å) without serious alteration in the remainder of the visible and ultraviolet absorption spectra.[9-12] Spectroscopic measurements have demonstrated the dimerization of the tetracyanoquinodimethane radical anion[13] and methylviologen radical cation[14] in aqueous solution, and both spectroscopic and epr data have shown that paramagnetic dimers result from a number of ketyls in ether solution.[15]

Pyridinyl radicals are in equilibrium with diamagnetic diradical dimers (eq 1) as shown by spectroscopic and epr results over a wide range of concentrations and temperatures.[16] Kosower and Waits note the presence of a small amount of triplet diradical dimer in equilibrium with the diamagnetic dimer (eq 2) from the appearance of wings separated by 83 G in the epr spectra of pyridinyl radicals in 2-methyltetrahydrofuran (MTHF) glasses at 77°K.[17]

$$\overset{\uparrow}{Py}\cdot + \overset{\uparrow}{Py}\cdot = (\overset{\uparrow}{Py}\cdot\overset{\downarrow}{Py}\cdot) \qquad (1)$$

$$Py\cdot = \mathbf{1},\ R = CH_3,\ CH_3CH_2,\ (CH_3)_2CH$$

(arrow indicates spin)

$$(\overset{\uparrow}{Py}\cdot\overset{\downarrow}{Py}\cdot) \rightleftharpoons (\overset{\uparrow}{Py}\cdot\overset{\uparrow}{Py}\cdot) \qquad (2)$$

The stable diradical **2** [1,1′-ethylene-bis(4-carbomethoxypyridinyl)] has a triplet ground state (by epr in MTHF glass at 77°K) in dilute solution but associates at higher concentrations to form monoradical-like species[18] (eq 3). Waring and Sloan[19] report that the paramagnetic species present in solutions of Chichibabin's hydrocarbon is probably a dimer. Equation 4 presents a simplified view of the situation. The dimer

2

$$\overset{\uparrow}{Py}\cdot\text{–}CH_2CH_2\text{–}\overset{\uparrow}{Py}\cdot + \overset{\uparrow}{Py}\cdot\text{–}CH_2CH_2\text{–}\overset{\uparrow}{Py}\cdot \rightleftharpoons \left[\begin{array}{ll} \overset{\uparrow}{Py}\cdot\text{–}CH_2CH_2\text{–}\overset{\uparrow}{Py}\cdot & \\ & \underset{\downarrow}{Py}\cdot\text{–}CH_2CH_2\text{–}\underset{\downarrow}{Py}\cdot \end{array}\right] \qquad (3)$$

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[1] Article III in this series: E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

[2] Preliminary communication: M. Itoh and E. M. Kosower, *ibid.*, **89**, 3955 (1967).

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[4] Support from the National Institutes of Health, the National Science Foundation, the Army Research Office (Durham), and the Research Laboratories, Edgewood Arsenal (through Contract DA 18-035-AMC-138(A)), is gratefully acknowledged.

[5] To whom requests for reprints should be addressed.

[6] W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Am. Chem. Soc.*, **83**, 3164 (1961).

[7] E. M. Kosower and E. J. Poziomek, *ibid.*, **85**, 2035 (1963).

[8] E. M. Kosower and E. J. Poziomek, *ibid.*, **86**, 5515 (1964).

[9] K. H. Hausser, *Z. Naturforsch.*, **11a**, 20 (1956).

[10] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957) (findings confirmed by Ooshika and coworkers).[11,12]

[11] K. Uemura, S. Nakayama, Y. Sao, K. Suzuki, and Y. Ooshika, *Bull. Chem. Soc. Japan*, **39**, 1348 (1966).

[12] A. Kawamori, A. Honda, N. Joo, K. Suzuki, and Y. Ooshika, *J. Chem. Phys.*, **44**, 4363 (1966).

[13] R. H. Boyd and W. D. Phillips, *ibid.*, **43**, 2927 (1965).

[14] E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5521 (1964). The decrease in paramagnetism with increasing concentration reported by M. J. Blandmer, M. F. Fox, M. C. R. Symons, and G. S. P Verma, *Chem. Commun.*, 844 (1966), is in accord with the formation of diamagnetic dimer.

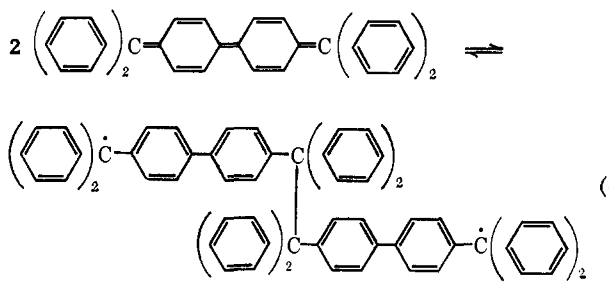
[15] N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).

[16] M. Itoh and S. Nagakura, *ibid.*, **89**, 3959 (1967).

[17] E. M. Kosower and H. P. Waits, 150th National Meeting of the American Chemical Society, Sept 1965, Atlantic City, N. J., Abstracts, 109S.

[18] E. M. Kosower and Y. Ikegami, *J. Am. Chem. Soc.*, **89**, 461 (1967).

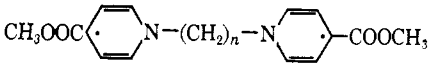
[19] R. K. Waring, Jr., and G. J Sloan, *J. Chem. Phys.*, **40**, 772 (1964).



(4)

in this case involves covalent bond formation, but the epr of the dimers illustrated in both eq 3 and 4 is that of a "monoradical." In addition to puzzles like the "biradical paradox,"[19,20] a number of important chemical problems require a detailed understanding of the properties of diradicals. The rearrangement of *cis*- to *trans*-cyclopropane-1,2-d_2 probably proceeds *via* the 1,3 diradical trimethylene ($\cdot CH_2CH_2CH_2\cdot$).[21,22] The same type of intermediate may be produced from the reaction of triplet methylene with an alkene.[23] Theoretical calculations indicate that 1,3 interaction in diradicals may be considerable.[24] Dimerization of certain alkenes substituted with electron-withdrawing groups proceeds by way of 1,4 diradicals.[25]

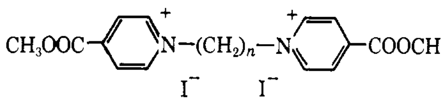
In the present paper, we report the preparation and properties of three diradicals, **3** [1,1′-trimethylene-bis-(4-carbomethoxypyridinyl)], **4** [1,1′-tetramethylene-bis-(4-carbomethoxypyridinyl)], and **5** [1,1′-pentamethylene-bis(4-carbomethoxypyridinyl)].



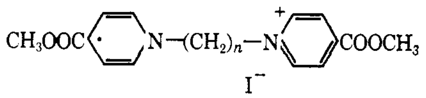
3, $n = 3$
4, $n = 4$
5, $n = 5$

Results

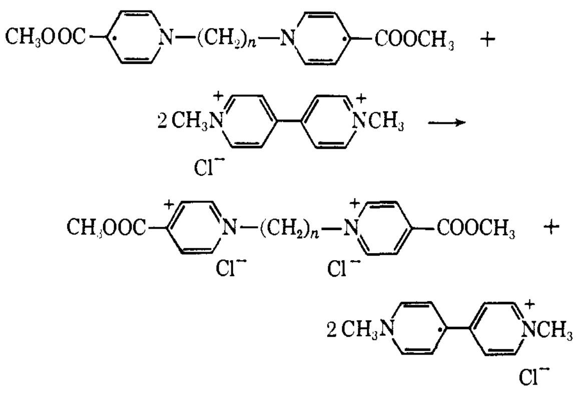
Preparation of Diradicals. The bis(pyridinium diiodides), **3**$^{2+}$, **4**$^{2+}$, and **5**$^{2+}$, were reduced by treatment with 3% sodium amalgam in acetonitrile.[17,18] The most effective procedure involved initial stirring at low temperatures (1 or 2 hr between −40 and 0°) followed by standing at room temperature for about 1 week. The course of the reaction was monitored spectrophotometrically. In the case of **3** and **4**, the intermediate stage of the monocation radicals, **3**$\cdot^+$ and **4**$\cdot^+$, was clearly distinguishable from the final diradical by ultraviolet epr spectroscopy (see Figures 1 and 2). It was not possible to ascertain whether or not **5**$\cdot^+$ was present in appreciable amounts. After the yield of diradical had reached a maximum, acetonitrile was removed and the diradical extracted with isopentane containing 10% 3-methylpentane (PMP). (The time chosen for the isolation of **5** was based on results for **3** and **4**.) The concentration of diradical was determined by reaction with excess solid methylviologen dichloride in acetonitrile,[18] utilizing the known absorption coefficients for the methylviologen radical cation[14] (eq 5).



3^{2+}, $n = 3$
4^{2+}, $n = 4$
5^{2+}, $n = 5$



3$\cdot^+$, $n = 3$
4$\cdot^+$, $n = 4$
5$\cdot^+$, $n = 5$



(5)

In the case of diiodide **3**$^{2+}$, the reduction solution at first exhibited a rising absorption in the visible region at 6100 Å. Further reaction caused this band to be replaced by another at 7000 Å. In the ultraviolet region, a sharp absorption band at 3820 Å appeared for the monoradical cation, **3**$\cdot^+$, and was gradually replaced by a broad band at 3800–3900 Å assigned to the diradical **3** (Figures 1 and 2).

Epr Spectra. A. Solution. The epr spectra of **3**, **4**, and **5** were measured at room temperature in both isopentane (PMP) and MTHF solution. The hyperfine structure of the spectra increased with the number of methylene groups separating the pyridinyl radical moieties, as illustrated for PMP solution in Figure 3. A modest solvent effect on some of the splitting constants resulted in a somewhat different appearance for the epr spectra in MTHF solution (Figure 4). The epr spectra of solutions of **3** were measured for relatively high concentrations (somewhat below 10^{-3} *M*). The appearance of the epr spectrum of **3** in PMP altered upon dilution, with loss of hyperfine structure, as shown in Figure 5. A comparison of the diradical epr spectra with that of the monoradical, 1-methyl-4-carbomethoxypyridinyl, was made in Figure 3. No change in the hyperfine structure of the spectra of **4** and **5** was noted with concentration change.

B. Signal Strength. It was noted that the strength of the epr signal obtained for **3** and **4** fell considerably below that expected on the basis of ultraviolet spectroscopy. The spin concentrations of **3**, **4**, and **5** were therefore determined by comparison of signal strengths obtained from solutions of the diradicals **3**, **4**, and **5** with that from a solution of 1-methyl-4-carbomethoxypyridinyl (**1**-CH_3, *i.e.*, **1**, with R = CH_3) of known con-

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(20) H. M. McConnell, *J. Chem. Phys.*, **33**, 1868 (1960).

(21) B. S. Ravinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, **28**, 504 (1958).

(22) S. W. Benson, *ibid.*, **34**, 521 (1961).

(23) See the summary in E. M. Kosower, "An Introduction to Physical Organic Chemistry," Part 3, John Wiley and Sons, Inc., New York, N. Y., 1968.

(24) R. Hoffmann, to be published.

(25) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

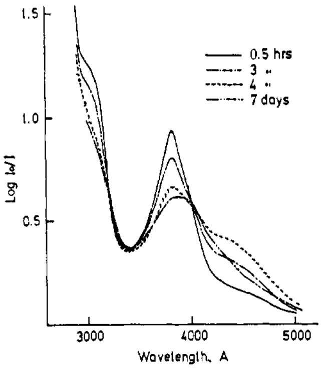


Figure 1. Changes in ultraviolet spectrum observed during the reduction of 1,1′-trimethylene-bis(4-carbomethoxypyridinium) diiodide (3^{2+}) (5.7 mg) with 3% sodium amalgam in acetonitrile (6 ml), light path length, 1 mm.

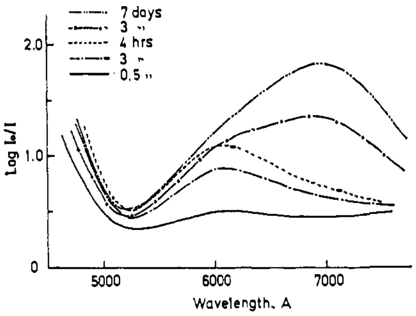


Figure 2. Changes in visible spectrum of the reduction solution described by Figure 1, light path length 10 mm.

centration.[8] Dilute solutions of **1**-CH_3 were found to be almost entirely monomeric.[16] Although spin concentration determinations are probably subject to an error of ±20%, the divergence between the values found and those expected was so large as to preclude any doubt about the phenomenon.

In comparison to radical concentrations measured according to eq 5, the spin concentrations of the diradicals were: **3** (2%), **4** (20%), and **5** (100%), with **1**-CH_3 assumed at 100%. The concentration of paramagnetic species was therefore far below that expected for solutions of **3** and **4**.

The signal strengths of solutions of **4** and **5** decreased with increasing concentration in the way previously found for the diradical **2**.[18]

C. Low Temperatures. MTHF Glass. The epr spectra of **3** and **4** are gradually broadened from 42–43 G at room temperature to 70–80 G in PMP solution (~193 and 173 °K) and in MTHF glass at 77 °K. It may be that a small amount of triplet contributes to the epr spectrum as in the case of the dimers of the pyridinyl radical **1** (eq 2),[17] but it is certainly minor in importance. The triplet levels must be more than 0.8 kcal/mol above the singlet level. No significant amount of triplet in which the rings are close together (*i.e.*, under 6 Å) can be present.

Ultraviolet and Visible Absorption Spectra. A. Dilute Solution. The light absorption spectrum of a pyridinyl monoradical (**1**) has maxima near 6300 Å ($\epsilon < 100$), 4000 Å (ϵ ~5000), and 3000 Å (ϵ ~10,000). The spectrum of the diradical **5** is very similar to that of a monoradical and is shown in Figure 6.

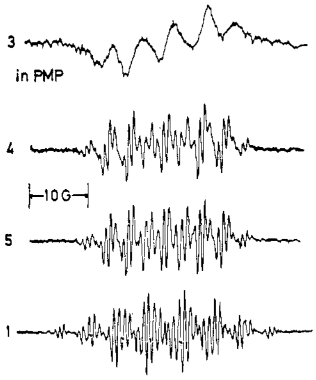


Figure 3. Epr spectra of diradicals **3**, **4**, and **5** compared to that of 1-methyl-4-carbomethoxypyridinyl (**1**) in PMP (isopentane–3-methylpentane, 9:1) solution at 25°. Approximate concentrations of the materials are **3**, 5×10^{-4} *M*; **4**, 5×10^{-5} *M*; **5**, 1×10^{-5} *M*; **1**, 1×10^{-5} *M*.

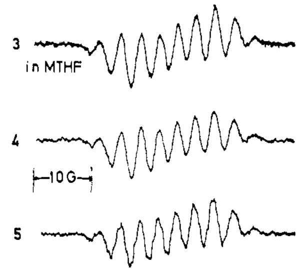


Figure 4. Epr spectra of the diradicals **3**, **4**, and **5** in MTHF (2-methyltetrahydrofuran) solution at 25°.

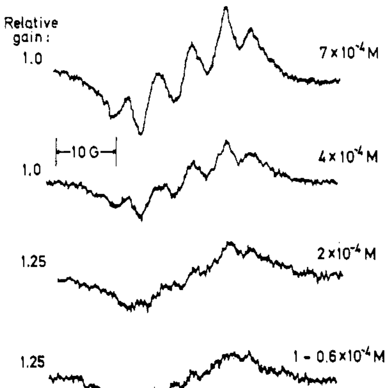


Figure 5. Epr spectra of the diradical **3** in PMP solution over a series of concentrations, which are indicated next to the curves.

The ultraviolet spectra of the diradicals **3** and **4** resemble that of **5**, although the absorption bands are broader and of lower intensity. The visible spectra of the diradicals **3** and **4** are markedly different from the visible spectrum of **5**. The intense absorption band found in the visible region near 6600 Å for **3** and **4** is very much like that assigned to the diamagnetic diradical dimer in solutions of the pyridinyl monoradical **1** by Itoh and Nagakura,[16] and contrasts to the weak visible absorption of **1** and **5**.

The absorption data are summarized in Table I and illustrated for the case of PMP solution at 25° in Figure 6.

B. Concentration Dependence. The visible absorption band of pyridinyl monoradical **1** exhibits an in-

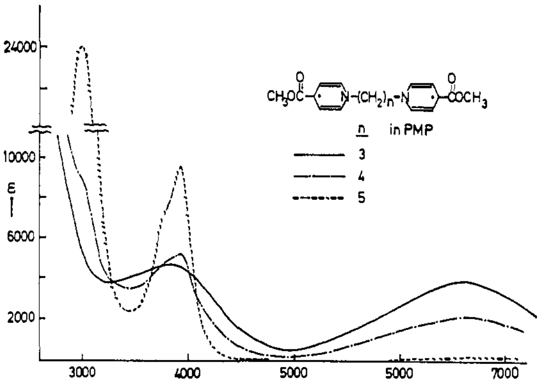


Figure 6. Ultraviolet and visible spectra of the pyridinyl diradicals **3**, **4**, and **5** in PMP solution at 25°.

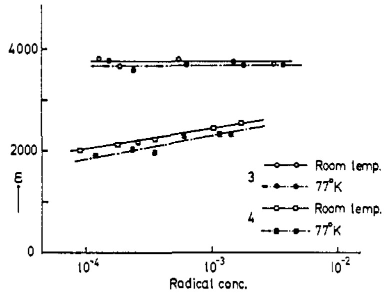


Figure 7. Absorption coefficient of diradicals **3** and **4** as a function of concentration at 25° (room temperature) in PMP and at 77°K in PMP glass; ϵ_{6600} and ϵ_{6500} of diradicals **3** and **4** were plotted at 25°, and ϵ_{7400} of both diradicals at 77°K, respectively.

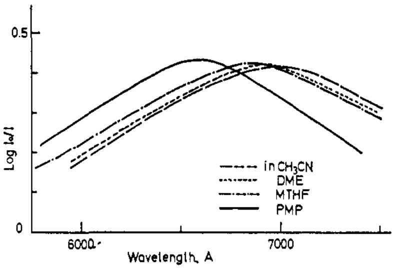


Figure 8. The effect of solvent on the positions of the visible absorption spectra of diradical **3**. The solvents used are PMP, MTHF, DME (1,2-dimethoxyethane), and acetonitrile.

tensity which is concentration dependent, as would be expected for the formation of a strongly absorbing dimer from a weakly absorbing monomer.[16] The intensity of the strong visible absorption of the diradical **3** is virtually independent of concentration, and that of diradical **4** only weakly dependent upon concentration. The absorption coefficient for **4** rises less than 25% for a tenfold increase in concentration, in contrast to the 700% observed for a fourfold increase in the concentration of **1**-CH_2CH_3 in PMP at 77°K.[16] The magnitude of the absorption coefficient changes with concentration at 77°K for **3** and **4** are parallel to those observed at room temperature (Figure 7).

Table I. Spectroscopic Data for Pyridinyl Radicals in PMP Solution or Glass[a]

Pyridinyl radical	Temp, °C	Absorption maxima (in Å) and absorption coefficients[b]
3	25	3820 (4600), 6600 (3800)
	77°K	4080 ($\sim$5000), 7400 ($\sim$3800)
4	25	2950 (s), 3750 (s), 3920 (5120), 6650 (2060)
	77°K	4050 ($\sim$5000), 7450 ($\sim$2000)
5	25	2990 (24,000), 3820 (s), 3930 (9660), 6400 (–[c])
	77°K	3850 ($\sim$8500), 4020 ($\sim$8900), 6200–6300 ($\sim$1500)[d]
1-CH_3 (monomer)	25	2950 (11,000), 3920 (4500), 6400 (90)
(dimer)[e]	77°K	2880 ($\sim$8000), 3750 (5000), 6230 (3860)

[a] PMP = isopentane–3-methylpentane (9:1). [b] s = shoulder. [c] Not observed clearly at low concentration, estimated ϵ <100. [d] Observed at relatively low concentration; probably much less than maximum absorption coefficient. [e] Data derived from results of ref 16.

The difficulty in preparing large quantities of **5** prevented us from observing the visible absorption band at concentrations higher than 10^{-4} *M*.

C. Solvent Effect. The position of the visible absorption band of pyridinyl monoradical monomers (**1**) exhibits only a modest solvent dependence.[16,17] Pyridinyl diradicals **3** and **4** have visible absorption bands which shift considerably to longer wavelengths with increasing polarity of the solvent. The absorption spectra of **3** in PMP, MTHF, dimethoxyethane (DME), and acetonitrile are shown in Figure 8. Data for **3**, **4**, and **1** are included in Table II.

Table II. Solvent Effect on Pyridinyl Diradical Maxima

Pyridinyl diradical	Solvent			
	PMP[a]	MTHF[b]	DME[c]	CH_3CN
3	6600	6880	6930	7030
4	6650	6920	6960	7080

[a] Isopentane–3-methylpentane (9:1). [b] 2-Methyltetrahydro furan. [c] 1,2-Dimethoxyethane.

D. Temperature Effect. A remarkable temperature dependence of the position of the visible absorption band of **3** and **4** is observed. In PMP solution, for example, the maximum at 6600 Å found at room temperature for **3** shifts to 7400 Å at 77°K. (We might remark that the maximum in acetonitrile, the most polar solvent utilized for spectroscopic measurements, is found at 7030 Å for **3**.) The position shift is accompanied by very little change in absorption coefficient.

The absorption spectrum changes smoothly from that observed at room temperature to the one found for 77°K as illustrated by the curves for intermediate temperatures displayed in Figure 9. Data for the temperature effect on the absorption maxima of **3** and **4** are found in Table I.

The absorption spectrum of **5** at 77°K in PMP exhibits a visible band similar to that found for monoradical **1** under the same conditions (Figure 10).

Discussion

Stable free radicals may be studied under conditions very different from those under which they were generated. Variation of the environment (temperature, medium, or concentration) can thus be utilized to elicit

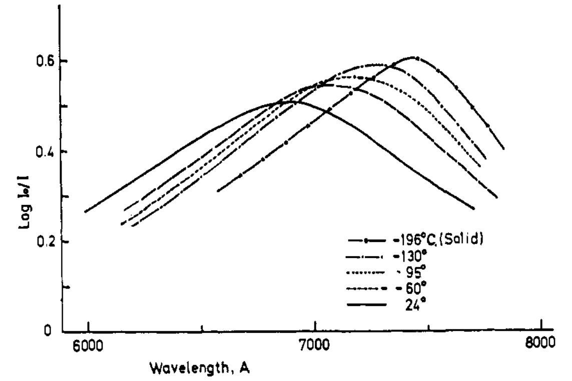


Figure 9. The effect of temperature on the visible absorption band of diradical **3** in MTHF solution (or glass).

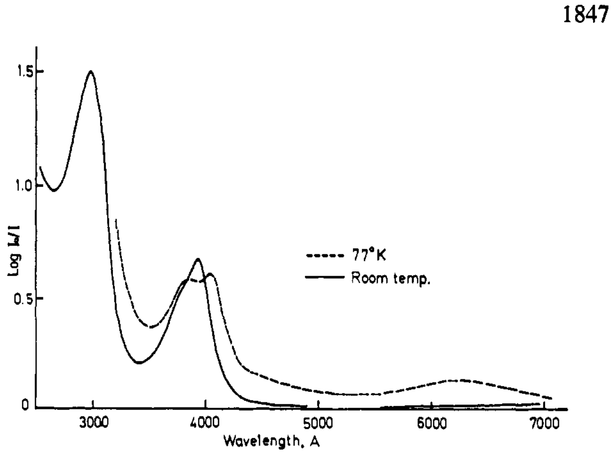


Figure 10. The effect of temperature on the absorption spectrum of diradical **5** at a concentration of 7×10^{-5} *M* in PMP solution.

much valuable information about radical behavior. Pyridinyl radicals (**1**) are sufficiently stable to be manipulated in this way.[1,6,8,16,17] Our sucess in preparing a moderately stable pyridinyl diradical[18] in which the pyridinyl radical moieties were separated by two methylene groups (**2**) encouraged us to examine a series of diradicals in which the number of methylene groups was increased to three (**3**), four (**4**), and five (**5**). We hoped to compare the properties of the radical ends of the diradicals with the behavior of the monoradical. As Itoh and Nagakura[16] have so carefully demonstrated, pyridinyl monoradicals (**1**) dimerize to diradical diamagnetic dimers (with only a minor contribution from triplet dimers[17]). Dimerization causes the loss of epr signal strength and is accompanied by the appearance of a strong visible band best interpreted as a charge-transfer band. (We might thus label the diradical dimers as "charge-transfer complexes.")

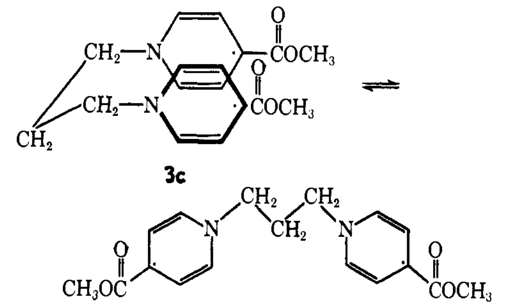
Our most important finding is that association of the radical ends of diradicals separated by either three or four methylene groups does occur. Measurement of the radical concentration by a straightforward titration method yields the gross radical concentration. Observation of the radical signal strength by means of comparison with the signal from a pyridinyl monoradical *in dilute solution* (that is, in monomeric form) indicates that the paramagnetism of the solution is far less than expected. Accompanying the decrease in spin concentration is a marked rise in the visible light absorption coefficient. These data are summarized in Table III.

Table III. Properties of Pyridinyl Monoradical and Diradicals

	Radical				
	Monoradical, **1**-CH_3[b]				
	Monomer	Dimer	**3**	**4**	**5**
Spin/radical × 100[a] %	[100]	[0][d]	2	20	100
ϵ_{max} (visible absorption band)	90	3840	3800	(2060)[c] 2600	<100

[a] Spin concentration as measured by comparison of the epr signal strength with that of pyridinyl monoradical **1**. In dilute solution, light absorption measurements indicate that **1** is completely in the monomeric form. Radical concentration as measured by titration with excess methylviologen dichloride. [b] 1-Methyl-4-carbomethoxypyridinyl.[16] [c] Figure in parentheses is that found experimentally. Larger value is estimated for pure closed form **4c**. [d] Triplet dimer would, of course, contribute spin, but is present only in a very low concentration.

The results are readily accommodated by postulating two forms of the diradicals: **c**, closed, and **o**, open. (Although we shall indicate only one variety of open form, a fully extended diradical, it is likely that a number of energetically similar arrangements are in equilibrium with the one shown.) The closed (**3c**) and open (**3o**) forms of the diradical **3** are illustrated. The closed



form of the diradical has properties like those of the pyridinyl monoradical dimer. The ground state is diamagnetic (spins paired) and has a strong visible absorption band which has been assigned by Itoh and Nagakura[16] as a charge-transfer transition. Although some perturbation of the energy levels results in decreased intensity and small shifts in maxima in the ultraviolet region, the appearance of the absorption bands in the 3000- and 4000-Å region is characteristic of the pyridinyl monoradical (Figure 6). Formation of a covalent bond would have produced a gross alteration in the light absorption spectrum. Thus, the closed form of the diradical must possess pyridinyl monoradical groups.

The closed form of radical **4** (**4c**) is less stable relative to the **4o** form than is the **3c** species relative to **3o**. From an examination of models, we may infer that maximization of radical–radical attraction leads to somewhat greater H–H repulsion in the methylene chain for **4c** than for **3c**. The failure of diradical **2** to yield the **2c** form (the triplet *s-trans* or *s-gauche* form is the main component of the ground state[18]) is best understood in terms of the repulsions created by causing all the bonds around the central ethylene group to be eclipsed. The absorption coefficient observed for the visible band of **4** is lower than that for **3**, consistent with less effective overlap between the two rings.

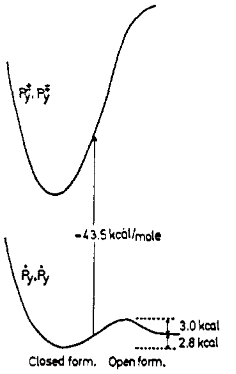
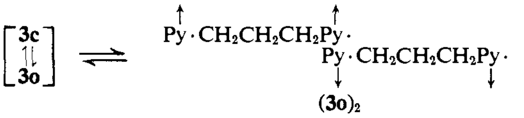


Figure 11. Free energy curves for the ground state and excited state of the diradical **3**. The free energy difference between the open and closed form of the diradical is based on the ratio of spin concentration to radical concentration. The activation energy for the transformation of the open form into the closed form is at least that required to eclipse all of the bonds in an ethane moiety or 3.0 kcal/mol. The curves shown are profiles through free energy surfaces on the coordinate involving stronger interaction between the rings.

The diradical **5** exists entirely in the **5o** form.[26]

The results of studies of the effect of concentration of diradical on epr and visible absorption are in accord with our interpretation of an equilibrium between closed and open forms for diradicals **3** and **4**. Concentration change has virtually no influence on the epr signal strength or the intensity of the visible absorption band for diradical **3** (Figure 7). The hyperfine structure of the epr spectrum of **3** decreases with dilution, suggesting that the pyridinyl radical ends can engage in *intermolecular* association (Figure 5). Diradical dimers would behave like monoradicals (like Chichibabin's hydrocarbon dimers) (eq 6).



$$\begin{bmatrix}\mathbf{3c}\\ \uparrow\downarrow\\ \mathbf{3o}\end{bmatrix} \rightleftharpoons \begin{array}{l} \overset{\uparrow}{\mathrm{Py}}\cdot\mathrm{CH_2CH_2CH_2}\overset{\uparrow}{\mathrm{Py}}\cdot \\ \qquad\qquad\qquad\quad \underset{\downarrow}{\mathrm{Py}}\cdot\mathrm{CH_2CH_2CH_2}\underset{\downarrow}{\mathrm{Py}}\cdot \\ \qquad\qquad\qquad\quad (\mathbf{3o})_2 \end{array} \qquad (6)$$

Properties of Diradicals. Investigation of the epr spectra of diradicals **3, 4,** and **5** in PMP glasses revealed no sign of triplet signals, implying that the triplet level is at least 0.8 kcal/mol above the singlet level in these diradicals. ($\Delta E = 2.3RT \log K$, with the assumption that somewhat less than 1% triplet might not be observed.)

The most surprising property of diradicals **3** and **4** was the sensitivity of the position of the visible absorption band to solvent and temperature. The latter effect is remarkable, with a shift from 6600 to 7400 Å for diradical **3**, corresponding to a change of 4.6 kcal/mol in transition energy. We propose as a possible explanation for this sensitivity the idea that the ground-state free energy curve is far more shallow and broad than the excited-state free energy curve so that some relatively small variation in the average position of the molecule on the ground-state curve has a substantial effect on the transition energy to the excited state. Given the interpretation of the excited state as a charge-transfer state (eq 7), we would expect the curve to be steeper on the side of dissociation than the curve for the ground state because of electrostatic attraction between the rings. The shallow ground-state curve implies that there are many molecules in thermally populated vibrational states. We can then explain the shift of the visible band to longer wavelengths by a polar solvent as due to a stabilization of the ground state. Lowering the temperature also changes the average energy of the ground state and causes a large shift in the transition energy. These possibilities are illustrated in Figure 11,

$$\mathrm{Py}\cdot\mathrm{Py}\cdot \xrightarrow{h\nu} \mathrm{Py}^{\pm}\mathrm{Py}^{\mp} \qquad (7)$$

for the case of diradical **3**.

If we make the assumption that solvent molecules are organized by the ground state in a way appropriate for stabilizing the excited state formed through an electronic transition, we can explain the solvent effect on the charge-transfer band. In this view, the more polar the solvent, the lower the transition energy which might be observed, since the excited state (a charge-transfer state) should interact more strongly with the solvent than the ground state. It may well be that both factors (free energy reaction coordinate surface shapes and solvent interaction) contribute to the changes of the visible absorption maxima. The interpretation of substituent and environmental effects upon charge-transfer transitions requires careful consideration of both ground and excited states, as has been emphasized elsewhere.[27]

Solutions of diradicals **3**, **4**, and **5** could be stored without appreciable change for several weeks. After 1 to 2 months, a noticeable decrease in epr signal strength is found.

We believe that our results on intramolecular association of pyridinyl diradicals require that careful consideration be given to the possibility of intramolecular association in other diradicals. Estimates of the competition between rates of ring closure and rotation around certain bonds in 1,3 and 1,4 diradicals may need revision.[24,28]

The association of free radicals to diamagnetic and paramagnetic diradical dimers (or polymers for diradical monomers) is a phenomenon with many chemical and biochemical implications. Only careful investigations of many systems will make possible decisions about the relationship of diradical dimer formation and structure. The driving force for the association is probably complex, with contributions from charge-transfer forces, dipole–dipole attraction, and mutual polarization. No generalization is yet possible on the basis of the limited information now available.

Experimental Section

Materials. Three bis(pyridinium iodides) were obtained from 4-carbomethoxypyridine and three corresponding diiodoalkanes: 1,1′-trimethylene-bis(4-carbomethoxypyridinium iodide) ($\mathbf{3}^{2+}$), mp 177–178° dec (*Anal.* Calcd for $C_{17}H_{20}O_4N_2I_2$: C, 35.81; H, 3.53; N, 4.91. Found: C, 35.76; H, 3.58; N, 4.97); 1,1′-tetramethylene-bis(4-carbomethoxypyridinium iodide) ($\mathbf{4}^{2+}$), mp 200° dec (*Anal.* Calcd for $C_{18}H_{22}O_4N_2I_2$: C, 37.00; H, 3.79; N, 4.79. Found: C, 37.13; H, 3.89; N, 4.74); 1,1′-pentamethylene-bis(4-carbomethoxypyridinium iodide) ($\mathbf{5}^{2+}$), mp 161–162° dec (*Anal.* Calcd for $C_{19}H_{24}O_4N_2I_2$: C, 38.14; H, 4.04; N, 4.68. Found: C, 38.10; H, 4.04; N, 4.60).

The acetonitrile, isopentane, and 3-methylpentane were spectrograde. 2-Methyltetrahydrofuran and 1,2-dimethoxyethane

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[26] Preliminary results on a pyridinyl diradical with ten methylene groups separating the radical ends indicate no appreciable radical–radical interaction.

[27] E. M. Kosower, *Progr. Phys. Org. Chem.*, 3, 81 (1965).

[28] E. M. Kosower, "Introduction to Physical Organic Chemistry," Part 3, John Wiley and Sons, Inc., New York, N. Y., 1968.

were refluxed with potassium metal for several hours and distilled. Refluxing and distillation were repeated three times.

Epr Spectra. All epr measurements were made with a Varian 4502 spectrometer with 100-kc modulation.

Absorption Spectra. A Cary Model 14 recording spectrophotometer was used. In the determination of low-temperature spectra, a Pyrex dewar was used.

Preparation of Diradicals. Bis(pyridinium iodide) (0.12 g), 3% sodium amalgam (1.0 g) (excess), and a stirring bar were sealed into the reaction flask. After pumping down to $\sim 10^{-6}$ mm, degassed acetonitrile (about 20 ml) was introduced by using a vacuum line. The reaction mixture was stirred for about 1 hr at 0 $\sim -30°$. The mixture gradually became greenish blue in color. After about 1 week at room temperature, the solvent was removed and residue extracted with degassed isopentane–3-methylpentane, 9:1 (PMP). Extraction was performed two or three times. In the cases of the diradicals **3** and **4**, a slightly greenish blue solution of the diradicals were obtained. The PMP solution of diradical **5** was almost colorless. The concentrations of the diradical solutions obtained were $\sim 10^{-4}$ *M*, because the diradicals were only slightly soluble in PMP.

Determination of Concentration of Diradicals. The PMP solvent (4.5 ml) of the diradical **3** solution was replaced by degassed acetonitrile (6.4 ml). The absorption spectrum of the acetonitrile solution as well as that of PMP solution was carefully determined. Methylviologen dichloride (2 mg) was added to the acetonitrile solution. The solution gradually became blue and the absorption maximum at 6050 Å associated with methylviologen cation radical increased. Absorbance at 6050 Å reached a maximum (1.6) in 5 days. From reported data on methylviologen cation radical (ϵ_{6050} 10060),[14] the concentration of the diradical solution **3** was determined to 2.26×10^{-4}. Determinations of concentrations were performed for the diradicals **4** and **5** by the same method.

Determination of Relative Spin Concentration. The epr spectrum of a PMP solution of diradical **3** of known concentration (8×10^{-4} *M* from absorption spectrum) was measured by the overmodulation method. The epr spectra of dilute solutions of the diradicals **4** (2×10^{-4} *M*) and **5** ($\sim 1 \times 10^{-4}$ *M*) were also determined with the same modulation frequency and almost the same signal gain of spectrometer as in the case of diradical **3**. The epr spectrum of a very dilute solution ($\sim 5 \times 10^{-5}$) of 1-methyl-4-carbomethoxypyridinyl radical was measured under the same conditions. The epr tubes chosen for these measurements had very similar dimensions.

The low-resolution epr spectra obtained were utilized to derive total epr absorptions (by measurement of the areas) from which the relative intensities of the epr spectra were calculated. By assuming that the monoradical **1** is completely in the paramagnetic form under the conditions used (room temperature, low concentration[16]), concentrations of the paramagnetic species in PMP of diradicals **3**, **4**, and **5** were calculated by comparison with the result for monoradical.

Acknowledgment. We are grateful to Dr. P.-k. C. Huang for preparation of the bis(pyridinium iodides).

Attempts to Generate Diphenylcyclopropenylidene. IV[1,2]

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Abstract: Attempts have been made to generate the potentially nucleophilic carbene, 2,3-diphenylcyclopropenylidene, and the corresponding diphenyldiazocyclopropene. The methods explored include oxidation of the hydrazone, decomposition of salts of the tosylhydrazone, reaction of the appropriate N-nitrosocarbamate with base, and α eliminations of carboxylic acids from the diphenylcyclopropenyl acetate, benzoate, *p*-nitrobenzoate, and N,N-dimethylcarbamate. Oxidation of the hydrazone failed at the hydrazone synthesis stage. Only the azine could be isolated under acidic conditions, and basic conditions opened the ring. Although the lithium, sodium, and potassium salts of the tosylhydrazone were successfully prepared, under no conditions attempted (from photolysis at Dry Ice temperature to pyrolyses at temperatures as high as 200°) was there observed any evidence for diazocyclopropene or carbene formation. Reaction of the N-nitrosocarbamate with base tended to give products resulting from formation of the diphenylcyclopropenyl cation but, in the presence of dimethyl fumarate, there was formed a small amount (less than 10%) of the spiropentene **13** suggesting that under these conditions there was formed at least a little of the carbene and/or possibly the diazocyclopropene. α Elimination of acetic acid, benzoic acid, and *p*-nitrobenzoic acid from the esters **22a–c** occurred with base in the presence of dimethyl fumarate to the extent of up to 14% as was indicated by amount of methylenecyclopropene **14** formed. Finally, base-induced decomposition of the N,N-dimethyl-O-carbamate **12** was by far the best method for generating what is believed to be the diphenylcyclopropenylidene. In the presence of dimethyl fumarate it gave the 1:1 adduct in yields up to almost 70% (determined spectrophotometrically). The mechanism of the carbamate reaction is discussed.

Sufficient suppression of the normal electrophilicity[4] of a singlet carbene by delocalization of electrons into its vacant p orbital should give rise to a species with nucleophilic properties due to the ever-present pair of nonbonded electrons on the carbene carbon atom. This has, in fact, been found to be the case in a number of instances where the nonbonded electrons of heteroatoms[5] (oxygen and nitrogen are apparently the only

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[1] This research was supported by the U. S. Army Research Office (Durham) and by the National Science Foundation.

[2] Taken in part from the Ph.D. Thesis of M. E. Stowe and from the M.S. Thesis of E. W. Lester.

[3] Alfred P. Sloan Fellow, 1963–1967.

[4] *Cf.* J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p 43; W. Kirmase, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 164.

[5] The question of the actual intermediacy of nucleophilic carbenes in many cases has been clouded by the fact that the correspondng carbene dimer (*e.g.*, tetraminoethylenes) give many of the same products with electrophiles[6] as would be expected from the carbene itself. However, there are still a number of cases that probably do indeed involve intermediate carbene formation (including, in fact, reactions of the dimer with electrophiles[6]). For examples of these as well as leading references to earlier work, see: D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966); R. W. Hoffmann and H. Hauser, *Tetrahedron*, **21**, 1891 (1965); H. Quast and S. Hunig, *Chem. Ber.*, **99**, 2017 (1966); *Angew. Chem. Intern. Ed. Engl.*, **3**, 800