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Electronic Structures and Spectra of Pyridinyl Hetero Diradicals. Charge-transfer Interaction between Two Different Radicals

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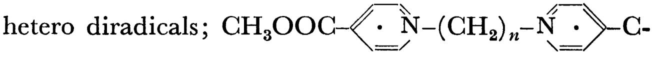
Pyridinyl hetero diradicals, Py(Ac)·$(CH_2)_n$ Py(Car)·, (in which Py(Ac)· and Py(Car)· are 4-$CH_3OCC_5H_4N$· and 4-$CH_3OOCC_5H_4N$·, respectively, and $n=3$, 4, and 5) were obtained. Equilibrium between the open and closed forms in the hetero diradical $n=3$ was directly observed by temperature dependence of absorption spectra ($-\Delta H=5.6$ kcal and $\Delta S=-10.5$ e.u.). Electronic absorption spectroscopy and SCF–CI molecular orbital calculation reveal that the closed form shows a strong charge-transfer band from Py(Car)· to Py(Ac)· moieties. The electronic structure of the hetero diradical was discussed in relation to the electronic interaction between two different radicals.

Molecular complexes between two different free radicals, the hetero radical dimers may be considered to be a special case of the electron-donor-acceptor complex, both components of which are electron excess systems. From the viewpoint of the electronic structure, the hetero radical dimers may be isoelectronic with hetero nuclear diatomic molecule, although the hetero dimer involves no covalent bond between radical moieties.

While numerous investigations of the radical dimers[1-3] have been carried out, only few spectroscopic studies of the electronic interaction between two different radicals have been reported.[4,5] Recently, Yamazaki and Kimura[5,6] have demonstrated the complex formation of tetracene and perylene cation radicals in concentrated sulfuric acid at low temperature, where the cation dimers of each component were also observed.[7] In the previous papers, Itoh and Kosower[8] reported a strong intramolecular interaction of two pyridinyl moieties in the 1,3-dipyridinylpropane, Py(Car)·$(CH_2)_3$Py(Car)·. Subsequently, Itoh[9] demonstrated that the closed form of the pyridinyl cation radical, $Py(Car)^+(CH_2)_3Py(Car)$· was regarded to be the dimer cation which could not be observed in the mixed solution of the pyridinyl and pyridinium salt without tri- or tetramethylenes. On the other hand, importance and efficiency of the trimethylene group for the intramolecular interaction have been also emphasised in the excimer formation,[10,11] energy transfer[12] and fluorescence quenching.[13]

This paper presents a study of a new series of pyridinyl hetero diradicals; 

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OCH_3, $n=3$, 4, and 5 which exhibit intramolecular charge-transfer interaction between two different pyridinyl radicals in solution at room temperature. Electronic structure of the closed form of the hetero diradical which is considered to be a hetero radical dimer was calculated by the aid of the SCF–CI method. Spectroscopic and theoretical results for the hetero diradical were compared with those for the diradicals, $\mathrm{Py(Car)\cdot(CH_2)_3Py(Car)\cdot}$[8] and $\mathrm{Py(Ac)\cdot(CH_2)_3Py(Ac)\cdot}$.[14] (abbreviated to Car-3-Car, and Ac-3-Ac, respectively.).

Results and Discussion

Electronic Absorption Spectra. The pyridinyl hetero diradicals (**3** for $n=3$, **4** for 4, and **5** for 5) were prepared by reduction of the corresponding diiodides or bromides in the manner previously described.[8,9] The electronic absorption spectra of the 2-methyltetrahydrofuran (abbreviated to MTHF) solutions of **3**, **4**, and **5** were determined at room temperature (27—28°C), as shown in Fig. 1. While the spectra of **4** and **5** are very much similar to the sum of the spectra of 1-methyl-4-carbomethoxy-[2,15] and 1-methyl-4-acetylpyridinyls,[15] **3** shows a remarkable absorption band in 600—650 nm region. Concentration independence of the spectrum of **3** at room temperature (1×10^{-3}—5×10^{-5}M) suggests that the spectrum of **3** may be ascribed to an intramolecular interaction. From spectroscopic behavior of **3** in comparison with that of the diradical, Car-3-Car reported in the previous paper, the visible absorption band at 615 nm may be a charge-transfer band between two kinds of pyridinyl moieties. This assignment is supported by the theoretical consideration based on the SCF–CI calculation, as will be mentioned later. Yamazaki and Kimura[6] reported two charge-transfer bands between tetracene and perylene cations at 800—950 nm region. In this paper, theoretical study suggests that a strong charge-transfer band from Py(Car)· to Py(Ac)· moieties and another very weak charge-transfer band in the reverse direction may appear by the electronic interaction between two different pyridinyl radicals. However, only one strong absorption band was observed as mentioned above.

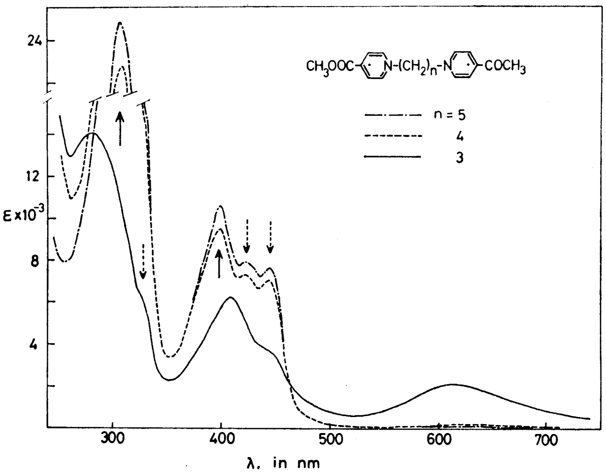

Fig. 1. The absorption spectra of the hetero diradical, **3**, **4**, and **5** in MTHF at room temperature (27—28°C); ←— and ←--- show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively.

An absorption maximum at 400—420 nm region appears in the MTHF solution of **3**, and a band at 300—340 nm region due to the pyridinyl moiety shifts to the shorter wavelength region compared to **4** and **5**, as shown in Fig. 1. These two absorption bands in the UV region which seem to be due to shifted local excitations decrease in intensity compared with those of the hetero diradicals **4** and **5**. Similar decrease of intensity at UV region was also observed in the diradicals, Car-**3**-Car and Ac-**3**-Ac. Leonard *et al.*[16] demonstrated the hypochromism in the absorption spectra of a series of dinucleotide analogs in which the bases are connected by a trimethylene; $B\text{–}C_3\text{–}B$ or $B\text{–}C_3\text{–}B'$. It seems that the decrease of the intensity in the UV region in the diradicals is attributed to the hypochromism, and/or intensity borrowing by the charge-transfer band.[17]

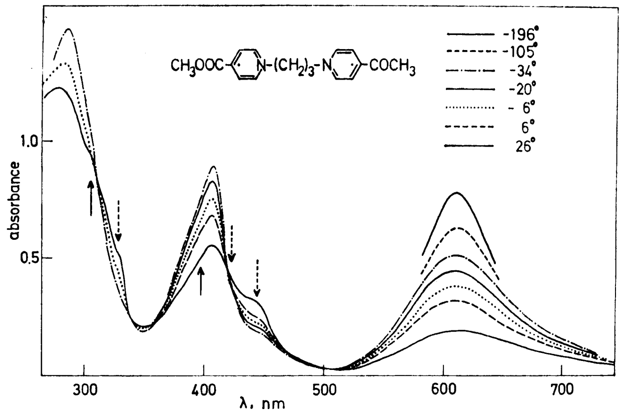

Fig. 2. Temperature dependence of the spectrum of **3** in MTHF. Concentration is 0.85×10^{-4}M: ←— and ←--- show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively. A visible absorption band at −196°C is shown as an extreme case of the equilibrium.

As mentioned in the previous communication,[18] the spectrum of the MTHF solution of **3** shows a remarkable temperature dependence (Fig. 2). The intensities of the 615 and 319 nm bands increased with decreasing temperature, while the absorption due to the each pyridinyl moiety decreased. This temperature dependence of the spectrum was ascribed to an equilibrium of the open and closed forms in **3** (an analog of the monomer dimer equilibrium). The thermodynamic data ($-\Delta H=5.6$ kcal and $\Delta S=-10.5$ e.u.) are compared with those on the complex formation of tetracene and perylene cations ($-\Delta H=7.7$ kcal and $\Delta S=-1.6$ e.u. at 20°C.[6] The complex formation of two different pyridinyls in **3** (the closed form) seems to be more

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16) D. T. Browne, J. Eisinger, and N. J. Leonard, *J. Amer. Chem., Soc.*, **90**, 7302 (1968).

17) Especially, a mixing between the charge-transfer and the local excitation appears in the slided model.

18) M. Itoh, *J. Amer. Chem. Soc.*, **94**, 1034 (1972).

Table 1. Spectroscopic and calculated data of electronic transitions in pyridinyl hetero diradical **3**

Obsd ΔE, eV	Calcd					
	ΔE, eV	f-value[a)]	μ_X[b)]	μ_Y	μ_Z	Character[c)]
—	1.69	0.01	−0.09	0.02	0.28	0.989(10→11)
2.02 (7800)[d)]	1.74	0.85	−0.25	−0.10	−2.34	0.989(10→12)
3.04 (11500)[d)]	3.47	0.17	0.07	0.74	−0.08	0.855(10→14) −0.495 (9→11)
4.35 (14000)[d)]	4.35	0.95	−0.06	1.57	0.09	0.791 (9→11) 0.441(10→14) 0.343(10→15)

a) Oscillator strength. b) Transition moment, x, y and z are the molecular axes shown in Fig. 3. c) Only configurations whose coefficients in the total wave function exceed 0.3 are shown in the table. d) Molar coefficient of absorption maximum in **3** at 77 K, because the diradical is assumed to be in the purely closed form at the temperature.

efficient than that without any methylene chain of which the open form may be more predominant on the energetic ground. Similar equilibrium between the open and closed forms was observed in the diradical, Ac-**3**-Ac.[14)] In the diradical Car-**3**-Car reported in the previous paper, a strong charge-transfer interaction of two moieties seems to make the diradical to be in the closed form, and to prevent direct observation of the equilibrium mentioned above.

Electronic Structure of Pyridinyl Hetero Diradical. In the previous paper,[2)] Itoh and Nagakura reported molecular orbital calculation of the pyridinyl radical, and semiquantitatively estimated the transition energy of the charge-transfer band in the pyridinyl dimer. In order to bear out the quantitative discussion on the charge-transfer interaction between two different radicals in the hetero diradical, the SCF–CI calculations were made. Most of the calculations of the radical dimers[7,19,20)] and/or dimer radical[21)] have been made with the method of "composite molecule", which consists of configuration interaction including the charge-transfer configuration between two SCF MO's of the radical monomers. In this paper, molecular orbitals (closed shell) were considered to be delocalized over two different radicals (open shell).[22)]

The standard program for restricted SCF–CI procedures was used in the diradicals as well as in the hetero diradical.[23,24)] Interatomic overlap integrals between two pyridinyl moieties were calculated by the aid of the data in Clementi's Table.[25)] Both intra- and intermolecular electron-electron repulsions were approximated by the Nishimoto-Mataga formula. The calculated results of the electronic transitions in the hetero diradical are summarized in Table 1, in comparison with the spectral data of **3**, where the molecular geometry was assumed to be a sandwich structure as shown in Fig. 3. Several other sandwich structures such as a twisted model[26)] and a slided model along x axis were assumed for calculation. However, the results suggested that the structure shown in Fig. 3 was the most reasonable both in their transition energies and intensities. For the sake of simplicity, the results calculated based on the structure shown in Fig. 3 are discussed in this paper. The transition energies show fairly good agreement with the spectral data of the hetero diradical **3**, although no parameterization in SCF–CI calculation was made for adjusting the theoretical results to the spectral data. Similar molecular orbital calculations were done for the diradicals, Car-**3**-Car and Ac-**3**-Ac. These calculated results are shown in Fig. 4, together with the absorption spectra.

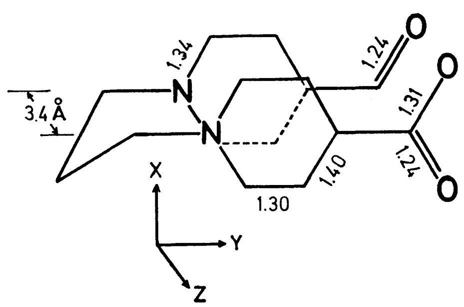

Fig. 3. Molecular geometry of the hetero diradical, **3** assumed in the calculation. A molecular model says that two pyridinyls are non-parallel in the spacing of ~3.4 Å.[2,14)]

Comparison of both theoretical and spectral results in the hetero diradical with those in two diradicals, Ac-**3**-Ac and Car-**3**-Car, suggests that the electronic interaction between two different radicals seems to be rather similar to that in the same radical species. This argument may be justified by the following consideration from the results in SCF–CI calculation of the pyridinyl mono radicals, Py(Ac)· and Py(Car)·, which are components of the hetero diradical. Figure 5 demonstrates the energy levels of two pyridinyls and the hetero diradical. Energy difference of half-occupied

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20) K. Kimura and N. Mataga, *J. Chem. Phys.*, **51**, 4167 (1969).

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23) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. Sec. A*, **68**, 591 (1955).

24) The computer program of the SCF-CI calculation used here was developed by Dr. S. Iwata.

25) E. Cleminti, *Tables of Atomic Functions* (IBM Co, San Jose, Calif., 1965).

26) Two pyridinyls were twisted in the molecular planes by 10—20° around a z-axis through a center of pyridinyl ring. M. Itoh, *Chem. Phys. Lett.*, **2**, 371 (1968).

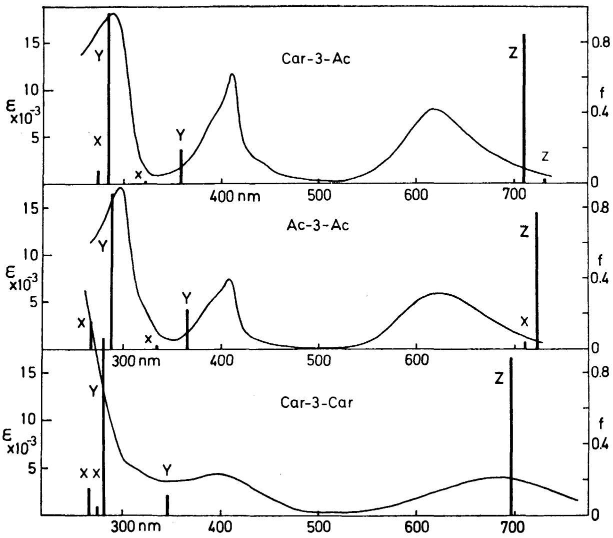

Fig. 4. Electronic absorption spectra of the MTHF solutions of **3** (at 77 K), Ac–**3**–Ac (at 77 K), and Car–**3**–Car (at room temperature), respectively. The sticks represent the calculated transition energies and osscillator strengths.

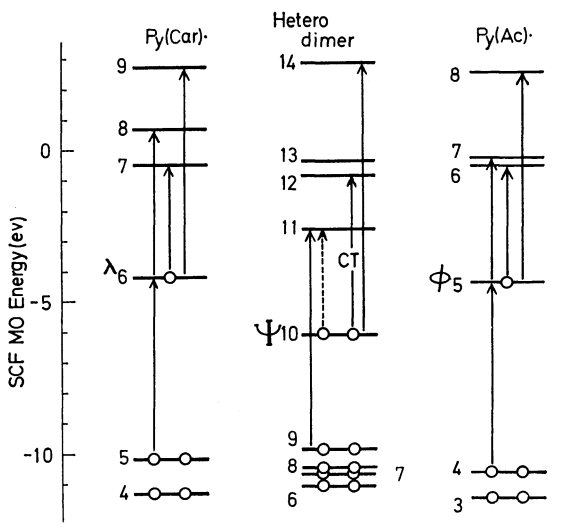

Fig. 5. Energy levels of molecular orbitals in the pyridinyl mono radicals and hetero diradical, respectively. In Py(Car)·, (6→7) is corresponding to ~640 nm (ε:<100) band, (5→6) and (6→7) are ~390 nm (4500), and (6→8) and (6→9) are 295 nm (11000), respectively. Electronic transitions in Py(Ac)· are very much similar to those in Py(Car)·.

molecular orbitals in two pyridinyls (ϕ_5 and λ_6) is unexpectedly only 0.185 eV. In the complex of tetracene⁺–perylene⁺ system, the energy difference of two half-occupied MO's was also very small. The half-occupied MO's in both radical components in the diradical (radical dimer) are degenerate, and only one charge-transfer band in the dimer is an allowed transition, which is from the ground state to the antisymmetric combination in the following equations;[1]

$$\frac{1}{\sqrt{2}}[\Psi(R_1^+, R_2^-)\pm\Psi(R_1^-, R_2^+)]$$

where (R_1^-, R_2^+) is the charge-transfer configuration in the radical pair. Yamazaki and Kimura[6] estimated two charge-transfer energies in the complex mentioned above from the following conventional equations; $I_\mathrm{I}-A_\mathrm{P}+C_\mathrm{TP}=CT_1$ and $I_\mathrm{P}-A_\mathrm{T}+C_\mathrm{PT}=CT_2$, where I and A are the ionization potential and electron affinity of the cations, respectively, and C is electrostatic force. However, they did not mention about the intensity of the charge-transfer bands. In this paper, theoretical results which was calculated by assuming electron delocalization over radical moieties show a strong charge-transfer transition from Py(Car)· to Py(Ac)· moieties, and another very weak charge-transfer in the reverse direction. These electronic transitions (energy, f-value and transition moment) and electronic configurations are summarized in Table 1. Then, the strong charge-transfer band observed at 615 nm in the hetero diradical **3** can be ascribed to transition, $\Psi_{10}\rightarrow\Psi_{12}$, of which MO's are shown in Fig. 6. Figure 6 clearly demonstrates a strong charge-transfer mentioned above, while $\Psi_{10}\rightarrow\Psi_{11}$ has a very small f-value with the reverse direction compared with that of $\Psi_{10}\rightarrow\Psi_{12}$.

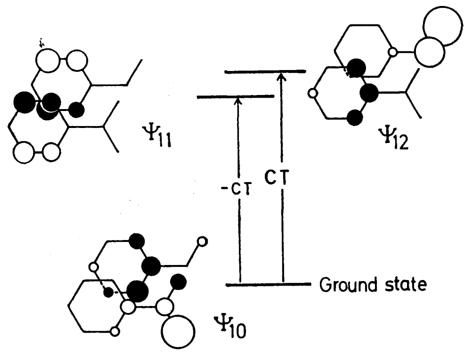

Fig. 6. Highest occupied orbitals of the ground (Ψ_{10}) and two charge-transfer states (Ψ_{11} and Ψ_{12}).

On the other hand, the electron transfer reaction from 1-methyl-4-carbomethoxypyridinyl to 1-methyl-4-acetylpyridinium occurred by adding the latter to an acetonitrile solution of the former. This suggests that Py(Ac)· may be an electron acceptor in the hetero diradical. The argument is successfully consistent with the direction of the charge-transfer mentioned above. Furthermore, total electron density on the each pyridinyl moiety in the diradical **3** demonstrates ~5% charge-transfer structure in the ground state;

$$\mathrm{Py(Car)^+-Py(Ac)^-}\ \sim5\%$$
$$\mathrm{Py(Car)\cdot-Py(Ac)\cdot}\ \sim95\%.$$

If two different radical species (R_1 and R_2) of which the energy levels of each half-occupied MO are sufficiently different from each other, a complete electron transfer in this radical pair would occur to produce an ion pair (R_1^+,R_2^-) in the ground state. Conclusively, it seems that only two radical species where the half-occupied MO's are nearly degenerate have a possibility to make the molecular complex between them. In this molecular complex, *i.e.*, the hetero radical dimer with a conceivable conformational structure, a strong charge-transfer band and another very weak transition (nearly forbidden) in the reverse direction might be observed in the visible or near IR region.

Experimental

Materials. Three α-(4-carbomethoxypyridinium)-ω-(4-acetylpyridinium) alkane diiodides were prepared from 4-carbomethoxy- and 4-acetylpyridines, and three corresponding alkyl diiodides or bromides. 1-(4-Carbomethoxypyridinium)-3-(4-acetylpyridinium)propane dibromide, mp 150—151°C. Found: C, 43.94; H, 4.77; N, 5.88%. Calcd for $C_{17}H_{20}O_3N_2Br_2$: C, 44.34; H, 4.34; N, 6.08%. 1-(4-Carbomethoxypyridinium)-4-(4-acetylpyridinium)butane diiodide, mp 203°C. Found: C, 38.03; H, 4.00; N, 4.48%. Calcd for $C_{18}H_{22}O_3N_2I_2$: C, 38.05; H, 3.88; N, 4.93%. Non-crystalline products of 1-(4-carbomethoxypyridinium)-5-(4-acetylpyridinium)pentane diiodide and dibromide were used. The structure and purity were checked by IR, UV, and NMR spectroscopies. Purification of the solvents was mentioned in the previous papers.

Preparation of Hetero Diradicals. α,ω-Dipyridinium diiodides (~0.02 g) and 3% sodium amalgam (~0.2 g) were sealed into the reaction tube. After evacuating to 10^{-5} Torr, degassed acetonitrile (~7 ml) was introduced by using a vacuum line. The reaction tube was shaken several times for about 3—5 hr at room temperature. The solvent was removed by using a vacuum line, and the diradical was extracted with MTHF (~10 ml).

Measurements. Electronic absorption spectra were determined with a Cary Model 11 recording spectrophotometer. A quartz dewar with windows was used for low-temperature spectra. ESR measurements were made with JEOLCO P-10 ESR spectrometer with 100 kHz modulation. Determinations of concentration of the diradical and of relative spin concentration were done using the same procedures as described in the previous papers.

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