2,2-cyclobutanetetracarboxylate (**3**) (125.5 g, 0.36 mole) was converted to 15.5 g (36% yield) of *cis*-cyclobutane-1,2-dicarboxylic anhydride (**4**), as described in the literature,[18–20] bp 102–104° (1.1 mm), mp 76–78° [lit.[18] bp 113–114° (2 mm), mp 78°].

***cis*- and *trans*-1,2-Dibromocyclobutane-1,2-dicarbonyl Bromide (5).** A modification of the methods of Perkin[19] and Kipping and Wren[21] was used to prepare *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromide (**5**). To a mixture of 12.6 g (0.10 mole) of cyclobutane-1,2-dicarboxylic anhydride (**4**) and 20 ml (0.20 mole) of phosphorus tribromide, which had been stirred for 15 min, was added 30 ml (0.42 mole) of dry bromine over a 25-min period. The addition of bromine was accompanied by an evolution of heat and the precipitation of phosphorus pentabromide. After the mixture was heated at 85–90° for 2 hr, 5 ml of bromine was added and the heating continued for 16 hr. An additional 1 ml of bromine was then added and the heating at 85–90° continued for 2 hr more. The reaction mixture was then cooled to room temperature, during which time nitrogen was bubbled in to remove part of the unreacted bromine, and extracted with two 40-ml portions of benzene. The benzene extracts were shaken with 150 ml of ice water; the aqueous phase was separated and extracted with two 25-ml portions of benzene, and the combined benzene extracts were dried over anhydrous sodium sulfate. The benzene was removed under reduced pressure and the pale yellow liquid which remained was distilled through a 2-in. short-path distillation column to yield 37.6 g (80%) of *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromide (**5**), bp 98–100° (0.08 mm) [lit.[21] bp 104–117° (0.4 mm)].

***cis*- and *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane (6).** The *cis*- and *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutanes (**6**) were prepared and separated according to a variation of the method reported by Kipping and Wren.[21]

To a stirred solution of 4.2 ml (0.04 mole) of N,N-dimethyl aniline, 25 ml of anhydrous methanol, and 15 ml of anhydrous ether was added, over a 0.5-hr period, a solution of *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromides (**5**) in 5 ml of dry ether. During the addition, refluxing of the ether occurred. The reaction mixture was then cooled to room temperature, washed with two 20-ml portions of water, two 20-ml portions of 9% hydrochloric acid, one 20-ml portion of saturated sodium bicarbonate solution, and three 20-ml portions of water, and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure (water aspirator) gave 6.1 g (92%) of crude *cis*- and *trans*-dibromo esters, which upon recrystallization from 20 ml of *n*-heptane yielded 1.7 g (26%) of *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$), mp 86–87°. Further recrystallization from 15 ml of *n*-heptane containing decolorizing charcoal yielded 1.1 g of pure *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$), mp 87–88° (lit.[21] mp 87–87.5°).

A mixture of 3.0 g (0.02 mole) of sodium iodide, 15 ml of absolute ethanol, and 2.1 g of the concentrated mother liquor from the above recrystallizations was refluxed for 2 hr. The dark solution formed was cooled and diluted with 20 ml of water and 10 ml of 10% sodium thiosulfate solution. The colorless solution thus obtained was extracted with three 15-ml portions of ether; the combined ether extracts were washed with 5 ml of 10% sodium thiosulfate solution and three 5-ml portions of water and dried over anhydrous magnesium sulfate. The ether solution was concentrated to 15 ml and cooled in a Dry Ice–acetone bath to yield 1.5 g of crude *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_c$), mp 37–40°. One recrystallization of the *cis*-dibromo ester from 2 ml of *n*-heptane gave 1.3 g (20%) of pure *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_c$), mp 40.5–41.5° (lit.[21] mp 41–42°).

Debromination of *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane (6$_t$). A 0.6-g (0.0018 mole) sample of *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$) was debrominated by refluxing for 3.5 hr a solution of the ester in 25 ml of dry ethanol containing 0.9 g (0.006 mole) of sodium iodide. The dark solution was diluted with 30 ml of 3% sodium thiosulfate solution and the resultant clear solution extracted with three 20-ml portions of ether. The combined ether extracts were washed with two 10-ml portions of water and dried over magnesium sulfate. Removal of the ether under reduced pressure afforded 0.31 g of impure 1,2-dicarbomethoxycyclobutene (**7**), mp 41–45°. One recrystallization from *n*-hexane gave 0.16 g (52%) of pure[22] 1,2-dicarbomethoxycyclobutene (**7**), mp 45–46° (lit.[21] mp 45–46°). The nmr spectrum showed two absorption bands, at τ 7.37 for the six methyl protons and τ 6.26 for the four ring protons, with an intensity ratio of 3:2.

Acknowledgments. We are greatly indebted to Dr. W. B. Moniz (Naval Research Laboratory) for the early 100-MHz spectra, to Dr. R. Freeman (Varian Associates) for reading the manuscript, and to Professor R. M. Moriarty (Catholic University) for helpful comments.

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[19] W. H. Perkin, Jr. *J. Chem. Soc.*, **65**, 572 (1894).

[20] K. B. Alberman and F. B. Kipping, *ibid.*, 779 (1921).

[21] F. B. Kipping and J. J. Wren, *ibid.*, **1733** (1957).

[22] A gas chromatogram of the 1,2-dicarbomethoxycyclobutene, obtained by the use of a TC detector and a 10 ft × 0.25 in. column packed with 20% SE-30 on 30–60 mesh Chromosorb W acid washed with a column temperature of 210° and a flow rate of 100 cc/min, gave only one peak.

Charge-Transfer Complexes between Substituted Pyridinyl Radicals

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Contribution from the Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Tokyo, Japan, and The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo, Japan. *Received March 8, 1967*

Abstract: The reversible dimerization of 1-alkyl-4-carbomethoxypyridinyl radicals in isopentane solution was studied by measuring electronic absorption spectra at low temperature. Charge-transfer bands associated with the radical dimers were observed for the 1-methyl-, 1-ethyl-, and 1-isopropyl-4-carbomethoxypyridinyl radicals. Analysis of the spectra yields monomer–dimer equilibrium constants at 77°K and molar extinction coefficients of charge-transfer bands of dimers for three radicals. A theoretical study has been undertaken with the pyridinyl monomer and dimer.

Hausser and Murrell[1] reported that the 9-ethylphenazyl radical and the tetramethyl-*p*-phenylenediamine cation radical form dimers in ethanol at low temperature, and that charge-transfer (abbreviated hereafter to CT) bands associated with π–π interaction

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[1] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

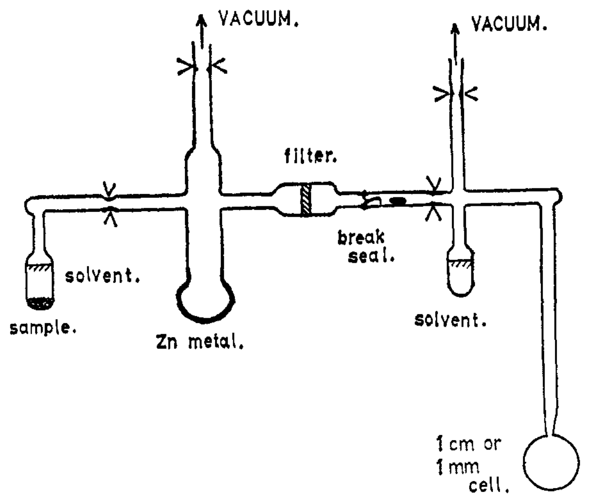

Figure 1. The vacuum-line system used for the preparation of the radical and for the measurement of the absorption spectra.

between the radicals could be observed at about 800 mμ. Hirota and Weissman studied electronic interaction in ketyl radicals by electron spin resonance and electronic spectra.[2] Boyd and Phillips found the reversible dimerization of the anion radical of 7,7,8,8-tetracyanoquinodimethane in aqueous solution at room temperature.[3] Kosower and Cotter also proposed the dimerization of the methylviologen cation radical.[4]

In a previous paper,[5] we have reported the esr and electronic absorption spectra of the 1,4-disubstituted pyridinyl radicals. In the course of our studies of the pyridinyl radicals, the 1-alkyl-4-carbomethoxypyridinyl radicals were found to exist as dimers in isopentane solution and at low temperature. Therefore, spectroscopic studies of the monomer–dimer equilibrium of the pyridinyl radicals have been made with the 1-methyl-4-carbomethoxy-, 1-ethyl-4-carbomethoxy-, and 1-isopropyl-4-carbomethoxypyridinyl radicals. In the present paper, special attention has been paid to the CT bands in the 600–700-mμ region due to π–π interaction between these radicals and to the electronic structures of these pyridinyl radical dimers. The theoretical study has been undertaken with the pyridinyl radical monomer and dimer by combining open-shell SCF molecular orbital method with the configuration interaction. The observed spectrophotometric behaviors of the monomer and dimer were discussed on the basis of the theoretical results.

Experimental Section

1-Methyl-4-carbomethoxypyridinium iodide,[5] mp 190°, 1-ethyl-4-carbomethoxypyridinium iodide,[6] mp 111°, and 1-isopropyl-4-carbomethoxypyridinium iodide, mp 137°, were prepared from 4-carbomethoxypyridine and three corresponding alkyl iodides by the method described in the literature. Acetonitrile was purified by repeated distillations from phosphorus pentoxide. Isopentane was shaken with concentrated sulfuric acid, washed with water, and dried over calcium chloride. After that, it was refluxed with potassium metal and finally distilled.

The substituted pyridinyl radicals were prepared at room temperature by bringing the corresponding pyridinium salts into contact with zinc mirror in acetonitrile. The procedures for the radical preparation were shown in the previous paper.[5] After the solvent acetonitrile was taken off, isopentane was transferred by distillation into a reaction tube from a solvent vessel with a break seal (see Figure 1). Only the pyridinyl radical was extracted from the residue with the isopentane. This is because the pyridinium salts were insoluble in isopentane. All these procedures were performed under high vacuum (*ca.* 10^{-6} mm).

The spectrophotometric measurements were made with a Cary recording spectrophotometer, Model 14 M. The spectra at low temperature were measured by making use of a quartz dewar vessel.

Theoretical Section

In order to study the electronic structures of the π–π-type dimers of the neutral radicals, the electronic structure of the 1-alkyl-4-carbomethoxypyridinyl radical monomer was calculated by the method combining the open-shell, self-consistent-field procedures of Longuet-Higgins and Pople[7] with the configuration interaction.

Ishitani and Nagakura[8] have already reported the electronic structures of the anion radicals of some aromatic hydrocarbons and substituted benzenes by the open-shell SCF method and the configuration interaction procedures. Almost the same method was applied to the 1-alkyl-4-carbomethoxypyridinyl radicals. In the actual calculation the approximation of the zero-differential overlap was adopted and the two-center Coulomb repulsion integrals of the type $(pp|qq)$ were calculated by Pariser–Parr approximation.[9] The Coulomb integral α_p was obtained by the following equation on the assumption neglecting penetration integrals

$$\alpha_p = -I_p - \sum_{p \neq q}(pp|qq)\gamma_q$$

where I_p is the valence-state ionization potential of the electron of the pth atom, and $\gamma_q = 1$ or 2 according to the core charges of the qth atoms, $+$e or $+$2e. All of these atomic integrals are summarized in Table I.

Table I. Parameters Used for the Calculation of the Substituted Pyridinyl Radical (in ev)

For Pyridinyl Ring Carbon atom I_p	 $(pp\|qq)$	 Nitrogen atom I_p	 $(pp\|qq)$	 β_{CC}	 β_{CN}
11.22	10.60	14.46	12.27	−2.39	−2.57
		17.34	13.34		−2.60
		19.06	14.06		−2.63
		20.73	14.73		−2.65
		25.46	15.65		−2.68

For Carboxyl Group	$=O_8$[a]	$-O_9$[a]	$C=O_8$	$C-O_9$	$C-C$
I_p	17.25	34.43	β −2.75	−2.0	−2.5
$(pp\|qq)$	15.38	18.85			

[a] M. K. Orloff and O. Sinanoğlu, *J. Chem. Phys.*, **43**, 49 (1965).

Now let us turn our attention to the problem of the valence state of the nitrogen atom in the pyridinyl radical. The ionization potentials of the pyridine-type nitrogen and pyridinium-type nitrogen atoms have been reported to be 14.4[10] and 28.85 ev,[11] re-

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

(3) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

(4) E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

(5) M. Itoh and S. Nagakura, *Bull. Chem. Soc. Japan*, **39**, 369 (1966).

(6) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(7) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 591 (1955).

(8) A. Ishitani and S. Nagakura, *Theoret. Chim. Acta*, **4**, 236 (1966).

(9) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

Table II. The Energy and Wave Function of Molecular Orbital of the 1-Alkyl-4-carbomethoxypyridinyl Radical[a]

	Wave function								
Energy, ev	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8	χ_9
−12.7069	0.0363	0.0267	0.0491	0.1244	0.0467	0.0261	0.3242	0.1748	0.9173
−11.2048	0.7928	0.3624	0.2048	0.1492	0.1890	0.3560	0.0319	0.0218	−0.1084
−8.8491	−0.2524	−0.0091	0.2294	0.4247	0.1974	−0.0227	0.4427	0.5940	−0.3387
−6.9961	0.3110	−0.1035	−0.4583	−0.4466	−0.3418	−0.0270	0.1604	0.5782	−0.0729
−5.9897	−0.0257	−0.4515	−0.4952	0.0713	0.5625	0.4754	0.0040	−0.0510	−0.0028
0.7071	0.3185	−0.2851	−0.2939	0.4968	−0.2750	−0.3520	0.3754	−0.3667	−0.0947
5.5942	0.0368	−0.5779	0.4634	0.0071	−0.4642	0.4839	−0.0037	−0.0010	0.0009
6.2191	−0.2784	0.3884	−0.1438	−0.2059	−0.2038	0.4344	0.5950	−0.3333	−0.1134
8.7412	−0.1690	0.2948	−0.3547	0.5366	−0.3963	0.3135	−0.4206	0.1829	0.0694

[a] $\chi_1, \chi_2, \ldots \chi_9$ are atomic orbitals. The atoms of the 1-alkyl-4-carbomethoxypyridinyl radical are marked as shown in Figure 3.

spectively. The valence state of the nitrogen atom in the pyridinyl radical is supposedly between those of the two types of the nitrogens. We tentatively adopted several values as the valence-state ionization potential of the nitrogen atoms. The effective nuclear charge of the nitrogen atom corresponding to the adopted valence-state ionization potential was obtained by the aid of the method reported by Brown.[12] Actually, the quadratic equation was obtained from the isoelectronic series C^-, N, and O^+. The electron affinities of these nitrogen atoms were also evaluated from the effective nuclear charge by using the similar quadratic equation obtained from the isoelectronic series to that as mentioned above. A two-center, electron-repulsion integral $(pp|qq)$ was calculated from the uniformly charged sphere model.[9] The parameters obtained are summarized in Table I. The SCF procedures based on these parameters were performed by an electronic computer Facom 202 in the Institute for Solid State Physics.[13] A set of the evaluated molecular orbitals and energies are shown as an example in Table II.

By putting 11 electrons in the SCF molecular orbitals, a ground and 13 excited configurations were constructed. In the present configuration calculation, only the singly excited configurations were taken into account. The energy values of these electron configurations are summarized in Table III. The transition energies and moments were evaluated for the several sets of parameters for each valence state of nitrogen. The transition energies calculated from the tentatively adopted I_p's are shown in Figure 2. From the comparison of the observed energies with the theoretical values, it is revealed that the valence-state ionization potential of the nitrogen atom may be estimated to be 19–20 ev, as shown in Figure 2.

Table III. The Ground and Excited Configurations and Their Energies

Configuration	Energy, ev	Configuration	Energy, ev
Ground	0	$(5\rightarrow7)^\beta$	5.500
$(5\rightarrow6)$	4.150	$(5\rightarrow8)^\alpha$	7.038
$(4\rightarrow6)$	4.890	$(5\rightarrow8)^\beta$	8.437
$(6\rightarrow7)$	2.221	$(4\rightarrow7)^\alpha$	7.516
$(6\rightarrow8)$	3.157	$(4\rightarrow7)^\beta$	8.084
$(6\rightarrow9)$	5.106	$(4\rightarrow8)^\alpha$	8.012
$(5\rightarrow7)^\alpha$	6.435	$(4\rightarrow8)^\beta$	9.226

$$(i\rightarrow m) = |\phi_1\bar{\phi}_1\ldots\phi_i\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_m\bar{\phi}_m|$$

$$(m\rightarrow k) = |\phi_1\bar{\phi}_1\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_k|$$

$$(i\rightarrow k)^\alpha = \frac{1}{\sqrt{2}}[\,|\phi_1\bar{\phi}_1\ldots\phi_i\bar{\phi}_k\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| + |\phi_1\bar{\phi}_1\ldots\phi_k\bar{\phi}_i\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_m|\,]$$

$$(i\rightarrow k)^\beta = \frac{1}{\sqrt{6}}[\,|\phi_1\bar{\phi}_1\ldots\phi_i\phi_k\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| - |\phi_1\bar{\phi}_1\ldots\phi_k\bar{\phi}_i\ldots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| + 2|\phi_1\bar{\phi}_1\ldots\phi_i\phi_k\ldots\phi_{m-1}\bar{\phi}_{m-1}\bar{\phi}_m|\,]$$

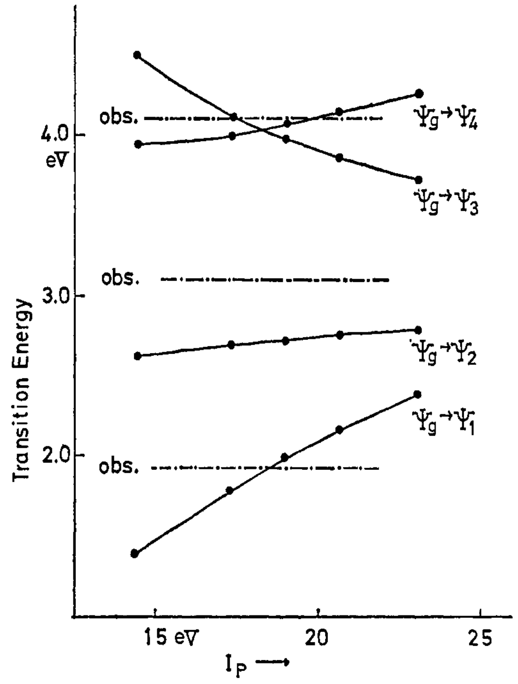

Figure 2. Relationship between calculated electronic transition energies of the 1-alkyl-4-carbomethoxypyridinyl radical and the valence-state ionization potential of the nitrogen atom.

Now we consider the electronic interaction between two neutral radicals. The ground and excited states which give rise to the intense absorption bands of the pyridinyl radical monomer are all doublets. For the radical dimer, both singlet and triplet functions may be constructed. But, the triplet function was omitted in considering the absorption spectra, because the ground state may be thought to be the singlet state.

By transferring an odd electron from the unpaired electron orbital φ_6^A of one component radical to the unpaired electron orbital φ_6^B of the other radical,

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(10) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

(11) S. Mataga and N. Mataga, *ibid.*, **19**, 231 (1959).

(12) R. D. Brown and M. L. Hefferman, *Trans. Faraday Soc.*, **54**, 757 (1958).

(13) In actual calculation, a computer program made by Dr. S. Iwata and Dr. A. Ishitani was used. The authors are grateful to them for the computer program.

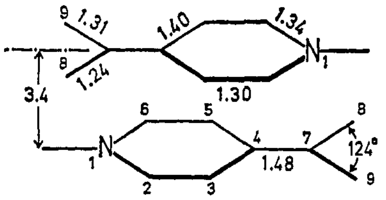

Figure 3. The assumed geometrical structure of the radical dimer (in Angstrom units).

we can obtain the lowest electron-transfer configuration which is described as an anion–cation pair ($P_y{}^{\pm}{}_A$, $P_y{}^{\mp}{}_B$). The energy necessary for the electron transfer can be given by the following well-known equation, $E = I - A + C$, where I and A are the ionization potential and electron affinity of the pyridinyl radical, respectively, and C is the coulombic energy of the anion–cation pair caused by the electron transfer.

By an analogy with Pariser's consideration on the atomic integrals, it is seen that $I - A$ is set equal to the mutual repulsion energy of the two electrons in the φ_6 molecular orbital of the pyridinyl radical as

$$I - A = \int \varphi_6(k)\varphi_6(k)\frac{e^2}{\gamma_{kl}}\varphi_6(l)\varphi_6(l)\,\mathrm{d}\tau_{kl} = (66|66) \quad (1)$$

The mutual repulsion integral (66|66) was calculated by the aid of the two-center Coulomb repulsion integrals evaluated by the Pariser–Parr approximation.[9] The resulting values are summarized in Table IV. In the actual evaluation of C, we assumed the geometric arrangement of the radical dimer to be as shown in Figure 3. The results for different I_p values are summarized in Table IV.

Table IV. The ($I - A$) and Coulombic Energy in the Substituted Pyridinyl Radical Dimer (ev)

I_p	$(I - A) =$ (66|66)	C
17.34	6.45	3.65
19.06	6.47	3.73
20.73	6.48	3.80

By virtue of the symmetry of the system, the symmetric and antisymmetric electron-transfer states are given as

$$\sqrt{\frac{1}{2}}[{}^1\Psi_1(P_y{}^+{}_A,P_y{}^-{}_B) \pm {}^1\Psi_1(P_y{}^-{}_A,P_y{}^+{}_B)] \qquad (2)$$

Hausser and Murrell[1] reported that the ground configuration will mix with only the symmetric electron-transfer state, and the stabilization energy depends on the amount of overlap between the singly occupied orbitals of two radicals. In the radical dimer, the stabilization of the ground state may depend on the value of the overlap integral between the $\varphi_6{}^A$ and $\varphi_6{}^B$ orbitals of the two radicals.

Results and Discussion

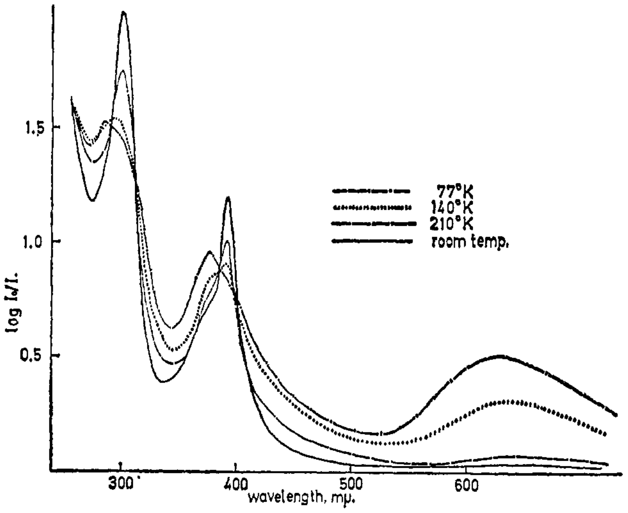

Figure 4. Temperature dependence of the absorption spectra of the 1-methyl-4-carbomethoxypyridinyl radical in isopentane: concentration, 4 × 10^{-4} *M;* light path length, 1 cm.

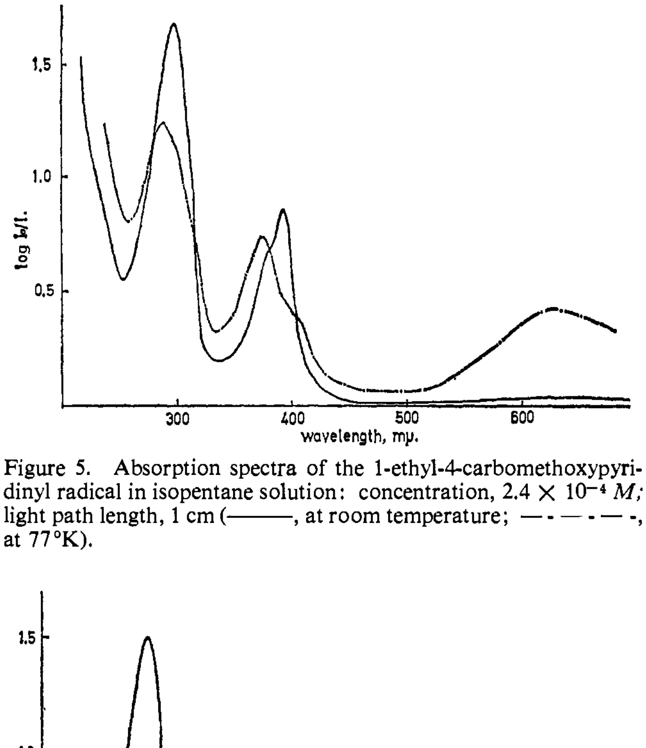

Figure 5. Absorption spectra of the 1-ethyl-4-carbomethoxypyridinyl radical in isopentane solution: concentration, 2.4 × 10^{-4} *M;* light path length, 1 cm (———, at room temperature; —·—·—, at 77°K).

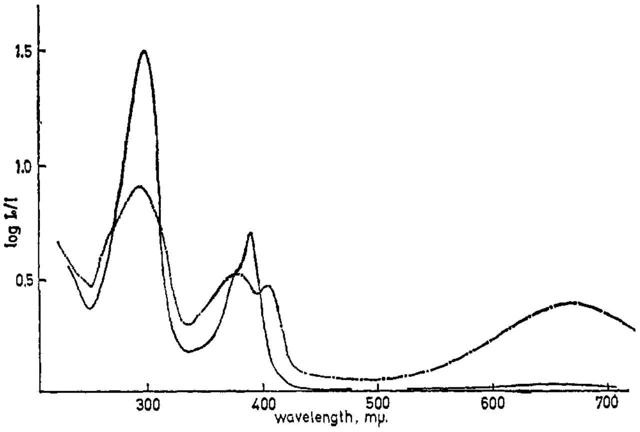

Figure 6. Absorption spectra of the isopentane solution of the 1-isopropyl-4-carbomethoxypyridinyl radical: concentration, 2.4 × 10^{-4} *M;* light path length, 1 cm (———, at room temperature; —·—, at 77°K).

The Absorption Spectra of the Pyridinyl Radical Monomers. The electronic spectrum of the acetonitrile solution of the 1-methyl-4-carbomethoxypyridinyl radical was shown in the previous paper.[5] The absorption spectra of the isopentane solutions of the three pyridinyl radicals were measured at room temperature with the results shown in Figure 4–6. When the isopentane solutions of the radicals were exposed to air, almost all absorption disappeared. The radical concentration and molar extinction coefficient were estimated by determining the weight of the radicals, after the solvent was completely removed from the isopentane solution of these radicals after exposure to air. The molar extinction coefficients obtained showed a good agreement with the result of the 1-ethyl-4-carbomethoxypyridinyl radical reported by Kosower and Poziomek.[14] Figures 4–6 show that the absorption spectra of these pyridinyl radicals are similar to one another.

The transition energies and transition moments of the 1-alkyl-4-carbomethoxypyridinyl radicals were calculated by the methods combining open-shell, self-consistent-field theory with configuration interaction.[7,8] The observed and theoretical values of the transition energies and transition moments are tabulated in Table V, taking as an example the case of the valence-state ionization potential of the nitrogen atom, I_p = 19.06 ev. The bands at ~300, ~390, and 640–650 mμ can be ascribed to the $\Psi_g \rightarrow \Psi_3$, $\Psi_g \rightarrow \Psi_2$, and $\Psi_g \rightarrow \Psi_1$ transitions, respectively. The calculated transition moments fit the observed tendency, as shown in Table V and Figures 4–6. The longest wavelength band is very weak. The characters of the ground and excited states associated with these electronic transitions are shown in Table VI by the percentages of the configurations mainly contributing to each state.

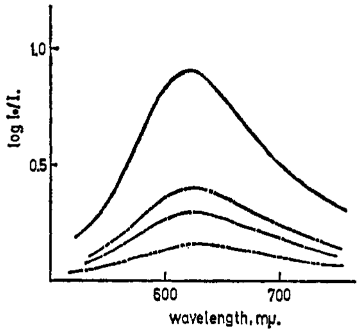

Figure 7. Concentration dependence of the visible absorption spectra of the 1-methyl-4-carbomethoxypyridinyl radical in isopentane solution at 77°K: ———, 6.3 × 10^{-4} *M*; — - —, 3.0 × 10^{-4} *M*; — — —, 2.4 × 10^{-4} *M*; — - - —, 1.6 × 10^{-4} *M* (light path length, 1 cm).

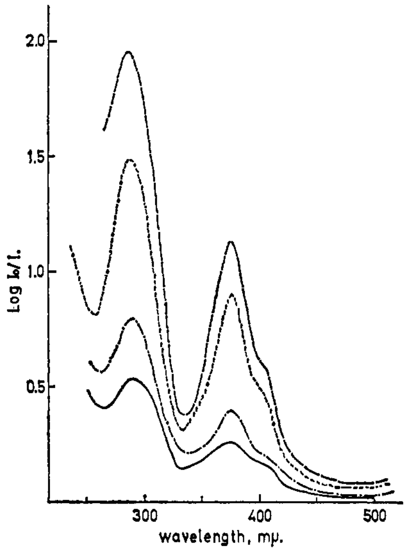

Figure 8. Concentration dependence of the ultraviolet absorption spectra of the 1-ethyl-4-carbomethoxypyridinyl radical in isopentane at 77°K (light path length, 1 cm): — — —, 2.7 × 10^{-4} *M*; - - - -, 2.4 × 10^{-4} *M*; — - —, 1.1 × 10^{-4} *M*; ———, 7.0 × 10^{-5} *M*.

Table V. The Observed and Calculated Data for the Absorption Spectra of the 1-Alkyl-4-carbomethoxypyridinyl Radical Monomer

	ΔE_{obsd}	ΔE_{calcd}	f_{calcd}[a]	y/x[b]
$\Psi_g \rightarrow \Psi_1$	1.9 eV	2.01 eV	2.63×10^{-3}	0.77
$\Psi_g \rightarrow \Psi_2$	3.1	2.71	6.67×10^{-1}	8.60
$\Psi_g \rightarrow \Psi_3$	4.1–4.2	4.00	1.31×10^{-1}	0.12
$\Psi_g \rightarrow \Psi_4$	—	4.08	8.23×10^{-3}	0.63

[a] $f_{\text{calcd}} = 4.704 \times 10^{-7} \tilde{\gamma} Q^2$ ($\tilde{\gamma}$ in cm^{-1}, Q in Debye units). [b] x and y axes are as follows

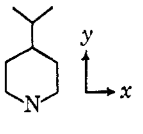

Table VI. The Theoretical Results of the Ground and the Lower Excited States of the 1-Alkyl-4-carbomethoxypyridinyl Radical Monomer

Wave function	Energy, ev	Configurations mainly contributed
Ψ_g	−0.117	G(98.5%)
Ψ_1	1.901	$6 \rightarrow 7$(93.5%), $5 \rightarrow 8^{\beta}$(1.4%), $4 \rightarrow 7^{\beta}$(1.4%)
Ψ_2	2.598	$4 \rightarrow 6$(8.4%), $6 \rightarrow 8$(81%), $5 \rightarrow 7^{\beta}$(7.2%)
Ψ_3	3.885	$5 \rightarrow 6$(84.7%), $6 \rightarrow 9$(4%)
Ψ_4	3.964	$6 \rightarrow 9$(43.6%), $5 \rightarrow 7^{\beta}$(28.6%), $4 \rightarrow 6$(10%) $5 \rightarrow 6$(6.9%)

Monomer–Dimer Equilibrium. The electronic spectra of the isopentane solution of the pyridinyl radicals were measured at various temperatures. The results for the 1-methyl-4-carbomethoxypyridinyl radical are shown in Figure 4. When the temperature of the radical solution is decreased from room temperature to liquid nitrogen temperature, an absorption in the 600–700-mμ region gradually increases the intensity and is intensified by 10 or 15 times at liquid nitrogen temperature, while the two shorter wavelength bands at ~300 and ~390 mμ decrease their maximum intensities and become broader, as is shown in Figure 4. A similar temperature dependence was also observed with the 1-ethyl-4-carbomethoxy- and 1-isopropyl-4-carbomethoxypyridinyl radicals. Their absorption spectra are shown in Figures 5 and 6, respectively. These temperature dependences of the absorption spectra are completely reversible.

Furthermore, the spectra of the radical solutions with various concentrations were measured at 77°K. The results are shown in Figures 7–11. From the above-mentioned results in the temperature and concentration dependences of the spectra in isopentane, it is inferred that these substituted pyridinyl radicals form dimers in isopentane and at low temperature. In order to check quantitatively these monomer–dimer equilibria, we analyzed the observed concentration dependence of the absorption spectra given in Figures 7, 9, and 11.

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(14) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964).

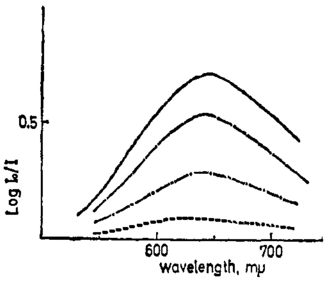

Figure 9. Concentration dependence of the visible absorption spectra of the 1-ethyl-4-carbomethoxypyridinyl radical in isopentane at 77°K (light path length, 1 mm): ———, 2.9×10^{-3} *M;* — — —, 2.4×10^{-3} *M;* — - —, 1.1×10^{-3} *M;* -----, 6.0×10^{-4} *M.*

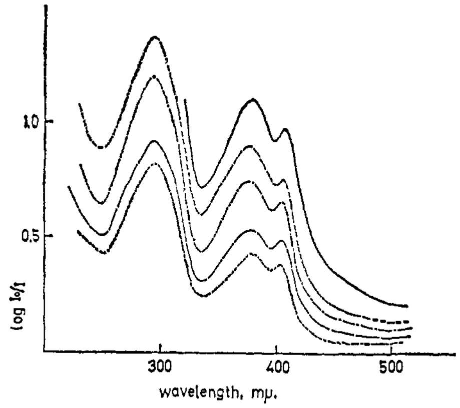

Figure 10. Concentration dependence of the ultraviolet absorption spectra of the 1-isopropyl-4-carbomethoxypyridinyl radical in isopentane at 77°K (light path length, 1 mm): ———, 5.5×10^{-3} *M;* -----, 4.0×10^{-3} *M;* — - —, 2.9×10^{-3} *M;* — — —, 2.0×10^{-3} *M;* - - - - -, 1.6×10^{-3} *M.*

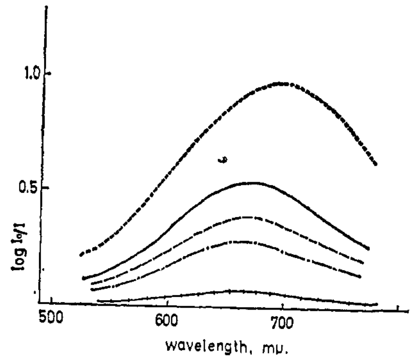

Figure 11. Concentration dependence of the visible absorption spectra of the 1-isopropyl-4-carbomethoxypyridinyl radical in isopentane at 77°K (light path length, 1 mm): -----, 5.5×10^{-3} *M;* ———, 2.9×10^{-3} *M;* - - - -, 2.0×10^{-3} *M;* — - —, 1.6×10^{-3} *M;* —·—·—, 5.2×10^{-4} *M.*

The monomer–dimer equilibrium constant K of the pyridinyl radical can be determined by eq 3, where ϵ

$$K = (\epsilon - \epsilon_m)(\epsilon_d - \epsilon_m)/2a(\epsilon - \epsilon_d)^2 \qquad (3)$$

is the apparent molar extinction coefficient at a certain wavelength; ϵ_m and ϵ_d are the molar extinction coefficients at the same wavelength of the monomer and the dimer, respectively; a is the radical concentration as the monomer form in isopentane. By assuming that the pyridinyl radicals in the solution of low concentration (10^{-5}–10^{-3} *M*) are mostly in monomer form at room temperature, the value, a, of each solution can be determined from the observed absorbancy of the solution at room temperature and the molar extinction coefficient of the corresponding monomer radical at certain wavelength (392 mμ for the 1-methyl-4-carbomethoxypyridinyl (I) and for the 1-ethyl-4-carbomethoxypyridinyl (II) and 390 mμ for the 1-isopropyl-4-carbomethoxypyridinyl (III) radicals). From the observed spectra at 77°K shown in Figures 7, 9, and 11, the apparent molar extinction coefficients, ϵ, can be obtained for each solution. In actuality, the ϵ values at 623, 646, and 694 mμ were adopted for the I, II, and III radicals, respectively. The value of K, ϵ_m, and ϵ_d were evaluated by inserting the observed a and ϵ into eq 3. The least-squares method was applied to the actual evaluation of the K, ϵ_m, and ϵ_d. Furthermore, it was shown that the value of log $[(\epsilon - \epsilon_m)\cdot(\epsilon_d - \epsilon_m)/(\epsilon - \epsilon_d)^2]$ is proportional to the logarithm of the radical concentration, a. The slopes of the straight lines are about 1, as is shown in Figure 12. This means that the concentration dependences of the absorption spectra of these pyridinyl radicals at 77°K can be explained by the equilibrium between monomer and dimer.[15]

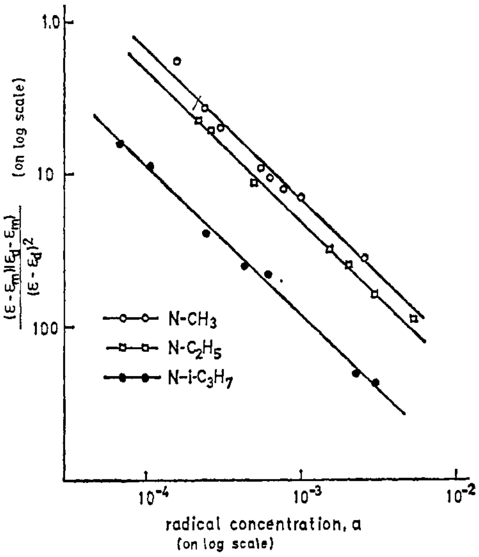

Figure 12. Plots of log $[(\epsilon - \epsilon_m)(\epsilon_d - \epsilon_m)/(\epsilon - \epsilon_d)^2]$ against log a for the monomer–dimer equilibrium of the pyridinyl radical in isopentane at 77°K.

The peak molar extinction coefficients, $\epsilon_d{}^1$ and $\epsilon_d{}^2$, for the two shorter wavelength bands of the pure dimer were obtained by combining the apparent molar extinction coefficients ϵ^1 and ϵ^2 with K. Here the superscripts 1 and 2 are referred to the ~300- and 390-mμ bands, respectively. Final obtained peak wavelengths and intensities of the pure monomers and dimers are summarized in Table VII, together with the evaluated equilibrium constants (K) at 77°K.

Absorption Spectra and Electronic Structures of Radical Dimers. As is shown in Table VII, the pure radical dimers show absorption bands in the 600–700-mμ region with considerably greater intensities than the monomers. By an analogy with the case of ethylphenazyl and tetramethyl-*p*-phenylenediamine cation radicals discussed by Hausser and Murrell,[1] we

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[15] H. Hosoya, J. Tanaka, and S. Nagakura, *J. Mol. Spectry.*, **8**, 257 (1962).

Table VII. The Equilibrium Constant (K) at 77 °K, the Maximum Wavelength (mμ), and Molar Extinction Coefficients (in parentheses) of the Radical Monomer and Dimer

	Monomer			Dimer				K, mole^{-1}
N–CH_3	295	392	640	288	375	623		7.1×10^3
	(11,000)	(4500)	(90)^a	...	(2500)^b	(1930)^a		
N–C_2H_5	297	392	650	287	375	646		3.45×10^4
	...	(4400)	(100)^a	...	...	(2620)^a		
N–i-C_3H_7	297	390	650–670	293	378	406	694	8.2×10^3
	(10,000)	(4500)	(90)^a	...	(2300)^b	(2080)^b	(2000)^a	

^{a} Obtained by the least-squares method. ^{b} Obtained from the observed ϵ^2 and $\epsilon_m{}^2$ by the aid of K.

may assign this absorption band to the CT band characteristic of the radical dimer which corresponds to the transition from the singlet ground state to the antisymmetric CT state represented by eq 2.[16] The energy of the CT configuration was estimated to be 2.7 ev from the equation $I - A + C$, as mentioned in the theoretical section. This value of 2.7 ev may be decreased by the configuration interaction with the locally excited configuration corresponding to the excitation within each radical ($\Psi_g \rightarrow \Psi_2$ and $\Psi_g \rightarrow \Psi_3$).[17] This estimation of the CT energy seems to support the interpretation that the longest wavelength bands (*ca.* 2.0 ev) may be the CT band. The moment of this CT transition is directed from one radical to another. This means that the CT band may be polarized mainly perpendicular to the plane of each radical, while the weak absorption band of the radical monomer (600–700 mμ) may be polarized in the radical plane.

The observed CT absorption bands shift by changing the N-alkyl group to longer wavelength in the following order: $CH_3 < C_2H_5 < i\text{-}C_3H_7$, as shown in Table VII. This tendency seems to be attributed not only to the change in the $I - A + C$, but also the stabilization energy of the dimer. The former depends on the electronic effects of the alkyl substituents to the pyridinyl radicals and the latter mainly depends on the overlap integrals between two singly occupied orbitals of each radical in the dimer, which are affected by the steric factors of the alkyl substituents of the pyridinyl radicals.

Judging from the fact that the ionization potential of alcohols decreases in the order of methanol > ethanol > 2-propanol, it may be tentatively inferred that the $I - A + C$ value might decrease in the order of methyl > ethyl > isopropyl derivatives. This is apparently coincident with the order in the observed peak wavelengths of the 600–700-mμ band. That is to say, we can roughly explain the observed wavelength shift of the CT bands by considering the $I - A + C$ value alone. However, a more detailed inspection of Table VII shows that the shift of the CT bands is extraordinarily large in the case of the 1-isopropyl-4-carbomethoxypyridinyl dimer. This may be due to the steric hindrance of the isopropyl group. The bulkiness of this group may prohibit the two ring planes of the dimer from approaching each other and may cause the decrease in the overlap integral S_{66} and therefore in the stabilization energy. This means that the CT band of the dimer of the isopropyl derivative shifts additionally to longer wavelength compared with the cases of the other two derivatives. The fact that the peak molar extinction of the 600–700-mμ band is smaller for the dimer of isopropyl derivative than for that of ethyl derivative seems also to support the above consideration.[18]

The shorter wavelength bands of the dimers may be regarded as the shifted locally excited bands of the monomer radicals. Concerning these bands, our attention must be paid to the fact that two absorption bands appear in the 370–410-mμ region for the 1-ethyl- and 1-isopropyl-4-carbomethoxypyridinyl radical dimer, although for the former one of the two bands was observed only as a shoulder. Moreover, a careful inspection of the spectrum of the dimer of 1-methyl-4-carbomethoxypyridinyl radical shows that a small absorption might be covered by the shorter wavelength band (λ_{max} 392 mμ). Therefore, it may be concluded that two absorption bands appear in this region for the respective radical dimers, while only one absorption band appears for the corresponding monomer. This may conceivably be due to the splitting of the locally excited band of the monomer radical (about 390 mμ) by virtue of dimer formation.

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(16) The transition from the ground state to the symmetric CT state may be thought to be forbidden on symmetry grounds.

(17) The interaction energy, *i.e.*, off-diagonal matrix element between the antisymmetric CT state and $\Psi_g \rightarrow \Psi_1$, is approximately zero.

(18) According to Hausser and Murrell,[1] the absorption intensity of the CT band of this kind can approximately be assumed to be proportional to the value of the overlap integral S_{66}.