A Study on the Nature of the Electronic Absorption Bands of Formylpyrroles and Acetylpyrroles[1]

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The electronic spectra of formyl- and acetylpyrroles were studied from both experimental and theoretical viewpoints. On the basis of the solvent effect and pH-dependence of the absorption spectra, the lowest energy transitions of 2- and 3-acetylpyrroles and the corresponding formylpyrroles, as well as the second lowest energy transitions of 3-acylpyrroles, were suggested to be accompanied by the electron-transfer from the pyrryl to carbonyl group. As to 1-acetylpyrrole (or 1-formylpyrrole), the longest wavelength absorption bands disappeared when the conjugation between the pyrryl and carbonyl groups were inhibited by steric hindrance. Solvent effects on the absorption band, however, were so small that the extent of electron-transfer was considered to change little during the transition. The results of VESCF MO calculations also supported the above suggestion based on experimental observations. The behaviors of the second lowest energy transitions of 1- and 2-acylpyrroles were too complicated to be accounted for straightforwardly.

Aside from pyrrole itself, no theoretical studies have been made on the electronic spectra of substituted pyrroles. In the case of monosubstituted benzenes, the composite-molecule method has been successfully applied to interpret electronic spectra. Taking the case of benzaldehyde, as an example, the absorption band at 43 kK was assigned to an intramolecular charge-transfer band from calculations based on the composite-molecule method.[2] Similar treatment is expected to be successful also in the case of substituted pyrroles because the pyrryl group is known to be a good electron donor as can be seen in studies on charge-transfer complexes[3] and the electronic spectra of 1-(*p*-substituted phenyl)-pyrroles.[4] Since the ionization potential of a pyrryl group is lower than that of a phenyl group, the charge-transfer configuration is expected to make a significant contribution to the electronic structures of pyrrole derivatives with a carbonyl group. In fact, the internal rotation around the C–N bond in 1-acylpyrroles was found to be fairly restricted due to the presence of double bond character ascribed to the contribution of charge-transfer configurations.[5]

In the present study, we investigated the characteristic absorption bands of formyl- and acetylpyrroles in the ultraviolet region which is usually accessible, to examine how well one can interpret the nature of these spectra on the basis of the electron transfer from the pyrryl to carbonyl group.

Results and Discussion

The lowest energy electronic transition of pyrrole is located at 47.6 kK. If an acyl group is attached to a pyrryl group, strong characteristic absorption bands are found for each isomer in the region between 35 and 45 kK (Fig. 1). The electronic spectra of formylpyrroles closely resemble those of the corresponding acetylpyrroles. The observed absorption maxima of these compounds together with their 1-methyl-substituted derivatives are listed in Table 1.

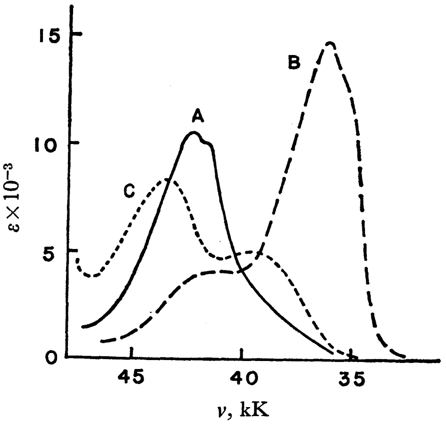

Fig. 1. The ultraviolet absorption spectra of acetylpyrroles in *n*-hexane.
A, 1-acetylpyrrole; B, 2-acetylpyrrole; C, 3-acetylpyrrole.

If the contribution of charge-transfer configurations in the electronic structure is more significant in an excited state than in the ground state, the corresponding absorption band should show an appreciable red-shift as the polarity of solvent increases. The behavior of the first absorption band of 2-acetylpyrrole is in accordance with this expectation. As an alternative explanation for the red-shift observed in the ethanol solution, the hydrogen bonding between pyrrole and ethanol molecules might be suggested. However, the absorption maximum of the first band of 1-methyl-2-acetylpyrrole is located very close to that of 2-acetylpyrrole not only in *n*-hexane but also in ethanol. The same situation is also encountered when we compare the first absorption bands of 2-formylpyrrole and 1-methyl-2-formylpyrrole. It is thus very unlikely that the hydrogen bonding plays an important role in the solvent-induced red-shift given in Table 1. The second absorption bands of 2-acetylpyrroles and 2-formylpyrroles, on the other hand, are not shifted appreciably by the change of solvent from *n*-hexane to alcohol.

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[2] K. Kimura and S. Nagakura, *Theoret. Chim. Acta*, **3**, 164 (1965).

[3] T. Matsuo and H. Shosenji, This Bulletin, **41**, 1068 (1968).

[4] T. Matsuo, H. Shosenji, and R. Miyamoto, *ibid.*, **41**, 2849 (1968).

[5] T. Matsuo and H. Shosenji, *Chem. Commun.*, **1969**, 501.

Table 1. Electronic absorption spectra of formylpyrroles and acetylpyrroles

Compound	in n-Hexane				in Ethanol			
	1st Band		2nd Band		1st Band		2nd Band	
	ν a)	ε b)	ν a)	ε b)	ν a)	ε b)	ν a)	ε b)
1-Formylpyrrole	38.0 c)	1.5	41.5 c) 42.4	9.5 11.2	38.0 c)	1.6	42.2	11.3
1-Acetylpyrrole	38.0 c)	2.0	41.6 c) 42.4	10.0 10.5	38.0 c)	2.0	41.9	10.6
2-Formylpyrrole	35.9	15.1	40.7	4.7	34.6	15.6	40.1 c)	4.4
1-Methyl-2-formylpyrrole	35.7	16.2	40.7	6.2	34.6	15.2	40.2	5.9
2-Acetylpyrrole	35.4 c) 36.2	12.7 14.7	40.7 41.8 c)	4.1 4.0	34.8	14.9	41.2 c)	3.3
1-Methyl-2-acetylpyrrole	36.0	15.5	40.8 c)	5.0	34.8	15.1	40.5 c)	4.5
3-Acetylpyrrole	38.6	4.3	43.6	7.9	35.8	4.8	41.0	9.4
1-Methyl-3-acetylpyrrole	38.2	5.3	41.5	8.6	d)		39.8	8.8

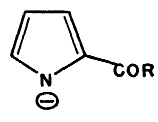
a) The values are in kK units. Errors are within 0.1 kK unless specified.

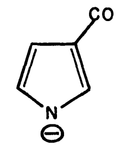
b) The values are in 10^3 l/mol·cm units. Errors are within 100 l/mol·cm except for the case of the shoulder of an absorption band, where the error may be twice as large as that for the case of a distinct peak.

c) The shoulder of an absorption band. Errors are estimated to be within 0.3 kK.

d) The absorption maximum could not be located on account of the band being hidden under the tail of the second absorption band.

In the case of 3-acetylpyrrole and its 1-methyl-substituted derivative, both the first and the second absorption bands show a red-shift when the solvent is changed from n-hexane to ethanol. In order to further investigate the electronic origin of the above described absorption bands of 2- and 3-acylpyrroles, we measured the electronic spectra in alkaline solutions. The results are shown in Figs. 2 and 3 for 2-formylpyrrole and 3-acetylpyrrole, respectively. In both cases, the longest wavelength absorption bands in 10N sodium hydroxide are found in a considerably longer wavelength region in neutral solutions. The spectra of 2-acetylpyrrole show a similar pH-dependence as observed in the case of 2-formylpyrrole. In alkaline solutions, these compounds are considered to exist as the anions as shown by structures (I) and (II).[6]


(I)


(II)

Since the ionization potential of the pyrryl anion should be considerably lower than that of neutral species, the large red-shift in alkaline solutions can be taken as sufficient evidence for assigning the absorptions to charge-transfer bands.

The longest wavelength absorption band of 1-acetylpyrrole is almost the same as that of 1-formylpyrrole, both of them being found in energy regions lower by about 5 kK than that of pyrrole. The absorption bands of 1-formylpyrrole, as well as those of 1-acetylpyrrole, consist of two components: a strong main peak (Band A) at about 42 kK and its shoulder (Band B) at approximately 38 kK. As to 1-formyl- and 1-acetylpyrrole, Band B is observed only as a small hump on the tail of Band A. On substitution of the proton at the 2-position by a methyl group, Band B appears clearly because

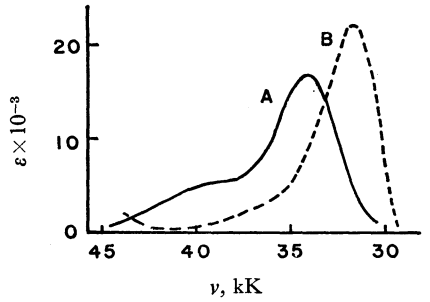


Fig. 2. The pH-dependence of the abosrption spectra of 2-formylpyrrole.
A, in water; B, in 10N aqueous sodium hydroxide solution.

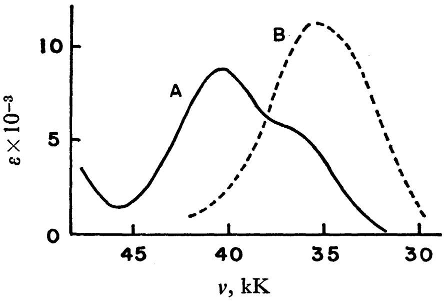


Fig. 3. The pH-dependence of the absorption spectra of 3-acetylpyrrole.
A, in water; B, in 10N aqueous sodium hydroxide solution.

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[6] Bonino and Mirone isolated the sodium salt of 2-formylpyrrole.[7] On inspecting the IR spectra, they concluded that the NH proton dissociated to yield the sodium salt. The evidence for the presence of anions (I) and (II) is also given by the fact that a methyl group is introduced to the nitrogen atom of 2-formylpyrrole,[8] 2-acetylpyrrole,[9] and 3-acetylpyrrole (present experiment), respectively, when the alkaline solutions are treated with dimethyl sulfate.

[7] G. B. Bonino and P. Mirone, *Atti accad. Nazl. Lincei. Rend (Classe sci fis., mat. e nat.)*, **17**, 167 (1954); *Chem. Abst.*, **49**, 15488b (1955).

[8] E. Fischer, *Ber.*, **46**, 2509 (1913).

[9] P. Fournari, *Bull. Soc. Chim. France*, **1963**, 488.

a hypochromic effect is observed on Band A while Band B is slightly shifted to longer wavelength with no change in its intensity. The absorption maximum of 2-methyl-1-acetylpyrrole in the vapor phase is slightly shifted to longer wavelength in comparison with that in the solution, but the shapes of the spectra in the two phases are essentially the same. The intensity of Band B is rather weak ($f \sim 0.02$), but stronger than that of ordinary n-π^* absorption bands. The solution spectra are not affected even by the addition of trifluoroacetic acid. Thus we can disregard the possible contribution of the lone pair electrons of the carbonyl group to the appearance of the absorption bands. In other words, both Bands A and B are assigned to π-π^* transitions. In the case of 2,5-dimethyl-1-acetylpyrrole, the plane of the acetyl group is twisted to almost a perpendicular position to that of the pyrryl group. As a consequence, both Band A and B disappear as can be seen in Fig. 4. The above results are also summarized in Table 2. It is clearly understood that the conjugation between the pyrryl and carbonyl groups is definitely required for the presence of both Bands A and B. Introduction of methyl groups into the 3- and 4-positions of the pyrryl group causes a large red-shift (1.8 kK) of Band A of 1-acetylpyrrole. Band B, on the other hand, is not affected and almost concealed under the shifted Band A (Fig. 4). Considering the fact that the first charge-transfer band of the chloranil complex of 3-methylpyrrole is also shifted to a wavelength longer by 1.7 kK than that of the chloranil-pyrrole system,[3] we would like to assign Band A to the intramolecular charge-transfer band. However, on the basis of the solvent effects, it is difficult to assign either Band A or B to charge-transfer absorptions, because the absorption maxima of these bands of 2-methyl-1-acetylpyrrole are hardly shifted by the change of the solvent from n-hexane to ethanol.

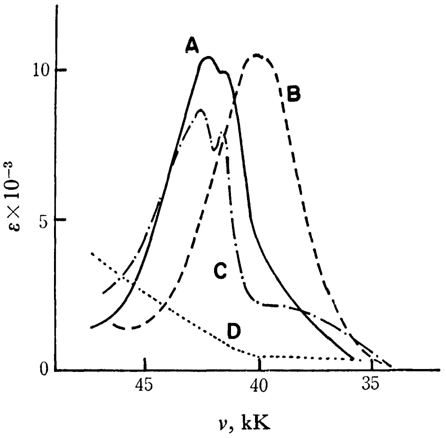


Fig. 4. The ultraviolet absorption spectra of methylsubstituted 1-acetylpyrroles in n-hexane.
A, 1-acetylpyrrole; B, 3,4-dimethyl-1-acetylpyrrole; C, 2-methyl-1-acetylpyrrole; D, 2,5-dimethyl-1-acetylpyrrole.

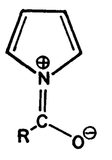
TABLE 2. ELECTRONIC ABSORPTION BANDS OF METHYLSUBSTITUTED 1-ACETYLPYRROLES[a)]

Compound	Band A		Band B	
	ν[b)]	ε[c)]	ν[b)]	ε[c)]
1-Acetylpyrrole	41.6±0.1	10.0±0.1	38.0±0.5	2.0±0.2
	42.4±0.1	10.5±0.1		
3,4-Dimethyl-1-acetylpyrrole	40.2±0.1	10.5±0.1	d)	
2-Methyl-1-acetylpyrrole	41.7±0.1	7.9±0.1	38.0±0.5	2.0±0.2
	42.6±0.1	8.7±0.1		

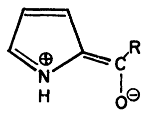
a) In n-hexane
b) Values in kK units
c) Values in 10^3 l/mol·cm units
d) The absorption maximum could not be located on account of the band being hidden under the tail of Band A.

The results are well accounted for if one assigns the longest wavelength absorption bands of 2- and 3-acetylpyrroles to charge-transfer bands. This is also true for 2- and 3-formylpyrroles. In the case of 1-acetyl- or 1-formylpyrrole, however, it is difficult to assign the longest wavelength absorption band to charge-transfer absorption straightforwardly.

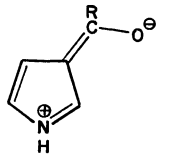
In the NMR spectroscopic rate studies, on the other hand, the barrier to internal rotation in 1-formyl- or 1-acetylpyrrole has been found to be clearly higher than that in the isomers correspondingly substituted at the 2- or 3-position.[5,10] The result indicates that the ionic form (III) makes more significant contribution to the ground state of the 1-substituted pyrroles than the ionic forms (IV) and (V) to the ground states of 2- and 3-acylpyrroles, respectively.



(III)



(IV)



(V)

In order to explain the above results, spectroscopic differences between the isomers of formyl- or acetylpyrroles and the electronic structures of these molecules were examined by the use of pi-electron approximation. Brown and Heffernan's VESCF MO with CI was adopted for this purpose. Geometries of the investigated molecules were estimated from those of the closely related compounds.[11] The one-center electron repulsion integrals were calculated by the use of Paolini's approximation,[15] and the two-center integrals were

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[10] L. Arlinger, K.-I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, **24**, 672 (1970).

[11] The geometry of the pyrryl group was assumed to be the same as that of pyrrole itself.[12] Referring to the cases of acetamides[13] and acetaldehyde,[14] it was assumed that the bond between the pyrryl and carbonyl groups is either 1.36 Å (1-acylpyrroles) or 1.4 Å (2- and 3-acylpyrroles), and also that the bond bisects the angle between the adjacent two bonds in the pyrryl group. Similarly, the bond length of the carbonyl group was assumed to be 1.21 Å. The bond angles associated with the carbonyl carbon were taken to be those for the ideal sp^2 hybridization.

[12] B. Bak, D. Christensen, L. Hansen-Nyagard and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

[13] K. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).

[14] D. P. Stevenson, H. D. Burnham, and V. Schomaker, *J. Amer. Chem. Soc.*, **61**, 2922 (1939).

[15] L. Paolini, *Nuovo Cimento*, **4**, 410 (1956).

evaluated by the use of the Nishimoto and Mataga equation. The penetration integrals were not taken into consideration. Pariser and Parr's formula was used for the estimation of the core resonance integrals (H_{pq}), except for the case of $H_{C=O}$, where Tanaka's value for formamide (−3.35 eV)[16] was adopted. The valence ionization potentials were estimated by means of Brown's approximation based on the effective nuclear charges on the atoms.[17] The lower nine of the singly-excited configurations were included in the CI calculation. The values thus obtained for transition energy, oscillator strength and the electronic configurations mainly contributing to the relevant, low excited states of the acylpyrroles are given in Table 3. The coefficients for the 2*p* orbital of each atom in the relevant π orbitals are shown in Fig. 5. The results for only one conformer of each isomer are shown here, because no significant difference between the rotamers was found as far as the carbonyl group was assumed to be coplanar with the pyrryl group. Similarly, the difference between acetyl and formyl groups was also disregarded in the calculation, because the observed electronic spectra of formylpyrroles are almost the same as those of the corresponding acetylpyrroles in the investigated region.

Table 3. Calculated values for the transition energy (ΔE_k), oscillator strength (f_k), and wave functions (Φ_k) for low-excited states of acylpyrroles

ΔE_k (eV)	f_k	Φ_k[a)]
1-Acylpyrrole		
5.87	0.23	$0.875\Phi_{35}-0.446\Phi_{46}$
6.03	0.20	$0.997\Phi_{45}+0.045\Phi_{26}$
7.53	0.16	$0.828\Phi_{47}+0.387\Phi_{36}$
2-Acylpyrrole		
5.55	0.42	$0.902\Phi_{45}+0.372\Phi_{35}$
5.89	0.23	$0.751\Phi_{35}+0.468\Phi_{46}$
7.04	0.33	$0.748\Phi_{46}-0.459\Phi_{35}$
3-Acylpyrrole		
5.85	0.01	$0.765\Phi_{35}-0.540\Phi_{46}$
6.07	0.24	$0.942\Phi_{45}+0.251\Phi_{35}$
6.60	0.71	$0.781\Phi_{46}+0.561\Phi_{35}$

a) Φ_{ij} denotes an electronic configuration which is obtained by the promotion of a π electron from the *i*th MO to the *j*th MO, when the pi-electron approximation was adopted in the calculation. The most important two electronic configurations for each energy level are shown for the sake of simplicity.

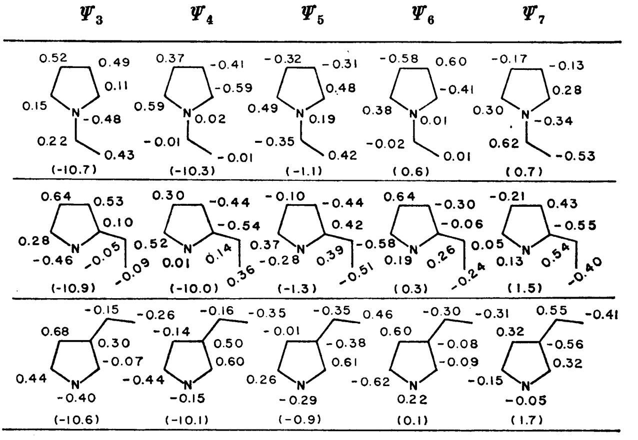

Fig. 5. The coefficients for the atomic orbitals in the relevant MO associated with the low energy transitions of acylpyrroles. The energy of each orbital, in eV units, is given by the numeral in parentheses under the corresponding structure.

The calculated π–π* transition energies are higher than the values obtained experimentally by approximately 1 eV. It is clear that more advanced treatment is required to obtain a satisfactorily quantitative agreement between the observed and the calculated values. Several important features of the electronic spectra of acylpyrroles are noticed, however, even in the present results. On the basis of the data in Table 3, it is expected that two absorption bands for each isomer will be found in the energy region (200—300 mμ), and that the lowest energy transition of 2-acylpyrroles will be found at the longest wavelength side as a rather strong peak, which is distinctly separated from those of the other isomers. These predictions are in fair agreement with observations. On examination of the electron configurations concerned, it is easily found also that these low energy transitions are originated from the simultaneous excitation of both the pyrryl and the carbonyl groups. In other words, a strong conjugation between the two groups are theoretically required for the presence of the observed absorption bands, as was verified in the case of methylsubstituted 1-acetylpyrrole (Fig. 4).

Table 4. π-Electron density on the carbonyl group of acylpyrroles in the ground state and the two low-excited states

Compound	Ground State	1st Excited State	2nd Excited State
1-Acylpyrrole	0.065	0.056	0.383
2-Acylpyrrole	0.024	0.313	0.163
3-Acylpyrrole	0.026	0.162	0.226

The π electron densities on the carbonyl groups were evaluated in order to find an explanation for the different solvent-induced shifts of the absorption maxima of the acylpyrroles. The results are shown in Table 4. The extent of electron transfer in the ground state from the pyrryl to carbonyl group in 1-acylpyrrole is suggested to be larger than that in 2- and 3-acylpyrroles. This is in line with the fact that the barrier to internal rotation of carbonyl group in 1-acylpyrrole is higher than that in 2- and 3-acylpyrroles. In the first excited state, the π electron densities on the carbonyl groups of 2- and 3-acylpyrroles increase in comparison with those in the ground states. Thus, the first absorption bands of these compounds in ethanol are shifted to longer wavelength than those in *n*-hexane (Table 1). Similarly, the negligibly small solvent effects on the absorption bands of 1-acylpyrroles can be accounted for by the minute change in the calculated π electron density on the carbonyl group on going from the ground state to the first excited state.

The situation is much more complicated in the case

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[16] J. Tanaka, *Nippon Kagaku Zasshi*, **78**, 1636 (1957).

[17] R. D. Brown and M. L. Heffernan, *Aust. J. Chem.*, **12**, 554 (1959).

of the second excited states of acylpyrroles. The correlation between the solvent-induced shift and the change in electron density at the carbonyl group is found only in the case of 3-acylpyrroles. From the values given in Table 4 we might expect a fairly strong solvent-dependence of the absorption due to the second lowest energy transition of 1-acylpyrrole. The experimental results are not in agreement with this expectation. Almost the same thing could be said with the second excited states of 2-acylpyrroles. It should be remembered that Band A of 1-acetylpyrrole shows an appreciable red-shift (1.8 kK) on the introduction of methyl groups at the 3- and 4-positions. A possible case might be where the π electron is actually transferred from the pyrryl to carbonyl group in the second excited state as indicated by calculation and also by the effect of methyl substitution at the 3- and 4-positions of 1-acetylpyrrole. The migration of π electrons thus induced might be counter-balanced by the polarization of σ electrons.

Experimental

Materials. The following compounds were prepared according to the method described in the literature given in parentheses or its modification: 1-formylpyrrole (Ref. 18, bp 81—83°C/60.5 mmHg), 1-acetylpyrrole (Ref. 19, bp 86.5°C/29 mmHg), 3,4-dimethyl-1-acetylpyrrole (Ref. 19, bp 120°C/27 mmHg), 2-methyl-1-acetylpyrrole (Ref. 20, bp 94—95°C/27.5 mmHg), 2,5-dimethyl-1-acetylpyrrole (Ref. 20, bp 110°C/23 mmHg), 2-formylpyrrole (Ref. 21, mp 44.4—44.9°C), 1-methyl-2-formylpyrrole (Ref. 21, bp 87—92°C/22 mmHg), 2-acetylpyrrole (Ref. 22, mp 92.0—92.7°C), 1-methyl-2-acetylpyrrole (Ref. 23, bp 92.3—94.0°C/22 mmHg), 3-acetylpyrrole (Ref. 24, mp 115.9—116.5°C), 1-methyl-3-acetylpyrrole (Ref. 9, bp 97.5—102.0°C/3 mmHg). All the above compounds were identified by elementary analyses, IR, and NMR spectra.

n-Hexane and ethanol were purchased from Wako Pure Chemicals Industries Ltd. They were repeatedly purified by the usual methods until they proved to be pure spectroscopically.

Spectroscopic Measurements. The electronic spectra were measured with a Bausch & Lomb Spectronic 505 Recording Spectrophotometer at temperatures between 17 and 19°C. The concentrations of the solutions were between 10^{-4} and 10^{-5} mol/*l*.

The authors are greatly indebted to the members of the Computer Center, Kyushu University, for their help in carrying out the VESCF MO calculations on a model OKITAC-5090H computer. Thanks are also due to Mr. Hajime Koga for his help in the study of the solvent effect on the spectra of 2-methyl-1-acetylpyrrole.

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18) L. Alessandri, *Atti Accad Lincei*, **24**, **II**, 194 (1955); *Chem. Abst.*, **10**, 1350 (1916).

19) G. S. Reddy, *Chem. Ind.*, **1965**, 1426.

20) R. W. Guy and R. A. Jones, *Aust. J. Chem.*, **19**, 107 (1966).

21) R. M. Silverstein, E. E. Ryskiewicz, C. Williard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1958).

22) G. L. Ciamician and M. Dennstadt, *Ber.*, **16**, 2348 (1883).

23) A. Ermili, A. J. Castro, and P. A. Westfall, *J. Org. Chem.* **30**, 339 (1965).

24) H. J. Anderson and C. W. Huang, *Can. J. Chem.*, **45**, 597 (1967).