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A Study of Charge-Transfer Complexes. VII. Interactions between the Alkyl- or Arylsubstituted Pyrroles and Chloranil or Tetracyanoethylene*1,*2

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The charge-transfer (CT) bands of complexes of alkylsubstituted pyrroles and chloranil or tetracyanoethylene (TCNE) were found to consist of two closely situated peaks. The peaks were assigned to transitions originated from the highest occupied, and second-highest occupied orbitals of the donor. The energy of the CT absorption band is hardly affected even by the presence of a bulky substituent such as a *t*-butyl group at the pyrrole nitrogen. Hence, the acceptor molecules were thought not to be close to the 1-position of the pyrryl group. In the case of 1-phenylpyrrole, the first CT bands are at almost the same positions as those of the corresponding complexes of 1-methylpyrrole. The bands show red shifts if methyl groups are introduced either on the pyrryl group or on the phenyl group, so that the planes of the two groups are twisted around the N-C bond between them. Thus the acceptor molecules were concluded to interact mainly with the pyrryl group.

The electronic spectra of pyrrole derivatives have been less investigated than those of benzene derivatives. The situation is the same for the intermolecular charge-transfer (abbreviated to CT hereafter) absorption bands of these compounds.[1] Only a few examples have been known of CT complexes of pyrrole derivatives.[3a,3b] In the present paper, the results of a systematic study on the nature of the CT absorption bands of alkyl- or aryl-substituted pyrroles will be described.

Results and Discussion

(A) Chloranil Complexes of Alkylpyrroles. The CT spectra of chloranil complexes of alkylpyrroles consist of two peaks, which overlap each other as shown in Fig. 1. The wave numbers for the peak positions are summarized in Table 1. In the case of chloranil complexes of *N,N*-dimethylaniline analogues, which will be described later, there are no signs of absorption bands within 10 kK of the first CT band. Therefore, the two peaks of the pyrrole complexes should be due to the intrinsic nature of the donor molecule. As suggested by several investigators,[3a,3b] the first and second CT bands of pyrrole complexes may be assigned to electronic transitions originated from the highest occupied, and

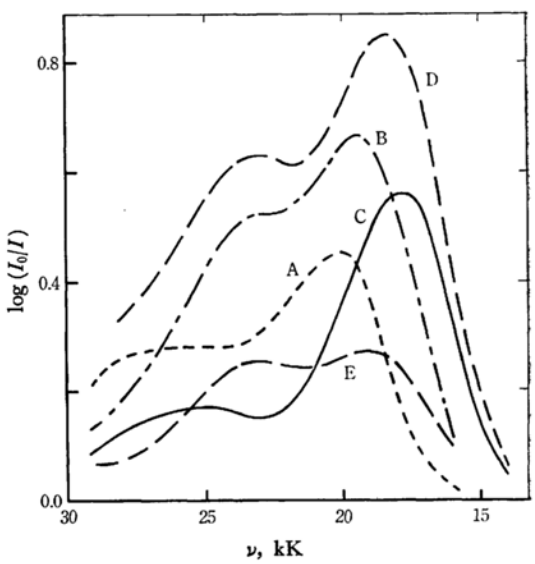

Fig. 1. The CT bands of the chloranil complexes of alkylpyrroles in carbon tetrachloride. The donors are indicated by the capital letters as the following: pyrrole (A), 1-methylpyrrole (B), 2-methylpyrrole (C), 3-methylpyrrole (D), 1-*t*-butylpyrrole (E). The concentrations of the acceptor are 0.0013 mol/*l*; the concentrations of the donors are 0.33 (A, C, D, E) or 0.073 mol/*l* (B).

*1 Previous paper: T. Matsuo and O. Higuchi, This Bulletin, **41**, 518 (1968); The contribution No. 144 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

*2 Presented in parts at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

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1) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe" Springer-Verlag, Berlin (1961).

2. A. R. Cooper, C. W. P. Crowne and P. G. Farrell, *Trans. Faraday Soc.*, **62**, 18 (1966).

3) a) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 4438 (1962); b) Z. Yoshida and T. Kobayashi, The paper presented at the Discussion Meeting on the Molecular Structure, Osaka, October, 1966.

Table 1. The CT bands of the chloranil complexes of alkylpyrroles in carbon tetrachloride[a)]

Donor	The 1st band	The 2nd band
Pyrrole	20.1±0.1	26.2±0.5
1-Methylpyrrole	19.5±0.1	24.0±0.2
2-Methylpyrrole	17.8±0.1	25.3±0.5
3-Methylpyrrole	18.4±0.1	23.8±0.2
1-*t*-Butylpyrrole	18.9±0.1	22.9±0.2

a) The values are in kilokayser units.

second-highest occupied orbitals of pyrrole, respectively. The semiempirical SCF-LCAO-MO method of Pariser-Parr-Pople was utilized to study the π electronic structure of pyrrole by Solony *et al.*[4] According to the calculation, the highest occupied orbital of pyrrole is antisymmetric with respect to the C_2 axis of the molecule. The second highest occupied orbital, on the other hand, is symmetric with respect to the same axis. In other words, the nitrogen atom of the pyrrole molecule is involved in the second highest occupied orbitals but not in the highest occupied orbital. The separation between the energy levels of the two orbitals is estimated to be only 0.4 eV. The above assignment of the CT bands of pyrrole complexes is in good agreement with the predicted natures of the two occupied molecular orbitals; the second CT band is approximately 0.7 eV higher than the first band, and methyl substitution at a carbon atom causes an appreciably larger red shift of the first CT band than that at a nitrogen atom.

To a first order approximation, the effect of methyl substitution may be treated as an increase in the Coulomb integral for the atom to which the methyl group is attached. According to simple LCAO-MO theory, a variation in the Coulomb integral for the rth atom ($\delta\alpha_r$) is expected to cause the following change in the energy level of the ith orbital:

$$\delta\varepsilon_i = C_{ir}^2\delta\alpha_r + \sum_{k(\neq i)}^{n} \frac{(C_{ir}C_{kr})^2}{\varepsilon_i - \varepsilon_k}(\delta\alpha_r)^2 + \cdots \quad (1)$$

where ε_i and C_{ir} have the usual meaning. Using the coefficients (C_{ir}) obtained by Solony *et al.*,[4] the effect on the highest occupied orbital is calculated as summarized in Table 2. The experimental values for the red shifts of the first CT bands, as measured by taking unsubstituted pyrrole as standard, are also tabulated in the same table for comparison. The value of $\delta\alpha_r$ is positive for methyl substitution. It is clear, then, that the red shifts of the first CT bands correlated well with the perturbation effects of the methyl group on the highest occupied orbital.

Table 2. The effect of methyl substitution on the π energy levels of pyrrole molecule

Substitution position	C_{ir}^2	$\sum(C_{ir}C_{kr})^2/(\varepsilon_i-\varepsilon_k)$	Red shift of the 1st band
1	0.0	0.0	0.6±0.1 kK
2	0.34	0.12	2.3±0.1
3	0.16	0.12	1.7±0.1

4) N. Solony, F. W. Birss and J. B. Greenshield, *Can. J. Chem.*, **43**, 1569 (1965).

In the case where 1-*t*-butylpyrrole is used as the π donor, the first CT band, as well as the second band, moves to lower wave numbers in comparison with the case of 1-methylpyrrole. The red shift may be explained as due to the fact that the inductive effect of the *t*-butyl group raises the π-energy levels of the pyrryl group. If the steric effect of the *t*-butyl group is of any importance, on the other hand, just the opposite shift will be expected because the increased donor-acceptor distance reduces the value of the electrostatic term C in the following equation:

$$h\nu_{CT} \cong I_p - E_A - C \quad (2)$$

Since the actual shifts are more or less bathochromic, the present authors speculate that the chloranil molecule is not close to the 1-position of the pyrryl group.

(B) Tetracyanoethylene Complexes of Alkylpyrroles. It is known that tetracyanoethylene (TCNE) reacts with pyrroles to form tricyanovinyl compounds.[5] In the present experiment, the CT bands were observed to decay with time. In return, new absorption bands appeared in the region between 300 and 500 mμ, which were due to the accumulation of reaction products. In the case of the

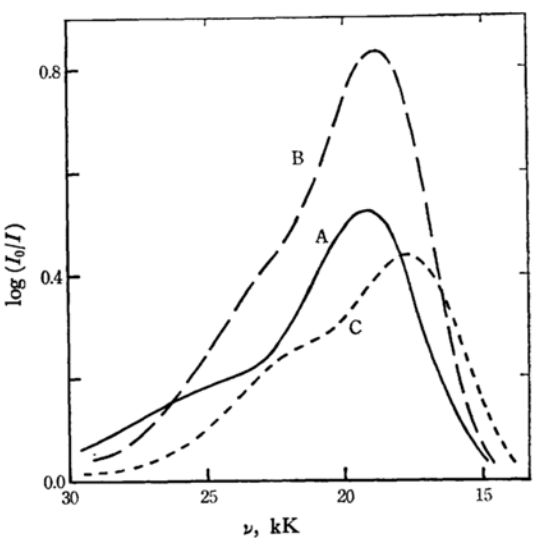

Fig. 2. The CT bands of the TCNE complexes of alkylpyrroles in *n*-hexane. The donors are indicated by the capital letters as follows: pyrrole (A), 1-methylpyrrole (B), 1-*t*-butylpyrrole (C). The concentrations of the acceptor are 3.0×10^{-4} mol/*l*; the concentrations of the donors are 0.10 (A), 0.15 (B) or 0.20 mol/*l* (C).

5) a) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958); b) R. Bonnet and J. D. White, *J. Chem. Soc.*, **1963**, 1648.

TABLE 3. THE CT BANDS OF TCNE COMPLEXES OF ALKYLPYRROLES IN VARIOUS SOLVENTS[a,b]

Donor	In n-C_6H_{14}		In CCl_4		In $(CHCl_2)_2$	
	1st band	2nd band	1st band	2nd band	1st band	2nd band
Pyrrole	19.3	25.6	18.9	25.5	18.4	25.1
1-Methylpyrrole	18.9	23.8	18.5		18.0	
1-*t*-Butylpyrrole	17.8	22.5	17.3	22.1	17.0	

a) The values are in the same units as in Table 1.
b) The accuracies in the values of the absorption maxima for the first and the second CT bands are 0.1 and 0.2 kK, respectively.

TABLE 4. THE CT BANDS OF THE CHLORANIL AND TCNE COMPLEXES OF 1-PHENYLPYRROLE ANALOGUES WITH METHYL SUBSTITUENTS[a]

Donor	Chloranil complex[b]		TCNE complex[c]	
	1st band	2nd band	1st band	2nd band
1-Phenylpyrrole	20.9±0.1		18.4±0.1	31.8±0.2
1-*p*-Tolylpyrrole	20.3±0.1		18.1±0.1	30.3±0.1
1-*o*-Tolylpyrrole	19.0±0.1	24.7±0.2	16.1±0.1	23.2±0.2
1-(2′,6′-Xylyl)-pyrrole	19.0±0.2	25.1±0.1	16.0±0.2	22.0±0.1
1-Phenyl-2,5-dimethylpyrrole	15.8±0.1	23.0±0.1	d)	d)

a) The values are in the same units as in Table 1.
b) In carbon tetrachloride.
c) In tetrachloroethane.
d) The measurement was unsuccesful because the reaction was rapid.

2-methylpyrrole-TCNE system, the decay of the CT bands was so rapid that the complete spectra could not be followed even by using the fastest scanning speed. A solution of the 3-methylpyrrole-TCNE system also shows extraordinary behavior. The spectra are not only time dependent, but also consist of several sharp peaks indicating at least three species besides the component molecules. Thus, the location of the CT bands could not be definitely determined. A detailed study of this peculiar system is under way, and the results will be reported in the near future. The time dependences of the TCNE complexes of pyrrole, 1-methylpyrrole and 1-*t*-butylpyrrole are small enough to be measured without any appreciable change taking place during measurement, if measurement is made within five minutes of mixing the acceptor and donor components. The spectra thus measured in *n*-hexane are shown in Fig. 2. Analogous to the cases of chloranil complexes, one can observe two CT bands for each system. The second CT band, however, is much weaker than the first band, and the former appears just as a shoulder of the latter. Both the first and second bands show similar red shifts as the solvent is changed in the order of *n*-hexane, carbon tetrachloride and tetrachloroethane, as summarized in Table 3. The shapes of the spectra are quite alike in all solvents. Thus, it is suggested that the nature of the donor-acceptor interactions between TCNE and alkylpyrroles is essentially the same as that of the chloranil-alkylpyrrole system.

(C) Chloranil and TCNE Complexes of 1-Phenylpyrrole Analogues. On the basis of the size of the dipole moment, 1-phenylpyrrole has been suggested to have a nearly planar structure, where the π-electrons of the pyrryl group are easily delocalized to the phenyl group without much disturbance.[6] The suggested conformation may be reasonable because the van der Waals radii of the protons at the 1- and 1′-positions barely overlap each other. In the case of 1-phenyl-2,5-dimethylpyrrole, however, the dipole moment[6] and the electronic spectra[7,8] indicate that the dimethylpyrryl group and the phenyl group are twisted around the N–C bond axis joining the two groups. The electronic spectra of 1-(2′,6′-xylyl)-pyrrole also have been interpreted as indicating the presence of twisting around the N–C bond axis. This twisting is, of course, due to the steric hindrance exerted by the methyl groups. A more or less similar situation is expected for the conformation of 1-(*o*-tolyl)-pyrrole. These compounds were also used as the electron donors in the present experiment. The CT absorption spectra of the chloranil complexes are shown in Fig. 3. The wave numbers for the absorption maxima, together with those for the TCNE complexes, are summarized in Table 4. In either series, the

6) H. Kofod, K. E. Sutton and J. Jackson, *J. Chem. Soc.*, **1952**, 1467.
7) J. Davoll, *ibid.*, **1953**, 3802.
8) Y. Chiang, R. L. Hinman, S. Theodoropulos and E. B. Whipple, *Tetrahedron*, **23**, 745 (1967).

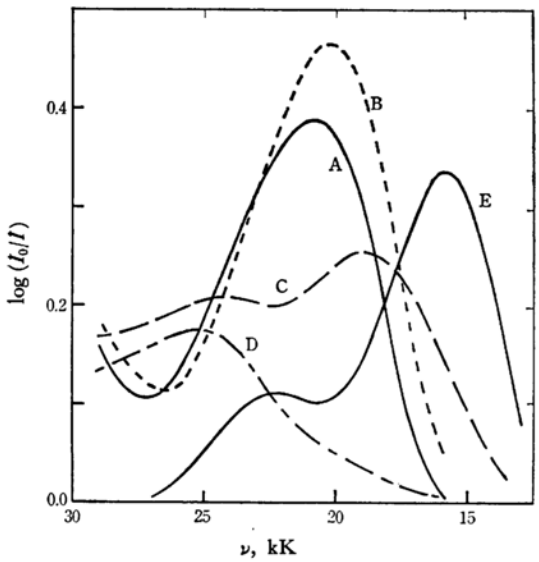

Fig. 3. The CT bands of the TCNE complexes of 1-phenylpyrrole analogues with methyl substituents in carbon tetrachloride. The donors are indicated by the capital letters as the following: 1-phenylpyrrole (A), 1-*p*-tolylpyrrole (B), 1-*o*-tolylpyrrole (C), 1-(2′,6′-xylyl)-pyrrole (D), 1-phenyl-2,5-dimethylpyrrole (E). The concentrations of the acceptor are 0.0013 mol/*l*; the concentrations of the donors are 0.33 (A, B, C, D) or 0.12 mol/*l* (E).

wave numbers for the absorption maxima of the first CT bands are in the following order: 1-phenyl-2,5-dimethylpyrrole < 1-(2′,6′-xylyl)-pyrrole < 1-(*o*-tolyl)-pyrrole < 1-(*p*-tolyl)-pyrrole ≈ 1-phenylpyrrole. It is interesting that the CT bands for donors with twisted conformations are at a lower energy than for those with planar structures. It should be noticed also that the first CT bands of 1-phenylpyrrole complexes are at almost the same positions as those of the corresponding complexes of 1-methylpyrrole. These observations appear to be against the general expectation that the ionization potential of an aromatic molecule decreases as the degree of conjugation is extended. An explanation may be the fact that the π-electrons of the pyrryl group are withdrawn to the more electronegative phenyl group. As a consequence, the energy level for the highest occupied orbital is lower than the case where conjugation between the two groups is forbidden. From this point of view, the rather large red shift of the first CT band for the chloranil complex of 1-phenyl-2,5-dimethylpyrrole may also be understood as due to the inductive effect of the methyl group on the π-electron system of the pyrryl group. Thus, it is suggested that the acceptor molecules interact mainly with the pyrryl group rather than with the phenyl group. In other words, the electronic state of the pyrryl group may be the most important factor determining the energy of the first CT band of the 1-phenylpyrrole analogues with alkyl substituents.

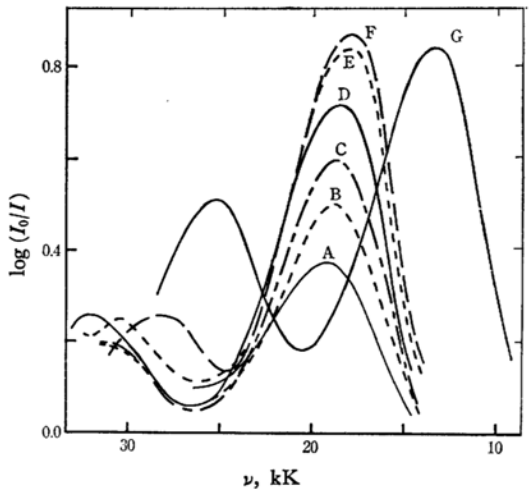

Fig. 4. The CT bands of the chloranil complexes of 1-(*p*-substituted phenyl)-pyrroles in the tetrachloroethane. The substituents are indicated by the capital letters as follows: acetyl (A), bromo (B), chloro (C), hydrogen (D), methyl (E), methoxy (F) and dimethylamino (G). The concentrations of the acceptor are 0.0020 mol/*l*; the concentrations of the donors are 0.10 (A, B, D, E, F), 0.12 (C) or 0.013 mol/*l* (G).

Table 5. The CT bands of the chloranil and TCNE complexes of 1-(*p*-substituted phenyl)-pyrroles[a)]

Substituent group	Chloranil complex[b)]	TCNE complex[c)]	
	1st band	1st band	2nd band
Acetyl	21.4±0.1	19.2±0.1	
Bromo	21.4±0.1	18.8±0.1	29.4±0.3
Chloro	21.3±0.1	18.6±0.1	31.0±0.4
Hydrogen	20.9±0.1	18.4±0.1	31.8±0.2
Methyl	20.3±0.1	18.1±0.1	30.3±0.1
Methoxy	20.0±0.1	18.0±0.1	28.3±0.1
Dimethylamino	14.7±0.1	13.2±0.1	25.2±0.1

a) The values are in the same units as in Table 1.
b) In carbon tetrachloride.
c) In tetrachloroethane.

In order to obtain further information on the role of the phenyl group, the CT spectra of various 1-(*p*-substituted phenyl)-pyrrole complexes were also investigated (Fig. 4, Table 5). Since the variations of the first CT bands of the chloranil complexes in Table 5 are almost the same as those of the TCNE complexes, the substituent effects on the former may be taken as representative. For comparison, the first CT bands of the chloranil complexes of *p*-substituted *N*,*N*-dimethylanilines were also measured (Table 6, Fig. 5). As for substituents other than the *N*,*N*-dimethylamino group, the effects observed in the 1-(*p*-substituted phenyl)-pyrrole complexes are slightly less than those in the *p*-substituted aniline

Table 6. The CT bands of the chloranil complexes of *p*-substituted *N,N*-dimethylanilines in carbon tetrachloride[a)]

Substituent group	1st band
Acetyl	15.8±0.1 kK
Bromo	15.0±0.1
Chloro	15.2±0.1
Hydrogen	15.5±0.1
Methyl	14.9±0.1
Methoxy	13.9±0.1
Dimethylamino	11.2±0.1

a) There are no signs of absorption bands within 10 kK from the first CT bands in these systems.

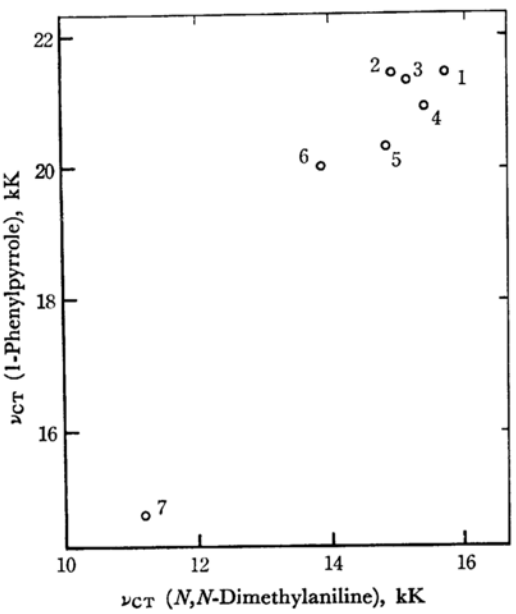

Fig. 5. The comparison of the first CT band of the chloranil complexes of 1-(*p*-substituted phenyl)-pyrrole with that of *p*-substituted *N,N*-dimethylaniline in carbon tetrachloride. The substituents are indicated by numbers as follows: acetyl (1), bromo (2), chloro (3), hydrogen (4), methyl (5), methoxy (6) and dimethylamino (7).

complexes. In the case of the dimethylamino group, the first CT bands are at considerably longer wavelengths than in the cases of other substituents. In comparison with the first CT bands of the chloranil complex of 1-phenylpyrrole, for example, the corresponding band of 1-(*p*-*N,N*-dimethylaminophenyl)-pyrrole is shifted to the longer wavelength side by 6.2 kK. The corresponding red shift in the *p*-*N,N*-dimethylaniline series, on the other hand, is only 4.3 kK. This interesting effect may be due to the fact that the *N,N*-dimethylaminophenyl group is a stronger electron donor than the pyrryl group, as may be seen by comparing the values in Table 1 with those in Table 6. As pointed out in the preceding paragraph, the acceptor molecules appear to be coordinated to the pyrryl group in 1-phenylpyrrole. The situation may be unchanged if the substituent at the phenyl group is either an electron-withdrawing or weakly electron-donating one. In the case of 1-(*p*-*N,N*-dimethylaminophenyl)-pyrrole, the electron-donating ability of the pyrryl group is exceeded by that of the substituent. As a consequence, the acceptor molecule may be coordinated to the *p*-*N,N*-dimethylamino group rather than to the pyrryl group.

Experimental

Measurements of the CT Spectra. Solutions of CT complexes were prepared by properly adjusting the concentrations of the donor (0.02—1.0 mol/*l*) and the acceptor molecules (0.00015—0.05 mol/*l*) in suitable solvents. The spectra were measured at room temperature (17—20°C) by the use of either a Bausch & Lomb Spectronic 505, or a Hitachi model EPS-2 recording spectrophotometer. The absorptions due to the donor and the acceptor were numerically subtracted from the recorded spectra to obtain the absorption bands of the pure complexes.

Materials. Carbon tetrachloride, *n*-hexane and tetrachloroethane were purchased from the Wako Pure Chemicals Co., Ltd., and purified by standard procedures. Chloranil (mp 292.5—293.0°C), pyrrole (bp 60—61°C/55 mmHg), 1-methylpyrrole (bp 44.9°C/42.5 mmHg), *N,N*-dimethylaniline (bp 85°C/20 mmHg), *N,N*-dimethyl-*p*-aminoacetophenone (mp 108.2—108.7°C), *N,N*-dimethyl-*p*-bromoaniline (mp 55.2— 55.9°C), *N,N*-dimethyl-*p*-chloroaniline (mp 34.5—35.0°C), *N,N*-dimethyl-*p*-toluidine (bp 114—115°C/34 mmHg), *N,N*-dimethyl-*p*-anisidine (mp 48.0—48.5°C) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (mp 51.0—52.0°C) were reagent-grade chemicals as supplied by the Wako Pure Chemicals Co., Ltd., and were repeatedly purified until they showed the melting points or boiling points given above. The following compounds were synthesized according to methods given in the references in parentheses: TCNE (Ref. 9, mp 199—200°C), 2-methylpyrrole (Ref. 10, bp 82.5°C/70 mmHg), 1-phenyl-2,5-dimethylpyrrole (Ref. 11, mp 51.5—52.5°C), 1-*p*-bromophenylpyrrole (Ref. 12, mp 96.2—96.5°C), 1-(*p*-*N,N*-dimethylaminophenyl)-pyrrole (Ref. 12, mp 152.5—153.2°C), 1-*o*-tolylpyrrole (Ref. 12,*4 bp 80°C/3 mmHg), 1-2',6'-xylylpyrrole (Ref. 12,*4 mp 47.2—47.6°C), 1-*p*-acetylphenylpyrrole (Ref. 12,*4 mp 120.0—121.0°C), 1-*t*-butylpyrrole (Ref. 13,*4 bp 65°C/38.5 mm-

9) T. L. Cairno, R. A. Carboni and D. D. Coffman, *J. Am. Chem. Soc.*, **80**, 2775 (1958).
10) A. J. Castro, J. F. Deck, M. T. Hugo, E. J. Lowe, J. P. Marsh, Jr., and R. J. Pfeifer, *J. Org. Chem.*, **20**, 668 (1955).
11) L. Knorr, *Ann.*, **236**, 290 (1886).
12) R. A. Jones, *Aust. J. Chem.*, **19**, 289 (1966).
13) The oral report by Altmann as quoted by L. Leichtenstein (*Ber.*, **14**, 933 (1881)).
*4 The materials used in the present syntheses are different from those in the references. The method, however, are essentially the same except for a little modification.

Hg), 1-phenylpyrrole (Ref. 13, mp 58.1—58.3°C), 1-*p*-chlorophenylpyrrole (Ref. 13,[*4] mp 87.9—88.3°C), 1-*p*-tolylpyrrole (Ref. 13, mp 82.2—82.7°C) and 1-*p*-anisylpyrrole (Ref. 13,[*4] mp 111.0—111.5°C). The synthesis of 3-methylpyrrole was accomplished by the alkali fusion of 3,5-dicarbethoxy-4-methyl-2-pyrrolecarboxylic acid, bp 76°C/53 mmHg. The purities of the above synthesized materials were determined by means of elementary analyses, NMR spectra and gas chromatography, where possible.