UDC 547.74/.75 : 543.422.4

54. **Yuichi Kanaoka, Yoshio Ban, Takeshi Oishi, Osamu Yonemitsu, Masanao Terashima, Tetsuo Kimura, and Masako Nakagawa**: Infrared Spectra of Some Indole and Pyrrole Compounds.[*2]

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Although a large number of papers contain the data of infrared spectra of indoles,[1a~z] only few systematic studies have been published so far.[2] Investigation of indole series[3] made it necessary to prepare many indole compounds and examine their infrared spectra. This paper describes the results thus obtained and associated spectral data on some related methylpyrroles.

I. The NH Region

Witkop[1b] observed the NH absorption of indole compounds in the range of 3472~3378 cm^{-1}. A review of reported data on methyl derivatives of indole[4] also showed that they appeared within the range of 3450 to 3375 cm^{-1} as strong and sharp bands.

In Table I are given the results obtained with indole compounds possessing a basic nitrogen atom. In the case of (II), (III), (VII), and (VIII), the bands near 3400 cm^{-1} were very weak or merely formed shoulders. These changes in the intensity and position of the NH band are ascribed to the intermolecular association. In the case of tertiary amines such as (IX) and (X), however, strong and sharp NH bands occurred which indicated that association was hindered by the sterical requirement of the annular nitrogen atom. The data taken from the literature[5] also agreed with this observation.

Whenever NH vibrations were masked by association in the solid phase, it was invariably possible to detect the unassociated NH vibration band at about 3490 cm^{-1}[6] in

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[*2] Presented at the 1st Hokkaido Local Meeting of the Pharmaceutical Society of Japan, July 20, 1958.

1) *a*) H. R. Snyder, E. L. Eliel: J. Am. Chem. Soc., **70**, 1857(1948). *b*) B. Witkop, *et al.*: *Ibid.*, **72**, 614, 619(1950); **73**, 1558, 2188(1951). *c*) J. B. Brown, H. B. Henbest, E. R. H. Jones: J. Chem. Soc., **1952**, 3174. *d*) T. A. Geisman, A. Armen: J. Am. Chem. Soc., **74**, 3916(1952). *e*) P. Mirone, M. Vampiri: Atti accad. nazl. Lincei, **12**, 405(1952). *f*) N. Neuss, H. E. Boaz, J. W. Forbes: J. Am. Chem. Soc., **76**, 2463(1954), **77**, 4087(1955). *g*) R. Goutarel, M. M. Janot, A. Le Hir, H. Corrodi: Helv. Chim. Acta, **37**, 1085(1954). *h*) A. Hofmann, J. Kelbe: *Ibid.*, **37**, 849 (1954), **39**, 116(1956). *i*) A. Stoll, A. Hofmann, R. Brunner: *Ibid.*, **38**, 270(1955). *j*) A. Stoll, F. Troxler, J. Peyer, A. Hofmann: *Ibid.*, **38**, 1454(1955). *k*) R. J. Koegel, J. P. Greenstein, W. Winitz, S. M. Birnbaum, R. A. McCallum: J. Am. Chem. Soc., **77**, 5708(1955). *l*) W. R. Vaughan, G. K. Finch: J. Org. Chem., **21**, 1201(1956). *m*) J. S. Moffatt: J. Chem. Soc., **1957**, 1442. *n*) J. A. Ballantine, C. B. Barret, R. J. S. Beer, B. G. Boggiano, S. Eardley, B. E. Jennings, A. Robinson: *Ibid.*, **1957**, 2227. *o*) J. M. Bruce, F. K. Sutcliffe: *Ibid.*, **1957**, 4789. *p*) R. B. Carlin: J. Am. Chem. Soc., **79**, 934(1957). *q*) C. Djerassi, J. Fishman, M. Gorman, J. P. Kutney, S. C. Pakarashi: *Ibid.*, **79**, 1217(1957). *r*) M. W. Klohs, F. Keller, R. E. Williams, G. W. Kusserow: *Ibid.*, **79**, 3763(1957). *s*) W. Schindler: Helv. Chim. Acta, **40**, 1130(1957). *t*) J. Schmutz, F. Hunziker, R. Hirt: *Ibid.*, **40**, 1189(1957). *u*) A. Hofmann, R. Brunner, H. Kobel, A. Brack: *Ibid.*, **40**, 1358(1957). *v*) F. Troxler, A. Hofmann: *Ibid.*, **40**, 1706, 1721, 2160(1957). *w*) C. Vamvacas, W. Philipsborn, E. Schlittler, H. Schmidt, P. Karrer: *Ibid.*, **40**, 1793(1957). *x*) D. Stauffacher, E. Seebeck: *Ibid.*, **41**, 169(1958). *y*) J. Schmutz, F. Hunziker: *Ibid.*, **43**, 288(1958). *z*) F. Millich, E. I. Becker: J. Org. Chem., **23**, 1096(1958).

2) After this work had been presented, a leading reference was published. A. Fujino, M. Yamaguchi: Kagaku-no-Ryoiki, Supplement No. 32, 78(1958). Nankodo, Tokyo.

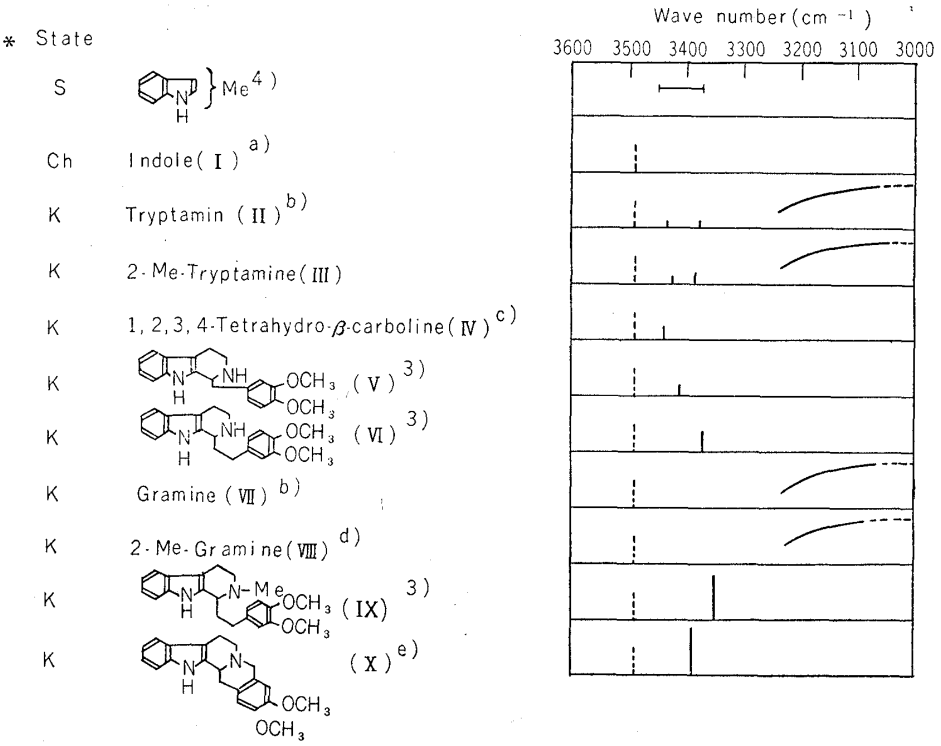
3) Y. Kanaoka: This Bulletin, **7**, 597(1959); Y. Ban, T. Oishi: Unpublished data.

4) D. M. S. Nos. 147~149, 547, 549, 1231~1233.

5) D. M. S. Nos. 197, 198, 992.

6) N. Fuson, M. L. Josien, R. L. Powel, E. Utterback: J. Chem. Phys., **20**, 145(1952).

Table I. The NH Region of Indole Amines



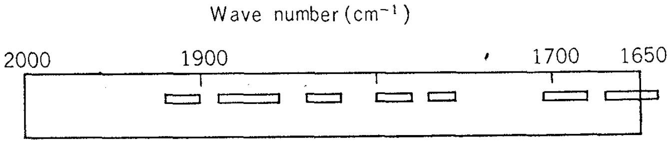
a) Commercially available.
b) J. Thesing, F. Schülde: Chem. Ber., **85**, 324(1952).
c) E. Späth: Ber., **63**, 2102(1930).
d) H. N. Rydon: J. Chem. Soc., **1948**, 708.
e) K. T. Potts, R. Robinson: *Ibid.*, **1955**, 2675.
* S: solid; Ch: chloroform solution; K: potassium bormide.

diluted carbon tetrachloride or chloroform solution. An attempt to correlate the associated NH vibration in solution to that in the solid state by increasing the concentration of solution failed owing to the limited solubility of these indole compounds in usual organic solvents. Salts of these indole amines exhibited the NH band in the wide range of 3400~3100 cm^{-1}, the intensity varied widely, and they were accompanied by salt bands.7) The interpretation of spectra in the solid state is thus rather difficult.

II. Region of 2000~1650 cm^{-1}

In this region there were usually observed a group of seven very weak combination or overtone vibrations,8) the patterns of which are not yet correlated to the mode of ring substitution (Table II). Of these, the bands near 1700 and 1650 cm^{-1} are often relatively stronger than others.

Table II. Region of 2000~1650 cm^{-1}



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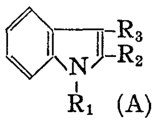
7) K. Nakanishi, T. Goto, M. Ohashi: Bull. Chem. Soc. Japan, **30**, 403(1957).
8) L. J. Bellamy: "The Infra-red Spectra of Complex Molecules," 67 (1958). Methuen & Co., London.

Table III. Infrared Absorptions of Aliphatic Derivatives of Indole[f]



(A)

Compd. No.	R_1	R_2	R_3	Region of 1650~900 cm^{-1}							
				1625~1615	1600~1575	1565~1540	1520~1470	1350	1250	1010	920
(I)	H	H	H	1614w	1578 v w		1503 v w 1487 v w	1361m 1347m	1250m	1007w 1002w	931w
(XI)[a,g]	Me	〃	〃	1615w	1576 v w		1515 s 1480m	1340 s	1246 s	1010m	924 v w
(XII)[b]	H	Me	〃	1621m	1598m	1552 s	1490w	1355 s	1240m	1008m 995w	926m
(VII)	〃	H	CH_2NMe_2	1618 v w	1592 v w	1550w	1503 v w	1362m 1350w	1254w 1244 s	1007w 993 s	922 v w
(VIII)	〃	Me	〃	1620w	1589 v w	1563w	1503w	1355m	1254w 1240m	1005m 999 s	920 v w
(XIII)[c]	〃	H	CH_2NMe_3	1615 v w	1580 v w	1535w	1494m	1353w	1255 s	1002 s 990m	923 v w
(XIV)[c]	〃	〃	CH_2CN	1623m	1599w 1587w	1560w	1495w	1367 s 1351 s	1260w 1232m	1010m	928w 922w
(XV)[24]	〃	Me	〃	1621w	1593 v w 1571 v w		1464 s	1351w	1253w	1015w 1004w	918w
(II)[c]	〃	H	$CH_2CH_2NH_2$	1619m	1603w 1592m 1581w	1560w	1502w 1490w	1352 s	1238m	1005 s	934 s
(III)	〃	Me	〃	1620m	1592m 1579m		1507m	1353m	1240m	1013m 1007m 988m	913 s
(XVI)[25]	〃	〃	CH_2COOH	1623w	1595w		1487 v w	1352m 1339m	1238 s	1000w	927m
(XVII)[d]	〃	$-(CH_2)_4-$		1615w	1588w	1563 v w		1369m	1235m	1005w	917w
(IV)	〃	$-(CH_2)_2NHCH_2-$		1616m	1578w	1560 v w 1540 v w	1485m	1345m	1240w	1012w	918w
(XVIII)[e]	〃	$-(CH_2)_2-NHCH_2-$ HCl		1618m	1585m	1550 v w	1485m	1354 s		1010w	

a) E. Fischer: Ann., **236**, 198(1886); Ber., **17**, 559(1884). This was prepared by Mr. T. Takeda in this laboratory.
b) H. M. Kissman, *et al.*: J. Am. Chem. Soc., **74**, 3948(1952).
c) J. Thesing, F. Schülde: Ber., **85**, 324(1952).
d) Org. Syntheses, **30**, 90.
e) E. Späth: Ber., **63**, 2102(1930).
f) KBr tablet, unless otherwise noted.
g) Liquid.
s: strong; m: medium; w: weak; v: very.

III. Region of 1650～1000 cm^{-1}

a) Aromatic Bands: Witkop⁹⁾ suggested that bands near 1600 cm^{-1} were characteristic of indole compounds. Houff, *et al.*¹⁰⁾ and Szmuszkoviz¹¹⁾ pointed out that several bands below 1620 cm^{-1} were due to C=C stretching vibrations, while Quilico¹²⁾ reported that three bands near 1605, 1570, and 1400 cm^{-1} originated from vibration of the phenyl ring of indoles. In Table III are given bands of aliphatic derivatives of indole having no polar substituents directly attached to the ring. There occurred almost invariably four groups of medium to weak bands at about 1625～1615, 1600～1575, 1565～1540, and 1520～1470 cm^{-1}, which were regarded as the indole aromatic bands. Common bands near 1380 cm^{-1} due to the usual methyl or methylene deformation vibration were excluded.

These aromatic bands vary in their intensity; the position of the band with the highest frequency (near 1615 cm^{-1}) was almost constant and, although the intensity was weak, it could be detected almost invariably.*[3] Even when a molecule has another phenyl group, it may be found as a shoulder of the 1600 cm^{-1} phenyl band. These aromatic bands are also present in the published spectra of the methyl derivatives of indole.(13) Of these, the third band varies the most and is sometimes lost. These behaviors of aromatic bands of indole derivatives are diagnostic to some extent.

b) Region of 1400～900 cm^{-1}: Quilico(12) assigned the bands at 1300 and 1250 cm^{-1}, and at 1170 and 1040 cm^{-1} respectively to C–N vibration and ring vibration. As shown in Table III, the majority of aliphatic derivatives exhibited five common bands at about 1350, 1250, 1010, and 920 cm^{-1}.

These bands are likely to be characteristic of the indole ring and probably arise from the C–N skeletal vibration and N–H in-plane bending vibration, but further studies are required.

IV. Region of 900～700 cm^{-1}

It is well known that indole compounds with no substituent in the benzene ring show a very strong band in the region of about 750 cm^{-1}.(14～16) These bands were assigned to the out-of-plane CH bending vibration of the benzene hydrogens and the frequency range agrees well with that of *ortho*-disubstituted benzene.(17)

In view of the fact that the correlation rule for the out-of-plane CH bending vibration in benzene ring holds for heterocyclic ring systems,(18) the pyrrole moiety of indole derivatives were now taken into consideration and examined. Leete and Marion(14) tentatively assigned the weak absorption at 757 cm^{-1} of skatole to the out-of-plane bending vibration of the hydrogen atom attached to the 2-carbon atom (indicated hereafter as C^2–H) and this is the only description which has appeared to date in connection with this view point.

Many indole derivatives show one or more absorptions of strong or medium intensity in the range of 900～700 cm^{-1}.

Meanwhile, indoles in which both hydrogen atoms attached to the carbon-2 and -3 (indicated as C^2–H and C^3–H, respectively) were substituted with aliphatic groups exhibited

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*[3] The enhancement of this first aromatic band by ring substitution will be discussed later in (2).

9) B. Witkop: J. Am. Chem. Soc., **79**, 3193(1957).

10) W. H. Houff, O. N. Hinsvark, H. M. Sell, L. E. Weller, S. H. Wiffer: *Ibid.*, **76**, 5654(1954).

11) J. Szmuszkoviz: *Ibid.*, **79**, 2819(1957).

12) A. Quilico, C. Cardani, F. Piozzi: Gazz. chim. ital., **85**, 3(1955).

13) D. M. S. Nos. 147, 149, 546～550, 1231～1233.

14) E. Leete, L. Marion: Can. J. Chem., **31**, 778(1953).

15) E. M. Tanner: Spectrochim. Acta, 282(1957).

16) D. M. S. Nos. 547, 550.

17) L. J. Bellamy: *loc. cit.*, p. 77.

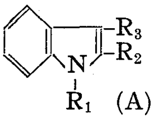
18) H. Shindo, N. Ikekawa: This Bulletin, **4**, 192(1956).

only one strong absorption in the range of 738~740 cm^{-1}. This is exemplified by tetrahydrocarbazole (XVII), tetrahydrocarboline (IV), and 2,3-dimethylindole (Table V).

It may be assumed that the benzene and pyrrole parts in indole compounds exhibit their CH bending vibrations independently, since in these molecules, couplings are expected to occur only between nearby CH groups, i.e., those located on the same ring of the molecule.[19,20] From the above observations and assumption, one may expect that the bands in the 850~700 cm^{-1} region, excluding the strong band of a phenyl ring at 745 cm^{-1}, are due to the CH bending vibration of the pyrrole moiety.

a) C^2-H Out-of-plane bending vibration : The absorption of five pairs (a~e) in the 850~700 cm^{-1} region is compared in Table IV. In each pair, the latter is substituted at C-2 with a methyl group, while the former is unsubstituted. As shown in Table IV, it is observed in most cases (a, b, c, e) that the peak near 800 or 760 cm^{-1} practically disappears in going from the C-2-unsubstituted indole (A : R_2=H) to the substituted indole (A: R_2=Me). In the case of (d), however, both exhibit one absorption (XIV, 773m; XV, 768m) and masking of the C-2 with a methyl produced no clear-cut change in this region.

TABLE IV. C^2-H and C^3-H Out-of-plane Bending Vibrations**


(A)

		R_1	R_2	R_3	Wave number (cm^{-1})			
a	(XXI)[a]	H	H	Me	847 v w	797 s *	760 sh*	743 v s
	(XIX)[b]	〃	Me	〃	845 v w	—	—	740 v s
b	(XXII)[c]	Et	H	〃	841 v w	798m* 789 v w	753 sh*	738 v s
	(XX)[d]	Et	Me	〃	840 v w	806 v w 789 v w	770 v w	738 v s
c	(VII)	H	H	CH_2NMe_2	827 s	778m*	762 w*	747 v s
	(VIII)	〃	Me	〃	843 s	784 v w	—	745 v s
d	(XIV)	〃	H	CH_2CN	850 w	810 w 788 v w	773m	747 v s
	(XV)	〃	Me	〃	840 v w	—	768m	752 v s
e	(II)	〃	H	$CH_2CH_2NH_2$	830 v w	809m* 805m*	755 sh*	747 v s
	(III)	〃	Me	〃	827 w	—	—	743 s 737 s
f	(XII)	〃	〃	H		787 v s *		753 s 747 sh 738 v s
	(XIX)	〃	〃	Me	845 v w	—		740 v s
g	(XXIII)[e]	Me	〃	H	841 w	770 s *		747 v s 733m
	(XX)	Et	〃	Me	840 v w	789 w 770 w		738 v s
h	(XXIV)[f]	H	〃	H 7-Me		792 v s		745 v s
	(XXV)[g]	〃	〃	Me 7-Me		798 sh 787 sh 777 s		745 v s
i	(XXVI)[h]	〃	〃	H 5,7-diMe	845 s	777m*		748 s
	(XXVII)[i]	Me	〃	Me 5,7-diMe	836 s	804 w		754 s

a) D. M. S. 1232. *b*) D. M. S. 547. *c*) D. M. S. 548. *d*) D. M. S. 550. *e*) D. M. S. 546.
f) D. M. S. 147. *g*) D. M. S. 549. *h*) D. M. S. 148. *i*) D. M. S. 1234.
* Band assigned. ** Potassium bromide. sh : shoulder.

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[19] M. P. Groenewege : Spectrochim. Acta, Suppl., 579(1957).

[20] T. Shimanouchi, Y. Kakiuchi, K. Gamoh : J. Chem. Phys., **25**, 1245(1956).

Both groups of bands are here assigned to the C^2–H bending vibration and the rather broad range from 810 to 760 cm^{-1} is indicated for them.

b) C^3–H Out-of-plane bending region : The comparison of four pairs (f～i) in the 850～700 cm^{-1} region is given in Table IV. In each pair, the former is unsubstituted at C^3–H (R$_3$=H) while the latter is substituted by a methyl group (R$_3$=Me). Provided that one or two strong bands[21] near 740 cm^{-1} are regarded as bands related to the benzene part, it is found that one strong band in the range between 785 and 770 cm^{-1} in the former member of each pair (f, g) is absent in the latter. In (h), no marked change was caused by the masking of C^3–H, and the band near 750～740 cm^{-1} in (i) made the interpretation obscure. From the result based on a rather limited number of compounds, the bands in the region of 785～770 cm^{-1} are tentatively assigned to the C^3–H vibration. Since the ranges assigned to the C^2–H and C^3–H bending vibration overlap with each other, they are of little diagnostic value for the substitution mode on the pyrrole part of indole compounds.

c) C^2–H and C^3–H Out-of-plane bending region : As shown in Table V, indole (I) and 1-methylindole (XI) have three peaks, while 2,3-disubstituted indoles (XIX, XX, XVII, IV) have only one strong peak. If the strong benzene band near 740 cm^{-1} is excluded, the bands in the range of 725～710 cm^{-1} remains to be assigned tentatively to the two adjacent hydrogen atoms (C^2–H, C^3–H) on the pyrrole ring. However, an examination of a larger number of compounds is necessary to confirm this.

TABLE V. Infrared Absorptions of 2,3-Disubstituted Compounds (in KBr)

	Wave number (cm^{-1})			
Indole (I)		767 m	748 v s	726 s *
1-Methylindole (XI)	842 v w	763 m	740 v s	712 s *
2,3-Dimethylindole (XIX)	845 v w	—	740 v s	—
1-Ethyl-2,3-dimethylindole (XX)	840 v w	770 w	738 v s	—
1,2,3,4-Tetrahydrocarbazole (XVII)		756 v w	741 v s	722 v w
1,2,3,4-Tetrahydro-β-carboline (IV)		795 v w	741 v s	—

V. CH Out-of-plane Bending Vibration of Some Methylpyrrole Compounds

The infrared spectra and Raman effect of pyrrole compounds have been studied by Bonino[22a] and many workers.[22b～u]

Lord has analyzed the fundamental vibrations of pyrrole and deuterium derivatives with the aid of Raman spectra[22c] and his results were later supported by Lecomte[22d] and Mirone.[22k]

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[21] T. Shimanouchi : Kagaku-no-Ryoiki, **12**, 314(1958).

[22] *a*) G.B. Bonino : Atti del II Congr. Internaz. de Chimica, **2**, 141(1938) [C.A., **33**, 7195(1939)]; G.B. Bonino, R. Manzoni-Ansidei, P. Pratesi : Z. physik. Chem., B., **22**, 21(1933), etc. *b*) A. Fujino, M. Yamaguchi : Kagaku-no-Ryoiki, Suppl. No. 32, 74(1958). *c*) R.C. Lord, F.A. Miller: J. Chem. Phys., **10**, 328(1942). *d*) J. Lecomte : Bull. soc. chim. France, **1946**, 415. *e*) H. Randall, R.G. Fowler, N. Fuson : "Infrared Determination of Organic Structures," New York(1949). *f*) P. Mirone : Atti accad. naz. Lincei, **11**, 365(1951). *g*) P. Mirone, A.M. Drusiani : *Ibid.*, **16**, 69(1954). *h*) P. Chiorboli : Gazz. chim. ital., **84**, 269(1954). *i*) P. Tuomikoski : J. phys. radium, **15**, 318(1954) [C.A., **48**, 9196]. *j*) W. Otting : Chem. Ber., **89**, 1940(1956). *k*) P. Mirone : Gazz. chim. ital., **86**, 165, 1079(1956) [C.A., **50**, 16388(1956)]. *l*) P. Mirone, A.M. Drusiani, V. Lorenzelli : Ann. Chim. (Rome), **46**, 1217(1956) [C.A., **51**, 7149(1957)]. *m*) J.M. Lebas, M.J. Josien: Bull. soc. chim. France, **1957**, 251. *n*) H.A. Staab : Chem. Ber., **90**, 1320(1957). *o*) M. Yamaguchi : Nippon Kagaku Zasshi, **78**, 1236(1957). *p*) M. Scrocco : Atti accad. naz. Lincei, **22**, 500 (1957). *q*) P. Mirone : Ann. Chim.(Rome), **48**, 72(1958). *r*) U. Eisner, R.L. Erskine : J. Chem. Soc., **1958**, 971. *s*) S.F. Mason : *Ibid.*, **1958**, 976. *t*) M. Yamaguchi : Bunseki Kagaku, **7**, 210 (1958). *u*) P.A. Cantor, C.A. Vanderwerf : J. Am. Chem. Soc., **80**, 970(1958).

However, little is known of the CH out-of-plane bending vibration of pyrrole derivatives and the only reference to this problem is the one by Mirone[22a] who reported that some bands in the range of 770~740 cm^{-1} could be assigned to the CH out-of-plane vibration in 2-formyl- and 1-methyl-2-formyl-pyrrole.

In an attempt to correlate the CH out-of-plane vibration of pyrroles to that of the pyrrole moiety of the indole ring, some methyl derivatives of pyrroles were prepared and their infrared spetra examined.

Dimethyl- and trimethyl-pyrroles (XXVIII, XXIX, XXX) showed a very strong band in the range of 900~700 cm^{-1}, which was lacking in tetramethylpyrrole (XXXI). This band is now assigned to the annular CH out-of-plane bending vibration on account of its marked intensity and frequency range, and this interpretation was further confirmed by the fact that tetramethylpyrrole (XXXI) did not show any strong band in this region. The possibility that the band is due to an N-H out-of-plane bending vibration is unlikely since Lord reported that in pyrrole itself this vibration occurred in a far lower frequency.[22c]

These results show that the correlation rule holds also for pyrrole compounds. The bands, however, occur at frequencies slightly lower than those of benzene derivatives. There is some coincidence between those observed in pyrrole compounds and those observed in the pyrrole part of corresponding indole rings as shown in Table VI (XXVIII and XXXII; XXX and XXXIV). In the case of (XXIX) and (XXXIII), the frequency ranges differ and this may be due to the effect of the benzene ring in the indole group.

TABLE VI. CH Out-of-plane Bending Vibration of Methylpyrroles
(taken as a liquid)

	Wave number (cm^{-1})		
2,3-Dimethylpyrrole (XXVIII)	836 m	780 v w	715 v s [a]
2,3,4-Trimethylpyrrole (XXIX)			728 v s [a]
2,4,5-Trimethylpyrrole (XXX)		787 v s [a]	
2,3,4,5-Tetramethylpyrrole (XXXI)		745 v w	725 v w
2,3-Unsubstituted indole (XXXII)		725~710[b]	
2-Unsubstituted indole (XXXIII)		810~760[b]	
3-Unsubstituted indole (XXXIV)		785~770[b]	

a) Band assigned. *b*) Region assigned.

Experimental

Spectral Measurement—Infrared absorption spectra in the range of 3600~700 cm^{-1} were determined by the Koken Model DS-301, equipped with NaCl optics. Samples were measured in KBr disks or as Nujol mull. Unassociated NH absorption of free bases were measured in CCl_4 or $CHCl_3$ solution (concentration × path-length, ca. 0.01~0.001 mol./cm.).

Materials—Compounds were synthesized as described in the literature unless otherwise specified.

2-Methyltryptamine (III)—(III) was prepared by the reduction of 3-(2-methylindolyl)acetonitrile[23] as described by Hoshino, *et al.*,[24] and also by catalytic reduction at 90 atms. and room temperature over Raney Ni in MeOH saturated with NH_3. Though the m.p. of the free base was different from that reported,[24] its validity was established by microanalysis, m.p. of its salts, and direct comparison with a specimen prepared through another route.[*4] Free base: Colorless prisms, m.p. 87°. *Anal.* Calcd. for $C_{11}H_{14}N_2$: C, 75.86; H, 8.05; N, 16.09. Found: C, 75.8; H, 8.5; N, 15.8. Picrate: Orange needles, m.p. 217°. *Anal.* Calcd. for $C_{17}H_{17}O_7N_5$: C, 50.62; H, 4.21; N, 17.36. C, 50.4; H, 4.5; N, 17.1.

[*4] A sample was kindly supplied by Dr. Noland. [cf. W. E. Noland, R. F. Lange: J. Am. Chem. Soc., **81**, 1203(1959)]. The picrate was obtained as red needles (from ether), m.p. 218~219°, or orange needles (from EtOH) of m.p. 217°. The former sample was shown to be identical with the above specimen by mixed m.p. and infrared spectral comparison; the latter had a different infrared spectrum, probably arising from dimorphism.

23) J. H. Gaddum, *et al.*: Quart. J. Exptl. Physiol., **40**, 49(1955).

24) T. Hoshino, K. Tamura: Ann., **500**, 42(1933).

Hydrochloride : Colorless needles, m.p. 193~194°. *Anal.* Calcd. for $C_{11}H_{15}N_2Cl$: C, 62.71; H, 7.12; N, 13.30. Found : C, 62.8; H, 7.45; N, 13.2.

The m.p. of (III) and its salts are given in Table VII.

TABLE VII. Melting Points of (III) and its Salts

	m.p. (°C)			
	Free base	Picrate	Hydrochloride	Acetate
Hoshino, *et al.*[24]	107~108	218~219	194~195	158~159
The present preparation	87 ($b.p_{0.04\sim0.05}$ 133~135)	218~219 (red needles)	193~194	158
Noland, *et al.*[25]	—	218~219	—	—

Methyl-substituted Pyrroles—(XXVIII) was prepared by Fischer's method.[25] (XXIX) and (XXXI) were prepared by the method of Treibs, *et al.*[26] 2,4,5-Trimethylpyrrole (XXX) was obtained by a similar method, in which 2,5-dimethyl-4-ethoxycarbonylpyrrole[27] was reduced with $LiAlH_4$ in dehyd. Et_2O. Slightly colored oil, $b.p_{12}$ 77° (reported $b.p_{14\sim15}$ 75~76°[29]). These pyrroles were unstable in air.

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Summary

Infrared spectra of a number of indole compounds have been examined and the characteristic frequencies of indole group are given. The CH out-of-plane bending vibration of the pyrrole moiety of the indole ring and related methylpyrroles are discussed.

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25) H. Fischer, E. Fink : Z. physiol. Chem., **283**, 152(1948).
26) A. Treibs, H. Derra-Scherer : Ann., **589**, 188(1954).
27) N. Sugimoto : Yakugaku Zasshi, **64**, 192(1944).
28) G. Korschun : Ber., **38**, 1129(1905).