

195. The Light Absorption of Pyrroles. Part II.* Infrared Spectra.

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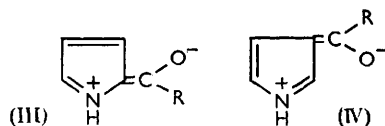
The infrared spectra of a number of pyrroles have been measured. The relation between structure and N-H and C=O frequencies is discussed. A band in the 1470—1600 cm^{-1} region, present in all the pyrroles examined, is assigned to bond-stretching vibrations of the ring.

THE infrared and Raman spectra of substituted pyrroles show some anomalies, particularly a lowering of the C=O stretching frequency in carbonyl-substituted pyrroles. Although data for a number of pyrroles have been recorded¹⁻⁹ comparatively little has been done to interpret the results and establish correlations. Since a number of pyrroles were available to us, their infrared spectra have been determined. The present work, however, is not a systematic study since there are not sufficient data for mono- and di-substituted derivatives.

The carbonyl-stretching frequency of $\alpha\beta$ -unsaturated β -amino-ketones (I) occurs at lower frequencies than that of ordinary $\alpha\beta$ -unsaturated ketones as the nitrogen atom



stabilises the dipolar form¹⁰ (II). Carbonyl-substituted pyrroles can also exist in dipolar forms (III, IV) which shift the carbonyl band to lower frequencies, 2- and 3-carbonyl



substituents being similarly affected. The hydrogen atom on the nitrogen is not essential for this perturbation^{1,4,7,10} and this has been confirmed in our work, since the 1-methylpyrrole (17 †) has the same carbonyl-stretching frequency as the 1-unsubstituted analogue (16). Intramolecular hydrogen bonding is excluded in the 2-substituted compounds (see below).

Furan and thiophen derivatives containing carbonyl substituents show similar shifts^{3,11,12} which are less pronounced than those observed for the corresponding pyrroles.

* Part I, *J.*, 1958, 922.

† This and similar Arabic numbers in parentheses refer to the numbers in the Table.

¹ Ansidei, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1940, **11**, 669.

² Bonino and Chiorboli, *ibid.*, 1951, **10**, 104.

³ Chiorboli, *ibid.*, 1952, **12**, 92, 558.

⁴ Bonino and Mirone, *ibid.*, 1954, **17**, 167, 254.

⁵ Mirone, Drusiani, and Lorenzelli, *Ann. Chim. (Italy)*, 1956, **46**, 1217.

⁶ Nicolaus and Oriente, *Gazzetta*, 1954, **84**, 230.

⁷ Nicolaus and Mangoni, *ibid.*, 1955, **85**, 1378.

⁸ Scrocco and Nicolaus, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1956, **20**, 795.

⁹ *Idem*, *ibid.*, 1956, **21**, 103.

¹⁰ Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.

¹¹ Mirone, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **16**, 483.

¹² Chiorboli and Mirone, *ibid.*, p. 243.

The infrared measurements for chloroform solution and for the solid state are summarised in the Table. This shows separately the N-H bands, bands in the C=O stretching region and at 1600—1475 cm^{-1} , and other marked bands in the "finger-print" region. The apparent maximal extinction coefficients are given in parentheses for measurements on solutions representing intensities more accurately than the symbols s(strong), m(medium), and w(weak). The estimated error is about $\pm 5\%$, and all measurements were made from the 100% *T* line except for the "free" NH band where some attempt was made to cancel out the absorption due to the "bonded" NH band when this was present.

The solid-state spectra (paraffin mulls) showed a marked inconsistency between very similar compounds which must be due to the intermolecular bonding effects in the crystals. This was especially noticeable in the pairs (13) and (14), and (5) and (6), where the difference in structure was due only to the alkyl substituents. Consequently identification of these compounds from their solid-state spectra is not to be recommended and only solution spectra give consistent results.

The discussion of the spectra therefore concerns solution results unless otherwise indicated. Bands in the 3000—2775 and 1480—1330 cm^{-1} ranges are not quoted because they were masked by solvent bands in solution and by the C-H bands in paraffin. Similarly bands below 800 cm^{-1} for chloroform solution are not recorded owing to the absorption of the solvent.

The N-H Stretching Region.—In chloroform solution the N-H absorption appears as a sharp band in the range 3435—3400 cm^{-1} . The N-H stretching frequency of pyrrole itself in carbon tetrachloride is a little higher at 3488 cm^{-1} ; there appears to be a small solvent effect as this frequency is lowered by 13 cm^{-1} in chloroform solution. Since the N-H stretching frequency is not appreciably altered by the presence of 2-carbonyl substituents, intramolecular hydrogen bonding is ruled out and this absorption is therefore due to the "free" N-H group.

In the solid state the N-H stretching frequency occurs in a much wider range at lower frequencies, *viz.*, 3315—3085 cm^{-1} . There is no apparent relation between the position of this bonded N-H absorption and the chemical nature of the substituents, although large 2-substituents [cf. compounds (7), (13), (14), (22)] seem to hinder intermolecular hydrogen bonding of the N-H group, giving weak hydrogen bonds with higher frequencies, whereas stronger hydrogen bonds are formed when the 2-substituents are small [cf. (15), (12)].

Scrocco and Nicolaus⁹ have shown that there is a linear relationship between the $\text{p}K_a$ value of the pyrrole and the difference, $\Delta\nu$, in the frequency of the free and bonded N-H vibrations, both determined in solution. While we have not determined any $\text{p}K_a$ values, our $\Delta\nu$ values correspond in magnitude to those given by Scrocco and Nicolaus. In those spectra where the bonded N-H band was visible, the largest $\Delta\nu$ value was given by compound (37) with 210 cm^{-1} and the smallest by (3) with 115 cm^{-1} .

Our determinations were made with a rock-salt prism and the estimated error in frequency is about $\pm 10 \text{ cm}^{-1}$ so that the extent of the range of the N-H frequency, particularly in solution, is probably due to experimental error rather than to real differences in the positions of the N-H stretching frequencies. As a check on the accuracy of our results the N-H frequency of pyrrole was redetermined; it was found to be in excellent agreement with the results recorded by Fuson.¹³ A discrepancy was noted between our results and those of Scrocco and Nicolaus⁹ for pyrroles (16) and (31) even after corrections for solvent effect were made. Similarly our N-H frequencies were found to be lower than the values recorded by Mirone *et al.*⁵ for pyrroles (28), (29), and (31). Since the above workers used a lithium fluoride prism it is likely that the differences observed are due to this.

The Carbonyl Stretching Region.—A comparison of the solution and the solid-state spectra in the carbonyl-stretching region near 1670 cm^{-1} shows a marked dissimilarity in

¹³ Fuson, Josien, Powell, and Utterback, *J. Chem. Phys.*, 1952, **20**, 145.

the absorption. This is probably due to intermolecular N-H...O=C hydrogen bonding and consequently solid-state spectra do not give consistent results even among similar compounds as the carbonyl-stretching frequency depends on the packing and hydrogen bonding in the crystals. Mirone, Drusiani, and Lorenzelli⁵ have found similar inconsistencies in a series of substituted pyrrole aldehydes. The solution spectra give much more consistent results which will now be discussed.

The pyrrolic monoesters (4), (5), (6), and (10) have essentially the same carbonyl-stretching frequency irrespective of whether the ester group is in the 2- or 3-position. This indicates that the dipolar forms (III) and (IV) can be formed with equal ease, and hence that it is not possible to determine the position of a pyrrolic carbonyl substituent from the C=O stretching frequency. Similarly the C=O frequency of the 2-acetyl derivative (11) lies very close to that of the 3-acetylpyrrole (12). The ketones absorb at a frequency about 40 cm.⁻¹ lower than that of the esters, the shift being of the same order as that observed in normal ketones and esters.

Pyrroles carrying two ester groups, (13—17), give rise to one asymmetrical carbonyl-stretching band. This is probably due to the fact that the two ester groups absorb at frequencies very close to each other so that the bands are not resolved. As both the symmetrical 2 : 5-diester (13), (14), and the 3 : 4-diester (15) have asymmetric carbonyl bands, there must be weak mechanical interaction between the two vibrations rather than preferential perturbation of one of the ester groups which might be postulated, for example, with diethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate (16). Mechanical interaction would be strongest when the two ester groups are in adjacent positions in the ring and this is confirmed by our data, although the triester (30) appears to be abnormal in this respect.

The spectrum of one 1-substituted pyrrole (17) was recorded to confirm (cf. refs. 1, 4, 7) that the hydrogen attached to the nitrogen atom is not essential for the perturbation, and to rule out the possibility of hydrogen bonding between the N-H group and adjacent 2-carboxyl substituent. The carbonyl-stretching frequency of diethyl 1 : 2 : 4-trimethylpyrrole-3 : 5-dicarboxylate (17) is identical with that of diethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate (16).

Pyrroles (23—29), containing both ester and carbonyl groups, have a much more complex absorption, giving rise to two, and sometimes three or more, bands. Mirone *et al.*⁵ have differentiated four types of carbonyl frequencies in a series of pyrrolic ester-aldehydes in the solid state which are called "associated" and "unassociated" ester and aldehyde bands, but there is not sufficient evidence in our work for such a definitive assignment.

The dipyrrolymethanes (8) and (9) show the expected shift of the carbonyl band in solution, but in the solid state strong intermolecular hydrogen-bonding splits the bands into two sharp maxima at 1688, 1644 cm.⁻¹ and 1699, 1647 cm.⁻¹ respectively.

The pyrrolic nitriles (36—40) absorb normally and there appears to be no effect of the pyrrole ring on the stretching frequency of the C≡N group. This frequency at about 2230 cm.⁻¹ is comparable with the C≡N stretching frequency of benzonitrile¹⁴ also at 2230 cm.⁻¹.

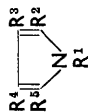
The effect of alkyl substituents on the C=O frequency has not been fully elucidated, chiefly owing to the lack of data. Mirone *et al.*⁵ found that, in the solid state, the C=O frequency is lowered by increasing alkyl-substitution. We have confirmed this effect in the case of the trisubstituted monoester (4) which absorbs at 1678 cm.⁻¹ and the tetrasubstituted monoesters (5) and (6) which absorb at 1669 cm.⁻¹ in chloroform. However, there is a slight increase in the C≡N band when going from the trisubstituted nitrile (36) (2229 cm.⁻¹) to the tetrasubstituted derivatives (37) and (38) which absorb at 2237 and 2234 cm.⁻¹ respectively.

The 1600—1470 cm.⁻¹ Region.—All the compounds which have been examined have absorption in the 1600—1470 cm.⁻¹ region which generally consists of two bands of variable intensity and position. In most cases, one band was near 1565 cm.⁻¹ and the other near

¹⁴ Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.

Infrared maxima (cm^{-1}) of pyrroles (C = in CHCl_3 , N = in Nujol)

No.	R ¹	R ²	R ³	R ⁴	R ⁵	N-H stretching	C=O stretching	1600—1475	Other bands
1	H	H	H	H	H	C 3475*	—	1564w 1516w	1070s 1035m 950w 891m 797m 778m
2	H	H	Et	Et	H	C 3370s ^b	—	1623m	1299m 1154w 1113m 1088m 1049m 985w 877w
3	H	H	Et	Et	H	C 3425m 3310m	—	1678(500)	1100(307) 1020(52) 1011(59) 928(62)
4	H	CO ₂ Et	Me	H	Me	C 3435(117) N 3251m	—	1575w 1545w 1495w	1269s 1215s 1101s 1025m 801s
5	H	CO ₂ Et	Me	Me	Me	C 3420(119) N 3241m	—	1669(456) 1668s	1323(106) 1110(260) 1065(161) 926(125) 1271s 1223m 1175m 1121m 1112m 1025m 773s 761s
6	H	CO ₂ Et	Et	Et	Me	C 3420(115) N 3448w 3273m	—	1576(55) 1493(171) 1496m	1120(284) 1095(149) 1083(218) 1022(189) 1277s 1259s 1170m 1122m 1098m 1029m 776m
7	H	CO ₂ Et	Me	Me	CH ₃ OMe	C 3257m	—	1545w 1497w*	1270s 1245s 1121s 1085s 1021m 951m 774m 740m
8	Substance A ^d	—	—	—	—	C 3415(125) 3290(63)	—	1600(71) 1580(71) 1493sh	1297(265) 1151(218) 1096(352) 1064(234) 941(71)
9	Substance B ^e	—	—	—	—	N 3315m	—	1581w 1501sh	1308s 1279s 1260s 1221s 1134s 1103m 768m 675w
10	H	Me	CO ₂ Et	Me	H	C 3420(125) 3268(14) N 3273m	—	1603(106) 1580(71) 1493sh	1299(310) 1152(267) 1111(297) 1072(356) 1017(115)
11	H	Ac	H	H	H	C 3420(122) 3236(22) N 3210m	—	1577w 1501sh	1302m 1280s 1254s 1224m 1139s 1110m 1083m 1019m 768m 723w
12	H	Me	Ac	Me	H	C 3435(80) 3250(43) N 3190m	—	1575(53) 1511(41)	1319(233) 1116(385) 1079(310)
13	H	CO ₂ Et	Me	Me	CO ₂ Et	C 3420(130) N 3450w 3250m	—	1580m 1521 } dbt w 1506 } 1506 }	1326m 1264s 1131s 1093s 1019m 788m 745m 733s
14	H	CO ₂ Me	Et	Et	CO ₂ Me	C 3425(137) N 3425w 3245m	—	1538(105) 1508(57) 1542m 1501w	1316(173) 1140(87) 1109(180) 1038(137) 925(56) 1140m 1127m 1042m 972m 926m 841m 773s 750s
15	H	H	CO ₂ Et	CO ₂ Et	H	C 3430(125) 3265(51)	—	1563(105) 1576w 1508w	1325(66) 1052(43) 941(123) 1239m 1071w 1021w 943m 752m
16	H	Me	CO ₂ Et	Me	CO ₂ Et	C 3420(116) 3265(20) N 3210m	—	1565(73) 1499sh 1564w 1505sh	1140(400) 1091(263) 1017(142) 1269s 1253s 1193m 1138m 1019m 783m
17	Me	Me	CO ₂ Et	Me	CO ₂ Et	C 3425(137) N 3425w 3245m	—	1560(134) 1546m	1143(335) 1087(246) 1062(83) 1016(61) 983(77) 1254s 1135m 1085m 982m 786s
18	H	CHCl ₃	CO ₂ Et	Me	CO ₂ Et	C 3430(125) 3265(51)	—	1519(152)	1326(279) 1286(635) 1175(302) 1134(231) 1058(538)
							—	1526m	1284s 1197m 1136m 1055s 813m 768s
							—	1572(164) 1504(155)	1111(208) 1085(452) 1073(445) 1018(87)
							—	1570w 1506w	1260s 1195s 1086s 1025m 893m 787m 773m
							—	1541(144) 1477(224)	1152(496) 1110(385) 1091(534) 1048(106)
							—	1635m 1483sh	1262s 1244s 1160m 1121m 1107m 1082m 786w
							—	1564(153) 1473(210)	1284(471) 1113(160) 1073(434) 1014(119)
							—	1718sh 1691(782)	



19	H	CO ₂ Et	CO ₂ Et	H	Me	N	3245m	1721s 1665s	1579w 1494m	1276s 1235m 1206s 1072s 1024m 850m 776m
20	H	CO ₂ Et	CO ₂ Et	Me	Me	N	3250m	1702m 1660s	1574w 1493w	1258s 1082m 1028m 790m 778m 731m
21	H	CO ₂ Et	CO ₂ Et	Br	Me	N	3210m	1733s 1681s	1574w 1528m	1275s 1238m 1207s 1079m 1053m 1025m 772s
22	H	Ac	H	H	Ac	C	3405(127)	1674(823) 1656sh	1529(90)	1078(67) 1050(100) 1020(32) 988(49) 921(80)
						N	3250m	1775w 1657sh 1644s	1523m	1259s 1241s 1066w 939m 891w 800m
23	H	f	H	H	CO ₂ Me	N	3250m	1732 } dbt s 1714 }	1537m	1311m 1222s 1062m 1054m 1003m 970m 882m 824m 796m 763s 725w
24	H	CHO	Et	Et	CO ₂ Et	C	3415(161)	1657s 1688(482) 1650(700)	1494w 1547(77)	1114(207) 1089(189) 1062(77) 1015(136) 960(34) 922(27)
25	H	Me	CHO	CO ₂ Et	Me	C	3415(113) 3220(37)	1688 } dbt s 1663 }	1547m 1477w	1256s 1133m 1024m 834m 756s
						N	3170w 3075m	1701s 1655w 1634s	1589m 1522m	1288(151) 1259(193) 1170(489) 1089(386) 1028(51)
26	H	Me	Ac	Me	CO ₂ Et	C	3430(136) 3245(36)	1770(6) 1704sh 1678(430) 1650(515)	1559(264) 1505(114) 1474(161)	1101(230) 1062(203) 1018(79) 947(142)
27	H	Me	Ac	Et	CO ₂ Et	N	3235m	1642s	1554m 1513m	1278s 1202s 1100m 1024m 942m 795m
						C	3430(127) 3250(29)	1704sh 1680(429) 1652(586)	1553(189) 1496(100) 1473sh	1276(346) 1105(170) 1072(146) 1052(127) 1018(105) 951(103)
28	H	Me	CHO	Me	CO ₂ Et	N	3150m	1703s 1625s	1562m 1505m	1286s 1271s 1185s 1096s 1070s 1051s 723w
						C	3415(115) 3240(28)	1712sh 1666(930)	1567(294) 1506(130)	1253(509) 1095(183) 1019(74) 924(33)
29	H	CHO	Me	CO ₂ Et	Me	C	3415(93) 3210(53)	1667s 1697(444) 1642 } dbt (776)	1561m 1513m 1565(107) 1488(187)	1284s 1187m 1100m 1020m 793m 774m 1266(406) 1138(346) 1095(430) 882(40) 853(50)
30	H	CO ₂ Me	CO ₂ Et	Me	CO ₂ Et	N	3205m	1694m	1560m	1284s 1258s 1133s 1097s 887m 780m 768m 704m
31	H	CHO	CO ₂ Et	Me	CO ₂ Et	C	3400(116)	1701(886) 1664(486)	1563(168) 1492sh 1553(142) 1489sh	1284(665) 1069(406) 1015(137) 960(62) 854(62) 1123(145) 1071(464) 1013(96) 885(20) 858(49)
32	H	CO ₂ H	Et	Et	CO ₂ Et	N	3230m	1709sh 1692s	1552m	1260s 1136m 1086m 1018m 863w, 785m 768m
33	H	CO ₂ H	Et	Et	CO ₂ H	N	3185m 2645m ^φ	1697w 1667s	1552m	1284s 1260s 1151s 1019m 916w 786m 770m
34	H	CO ₂ H	Me	CO ₂ Et	Me	N	3420m 2600m ^φ 3240m 2654m ^φ	1672sh 1650s 1695sh 1667s	1550m 1512w 1554m 1507w	1272s 1192s 1061m 934m 788m 1292s 1264s 1217m 1129m 1078m 916w 782m 725s
35	H	CO ₂ Et	Me	CO ₂ H	Me	N	3225m 2605m ^φ	1656s (broad)	1552m 1507sh	1279s 1202s 1133m 1089s 1024m 928w 788m 780m 771m 736m
36	H	Me	CN	H	Me	C	3425(77) 3245(47) 2229(250) ^Δ	—	1600(46) 1515(31)	1309(24) 1146(26) 1133(28) 1005(12)
37	H	Me	CN	CN	Me	C	3405 3195 2237 ^Δ	—	1600 1542	Saturated solution 1284(300) 1139(366) 1095(308) 1015(41)
38	H	Me	CN	CO ₂ Et	Me	C	3405(65) 3205(75) 2234(198) ^Δ	1697(549)	1597(45) 1541(147)	1284(300) 1139(366) 1095(308) 1015(41)
39	H	Me	CN	CHO	Me	N	3160w 3115m 2220m ^Δ	1637 } dbt s 1623 }	1591m 1530m	1096w 936m 817m 723w 683w
40	H	Me	CN	:NOH	Me	N	3245sh 3145m 2220m ^Δ	1626m (C=N)	1586w 1522w	1088w 965m 909s 780m 747m 723w

^φ At 3488 in CCl₄. ^Δ Spectrum for liquid. ^ε CH₂-N < [CH₂]_n. ^δ Substance A, di-(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolyl)methane. ^ε Substance B, di-(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolyl)methane. ^ζ CO₂Me. ^η OH band. ^θ CN band. ^ι strong. ^κ medium. ^λ weak. ^μ shoulder. ^ν doublet.

1500 cm^{-1} . Pyrrole itself has absorption at 1575, 1561, and 1531 cm^{-1} which has been ascribed to the asymmetrical and symmetrical vibrations of the double bonds in the pyrrole ring.¹⁵ These vibrations would be expected to depend considerably on the substitution of functional groups which would affect the symmetry of the molecule, and hence the position and intensity of these bands. Although there appears to be no empirical relation between the positions of the bands and the substitution on the pyrrole ring, it seems that the band near 1565 cm^{-1} is most intense when the functional substitution is at positions 2 : 4 or 3 : 4, and weakest in the 2 : 5-disubstituted pyrroles. This might be expected from a consideration of the symmetry of these vibrations.

Cromwell *et al.*¹⁰ also found strong absorption in this region in $\alpha\beta$ -unsaturated β -amino-ketones which was ascribed to a modified C=C or C-N stretching vibration similar to the amide II band. However, the absorption bands of the carbonyl-substituted pyrroles are of only weak or medium intensity and so the assignment to a ring vibration, similar to that in pyrrole itself, is preferred.

Experimental.—The spectra were recorded on a Grubb-Parsons D.B.I. double-beam infrared spectrometer with sodium chloride optics. Solid-state spectra were determined as paraffin mulls and solution spectra in chloroform using solutions of concentration about 0.5% w/v in a 0.5 mm. cell.

The preparation of the pyrroles was described in Part I. In addition, the pyrrole (4) was prepared as in ref. 16 and the pyrroles (6) and (27) as in ref. 17.

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¹⁵ Mirone, *Gazzetta*, 1956, **86**, 165.

¹⁶ Eisner, Linstead, Parkes, and Stephen, *J.*, 1956, 1655.

¹⁷ Eisner, Lichtarowicz, and Linstead, *J.*, 1957, 733.
