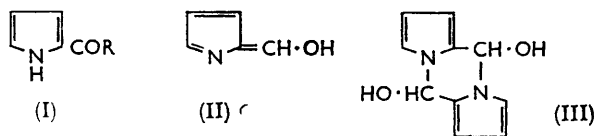


### 494. The Infrared Spectra and Structure of some 2-Acylpyrroles.

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The infrared spectra of simple 2-acylpyrroles in a wide range of solvents have been examined and are consistent with a polarised ketonic structure; but no equilibrium involving hemiacetal formation or keto-enol tautomerism has been detected spectroscopically. A series of *ortho*- and *para*-substituted 2-benzoylpyrroles have been prepared and shown to behave similarly. The steric requirements of 2-benzoylpyrrole and benzophenone are similar and lead to analogous spectroscopic effects.

THE reactivity of 2-acylpyrroles does not conform to the general pattern established for aromatic aldehydes and ketones. Thus pyrrole-2-aldehyde, unlike furfural, is stable to all but vigorous oxidation, to sodium hydroxide and to sodium cyanide; it gives condensation reactions only under forcing conditions.<sup>1</sup> To explain this behaviour it has been suggested that, *e.g.*, pyrrole-2-aldehyde (I; R = H) is better formulated as the enol<sup>2</sup> (II) or the dimer<sup>3</sup> (III); alternatively the abnormal reactivity has been ascribed to chel-



ation<sup>4</sup> and to the increased stability of the anion.<sup>5</sup> Similar structures have been advanced for other 2-acylpyrroles, but the properties of all these compounds are interpreted more convincingly in terms of the ready polarisability of the pyrrole ring. This receives support from the reactivity of 1-methylpyrrole-2-aldehyde which, contrary to earlier claims,<sup>2</sup> is similar to that of the unsubstituted aldehyde.<sup>6</sup>

More direct evidence for the structure of 2-acylpyrroles is provided by their infrared spectra. The spectra of 2-formyl-, 2-acetyl-, and 2-benzoyl-pyrrole, both as solids and as solutions in carbon tetrachloride, have been described by previous authors;<sup>7</sup> this work has now been extended to a wider range of solvents and concentrations in order to obtain a more comprehensive picture of the spectral and structural relationships among these compounds.

#### EXPERIMENTAL

Pyrrole-2-aldehyde was prepared by the action of dimethylformamide and phosphorus oxychloride on pyrrole.<sup>8</sup>

2-Acetyl- and 2-benzoyl-pyrrole were obtained by the action of pyrrolylmagnesium iodide on the acid chlorides. Similarly prepared were the following substituted pyrroles: 2-*o*-toluoyl-, m. p. 60—61° (from aqueous methanol) (Found: C, 77·8; H, 6·0. C<sub>12</sub>H<sub>11</sub>NO requires C, 77·7; H, 6·1%); 2-*p*-toluoyl-, m. p. 119° (from aqueous ethanol) (Found: C, 77·8; H, 5·8%); 2-*o*-anisoyl-, m. p. 131—132° (from aqueous ethanol) (Found: C, 71·5; H, 5·6; C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub> requires C, 71·6; H, 5·5%); 2-*p*-anisoyl-, m. p. 110—111° (from light petroleum) (Found: C,

<sup>1</sup> Fischer and Orth, "Die Chemie des Pyrrols," Akademische Verlagsgesellschaft, Leipzig, 1934, Vol. I, p. 150.

<sup>2</sup> Rastelli and Mingozzi, *Gazzetta*, 1925, **55**, 549.

<sup>3</sup> Emmert and Diehl, *Ber.*, 1931, **64**, 130.

<sup>4</sup> Scaramelli, *Ber.*, 1942, **B**, **75**, 1948.

<sup>5</sup> Treibs and Kolm, *Annalen*, 1957, **606**, 166.

<sup>6</sup> Herz and Brasch, *J. Org. Chem.*, 1958, **23**, 1513.

<sup>7</sup> Mirone, Drusiani, and Lorenzelli, *Ann. Chim. (Italy)*, 1956, **46**, 1217; Mirone and Lorenzelli, *ibid.*, 1958, **48**, 72, 881; 1959, **49**, 59; Scrocco, Caglioto, and Caglioto, *Atti Acad. naz. Lincei*, 1958, **24**, 316; Eisner and Erskine, *J.*, 1958, 971.

<sup>8</sup> Smith, *J.*, 1954, 3842.

71.5; H, 5.6%); 2-*o*-chlorobenzoyl-, m. p. 92—93° (from light petroleum) (Found: C, 64.2; H, 3.9.  $C_{11}H_8NOCl$  requires C, 64.2; H, 3.9%); 2-*p*-chlorobenzoyl-, m. p. 114—115° (from ethanol) (Found: C, 64.0; H, 3.9%); 2-*o*-nitrobenzoyl-, m. p. 145° (from methanol) (Found: C, 61.3; H, 3.9.  $C_{11}H_8N_2O_3$  requires C, 61.1; H, 3.7%); 2-*p*-nitrobenzoyl-, m. p. 160—161° (from aqueous ethanol) (Found: C, 61.3; H, 3.7%).

*o*-Nitrobenzophenone (35%), m. p. 102—103° (from ethanol), was prepared by the action of phenyl Grignard reagent on *o*-nitrobenzaldehyde and oxidation of the benzhydrol with aqueous potassium dichromate. Other substituted benzophenones were prepared by standard methods and showed the following characteristics: *o*-methyl-, b. p. 185°/25 mm.,  $n_D^{15}$  1.5974; *o*-methoxy-, b. p. 125°/0.3 mm., m. p. 35—36°; *p*-methoxy-, b. p. 150°/0.5 mm., m. p. 57° (from light petroleum); *o*-chloro-, b. p. 145°/2.5 mm., m. p. 45° (from light petroleum); *p*-chloro-, m. p. 78° (from light petroleum); *p*-nitro-, m. p. 138° (from ethanol).

Solvents were of spectroscopic grades or were purified by conventional means. Infrared spectra were measured on a Perkin-Elmer model 21 spectrometer with sodium chloride optics and cells of nominal thicknesses 0.1, 1.0, and 10 mm.; extinction coefficients are uncorrected empirical values; frequencies were calibrated against polystyrene. Ultraviolet spectra were measured for methanol solutions with a Cary 14 spectrometer.

## RESULTS AND DISCUSSION

*Simple 2-acylpyrroles.*—The suggested alternative structures for 2-acylpyrroles, *i.e.*, the enol (*e.g.*, II) or the dimeric hemiketal (*e.g.*, III), imply the existence of notional equilibria where the second component in each is the free or chelated 2-acylpyrrole (I). Further, 2-acylpyrroles may associate by the formation of intermolecular N—H····O=C hydrogen bonds. Consequently the most accessible spectral bands that can give useful structural information are those in the single-bond stretching region (N—H, O—H) and in the carbonyl region. In these regions the spectra of the solids contain single, broad bands, whereas those of solutions in non-polar solvents contain doublets (Tables 1 and 2). The relative intensity of the components of both doublets varies with concentration. At high dilutions the spectra

TABLE 1.

Effect of solvents on the amino stretching frequencies ( $cm^{-1}$ ) of 2-acylpyrroles.

Solvent	2-Formylpyrrole				2-Acetylpyrrole				2-Benzoylpyrrole			
	Free N—H band		Associated N—H band		Free N—H band		Associated N—H band		Free N—H band		Associated N—H band	
	$\nu$	$\epsilon^a$	$\nu$	$\epsilon^a$	$\nu$	$\epsilon^a$	$\nu$	$\epsilon^a$	$\nu$	$\epsilon^a$	$\nu$	$\epsilon^a$
$C_6H_{14}$	3470	60	3280	290	3470	80	3290	260	3470	70	3285	160
$C_2Cl_4$	3460	90	3275	200	3460	110 <sup>b</sup>	3290	150 <sup>b</sup>	3460	110	3280	80
$CCl_4$	3460	90	3280	150	3460	110	3290	100	3450	90 <sup>b</sup>	3285	100 <sup>b</sup>
$CS_2$	3450	90	3275	170	3450	100	3280	90	3450	90	3280	80
$CHCl_3$	3450	140	—	—	3450	150	—	—	3445	140	—	—
$CH_2Cl_2$	3450	150	—	—	3440	190	3280	—	3425	120 <sup>b</sup>	—	—
$MeNO_2$	3420	190	—	—	3420	100 <sup>d</sup>	—	—	3420	90 <sup>d</sup>	—	—
MeCN	3350	180	—	—	3360	90 <sup>d</sup>	—	—	3360	75	—	—
Dioxan	3230	150 <sup>c</sup>	—	—	3250	80 <sup>d</sup>	—	—	3250	120	—	—

*a*, extinction coefficient (=  $1 \log I_0/I$ ) for 0.01 molar solution unless otherwise stated; *b*, 0.02 molar; *c*, 0.05 molar; *d*, 0.1 molar.

show only the higher-frequency bands; the intensities of the lower-frequency bands increase smoothly with concentration (Table 3). This is consistent with an equilibrium of free and associated molecules (the lower-frequency bands of each doublet being assigned to the associated form), but it cannot be reconciled with the occurrence of significant amounts of dimeric hemiacetal (III), for then the intensity of both bands in the carbonyl region would vary inversely with concentration. Further, the one residual band in both single-bond and carbonyl stretching regions at high dilution indicates the absence of any

TABLE 2.

Effect of solvents on the carbonyl stretching frequencies (cm.<sup>-1</sup>) of 2-acylpyrroles.

Solvent	2-Formylpyrrole		2-Acetylpyrrole			2-Benzoylpyrrole *			2-Formyl-1-methylpyrrole
	Free C=O	Bonded C=O	Free C=O	Bonded C=O	Free C=O	Free C=O	Free C=O	Free C=O	
C <sub>6</sub> H <sub>14</sub>	1671	450	1659	1666	470	1646	1633	280 <sup>d</sup>	1676
Et <sub>3</sub> N	1671	980 <sup>c</sup>	—	1663	620	—	1631	460	—
C <sub>2</sub> Cl <sub>4</sub>	1668	600	1657	1661	530	1645	1629	390	1672
CCl <sub>4</sub>	1667	680	1657	1658	540 <sup>b</sup>	1645	1629	420 <sup>b</sup>	1672
CS <sub>2</sub>	1666	790	1657	1657	560	1644	—	—	1670
Dioxan	1663	950 <sup>c</sup>	—	1655	300 <sup>d</sup>	—	1625	—	1669
MeCN	1662	940	—	1654	500	—	1626	270 <sup>d</sup>	1668
Pyridine	1661	970 <sup>c</sup>	—	1650	480	—	1623	108 <sup>d</sup>	1666
MeNO <sub>2</sub>	1661	760 <sup>c</sup>	—	1648	384 <sup>c</sup>	—	1621	—	—
CH <sub>2</sub> Cl <sub>2</sub>	1659	850	—	1650	500 <sup>b</sup>	—	1620	380 <sup>b</sup>	1666
CHCl <sub>3</sub>	1658	770	—	1647	460	—	1615	390	1663
Pr <sup>n</sup> -OH	1655	615	—	1642	540	—	1613	315	1655
CHBr <sub>3</sub>	—	—	—	1641	—	—	1611	—	1660

\* The proximity of other strong bands did not allow satisfactory observation of the frequencies of the bonded carbonyl group.

*a*, extinction coefficient for 0.01 molar solution unless otherwise stated; *b*, molar; *c*, 0.05 molar; *d*, 0.1 molar.

TABLE 3.

Effect of concentration on intensity of the N-H stretching frequencies of carbon tetrachloride solutions of 2-acylpyrroles.

Concn. (g.-mol./l.)	2-Formylpyrrole				2-Acetylpyrrole				2-Benzoylpyrrole			
	Free N-H band		Associated N-H band		Free N-H band		Associated N-H band		Free N-H band		Associated N-H band	
	$\epsilon$	<i>t</i>	$\epsilon$	<i>t</i>	$\epsilon$	<i>t</i>	$\epsilon$	<i>t</i>	$\epsilon$	<i>t</i>	$\epsilon$	<i>t</i>
0.0005	150	4.5	—	—	160	4.8	—	—	150	4.9	—	—
0.005	120	3.6	90	6.1	130	3.9	60	4.1	130	3.9	50	3.7
0.01	90	2.7	150	10.5	110	3.3	100	6.8	—	—	—	—
0.02	—	—	—	—	120	3.8	150	10.2	90	2.2	100	7.0
0.05	50	1.5	190	14.2	—	—	—	—	—	—	—	—
0.1	—	—	—	—	50	1.5	180	12.2	60	1.8	190	14.2
0.2	30	0.9	300	21.0	50	1.4	240	16.1	50	1.4	250	18.7
0.4	20	0.7	280	21.6	40	1.4	280	20.4	—	—	—	—

$$\epsilon = \frac{1}{d} \log I_0/I. \quad t = 10^{-3} \Delta \nu \epsilon.$$

TABLE 4.

Infrared spectral data for solutions of substituted 2-benzoylpyrroles and benzophenones.

Solvent	2-Benzoylpyrroles				<i>m</i> <sub>C=O</sub>	Benzophenones	
	CCl <sub>4</sub>		CHCl <sub>3</sub>			CCl <sub>4</sub>	CHCl <sub>3</sub>
	$\nu_{N-H}$	$\nu_{C=O}$	$\nu_{N-H}$	$\nu_{C=O}$		$\nu_{C=O}$	$\nu_{C=O}$
Phenyl-substituent	cm. <sup>-1</sup>	cm. <sup>-1</sup>	cm. <sup>-1</sup>	cm. <sup>-1</sup>		cm. <sup>-1</sup>	cm. <sup>-1</sup>
H	3450	1629	3445	1615	0.74	1665 <sup>b</sup>	1657 <sup>b</sup>
<i>p</i> -Me	3460	1627	3450	1615	0.83	1664 <sup>b</sup>	1653 <sup>b</sup>
<i>p</i> -OMe	3450	1627	3450	1620	1.20	1658	1650
<i>p</i> -Cl	3445	1630	3440	1620	1.02	1666	1659
<i>p</i> -NO <sub>2</sub>	3450	1633	3445	1625	1.13	1673	1664
<i>o</i> -Me	3460	1632	3450	1620	0.83	1669	1662
<i>o</i> -OMe	3445	1640	3445	1621	0.61	1670	1663
<i>o</i> -Cl	3455	1643	3450	1625	0.61	1678	1668
<i>o</i> -NO <sub>2</sub>	3455	1646	3450	1632	0.64	1684	1676

*a*, Acetophenone as reference compound; *b*, Thompson, Needham, and Jameson, ref. 20.

effective keto-enol tautomerism in non-polar solvents. Since from bond-energy data<sup>9</sup> it appears that the enol (II) is destabilised by at least 7 kcal./mole relative to the keto form, it is probable that the only species present in significant amounts under these conditions is the acylpyrrole (I).

The relative intensities of the two bands, which can now be ascribed to the non-associated and associated N-H stretching frequencies, are markedly affected by the solvent, as also is the position of the higher-frequency (*i.e.*, non-associated) N-H band. As the displacement of this band relative to its position in hexane solution increases so also does its relative intensity, and in polar solvents only one band appears in the single-bond stretching region. The variation of frequency of the non-associated N-H band with solvent is similar to that observed with pyrrole,<sup>10</sup> and plots of these frequencies give excellent straight lines of the form:  $\nu_{\text{N-H}}(\text{pyrrole}) = m\nu_{\text{N-H}}(2\text{-acylpyrrole}) + d$ , where the gradient,  $m$ , of all three lines has the value 0.66. Consequently the non-associated N-H band must be ascribed to a free rather than to a chelated amino-group, for solvents affect the latter differently.<sup>12</sup> The excellent fit of the straight lines and the absence of any additional bands in this spectral region exclude the possibility of enolisation induced by solute-solvent interaction in the more polar solvents. The frequency of the associated N-H band, which can be ascribed to intermolecular hydrogen bonding is, in accordance with expectation,<sup>13</sup> less dependent on solvent, although the range of solvents in which it has been studied is small.

The bands in the carbonyl region appear at values lower than those normally encountered with aromatic aldehydes and ketones (*e.g.*, in carbon tetrachloride solution: benzaldehyde,<sup>14</sup> 1708  $\text{cm}^{-1}$ ; acetophenone, 1692  $\text{cm}^{-1}$ ; benzophenone, 1664  $\text{cm}^{-1}$ ). However, these low values are similar to those recorded for other unsaturated amino-ketones<sup>15</sup> and reflect a mesomeric release of electrons from the pyrrole ring to the carbonyl group to give a structure whose ground state shows considerable charge separation. Support for this interpretation is provided by the low carbonyl frequency of 1-methylpyrrole-2-aldehyde, in which the band cannot be due to the C=N stretching frequency of the pyrrolenine (enol) form.

The two carbonyl bands behave similarly to the amino bands in solvents of low polarity. The relative intensity of the higher-frequency band, which can be assigned to the free-carbonyl stretching frequency, increases on dilution, and its position depends on the solvent. In more polar solvents only one band is observed; that this is due to a free carbonyl group is confirmed by plotting its frequency in a variety of solvents against that of acetophenone.<sup>16</sup> Excellent straight lines are obtained, whose gradients, unlike those from the corresponding amino-bands, differ (*viz.*, -CHO, 1.02; -COCH<sub>3</sub>, 0.68; -COC<sub>6</sub>H<sub>5</sub>, 0.74) and reflect the sensitivity of the system to the interactions of the acyl substituents: the carbonyl bond—but not the amino-bond—forms part of the extended conjugation of these compounds. Similar straight lines are obtained when 1-methylpyrrole-2-aldehyde is used as the reference compound, confirming that the solvent has not induced any enolisation. As with the associated amino group, the environment of the associated carbonyl group scarcely varies and its stretching frequency is largely independent of solvent.<sup>17</sup>

The simple correlation between the magnitude of the frequency shift and solvent-solute interaction in effectively monofunctional systems, *e.g.*, alcohols<sup>10</sup> and carboxylic

<sup>9</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 111.

<sup>10</sup> Cf. Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120; Bellamy and Hallam, *ibid.*, 1959, **55**, 220.

<sup>11</sup> Collings and Morgan, *J.*, 1963, 3437.

<sup>12</sup> Allerhand and Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 371.

<sup>13</sup> Cf. Josien and Fuson, *J. Chem. Phys.*, 1954, **22**, 1169.

<sup>14</sup> Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626.

<sup>15</sup> Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.

<sup>16</sup> Bellamy, Conduit, Pace, and Williams, *Trans. Faraday Soc.*, 1959, **55**, 1677.

<sup>17</sup> Cf. Cannon, *Microchem. Acta*, 1955, 555.

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acids,<sup>11</sup> is not valid for such polyfunctional systems as 2-acylpyrroles. Thus, while the carbonyl frequencies of these compounds in triethylamine solution indicate little solvent-solute interaction, no associated carbonyl band can be detected; in hexane, with which there is necessarily little interaction, the associated carbonyl band is notably the stronger. Here the interaction of triethylamine with the amino function, through its ability to form the stronger hydrogen bond, generates a free carbonyl group. The generally stronger interactions accompanying hydrogen-bonding make the converse effect difficult to detect, but it is possible that the weak associated amino-bands of 2-acylpyrroles in chloroform and methylene chloride are due to the strong interactions of these solvents with carbonyl groups.

*2-Aroylpyrroles.*—Although no enolic tautomer was detected in the spectra of the simple ketones, it seemed possible that after relatively minor structural modifications the notional equilibrium might be detectable. In related tautomeric systems it has been noted that the introduction of substituents which can stabilise one form, *e.g.*, by hydrogen-bonding, can markedly affect the position of equilibrium. Thus in the phenylazonaphthols, the introduction of *o*-chloro-, *o*-methoxy-, and *o*-nitro-substituents into the phenyl group displaces the equilibrium towards the hydrazone form.<sup>18</sup> To determine whether a similar effect could operate on 2-acylpyrroles a number of *o*-substituted 2-benzoylpyrroles were prepared; for comparison the *para*-substituted isomers were also prepared.

The spectra of solutions of these compounds in a variety of solvents were examined. The pattern and behaviour of the bands in the single-bond and carbonyl stretching regions were entirely similar to those observed for the simple ketones. Excellent straight lines were obtained when the observed frequencies of the free amino and carbonyl bands were plotted against those of pyrrole and acetophenone, respectively; there was no discontinuity in the lines or appearance of new bands to suggest the presence of the tautomeric enol.

The frequency of the free N-H stretching band is scarcely affected by the nature of the acyl group, and the gradient of all the plots is again close to 0.66 (pyrrole as standard). The insensitivity to substituents is reasonable, since the N-H bond does not form part of the conjugated system; but a more precise examination would probably reveal small variations both in frequency and gradient. The uniformity of behaviour further demonstrates that the introduction of *o*-substituents into the benzoyl group effects no significant changes at the amino function and consequently that intramolecular hydrogen-bonding between the *o*-substituent and any enolic hydroxyl group provides no useful stabilisation.

Conversely, the frequency of the free carbonyl band is markedly dependent on both the position and nature of the substituents. A group can modify the stretching frequency of an attached carbonyl system through three factors: (*a*) a mass effect; (*b*) steric compression acting on the X-CO-Y bond-angle; (*c*) electrical effects, which include modifications of the force constant of the carbonyl bond through mesomeric, inductive and direct-field effects. The frequency shifts for some series of related compounds can, however, be discussed largely in terms of the electrical factors. This is clearly justified empirically, *e.g.*, by the correlation between Hammett sigma values and the carbonyl frequencies of substituted aceto- and benzo-phenones.<sup>19-21</sup> Consequently, while the reduction in carbonyl frequency from 1658 cm.<sup>-1</sup> (CCl<sub>4</sub>) for 2-acetylpyrrole to 1629 cm.<sup>-1</sup> (CCl<sub>4</sub>) for 2-benzoylpyrrole may well be due to all three factors, the further influence of substituents in the *para*-position of the benzoyl group will be effective only through electrical factors. The carbonyl frequency in substituted 2-benzoylpyrroles in carbon tetrachloride solution follows the sequence of Hammett sigma constants, *i.e.*, *p*-NO<sub>2</sub> > *p*-Cl > H > *p*-Me, *p*-OMe, but is notably less perturbed by *para*-substituents than is that of either aceto- or benzo-phenone. A carbonyl group will obviously interact more strongly with a pyrrole ring than with a

<sup>18</sup> Morgan, *J.*, 1961, 2151.

<sup>19</sup> Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526.

<sup>20</sup> Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

<sup>21</sup> Jones, Forbes, and Mueller, *Canad. J. Chem.*, 1957, **35**, 504.

benzene ring: the consequently lower energy of the 2-pyrrolyl system will make smaller demands on an attached phenyl group than will, *e.g.*, the benzoyl system of benzophenone. Under these conditions the electrical effects of substituents attached to the phenyl group become less important in determining the carbonyl frequency; this will particularly affect the contributions of highly polarisable groupings and may well account for the relatively high frequency of 2-anisoylpyrrole.

The solvent-induced displacements of the carbonyl frequency provide further illustration of this effect. The gradient indicates decreasing sensitivity of carbonyl frequency to solvents in the order:  $H \approx p\text{-Me} > p\text{-Cl} > p\text{-NO}_2 \approx p\text{-OMe}$ , which would be expected from the electrical properties of the substituents, with the exception of the methoxyphenyl group, which is probably free to interact more strongly than usual with solvents. It is reasonable to expect that interaction with the lone pairs of electrons on the ethereal oxygen will follow linearly the interaction with those on the carbonyl oxygen atom so that the solvent plot retains its linearity. Consequently the donor effect of the methoxyphenyl group on the conjugated system will be progressively reduced as the carbonyl frequency is reduced, until, for solutions in chloroform, the frequency of 2-*p*-anisoylpyrrole (1620  $\text{cm}^{-1}$ ) is greater than that of 2-benzoylpyrrole (1615  $\text{cm}^{-1}$ ). Satisfactory comparison of frequencies for solutions in more polar solvents is precluded by the proximity of other bands. An analogous solvent effect on the donor properties of substituents has been detected by nuclear magnetic resonance spectroscopy of a series of aryl fluorides.<sup>22</sup>

In contrast to the *para*-substituted isomers, the *ortho*-substituted 2-benzoylpyrroles have higher carbonyl frequencies than does the parent compound. The reason for this and the failure of the *ortho*-substituent to play any part in stabilising the enol form is made apparent by extending the formal analogy between 2-benzoylpyrrole and benzophenone. There is much evidence to show that benzophenone has a non-planar structure with the phenyl groups forced by steric crowding to an inclination of *ca.* 12° with the plane containing the carbonyl group.<sup>23,24</sup> This twisting is insufficient to prevent effective conjugation of the carbonyl and aryl groups in benzophenone and its *meta*- and *para*-substituted derivatives<sup>25</sup> but when *ortho*-substituents are introduced further distortion occurs.<sup>26</sup> Thus the ultraviolet spectra of *ortho*-substituted benzophenones show characteristically weaker bands at shorter wavelengths than the *para*-isomers.<sup>27,28</sup> The tendency for the most stable rotational isomer to be that in which the better electron donor retains conjugation with the carbonyl group is illustrated by the ultraviolet spectrum of *o*-nitrobenzophenone, which shows no conjugation between the carbonyl and *o*-nitrophenyl groups.<sup>24,29</sup> Such conjugation depends on whether the system can accommodate the steric requirements and the field-effects of the substituent: the spectrum of *o*-methoxybenzophenone suggests diminished conjugation between the methoxyphenyl and carbonyl groups. The ultraviolet spectra of 2-benzoylpyrroles have similar variations of intensity and wavelength, although the effects of substitution are partly masked by the longer wavelength and high intensity of the absorption due to the pyrrolyl chromophore.

The infrared spectra of the *ortho*-substituted derivatives show analogous perturbations, but these cannot be discussed satisfactorily in terms of electrical effects alone, since the influence of steric compression on the carbonyl frequency cannot be readily assessed. Nevertheless, in the benzophenones and 2-benzoylpyrroles the carbonyl frequencies lie in

<sup>22</sup> Taft, Glick, Lewis, Fox, and Ehrenson, *J. Amer. Chem. Soc.*, 1960, **82**, 756.

<sup>23</sup> Bergmann, Engle, and Meyer, *Ber.*, 1932, **65**, 446; Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.

<sup>24</sup> Rekker and Nauta, *Rec. Trav. chim.*, 1961, **80**, 747.

<sup>25</sup> Cf. Karle, Hauptman, Karle, and Wing, *Acta Cryst.*, 1958, **11**, 257.

<sup>26</sup> Smith and Antoniadis, *Tetrahedron*, 1960, **9**, 210.

<sup>27</sup> Ingraham, "Steric Effects in Organic Chemistry," ed. Newman, Wiley, New York, 1956, p. 479.

<sup>28</sup> O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906; Rekker and Nauta, *Rec. Trav. chim.*, 1954, **73**, 969; 1958, **77**, 714.

<sup>29</sup> Szmant and Harmuth, *J. Amer. Chem. Soc.*, 1959, **81**, 962; Moricani, O'Connor, and Forbes, *ibid.*, 1960, **82**, 5454.

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the same order ( $H < o\text{-CH}_3 < o\text{-OCH}_3 < o\text{-Cl} < o\text{-NO}_2$ ), which suggests that similar steric and field effects are operating. Models of 2-benzoylpyrroles show that the introduction of *ortho*-substituents must again be accompanied by considerable distortion. In view of the strong pyrrolyl-carbonyl interaction and the correspondingly high bond-order of the  $C_2$ -carbonyl bond, it is likely that these groups remain largely coplanar in the *ortho*-substituted derivatives and that it is the phenyl-carbonyl bond that twists. Any ability of the *ortho* substituent to stabilise the enol form is minimised by this skewed structure which is necessarily badly orientated for hydrogen bonding. That the carbonyl frequencies in 2-*o*-chloro-, -methoxy-, and -nitro-benzoylpyrroles show almost the same solvent-dependence suggests that the non-bonded interactions in these compounds are closely similar (it may well be fortuitous that the same solvent-dependence is shown by

TABLE 5.

Bands in the ultraviolet spectra of acylpyrroles and acylbenzenes.

Acyl groups	2-Acylpyrroles				Acylbenzenes			
	$\lambda$ ( $m\mu$ )	$\log \epsilon$	$\lambda$ ( $m\mu$ )	$\log \epsilon$	$\lambda$ ( $m\mu$ )	$\log \epsilon$	$\lambda$ ( $m\mu$ )	$\log \epsilon$
CHO .....	237	3.88	287	4.23	240 <sup>a</sup>	4.12	278 <sup>a</sup>	3.08
Ac .....	237	3.83	286	4.22	242 <sup>b</sup>	4.0	(280) <sup>b</sup>	3.0
Bz .....	239	4.01	307	4.20	253 <sup>c</sup>	4.27	—	—
R in $CO \cdot C_6H_4R$								
<i>o</i> -Me .....	251	3.75	299	4.25	250	4.28	(292)	3.40
<i>p</i> -Me .....	254	3.97	307	4.24	259 <sup>d</sup>	4.24	—	—
<i>o</i> -OMe .....	(255)	3.63	301	4.22	248	4.26	(293)	3.54
<i>p</i> -OMe .....	(260)	3.88	311	4.27	250	3.96	290	4.21
<i>o</i> -Cl .....	247	3.59	301	4.20	251	4.27	(293)	3.34
<i>p</i> -Cl .....	252	3.99	310	4.17	256	4.32	—	—
<i>o</i> -NO <sub>2</sub> .....	(255)	3.85	297	4.10	249	4.21	—	—
<i>p</i> -NO <sub>2</sub> .....	263	4.12	323	3.99	266	4.33	—	—

*a*, Van Allan and Tinker, ref. 30; *b*, Rasmussen, Tunncliff, and Brattain, ref. 31; *c*, Szmant and McGinnis, ref. 32; *d*, Kaplan, Parton, and Vaughan, ref. 33.

2-acetylpyrrole). Consequently the geometrical relations of the carbonyl and pyrrolyl amino-groups in these compounds are also likely to be similar. The dipole moment<sup>34</sup> of 2-formylpyrrole indicates that it has the *syn* structure, and, although there is no direct evidence, the closely similar spectroscopic behaviour, notably of the amino-groups, suggests a similar structure for all the 2-acylpyrroles.

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<sup>30</sup> Van Allen and Tinker, *J. Org. Chem.*, 1954, **19**, 1243.

<sup>31</sup> Rasmussen, Tunncliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

<sup>32</sup> Szmant and McGinnis, *J. Amer. Chem. Soc.*, 1952, **74**, 240.

<sup>33</sup> Kaplan, Parton, and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 4341.

<sup>34</sup> Marinangeli, *Ann. Chim. (Italy)*, 1954, **44**, 219.