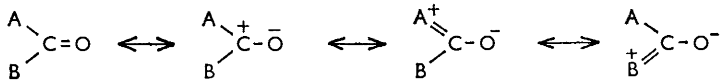
958. *Infrared Spectra of Pyrrolic Esters*

By R. GRIGG

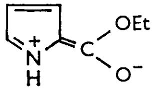
The infrared spectra of a number of pyrrolic esters have been examined in the NH stretching region and in the carbonyl stretching region. Pyrroles with a 2-ester substituent are shown to exhibit rotational isomerism. The carbonyl stretching frequencies of the 2-esters occur at higher frequencies than those of the 3-esters, indicating that a spectroscopic distinction between the two is possible.

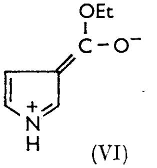
SUBSTITUENT vibrations can give information about the electron donor and acceptor abilities of heteroaromatic rings. The force constant of the C=O bond, and hence the carbonyl stretching frequency, depends on the electronegativities of the groups A and B (I). The greater the electron release from A and B (II—IV), the lower the carbonyl stretching frequency.

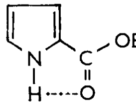

(I) (II) (III) (IV)

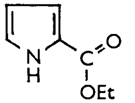
The pyrrole nucleus has been recognised as a good electron source from chemical evidence,[1] and infrared (i.r.) measurements have demonstrated that it releases electrons to electron-withdrawing substituents in the ground state.[2-5] A study of formylpyrroles [6] has shown that the carbonyl stretching frequency of 3-formylpyrroles occurs at *ca.* 30 cm.$^{-1}$ higher than that of the 2-aldehydes. These results have been interpreted as indicating that the pyrrole nucleus releases electrons more readily at the 2-position than at the 3-position [7] in the ground state. A similar study on carboxythiophens and formylthiophens [8] indicated that thiophens also release electrons more readily at the 2-position.

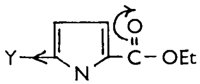
In a recent Paper [4] it was reported that the carbonyl stretching frequencies of 2- and 3-monoalkoxycarbonylpyrroles occurred at the same frequency. The coincidence of the absorptions led to the suggestion that esters of this type could not be distinguished by i.r. spectroscopy and was taken to indicate that the "dipolar structures" (V) and (VI) could be formed with equal ease.

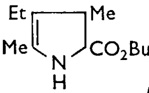

(V)


(VI)


(VII)


(VIII)


(IX)


(X)

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[1] H. Fischer and H. Orth, " Die Chemie des Pyrrols," Akademische Verlag. M.B.H., Leipzig, 1934, vol. I.

[2] M. Scrocco and R. Nicolaus, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1956, **20**, 795; 1957, **22**, 500.

[3] M. Scrocco, L. Caglioti, and V. Caglioti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1958, **24**, 316.

[4] U. Eisner and R. L. Erskine, *J.*, 1958, 971.

[5] R. Grigg and A. W. Johnson, *J.*, 1964, 3315.

[6] P. Mirone and V. Lorenzelli, *Ann. Chim.* (*Italy*), 1958, **48**, 72.

[7] A. R. Katritzky and A. P. Ambler, " Physical Methods in Heterocyclic Chemistry," ed. A. R. Katritzky, Academic Press, New York and London, 1963, vol. II, p. 310.

[8] S. Gronowitz and A. Rosenberg, *Arkiv Kemi*, 1955, **8**, 23.

It was further reported that 2,4-diethoxycarbonylpyrroles had a single asymmetric carbonyl band, indicating that the two ester carbonyl stretching frequencies were overlapping. These spectra were determined for solutions in chloroform, which is known to have an effect on carbonyl stretching frequencies.[9]

It appeared from a study of 2,2′-bipyrroles and related pyrroles [5] that the 2- and 3-esters could be distinguished by i.r. spectroscopy. The spectra of 23 tri- and tetra-substituted pyrroles bearing one or two ester substituents have been determined in carbon tetrachloride. In the case of the monoesters it was found that the free carbonyl stretching frequency of the 2-esters occurred in the range 1710—1732 cm.$^{-1}$ (Table 1, nos. 1—11), whilst the 3-esters studied absorbed in the range 1701—1711 cm.$^{-1}$ (Table 1, nos. 12—16). The 2,4-diesters (Table 1, nos. 17—23) conform to the same pattern; thus the carbonyl stretching frequency of the 2-ester group occurs in the range 1718—1735 cm.$^{-1}$, and that of the 4-ester group in the range 1697—1715 cm.$^{-1}$.

In addition to a free carbonyl stretching frequency, the majority of the 2-monoesters have two other bands in the carbonyl region attributable to the ester group. Dilution studies enabled these to be assigned to an intermolecular and an intramolecular hydrogen-bonded ester group. The carbonyl stretching frequency of the intramolecular hydrogen-bonded ester group occurred between that of the free carbonyl and the intermolecular hydrogen-bonded carbonyl stretching frequencies. Pyrrole 2-esters may show rotational isomerism and the intramolecularly bonded ester group is due to the presence of the rotational isomer (VII). The free carbonyl stretching frequency is probably due to the rotational isomer (VIII). The 3-monoesters exhibit only two carbonyl bands, due to a free ester group and an intermolecularly hydrogen-bonded ester group, respectively. The expected absorption associated with the intramolecularly bonded 2-ester group of the pyrrole diesters is probably obscured by the carbonyl absorption of the non-bonded 4-ester group. When the electronic requirements of the 2-ester group are set in opposition to another electron-withdrawing substituent Y (IX), the free carbonyl stretching frequency exhibits the expected shift to higher frequencies as the electron-withdrawing ability of Y increases. (Table 1, nos. 2, 5, 7, 9, and 11).

The carbonyl stretching frequencies recorded in Table 1 clearly indicate that the 2-esters have higher frequencies than the 3-esters. This contrasts sharply with the results obtained with formylpyrroles [6] and indicates that caution should be exercised when generalising data obtained with only one type of electronegative substituent.[7] An anomalous result was obtained with the t-butyl ester (X), which exhibited carbonyl bands at 1667, 1681, 1705 cm.$^{-1}$ and N–H bands at 3325, 3461, and 3481 cm.$^{-1}$.

The NH stretching frequencies provided further evidence for the type of hydrogen bonding present in these pyrroles (Table 2). All the monoesters had an intermolecularly hydrogen bonded NH band in the range 3248—3346 cm.$^{-1}$. The relative intensity of this band decreased on dilution, as expected for a system showing intermolecular hydrogen bonding. The 3-monoesters had an NH band in the range 3438—3476 cm.$^{-1}$ due to a free NH group (Table 2, nos. 12—16), with a weak shoulder on the low-frequency side of this band, (Table 2, nos. 12—15). Several workers [10,11] have observed a shoulder on the low-frequency side of the free NH stretch in pyrrole. This had previously been interpreted as due to a monomer–dimer equilibrium [11] but has recently been reassigned [12] to a hot band which is due to the same spectral transition as the free NH stretch, but for molecules in a low-lying energy level above the ground state.

The 2-monoesters had two bands or an asymmetric band which were concentration-independent in the range 3437—3486 cm.$^{-1}$. The lower-frequency band is assigned to the

[9] R. N. Jones and C. Sandorfy, " Chemical Applications of Spectroscopy," ed. A. Weissberger, Interscience Publishers, New York, 1956, p. 471.

[10] N. Fuson, P. Pineau, and M. L. Josien, *J. Chim. phys.*, 1958, **55**, 454.

[11] H. Wimette and R. H. Linnell, *J. Phys. Chem.*, 1962, **66**, 546.

[12] R. H. Linnell, *J. Chem. Phys.*, 1964, **41**, 3274.

TABLE 1

Infrared absorptions of pyrrolic esters: carbonyl stretching frequencies

	Substituents				Free C=O (cm.$^{-1}$)		Bonded C=O (cm.$^{-1}$)		Other C=O (cm.$^{-1}$)
No.	2	3	4	5	2-Ester	3(4)-Ester	Intra	Inter	
1	CO_2Et	Me	Et	CHO	1725		1712	1702sh	1668
2	CO_2Et	Me	Me	CHO	1726		1712	1702sh	1669
3	CO_2Et	Me	CHO	Me	1724			1694	1679, 1665
4	CO_2Et	Me	Et	H	1716		1690asym.		
5	CO_2Et	Me	Me	H	1716		1692	1678sh	
6	CO_2Et	Me	H	Me	1715		1685	1670	
7	CO_2Et	Me	Me	I	1719		1696	1678	
8	CO_2CH_2Ph	Me	Me	I	1722		1697	1682	
9	CO_2Et	Me	Me	Me	1710		1683	1669	
10	CO_2CH_2Ph	Me	Me	Me	1712		1689asym.		
11	CO_2Et	Me	Me	NO_2	1732		1713	1701sh	
12	Me	CO_2CH_2Ph	Me	I	—	1709	—	1683sh	
13	Me	CO_2Et	Me	H	—	1701	—	1683sh	
14	Me	CO_2Et	Me	Me	—	1702	—	1683sh	
15	Me	CO_2Et	H	Me	—	1711	—	1693	
16	Me	CO_2Et	Me	CHO	—	1710	—		1652, 1647, 1638
17	CO_2Et	Me	CO_2Et	Br	1721	1701		1679	
18	CO_2CH_2Ph	Me	CO_2Et	CH_2OMe	1720	1700			
19	CO_2CH_2Ph	Me	CO_2Et	CH_2OEt	1719sh	1699			
20	CO_2Et	Et	CO_2Et	I	1718	1701		1680	
21	CO_2CH_2Ph	Me	CO_2Et	CHO	1735	1715			1675
22	CO_2Et	Me	CO_2Et	H	1724	1697		1676	
23	CO_2CH_2Ph	Me	CO_2Et	H	1723	1701		1681sh	

sh = Shoulder. asym = Asymmetric band.

TABLE 2

Infrared absorptions of pyrrolic esters: NH stretching frequencies

	Substituents				Free NH (cm.$^{-1}$)	Bonded NH (cm.$^{-1}$)		Hot band? (cm.$^{-1}$)
No.	2	3	4	5		Intra	Inter	
1	CO_2Et	Me	Et	CHO	3450	3441sh	3295	
2	CO_2Et	Me	Me	CHO	3453	3443sh	3298	
3	CO_2Et	Me	CHO	Me	3451sh	3437	3291	
4	CO_2Et	Me	Et	H	3486	3468	3327	
5	CO_2Et	Me	Me	H	3486	3468	3325	
6	CO_2Et	Me	H	Me	3480	3465	3316	
7	CO_2Et	Me	Me	I	3466sh	3455	3278	
8	CO_2CH_2Ph	Me	Me	I	3462sh	3452	3282	
9	CO_2Et	Me	Me	Me	3476	3459	3317	
10	CO_2CH_2Ph	Me	Me	Me	3475sh	3461	3323	
11	CO_2Et	Me	Me	NO_2	3444 *		3258	
12	Me	CO_2CH_2Ph	Me	I	3463		3320	3446
13	Me	CO_2Et	Me	H	3476		3345	3461
14	Me	CO_2Et	H	Me	3467		3336	3449
15	Me	CO_2Et	Me	Me	3463		3346	3451
16	Me	CO_2Et	Me	CHO	3438		3248	
17	CO_2Et	Me	CO_2Et	Br	3447sh	3436	3248	
18	CO_2CH_2Ph	Me	CO_2Et	CH_2OMe	3446asym		3280	
19	CO_2CH_2Ph	Me	CO_2Et	CH_2OEt	3461sh	3451	3278	
20	CO_2Et	Et	CO_2Et	I	3445sh	3436	3259	
21	CO_2CH_2Ph	Me	CO_2Et	CHO	3426asym		3278	
22	CO_2Et	Me	CO_2Et	H	3466sh	3451	3297	
23	CO_2CH_2Ph	Me	CO_2Et	H	3453		3300	

sh = Shoulder. asym = Asymmetric band.

* Broad band.

rotational isomer (VII), and the free NH band is probably due to the rotational isomer (VIII). The intramolecular hydrogen bonding results in a small frequency shift ($\Delta\nu$ = 9—18 cm.$^{-1}$) compared to the intermolecular hydrogen bonding ($\Delta\nu$ = 117—119 cm.$^{-1}$). The pyrrole diesters (Table 2, nos. 17—23) had an intermolecularly bonded NH band in the range 3248—3300 cm.$^{-1}$, and two bands or an asymmetric band which were concentration-independent in the range 3426—3466 cm.$^{-1}$, again indicating the presence of the rotational isomer (VII).

Since this investigation was completed, work on the NH stretching frequencies of pyrrolic esters has been reported.[13] The conclusions were in agreement with those described above, but were unsupported by evidence from the carbonyl region of the spectra.

EXPERIMENTAL

The i.r. spectra were determined for solutions in carbon tetrachloride in compensated potassium bromide cells on a Unicam S.P. 100 spectrophotometer fitted with a prism-grating double monochromator. The compounds studied were prepared by standard methods and were recrystallised before use.

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UNIVERSITY CHEMICAL LABORATORIES, CAMBRIDGE. [*Received, March 8th,* 1965.]

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[13] R. A. Jones and A. G. Moritz, *Spectrochim. Acta,* 1965, **21**, 295.