186. *The Light Absorption of Pyrroles. Part I. Ultraviolet Spectra.*

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The ultraviolet light absorption of a number of pyrroles has been determined. The spectra are discussed, and correlations between structure and light absorption attempted.

THE ultraviolet light absorption of certain pyrroles has recently been reported,[1-5] but interpretation of the data has been scanty. The aim of the present contribution is to record some further light absorption data (see Table 1) and to establish a number of correlations. The work was initiated in 1952, so there is some duplication of our results with those of Cookson.[1]

Pyrrole itself possesses a strong band (*A*) in the 210 mμ region (ε 15,000),[6] and a weak one (band *B*) at 240 mμ (ε 300). Cookson [1] observed that alkyl-substitution lowered the intensity of band *A*, and caused band *B* to disappear. Six alkyl-substituted pyrroles (1—6) * have now been investigated, the hypochromic effect being confirmed. Band *B* is absent in the simple alkylpyrroles (1), (2), (3), but appears in the more complex compounds (4), (5), (6), shifted by up to 20 mμ towards the visible region. The spectra of the pyrrole–acetone (5) and pyrrole–butanone (6) adducts are in keeping with their structures, as recently confirmed by chemical evidence.[7]

A new band makes its appearance when the pyrrole nucleus is substituted by $-M$ substituents [compounds (7—42)]. There is also selective light absorption in region *B*,[1] *viz.*, ~250—270 mμ, but as the intensities are very much higher than those found for certain alkylpyrroles and pyrrole itself, it is likely that these maxima are here due to a new type of transition. This band is probably of normal *K*-type, because (i) it is present for all conjugated, and absent for non-conjugated, pyrroles, and (ii) the transition energy decreases (*i.e.*, $\lambda_{max.}$ shifts towards the visible region) with increasing conjugative powers

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* These and similar numbers in parentheses refer to Tables.

[1] Cookson, *J.*, 1953, 2789.

[2] Andrisano and Pappalardo, *Gazzetta*, 1955, **85**, 1430.

[3] Bonino and Marinangeli, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1955, **19**, 222, 393.

[4] Scrocco and Nicolaus, *ibid.*, 1956, **20**, 795.

[5] Grob and Ankli, *Helv. Chim. Acta*, 1949, **32**, 2033; Grob and Camenish, *ibid.*, 1953, **36**, 49; Cookson and Rimington, *Nature*, 1953, **171**, 875; *Biochem. J.*, 1954, **57**, 476; Davoll, *J.*, 1953, 3802.

[6] Bowden, Braude, and Jones, *J.*, 1946, 948.

[7] Rothemund and Gage, *J. Amer. Chem. Soc.*, 1955, **77**, 3340.

TABLE 1. *Light absorption*[a] *of substituted pyrroles*

No.	Subst. at position				Band *A*		Band *B*		Band *K*	
	2	3	4	5	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
1	—	Et	Et	—	~208	5900	—	—	—	—
2	Me	—	Me	—	218	4700	—	—	—	—
3	Me [b]	Et	Me	—	214	7000	—	—	—	—
4	CH$_2$·NC$_5$H$_{10}$	Et	Et	—	208	9200	270	40	—	—
5	Me$_2$C< [c]	—	—	Me$_2$C<	219 227	4700 3700	280	110	—	—
6	MeEtC< [c]	—	—	MeEtC<	227	4600	266 278	600 530	—	—
7	CO$_2$Et	Me	Me	—	—	—	—	—	273	14,500
8	CO$_2$Et [d]	Me	Me	Me	—	—	253	6800	285	15,800
9	CO$_2$Et [e,f]	Me	Me	–CH$_2$–	—	—	—	—	290	15,700
10	CO$_2$Et [e]	Me	Et	–CH$_2$–	—	—	—	—	290	15,700
11	CO$_2$Et	Me	Me	CH$_2$·OMe	—	—	—	—	271 282	15,000 17,500
12	CH:N·OH	—	—	—	—	—	—	—	272	17,600
13	CHO [g]	—	—	—	—	—	251	3100	287	13,300
14	COMe [h,i]	—	—	—	—	—	251	4100	290	16,400
15	CH:CH·COMe	—	—	—	—	—	—	—	352	16,900
16	CH:CH·COPh	—	—	—	—	—	262	9300	386	24,500
17	Me	CN	—	Me	—	—	—	—	246	5500
18	Me [j]	CO$_2$Et	Me	—	232	9000	—	—	258	5300
19	Me [k]	COMe	Me	—	209	10,300	250	10,400	282	4900
20	CO$_2$Et	Me	Me	CO$_2$Et	220	16,700	—	—	282	22,000
21	CO$_2$Me	Et	Et	CO$_2$Me	222	17,700	—	—	282	19,800
22	CO$_2$H	Et	Et	CO$_2$Et	222	17,900	—	—	280	19,100
23	CO$_2$H	Et	Et	CO$_2$H	220	19,600	—	—	280	19,200
24	COMe [h]	—	—	COMe	229	12,800	—	—	305	16,400
25	CHO [m]	Et	Et	CO$_2$Et	232	12,500	—	—	305	17,400
26	CO·CO$_2$Me [h]	—	—	CO$_2$Me	227	7500	—	—	312	13,200
27	Me	CN	CN	Me	—	—	—	—	252	8100
28	Me	CO$_2$Et	CN	Me	—	—	—	—	262	9200
29	—	CO$_2$Et	CO$_2$Et	—	209	13,200	—	—	253	7500
30	Me	CN	CH:N·OH	Me	—	—	240	7500	280	9800
31	Me	CHO	CN	Me	222 227	11,000 10,800	255	8700	285	7400
32	Me	CO$_2$Et	CHO	Me	232	11,300	264	6600	295	8000
33	CO$_2$Et	Me	CO$_2$Et	Me	221	27,500	—	—	273	16,700
34	CO$_2$Et [n]	Me	CO$_2$Et	Me	226	29,100	—	—	274	14,400
35	CO$_2$Et	Me	CO$_2$H	Me	220	23,600	—	—	273	15,200
36	CO$_2$H	Me	CO$_2$Et	Me	220	24,100	—	—	271	15,200
37	CO$_2$Et	Me	CO$_2$Et	CHCl$_2$	222	21,400	—	—	260	11,100
38	CO$_2$Et [o]	Et	COMe	Me	236	22,000	—	—	286	11,700
39	CO$_2$Et	Me	CHO	Me	240	22,400	—	—	288	10,100
40	Me	CO$_2$Et	Me	CHO	220 228	15,400 15,200	—	—	297	20,900
41	CO$_2$Et	Me	CO$_2$Et	CO$_2$Me	224	24,000	—	—	276	17,500
42	CO$_2$Et	Me	CO$_2$Et	CHO	237	21,500	270	7600	308	11,100

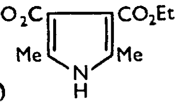
[a] In EtOH unless otherwise stated. [b] Cookson[1] gives $\lambda_{max.}$ ~200 mμ (ε 7450). [c] Pyrrole–ketone adducts; ε given per pyrrole unit. [d] In dioxan, $\lambda_{max.}$ 281 mμ (ε 16,400). [e] Dipyrrylmethane (II); ε given per pyrrole unit. [f] In dioxan, $\lambda_{max.}$ 287 mμ (ε 15,900). [g] Andrisano and Pappalardo[2] give $\lambda_{max.}$ ~252, 289·5; (ε 5000; 16,600). [h] In MeOH. [i] Andrisano and Pappalardo[2] give $\lambda_{max.}$ ~250, 287 mμ (ε 4400; 15,800). [j] Cookson[1] gives $\lambda_{max.}$ 232, 259 mμ (ε 8480; 5030). [k] Cookson[1] gives λ_{max} <210, 251, 271—285 mμ (ε >10,000; 10,000; 4760). [l] Cf. ethyl 4-ethyl-5-methoxycarbonyl-3-methylpyrrole-2-carboxylate for which Cookson gives $\lambda_{max.}$ 221, 282 mμ (ε 17,700; 21,900). [m] Cf. ethyl 4-ethyl-5-formyl-3-methylpyrrole-2-carboxylate, for which Cookson gives $\lambda_{max.}$ 231, 303 mμ (ε 14,200; 21,100). [n] *N*-Methyl derivative. [o] Cf. ethyl 4-acetyl-3 : 5-dimethylpyrrole-2-carboxylate, for which Cookson gives $\lambda_{max.}$ 235, 283 mμ (ε 22,800; 11,800), with an inflection at 255 mμ (ε 12,000).

of substituents, *viz.*, in the approximate sequence CN < CO$_2$H < CO$_2$R < CH:N·OH < CHO ~COMe < CO·CO$_2$R < CH:CH·COMe < CH:CH·COPh (cf. ref. 2). For example, the absorption at longer wavelength of the compound (40), compared with that of the isomer (39), is clearly due to the predominating influence of the more strongly conjugating 2-formyl group. We find the difference between the $\lambda_{max.}$ values of CO$_2$H and CO$_2$R derivatives to be only about 2 mμ, compared with ~6 mμ previously reported.[2]

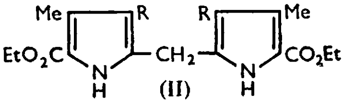
The *K*-band maxima are shifted by approximately 7 mμ towards the red region for each nuclear alkyl group (cf. refs. 1, 3), independently of the position of substitution. It appears possible that steric interference could take place between a bulky alkyl group and a vicinal chromophoric substituent.* This would reduce π-electron interaction between the substituent and the pyrrole nucleus, thus reducing the ε value, or, in extreme cases, producing a hypsochromic shift. In the related system of *o*-methyl-substituted benzaldehydes and acetophenones,[8] a reduction in ε was the only observed effect. In the pyrrole series a similar effect appears to take place. Thus replacement of the two nuclear methyl groups in the diester (20) by ethyl groups (21) reduces the ε value by 2200. Similarly comparison of the diester (29) with Cookson's pyrrole [1] (I), which contains two additional methyl groups, shows a lowering of ε by 950.

Pruckner and Dobeneck [9] have recorded values of 281 mμ for the dipyrrylmethanes (II; R = Me; compound 9) and (II; R = Et; compound 10) (in dioxan), a result which we considered rather too low. On repeating the measurements in ethanol, we found values of 290 mμ in each case [in dioxan compound (9) had $\lambda_{max.}$ 287 mμ]. The corresponding mononuclear trialkylpyrrole ester (8) had a maximum at 285 mμ (281 mμ in dioxan). Thus a bathochromic shift of 5—6 mμ occurs when two pyrrole units are separated by a methylene bridge, pointing to conjugation (in the excited state) across the methylene bridge equivalent to 1·7 kcal./mole.† Analogously there is evidence of electronic interaction in diphenylmethane [10] between the two benzene rings across the methylene bridge.

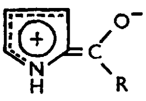
3-Substituted pyrroles absorb at shorter wavelengths (15—20 mμ) than the corresponding 2-derivatives. This indicates that conjugation in the excited state, with a resulting lowering of energy, is more pronounced in the latter, so that the absorption maximum occurs at longer wavelengths in the former. Calculations on two matched pairs of derivatives ‡ point to a difference in conjugation energy (in the excited states) of 6·0 and 6·1 kcal./mole, respectively. The differences in conjugation energy in the ground state of 2- and 3-derivatives are of the order of 2·5—3·0 kcal./mole, as determined by combustion methods.[11]



(I)



(II)



(III)

The relative conjugating power of the pyrrole, furan, and benzene nuclei may be compared by examining the $\lambda_{max.}$ values of the *K*-bands in, say, the corresponding 2-Ar·CH:CH·COMe derivatives. They are in the order of 2-pyrryl ($\lambda_{max.}$ 352 mμ) > 2-furyl ($\lambda_{max.}$ 310 mμ) [12] > phenyl ($\lambda_{max.}$ 285 mμ),[13] a sequence expected from the recorded data on chemical reactivity.

The nature of the *K*-band of pyrroledicarboxylic acids and esters is more complex (cf. ref. 4), as there appears to be no direct correlation between the energy of the *K*-type transition and the conjugation effects that can be predicted for the 2- and 3-positions. *A priori* it was considered unlikely that —*M* substituents would interact conjugatively

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* Inspection of models shows that there would be more steric interference in the 2 : 3-positions than in the 3 : 4-positions.

† The calculated difference in energy between transitions occurring at 285 mμ and 290 mμ.

‡ Compounds (7) and (18); and 2-acetyl-4-ethyl-3 : 5-dimethylpyrrole for which Cookson [1] gives $\lambda_{max.}$ 308 mμ, and compound (19), corrected for a third alkyl group, *i.e.*, $\lambda_{max.}$ 289 mμ.

[8] Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117; Braude and Sondheimer, *J.*, 1955, 3754.

[9] Pruckner and Dobeneck, *Z. phys. Chem.*, 1941, **190**, *A*, 43.

[10] Braude, *J.*, 1949, 1902.

[11] Stern and Klebs, *Annalen*, 1932, **500**, 107; 1933, **504**, 296.

[12] Hughes and Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 737.

[13] Braude, *Ann. Reports*, 1945, **42**, 105.

with each other *via* the nucleus either in the ground or the transition state; thus the spectra of esters were expected for follow an additive scheme, *i.e.*, the sequence of increasing wavelengths: 3- < 3 : 4- < 2- < 2 : 3- and 2 : 4- < 2 : 5-. This order is approximately followed, as seen from Table 2 in which are listed $\Delta\lambda$ and $\Delta\varepsilon$ values of the various esters investigated. The 2- and the 3-carboxylic acids are used as a basis for comparison, together with values given by Scrocco and Nicolaus[4] for the acids.

It appears that further substitution of a CO_2R group into a molecule containing an acid or an ester group lowers the transition energies of the *K*-band appreciably. This applies not only to CO_2R groups, but to any $-M$ group, as seen from Table 1. Substitution of such a group will cause increased contributions from polar forms, such as (III) (*i.e.*, conjugation of one of the $-M$ substituents with the nucleus), in the excited state, thereby lowering its energy and decreasing the energy of the total transition.

This effect is remarkably powerful in the 2 : 3-derivatives which have very high $\lambda_{max.}$ values. It is striking that the introduction of further CO_2R groups causes a distinct hypsochromic shift, which is most pronounced when the group enters the 5-position.

In all cases listed in Table 2, in which a CO_2R grouping is being substituted in the 3-position next to a 2-CO_2R group already present, a sharp reduction in ε is observed. Since normally a bathochromic displacement of a *K*-band is accompanied by an increase in the ε value, this effect must be due to appreciable hindrance between the CO_2R groups, causing displacement from coplanarity (or angular displacement) similar to those referred to above.

TABLE 2.[d]

Acids[a]

Position substd.	$\lambda_{max.}$	ε	$\Delta\lambda_\alpha$	$\Delta\varepsilon_\alpha$	$\Delta\lambda_\beta$	$\Delta\varepsilon_\beta$
2-	262	12·0	0	0	—	—
3-	245	4·8	—	—	0	0
2 : 3-	282	4·2	+20	−7·8	+37	−0·6
2 : 4-	—	—	—	—	—	—
2 : 5-	272	20·1	+10	+8·1	—	—
3 : 4-	259	7·3	—	—	+14	+2·5
2 : 3 : 4-	279	8·0	+17	−4·0	+34	+3·2
2 : 3 : 5-	270	10·3	+ 8	−1·7	+25	+5·5
2 : 3 : 4 : 5-	277	7·6	+15	−4·4	+32	+2·8

Ethyl esters[b, c]

Position substd.	$\lambda_{max.}$	ε	$\Delta\lambda_\alpha$	$\Delta\varepsilon_\alpha$	$\Delta\lambda_\beta$	$\Delta\varepsilon_\beta$
2-	273	14·5	0	0	—	—
3-	258	5·3	—	—	0	0
2 : 3-	293[c]	10·5	+20	−4·0	+35	+ 5·2
2 : 4-	273	16·7	0	+2·2	+15	+11·4
2 : 5-	282	22·0	+ 9	+7·5	—	—
3 : 4-	267·5[e]	8·5	—	—	+ 9·5	+ 3·2
2 : 3 : 4-	—	—	—	—	—	—
2 : 3 : 5-	283	18·0	+10	+3·5	+25	+12·7
2 : 3 : 4 : 5-	—	—	—	—	—	—

[a] Scrocco and Nicolaus.[4] [b] Present work unless otherwise stated. [c] The data extrapolated where necessary to two nuclear methyl groups, assuming that substitution of one methyl group produces $\Delta\lambda$ + 7 mμ and $\Delta\varepsilon$ + 500. [d] $\Delta\lambda_\alpha$, $\Delta\varepsilon_\alpha$ represent the increase, respectively, of $\lambda_{max.}$ (mμ) and $\varepsilon \times 10^{-3}$, of the substance over the parent 2-derivative; $\Delta\lambda_\beta$, $\Delta\varepsilon_\beta$ refer to the corresponding values compared to those of 3-derivative. ε values to be multiplied by 10^3. [e] Ref. 1.

From a careful examination of the various types of pyrroles substituted with $-M$ groups, a regular pattern may be seen, *viz.*, that the ε values are very largely, though not exclusively, governed by the positions of substitution rather than by the type of substituent, a phenomenon not observed in, say, the benzene system. The orders of magnitude of ε values shown by substituted pyrroles have been collated in Table 3, and should be of use in determining structural details of pyrrole derivatives. Thus, for example, during other work, the preparation[14] of diethyl 5-formyl-3-methylpyrrole-2 : 4-dicarboxylate (42) was repeated. It is now shown that, under the conditions specified, the corresponding 2-dichloromethyl derivative (37), having the same m. p. as the aldehyde, is not hydrolysed, contrary to the findings of previous workers. Its ultraviolet absorption was quite different from that expected for the 2-formyl derivative (42). The latter may be formed under more vigorous hydrolytic conditions, and its light absorption is in agreement with data given in Table 2 and 3.

TABLE 3. *Range of ε values* (× 10^{-3}) *for pyrrole derivatives substituted by —M groups*

	Band *A*	Band *B*	Band *C*		Band *A*	Band *B*	Band *C*
2-	—	5—9 *	13—20	2 : 5-	12—20	—	17—22
3-	8—10	10 *	4—5	2 : 3-	8—12	4—6 *	10—12
3 : 4-	11—13 †	6—8 *	7—10	2 : 3 : 5-	21—24 †	7—10 †	9—17
2 : 4-	20—25	10—12 *	10—17				

* Or submerged. † Or absent.

[*Added, January 8th*, 1958.—Further ultraviolet data for pyrrolecarboxylic acid and esters were presented recently.[14a] A case of 3 : 4-interaction is given in that 4-methyl substitution in ethyl pyrrole-3-carboxylate gave a hypsochromic shift of 13 mμ. The effect on extinction coefficients was not reported.]

EXPERIMENTAL

The spectroscopic measurements were carried out on a Unicam S.P. 500 spectrophotometer; some preliminary results were obtained on a Hilger-Spekker spectrophotometer.

Preparation of Pyrroles.—Unless otherwise stated, the pyrroles were prepared by the standard methods due to Fischer.[15] The methods for preparing the remaining pyrroles have been recorded in the following publications: compounds (8), (20), (35), (39), Eisner *et al.*;[16] compounds (1), (4), (21), (22), (23), (25), (38), Eisner *et al.*;[17] compounds (17), (27), (28), (30), (31), (32), Bilton and Linstead;[18] compound (29), Kornfeld and Jones;[19] compound (7), Kleinspehn;[20] compound (40) by a modification of the method of Chu and Chu;[21] compound (41), Corwin *et al.*;[14] compounds (5), (6), Rothemund and Gage;[7] compound (16), Ross and Waight.[22] They were purified to constant m. p. by crystallisation and sublimation under reduced pressure, or by distillation where appropriate.

The esters (18)[15] and (34)[23] were purified by chromatography on alumina with benzene–light petroleum (b. p. 60—80°) (1 : 1) as eluant.

Diethyl 3-Dichloromethyl-5-methylpyrrole-2 : 4-dicarboxylate (37).—The method of Corwin *et al.*[14] for the preparation of diethyl 3-formyl-5-methylpyrrole-2 : 4-dicarboxylate (42) was followed. The solid isolated, after recrystallisation and sublimation under reduced pressure, had m. p. 124°, and gave a positive Beilstein test. Elementary analysis indicated that it was the dichloromethyl derivative (37) (Found: C, 47·6; H, 5·2; N, 4·6. Calc. for $C_{12}H_{15}O_4NCl_2$: C, 46·8; H, 5·1; N, 4·55%). It was boiled with aqueous alcohol for 3 hr., which converted it into the aldehyde (42), m. p. 126°, after crystallisation from aqueous alcohol (Found: C, 57·4; H, 6·2. Calc. for $C_{12}H_{15}O_5N$: C, 56·9; H, 6·0%). A mixture of the two substances melted at 95°.

Ethyl 5-Methoxymethyl-3 : 4-dimethylpyrrole-2-carboxylate (11).—To the ester (8) (3·75 g.) in "AnalaR" acetic acid (120 c.c.) lead tetra-acetate (9·19 g.) was added during 1 hr. The solution was stirred at room temperature for 1·5 hr., the solvent removed under reduced pressure (<60°), and the residue dissolved in chloroform and washed with water until free from lead salts. The

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[14] Corwin, Bailey, and Viohl, *J. Amer. Chem. Soc.*, 1942, **64**, 1267.

[14a] Scrocco and Nicolaus, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1957, **22**, 311, 500.

[15] Fischer–Orth, "Die Chemie des Pyrrols," Akademische Verlag Gesellschaft, Leipzig, 1937, Vol. I.

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

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

[18] Bilton and Linstead, *J.*, 1937, 922.

[19] Kornfeld and Jones, *J. Org. Chem.*, 1954, **19**, 1671.

[20] Kleinspehn, *J. Amer. Chem. Soc.*, 1955, **77**, 1546.

[21] Chu and Chu, *J. Org. Chem.*, 1954, **19**, 266.

[22] Ross and Waight, unpublished results.

[23] Corwin and Quattlebaum, *J. Amer. Chem. Soc.*, 1936, **58**, 1083.

solution was dried, the solvent removed, and the residue crystallised from aqueous methanol, affording a small amount of an impure solid, m. p. 158—178°, and a filtrate A. The solid was sublimed at 120°/20 mm., affording a sublimate, m. p. 69—72°, and a residue which after crystallisation from ethanol had m. p. 196—198°. It was identified as the dipyrrylmethane (9) (Found: C, 65·7; H, 7·7; N, 7·95. Calc. for $C_{19}H_{26}O_4N_2$: C, 65·9; H, 7·6; N, 8·1%). The filtrate A was diluted with water and extracted with chloroform. Removal of the solvent under reduced pressure and crystallisation from light petroleum (b. p. 60—80°) afforded *ethyl 5-methoxymethyl-*3 : 4-*dimethylpyrrole-*2-*carboxylate*, which after sublimation at 80°/20 mm. had m. p. 68—70° (Found: C, 62·5; H, 8·3; N, 6·7; OMe, 34·7. 34·6. $C_{11}H_{17}O_3N$ requires C, 62·5; H, 8·1; N, 6·6; OMe, 36·9%).

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