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ELECTRONIC ABSORPTION SPECTRA OF ALKYL- AND PHENYL-SUBSTITUTED PYRYLIUM SALTS

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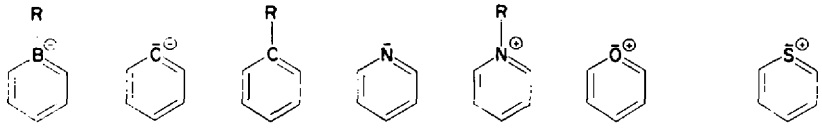
Abstract—Absorption spectra in the region 220–400 mμ have been determined for alkyl- and phenyl-substituted pyrylium salts. Three bands are apparent, in the decreasing order of wavelength, *x*, *y*, and *x'* bands. These bands are differently influenced by substitution in α and γ positions. Relationships of these bands with transitions in other aromatic compounds are established, and the effect of heteroatom variation in the series III–VI on the spectrum is discussed.

FROM the following series of six-membered monocyclic monoheteroaromatic systems, compounds II–VI are known (as well as the thiapyrylium cation VII, related to VI). The pyrylium cation VI contains a heteroatom $O^{\oplus}$ with the greatest electronegativity in the series I–VI[1] and therefore, although it is much more stable than an ordinary oxonium cation (because of the aromatic conjugation), it is much more reactive than the other aromatic systems and it can easily be converted into them.[2]

VI → III, IV, V or VII



I II III IV V VI VII

The electronic absorption spectra of the pyrylium cation or its derivatives with simple alkyl or phenyl substituents have been determined only in two isolated cases. The ultra-violet absorption spectrum of 2,4,6-trimethylpyrylium perchlorate* in ethanol solution has been determined in connection with the problem of pyrone mesomerism.[3] More systematically, the visible and ultra-violet absorption spectra of substituted pyrylium salts have been determined by Wizinger *et al.*;[4–8] they have described the spectrum of 2,4,6-triphenylpyrylium perchlorate in acetic acid[4–7] and of many other pyrylium salts with auxochromes, in a comprehensive study of the

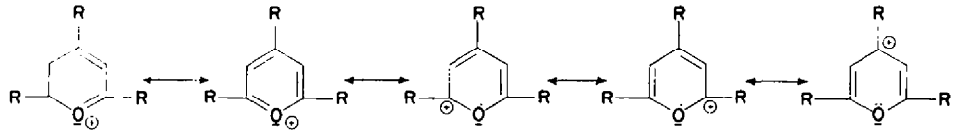
* It had been qualitatively reported in H_2SO_4 by A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **52**, 1535 (1919).

[1] A. T. Balaban, *Studii Cerc. Chim.* **7**, 257 (1959).
[2] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann.* **625**, 74 (1959).
[3] R. C. Gibbs, J. R. Johnson and E. C. Hughes, *J. Amer. Chem. Soc.* **52**, 4895 (1930).
[4] R. Wizinger and K. Wagner, *Helv. Chim. Acta* **34**, 2290 (1951).
[5] R. Wizinger, A. Grüne and E. Jacobi, *Helv. Chim. Acta* **39**, 1 (1956).
[6] R. Wizinger, S. Losinger and P. Ulrich, *Helv. Chim. Acta* **39**, 5 (1956).
[7] R. Wizinger and P. Ulrich, *Helv. Chim. Acta* **39**, 207 (1956).
[8] R. Wizinger and P. Ulrich, *Helv. Chim. Acta* **39**, 217 (1956).

influence of auxochromes on the spectra of cations V, VI and VII and the respective cyanines (but limiting themselves to the band with longer wavelength and not giving extinction coefficients).

The electronic absorption spectra of simple substituted, auxochrome-free pyrylium salts (which should reflect the electronic correlations in the series I–VI) have not yet been systematically investigated. Such studies exist in the benzopyrylium series[9] and in other polycyclic pyrylium compounds. The scope of the present paper is to fill this gap, and to furnish the basis for a comparative discussion of the systems I–VI. All but one pyrylium salt studied in the present paper have been obtained by a new simple synthetic method.[2]

The unsubstituted pyrylium cation is very unstable;[10] it may be isolated only at low temperature but it decomposes quickly. This may be explained by the mesomerism depicted in the formulae VIII. The large electronegativity of the oxygen heteroatom causes the positive charge to appear in positions 2 and 6(α) and somewhat less in position 4(γ).



VIII a VIII b VIII c VIII d VIII e

In the case of unsubstituted pyrylium salts (VIII, R = H), the 2,4 and 6 carbon atoms behave as secondary carbonium ions which are highly reactive and unstable. But the systems bearing substituents in these positions (VIII, R = Alk or Ar) are stable, because tertiary carbonium ions are stable (even the simplest tertiary carbonium ion, $(H_3C)_3C^{\oplus}$ has been spectroscopically identified in dilute solution).[11] These substituted systems constitute the object of the present study.

The perchlorate anion has been chosen for all pyrylium salts because it is synthetically and spectroscopically convenient, and gives stable and easily purified salts. Owing to the very small basicity of the $ClO_4^{\ominus}$ anion, no electronic interactions[12] are to be expected.

TABLE 1. EFFECT OF THE SOLVENT ON THE ABSORPTION SPECTRUM OF 2,4,6-TRIMETHYLPYRYLIUM PERCHLORATE (IX, $R_1 = R_3 = R_4 = CH_3$, $R_2 = H$, $X = ClO_4$)

No.	Solvent	Conc. moles/l	*y* Band		*x* Band	
			λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{max}
1.1	water	10^{-3}	233	5450	284	7900
1.2	ethanol*	10^{-3}	232	4500	286	9260
1.3	acetic acid	10^{-3}	—	—	284	12020
1.4	0·05 N $HClO_4$	10^{-3}	230	4550	285	12000

* Literature values[3] λ_{max} 230 mμ, ε_{max} 3650 and λ_{max} 286 mμ, ε_{max} 10400

[9] A. N. Nesmeyanov, L. A. Kazytsina, N. K. Kochetkov and M. I. Rybinskaya, *Izv. Akad. Nauk, OHN* 784 (1954).

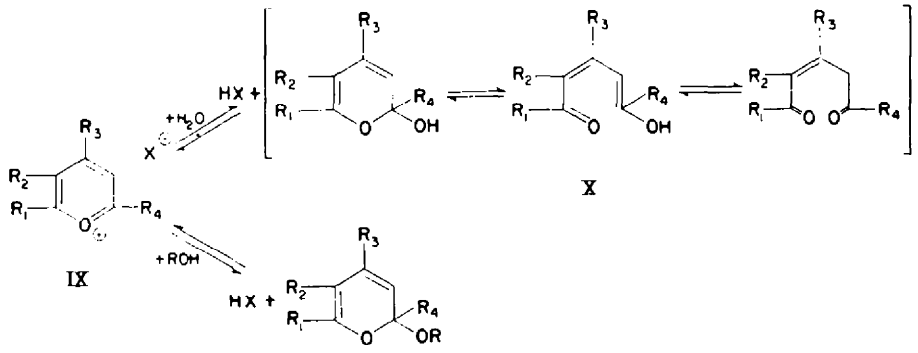
[10] F. Klages and H. Träger, *Chem. Ber.* **86**, 1327 (1953).

[11] J. Rosenbaum and M. C. R. Symons, *Proc. Chem. Soc.* 92 (1959).

[12] F. Kröhnke and H. Dickoré, *Chem. Ber.* **92**, 46 (1959) and especially p. 53.

1. *The effect of the solvent* has been studied for 2,4,6-trimethylpyrylium perchlorate (Table 1). The absorption maxima in water, ethanol, acetic acid and aqueous 0·05 N perchloric acid appear at nearly equal wavelengths, but in the first two cases (1.1 and 1.2) the extinction coefficients are smaller, and prolonged irradiation or conservation is reducing and shifting these maxima.

This may be explained by admitting partial solvolysis leading to tautomeric pseudobases X[13] or to ethers XI:



IX X XI

In acid solution, the formation of such compounds X or XI which polymerize or decompose on irradiation or conservation, is prevented by shifting the equilibrium towards the pyrylium cation IX.

The work was therefore continued only with solutions in aqueous 0·05 N perchloric acid (for pyrylium salts containing 0 or one phenyl group) or in acetic acid (for pyrylium salts containing two or more phenyl groups, which are sparingly soluble in water). These solutions are stable to irradiation giving reproducible results. The lower limit of the spectrum is 220 mμ for solutions in aqueous perchloric acid and 235 mμ for solutions in acetic acid.

2. *The spectra of pyrylium salts with alkyl groups in* 2,4 *and* 6 *positions* contain two bands with maxima at 230–235 mμ (designated *y band*) and at 285–290 mμ (*x band*); the effect of the alkyl groups is rather small, as shown in Table 2.

Though the variations are small, they are greater than experimental errors, so that some general conclusions may be reached.

In Fig. 1, λ_{max} and ε_{max} of alkyl-substituted pyrylium perchlorates have been related to the number of carbon atoms in their formulae (Table 2). Each point in Fig. 1 is numbered in accordance with Table 2. The effects of substitutents upon wavelength and absorption intensity have been separately represented for the *x* and *y* bands. The following general trends may be observed.

(*a*) The increase of the alkyl group in α-position in the order Me → Et → iPr → tBu corresponding to the increase of the number of carbon atoms, of the volume, and of the electron-repelling inductive effect (2.1, 2.3, 2.5, 2.6 and 2.7), has a small effect on the *y* band (λ_{max} and ε_{max} have a very slight increase), but has a sensible influence on the *x* band (λ_{max} increases little and ε_{max} increases appreciably). These variations are indicated by the full lines in Fig. 1.

[13] J. A. Berson, *J. Amer. Chem Soc.* **74**, 358 (1952).

TABLE 2. ABSORPTION SPECTRA OF ALKYL-SUBSTITUTED PYRYLIUM PERCHLORATES
(IX, X = ClO_4; 10^{-3} molar solutions in 0·05 N perchloric acid)

No.	Substituents in IX			Formula	*y* Band				*x* Band			
	R_1	R_2 R_3	R_4		λ_{max} (mμ)	ν_{max} (cm^{-1})	ε_{max}	lg ε_{max}	λ_{max} (mμ)	ν_{max} (cm^{-1})	ε_{max}	lg ε_{max}
2.1	CH_3	H CH_3	CH_3	$C_9H_{11}O^{\oplus}$ $ClO_4^{\ominus}$	230	43480	4550	3·658	285	35090	12000	4·079
2.2	CH_3	H C_6H_5	CH_3	$C_{14}H_{13}O^{\oplus}$ $ClO_4^{\ominus}$	233	42920	5950	3·775	285	35090	12200	4·086
2.3	CH_3	H CH_3	C_2H_5	$C_{10}H_{13}O^{\oplus}$ $ClO_4^{\ominus}$	231	43290	4610	3·664	286	34960	12900	4·111
2.4	CH_3	H $CH(CH_3)_2$	CH_3	$C_{11}H_{15}O^{\oplus}$ $ClO_4^{\ominus}$	236	42370	6120	3·787	285	35090	11560	4·063
2.5	C_6H_5	H CH_3	C_2H_5	$C_{15}H_{15}O^{\oplus}$ $ClO_4^{\ominus}$	231	43290	4650	3·667	287	34840	13250	4·122
2.6	$(H_3C)_2CH$	H CH_3	$CH(CH_3)_2$	$C_{13}H_{19}O^{\oplus}$ $ClO_4^{\ominus}$	232	43100	4680	3·670	288	34720	13860	4·142
2.7	$(H_3C)_3C$	H CH_3	$C(CH_3)_3$	$C_{14}H_{23}O^{\oplus}$ $ClO_4^{\ominus}$	232	43100	5050	3·703	288	34720	14250	4·154

(*b*) The increase of the alkyl group in γ-position in the order Me → Et → iPr (2.1, 2.2 and 2·4) has the opposite effect; a pronounced effect on the *y* band (λ_{max} and ε_{max} increase sensibly) and a negligible effect on the *x* band (λ_{max} is not affected, and ε_{max} first increases, then decreases). These variations are indicated by the broken lines in Fig. 1.

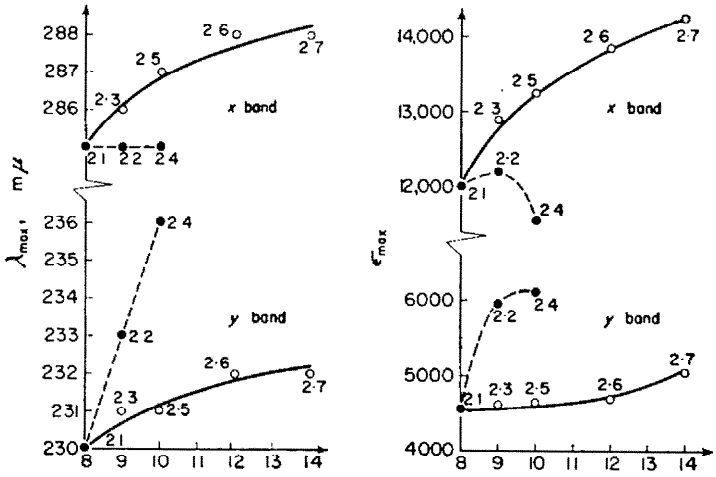


FIG. 1. Effect of alkyl groups. In abscissa, the number of carbon atoms in the formula.
—○— α positions; —●— — — γ position.

The variation of alkyl substituents in the order Me → Et → iPr → tBu has a bathochromic and hyperchromic effect on the *y* band when the substituent is in γ-position (broken lines are above full lines in Fig. 1 for the *y* band) and on the *x* band when the substituent is in α-position (full lines above broken lines in Fig. 1 for the *x* band).

TABLE 3. COLOUR AND FLUORESCENCE OF SOLUTIONS OF PHENYL-SUBSTITUTED PYRYLIUM PERCHLORATES

Number of Ph-groups	Position	Colour	Fluorescence
0	—	colourless	no
1	γ	colourless	violet, very slight
1	α	colourless	violet
2	α, γ	colourless	blue
2	β, γ	colourless	violet, slight
2	α, α	pale yellow	blue, strong
3	α, α, γ	yellow	blue–green
4	$\alpha, \alpha, \beta, \gamma$	pale yellow	green

3. *The effect of phenyl groups* on the absorption spectra of pyrylium cations is much more pronounced than the effect of alkyl groups. This may be seen by the colour and fluorescence of the solutions (shown qualitatively in Table 3).

The absorption maxima are indicated in Table 4.

TABLE 4. ABSORPTION SPECTRA OF PYRYLIUM PERCHLORATES WITH ALKYL- AND PHENYL-SUBSTITUENTS (IX, X = ClO_4)

No.	Substituents in IX				Formula	No of phenyl groups				Solvent	Conc. (moles/l.)	x' Band				y Band				x Band			
	R_1	R_2	R_3	R_4		α	β	γ	Total			λ_{max} (mμ)	ν_{max} (cm^{-1})	ε_{max}	lg ε_{max}	λ_{max} (mμ)	ν_{max} (cm^{-1})	ε_{max}	lg ε_{max}	λ_{max} (mμ)	ν_{max} (cm^{-1})	ε_{max}	lg ε_{max}
4.1	CH_3	H	CH_3	CH_3	$C_8H_{11}O^{\oplus}\ ClO_4^{\ominus}$	0	0	0	0	0·05 N $HClO_4$	10^{-3}					230	43480	4550	3·658	285	35090	12000	4·079
4.2	CH_3	H	CH_3	C_6H_5	$C_{13}H_{13}O^{\oplus}\ ClO_4^{\ominus}$	1	0	0	1	0·05 N $HClO_4$	$5\cdot10^{-4}$	227	44050	11260	4·052	244	40980	10220	4·009	345	28990	24000	4·380
4.3	CH_3	H	C_6H_5	CH_3	$C_{13}H_{13}O^{\oplus}\ ClO_4^{\ominus}$	0	0	1	1	0·05 N $HClO_4$	$5\cdot10^{-4}$					304*	32890	20000	4·301	327	30580	23400	4·369
4.4	C_6H_5	H	C_6H_5	CH_3	$C_{18}H_{15}O^{\oplus}\ ClO_4^{\ominus}$	1	0	1	2	0·05 N $HClO_4$	$5\cdot10^{-4}$	254	39370	14640	4·166	338	29590	23600	4·373	374	26740	29100	4·464
4.5	C_6H_5	H	CH_3	C_6H_5	$C_{18}H_{15}O^{\oplus}\ ClO_4^{\ominus}$	2	0	0	2	CH_3COOH	10^{-3}	236	42370	13800	4·140	277	36100	18760	4·273	392	25510	26900	4·430
4·6	CH_3	C_6H_5	C_6H_5	CH_3	$C_{19}H_{17}O^{\oplus}\ ClO_4^{\ominus}$	0	1	1	2	CH_3COOH	10^{-3}					245	40820	8900	3·949	308	32470	11800	4·072
4.7	C_6H_5	H	C_6H_5	C_6H_5	$C_{23}H_{17}O^{\oplus}\ ClO_4^{\ominus}$	2	0	1	3	CH_3COOH	10^{-3}	278	35970	18000	4·255	361†	27700	30000	4·477	408†	24510	24500	4·389
4.8	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$C_{29}H_{21}O^{\oplus}\ ClO_4^{\ominus}$	2	1	1	4	CH_3COOH	10^{-3}	296	33780	17500	4·243	379	26380	20400	4·310	412	24270	19200	4·283

* Imprecise value: inflexion, the *x* and *y* bands are very near to one another, and partially overlapped.
† Literature values[6,7] 360 and 408 mμ.

In order to study systematically the effect of phenyl groups, absorption spectra have been determined for all six possible compounds having methyl and/or phenyl groups in the 2,4 and 6 positions (4.1, 4.2, 4.3, 4.4, 4.5 and 4.7) and for compounds containing a phenyl group in β position (4.6 and 4.8). For comparison purposes, the spectrum of 2,4,6-trimethylpyrylium perchlorate has been included also in Table 4 (1.4 = 2.1 = 4.1).

To observe the effect of phenyl groups, Fig. 2 represents the data from Table 4.

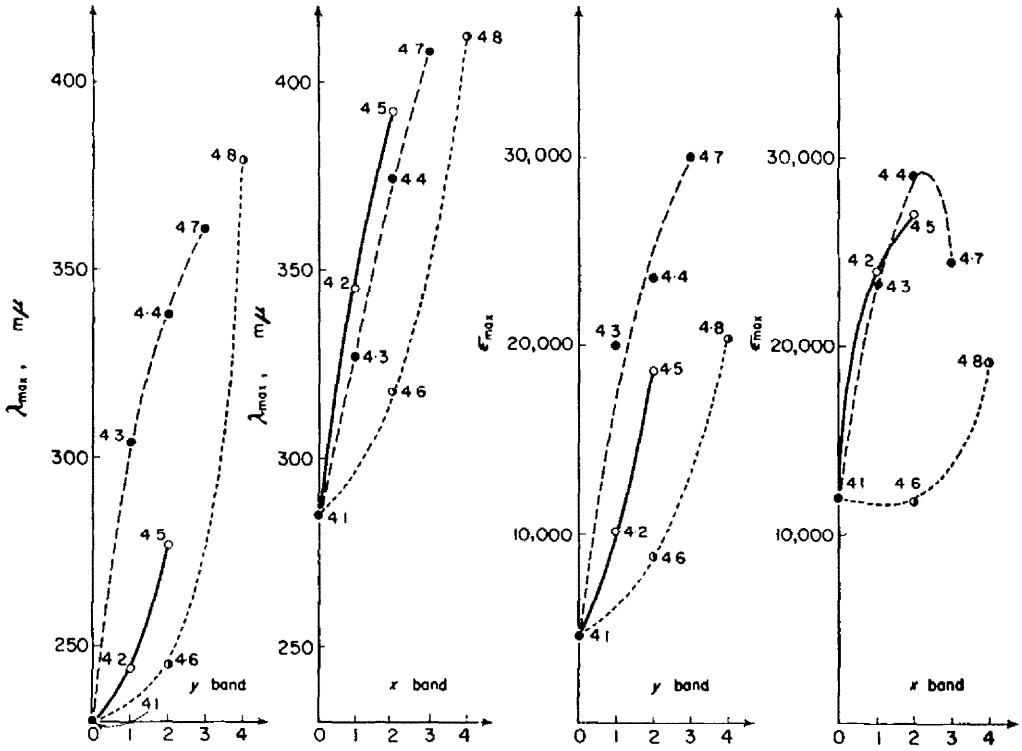


FIG. 2. Effect of phenyl groups. In abscissa, the number of phenyl groups.
—○——— α positions; —●— — — γ position; .◑.... β position.

The following general remarks may be made:

(*a*) Phenyl groups cause batho- and hyper-chromic effects which are much larger than those due to alkyl groups: while the latter are less than 10 mμ (for λ_{max}) and 30 per cent (for ε_{max}), the former are about 100 mμ and 300 per cent. This is easy to explain, taking into account that aryl groups may stabilize more effectively, through electronic effects, the positive charges in α and γ positions (VIII, R = Ar) than alkyl groups through their inductive effects. It must be emphasized that these large influences of the phenyl groups on the spectrum of the pyrylium nucleus arise only from phenyl–pyrylium, and not from phenyl–phenyl interactions, since the phenyl groups in the 2,4 and 6 positions are mutually in *meta* position, and it is established[14] that in the *m*-polyphenyl series, only ε_{max} and not λ_{max} is increasing

[14] A. E. Gillam and D. H. Hey, *J. Chem. Soc.* 1170 (1930); A. E. Gillam and E. S. Stern, *An Introduction to Electron Absorption Spectroscopy in Organic Chemistry*. Arnold, London (1954); J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Soc.* 2552 (1955).

with the number of phenyl groups. The sole cases when an interaction between two phenyl groups is plausible are those with two phenyl groups in *ortho* to one another (4.6 and 4.8), when both electronic and steric effects are probably involved (these cases have therefore been separately represented by broken lines in Fig. 2).

(*b*) Because of the different orders of magnitude alkyl effects may be neglected as a first approximation relative to phenyl effects.

(*c*) Phenyl groups in α positions (4.1, 4.2 and 4.5) have a bathochromic effect which is greater for the x band than for the y band, just as in the case of alkyl groups (full lines in Fig. 2).

(*d*) Phenyl groups in γ positions (4.1, 4.3, 4.4 and 4.7) have a batho- and hyperchromic effect which is greater for the y band than for the x band, just as in the case of alkyl groups (broken lines in Fig. 2).

(*e*) The introduction of a phenyl group in β position besides a γ-phenyl group (4.6 and 4.8) has a smaller effect than the two preceding ones, and the x and y bands behave similarly.

(*f*) When there are one or two phenyl groups in α-position, a third band appears in the experimentally accessible spectral region (designated x' band in Table 4). It is influenced by phenyl groups similarly to the x band, but no conclusions can be drawn until the λ_{max} and ε_{max} will be known for this x' band in the whole series.

(*g*) While in the alkyl-substituted series the x band presented an absorption coefficient ε_{max} 2–3 times greater than the y band, in the phenyl-substituted series, especially when a γ-phenyl is present, ε_{max} values become comparable for the x and y bands and for the last two compounds in Table 4 (4.7 and 4.8) the absorption intensity is greater for the y band than for the x band. This is to be expected in view of the different effects of phenyl groups on the x and y bands. These different effects are responsible for the appearance of the y band for 4.3 as a shoulder (inflexion) on the ascending branch of the absorption curve.

(*h*) The only exception to the rule that phenyl groups cause bathochromic and hyperchromic effects, is the hypochromic effect observed for the x band when the substituent is in γ-position. The same exception may be observed in the alkyl-substituted series (Figs. 1 and 2, ε_{max} for the x band, broken lines).

The qualitative conclusions are similar to those from the case of alkyl derivatives: increasing the number of phenyl groups generally causes a batho- and hyper-chromic effect, but this is more pronounced for the y band when the γ position is involved (broken lines are above full lines for the y band in Fig. 2) and for the x band when α-positions are involved (full lines above broken lines for the x band in Fig. 2). Phenyl groups in β exert a smaller influence.

The data published by Wizinger and Ulrich[7] relative to 2,4,6-triphenyl-substituted pyrylium perchlorates with NMe_2 and/or OMe auxochromic groups in the *para* positions of the phenyl groups bear out these conclusions, though the comparison can be made only for λ_{max} of the x band.

The data reproduced in Table 5 refer to acetic acid solution.

In Fig. 3 the wavelengths have been represented as function of the number of auxochromic groups in the same way as in Figs. 1 and 2, using Wizinger and Ulrich's data. Each point in Fig. 3 is numbered as in Table 5.

It may be observed that again increasing the number of auxochromic groups leads to bathochromic shifts which are greater when α-positions are involved (full lines

are above broken lines in Fig. 3). A hypsochromic effect is evident for the compound with three NMe_2 groups (see above under *h*). It is apparent that *p*-methoxyphenyl,

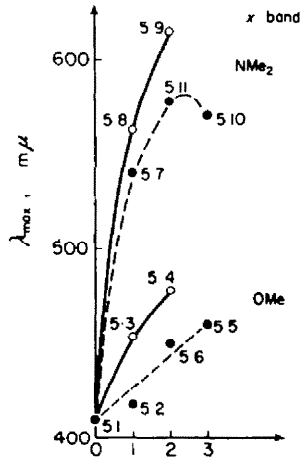


FIG. 3. Effect of auxochromic groups. In abscissa, the number of auxochromic groups. —○— α positions; —●— — γ position.

TABLE 5. ABSORPTION SPECTRA OF 2,4,6-TRIPHENYLPYRYLIUM PERCHLORATES WITH AUXOCHROMES IN *para*-POSITIONS AFTER WIZINGER AND ULRICH[7]

No.	Notation in Wizinger and Ulrich's paper[7]	Substituents in *para*-positions of the phenyl groups			*y* band	*x* band
		2	4	6	λ_{max} (mμ)	λ_{max} (mμ)
5.1	Ic	H	H	H	360	ca. 408
5.2	IIc	H	OMe	H		418
5.3	IIIc	H	H	OMe		454
5.4	IVc	OMe	H	OMe		478
5.5	Vc	OMe	OMe	OMe	420	ca. 460
5.6	VIc	H	OMe	OMe	416	ca. 450
5.7	VIIc	H	NMe_2	H		540
5.8	VIIIc	H	H	NMe_2		563
5.9	IXc	NMe_2	H	NMe_2		615
5.10	Xc	NMe_2	NMe_2	NMe_2	533	ca. 570
5.11	XIc	H	NMe_2	NMe_2		578

and even more *p*-dimethylaminophenyl, groups may stabilize more effectively positive charges than do phenyl groups.

Discussion of the results

No evidence has been obtained in favour of hyperconjugation in the series of alkyl-substituted pyrylium salts.[15]

The three bands found in the absorption spectrum of pyrylium salts VI are clearly related to the bands in the spectrum of benzene III, pyridine IV, and pyridinium compounds V. Two facts are apparent. Firstly, the vibrational structure of the bands, manifest for III is less pronounced for IV,[16] still less for V (for instance, the U.V. spectrum of pyridine-N-oxide has no vibrational structure[17]), and completely vanishes for VI. Apparently, the absence of vibrational structure in the spectra of pyrylium salts is not therefore attributable to the polar solvents employed, but is intimately associated with the absorbent cation (probably it is not due to a loose-bolt effect, since these cations are strongly fluorescent).

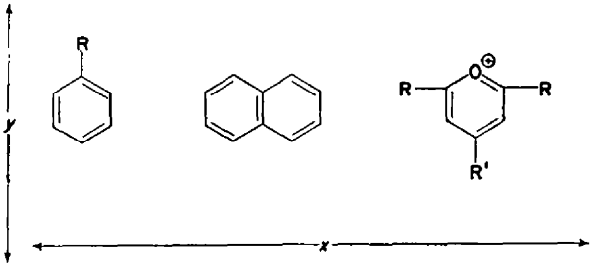


FIG. 4.

Secondly, the absorption intensities show a regular trend in the series III–VI: as the electronegativity of the heteroatom increases, the forbiddeness of the π–π^* transitions decreases, so that the absorption intensities are considerably changed. In the case of trimethylpyrylium perchlorate in 0·05 N perchloric acid, the oscillator strength values f are about 0·175 for the x band and 0·043 for the y band.

Thus, neither vibrational structure, nor absorption intensity can help in establishing relationships between the absorption spectra of compounds III–VI; this must be done only on the basis of sequence of bands in the spectrum and effect of substituents. But these two latter factors are consistent with one another as shown in the following.

Judging from the sequence of bands, the x band with longest wavelength is related to the $^1A_{1g}$–$^1B_{2u}$ π–π^* singlet transition in the benzene spectrum (Platt symbol: ^1L_b[18]; Clar symbol: α band[19]; Moffit symbol: V[20]), the y band is related to the $^1A_{1g}$–$^1B_{1u}$ π–π^* singlet transition in the benzene spectrum (Platt symbol: ^1L_a; Clar symbol: p band; Moffit symbol: U) and the x' band which is shifted

[15] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron* **5**, 166 (1959).
[16] cf. F. Matsen, *Chemical Applications of Spectroscopy* (Edited by F. West) pp. 629–706. Interscience, New York (1956); H. A. Staab, *Einführung in die theoretische organische Chemie* pp. 292–419. Verlag Chemie, Weinheim (1959).
[17] H. H. Jaffé, *J. Amer. Chem. Soc.* **77**, 4451 (1957); M. Ito and W. Mizushima, *J. Chem. Phys.* **24**, 495 (1956).
[18] J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949); **19**, 101 (1951).
[19] E. Clar, *Aromatische Kohlenwasserstoffe* (2nd Ed.) p. 36. Springer, Berlin (1952); *Chem. Ber.* **82**, 495 (1949).
[20] W. Moffitt, *J. Chem. Phys.* **22**, 320 (1954).

into the accesible ultra-violet region only in a few pyrylium salts is related to the $^1A_{1g}$–$^1E_{1u}$ π–π^* singlet transition in the benzene spectrum (Platt symbol: ^1B; Clar symbol: β band; Moffitt symbol: X, Y). This x' band is expected to be followed by another band at shorter wavelengths, which should be called y' band: then the x' band should correspond to the ^1B_b or β band, and the y' band to the ^1B_a or β' band in the spectrum of aromatic compounds.†

This assignment leads to the prediction that the x and x' bands must be polarized in the x direction (Fig. 4), having a nodal line through the heteroatom, while the y (and the predicted y') bands must be polarized in the y direction, having a nodal line between the atoms.[18]

(The notations x, x', y and y' have been chosen to emphasize the relationship with other bidimensional molecules with mobile π-electrons[21]).

TABLE 6. COMPARISON OF SPECTRA OF SYM-TRIMETHYL-DERIVATIVES OF COMPOUNDS III–VI

	y Band		x Band	
	λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{max}
Mesitylene[22]	215	7420	265[a]	219[a]
sym-Collidine[23]	ca. 216	6900	267	4000
1,2,4,6-Tetramethylpyridinium perchlorate[b]	221	5100	268	7340
2,4,6-Trimethylpyrylium perchlorate[b]	230	4550	285	12000

[a] Main vibrational peak
[b] Present work

This prediction is borne out by the effect of substituents: the x and x' bands are influenced by substituents in α and α' positions, while the y band is influenced by substituents in γ position. One could assume that in the first and third electronically excited state of the pyrylium cation, structures VIIIc + VIIId are contributing more than in the ground state, while in the second excited state structure VIIIe is contributing more‡.

Comparison between the absorption spectra of mesitylene,[22] collidine [23] and trimethylpyrylium perchlorate is also instructive, and we recorded the spectrum of

† See Y. Burawoy and J. P. Critchley, *Tetrahedron* **5**, 340 (1959) for a different assignment of the p and β bands in the benzene spectrum.

‡ This is a possible explanation of the specific reaction of pyrylium compounds with nucleophilic reagents in α-positions, since the first electronically excited state of the molecule (responsible for the x band) is somewhat associated with the presence of positive charges in α-positions. Alternative explanations are the presence of two structures with positive charge in α (VIIIc and VIIId) and only one structure for γ position (VIIIe), or the smaller charge separation in the former than in the latter.

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[22] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.* **71**, 2932 (1949); C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.* **17**, 460 (1949).

[23] N. Ikekawa, N. Maruyama and Y. Sato, *Pharm. Bull. Japan* **2**, 209 (1954); D. Rostafinska, *Roczn. Chem.* **29**, 803 (1955).

1,2,4,6-tetramethylpyridinium perchlorate in 0·05 N $HClO_4$ (10^{-3} molar solution). The results are summarized in Table 6.

It is apparent that with increasing electronegativity of the heteroatom in the sequence mesitylene → collidine → N-methyl-collidinium → trimethylpyrylium both the x and y bands are shifted towards longer wavelengths, that ε decreases for the y band and strongly increases for the x band, and that the last two compounds are completely devoid of vibrational structure.

EXPERIMENTAL

A CΦ4 spectrophotometer was employed. All pyrylium compounds mentioned were prepared as described,[3] with the exception of 2,4-diphenyl-6-methylpyrylium perchlorate (4·4) which was obtained according to Diels and Alder.[24] Pyrylium perchlorates with alkyl substituents or with one phenyl group were purified by recrystallization from aqueous 0·05 N perchloric acid. Pyrylium perchlorates with two or more phenyl groups were recrystallized from acetic acid. Commercial reagents and solvents were employed, without further purification.

1,2,4,6-Tetramethylpyrydinium perchlorate was prepared from 2,4,6-trimethylpyrylium perchlorate and methyl amine and had m.p. 204–205° (uncorr.) from water: literature values m.p. 206–207°[25], 202°[26], 201°[27].

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[27] B. Emmert and O. Varenkamp, *Ber. Dtsch. Chem. Ges.* **56**, 491 (1923).