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CHARGE-TRANSFER SPECTRA OF PYRYLIUM IODIDES

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Abstract—New methods are described for the preparation of substituted pyrylium halides. Pyrylium iodides have a different colour and an additional charge-transfer absorption band in the crystalline state and in dichloromethane solution as compared with the corresponding perchlorates. The position of the CT band is intermediate between that of tropylium and pyridinium halides. The effect of phenyl groups on the CT band of pyrylium iodides, which is markedly different from the effect on the x-band from the absorption spectrum or on the polarographic half-wave potentials is tentatively explained by the symmetry properties of the lowest empty molecular orbital, thus accounting for the correlation with the y-band from the absorption spectrum.

PYRYLIUM salts (sulphates, perchlorates, fluoborates, etc.) with alkyl substituents in positions 2, 4 and 6 are colourless, those with one phenyl substituent are straw-coloured, and those with two or three phenyl groups are yellow. By contrast, it has long been known that diphenylmethylpyrylium iodides are red[1,2] and that triphenylpyrylium iodide is dark red.[3,*]

No explanation of this colour difference has hitherto been offered. In previous studies of electronic absorption spectra of pyrylium salts,[6] only perchlorates were selected in order to avoid interactions with the anion. In the present paper a spectral study of pyrylium iodides is reported.

New methods (Experimental) were devised for the preparation of alkyl-substituted pyrylium iodides. Similar colour differences also exist in the alkyl-substituted series—instead of being colourless like the perchlorates, the iodides are yellow in the crystalline state.[7] Dilute solutions of pyrylium iodides in water, acetic acid or ethanol present no colour difference when compared with solutions of perchlorates and only minor spectral differences attributable to the variation in dielectric constant or Z-value.[8]

No trace of absorption beyond 320 mμ is visible in ethanol solutions of 2,4,6-trimethylpyrylium iodide—the solution is colourless unless it is very concentrated, and no new band is visible in the spectrum, but, when it is dissolved in non-ionizing solvents such as methylene dichloride, a yellow solution results which presents, in

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[*] Lighter-coloured forms of pyrylium iodides, possibly covalently-bonded,[4] have been reported.[1,5]

[1] W. Schneider and F. Seebach, *Ber. Dtsch. Chem. Ges.* **54**, 2285 (1921).

[2] W. Schneider and A. Ross, *Ber. Dtsch. Chem. Ges.* **55**, 2775 (1922).

[3] W. Dilthey, *J. Prakt. Chem.* **94**, 53 (1916).

[4] F. Kröhnke and H. Dickoré, *Chem. Ber.* **92**, 46 (1959).

[5] W. Schneider, *Liebigs Ann.* **432**, 297 (1923).

[6] A. T. Balaban, V. A. Sahini and E. Keplinger, *Tetrahedron* **9**, 163 (1960;) A. T. Balaban and C. D. Nenitzescu, *Izvestia Akad. Nauk SSSR, Otdel. khim. Nauk* 2064 (1960).

[7] M. Feldman and S. Winstein, *Tetrahedron Letters* 853 (1962).

[8] E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3253, 3261 (1958).

addition to the two bands at 230 and 285 mμ shown by the perchlorate in water,[6,*] two supplementary bands at 360 and 450 mμ, as shown in Fig. 1 and 2. Similarly, 2,4,6-triphenylpyrylium iodide in methylene dichloride presents a supplementary band at 550 mμ (cf. Fig. 3). Although these additional bands of pyrylium iodides have low extinction coefficients, they are broad and sufficiently remote from the highest wavelength absorption band of perchlorates to cause a significant colour difference between perchlorates and iodides in the crystalline state or in non-polar solvents. This phenomenon which has also been reported for pyridinium[8–11] and tropylium[12] halides is due to charge transfer from the anion to the cation. This charge transfer requires a close proximity of cation and anion, such as that existing in the crystalline state or in solutions in non-ionizing solvents which contain ion pairs.

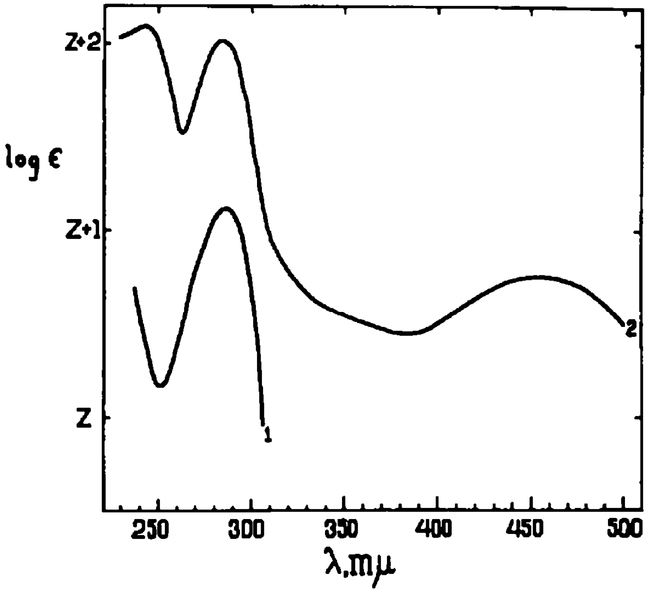

FIG. 1. Absorption spectra of 2,4,6-trimethylpyrylium perchlorate (curve 1, $z = 3$) and iodide (curve 2, $z = 2$, $9 \cdot 10^{-4}$ moles/l) in dichloromethane.

Although many papers and reviews as well as a book on donor-acceptor complexes have recently appeared (cf.[13]), the case of organic cation–halide anion charge-transfer complexes has received little consideration. Halides (especially iodides) of

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[*] 2,4,6-Trimethylpyrylium perchlorate, like other pyrylium perchlorates, is slightly soluble in dichloromethane (whence it may be precipitated by ether) and presents in this solvent λ_{max} 286 mμ (lg ε 4·11).

[9] E. M. Kosower, J. A. Skorcz, W. M. Schwarz Jr., and J. W. Patton, *J. Amer. Chem. Soc.* **82**, 2188 (1960).

[10] E. M. Kosower and J. A. Skorcz, *J. Amer. Chem. Soc.* **82**, 2195 (1960).

[11] E. M. Kosower, *J. Amer. Chem. Soc.* **77**, 3883 (1955); E. M. Kosower and P. E. Klinedinst Jr., *Ibid.*, **78**, 3493 (1956); E. M. Kosower, D. Hofmann and K. Wallenfels, *Ibid.* **84**, 2755 (1962).

[12] K. M. Harmon, F. E. Cummings, D. A. Davis and D. J. Diestler, *J. Amer. Chem. Soc.* **84**, 120, 3349 (1962); W. E. Doering and H. Krauch, *Angew. Chem.* **68**, 661 (1956).

[13] R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.* **13**, 107 (1962); V. P. Parini, *Uspekhi khim.* **31**, 822 (1962); G. Cauquis and J. J. Basselier, *Ann. Chim., Paris*, **7**, 745 (1962); J. W. Smith, *Science Progress* **50**, 607 (1962).

other organic aromatic cations besides tropylium, pyridinium and pyrylium, namely thiopyrylium,[14] azapyrylium,[15] dithiolium,[16] etc., and their benzoderivatives, have been reported to possess a deeper colour than the corresponding perchlorates, therefore charge-transfer is general in such compounds and deserves special attention.

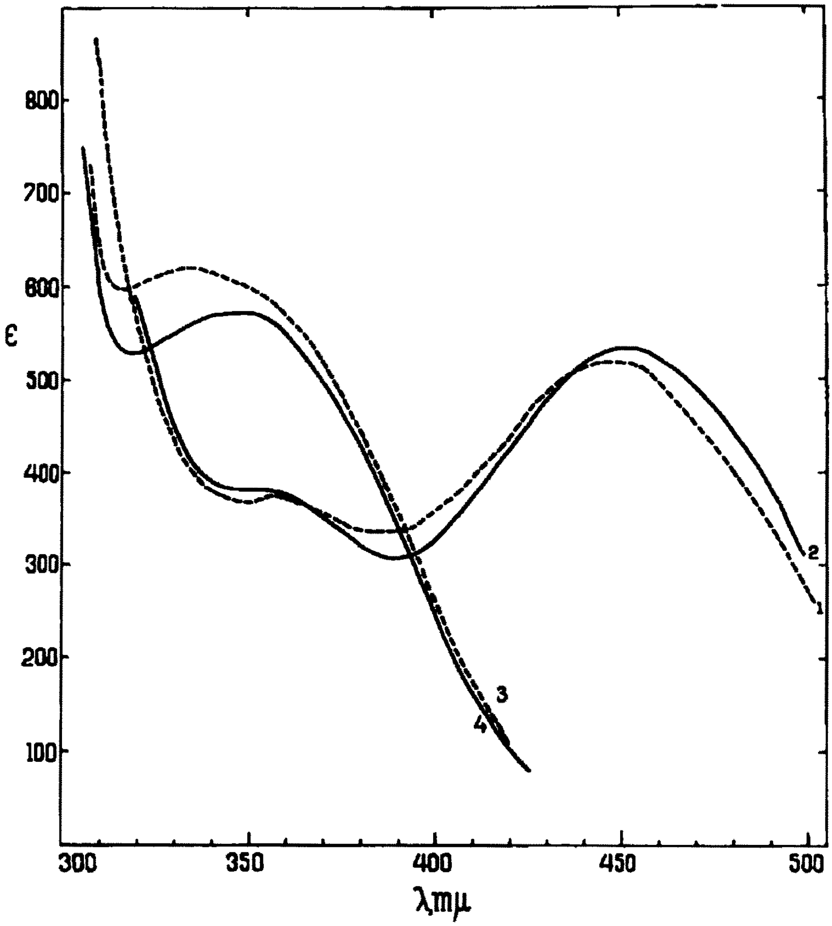

FIG. 2. Spectra of 2,4,6-trimethylpyrylium iodide (curves 1 and 2, $9\cdot10^{-4}$ moles/l) and bromide (curves 3 and 4, $4\cdot7\cdot10^{-4}$ moles/l) in CH_2Cl_2 (full line) and CH_2Cl_2 saturated with SO_2 (dashed line).

Detailed spectral investigations provide the means of comparing the excited states of various cationic aromatic systems acting as electron acceptors from iodide ions. In Mulliken's classification[17] the iodide anion is a donor of type n′ but the aromatic cation could be classified either as an acceptor of type xπ (neutral π acceptor) or of type v* (vacant orbital acceptor); a special acceptor type is perhaps indicated (aromatic cation).

[14] R. Wizinger and P. Ulrich, *Helv. Chim. Acta* **39**, 207 (1956).

[15] S. Hünig and K. Hübner, *Chem. Ber.* **95**, 937 (1962).

[16] E. Klingsberg, *J. Amer. Chem. Soc.* **84**, 3410 (1962); A. Lüttringhaus, *Liebigs Ann.* **661**, 85 (1963).

[17] R. S. Mulliken, *J. Phys. Chem.* **56**, 801 (1952).

EXPERIMENTAL

The preparation of pyrylium iodides was effected by known methods[18] in the case of 2,4,6-triphenylpyrylium[9] m.p. 224° and 2-methyl-4,6-diphenylpyrylium[1] m.p. 222°. The products were recrystallized from ethanol containing SO_2 in order to avoid the presence of triiodide. The other pyrylium salts were obtained by Friedel-Crafts diacylation of olefins.[19] In the case of pyrylium salts with bulky substituents (phenyl, t-butyl) in positions 2 and 6, chloroaluminates were isolated, dissolved in dil. HCl and treated with NaI aq., when pyrylium iodides precipitated. In all other cases the iodides were prepared from perchlorates and by using one of the following methods, the hitherto unknown unsubstituted and alkyl-substituted pyrylium halides were prepared.

A. The perchlorate was dissolved by mild heating in conc HCl, excess $FeCl_3$ solution in conc HCl added in the cold, and the precipitated tetrachloroferrate filtered off on a sintered glass filter, washed thoroughly with conc HCl, and recrystallized from dil. HCl by addition of conc HCl. Pyrylium chloroferrates are far more soluble in water and far less soluble in conc HCl than perchlorates.

A saturated aqueous solution of the chloroferrate, slightly acidified with HCl was reduced with H_2S until no more sulphur precipitated (4–8 hr). The greenish solution on cooling deposited $FeCl_2$ and after standing overnight in the refrigerator was rapidly filtered (oxygen reoxidizes Fe^{2+} into Fe^{3+}), and treated with saturated NaI aq. into which SO_2 had been introduced. The pyrylium iodide was filtered off and washed (sat. NaI aq.).

B. The reduction of the tetrachloroferrate may be obviated by gradually adding a conc aqueous solution of the chloroferrate into saturated NaI aq. containing solid $NaHSO_3$. The iodine set free by Fe^{3+} is slowly reduced by the sulphite, and a new portion of the chloroferrate added when the dark colour has disappeared. After filtration, the pyrylium iodide was extracted from the precipitate with hot ethanol or methylene dichloride, and the solvent evaporated.

C. The previous methods are particularly suitable for alkyl-substituted pyrylium iodides, but a simple and general method for their preparation directly from perchlorates consists in treating solid perchlorates with 56% HI in the cold. A brown precipitate of pyrylium iodide (with some triiodide) is immediately formed, which should be filtered off on a sintered glass filter and washed thoroughly with 56% HI, dissolved in ethanol, SO_2 bubbled through the solution to reduce triiodide, and the iodide precipitated by addition of ether.

D. A more general method for the preparation of pyrylium halides, especially chloride and bromide consists in the treatment of the pseudobase in benzene with gaseous hydrogen halide. The pseudobase may be prepared by the addition of an aqueous solution of the chloroferrate to a stirred mixture of benzene and aqueous sodium acetate.

Unsubstituted pyrylium iodide. The yellow, non-hygroscopic *iodide* obtained from the perchlorate[20] (procedure C) decomposed at about 130° evolving iodine. (Found: C, 28·68; H, 3·25. C_5H_5I requires: C, 28·87; H, 2·42%).

2,4,6-*Trimethylpyrylium salts.* The tetrachloroferrate m.p. 53° obtained from the perchlorate (method A) was described previously.[21] By method A or B it was converted into the lemon-yellow *iodide* which can also be obtained from the perchlorate by method C. On recrystallization from acetic acid a product which decomposes at ca. 200° was obtained,[7] but recrystallization from absolute ethanol or from ethanol-ether afforded a product m.p. 224° dec. (Found: C, 38·03; H, 4·38; I, 50·16. $C_8H_{11}IO$ requires: C, 38·43; H, 4·44; I, 50·75%). The iodide is non-hygroscopic and readily soluble in water yielding colourless solutions which react with ammonia giving sym-collidine (picrate, m.p. and mixed m.p. 157°). The iodide sublimed in vacuum with only slight decomposition. The *bromide* was prepared (method D) by addition of a cold aqueous solution of trimethylpyrylium chloroferrate to a stirred mixture of aqueous sodium acetate and benzene, separating and washing the benzene layer with water and drying ($MgSO_4$). The bromide was precipitated by passing dry HBr into the benzene solution of the pseudobase. After being pressed on porous plate it was recrystallized by dissolution in the minimum amount of abs. ethanol, and addition of benzene and pet. ether,

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[18] K. Dimroth, *Angew. Chem.* **72**, 331 (1960).

[19] A. T. Balaban and C. D. Nenitzescu, *Revue de Chimie Acad. R.P.R.*, **6**, 269 (1961); *Studii si Cercetări Chim. Acad. R.P.R.*, **9**, 251 (1961).

[20] F. Klages and H. Träger, *Chem. Ber.* **86**, 1327 (1956).

[21] A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* 3553 (1961).

colourless hygroscopic crystals m.p. 199°. (Found: C, 47·20; H, 5·49; Br, 38·89. $C_8H_{11}BrO$ requires: C, 47·31; H, 5·46; Br, 39·35%). The *chloride* similarly obtained is so hygroscopic that it could not be conveniently handled and analysed.

2,6-*Diethyl-4-methylpyrylium salts*. The *iodide* (method C) is yellow, m.p. 175° (from ethanol–ether in the presence of SO_2) (Found: C, 43·19; H, 5·79; I, 45·01. $C_{10}H_{15}IO$ requires: C, 43·18; H, 5·43; I, 45·63%).

2,6-*Di-t-butyl-4-methylpyrylium iodide*, yellow (method C) was recrystallized from SO_2-containing ethanol and ether, m.p. 170°. It is very soluble and undergoes discoloration on keeping. (Found: C, 48·87; H, 6·74; I, 36·84. $C_{14}H_{23}IO$ requires: C, 50·30; H, 6·93; I, 37·98%). The *triiodide* m.p. 95°, was obtained by recrystallization from ethanol of the crude product obtained by method C. (Found: C, 28·66; H, 4·07; I, 64·57. $C_{14}H_{23}I_3O$ requires: C, 28·60; H, 3·94; I, 64·75%).

2,6-*Dimethyl-4-ethylpyrylium chloroferrate*, m.p. 43° (from HCl) (Found: C, 34·10; H, 4·18; $C_9H_{13}Cl_4FeO$ requires: C, 36·27; H, 4·40%).

2,4-*Dimethyl-6-phenylpyrylium salts*. *The chloroferrate* m.p. 148° (from HCl) (Found: C, 44·84; H, 3·57; Cl, 40·34. $C_{13}H_{13}Cl_4FeO$ requires: C, 45·12; H, 3·79; Cl, 40·99%). The *iodide*, orange-yellow (method C) was washed with aqueous SO_2 solution and recrystallized from ethanol–ether, m.p. dec. 198° (Found: C, 50·01; H, 4·14; I, 40·12. $C_{13}H_{13}IO$ requires: C, 50·02; H, 4·19; I, 40·66%).

2,6-*Dimethyl-4-phenylpyrylium salts*. The *chloroferrate*, m.p. 152° (from HCl) was obtained from the perchlorate prepared from α-methylstyrene, acetic anhydride and 70%-perchloric acid. (Found: C, 45·17; H, 4·30; Cl, 41·00. $C_{13}H_{13}Cl_4FeO$ requires: C, 45·12; H, 3·79; Cl, 40·99%). The iodide obtained from the perchlorate (method C) m.p. 210° (from ethanol–ether in the presence of SO_2) is brick-red. Lit.[5] m.p. 203° (Found: C, 50·44; H, 4·48; I, 40·48. Calc. for $C_{13}H_{13}IO$: C, 50·02; H, 4·19; I, 40·66%).

2,6-*Diphenyl-4-methylpyrylium iodide*, brick-red, m.p. dec. ca. 245° was obtained from the chloroaluminate and recrystallized from ethanol. Lit. m.p. dec. 240°,[9] 238°.[22] (Found: C, 57·99; H, 4·50; I, 33·35. Calc. for $C_{18}H_{15}IO$: C, 57·77; H, 4·04; I, 33·91%).

2,3,4,6-*Tetraphenylpyrylium iodide*, brown, m.p. 218° was obtained from the perchlorate and HI (method C) (Found : C, 67·87; H, 4·53; I, 24·52. $C_{29}H_{21}IO$ requires: C, 67·98; H, 4·13; I, 24·77%).

2,3,6-*Triphenyl-4-methylpyrylium salts* were prepared from the perchlorate.[23] *Chloroferrate* m.p. 170° (Found: C, 55·35; H, 3·86. $C_{24}H_{19}Cl_4FeO$ requires: C, 55·32; H, 3·67%). The yellow *iodide* obtained by method C melts with decomposition at 252°.

A preliminary account of these methods of preparation of pyrylium halides has been published.[24]

UV and visible absorption spectra were measured with a Jena VSU-1 spectrophotometer with quartz and glass prisms at room temp. Solvents were carefully purified, dried and fractionated.

RESULTS AND DISCUSSION

Absorption maxima of ten pyrylium salts are presented in Table 1 and in Figs. 1–4. The data referring to pyrylium perchlorates are partly taken from a previous paper. Oscillator strength values f were calculated by the approximate formula $f = 4{\cdot}32{\cdot}10^{-9}\ \varepsilon_{max}\cdot \Delta\tilde{\nu}_{1/2}$ when both the left and right slope were free from overlap with other bands (when overlap was present, $\Delta\tilde{\nu}_{1/2}$ was taken twice the difference between $\tilde{\nu}_{1/2}$ of the free slope and $\tilde{\nu}$ of the band axis). As seen from Table 1, in most cases on replacing the polar solvent of the perchlorate by dichloromethane for the iodide, all bands are bathochromically shifted; however the shift is different for different bands and for different salts.

The data for the charge-transfer band have specified concentrations because this band does not obey the Lambert-Beer law.[11] This was verified for 2,4,6-triphenylpyrylium iodide as shown in Table 2 and Fig. 3. A 45-fold concentration increase doubles the f value and causes a more than double increase of ε_{max}.

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[22] K. Dimroth, G. Arnoldy, S. v. Eicken and G. Schiffler, *Liebigs Ann.* **604**, 221 (1957).

[23] A. T. Balaban, *Tetrahedron Letters* 91 (1963).

[24] A. T. Balaban, *C. R. Acad. Sci., Paris* **256**, 4041 (1963).

TABLE 1. ABSORPTION MAXIMA OF PYRYLIUM SALTS[a]

No.	Substituent in position				Perchlorate[6]				Iodide in dichloromethane[b]					
												CT-Band		
	2	3	4	6	Solvent	x'-Band	y-Band	x-Band	x'-Band	y-Band	x-Band		Conc. (m moles/l)	10^4f
1	Me	H	Me	Me	H_2O[c]	—	230	285	—	243	285	360		68
							4550	12000		12600	10700	370		
												450	0·09	110
												530		
2	Et	H	Me	Et	H_2O	—	231	287	—	—	—	356		54
							4650	13200				280		
												449	1·1	69
												320		
3	Ph	H	Me	Me	H_2O	227	244	345	—	246	356	480	1·1	76
						11300	10200	24000		20800	20600	340		
4	Me	H	Ph	Me	H_2O	233s[b]	304s	327	243	300	342	503	2·1	107
						3300	20000	23400	14300	14200	22000	540		
5	Ph	H	H	Ph	CH_2Cl_2	243[b]	283[b]	415[b]	244	284	415	486	0·77	—
						10500	18500	30000	18400	14400	20400	110		
6	Ph	H	Ph	Me	H_2O	254	338	374	248	346	380	530	1·1	110
						14600	23600	29100	20200	20700	26200	540		
7	Ph	H	Me	Ph	CH_3CO_2H	236	277	392	242	281	398	485	1·1	110
						13800	18800	26900	18800	13600	19500	350		
8	Ph	H	Ph	Ph	CH_3CO_2H	278	361	408	283[d]	368	415	551	4·5	83
						36000	30000	24500	18300	36000	26100	400		
9	Ph	Ph	Me	Ph	CH_3CO_2H	—	284[b]	392[b]	239	289	400	490s	0·86	—
							19600	25400	19300	19300	23300	—		
10	Ph	Ph	Ph	Ph	CH_3CO_2H	296	379	412	296[e]	374	438	550s	0·93	—
						17500	20400	19200	35600	27500	11100	—		

[a] Wavelengths λ_{max} in mμ (upper row) and molar absorptivities ε_{max} (lower row) are given ; s denotes shoulder.

[b] Newly-determined bands.

[c] In dichloromethane, λ_{max} 286 mμ (ε 13000); in acetonitrile 244 (12300) and 284 mμ (ε 13100).

[d] Additional band at 242 mμ (ε 25200).

[e] Additional band at 248 mμ (ε 1900).

Alkyl-substituted pyrylium salts (Nos. 1 and 2 in Table 1) present two CT bands, while phenyl-substituted salts present one band, probably because the lower-wavelength CT band is submerged by the x-band, whose bathochromic effect on substitution with phenyl is far larger than the corresponding effect of the CT bands.

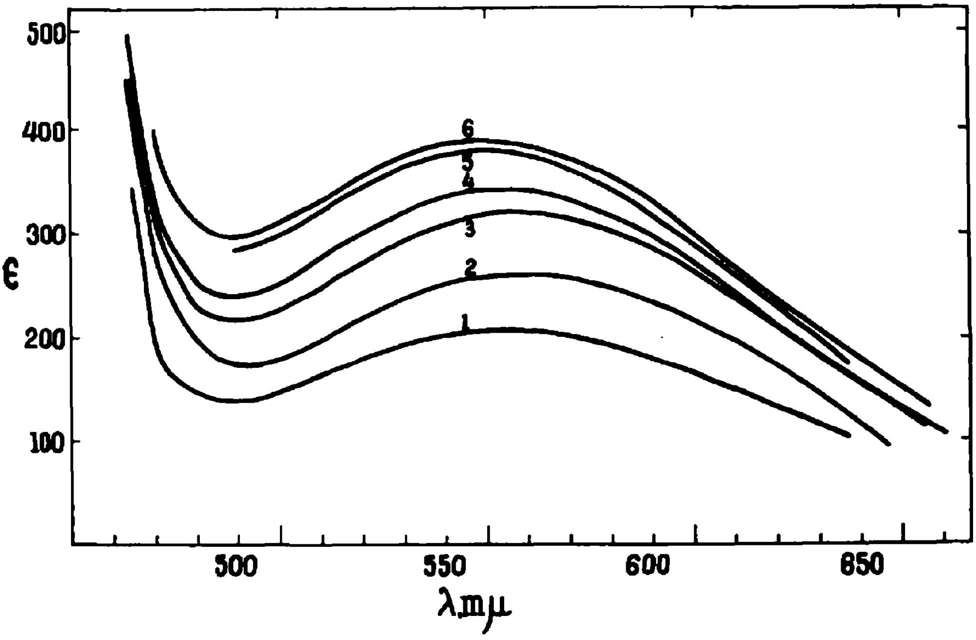

Fig. 3. Spectra of 2,4,6-triphenylpyrylium iodide in dichloromethane. Numbers and concentrations as in Table 2.

The lower-wavelength CT band falls in a region where the triiodide anion also absorbs (360 mμ).[9,10,25] By using solutions saturated with SO_2 (sulphur dioxide is itself an acceptor,[26] and its CT band with $I^{\ominus}$ is at 341 mμ in water and at 350 mμ in methanol), both CT bands of the two alkyl-substituted iodides persisted (cf. Fig. 2), evidencing therefore that they are not due to triiodide formed by decomposition (pyrylium iodides are thus more stable than tropylium iodides[12]). The energy difference between the two CT bands of 2,4,6-trimethylpyrylium iodide (5100 cm^{-1}) is smaller than that observed between the two bands of the iodide ion[27] or of 1-methylpyridinium iodide[9] (7400 cm^{-1}), but is of the same order of magnitude as the energy difference between the two CT bands of other pyridinium iodides,[10] therefore Kosower's arguments[9] may be considered valid also for pyrylium iodides.

A comparison may be made between the CT bands of pyridinium, pyrylium and tropylium iodides. It appears that the wavelengths of the CT bands increase in the above order: for 1-methylpyridinium in chloroform the CT maxima are at 379·6 and

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[25] F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *J. Chem. Soc.* 1092 (1931).

[26] D. Booth, F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.* **55**, 1293 (1959); J. Jander and G. Türk, *Angew. Chem.* **75**, 792 (1963).

[27] E. Lederle, *Z. physik. Chem.* **B10**, 121 (1930).

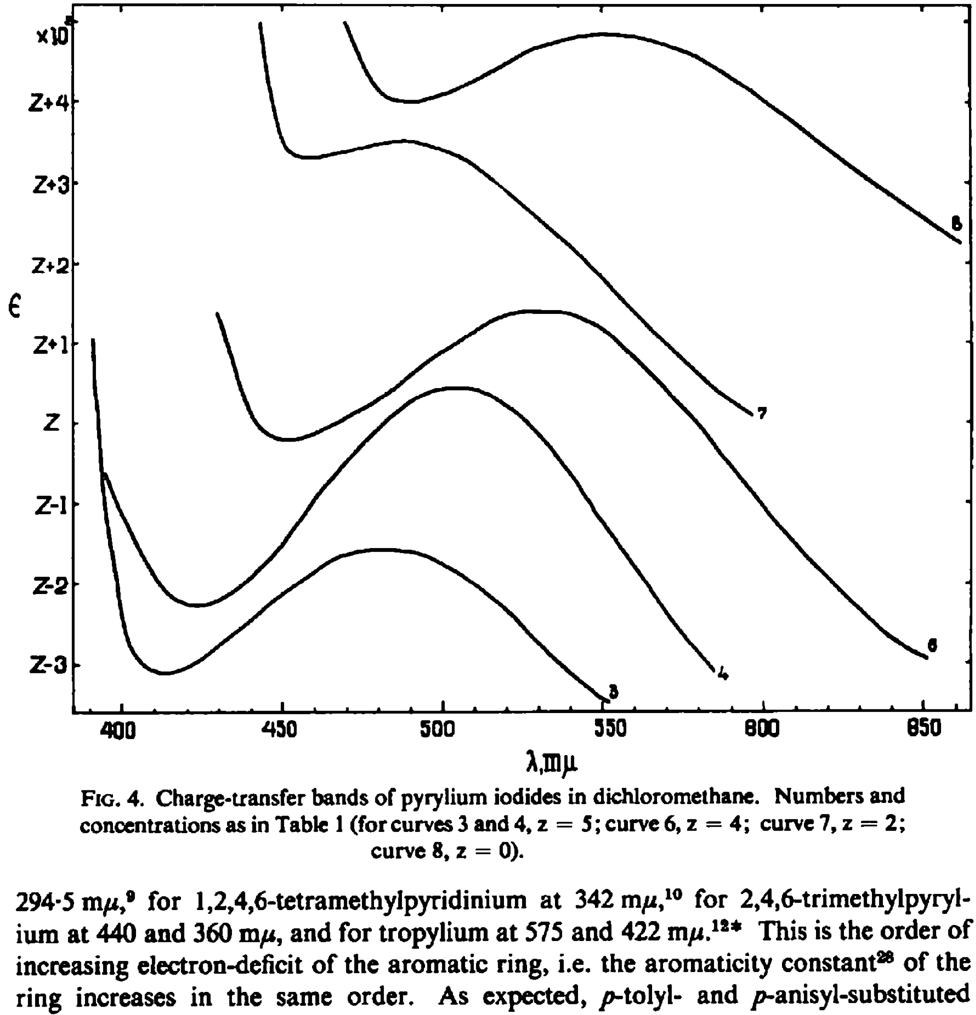

Fig. 4. Charge-transfer bands of pyrylium iodides in dichloromethane. Numbers and concentrations as in Table 1 (for curves 3 and 4, z = 5; curve 6, z = 4; curve 7, z = 2; curve 8, z = 0).

294·5 mμ,[9] for 1,2,4,6-tetramethylpyridinium at 342 mμ,[10] for 2,4,6-trimethylpyrylium at 440 and 360 mμ, and for tropylium at 575 and 422 mμ.[12*] This is the order of increasing electron-deficit of the aromatic ring, i.e. the aromaticity constant[28] of the ring increases in the same order. As expected, *p*-tolyl- and *p*-anisyl-substituted pyrylium iodides[29] present no CT band because electron-donating substituents cause a hypsochromic effect on the CT band and a bathochromic effect on the x absorption

Table 2. Data for the CT band of 2,4,6-triphenylpyrylium iodide in methylene dichloride

No.	Conc. moles/l	λ_{max}(mμ)	ϵ_{max}	10^4 f
1	0·9 . 10^{-4}	558	208	43
2	2·0	561	262	50
3	4·5	560	324	64
4	9·0	556	345	69
5	20	551	383	77
6	45	551	390	83

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[*] Revised values: 571·5 and 409 mμ (E. M. Kosower, personal communication.)

[28] A. T. Balaban and Z. Simon, *Tetrahedron* **18**, 315 (1962).

[29] A. T. Balaban, M. Gavăt and C. D. Nenitzescu, to be published.

band so that the former band is submerged under the latter. Electron-attracting substituents are expected to exert the opposite effect.

The effect of phenyl groups on the position of the CT band is rather difficult to interpret. As shown by the data from Table 3, the higher the number of substituent phenyl groups, the lower the half-wave potentials $E_{1/2}$ for monoelectronic electroreduction of pyrylium salts[30] and the lower the transition energy $\tilde{\nu}_{max}$ of the x-band.[6] The ranges corresponding to monophenyl-substituted and diphenyl-substituted pyrylium salts do not overlap in these cases; phenyl groups in α-position exert a slightly larger effect than those in γ-position. In the case of the CT band, however, the ranges corresponding to monophenyl- and diphenyl-substituted derivatives overlap considerably and phenyl groups in γ-position exert a much larger effect than those in α-position (one phenyl in γ-position produces a larger bathochromic effect on the CT band than two phenyl groups in α-position).

As emphasized by Dewar *et al.*[31] there exist locally-excited transitions in the acceptor organic cation leading to the absorption bands (x-bands of the iodides are practically identical to those of the perchlorates, due account being taken of the solvatochromy; for the other bands, some intensity differences are manifest), as well as charge-transfer transitions from the highest occupied "molecular" orbital (HOMO) of the donor iodide anion to the lowest empty molecular orbital (LEMO) of the organic cation. Since the donor is the same for the whole series of pyrylium iodides, a correlation should exist between $\tilde{\nu}_{CT}$ and the energy E_{LEMO}. Values of E_{LEMO} were calculated by the Hückel MO method using two sets of parameters: according to[32] with all $\beta = 1$, $\alpha_{O}\odot = \alpha + 2{\cdot}0\beta$, and for carbon atoms in α-position, neighbours of the $O^{\oplus}$ heteroatom, $\alpha_{C(O^{\oplus})} = \alpha + 0{\cdot}7\beta$ through a perturbational method, neglecting the two orbitals with the lowest and highest energy of each pyrylium and phenyl ring; and with parameters recommended by Streitwieser[33] $\alpha_{O^{\oplus}} = \alpha + 2{\cdot}5\beta$; $\alpha_{Me} = \alpha + 2{\cdot}0\beta$; $\alpha_{C(O^{\oplus})} = \alpha + 0{\cdot}25\beta$; $\alpha_{C(Me)} = \alpha - 0{\cdot}20\beta$; $\alpha_{C(O^{\oplus})(Me)} = \alpha$; $\beta_{ring} = \beta$; $\beta_{C-ring} = 0{\cdot}9\beta$; $\beta_{Me-ring} = 0{\cdot}7\beta$, using the digital IFA-101 computer for the complete solution.* Energies of the LEMO orbital, E_{LEMO}, thus found are included in Table 3, and show a satisfactory correlation with $E_{1/2}$, but no correlation with $\tilde{\nu}_{CT}$ (a rough correlation also exists between $E_{1/2}$ and $\tilde{\nu}_{x\text{-band}}$[30]).

Similarly, it was not possible to correlate $\tilde{\nu}_{CT}$ with the difference ΔE_{res} between the resonance energy of the substituted pyrylium cation and the resonance energy of the molecule resulted by covalent bonding of iodine to that position of the cation for which this difference is smallest (generally this position is the most electron-deficient α-position; in the case of 2,4-dimethyl-6-phenylpyrylium (No. 3), this position is the α-position bearing the methyl group). Calculations of ΔE_{res} were performed by a pertubational method using Streitwieser's parameters.

The following explanation is tentatively proposed for these CT spectra. In the

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* Thanks are due to Mr. I. Zamfirescu for computations.

[30] E. Gîrd and A. T. Balaban, *J. Electroanal. Chem.* **4**, 48 (1962); A. T. Balaban, C. Bratu and C. N. Rentea, *Tetrahedron* in press.

[31] M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.* **83**, 4560 (1961); M. J. S. Dewar and H. Rogers, *Ibid.* **84**, 395 (1962).

[32] Z. Simon, *Optika i Spektroskopyia* **12**, 22 (1962).

[33] A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists* Chap. 5. J. Wiley, New York (1961).

case of electroreduction one cannot consider an overlap between the LEMO of the pyrylium cation and the "electron orbital" of the dropping mercury electrode; however, in the case of pyrylium iodides the LEMO presents considerable overlap with the iodide orbital whence the electron is transferred. The electronic configuration

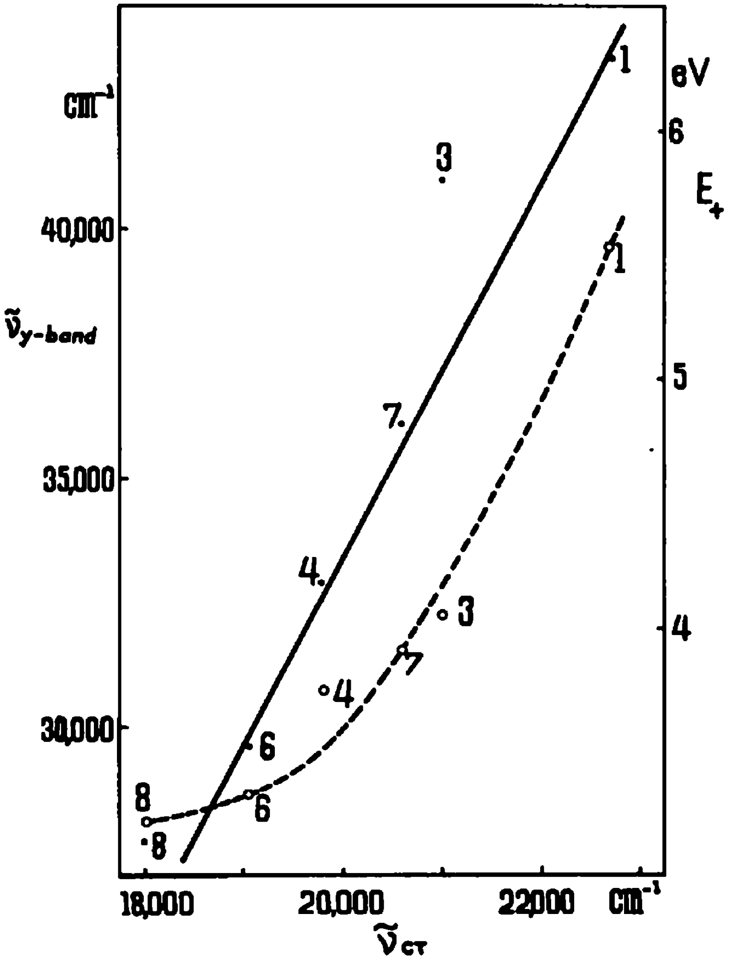

FIG. 5. Correlation of $\tilde{\nu}_{CT}$ with E_+ (dashed line) and with $\tilde{\nu}_{\gamma\text{-band}}$ (full line), cf. Table 3.

resulted by charge transfer may interact with electronic configurations of the pyrylium cation produced by locally-excited transitions, provided that certain symmetry conditions are fulfilled. These conditions refer to the symmetry plane δ perpendicular on the pyrylium ring, passing through the oxygen and the γ-carbon atoms (in a coarse approximation even in the case of the asymmetric salts). It seems reasonable to suppose that the electron is transferred form a 5p iodide orbital directed towards the pyrylium cation, and that the CT electronic configuration is symmetric relative to plane δ, since calculations show[32] that in all cases the LEMO is symmetric or approximately symmetric relative to this plane.

TABLE 3. COMPARISON OF EXPERIMENTAL AND CALCULATED DATA

				Experimental				Calculated			
No.	Substituent in position			Absorption spectrum of perchlorate[6] (cm^{-1})		Half-wave potential $E_{1/2}$(mV)[30]	Charge-transfer band of iidide $\tilde{\nu}_{CT}$(cm^{-1})	$(E_{LEMO} - \alpha)/\beta$		$\Delta E_{res}/\beta$	$E_+(A_1)$ after[32,35] (eV)
	2	4	6	$\tilde{\nu}_{x\text{-band}}$	$\tilde{\nu}_{y\text{-band}}$			after[32]	after[33]		
1	Me	Me	Me	35100	43500	−870	22700	−0·35	−0·663	1·320	5·53
3	Ph	Me	Me	29000	41000	588	21000	0·30	0·420	1·337	4·05
4	Me	Ph	Me	30600	32900	577	19800	0·30	0·433	1·333	3·75
6	Ph	Ph	Me	26700	29600	408	19050	0·26	0·296	—	3·33
7	Ph	Me	Ph	25500	36100	394	20600	0·26	0·215	—	3·91
8	Ph	Ph	Ph	24500	27700	300	18000	0·23	—	—	3·22

The data from Table 1 show that the energies of locally-excited transitions are greater than those of CT transitions. The closer these two energies, the more marked will be the lowering of the CT transition energy by configuration interaction. Table 3 includes locally-excited transition energies E_+ that are symmetrical relative to plane δ; they were calculated[32] using a modified Goodman and Shull procedure[34] and may be found, under the heading of the first A_1 band with calculated longitudinal polarization, in Table 3 from ref.[32] (for the trimethylpyrylium salt cf.[35]). It may be seen that for γ-phenyl-substituted pyrylium salts these symmetrical configuration lie lower than for salts with phenyl groups in α-position. Configuration repulsion will therefore cause a larger bathochromic effect in the former case than in the latter, leading to deviations from the parallelism between $\tilde{\nu}_{CT}$ and $E_{1/2}$ which would exist in the absence of this repulsion. Fig. 5 shows that a satisfactory correlation holds between E_+ and $\tilde{\nu}_{CT}$.

These energies E_+ with calculated longitudinal polarization correspond to the second locally-excited transition in the absorption spectrum of pyrylium salts, i.e. to the so called y-band[6] (the calculations[32] which indicated that an inversion of x- and y-bands occurs in the case of 2,6-dimethyl-4-phenylpyrylium are not confirmed by the present Hückel MO calculations; the difference is, however not essential, because the x and y bands are very close to one another in this case). Therefore, a correlation should exist between the CT band and the experimental data for the y-band.

As shown in Table 3 and Fig. 5, such a correlation is indeed found, and is more linear than that between $\tilde{\nu}_{CT}$ and E_+. Point 3 would require a higher $\tilde{\nu}_{CT}$ value than that experimentally observed; in this case, owing to the asymmetry of the molecule, the state corresponding to the x band contains an appreciable amount of locally-excited configuration symmetric relative to plane δ, so that it contributes to the bathochromic effect of the CT band.

Note added in proof—Recent investigations on the UV spectra of 2,6-dimethyl-4-arylpyrylium, where the aryl is phenyl, *p*-tolyl, or *p*-anisyl, showed that the assignment of x and y bands in compound No. 4 must be reversed (*Rev. Roumaine Chim.*, in press). This reassignment does not affect the discussion, but Tables 1 and 3 and Fig. 5 must be corrected.

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[34] L. Goodman and H. Shull, *J. Chem. Phys.* **22**, 1338 (1954).

[35] Z. Simon and C. Volanschi, *Studii şi Cercetări Chim. Acad. R.P.R.* **8**, 641 (1960).