

THE SPECTROSCOPY OF PYRYLIUM SALTS

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Abstract—The spectra of pyrylium perchlorate, various alkyl and aromatic derivatives, and cyanine-like dyes derived from pyrylium salts are discussed. These molecules are closely related to molecules which belong to the C_{2v} point group, and the existence of the symmetry permits a more detailed discussion of the spectra than has been attempted heretofore.

Through the efforts of Wizinger *et al.*¹⁻⁸ and Balaban *et al.*,⁹ the spectra of a number of pyrylium derivatives have become available. Calculations have been performed¹⁰⁻¹² which indicate that the low-energy spectra of these materials can be understood in terms of Hückel molecular orbital theory. In spite of the large number of data and the calculations, however, no particular attempt has been made to relate the spectra of these materials to one another, or to explore the relations that the spectra of pyrylium salts might bear toward the spectra of other classes of molecules. In this communication the spectra of several new derivatives of pyrylium salts are reported, the spectra of some previously reported derivatives are reported in more detail, and the relations between the spectra of the various derivatives are explored with some attention to their relation to other types of molecules.

The spectrum of pyrylium salts and alkyl derivatives

The spectrum of the pyrylium cation consists of two bands with $\lambda_{\max} = 269 \text{ nm}$ ($\epsilon = 8800 \text{ M}^{-1}\text{cm}^{-1}$) and 219 nm ($\epsilon = 2100 \text{ M}^{-1}\text{cm}^{-1}$).^{13,14} This spectrum is conveniently regarded as a member of the progression, benzene-pyridine-pyridinium-pyrylium. In this progression, the pi-electron structure of pyridine is similar to that of benzene, the difference being a lone electron pair on the nitrogen atom. The other major difference is the symmetry of the molecule which is D_{6h} in benzene and C_{2v} in pyridine. Thus pyridine can be compared to benzene by evaluating the effect of reducing the symmetry of benzene itself from D_{6h} to C_{2v} .

The pi-electronic structure of benzene and the associated low-energy spectrum can be regarded as well understood.¹⁵⁻¹⁷ The ground-state pi-electron configuration of benzene is $a_{2u}^2 e_{1g}^4 e_{2u} b_{2g}$, and the

three low-energy pi-electronic transitions are B_{2u} (4.68 eV), B_{1u} (5.99 eV), and E_{1u} (6.81 eV). These transitions are all derived from the electron configuration $e_{1g} \rightarrow e_{2u}$. Reducing the symmetry from D_{6h} to C_{2v} simply involves changing the labels; when the C_2 axis includes two carbon atoms (the situation appropriate to the problem at hand), the ground-state electron configuration of benzene becomes $b_1^2(b_1^2 a_2^2)(b_1 a_2) b_1$, and the low-energy transitions become B_2 , A_1 and $(B_2 + A_1)$, respectively, where the parentheses imply energy degeneracy. The B_2 pi-electronic transition arises from an equal mixture of $b_1 \rightarrow a_2$ and $a_2 \rightarrow b_1$ electron configurations; the A_1 transitions arise from equal mixtures of $a_2 \rightarrow a_2$ and $b_1 \rightarrow b_1$ configurations.

Since pyridine is iso-pi-electronic with C_{2v} benzene, the low-energy pi-electronic spectrum of pyridine consists of a B_2 , and A_1 , and $B_2 + A_1$, located near 4.68 eV, 5.99 eV, and 6.81 eV, respectively. Investigations by various authors have verified these relations,¹⁸⁻²¹ which are shown in Fig 1.

Protonation of pyridine to form pyridinium does not affect the pi-electron structure of the molecule, it merely eliminates the lone electron pair on the N atom. This change should accentuate the C_{2v} symmetry of the molecule, thus increasing the splittings, and renders the nonbonding electrons sigma-bonding once again, the result of which is the elimination of the $n\pi^*$ transition. The band assignments have been established in the case of pyridinium^{22,23} and are shown in Fig 1.

Pyrylium is iso-pi-electronic with pyridinium, the major difference being a lone electron pair on the O atom; the symmetry of the molecule is the same. The spectrum of pyrylium is shown in Fig 1. This spectrum is easily understood in view of the preceding series, as is the spectrum of 2,4,6-trimethylpyrylium, which has been reported by Balaban *et al.*⁹ and is also shown in Fig 1. In these molecules, the lowest-energy pi-electronic transition is most probably a B_2 , the second transition an A_1 , and the correlations are as indicated in Fig 1. The spectrum

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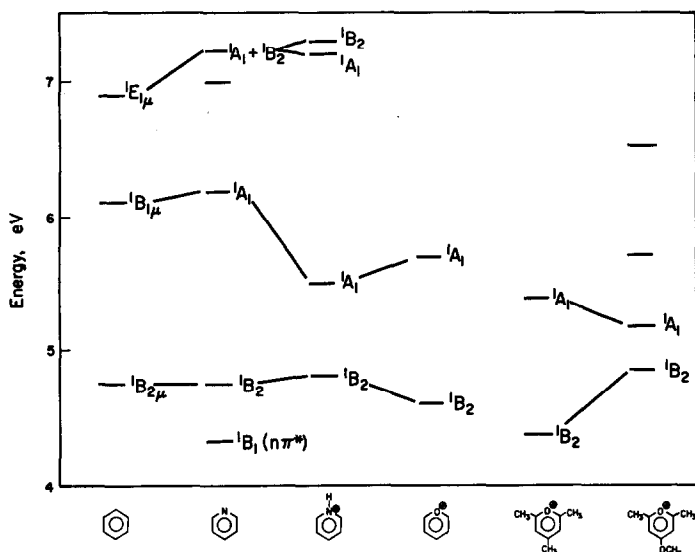


Fig 1. Correlation diagram relating low-energy electronic transitions of benzene, pyridine, pyridinium, pyrylium, 2,4,6-trimethylpyrylium, and 2,6-dimethyl-4-methoxy-pyrylium.

of 2,6-dimethyl-4-methoxypyrylium perchlorate has been investigated as a part of this work. It has been included in Fig. 1 and shown in detail in Fig. 2.

In this paper structural formulas and chemical names are given in the figures together with the spectra. Materials are therefore referred to by figure number, as 2, 3A, etc. Addition of the oxygen atom in the 4-position adds a b_1 molecular orbital to the pi-electron structure of the pyrylium. The

situation is similar to that found recently in the case of aniline,²⁴ i.e., the b_1 derived from the oxygen is far down the pi-manifold and has the effect of raising the energy of the b_1 orbitals above it, nearby b_1 orbitals being raised relatively more, and higher energy b_1 's being raised relatively less. Thus the low-energy B_2 transition, which is derived for the most part from an $a_2 \rightarrow b_1$ configuration, is raised in energy, whereas the low-energy A_1 is decreased in energy, since it is derived from $b_1 \rightarrow b_1$ configuration. Thus the assignments given in Fig 1 can be considered reasonably firm, although they have not been proved by the observation of polarized single-crystal spectra in the cases of the pyrylium salts.

Before we leave this class of molecules, it is worthwhile to call attention to the absence of low-energy $n\pi^*$ transitions in the pyryliums. The pyrylium salts do possess nonbonding electrons, and it might be expected that the lowest-energy electronic transition would be an $n\pi^*$, as is the case with pyridine. No such transition has been reported for pyrylium salts, and no such transition was located in 2 perchlorate in the course of this work despite an extensive search, which would have turned up any transition with an extinction coefficient larger than $1.0 M^{-1}cm^{-1}$. The $n\pi^*$ of pyridine is estimated by Stephenson¹⁹ to have an extinction coefficient of several hundred, and it is expected that such a band would have been observed in 2 if it existed below the lowest $\pi\pi^*$. It seems necessary to infer that the $n\pi^*$'s of pyrylium salts lie at higher energy than the lowest $\pi\pi^*$. Such an assertion makes sense if one recalls that the oxygen atom of pyrylium bears some fraction of a positive charge,

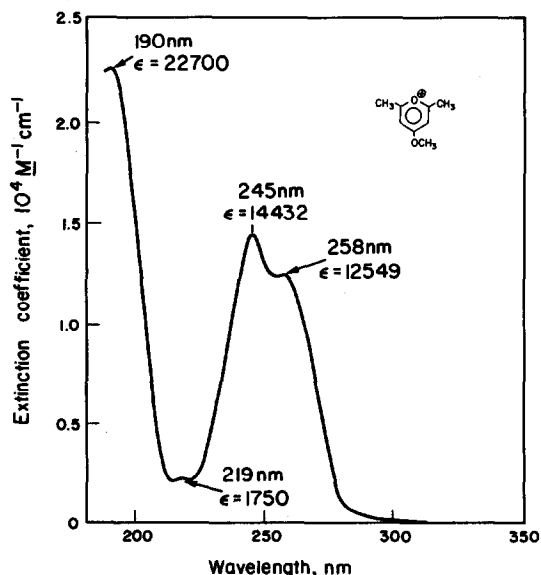


Fig 2. Absorption spectrum of 2,6-dimethyl-4-methoxy-pyrylium perchlorate in MeCN.

and that an $n\pi^*$ transition must result in a much larger positive charge being localized on the oxygen atom, since the nonbonding electron must come completely from the oxygen atom to be shared around the ring. Thus the $n\pi^*$ transitions of pyrylium are shifted to higher energy by an electrostatic effect not present in pyridine.

The spectra of aromatic pyrylium derivatives

These materials can be divided into three classes according to the positions of the substituents: molecules with substituents in the 2- and 6-positions, those with substituents in the 4-position, and those with substituents in 2-, 4-, and 6-positions. If it is assumed that the pi-electron systems of the derivatives remain in C_{2v} , these classes are divided according to the transformation properties of the substituents under the operations of C_{2v} ; substituents in the 2- and 6-positions transform into one another under C_2 and σ_v , but substituents in the 4-position transform only into themselves. This difference in transformation properties gives rise to differences in the substituent effects, which is the basis for the utility of the division of these materials into the classes.

As an example of the sort of behavior experienced in each of these classes, spectra of various aromatic pyrylium salts are shown in Figs 3 and 4.

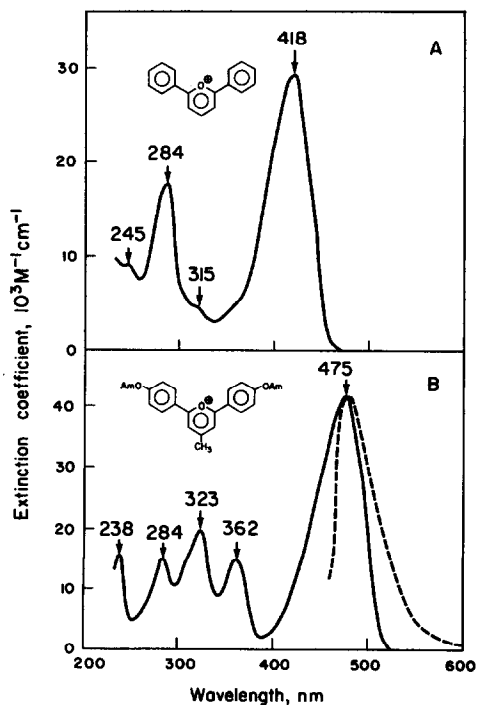


Fig 3. A: Absorption spectrum of 2,6-diphenylpyrylium perchlorate in CH_2Cl_2 . B: Spectra of 2,6-bis(4-amyloxyphenyl)-4-methylpyrylium perchlorate. — Absorption in CH_2Cl_2 . - - - Emission in MeOH. $\lambda_{\text{exc}} = 450 \text{ nm}$.

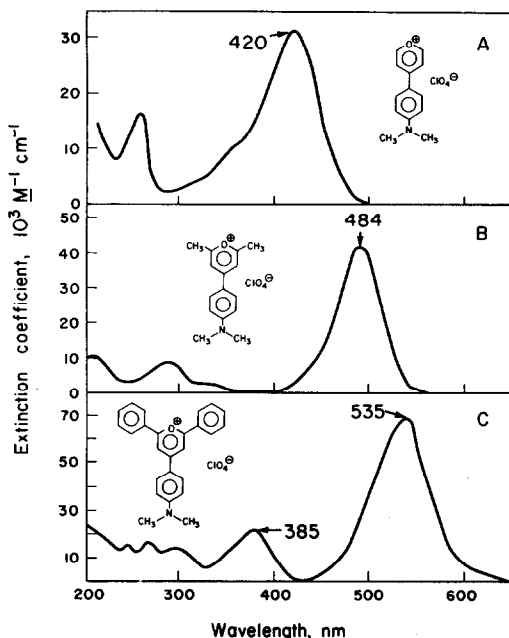


Fig 4. Absorption spectra in MeCN. A: 4-(4-dimethylaminophenyl)pyrylium perchlorate. B: 2,6-dimethyl-4-(4-dimethylaminophenyl)pyrylium perchlorate. C: 2,6-diphenyl-4-(4-dimethylaminophenyl)pyrylium perchlorate.

Intensity data for the longest-wavelength bands of a number of aromatic pyrylium derivatives are shown in Table 1.

If these molecules are all in C_{2v} , symmetry requirements prevent charge from migrating between substituents in the 2- and 6-positions; corresponding positions in the 2- and 6-substituents must bear the same charge. As a consequence, 2- and 6-position substituents are not as effective in producing low-energy transitions as are 4-position substituents. Aromatic substituents in the 4-position have two or more carbon atoms in the pi-electron system and also on the C_2 axis. There are no symmetry restrictions of charge density changes on these atoms; charge can move freely from one end of the molecule to the other.

The highest occupied orbital of aniline is a b_1 ,²⁴ and the positively charged pyrylium ring must certainly be regarded as an acceptor with a low-lying unoccupied b_1 (derived from benzene e_{2u}); it is therefore reasonable to suppose that the lowest electronic transition of **4a** is an A_1 ($b_1 \rightarrow b_1$), as was found in the similar case of *p*-nitroaniline.²⁵

The situation in **4A** is also similar to that in *p*-nitroaniline in that the symmetry axes of the composite molecule are the same as those of the substituents. It is therefore possible to use the wavefunctions of the substituents as a starting point from which to consider the spectrum. No such simplification is possible in the case of the 2- and 6-position sub-

Table 1. Positions and intensities of longest-wavelength electronic absorption bands of aromatic pyrylium derivatives

Material	λ (nm)	E (eV)	ϵ ($M^{-1}cm^{-1}$)	$\Delta\epsilon^a$	f^b	Ref.
3A	418	2.96	29,400	200	0.39	c
2,6-Diphenyl-4-methylpyrylium	392	3.16	26,900			9
3B	475	2.61	42,200	200	0.54	c
2,6-Dimethyl-4-phenylpyrylium	327	3.79				10
4A	420	2.95	31,200		0.52	c
4B	484	2.56	41,500		0.82	c
2,4,6-Triphenylpyrylium	405	3.06	27,600	200	0.31	9, 10 ^c
4C	535	2.32	67,500		0.74	c

^aFrom a least-squares fit to Beer's Law using the "t" distribution at 50% confidence limits.

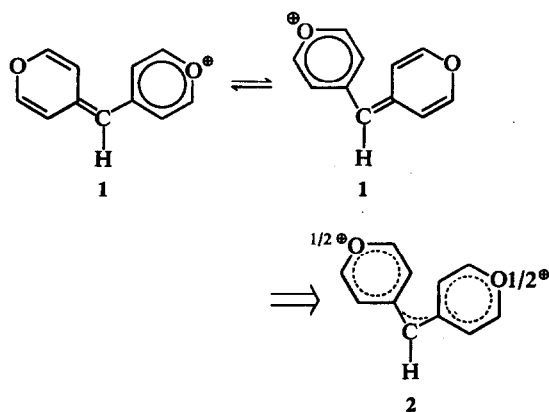
^bCalculated from $f = 4.312 \times 10^{-9} \int \epsilon d\nu$.

^cThis work.

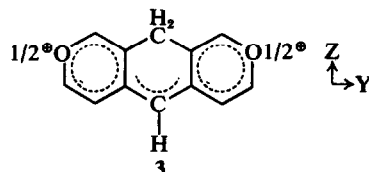
stituents, since the symmetry axis of the pyrylium ring does not coincide with any symmetry axis of the 2- and 6-position groups. An absorption band at 385 nm does appear to be characteristic of the 2,6-diphenylpyrylium group, as in 3A, 4C, 5A, 5C, 6B and 7B; a band in the 435–485-nm region seems to be characteristic of the 2,6-bis(4-amyloxyphenyl)pyrylium grouping (3B, 5B, 6C, 7A). These bands would seem most probably to be B_2 bands of the ($a_2 \rightarrow b_1$) type; charge migrates from the substituents into the pyrylium ring. This is consistent with the previous assumption that the highest occupied orbital of pyrylium is an a_2 , and the lowest empty orbital of pyrylium is a b_1 . In such discussion it must be remembered that the orbitals involved in the transitions of the 2,6-aromatic substituted molecule are not simply related to the corresponding orbitals in benzene, as was the case in 4-substituted derivatives.

The spectra of cyaninelike pyrylium dyes

If two pyrylium moieties are connected to a common methylene group and a proton is removed from the methylene group, a simple cyaninelike pyrylium derivative is formed.



For the moment it will be assumed that the molecule is formed as



and is in C_{2v} . The $—CH_2$ group makes no contribution to the pi-electron system of the molecule, and is neglected except for the fact that its presence enforces C_{2v} symmetry on the molecule. For molecule (3), symmetry considerations permit some deductions to be made concerning the electronic structure and spectra. These deductions can then be applied to other molecules in the same class which can be regarded as perturbations on (3).

Since electron densities are the squares of wavefunctions, they must belong to the totally symmetric representation of the molecular point group. Thus the positive charge of molecule (3) can be localized on the methine group to any extent desired, since the methine carbon is not interchanged with any other atom by any operation contained in C_{2v} , but the charge remaining must be distributed equally between corresponding positions, i.e., positions interchanged by C_2 and σ_v of the two six-membered rings. Since corresponding positions of each ring bear the same charge at any instant, it makes little sense to discuss the spectra in terms of charge migrating between the substituent rings.

Since the pi-wavefunctions of 3 belong either to an a_2 or b_1 irreducible representation of C_{2v} and the central methine group has a node in the a_2 wavefunctions, clearly the methine group must play a central role in the chemistry and spectroscopy of these materials. For B_2 (y-polarized) transitions, the methine group must act either as an electron source ($b_1 \rightarrow a_2$) or as an electron sink ($a_2 \rightarrow b_1$). For one class of A_1 (z-polarized) transitions, the methine group does not permit direct interaction

between the rings ($a_2 \rightarrow a_2$), although interaction can occur through configuration interaction, or through interaction of the fields associated with the transition moments. For only one class of pi-electronic transitions, the A_1 ($b_1 \rightarrow b_1$), does the methine group enter both ground and excited states, as a source or a sink, since the electron density gained or lost by the methine group must be symmetrically distributed over the two rings.

Intuition leads to the postulate that in the ground state of **3**, the positive charge is localized more in the rings than on the methine group, and that the lowest-energy electronic transition is likely to involve migration of an electron from the methine group into the rings to the positively charged centers. This is equivalent to asserting that the lowest-energy electronic transition is a B_2 (y -polarized) of the ($b_1 \rightarrow a_2$) type. This intuitive assertion can be

experimentally verified to some extent by observing the spectra of substituted derivatives; provision of an electron donor in the place of the methine hydrogen should shift the lowest absorption to lower energy if intuition is correct or to higher energy if the transition is a B_2 of the ($a_2 \rightarrow b_1$) type, have very little effect if the transition is an A_1 of the ($a_2 \rightarrow a_2$) sort, and have an unpredictable effect if the transition is of the ($b_1 \rightarrow b_1$) type.

The difference between **2** and **3** is that in **2** the rings are twisted slightly with respect to one another; **2** is therefore not in C_{2v} . This difference is relatively small, however, and it might be expected that the discussion given above for the case of **3** would apply in the case of **2**. No molecules of the **3** type are known, but spectra of several derivatives **2** are known; three of these are shown in Fig. 5.

The spectra shown in Fig 5, as well as the spectra

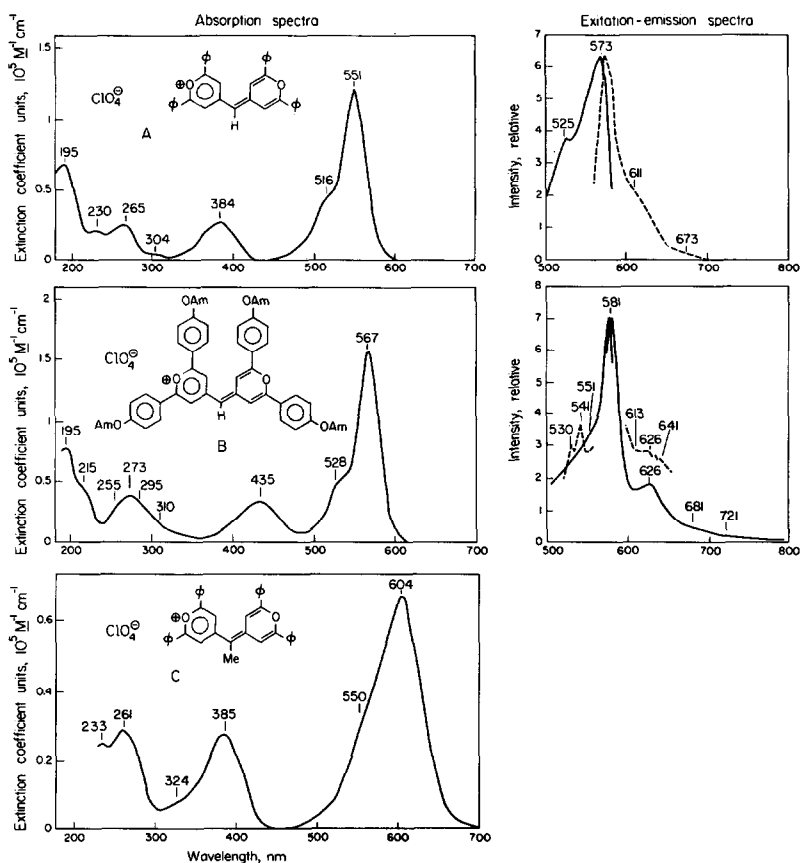


Fig 5. A: Spectra of 2,6-diphenyl-4-[2,6-diphenyl-4H-pyran-4-ylidene)methyl]pyrylium perchlorate. — Absorption in MeOH. — Action spectrum for emission at 590 nm. - - - Emission spectrum for excitation at 520 nm. B: Spectra of 2,6-bis(4-amyloxyphenyl)-4-[2,6-bis(4-amyloxyphenyl)-4H-pyran-4-ylidene)methyl]-pyrylium perchlorate. — Absorption in MeCN. — Action spectrum for emission at 625 nm. - - - Action spectrum for emission at 580 nm. — Emission spectrum for excitation at 570 nm. - - - Emission spectrum for excitation at 580 nm. C: Absorption spectrum of 2,6-diphenyl-4-[1-(2,6-diphenyl-4H-pyran-4-ylidene)ethyl]pyrylium perchlorate in MeCN.

of trimethinecyanine-type pyrylium dyes shown in Figs 6 and 7, exhibit the shoulder about 1400 cm^{-1} to the blue of the long-wavelength absorption characteristic of cyanine dyes. Since this band has a similar shoulder in the emission spectrum which is partly resolved at low temperature, the shoulder must be assigned to vibrations. The shoulder decreases dramatically in importance when the hydrogen atoms of the methine chain are replaced by methyl groups, as is evident on comparing the spectra of **5A** and **5C**, and the spectrum of **6B** with that of **7B**. The vibrations that produce the shoulder must therefore be associated with the methine chain.

In addition to decreasing the importance of the short-wavelength shoulder, substitution of methyl groups in the methine chain shifts the lowest-energy electronic absorption to substantially lower energy. Since the methyl group is an electron donor, the shift to lower energy implies that the C atoms of the methine chain lose electron density on transition to the excited state, in agreement with the intuitive

picture that the electron comes from the methine chain and goes to the rings (formally to the oxygen atoms) on excitation. Such a transition is a $B_2 (b_1 \rightarrow a_2)$ in the C_{2v} molecule **3**.

Aromatic substitution in the 2- and 6-positions of the pyrylium rings gives rise to characteristic electronic absorption bands in the 375–500-nm spectral region. The 385-nm band present in **5A**, **5C**, **6B** and **7B** can be considered characteristic of 2,6,2',6'-tetraphenyl substitution, and the bands at 435–445 nm in molecules **5B** and **6C** characteristic of 2,6,2',6'-tetra(4-amyloxyphenyl) substitution. These bands are very similar to the corresponding bands of simple pyryliums (Fig 3) or aromatic pyryliums (Fig 4). The 2,6- and 2',6'-chromophores do not interact strongly with one another, since the spectra of the cyanine derivatives are so similar to those of the simple pyryliums; the molecule with both chromophores, **7A**, exhibits bands at 385 and 470 nm, each with about half the intensity of the band in the tetrasubstituted molecules **5A** and **5B**.

Comparison of the spectra of the tetra-*t*-butyl-

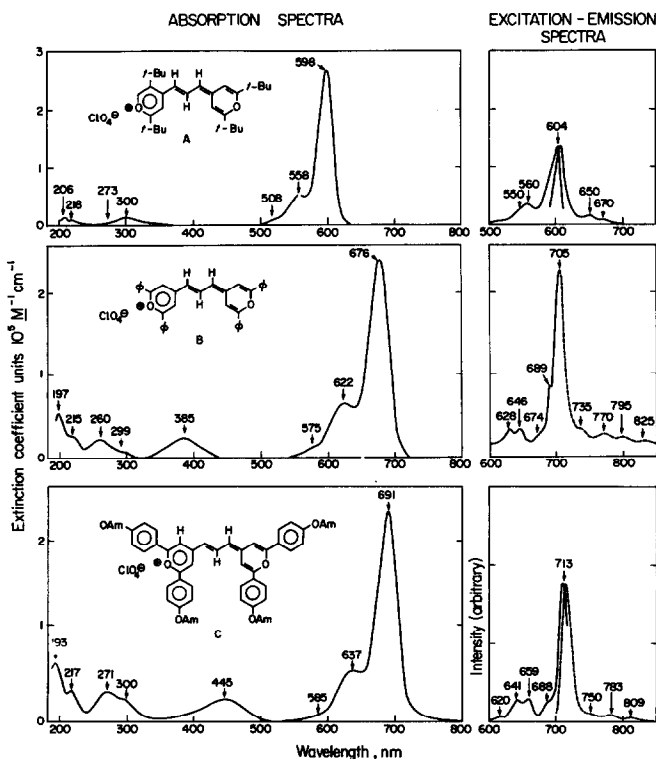


Fig 6. A: Spectra of 2,6-di-*t*-butyl-4-[3-(2,6-di-*t*-butyl-4H-pyran-4-ylidene)propenyl]pyrylium perchlorate. — Absorption in MeOH. — Emission spectrum for excitation at 570 nm. — Action spectrum for emission at 720 nm. B: Spectra of 2,6-diphenyl-4-[3-(2,6-diphenyl-4H-pyran-4-ylidene)propenyl]pyrylium perchlorate. — Absorption in MeCN. — Emission spectrum for excitation at 650 nm. — Action spectrum for emission at 720 nm. C: Spectra of 2,6-bis(4-amyloxyphenyl)-4-[3-(2,6-bis(4-amyloxyphenyl)-4H-pyran-4-ylidene)propenyl]pyrylium perchlorate. — Absorption in MeCN. — Emission spectrum for excitation at 640 nm. — Action spectrum for emission at 740 nm.

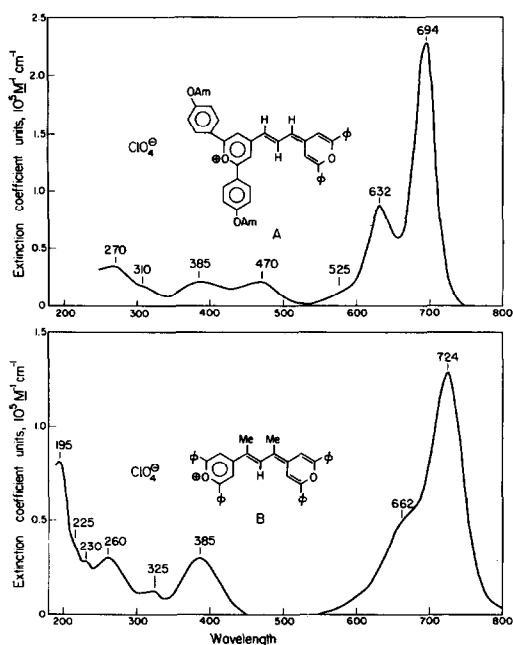


Fig 7. A: Absorption spectrum of 2,6-bis(4-amyloxyphenyl)-4-[3-(2,6-diphenyl-4H-pyran-4-ylidene)propenyl]-pyrylium perchlorate in CHCl_3 . B: Absorption spectrum of 2,6-diphenyl-4-[3-(2,6-diphenyl-4H-pyran-4-ylidene)-1,3-dimethylpropenyl]pyrylium perchlorate in MeCN.

Table 2. Band position and intensity data for cyanine-type pyrylium dyes

Molecule	λ (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	f^a
5A	551	129000	0.94
	384	27800	0.39
5B	567	163000	1.08
	435	33900	0.465
5C	604	66800	0.60
	385	27300	0.46
6A	598	267000	1.20
6B	686	117000	1.21
	385	12500	0.20
6C	691	210000	1.00
	445	19700	0.31
	694	228000	1.13
7A	470	19200	
	385	21200	
7B	724	139200	1.0
	385	30600	0.51

^aCalculated from $f = 4.312 \times 10^{-9} \int \epsilon d\nu$.

substituted dye **6A** with the tetraphenyl- and tetra-(4-amyloxyphenyl)-substituted dyes **6B** and **6C** gives an idea of the interaction between aromatic 2,6-substituents and the main low-energy chromophore. Once aromatic 2,6-substitution has been provided, little change is produced in the low-

energy transition by altering the character of the aromatic substituent. This is an indication that the interaction observed between the chromophores is not primarily due to direct modification of the electron density at a sensitive position in the molecule, but is an interaction by more indirect means. The dramatic effect produced by methyl substitution in the methine chain is apparently due to modification of the electron density at a sensitive position in the molecule.

DISCUSSION

The spectra of pyrylium derivatives are most easily interpreted if it is assumed that the highest occupied pi-orbital of pyrylium is an a_2 and the lowest empty pi-orbital is a b_1 . The spectra of simple pyrylium derivatives are very closely related to those of benzene and aniline.

The spectra of pyrylium derivatives formed by placing aromatic groups in the 4-position can be interpreted in terms of the concept of intramolecular charge transfer when the aromatic substituent possesses a b_1 highest occupied molecular orbital. Spectra of these derivatives, such as 4-(4-dimethylaminophenyl)-pyrylium perchlorate, contain a very strong, low-energy band that is best interpreted as an A_1 ($b_1 \rightarrow b_1$) in which the main effect is an electron migrating from the 4-aminophenyl group to the pyrylium ring. Previous work²⁴ indicates that the electron that migrates in this transition comes from the phenyl part rather than the 4-amino part of 4-aminophenyl.

The spectra of 2,6-diaromatic pyrylium derivatives are somewhat more difficult to interpret than those of 4-aromatic derivatives, since the symmetry axes of the pyrylium do not coincide with the axes of the substituents. The 2,6-diaromatic derivatives do have characteristic absorption bands that are changed very little on substitution at the 4-position. These bands are best interpreted as B_2 ($a_2 \rightarrow b_1$) transitions, which would be little affected by aromatic substituents in the 4-position when the 4-substituent has a b_1 highest occupied molecular orbital and an a_2 lowest empty molecular orbital. In this case, exemplified by 4-aminophenyl or 4-amyloxyphenyl substituents, the orbitals which have the correct symmetry to interact are well separated in energy, and the spectrum of the 2,6-diaromatic fragment is perturbed relatively little.

Cyaninelike dyes formed by coupling pyrylium groups through a methine linkage possess low-energy absorption bands that can be identified as B_2 ($b_1 \rightarrow a_2$) transitions of the corresponding C_{2v} species. Some care must be used in interpreting these spectra, since the symmetry elements of the cyaninelike molecule do not coincide with the elements of the pyrylium fragments. In these cyaninelike dyes the shoulder, which appears about 1400 cm^{-1} to the blue of the lowest-energy absorption band in many cyanines, is shown to be a super-

position of several vibrations of the methine chain. Substitution of Me groups for the H atoms of the methine chain greatly reduces the prominence of these vibrations.

EXPERIMENTAL

Spectra. Absorption spectra were obtained in appropriate solvents over a range of concentrations using a Cary Model 14 spectrophotometer. Emission spectra were obtained with an instrument of conventional design. A 1000-W xenon lamp operating through a 500-mm Bausch and Lomb grating monochromator provided the exciting light. Emitted light was analyzed by another 500-mm Bausch and Lomb monochromator equipped with an EMI 9558 photomultiplier, the signal from which was fed to the y-axis of an appropriately damped recorder. The x-axis of the recorder was driven by a voltage derived from the wavelength drive of the monochromator. Experimental conditions were chosen so that the spectral bandwidth of each monochromator was 1 nm. The angle between exciting and analyzing beams was 135°, and samples were run at 77°K and below 10⁻⁵ M. The phototube was run at 196°K and 2000 V. Emission spectra are uncorrected for variations of the detection system efficiency with wavelength.

Materials. The following compounds were prepared as described in the indicated references: Material 2,²⁸ 3A,²⁷ 4C.⁵

Material 3B. The method of Light and Hauser²⁸ was used to prepare 2,6-bis(4-amyloxyphenyl)-4H-pyran-4-one, m.p. 66–75°. (Found: C, 76.8; H, 7.8. Calc. for C₂₇H₃₂O₄: C, 77.1; H, 7.7%)

A mixture of 10 g of the pyrone and 50 ml of dimethyl sulfate was heated on a steam bath for 2 h, cooled, diluted with ether, and chilled. The solid was collected, dissolved in MeOH, and 10 ml of 70% HClO₄ added. The yellow solid was collected and crystallized (MeOH) yielding 7.2 g of 2,6-bis(4-amyloxyphenyl)-4-methoxypyrylium perchlorate, m.p. 170–171°. (Found: C, 62.7; H, 6.8; Cl, 6.7. Calc. for C₂₈H₃₅ClO₆: C, 62.8; H, 6.6; Cl, 6.6%)

A mixture of 6 g of the pyrylium salt, 2 g of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), 4 ml of N,N-diisopropylethylamine, and 50 ml of MeCN was stirred for 10 min and chilled overnight; the solid was collected and crystallized from MeCN yielding 5.9 g of 2,6-bis(4-amyloxyphenyl)-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-4H-pyran, m.p. 134–136°. (Found: C, 72.5; H, 6.7. Calc. for C₃₃H₃₈O₇: C, 72.5; H, 7.0%)

A solution of 3 g of the above pyran in 20 ml AcOH and 2.5 ml of 70% HClO₄ was heated on a steam bath for 10 min, cooled, and the solid collected and crystallized from AcOH giving 1.5 g of 3B, m.p. 194–196°. (Found: C, 64.8; H, 6.7; Cl, 6.8. Calc. for C₂₈H₃₅ClO₇: C, 64.8; H, 6.8; Cl, 6.8%)

Material 4B. A Grignard reagent was prepared from 15 g of *p*-bromo-N,N-dimethylaniline and 2.5 g of Mg in THF (100 ml) and added to a solution of 6 g of 2,6-dimethyl-4H-pyran-4-one in THF (100 ml) with stirring and cooling. The red mixture was stirred for 0.5 h in an ice bath and added to a large excess of cold, dilute HClO₄. The solid was collected and crystallized from alcohol yielding 8 g of 4B, m.p. 236–238°. (Found: C, 55.3; H, 5.6; N, 4.6. Calc. for C₁₅H₁₈ClNO₅: C, 55.0; H, 5.5; N, 4.3%)

Material 4A. This compound was prepared by the method described for 4B except that the 2,6-dimethyl-4H-pyran-4-one was replaced by 4H-pyran-4-one. The

product was obtained in 56% yield, m.p. 195–196°. (Found: C, 52.0; H, 4.6; N, 4.8. Calc. for C₁₃H₁₄ClNO₅: C, 52.1; H, 4.7; N, 4.7%)

Material 5A. A mixture of 1.2 g of 2,6-diphenyl-4-pyrone, 1.7 g of 2,6-diphenyl-4-methylpyrylium perchlorate,²⁹ and 20 ml Ac₂O was refluxed for 20 min, cooled, and the solid collected. The product was purified by extraction in a Soxhlet extractor to give 3.3 g 5A, m.p. 324–325°. (Found: C, 72.4; H, 4.6; Cl, 6.0. Calc. for C₃₅H₂₅ClO₆: C, 72.8; H, 4.4; Cl, 6.2%)

Material 5B. A mixture of 3.7 g of 3B, 3.1 g of 2,6-bis-4-amyloxyphenyl-4H-pyran-4-one, and 20 ml of Ac₂O was refluxed for 10 min, chilled, and the solid collected and crystallized from AcOH yielding 5.7 g of 5B, m.p. 93–94°. (Found: C, 71.4; H, 7.1; Cl, 3.9. Calc. for C₅₅H₆₅ClO₁₀: C, 71.7; H, 7.1; Cl, 3.9%)

Material 5C. A mixture of 0.72 g of 2,6-diphenyl-4-ethyl-pyrylium perchlorate, 0.5 g of 2,6-diphenyl-4H-pyran-4-one, and Ac₂O (12 ml) was refluxed for 40 min, cooled, and the dye was crystallized by extraction with MeOH in a Soxhlet extractor; yield 0.9 g of 5C, m.p. 283–284°. (Found: C, 73.5; H, 5.0; Cl, 5.9. Calc. for C₃₆H₂₇ClO₆: C, 73.2; H, 4.6; Cl, 6.0%)

Material 6A. A mixture of 5 g of 2,6-di-*t*-butyl-4-methyl-pyrylium perchlorate,²⁹ 5 ml of DMF, and 50 ml of Ac₂O was refluxed for 15 min, cooled, diluted with ether, chilled, and the solid collected. The solid was added to CH₂Cl₂ (75 ml) and 5% NaOH aq (25 ml), and the mixture was stirred overnight. The organic phase was separated, water washed, dried, and the solvent removed to give 3.5 g of 2,6-di-*t*-butyl-4-formylmethylene-4H-pyran. A mixture of the crude pyran, 3 g of 2,6-di-*t*-butyl-4-methylpyrylium perchlorate, and 50 ml of 1,2,3-trichloropropane was refluxed for 0.5 h, the trichloropropane was removed under reduced pressure, and the residue recrystallized from AcOH giving 4.8 g of 6A, m.p. 163–164°. (Found: C, 66.7; H, 8.5; Cl, 6.8. Calc. for C₂₉H₄₅ClO₆: C, 66.6; H, 8.3; Cl, 6.8%)

Material 6B. A mixture of 3.5 g of 4-methyl-2,6-diphenylpyrylium perchlorate,²⁹ 0.8 g of methyl diethoxyacetate, and 25 ml Ac₂O was refluxed for 10 min, 0.4 g of NaOAc added and the refluxing continued for 15 min. The solution was cooled and the solid collected and boiled with MeCN (100 ml). The mixture was filtered hot, and the insoluble material extracted in a Soxhlet extractor to give 1.9 g of 6B, m.p. 332–333°. (Found: C, 73.5; H, 4.2; Cl, 5.9. Calc. for C₃₇H₂₇ClO₆: C, 73.7; H, 4.5; Cl, 5.9%)

Material 7A. A mixture of 2,6-diphenyl-4-formylmethylene-4H-pyran³⁰ and 4 g of 3B in 50 ml of 1,2,3-trichloropropane was refluxed for 0.5 hr, cooled, diluted with ether, and the solid collected. The solid was crystallized from Ac₂O giving 2.1 g 7A, m.p. 132–134°. (Found: C, 72.4; H, 6.0; Cl 4.7. Calc. for C₄₇H₄₇ClO₆: C, 72.8; H, 6.1; Cl, 4.6%)

Material 7B. A mixture of 1.8 g of 4-ethyl-2,6-diphenylpyrylium perchlorate and 1.4 g of 2-(2,6-diphenyl-4H-pyran-4-ylidene)propionaldehyde (prepared from 4-ethyl-2,6-diphenyl-pyrylium perchlorate, DMF, and Ac₂O by a described procedure³⁰ in 2.5 ml of 1,2,3-trichloropropane was refluxed for 0.5 h, chilled, and the solid crystallized from MeCN, giving 0.7 g of 7B, m.p. 288–289°. (Found: C, 73.9; H, 5.1; Cl, 5.6. Calc. for C₃₉H₃₁ClO₆: C, 74.2; H, 5.0; Cl, 5.6%)

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