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Nature of the absorption bands of pyrylocyanines. 2. Influence of *t*-Bu, Ph and Th ring substituents

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Abstract

The effects of *t*-Bu, Ph and Th substituents on the absorption spectra of α-and γ-pyrylocyanines and their heteroanalogues have been investigated using experimental and quantum-chemical methods. It has been found that changes in the position of the absorption band depend on the electronegativity of the ring heteroatom (O, S, N CH_3), polymethine length, and the position of the bond between the chain and the end group. In the case of dye molecules, the effect of two substituents was additive, in contrast to the corresponding salts of the intial heterocycles. An explanation for the significant shifts in the absorption maximum of the thienylcyanines has been presented. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In a previous paper [1], the dependence of spectroscopic characteristics of tetraphenyl pyrylocyanines and their heteroanalogues on heteroatom type and isomerization, was described. It is well known that introducing phenyl groups and other substituents in the pyrylo residues has a substantial effect on electron transitions [2]. Also, significant spectral shifts can be achieved by introducing thienyl substituents [3], the net effect of which is extended conjugation. For a quantitative estimation of the increase in the conjugated system, the so called effective length of end groups (L) was proposed [4,5]. A topological parameter Φ_o, the so called electron donor ability of end group, has been used to define the position of the frontier levels with respect to the non-bonding level of π-electrons. In the approximation of quasi-long polymethines, it has been found that parameters L and Φ_o can be calculated using the minor coefficients of end group polynomials [4,5].

In addition, the use of complex heterocycles as terminal groups often gives deep colors and, hence, can be regarded as local chromophores [6]. As a rule, local electron transitions interact with the transitions in the basic chromophores (so called polymethine transitions). This leads to additional deepening of color.

The present work is concerned with spectral effects arising from incorporating an alkyl substituent, *t*-Bu, an aromatic group, (Ph), and the isovalence sulfur-analogue, thienyl (Th) in terminal nuclei in both γ- and α-pyrylocyanine dyes and the corresponding chlorate salts.

The polymethine dye cations and salts involved in this study have general formulae **1**–**4**.

2. Experimental

The synthesis of compounds **1**–**4** have been described previously [7–12]. Quantum-chemical calculation of molecular geometry and electron transition were performed using the standard AM1 semi-empirical method (HyperChem package).

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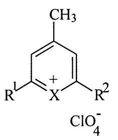

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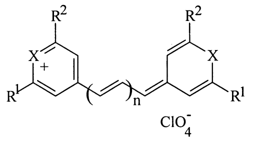

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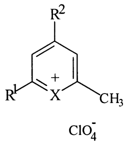

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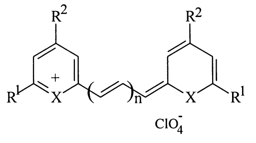


4

R^1, R^2 = *t*-Bu, Ph, Th; X = NCH_3, O, S; *n* = 0, 1, 2

3. Molecular geometry and spectral properties of heterocyclic salts

In determining the optimized geometries, *t*-Bu groups in initial heterocyclic residues were simulated by methyl groups ($R = CH_3$). This substituent change does not have a significant affect on bond length and bond and dihedral angles in the basic pyrylium structure and the heteroanalogues, and it is known that the spectral properties of *t*-Bu and methyl substituted pyrylocyanines are similar [13]. The calculated results are presented in Fig. 1. Replacing two methyl groups in the model compounds ($R^1 = R^2 = CH_3$) by phenyl groups does not lead to a significant change in molecular geometry in the α- and γ-methylsubstituted salts (**1** and **3**). Steric hindrances in diphenyl derivatives cause the phenyl rings to rotate out of the plane of the heterocycle. So, in the γ-series (**1**), the calculated dihedral angles between the phenyl group and the heterocycle φ(Ph–Het) are 60° ($X = NCH_3$), 8° ($X = O$) and 40° ($X = S$). These values are close to the experimental values [14]. Similarly, the thienyl-substituted pyridinium salts were found to be non planar: $\varphi(\text{Th–Het}) = 42°$ ($X = NCH_3$). However, the dihedral angles are close to zero for the pyrylium and thiopyrylium salts. In the α-series (**3**), the angles between the Ph or Th group and the attached heterocycle are different for positions 2 and 4. This is due to differencies in spatial effects.

Three conformers are possible for 2,6-dithienyl substituted salts, namely: ZEEZ, EEEE and ZEEE.

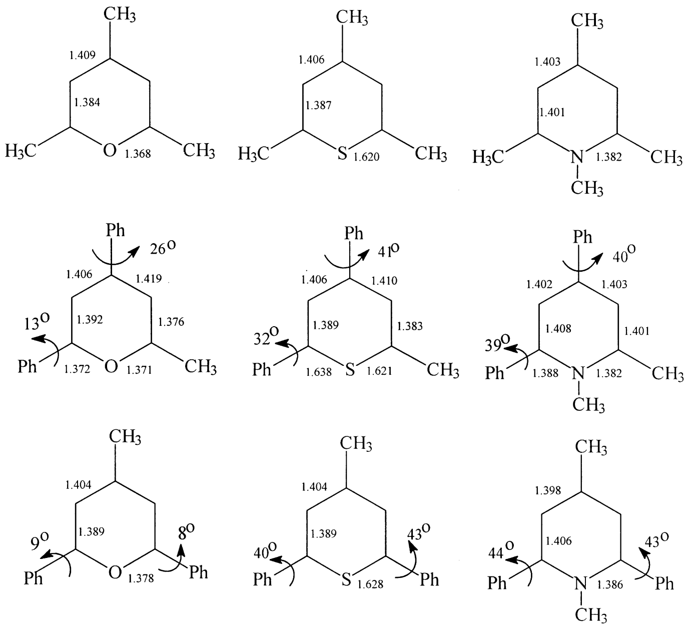
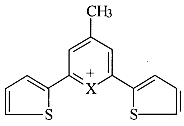
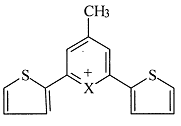


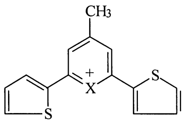
Fig. 1. Bond lengths and dihedral angles of Ph groups (arrows) in heterocyclic salts **1** and **3**.



ZEEZ



EEEE



ZEEE

Calculations show the EEEE isomer to be the most stable, but the energy difference between this conformer and ZEEZ and ZEEE conformers is equal less 2 kcal/mol. However, in conformer ZEEZ an S–S resonance interaction can occur. According to perturbation theory, a through space S–S interaction should lead to destabilization in the π-system, with an even number of atoms and to stabilization in system containing an odd number of atoms in the π-system. Simulation of S–S interactions using the PPP method ($\beta = -0.3$ eV) gave a destabilization energy of 0.042 EV.

Experimental studies involving the assessment of nuclear Overhauser effects have shown that the EEEE conformer of pyrylium and thiopyrylium salts is the most stable in solution [12]. The authors have explained the increased stability of this conformer to be the result of solvatation effects.

It was found that the absorption spectra of salts **1** and **3** are highly sensitive to the nature of substituents R^1 and R^2. Replacing a *t*-Bu group by a Ph or Th group led to appreciable lengthening of the conjugated system and hence to a decrease in the energy gap. As a result, the first absorption band shifts to longer wavelengths. It can be seen from Fig. 2. that electron density changes upon excitation are similar to that reported for linear odd-atom polymethine systems [15], which exhibit comparable deep colours.

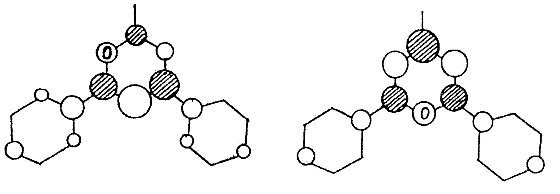


Fig. 2. Electron density redistribution upon excitation in α- and γ-pyrylium salts: shaded circles — electron density increases; empty circles — electron density decreases.

Table 1
Spectroscopic data for heterocyclic salts **1** and **3**

Salt	R^1	R^2	X	λ_{max}, nm	$\Delta\lambda$, nm[a]
1	*t*-Bu	*t*-Bu	NCH_3	275	–
γ-series			O	290	–
			S	305	–
	Ph	Ph	O	402	112
			S	405	100
	Th	Th	O	470	180
			S	492	187
3	*t*-Bu	*t*-Bu	NCH_3	272	–
α-series			O	285	–
			S	306	–
	Ph	*t*-Bu	O	360	75
			S	370	64
	t-Bu	Ph	O	342	57
			S	360	54
	Ph	Ph	O	384	99
			S	372	66
	Th	Th	O	443	158
			S	458	152

[a] $\Delta\lambda$ is calculated with respect to the corresponding di-*t*-Bu-substituted compound. Ph = phenyl, Th = 2-thienyl.

The observed absorption maxima of salts **1** and **3** are presented in Table 1. It can be seen that the effects of replacing a *t*-Bu group by phenyl in positions 2 and 4 in the α-series are different. Also, the nature of the heteroatom effects ($\Delta\lambda$) is reported, with a greater effect observed for the pyrylium compound than the thiopyrylium analogue. This may be explained by the lower position of HOMO level in pyrylium compounds containing the more electronegative oxygen atom, which leads to a stronger interaction between the HOMO of the heterocycle and the energy levels of the phenyl group.

Introducing a second phenyl group further shifts the absorption band; however, the effect of the second group is less pronounced (see Table 1). This is caused by the fact that the distance between the HOMO of the monophenyl-substituted compound and the energy level of the phenyl group is greater than that in the di-*t*-Bu-substituted compounds. As a result, the interaction between the energy levels involved is reduced. It can also be seen from Table 1 that the effect of two phenyl groups is greater in the γ-series.

Replacing *t*-Bu groups by thienyl residues leads to a substantial bathochromic shift. Like Ph substituents, the influence of thienyl groups is greater in the γ-series. However, the effect of replacing a phenyl group by thienyl is similar in the two series, e.g. 68 nm in γ-pyrylium and 59 nm in α-pyrylium, and 87 and 86 nm in the corresponding thioanalogues. Further, it is clear from Table 1 that $\Delta\lambda$ depends essentially on the electronegativity of the heteroatom.

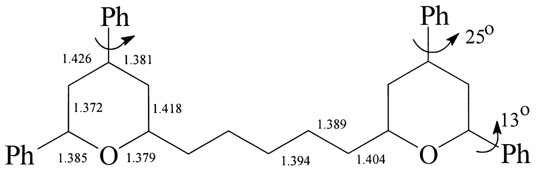
4. Substituent effects in dyes

4.1. Optimized molecular geometry

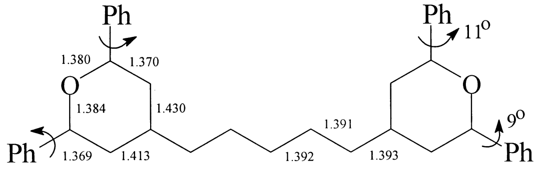
As an example, the optimized structure of the pyrylodicarbocyanines **2** and **4** ($n = 2$) is presented in Fig. 3. It can be seen that the carbon–carbon bond lengths are about the same and are close to 1.4 Å, which is typical for polymethine dyes [15]. Calculations showed similar bond length comparisons for the other dyes.

Comparison of Fig. 1 and 3 shows that the bond lengths in the heterocyclic moiety of dyes **2** and **4** are less equivalent than those in the corresponding salts (**1** and **3**), while the dihedral angles between the Ph or Th substituent and the heterocycle are practicaly the same in dyes and salts.

Information about molecular geometry of type **4** cyanine dyes was obtained by X-ray analysis [16]. Results show that the experimental C2–C3 bond distance is shorter than the calculated value, while the C3–C4 bond length is longer. Since then, experimental studies on dye solution have confirmed the calculated data [17]. It is possible that bond length differences arise because modeling studies do not take into consideration intermolecular interactions and the relative positions of dye cations and counterions in crystals.



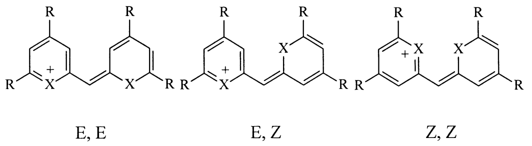
Type 4 dye



Type 2 dye

Fig. 3. Bond lengths and dihedral angles in α- and γ-dicarbopyrylocyanines.

It is known that the polymethine chain in dyes having $n > 2$ is mainly in an all-*trans* conformation. But there are three possible spatial isomers for α-monomethines, namely: E,E; E,Z and Z,Z:



A pyrydo-2-monomethinecyanine (**4**; $X = \mathrm{NCH_3}$, $n = 0$) was found by PMR spectroscopy to exist as the E,E conformer [10,18]. In other isomers, considerable steric hindrance arise between a hydrogen atom and methyl group (E,Z conformer) or between two methyl groups (Z,Z conformer). Calculation of the structures of model unsubstituted dyes shows that the E,Z conformer is less stable by 10.3 kcal/mol than the E,E conformer, while the Z.Z comformer is more stable than E,Z by 5.1 kcal/mol.

Unlike pyrydocyanines, in pyrylo- and thiopyrylocyanines, the E,E conformer is less stable. Calculated energies of the corresponding forms are follows: $X = \mathrm{O}$, −2298.9 (EE), −2302.8 (EZ), −2304.2 kcal/mol (ZZ); $X = \mathrm{S}$, −2258.2 (EE), −2259.6 (EZ), −2267.5 (ZZ) kcal/mol. It was found experimentally that pyrylo-2-monomethinecyanines ($X = \mathrm{O}$, $n = 0$, $R^1 = R^2 = t$-Bu) molecules exist in solutions as EZ conformer while the ZZ isomers are most likely for thioanalogues ($X = \mathrm{S}$) [10]. The additional stability of the ZZ structure probably arises from resonance interactions between the sulfur atoms. This assumption is confirmed by the unsually large vinylene shift (212 nm for $n = 1$ and 0 observed in absorption spectra, due to S–S interactions in the thiopyrylomonomethinecyanine ZZ conformer, which should be accompanied by a considerable hypsochromic shift in the longwave band maximim [10]. A similar interaction is absent

Table 2
Effective length (L) and electron donor ability (Φ_o) for the end groups of dyes **2** and **4**

X	$R^1 = R^2$	Φ_o	$\Delta\Phi_o$	L	ΔL
NCH_3	H	69°	–	2.93	–
	Ph	69°	0°	3.30	0.37
	Th	71°	2°	3.20	0.27
O	H	44°	–	4.43	–
	Ph	44°	0°	6.07	1.64
	Th	56°	12°	5.49	1.06
S	H	42°	–	5.19	–
	Ph	42°	0°	6.24	1.05
	Th	53°	11°	6.20	1.01

Table 3
Spectroscopic data for dyes **2** and **4** (in CH_2Cl_2)

Dye	X	R^1	R^2	n	λ_{max}, nm	$\Delta\lambda_1$, nm[a]	$\Delta\lambda_2$, nm[b]
2	NCH_3	*t*-Bu	*t*-Bu	1	638	–	–
γ-series		Ph	Ph	1	644	–	–
				2	758	–	–
	O	*t*-Bu	*t*-Bu	1	607	–	–
				2	715	–	–
		Ph	Ph	1	676	69	–
				2	798	83	–
		Th	Th	1	720	113	44
	S	*t*-Bu	*t*-Bu	1	703	–	–
		Ph	Ph	1	755	52	–
		Th	Th	1	813	110	58
4	NCH_3	*t*-Bu	*t*-Bu	1	575	–	–
α-series				2	675	–	–
		t-Bu	Ph	1	620	45	–
				2	722	47	–
		Ph	*t*-Bu	1	584	9	–
				2	685	10	–
		Ph	Ph	1	630	55	–
				2	728	53	–
	O	*t*-Bu	*t*-Bu	1	668	–	–
				2	763	–	–
		t-Bu	Ph	1	734	66	–
				2	844	81	–
		Ph	*t*-Bu	1	725	57	–
				2	829	66	–
		Ph	Ph	1	806	138	–
				2	910	147	–
		Th	Th	1	870	202	64
	S	*t*-Bu	*t*-Bu	1	782	–	–
				2	876	–	–
		t-Bu	Ph	1	814	32	–
				2	948	72	–
		Ph	*t*-Bu	1	808	26	–
				2	926	50	–
		Ph	Ph	1	865	83	–
				2	1000	124	–
		Th	Th	1	960	178	95

[a] $\Delta\lambda_1$ — with respect to *t*-Bu.
[b] $\Delta\lambda_2$ — with respect to Ph.

in dyes with a long conjugated chain and hence the next vinylene shift ($n = 2$ and 1) is 94 nm [9].

For all longer dyes of type **4**, two orientations for each heterocycle are possible (*trans*- and *cis*-conformer in respect to heteroatom X), and the stability of the isomers depends mainly on differences in steric hindrance between the hydrogen atoms in the β-positions of the polymethine chain and the heterocycle (*trans*-conformer) or the atom X (*cis*-conformer). When $X = O$, the steric hindrance is greater in the former conformer, while when $X = S$, NCH_3, spatial effects are greater in the latter comformer. It has been established by nuclear Overhauser effects [19] that dyes **4** ($n > 0$) exist in solutions as equilibrium mixtures of different conformers, one of them being predominant. The concentration of the ZEEZ conformer is higher in a solution of pyrylocarbocyanine, while the thiopyrylo- ($X = S$) and pyridocarbocyanines ($X = NCH_3$) exist mainly as EEEE conformers.

4.2. Spectral properties

It has been shown [1] that the first electron transition in dyes **2** and **4** involves mainly the polymethine chain, and is accompanied by the transfer of electron density from the carbon atoms in odd positions along the chain to neighbouring atoms (polymethine transition). The second and third electron transitions involve one of the quasi-degenerated occupied levels of the end groups, with electron density transfering from the polymethine chain to the heterocycle. Replacing *t*-Bu substituents in the end groups does not lead to changes in the nature of the first electron transition, because the electron levels of the Ph and Th moieties are far enough apart from the frontier levels of the basic polymethine chromophore.

To estimate the influence of the end group topology on the wavelength of the first transition, topological indices L and Φ_o have been calculated (Table 2). It can be seen that introducing Ph and Th substituents increases the effective length (L)

of the end groups, which is in agreement with experimental data. The data show that switching from tetra-*t*-Bu-substituted cyanines to phenyl- or thienyl derivatives is accompanied by a bathochromic shift in the absorption maximum, $\Delta\lambda$, depending on the electronegativity of the heteroatom. In the highly basic pyridocyanines ($X = NCH_3$), the frontier levels are shifted upward and hence are more separated from local Ph or Th levels than the frontier levels in the weakly basic pyrylo- or thiopyrylocyanines. As a result, the interaction between the frontier delocalized levels and local levels in pyridinium dyes is smaller, and hence $\Delta\lambda$ is less. However, it is necessary to take into consideration the energy gap or the absolute energy level positions, when comparing spectral effects of pyrylo- and thiopyrulocyanines. The observed shifts in the absorption bands are presented in Table 3. One can see that the bathochromic effects of Ph and Th groups depend on the molecular topology of terminal groups, and that these effects are different for the α- and γ-isomers. Also, replacing *t*-Bu substituents in the 4,4′-positions causes a greater $\Delta\lambda$ than in the 6,6′-positions, especially in pyrido-2-cyanines and thiopyrylo-2-cyanines. The additive effects of two substituents, in the case of the dyes, can be explained by the fact that introducing substituents causes only a small perturbation which does not influence the nature of the first electron transition. The presence of Ph groups increases the length of the polymethine chain, especially in thiopyrylocyanines, i.e. 83 nm ($n = 1$) and 124 nm ($n = 2$).

There are specific difficulties in the interpretation of the observed $\Delta\lambda$ values when thienyl groups are introduced. It can be seen from Table 3 that the experimental $\Delta\lambda$ values from Th are greater than those from Ph substituents. The difference is 44 nm for pyrylo-4-cyanines and 58 nm for its thio analogue. In the α-series of dyes (**4**), the effects of these changes were greater, with thieyl derivatives absorbing at 64 nm (pyrylocyanines) and 95 nm (thiopyrylocyanines) higher than the corresponding dyes containing Ph residues. However, it is clear from Table 2 that the effective lengths of end groups with Th substituents are less

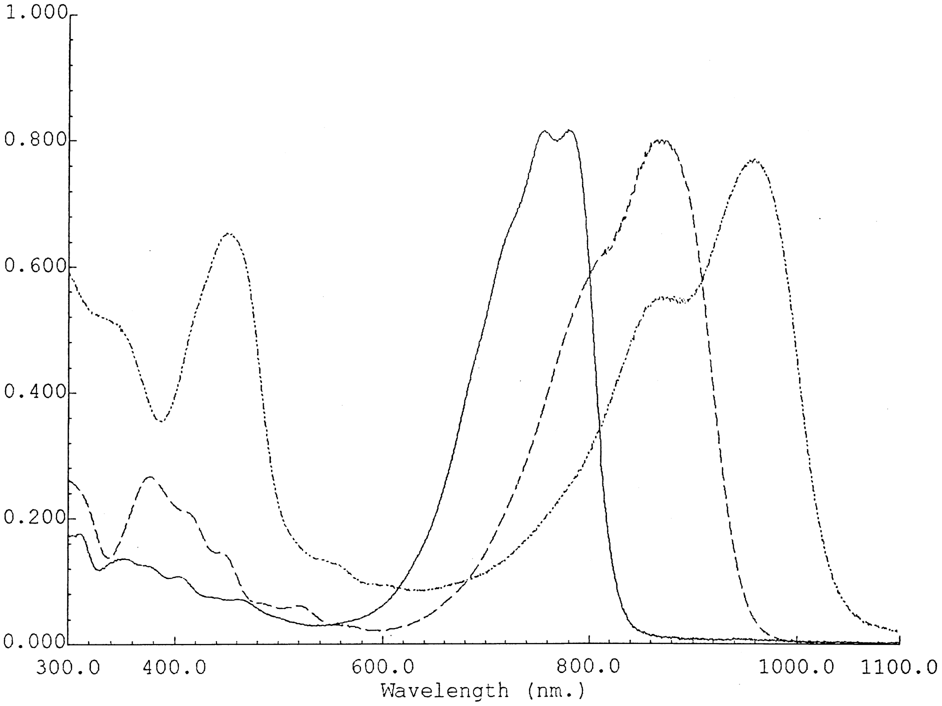


Fig. 4. Absorption spectra of α-thiopyrylocyanines **4** ($X = S$, $n = 1$): — $R = t$-Bu, - - - $R =$ Ph, ... $R =$ Th.

than those with Ph substituents. Consequently, there must be another cause for these spectral effects. It has been noted above that the second and third transitions in dyes **2** and **4** are localized on the end group atoms. The distance between frontier levels of polymethine dyes and the local levels of Th residues is small, and hence the polymethine and quasi-local transitions should strongly interact within these levels. In the process, the energy of the polymethine transition are reduced while the energies of the quasi-local transitions increase. It can be seen from Fig. 4, in the spectra of thienylsubstituted dyes, the second band is shifted bathochromically by 70–80 nm more than the corresponding band of the Ph-derivative. In this case, interactions between the polymethine and local transitions are greater, leading to a greater shift in absorption maxima in Th-containing dyes. Also, the shortwave bands in Th-substituted cyanines are shifted hypsochromically with respect to the same band of the corresponding salts. This behavior was not observed in Ph-substituted dyes [13].

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