Synthesis, Structure, and Spectral Properties of Pyrylium Salts and Their Derivatives. II.5-(Benzyliden)- and 5-(Cinnamyliden)-5,6,7,8-Tetrahydro-1,3-Diphenyl-2-Benzopyrylium Salts

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Z. Naturforsch. **43a,** 793–796 (1988); received March 16, 1988

The synthesis, structure and spectral properties of a group of dyes with a pyrylium ring are described. Quantumchemical calculations indicate that the chromophore system has a structure corresponding to that of the polymethine dyes.

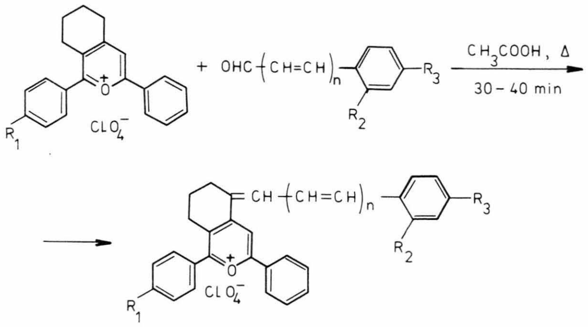
1. Introduction

The present paper contains results of experimental and theoretical studies of new dyes containing a pyrylium ring. These studies are a continuation of [1] and an extension to dyes known in the literature [2] as pyrylocyanine dyes. Several of these little investigated dyes find application as laser dyes [3, 4].

2. Synthesis

All studied dyes are not described in the literature. They were obtained according to a well-known method by condensation of the corresponding benzaldehydes or cinnamyl aldehydes with 5,6,7,8-tetrahydro-1,3-diphenyl-2-benzopyrylium salts [5] in acetic acid [6, 7].

The dyes were obtained according to the following general synthetic scheme:



The substituents R_1, R_2, R_3, the values of *n* and the data from the elemental analysis are given in Table 1.

0.01 mol 5,6,7,8-tetrahydro-1,3-diphenyl-2-benzopyrylium salts, 0.01 mol benzaldehyde or cinnamyl aldehyde and 40 ml glacial acetic acid are refluxed for 30–40 minutes. The reaction mixture is cooled down to room temperature. The precipitate is filtered, washed with diethyl ether on the filter funnel, dried and recrystallized from an appropriate solvent.

The good agreement (see the theoretical part) between the experimental and the with standard parameters [1, 16] computed transition energies of the investigated molecules also indicates that the above structures are correct.

3. Spectral characteristics

The equipment and conditions for recording the spectral characteristics are described in [1]. To avoid some concentration effects observed in compounds of this type [8, 9], the concentration of the studied solutions was $< 10^{-4}$ mol/l.

Like other dyes from the group of pyrylium salts [10, 11], the absorption spectra of the investigated compounds in solution are characterized by well-defined bands (Figure 1). The molar absorbtivity ε of the bands is high – for some compounds up to about $80\,000\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ (Table 2). Changing the R_1 substituent in some cases leads to a change in the relative intensity of the two bands (Table 2), but the energy of the Franck-Condon absorption transitions is practically not influenced by R_1.

For the polymethines [12] (Brooker rule), the elongation of the polymethine chain by one vinyl group is connected with a bathochromic shift of the

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Table 1. Substituents, melting points and results from the elemental analysis of the compounds investigated.

Compound No.	R_1	R_2	R_3	*n*	m.p. °C	Yield	C%cal/fomd[a]	H% cal/fomd	Cl% cal/fomd
1	H	H	$(CH_3)_2N$	0	250–251[b]	68	69.56/69.60	5.45/5.41	6.85/6.58
2	H	H	$(C_2H_5)_2N$	0	218–220[b]	53	70.38/70.39	5.90/5.93	6.49/6.55
3	H	H	$H_5C_2-N-C_2H_4Cl$	0	225–227[b]	47	66.20/66.50	5.38/5.59	12.22/12.03
4[a]	H	H	$H_5C_2-N-C_2H_5CN$	0	204–205[b]	59	67.28/67.44	5.65/5.75	6.02/5.95
5	OCH_3	H	$H_5C_2-N-C_2H_4Cl$	0	212–214[c]	37	64.92/65.29	5.45/5.64	11.60/10.92
6	OCH_3	H	$(CH_3)_2N$	0	260–261[b]	29	67.94/67.94	5.52/5.47	6.47/6.67
7	H	Cl	$(C_2H_5)_2N$	0	225–227[c]	73	66.20/66.39	5.38/5.62	12.21/12.08
8	H	H	$H_5C_2-N-CH_2C_6H_5$	0	229–231[b]	41	73.07/73.32	5.63/5.71	5.83/6.10
9	OCH_3	H	$H_5C_2-N-CH_2C_6H_5$	0	244–246[b]	35	71.52/71.28	5.69/5.95	–
10[a]	OCH_3	H	$(C_2H_5)_2N$	0	223–226[b]	40	65.71/65.26	6.18/6.12	5.88/6.09
11	H	H	$(CH_3)_2N$	1	272–274[c]	37	70.66/70.64	5.56/5.35	–
12	CH_3	H	$(CH_3)_2N$	1	275–277[c]	33	71.02/70.78	5.78/5.80	–
13[a]	H	H	$(CH_3)_2N$	1	237–239[c]	20	66.94/67.08	5.78/5.71	–
14[a]	Cl	H	$(CH_3)_2N$	1	252–254[c]	44	65.42/65.72	5.15/5.09	–
15	CH_3	H	H	1	289–291[c]	22	72.29/72.10	5.28/5.32	–
16	OCH_3	H	H	1	275–277[c]	13	70.11/70.03	5.12/5.49	–
17	Cl	H	H	1	299–301[c]	43	67.29/66.99	4.52/4.56	–

[a] **4** and **13** crystallize with one molecule of water, **10** and **14** with 0.5 molecules of water.
[b] recrystallized from acetic acid: acetonitrile 3:1.
[c] recrystallized from acetic acid.

Table 2. Experimental spectral characteristics of the investigated compounds in C_2H_5OH at room temperature and 77 K, ν^A, ν^F: energies of the two longest wavelength absorption Franck-Condon transitions and Fluorescence transition in [cm^{-1}], ε: molar absorptivity in [$l\,mol^{-1}\,cm^{-1}$], I^F: fluorescence intensity at the respective ν^F.

No	ν^A		ε		ν^F	$\frac{I^F(77\,K)}{I^F(293\,K)}$
1	30 720	15 880	13 850	70 250	14 700	2000
2	30 600	15 680	23 430	59 450	14 390	980
3	30 880	16 160	60 330	19 919	14 600	2600
4	31 160	16 360	62 860	8 510	14 600	2700
5	31 200	16 200	73 760	13 900	14 660	550
6	21 260	16 040	14 590	63 560	14 490	1460
7	30 560	16 040	[a]		14 560	1940
8	30 520	15880	60 120	16 220	14 430	580
9	30 720	16 000	70 600	72 700	14 350	820
10	30 600	15 720	75 200	12 500	14 490	690
11	26 240	13 960	12 420	23 680	12 580	69
12	25 000	14 050	17 960	82 250	12 660	41
13	23 750	13 940	19 140	81 360	12 660	33
14	25 640	13 810	11 600	46 240	12 500	32
15	30 000	20 240	21 040	10 250	17 240	90
16	34 480	20 160	18 700	33 600	17 540	17
17	24 270	20 040	[b]		17 240	4

[a] thermally and photochemically unstable
[b] inadequate solubility

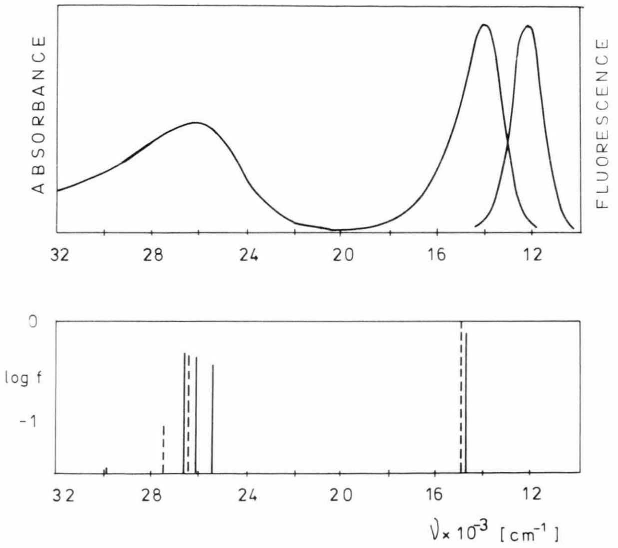


Fig. 1. *Above*: Absorption and fluorescence spectrum of **11** in ethyl alcohol. *Below*: Calculated transition energies for **11**. The length of the solid lines equals log *f*, where *f* is the calculated oscillator strength. Dashed lines are results of the calculations for fragment **A**, which is the main chromophore.

longest wavelength transition of ~100 nm. For the investigated molecules, the elongation of the conjugated system by one vinyl group leads to a bathochromic shift of ~60 nm (cf. for example **1** and **11**, **6** and **13** in Table 2).

All studied compounds fluoresce in solution at room temperature, but in contradistinction to other pyrylium salts [1, 13, 14], the fluorescence quantum yield Q_f is low – about 0.001 and does not depend on the length of the conjugated system ($n = 0, 1$), or on R_1.

The fluorescence band is mirror symmetrical to the longest wavelength absorption band, the excitation spectrum is identical to the absorption spectrum, the

Stokes shift is of the order of 2000 cm^{-1}; consequently the electron excitation leads only to geometry changes of the fluorescence state.

The effect of the elongation of the conjugated system ($n = 0, 1$) on the energy of the Franck-Condon fluorescence transition is the same as for the absorption transitions: a bathochromic shift of ν^F by about 2000 cm^{-1}, cf. Table 2.

The freezing of the ethanol solutions to 77 K leads to the well-known [8, 15] "blue shift" of the fluorescence band by about 500 cm^{-1}, and the excitation spectrum does not change relative to that at 293 K.

The fluorescence intensity of the studied pyrylium salts does practically not depend on whether R_3 is a substituted aminogroup or H. Such a dependency is not observed in solution at room temperature or in frozen matrix at 77 K.

From the experimental data in Table 2 it is seen that for the compounds with $n = 0$ the fluorescence intensity in frozen matrix is higher by an order of 3 (relative to 293 K) and Q_f is near unity, while for compounds with $n = 1$ the increase in the fluorescence intensity as a result of the freezing is considerably weaker.

None of the studied compounds phosphoresces at 77 K, and this is in line with some general considerations on the luminescence of pyrylium salts, expressed in [14].

The studied pyrylium salts dissolve only slightly in saturated hydrocarbons. To study the solvent effect, the ethanol solutions were diluted with cyclohexane (volume ratio 1:50). In analogy to the results in [1], under these conditions one observes a weak hypsochromic shift of the spectral peaks by about 10 nm; the fluorescence intensity practically does not change relative to ethanol solutions of the same concentration.

4. Quantum-Chemical Considerations

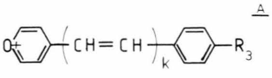
The theoretical treatment aims at identifying the main chromophore in the studied class of dyes. The numerical quantum-chemical calculations were carried out in π-electron approximation by the Pariser-Parr-Pople (PPP-SCF-CI) method, using a parametrization described in the previous communication [1].

Table 3. Theoretical values of the energies of the first $\pi\pi^*$ electron transition (in eV), oscillator strengths (f) and coefficients of the predominating configurations $d_{kk'}$ in the CI wavefunctions for compounds **1, 11** and corresponding chromophores A: **1** A, **11** A and **15** A. Parametrisation [16]. Compound **1*** with phenyl rings rotated at an angle of 45°.

N°	ΔE	f	$d_{kk'}$
1	2.06	1.489	$0.95\, V_1^{1'}$
	3.17	0.399	$0.68\, V_1^{2'} + 0.66\, V_2^{1'} + 0.24\, V_3^{2'}$
	3.32	0.297	$0.69\, V_2^{1'} - 0.66\, V_1^{2'}$
	3.70	0.217	$0.66\, V_3^{1'} - 0.58\, V_1^{3'} - 0.29\, V_1^{1'}$
1*	2.11	1.527	$0.95\, V_1^{1'}$
	3.36	0.138	$0.82\, V_1^{2'} + 0.44\, V_2^{1'} + 0.24\, V_3^{2'}$
	3.51	0.367	$0.74\, V_2^{1'} - 0.48\, V_1^{2'} + 0.35\, V_3^{1'}$
	3.77	0.140	$0.54\, V_3^{1'} + 0.52\, V_4^{1'} - 0.43\, V_1^{3'}$
1 (A)	2.10	1.312	$0.97\, V_1^{1'}$
	3.29	0.002	$0.96\, V_1^{2'} + 0.26\, V_3^{2'}$
	3.64	0.001	$0.92\, V_2^{1'} - 0.29\, V_1^{4'}$
	3.78	0.244	$0.77\, V_3^{1'} - 0.55\, V_1^{3'} - 0.22\, V_1^{1'}$
11	1.85	1.486	$0.94\, V_1^{1'}$
	3.16	0.282	$0.79\, V_1^{2'} + 0.49\, V_4^{1'} - 0.29\, V_2^{2'}$
	3.24	0.319	$0.60\, V_2^{1'} + 0.56\, V_4^{2'} - 0.34\, V_1^{3'}$
	3.29	0.562	$0.60\, V_3^{1'} - 0.51\, V_2^{1'} - 0.46\, V_1^{2'}$
11 (A)	1.89	1.637	$0.96\, V_1^{1'}$
	3.29	0.306	$0.81\, V_2^{1'} - 0.43\, V_1^{2'} + 0.27\, V_1^{1'}$
	3.42	0.005	$0.92\, V_1^{2'} + 0.34\, V_2^{2'}$
	3.70	0.0	$0.90\, V_3^{1'} - 0.30\, V_3^{3'}$
15 (A)	2.53	1.356	$0.96\, V_1^{1'}$
	3.51	0.015	$0.94\, V_2^{1'} + 0.27\, V_2^{3'}$
	4.07	0.002	$0.92\, V_3^{1'} + 0.35\, V_3^{2'}$
	4.23	0.053	$0.93\, V_3^{1'} + 0.23\, V_5^{2'}$

Along with this parametrization, another set of parameters [16] for the Coulomb and resonance integrals for the carbon atoms and heteroatomic groups was used. The calculations with both sets of parameters give good results for the energies and probabilities of the singlet $\pi\pi^*$ transitions for all compounds. Since the results from the two parametrisations are similar, qualitatively and quantitatively, the numerical values for only one of them i.e. that of [16], are presented in the tables and figures. In Fig. 1 and Table 3 the theoretical results for various conjugated structures are presented.

To identify the main chromophore in the investigated molecules, the methods described in the previous communication [1] were used: analysis of the wavefunctions and a comparison of the transition energies in the molecules and their fragments. The application of these methods shows that the main chromophore is the fragment **A** ($k = 1, 2$):



The analysis of the wave functions indicates (Table 3) that for all molecules and their corresponding fragments of type **A**, the longest wavelength $\pi\pi^*$ transition is determined by the HOMO → LUMO transition, for which, in all cases, the statistical weight

Table 4. Values of L_f, indicating degree of localization of the longest wavelength $^1S_0 \rightarrow {}^1S_i$ ($i = 1, 2$) $\pi\pi^*$ transitions for **11** and its various fragments.

Fragment	I	II	III	IV	V
$L_f(^1S_0 \rightarrow {}^1S_1)$	0.641	0.251	0.075	0.016	0.017
$L_f(^1S_0 \rightarrow {}^1S_2)$	0.408	0.234	0.178	0.102	0.078

of the $V_1^{1'}$ configuration (electron transition from HOMO to LUMO) is ≥ 0.90. For example, for **11**, the coefficient in front of the $V_1^{1'}$ configuration is 0.94, and for the corresponding fragment **A** the $V_1^{1'}$ coefficient is 0.96. An indication that the fragments of type **A** are the main chromophores is also the fact that the numerical results for the energy of the longest wavelength $^1S_0 \rightarrow {}^1S_1^*$ ($\pi\pi^*$) transition practically do not depend on the angle between the plane of the pyrylium ring and the phenyl rings connected to it.

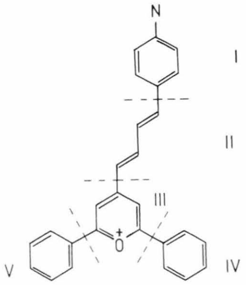
Another criterion for the characterization of the main chromophore in complex conjugated systems is the theoretical determination of that part or fragment of the molecule, in which the electron transition is localized. For this purpose the approach of Lusanov [17] is convenient and estimates the contribution of each fragment of the molecule to the total electron excitation. This analysis was carried out by calculating the values of L_f ($0 \leq L_f \leq 1$), which for a fragment with index f are defined by the expression [17]

$$L_f = \sum_{\mu \in f} \sum_{v} \left[\frac{1}{\sqrt{2}} \sum_{k,k'} d_{kk'} \left(c_{\mu k} c_{v k'} + c_{v k} c_{\mu k'} \right) \right]^2 .$$

Obviously

$$\sum_f L_f = 1 .$$

Above, $d_{kk'}$ denote the coefficients in the expansion of the wavefunction over the singly excited configurations $V_k^{k'}$, and $c_{\mu k}$ (c_{vk}) are the AO coefficients in the MO of a given fragment, respectively in the MO of the whole molecule. Table 4 gives the values of L_f for the first two longest wavelength $\pi\pi^*$ singlet transitions ($^1S_0 \rightarrow {}^1S_1^*$ and $^1S_0 \rightarrow {}^1S_2^*$) for **11** and its various fragments:



It is seen from the table that for the first transition $L_{\mathrm{I}} + L_{\mathrm{II}} + L_{\mathrm{III}} = 0.967$, i.e the longest wavelength singlet transition is practically localized in the fragment **A**, and this tendency continues for the next high-lying $\pi\pi^*$ transitions.

Acknowledgement

The authors thank to Mrs. Dipl. Chem. M. Taseva for the assistance in the quantum-chemical work.

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