Synthesis, Structure and Spectral Properties of Pyrylium Salts and Their Derivatives.
I. 5,6-Dihydro-benzo(c)xanthylium Salts

T. G. Deligeorgiev
Department of Chemistry, University of Sofia, Sofia

P. Nikolov and N. Tyutyulkov
Bulgarian Academy of Sciences, Institute of Organic Chemistry, with Center for Phytochemistry, Sofia

Z. Naturforsch. **42a,** 43–48 (1987); received May 2, 1986

The synthesis and spectral properties of a group of xanthylium salts are described. The longest wavelength absorption maximum in organic solvents (ethanol, 1,4-dioxane, acetonitrile) is the region 17 000–20 000 cm^{-1}, the molar absorptivity exceeding 30 000 $l \cdot mol^{-1} cm^{-1}$. The fluorescence Frank Condon transition is in the region 16 000–19 000 cm^{-1}, the fluorescence quantum yield of some of the compounds is greater than 0.9. The relation between the structure and the spectral properties of the molecules is interpreted by means of PPP-quantumchemical calculations.

1. Introduction

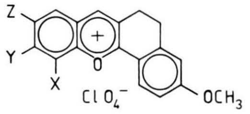
The practical and theoretical interest [1] in pyrylium salts has different reasons. Together with being starting compounds for many syntheses, their fluorescence characteristics make them applicable as dyes [2, 3, 4] and Q-switchers in laser techniques. Some of them are used as precursors for dyes, absorbing in the infrared [3, 4], while others – like flavylium salts, are natural compounds. These substances are of theoretical interest also because the problem of the chromophore in the different pyrylium salts cannot be said to be solved [6].

This paper reports on first results of systematic investigations, now in progress, on different groups of pyrylium salts. The synthesis and spectral properties of the 5,6-dyhydrobenzo(c)xanthylium salts of Fig. 1 are discussed, and a quantum-chemical interpretation of their electronic spectra is suggested.

2. Synthesis

The compounds **2–6** are newly synthesized [7] following a well-known method [8], while **1** and **7** are proposed as laser dyes [9], but no detailed description of their synthesis and photophysical characteristics are quoted there.

0.01 gmol of a corresponding 2-hydroxybensaldehyde or N-(2-hydroxy)arylidennitroaniline, 1.76 (0.01 gmol) 6-methoxy-1-tetralone, 30 ml glacial



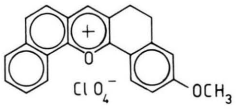
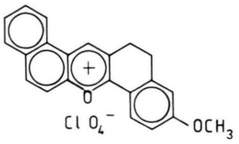
Nº	X	Y	Z
1	H	H	H
2	H	$N[CH_3]_2$	H
3	H	$N[C_2H_5]_2$	H
4	H	H	NO_2
5	NO_2	H	H
6			
7			

Fig. 1. Structure of the investigated 5,6-dihydro-benzo(c)xanthylium salts.

Reprint requests to Prof. Dr. N. Tyutyulkov, Institut für Organische Chemie, Akademie der Wissenschaften, 1113 Sofia (Bulgarien).

0340-4811 / 87 / 0100-0043 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Melting points and results of the elemental analysis of the 5,6-dihydro-benzo(c)xanthylium salts.

Compound	m.p. (°C)	Yield^{a}	C% calc./found	N% calc./found
1	225–227	90^{b}	59.58/59.85	4.14/4.39
2	> 300	75^{b}	59.18/59.12	4.93/4.87
3	273–275	71^{b}	60.90/60.93	5.53/5.40
4	> 300	94^{c}	53.00/53.01	3.43/3.73
5	246–248	78^{c}	53.00/53.42	3.43/3.61
6	> 300	87^{c}	64.00/64.00	4.12/4.12
7	273–275	93^{c}	64.00/64.00	4.12/4.00

[a] The melting points are not corrected; they are not well defined, melting being accompanied by decomposition.

[b] Recrystallized from acetic acid.

[c] Recrystallized from acetic acid: dimethylsulfoxide in volume ratio 1:1.

acetic acid and 3 ml 70% perchloric acid were refluxed for 30–45 min. The reaction mixture is cooled down to room temperature. The precipitate is filtered, washed with two portions of 30 ml diethyl ether, dried and recrystallized from an appropriate solvent.

Some physical characteristics of compounds **1–7** and the data of the elemental analysis are given in Table 1.

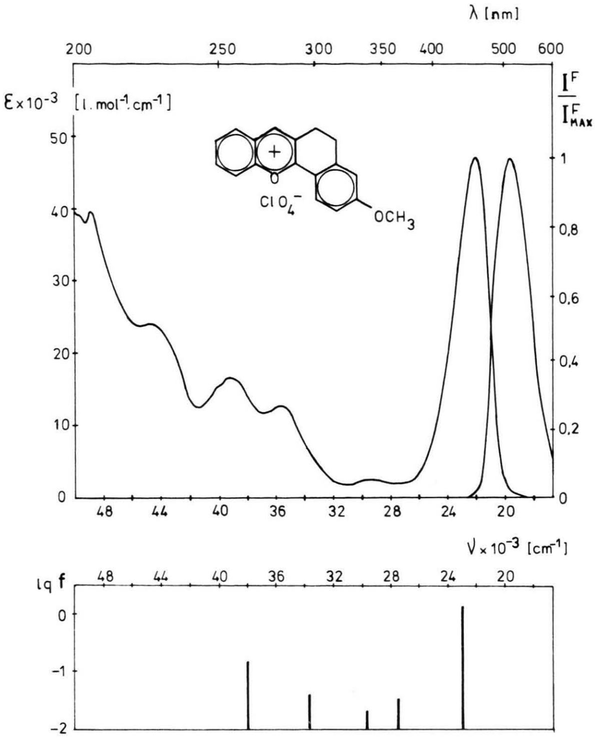


Fig. 2. Electronic spectrum of compound **1** in $C_2H_5OH + 1\% HClO_4$ at 20 °C. The vertical lines denote the computed energies of the $\pi\pi^*$ transitions and the corresponding oscillator strengths.

3. Spectral Characteristics

The absorption spectra are recorded on a double beam spectrophotometer Specord M40, Carl Zeiss, Jena, DDR.

The corrected excitation and emission spectra are taken on a fluorescence spectrophotometer Perkin-Elmer MPF 44 at room temperature and at 77 °K. The low-temperature measurements at 77 °K are performed in a standard phosphorescence accessory to MPF 44 in a quarz tube of diameter 5 mm.

3-amino-phthalimid ($Q_f = 0.6$ in ethanol [10]) is used as a standard for the determination of the relative fluorescence quantum yield Q_f. The concentration of the investigated solutions is kept below 10^{-4} M/l in order to avoid concentration effects observed in similar system [11]. All solutions are stabilised by adding of an approximately 1 vol.% $HClO_4$ to a 10^{-4} M solution. It should be noted that depending on the substituents (X, Y, Z) the portion of $HClO_4$ was varied to obtain maximum optical density of the longest wavelength absorption maximum. Most acidic are the solutions of compounds **4, 5** (2 vol.% $HClO_4$); least acidic (below 0.1 vol% $HClO_4$) are those of **2** and **3.** Lowering of the pH of the solutions of compounds **2** and **3** leads to a protonation of the $N(CH_3)_2$, resp. the $N(C_2H_5)_2$ group, resulting in a strong hypsochromic shift of the longest wavelength absorption maximum of about 4000 cm^{-1}; the absorption spectrum closely resembles the spectrum of the unsubstituted compound **1.**

3a) Absorption Spectra

The absorption spectra of the xanthylium salts (Fig. 1) do not differ significantly from the absorption spectra of the compounds with similar structure described in [1, 12, 13]. The longest wavelength absorption $\pi\pi^*$ band of compounds **1–7** is the most intensive one in the spectrum; at shorter wavelength, in the region 24000–40000 cm^{-1}, a series of absorption bands of lower intensity is observed. Fig. 2

Table 2. Experimental spectral characteristics of the investigated compounds; the numbers of the compounds correspond to those in Fig. 1. ν^A, ν^F = frequency of the longest wavelength absorption Frank Condon transition, $[\nu] = \text{cm}^{-1}$; Q_f = fluorescence quantum yield; ε = molar absorptivity, $[\varepsilon] = 10^3\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$ (/-very poor solubility).

	C_2H_5OH				CH_3CN			1,4-dioxane		
No.	ν^A	ν^F	Q_f	ε	ν^A	ν^F	Q_f	ν^A	ν^F	Q_f
1	21 930	19 660	0.82	47.9	22 030	19 880	0.97	22 170	19 230	0.82
2	18 000	16 000	0.05	35.5	18 020	15 940	0.05	/	/	/
3	17 730	15 970	0.05	33.8	17 860	18 870	0.05	18 020	16 950	0.06
4	21 520	19 290	0.56	27.4	21 520	19 460	0.76	21 690	19 200	0.48
5	21 360	19 200	0.61	31.7	21 360	19 200	0.72	/	/	/
6	20 450	18 230	0.83	35.9	20 480	18 460	0.90	/	/	/
7	20 450	18 830	0.91	55.8	20 560	18 940	0.96	10 620	18 800	0.99

shows the electronic spectrum of **1**; some spectral characteristics of the investigated compounds are given in Table 2.

The longest wavelength absorption Frank Condon transition of the primary compound **1**, in 1,4-dioxane, ethanol and acetonitrile is at about $22000\ \text{cm}^{-1}$, the absorption band is intensive ($\varepsilon = 47900\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$ in $C_2H_5OH + 1\%\ HClO_4$), symmetrical, and has no vibrational structure.

The quantum-chemical calculations show that the absorption in this region can be attributed only to the $^1S_0 - {}^1S_1$ ($\pi\pi^*$) transition (Fig. 1, see Section **4**).

The shorter wavelength transitions of **1** are of considerably lower intensity: $\nu = 28000\ \text{cm}^{-1}$, $\varepsilon = 2300\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$; $\nu = 39000\ \text{cm}^{-1}$, $\varepsilon = 11800\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$ in ethanol + 1% $HClO_4$.

The nitro-group in positions 9 and 11 (**4** and **5**) as well as the condensed aromatic ring in positions 8, 9 and 10, 11 (**6** and **7**) do not change the character of the absorption spectrum, relative to **1**.

Strong electron-donating substituents, $N(CH_3)_2$ and $N(C_2H_5)_2$, lower the energy of the longest wavelength $\pi\pi^*$ transition with about $4000\ \text{cm}^{-1}$ relative to **1** (Table 2). Besides the difference between the extinction coefficients of the $^1S_0 - {}^1S_1$ ($\pi\pi^*$) transition and the shorter wavelength transitions diminished; e.g. the first four $\pi\pi^*$ transition of **2** in ethanol have the following energies: $\nu = 18000\ \text{cm}^{-1}$, $\varepsilon = 35500\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$; $\nu = 26000\ \text{cm}^{-1}$, $\varepsilon = 10800\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$; $\nu = 35000\ \text{cm}^{-1}$, $\varepsilon = 12900\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$; $\nu = 38400\ \text{cm}^{-1}$, $\varepsilon = 14500\ \text{l} \cdot \text{mol}^{-1}\ \text{cm}^{-1}$. As a result the absorption spectra of compounds **2** and **3** consist of a series of well defined absorption bands.

3b) *Fluorescence Characteristics in Solution*

The xanthylium salts **1–7** fluoresce in solution; with the exception of **2** and **3** their fluorescence quantum yield is high, over 0.5 (see Table 2). Most intensive is the fluorescence of **7** in 1,4-dioxane: $Q_f = 0.99$. In all cases the fluorescence band is symmetrical to the longest wavelength absorption band and the corrected excitation spectrum is identical with the absorption spectrum in the whole region $17000-48000\ \text{cm}^{-1}$; the Stokes shift is about $2000\ \text{cm}^{-1}$. Consequently, the electronic transitions give rise only to geometric but not structural changes in the $^1S_1$ ($\pi\pi^*$) state of the compounds investigated.

It is known that some xanthylium salts have intensive fluorescence in solution [14, 15, 16]. The fluorescence quantum yields of the compounds, listed in Fig. 1, is higher than Q_f of the substances with similar structure studied in [16]. This fact may be explained with the longer conjugated system and the fixed planar structure of **1–7**. The fixed planar structure results in greater electronic delocalization in both the $^1S_0$ and in the fluorescent $^1S_1$ ($\pi\pi^*$) state, diminishing the probability for intramolecular motions of great amplitude, quenching the emission [17].

3c) *Solvent Effect*

The compounds studied have a very poor solubility in saturated hydrocarbons. In order to estimate their spectral behaviour in non-polar solvents, mixtures of ethanol solutions with C_6H_6 in different volume ratios were used keeping the molar concentration of the compound 10^{-5} gmol/l. The change in the position of the spectral maxima is less than 10 nm for ratio in the range 100 : 1 $C_2H_5OH : C_6H_6$; Q_f changes within about 5%.

A change of the solvent polarity (1,4-dioxane, C_2H_5OH, CH_3CN) leads to a slight shift (no more than 500 cm^{-1}) of the Frank Condon transitions and an insignificant change of the Stokes loss. The fluorescence quantum yields of **1**–**7** cannot be correlated with the solvent polarities (Table 2).

In frozen ethanol solution at 77 °K the Frank Condon fluorescence transition shifts to the blue (10–20 nm); the fluorescence intensity slightly increases, while the excitation spectra remain practically unchanged.

The considerable increase of the fluorescence intensity at low temperatures is usually connected with the hindered intramolecular motion of certain fragments in the molecule. Because of the fixed planar structure of the compounds **1**–**7** one could not expect such quenching processes. The latter is supported by the high fluorescence quantum yields in solution at room temperature, as well as by the insignificant increase of the fluorescence intensity in a solid matrix at 77 °K. The ethanol solutions of the compounds **1**–**7** do not phosphoresce at 77 °K, and no luminescence from the solid phase is observed.

4. Quantum-Chemical Considerations

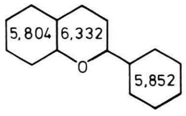
The quantum-chemical calculations performed by the Pariser-Parr-Pople (PPP) method (SCF-CI), taking into account all singly excited configurations, with a standard parametrization [18], are in good agreement with the absorption spectra.

The difference between the calculated and the experimental $\pi\pi^*$ Frank Condon transition energies is within the accuracy of the PPP method. Figure 2 allows comparison of the absorption spectrum of **1** and the calculated energies of the $\pi\pi^*$ transitions (the length of the lines is proportional to the calculated oscillator strength f).

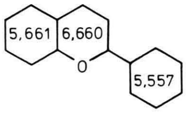
The geometry of the investigated molecules was determined by an iterative procedure; the bond length R were determined via the bond order p [19] ($p(\text{Å}) = 1.517 - 0.18p$). The dependence of the resonance integrals between adjacent carbon atoms on the bond lengths was accounted for using the formula: $\beta = -2.318 \dfrac{S(R)}{S_0}$ eV (S_0 is the overlap integral for $R = 1.39$ Å).

For all molecules, in agreement with the experiment, the longest wavelength $\pi\pi^*$ transition is the most intensive one, with an oscillator strength $f \cong 1.0$, while the next shorter wavelength $\pi\pi^*$ transition are of low intensity ($f \leqq 0.1$) (see Table 3).

The longest wavelength $\pi\pi^*$ transition of all the compounds treated is related to a partial charge transfer between the six-membered rings. This can be seen from the following scheme, where the total π-electronic charges $Q = \sum q_\mu$ on the cycles in the ground $^1S_0$ and the first excited singlet state $^1S_1$ ($\pi\pi^*$) of the unsubstituted basic fragment (A) are shown.



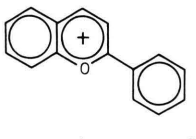
A - $^1S_0$



A - $^1S_1(\pi\pi^*)$

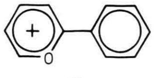
According to the calculations, the difference of the dipole moments $\Delta\mu = \mu(^1S_1) - \mu(^1S_0)$ for **2** and its fragment F are 2.97 and 2.55 D, resp., the angle between the direction of the dipole moments in $^1S_1$ and $^1S_0$ being 15° and 13°, resp. As the system is an ion (a cation) the absolute value of the calculated dipole moment depends on the coordinate system, but the change of the dipole moment $\Delta\mu$ is invariant. The small change of the dipole moment upon excitation explains the weak influence of the solvent polarity on the absorption and fluorescence spectra. The change of the dipole moment is not the only factor determining the influence of the solvent. For systems similar to the compounds investigated, the influence of the solvent is determined by the possibility for formation of aggregates and ion pairs [6].

The π-electronic system of the dihydroxanthylium cation, responsible for the $\pi\pi^*$ transitions of all the molecules under investigation, is fragment A:

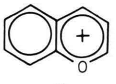


A

However, it cannot be said a priori whether the main chromophore is this fragment or either of the subfragments



B



C

D

Before discussing the problem for the main chromophore, it has to be emphasized that for polyatomic molecules one cannot always expect an unambiguous solution. The answer of the question "Which is the main chromophore" depends on the choice of the method of comparison [20]. Frequently, the different methods give preference to different chromophore systems within the same group of molecules. For systems with a complex system of conjugation a comparison of the results of the application of different criteria is necessary [20].

Besides the above fragmentation, another one (treated further) with the diarylmethane system as a main chromophore is also possible. If we denote with $i = 1, 2, 3$, resp. with $j = 1', 2', 3', \ldots$ the frontier orbitals of the molecules, and with V_{ij} the singlet configuration, corresponding to a transition of an electron from the i-th bonding MO to the j-th antibonding MO, the wave functions of the excited states will be written as

$$\psi = \sum c_{ij} V_{ij} . \qquad (1)$$

The longest wavelength intensive $\pi\pi^*$ transition of all the compounds **1**–**7** is determined predominently by the $V_{11'}$ configuration, i.e. it is a HOMO-LUMO transition. The next shorter wavelength transitions of lower intensity are determined mainly by $V_{i1'}$ configurations ($i = 2, 3$). This can be seen from Table 3, giving the results for **1** and some fragments.

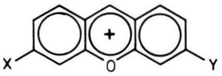
Table 3. Computed energies ΔE (eV) of the first three $\pi\pi^*$ transitions, oscillator strengths f, and the coefficients of the main configurations in the expansion of the wavefunction over configurations (1) for **1** and the fragments A, B, C, D, E.

Fragment	ΔE	f	Coefficients of the dominating configurations
1	2.84	1.096	$0.960\, V_{11'}$
	3.41	0.032	$0.964\, V_{21'}$
	3.63	0.020	$0.940\, V_{31'}$
A	3.08	0.950	$0.952\, V_{11'}$
	3.34	0.046	$0.908\, V_{21'}$
	3.50	0.034	$0.907\, V_{31'}$
B	3.46	0.868	$0.979\, V_{11'}$
	3.84	0.043	$0.950\, V_{21'}$
	5.08	0.169	$0.962\, V_{12'}$
C	3.39	0.100	$0.981\, V_{11'}$
	4.01	0.389	$0.937\, V_{21'} + 0.289\, V_{12'}$
	5.39	0.621	$0.272\, V_{21'} - 0.823\, V_{12'} + 0.410\, V_{23'}$
D	4.76	0.315	$0.964\, V_{11'}$
	5.83	0.044	$0.843\, V_{21'} + 0.533\, V_{12'}$
	7.06	1.103	$0.532\, V_{21'} + 0.845\, V_{12'}$
E	2.31	1.159	$0.964\, V_{11'}$
	3.00	0.052	$0.973\, V_{21'}$
	3.11	0.022	$0.975\, V_{31'}$

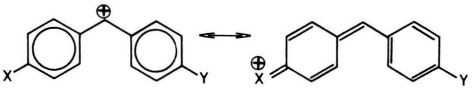
The results for the computed transition energies, the oscillator strengths, and the coefficients C_{ij} of the predominating configurations in the expansion (1) are also presented in Table 3. It can be seen that the character of the transitions, the energies and the oscillator strengths of **1** are identical with those of fragment A, which can be regarded as the main chromophore.

The character, energies and oscillator strengths of the transitions of fragments B, C and D do not correspond to those of **1**. For C and D, together with the substantial inaccuracy in the calculated energy of the third transition, a strong mixing of the configurations is also observed. An analogous comparative analysis for molecules **2**–**7** yields the same result: for all of them A is the main chromophore.

Another way of interpreting the spectral properties of the molecules in question is implied by the theoretical studies [8, 20, 21], according to which in systems of type

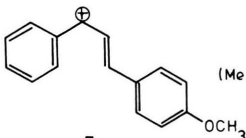


the oxygen atom could be considered only a perturbing factor. This means that the main chromophore is the diarylmethane system [8, 20, 21]:

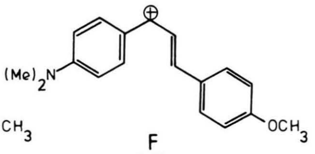


(According to Dähne [22] the chromophore of the diarylmethane systems is a polymethine system.)

From this point of view [8, 20, 21], the chromophore of **1** will be the fragment E, while the chromophore of **2** will be the fragment F.

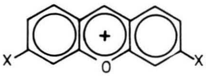


E

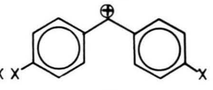


F

The results for fragment E are given in Table 3. For symmetrical systems of type G:



G



H

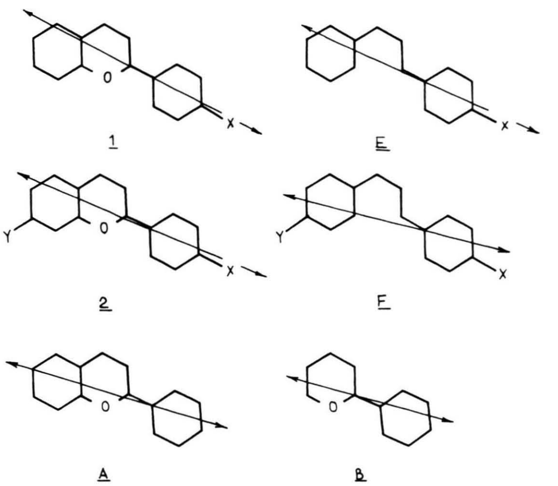


Fig. 3. Direction of the computed transition moment for the $^1S_0-{}^1S_1$ $(\pi\pi^*)$ transition for **1** and **2** and some of their fragments; $X = OCH_3$, $Y = N(CH_3)_2$.

it was experimentally shown [20, 21] that the longest wavelength $\pi\pi^*$ transition in the diarylmethane system H is batochromically shifted compared to the cyclic system G. A similar result is obtained for **1** and fragment E (Table 3).

This result, as well as the configuration analysis (Table 3) show that the diarylmethane fragment E can also be regarded as a chromophore of **1.** A similar result is obtained for fragment F, which can be regarded as a chromophore of **2.**

The method of Longuet-Higgins-Murrell [23, 24] "Molecule in molecule" (MIM method) leads practically to the same results. The results of the calculations show that, if the MO fragment E (resp. F) and the $2P_z$ AO of the oxygen atom are taken as basis functions in the expansion (1), the first three $\pi\pi^*$ transitions are localized on fragment E, (fragment F, resp.). The fourth transition is a CT transition – a transition of an electron from the oxygen atom to fragment E (resp. F).

It follows from the analysis made above that for the class of molecules treated, where a complex π-electronic conjugated system exists the basic chromophore cannot be defined reliably. This conclusion is supported by the results shown in Fig. 3, where the direction of the calculated transition moments for the $^1S_0-{}^1S_1$ $(\pi\pi^*)$ transitions of molecules **1, 2** and fragments A, B, E and F are presented.

As seen in Fig. 3 there is no significant difference in the direction of the calculated transition moments for molecules **1, 2** and their respective fragmentations, thus making it impossible to select a main chromophore on this basis.

An extention of the investigations towards some other pyrylium salts and derivatives, the studies now in progress, will probably give a more reliable answer to the question, which is the main chromophore of such heterocyclic systems.

[1] A. Balaban, A. Dinculescu, G. Dorofeenko, G. Fischer, A. Koblik, V. Mezheritki, and W. Schroth, Pyrylium Salts: Syntheses, Reactions and Physical Properties, Academic Press, New York 1982.
[2] M. Maeda, Laser Dyes, Academic Press, New York 1984.
[3] G. A. Reynolds and K. H. Drexhage, J. Org. Chem. **42(5),** 885 (1977).
[4] B. Kopainsky, P. Qiu, W. Kaiser, B. Sens, and K. Drexhage, Appl. Phys. **B 29,** 15 (1982).
[5] J. Williams and G. Reynolds, J. Appl. Phys. **39,** No. 11, 5327 (1968).
[6] J. Fabian and H. Hartmann, Light Absorption of Organic Colorants, Springer, Berlin 1980, p. 159.
[7] Patent Bulg., reg. No. 69657, 09. 04. 1985.
[8] M. J. Dewar, J. Chem. Soc. London **1950,** 2329; **1952,** 3532, 3544.
[9] DOS 2109040; Chem. Abstr. **76,** 40148e (1972).
[10] N. Borisovitch, V. Zelinskii, and B. Neporent, Dokl. Acad. Nauk USSR **94,** 37 (1954).
[11] V. Wintgens, J. Poulique, and J. Kossanyi, to be published.
[12] P. Czerney and H. Hartmann, J. Prakt. Chemie, Bd. **325(1),** 161 (1983).
[13] J. Wilt, G. Reynolds, and J. Van Allan, Tetrahedron **29,** No. 6, 795 (1973).
[14] B. Krasovitskii and B. Bolotin, Organic Luminophores (Russ.), Khimia, Ed. 1976, Leningrad, USSR.
[15] W. Karmazin, M. Knejanskii, E. Olehowich, and G. Dorofeenko, Zh. Prikl. Spectrosk. (Russ.) **22,** 234 (1975).
[16] S. Tripathi, M. Simalty, and J. Kossanyi, Tetrahedron Lett. **26,** No. 16, 1995 (1985).
[17] F. Fratev, Z. Naturforsch. **30a,** 1691 (1975); F. Fratev, J. Mol. Struct. **30,** 217 (1976).
[18] N. Tyutyulkov and G. Hiebaum, Theor. Chim. Acta Berlin **14,** 39 (1969).
[19] C. A. Coulson and A. Golebiewsky, Proc. Phys. Soc. London **78,** 1310 (1961).
[20] J. Fabian, A. Mehlhorn, F. Dietz, and N. Tyutyulkov, Mh. Chemie **115,** 21 (1984).
[21] G. G. Dyadyusha, Ukr. Khim. Zh. USSR **30,** 929, 1186 (1984).
[22] S. Dähne and F. Moldenhauerm, Progress in Phys. Organic Chemistry, Ed. R. Taft, **15,** Wiley, New York 1985.
[23] H. C. Longuet-Higgins and J. N. Murrell, Proc. Phys. Soc. London **A 68,** 601 (1955).
[24] J. Fabian, J. Signalaufzeichenmaterialien **6,** 307 (1978); **7,** 67 (1979).