- 3. T. T. Basiev, Yu. K. Voron'ko, V. V. Osiko, and A. I. Prokhorov, The Spectroscopy of Crystals [in Russian], Moscow (1966), pp. 57-82.
- 4. M. I. Gaiduk, V. F. Zolin, and L. S. Gaigerova, The Luminescence Spectra of Europium [in Russian], Moscow (1974).
- 5. H. J. Rother, S. Kemmler-Sack, U. Treiber, and W. R. Cyris, Z. Anorg. Allgem. Chem., <u>466</u>, 131-138 (1980).
- 6. A. A. Kaminskii, Zh. Eksp. Teor. Fiz., <u>58</u>, 407-409 (1970).
- 7. M. I. Weber, T. E. Vartimos, and B. H. Matsinger, Phys. Rev. B, 8, 48-51 (1973).
- M. V. Artamonova, Ch. M. Briskina, A. I. Burshtein, et al., Zh. Eksp. Teor. Fiz., <u>62</u>, 864-871 (1972).
- 9. Yu. K. Voron'ko, T. G. Mamedov, V. V. Osiko, et al., Preprint No. 16, Moscow (1976).

SPECTRAL-LUMINESCENT PROPERTIES OF CERTAIN PYRYLIUM AND THIOPYRYLIUM SALTS

G. N. Ten, I. F. Kovalev, V. P. Bazov, and V. G. Kharchenko

Salts of thiopyrylium and its oxygen-containing analogs are widely applied as dyes for polymers and photosensitizers in photography [1]. This stimulates the search for new compounds and study of their physicochemical properties [2-10]. We decided to measure the electronic absorption spectra and fluorescence spectra of a series of pyrylium and thiopyrylium salts to show that these spectra reveal structural features of the molecular systems and electron charge redistributions as a function of their substituents. Only fragmentary information is available in [2-10] on these problems.

Thiopyrylium salts I-VI, IX were obtained by a known method, by reacting the corresponding 1,5-diketones with hydrogen sulfide and perchloric acid at room temperature. Pyrylium salts VII, VIII, X were obtained similarly by the action of perchloric acid in an acetic acid medium on the corresponding 1,5-diketones [1].

Salts XI, XII were obtained by the reaction of methylenebis(cyclohexane) with hydrogen sulfide, $SbCl_5$ and HCl in an acetic acid medium.

The absorption spectra were measured on a Perkin-Elmer 554 spectrophotometer in the wavelength range of 200-900 nm at room temperature. Recording conditions: solvent CH_2Cl_2 , concentration C = 10^{-4} mole/liter, optical path of the cuvette ℓ = 1 mm.

The fluorescence spectra were obtained on a MPF spectrofluorimeter with an array of 1200 str/mm at an excitation by different lines of a xenon lamp.

The fluorescence spectra were measured at optical densities of 0.2-0.6.

For a long-wave absorption band, the oscillator forces were calculated according to the formula [11]

$$f = 4,32 \cdot 10^{-9} n^2 \int_{v_1}^{v_2} \varepsilon(v) \, dv.$$

The limits of numerical integration were sharply determined by the relative position of the long-wave absorption band, since it practically does not overlap other bands $[nD^{20} = 1.4337 \text{ for } CH_2Cl_2;$ the values of the extinction coefficient $\varepsilon(v)$ are listed in Table 1]. The relative quantum yield was calculated from the formula [11]

$$\frac{F_2}{F_1} = \frac{Q_2}{Q_1} = \frac{\operatorname{area}}{\operatorname{area}} \frac{2}{1} = \frac{I_0 \varepsilon_2 C_2 l \varphi_2}{I_0 \varepsilon_1 C_1 l \varphi_1} = \left(\frac{\varphi_2}{\varphi_1}\right) \frac{D_2}{D_1},$$

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 45, No. 3, pp. 429-433, September, 1986. Original article submitted March 26, 1985.

UDC 535.37



Fig. 1. Structural formulas of pyrylium and thiopyrylium salts.

TABLE 1. Spectral-Luminescent Characteristics of Pyrylium and Thiopyrylium Salts

pq		Fluorescence	
No. of compou	Absorption. λ_{max} , nm ($\epsilon = 10^{-3}$ mole liter.cm ⁻¹ ; fosc)	λ _{max} , nm	Φį
I	220 (11,35), 255 (11,25), 330 (2,1), 415 (13,9; 0,472)	490 (490) [2]	0,0067 (0,0072) [2]
11	222 (19,5), 262 (34,0), 400 (24,5; 0,964)	475	0,096
111	228 (14,0), 250 (17,8), 270 (16,0) 380 (21,6; 0,638), 415 sh. (16,2; 0,480)	475 (465) [2]	0,004 (0,0041) [2]
IV	205 (33,5), 262 (17,05), 410 sh. (21,25; 0,531) 450 (30,7; 0,763)	545,585 sh	
V VI	220 (20,5), 250 (19,0), 378 (118; 0,457) 220 (20,1), 260 (25,12), 400 (23,7;	478	
VII	0,767, 440 (23,9; 0,722) 220 (13,0), 280 (11,55), 310 sh. (4,75),	555,590 sh. 457 (465) [2] (467) [6]	0,004 0,132 (0,0301) [2]
VIII	412 (18,4; 0,610) 230 (24,9), 270 (22,0), 304 sh. (9,0), 385 (35.8; 1.617)	(407) [0] 452	0,014
IX	220 (11,16), 247 (9,53), 280 sh. (6,28), 380 (4,96; 0,217)	460	0,005
X	250 (9,55), 370 (17,25; 0,668) 205 206 (40.0) 268 - 270 (12.04)	418	0,163
XII	203-203 (12,01), $203-270$ (12,01), 330 (9,15; 0,248) 221 (28,8), 274 (14,25), 330 (95; 0,268)	435 435	10-4 10-4

<u>Note</u>. In λ_{\max} and φ_t columns, the literature values of parameters are shown in brackets.

where φ_1 is known absolute fluorescence quantum yield of standard; F, fluorescence intensity; Q, absolute rate of fluorescence emission of solution; I_0 , intensity of exciting light; ε , molar extinction coefficient; C, concentration; ℓ , optical path of a layer; D, optical density.

Index 1 refers to standard; a solution of anthracene in ethanol was used as standard, which has $\varphi_f = 0.27$ at $\lambda_{exc} = 366$ nm.

In the present work, the results are reported on investigation of spectral-luminescent characteristics of the following heterocyclic compounds (see Table 1 and Fig. 1):

I. X = S, $R_1 = R_2 = R_3 = H - 2$,6-diphenylthiopyrylium perchlorate;

II. X = S, $R_1 = R_3 = H$, $R_2 = CH_3 - 2$, 6-diphenyl-4-methylthiopyrylium perchlorate;

III. X = S, $R_1 = R_3 = H$, $R_2 = C_6H_5 - 2,4,6$ -triphenylthiopyrylium perchlorate;

IV. X = S, $R_1 = R_3 = H$, $R_2 = C_6H_4OCH_3 - 2,6$ -diphenyl-4-(para-methoxyphenyl)-thiopyrylium perchlorate;

V. X = S, $R_1 = R_3 = CH_3$, $R_2 = H - 2$, 6-dipheny1-3, 5-dimethylthiopyrylium perchlorate;

VI. X = S, $R_1 = R_3 = CH_3$, $R_2 = C_6H_4OCH_3 - 2,6$ -diphenyl-3,5-dimethyl-4-(para-methoxy-phenyl)thiopyrylium perchlorate;

VII. X = 0, $R_1 = R_2 = R_3 = H - 2,6$ -diphenylpyrylium perchlorate;

VIII. X = 0, $R_1 = R_3 = CH_3$, $R_2 = H - 2$, 6-diphenyl-3, 5-dimethylpyrylium perchlorate;

IX. X = S - 2-phenyl-5,6-(trimethylene)thiopyrylium perchlorate;

X. X = 0 - 2-phenyl-5,6-(trimethylene)pyrylium perchlorate;

XI. R = H - symm-octahydrothioxanthylium hexachloroantimonate;



Fig. 2. Absorption and fluorescence spectra of series of pyrylium and thiopyrylium salts. Solvent - CH_2Cl_2 , T = 290°K.

XII. $R = C_6H_5 - 9$ -phenyl-symm-octahydrothioxanthylium hexachloroantimonate.

Figure 2 shows the absorption and fluorescence spectra for individual compounds.

The UV spectra of polynuclear thiopyrylium salts are similar to the spectra of the corresponding hydrocarbons, where X = CH. This is explained by the specific properties of the sulfur atom: the relatively easy ionization of the valence electrons and fairly small overlap of their $3p\pi$ -orbitals with the $2p\pi$ -AO of the neighboring carbon atoms [4]. Thiopyrylium salts usually absorb in longer-wave region of the UV spectrum than do the corresponding pyrylium salts.

For the unsubstituted thiopyrylium cation, two absorption bands are observed in the electronic spectrum, at 246 nm ($\varepsilon = 3.74 \cdot 10^3$ liter/mole·cm⁻¹) and 285 nm ($\varepsilon = 3.55 \cdot 10^3$ liter/mole·cm⁻¹) [8]. For 2-, 3-, and 4-methylpyrylium perchlorates, it was shown that the presence of methyl groups changes inappreciably the spectrum of the cation [9]. Aryl substituents do not appreciably complicate the electronic spectrum: there is a bathochromic shift of 20-70 nm of the long-wave absorption band, and a considerable broadening of this band with unresolved vibrational structure [10]. Since the appearance of broad structureless bands is due to intramolecular processes, one of these processes may be an intramolecular charge transfer (ICT). In our case, the acceptor is possibly a heterocycle, and the donor - aryl groups at 2,4,6-positions (see Table 1, compounds I-VI).

For 2,4,6-triphenyl-substituted pyrylium and thiopyrylium salts III, IV, VI, the appearance of an additional long-wave absorption band in the 380-450 nm region is characteristic. In the presence of a hetero atom in the cation, there is no degeneration of the upper occupied orbital characteristic of 1,3,5-triphenylbenzene [5]. Two levels with similar energy are formed, and electron transitions from them give two appreciably overlapping longwave absorption bands.

In our work, we discuss mainly the long-wave absorption bands, which are most sensitive to structural changes of the molecule and are responsible for the fluorescence (compounds I, II, V, VII, VIII, IX-XII are characterized by one, and salts III, IV, VI by two bands in the long-wave regions; see Table 1).



Fig. 3. Dependence of inductive effect constants σ_X^+ on shift of the long-wave band for compounds II, III, IV (with reference to I).



Fig. 4. Position of maximum of absorption band at $\lambda_{max} = 412$ nm of compound VII in CH₃CN-CH₂Cl₂ binary solvent, depending on increase in the fraction of nonpolar component. Percent of CH₃CN content - 100 (1), 50 (2), 20 (3), and 5 (4).

It was noted that the position of the maximum of the long-wave absorption band in the spectrum of the 2,6-diphenylthiopyrylium salt I (415 nm) changes inappreciably when a phenyl (III) or methoxyl group (IV) is introduced at the 4-position. This is possibly due to steric factors. In fact, these groups have the same tendency to steric interaction (the CH₃ group was chosen as a standard substituent). The steric state E_8^{0} for the C_6H_5 group and H atom is equal to 0.24 [12]. A similar effect is observed for pyrylium salts also. Thus, for 2,4,6-triphenylpyrylium perchlorate, the maximum of the long-wave band is at 416 nm [3] (compare with compound (VII). The position of the maximum of the long-wave absorption band at 330 nm in the spectrum of the symm-octahydrothioranthylium salt (XI) also does not change if a phenyl group is introduced into the 9-position (XII). The steric interaction between the phenyl group and the heterocycle hinders charge transfer and as a result the integral intensity of the long-wave band at 415 nm in the spectra of compounds I, III, and at 330 nm in XI, XII, with substituents H and C_6H_5 at positions 4 and 9, respectively, practically do not change. The second long-wave band at 380 nm of compound III behaves differently. This is characterized by high integral intensity (see Table 1, fosc). Increase in intensity may be due to the contribution of ICT to this band. The presence of a strong donor OCH_3 group (salt IV) at the 4-position of the benzene ring leads to a considerable bathochromic shift of the 380-nm band (salt III) to 450 nm (salt IV). The second long-wave band at 410 nm in the spectrum of compound IV changes inappreciably with respect to position and integral intensity, compared with the same spectral characteristics of compounds I and III. A correlation is observed between the shift of the long-wave band due to ICT and the inductive effect constants σ_n^+ [13] (cf. in Fig. 3).

Methyl substituents at the 3-position of the thiopyrylium cation lead to a certain decrease in the integral intensity of the ICT band (salts V, VI) in contrast to the case of oxygen-containing analog VIII, which may be due to the different electronegativity of the hetero atoms and the possible manifestation of the hyperconjugation effect of the methyl group for the pyrylium salts [7]. Table 1 shows that the relative quantum yield for thiopyrylium salts is $10^{-2}-10^{-3}$. A comparison of our results on φ t with the literature data (see Table 1) shows that there is good correspondence for the thiopyrylium salts I and III. In contrast, for 2,6-diphenylpyrylium salt VII, there are appreciable differences between the φ t and ε values that we calculated and those determined in [6, 2]. To clarify the reason for these differences, we studied the concentrational dependence of the long-wave absorption band of VII in acetonitrile. The results of the investigation show no deviations from Beer's law if the concentrations are varied within $10^{-3}-10^{-5}$ mole·liter⁻¹, i.e., in a polar solvent 2,6-diphenylpyrylium perchlorate VII is present in a monomolecular state.

In a $CH_3CN-CH_2Cl_2$ binary solvent, with increase in the fraction of the nonpolar CH_2Cl_2 component (Fig. 4), a shift in the maximum of the long-wave band at $\lambda_{max} = 412$ nm of compound VII is observed. Simultaneously, the overall absorbability of the molecule first increases, and then decreases. This behavior in binary mixtures is possible if the molecules are combined into fluorescing associates in the form of ion pairs K⁺A⁻...K⁺A⁻ [14]. The

formation of associates may explain the inconsistency of the experimental data with respect to φ_t and ε , obtained by different authors for compound VII.

It was thus shown that one of the long-wave absorption bands is due to ICT, and the position of the second band is dependent on steric factors. The integral intensity of the long-wave band and the quantum yield of 2,6-diphenylpyrylium are determined by the degree of formation of the fluorescing associates.

LITERATURE CITED

- 1. V. G. Kharchenko, S. N. Chalaya, and T. M. Konovalov, Thiopyrans and Thiopyrylium Salts [in Russian], Saratov (1975).
- 2. R. Mayer, J. Sühnel, H. Hartmann, and J. Fabian, Z. Phys. Chem., 256, 792-800 (1975).
- 3. A. Mistr and R. Zahradnik, Collect. Czech. Chem. Commun., <u>38</u>, No. 6, 1668-1673 (1973).
- 4. V. G. Kharchenko, A. D. Shebaldova, V. N. Kravtsova, et al., Certain Problems of Chemistry of Diketones and Compounds Based on Them [in Russian], Saratov (1979).
- 5. A. Mistr, M. Vavra, J. Skoupý, and R. Zahradnik, Collect. Czech. Chem. Commun., <u>37</u>, No. 5, 1520-1532 (1972).
- 6. V. P. Karmazin, M. I. Knyazhanskii, E. P. Olekhnovich, and G. N. Dorofeenko, Zh. Prikl. Spektrosk., 23, No. 2, 234-239 (1975).
- 7. M. I. Knyazhanskii, V. P. Karmazin, E. P. Olekhnovich, and G. N. Dorofeenko, Zh. Prikl. Khim., 23, No. 2, 328-331 (1975).
- 8. I. Ya. Evtushenko, Candidate's Dissertation, Mathematical Sciences, Saratov (1977).
- 9. I. Degani and C. Vincenzi, Boll. Schi. Fac. Chim. Industr. Bologna, 23, 249-250 (1965).
- 10. Z. Yozhida, H. Sugimoto, and S. Yoneda, Tetrahedron, 28, No. 24, 5873-5881 (1972).
- 11. S. Parker, Photoluminescence of Solutions [Russian translation], Mir, Moscow (1972).
- 12. V. A. Pal'm, Introduction to Theoretical Organic Chemistry [in Russian], Vysshaya Shkola, Moscow (1974).
- 13. K. Johnson, The Hammett Equation [Russian translation], Mir, Moscow (1977).
- 14. N. Nizamov, U. Zakhidov, A. K. Atakhodzhaev, et al., Zh. Prikl. Spektrosk., <u>36</u>, No. 3, 422-430 (1982).

EDGE RADIATION SPECTRA OF LUMINESCENT CERAMIC A²B⁶

A. I. Proskura and I. V. Zakharchenko

UDC 535.372:537.226

The edge radiation (ER) spectra of wide-gap A^2B^6 compounds were studied by F. Kreger in 1940. Since that time the ER spectra and mechanisms of the corresponding electronic transitions have been studied intensively in different objects. The main studies were performed with single crystals, which make it possible to study the ER as one of the fundamental properties of the semiconductor. Historically, however, ER studies began with more accessible objects - polycrystalline powders. As interest in the photoluminescence of ZnS and photoconductivity of CdS increased, the radiative recombination in the region of edge absorption was also studied in films and single crystals. Extensive information about ER in different traditional materials has now been accumulated [1, 2]. However, the ER of luminescent ceramic has not been previously studied.

In view of the promising outlook for ceramic materials, we thought it would be useful to study ER of a series of A^2B^6 compounds in the ceramic variant. Their intrinsic and impurity luminescence was studied in [3].

The samples were prepared by the method of hot pressing. The ceramic was not purposefully doped. The measurements were performed at temperatures of 77 and 293°K with excitation by radiation from a laser of the type LG-21 with $\lambda = 337$ nm, a pulse power of P = 1.6 kW, and a pulse repetition frequency of 80 Hz in a state with externally triggered mode-

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 45, No. 3, pp. 434-438, September, 1986. Original article submitted April 23, 1985.