
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

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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 in the region 17 000–20 000 cm⁻¹, the molar absorptivity exceeding 30 000 1·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-dihydrobenzo(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.

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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. (°C)</th>
<th>Yield*</th>
<th>C% calc./found</th>
<th>N% calc./found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>225-227</td>
<td>90b</td>
<td>59.58/59.85</td>
<td>4.14/4.39</td>
</tr>
<tr>
<td>2</td>
<td>&gt;300</td>
<td>75b</td>
<td>59.18/59.12</td>
<td>4.93/4.87</td>
</tr>
<tr>
<td>3</td>
<td>273-275</td>
<td>71b</td>
<td>60.90/60.93</td>
<td>5.53/5.40</td>
</tr>
<tr>
<td>4</td>
<td>&gt;300</td>
<td>94c</td>
<td>53.00/53.01</td>
<td>3.43/3.73</td>
</tr>
<tr>
<td>5</td>
<td>246-248</td>
<td>78c</td>
<td>53.00/53.42</td>
<td>3.43/3.61</td>
</tr>
<tr>
<td>6</td>
<td>&gt;300</td>
<td>87c</td>
<td>64.00/64.00</td>
<td>4.12/4.12</td>
</tr>
<tr>
<td>7</td>
<td>273-275</td>
<td>93c</td>
<td>64.00/64.00</td>
<td>4.12/4.00</td>
</tr>
</tbody>
</table>

* 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.

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 quartz tube of diameter 5 mm.

3-amino-phthalimid \((Q_f = 0.6 \text{ in ethanol} [10])\) 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 \(10^{-4} \text{ M/l}\) 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 \(10^{-4} \text{ M}\) 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\(_2\)H\(_5\))\(_2\) 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
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 22 000 cm\(^{-1}\), the absorption band is intensive (\(\varepsilon = 47900 \text{ 1·mol}^{-1}\text{·cm}^{-1}\) in C\(_2\)H\(_5\)OH + 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 \(1S_0 \rightarrow 1S_1 (\pi\pi^*)\) transition (Fig. 1, see Section 4).

The shorter wavelength transitions of 1 are of considerably lower intensity: \(\nu = 28 000 \text{ cm}^{-1}\), \(\varepsilon = 2300 \text{ 1·mol}^{-1}\text{·cm}^{-1}\); \(\nu = 39 000 \text{ cm}^{-1}\), \(\varepsilon = 11 800 \text{ 1·mol}^{-1}\text{·cm}^{-1}\) 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\(_2\)H\(_5\))\(_2\), lower the energy of the longest wavelength \(\pi\pi^*\) transition with about 4000 cm\(^{-1}\) relative to 1 (Table 2). Besides the difference between the extinction coefficients of the \(1S_0 \rightarrow 1S_1 (\pi\pi^*)\) transition and the shorter wavelength transitions diminished; e.g. the first four \(\pi\pi^*\) transition of 2 in ethanol have the following energies: \(\nu = 18 000 \text{ cm}^{-1}\), \(\varepsilon = 35 500 \text{ 1·mol}^{-1}\text{·cm}^{-1}\); \(\nu = 26 000 \text{ cm}^{-1}\), \(\varepsilon = 10 800 \text{ 1·mol}^{-1}\text{·cm}^{-1}\); \(\nu = 35 000 \text{ cm}^{-1}\), \(\varepsilon = 12 900 \text{ 1·mol}^{-1}\text{·cm}^{-1}\); \(\nu = 38 400 \text{ cm}^{-1}\), \(\varepsilon = 14 500 \text{ 1·mol}^{-1}\text{·cm}^{-1}\). 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 17 000–48 000 cm\(^{-1}\); the Stokes shift is about 2000 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\(_6\)H\(_6\) 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] ($p(A) = 1.517 \pm 0.18 p$). The dependence of the resonance integrals between adjacent carbon atoms on the bond lengths was accounted for using the formula: $\beta = -2.318 \frac{S(R)}{S_0} \text{eV}$ ($S_0$ 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 $f \approx 1.0$, while the next shorter wavelength $\pi\pi^*$ transition are of low intensity ($f \leq 0.1$) (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 $\pi$-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.

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 $\pi$-electronic system of the dihydroxanthylium cation, responsible for the $\pi\pi^*$ transitions of all the molecules under investigation, is fragment $\Delta$:
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 \( j = 1', 2', 3' \), ... 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

\[
\psi = \sum c_{ij} V_{ij}.
\]

The longest wavelength intensive \( \pi \pi^* \) transition of all the compounds 1 – 7 is determined predominantly by the \( V_{11'} \) configuration, i.e. it is a HOMOLUMO 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.

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 \( \Delta \), 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 \( \Delta \) 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

\[
\text{[According to Dähne [22] the chromophore of the diarylmethane systems is a polymethine system.]}\]

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.

![Diagram](image)

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

![Diagram](image)
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 $\pi$-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 $S_0-S_1$ ($\pi\pi^*$) 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 extension 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.