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Anion Nature Influence on Spectral and Some Physico-Chemical Properties of 6,7-Dihydroxy-4-methyl-2-phenylchromenylium Salts

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Abstract—The influence of the nature of anions (Cl^-, Br^-, I^-, ClO_4^-, and PF_6^-) on the physico-chemical properties (solubility, solvatochromism, and spectral characteristics) of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts was studied. The main spectrophotometric characteristics were determined. It was noted that the molar absorption coefficient increases on passing to polar solvents. The highest molar absorption coefficient was observed for the hexafluorophosphate anion, which has weak coordinating power that favors more efficient solvation of the organic cation.

Keywords: 6,7-dihydroxy-4-methyl-2-phenylchromenylium, spectrophotometry, IR spectroscopy, solubility, solvatochromism

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Organic analytical reagents represent a large class of synthetic compounds that are used to identify, separate, and concentrate both organic compounds and inorganic ions. An important aspect of studying organic reagents is the determination of their physico-chemical and acid-core properties and spectral characteristics [1]. Among them, spectrophotometric, fluorescent, and solvatochromic properties occupy a special position. These latter are related to the interaction between solvent molecules differing in dipole moments and chromophoric groups of dissolved substances [2]. In addition, in solvents of various natures differing in physico-chemical properties, spectrophotometric characteristics of equilibrium forms of a dye can be caused not only by solvatochromism, but also by tautomerism [3–5].

In turn, derivatives of oxygen-containing heterocyclic compounds, *ortho*-dioxychromenoles, are of considerable interest. Among these latter, the most studied are complex-forming properties of 6,7-dihydroxychromenylium derivatives in relation to polyvalent metal ions, and techniques for their direct or extraction-spectrophotometric determination are developed [6, 7]. It should be noted that the publications on the study of these compounds are few in number and are dedicated to their acid-base properties [8] or special features of their synthesis [9, 10].

The aim of this work is to study the effect of the nature of the anions Cl^-, Br^-, I^-, ClO_4^-, and PF_6^- on the spectral characteristics, solubility, and solvatochromism of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts.

One of essential parameters to be taken into account in rational choosing a reagent for direct or extraction-(sorption) spectrophotometric determination of metal ions is the solubility of this reagent and the corresponding complex compound. The results of HPLC determination of the solubility of the compounds under study are presented in Table 1. These data show that among the studied set of solvents, methanol dissolves best 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts and water, worst. It should be noted that the solubilities in water, methanol, and ethanol (96%) decrease almost linearly (R^2 = 0.95, 0.94, 0.85) for the series of anions Cl^-, Br^-, I^-, ClO_4^-, and PF_6^- with increase in the anion radii (r = 181, 196, 220, 240, 242 pm, respectively) [11, 12].

It was interesting to study the influence of the anion nature on the spectral properties of dihydroxychromenyliums. Thus, in the IR spectra there are a widened band of OH-groups stretching vibrations at 3270–3460 cm^{-1} and a band of C-H stretching vibrations at 2900–3080 cm^{-1}. There are also characteristic bands

Table 1. Solubility of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts in certain solvents

Anion	Solubility, mmol/L			
	water	methanol	ethanol	acetonitrile
Chloride	0.55	180.31	13.53	1.21
Bromide	0.50	179.28	7.69	0.92
Iodide	0.16	53.13	5.45	2.21
Perchlorate	0.10	33.01	4.84	12.65
Hexafluorophosphate	0.07	14.75	3.62	9.33

Table 2. Spectral characteristics of solutions of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts in various solvents

Solvent		Cl^-		Br^-		I^-		ClO_4^-		PF_6^-	
		λ, nm	$\varepsilon\times10^{-4}$	λ, nm	$\varepsilon\times10^{-4}$	λ, nm	$\varepsilon\times10^{-4}$	λ, nm	$\varepsilon\times10^{-4}$	λ, nm	$\varepsilon\times10^{-4}$
Polar protic	Water	460	2.32	459	2.63	460	2.62	459	2.24	459	3.26
	Methanol	470	2.31	462	2.55	454	2.42	469	2.09	461	2.90
	Ethanol	470	2.14	462	2.33	466	2.36	464	2.04	471	2.90
	Isopropanol	444	2.66	455	2.35	457	2.39	455	1.96	440	3.93
	n-Propanol	473	2.13	471	2.48	470	2.39	469	2.07	471	3.06
	n-Butanol	472	2.02	469	2.39	471	2.38	469	2.09	470	2.98
	Isoamyl alcohol	473	2.08	471	2.37	471	2.38	471	2.02	466	2.88
Polar aprotic	THF	460	1.74	446	2.34	456	1.99	438	1.79	447	2.63
	Dioxane	462	1.69	462	2.31	464	2.16	459	1.54	458	2.58
	Acetonitrile	466	1.79	464	2.31	454	2.14	465	1.74	461	2.58
	Acetone	460	1.81	455	2.34	442	2.13	448	1.86	452	2.56
	Ethyl acetate	461	1.80	456	2.19	451	2.11	451	1.66	458	2.60
	Butyl acetate	460	1.73	455	2.23	458	1.97	454	1.63	459	2.44

at 1623–630 cm^{-1} (pronounced in the IR spectrum) and 1596–1602 cm^{-1} (intense in the IR spectrum), which correspond to the vibrations of the benzopyrylium C-O and C–S bonds [13, 14]. There is also a characteristic band of skeletal vibrations of the benzene ring about 1000 cm^{-1}, of medium intensity in the IR spectrum and of low in intensity in the IR spectrum. It is interesting to note that the effect of anions on the intensity of the C–O and C–C benzopyrylium cycle bands is noticeable in the IR spectrum: in passing from Cl^- to PF_6^- the intensity of the band at 1623–1630 cm^{-1} decreases relative to the band at 1596–1602 cm^{-1} as the anion radius increases. This effect may be associated with a change in the charge localization in the pyrylium cycle, and hence with the change in the polarity of the benzopyrylium cation, which in turn affects solubilities of the corresponding salts.

The study of the electronic absorption spectra of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts has shown that the position and intensity of the absorption bands are affected not only by the solvent nature (solvatochromism), but also by the counter-anion nature. On the basis of the experimental results and related calculations we constructed the dependences of the molar light absorption logarithm on the Dimrot–Reichardt empirical parameter of solvents polarity $E_T(30)$ [15]. Molar absorption coefficients and positions of absorption maxima for all studied salts are summarized in Table 2. Examination of these results allow us to conclude that the logarithms of molar absorption coefficients in solvents of different natures almost linearly increase with the increase in their polarity parameter $E_T(30)$ for all the salts under study ($R^2 = 0.80–0.90$).

According to the data of Table 2, it can be concluded that in most cases a bathochromic shift of 2–15 nm, as compared to the aqueous solution, is observed in the alcohols solutions, but in the isopropanol solutions a hypsochromic shift of 5–20 nm was recorded. The anion nature does not significantly affect the position of the absorption maximum, and the corresponding Δλ values do not exceed 14 nm in passing from one 6,7-dihydroxy-4-methyl-2-phenylchromenylium salt to another. The molar absorption coefficient is greater in polar protic solvents (water and alcohols) than in aprotic solvents. Among the anions, hexafluorophosphate of

6,7-dihydroxy-4-methyl-2-phenylchromenylium has the highest absorption coefficient, which is probably caused by the weak coordinating effect of this anion that favors a more efficient solvation of the 6,7-dihydroxy-4-methyl-2-phenylchromenyl cation.

Thus, the effect of the anion nature on the physical and chemical properties of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts has been studied. It has been found that thermochemical radii of anions correlate with solubilities of the salts in polar protic solvents and also with characteristic bands in vibrational spectra. The influence of solvation by protic and aprotic polar solvents on the position of light absorption maxima of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts has been pointed out. Dependences of the molar light absorption logarithms of the 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts on the empirical parameters of solvents polarity $E_T(30)$ have been established.

EXPERIMENTAL

The salts (chloride, bromide, and perchlorate) of 6,7-dihydroxy-4-methyl-2-phenylchromenylium were obtained by condensation of pyrogallol A with benzoylacetone in glacial acetic acid with the direct introduction of the corresponding acid into the reaction mass or by the exchange reaction of 6,7-dihydroxy-4-methyl-2-phenylchromhen chloride with the formation of a soluble salt. All reagents were of no less than analytical grade.

Identification of the reaction products and their purity determination were carried out by the HPLC method using an Infinity 1260 chromatograph with a 6530 Accurate Mass-TOF (Agilent Technologies, USA) mass detector and a diode-matrix UV detector. The holding time of the 6,7-dihydroxy-4-methyl-2-phenylchromenylium cation, regardless of anion, is 3.25±0.05 min. According to the internal normalization, the purity of the synthesized products is no less than 99.0%. In the mass-spectra (ionization with a double electrospray at atmospheric pressure in a positive field) there is a peak with *m/z* 253.20±0.05; calculated for the cation 6,7-dihydroxy-4-methyl-2-phenylchromenylium cation $C_{16}H_{13}O_3^+$: 253.27 [M^+]. Ionization in the negative field was used to detect anions (except for Cl^-, the *m/z* value of which does not reach the working range 50–3000 Da of the mass detector).

The IR spectra were recorded by the frustrated total internal reflection (FTIR) method in the range of 400–4000 cm^{-1} with a baseline correction using an FT-IR-8400S (Shimadzu) IR spectrometer and a Quest Specac attachment. The Raman spectra were obtained on a DXR Raman Microscope Thermo Sientific instrument with a 780 nm laser in the working interval of 100–3500 cm^{-1} with the baseline correction and fluorescence suppression. We were not able to detect Raman spectra for the hexafluorophosphate and chloride, because fluorescence overlaps with valid signals in their spectra. The ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance III (400 MHz) spectrometer in DMSO-d_6.

Solubility of 6,7-dihydroxy-4-methyl-2-phenylchromenylium salts was studied by the HPLC method with a UV detection at λ = 260 nm. Deionized water, methanol, ethanol (96%), and acetonitrile were taken as solvents. To construct the calibration graph, 6,7-dihydroxy-4-methyl-2-phenylchromenylium chloride solutions in acetonitrile with concentrations of 0.2, 0.4, 0.6, 1.0, 2.0, 3.0, 6.0, 9.0, and 12.0 mmol/L were prepared. The injection volume was 1 μL. Along this range, the dependence of the 6,7-dihydroxy-4-methyl-2-phenylchromenylium concentration on the peak area in the chromatogram is linear with $R^2 = 0.999$. In each of five 5 mL flasks, 0.1 g of 6,7-dihydroxy-4-methyl-2-phenylchromenylium chloride, bromide, iodide, perchlorate, or hexafluorophosfate were injected and 4.0–4.5 mL of water were added. The mixture was stirred and after complete dissolution 0.05 g more of a salt was added in small portions to obtain an undissolved precipitate and a saturated solution of a 6,7-dihydroxy-4-methyl-2-phenylchromenylium salt above it. The resulting mixture was left for 2 h up to reaching equilibrium, and then the saturated solution was taken off with a syringe, filtered through a syringe teflon membrane filter with a 2 μm pore size, and chromatographed. The solubilities in methanol and ethanol were studied similarly. The injections were varied so that the signal falls into the middle of the graduation graph. Further, according to the HPLC-UV data, the molar concentrations of saturated solutions were calculated, taking into account the injection volume.

Solvatochromism was studied in the way similar to the procedure described in the work [16]. In a glass-stoppered test tube, 0.1 mL of 1×10^{-3} M methanol solution of a corresponding 6,7-dihydroxy-4-methyl-2-phenylchromenylium salt and 5 mL of an organic solvent were injected, the mixture was stirred, and the absorption spectrum was recorded on an SF-56 (LOMO-Spectr, Russia) spectrophotometer in the wavelength range of

380–780 nm in quartz cells thermostatted at 25°C (*l* = 1 cm).

6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium perchlorate. To a mixture of pyrogallol A (2.52 g, 10 mmol) and benzoylacetone (1.62 g, 10 mmol) in 10 mL of glacial acetic acid, 6 mL of 50% chloric acid (40 mmol of $HClO_4$) was added. The reaction mixture was boiled for 30 min. After cooling to room temperature, a light brown crystalline precipitate was filtered off on a Schott filter under vacuum and washed with distilled water (3×5 mL). Yield 70%. IR spectrum, ν, cm^{-1}: 3426.5 (O–H), 3070.2 (C–H, Ar), 1626.0. 1602.2 (C–O, C–C, Het), 1579.1, 1509.0, 1489.7, 1463.7, 1444.9, 1410.3, 1371.3, 1343.5, 1297.0, 1271.0, 1218.4, 1173.5, 1092.4. 1052.1 (Cl–O), 997.9 (C–C, Ph), 896.0, 868.9, 854.0, 780.8, 762.0, 738.5, 681.9, 663.4, 618.5, 517.6, 473.0. IR spectrum, ν, cm^{-1}: 1625.9. 1596.7(C–O, C–C, Het), 1532.0, 1508.5, 1466.2, 1425.7, 1379.5, 1342.9, 1240.9, 1194.9, 1168.8, 1001.5 (C–C, Ph), 898.2, 526.2. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.91 c (3H, CH_3), 7.48–7.49 d (2H, Ar, *J* = 4.64 Hz), 7.70–7.79 m (3H, Ar), 8.38–8.40 d (2H, Het, *J* = 7.43 Hz), 8.47 c (1H, Het). NMR spectrum ^{13}C (DMSO-d_6), δ_C, ppm: 20.72 (CH_3), 103.18, 107.11, 114.71, 120.82, 128.53, 129.88, 130.26, 134.84, 150.53, 154.65, 162.43, 164.48, 165.38. Mass-spectrum (ESI^-), *m*/*z*: 99.66 (calculated for ClO_4^-: 99.45).

6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium chloride. A current of dry hydrogen chloride was passed through a solution of pyrogallol A (2.52 g, 10 mmol) and benzoylacetone (1.62 g, 10 mmol) in 10 mL of glacial acetic acid at room temperature for 30–40 min, then 3 h more with heating on a boiling water bath. The reaction mass was poured into 100 mL of a water-ice mixture. A light brown precipitate was filtered off on a Schott filter under vacuum and washed with diisopropyl ether. Yield 55%. IR spectrum, ν, cm^{-1}: 3355.9 (O–H), 2903.0 (C–H, Ar), 2611.7 (C–H, Alk), 1625.0. 1597.2 (C–O, C–C, Het), 1578.5, 1554.6, 1525.1, 1490.8, 1410.4, 1368.3, 1294.8, 1253.8, 1214.9, 1214.9, 1201.4, 1201.4, 997.8 (C–C, Ph), 896.4, 850.4, 780.8, 763.1, 732.2, 705.6, 680.2, 660.4, 620.2, 554.8, 526.1, 502.9, 472.1.

6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium bromide. To a solution of pyrogallol A (2.52 g, 10 mmol) and benzoylacetone (1.62 g, 10 mmol) in 10 mL of glacial acetic acid, 8 mL of 40% hydrobromic acid (60 mmol of HBr) was added. The reaction mixture was boiled for 30 min, and then the light brown crystalline precipitate was filtered off on a Schott filter under vacuum and washed with several portions of water. Yield 50%. IR spectrum, ν, cm^{-1}: 3404.7. 3375.5 (O–H), 3043.4 (C–H, Ar), 2641.5 (C–H, Alk), 1624.3. 1595.6 (C–O, C–C, Het), 1580.3, 1556.3, 1522.0, 1489.3, 1407.1, 1382.6, 1367.1, 1295.5, 1252.3, 1238.8, 1216.4, 1195.6, 1158.3, 1100.5, 1081.0, 1034.0, 997.4 (C–C, Ph), 895.9, 849.3, 780.4, 762.6, 727.6, 694.9, 677.8, 661.2, 622.0, 553.4, 525.0, 514.1, 470.7. IR spectrum, ν, cm^{-1}: 1630.2, 1596.9 (C–O, C–C, Het), 1527.8, 1508.9, 1468.0, 1427.2, 1383.8, 1369.1, 1322.9, 1291.5, 1255.2, 1238.3, 1185.1, 1159.0, 1083.4, 1000.5 (C–C, Ph), 898.0, 764.2, 708.6, 679.1, 6.17.9, 529.1. Mass-spectrum (ESI^-), *m*/*z*: 78.90, 80.90 [calculated for Br^-: 78.92 (^{79}Br), 80.92 (^{81}Br)].

6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium iodide. Chloride of 6,7-dihydroxy-4-methyl-2-phenylchromenylium (2.9 g, 10 mmol) was dissolved in 60 mL of a boiling water–ethanol mixture (30 : 70), and then 10 g (65 mmol) of sodium iodide was added. After 20 min a precipitation was observed. The mixture was left in air for 24 h, and then the red-brown precipitate was filtered off on a Schott filter under vacuum and washed with several portions of water. Yield 60%. IR spectrum, ν, cm^{-1}: 3278.2 (O–H), 3038.6 (C–H, Ar), 1624.2. 1595.8 (C–O, C–C, Het), 1510.6, 1490.0, 1461.9, 1444.2, 1408.9, 1347.5, 1297.4, 1269.2, 1216.4, 1190.1, 1156.6, 1103.6, 1079.2, 1058.9, 1021.1, 996.2 (C–C, Ph), 895.7, 858.9, 782.5, 761.0, 736.7, 680.9, 662.3, 619.3, 516.1, 472.7. IR spectrum, ν, cm^{-1}: 1620.0, 1596.1 (C–O, C–C, Het), 1539.7, 1508.6, 1465.4, 1425.6, 1380.1, 1343.9, 1274.2, 1237.7, 999.6 (C–C, Ph), 897.1, 527.4. Mass-spectrum (ESI^-), *m*/*z*: 127.12 (calculated for I^-: 126.90).

6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium hexafluorophosphate. Chloride of 6,7-dihydroxy-4-methyl-2-phenylchromenylium (2.9 g, 10 mmol) was dissolved in 60 mL of a boiling water-ethanol mixture (30:70), and then ammonium hexafluorophosphate (7 g, 43 mmol) was added. After 20 min a precipitation was observed. The mixture was left in air for 24 h, and then the red precipitate was filtered off on a Schott filter under vacuum and washed with several portions of water. Yield 70%. IR spectrum, ν, cm^{-1}: 3457.1 (O–H), 3078.4 (C–H, Ar), 2980.9 (C–H, Alk), 1629.3, 1596.4 (C–C, C–O, Het), 1574.7, 1531.3, 1505.5, 1490.6, 1403.6, 1371.1, 1342.8, 1256.1, 1227.1, 1204.8, 1103.5, 1079.3, 1027.3, 999.3 (C–C, Ph), 928.3, 877.3, 825.2 (P–F), 768.6, 702.1, 679.4, 658.2, 629.3, 554.0, 516.6, 471.4. Mass-spectrum (ESI^-), *m*/*z*: 144.93 (calculated for PF_6^-: 144.97).

CONFLICT OF INTEREST

No conflict of interest was declared by the he authors.

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