Chemistry of Heterocyclic Compounds, Vol. 44, No. 8, 2008

ELECTRONIC ABSORPTION SPECTRA OF PYRYLIUM AND BENZODIHYDRO-CHROMENYLIUM SALTS

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The electronic absorption spectra of benzodihydrochromenylium, tetrahydrochromenylium, and dichloropyrylium salts were studied for the first time. It was noticed that intramolecular charge transfer takes place mainly between the substituent at position 4 of the pyrylium ring and the π-system of the cation as a whole, while the bathochromic shift depends substantially on the geometry of the molecule. It was shown that the chlorine atoms have an effect on the form of the spectra when they are introduced into the ring of the pyrylium cation and into the aryl substituents.

Keywords: 1,5-diketones, benzodihydrochromenylium salts, chlorine-substituted pyrylium salts, intramolecular charge transfer.

Pyrylium salts exhibit extremely interesting optical characteristics, due mainly to the structure of the cation, which contains an electronegative oxygen atom. This opens up wide possibilities for the use of pyrylium salts as fluorescent materials, photosensitizers, organic photoconductors, and semiconductors [1].

It is known that the absorption bands in the spectra of the unsubstituted pyrylium cation at λ_{max} 269 and 219 nm correspond to $\pi \rightarrow \pi^*$ transitions. The introduction of aryl substituents at positions 2,4,6 of the pyrylium ring complicates the form of the spectrum with strong absorption bands in its long-wave region (λ_{max} 350-450 nm) [2, 3]. Here it is considered that these bands correspond to transitions with intramolecular charge transfer from the aryl substituent to the cation. The substituent at the C-4 atom of the pyrylium ring has the greatest effect on these transitions, since there are no symmetry restrictions for change of charge density at the atoms of the π–system and electron density accumulates at the heteroatom [4, 5].

In order to determine the effect of the nature of the absorption bands and the effect of the molecular geometry (the extent of the π–system and its nature) on their parameters we studied the electronic spectra of a series of pyrylium, tetrahydrochromenylium, and benzodihydrochromenylium salts.

We obtained 2-phenyl-4-R-7,8-dihydrochromenylium fluoroborates **3a-c** in the reaction of propanonyltetrahydronaphthalenones **1a-c** with boron trifluoride etherate in various solvents (glacial acetic acid, acetic anhydride, and toluene).

It was found that the yield of the fluoroborates **3a-c** in acetic anhydride increases to 65-67% (Table 1). This is determined by the accepting characteristics of the acetyl cation, which promotes removal of a hydride ion according to the general-theoretical concepts [6] from position 4 of the 2,4-R-7,8-benzo-5,6-dihydro-chromene, as intermediate, during heteroaromatization to the corresponding fluoroborate **3**. At 140°C

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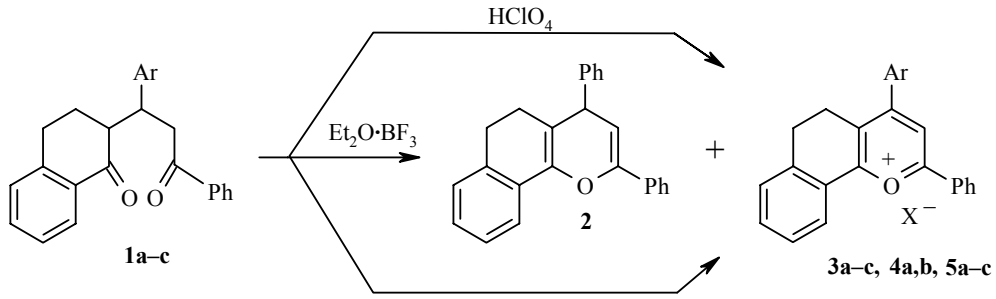
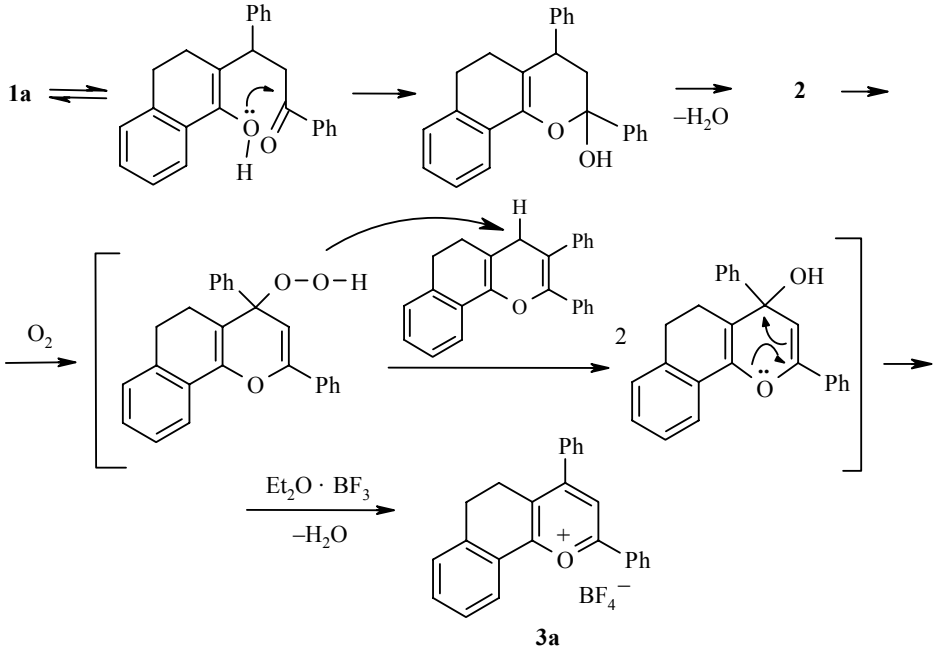


1, 3–5 a Ar = Ph, **b** Ar = 4-$MeOC_6H_4$; **1,3 c** Ar = 4-$Me_2NC_6H_4$; **3** X = BF_4, **4** X = ClO_4, **5a,b** X = Br; **5c** Ar = C_6H_4–$N^+HMe_2Br^-$, X = Br·$5H_2O$

2,4-diphenyl-7,8-benzo-5,6-dihydrochromene (**2**) (59%) is formed together with the salt **3a**, and this is probably due to the concurrent simple dehydration of the product from semi-ketalization of the diketone **1a** according to the usual mechanism [7]. It is not possible to isolate benzohexahydrochromene, which makes it possible to link salt formation to oxidative aromatization by the action of atmospheric oxygen according to the following scheme:



The possibility of such a transformation is supported by the formation of the fluoroborates **3a**,**b** (up to 55%) in toluene (Table 1) in the absence of hydride ion acceptors.

The respective perchlorates **4a**,**b** were isolated during the reaction of the diketones **1a**,**b** with perchloric acid in acetic acid.

The bromides **5a**,**b** and 4-(4-dimethylaminophenyl)-2-phenyl-7,8-benzo-5,6-dihydrochromenylium dibromide **5c** were synthesized by the action of bromine on propanonyltetrahydronaphthalenones **1a-c** in glacial acetic acid. According to the data from thermogravimetric analysis, compound **5c** was obtained in the form of a crystallohydrate with five molecules of water, the content of which amounts to 12% and is removed in the range of 60-180°C. The anhydrous dibromide **5c** is unstable under polythermal conditions – there is no horizontal area indicating a constant composition on the thermogravimetric curve. In the range of 200-480°C there is a slow

TABLE 1. The Yields of the Products from the Reaction of the Diketones **1a-c** with Boron Trifluoride Etherate and Bromine

Diketone	Solvent	Reagent	Reaction temperature,°C	Benzohydrochromenylium Salts **3** and **5**	Yield, %
1a	AcOH	$Et_2O{\cdot}BF_3$	20	**3a**	54
1a	Ac_2O	$Et_2O{\cdot}BF_3$	20	**3a**	67
1a	Ac_2O	$Et_2O{\cdot}BF_3$	140	**3a**	7*
1a	PhMe	$Et_2O{\cdot}BF_3$	110	**3a**	51*
1a	AcOH	Br_2	118	**5a**	40
1b	AcOH	$Et_2O{\cdot}BF_3$	20	**3b**	57
1b	Ac_2O	$Et_2O{\cdot}BF_3$	20	**3b**	65
1b*[2]	PhMe	$Et_2O{\cdot}BF_3$	110	**3b**	55
1b	AcOH	Br_2	118	**5b**	7
1c	AcOH	$Et_2O{\cdot}BF_3$	20	**3c**	52
1c*[2]	PhMe	$Et_2O{\cdot}BF_3$	110	**3c**	55
1c	AcOH	Br_2	20	**5c**	76

* Benzodihydrochromene **2** is formed in addition to the salt **3a** with yields of 59 and 13% respectively.

*[2] The corresponding benzodihydrochromenes were detected by chromatography.

decrease of weight as a result of the destruction of the substance and removal of the decomposition products. In this range of temperatures there are no thermal effects on the differential thermal curve. At 480-810° a significant exo effect for the oxidation of the free carbon and the products from decomposition of the investigated substance is observed on the differential thermal curve.

During comparison of the absorption spectra of 2,4-diphenyl-7,8-benzo-5,6-dihydrochromenylium (**4a**) and 2-phenyl-7,8-benzo-5,6-dihydrochromenylium (**6**) perchlorates [4], which have only one band in the long-wave region at λ_{max} 437 nm, it was found that the introduction of a phenyl substituent at position 4 does not substantially affect the parameters of the band, but a new band appears at λ_{max} 356 nm. The latter disappears in the transition to the electronic spectrum of 4-(4-methoxyphenyl)-2-phenyl-7,8-benzo-5,6-dihydrochromenylium perchlorate (**4b**), and strong absorption is only observed at λ_{max} 430 nm. A similar pattern is observed for the fluoroborates **3a** and **3b** (Table 2).

Thus, the absorption bands at λ_{max} 356-358 nm in the salts **3a** and **4a** can be interpreted as bands for intramolecular charge transfer from the π-system of the phenyl at position 4 to the cation. The absence of such bands in the spectra of compounds **3b** and **4b** indicates that the methoxyphenyl fragment is not coplanar in relation to the plane of the ring in the cation. The form of the electronic spectra of the salts **3a**,**b**, **4a**,**b**, and **5a**,**b** with various anions indicates that the counter-ion has little effect.

Theoretical calculations of the absorption bands for the investigated compounds by the semiempirical AM1 method confirm the relationships that we discovered. It is seen that the resolved band at λ_{max} 374 nm (intensity 0.671) in the gas phase for compound **3b** in acetic acid and methylene chloride disappears on account, apparently, of the effect of the solvent.

A distinguishing feature of the absorption spectra of the difluoroborate **3c** and dibromide **5c** is the presence of two absorption bands in the long-wave region (569 and 416 nm respectively), which belong to the charge transfer bands and, in our opinion, reflect their structure as bications.

TABLE 2. The Electronic Absorption Spectra* of the Salts **3a-c**, **4a**,**b**, **5a-c**, **6**, **8a**,**b**, and **10a-d**

Com-pound*[2]	CH_2Cl_2		AcOH		Quantum-chemical calculation	
	λ, nm	OD, A	λ, nm	OD, A	λ, nm	OD, A
3a	437	1.458	430	1.001	402	0.634
	358	1.001	347	0.599	344	0.653
	291	0.897	287	0.560	288	0.292
	233	1.120	235	0.978	239	0.109
3b	443	1.776	425	1.083	397	0.657
	287	0.990	285	0.455	374	0.671
	236	1.229	238	1.068	285	0.350
					241	0.169
3c	566	1.019			429	0.663
	413	0.495	—	—	306	0.503
	293	0.662			257	0.123
	247	1.503				
4a	434	0.695	431	0.725	434	0.695
	356	1.200	355	1.240	356	1.200
4b	430	2.525	427	2.130	—	—
5a	438	0.905			438	0.905
	356	0.687	—	—	356	0.687
	292	0.978			292	0.978
	232	1.755			232	1.755
5b	435	1.031			435	1.031
	288	0.479	—	—	288	0.479
	236	0.555			236	0.555
5c	569	1.020	554	1.017	569	1.020
	416	0.557	412	0.705	416	0.557
	295	0.756	287	0.930	295	0.756
	240	1.480	236	1.615	240	1.480
6	437	1.625			405	0.675
	269		—	—	296	0.477
	219				250	0.237
8a	365	1.738	360	1.913	372	0.816
	256	0.845	250	1.088	333	0.359
					266	0.314
8b	416	1.413	395	1.137	392	0.876
	370	1.423	365	1.286	344	0.394
	258	1.206	252	0.964	262	0.296
10a	409	0.226	397	0.255	408	0.532
					377	0.429
10b	467	0.478	453	0.323	415	0.515
	374	0.280	359	0.289	376	0.540
	320	0.495	305	0.474	327	0.179
10c	430	0.517	422	0.202	422	0.607
	380	0.429	360	0.233	382	0.456
	300	0.366			332	0.230
10d	420	0.111	357	0.342	428	0.648
	347	0.188			399	0.423

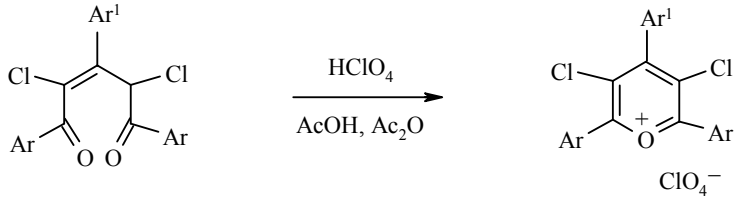
* λ = wavelength, OD = optical density.

*[2] For compounds **4a**,**b** and **5a-c** the wavelengths of the salts with various anions calculated by the quantum-chemical method are identical.

It is known that 2,6-diphenylpyrylium perchlorate has only one band in the long-wave region of the spectrum at λ_{max} 398 nm [1]. By comparing the spectra of the benzodihydrochromenylium salts **3a**,**b** and **4a**,**b** with those for 2,4,6-triphenylpyrylium **7a** (λ_{max} 416, 362 nm) and 4-(4-methoxyphenyl)-2,6-diphenylpyrylium (**7b)** [1] it is possible to observe a similar steric effect from the methoxyphenyl substituent at the C-4 atom (λ_{max} 422 nm).

In the spectra of 2,4-diphenyl- (**8a**) and 4-(4-methoxyphenyl)-2-phenyl-5,6,7,8-tetrahydrochromenylium (**8b**) perchlorates that we have described long-wave bands are observed at 365-370 nm, but in the spectrum of the latter a new band appears at 416 nm. Taking account of the fact that there is only one band at 376 nm in the spectrum of 2-phenyl-5,6,7,8-tetrahydrochromenylium perchlorate [8], the band in the low-frequency part of the spectrum of the salt **8b** can be assigned to intramolecular transfer of the charge of the substituent at the C-4 atom, and the absence of this in the spectrum of **8a** suggests that the phenyl substituent at position 4 is not coplanar. Thus, the introduction of an alicyclic fragment into the hetero system alters the geometry of the molecule and has a significant effect on the form of the spectra.

During the action of perchloric acid on the dichloropentenediones **9a-d** [9] in a mixture of acetic acid and acetic anhydride (1:1) the chlorine-substituted pyrylium salts **10a-d** were isolated with yields of 74-77%:



9a–d **10a–d**

9,10 a Ar = Ar^1 = Ph, **b** Ar = Ph, Ar^1 = 4-ClC$_6$H$_4$, **c** Ar = 4-ClC$_6$H$_4$, Ar^1 = Ph, **d** Ar = Ph, Ar^1 = 4-MeOC$_6$H$_4$

It was shown that the introduction of chlorine into the pyrylium ring changes the character of the spectrum. The long-wave band at 409 nm in 3,5-dichloro-2,4,6-triphenylpyrylium perchlorate (**10a**) remains in the same position, but the band at 362 nm characteristic of the unsubstituted analog **7a** disappears. Its presence in the gas phase, according to quantum-chemical calculations (377 nm), indicates that the phenyl substituent at the C-4 atom is not coplanar in relation to the plane of the cation on account of the steric effect of the chlorine atoms, ruling out intramolecular charge transfer from the substituent to the cation.

The opposite behavior is observed in the spectra of 4-(4-methoxyphenyl)-2,6-diphenylpyrylium (**7b**) and 3,5-dichloro-4-(4-methoxyphenyl)-2,6-diphenylpyrylium (**10d**) perchlorates. The retention of the long-wave band (420 nm) and the appearance of a new band at 347 nm in the spectrum of the salt **10d** favor the existence of intramolecular charge transfer from the substituent at the C-4 atom to the cation. Here it is worth mentioning the contribution from the chlorine atoms to conjugation, since the long-wave band in the spectrum observed in methylene chloride and belonging to the $n\rightarrow\pi$ transition disappears if glacial acetic acid is used as solvent.

The introduction of a chlorine atom in the substituents at positions 2, 6, or 4 in the salts **10b**,**c** complicates the spectrum by the appearance of new bands in their long-wave parts (Table 2). Here, in the case of compound **10c** a low-energy transition of the $n\rightarrow\pi$ type can be observed in the transition to acetic acid. (The band at 300 nm disappears.)

EXPERIMENTAL

The electronic absorption spectra of the compounds were recorded on a Akvilon SF 201 spectrometer with $c = 5\cdot10^{-4}$ M. The IR spectra were obtained on a Specord M-80 spectrophotometer in tablets with KBr, and the ^{1}H NMR spectra were obtained on a Bruker AM 300 instrument (300 MHz) in deuterochloroform with TMS as internal standard. The course of the reaction and the individuality of the compounds were monitored by TLC

on Silufol UV-254 plates with 3:1:1 hexane–ether–acetone as eluent. The standards used during the AM1 quantum-chemical calculations were the data from X-ray crystallographic analysis for the dihedral angles of rotation of the substituents to the plane of the cation in 2,4,6-triphenylpyrylium perchlorate: α(C-2) = 10.4, γ(C-4) = 18, α'(C-6) = 2.3° [10]. The differential thermal curve was recorded on the Derivatograph system of F. Paulik, J. Paulik, and L. Erdey.

The initial diketones **1a-c** [11] and the dichloropentenediones **9a-c** [12] and **9d** [13] were obtained by the known methods. The fluoroborates **3a-c** and bromides **5a**,**b** were prepared in acetic acid by the method in [11, 14], and the perchlorates **4a**,**b**, **8a**,**b**, and **10a-c** by the method in [8, 9, 15].

4-Aryl-2-phenyl-7,8-benzo-5,6-dihydrochromenylium Fluoroborates 3a-c. A. The compounds were prepared in acetic acid. Compound **3a**, yield 54%, mp 265-267°C (reprecipitation from Me_2CO with *i*-Pr_2O) [14]; compound **3b**, yield 57%, mp 246-248°C (reprecipitation from Me_2CO with *i*-Pr_2O). [11].

Compound 3c. Yield 52%; mp 222-223°C (reprecipitation from Me_2CO with *i*-Pr_2O). ^{1}H NMR spectrum, δ, ppm: 2.1 (4H, s, $2CH_2$); 2.8 (6H, s, $N(CH_3)_2$); 6.6 (1H, s, H-3); 7.0-7.9 (13H, m, H-2'3',4',5',6' + H-2",3",5",6" + H-11,12,13,14). Found, %: C 59.02; H 4.76; N 2.48. $C_{27}H_{24}BF_4NO$. Calculated, %: C 58.63; H 4.56; N 2.53.

B. To a solution of the diketones **1a**,**b** (28 mmol) in acetic anhydride (40 ml) with stirring we added drop by drop boron trifluoride etherate (5.4 ml, 42 mmol). After two days the precipitate was filtered off, washed with *i*-Pr_2O, and dried. We obtained compound **3a** (8.04 g, 67%), mp 265-267°C (reprecipitation from Me_2CO with *i*-Pr_2O) [14] and compound **3b** (8.00 g, 65%), mp 246-248°C (reprecipitation from Me_2CO with *i*-Pr_2O) [11].

C. To a solution of the diketones **1a-c** (2.8 mmol) in toluene (10 ml) we added drop by drop boron trifluoride etherate (0.5 ml, 4.2 mmol,), and we boiled the mixture for 3 h. The salts were precipitated with ether, filtered off, washed with ether, and dried. From the ether mother solution we obtained compound **2** (0.12 g, 13%); mp 103-104°C (alcohol). IR spectrum (thin layer), ν, cm^{-1}: 1247 (C–O–C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 (2H, m, H-5); 2.69 (2H, m, H-6); 4.16 (1H, d, $J_{3,4}$ = 13.2, H-4); 5.48 (1H, d, $J_{3,4}$ = 13.2, H-3); 7.25-7.90 (14H, m, H–Ar). Found, %: C 88.07; H 6.21. $C_{25}H_{20}O$. Calculated, %: C 88.29; H 5.95. Salt **3a**, yield 0.6 g (51%), **3b** 0.48 g (40%), **3c** 0.64 g (55%).

4-(4-N,N-Dimethylaminophenyl)-2-phenyl-7,8-benzo-5,6-dihydrochromenylium Dibromide (5c). To a boiling solution of the diketone **1c** (7.58 g, 191 mmol) in acetic acid (40 ml) we added drop by drop over 30 min a solution of bromine (4.5 g, 1.5 ml, 28 mmol,) in acetic acid (20 ml). The solvent was distilled, the mixture was treated with boiling ethanol and evaporated, and the crystals were filtered off and dried. We obtained the dibromide **5c** (8.3 g, 76%); mp 239-240°C (reprecipitation from chloroform with ether). According to data from thermogravimetric analysis, the compound was isolated from the reaction mixture in the form of the pentahydrate. IR spectrum (thin layer), ν, cm^{-1}: 1570 (pyrylium cation), 1590 (Ar), 3400 (H_2O). Found, %: C 51.75; H 5.56; Br 25.03; N 2.25. $C_{27}H_{24}Br_2NO_6$. Calculated, %: C 51.51; H 5.56; Br 25.43; N 2.23.

3,5-Dichloro-4-(4-methoxyphenyl)-2,6-diphenylpyrylium Perchlorate (10d). A solution of the diketone **9d** (1.06 g, 2.5 mmol) in glacial acetic acid (15 ml), Ac_2O (5 ml), and 70% perchloric acid 0.75 g (0.5 ml, 7.5 mmol,) were heated at 100°C, cooled, and diluted with ether (150 ml). The crystalline precipitate was filtered off, washed with ether, and dried. We obtained the perchlorate **10d** (0.89 g, 70%), mp 230-232°C (acetic acid). IR spectrum (thin layer), ν, cm^{-1}: 1610 (pyrylium cation), 1590 (Ar), 1150 (C–O–C), 1070 ($C1O_4$), 650 (C–Cl). For analysis the perchlorate **10d** was converted into the corresponding tetrachloroferrate. Found, %: C 48.10; H 2.61; Cl 35.09. $C_{24}H_{17}Cl_6FeO_2$. Calculated, %: C 47.61; H 2.76; Cl 35.14.

The work was carried out with financial support from the Russian Fundamental Research Foundation (grant 06-03-32667a).

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