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Absorption spectra and nature of electron transitions in azomethine dyes as 6-derivatives of 2H-2-chromenone

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Abstract

One of the main problems in expanding the application of the coumarin derivatives is a search of new ways for deeping the color and increasing the intensity of the spectral bands. A series of 6-derivatives of 2H-2-chromenone were synthesized. The UV–VIS, ^{1}H NMR spectra of azomethine dyes in the region 220–450 nm have been recorded. Quantum-chemical calculations and the nature of the electronic excitation process were carried out using the PPP and AM1 approximations. Dependence of long wavelength band intensity on the donor strength of the end groups was investigated. The spectral and quantum-chemical investigations show that the azomethine dyes based on the 2H-2-chromenone could be an effective way to influence spectral properties of their derivatives, particularly, position and intensity of the long wavelength absorption bands.

Keywords: 2H-2-Chromenone; Azomethine dyes; Bathochromic shift; Hyperchromic effect; Electron absorption spectra; Electron density redistribution

1. Introduction

Coumarins are widely used in numerous applications. Compounds based on the coumarin ring system give rise to one of the most extensively investigated and commercially significant group of organic fluorescent materials [1–6]. Coumarin derivatives provide some of the most important commercial brightening agents and are also used as fluorescent dyes for synthetic fibres and daylight fluorescent pigments. They also play a vital role in electrophotographic and electroluminiscent devices [7–9].

2H-2-Chromenone (or coumarin) and its derivatives are known as bioactive compounds, many of them possess antibacterial and antifungal properties [10]. Coumarins are also of considerable biological and medical interest. Many derivatives of these products show significant physiological effects: weakly toxic, anticarcinogenic, anticoagulant and antibiotic activities [11–13].

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The importance of the coumarin dyes as fluorescent brightening agents are derived from their efficient light emission properties, their reasonable stability and their relatively easy synthesis. The most commonly encountered fluorescent coumarins either absorb in the UV region and emit blue light or longer wavelengths [6]. There remains great interest in the molecular design and synthesis of new coumarin derivatives which would extend the available range of long wavelength emitting fluorescent materials. One of the main problems in the widening of the application of the coumarin derivatives is a search of new ways of deeping the color and increasing the intensity of the spectral bands. One possible way is to introduce complex π-electron substituents or even chromophore systems into coumarin molecule.

This paper represents the results of the spectral and quantum-chemical investigation of new synthesized coumarin derivatives—azomethine dyes.

2. Materials and equipment

Azomethine dyes studied were those of general structures **3a–i**, obtained by interaction of 6-amino-2H-2-chromenone **1** with the corresponding aldehydes **2a–i**:

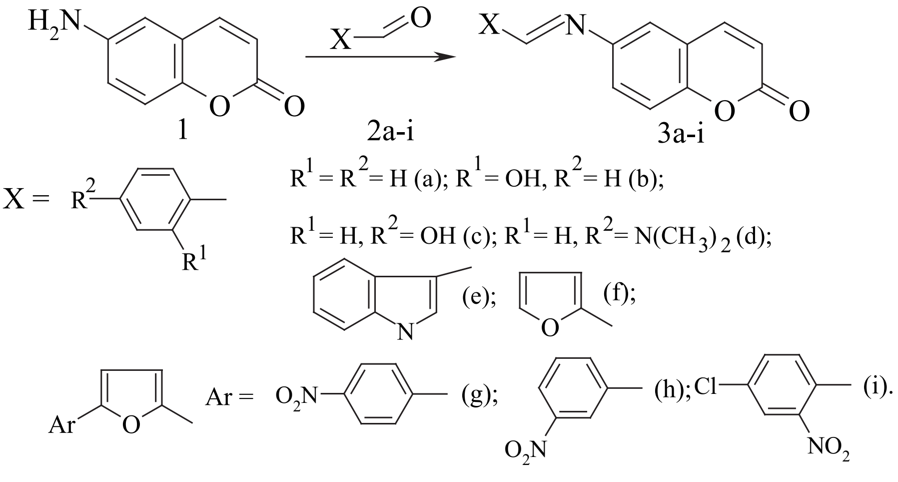
Also 2H-2-chromenone (coumarin) **4** of commercial origin was investigated; its spectral data correspond to that in the literature.

The spectra of ^{1}H NMR were recorded on a Varian VXR 300 spectrometer at 300.1 MHz in DMSO-d_6 with TMS as internal standard. Electron absorption spectra (UV spectra) were recorded with Shimadzu UV-3100 UV/visible spectrophotometer in the range of 220–450 nm. Using 1 cm quartz cells with concentration of azomethine dyes 4×10^{-5} mol l^{-1} in ethanol solution.

The equilibrium molecular geometry of dyes in the ground state was optimized in AM1 approximation until the gradient was 0.01 kcal/mol. The electron distribution and electron transition energies were calculated in the AM1 and PPP approximations (with spectral parametrization) using the lowest singly excited configurations: 35 for coumarins **1**, **4** and 90 for azomethine dyes (only π-levels and the highest *n*-levels are taken into consideration).

3. Results and discussion

The series of 2H-2-chromenone **4**, 6-amino-2H-2-chromenone **1** and azomethine dyes **3a–i** investigated were divided, for convenience, into



four groups so that the compounds in each subseries can be considered as derivatives of the main dye:

1. 2H-2-chromenone **4** and its 6-aminosubstituted derivative **1**;
2. 6-Phenylmethylideneamino-2H-2-chromenone **3a** and its substitutes in the phenyl cycle **3b–d**: 6-(2-hydroxyphenyl)methylideneamino-2H-2-chromenone **3b**, 6-(4-hydroxyphenyl) methylidene amino-2H-2-chromenone **3c**, 6-(4-dimethylaminophenyl)methylideneamino-2H-2-chromenone **3d**;
3. 6-Phenylmethylideneamino-2H-2-chromenone **3a**, 6-(2-furyl)methylideneamino-2H-2-chromenone **3f**, 6-(1H-3-indolyl)methylideneamino-2H-2-chromenone **3e** as azomethine dyes containing end groups with various donor strength;
4. Substituted 6-(2-furyl)methylideneamino-2H-2-chromenone **3f** derivatives: 6-[5-(4-nitrophenyl)-2-furyl]methylideneamino-2H-2-chromenone **3g**, 6-[5-(3-nitrophenyl)-2-furyl]methylideneamino-2H-2-chromenone **3h**, 6-[5-(4-chloro-2-nitrophenyl)-2-furyl] methylideneamino-2H-2-chromenone **3i**.

Such division of the studied dyes enables a more correct interpretation of the observed effects in their absorption spectra to be carried out.

The two base compounds, **1** and **4**, were investigated in detail by both spectral and quantum-chemical methods [1,14–18]. Their spectra are presented in Fig. 1. Analysis of the spectral data and quantum-chemical results obtained in the both AM1 and PPP approximations has shown that the long wavelength band is associated with two allowed π→π*-electron transitions and one forbidden *n*→π*-transition involving the lone electron pair (LUP) of the exocyclic oxygen atom [18]. Introduction of the amino-group in position 6 is accompanied by appearance of the wide spectral band shifted bathochromically while the short wavelength bands remain similar to spectral picture in this region for **4** [1] (see also Fig. 1).

Such considerable changes in the absorption spectra of **1** in comparison with the initial **4** could be explained by quantum-chemical modelling. The highest occupied and lowest vacant levels for compounds **1** and **4** are presented in Fig. 2.

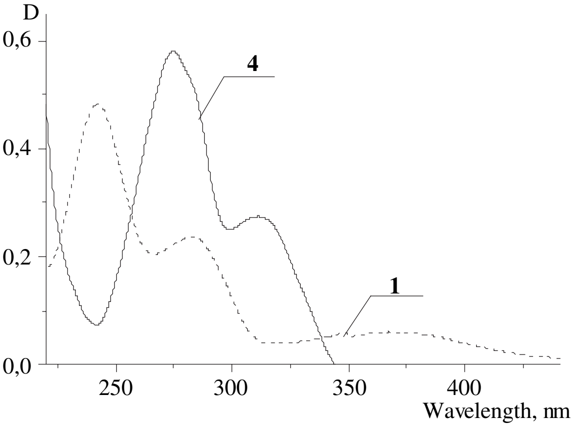


Fig. 1. Absorption spectra of 6-amino-2H-2-chromenone **1** and unsubstituted coumarin **4**.

It is seen that the introduction of an amino-group with its LUP conjugated with the main π-electron system leads to the frontier and nearest levels to be shifted upward relative to corresponding levels in the coumarin **4**. The calculations show the HOMO to undergo an essential shift (0.75 eV) while other involved levels seen in Fig. 2 are shifted only slightly (≅0.1 eV). It was found that LUP of the nitrogen atom has considerable influence on the HOMO so that the coefficient $C_{\mathrm{HOMO,\,N}} = 0.44$ (AM1) or 0.63 (PPP). Thus, the introduction of the amino-group causes mainly, the energy gap to decrease (in 0.7 eV). At the same time, Fig. 2 (for **1**) demonstrates the considerable

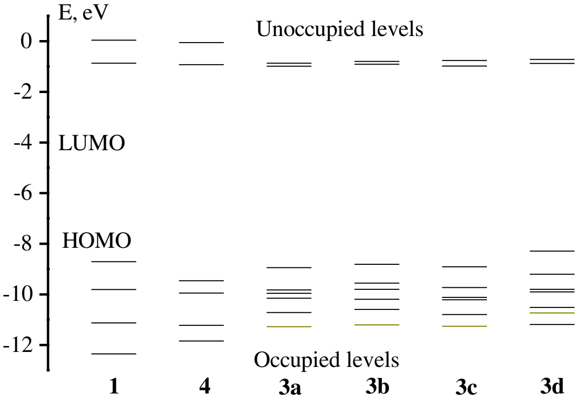


Fig. 2. Electron levels of coumarins **1**, **4** and azomethine dyes **3a**, **3b**, **3c**, **3d** (AM1).

increase of the distance between the highest and next occupied levels. However, no additional electron level appears in this energetic interval (0/− 11.5 eV).

It could be also noted that orbital |HOMO-2> which can be predominantly considered as a LUP of the exocyclic oxygen atom is maintained in its character and position.

Taking into consideration our previous conclusion that two $\pi\rightarrow\pi^*$-electron transitions (and one $n\rightarrow\pi^*$-electron transition) correspond to the first absorption band with $\lambda_{max} = 311$ nm in the initial **4**, we could assume that the decrease of the energy gap and simultaneous increase of the distance between two highest occupied MOs should be accompanied by splitting of these transitions in **1** and 6-azomethine dyes so that both $\pi\rightarrow\pi^*$-electron transitions manifest themselves as separated spectral bands. The calculations also give the similar results: the difference $\Delta\lambda_{12} = \lambda_1 - \lambda_2$ for **1** reaches 96 nm (PPP) and 98 nm (AM1) while value $\Delta\lambda_{12}$ is equal to 39 nm (PPP) and 83 nm (AM1) for **4**. The low intensity and considerable width of the long wavelength spectral band for the 6-azomethine dyes can be connected with the relative low conjugation between amino-group and the main heterocycle: the calculated rotation barrier $B = 19.29$ J/mol (AM1). On the contrary, the rotation barrier of amino-group in position 7 is approximately twice as high: 33.81 J/mol; and hence, the corresponding spectral band in the 7-aminocoumarin is observed as more narrow and intensive [1].

The calculations performed in the all-valence approximation AM1, give additional results for the forbidden $n\rightarrow\pi^*$-transition. It is seen from data presented in Table 1, that $n\rightarrow\pi^*$-transition in compound **1** should be bathochromically shifted as compared with compound **4**, but it cannot be detected experimentally because of the oscillator strength $f\approx 0$. Also, the $n\rightarrow\pi^*$-transition is overlapped by the higher intensive $\pi\rightarrow\pi^*$-transition.

It is convenient to use the diagrams of electron densities redistribution at atoms on excitation in order to analyse the nature of the electron transitions. Fig. 3 shows such diagrams for compounds **4** and its 6-aminoderivative **1**.

One could see that first electron transition in start compound **4** (Fig. 3a) is accompanied by electron transferring from the exocyclic one-coordinated oxygen atom to coumarin ring. In contrast, excitation in **1** (Fig. 3b) leads the electron transferring mainly from the amino-group. This effect is related to the considerable contribution of the LUP at nitrogen atom in the HOMO.

Going from **1** to azomethine dyes **3a**–**d** containing phenyl or its OH– and $N(CH_3)_2$-substituted derivatives as a terminal group are accompanied by the hypsochromic shift of the long wavelength band and by increase of its intensity as compared with the spectra of the **1** (Fig. 4).

Table 1
Comparison of experimental and PPP-MO, AM1 calculated electronic spectral data for coumarins **1**, **4** and azomethine dyes **3a**–**i**

Compound	λ_{max}, nm ($\varepsilon\times10^{-4}$)	PPP-MO: λ_{max}, nm	AM1: λ_{max}, nm (f)
4	311 (0.69), 275 (1.45)	308, 269	346 (0.073), 326 (0.031), 285 (0.000)[a], 264 (0.415)
1	370 (0.15), 283 (0.59)	374, 278, 269	379 (0.083), 338 (0.012), 283 (0.003)[a], 278 (0.614)
3a	319 (1.24), 277 (3.11)	334, 316, 283, 274	362 (0.084), 348 (0.315), 324 (0.005)[a], 320 (0.010)[a], 311 (0.718)
3b	344 (1.61), 320 (1.35), 278 (2.72)	339, 319, 291, 281	364 (0.126), 351 (0.364), 323 (0.008)[a], 324 (0.014)[a], 314 (0.410)
3c	321 (2.10), 293 (2.30)	338, 318, 282, 277	363 (0.181), 352 (0.411), 326 (0.051)[a], 328 (0.004)[a], 320 (0.205)
3d	365 (4,65), 278 (1.53)	366, 324, 298, 282	375 (0.687), 358 (0.222), 344 (0.017)[a], 328 (0.145), 320 (0.047)
3e	328 (2.20), 274 (1.97)	354, 321, 286, 275	367 (0.521), 353 (0.213), 345 (0.008)[a], 328 (0.032)[a], 301 (0.824)
3f	332 (1.80), 282 (3.80)	345, 322, 285	370 (0.438), 354 (0.227), 331 (0.017)[a], 318 (0.557)
3g	385 (3.0), 279 (1.50)	394, 317, 301, 298, 273	401 (1.14), 349 (0.080), 331 (0.011)[a], 328 (0.000)[a], 327 (0.070)
3h	356 (3.20), 269 (1.95)	372, 339, 317, 281, 270	376 (1.160), 317 (0.240), 294 (0.300), 283 (0.230)
3i	352 (2.32), 270 (4.81)	387, 318, 308, 301, 287	—

f is oscillator strength.

[a] This transition is mainly $n\rightarrow\pi^*$-transition.

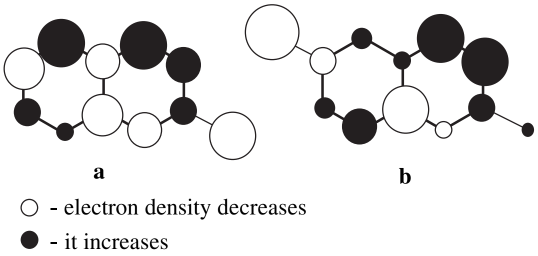


Fig. 3. Electron density redistribution on excitation $S_0 \rightarrow S_1$ of coumarins **4**—(a), **1**—(b) (PPP).

Nevertheless, the first two spectral bands remain separated. This agrees with relatively great distance between the two highest occupied levels (Fig. 2) which constitute main part in the first two electron transitions: $|\text{HOMO}> \rightarrow |\text{LUMO}>$ and $|\text{HOMO}-1> \rightarrow |\text{LUMO}>$. It should be noted that calculation predicts the lower splitting of the first two transitions (Table 1). In the azomethine dyes additional $n \rightarrow \pi^*$-transitions could appear as compared with coumarins **1** and **4**. They are related to the LUP of nitrogen atom of the azomethine chain.

Also, the hyperchromic effect is observed on going from **1** to the azomethine dyes **3a**–**3d**. The influence of the donor residues could be estimated quantitatively by $I_{\text{lw}}/I_{\text{sw}}$ ratio, where I_{lw} is the intensity of the long wavelength band and I_{sw} is the intensity of the short wavelength one. For the dyes in the series **1**→**3a**→**3b**→**3c**→**3d**, the ratio $I_{\text{lw}}/I_{\text{sw}}$ is equal correspondently: 1:1.6:2.4:3.6:12.2 (for convenience, the ratio $I_{\text{lw}}/I_{\text{sw}}$ of compound **1** is adopted as 1). Thus, the greatest bathochromic shift, 55 nm, (in respect to unsubstituted **4**) and the highest hyperchromic effect are observed for 6-(4-dimethylaminophenyl)methylideneamino-2H-2-chromenone **3d** as a strongest donor substituent, while the unsubstituted phenyl group exhibits the lowest spectral shift: 8 nm. The calculated data (PPP and AM1), seen from Table 1, are in good agreement with experimental maxima, and hence could be used for studying the electron transition nature in the dyes. Fig. 5 demonstrates that the first transition is virtually delocalized along whole dye molecule **3d**, although electron density redistribution at atoms of the 4-dimethylaminophenyl-substitutent is greater than in unsubstituted coumarin residue. In this case electron transferring occurs from the nitrogen atom of dimethylamino-group to the azomethine chain.

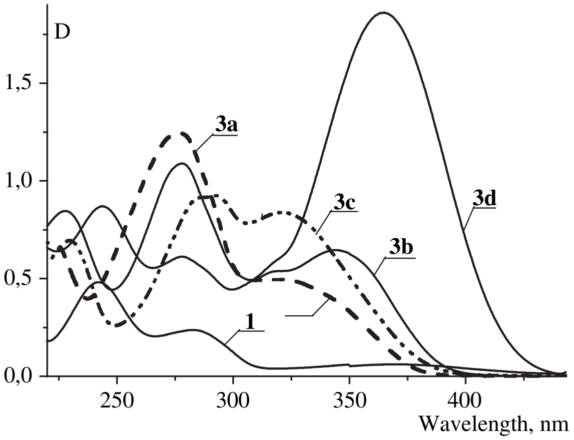


Fig. 4. Absorption spectra of compound **1** and azomethine dyes **3a**, **3b**, **3c**, **3d**.

The dependence of long wavelength band intensity on the donor strength of the terminal group can be clearly demonstrated in the next series of the azomethine dyes: **3a**→**3f**→**3e** containing the phenyl, furyl and indolyl residues correspondently. The long wavelength band of these three dyes are positioned relatively close and shifted bathochromically in comparison with **4**. It is seen on Fig. 6 that increase of donor strength of the residue in series **3a**→**3f**→**3e** leads to regular increase of band intensity, so that ratio $I_{\text{lw}}/I_{\text{sw}}$ is equal: 0.40:0.47:1.12. The calculated oscillator strength f increases also in this series (Table 1). However, it should be noticed that introduction of furyl or indolyl residues cause the lower bathochromic shift and hyperchromic effect than the highly-effective p-dimethylaminophenyl terminal group (compare Figs. 4 and 6).

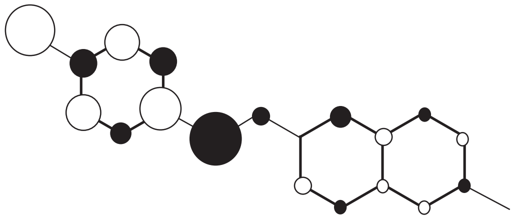


Fig. 5. Electron density redistribution on excitation of 6-(4-dimethylaminophenyl)methylideneamino-2H-2-chromenone **3d** (PPP).

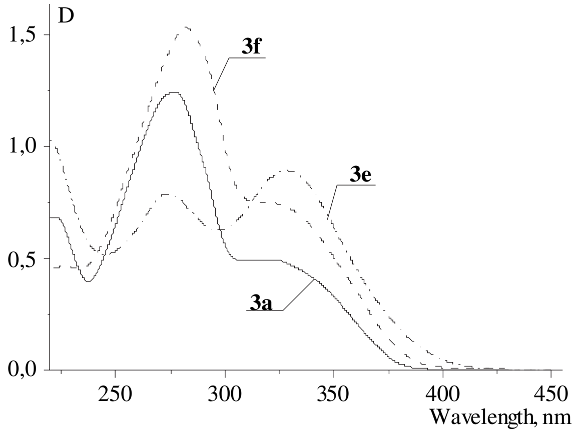


Fig. 6. Absorption spectra of azomethine dyes **3a**, **3f**, **3e**.

Finally, the influence of the additional acceptor substituent, introduced in furan heterocycle, has been investigated (dyes **3g**, **3h**, **3i**) in comparison with **3f**. It is seen from spectra (Fig. 7) and Table 1 that the NO_2-group increases the effective length of the π-electron system and hence leads to the considerable bathochromic shift of the long wavelength band.

The maximum spectral effect is observed for compound **3g**. Calculations also predict the essential increase of the first electron transition wavelength for the NO_2-substituted dyes **3g** and **3h** in comparison with dye **3f**. Similar widening of the spectral band occurs for the dye **3i**, containing an NO_2-group in *ortho*-position. Besides, the calculated oscillator strength is higher for compounds **3g** and **3h**. However, this leads only to widening of the spectral band while the intensity (Fig. 7) is even lower than the intensity of the band of dye **3f** containing unsubstituted furan cycle.

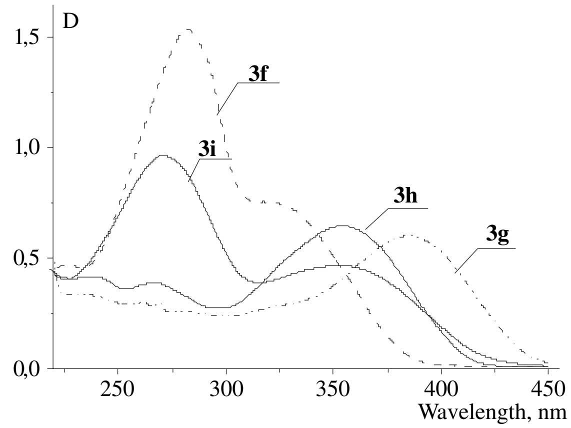


Fig. 7. Absorption spectra of azomethine dyes **3f**, **3g**, **3h**, **3i**.

Thus, the spectral and quantum-chemical investigations show that the azomethine dyes based on the 2H-2-chromenone could be an effective way to influence spectral properties of their derivatives, particularly, wavelength and intensity of the long wavelength absorption bands.

4. Experimental

The 6-azomethine dyes **3a–i** were obtained by general procedure of the condensation reaction of 6-amino-2H-2-chromenone **1** with aldehydes **2a–i**: 0.01 mole of **1** and 0.01 mole of **2a–e** were heated under reflux in 10 cm^3 of absolute ethanol (for **2f–i** in anhydrous dioxane) in the presence of a few drops of piperidine for 3 h. Then the mixture was cooled to room temperature and after standing overnight, the azomethines **3a–i** appeared. The solid was filtered and dye in the mother liquor was precipitated by evaporation of solvent. All products were purified by recrystallization: **3a–d** from EtOH, **3e** from EtOH:DMF, **3g–i** from dioxane.

The 6-azomethine dyes **3a–d** were obtained with better yields than that described in [19].

6-Amino-2H-2-chromenone **1** was prepared by the nitration of 2H-2-chromenone **4** and subsequent reduction with iron and hydrochloric acid by the literature [20].

^1H NMR data for the azomethine dyes **3b–i** are given in Table 2.

4.1. *6-Phenylmethylideneamino-2H-2-chromenone **3a***

Yield 68%, m.p. 149–150 °C. Anal. calcd. for: C, 77.11%; H, 4.12%; N, 5.62%. Found: C, 77.03%; H, 4.08%; N, 5.58%.

4.2. *6-(2-Hydroxyphenyl)methylideneamino-2H-2-chromenone **3b***

Yield 65.5%, m.p. 170–171 °C. Anal. calcd. for: C, 72.45%; H, 4.15%; N, 5.28%. Found: C, 72.26%; H, 4.08%; N, 5.15%.

Table 2
^{1}H NMR data for the azomethine dyes **3b–i**

Entry	^{1}H NMR δ (ppm)			
	H^{9} (–CH=)	$\mathrm{H}^{3–5,\ 7–8}$ (coumarin)	$\mathrm{H}^{10–16}$ (arom. substit.)	H (other)
3b	9.01 (1H, s, 9-H)	8.08 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.79 (1H, s, 5-H), 7.70 (1H, dd, 7-H), 7.49 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.56 (1H, d, $^{3}J = 10$ Hz, 3-H)	7.67 (1H, d, $^{3}J = 8$ Hz, 10-H), 7.44 (1H, t, $^{3}J = 8$ Hz, 12-H), 7.01 (1H, t, $^{3}J = 8$ Hz, 11-H), 6,99 (1H, d, $^{3}J = 8$ Hz, 13-H)	12.85 (1H, s, OH)
3c	8.54 (1H, s, 9-H)	8.07 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.58 (1H, d, $^{4}J = 2$ Hz, 5-H), 7.51 (1H, dd, $^{3}J = 10$ Hz, $^{4}J = 2$ Hz, 7-H), 7.43 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.53 (1H, d, $^{3}J = 10$ Hz, 3-H)	7.79 (2H, d, $^{3}J = 8$ Hz, 10, 14-H), 6.90 (2H, d, $^{3}J = 8$ Hz, 11, 13-H)	10.18 (1H, s, OH)
3d	8.47 (1H, s, 9-H)	8.06 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.54 (1H, w.s, 5-H), 7.49 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.40 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.52 (1H, d, $^{3}J = 10$ Hz, 3-H)	7.76 (2H, d, $^{3}J = 9$ Hz, 10, 14-H), 6.79 (2H, d, $^{3}J = 9$ Hz, 11, 13-H)	3.02 (6H, s, $N(CH_3)_2$)
3e	8.78 (1H, s, 9-H)	8.10 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.58 (1H, w.s, 5-H), 7.52 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.43 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.54 (1H, d, $^{3}J = 10$ Hz, 3-H)	8.41 (1H, d, $^{3}J = 8$ Hz, 10-H), 8.06 (1H, s, 15-H), 7.52 (1H, d, $^{3}J = 8$ Hz, 13-H), 7.26 (1H, t, $^{3}J = 8$ Hz, 12-H), 7.21 (1H, t, $^{3}J = 8$ Hz, 11-H)	11.87 (1H, s, NH, 14-H)
3f	8.52 (1H, s, 9-H)	8.07 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.64 (1H, s, 5-H), 7.56 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.44 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.55 (1H, d, $^{3}J = 10$ Hz, 3-H)	8.00 (1H, w.s, 10-H), 7.21 (1H, w.s, 11-H), 6.50 (1H, w.s, 12-H)	
3g	8.59 (1H, s, 9-H)	8.05–8.10 (1H, m, 4-H), 7.70 (1H, s, 5-H), 7.61 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.45 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.54 (1H, d, $^{3}J = 10$ Hz, 3-H)	8.34 (2H, d, $^{3}J = 8$ Hz, 13, 14-H), 8.05-8.10 (2H, m, 12, 15-H), 7.54 (1H, s, 11-H), 7.38 (1H, s, 10-H)	
3h	8.58 (1H, s, 9-H)	8.07 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.70 (1H, s, 5-H), 7.62 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.45 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.55 (1H, d, $^{3}J = 10$ Hz, 3-H)	8.57 (1H, s, 15-H), 8.28 (1H, d, $^{3}J = 7$ Hz, 14-H), 8.22 (1H, d, $^{3}J = 8$ Hz, 12-H) 7.79 (1H, t, $^{3}J = 8$ Hz, 13-H), 7.52 (1H, d, $^{3}J = 4$ Hz, 11-H), 7.36 (1H, d, $^{3}J = 4$ Hz, 10-H)	
3i	8.52 (1H, s, 9-H)	8.08 (1H, d, $^{3}J = 10$ Hz, 4-H), 7.67 (1H, w.s, 5-H), 7.58 (1H, d, $^{3}J = 9$ Hz, 7-H), 7.45 (1H, d, $^{3}J = 9$ Hz, 8-H), 6.55 (1H, d, $^{3}J = 10$ Hz, 3-H)	8.22 (1H, s, 14-H), 7.93 (1H, d, $^{3}J = 9$ Hz, 12-H), 7.90 (1H, d, $^{3}J = 9$ Hz, 13-H), 7.35 (1H, d, $^{3}J = 4$ Hz, 11-H), 7.17 (1H, d, $^{3}J = 4$ Hz, 10-H)	

4.3. 6-(4-Hydroxyphenyl)methylideneamino-2H-2-chromenone **3c**

Yield 63.8%, m.p. 243–244 °C. Anal. calcd. for: C, 72.45%; H, 4.15%; N, 5.28%. Found: C, 71.98%; H, 4.02%; N, 5.18%.

4.4. 6-(4-Dimethylaminophenyl)methylideneamino-2H-2-chromenone **3d**

Yield 64%, m.p. 198–199 °C. Anal. calcd. for: C, 73.97%; H, 5.48%; N, 9.59%. Found: C, 73.15%; H, 5.32%; N, 9.52%.

4.5. 6-(1H-3-Indolyl)methylideneamino-2H-2-chromenone **3e**

Yield 53%, m.p. 234 °C. Anal. calcd. for: C, 75.0%; H, 4.17%; N, 9.72%. Found: C, 74.95%; H, 4.13%; N, 9.63%.

4.6. 6-(2-Furyl)methylideneamino-2H-2-chromenone **3f**

Yield 54%, m.p. 137–138 °C. Anal. calcd. for: C, 70.29%; H, 3.76%; N, 5.86%. Found: C, 69.98%; H, 3.67%; N, 5.75%.

4.7. 6-[5-(4-Nitrophenyl)-2-furyl]methylideneamino-2H-2-chromenone **3g**

Yield 56%, m.p. 259–261 °C. Anal. calcd. for: C, 66.67%; H, 3.33%; N, 7.78%. Found: C, 66.50%; H, 3.28%; N, 7.65%.

4.8. 6-[5-(3-Nitrophenyl)-2-furyl]methylideneamino-2H-2-chromenone **3h**

Yield 52%, m.p. 255–256 °C. Anal. calcd. for: C, 66.67%; H, 3.33%; N, 7.78%. Found: C, 66.55%; H, 3.15%; N, 7.65%.

4.9. 6-[5-(4-Chloro-2-nitrophenyl)-2-furyl]methylideneamino-2H-2-chromenone **3i**

Yield 45%, m.p. 218–219 °C. Anal. calcd. for: C, 60.91%; H, 2.79%; N, 7.11%; Cl, 9.01%. Found: C, 60.65%; H, 2.69%; N, 7.05%; Cl, 8.95%.

5. Conclusion

Introducing complex π-electron substituents or chromophore systems into the coumarin molecule produces bathochromic and hyperchromic shifts. The dependence of long wavelength band intensity on the donor strength of the end groups was investigated in detail by both spectral and quantum-chemical methods. Analysis of the spectral data and quantum-chemical results obtained in the both AM1 and PPP approximations has shown acceptable correlation between calculated and experimental data for a series of azomethine dyes.

References

[1] Christie RM, Chih-Hung L. Studies of fluorescent dyes: part 1. An investigation of the electronic spectral properties of substituted coumarins. Dyes Pigments 1999; 42:85–93.

[2] Nishizono N, Oda K, Ohno K, Minami M, Machida M. Synthesis of 3-aryl-7-diethylaminocoumarin derivatives: reaction with isatin and their fluorescent properties. Heterocycles 2001;55(10):1897–905.

[3] Umemoto H, Kitao T, Konishi K. Fluorescent whitening agents for synthetic fibers. XIII. Fluorescence of some coumarins as whitening agents. Kogyo Kagaku Zasshi 1970;73(6):1146–51.

[4] Zhang YY, Meng XM, Wang XL, Xu LH. Studies on the synthesis and spectra characteristics of stilbenylcoumarin organic materials. Dyes Pigments 2003;56:189–94.

[5] Urano T, Nagasaka H, Tsuchiyama M, Shimizu S, Kawazoe K, Shimizu M, et al. Laser flash photolysis in high-speed photopolymer coating layers. Bull Chem Soc Jpn 1995;68:1661–8.

[6] Griffiths J, Millar V, Bahra GS. The influence of chain length and electron acceptor residues in 3-substituted 7-*N*,*N*-diethylaminocoumarin dyes. Dyes Pigments 1995;28(4): 327–39.

[7] Fujimoto S, Sasaki O, Shibata T. (Konica Co). Electrophotographic photoreceptor. Jpn Kokai Tokkyo Koho JP 04,19,668. Chem Abstr 1992;117:121489j.

[8] Tanaka M. (Canon KK.). Electrophotographic photoreceptor and apparatus using same. Jpn Kokai Tokkyo Koho JP 04,343,362. Chem Abstr 1993;119:213954b.

[9] Sasaki K. (Sharp KK.). Semiconductor electroluminescent device. Jpn Kokai Tokkyo Koho JP 05,190,902. Chem Abstr 1994;120:310929a.

[10] Vijayakumar BS, Sivaram J. Antifungal activity of coumarin and its derivatives on pathogenic fungi. J Maharashtra Agric Univ 1997;22(3):346–7.

[11] Merchant JR, Gupta AS. Synthesis of coumarylthiohydantoins having antibercular activity. Indian J Chem 1978; 16(1):71–2.

[12] El-Sayed AM, Ghattas A-BAG, El-Wassimy MT, Allah OA. Synthesis of some new biologically active coumarin derivatives. Farmaco 1999;54(1–2):56–63.

[13] Kitagawa H, Iwaki R. Coumarin derivatives for medicinal purposes. Yakugaku Zasshi 1958;78: 491–7.

[14] Jacobson CR, Brower KR, Amstutz ED. Some new coumarins and chromones and their ultraviolet absorption spectra. J Org Chem 1953;18:1117–23.

[15] Ganguly BK, Bagchi P. Studies on the ultraviolet absorption spectra of coumarins and chromones. J Org Chem 1956;21:1415–9.

[16] Jones GII, Griffin SF, Choi C, Bergmark WR. Electron donor–acceptor quenching and photoinduced electron transfer for coumarin dyes. J Org Chem 1984;49:2705–8.

[17] Mangini A, Passerini R. Ricerche sugli eterociclici: spettri di assorbimento u.v. e proprieta cromoforiche. Nota V Cumarine Gazz Chim Ital 1957;3:243–92.

[18] Korotkova IV, Sakhno TV, Barashkov MM. Theoretical investigation of processes of non-radiative deactivation of coumarin derivatives. Teoreticheskaya i Eksperimentalnaya Khimia 1997;33(2):105–10 [Russian].

[19] Trkovnik M, Bobarevic B, Hadzimusic M. 6- and 8-Aminocoumarin azomethines. Glas Hem Technol Bosne Hercegovine 1968;16:117–8.

[20] Morgan T, Micklethwait FMG. 6-Aminocoumarin. J Chem Soc 1904;85:1230–8.