Chemistry of Heterocyclic Compounds, Vol. 48, No. 12, March, 2013 (Russian Original Vol. 48, No. 12, December, 2012)

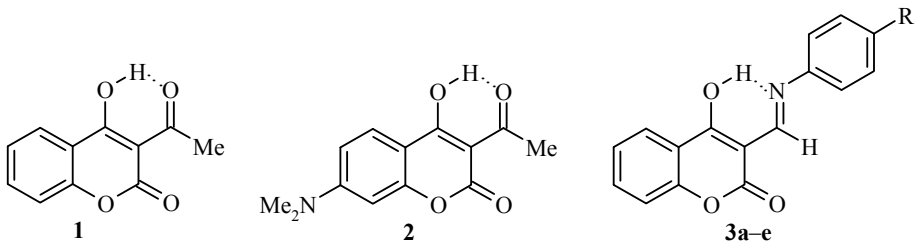
SYNTHESIS AND STRUCTURE OF SCHIFF BASES DERIVED FROM 3-FORMYL-4-HYDROXYCOUMARIN AND DIAMINES

B. G. Milevskii[1], T. A. Chibisova[1], N. P. Solov'eva[2], O. S. Anisimova[2], V. S. Lebedev[1], I. V. Ivanov[1], and V. F. Traven[1]*

The mono- and diimine products from the condensation of 3-formyl-4-hydroxycoumarin and various diamines were synthesized. It was shown by ^1H NMR and mass spectrometry that the obtained compounds in DMSO-d_6 solution and in gas phase exist in the E- and Z-keto-enamine forms.

Keywords: 3-formyl-4-hydroxycoumarin, enamines, *E*/*Z* isomerization, tautomerism.

Azomethines containing a π-conjugated imino group (C=N) and benzene ring in the main chain can potentially find broad use as ligands in catalysts, intermediates for thermostable materials, and complexones for metal ions [1-5]. Azomethines of the heterocyclic series are of particular interest. In particular, the 3-acyl-4-hydroxycoumarin imines represent remarkable examples of β,β′-tricarbonyl compound derivatives. For instance, compounds **1-3** have an increased tendency to undergo various isomeric transformations [6-9].



3 a R = H, **b** R = Me, **c** R = Br, **d** R = NO_2, **e** R = OMe

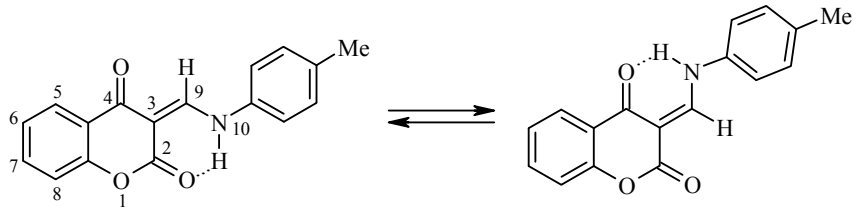
From the ^1H and ^{13}C NMR spectra, we previously established that the imino derivatives **3a-e** of 3-formyl-4-hydroxycoumarin mainly exist in the keto-enamine form as mixtures of *E*- and *Z*-isomers [8, 9]. For instance, the imine **3b** is a mixture of 70% of the *E*-isomer and 30% of the *Z*-isomer.

Study of the isomeric transformations is particularly important for the successful application of organic compounds that exhibit significant and stable changes in the absorption and emission spectra under the influence of various factors (irradiation, change in the solvent composition, etc.), in molecular electronics (e.g., as molecular switches) [10, 11].

*To whom correspondence should be addressed, valerii.traven@gmail.com.

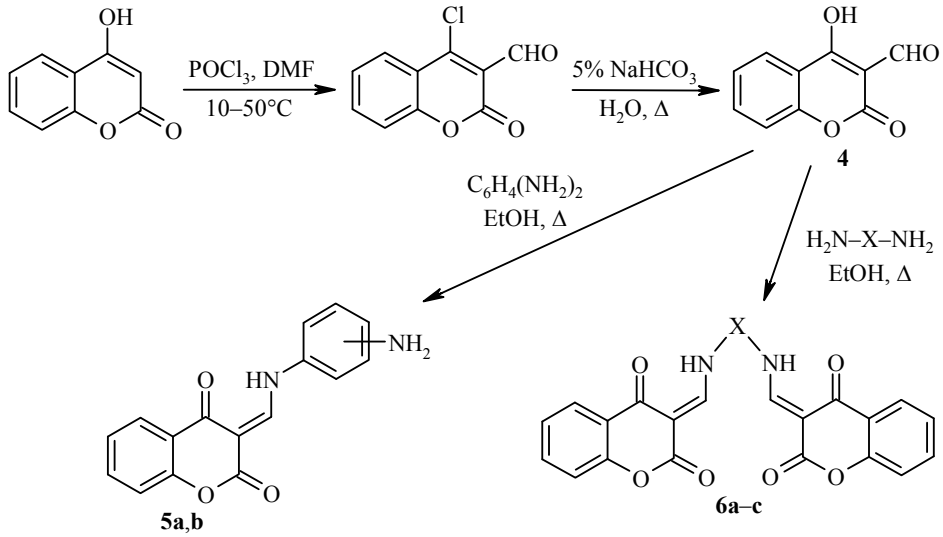
[1]D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Sq., Moscow 125047, Russia.
[2]Center of Drug Chemistry, 7 Zubovskaya St., Moscow 119815, Russia; e-mail: npsolovieva@mail.ru.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1903-1915, December, 2012. Original article submitted June 19, 2012.



3b, *Z*-keto-enamine **3b**, *E*-keto-enamine

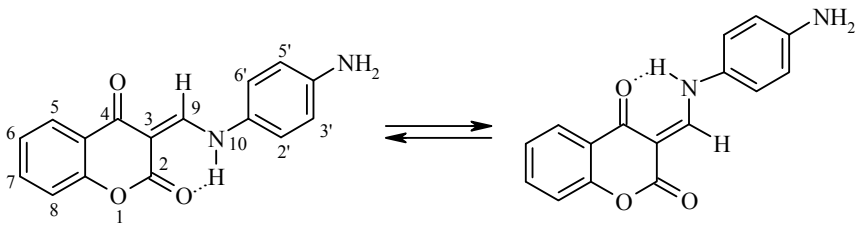
In the present work, we studied the structure of the diimines produced by the condensation of 3-formyl-4-hydroxycoumarin (**4**) and various diamines. The choice of the targeted structures **5a**,**b** and **6a-c** was based on the fact that the presence of the *ortho*-positioned azomethine and hydroxyl groups is required for the formation of an effective ligand unit that is potentially capable of forming stable metal complexes.



5a,**b** **6a–c**

5 a = *para*-NH_2, **b** = *ortho*-NH_2; **6 a** X = 1,2-C_6H_4, **b** X = 1,2-C_2H_4, **c** X = 1,2-C_6H_{10}

Compounds **5a**,**b** and **6a-c** were obtained from 4-hydroxycoumarin in three stages: formylation of 4-hydroxycoumarin with a mixture of DMF and phosphorus oxychloride [12], hydrolysis of 4-chloro-3-formyl-coumarin by boiling in a 5% solution of sodium bicarbonate, and condensation of the obtained 3-formyl-4-hydroxycoumarin (**4**) with various diamines. When carrying out the reaction in ethanol, a twofold excess of the aldehyde allowed to obtain the targeted diimines **6b**,**c**. Condensation with *o*-phenylenediamine under the same conditions produced only the monoimine **5b**. The diimine **6a** was successfully synthesized only by using a threefold excess of the aldehyde **4**.



5a, *Z*-keto-enamine **5a**, *E*-keto-enamine

In acetic acid, the condensation proceeded differently; even with a 1:1 reagent ratio the diimine **6a** was formed in 50% yield, while the diimine **6b** was formed in about 40% yield.

Compound **5a** is structurally similar to the previously studied 3-(*p*-tolylaminomethylidene)chroman-2,4-dione **3b** [8, 9]. According to ^{1}H NMR data for DMSO-d_6 solution, the monoimine **5a** also exists in the form of a mixture of *E*- and *Z*-keto-enamines.

A characteristic feature of the ^{1}H NMR spectrum of compound **5a** is the presence of two downfield signals corresponding to the protons of the NH group at 13.61 and 11.82 ppm. The more downfield signal corresponds to the *E*-isomer, which is stabilized by a strong intramolecular hydrogen bond of the chelate type with the oxygen of the C(4)=O group. The signal for the protons of the NH group in the more upfield region corresponds to the *Z*-isomer. The formation of another intramolecular hydrogen bond with oxygen atom of the C(2)=O fragment is possible in this isomer, but as established earlier [9], this hydrogen bond is significantly weaker than the hydrogen bond between the N(10)H and C(4)=O groups. With such an assignment the integral intensities of the N(10)H signals allow quantitative determination of the corresponding isomer content in the equilibrium mixtures: the *E*-isomer from the signal at 13.61 ppm (73%) and the *Z*-isomer from the signal at 11.82 ppm (27%). The difference between the H-9 proton chemical shift values for the two geometric isomers is substantially smaller, and the H-9 signal from the *Z*-isomer is located downfield. It is interesting to note the difference between the values of the vicinal spin-spin coupling constants $J_{9,10}$ of the H-9 and N(10)H protons for the two isomeric forms: for the *E*-keto-enamines these constants are 13.7 (imine **3b**) and 13.5 Hz (imine **5a**), whereas the values for the *Z*-keto-enamines are increased to 14.5 (imine **3b**) and 14.8 Hz (imine **5a**), indicating a transoid arrangement of the N(10)–H and C(9)–H bonds in relation to the C(9)–N(10) bond and a small change in the geometry (bond lengths and dihedral angles) of these fragments.

In comparison with the azomethine **5a**, the azomethine **5b** has a significantly more complicated ^{1}H NMR spectrum. The spectrum of 3-[(2-aminophenyl)aminomethylidene]chroman-2,4-dione (**5b**) contains four signals for the protons of the NH group and the corresponding signals of the CH protons. The doubling of the number of signals is probably due to the fact that steric hindrances between the NH_2 group and the enamine fragment arise in the *ortho* derivative, leading to the appearance of two conformational forms for each geometric *E*- and *Z*-isomer.

The ^{1}H NMR spectra of compound **5b**, recorded immediately after preparation of the solution and 48 h later, hardly differ at all: the form that predominates in solution (51%) is represented by doublets for the N(10)H proton at 13.43 ppm and the H-9 proton at 8.73 ppm ($J_{9,10}$ = 13.1 Hz). In the remaining three minor forms the observed signals of the N(10)H and H-9 protons are appreciably broader. This leads to representation of the H-9 proton in the spectrum by two groups of signals – at 8.50-8.65 and 8.70-8.80 ppm. The paired H-9 and N(10)H signals were assigned to the specific forms by means of a double resonance experiment.

By analogy with compounds **3b** and **5a**, the isomeric forms of compound **5b**, which exhibit relatively downfield signals for the N(10)H proton (13.25 and 13.43 ppm), were assigned as *E*-isomers, while the forms for which the signal of this proton is at 11.65 and 11.99 ppm were assigned as *Z*-isomers. Figure 1 shows the downfield part of the ^{1}H NMR spectrum of compound **5b**, on which the N(10)H and H-9 proton signals of all four forms are indicated. Of the two *E*-isomers, the more energetically favorable is the form with the *s-cis* orientation* of the N(10)–H and C(2')–NH_2 groups in relation to the N(10)–C(Ar) single bond (content of this form 51%). The second *E*-isomer, in which these groups have the *s-trans* arrangement, is less stable, and its content amounts to 16%.

*The designations of the *s-cis*/*s-trans* isomers refer to the mutual arrangement of the N(10)–H bond and the C(2')–NH_2 fragment of the phenyl ring.

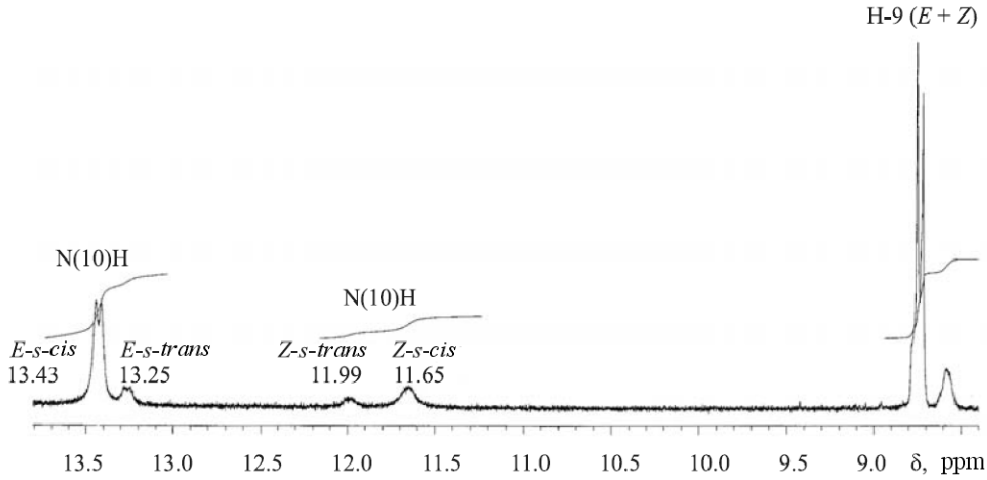
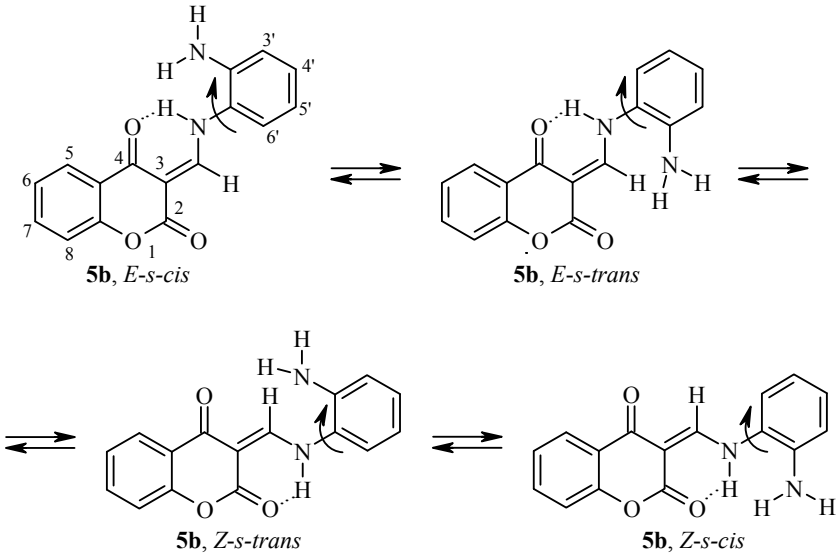


Fig. 1. The downfield part of the ^{1}H NMR spectrum of compound **5b**.

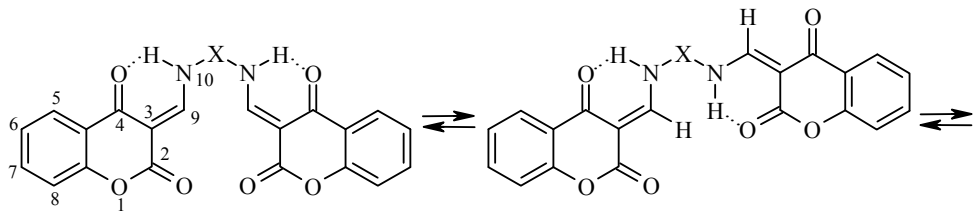
As already mentioned above, the *Z*-isomers were found to be substantially less favorable energetically than the corresponding *E*-isomers. As in the case of the *E*-isomer, favored among the two *Z*-isomers was the one in which the N(10)–H and C(2')–NH_2 fragments are in the *cis* orientation in relation to the N(10)–C(Ar) bond (22%). The fraction of the second *Z*-isomer with the *s-trans* N(10)–H and C(2')–NH_2 groups amounted to 11%. Thus, the spectrum of compound **5b** contained the signals of four forms: *E-s-cis* (51%), *E-s-trans* (16%), *Z-s-cis* (22%), and *Z-s-trans* (11%). As in the case of the azomethines **3b** and **5a**, the total content of the *E*-isomers (67%) for the azomethine **5b** was higher than the total content of the *Z*-form (33%).



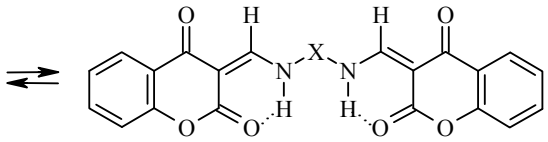
Earlier [8, 9] it was established that 3-(*p*-tolylaminomethylidene)chroman-2,4-dione **3b** undergoes *E*/*Z* isomerization in $CDCl_3$ solution. Immediately after dissolution, the *Z*-isomer signal predominated in the ^{1}H NMR spectrum (its content in the solution exceeds 95%), but after 25 h the opposite ratio of isomers was observed, and the signal of the more stable *E*-isomer became dominant, with its fraction increasing from 5 to 66%. In DMSO-d_6 solution, the thermodynamic equilibrium for this compound was established in 4 h. However, analogous changes were not observed in the ^{1}H NMR spectra of compounds **5a**,**b**.

In that case the signals of the more stable *E*-isomer remained constant over time. Only the nature of splitting in the signals changed. In the ^{1}H NMR spectrum of a freshly prepared solution of compound **5a**, the multiplicity of all the presented signals was not sufficiently clear, since the spectrum is reflecting the kinetic state of the solution. In the spectrum recorded after 25 h the multiplicity of all the signals became very clear; mutual splitting of the signals for the H-9 and N(10)H protons was observed, indicating an equilibrium between the keto-enamine forms.

In the transition to the biscoumarinylimines **6a-c** the spectra are significantly more complicated, since these compounds can exist as a set of two symmetrical forms and one unsymmetrical form – *Z*,*Z*-, *E*,*E*-, and *E*,*Z*-keto-enamines.



6a–c, *E*,*E*-keto-enamine **6a–c**, *E*,*Z*-keto-enamine



6a–c, Z,*Z*-keto-enamine

In the ^{1}H NMR spectrum, each symmetrical form (*E*,*E* and *Z*,*Z*) is represented by its own set of proton signals corresponding to half of the molecule, but the intensity of all the signals is doubled. In the unsymmetrical structure of the *E*,*Z*-keto-enamine, the chemical shifts of the proton signals of the two NH and two CH groups differ from each other, but the intensity ratio of the corresponding signals is identical, as expected. Here the N(10)H and H-9 proton chemical shifts for the molecular fragments with the *E*-configuration in the unsymmetrical (*E*,*Z*) and symmetrical (*E*,*E*) structures differ only slightly. The chemical shifts of the N(10)H and H-9 signals in the *Z*-configuration fragments of the unsymmetrical (*E*,*Z*) and symmetrical (*Z*,*Z*) structures also exhibit only minor differences.

The nature of the spectra and the fraction of the diimine isomers **6a**,**b** remained constant over time, as was the case for the monoimines **5a**,**b**. It can be assumed that the studied compounds also existed in the keto-enamine forms in the solid state, as a result of which their dissolution in DMSO-d_6 was not accompanied by isomeric transformations. At the same time, the spectrum recorded after two days had significantly more distinct multiplicity in all signals. Mutual splitting of the signals of the H-9 and N(10)H protons was observed in all the spectra, thus confirming unambiguously that the keto-enamine forms of the diimines were in equilibrium.

The assignment of the N(10)H and H-9 signals to the specific forms and assessments of the isomeric form fractions were achieved by successive spin-spin decoupling of the H-9 and N(10)H protons (Fig. 2). During spin-spin decoupling of the N(10)H protons the spectrum exhibited changes in the multiplet structure of the H-9 proton signal, which contained the signals of this proton in all three forms (*E*,*E*, *Z*,*Z,* and *E*,*Z*).

It can be stated on the basis of the ^{1}H NMR spectral data that the *E*,*E* and *E*,*Z* isomers were also the most stable for compound **6a**. This led to a high content of both forms (45% of *E*,*E* and 42% of *E*,*Z*) in the equilibrium mixture, while the amount of the *Z*,*Z* form was only 13%.

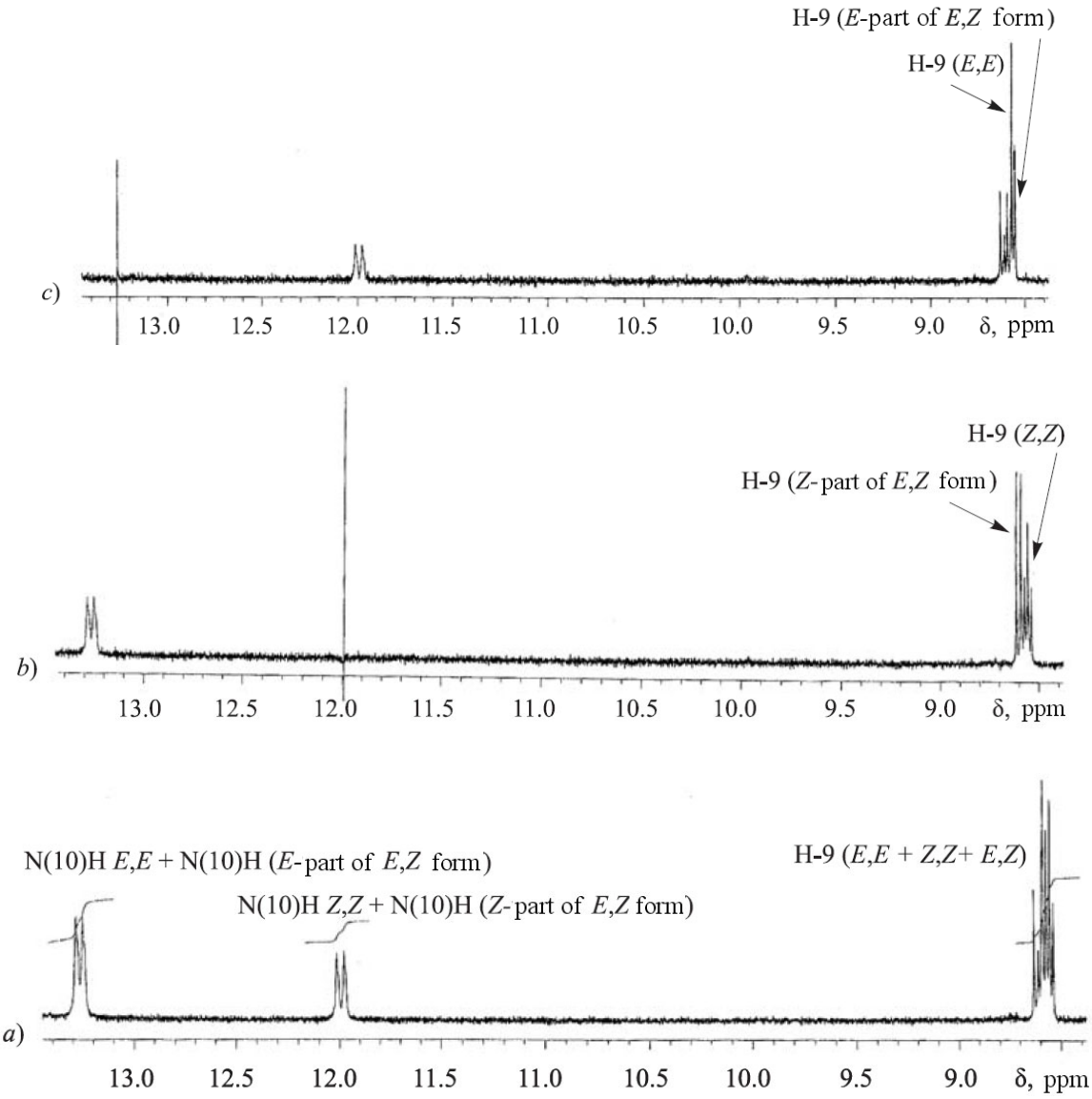


Fig. 2. The downfield part of the ^{1}H NMR spectrum of compound **6a**: *a*) The spectrum without spin-spin decoupling from the N(10)H and H-9 protons; *b*) the spectrum with suppression of the N(10)H signals from the *Z*,*Z* isomer; *c*) the spectrum with suppression of the N(10)H signals from the *E*,*E* isomer.

Compound **6b**, in which the central phenyl fragment is substituted by an ethylene chain, also existed in the form of an equilibrium mixture of the two symmetrical *E*,*E* and *Z*,*Z* isomers and one asymmetrical *E*,*Z* isomer. However, their relative contributions to the composition of the equilibrium mixture of compound **6b** differed from those for the imine **6a**: *E*,*E* – 60%, *E*,*Z* – 31%, and *Z*,*Z* – 9%, i.e., the symmetrical *E*,*E* isomer became energetically more favorable while the *Z*,*Z* isomer was less favorable than in the case of compound **6a**.

For compound **6c**, in which the central part of the molecule is a cyclohexane ring, the ^{1}H NMR spectra indicated a more complex situation, since in addition to the three already mentioned geometrical isomers, the diversity of forms was enriched by the various conformers of the cyclohexane ring.

TABLE 1. The Chemical Shifts of the Characteristic Signals for the N(10)H and H-9 Protons, the Spin-Spin Coupling Constants, and the Relative Content of the Isomeric Forms of Compounds **3b***, **5a**,**b**, and **6a**,**b**

Compound	Type of isomer	*E*-isomer or *E*-part of *E*,*E*, *E*,*Z* isomer				*Z*-isomer or *Z*-part of *Z*,*Z*, *E*,*Z* isomer			
		$\delta_{N(10)H}$, ppm	δ_{H-9}, ppm	$J_{9,10}$, Hz	Relative content of form, %	$\delta_{N(10)H}$, ppm	δ_{H-9}, ppm	$J_{9,10}$, Hz	Relative content of form, %
3b	—	13.60 (d)	8.87 (d)	13.7	66	11.91 (d)	8.98 (d)	14.5	34
5a	—	13.61 (d)	8.66 (d)	13.5	73	11.82 (d)	8.70 (br. s)	14.8	27
5b	*s-cis*	13.43 (d)	8.73 (d)	13.1	51	11.65 (br. s)	8.76 (br. s)	—*[2]	22
	s-trans	13.25 (br. s)	8.57 (br. s)	—*[2]	16	11.99 (br. s)	8.61 (br. s)	—*[2]	11
6a	*E*,*E*	13.26 (d)	8.57 (d)	13.8	45	—	—	—	—
	Z,*Z*	—	—	—	—	11.98 (d)	8.59 (d)	14.8	13
	E,*Z*	13.24 (d)	8.55 (d)	13.8	—*[3]	12.00 (d)	8.61 (d)	14.8	—*[3]
6b	*E*,*E*	11.57 (br. s)*[4]	8.44 (d)	14.5	60	—	—	—	—
	Z,*Z*	—	—	—	—	10.38 (br. s)*[4]	8.51 (d)	15.1	9
	E,*Z*	11.57 (br. s)*[4]	8.41 (d)	14.5	—*[3]	10.38 (br. s)*	8.55 (d)	15.1	—*[3]

*The spectra of compounds **5a**,**b** and **6a**,**b** were recorded in DMSO-d_6. The chemical shifts of the remaining fragments are given in the experimental section. The spectral data of compound **3b** were taken from [8, 9], the solvent was $CDCl_3$.

*[2]In the minor isomers of compound **5b** it was difficult to determine $J_{9,10}$ due to the fast conformational exchanges leading to smoothing of the N(10)H and H-9 signal shapes.

*[3]For compound **6a**, the relative content of the unsymmetrical *E*,*Z* form amounted to 42%, and 31% for compound **6b**.

*[4]The signal of the N(10)H proton was a broadened singlet on account of spin-spin coupling with the CH_2 protons.

In the ^{1}H NMR spectrum of compound **6c** in the downfield region (10.23, 11.48, and 12.13 ppm) there were broad, weakly split signals of various intensity for the N(10)H protons, the relative intensity of which amounted to 0.35H, 1.03H, and 0.62H (with the combined intensity of 2H).*

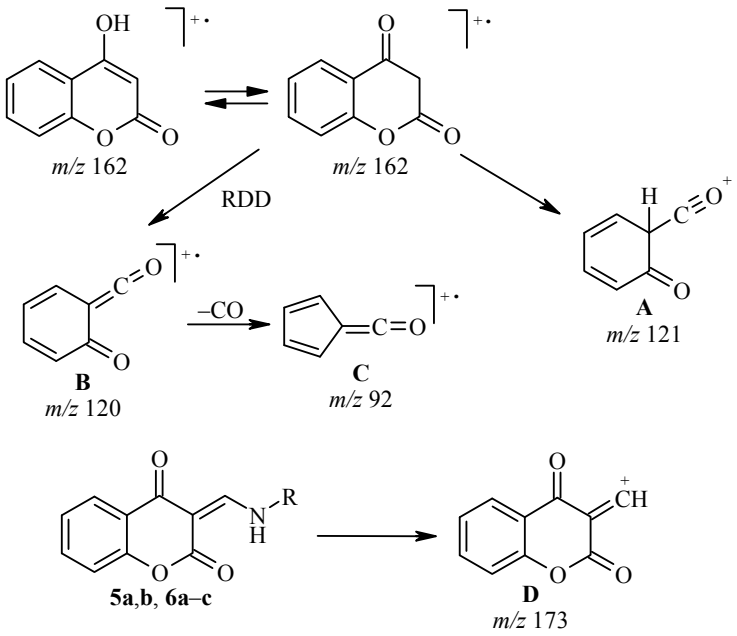
The signals of the H-9 protons formed a group of seven doublets ($J_{9,10}$ = 13.6-14.9 Hz) located in the range of 8.32-8.68 ppm, while their overall intensity corresponded to 2H. The protons of the coumarin ring formed multiplets in the regions of 7.16-7.34 ppm (H-6,8), 7.57-7.70 ppm (H-7), and 7.79-7.92 ppm (H-5) with relative contents of 2:1:1. In the spectrum, the methylene protons of the cyclohexane ring formed a multiplet in the region of 1.27-2.10 ppm (8H); the methine protons H-1' and H-2' were represented by broad signals at 4.00-4.38 ppm, the combined intensity of which amounted to 2H.

The results from ^{1}H NMR structural study of the imines **5a**,**b** and **6a-c** by ^{1}H NMR showed that their most stable tautomeric form was the keto-enamine form, both isomers of which (the *E*- and *Z*-isomers) were stabilized by strong intramolecular hydrogen bonds. The 4-hydroxyimine form was not detected in any of the investigated structures. This conclusion applies not only to the solution phase in organic solvents, but also to the solid phase. As we showed earlier, in the crystalline state 3-formyl-4-hydroxycoumarin imines (**4**) exist in the form of keto-enamines [9].

While continuing the investigation of the structural characteristics of the imines we also studied them in the gas phase by mass spectrometry. It was established that the compounds **5a**,**b** and **6a-c** have similar fragmentation patterns. The characteristic peaks present in the mass spectra of all the imines were the peaks of fragment ions with *m*/*z* 173, 121, and 92.

The fragmentation of 4-hydroxycoumarin under electron impact has been studied earlier [13]. It was shown that the ions with *m*/*z* 120 (fragment **B**), 121 (fragment **A**), and 92 (fragment **C**) were formed as a result of retrodiene decomposition (RDD) or a retro-Diels–Alder reaction followed by ejection of a CO molecule from the fragment **B**.

Thus, in the mass spectra of compounds **5a**,**b** and **6a-c**, the formation of the fragment ions with *m*/*z* 121 and 92 was due to dissociation of the coumarin part of the molecule. As a result of homolytic cleavage of the =CH–NH– bond, a stable ion with *m*/*z* 173 was formed (fragment **D**).

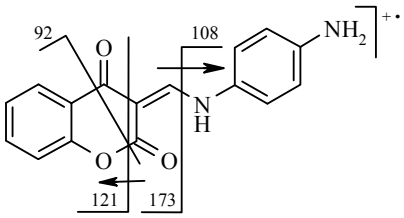


*The intensity was normalized against the signal of the H-5 proton (δ = 7.79-7.92 ppm, 2H).

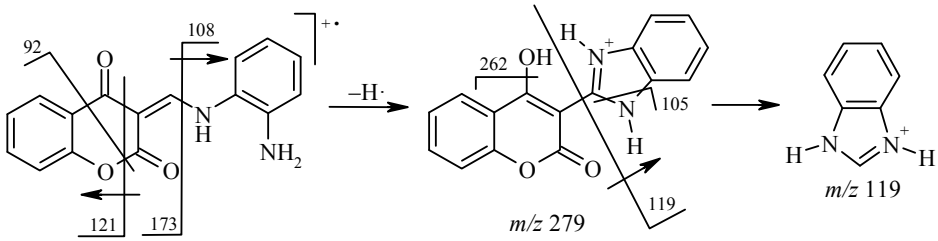
Such dissociation is unusual for azomethines characterized by increased concentration of electron density at the –HC=N– bond [14].

In consideration of the facts discussed above and also taking into account the opinion that there are no tautomeric transformations in the ionization chamber [13], it can be concluded that compounds **5a**,**b** and **6a-c** existed predominantly in the keto-enamine form at the moment of electron impact in the gas phase (similarly as in the liquid and in the solid phases).

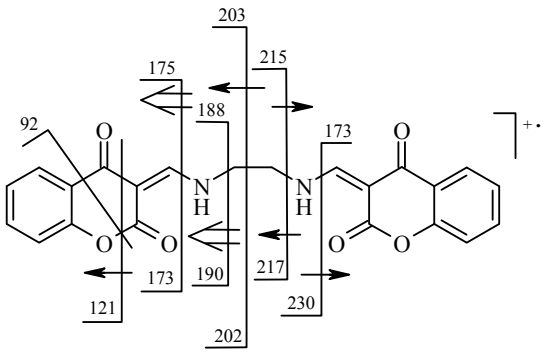
A molecular ion peak was observed in the mass spectrum of the keto-enamine **5a** at *m*/*z* 280. The fragmentation of this compound is shown in the scheme:



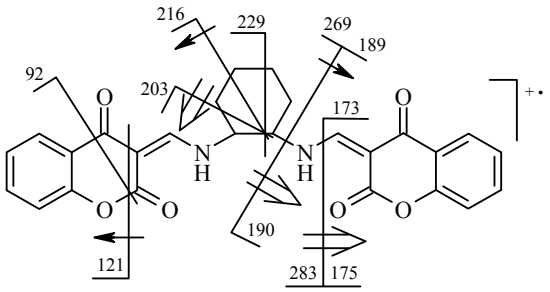
The azomethine **5b**, isomeric with compound **5a**, had a considerably more complicated mass spectrum. In addition to the molecular ion peak at *m*/*z* 280 and the peaks of the fragment ions (*m*/*z* 173, 108), formed as a result of its dissociation, the spectrum also contained a strong peak for the $[M-H]^+$ ion, which apparently corresponds to the structure of protonated 3-(benzimidazol-2-yl)-4-hydroxycoumarin formed as a result of a hydrogen atom elimination from the initial structure. Thus, two independent fragmentation paths were observed in the spectrum. The dominant peak most likely belonged to the stable cation of protonated benzimidazole, the appearance of which was observed earlier in the mass spectra of *o*-phenylenediamine derivatives [15].



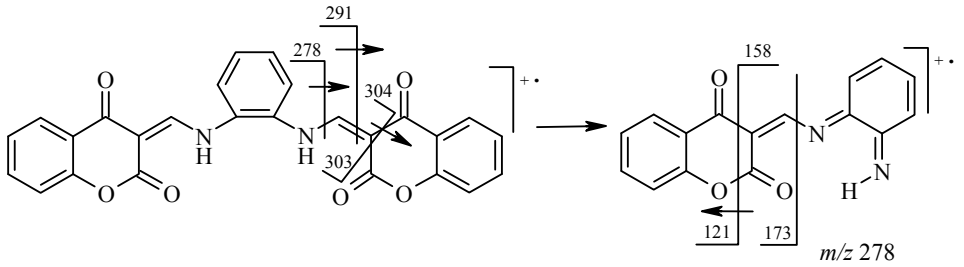
The mass spectrum of compound **6b** contained a molecular ion peak at *m*/*z* 404 and also peaks for fragments arising from stepwise cleavage of the bonds as shown below.



In the mass spectrum of compound **6c**, there was a molecular ion peak at *m*/*z* 458. Its dissociation under electron impact is shown in the following scheme.



A molecular ion peak at *m*/*z* 452 was not recorded in the mass spectrum of compound **6a** (only peaks in the range of *m*/*z* 25-320 were present in the spectrum), but the peaks of daughter ions observed in the region of large masses agreed with the structure of compound **6a**. The formation of the main fragments is shown in the scheme below. The highest peak belonged to an ion with *m*/*z* 278, the preferential formation of which was apparently due to the *ortho* arrangement of the NH group and the =N–CH= fragment. The structure presented below can be assigned to this ion. Further dissociation of the ion at *m*/*z* 278 led to the appearance of ions at *m*/*z* 121, 158, and 173. The spectrum also contained ions at *m*/*z* 212 $[M\text{-}2COC_6H_4O]^{+\cdot}$, 211 $[M\text{-}COC_6H_4O\text{-}COC_6H_4OH]^{+\cdot}$, 184 $[M\text{-}2COC_6H_4O\text{-}CO]^{+\cdot}$, and 183 $[M\text{-}COC_6H_4O\text{-}COC_6H_4OH\text{-}CO]^{+\cdot}$, which also agreed with the proposed structure.



Thus, structural study of new mono- and diimines (the products from 3-formyl-4-hydroxycoumarin condensation with various diamines) by ^{1}H NMR and mass spectrometry has shown that the obtained compounds in DMSO-d_6 solution and in the gas phase exist in the *E*- and *Z*-keto-enamine forms, where the most stable isomer is the *E*-somer. It can be noted in this connection that the assignment of the signals for the *E*- and *Z*-isomers in earlier papers investigating the structures of analogous compounds, i.e., 3-(*p*-tolyl-aminomethylidene)chroman-2,4-dione, 3-(phenylaminomethylidene)chroman-2,4-dione, 3-(*p*-methoxy-phenyl-aminomethylidene)chroman-2,4-dione, and 3-(*n*-propyl-aminomethylidene)chroman-2,4-dione by IR and ^{1}H NMR spectroscopy was not in our opinion sufficiently well-grounded.

EXPERIMENTAL

The IR spectra were recorded on a Thermo Electron Corp. Nicolet Avatar 330 spectrometer in KBr pellets. The ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Unity Plus spectrometer (400 MHz) with the solvent signal as standard (δ 2.50 ppm). The mass spectra were recorded on a Finnigan MAT SSQ-710 mass spectrometer, ionizing electron energy 70 eV, direct injection of the sample into the ion source, and ionization chamber temperature 150°C. Elemental analysis was performed on a EuroVector Euro EA 3000 analyzer.

The melting points were determined on a PTP instrument (Khimlaborpribor, Russia). The 3-formyl-4-hydroxycoumarin was synthesized according to the method described in [12]. The reactions were monitored by TLC on Silufol UV-254 plates in the following solvent systems: a) $CHCl_3$; b) $CHCl_3$–acetone, 16:1.

Compounds 5a,b and 6a-c (General Method). A mixture of 3-formyl-4-hydroxycoumarin **4** and the diamine in alcohol (6-15 ml) was heated for 1-3 h and then cooled to 25°C. The precipitate was filtered off, washed with water, recrystallized from EtOH, and dried.

3-{[(4-Aminophenyl)amino]methylidene}-2*H*-chromene-2,4(3*H*)-dione (5a). This compound was obtained from the aldehyde **4** (100 mg, 0.526 mmol) and *p*-phenylenediamine (57 mg, 0.526 mmol). Yield 118 mg (80%). Dark-yellow crystals; mp 240-242 °C. IR spectrum, ν, cm^{-1}: 1612 (C=O), 1683 (O–C=O), 3212 (NH), 3347 (N–H), 3449 (H–N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 13.61 (0.73H, d, $J_{9,10}$ = 13.5, NH (*E*)); 11.82 (0.27H, d, $J_{9,10}$ = 14.8, NH (*Z*)); 8.70 (0.27H, br. s, H-9 (*Z*)); 8.66 (0.73H, d, $J_{9,10}$ = 13.5, H-9 (*E*)); 7.97 (1H, dd, $J_{5,6}$ = 7.8, $J_{5,7}$ = 1.5, H-5); 7.70-7.66 (1H, m, H-7); 7.38-7.30 (4H, m, H-6,8,2',6'); 6.61-6.65 (2H, m, H-3',5'); 5.49 (2H, s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 280 $[M]^{+\cdot}$ (100), 173 $[M\text{-}C_6H_7N_2]^+$ (35), 121 $[M\text{-}C_6H_7N_2\text{-}C_3O]^+$ (17), 108 $[M\text{-}C_{10}H_4O_3]^+$ (20), 92 $[M\text{-}C_6H_7N_2\text{-}C_3O\text{-}CHO]^{+\cdot}$ (13). Found, %: C 68.75; H 4.36; N 10.07. $C_{16}H_{12}N_2O_3$. Calculated, %: C 68.57; H 4.32; N 9.99.

3-{[(2-Aminophenyl)amino]methylidene}-2*H*-chromene-2,4(3*H*)-dione (5b). This compound was obtained from the aldehyde **4** (100 mg, 0.526 mmol) and *o*-phenylenediamine (114 mg, 1.052 mmol). Yield 110 mg (75%). Yellow crystals; mp 208-211°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 13.43 (0.51H, d, $J_{9,10}$ = 13.1, NH (*E, s-cis*)); 13.25 (0.16H, br. s, NH (*E, s-trans*)); 11.99 (0.11H, br. s, NH (*Z, s-trans*)); 11.65 (0.22H, br. s, NH (*Z, s-cis*)); 8.76 (0.22H, br. s, H-9 (*Z, s-cis*)); 8.73 (0.51H, d, $J_{9,10}$ = 13.1, H-9 (*E, s-cis*)); 8.61 (0.11H, br. s, H-9 (*Z, s-trans*)); 8.57 (0.16H, br. s, H-9 (*E, s-trans*)); 8.02-7.93 (1H, m, H-5); 7.76-7.67 (1H, m, H-7); 7.57-7.46 (1H, m, H-6'); 7.43-7.32 (2H, m, H-6,8); 7.13-7.08 (1H, m, H-4'); 6.94-6.89 (1H, m, H-3'); 6.78-6.74 (1H, m, H-5'); 5.28 (2H, s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 280 $[M]^{+\cdot}$ (50), 279 $[M\text{-}H]^+$ (55), 262 $[M\text{-}H\text{-}OH]^{+\cdot}$ (4), 173 $[M\text{-}C_6H_7N_2]^+$ (5), 121 $[M\text{-}C_6H_7N_2\text{-}C_3O]^+$ (33), 119 $[M\text{-}H\text{-}C_9H_4O_3]^+$ (100), 108 $[M\text{-}C_{10}H_4O_3]^{+\cdot}$ (12), 105 $[M\text{-}H\text{-}C_9H_4O_3\text{-}N]^{+\cdot}$ (14), 92 $[M\text{-}C_6H_7N_2\text{-}C_3O\text{-}CHO]^{+\cdot}$ (31). Found, %: C 68.42; H 4.38; N 9.93. $C_{16}H_{12}N_2O_3$. Calculated, %: C 68.57; H 4.32; N 9.99.

3,3'-[1,2-Phenylenebis(iminomethylidene)]bis(2*H*-chromene-2,4(3*H*)-dione) (6a). This compound was obtained from the aldehyde **4** (300 mg, 1.578 mmol) and *o*-phenylenediamine (114 mg, 0.526 mmol). Yield 214 mg (90%). Yellow crystals; mp 279-281°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 1720 (O–C=O), 3062 (N–H), 3435 (br., N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 13.26 (0.90H, d, $J_{9,10}$ = 13.8, NH (*E,E*)); 13.24 (0.42H, d, $J_{9,10}$ = 13.8, NH (*E-part E,Z*)); 12.00 (0.42H, d, $J_{9,10}$ = 14.8, NH (*Z-part E,Z*)); 11.98 (0.26H, d, $J_{9,10}$ = 14.8, NH (*Z,Z*)); 8.61 (0.42H, $J_{9,10}$ = 14.8, H-9 (*Z*-part *E,Z*)); 8.59 (0.26H, d, $J_{9,10}$ = 14.8, H-9 (*Z,Z*)); 8.57 (0.9H, d, $J_{9,10}$ = 13.8, H-9 (*E,E*)); 8.55 (0.42H, d, $J_{9,10}$ = 13.8, H-9 (*E*-part *E,Z*)); 8.03-7.93 (2H, m, H-5); 7.79-7.67 (4H, m, H-7,4',5'); 7.56-7.47 (2H, m, H-3',6'); 7.39-7.32 (4H, m, H-6,8). Mass spectrum, *m/z* (I_{rel}, %): 304 $[M\text{-}C_8H_4O_3]^{+\cdot}$ (5), 303 $[M\text{-}C_8H_5O_3]^{+\cdot}$ (5), 291 $[M\text{-}C_9H_5O_3]^+$ (17), 278 $[M\text{-}C_{10}H_6O_3]^{+\cdot}$ (100), 212 $[M\text{-}2C_7H_4O_2]^{+\cdot}$ (2), 211 $[M\text{-}C_7H_4O_2\text{-}C_7H_5O_2]^{+\cdot}$ (4), 184 $[M\text{-}2C_7H_4O_2\text{-}CO]^{+\cdot}$ (3), 183 $[M\text{-}C_7H_4O_2\text{-}C_7H_5O_2\text{-}CO]^{+\cdot}$ (1), 173 $[M\text{-}C_{16}H_{11}O_3N_2]^+$ (7), 158 $[M\text{-}C_{10}H_6O_3\text{-}C_7H_4O_2]^{+\cdot}$ (10), 121 $[M\text{-}C_{16}H_{11}O_3N_2\text{-}C_3O]^+$ (28). Found, %: C 69.10; H 3.66; N 6.25. $C_{26}H_{16}N_2O_6$. Calculated, %: C 69.03; H 3.56; N 6.19.

3,3'-[Ethane-1,2-diylbis(iminomethylidene)]bis(2*H*-chromene-2,4(3*H*)-dione) (6b). This compound was obtained from the aldehyde **4** (200 mg, 1.052 mmol) and 1,2-diaminoethane (35 μl, 0.526 mmol). Yield 189 mg (89%). Colorless crystals; mp 364-365°C. IR spectrum, ν, cm^{-1}: 1631 (C=O), 1711 (O–C=O), 3253 (N–H), 3434 (br., N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.57 (1.51H, br. s, NH (*E,E*+*E*-part *E,Z*)); 10.38 (0.49H, br. s, NH (*Z,Z*+*Z*-part *E,Z*)); 8.55 (0.31H, d, $J_{9,10}$ = 15.1, H-9 (*Z*-part *E,Z*)); 8.51 (0.18H, d, $J_{9,10}$ = 15.1, H-9 (*Z,Z*)); 8.44 (1.20H, d, $J_{9,10}$ = 14.5, H-9 (*E,E*)); 8.41 (0.31H, d, $J_{9,10}$ = 14.5, H-9 (*E*-part *E,Z*)); 7.93-7.84 (2H, m, H-5); 7.68-7.61 (2H, m, H-7); 7.34-7.23 (4H, m, H-6,8); 3.91 (4H, s, CH_2CH_2). Mass spectrum, *m/z* (I_{rel}, %): 404 $[M]^{+\cdot}$ (6), 230 $[M\text{-}C_{10}H_6O_3]^{+\cdot}$ (9), 217 $[M\text{-}C_{10}H_5NO_3]^{+\cdot}$ (13), 215 $[M\text{-}C_{10}H_7NO_3]^{+\cdot}$ (33), 203 $[M\text{-}C_{11}H_7NO_3]^{+\cdot}$ (55), 202 $[M\text{-}C_{11}H_8NO_3]^+$ (55), 190 $[M\text{-}C_{12}H_8NO_3]^+$ (17), 188 $[M\text{-}C_{12}H_{10}NO_3]^+$ (17), 175 $[M\text{-}C_{12}H_9N_2O_3]^+$ (54), 173

$[M\text{-}C_{12}H_{11}N_2O_3]^+$ (23), 121 $[M\text{-}C_{12}H_{11}N_2O_3\text{-}C_3O]^+$ (100), 92 $[M\text{-}C_{12}H_{11}N_2O_3\text{-}C_3O\text{-}CHO]^{+\cdot}$ (31). Found, %: C 65.21; H 4.27; N 6.90. $C_{22}H_{16}N_2O_6$. Calculated, %: C 65.34; H 3.99; N 6.93.

3,3'-[Cyclohexane-1,2-diylbis(iminomethylidene)]bis(2*H*-chromene-2,4(3*H*)-dione) (6c). This compound was obtained form the aldehyde **4** (200 mg, 1.052 mmol) and 1,2-diaminocyclohexane (64 μl, 0.526 mmol). Yield 217 mg (90%). Light-yellow crystals; mp 316-318°C. IR spectrum, ν, cm^{-1}: 1642 (C=O), 1692 (O–C=O), 3230 (N–H), 3439 (br. s, N–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 12.13 (0.35H, br. s, NH); 11.48 (1.03H, br. s, NH); 10.23 (0.62H, br. s, NH); 8.68-8.32 (2H, m, H-9); 7.92-7.79 (2H, m, H-5); 7.70-7.57 (2H, m, H-7); 7.34-7.16 (4H, m, H-6,8); 4.38-4.00 (2H, m, H-1',2'); 2.10-1.27 (8H, m, 3',4',5',6'-CH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 458 $[M]^{+\cdot}$ (40), 283 $[M\text{-}C_{10}H_7O_3]^+$ (12), 269 $[M\text{-}C_{10}H_7NO_3]^{+\cdot}$ (97), 229 $[M\text{-}C_{13}H_{11}NO_3]^{+\cdot}$ (6), 216 $[M\text{-}C_{14}H_{12}NO_3]^{+\cdot}$ (13), 203 $[M\text{-}C_{15}H_{13}NO_3]^{+\cdot}$ (24), 190 $[M\text{-}C_{16}H_{14}NO_3]^+$ (63), 189 $[M\text{-}C_{16}H_{15}NO_3]^{+\cdot}$ (26), 175 $[M\text{-}C_{16}H_{15}N_2O_3]^+$ (27), 173 $[M\text{-}C_{16}H_{17}N_2O_3]^+$ (21), 121 $[M\text{-}C_{16}H_{17}N_2O_3\text{-}C_3O]^+$ (100), 92 $[M\text{-}C_{16}H_{17}N_2O_3\text{-}C_3O\text{-}CHO]^{+\cdot}$ (30). Found, %: C 68.12; H 5.16; N 6.26. $C_{26}H_{22}N_2O_6$. Calculated, %: C 68.11; H 4.84; N 6.11.

Condensation of Aldehyde 4 with *o*-Phenylenediamine and 1,2-Diaminoethane in Acetic Acid. The aldehyde **4** (1.3 g, 7 mmol) and the corresponding amine (7 mmol) were dissolved with heating in glacial acetic acid (50 ml) and refluxed for 5 h. After the reaction mixture had cooled, the crystals that formed were filtered off and recrystallized from acetic acid.

Compound 6a. Yield 1.6 g (50%). Yellow crystals; mp 279-281°C.

Compound 6b. Yield 1.1 g (40%). Colorless crystals; mp 364-365°C.

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