E/*Z*(C=C)-Isomerization of enamines of 3-formyl-4-hydroxycoumarin induced by organic solvents

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According to ^{1}H and ^{13}C NMR data, enamines of 3-formyl-4-hydroxycoumarin exist in the keto enamine tautomeric form and undergo *Z*/*E*-isomerization around the C=C bond in $CDCl_3$, DMSO-d_6, and CD_3OD at room temperature. The activation energies of *E*/*Z*-isomerization were measured experimentally and calculated by the B3LYP/6-311++G(d,p) method. An X-ray diffraction study showed that 3-(benzyliminomethyl)chromane-2,4-dione in the crystalline state exists as a mixture of two keto enamine isomers.

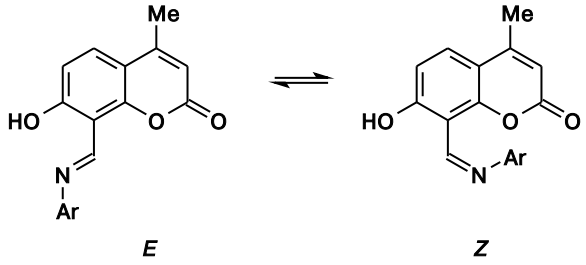
Key words: imines, isomerization, tautomerism, keto enamines, hydroxy imines, coumarin derivatives.

Noncovalent interactions play an important role in organic chemistry, in the formation of supramolecular systems, and in interactions of biological substrates.[1—3] In particular, these interactions are responsible for isomerizations of solvatochromic compounds used for the design of various types of sensors, elements of molecular electronics devices, and information recording and storage systems.[4,5]

Aromatic and heteroaromatic imines are particularly prone to isomerization.[6—8] Earlier, we have reported on solvatochromism in imines derived from 8-formyl-7-hydroxy-4-methylcoumarin.[9] It was found that these compounds mainly exist in the enol form and no keto-enol tautomerism was observed. Some compounds of this series (in particular, imines containing strong electron-withdrawing groups in the *para*-position of the phenyl ring) can undergo *E*/*Z*-isomerization around the C=N bond (Scheme 1).

4-Hydroxycoumarins representing the enol forms of 2,4-diketochromone are also prone to tautomerism. Tautomeric transformations of derivatives of 4-hydroxycoumarin and 3-acyl-4-hydroxycoumarins (**1**) are induced by changes in the solvent polarity and are sometimes accompanied by changes in both electronic absorption spectra and fluorescence spectra.[10,11]

Scheme 1



E *Z*

In the present work, we have synthesized imines of 3-formyl-4-hydroxycoumarin **2—4** and studied their isomerization in organic solvents.

Like other derivatives of 4-hydroxycoumarin, imines **2—4** can potentially undergo tautomeric transformations. Scheme 2 presents selected tautomeric forms. Nevertheless, we inferred from our studies of ^{1}H NMR spectra of imines **2—4** that all of them exist in solution in the same tautomeric form, namely, as a mixture of two *E*- and *Z*-isomers of the keto enamine form (Scheme 2). The rate of equilibration between isomers depends strongly on the solvent polarity and on the imine structure.

The isomerization of imine **2b** was studied in most detail. For this compound, an equilibrium between the

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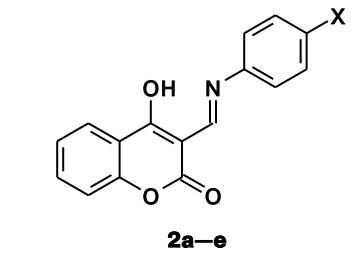
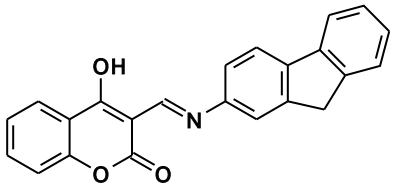


2a—e



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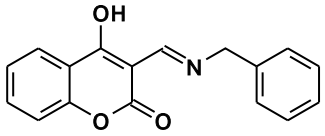

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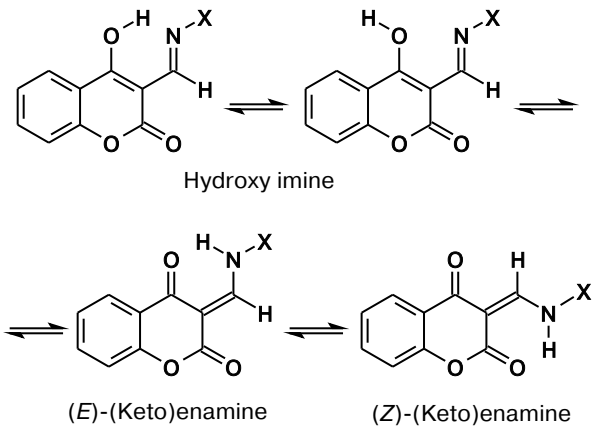
X = H (**a**), Me (**b**), OMe (**c**), Br (**d**), NO_2 (**e**)

Scheme 2



E- and *Z*-isomers is established almost immediately after dissolution in methanol, 4 h after dissolution in DMSO, and 24 h after dissolution in chloroform.

The isomerization is clearly detected by NMR spectroscopy. The ^{1}H NMR spectrum of compound **2b** immediately after dissolution in chloroform-d exhibits a signal for the NH-proton at δ 11.9 corresponding to one major isomer whose content in solution is 95%. After 24 h, the isomer characterized by the signal for the NH proton at δ 13.6 becomes dominant. The content of this isomer increases from 5 to 70% (Fig. 1).

The ^{13}C NMR spectrum of the equilibrium solution of compound **2b** in $CDCl_3$ also exhibits signals of two isomers (Table 1). The signal for the C(4) atom of the major isomer at δ 181.6 is shifted downfield compared to the signal of the minor isomer at δ 178.5. The reverse is observed for the signal for the C(2) atom. This can be explained by the effect of the C(2)=O...H—N and C(4)=O...H—N hydrogen bond in the *Z*- and *E*-keto enamine, respectively. The signal for the C(2) atom is a doublet owing to the spin-spin coupling between this atom and the H(9) proton. The constant of heteronuclear spin-spin coupling C—H for the minor isomer is much larger than for the major isomer, namely, $J_{C(2)H(9)}$ = 9.94 and 3.07 Hz, respectively. These values suggest that the minor isomer is the *Z*-keto enamine with a *trans*-orientation of the bonds C(2)—C(3) and C(9)—H and, correspondingly, large $J_{C(2)H(9)}$. Thus, the major isomer is the *E*-isomer. The chemical shifts in the ^{13}C NMR spectrum ($CDCl_3$) of compound **2b** are listed in Table 1.

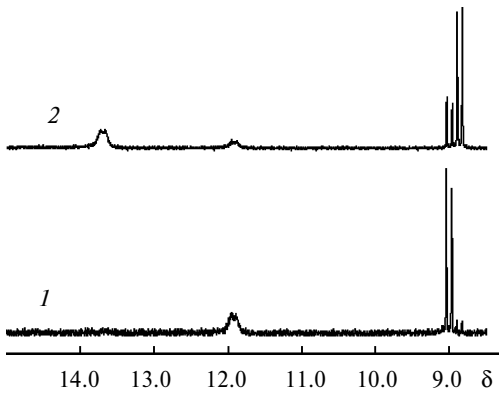


Fig. 1. ^{1}H NMR spectra recorded immediately (*1*) and 24 h (*2*) after dissolution of imine **2b** in chloroform-d.

According to our B3LYP/6-311++G(d,p) calculations using the GAUSSIAN-98 program,[12] the energy of for-

Table 1. Chemical shifts (δ) in the ^{13}C NMR spectrum ($CDCl_3$) of imine **2b**

Atom, group	*E*-Isomer	*Z*-Isomer
2	163.60	165.30
3	98.37	98.39
4	181.60	178.50
5	125.70	126.40
6	124.70	124.30
7	134.60	134.50
8	117.30	117.40
9	154.60	153.20
4a	120.30	120.60
8a	154.20	154.90
10	137.60	134.50
11, 15	118.30	118.40
12, 14	130.60	130.60
13	135.20	135.20
CH_3	20.30	20.90

mation of *E*-keto enamine is lower than that of the *Z*-keto enamine form. The energy difference $\Delta E = 0.65$ kcal mol^{-1} corresponds to a thermodynamic equilibrium between two isomers in a 75 : 25 ratio, being in good agreement with the experimental *E* : *Z* ratio of nearly 70 : 30. The calculated energies of formation of the hydroxy imine form are 6.35 and 12.72 kcal mol^{-1} (for the 4- and 2-hydroxy forms, respectively) higher than that of the *E*-keto enamine. As a consequence, the amount of the hydroxy imine form can be at most 10^{-3} and 10^{-8}%, respectively.

The hydrogen bond NH...O=C(4) in the *E*-isomer (1.81 Å) is much shorter and, therefore, stronger than the corresponding bond NH...O=C(2) in the *Z*-isomer (1.87 Å). The relative strengths of the two hydrogen bonds can be estimated from the partial charges on the donor and acceptor atoms. Our DFT calculations showed that the partial charges on the imine proton and carbonyl oxygen atoms bound to the C(2) and C(4) atoms in the *E*-isomer are +0.440, −0.297, and −0.269, respectively. The corresponding values for the *Z*-isomer are +0.417, −0.292, and −0.267. As can be seen, the positive charge of the imino proton involved in the formation of the hydrogen bond is higher in the *E*-isomer.

We calculated the chemical shifts of protons and carbon atoms for both isomers of compound **2b** by the B3LYP GIAO/6-311++G(2d,p) method. The calculated values are in good agreement with the experimental data (Table 2). The relative chemical shifts of NH-protons excellently correlate with the strengths of the hydrogen bonds in the *E*- and *Z*-isomers. The largest changes in the ^{13}C chemical shift on going from one isomer to the other were found for the C(2) and C(4) atoms. The calculated differences in the chemical shifts are different for the C(2) and C(4) atoms of two isomers (−1.6 and +3.1, respectively) and agree with the corresponding experimental values (−1.5 and +4.0). The results of the GIAO calculations also enable reliable assignment of the signals for the H(9) proton in the *E*- and *Z*-isomers, *viz.*, the signal for H(9) in the *E*-keto enamine is shifted upfield (δ 8.9) relative to the proton signal in the spectrum of the *Z*-isomer (δ 9.0).

Examples of *E*/*Z*-isomerization around the C=C bond were reported earlier.[13–17] In particular, we have established[14,15] that the merocyanine derivatives of 3-formyl-4-hydroxycoumarin exist as mixtures of *E*- and *Z*-isomers. An unprecedented coexistence of spirooxazine and photomerocyanine in four *trans*-conformations is documented.[16] *Trans-trans-cis*/*trans-trans-trans*-isomerism in photochromic spiropyran-merocyanines was studied experimentally and using DFT calculations.[17] At the same time, only one isomer of the keto enamine form was detected in a study of the ^{1}H NMR spectra of imines of 3-formyl-4-hydroxycoumarin.[18]

We also determined the kinetic parameters of *Z*/*E*-isomerization of imine **2b**. To this end, we measured changes in the intensities of the signals of the *E*- and *Z*-isomers of imine **2b** with time in the temperature range from 30 to 50 °C and calculated the rate constants. It was found that the decrease in the intensities of the signals of the *Z*-isomer and an increase in the intensities of the signals of the *E*-isomer in the initial stage of the reaction is correctly described by a first-order kinetic equation.

Taking into account the linear dependence of ln*k* on $1/T$ (Fig. 2), the calculated activation energy of isomerization of imine **2b** from *Z*-keto enamine to the corresponding *E*-isomer is 84±6 kJ mol^{-1}.

The activation energy of rotation about the C(3)—C(9) bond in compound **2b** was also calculated by the B3LYP/6-311++G(d,p) method, which gave a value of 148 kJ mol^{-1}. This is much higher (by 64 kJ mol^{-1}) than the experimental value. Probably, the real mechanism of *E*/*Z*-isomerization is more complex than a simple rotation about the C(3)—C(9) bond assumed in the quantum chemical calculations. For instance, isomerization may involve keto-enol tautomeric transformations accompanied by intramolecular proton migration, which may cause

Table 2. ^{1}H and ^{13}C chemical shifts (δ) for *E*- and *Z*-isomers of compound **2b** obtained from GIAO calculations and experimental data (in parentheses)

Atom, group	*E*-Isomer	*Z*-Isomer
NH	12.60 (13.60)	11.40 (12.00)
H(9)	9.07 (8.90)	9.46 (9.00)
C(2)	167.80 (163.60)	169.30 (165.20)
C(3)	105.10 (98.37)	107.10 (98.39)
C(4)	188.30 (181.60)	184.30 (178.50)
C(9)	161.62 (154.60)	160.67 (153.20)
C(10)	124.32 (137.62)	124.24 (134.48)

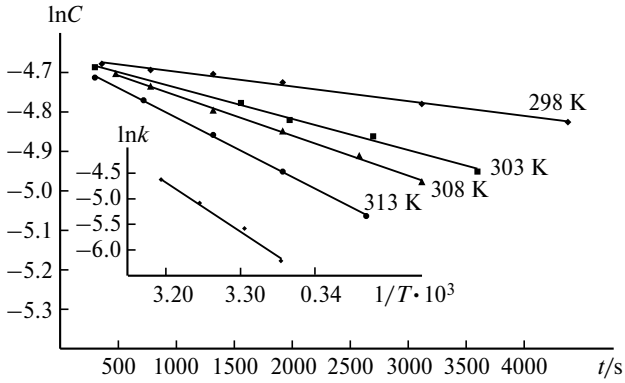


Fig. 2. Changes in the signal for the H(9) proton in the *Z*-isomer in chloroform-d at different temperatures. Inset: the plot of ln *k* *vs.* $1/T$ calculated using the expression ln k = = −9566.4 $(1/T)$ + 25.985.

a decrease in the activation energy. At the same time, the much higher energies of formation of the 4- and 2-hydroxy forms compared to that of the keto enamine form suggest that their involvement in isomerization is unlikely. Probably, there is also a contribution of the solvent effect because calculations were carried out for a molecule in the gas phase while the experimental value was obtained for the compound dissolved in chloroform. In addition, the difference between the calculated and experimental activation energies (46 kJ mol^{-1}) obtained in the present work is close to the activation energy difference between the gas phase and $C_2H_2Cl_2$ solution (55 kJ mol^{-1}) for *E*/*Z*-isomerization of spiropyran-merocyanine obtained analogously.[19]

We found that the higher the solvent polarity the stronger the effect of solvent on *E*/*Z*-isomerization. For instance, the isomerization of imine **2b** in DMSO-d_6 proceeds at a much higher rate. Immediately after dissolution, the signal for the H(9) atom is observed as a broadened singlet. It splits into two doublets at δ 8.66 (*E*-isomer, $J_{9,10a}$ = 13.5 Hz, 73%) and 8.72 (*Z*-isomer, $J_{9,10a}$ = 14.8Hz, 27%) after 4 h and then the signal intensities remain unchanged. The same can be observed in a lower field (δ 11—14) for the signals for the NH protons. Two broad NH proton signals at δ 13.4 (*E*-isomer) and 11.7 (*Z*-isomer) are observed in the ^{1}H NMR spectrum immediately after dissolution of imine **2b** in DMSO-d_6 (Fig. 3).

When dissolved in methanol-d_4, the thermodynamic equilibrium between two isomers of imine **2b** is attained immediately as well. The ^{1}H NMR spectrum recorded immediately after dissolution exhibits two broadened singlet signals for H(9) of different intensity. The stronger signal at δ 8.94 was assigned to the *E*-isomer while the weaker signal at δ 9.06 was assigned to the *Z*-isomer. The intensity ratio of these signals remains unchanged with time. Low resolution of both signals is most likely due to fast H/D-exchange of NH-protons of the keto enamine form in methanol. The $J_{H,D}$ coupling constant is 6.5 times smaller than the corresponding $J_{H,H}$ constant; therefore, the $^3J_{H,D}$ constant in the ^{1}H NMR spectra of imine **2b** after exchange of NH-proton by a deuterium atom from the solvent should be about 2 Hz. Moreover, the signal for the H(9) proton should appear as a triplet due to the interaction with the quadrupole deuterium atom (S = 1). The joint effect of these factors leads to broadening of this signal (the width at half-height is 5.4 Hz).

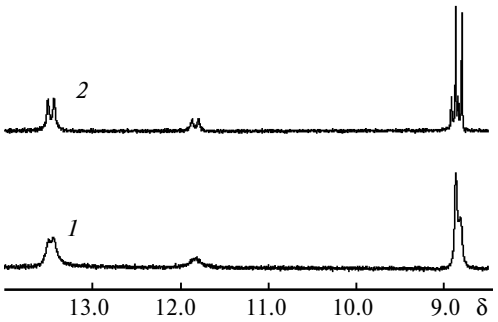


Fig. 3. ^{1}H NMR spectra recorded immediately (*1*) and 4 h after dissolution of imine **2b** in DMSO-d_6 (*2*).

Other imines **2—4** exhibit similar spectral and isomerization properties. The ^{1}H NMR spectra of all compounds show signals of *Z*- and *E*-isomers. The chemical shifts for the NH-protons and H(9) atom are listed in Table 3.

In addition, all imines are characterized by a similar isomeric composition (*Z* : *E* ratio), as shown below.

Compound	**2a**	**2b**	**2d**	**3**	**2c**	**2e**	**4**
Z/*E* (%)	31/69	34/66	24/76	30/70	27/73	30/70	30/70

However, compounds **2—4** differ in equilibration rates for the *Z*- and *E*-forms in chloroform. For compounds **2a,d** and **3**, equilibration takes a few hours to complete as for compound **2b**. However, for compounds **2c,e** and **4**, the equilibrium is attained immediately after dissolution, as indicated by the lack of changes in their ^{1}H NMR spectra which show two groups of doublet signals of the *E*- and *Z*-isomers near δ 9 for H(9) proton and at δ 11—14 for NH-protons. Like the ^{1}H NMR spectra of the solutions in chloroform, those recorded in DMSO-d_6 also remain unchanged and immediately after dissolution they show well-defined doublets of H(9) proton and NH-protons. The properties of compound **2c** deserve particular attention. In its ^{1}H NMR spectrum in DMSO-d_6, the signal for the H(9) proton appears as a singlet at δ 8.78

Table 3. Chemical shifts (δ) of protons in compounds **2—4** in chloroform

Compound	N—H		H(9)		H(5)	
	E-Isomer	*Z*-Isomer	*E*-Isomer	*Z*-Isomer	*E*-Isomer	*Z*-Isomer
2a	13.72	11.98	8.90	9.04	8.08	8.14
2b	13.68	11.94	8.86	9.01	8.07	8.14
2c	13.75	11.94	8.79	8.93	8.07	8.14
2d	13.70	11.90	8.84	8.98	8.07	8.14
2e	13.79	12.00	8.92	9.04	8.08	8.14
3	13.82	12.04	8.93	9.07	8.08	8.15
4	12.12	10.49	8.49	8.67	7.96	8.06

and a strongly broadened singlet at δ 13.0 is observed in the region δ 11—14. The spectrum remains unchanged with time. One would assume that compound **2c** exists in DMSO-d_6 in the hydroxy imine form. To refine the structure of compound **2c**, we studied the multiplicity of the signal for the C(9) atom. In the ^{13}C NMR spectrum of the hydroxy imine form, one would expect for this atom the appearance of a doublet with a direct heteronuclear spin-spin coupling constant C(9)—H of 140—160 Hz. In the case of the keto enamine form, one would expect the appearance of a doublet of doublets with the direct spin-spin coupling constant C(9)—H and the spin-spin coupling constant through two bonds C(9)—H(N). A DEPT90 experiment revealed that the signal for the atom C(9) is a doublet of doublets with a direct spin-spin coupling constant of 153.6 Hz and a spin-spin coupling constant through two bonds of 8.5 Hz. An increase in the concentration of compound **2c** in solution led to splitting of the singlet signal for the H(9) proton into two doublets and the appearance of corresponding doublet signals for the NH-proton at δ 11.8 and 13.5. Therefore, the appearance of a singlet signal for the H(9) proton at a lower concentration may be a consequence of intense proton exchange of NH groups with water containing in DMSO-d_6.

From analysis of the ^1H NMR spectrum of compound **4** it follows that, as in the case of compound **2b**, the *E*-keto enamine form is the major isomer, the *Z*-keto enamine form being the minor one.

Our X-ray diffraction study of crystals of compound **4** showed that, as in solution, this compound exists in the crystalline phase as a mixture of two keto enamine isomers (Fig. 4). In the solid state, both isomers are characterized by well-defined intramolecular interactions between N—H...O=C(4) and N—H...O=C(2) groups in the *E*- and *Z*-keto enamine forms, *viz.*, the lengths of the corresponding hydrogen bonds are 2.00 and 2.16 Å.

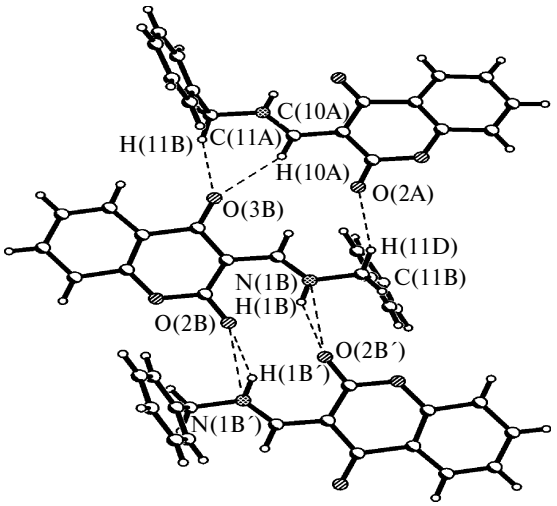


Fig. 4. Intermolecular hydrogen bonds between *E*- and *Z*-isomers in crystals of compound **4**.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker WP200-SY (200 MHz) and Unity Plus (Varian, 400 MHz) spectrometers in CD_3OD, $CDCl_3$, and DMSO-d_6. The chemical shifts were calculated using Me_4Si as the internal standard. Mass spectra were obtained on a Finnigan mass spectrometer (electron ionization energy 70 eV, $T = 443$ K).

The rates of *Z*/*E*-isomerization were determined at imine concentrations of 1—3 mmol L^{-1}. Signals of the *E*- and *Z*-keto enamine forms were recorded within the time interval 6—70 min. The first spectrum was recorded 6 min after preparation of the sample. The relative concentrations of isomers were determined from the integrated intensities of the H(9) proton signals. The rate constants k were calculated from the first-order kinetic equation $\ln c = kt$.

Quantum chemical calculations were carried out using the GAUSSIAN 98 program.[12] Geometry optimization was performed within the density functional theory (DFT) using the B3LYP functional and 6-311++G(d,p) basis set. The ^1H and ^{13}C NMR chemical shifts were calculated by the GIAO method in the 6-311++G(2d,p) basis set.[20—22] To determine the absolute values of the chemical shifts, the isotopic shielding was calculated for Me_4Si with the same basis set.

The energy profile for rotation about the C(3)—C(9) bond was obtained from the Hartree—Fock calculations in the 6-31++G(d,p) basis set. Geometry optimization was performed for all intermediate structure with a fixed value of the torsion angle with respect to the C(3)—C(9) bond with an increment of 5 or 30°. Geometric parameters obtained for the structure with the maximum energy were then used as the initial approximation in the search for a first-order saddle point.

X-ray diffraction analysis. A single crystal was grown from isopropyl alcohol. An X-ray study of the crystals of **2** was carried out on a Bruker SMART APEX2 CCD diffractometer (Mo-Kα radiation) at 20 °C. The crystal structure was solved by the direct methods followed by the Fourier syntheses using the SHELXS-97 software. The structure was refined by the least squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms using the SHELXL-97 software. Positions of hydrogen atoms were calculated geometrically.

The atomic coordinates, bond lengths, and bond angles were deposited at the Cambridge Structural Database (www.ccdc.cam.uk/conts/retrieving.html, CCDC, record No. 700853).

Selected geometric parameters of the crystal and experimental data are as follows: $C_{17}H_{13}NO_3$, $M = 279.28$, triclinic crystal system, space group *P*-1, $a = 10.669(2)$ Å, $b = 11.983(2)$ Å, $c = 12.169(2)$ Å, $\alpha = 62.38(3)°$, $\beta = 89.29(3)°$, $\gamma = 81.67(3)°$, $V = 1361.3(5)$ Å^3, $Z = 4$, $d_{calc} = 1.36$ g cm^{-3}, $\mu = 0.094$ mm^{-1}, the total number of reflections is 9513, the number of independent reflections is 5301, 379 parameters refined, $R = 0.075$ for 2608 reflections with $F_0 > 4\sigma(F_0)$.

Synthesis of imines of 3-formyl-4-hydroxycoumarin (general procedure). A mixture of 3-formyl-4-hydroxycoumarin (0.1 g, $0.53 \cdot 10^{-3}$ mol) and *p*-toluidine (0.05 g, $0.53 \cdot 10^{-3}$ mol) in EtOH (10 mL) was heated for 2 h and cooled. The precipitate was filtered off, washed with water, and dried in air. Needle-shaped crystals were obtained (from EtOH).

3-(Phenyliminomethyl)chromane-2,4-dione (2a).[15] White powder, m.p. 208—210 °C (*cf.* publ. data: m.p. 209—210 °C). ^1H NMR (200 MHz, $CDCl_3$, δ,, *J*/Hz): 13.72 (d, 0.7 H, NH,

$J_{NH,H(9)}$ = 13.6); 11.96 (d, 0.3 H, NH, $J_{NH,H(9)}$ = 14.9); 9.04 (d, 1 H, H(9), $J_{NH,H(9)}$ = 14.9); 8.90 (d, 0.7 H, H(9), $J_{NH,H(9)}$ = 13.7); 8.14 (dd, 0.3 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 2.0); 8.08 (dd, 0.7 H, H(5), J = 8.2, J = 1.5); 7.74 (m, 1 H, H(7)); 7.43—7.55 (m, 2 H, H(6), H(8)); 7.24—7.41 (m, 5 H, H(2′), H(3′), H(4′), H(5′), H(6′)).

3-(*p*-Tolyliminomethyl)chromane-2,4-dione (2b).[15] White powder, m.p. 192—194 °C. (*cf.* publ. data: m.p. 191 °C). ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 13.60 (d, 0.66 H, NH, $J_{NH,H(9)}$ = 13.7); 11.91 (d, 0.34 H, NH, $J_{NH,H(9)}$ = 14.5); 9.98 (d, 0.34 H, H(9), $J_{H(9),NH}$ = 14.5); 9.87 (d, 0.66 H, H(9), $J_{H(9),NH}$ = 13.7); 8.14 (dd, 1 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.7); 8.07 (dd, 1 H, H(5), $J_{5,6}$ = 8.2, $J_{5,7}$ = 1.5); 7.66—7.70 (m, 1 H, H(7)); 7.53—7.58 (m, 2 H, H(6), H(8)); 7.20—7.40 (m, 4 H, H(1′), H(2′), H(4′), H(5′)); 2.39 (s, 3 H, Me).

3-[(4-Methoxyphenylimino)methyl]chromane-2,4-dione (2c). Pale yellow powder, m.p. 249—250 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 13.75 (d, 0.7 H, NH, $J_{NH,H(9)}$ = 13.9); 11.94 (d, 0.3 H, NH, $J_{NH,H(9)}$ = 14.4); 8.93 (d, 0.3 H, H(9), $J_{H(9),NH}$ = 14.4); 8.79 (d, 0.7 H, H(9), $J_{H(9),NH}$ = 13.9); 8.14 (dd, 0.3 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 2); 8.08 (dd, 0.7 H, H(5), $J_{5,6}$ = 8.21, $J_{5,7}$ = 1.5); 7.52—7.65 (m, 1 H, H(7)); 7.22—7.35 (m, 4 H, H(6), H(8), H(2′), H(6′)); 6.97 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 9.24); 3.84 (s, 3 H, OCH_3). Mass spectrum, m/z (I_{rel} (%)): 279 $[M]^+$ (80). Found (%): C, 73.14; H, 5.16; N, 5.07. $C_{17}H_{13}NO_3$. Calculated (%): C, 73.11; H, 4.69; N, 5.02.

3-[(4-Bromophenylimino)methyl]chromane-2,4-dione (2d). White crystals, m.p. 249—250 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 13.57 (d, 0.76 H, NH, $J_{NH,H(9)}$ = 13.3); 11.8 (d, 0.24 H, NH, $J_{NH,H(9)}$ = 14.4); 8.88 (d, 0.24 H, H(9), $J_{H(9),NH}$ = 14.4); 8.79 (d, 0.76 H, H(9), $J_{H(9),NH}$ = 13.3); 7.89—8.06 (m, 1 H, H(5)); 7.47—7.61 (m, 3 H, H(7), H(2′), H(6′)); 7.13—7.34 (m, 4 H, H(6), H(8), H(3′), H(5′)). Mass spectrum, m/z (I_{rel} (%)): 344 $[M]^+$ (100). Found (%): C, 55.19; H, 2.61; N, 3.79. $C_{16}H_{10}BrNO_3$. Calculated (%): C, 55.84; H, 2.93; N, 4.07.

3-[(4-Nitrophenylimino)methyl]chromane-2,4-dione (2e). Yellow powder, m.p. 308—310 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 13.77 (d, 0.7 H, NH, $J_{NH,H(9)}$ = 13.1); 12.0 (d, 0.3 H, NH, $J_{NH,H(9)}$ = 13.8); 9.04 (d, 0.3 H, H(9), $J_{H(9),NH}$ = 13.8); 8.92 (d, 0.7 H, H(9), $J_{H(9),NH}$ = 13.1); 8.36 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 9); 8.11 (dd, 0.3 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.8); 8.08 (dd, 0.7 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.5); 7.74 (m, 1 H, H(7)); 7.48 (d, 2 H, H(2′), H(6′), $J_{3',2'}$ = 9); 7.16—7.41 (m, 2 H, H(6), H(8)). Mass spectrum, m/z (I_{rel} (%)): 310 $[M]^+$ (100). Found (%): C, 62.03; H, 3.17; N, 25.82. $C_{23}H_{15}NO_3$. Calculated (%): C, 61.94; H, 3.25; N, 25.78.

3-[(9*H*-Fluoren-2-ylimino)methyl]chromane-2,4-dione (3). Yellow powder, m.p. 300—302 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 14.53 (d, 0.7 H, NH, $J_{NH,H(9)}$ = 13.8); 12.75 (d, 0.3 H, NH, $J_{NH,H(9)}$ = 14.4); 9.76 (d, 0.3 H, H(9), $J_{H(9),NH}$ = 14.4); 9.64 (d, 0.7 H, H(9), $J_{H(9),NH}$ = 13.8); 8.85 (dd, 0.3 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.5); 8.78 (dd, 0.7 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.5); 7.54 (d, 1 H, H(4′), $J_{4',3'}$ = 8.2); 7.48 (dd, 1 H, H(5′), $J_{3',4'}$ = 7.2, $J_{5',6'}$ = 1.5); 8.22—8.37 (m, 3 H, H(7), H(1′), H(8′)); 7.92 (m, 5 H, H(6), H(8), H(3′), H(6′), H(7′)); 4.66 (s, 2 H, H(9′)). Mass spectrum, m/z (I_{rel} (%)): 353 $[M]^+$ (100). Found (%): C, 78.29; H, 4.07; N, 3.88. $C_{23}H_{15}NO_3$. Calculated (%): C, 78.17; H, 4.28; N, 3.96.

3-(Benzyliminomethyl)chromane-2,4-dione (4).[12] White crystals, m.p. 165—167 °C (*cf.* lit. data[12]: m.p. 167—168 °C). ^{1}H NMR (200 MHz, $CDCl_3$, δ,, J/Hz): 12.30 (m, 0.7 H, NH); 10.50 (m, 0.3 H, NH); 8.66 (d, 0.3 H, H(9), $J_{H(9),NH}$ = 14.9); 8.49 (d, 0.7 H, H(9), $J_{H(9),NH}$ = 13.8); 8.07 (dd, 0.3 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.07); 8.08 (dd, 0.9 H, H(5), $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.5); 7.55—7.66 (m, 1 H, H(7)); 7.42—7.53 (m, 2 H, H(6), H(8)); 7.20—7.40 (m, 5 H, H(1′), H(2′), H(3′), H(4′), H(5′)).

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