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Unusual *E*/*Z*-isomerization of 7-hydroxy-4-methyl-8-[(9*H*-fluoren-2-ylimino)methyl]-2*H*-1-benzopyran-2-one in acetonitrile

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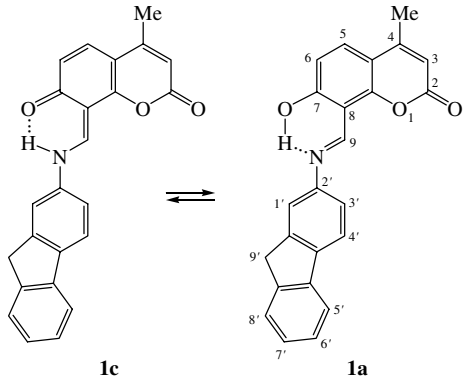
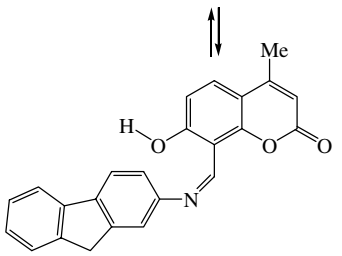
The title compound has an *E*-configuration in a solid state but undergoes *E*/*Z*-isomerization in an acetonitrile solution.

We found an unusual isomerization of 7-hydroxy-4-methyl-8-[(9*H*-fluoren-2-ylimino)methyl]-2*H*-1-benzopyran-2-one **1**.‡

The IR spectrum of **1** in KBr pellets exhibits absorption bands at 1630, 1715 and 3424 cm^{-1}, which correspond to the CH=N group, the pyrone ring and the OH function, participating in the intramolecular H-bonding in accordance with the structure of *E*-hydroxyimine **1a**.



1c *Z*-ketoenamine ⇌ **1a** *E*-hydroxyimine



1b *Z*-hydroxyimine

In the ^{1}H NMR spectrum of **1** in $CDCl_3$, the signal of OH protons is observed at 15.1 ppm and the signal of the methyne (CH=N) proton is seen at 9.3 ppm. In the spectrum there is no signal of the NH proton. The low-field region of the spectrum of imine **1** contains several multiplets, which correspond to nine aromatic protons. Their assignment was made with the use of a COSY DQF experiment. The signals of coumarin fragment protons are observed as two doublets at 6.9 and 7.8 ppm (5-H and 6-H) and two singlets at 6.2 (3-H) and 2.4 ppm (4-Me). The signals of fluorene fragment are located at 7.3–7.4 (m, 6′-H and 7′-H), 7.5–7.6 (m, 3′-H and 5′-H), 7.7 (s, 1′-H) and 7.9–8.0 ppm (m, 4′-H and 8′-H). Sterical interaction of 9-H with 1′- and 3′-protons is seen from the NOE experiment (Figure 1).

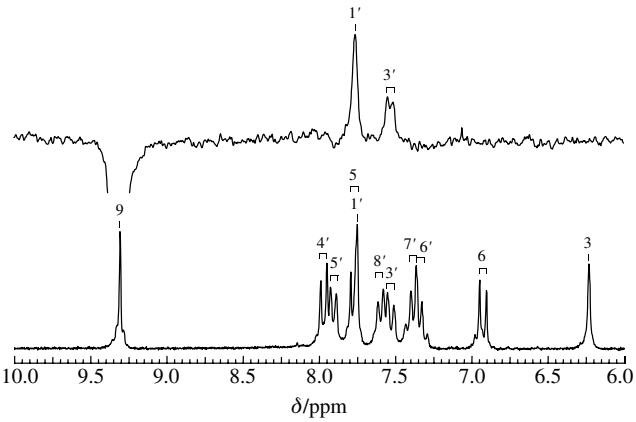


Figure 1 Interaction of 1′-H and 3′-H with 9-H in the ^{1}H NMR NOE experiment.

Note that spectral data of imine **1** do not change with time when recorded in $CDCl_3$. However, its electron absorption spectrum definitely transforms when imine **1** is dissolved in acetonitrile. EA-spectral curves of imine **1** are shown in Figure 2 at different intervals of time after its dissolution in MeCN. One can see that the absorption maximum moves to shorter wavelengths with larger intervals of time: the hypsochromic shift of the λ_{max} is about 50 nm.

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‡ ^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200 MHz). IR spectra were measured on a Specord M-80 spectrophotometer. Electron absorption spectra were obtained on a Specord M-400 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter. Mass spectrum was recorded on a GCQ mass spectrometer at an electron energy of 70 eV and 200 °C. Quantum-chemical calculations were performed by the PM3 and ZINDO/S methods.

A mixture of 8-formyl-7-hydroxy-4-methylcoumarin (2 g, 0.01 mol), 2-aminofluorene (1.8 g, 0.01 mol) and anhydrous ethanol (10 ml) was heated for 2 h. Then, the reaction mixture was cooled until a precipitate was formed. The precipitate was filtered off, dried and recrystallized from ethanol to give compound **1**: yellow crystals, yield 72%, mp 246–247 °C, R_f 0.69. ^{1}H NMR ($CDCl_3$) δ: 6.18 (s, 1H, 3-H), 2.46 (s, 3H, 4-Me), 7.81 (d, 1H, 5-H, $J_{5,6}$ 8.96 Hz), 6.93 (d, 1H, 6-H, $J_{6,5}$ 8.96 Hz), 9.35 (s, 1H, CH=N), 15.00 (s, 1H, 7-OH), 4.01 (s, 2H, CH_2), 7.30–7.92 (m, 7H, 1′-H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H). IR (ν/cm^{-1}): 1715 (α-pyrone), 1630 (CH=N). UV [λ_{max}/nm (lg ε)]: 472 (3.62). MS, *m*/*z* (%): 367 (56). Found (%): C, 78.28; H, 4.71; N, 3.85. Calc. for $C_{24}H_{17}NO_3$ (%): C, 78.47; H, 4.63; N, 3.81.

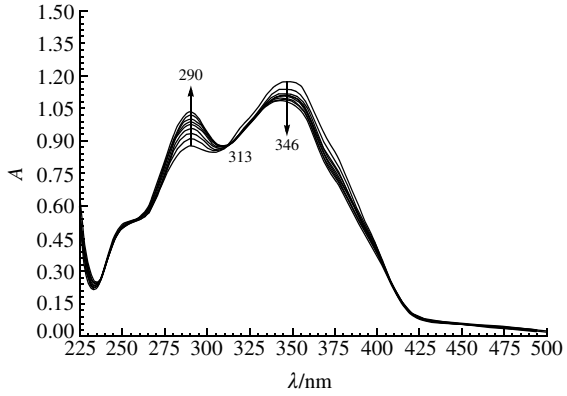

Figure 2 Electron absorption spectra of imine **1** in MeCN at different intervals of time (4–24 min).

Similar changes of the electron absorption spectra are seen when imine **1** is dissolved in DMF–DMSO mixtures containing from 100% DMF to 100% DMSO. This spectral behaviour of imine **1** can be explained by a monotonic change of its geometry, for example, due to rotation of imine fragments around the C_{Ar}–N bond. However, such an explanation disagrees with several isosbestic points, which are seen in the curves (Figure 2). These points illustrate an equilibrium between two definite isomers.

Geometric isomers **1a** and **1b** seem to be equilibrated forms of imine **1**, which explain its spectral properties. This conclusion is in accordance with quantum-chemical calculations of the electron absorption spectra (Table 1). By ZINDO/S calculations, transformation of *E*-isomer **1a** into *Z*-isomer **1b** should lead to the hypsochromic shift of the longest wavelength band absorption maximum as we see in the experimental spectrum. Suggestion of the *E*-hydroxyimine **1a** isomerization into *Z*-ketoenamine **1c** does not agree with the calculated results: by ZINDO/S, **1a** → **1c** isomerization should result in the significant bathochromic shift of the longest wavelength band absorption maximum (Table 1). However, due to evident sterical hindrance in the planar *Z*-hydroxyimine structure, one can suggest that the acetonitrile-induced **1a** → **1b** transformation leads to the sterically crowded *Z*-configuration of imine **1b**.

Isomeric transformations of imine **1** in acetonitrile can also be seen in the electron emission spectra. Fluorescent spectral curves of imine **1** are shown in Figure 3 at different intervals of time after its dissolution in acetonitrile. One can see that an emission maximum moves to shorter wavelengths with larger intervals of time: a hypsochromic shift of the λ_{max} is about the same as in the electron absorption spectra.

There are some examples of *E*/*Z*-isomerization of imines at the CH=N bond due to their interaction with solvent.[1,2] The inversion mechanism of *E*/*Z*-isomerization of imines provides significant decrease of the energy barrier when compared with that of alkene *E*/*Z*-isomerization.[3,4] For example, equilibrium of *E*- and *Z*-isomers of the merocyanine form of 5′-hydroxy-1,3,3-trimethylspiro(indoline-2,3′-[3*H*]naphtho[1,2-*b*][1,4]oxazine) was found at –50 °C in $CDCl_3$.[5]

Table 1 Quantum-chemical calculations (ZINDO/S) of formation energies ΔH_f and λ_{max} of tautomers in the electron absorption spectra of imine **1**.

Tautomer	ΔH/kcal mol^{-1}	λ_{max}/nm
1a	2.69	293.0 (1.0), 274.0 (0.35), 238.0 (0.55)
1b	5.86	288.0 (1.0), 254.0 (0.55)
1c	0.59	402.8 (0.75), 321.4 (1.0), 264.8 (0.6)

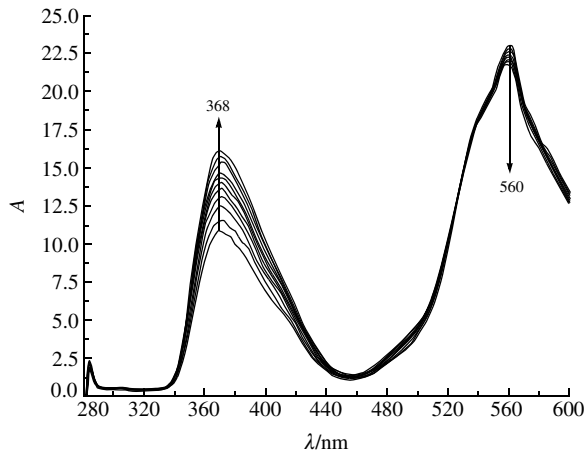

Figure 3 Fluorescent spectra of imine **1** in MeCN at different intervals of time (9–31 min).

Using PM3 quantum-chemical calculations, we found that interaction with acetonitrile as a solvent leads to the non-planarity of imine **1** and then to its *E*/*Z* isomerization. Thus, the use of acetonitrile controls the isomeric transitions of imine **1** at the CH=N bond. These structural transformations due to noncovalent substrate–solvent interactions are of interest with respect to the self-assembly of molecules in supramolecular chemistry.[6,7]

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