



## Unusual Behaviour of 7-Diethylamino-3-(3,4-ethylen-dioxybenzoyl)coumarin Towards Group IIA Cations: A Potential Photoactive Probe for Magnesium

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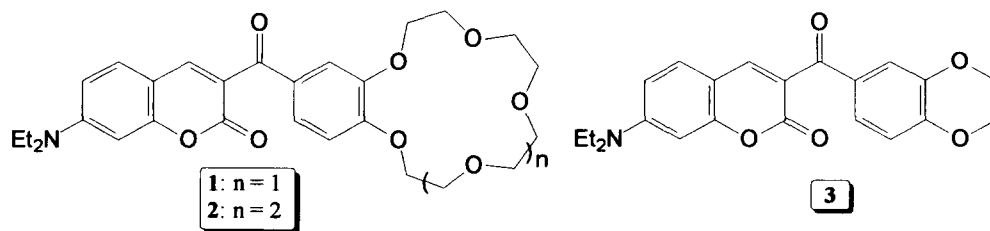
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**Abstract:** The titled compound showed, upon spectrophotometric titrations with Group IIA cations, a spectacular bathochromic shift (*c.a.* 50 nm) with  $Mg^{2+}$  but not with the other cations. This result is understood in terms of internal charge-transfer species expressly favored by  $Et_2N$  and ArCO substituents and best matching of ionic diameter and charge density of  $Mg^{2+}$ . This finding may lead to new simple photoactive probes. © 1997 Elsevier Science Ltd.

The coumarin nucleus has been the focus of our recent research concerning photoactive compounds and luminescent probes. We are currently investigating how the suitable attachment of several complexing systems (crown ethers, aminopolycarboxylic units, etc.) to coumarins can render useful photoactive compounds, namely bioaffinity-assay markers,<sup>1</sup> fluorescence signalling systems,<sup>2</sup> triplet sensitizers for lanthanide luminescence, etc.<sup>3</sup> Some of the studied compounds so far did in fact display useful emission properties which resulted strongly dependent on metal ions and coumarin substitution.

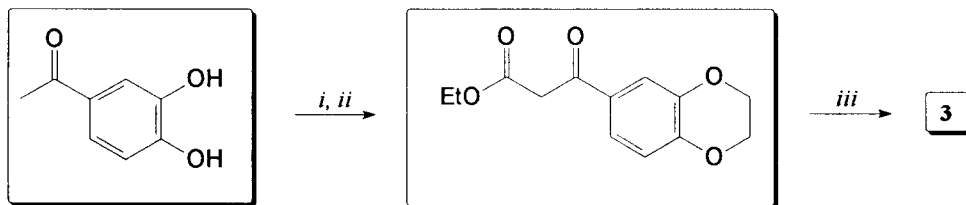
In the course of our research on the complexation properties of crown ethers attached to coumarins we found that compounds **1** and **2** (Scheme I) gave UV-vis spectra, upon spectrophotometric titrations with Group IIA cations, which were compatible with the presence of a mixture of two different complexes of 1:1 stoichiometry, in which the cation is complexed respectively to the carbonyl groups or to the crown ethers. Data suggested that the complex formed through the crown is less important for **2** than for **1**.



Scheme I

To scrutinize the role played by the crown rings in these systems we then prepared 7-diethylamino-3-(3,4-ethylenedioxybenzoyl)coumarin (**3** in Scheme I), in which the 1,4-dioxane moiety would mimic the electronic effects exerted by the corresponding crown rings to the 3-aryl coumarin nucleus in **1** and **2**. We found, and hereby describe, the very unusual spectroscopic conduct of **3** when it complexes with Group IIA cations, especially magnesium. Its surprising behaviour may lead to a new series of simple compounds, easy to prepare, with potential application as photoactive probes for cations of group II.

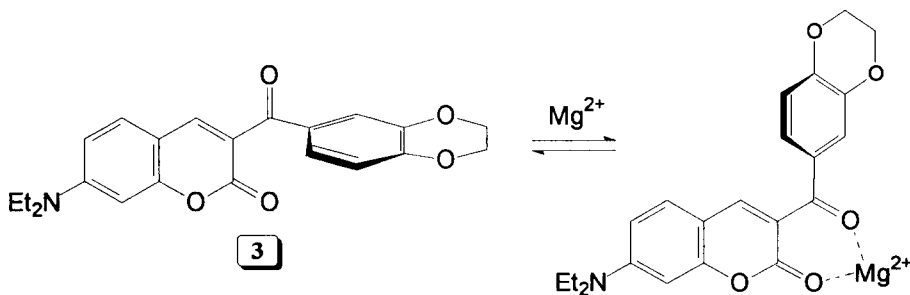
Synthesis of compound **3**<sup>4</sup> was straightforward and accomplished as shown in Scheme II.



Scheme II

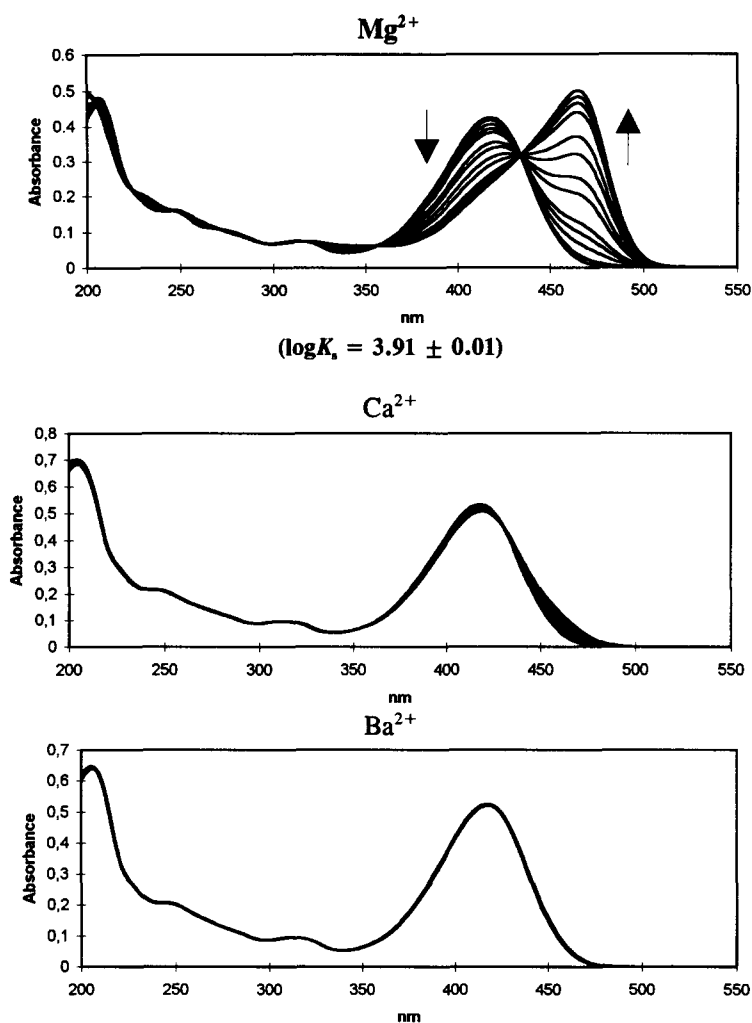
*Reagents and conditions:* *i*) 1,2-Dibromoethane,  $\text{Na}_2\text{CO}_3$ /acetone (60°C, 12h); *ii*) NaH, diethylcarbonate/THF (reflux, 1.5h); *iii*) 4-Diethylaminosalicylaldehyde, piperidine/ethanol (reflux, 2h).

Figure 1 shows the spectrophotometric titrations<sup>5</sup> of **3** with the Group IIA cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ . The spectacular bathochromic shift (*c.a.* 50 nm) shown by **3** with  $\text{Mg}^{2+}$ , but not with the other cations, should be the result of the equilibrium displayed in Scheme III.<sup>6</sup>



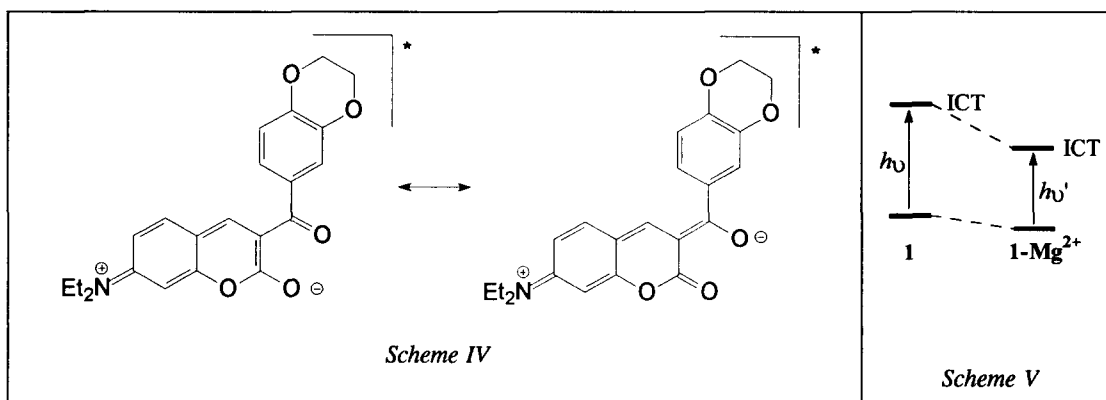
Scheme III

It is known that coumarins bearing an electron-donor substituent (as  $\text{Et}_2\text{N}$ ) at 7-position gives an excited state whose electronic structure can be at least partially described as internal charge-transfer (ICT) species (Scheme IV).<sup>7</sup> This ICT is even more favored when, in addition to the lactone carbonyl group, there exists a second strong electron acceptor ( $\text{ArCO}$ ) in 3-position of the coumarin ring.<sup>8</sup>



*Figure 1*

The complex of **3** with  $\text{Mg}^{2+}$ , presumably formed through the two carbonyl groups (Scheme III), should stabilize both ground and ICT states but the stabilization of the latter should be much higher to be compatible with the strong bathochromic shift observed (Scheme V). The selectivity of this phenomenon towards  $\text{Mg}^{2+}$  strongly supports the co-operation of both carbonyl groups in the chelation and should be attributed to the best matching of ionic diameter (1.32 Å) and charge density ( $3.03 \text{ q } \text{Å}^{-1}$ )<sup>9</sup> of  $\text{Mg}^{2+}$  compared to the other Group IIA metals.



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#### References and Notes

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- M.p. 121°-123°C; <sup>1</sup>H-NMR 200-MHz (CDCl<sub>3</sub>) δ (ppm): 8.01 (s, 1H), 7.42 (d, 1H, *J*=2.0 Hz), 7.39 (dd, 1H, *J*=2.0, 8.2 Hz), 7.35 (d, 1H, *J*= 8.9 Hz), 6.9 (d, 1H, *J*=8.2 Hz), 6.61 (dd, 1H, *J*=2.5, 8.9 Hz), 6.51 (d, 1H, *J*=2.5 Hz), 4.33-4.26 (m, 4H), 3.46 (q, 4H, *J*=7.1 Hz), 1.24 (t, 6H, *J*=7.1 Hz); MS (EI<sup>+</sup>): 379 (M<sup>+</sup>, 70%), 364 (M<sup>+</sup>-CH<sub>3</sub>, 100%), 351 (M<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>), 336 (M<sup>+</sup>-CH<sub>3</sub>-C<sub>2</sub>H<sub>4</sub>, 10%), 163 (ethylendioxiphenylCO<sup>+</sup>, 43%); Elemental analysis calcd. for C<sub>22</sub>H<sub>21</sub>NO<sub>5</sub>: C, 69.66%, H, 5.54%, N, 3.69%; Found: C, 69.47%, H, 5.32%, N, 3.54%.
- To 2.5 mL of a solution 3.210<sup>-5</sup> M of 3 in acetonitrile, portions of 2 μL (0.25 equivalents) of a solution 10<sup>-2</sup> M of metal perchlorate (previously dried over phosphorous pentoxide) in acetonitrile were added and the absorption spectrum recorded for each addition. *K<sub>a</sub>* was obtained by non-linear regression analysis.
- Conformers are depicted similar to those predicted by AM1 calculations as the most stable ones.
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