

New 2*H*-chromen-2-one derivatives potentially utilizable as memory media

Radoslav Flašík, Henrieta Stankovičová,* Jana Donovalová, and Anton Gáplovský

*Institute of Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH2, 842 15
Bratislava, Slovakia, stankovh@fns.uniba.sk*

Abstract

New coumarin derivatives, 2-oxo-2*H*-chromencarbaldehyde hydrazones were prepared. Photochromic and thermochromic properties of prepared compounds were investigated.

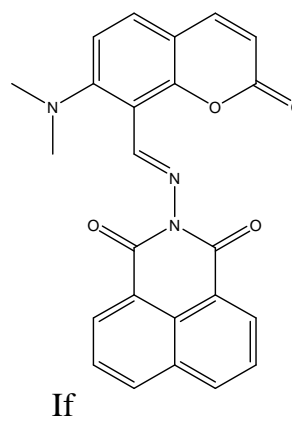
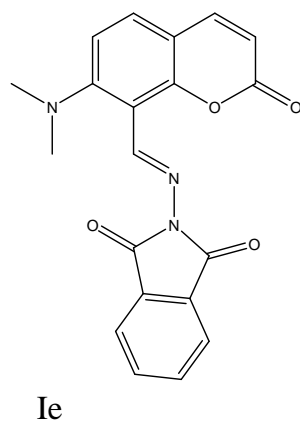
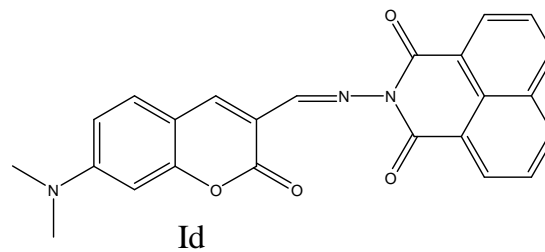
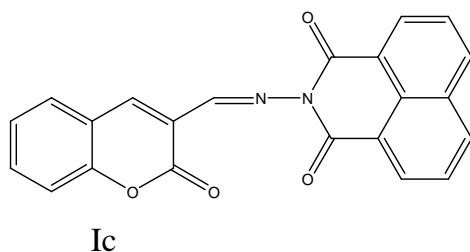
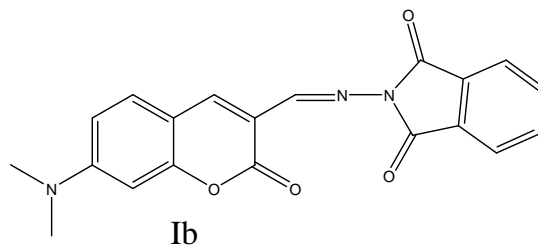
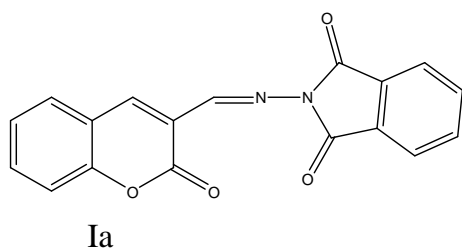
Introduction

Information technology has revolutionized daily life and the continuously increasing amount of data to be stored and manipulated strongly stimulated the search for switching and memory elements as tiny as a single molecule. Molecular switches can be converted from one state to another by an external stimulus such as light, temperature, electricity or a chemical reaction. The operation of any optically controlled device is critically dependent upon the efficiency of light absorption by the input chromophore, and its ability to undergo electron transfer. Three characteristics make an excellent input chromophore: a large extinction coefficient, long-lived excited state, and a high fluorescence quantum yield.

Results and discussion

The aim of this work was to synthesize new coumarin derivatives with C=N double bond, which can potentially be used as a memory media. Isomerization around C=N double bond can serve as a process on which the molecular switch is based.¹

New coumarin derivatives, 2-oxo-2*H*-chromencarbaldehyde hydrazones Ia-f, were prepared by reaction of substituted 2-oxo-2*H*-chromencarbaldehydes with various *N*-aminoimides in ethanol in the presence of *p*-toluenesulfonic acid as catalyst in 45-73 % yield. It was found according to UV-VIS absorption spectra that the formed compounds are trans isomers.



We have investigated photochromic and thermochromic properties of prepared compounds. The study was carried out in polar (methanol) as well as nonpolar (toluene) media. It was found that isomerization around C=N bond takes place. *E-Z* isomerisation undergoes with ultraviolet light. This isomerization is a reversible process. The back *Z-E* isomerization occurs photochemically with the visible light in polar and in non-polar solvent and thermally only in non-polar solvent. It is possible to conclude, that some of prepared compounds can potentially be used as memory media. Basic requirement for this use is good photochromic behaviour of prepared compounds in more organized systems. This study should be the next step of research.

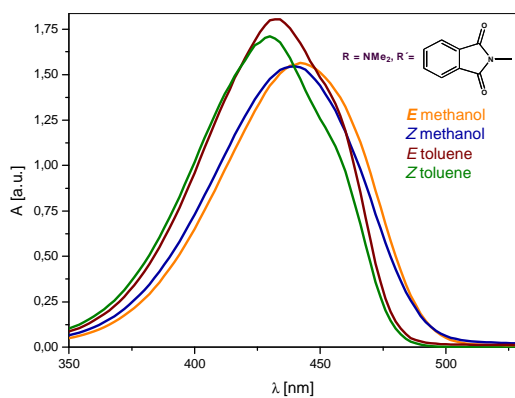


Fig. 1 UV-VIS spectra of isomers in various solvents

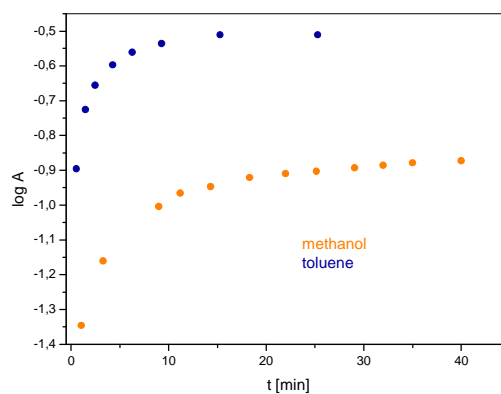


Fig. 2 Time change of absorbance due to reaching equilibrium state

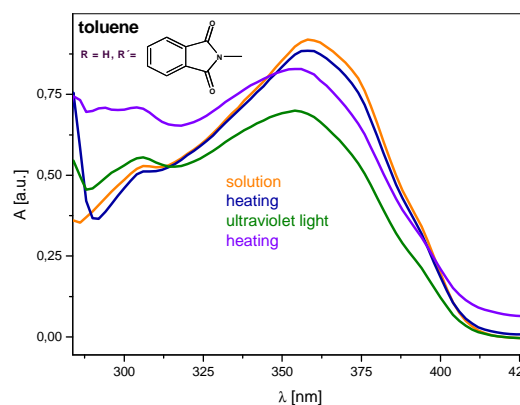
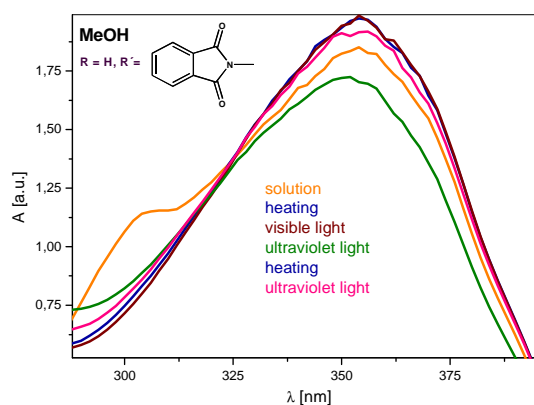


Fig. 3a, 3b Change of UV-VIS spectra (E-Z and Z-E isomerisation)

General experimental procedure

Starting materials

Chemicals were purchased from the major chemical suppliers as highest purity grade. 2-Oxo-2*H*-chromen-3-carbaldehyde² and 7-*N,N*-dimethyl-2-oxo-2*H*-chromen-3-carbaldehyde³ were prepared according to literature procedures. 7-*N,N*-Dimethyl-2-oxo-2*H*-chromen-8-carbaldehyde was prepared by Vismeyer-Haack formylation of 7-*N,N*-dimethyl-2*H*-chromen-2-one.

2-oxo-2H-chromenecarbaldehyde hydrazones

Aldehyde (0.46 mmol) was dissolved in 10 mL of hot ethanol. *N*-Aminoimide (0.46 mmol) was added to the solution and after its dissolution a crystal of *p*-toluenesulfonic acid was added to the reaction mixture. The mixture was refluxed for 15 minutes. After cooling, the precipitate was filtered off, washed with ethanol, dried and recrystallized from ethanol.

Acknowledgements

This work was supported by Slovak Grant Agency (Grant No 1/0639/08).

References

1. Gáplovský, A.; Donovalová, J.; Lácová, M.; Mračnová, R.; El-Shaar, H.M. *J. Photochem. Photobiol. A: Chem.* **2000**, *136*, 61-65.
2. Ito, K.; Nakajima, K. *J. Heterocyclic Chem.* **1988**, *25*, 511-515.
3. Kirpichenok, M.A.; Baukulev, V.M.; Karandashova, L.A.; Grandberg, I.I. *Khim. Geterosikl. Soedin.* **1991**, *11*, 1480-1487.