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The photochemical behaviour of 6-X-4H-3(bicyclo[2.2.1]-5-heptene-2,3-dicarboximidoiminomethyl)-4-chromones. Photochromism and thermochromism

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Abstract

The photochemical behaviour of 6-X-4H-3(bicyclo[2.2.1]-5-heptene-2,3-dicarboimidoximinomethyl)-4-chromones (X=CH_3, Cl, NO_2) was studied upon irradiation ($\lambda_{irr}\cong$310 nm) in CH_3OH and benzene. Direct *E–Z* or *Z–E* photoisomerization and thermal *Z–E* isomerization were observed. The activation energies of *Z–E* isomerization were in the range 8.7–69.5 kJ mol^{-1}. Prolongation of the irradiation of the title compounds till the equilibrium is reached between *E* and *Z* isomers results in the irreversible process. The products of this irreversible process were identified. Fluorescence emission and excitation spectra were measured.

Keywords: Chromones; Photochromism; Thermochromism

1. Introduction

Compounds with the exocyclic C=N bond as well as the C=C and N=N bonds respectively undergo the isomerization. The conversion from one isomer to the other can be initiated by light or by temperature [1–6]. In the case that *E–Z* isomerization is reversible photochemical process and both isomers have different absorption spectra, this phenomenon is called photochromism [7].

Besides *E–Z* isomerization about the C=N double bond, the possibility of conformer and tautomer formation should be considered in dependence on the structure of fragments. Structure of the fragment adjacent to C=N double bond can effect photochemical or thermal reactivity of the compounds with photochromic properties. In this paper, we describe the photochemical system where photochromism depends on the geometric isomerization of substituted 6-X-4H-3(bicyclo[2.2.1]-5-heptene-2,3-dicarboximidoiminomethyl)-4-chromones (Scheme 1). The photochemical reactivity of these compounds and thermochromism were studied.

2. Experimental details

2.1. General methods

All photolysis experiments were carried in quartz spectrophotometric cell using the filtered irradiation ($\lambda\cong$310 nm) from an UVP, Inc. Chromato VUE transilluminator, Model TM-15 or unfiltered light using from an Osram halogen lamp (150 W) in degassed methanol or benzene under nitrogen at room temperature. The course of photolysis was monitored by UV/VIS spectrophotometer HP 8452A Array spectrophotometer. After irradiation, the reaction mixture was concentrated under vacuum and analysed by gas chromatography. GC analysis of the samples was performed on a Helwett–Packard (HP) (Palo Alto, CA, USA) 5890A Series II gas chromatograph equipped with split–splitless injector (300°C, splitting ratio 1:30, splitless time 1′). Helium (TATRAGAS, 99.95%) was used as the carrier gas (inlet pressure 50 kPa). The injection volume was 1 μl. An HP 5890A Series II gas chromatograph interfaced to an HP 5917A mass-selective detector with an HP MS Chemstation data system was used for identification of the GC components. The column used was a cross-linked fused-silica capillary column (10 m×0.32 mm i.d.) coated with poly-

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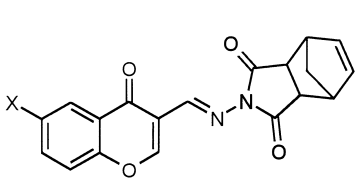
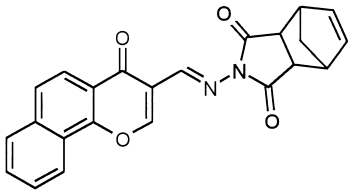


(I) X = Cl;

(II) X = CH_3;

(III) X = NO_2;



(IV)

Scheme 1. Structure of studied compounds.

dimethylsiloxane (0.20 μm phase thickness). The oven temperature was programed from 40 to 320°C at 15°C min^{-1}. The temperatures of the isolation chamber and of the transfer line were 180 and 280°C, respectively. The electron energy was 70 eV. Mass spectra and reconstructed total ion chromatograms were obtained by automatic scanning in the mass range *m*/*z* 45–450 at 2.2 scans s^{-1}. UV spectra were recorded with HP 8452A Array spectrophotometer. IR spectra were measured in KBr using a Perkin–Elmer 781 Infrared Spectrophotometer. H-NMR spectra were recorded in $CDCl_3$ with VARIAN GEMINY 2000 (300 MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. Elemental analysis were performed with Carlo–Erba CHN 1106.

2.2. Materials

Methanol and benzene (spectroscopic grade, Merck) were used as solvents. The study compounds 6-X-4H-3(bicyclo [2.2.1]-5-heptene-2,3-dicarboximidoimino-methyl)-4-chromones (I–IV) were synthetized according to the following procedure: Solution of *N*-aminobicyclo[2.2.1]-5-heptene-2,3-dicarboximid (10 mmol) in small amount of ethanol was added to ethanol solution of 6-X-3-formylchromones (10 mmol) and catalytic amount of *p*-toluenesulfonic acid (0.1 mmol). The mixture was stirred at the room temperature for 2 h. The solid compound was separated, washed with diethylether and recrystallized from xylene. The yields of the products I–IV were: (I) 58%; (II) 67%; (III) 60%; (IV) 85%.

The physical and spectroscopic data of compounds I–IV are as follows.

Compound (I): m.p. 224–225°C; IR (KBr) 1615, 1637, 1710, 1775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.57 (1H, d, *J*=3.6 Hz), 1.78 (1H, d, *J*=3 Hz), 3.36 (2H, dd, *J*=2.7, 1.5 Hz), 3.50 (2H, s), 6.23 (2H, t, *J*=1.93, 1.64 Hz), 7.47 (1H, d, *J*=8.79 Hz), 7.65 (1H, dd, *J*=9.06, 2.47 Hz), 8.22 (1H, d, *J*=2,48 Hz), 8.72 (1H, s), 9.18 (1H, s). Analysis calculated for $C_{19}H_{13}ClN_2O_4$: C, 61.88%; H, 3.55%; N, 7.60%; Cl, 9.61%. Found: C, 61.79%; H, 3.56%; N, 7.44%; Cl, 9.78%.

Compound (II): m.p. 212–214°C; IR (KBr) 1620, 1643, 1703, 1769 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.57 (1H, d, *J*=3 Hz), 1.77 (1H, d, *J*=2.9 Hz), 2.47 (3H, s), 3.36 (2H, dd, *J*=0.8, 0.5 Hz), 3.49 (2H, s), 6.23 (2H, t, *J*=1.64 Hz), 7.39 (1H, d, *J*=8.52 Hz), 7.51 (1H, dd, *J*=8.52, 2.2 Hz), 8.03 (1H, d, *J*=1.4 Hz), 8.71 (1H, s), 9.16 (1H, s). Analysis calculated for $C_{20}H_{16}N_2O_4$: C, 68.96%; H, 4.63%; N, 8.04%. Found: C, 69.08%; H, 4.64%; N, 8.05%.

Compound (III): m.p. 295°C; IR (KBr) 1625, 1645, 1710, 1755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58 (1H, d, *J*=9.06 Hz), 1.79 (1H, d, *J*=8.8 Hz), 3.37 (2H, dd, *J*=7.7, 1.1 Hz), 3.51 (2H, s), 6.63 (2H, d, *J*=3.3 Hz), 7.68 (1H, d, *J*=9.3 Hz), 8.55 (1H, dd, *J*=9.3, 2.7 Hz), 8.76 (1H, s), 9.12 (1H, d, *J*=2.74), 9.25 (1H, s); Analysis calculated for $C_{19}H_{13}N_3O_6$: C, 60.16%; H, 3.45%; N, 11.07%. Found: C, 59.97%; H, 3.41%; N, 11.02%.

Compound (IV): m.p. 229–231°C; IR (KBr) 1620, 1640, 1723, 1787 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.57 (1H, d, *J*=9.15 Hz), 1.78 (1H, d, *J*=8.79 Hz), 3.37 (2H, dd, *J*=2.74, 1.65 Hz), 3.51 (2H, s), 6.24 (2H, s), 7.18 (1H, m), 7.53 (1H, d, *J*=9 Hz), 7.65 (1H, m), 7.78 (1H, m), 7.92 (1H, d, *J*=7.9 Hz), 8.12 (1H, d, *J*=9 Hz), 8.75 (1H, s), 9.29 (1H, s). Analysis calculated for $C_{23}H_{16}N_2O_4$: C, 71.87%; H, 4.20%; N, 7.29%. Found: C, 71.54%; H, 4.33%; N, 7.14%.

3. Results and discussion

The study compounds absorb UV light in the range 220–430 nm. The absorption maximum is red shifted with increasing polarity of solvent by a few nanometer. This absorption corresponds to π,π^* band which overlap n,π^* band. Effect of substituents on the position of long-wavelength absorption is given in Table 1.

Substitution of phthalimide by NH–Ph fragment in the molecule has much more influence on absorption spectra (λ_{max}=355 nm in CH_3OH). This change of absorption spectra can be caused by the different electron-donor ability of both fragments on CH=N double bond. The fluorescence emission of the study compounds has a very low intensity in the range of λ=350–550 nm (Fig. 1). Maximum of

Table 1
Basic characteristics of the absorption and fluorescence spectra of I, II, III and IV in methanol

Compound	Absorbance		Fluorescence, λ_{max} (nm)
	λ_{max} (nm)	$\log \varepsilon$ (l mol cm^{-1})	
I	348[a]	3.76	435
	311	4.13	
	261	4.18	
II	308	4.15	424
	260	4.28	
III	330	4.19	421
	314	4.19	
IV	326[a]	4.07	436[a]
	292	4.37	398
	226	4.36	

[a] Shoulder.

the fluorescence emission is red shifted with decreasing electron-donor ability of the substituent.

Intensity of fluorescence emission in benzene is lower compared to that of methanol and increases with decreasing temperature. We were also interested to find out which part of the structure I–IV is important for the observed fluorescence. Spectra of parent chromone aldehydes were also measured. The fluorescence of I, II, III and IV compared to the fluorescence of corresponding chromone aldehydes has nearly the same position and shape (Fig. 2); only the intensity of fluorescence is different. For example, the intensity of the fluorescence of 6-methyl-3-formylchromone is 20 times higher than intensity of the fluorescence of II. From the foregoing it follows that the fluorescence occurs from the singlet state which is localised on the chromone fragment of II. The fluorescence spectrum of *N*-aminobicyclo[2.2.1]-5-heptene-2,3-dicarboximid is blue shifted ~60 nm compared to II or 6-methyl-3-formylchromone, respectively (Fig. 2).

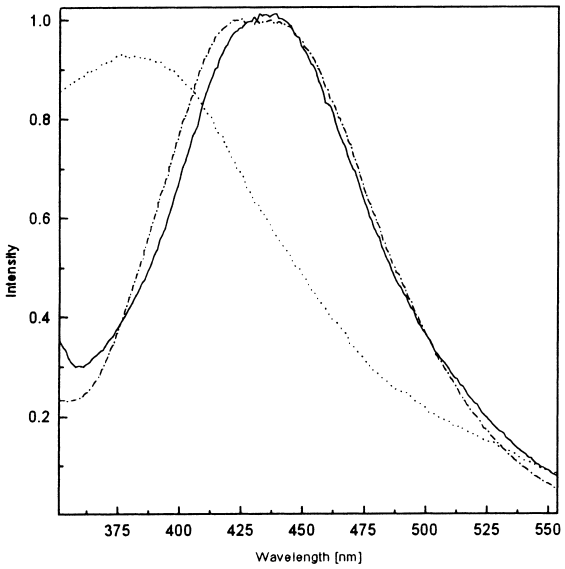


Fig. 2. Fluorescence emission spectra (λ_{ex}=310 nm) of II (—) correspond 6-methyl-3-formylchromone (---) and *N*-aminobicyclo[2.2.1]-5-heptene-2,3-dicarboximid (. . .).

Excitation spectra of the chromones depend on the wavelength of the emission (Fig. 3). Changes in excitation spectra are caused by the photolability of the *E*-isomer as well as the presence of their conformers in the solution which can be stabilized by intramolecular interactions as the interaction of H in position 2 of chromone fragment or H of HC=N

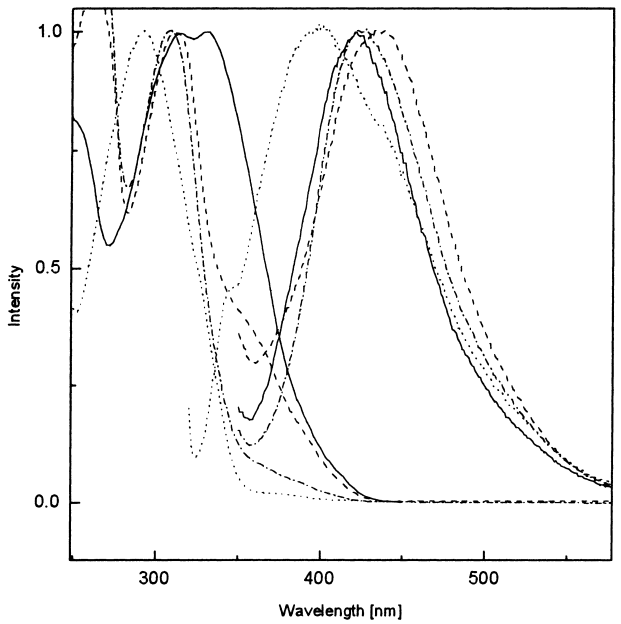


Fig. 1. Fluorescence emission and absorption spectra of the *E*-isomers of I (- -), II (---), III (—) and IV (. . .) in methanol (λ_{ex}=310 nm).

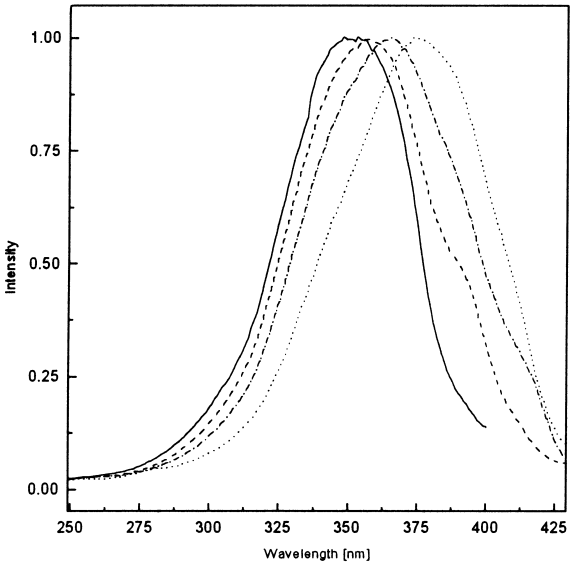
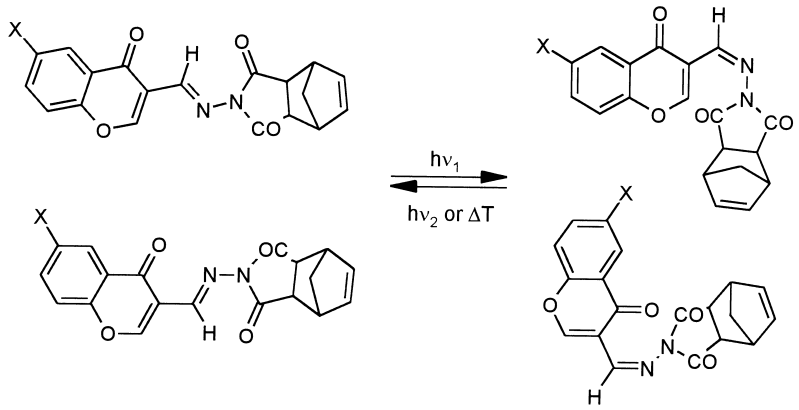


Fig. 3. Fluorescence excitation spectrum of the *E*-isomer of I in methanol [$\lambda_{em=}$420 nm (—), 450 nm (- - -), 480 nm (---), 540 nm (. . .)].



Scheme 2.

with C=O of chromone or phthalimide fragments, respectively (Scheme 2). UV irradiation of the studied compounds at $\lambda \cong 310$ nm in CH_3OH or benzene at the room temperature causes the blue shift of the absorption maximum as well as decreases in the absorption of long-wavelength band (Fig. 4). The change of long-wavelength absorption corresponds to *E–Z* geometric isomerization about the C=N double bond. This isomerization is a reversible process. The back *Z–E* isomerization occurs photochemically with the visible light in the polar (e.g. CH_3OH) or in the non-polar solvent (e.g. benzene) and thermally only in polar solvent. The molecular structure or substituent has a very small effect on the photochemical isomerization compared to thermal, where the effect is substantial.

We have also calculated the activation energies of the studied non-photochemical *E–Z* isomerization (Table 2). As can be seen from Table 2, the activation entropy is enhanced in the same direction as the activation energy. The negative activation entropies show that the transition state is less organized than initial state [8]. The change of the activation entropy cannot be explained by steric hindrance of the substituent. The major contribution has internal rotation entropy, which characterizes intramolecular rotation about the bonds in molecule.

Table 2
Thermodynamic data of the *Z–E* isomers of I, II, III and IV in methanol

Compound	$\Delta E^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
I	40.4	−133.2
II	50.9	−105.5
III	8.7	−236.4
IV	69.5	−54.5

The solvatation ability and polarity of the solvent play important role in the thermal isomerization. Contrary to

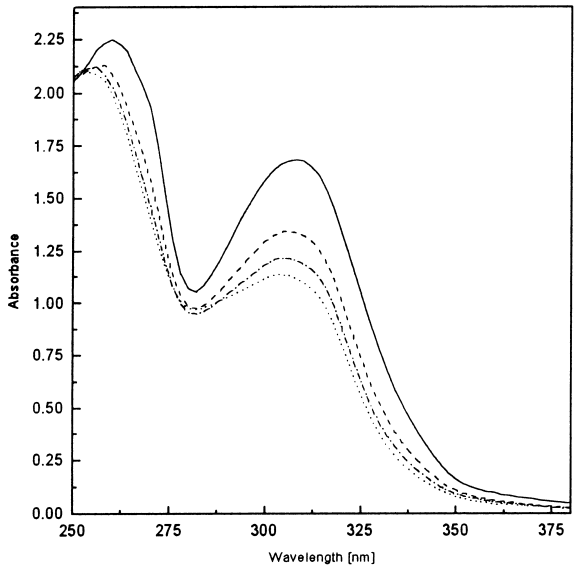


Fig. 4. UV spectrum of the *E*-isomer of II in methanol ($c=10^{-4}$ mol dm^{-3}) at the different time [s] of irradiation. 0 (—); 5 (- -); 10 (-·-); 600 (. . .).

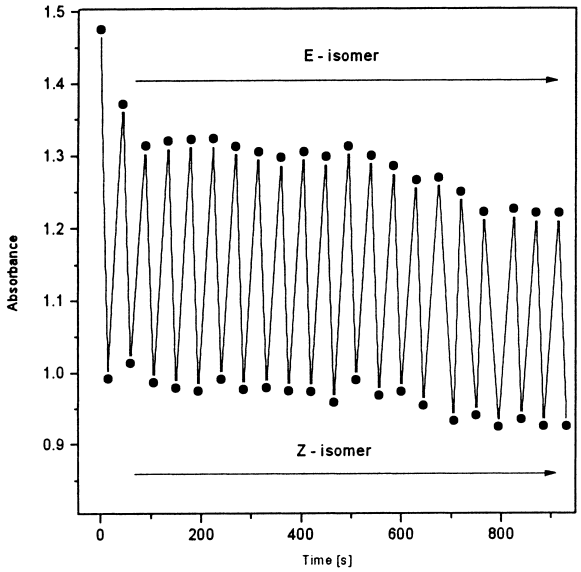


Fig. 5. Change of UV absorbance ($\lambda=308$ nm) of II after alternate irradiation by UV light (310 nm, $\Delta=15$ s) and VIS light (halogen lamp, $\Delta=30$ s) in CH_3OH.

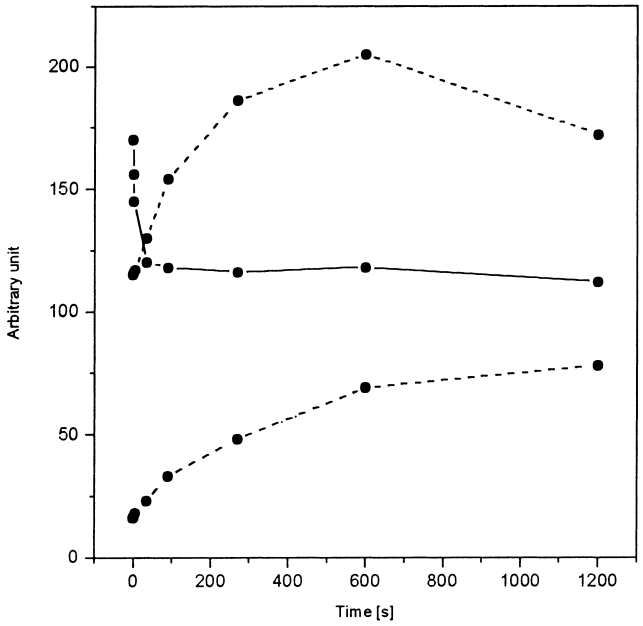


Fig. 6. Changes of absorption (λ=308 nm, —), emission (λ=350 nm, - - -) and excitation (λ=300 nm, -·-·-) spectra of II in methanol in dependence of the time of irradiation.

thermal isomerization in CH_3OH, thermal isomerization in benzene was not observed in the range 19–58°C. The long-wavelength absorption in UV spectra is blue shifted by ∼4 nm (λ_{max}=310 nm) in benzene compared to CH_3OH. Optimalization of the geometry of *E* and *Z* isomers by Hyperchem 3 confirms the assumption that these isomers are not planar. *E* and *Z* isomers have chromone fragment and C=N bond in one plane and phthalimide fragment is out of this plane. The lone pair of nitrogen of the *Z*-isomer can interact with p-electrons of phthalimide carbonyl group [9,10]. Substituent X effects the strength of the interaction. The strength of this interaction increases the thermal stability of the *Z* isomer. Light of the halogen lamp which is absorbed by the *Z*-isomer has enough energy to initialize *Z–E* isomerization in benzene.

The change of absorption of the *E*-isomer occurs very fast upon UV irradiation. After ∼15 s irradiation, the equilibrium of the *E* and *Z* isomers is reached in both solvent. Applying the light of the halogen lamp on the equilibrium mixture, *Z–E* isomerization occurs and the absorption returns to the initial state. This process was repeated many times (Fig. 5). Prolongation of irradiation (λ≅310 nm, *t*=50 min) has a small effect on the UV spectra. *Z–E* isomerization does not occur upon VIS irradiation at this stage of the reaction. UV absorbance as well as intensity of fluorescence decrease during the photochemical *E–Z* isomerization. Intensity of the fluorescence enhances with prolongation of the irradiation contrary to the intensity of UV absorbtion. The changes of absorption, emission and excitation spectra are depicted in Fig. 6. It follows from the spectral changes that after the *E–Z* equilibrium is reached the other photochemical changes occur. They are irreversible. We cannot decide if *E* or *Z* isomer undergoes to the additional photochemical conversion. The proof cannot be reached by separation methods as GC, HPLC either because the equilibrium process between *E–Z* isomers is so fast to compared with competitive photochemical reactions.

Abstraction of hydrogen from the carbon of CH=N group by the C=O of phthalimide fragment and α-cleavage is possible from photochemical point of view. In the reaction mixture was identified 3-cyanochromone, 6-X-3-formylchromone, bicyclo[2.2.1]-5-heptene-2,3-dicarboximid, *N*-aminobicyclo[2.2.1]-5-heptene-2,3-dicarboximid and another compounds, which can be products of the non-photochemical reactions.

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