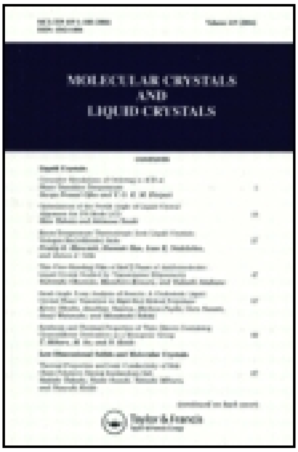

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NOVEL PHOTOCHROMIC 2H-CHROMENES WITH π–DONOR SUBSTITUENTS IN THE 2H-PYRAN RING

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Abstract A series of novel photochromic 2H-chromenes containing the ethynyl or ethoxy groups in position 4 (I, II) and an annelated pyrrole ring (III, IV) have been synthesized and their spectral and photochromic properties studied. The chromenes I - IV are characterized by high rates of thermal bleaching reaction in liquid solutions at room temperature. Longwave absorption bands of the chromenes I have their maxima at 295-308 nm, whereas their photoisomers absorb at $\lambda_{max} = 437$ nm (glassy isopentane-isopropanol, 4:1 solvent, T<200 K). For the type chromenes III, IV the longwave absorption bands are found in the regions of $\lambda_{max} = 323$-325 nm (ring-closed form A) and $\lambda_{max} = 675$-678 nm (ring-opened form B).

INTRODUCTION

2H-Chromenes continue attracting attention as important components of diverse variable transmission materials. An important modification of their structure and, thus, spectral properties is associated with annelation of pyridine and pyrazine rings to the benzene ring of a 2H-chromene unit [1].

In the present work we report on the synthesis and spectral study of novel 2H-chromenes in which a heterocyclic moiety is annelated with 2H-pyran ring of 2H-chromenes.

EXPERIMENTAL

Absorption spectra of the compounds I - IV were recorded on a spectrophotometer "Specord UV - VIS" (Germany) equipped with a device for irradiation on the base of a 250 W high-pressure mercury lamp (DRSH-250), glass filters being employed. The lamp flash photolysis device described in [2] was used. IR spectra were recorded on a Specord

IR-75 instrument. H^1 NMR spectra were obtained on a Varian XL-100 (100 MHz) and UNITY-300 (300 MHz) instruments with HMDS as an internal standard.

2,3-dimethyl-4-ethoxy-2H-1-benzopyran (I). A Grignard compound prepared from magnesium (1.6 g, 0.066 mole) and methyl iodide (4.2 ml, 0.066 mole) in anhydrous diethyl ether (50 ml) has been added dropwise within 10 minutes to a suspension of 4-ethoxychromilium perchlorate (12.5 g, 0.043 mole) in 50 ml of anhydrous ether cooled by ice-water. The reaction mixture was stirred during 10 minutes at room temperature and then a saturated solution of ammonium chloride was added to the mixture. The ether layer was separated, dried with sodium sulfate and the solvent removed by evaporation. The oily product obtained was distilled in vacuum to give I (8g) as a colorless liquid in 90% yield); b.p. 128-130°C (2 torr). IR spectrum (ν, cm $^{-1}$) : 1655 (C=C), 1605 (arom.), 1245 (C-O-C). H^1 NMR spectrum (δ, ppm, CCl_4): 1.2 (m, 6H, 2-CH_3 and OCH_2CH_3); 1.25 (d, 3H, J 6.8 Hz, 2-Me); 1.68 (s, 3H, 3-Me); 3.70 (q, 2H, J 7.3 Hz, OCH_2CH_3); 4.7 (q, 1H, J 6.8 Hz, 2-H); 6.5-7.2 (m, 4H, arom). Found % : C 76.61, H 6.72. $C_{13}H_{16}O_2$ requires % C 76.44; H 7.89.

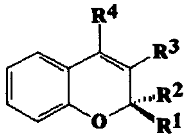
2-Methylamino-2-phenyl-3-methyl-4-phenylethynyl-2H-1-benzopyran (II) was prepared from 2-phenyl-3-methyl-4-phenylethynyl-1-benzopyrylium perchlorate by a treatment with an excessive amount of methylamine in acetonitrile. The compound was isolated in 71% yield on the solvent evaporation and recrystallization from acetonitrile-isopropanol (1:1) mixture. M.p. 128-129 °C. IR spectrum (ν, cm $^{-1}$) :3340 (NH), 1607, 1594, 1260, 1240. H^1 NMR spectrum (δ, ppm, $CDCl_3$): 1.84 (s, 3H, CH_3), 2.0 (s, 1H, NH), 2.31 (s, 3H, NCH_3), 6.87-7.74 (m, 14H, arom.). Found %: C 85.43; H 5.89; N 3.78. $C_{25}H_{21}NO$ requires %: C 85.44; H 6.02; N 3.99.

2,4-Diphenyl-3,5-dimethyl-2H-chromeno[3,4-b]-pyrrole (III) 2-Phenyl-3-methyl-4-phenylethynyl-1-benzopyrylium perchlorate was treated with an excessive amount of methylamine in ethanol, and then the reaction mixture was refluxed within a few hours. After evaporation of the solvent solid residue was recrystallized from mixture of ethanol and acetonitrile (1:1) to give III in 50% yield. M.p. 170-171 °C. IR spectrum (ν, cm $^{-1}$) 1600, 1554, 1527, 1500, 1207. H^1 NMR spectrum (δ, ppm, $CDCl_3$): 2.28 (s, 3H, CH_3), 3.06 (s, 3H, NCH_3), 6.33 (s, 1H, H^2), 6.63-7.59 (m, 14H, arom.). Found %: C 85.21; H 5.87; N 3.46. $C_{25}H_{21}NO$ requires % : C 85.44; H 6.02; N 3.99.

2,4-Diphenyl-3-methyl-2H-chromeno[3,4-b]-pyrrole (IV) was prepared as described in a previous procedure from 2-phenyl-4-phenylethynyl-1-benzopyrylium perchlorate. The yield of IV was 60%. M.p.153-154 °C (from an acetonitrile-isopropanol mixture). IR spectrum (ν, cm $^{-1}$) 1600, 1567, 1554, 1500, 1200. H^1 NMR spectrum (δ, ppm, $CDCl_3$): 3.30 s (3H, NCH_3), 6.45 (s, 1H, H^2), 6.55 (s,1H, H^5), 6.75-7.45 (m, 14H, arom.). Found %: C 85.55; H 5.76; N 3.90. $C_{24}H_{19}NO$ requires % : C 85.44; H 5.68; N 4.15.

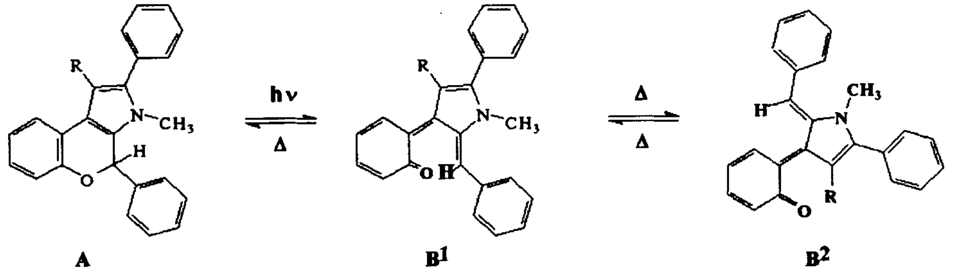
RESULTS AND DISCUSSION.

The 2H-chromenes I,II with electron releasing substituents in the 4th position of the 2H-pyran ring and III, IV with a fused pyrrole ring are characterized by longwave absorption bands with the maxima in the spectral regions of 295-310 and 323-325 nm respectively (Table 1).



I: $R^1 = H$; $R^2 = R^3 = CH_3$; $R^4 = OC_2H_5$

II: $R^1 = NHCH_3$; $R^2 = Ph$; $R^3 = H$; $R^4 = C{\equiv}CPh$



III: R = H; IV: R = CH_3

Unlike derivatives of 2-aminochromenes [1] the compounds I - IV in their ground state are stable in the ring-closed form A and do not reveal. No photocoloration of the solutions of I-IV is observed under illumination of solutions of I-IV at room temperature with the UV-light. However flash-photolysis of a solution of I in toluene results in an appearance of a transient absorption band with λ_{max} about 430 nm and lifetime τ = 5 ms which characteristics are typical for the metastable type B cisoid B^1 species[1] (Figure 1.).

TABLE 1. Spectral characteristics of the chromenes I-IV (isopentane-isopropanol, 4:1, 77 K)

Compound	λ_{max}^{A}, nm	λ_{max}^{B}, nm
I	308	437
II	295	-
III	325	411, 678
IV	323	407, 675

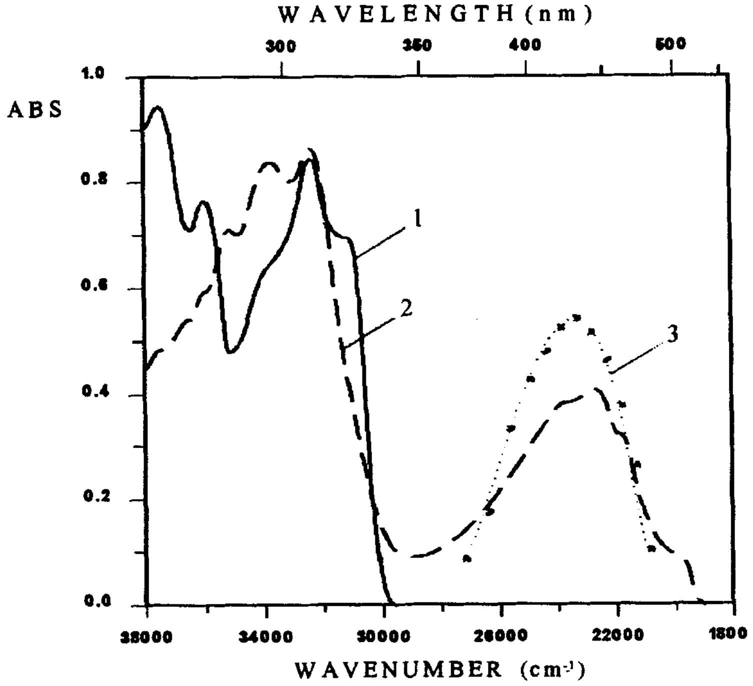


FIGURE 1. Absorption spectra of a isopentane-isopropanol, 4:1 solution of chromene I ($c = 6.3 \cdot 10^{-5}$ M, T = 165 K) before (1) and after irradiation (313 nm) for 2000 s; transient absorption spectra recorded upon 10^{-6} s lamp exitation of toluene solution of chromene I ($c = 6.3 \cdot 10^{-5}$ M, T=295 K) at the 10^{-6} s after the end of the pulse.

The same band arises under prolonged continuous UV- irradiation of a glassy solution of **I** at low temperature (T = 166 K), when the rate of dark bleaching reaction is low enough to make the isomeric **B** detectable. However, no photoisomerization was observed at 77 K. This observation points to an appreciable potential barrier in the excited state for the C_{sp} -O-bond cleavage leading to the formation (Figure 1) of the type **B** isomers. No photocoloration of the compound **II** was observed in the whole of the temperature interval, from room temperature to 77 K.

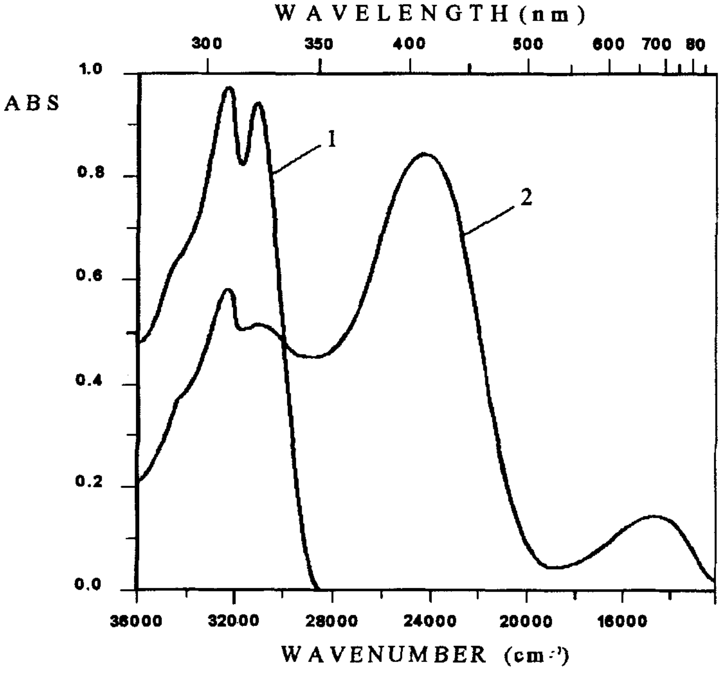


FIGURE 2. Absorption spectra of a isopentane-isopropanol, 4:1 solution of chromene **IV** ($c = 4.2 \cdot 10^{-5}$ M, T = 77 K) before (1) and after irradiation (313 nm) for 8500 s.

A continuous UV-irradiation of glassy solutions (T = 77K) of chromenes **III, IV** gives rise to the formation of photoproducts possessing two absorption bands (λ_{max} = 405-415 nm and 670-680 nm). These two bands originate, most probably, from electronic transitions in two different isomers of the photoproduct **B**, i.e. $\mathbf{B}^1$ (cis) and $\mathbf{B}^2$ (trans) respectively (Figure 2, Table 1). This suggestion is corroborated by that the ratio the absorbances in λ_{max} of $\mathbf{B}^1$ and $\mathbf{B}^2$ changes with the time of irradiation. The longer is the time of irradiation, the higher is the absorbance of the longer-wave absorbing species, presumably $\mathbf{B}^2$. Noteworthy is also that in the photostationary state, relative intensity of the $\mathbf{B}^2$-isomer in **III** is twice higher than that for the compound **IV**, in which case steric conditions for the formation of $\mathbf{B}^2$ are less favorable.

This interpretation of the origin of the absorption bands of the photocolored **B**-form in chromenes **III** and **IV** is confirmed by the results of study of 2-aminochromenes where distinct long-wave absorption bands for configurational isomers of the photoinduced quinoneaminoallydes [2,3].

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