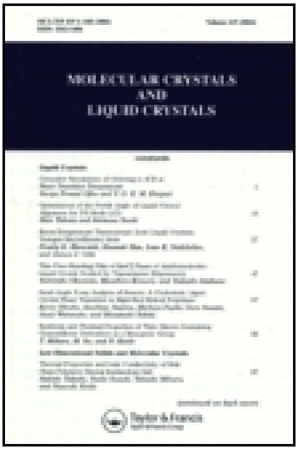

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic Behavior of Isochromenes (1H-Benzopyrans) as Studied by Transient Absorption Spectroscopy

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To cite this article: Eisuke Haba, Katsunori Segawa & Hirochika Sakuragi (2000): Photochromic Behavior of Isochromenes (1H-Benzopyrans) as Studied by Transient Absorption Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 221-226

To link to this article: http://dx.doi.org/10.1080/10587250008023922

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 221-226
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Photochromic Behavior of Isochromenes (1*H*-Benzopyrans) as Studied by Transient Absorption Spectroscopy

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3-Phenyl- and 3-(2-naphthyl)isochromene show light-intensity-dependent photochromic behavior; the excitations with low- and high-intensity laser pulses produce isomeric open forms by way of one-photon and two-photon processes, respectively, their lifetimes being in the hundred-nanosecond and hundred-microsecond orders, respectively.

Keywords: Isochromenes; Photochromism; Transient absorption spectroscopy; Two-color laser photolysis

INTRODUCTION

Organic photochromic materials have been extensively studied from the view point of potential applications in optical data storage and optical switching [1,2]. Chromenes (2*H*-benzopyrans), the simple models of spirobenzopyrans, are among the well studied photochromic compounds [3–5]; however, photochemical behavior of isochromenes (1*H*-benzopyrans) has not received much attention [6,7]. Recently, we have found that 3-arylisochromenes show light-intensity-dependent two-photon two-step photochromic behavior. Upon excitation with low- and high-intensity laser pulses, the isochromenes underwent a C-O bond cleavage to give isomeric open forms with short and long lifetimes, respectively. The two isomeric open forms were found to be photochemically interconverted.

3-Phenyl isochromene (3PI) and 3-(2-naphthyl)isochromene (3NI) were prepared by an intramolecular Wittig reaction with sodium *t*-amylate of [*o*-(benzoyloxymethyl)phenylmethyl]- and [*o*-(2-naphthoyloxymethyl)-phenylmethyl]triphenylphosphonium bromide, respectively, which were prepared from the corresponding sodium aroates and [*o*-(bromomethyl)-phenylmethyl]triphenylphosphonium bromide [8]. 3-Phenyl-1*H*-naphtho[2,3-*c*]pyran (3PN) was prepared in a similar way from 2,3-di(bromomethyl)naphthalene and sodium benzoate.

3PI: mp 119–120 °C (lit. 122–124 °C [7]); UV (cyclohexane) λ_{max} 326 nm (ε 17000), 236 (17000); ^{1}H NMR ($CDCl_3$): δ 5.22 (s, 2H, CH_2), 6.47 (s, 1H, =CH), 7.0–7.8 (m, 9H, phenyl H).

3NI: mp 164–166 °C; UV (cyclohexane) λ_{max} 337 nm (ε 16000), 240 (23000); ^{1}H NMR ($CDCl_3$): δ 5.29 (s, 2H, CH_2), 6.61 (s, 1H, =CH) 7.1–7.9 (m, 10H, aryl H), 8.23 (s, 1H, aryl H).

3PN: mp 210–211 °C; UV (cyclohexane) λ_{max} 333 nm (ε 28000), 246 (22000), 238 (22000); ^{1}H NMR ($CDCl_3$): δ 5.37 (s, 2H, CH_2), 6.63 (s, 1H, =CH) 7.3–7.9 (m, 11H, aryl H).

Cyclohexane and acetonitrile (Dojin, spectrograde) were used as received as solvents.

Laser-flash photolyses were performed using an excimer laser (Lambda Physik LPX-100, XeCl, 308 nm, 10-ns fwhm, 90 mJ/pulse) and a pulsed xenon arc (Ushio UXL-159, 150 W) as a monitoring light source. The laser pulses in the 390- and 425-nm regions were supplied from an excimer laser (Lambda Physik Lextra, XeCl, 308 nm)-pumped dye laser (Lambda Physik Scanmate; dye: QUI, 10-ns fwhm, 10 mJ/pulse in the 390-nm region and Stilbene 3, 10-ns fwhm, 10 mJ/pulse in the 425-nm region).

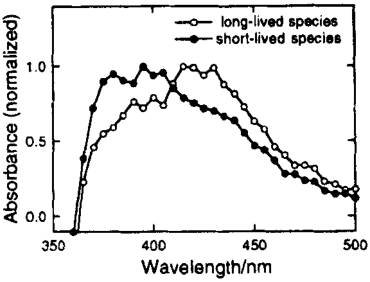
Molecular orbital calculations (PM3-CI) of the potential energy surfaces for C-O bond cleavage and C-C double bond twisting (*Z*-*E* isomerization) were carried out [9]. In the bond cleavage the molecular structure was optimized for every 2 nm increase in the C-O distance from the closed form to the open (*Z*)-form, and in the double bond twisting for every 15 degrees from *Z* to *E*, at the SCF calculation. The CI calculation includes complete active space configurations constructed from the four highest occupied and the four lowest unoccupied MO's of the ground configuration.

RESULTS AND DISCUSSION

Light Intensity Dependent Photochromic Behavior

Pulsed laser excitation of 3-phenylisochromene (3PI) in a low concentration (5×10^{-4} mol dm^{-3}) in cyclohexane at 308 nm (ca. 4 mJ/pulse) under argon exhibited an absorption band with a lifetime of 200 ns around 400 nm (λ_{max} ca. 390 nm), at the longer wavelength region than did the original 3PI, as shown in Figures 1 and 2. The spectral profile and the decay rate were neither affected under air in cyclohexane nor under argon in acetonitrile. In comparison with the photochromic behavior of chromenes [3,7], the present absorption band can be reasonably assigned to an open keto-form of 3PI.

Upon photolysis of 3PI (1×10^{-4} mol dm^{-3}) with laser pulses of much higher intensity (ca. 40 mJ/pulse), a longer-lived component (lifetime: 500 μs) appeared in almost the same but slightly longer wavelength region (λ_{max} ca. 425 nm; Figures 1 and 2). This component increased with increasing light intensity, and the spectral intensity showed a nearly second-order dependence on the light intensity. The short- and long-lived components can be attributed to the isomeric open forms, (*Z*)- and (*E*)-forms, respectively (Scheme 1); the former may be produced directly by photocleavage of the original closed form, and the latter from photoisomerization of the (*Z*)-form through a biphotonic process within the duration of a laser pulse.



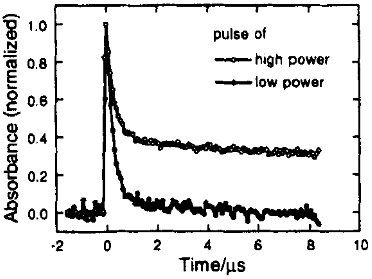
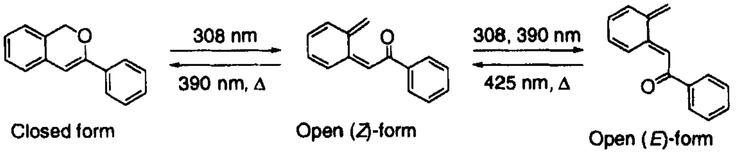


FIGURE 1 Absorption spectra of a short- and a long-lived species observed on laser photolysis of 3PI in cyclohexane.

FIGURE 2 Time profiles of the transient absorptions monitored at 420 nm on laser photolysis of 3PI with different laser powers.



Scheme 1

The activation energy for ring closure of the open (Z)-form was calculated to be 29 kJ mol^{-1} (log (A/s^{-1}) = 11.6) from the decay rate constants obtained by monitoring the transient absorption band at 390 nm in the range of 10–40°C. This value is close to the activation energies for ring closure of the open forms of 2,2-dipheny- and 2,2,4-triphenylchromenes (29–34 kJ mol^{-1}) [10].

3-(2-Naphthyl)isochromene (3NI) showed a light-intensity-dependent photochromism similar to that of 3PI; the two open forms of 3NI exhibited the absorption spectra in the wavelength region at 380–500 nm (λ_{max} 400–425 nm) with lifetimes of 300 ns and 200 μs.

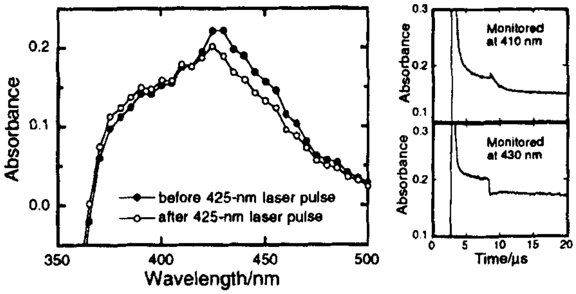


FIGURE 3 Spectral change and time profiles observed on excitation at 425 nm of the long-lived species generated from the 308-nm photolysis of 3PI in cyclohexane.

However, 3-phenyl-1*H*-naphtho[2,3-*c*]pyran showed no bond cleavage upon 308-nm laser excitation. The excitation energy of the naphthopyran might be insufficient for the C-O bond cleavage.

Two-Color Laser Excitation

When the short- and long-lived species generated from the 308-nm photolysis of 3PI were excited with 390- and 425-nm laser pulses, respectively (two-color laser photolysis), rapid spectral changes were observed. For the short-lived species ((*Z*)-form) a bleaching of the absorption band and a recovery around 320 nm were observed. These observations indicate that the (*Z*)-form cyclizes not only thermally but also photochemically. The excitation of the long-lived species ((*E*)-form) exhibited a decrease and an increase in spectral intensity at 420-450 and 370-420 nm, respectively (Figure 3). This spectral change could be attributed to an isomerization of the (*E*)-form to the (*Z*)-form followed by the ring closure (Scheme 1).

Two-color laser photolyses of 3NI (308 nm + 395 nm and 308 nm + 425 nm for the short- and long-lived species, respectively) showed photochemical behavior essentially identical with that of 3PI.

Energy Surfaces of Photochromic Reactions

In order to determine the energy surfaces of C-O bond cleavage and C-C double bond twisting (*Z*-*E* isomerization) of 3PI, PM3-CI calculations were carried out. The open (*Z*)- and (*E*)-forms are located at 137 and 123 kJ mol^{-1} higher levels over the closed form, the (*E*)-form being 14 kJ mol^{-1} more stabilized than the (*Z*)-form. The energy barriers to the ring closure of the (*Z*)-form and to the thermal *E*→*Z* isomerization were estimated to be 60 and 134 kJ mol^{-1}. As mentioned above, the activation energy for ring closure was experimentally determined to be 29 kJ mol^{-1}. The difference in lifetime of the open forms (200 ns and 500 μs) can be rationalized by the energy barriers between the closed and the open forms.

The calculations also indicated that the photochemical ring closure and *Z*-*E* isomerization are reasonable processes from the lowest excited singlet state (S_1) of the open forms. On the energy surface of the S_1 state, the energy minima are located at the geometry (M_1) with a C-O distance of ca. 19 nm and at the perpendicularly twisted geometry (M_2) of the open form. The decay from M_1 leads to the closed form or the (*Z*)-form, and that from M_2 to the (*Z*)- or the (*E*)-form, by way of the ground-state energy maximum, respectively.

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