TRANSIENT OPTICAL ABSORPTION SPECTROSCOPY
OF THE PHOTOCHEMICAL SPIROPYRAN–MEROCYANINE CONVERSION

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The photochemical ring-opening reaction of 1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] has been followed by transient absorption spectroscopy, covering the range 370–650 nm with a temporal resolution of 0.42 ps. During the pump pulse, induced transient absorption is observed only at wavelengths shorter than 500 nm, with a maximum near 440 nm. The absorption at 440 nm decays within ≈ 5 ps, while a broad absorption band appears at 550 nm in the region characteristic of merocyanine absorption. The risetime of the absorption at 550 nm is approximately 1.3 ps. The reaction is described as a barrierless photoisomerisation on the excited singlet potential energy surface towards a nonplanar cisoid form, followed by internal conversion and rapid attainment of planarity.

1. Introduction

Spiropyrans can exist in two basic forms: the colourless parent spiropyran structure and an intensely coloured merocyanine structure (fig. 1). The spiropyran structure consists of two orthogonal π-electron systems with little interaction, so that its absorption spectrum is essentially the superposition of the spectra of the constituent chromophores [1]. Upon excitation of the pyran chromophore in the UV, the bond between the spiro carbon atom and the oxygen atom is broken and the molecule can unfold. The π electrons can eventually conjugate over the entire structure, so that the corresponding absorption spectrum is displaced far to the red compared to that of the parent form.

The "photochromism" of the spiropyrans has been studied intensively (an excellent review up to 1969 is given in ref. [2]), not least because of hopes for practical applications. One important class of photochromic spiropyrans is derived from 1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline],commonly termed BIPS (cf. fig.2, structure I). Of the derivatives, 6-nitro-BIPS has been examined most thoroughly.

The following topical areas have emerged:

(i) *Distinction of merocyanine isomers* [3–5], and the photochemical distribution of these isomers;

(ii) *Participation of triplet states* in the photochemical reaction of nitro-substituted compounds [6,7];

(iii) *Photoinduced aggregation* of the coloured structure from 6-nitro-BIPS, mediated through triplet states [8];

(iv) *Description of reaction intermediates*. The existence of a primary photoproduct in which the C_{spiro}–O bond is broken, and which still possesses the orthogonal parent geometry, was originally proposed in ref. [9]. This hypothetical photoproduct was labelled X; its approximate geometry is shown as structure II in fig. 2. However, its spectral properties, its states and their lifetimes are poorly characterized at present. By definition, X should be the first photochemical reaction product prior to geometrical
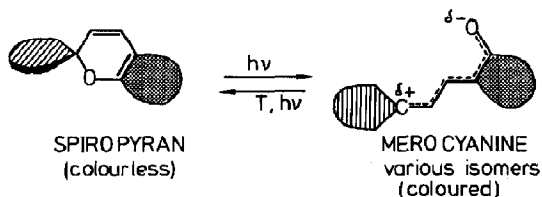

Fig. 1. General scheme for the photochromism of spiropyrans.

SPIROPYRAN
(colourless)
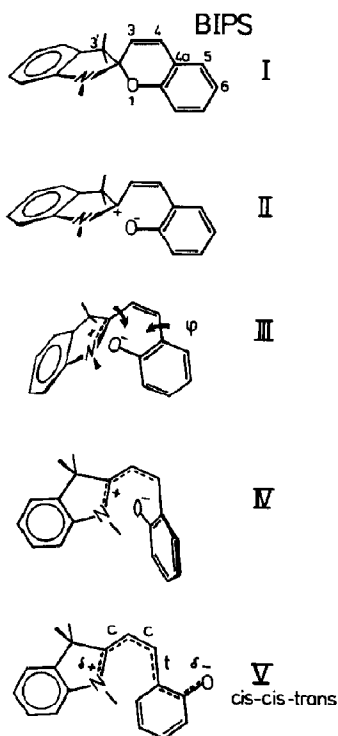
MEROCYANINE
various isomers
(coloured)

Fig. 2. The structure of BIPS (I), the hypothetical first photochemical reaction product X (II or III), the postulated non-planar cisoid intermediate (IV) and a merocyanine isomer (V). A possible photochemical reaction coordinate ϕ – twisting around the C_4–C_{4a} bond – is indicated.

change. Hence the most substantial evidence should come from the earliest spectral data after photolysis. Ref. [10] reported a transient absorption spectrum for 6-nitro-BIPS, taken 10 ps after UV excitation with 6 ps resolution. The spectrum consists of a dominant band centered at 440 nm and a weaker, red band at 585 nm. Both were attributed to X (in the ground state), although the red band resembles the merocyanine absorption into which the entire spectrum evolves. The decay of X was monitored at 440 nm, giving time constants of 30 and 300 ns. Other reports inferred the lifetime of X from the rise of merocyanine absorption, yielding values of 270 ps [8] or 22 ns [11]. Very weak phosphorescence from ^{3}X at 4.2 K was described in ref. [12], while an absorption at 430 nm with a decay time of 2 µs at room temperature was also attributed to ^{3}X [11].

The present study attempts to describe the early part of the photochemical conversion of a spiropyran into the corresponding merocyanine isomers. BIPS was chosen as a model compound because its photocoloration proceeds exclusively through singlet states [13]. Pump/probe absorption spectra were recorded at 0.33 ps intervals with 0.42 ps resolution, covering the photochemical reaction from its beginning up to 100 ps.

2. Experimental

2.1. The pump/probe absorption experiment

The pump/probe absorption experiment used a laser system combining an excimer laser with a colliding pulse mode (CPM) dye laser (see below). The pump pulse at 308 nm (with 360 µJ focused onto ≈ 3 mm^2) had a pulse duration of 0.24 ps. The probe continuum was generated over 1 mm of o-phosphoric acid [14], from a pulse at 616 nm (30 µJ, diffraction limited) of 0.150 ps duration.

The beam of white light was split into the probe beam proper and a reference beam. Both beams were focused onto the sample cuvette; the probe beam was superimposed by the copropagating pump beam. The pump pulse could be advanced in time, relative to the probe pulse, by translation of a mirror on a precision linear actuator. The probe and reference spots were imaged onto separate single quartz fibers which were fed into a spectrograph (Jobin–Yvon H25, 150 lines/mm) using adapting input optics. The probe beam was polarised at the magic angle relative to the pump polarisation by using a sheet polarisor after the sample cuvette. Probe and reference spectra were detected by two photodiode arrays which were intensified by a common multichannel plate (Princeton Instruments). A microcomputer controlled data acquisition and the relative delay between the pump and probe pulses. For each setting of the time delay, 100 separate spectra were recorded at 10 Hz and averaged numerically.

The temporal resolution is determined by the cross-correlation width of the pump pulses at $\lambda_1 = 308$ nm, with a spectral component at λ_2 of the white probe pulse. The cross-correlation was measured using two-photon absorption in neat benzene (for $\lambda_2 \leqslant 500$ nm) or ground-state bleaching of malachite green in

ethanol (for $\lambda_2 > 500$ nm). The cross-correlation width (fwhm) was less than 0.42 ps for all probe wavelengths.

An experimental time reference was provided by the peak of the cross-correlation at any probe wavelength λ_2. The cross-correlation peaks occurred simultaneously (within our time resolution) for $\lambda_2 > 430$ nm; this is taken as reference time zero. For shorter wavelengths, the peaks were shifted continuously to negative times due to residual dispersive effects: the shift amounted to -0.33 ps for $\lambda_2 = 395$ nm and -0.67 ps for $\lambda_2 = 370$ nm. This has to be borne in mind during the discussion of the spectral evolution.

BIPS was synthesized as in ref. [15]. A solution in ethanol (0.40×10^{-2} molar) was used in a 0.5 mm cuvette, giving an optical density of 0.84 at 308 nm.

2.2. The laser system

The CPM dye laser has the same design as in ref. [16] and was built from modular components (FSU Jena-Laserinstruments). It was pumped by 1.1 W at 514 nm, and produced 100 fs pulses at 616 nm. High stability was achieved through operation in the proper stability regime [17]. The output was amplified [18] in modified capillary prismatic dye cells using the first discharge channel of a XeCl* excimer laser with two channels (Lambda Physik EMG 150). A prism (de-)compressor [19] was used prior to amplification in order to compensate for the effects of group-velocity dispersion. Amplification proceeded along two branches. The first amplified beam was frequency-doubled; the resulting pulse at 308 nm was further amplified to 1.2 mJ on a double pass through the second discharge channel of the excimer laser [20]. The second amplified red beam was appropriately delayed for continuum generation. Details will be published elsewhere.

3. Results

The transient absorption spectra from an ethanolic solution of BIPS, following excitation at 308 nm with 0.24 ps pulse duration, are shown in fig. 3. The spectral development is characterized by the following:

(1) Appearance of a well-defined band at 400 nm for the earliest times.

(2) Fast evolution (fig. 3a) of this band, to a broad absorption maximising near 440 nm at 0.33 ps.

(3) From 0.67 ps onward (fig. 3b), the evolved absorption at 440 nm decays. During this decay, the broad absorption at longer wavelength increases to form a characteristic band at 550 nm.

The apparent spectral evolution of the primary band in the near UV is a measurement artifact: it may be accounted for by the dependence of time origins on the probe wavelength in this spectral region, as was mentioned in section 2. The true transient absorption spectrum at a given nominal time may then be constructed from the measured spectrum through substitution of the short-wavelength part by spectrally weighted portions of the two spectra preceding by 0.33 and 0.67 ps. In this way, the true absorption spectrum coincident with the pump pulse is seen to cover predominantly the region at wavelengths below 500 nm, with a peak near 440 nm. For later times, the spectral change at shorter wavelengths is relatively small so that this correction is not necessary.

The rise of the absorption at 550 nm, i.e. in the region which is typical for merocyanine absorption, is separately shown in fig. 4. This is compared to the ground-state bleaching of malachite green (in ethanol), which locates the time origin and illustrates the temporal resolution of the measurement. For BIPS, the rise of the absorption at 550 nm is reasonably well described by a single exponential with a risetime of 1.3 ps. A slower, minor component is needed to connect with the optical density at 550 nm measured for 104 ps delay (used for normalisation).

4. Discussion

The observations above contain a novel feature of spiropyran transient spectroscopy: the immediate appearance of transient absorption in the blue to near UV region only. On the other hand, a component of transient absorption around 450 nm has been much discussed, although only for 6-nitro-BIPS. In this case it was shown to be dominant at 8 ps, and it was assigned to the elusive X formed in the ground state from a higher triplet of the spiropyran parent [21]. A complication was presented by the simultaneous
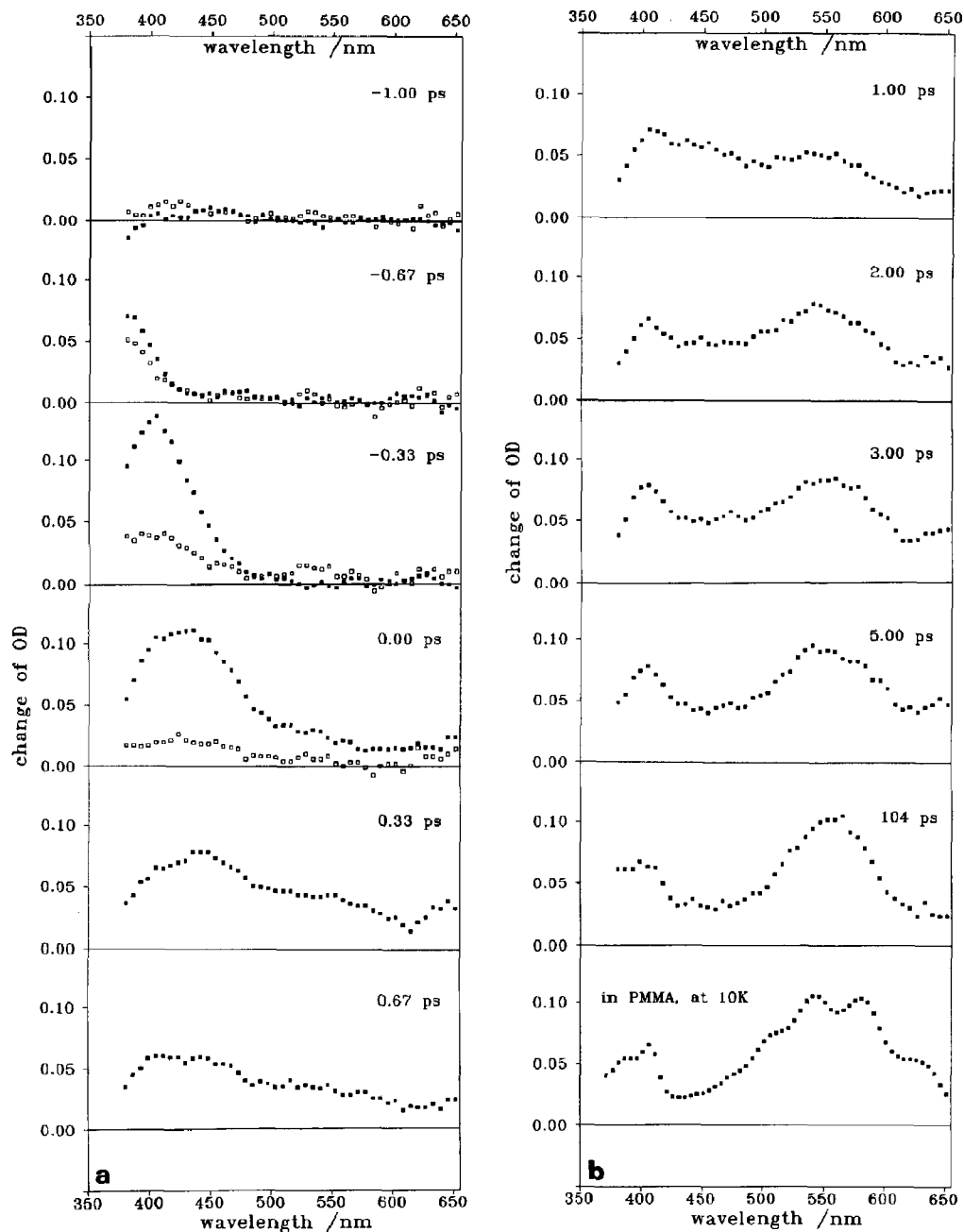
Fig. 3. Transient absorption spectra of BIPS following UV excitation with 0.24 ps pulse duration, and with 0.42 ps resolution. (Open squares indicate induced absorption changes in ethanol alone, due to two-photon absorption of the probe and pump.)
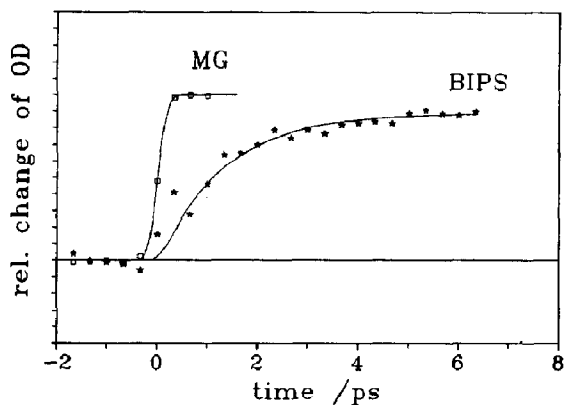
Fig. 4. Rise of transient absorption from an ethanolic solution of BIPS, at 550 nm. This is compared to ground-state bleaching of malachite green (MG) in ethanol. Excitation was at 308 nm in both cases.

existence of a well-defined red absorption band at this earliest resolved time; this band was also attributed to X. Lastly, the 450 nm region also shows transient absorption due to intermediate triplets [13].

The spectra shown in fig. 3 should not be complicated by intermediate triplets [13]. The spectral evolution distinguishes the 440 nm absorption from the characteristic red band.

4.1. Assignments

The latest recorded transient absorption spectrum, at 104 ps after excitation, strongly resembles the spectrum of the merocyanine products. This is seen by comparison with the stationary merocyanine absorption spectrum shown in the lowest panel of fig. 3b. We therefore assign the transient absorption spectrum at 104 ps to the merocyanine isomer distribution at this time, and in the electronic ground state. Its characteristic absorption band, at 550 nm, was shown to emerge continuously from the broad and unstructured absorption at 0.67 ps, with a rise-time of 1.3 ps.

At earliest times, up to 0.33 ps after excitation, transient absorption occurs only in the blue to near UV region. This absorption may then have two carriers: a primary photoproduct in its first excited singlet state S_1, or else a primary photoproduct in its ground state S_0, which evolves on the S_0 potential

energy surface into some merocyanine isomer distribution. The latter possibility requires that internal conversion take place within 0.3 ps. This does not appear reasonable in view of the wide electronic energy gap. Therefore, we assign the transient absorption around 440 nm, and at earliest times, to an S_1–S_n absorption.

It follows that the transient absorption spectra of fig. 3 should record an internal conversion where the spectral evolution from the near UV ends and the merocyanine band appears.

4.2. Relation to structural change

What is the likely structural change underlying the spectra? In ref. [22] two paths of spiropyran ring opening were examined by MNDO and INDO-2 calculations for small model systems. The photochemical path was associated with a change of the twist angle ϕ around the C_4–C_{4a} bond (cf. fig. 2). In the course of this internal rotation, the group attached to the spiro carbon atom rotates into planarity with the central cisoid C_{spiro}–C_3–C_4–C_{4a} structure. It will be shown below that our observations are consistent with this description of the photochemical reaction.

Fig. 5 shows potential energy curves for twisting of the C_4–C_{4a} bond in BIPS. These curves are not entirely arbitrary. The spiro form has an S_0–S_1 transition energy of ≈ 3.77 eV. The lowest S_0 reaction enthalpy was determined to be 0.19 eV [3]; the S_0 reaction enthalpy for an unfavourable CCT isomer (cf. fig. 2) was calculated to be 1.25 eV for chromene [22]; here we assume a reasonable value of 1.0
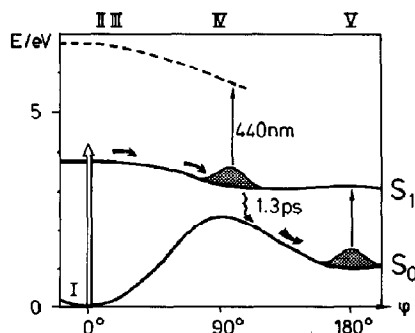

Fig. 5. Description of the photochemical ring-opening reaction along the twist angle ϕ. Roman numerals refer to structures in fig. 2.

eV. An S_0 barrier of 0.93 eV (in the forward direction) was determined experimentally from the thermal reaction [3]; the calculated value for the photochemical path of chromene is 2.4 eV [22], which is used here. Finally, the S_0–S_1 transition energy for the first merocyanine isomer, 2.2 eV, is taken from the transient absorption spectrum at 104 ps.

In combination with the spectral assignments made in section 4.1, we propose the following tentative description of the photochemical ring-opening reaction (figs. 2 and 5). Excitation of the spiropyran (**I**) leads to some primary, transient photoproduct (**II** or **III**) on the S_1 energy surface. For more viscous solvents, it should be detectable by its S_1–S_n absorption. The photoproduct evolves through barrierless isomerisation on the S_1 surface to an orthogonal form **IV** (cf. fig. 2) which is characterized by a broad S_1–S_n absorption maximising near 440 nm. From here, level crossing to the S_0 surface occurs through vibronic interaction, with a rate of 0.8×10^{12} s^{-1}. This is followed by faster (and hence unrecorded) ground-state relaxation to the first merocyanine form **V**.

5. Conclusion

In summary we conclude:

(1) There is no evidence for a reasonably stable primary photoproduct X having the parent geometry.

(2) The earliest transient absorption at 440 nm could be due to a cisoid, non-planar form on the S_1 surface, representing a local energy minimum which acts as a "funnel" for internal conversion. Internal conversion should be followed by rapid opening to some fully planar first isomer (which need not necessarily have the CCT conformation of structure **V** shown in fig. 2).

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