

## PRIMARY PROCESSES IN THE PHOTOCHROMISM OF A STERICALLY CROWDED PIPERIDINOSPIROPYRAN STUDIED BY NANOSECOND LASER PHOTOLYSIS

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### Summary

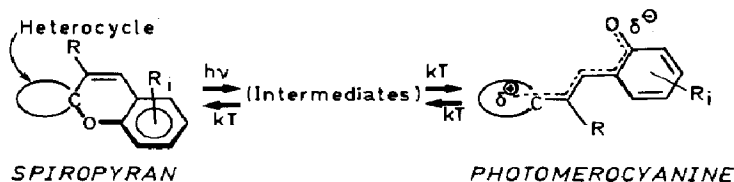
The primary processes in the photoisomerization of spiro[3-methyl-8-methoxy-6-nitro-2*H*(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] (Me-SP) in toluene were studied from 273 to 323 K by means of nanosecond laser photolysis using the third harmonic (353 nm) of a neodymium-glass laser as the excitation light (pulses with a full width at half-maximum of 6 ns). The results indicate that benzopyran ring opening in Me-SP occurs in both the excited singlet state and the lowest triplet state. Photoisomerization in Me-SP does not lead to an all-*trans* isomer because of steric hindrance due to the two methyl groups in the 3' position and the one methyl group in the 3 position, but instead leads to a cisoid isomer X characterized by a lifetime of about 3 s at 297 K and an absorption centred at 440 nm. X is formed exclusively from the excited singlet state of Me-SP. Two triplet species, one of which was formed from the other, were detected. Their lifetimes were 25 ns and 2.2  $\mu$ s respectively at 297 K. The first triplet T was assigned to the lowest triplet state of Me-SP and the second triplet <sup>3</sup>Y to the lowest triplet state of a species (different from X) formed just after C—O bond rupture. The triplet <sup>3</sup>Y relaxes towards the ground state of Me-SP. The activation energy of the T  $\rightarrow$  <sup>3</sup>Y process is about 5 kcal mol<sup>-1</sup>.

### 1. Introduction

The photochromic properties of the spiropyrans are well known. When the spiro-carbon atom forms part of a heterocycle (*e.g.* indoline), C—O bond

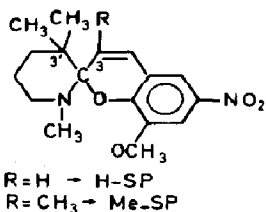
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rupture occurs easily on light excitation giving a highly coloured photomerocyanine which thermally (or photochemically) reverts to the initial colourless form:



The heterocyclic and benzopyran rings are orthogonal to each other in the spiropyran, whereas the photomerocyanine has a planar structure. Extensive structural rearrangement occurs in this photochromic reaction which therefore is most probably a multistep process as indicated above. Although the spiropyrans, and in particular the indoline class, have been investigated extensively [1 - 7], these studies have focused on the photochromic properties whereas the primary photoprocesses have received less attention and are still not satisfactorily understood. It has been shown that the triplet of the spiropyran is involved in the photoreaction as an upper excited triplet [8], as a higher vibrational level of the lowest triplet [6] or as the vibrationally relaxed lowest triplet [3 - 5, 7, 9 - 11]. The existence of a ground state intermediate (X) was inferred by Heiligman-Rim *et al.* [1] from studies of the photochromism of spiropyrans; X was suggested to be a cisoid isomer which was formed after rupture of the C—O bond in the benzopyran ring and retained a geometry close to that of the spiropyran. Recent time-resolved studies of spiropyran photoisomerization [3, 6, 7] support the existence of this intermediate. Spiropyran photolysis at 4 K studied by optically detected magnetic resonance and luminescence also provided further evidence for the appearance of such a cisoid isomer [12].

In contrast with the indolinospiropyrans, no detailed studies of the primary steps in the photoisomerization of the piperidinospiropyrans have been performed using time-resolved techniques. The photochromism of this class of compounds was reported by Maguet *et al.* [13]. The photoisomer of spiro[8-methoxy-6-nitro-2*H*(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] (H-SP) is similar to that of indoline and other classes of spiropyrans:



under light excitation a coloured photomerocyanine with all-*trans* geometry ( $\lambda_{\max} \approx 570$  nm) is obtained. However, if the hydrogen atom in position 3 on the benzopyran ring is substituted by a methyl group to form spiro[3-methyl-8-methoxy-6-nitro-2*H*(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] (Me-SP), the photoisomer is not the *trans*-photomerocyanine but a cisoid

isomer X characterized by an absorption peak at 440 nm [13]. This specific behaviour is probably due to steric hindrance to rotation arising from the presence of the three methyl groups in positions 3 and 3'. This isomer may correspond to the intermediate leading to the photomerocyanine which has been proposed for different classes of spiropyrans [13]. Me-SP was considered to be a suitable system for investigation of the early steps in spiropyran isomerization because of the absence of the complex thermal steps leading to the fully developed *trans*-merocyanine.

The purpose of the present study was to investigate the mechanism of the photoreaction of this crowded spiropyran by means of nanosecond laser photolysis. The results show that the cisoid isomer is formed exclusively from the excited singlet state of the spiropyran. In addition to this species two transients of triplet character were detected, one of which is formed from the other. The one appearing first was attributed to the lowest triplet of the spiropyran; this species leads by C—O bond rupture to the triplet state of an isomer which retains a geometry close to that of the initial compound.

## 2. Experimental details

### 2.1. Laser apparatus

The exciting light source was an Nd<sup>3+</sup>-doped glass laser (CILAS VD 231) emitting at 1060 nm. Laser pulses of wavelength 353.3 nm and a full width at half-maximum of 6 ns were generated using potassium dihydrogen phosphate crystals and a Pockels cell (CILAS DL11). Relative values of the laser energy were obtained by directing a small fraction of the laser light onto a pyroelectric joulemeter (Laser Precision Corporation model Rk3230 with an RE335 probe).

The laser beam was focused by means of cylindrical lenses onto an area of dimensions approximately 3 mm × 10 mm at the entrance of the silica cell containing the sample. A frosted silica plate was placed close to the cell to homogenize the laser light. Transient absorption changes were monitored perpendicularly to the laser beam using a xenon flash lamp, which was replaced by a constant-running Osram XBO 75W/2 lamp for decays longer than 20 μs, as the analysis light source. The detection set-up included a high intensity Jarrell-Ash monochromator (focal length, 0.25 m; bandwidth, 2 nm), a photomultiplier (RCA 1P28 or HTV R928 in the UV and visible ranges and HTV R406 in the IR range) and a double-beam oscilloscope (Tektronix 7844). The time response of the detection system was 1 - 2 ns. The oscilloscope screen was scanned using a high sensitivity video camera (Sofretec CF123V) and the video signal was digitized using a converter (Thomson CSF TSN1150) for storage on magnetic tape in a Tektronix 4051 computer.

### 2.2. Materials

Me-SP was synthesized according to the method described in ref. 14. Toluene (Merck Uvasol) was chosen as the solvent because spiropyrans are

known to have little tendency to aggregate in this liquid [15]. Indeed no deviation from Beer's law could be detected by spectrophotometry at concentrations of  $10^{-5}$  -  $10^{-3}$  M. In addition the absence of concentration effects was checked in the transient kinetics study. A concentration of  $9 \times 10^{-5}$  M was used in the present study.

The samples contained in silica cells of cross section 10 mm  $\times$  10 mm were deoxygenated by bubbling with argon for 15 min. Although no photo-degradation was observed, the samples were renewed frequently.

### 2.3. Triplet quantum yields

The triplet quantum yield was obtained by comparing the amount of triplet populated after laser excitation of Me-SP with that found on excitation of a reference compound of known triplet quantum yield at the same laser energy. Acridine in benzene was chosen as the reference; its triplet quantum yield is reported to be  $0.73 \pm 0.07$  and the triplet extinction coefficient at 442 nm (absorption maximum) is  $2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  [16].

In these measurements the laser energy was kept low enough to avoid light saturation effects; less than 15% of the Me-SP was converted to the triplet state. The acridine concentration was chosen to give the same optical density (OD) at 353 nm as that of Me-SP (0.14 across the 2 mm width of the analysis beam). The triplet concentration of Me-SP was monitored at 600 nm using a triplet extinction coefficient of  $4600 \text{ M}^{-1} \text{ cm}^{-1}$  and the triplet concentration of acridine was monitored at 442 nm.

## 3. Results and discussion

Transient optical density changes obtained on laser excitation at 353 nm of deoxygenated solutions of Me-SP ( $9 \times 10^{-5}$  M) at 297 K were monitored in the spectral range 290 - 800 nm over a time range extending from a few nanoseconds to a few seconds after the laser pulse. All the changes observed were proportional to the laser energy at low energies and displayed a saturation trend at high laser energies owing to depletion of the spiropyran ground state. This behaviour reflects the monophotonic character of the processes investigated.

### 3.1. Spectra and kinetics

Typical oscillograms are shown in Fig. 1. At the end of the pulse the oscillograms at 430 nm (Fig. 1(a)) and 560 nm (Fig. 1(b)) indicate that the species giving rise to transient absorption are formed within the laser pulse. On a longer time scale ( $200 \text{ ns division}^{-1}$ ) (Fig. 1(c)) the optical density at 430 nm decreases in two distinct time phases: a fast decay lasting about 200 ns and a slower decay extending into the microsecond range. The slower phase is clearly illustrated by the oscillogram at 560 nm (Fig. 1(d)) in which the optical density change has an evolution lasting about 20  $\mu\text{s}$ . In the same time scale the absorption at 440 nm (Fig. 1(e)) decreases slightly and after

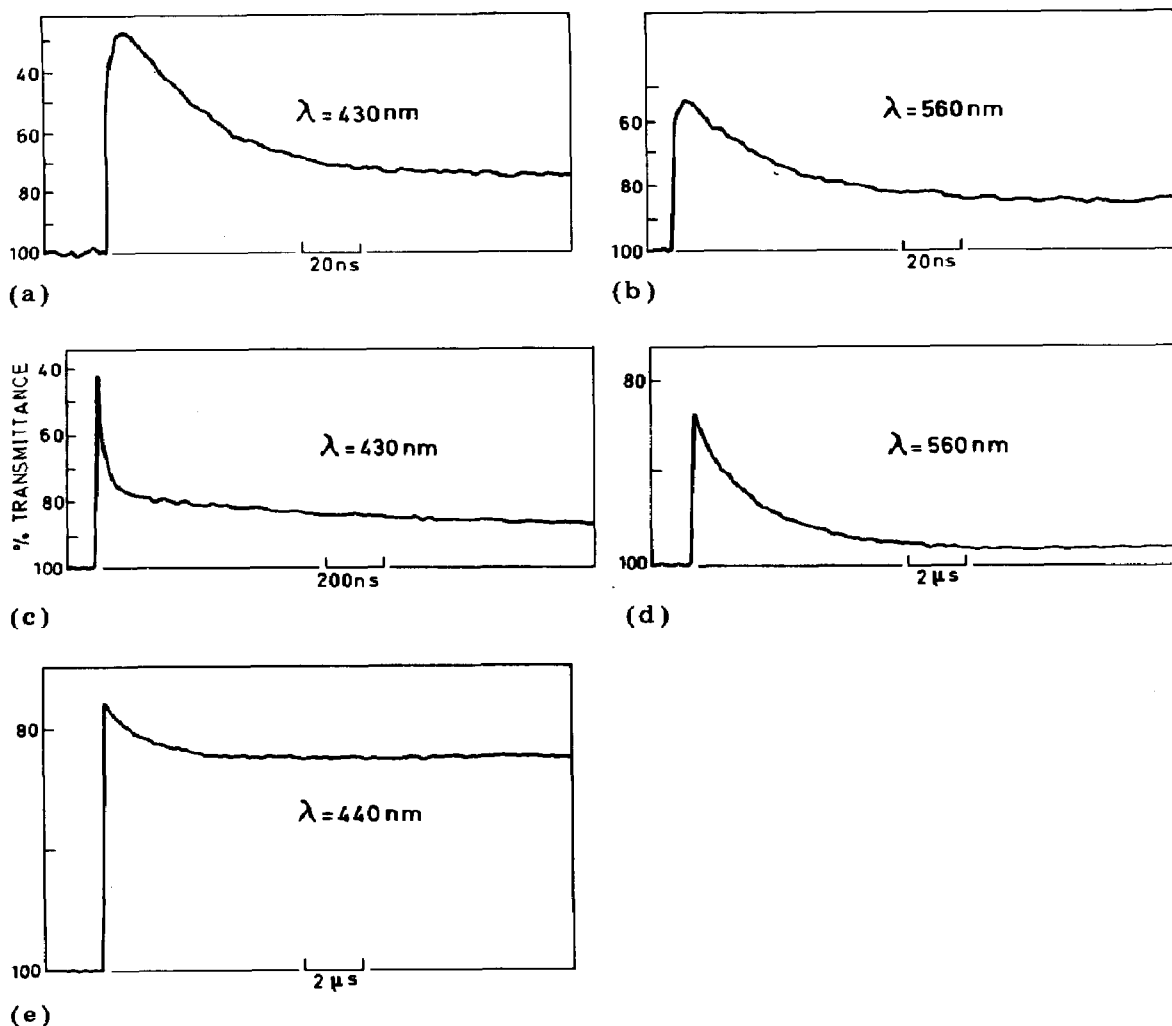
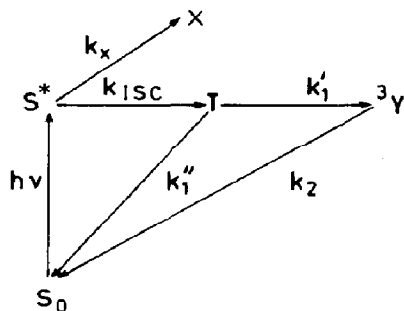


Fig. 1. Oscillograms showing the variation in the optical transmission at various wavelengths  $\lambda$  of  $9 \times 10^{-5}$  M Me-SP in degassed toluene at 297 K on excitation by a 353 nm laser pulse of 6 ns duration.

about 6  $\mu$ s reaches a plateau which is constant throughout hundreds of milliseconds and then decays in the range of seconds. At all wavelengths these three time phases were separately fitted by single exponentials with time constants of 25 ns, 2.2  $\mu$ s and 3 s respectively at room temperature. Since these time constants were unaffected by changes in either the initial spiropyran concentration or the laser excitation energy, it was concluded that they correspond to unimolecular decay processes of three different transients which are denoted T,  $^3$ Y and X in the following.

We propose the following scheme to account for the experimental results obtained from the observed oxygen and temperature effects on both the kinetics and the yields of the transient species:



$S^*$  represents the first excited singlet state of Me-SP,  $T$  represents the lowest triplet state of Me-SP,  ${}^3Y$  is an intermediate on the triplet energy surface which is formed just after the C—O bond opens and retains a geometry close to that of the initial spiropyran and  $X$  is a sterically hindered isomer which retains a cisoid non-planar configuration.

Difference spectra were constructed from changes in the transient absorption measured at three different characteristic times defined by the kinetics:  $t = 0$  (end of pulse),  $t = 160$  ns (end of the fast decay) and  $t = 20$   $\mu$ s (end of the slow phase). The spectra obtained are shown in Fig. 2. The absolute spectra of the three transients (Fig. 3) were calculated from the difference spectra combined with the kinetic results. Corrections due to overlapping of the transient spectra resulted in some uncertainty particularly for the spectrum of  ${}^3Y$  which has a minimum in a region of strong absorption of  $X$ . The spectrum of the  $X$  isomer was obtained from the difference

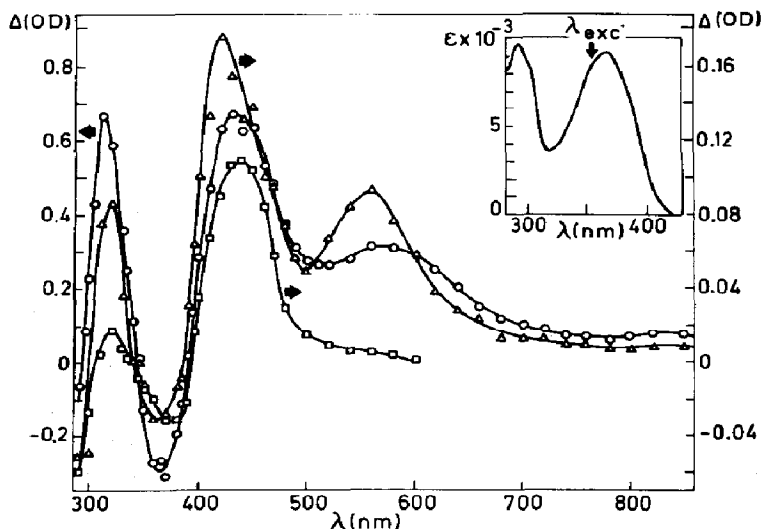


Fig. 2. Difference spectra observed on excitation of  $9 \times 10^{-5}$  M Me-SP in degassed toluene at 297 K by a 353 nm laser pulse:  $\circ$ , at the end of the pulse ( $t = 0$ ) (OD, left-hand scale);  $\triangle$ ,  $t = 160$  ns (OD, right-hand scale);  $\square$ ,  $t = 20$   $\mu$ s (OD, right-hand scale). The values are the average of at least two measurements. The extinction coefficients  $\epsilon$  (per mole per centimetre) of Me-SP in toluene at the laser wavelength  $\lambda_{\text{exc}}$  indicated are shown in the inset.

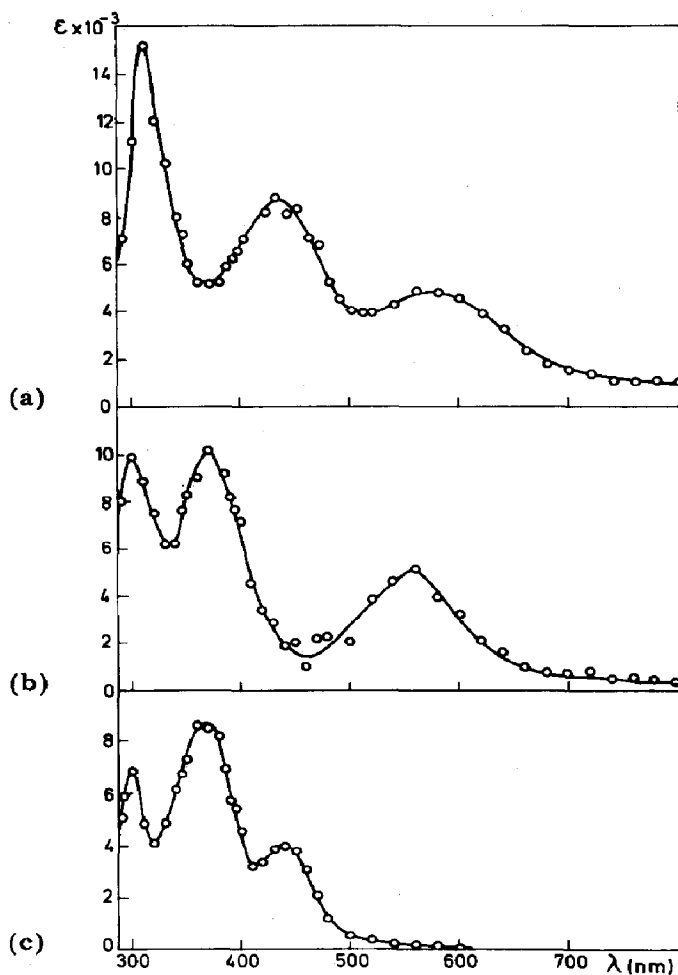


Fig. 3. Extinction coefficients  $\epsilon$  (per mole per centimetre) of Me-SP transients calculated from the difference spectra: (a) the lowest triplet state of Me-SP; (b) the second triplet  ${}^3Y$ ; (c) the isomer X.

spectrum at  $20 \mu\text{s}$ . At this time X is the only transient species still remaining. The oxygen and temperature effects, which are discussed below, show that only T and X are formed directly from the excited singlet state (lifetime less than  $10^{-11}$  s). The concentration of X was then deduced from the estimated value of the triplet concentration (see below) and the known value of the depletion of the Me-SP ground state (derived from the saturation curve obtained on varying the laser energy). The spectrum of X (Fig. 3(c)) has three maxima at 300 nm, 370 nm and 440 nm with  $\epsilon$  values of  $7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  respectively. Photomero-cyanines are known to have strong absorption maxima in the 500 - 600 nm region (with  $\epsilon_{\text{max}}$  values of  $(3 - 7) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) [2]. In contrast, X has a very low  $\epsilon$  between 500 and 600 nm and does not absorb at wavelengths greater than 600 nm. These characteristics imply that X is not an all-*trans* isomer: X probably retains a cisoid non-planar geometry because steric

hindrance introduced by the three neighbouring methyl groups prevents relaxation to planar geometry; however, twisting of the benzene group with respect to the piperidine group may occur. The absorption spectrum and lifetime of this isomer show that this species is the same as that detected by Maguet *et al.* [13] in flash experiments. The spectrum of the first transient T (Fig. 3(a)) was obtained from the end-of-pulse difference spectrum by subtracting the difference spectrum at 20  $\mu$ s and by assuming that conversion of the excited singlet state to T was 70% at saturation, the remainder being X. This assumption gives three bands with extinction coefficients  $\epsilon$  in good agreement with those observed in H-SP [17]; moreover it leads to a relatively small value for the  $\epsilon$  of X at 440 nm, which is expected for a cisoid form where delocalization and charge separation cannot develop to a great extent. The spectrum of T has three maxima at 310 nm, 430 nm and 570 nm with  $\epsilon$  values of  $15 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . However, the approximate nature of these values, because of the many corrections involved, must be stressed.

### 3.2. Oxygen effects

Saturation of the solution with oxygen ( $9 \times 10^{-3} \text{ M O}_2$  [18]) efficiently accelerated the decays of T and  $^3\text{Y}$  but did not affect either the concentration of X formed or its lifetime. The same trends were observed in air-saturated solutions but, as expected, were less pronounced. Kinetic analysis of the decays of T and  $^3\text{Y}$  yielded high values for the quenching rate constants:  $k_q = (3 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for both T and  $^3\text{Y}$ . These values are typical of triplet quenching by oxygen and confirm the triplet nature of these transient species. T was assigned to the lowest triplet state of Me-SP; the intersystem crossing in this compound is expected to be efficient since it does not fluoresce even at 77 K and is strongly phosphorescent at low temperatures [14]. The absence of any other transient formation concomitant with the quenching of T and  $^3\text{Y}$  shows that these two triplets are quenched toward the Me-SP ground state. It was inferred from the study of temperature effects that  $^3\text{Y}$  is formed from T. By analogy with results obtained for a nitrochromene [19], we attribute the evolution of T towards  $^3\text{Y}$  to C—O bond rupture on the triplet energy surface leading to a triplet with a geometry close to that of the initial compound. However, probably as a result of steric hindrance introduced by the three methyl groups in positions 3 and 3', this triplet does not lead to a *trans* isomer as observed in nitrochromene but decays back to the ground state of the closed form.

Since the lifetime of X is not affected by oxygen, X must be the ground state of an isomer of Me-SP. In addition, since its concentration does not depend upon the concentration of dissolved oxygen, X must be formed only from the first excited singlet state of Me-SP and not from the triplet state.

### 3.3. Temperature effects

The effect of temperature on the kinetics was studied in the range 273 - 323 K. In this range the isomer yield increases slightly while the T yield de-



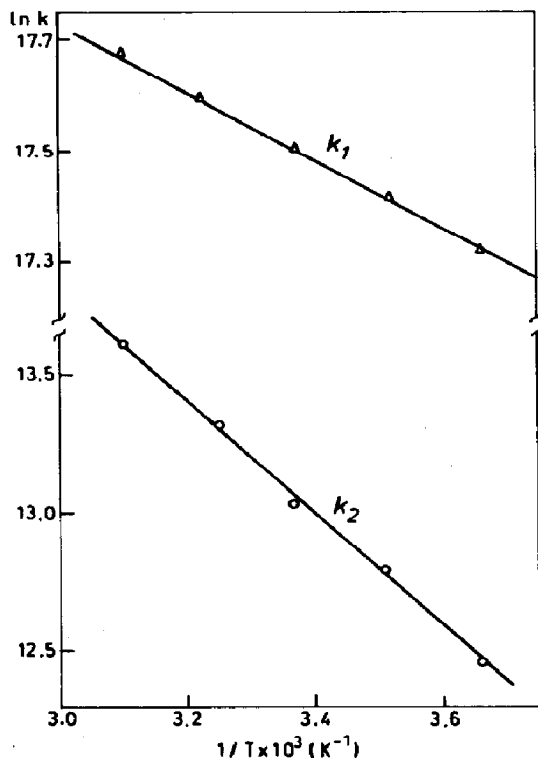


Fig. 4. Arrhenius plots of the decay rate constants of T ( $k_1$ ) and  $^3\text{Y}$  ( $k_2$ ).

creases to a very small extent. This observation supports the conclusion derived from the study of oxygen effects, *i.e.* X is formed only via the excited singlet state and not via the triplet path. The temperature dependence of the decays of triplets T and  $^3\text{Y}$  is shown in Fig. 4. On the basis of previous results obtained for the closely related nitrochromene system [19] it seems quite reasonable to assume that the formation of the triplet  $^3\text{Y}$  follows that of T. Even if we do not have direct experimental evidence for this fact, a self-consistent description of the kinetic and spectral results as a function of temperature can be given on this basis. Since reconstitution of the absorption spectrum of  $^3\text{Y}$  from difference spectra indicates that only part of the T population decays to  $^3\text{Y}$ , the remainder must decay to  $\text{S}_0$  so that the observed decay rate constant  $k_1$  is the result of two competing decay processes (rate constants  $k'_1$  and  $k''_1$  in the kinetic scheme). Simulation of experimental decays at various temperatures using this assumption leads to activation energies of about  $5.5 \text{ kcal mol}^{-1}$  and about  $0.3 \text{ kcal mol}^{-1}$  respectively and pre-exponential factors of  $1 \times 10^{11} \text{ s}^{-1}$  and  $5 \times 10^7 \text{ s}^{-1}$  respectively for  $k'_1$  and  $k''_1$ . The high value obtained for the pre-exponential factor of  $k'_1$  shows that the first triplet disappears without spin change. The activation energy for C—O bond rupture appears to be quite similar to that of nitrochromene [19], indicating that the mechanism of the rupture is similar. Model calculations [20] have shown that the most probable path

for C—O bond rupture occurs by torsion around the 4—5 bond. The experimental activation energy would then correspond to the energy required to reach the geometry necessary for C—O bond opening via this torsional movement ( $\phi > 30^\circ$ ). The process  $T \rightarrow S_0$  is characterized by a low pre-exponential factor as expected for a spin-forbidden process. It was calculated from the computed  $k_1'$  and  $k_1''$  values that a fraction 0.3 of T was converted to  ${}^3Y$  at 297 K and that the remainder was converted to  $S_0$ . (This fraction was used in the calculation of the absorption spectra of the transient given in Fig. 3.)

The decay of the triplet  ${}^3Y$  (rate constant  $k_2$ ) corresponds to a deactivation to  $S_0$  characterized by an activation energy of 4 kcal mol $^{-1}$  and a pre-exponential factor of  $4 \times 10^8$  s $^{-1}$ . The low value of the pre-exponential factor is consistent with the spin change involved in the relaxation of  ${}^3Y$  to a ground state. As it has been shown that no isomer is formed by oxygen quenching of  ${}^3Y$ , the isoenergetic state to which intersystem crossing leads must be a highly excited vibrational level of the electronic ground state  $S_0$ .

### 3.4. Quantum yields

The quantum yield of the Me-SP triplet was determined by comparing the triplet concentration obtained on excitation of Me-SP solutions with that of acridine in benzene which was used as a standard [16] (see Section 2.3). A value of about 0.5 was obtained for  $\Phi_T$  at 297 K. This  $\Phi_T$  value was used to calculate the quantum yield  $\Phi_X$  of the X isomer. The isomer formation and triplet formation from the excited singlet state compete with each other. Under light saturation conditions 70% of the excited singlet state is converted to the triplet state T and the remainder is converted to X (see Section 3.1). The yield of X is thus

$$\Phi_X = \Phi_T \times \frac{3}{7} \approx 0.20$$

It should be noted that in the case of nitrochromene [19], where isomerization occurs via both the excited singlet state and the lowest triplet state, the quantum yield for direct isomer formation via the excited singlet has a similar value (0.14).

## 4. Conclusions

It has been shown in the present study that C—O bond rupture in the benzopyran ring occurs in both the excited singlet state and the relaxed lowest triplet state of Me-SP. Mechanisms of ring opening involving both pathways have been proposed for spiropyran [3, 4, 7, 10, 11]. Photoisomerization of spiropyran leads ultimately to coloured photomercyanines. However, in the case of Me-SP isomerization stops at an early stage in both the singlet and triplet pathways owing to steric hindrance. C—O bond rupture occurs in the lowest triplet state of Me-SP without spin

change; the triplet  $^3Y$  formed in this process then returns to the initial spiropyran with spin change. This sequence of two relaxed triplets appears to be a common feature of the triplet path of the photoreaction for Me-SP, H-SP [17] and nitrochromene [19]. Direct evidence for the existence of such a sequence has not been reported for other classes of spiropyrans.

In the present study of Me-SP it has been shown that the X isomer is formed exclusively from the excited singlet state of the spiropyran. This isomer is characterized by an absorption maximum at 440 nm and by the absence of absorption at wavelengths greater than 600 nm in contrast with the photomerocyanine generally obtained in spiropyran photoisomerization. The relaxation to an all-*trans* photomerocyanine is probably not possible because the three neighbouring methyl groups prevent attainment of a planar geometry; however, twisting of the benzene ring with respect to the piperidine group may occur.

Our interpretation of the nature of X can be compared with the results of previous spiropyran photoisomerization studies. Heiligman-Rim *et al.* [1] first proposed that a cisoid isomer precedes the formation of the photomerocyanine. Later Murin *et al.* [3] in a nanosecond laser study of indolino-spiropyran observed a transient absorption with a maximum at 440 nm and a lifetime of about 200 ns. They proposed on the basis of the correlation between the decay of this transient and the formation of the photomerocyanine that this species is a cisoid isomer precursor of the photomerocyanine. Recently Krysanov and Alfimov [6] supported this assumption in a picosecond laser study in which they observed a photoinduced absorption at 440 nm appearing within the duration of the pulse (8 ps). Because of the similarity of the spectrum to that observed by Murin *et al.* [3] they assigned this transient to the same isomer. In another recent picosecond laser study Kalisky *et al.* [7] observed an isomer with an absorption maximum at 440 nm which was formed from the first excited singlet state of the spiropyran and had a lifetime of about 300 ps. Despite the different lifetimes, these workers tentatively proposed a unified scheme in which this intermediate is the same isomer as that proposed by Murin *et al.* [3] and Krysanov and Alfimov [6].

The isomer obtained in the present study has the same spectral characteristics as the isomers mentioned above, and therefore presumably corresponds to the same stage in configurational evolution in the isomerization process. Our results in Me-SP thus give further support to the existence of a cisoid ground state intermediate in the photoisomerization which was first postulated by Heiligman-Rim *et al.* [1].

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