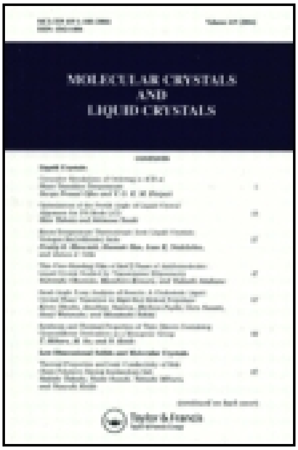

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Time-Resolved Resonance Raman and Absorption Spectroscopies of Reaction Intermediates in the Photochromism of Spiropyrans

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TIME-RESOLVED RESONANCE RAMAN AND ABSORPTION SPECTROSCOPIES OF REACTION INTERMEDIATES IN THE PHOTOCHROMISM OF SPIROPYRANS

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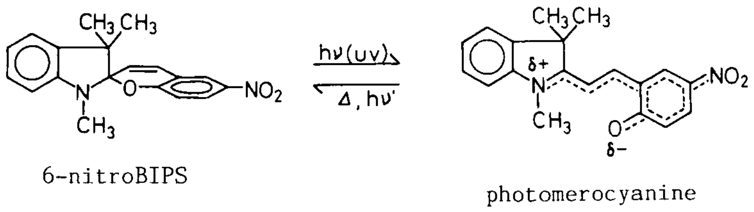
Abstract Time-resolved resonance Raman and absorption spectra have revealed that three transients are involved in the photochromic reaction of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] in the ns - μs time region. The firstly appearing transient is identified as the lowest excited triplet state T_1. The secondly appearing transient is assignable to the photomerocyanine generated from the T_1 state by the cleavage of the C(spiro)-O bond of the spiropyran ring, and the lastly appearing transient is considered to be a dimeric species of the photomerocyanine.

INTRODUCTION

Spiropyrans are known to exhibit photochromism in solution[1]. The basic photochemical reaction consists of the reversible cleavage of the C(spiro)-O bond by irradiation of UV light to generate colored transients having a merocyanine-like structure (photomerocyanines)[2].

In a preceding paper[3] we have shown by time-resolved resonance Raman spectra that two transients are involved in the photochromism of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitroBIPS) in deoxygenated cyclohexane in the 200 ns - 2 ms time region. In this study, the characterization of the transients involved as well as the time-dependence of the photochromism has been investigated in the 20 ns - 100 μs time region by means of time-resolved resonance Raman and absorption spectroscopies.



EXPERIMENTAL

Our experimental setup for nanosecond time-resolved Raman spectroscopy has been reported previously[4] and that for nanosecond laser flash photolysis will be described elsewhere.

RESULTS AND DISCUSSION

Resonance Raman spectra of 6-nitro-BIPS in deoxygenated cyclohexane observed at various delay times after UV irradiation are shown in Fig. 1. The solvent bands were subtracted from each spectrum.

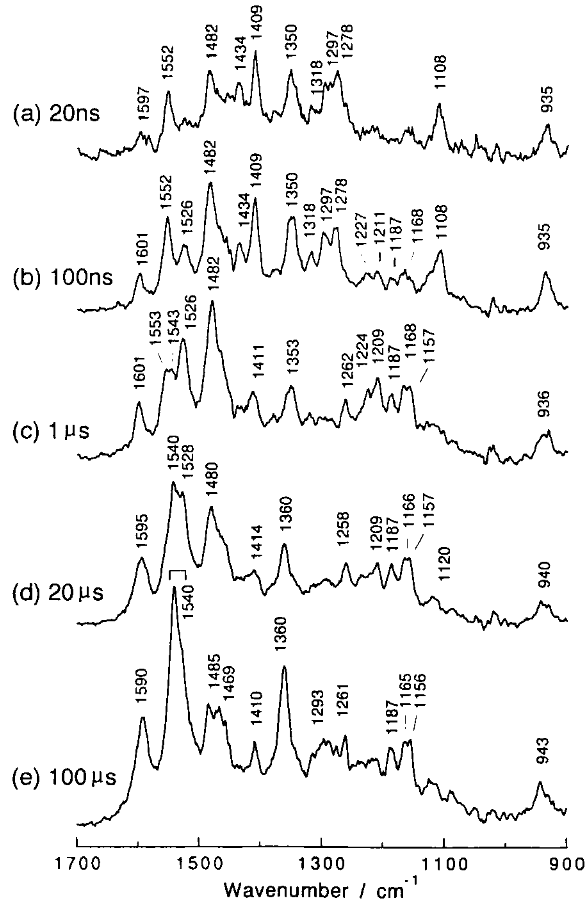


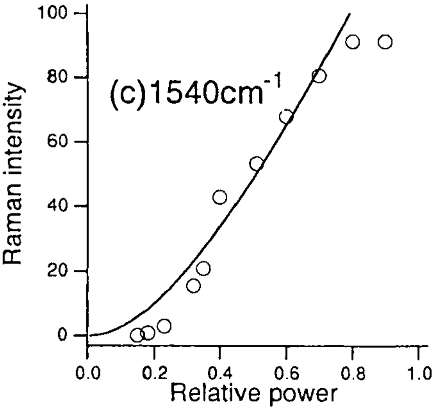
FIGURE 1 Time-resolved resonance Raman spectra of 6-nitroBIPS in deoxygenated cyclohexane measured at various delay times after UV (308 nm) irradiation. Probe wavelength, 460 nm.

At 20 ns delay time, a transient exhibiting the bands at 1552, 1482, 1434, 1409, 1350, 1278, 1108 and 935 cm^{-1} (transient I) is predominant. As the time goes on, this transient rapidly fades out and is no longer detectable at 20 μs, while a transient exhibiting the bands at 1601, 1526, 1482, 1262, 1209, 1187 and 1168 cm^{-1} (transient II) comes into prominence and in addition, another transient characterized by the bands at 1590, 1540, 1360 and 943 cm^{-1} (transient III) grows apparent. At 100 μs delay time, the transient III becomes abundant, while the transient II is only barely detectable. These spectral changes indicate that the three transients, I, II and III are generated sequentially in the photochromic reaction of 6-nitroBIPS in the nanosecond time regime.

In oxygen saturated solutions, the transient I is hardly detectable as early as at 100 ns delay time, while the transient II is distinctly detectable at 20 ns. The shortening of the lifetime of the transient I by the presence of oxygen indicates that the transient I is assignable to the lowest excited triplet state T_1. From the dependence of the intensities of the Raman bands of the transient I and II on the delay time, the lifetime of the transient I is estimated to be 330 ns which is virtually identical with the rise time of the transient II. This suggests that the transient II is generated from the T_1 state. The lifetime of the transient II is not affected by the presence of oxygen. Thus, the transient II is reasonably be assigned to the photomerocyanine. The production of the photomerocyanine of 6-nitroBIPS from the T_1 state provides a striking contrast to the observations that photomerocyanines of the majority of spiropyrans are generated from the lowest excited singlet state S_1.

We found that the production of the transient III is strongly dependent on the UV pump power. When the pump power is weak, the transient III is not detectable. It is observable once the pump power is sufficiently large. In Fig. 2 is plotted the relative intensity of the Raman band at 1540 cm^{-1} against the UV pump power (arbitrary unit). The non-linear dependence of the intensity on the pump power observed for the 1540 cm^{-1} band is commonly observable for other bands of the transient III. Since the yield of photomerocyanine should be proportional to the concentration of its precursor, T_1, which is proportional to the UV pump power, the non-linear dependence obtained in Fig. 2 indicates that the dependence of the yield of the transient III on the concentration of its precursor, photomerocyanine, should also be non-linear, and suggests the assignment of the transient III to a dimeric species of the photomerocyanine. This assignment is supported by a similar non-linear dependence of the intensities of the bands of the transient III on the concentration of 6-nitroBIPS.

Time-resolved absorption spectra of 6-nitroBIPS shown in Fig. 3 are consistent with the Raman results. The band at 435 nm observed at 100 ns delay time and no longer detectable at 1 μs in deoxygenated cyclohexane can be attributed to the T_1 state and the strong band at 580 nm to the photomerocyanine. The shoulder at 540 nm appearing under strong UV pump power is considered to arise from the dimeric species.



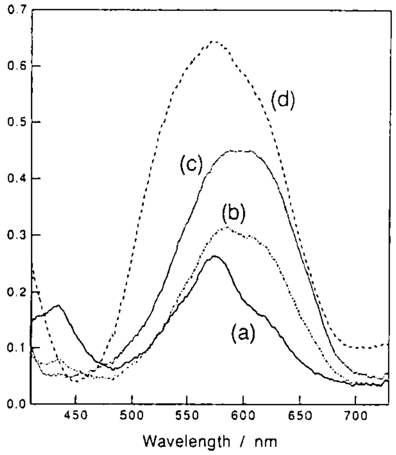


FIGURE 2 Dependence of the intensity of the Raman band at 1540 cm^{-1} of the transient III on the UV (308 nm) pump power.

FIGURE 3 Time-resolved absorption spectra of 6-nitroBIPS in deoxygenated cyclohexane at various delay times: (a) 100 ns; (b) 1 μs; (c) 100 μs; (d) 100 μs, under strong UV pump power.

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