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TIME-RESOLVED RESONANCE RAMAN AND MOLECULAR ORBITAL STUDIES OF THE STRUCTURES OF THE TRANSIENT SPECIES INVOLVED IN THE PHOTOCHROMIC REACTION OF 2,2′-SPIROBI[2H-1-BENZOPYRAN]*

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ABSTRACT

Resonance Raman spectra of the transient species of 2,2′-spirobi[2H-1-benzopyran] in various solvents reveal that at least two isomers exist in solution, the relative abundance of which depends on the polarity and hydrogen-bond donor ability of the solvent. Vibrational assignment of the transient species based on ^{13}C substitutions shows that the Raman bands mainly attributable to the vibrations of the open benzopyran part are enhanced by the Raman excitation wavelengths longer than 460 nm, whereas those assignable to the vibrations of the closed benzopyran part are observed only by the Raman excitation wavelengths shorter than 460 nm. Semi-empirical molecular orbital calculations show that the contribution of the *ortho*-quinoidal form to the resonance hybrid structure of the transient species is much larger than that of the zwitterionic form. Also, it is shown that the *trans-trans-trans* (*TTT*) configuration about the three C–C partial double bonds of the transient species is most stable.

INTRODUCTION

A great number of studies have been done on the photochromic properties of spiropyrans [1] yet the detailed photochromic reaction mechanism as well as the configurations of the colored transient species produced by the reaction are still open to conjecture.

The overall photochromic reaction of spiropyrans consists of the reversible heterolytic cleavage of a C–O spiro linkage involving the number 2 carbon atom of the pyran ring. This cleavage leads to the formation of transient species having a merocyanine-like structure represented as a resonance hybrid of *ortho*-quinoidal and zwitterionic forms and gives rise to extensive conjugation

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*Dedicated to Professor Masamichi Tsuboi on the occasion of his 65th birthday

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in the molecule, which is responsible for the strong coloration of the transient species.

Associated with this reaction, however, two important points remain to be clarified: (1) contributions of the *ortho*-quinoidal and zwitterionic forms to the resonance hybrid structure of the transient species; and (2) isomerization about the three C–C partial double bonds of the merocyanine-like structure.

Although it is naturally expected that the contribution of the more polar zwitterionic form to the resonance hybrid structure of the transient species would increase as the polarity of the solvent increases, the degree of π-electron delocalization along the merocyanine-like skeleton of the transient species is not well understood. Also, it has been suggested that in solution the transient species of a spiropyran exists as a mixture of several isomeric configurations with respect to the three C–C partial double bonds. However, the characterization of these isomers is quite difficult, because their relative abundance is strongly dependent on temperature as well as on the nature of the solvent [2–5].

2,2′-Spirobi[2H-1-benzopyran] (SBP) is an interesting spiropyran because it consists of two benzopyran rings connected by a common spiro carbon atom at the number 2 position of both rings (Fig. 1). On irradiation with UV light, one of the two benzopyran rings is opened and the remaining benzopyran ring may participate in the conjugation of the merocyanine part as shown in Fig. 1 [6–10]. It is expected that the highly extended conjugation over the entire molecule of the transient species of SBP compared with that of indolinospiropyrans may provide a clue to the understanding of the above problems.

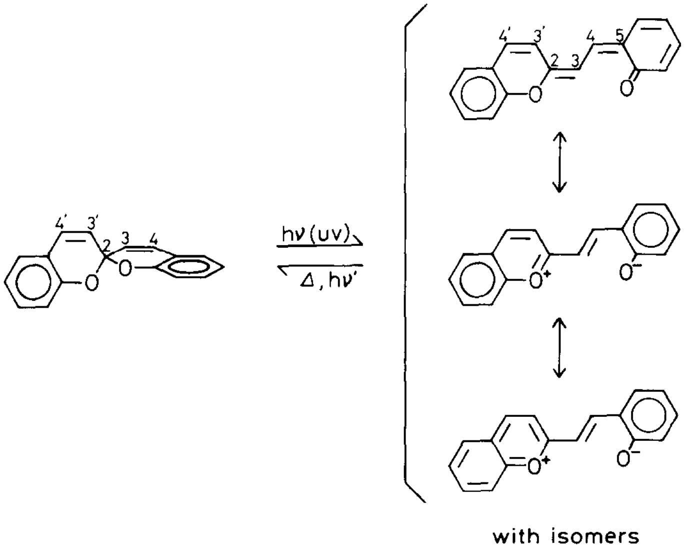

Fig. 1. Photochromic reaction of SBP.

EXPERIMENTAL

SBP and ^{13}C-substituted SBPs, namely, SBP-2-^{13}C, SBP-3,3′-^{13}C and SBP-2,3,3′-^{13}C, were synthesized according to the method of Appriou et al. [11] by the reaction of salicylaldehyde with acetone, acetone-1-^{13}C, acetone-2,2′-^{13}C and acetone-1,2,2′-^{13}C, respectively, in an acetic acid solution bubbling with dry HCl gas and were purified with charcoal and column chromatography.

The experimental arrangement of our nanosecond time-resolved Raman spectroscopy system is shown in Fig. 2. Two sets of excimer-laser-pumped dye lasers (Lambda Physik LPX120i, FL3002) were used as the pump and probe light sources. The delay time between the firing of the pump and probe lasers was electrically varied using a delay pulse generator (Stanford Research DG535). The Raman signals were collected on the slit of a monochromator (Spex 1877 Triplemate) and were detected using a multichannel analyzer (SMA D/SIDA-700G). The pump and probe laser pulses as well as the gate pulse of the multichannel analyzer were monitored by phototubes (Hamamatsu R1328U-02) and an oscilloscope (Sony Tektronix 11302-11A52).

The maximum pulse energy, the pulse width and the maximum repetition rate of the excimer laser are 150 mJ, 17 ns and 200 Hz at 308 nm and the conversion efficiency of the dye laser is 14% for Rohdamine 6G.

RESULTS AND DISCUSSION

Solvent dependence

Figure 3 compares the resonance Raman spectra of the transient species of SBP in different solvents. All the spectra were measured at 100 ns after UV

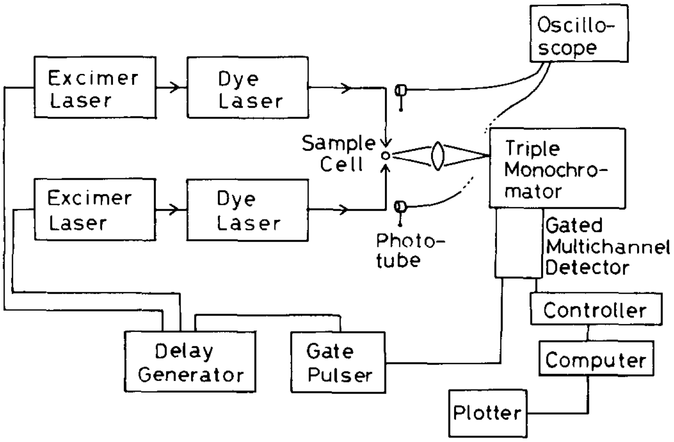

Fig. 2. Experimental system for time-resolved Raman spectroscopy.

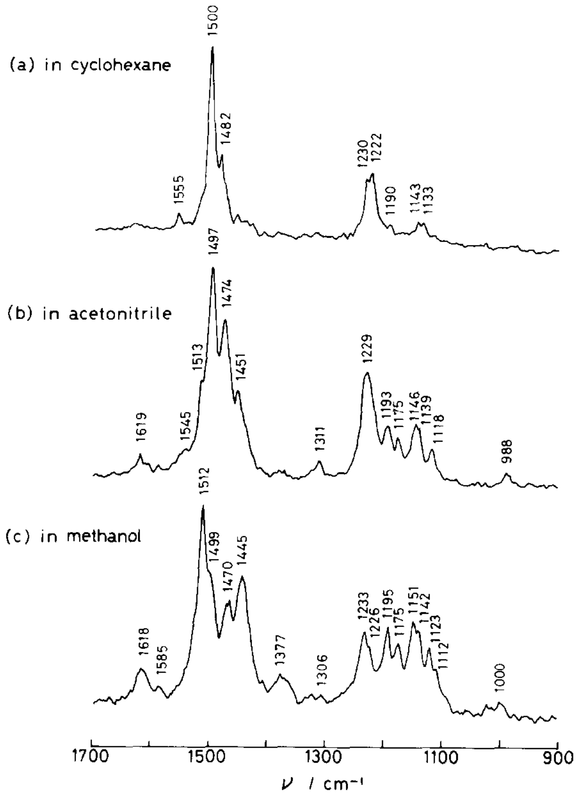

Fig. 3. Resonance Raman spectra of the transient species of SBP in different solvents taken 100 ns after UV (308 nm) irradiation: (a) in cyclohexane; (b) in acetonitrile; (c) in methanol. Concentration, 2.0×10^{-3} mol dm^{-3}; excitation wavelength, 490 nm; solvent bands have been subtracted.

(308 nm) irradiation. The Raman excitation wavelength is 490 nm and solvent bands were subtracted.

It is seen that the spectral feature changes drastically with the nature of the solvent. In nonpolar cyclohexane, the spectrum is quite simple; only the band at 1500 cm^{-1} and the doublet at 1230 and 1222 cm^{-1} are prominent. In polar acetonitrile, the spectrum is more complex; three strong bands are observed at 1497, 1474 and 1229 cm^{-1}, and several weaker bands are detectable in the region between 1650 and 950 cm^{-1}. In methanol, the spectral feature is even more complicated and is quite different from that in cyclohexane or in acetonitrile; the bands at 1512 and 1445 cm^{-1}, which are hardly detectable in cyclohexane and very weak in acetonitrile, are here the strongest bands. The bands at 1499, 1470 and 1229 cm^{-1}, which are strong in acetonitrile, are weak in methanol. Also, many weaker bands are observed in the region between 1650 and 950 cm^{-1}.

The above spectral changes may be explained if it is assumed that several isomers of the transient species exist in solution and the population of each isomeric species depends on the polarity and hydrogen-bond donor ability of the solvent. In cyclohexane, however, only one isomer is predominantly abundant.

The resonance Raman spectra of the transient species of SBP in various alcohols are shown in Fig. 4. All the spectra were measured at 100 ns after UV irradiation. The excitation wavelength is 490 nm and solvent bands were subtracted. It is readily recognized in this figure that these spectra show a distinct tendency with respect to the hydrogen-bond donor ability of the solvent.

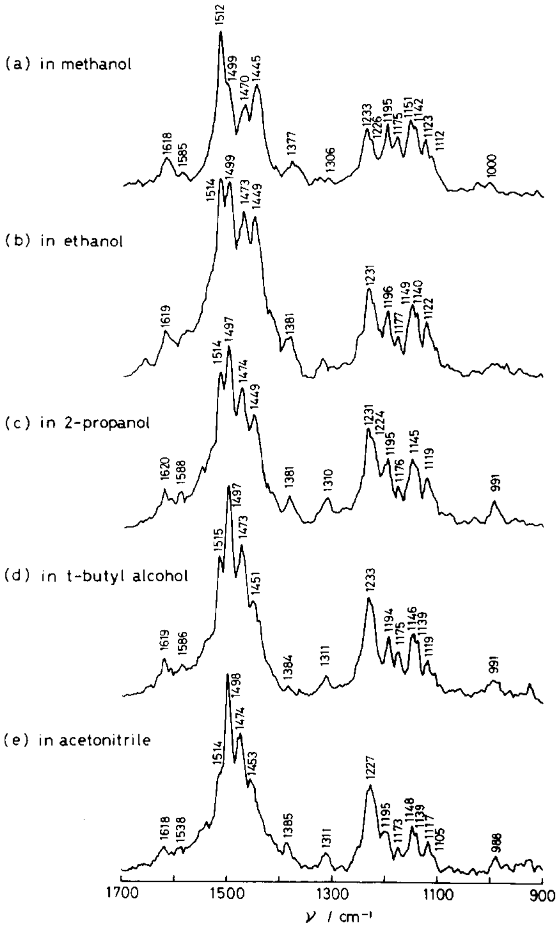

Fig. 4. Comparison of resonance Raman spectra of the transient species of SBP in various alcohols and in acetonitrile taken 100 ns after UV (308 nm) irradiation: (a) in methanol; (b) in ethanol; (c) in 2-propanol; (d) in t-butyl alcohol; (e) in acetonitrile. Concentration, 2×10^{-3} mol dm^{-3}; Raman excitation wavelength, 490 nm; solvent bands have been subtracted.

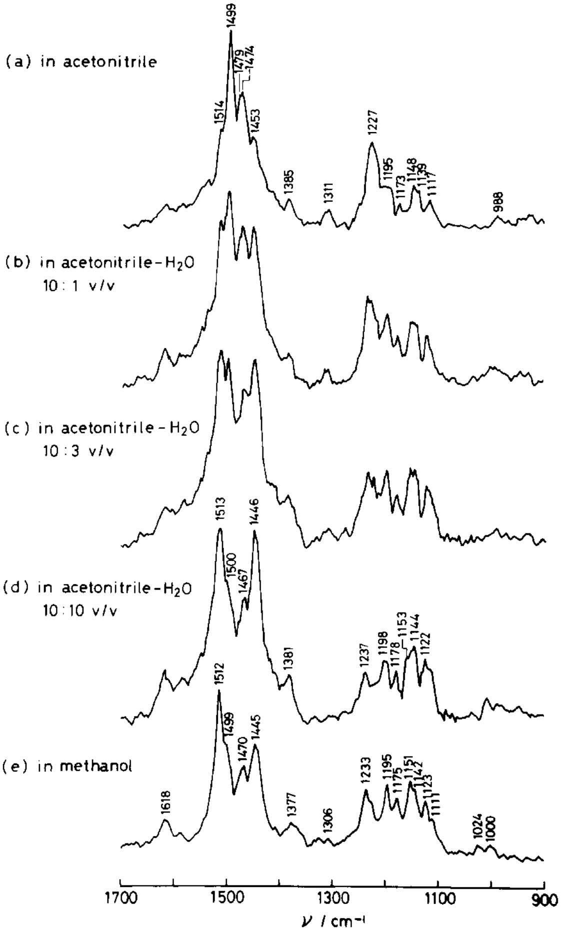

Fig. 5. Resonance Raman spectra of the transient species of SBP in acetonitrile/water mixed solvents with various volume ratios taken 100 ns after UV (308 nm) irradiation: (a) in CH_3CN; (b) in CH_3CN 10/H_2O 1 mixed solvent; (c) in CH_3CN 10/H_2O 3 mixed solvent; (c) CH_3CN 1/H_2O 1 mixed solvent. Raman excitation wavelength is 490 nm; solvent bands have been subtracted.

In methanol whose hydrogen-bond donor ability is largest among these alcohols, the bands at 1512 and 1445 cm^{-1} are strong compared with the bands at 1499 and 1470 cm^{-1}. As the hydrogen-bond donor ability of the solvent decreases in the order from methanol to ethanol, 2-propanol and t-butyl alcohol, the bands at 1512 and 1445 cm^{-1} become weaker and weaker, while the bands at 1499 and 1470 cm^{-1} become stronger and stronger. Finally, the spectrum in t-butyl alcohol is almost indistinguishable from that in acetonitrile which has no hydrogen-bond donor ability. This corresponds quite nicely to the very low hydrogen-bond donor ability of t-butyl alcohol on account of large steric hindrance of the t-butyl group.

The effect of water on the spectrum of the transient species of SBP in acetonitrile is shown in Fig. 5. As the concentration of water increases the spectrum gradually approaches, and ultimately strongly resembles, the spectrum in methanol.

Based on these spectral changes, it may be concluded that the isomer exhibiting the band at about 1512 cm^{-1} and the one exhibiting the band at 1445 cm^{-1} take the configurations which are stabilized by forming hydrogen bonds with hydrogen-bond donor solvents, whereas the isomer exhibiting the band at 1499 cm^{-1} and the one exhibiting the band at 1470 cm^{-1} take the configurations which cannot form strong hydrogen bonds with hydrogen-bond donor solvents. It is not clear, however, whether or not the isomer exhibiting the band at 1512 cm^{-1} is identical to that exhibiting the band at 1445 cm^{-1}. The same situation exists for the bands at 1499 and 1470 cm^{-1}. In other words, the above spectral changes indicate that there are at least two, and possibly four, stereoisomeric configurations of the transient species of SBP which exist in solution.

Wavelength dependence

Spectral dependence of the transient species of SBP in cyclohexane on the Raman excitation wavelength is shown in Fig. 6. All the spectra were measured at 100 ns after UV (308 nm) irradiation.

It is seen that the spectral changes occur quite distinctly with the Raman excitation wavelength at 460 nm. With the Raman excitation wavelength longer than 460 nm, the spectra are not very different; only the bands at 1500, 1482 and 1223 cm^{-1} are prominent. With 460 nm excitation, however, new bands start to appear at 1600, 1565, 1322 and 1171 cm^{-1}, and a dramatic increase in the relative intensity of these newly appeared bands is observed with 450 nm and shorter wavelength excitations.

Similar results were also obtained for acetonitrile and methanol solutions. The spectral changes, however, are much more complicated due to the probable existence of isomeric species.

Hirshberg and Fischer [7] reported that the transient species of SBP exhibits two absorption peaks at 490 and 420 nm at $-110\,°C$. It is conceivable that the strong dependence of the Raman spectrum of the transient species of SBP on the excitation wavelength is related to these two absorption peaks.

Vibrational assignment based on ^{13}C substitutions

The resonance Raman spectra of the transient species of ^{13}C-substituted SBPs in cyclohexane are compared in Fig. 7. All the spectra were measured 100 ns after UV (308 nm) irradiation and the excitation wavelength is 460 nm.

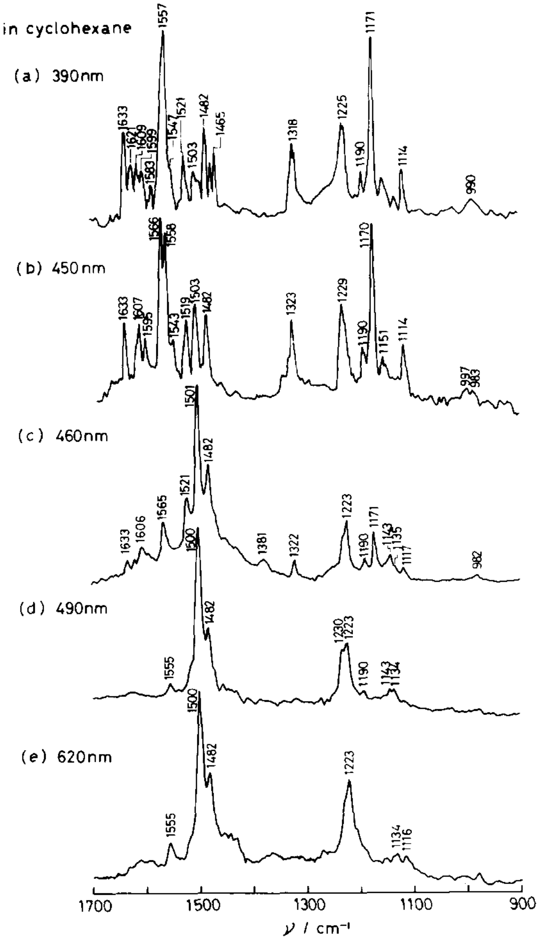

Fig. 6. Dependence of the resonance Raman spectra of the transient species of SBP in cyclohexane on the excitation wavelength: (a) 390 nm excitation; (b) 450 nm excitation; (c) 460 nm excitation; (d) 490 nm excitation; (e) 620 nm excitation. Spectra were measured at 100 ns after UV (308 nm) irradiation and the solvent bands have been subtracted.

The frequency shifts on the ^{13}C-substitutions are summarized in Table 1 along with the vibrational assignment.

The band at 1565 cm^{-1} does not shift upon 2-^{13}C substitution, but shifts to 1555 and 1554 cm^{-1} upon 3,3′-^{13}C and 2,3,3′-^{13}C substitutions, respectively. This band can be assigned to the C(3′)=C(4′) stretch, more precisely, to a vibrational mode to which the contribution of the C(3′)=C(4′) stretch is large. The band at 1521 cm^{-1} shifts to 1513 and 1517 cm^{-1} on the 2-^{13}C and 3,3′-^{13}C substitutions, respectively, and is hidden under the band at 1496 cm^{-1} on the 2,3,3′-^{13}C substitution. Thus, the band at 1521 cm^{-1} is assignable to the

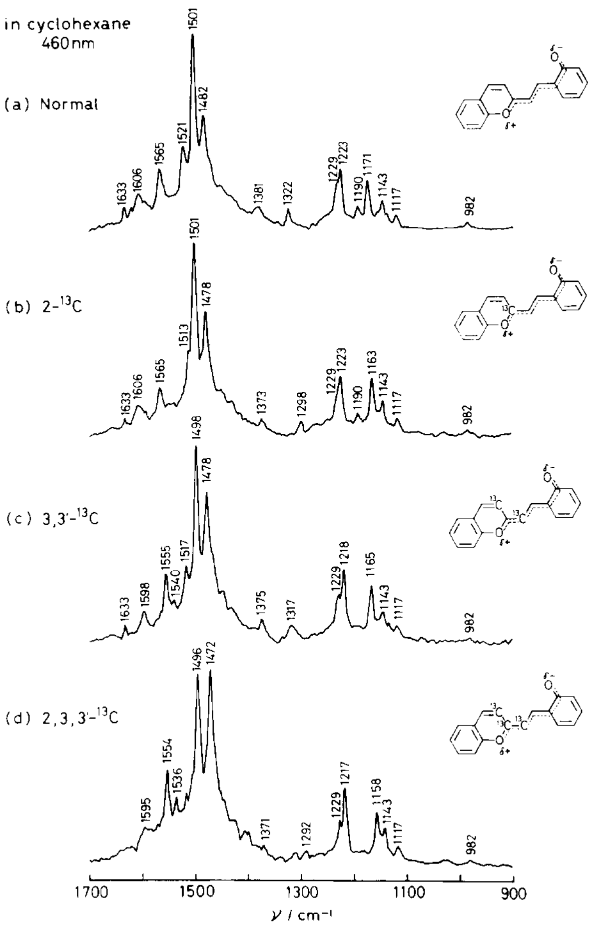

Fig. 7. Resonance Raman spectra of the transient species of ^{13}C substituted SBPs in cyclohexane taken 100 ns after UV (308 nm) irradiation: (a) normal species; (b) 2-^{13}C species; (c) 3,3′-^{13}C species; (d) 2,3,3′-^{13}C species. Excitation wavelength, 460 nm; solvent bands have been subtracted.

C(2)=C(3) stretch. The band at 1322 cm^{-1} shifts to 1298, 1317 and 1292 cm^{-1} on the 2-^{13}C, 3,3′-^{13}C and 2,3,3′-^{13}C substitutions, respectively. This band is attributable to the C(2)–O stretch. The band at 1171 cm^{-1} shifts to 1163, 1165 and 1158 cm^{-1} on 2-^{13}C, 3,3′-^{13}C and 2,3,3′-^{13}C substitutions, respectively. This band can be assigned to the C(2)–C(3′) stretch.

The above assignment indicates that almost all the bands which are detectable only in the spectra excited by light of wavelength shorter than 460 nm are attributable to the vibrations of the closed benzopyran part, whereas the bands which are most strongly enhanced with light of wavelength longer than 460 nm are assignable to the vibrations of the open benzopyran part, i.e. the merocyanine-like part.

TABLE 1

Vibrational assignment of the transient species of SBP in cyclohexane based on the frequency shifts on ^{13}C substitutions

Frequency SBP	Frequency shift			Assignment[a]
	SBP-2-^{13}C	SBP-3,3′-^{13}C	SBP-2,3,3′-^{13}C	
1633[b]	0	0	0	
1606[b]	0	−8	−11	
1565[b]	0	−10	−11	C(3′)=C(4′) str.
1521	−8	−6	−25	C(2)=C(3) str.
1501	0	−3	−5	quinoid C=C str.
1482	−3	−3	−9	C(4)=C(5) str.
1322[b]	−22	−3	−27	C(2)-O str.
1229	0	0	0	
1223	0	−5	−6	C(3)-C(4) str.
1171[b]	−5	−6	−13	C(2)-C(3′) str.
1143	0	0	0	
1117	0	0	0	
982	0	0	0	

[a] The numbering of carbon atoms is given in Fig. 1.

[b] The bands which are detectable only by the excitation wavelength shorter than 460 nm.

This leads to the conclusion that the absorption peak of the transient species at about 490 nm reported by Hirshberg and Fischer [7] is associated with the vertical transition to an excited singlet state, where the changes in molecular geometry are mainly confined to the merocyanine-like part, while the absorption peak at about 420 nm is related to the transition to another excited singlet state whose molecular structure is deformed mainly in the benzopyran part.

Time dependence

The time dependence of the resonance Raman spectra of the transient species of SBP in methanol is shown in Fig. 8. The excitation wavelength is 540 nm.

A distinct spectral change is observed at 500 μs after UV (308 nm) irradiation. Judging from the fact that the change occurs quite late after the UV irradiation, it may be attributable to aggregation of the transient species. The spectra in cyclohexane and in acetonitrile do not exhibit such time dependence, probably because the aggregated species is not soluble in nonpolar solvents and precipitates [12].

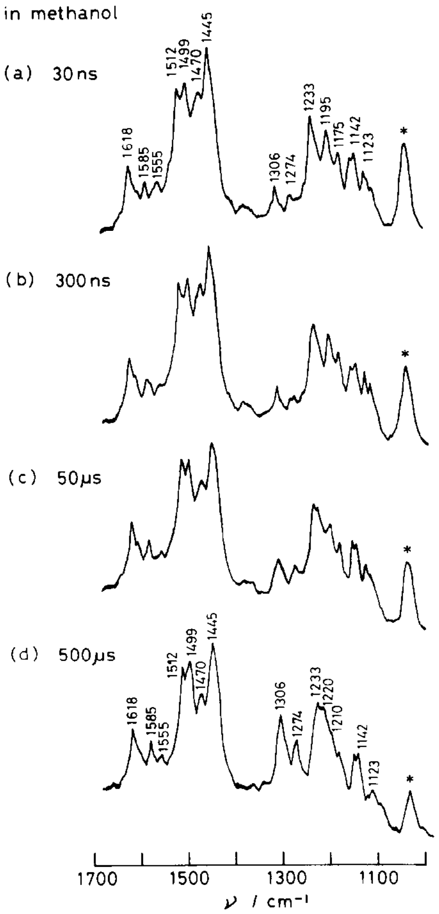

Fig. 8. Time-dependence of the resonance Raman spectra of the transient species of SBP in methanol: (a) 30 ns after UV (308 nm) irradiation; (b) 300 ns after UV irradiation; (c) 50 μs after UV irradiation; (d) 500 μs after UV irradiation. Excitation wavelength, 540 nm; solvent bands have been subtracted.

Molecular orbital calculations

Optimized geometries of SBP in the closed spiro form and in the merocyanine-like open form in the four different configurations, namely, *trans-trans-trans* (*TTT*), *TTC, CTT* and *CTC* configurations about the three partial C–C double bonds, were calculated using the semi-empirical AM1 (Austin method 1) method in the SCF level as shown in Figs. 9 and 10.

In the structure of the spiro form, the C(spiro)–O bond is calculated to be 1.436 Å which is significantly longer than the usual C–O single bond (1.427 Å in CH_3OH [13]). This accounts for the ease with which the cleavage of the C(spiro)–O bond of SBP takes place by UV irradiation.

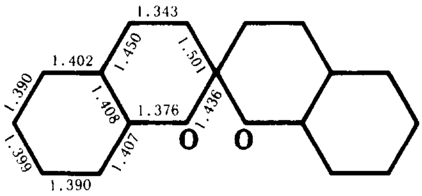

Fig. 9. Optimized geometry of SBP obtained by using the semi-empirical AM1 method (SCF level).

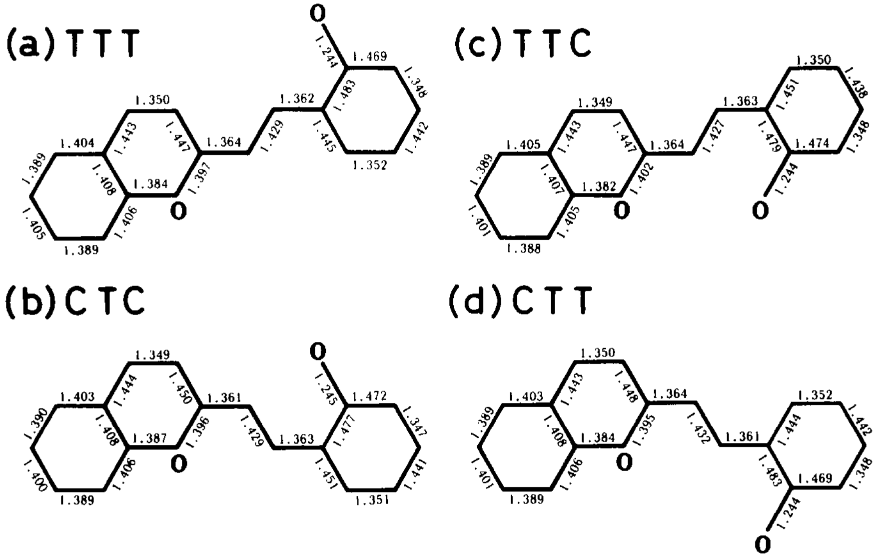

Fig. 10. Optimized geometries of the transient species of SBP in different configurations: (a) *TTT* configuration; (b) *CTC* configuration; (c) *TTC* configuration; (d) *CTT* configuration. The calculations were carried out using the semi-empirical AM1 method.

The calculated bond lengths of the merocyanine-like open structure are not much different for the four isomeric configurations. The bond lengths of the central three C–C bonds are calculated to be 1.364, 1.429 and 1.362 Å for the *TTT* configuration, 1.361, 1.429 and 1.363 Å for *CTC*, 1.364, 1.427 and 1.363 Å for *TTC*, and 1.364, 1.432 and 1.361 Å for *CTT*. The C–O bond length of the open benzopyran is calculated to be 1.244, 1.245, 1.244 and 1.244 Å for *TTT*, *CTC*, *TTC* and *CTT*, respectively, which are much shorter than the usual C–O single bond. These calculated values of the bond lengths indicate that the contribution of the quinoid form is definitely larger than the zwitterionic forms in the resonance hybrid structure of the transient species (Fig. 1).

The relative energies of the four configurations of the merocyanine-like structure were calculated using the MNDOC/MRSDCI (modified neglect of diatomic overlap-C/multi-reference single and double configuration interac-

TABLE 2

Calculated relative energies and dipole moments of different configurations of the transient species of SBP (the relative energies were obtained using the semi-empirical MNDOC/MR-SDCI method, and the dipole moments were calculated using the AM1 method)

Configuration	Relative energy (kcal mol^{-1})	Dipole moment (Debye)
TTT	0.0	4.5
CTT	0.5	5.2
CTC	2.0	4.2
TTC	3.1	4.7

tion) method taking into account 7 occupied and 7 unoccupied orbitals and 5 reference electronic configurations as shown in Table 2. In this approximation the number of configuration state functions amounts to 4604. It is seen that the energy of the *TTT* configuration is the lowest among the four configurations. The dipole moments of the four configurations calculated using the AM1 method are also shown in Table 2. We see that the dipole moment of the *TTT* configuration is the second lowest.

Based on the MO calculations, it may be concluded that the isomeric species which predominates in nonpolar cyclohexane takes the configuration which is energetically most stable and less polar, namely, the *TTT* configuration. The *CTT* configuration is only 0.5 kcal mol^{-1} more unstable than *TTT*, but is more polar. Therefore, the *CTT* configuration may also exist in polar solvents such as acetonitrile and methanol. The *CTC* and *TTC* configurations are very unstable and it is highly probable that their populations are too low to be detected by Raman spectra.

ACKNOWLEDGEMENT

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