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# Structures of transient species in the photochromic reaction of 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]: time-resolved resonance Raman study of isotopically substituted analogues

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**Abstract**—Time-resolved resonance Raman spectra of seven kinds of isotopically substituted analogues of 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] in the photomerocyanine form have disclosed that only the vibrations of the cleaved benzopyran part are resonance enhanced significantly in cyclohexane and in acetonitrile solutions with 460–390 nm probe light. Dramatic changes in the resonance Raman spectra of the photomerocyanine on going from non-hydrogen-bond donor solvents to hydrogen-bond donor solvents can be interpreted as being due to changes in the relative contribution of *ortho*-quinoidal and zwitterionic forms in the resonance hybrid structure of the photomerocyanine: in cyclohexane and in acetonitrile the contribution of the *ortho*-quinoidal form is substantial, while in methanol the zwitterionic form is stabilized by hydrogen bonding with the solvent and the photomerocyanine takes an almost zwitterionic structure.

## INTRODUCTION

IT HAS been established that the photochromic reaction of spiropyrans consists of a cleavage of the C(spiro)–O bond by irradiation with UV light to generate coloured transients having merocyanine-like structures [1, 2], commonly called photomerocyanine. However, the configuration of the photomerocyanine, as well as the electron distribution of the merocyanine-like skeleton, is not well understood.

In a preceding paper, we have shown by time-resolved resonance Raman spectroscopy that the photochromic reaction of 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (BIPS) in various solvents can be interpreted in terms of the involvement of four photomerocyanine isomers having TTC (*trans–trans–cis*), CTT, CTC and TTT configurations with respect to the three C–C partial double bonds of the skeleton, with their relative abundance being dependent on the polarity and hydrogen-bond donor ability of the solvent [3, 4].

The structure of the photomerocyanine may be expressed as a resonance hybrid of *ortho*-quinoidal and zwitterionic forms, as shown in Scheme 1 (TTC photomerocyanine isomer is shown as an example). Since the relative contribution of these two forms to the resonance hybrid structure is considered to be highly dependent on the polarity and particularly on the hydrogen-bond donor ability of the solvent, it is necessary for a proper understanding of the photochromic reaction of BIPS to take into account the changes in the relative contribution of the two forms in different solvents, in addition to the *trans–cis* isomerization about the three C–C partial double bonds of the photomerocyanine skeleton.

The present investigation was undertaken in order to obtain detailed information on the solvent dependence of the relative contribution of the *ortho*-quinoidal and zwitterionic forms in the resonance hybrid structure of the photomerocyanine by establishing its vibrational assignment based on isotopic substitutions.

## EXPERIMENTAL

The experimental arrangement of our time-resolved Raman spectroscopy system has been described previously [5] and that of our laser flash photolysis system will be given elsewhere.

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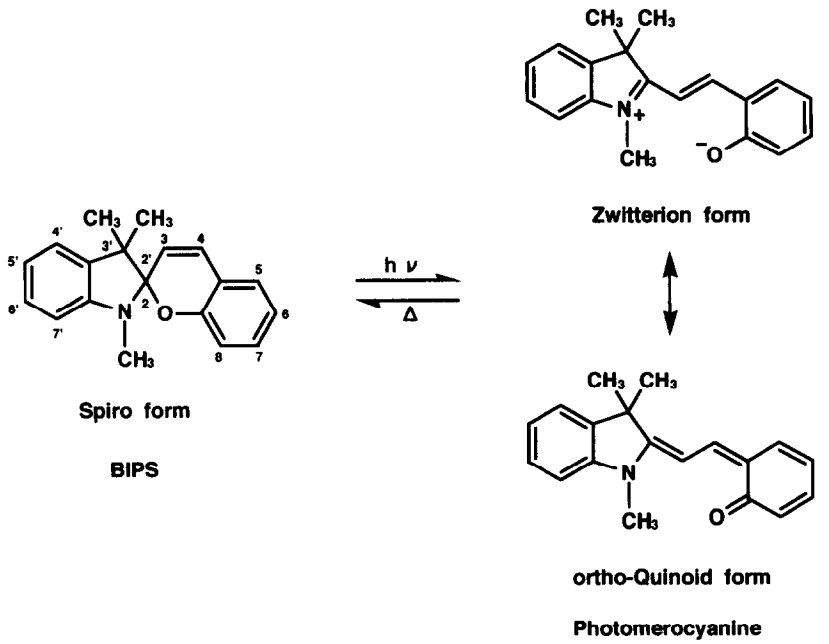


Scheme 1.

BIPS and its isotopically substituted analogues, namely BIPS-$d_1$ (4-position), BIPS-$d_3$ (N–$CD_3$), BIPS-$d_{4p}$ (phenyl group in the benzopyran moiety), BIPS-$d_{4i}$ (phenyl group in the indoline moiety), BIPS-$^{13}$C (N–$^{13}CH_3$), BIPS-$^{15}$N and BIPS-$^{18}$O, were synthesized by condensation of Fisher's base (1,3,3-trimethyl-2-methyleneindoline) or isotopically substituted Fisher's base with salicylaldehyde or isotopically substituted salicylaldehyde.

BIPS-$d_1$, BIPS-$d_{4p}$ and BIPS-$^{18}$O were synthesized by the condensation of Fisher's base with salicylaldehyde-$d_1$ [*o*-$C_6H_4$(OH)CDO], salicylaldehyde-$d_4$ [*o*-$C_6D_4$(OH)CHO] and salicylaldehyde-$^{18}$O [*o*-$C_6H_4$(OH)$CH^{18}O$], respectively. The salicylaldehyde-$d_1$ was synthesized from chloroform-$d_1$ (Merck, 99 atom% D) and phenol (Reimer–Tiemann reaction), the salicylaldehyde-$d_4$ from chloroform and phenol-$d_6$ (Toho Sanso, 99 atom% D), and the salicylaldehyde-$^{18}$O from chloroform and phenol-$^{18}$O prepared by the reaction of sodium benzenesulphonate with $K^{18}OH$ derived from $H_2{}^{18}O$ (Cambridge Isotope Lab., 99 atom% $^{18}$O).

BIPS-$d_3$, BIPS-$d_{4i}$, BIPS-$^{13}$C and BIPS-$^{15}$N were synthesized by the condensation of salicylaldehyde with Fisher's base-$d_3$ (N–$CH_3$), Fisher's base-$d_4$ (phenyl group), Fisher's base-$^{13}$C (N–$CH_3$) and Fisher's base-$^{15}$N, respectively. The Fisher's base-$d_3$ and Fisher's base-$^{13}$C were synthesized by the reaction of 2,3,3-trimethylindolenine with methyl iodide-$d_3$ (Merck, 99.5 atom% D) and methyliodide-$^{13}$C (Cambridge Lab., 99 atom% $^{13}$C), respectively. The Fischer's base-$d_4$ was synthesized by the reaction of methyl iodide with 2,3,3-trimethylindolenine-$d_4$, which was prepared by the reaction of isopropylmethylketone with phenylhydrazine-$d_6$ derived from aniline-$d_7$ (Toho Sanso, 98 atom% D), and the Fisher's base-$^{15}$N was synthesized by the same reaction using aniline-$^{15}$N (Toho Sanso, 99 atom% D).

## RESULTS AND DISCUSSION

### *Time-resolved absorption spectra*

Figure 1 shows transient absorption spectra of the photomerocyanine of BIPS in various solvents measured at 500 ns after UV (308 nm) irradiation. These spectra do not exhibit time dependence in any of these solvents in the time range between 20 ns and 5 ms. It is seen that the peak positions and absorption band shapes are dependent on the solvent. In non-polar solvents such as cyclohexane or benzene, both bands at around 550 and 400 nm have structures. These structures, however, are not distinctly seen in polar solvents such as acetonitrile or DMSO, and are completely smoothed out in alcohols. These results are in accord with those reported by MURIN *et al.* [6].

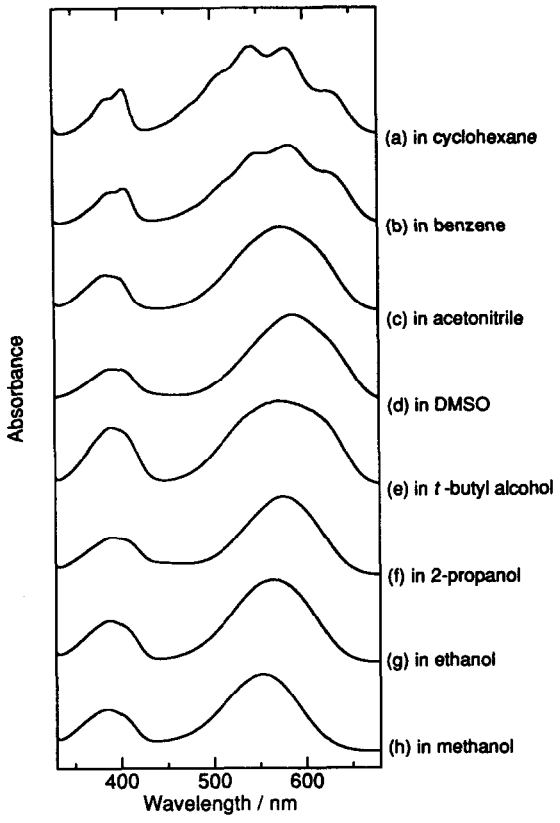


Fig. 1. Transient absorption spectra of the photomerocyanine of BIPS in various solvents measured 500 ns after UV (308 nm) irradiation: (a) in cyclohexane; (b) in benzene; (c) in acetonitrile; (d) in DMSO; (e) in t-butyl alcohol; (f) in 2-propanol; (g) in ethanol; (h) in methanol. Concentration, $5.0 \times 10^{-4}$ mol dm$^{-3}$.

One feature of interest is that the absorption peak at around 550 nm shifts to shorter wavelength as the hydrogen-bond donor ability of the solvent increases in the sequence: t-butyl alcohol, 2-propanol, ethanol and methanol. The spectrum in t-butyl alcohol is quite similar to that in acetonitrile. Closer examinations of the spectra of alcoholic solutions reveal that each of the bands at around 550 nm consists of at least three Lorentz-type bands, with the relative intensity of the shortest wavelength band increasing in the above sequence.

Two possible effects should be considered in this respect: (i) configurational isomerism around the three C–C partial double bonds of the merocyanine-like skeleton and (ii) changes in the relative contribution of the *ortho*-quinoidal and zwitterionic forms in the resonance hybrid structure of the photomerocyanine caused by formation of hydrogen bonds with the solvent. The former effect has been discussed in our previous paper [3] and will not be considered here in detail. Briefly, Raman spectral changes of BIPS photomerocyanine in different solvents can be interpreted in terms of four configurations, TTC (*trans–trans–cis*), CTC, CTT and TTT, with respect to the three C–C partial double bonds. In alcoholic solutions, in particular, two photomerocyanines having the TTT and CTT configurations are considered to be stabilized by hydrogen bond formation with the solvent. Although the three Lorentz-type bands at around 550 nm are most probably attributable to these different configurational isomers, the correspondence between them is not clear, except to say that the shortest wavenumber band arises from a hydrogen-bonded species. On the other hand, the latter effect has not been discussed in detail previously and therefore, is one of the main subjects of this investigation.

The hypsochromic shift of the absorption band of the photomerocyanine with increasing hydrogen-bond donor ability of the solvent shown in Fig. 1 should be ascribed

to an increase of the population of hydrogen-bonded photomerocyanines as compared with the population of free (non-hydrogen-bonded) photomerocyanines. Since the absorption coefficients of the bands at around 550 nm are quite large, $\varepsilon = 3.0 \times 10^4\ M^{-1}\ cm^{-1}$ [7], these bands are considered to be due to $\pi$–$\pi^*$ transitions. It is generally believed that an absorption band arising from a $\pi$–$\pi^*$ transition exhibits bathochromic shifts in polar solvents and particularly in hydrogen-bond donor solvents. Therefore, the observed hypsochromic shifts of the band at around 550 nm of the photomerocyanine of BIPS in hydrogen-bond donor solvents are quite unusual and suggest that the electron distribution of the photomerocyanine in hydrogen-bond donor solvents differs considerably from that in non-hydrogen-bond donor solvents. It seems plausible that the photomerocyanine takes an almost zwitterionic structure when it is hydrogen bonded with the solvent, while it takes a nearly *ortho*-quinoidal structure in non-polar solvents and also in polar (non-hydrogen-bonding) solvents with a slightly larger contribution of the zwitterionic form.

*Time-resolved resonance Raman spectra*

In Fig. 2 are shown the transient resonance Raman spectra of the photomerocyanine of BIPS in cyclohexane, in acetonitrile and in methanol measured at 100 ns after UV (308 nm) irradiation using 460 nm probe light. None of these spectra exhibit time dependence, in good agreement with the transient absorption spectra shown in Fig. 1. However, the Raman spectral changes in different solvents are quite dramatic. In cyclohexane the spectrum is comparatively simple and only one strong band is observed at 1501 $cm^{-1}$. In acetonitrile, the spectrum is more complex and several strong bands are observed in the 1530–1440 and 1250–1100 $cm^{-1}$ spectral regions. The strongest band at 1501 $cm^{-1}$ of cyclohexane solution appears to correspond to either of the doublet peaks at 1496 and 1485 $cm^{-1}$. In methanol, the band corresponding to the strongest band at 1501 $cm^{-1}$ in cyclohexane or the band corresponding to the doublet at 1496 and

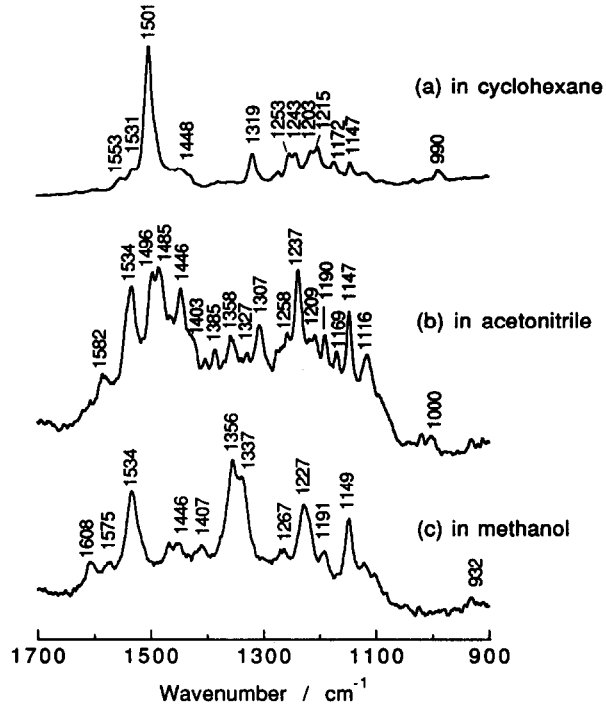


Fig. 2. Transient resonance Raman spectra of the photomerocyanine of BIPS in different solvents measured at 100 ns after UV (308 nm) irradiation with 460 nm probing: (a) in cyclohexane; (b) in acetonitrile; (c) in methanol. Concentration, $1.0 \times 10^{-3}$ mol $dm^{-3}$. Solvent bands were subtracted.

1485 $cm^{-1}$ in acetonitrile is missing and a strong doublet appears at 1356 and 1337 $cm^{-1}$, which is absent in both cyclohexane and acetonitrile solutions.

The spectral changes in alcoholic solutions are particularly interesting, as shown in Fig. 3. We see that the strong doublet peaks at 1356 and 1337 $cm^{-1}$ in methanol solution reduce in intensity as the hydrogen-bond donor ability of the solvent decreases in the order: methanol, ethanol, 2-propanol and t-butyl alcohol, while the doublet at 1496 and 1485 $cm^{-1}$, which is the characteristic band in polar solvents such as acetonitrile or DMSO, increases in intensity in the same sequence. The spectrum in t-butyl alcohol is quite similar to that in acetonitrile or in DMSO. Taking into account the fact that the hydrogen-bond donor ability of t-butyl alcohol is small due to steric hindrance, the close resemblance of the Raman and absorption spectra in t-butyl alcohol with those in acetonitrile or in DMSO indicates that the doublet at 1356 and 1337 $cm^{-1}$ in methanol arises from the photomerocyanine, which is hydrogen bonded with hydrogen-bond donor solvents. The spectral change in alcoholic solutions, therefore, can be interpreted as being due to the change in the relative populations of hydrogen-bonded and non-

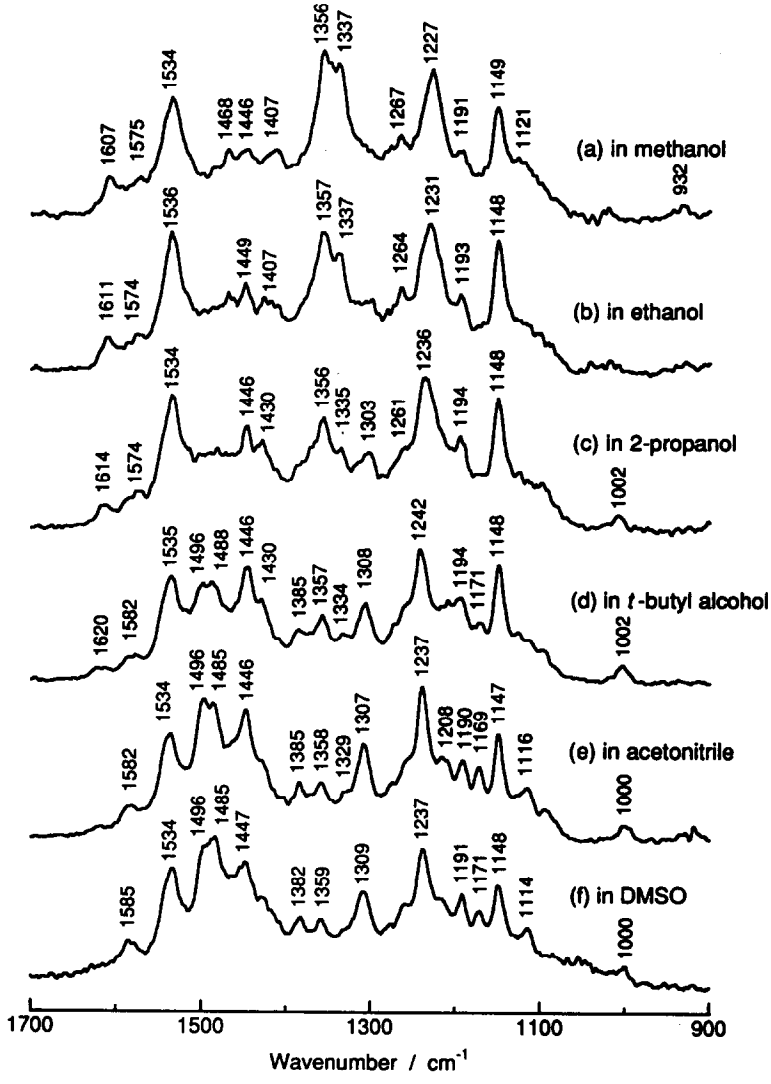


Fig. 3. Comparison of transient resonance Raman spectra of the photomerocyanine of BIPS in various alcohols with those in acetonitrile and in DMSO measured at 100 ns after UV (308 nm) irradiation with 460 nm probing: (a) in methanol; (b) in ethanol; (c) in 2-propanol; (d) t-butyl alcohol; (e) in acetonitrile; (f) in DMSO. Concentration, $1.0 \times 10^{-3}$ mol $dm^{-3}$. Solvent bands were subtracted.

hydrogen-bonded photomerocyanines with the solvent, depending on its hydrogen-bond donor ability.

Since the relative contribution of the zwitterionic form to the resonance hybrid structure of the photomerocyanine is considered to be predominant over that of the *ortho*-quinoidal form in the hydrogen-bonded photomerocyanine, the Raman spectrum of the methanol solution, where the photomerocyanines are almost completely hydrogen bonded with the solvent, may be attributable to the zwitterionic form.

*Frequency shifts on isotopic substitution*

Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in cyclohexane measured with 460 nm probe light are shown in Fig. 4. The strongest band at 1501 $cm^{-1}$ shifts to 1483 $cm^{-1}$ on the deuteration of the phenyl group in the benzopyran moiety (BIPS-$d_{4p}$), but does not exhibit appreciable shifting on other isotopic substitutions. This band is assignable to a stretching vibration

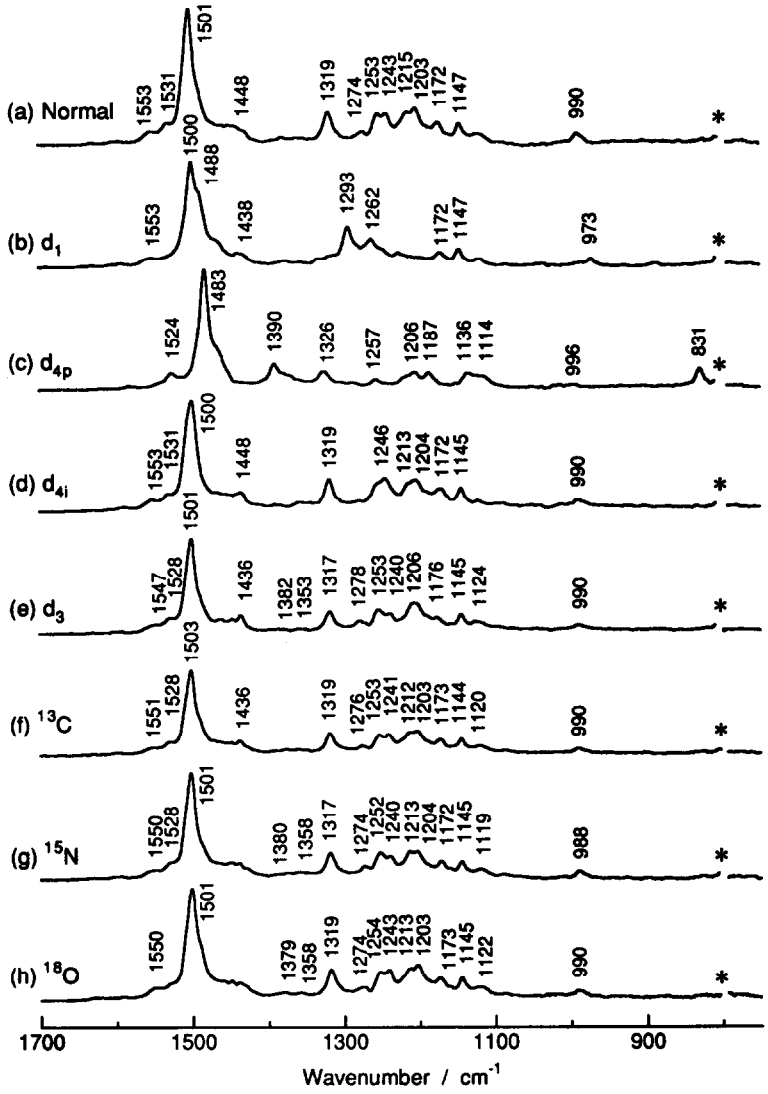


Fig. 4. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in cyclohexane measured at 100 ns after UV (308 nm) irradiation with 460 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (e) BIPS-$d_3$; (f) BIPS-$^{13}C$; (g) BIPS-$^{15}N$; (h) BIPS-$^{18}O$. Concentration, $1.0 \times 10^{-3}$ mol $dm^{-3}$. Solvent bands were subtracted. Asterisk denotes that the spectrum is obscured by a strong band of the solvent.

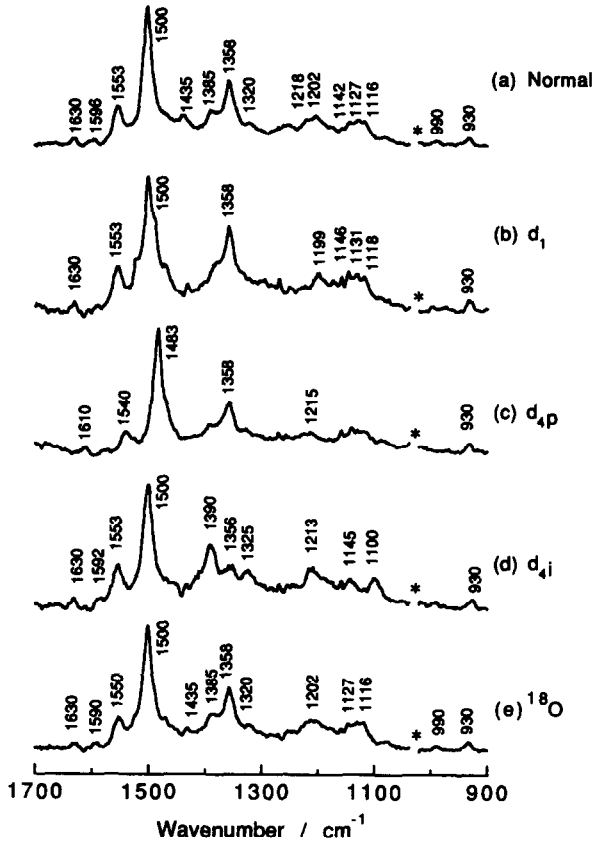


Fig. 5. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in cyclohexane measured at 100 ns after UV (308 nm) irradiation with 390 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (e) BIPS-$^{18}$O. Concentration, $1.0 \times 10^{-3}$ mol dm$^{-3}$. Solvent bands were subtracted. Asterisk denotes that the spectrum is obscured by a strong band of the solvent.

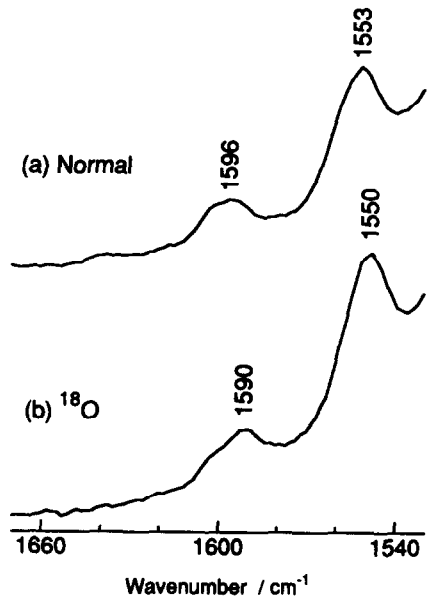


Fig. 6. Comparison of the transient resonance Raman spectra in the 1660–1540 cm$^{-1}$ region of the photomerocyanines of BIPS and BIPS-$^{18}$O in cyclohexane measured at 100 ns after UV (308 nm) irradiation with 420 nm probe light: (a) normal species; (b) BIPS-$^{18}$O. Concentration, $1.0 \times 10^{-3}$ mol dm$^{-3}$.

of the phenyl skeleton of the cleaved benzopyran part of the photomerocyanine. The resonance Raman spectra of the isotopically substituted analogues, BIPS-$d_1$, BIPS-$d_{4p}$, BIPS-$d_{4i}$ and BIPS-$^{18}O$, measured with 390 nm probe light, are compared in Fig. 5. The bands at 1630 and 1553 $cm^{-1}$, which are not clearly seen in the spectra with 460 nm probing, shift to 1610 and 1540 $cm^{-1}$, respectively, on deuteration of the phenyl group in the benzopyran moiety. These bands are also attributable to stretching vibrations of the phenyl group in the cleaved benzopyran part.

It is known that an *ortho*-disubstituted phenyl group in the benzenoid form usually exhibits bands at around 1600, 1590, 1490 and 1450 $cm^{-1}$, which are assignable to the skeletal stretches 8*b*, 8*a*, 19*b* and 19*a* [8] (WILSON vibrational number [9]) and are shifted to around 1570–1550 $cm^{-1}$ for 8*a* and 8*b* and 1370–1340 $cm^{-1}$ for 19*a* and 19*b* on deuteration. Therefore, the fact that the bands at 1630, 1553 and 1501 $cm^{-1}$ are attributable to the skeletal stretches of the phenyl group in the cleaved benzopyran part and are shifted on deuteration to 1610, 1540 and 1483 $cm^{-1}$, respectively, indicates that

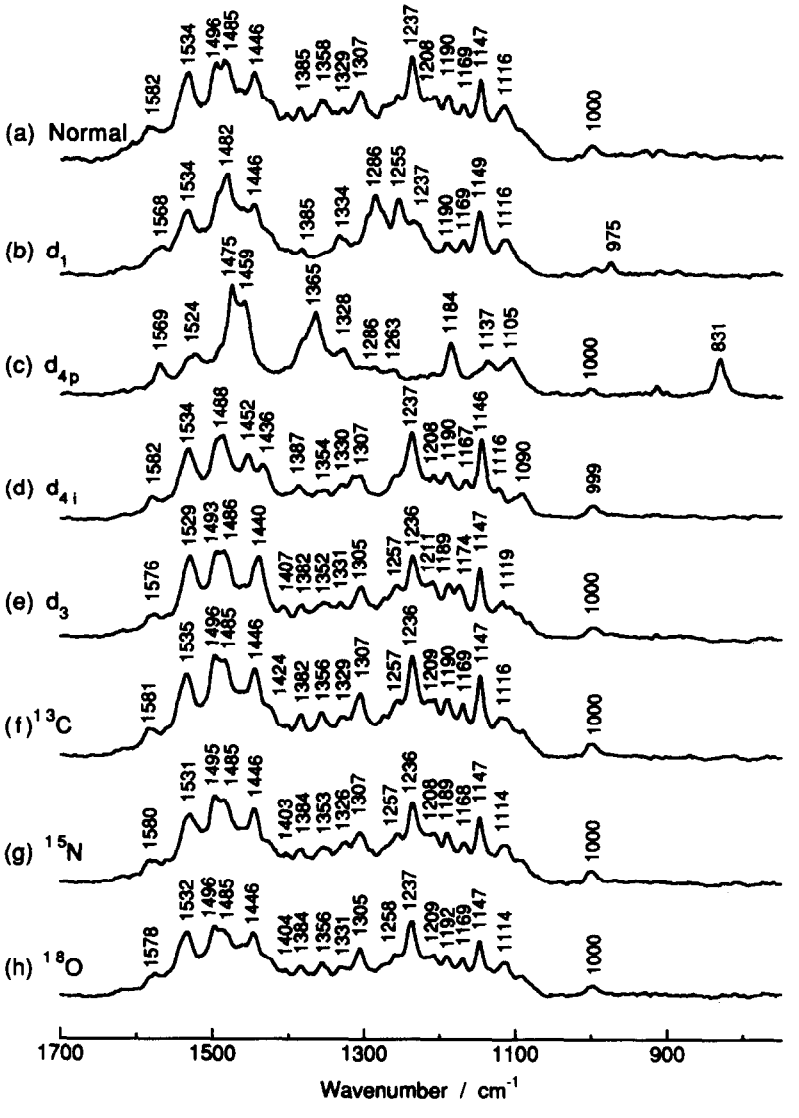


Fig. 7. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in acetonitrile measured at 100 ns after UV (308 nm) irradiation with 460 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (e) BIPS-$d_3$; (f) BIPS-$^{13}C$; (g) BIPS-$^{15}N$; (h) BIPS-$^{18}O$. Concentration, $1.0 \times 10^{-3}$ mol $dm^{-3}$. Solvent bands were subtracted.

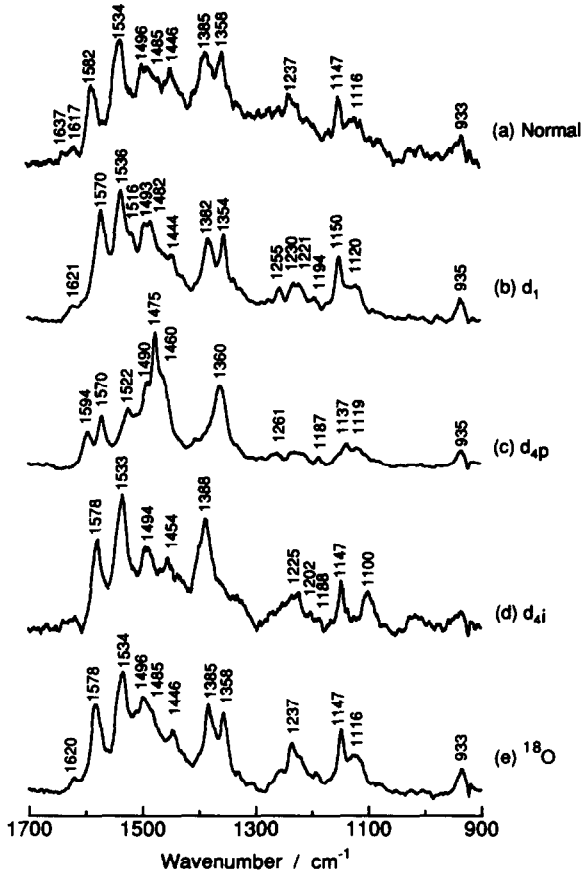


Fig. 8. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in acetonitrile measured at 100 ns after UV (308 nm) irradiation with 390 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (e) BIPS-$^{18}O$. Concentration, $1.0 \times 10^{-3}$ mol dm$^{-3}$. Solvent bands were subtracted.

the phenyl group in the cleaved benzopyran part of the photomerocyanine is not in a benzenoid form, but takes an almost *ortho*-quinoidal form in cyclohexane solution.

The spectra measured with 460 nm probing shown in Fig. 4 appear to indicate that the $^{18}O$ substitution does not affect the spectrum appreciably and the C=O stretch is not observable in the Raman spectrum due to its weak intensity, as is often the case. However, a closer examination of the spectra measured with 390 nm probing shown in Fig. 5 and with 420 nm probing shown in Fig. 6 (the spectra of the normal species and $^{18}O$ analogue are compared with enlarged scaling near the 1600 cm$^{-1}$ region) reveals that the band at 1596 cm$^{-1}$ definitely shifts to 1590 cm$^{-1}$ on $^{18}O$ substitution. This indicates that the band at 1596 cm$^{-1}$ can be assigned to a normal mode with an appreciable contribution of the C=O stretch.

It may appear that the frequency 1596 cm$^{-1}$ is somewhat lower compared, for example, with the C=O stretch frequencies of *p*-benzoquinone, 1673 (symmetric) and 1613 cm$^{-1}$ (antisymmetric) [10], and the downfield shift of 6 cm$^{-1}$ on $^{18}O$ substitution is much smaller than that of a usual C=O stretch (a downfield shift of about 40 cm$^{-1}$ is expected on $^{18}O$ substitution for a pure C=O stretch [11]). However, since the C=O group of the photomerocyanine is conjugated with the phenyl group in the cleaved benzopyran and the electron distribution of the photomerocyanine skeleton should be expressed as a resonance hybrid of *ortho*-quinoidal and zwitterionic forms, the C=O stretch is not isolated from C=C stretches of the phenyl group. The coupling with the C=C stretches of the phenyl group leads to a lowering of the C=O stretch frequency and a smaller $^{18}O$ isotopic shift than those of the usual C=O stretch. Nonetheless, the assignment of the band at 1596 cm$^{-1}$ observed in cyclohexane to a normal mode

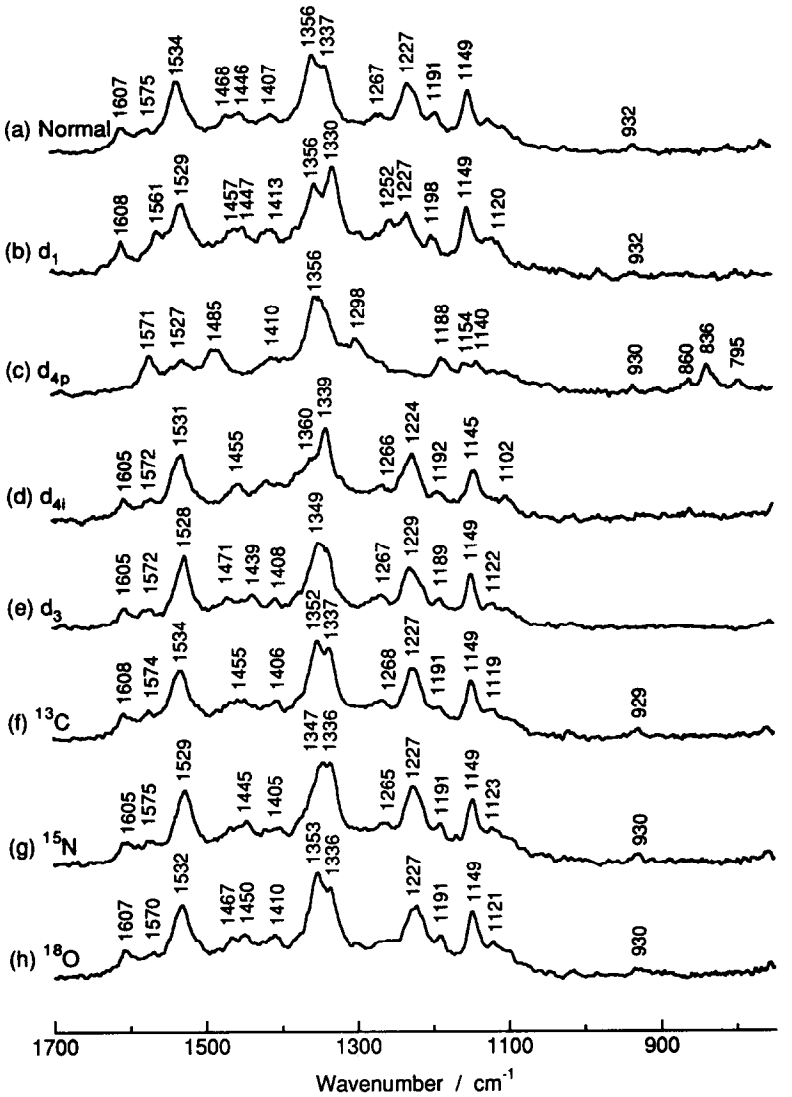


Fig. 9. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in methanol measured at 100 ns after UV (308 nm) irradiation with 460 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (c) BIPS-$d_3$; (f) BIPS-$^{13}C$; (g) BIPS-$^{15}N$; (h) BIPS-$^{18}O$. Concentration, $1.0 \times 10^{-3}$ mol dm$^{-3}$. Solvent bands were subtracted.

involving a considerable contribution of the C=O stretch gives support to the above conclusion that the contribution of the *ortho*-quinoidal form predominates over that of the zwitterionic form in the resonance hybrid structure of the photomerocyanine in cyclohexane.

It is seen in Figs 4 and 5 that the deuteration of the phenyl and N–$CH_3$ groups in the indoline moiety, and the $^{15}N$ and $^{13}C$ substitutions of the N–$CH_3$ group do not affect the spectrum, suggesting that the vibrations of the indoline part of the photomerocyanine are not appreciably resonance enhanced either by 460 nm or by 390 nm probing in cyclohexane solution. These results are consistent with the conclusion that the photomerocyanine in cyclohexane takes an approximately *ortho*-quinoidal structure in which the indoline phenyl group does not participate in the conjugation of the photomerocyanine skeleton.

Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in acetonitrile measured with 460 nm probe light are shown in Fig. 7 and those measured with 390 nm probe light in Fig. 8. The bands at 1582 and 1534 cm$^{-1}$ shift to 1569 and 1524 cm$^{-1}$, respectively, and the doublet peaks at 1496 and

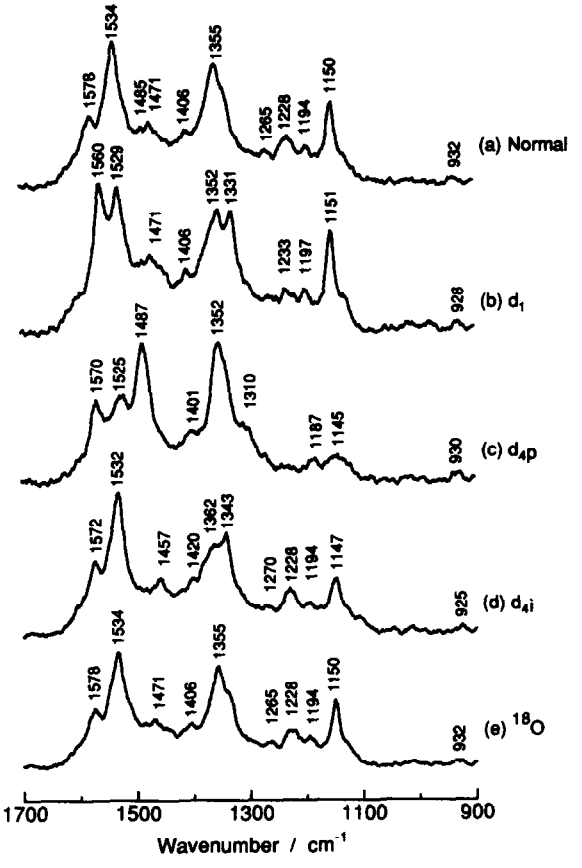


Fig. 10. Transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in methanol measured at 100 ns after UV (308 nm) irradiation with 420 nm probe light: (a) normal species; (b) BIPS-$d_1$; (c) BIPS-$d_{4p}$; (d) BIPS-$d_{4i}$; (e) BIPS-$^{18}O$. Concentration, $1.0 \times 10^{-3}$ mol dm$^{-3}$. Solvent bands were subtracted.

1485 cm$^{-1}$ shift to 1475 and 1459 cm$^{-1}$ on deuteration of the phenyl group in the benzopyran moiety. The band at 1582 cm$^{-1}$ shifts to 1570 cm$^{-1}$ on deuteration at the 4-position of the benzopyran moiety. These isotopic shifts indicate that the bands at 1582, 1534, 1496 and 1485 cm$^{-1}$ are assignable to the skeletal stretches of the cleaved benzopyran part and suggest that the photomerocyanine also takes an approximate *ortho*-quinoid structure in acetonitrile.

The results showing deuteration of the phenyl group in the indoline moiety and deuteration and $^{13}C$ and $^{15}N$ substitutions of the N–$CH_3$ group do not affect the spectrum appreciably indicate that the indoline phenyl group, as well as the N–$CH_3$ group, do not significantly participate in the conjugation of the photomerocyanine skeleton and are consistent with the approximate *ortho*-quinoidal structure. No band is identified positively as the C=O stretch or a normal mode with large contribution of the C=O stretch in the spectra of acetonitrile solution, due most probably to its weak intensity. Since the band assignable to the C=O stretch is expected to appear somewhat lower in acetonitrile than in cyclohexane because of the slightly larger contribution of the zwitterionic form to the resonance hybrid structure of the photomerocyanine in acetonitrile, it is also probable that the band assignable to the C=O stretch is buried under intense nearby bands in the 1550–1450 cm$^{-1}$ region.

The transient resonance Raman spectra of isotopically substituted analogues of the photomerocyanine of BIPS in methanol measured with 460 nm probe light are shown in Fig. 9 and those measured with 420 nm light in Fig. 10. Due to strong fluorescence from the sample, the 390 nm light could not be used for probing. The band at 1607 cm$^{-1}$ is seen to exhibit a shift to 1571 cm$^{-1}$ on deuteration of the phenyl group in the benzopyran

moiety. This isotopic shift is common to a phenyl group in the benzenoid form. Therefore, this band can be assigned to the 8*b* mode of the phenyl group of the benzopyran part, and suggests that the photomerocyanine takes a zwitterionic form in methanol. However, the band assignable to the C–$O^-$ stretch, which is expected to appear around 1300–1200 $cm^{-1}$, is not detected.

The band at 1575 $cm^{-1}$ shifts to 1561 $cm^{-1}$ on deuteration of the 4-position of the benzopyran moiety. This band is reasonably assigned to the central C=C bond of the cleaved pyran part of the merocyanine skeleton.

## CONCLUSIONS

Time-resolved absorption spectra and time-resolved resonance Raman spectra of isotopically substituted analogues of BIPS in various solvents reveal that the electron distribution of photochemically produced transient photomerocyanines can be represented by an *ortho*-quinoidal structure with a small contribution of the zwitterionic form in cyclohexane and also by an *ortho*-quinoidal structure but with a slightly larger contribution of the zwitterionic form in acetonitrile.

In alcoholic solutions, the photomerocyanine exists as a mixture of non-hydrogen-bonded and hydrogen-bonded forms, with their relative abundance being dependent on the hydrogen-bond donor ability of the solvent. The electron distribution of the non-hydrogen-bonded photomerocyanine in alcohols is similar to that of the photomerocyanine in polar solvents. On the other hand, the electron distribution of hydrogen-bonded merocyanine in alcohols is represented by an almost completely zwitterionic structure.

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