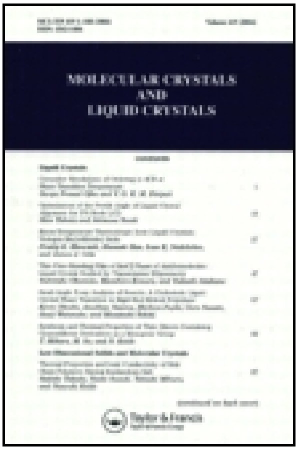

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Surface-Enhanced Resonance Raman Studies of Spiropyrans (Bips and Derivatives)

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SURFACE-ENHANCED RESONANCE RAMAN STUDIES OF SPIROPYRANS (BIPS AND DERIVATIVES)

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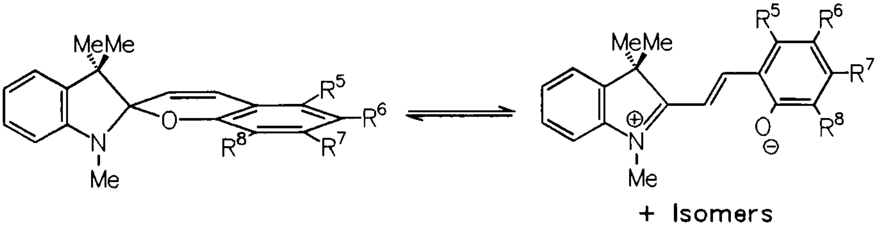
Abstract The merocyanine form of BIPS and three of its nitro derivatives were studied by surface-enhanced Raman spectroscopy. It was found that in case of the nitro derivates, the SERS spectra originated from the unprotonated open merocyanine forms, even if the solution was acidified. In case of 6-nitro BIPS, there exist two enantiomers of the closed spiro form with different properties. The photoinduced merocyanine form of the photoactive enantiomer is different from the thermal ring opening product of the photoinactive enantiomer.

INTRODUCTION

Since a complete understanding of the photochromic properties of spiropyrans and spirooxazines requires the knowledge of the isomeric distribution of the compounds in the open merocyanine form[1], several attempts have been made in the past to determine it as a function of solvent properties and substituents. Raman spectroscopy[2,3] is a most suitable tool to solve this task, except that fluorescence often prevents a tuning of the excitation wavelength into the long wavelength absorption band. This problem is avoided by using coherent anti-Stokes Raman scattering (CARS), in which case the signal to be detected is at shorter wavelength than the exciting radiation[4]. The draw backs of CARS spectroscopy are, however, the need of fairly high solute concentration and the complex line shapes. Since surface-enhanced Raman spectroscopy is known for its potential in investigating fluorescing compounds with minimum amounts of sample, we decided to apply this technique to the study of photochromic materials. In this contribution we will report our first results on BIPS and three of its nitro-derivatives.



	R^5	R^6	R^7	R^8
BIPS (**1**)	H	H	H	H
6-Nitro-BIPS (**2**)	H	NO_2	H	H
8-Methoxy-6-nitro-BIPS (**3**)	H	NO_2	H	OMe
5,7-Dimethoxy-6-nitro-BIPS (**4**)	OMe	NO_2	OMe	H

EXPERIMENTAL DETAILS

Materials

The above scheme shows the structure of the compounds investigated and introduces the numbering used. The samples were synthesized according to published procedures several years ago and stored in dry, crystaline form. A fraction of compounds **2** and **4** were recrystalized shortly before use from methanol solution.

Silver soles needed for surface-enhanced Raman (SER) spectroscopy were prepared according to a newly developed procedure.[5] Special attention was given to uniform particle size (50 nm) and neutral pH. Stabilisation of the sole was achieved by addition of chloride.

Methods

The compounds were dissolved in methanol (10^{-3} M). For UV-vis spectroscopic investigations, these solutions were titrated either with HCl or illuminated with the filtered light of a 250 W mercury lamp. For SER spectroscopy, the illuminated or acidified sample solutions were added to the silver sole. Then spectra were recorded in intervals up to 20 hours after mixing (λ_{ex} = 514.5 nm).

RESULTS

In Figure 1, the UV-vis absorption spectra of the four compounds in methanolic solution are shown. Compound **1** (BIPS) shows practically no absorption in the wavelength range 350-650 nm. Compound **2** (6-nitro BIPS) exhibits a weak absorption with maximum around 540 nm. Introduction of a methoxy group in position 8 (compound **3**) results in a relatively better stabilisation of the open merocyanine form. As a consequence two fairly intense absorption bands are observed with maxima around 550 nm and 370 nm. Introduction of two methoxy groups next to the nitro group (compound **4**) causes a further rela-

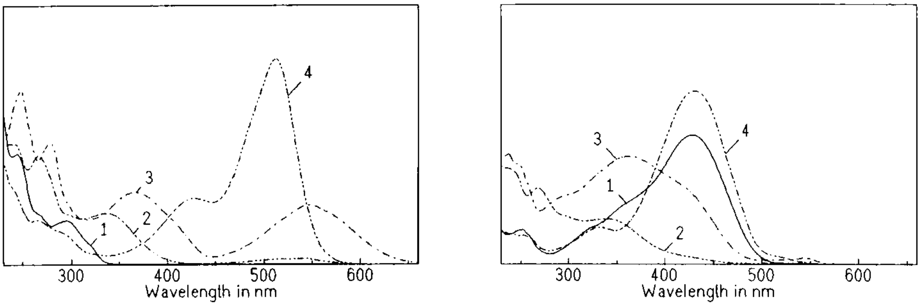


FIGURE 1 UV-vis absorption spectra of compounds **1** - **4** in neutral methanolic solution (left side) and acidified methanolic solution (right side).

tive stabilisation of the merocyanine form. The absorption spectrum is now dominated by an intense absorption at 515 nm and a weaker band around 425 nm.

Upon addition of HCl in excess, a new absorption band with maximum around 435 nm shows up in the spectrum of BIPS; it is assigned to a protonated open form. Qualitatively the same observation is made with nitro BIPS, **2**, except that the changes are much smaller. The weak band around 420 nm increases whereas the long wavelength maximum decreases in intensity. In case of the methoxy derivative, **3**, the band around 370 nm increases and a new transition indicated by a shoulder around 430 nm is found in the acidified solution. In the acidified solution of the di-methoxy derivative, **4**, the long wavelength absorption has disappeared and the formerly weak band around 425 nm has gained much intensity.

Using steady state UV-illumination, no increase in long wavelength absorption is found for BIPS. This is reasonable in view of the short lifetime of the open merocyanine form. Nitro BIPS, on the other hand, shows a significant increase of the long wavelength absorption due to the fairly slow back reaction to the closed spiro form. In the spectra of the methoxy derivatives **3** and **4**, no significant increase of the long wavelength absorption could be found upon steady state UV-illumination. Upon irradiation of **4** with 514.5 nm laser light, the red band disappears indicating a photoinduced ring closure. In the dark, the red absorption is recovered on the time scale of seconds.

In their open merocyanine forms (unprotonated) the investigated compounds have a high extinction coefficient for 514.5 nm radiation used in SER spectroscopy. The absorption of the protonated forms is, however, hypsochromically shifted. Nevertheless, one can expect to get good SER spectra of these species and despite of the fact that the total concentration of the spiro compounds in the sole solution is only on the order of 10^{-5} M.

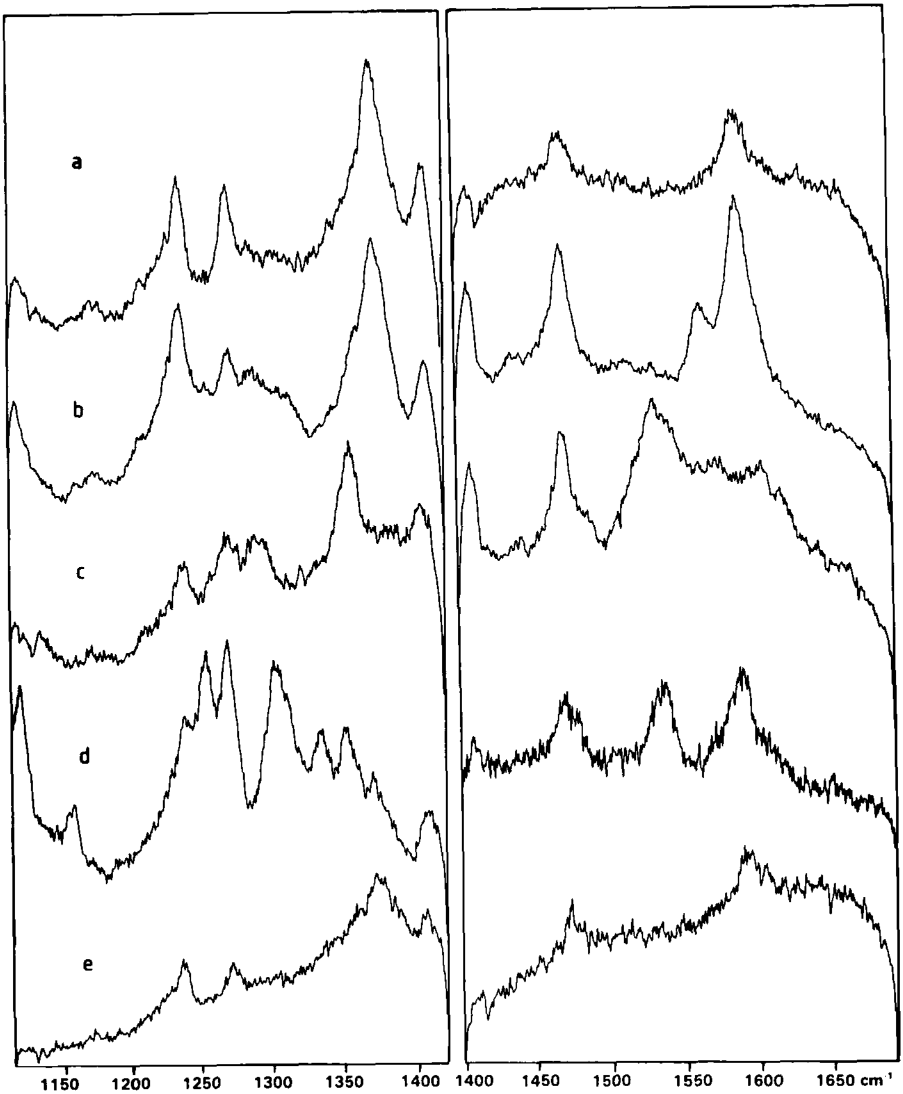


FIGURE 2 SER spectra of compounds **2** - **4** in neutral methanolic solution (a = **2**, b = **3**, c = **4**) and of BIPS (**1**) in acidified (d) and alkalified (e) methanolic solution.

In accordance with the lack of open form BIPS produced no SER spectrum in plain methanol. It is surprising, however, that the dimethoxy derivative, **4**, did not produce a SER spectrum within the first 20 min. after mixing despite of its intense band around 515 nm. Only after 18 hours of standing time in the sole a reasonable good spectrum could be recorded (trace c in Fig.2). In contrast, compounds **2** and **3** generated good SER spectra immediately after mixing (Fig.2a,

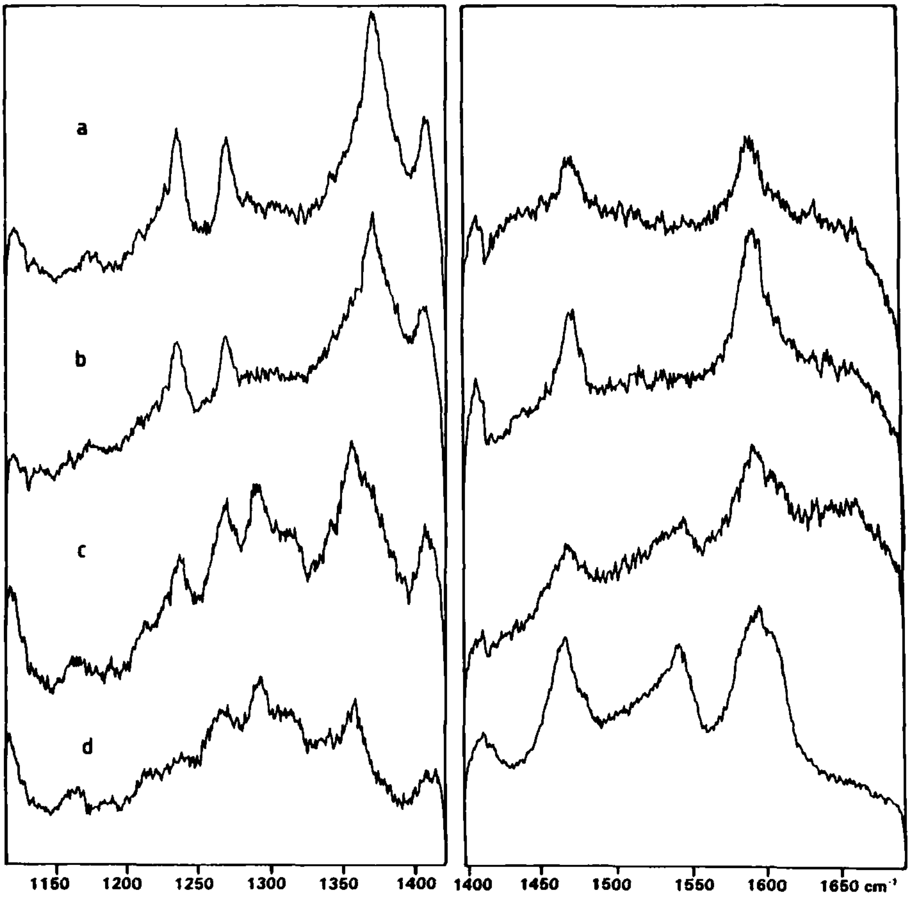


FIGURE 3 SER spectra of nitro BIPS (**2**) recorded with differently prepared solutions (for more details see text).

2b). In case of nitro BIPS, **2**, SER spectra of similar quality could be recorded up to 18 hours of standing time. During such a long standing time, the methoxy derivative, **3**, was obviously converted into another species, which showed high fluorescence, but no SER signal. Furthermore, it should be noted that the spectra of compounds **2** and **3** exhibit essentially the same strong bands (one exception is the medium strong band around 1560 cm^{-1} in compound **3**). In the spectrum of compound **4** several bands are observed with the same frequencies as in **3**. The most remarkable difference is the shift of the 1380 cm^{-1} band to 1360 cm^{-1} and the appearance of a new band around 1525 cm^{-1} instead of the band pair at 1560 and 1590 cm^{-1} in compound **3**.

To our great surprise we did not observe any changes in band positions upon acidification of the solution of compound **2** despite of the changes in the absorption spectrum.

The SER spectrum can only be recorded immediately after mixing and disappears with standing time. In case of the monomethoxy derivative, **3**, no new bands can be detected upon acidification of the solution. The fluorescence background is, however, increased relative to that of the neutral solution. Therefore, upon acidification, a species must be formed which is fluorescent but does not produce a SER signal. In an acidified methanolic solution, BIPS shows a good quality SER spectrum immediately after mixing of sole and dye solution (Fig.1d). In Fig.1e, the SER spectrum of a solution of BIPS with added NaOH is displayed. The difference between both spectra is obvious. Remarkable is, however, that trace 1e resembles very much trace 1a, the spectrum of nitro BIPS in neutral methanolic solution.

In accordance with the fact that steady state UV-illumination did not change significantly the UV-vis absorption spectra, no new bands are observed if the solutions of compounds **3** and **4** were illuminated before being added to the sole. In case of the monomethoxy derivative, **3**, one observes, however a different intensity distribution in the double bond stretching region (not shown). In the illuminated sample the band around 1560 cm^{-1} is enhanced relative to that at 1590 cm^{-1} and a new, weak band around 1530 cm^{-1} is seen. The ratio of intensities of the band pair at 1560 cm^{-1} and 1590 cm^{-1} changes with standing time of the solution after mixing. This could indicate that isomers produced by photolytic ring opening relax towards the thermal equilibrium distribution.

Extremely interesting effects are observed with nitro BIPS (compound **2**). Three different samples were studied. Sample 1 and 2 were made up from material, which was stored in crystaline form for a long time after synthesis. One stock solution was kept for a longer period of time before it was used in SER spectroscopy (sample 1); it produced the spectra shown in Fig.2. If such a solution was illuminated before mixing with the sole, no SER spectrum could be recorded because of a high fluorescence background. If the same irradiated sample was stored in the dark for 18 hours, a SER spectum could be recorded with band positions equivalent to that of the non-illuminated sample (Fig.3b). If, on the other hand, a new solution was prepared from the old crystaline material (sample 2), SER spectra could not be recorded immediately after mixing because of high fluorescence background. Fresh solutions illuminated prior to mixing with the sole produced a SER spectrum immediately after mixing, the band positions were, however, different (Fig.3c). New bands showed up around 1165, 1210, 1290, 1310, and 1360 cm^{-1}. In the double bond stretching region, a broad feature appeared between 1490 and 1550 cm^{-1} and a shoulder around 1610 cm^{-1}.

With a fresh solution prepared of recrystalized material (sample 3), no SER spectrum could be recorded immediately after mixing (like in the case of sample 2). If this stock solution was, however, illuminated before mixing with the sole, a SER spectrum with good signal to noise ratio could again be recorded immediately after mixing (Fig.3d). It resembles that shown in Fig.3c except that the bands around 1245 and 1380 cm^{-1} are extremly weak. The bands in the double bond stretching region are more pronounced and so is the shoulder around 1610 cm^{-1}. The spectra shown in Fig.4, prove that there are actually 2 bands between 1490 and 1560 cm^{-1}, whose intensity ratio changes with standing time. The final band pattern does, however, not resemble the spectra produced from stored stock solutions (sample 1) without (Fig.3a) or with illumination after standing time (Fig.3b).

DISCUSSION

Yoda et al.[3] have presented Raman spectra of BIPS in neutral (λ_{ex} = 488 nm) and in acidified methanolic solution (λ_{ex} = 647,1 nm), which were assigned to the neutral and monoprotonated open merocyanine forms. The spectrum taken of an alkaline solution (Fig.2e) should represent the spectrum of an unprotonated open form. Since the dominant bands do not coincide with those in the corresponding spectra by Yoda et al., we must conclude that due to the different conditions, different isomers are observed. In order to pursue this problem we have also recorded resonance-enhanced Raman (RR) spectra of acidified (compounds **1** - **4**) and neutral solutions (compounds **2** - **4**) with excitation wavelength λ_{ex} = 415 nm. We found that the RR and SER spectra of the acidified BIPS solution are so different that they must be assigned to different isomers again. This hypothesis is supported further by the fact that our SER spectra coincide in most features with the 647.1 nm-spectra by Yoda et al. for the protonated form.

The spectra of nitro BIPS and its methoxy derivative **3** resemble each other to great extent and exhibit a great similarity to that of BIPS in alkaline solution. From this and the fact that the spectra do not change significantly upon acidification of the solution, we conclude that it is only the neutral form which is adsorbed on the silver surface and gives rise to the SER spectra. This conclusion is supported by the fact that the SER spectrum of nitro BIPS resembles the spectrum of Takahashi et al.[2] for neutral **2** and is, from its general appearance, pronouncedly different from the 415 nm-RR spectrum of protonated **2**. The comparison of RR spectra of **3** and protonated **3** with the SER spectrum of **3** is also in favor of an assignment of the SER spectrum to the neutral, open merocyanine form of **3**. The same comparison made for the dimethoxy derivative **4** does not yield an unambigous answer.

The astounding dependence of the SER spectra of nitro BIPS on sample preparation can be explained easily by assuming that the closed spiro form exists in two enantiomeric forms, which possess vastly different quantum yields for the photoinduced ring opening reaction. During the recrystalization process, the photochemically active spiro form SA is enriched. Upon illumination of the freshly prepared stock solution (sample 3), two different isomers in the open merocyanine form MA and MA′ are produced. These forms exhibit only a weak fluorescence upon excitation with 514 nm radiation and adsorb quickly on the silver surface (Fig. 3d). With increasing standing time of the sole, one of the isomers (the 1540 cm^{-1} species) disappears on the time scale of minutes by conversion into the other form (the 1512 cm^{-1} species). If, in contrast, the stock solution is not irradiated no SER signal can be observed at any time after mixing. This suggests that the photoactive spiroform SA is inactive with respect to thermal ring opening.

The photochemically active form SA has obviously during the years of storage converted in part into a thermally active form SB. The freshly prepared stock solution (sample 2) produces in solution in the dark one open merocyanine form, MB, in low equilibrium concentration. This form does not adsorb readily on the silver surface but produces a high fluorescence signal immediately after mixing. During the course of 1 - 2 days, the molecules MB convert into a species MB′, which yields a SER signal characterised by bands at 1240, 1275 and 1590 cm^{-1} (Fig. 3a,3b). Upon irradiation of this stock solution, the remainder of the photochemically active species SA undergoes also ring opening. The sample yields a SER spectrum similar to that of the recrystalized, freshly prepared and illuminated solution (sample 3), except that additional bands at 1240 and 1370 cm^{-1} are seen.

If the stock solution is stored for a longer period of time (sample 1), then the photochemically active spiro form, SA, is converted completely into the thermally active form SB. As a consequence, one observes already immediately after mixing the bands of the open merocyanine form MB′ characterized by strong bands at 1240, 1370, 1475 and 1590 cm^{-1}. Due to the drain of molecules MB′ by adsorption on the silver surface, more molecules in spiro form SB undergo thermal ring opening during 1 - 2 days of standing time, thereby increasing the SER signal. The lack of photoactive form SA in aged stock solution explains the negligible effect of irradiation of this type of solution.

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