Low-temperature NMR and IR Spectra of Photomerocyanine Form of Spirophenanthrooxazine

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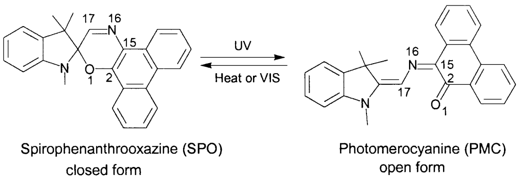
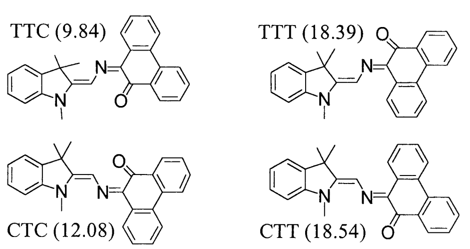
Low-temperature ^{13}C NMR and IR spectra of the metastable photomerocyanine (PMC) of spirophenanthrooxazine (SPO) show that PMC is in quinoidal structure. Especially, ^{13}C NMR study directly evidences the formation of two quinoidal PMCs in CD_2Cl_2 upon UV irradiation. The quantum chemical study of SPO shows that among open forms TTC and CTC are more stable than TTT and CTT because of the formation of the intramolecular hydrogen bond.

Upon UV irradiation, colorless spirooxazines (SO) and spiropyrans (SP) undergo a reversible photochemical transformation to their colored open form, photomerocyanine (PMC) (Scheme 1).[1,2] Although eight PMC isomers are theoretically conceivable, only four transoid isomers are believed to contribute to the equilibrium mixture at room temperature (Scheme 2).[3,4] SO exhibit greater photofatigue resistance than the more widely studied SP, a property which is advantageous in practical applications. However, the knowledge of the reaction mechanism of SO and the physical and chemical properties of their open forms is relatively limited because the isolation of the open forms of SO has been failed so far.

To extend the understanding of the structure of open forms of spironaphthooxazine (SNO), the most widely studied SO, theoretical calculations,[3,5] solvatochromic studies[6,7] and ^{1}H NMR nuclear overhauser effect (NOE) experiments[5,8] have been performed. However, it remains ambiguous whether the PMC is in quinoidal or zwitterionic form. Here we report the experimental evidences directly showing the electronic distribution on the carbonyl bond of metastable PMC of SO using low-temperature NMR and IR spectroscopy.



Scheme 1. Photochromism of SPO between closed and open forms.



Scheme 2. Four transoid isomers of SPO: The numbers in parentheses indicate the relative energies in kcal/mol obtained with RHF/3-21g method.

Because the thermal back reaction to the closed form significantly slows down at lower temperature,[1,9] NMR spectra of PMC were taken at −60 °C after the enrichment of the open form by irradiating spirophenanthrooxazine (SPO, 1,3-dihydro-1,3,3-trimethyl-spiro[2*H*-indol-2,3′-[3*H*]phenanthro[2,1-*b*][1,4] oxazine]) at −84 °C with 355 nm light pulses from a Nd: YAG laser. Similarly, IR spectra of PMC were measured after UV irradiation at 77 K.

In order to obtain the evidence directly showing the electronic structure of O1–C2 bond, we measured ^{13}C NMR spectra of PMC at low temperatures. The ^{13}C NMR spectrum obtained in CD_2Cl_2 before UV irradiation (Figure 1a) shows no peaks at 170–180 ppm region, where the peaks of carbonyl carbon typically appear. However, the spectrum (b) obtained after the UV irradiation clearly shows two peaks at 172.6 ppm and at 178.0 ppm. This observation directly indicates that two different PMC isomers are produced in CD_2Cl_2 by UV radiation and both PMCs are in quinoidal form. Because the open forms of SO have not been isolated so far, the spectrum (b) actually corresponds to a mixture containing both the closed and open forms (ca. 35% based on the integration of ^{1}H NMR spectrum). Because the electronic structure of PMC depends on its environment, the zwitterionic PMC form might be obtained in different solvent.

The structures of closed form and four open forms of SPO were optimized at HF/3-21G level using Gaussian 98W

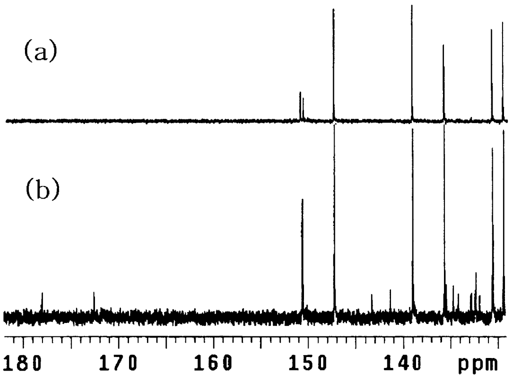


Figure 1. ^{13}C NMR spectra of SPO in CD_2Cl_2 at −60 °C: (a) before UV irradiation and (b) after UV irradiation.

program.[10] During the optimization, all degrees of the freedom were optimized without any symmetry constraints. Important bond angles and bond lengths of the closed form obtained in this method are in reasonable agreement with those obtained from X-ray data of SNO[11] and its related compounds.[12] The stabilities of four open forms (transoids) relative to the closed form are presented in Scheme 2. TTC is the most stable PMC and CTC is the next stable one. This result is similar to that obtained for SNO.[5] However, CTT and TTT have much higher energy than TTC or CTC. The stability of TTC and CTC can be understood in terms of the particularly short distance (2.093 and 2.090 Å, respectively) of O1···H17, which stabilizes the molecule highly by inducing strong intramolecular hydrogen bonding. Therefore, we interpret that two carbonyl carbon peaks in Figure 1b are related with TTC and CTC isomers. Meanwhile, the fact that the calculated bond distance of O1–C2 and charges on O1 and C2 atoms (1.226 Å, −0.631 and 0.602) of TTC and CTC are comparable to those of acetone also supports the quinoidal form of PMC rather than zwitterionic character.

Figures 2a and 2b represent the IR spectra of the amorphous SPO film[13] before and after UV irradiation, respectively. The remarkable change in IR spectra implies the production of PMC upon the UV irradiation. However, spectrum (b) shows no noticeable peaks are produced in 1650–1800 $\mathrm{cm^{-1}}$ region, where the peaks of the carbonyl stretching typically appear. And the difference spectrum (c) shows there are only small absorption increases at $\approx$1625 $\mathrm{cm^{-1}}$ and $\approx$1597 $\mathrm{cm^{-1}}$ and a decrease at $\approx$1610 $\mathrm{cm^{-1}}$. To interpret the results, IR spectrum of TTC is calculated using density-functional theory method (B3LYP/6-31g(d)) and IR frequencies are scaled using scale factor 0.9613. The calculated spectrum (d) shows that the carbonyl stretching and the C=C stretching of aromatic ring in TTC appear at 1629 $\mathrm{cm^{-1}}$ and 1589 $\mathrm{cm^{-1}}$, respectively, which are in good agreement with 1625 $\mathrm{cm^{-1}}$ and 1597 $\mathrm{cm^{-1}}$. Furthermore, it predicts the band intensity of the carbonyl stretching is very weak. Therefore, the peak at 1625 $\mathrm{cm^{-1}}$ can be attributed to the carbonyl stretching and this assignment indicates quinoidal structure of TTC. Because some merocyanine dyes containing carbonyl group at the end of the conjugated system also give very weak carbonyl stretching bands in this region,[14] our interpretation carries validity. The absorption decrease at 1610 $\mathrm{cm^{-1}}$ can be attributed to the C=C stretching of the aromatic rings of the closed form.

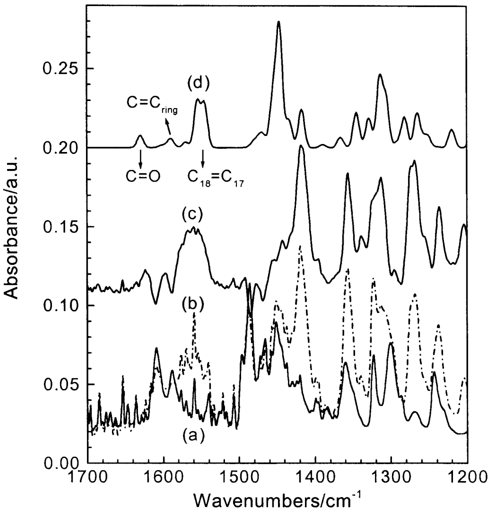


Figure 2. IR spectra of SPO: (a) before UV irradiation, (b) after UV irradiation, (c) difference spectrum (b)−(a), and (d) IR spectrum of TTC calculated in B3LYP/6-31g(d) level. (a) and (b) were measured at 77 K for the amorphous SPO film deposited on KBr plate.

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