Stabilization of the merocyanine form of photochromic compounds in fluoro alcohols is due to a hydrogen bond

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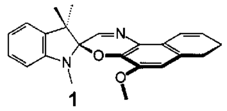
Fluoroalcohols [1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), 2,2,2-trifluoroethanol (TFE) and 2-fluoroethanol (FE)], acting as Lewis acids, stabilize the π-conjugated, colored merocyanine forms of spiropyran and spirooxazine photochromic compounds as metal ions do.

We[1] and others[2] have been interested in the interactions of metal ions with photochromic compounds such as spiropyrans, spironaphthoxazines, and chromenes for potential applications in optical switching, memory and sensors. In these photochromic compounds, light is used to cleave a single C–O bond in the pyran or oxazine ring (so-called closed form) which results in the creation of a relatively more polar species (so-called open or merocyanine form). Metals influence this process by associating with this now electron-rich oxygen atom in the open form. It has been reported that 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) stabilizes the merocyanine form of polymer-bound nitrospiropyran through a general effect of the solvent's 'polarity'.[3] We wondered if HFP and other fluoro alcohols[4] known as good H-bond donors could stabilize the open form of spirooxazines in particular, and other similar photochromics in general, and if so, do they work as the metal ions do, through a specific Lewis acid/Lewis base interaction?



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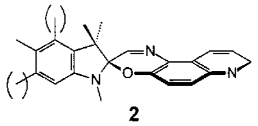

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Compound **1**, 1,3-dihydro-5-methoxy-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] is purple at room temperature at equilibrium without photolysis in HFP-*d* (2 atom% ^{1}H on the hydroxy group). ^{1}H NMR integration shows that about 50% of **1** exists in the open form(s) **1′**. ^{1}H ROESY spectra for these solutions have cross peaks between the solvent hydroxy proton and the *N*-methyl protons in **1**. There is also a cross peak between the solvent hydroxy proton and the methoxy methyl in the merocyanine form of the molecule **1′**. There is evidence for both so-called TTC[5] and TTT isomers of **1′**; cross peaks are indicated as arrows in Fig. 1.

Compound **2** (1,3,3-trimethyl 5,6-dimethylspiro[2*H*-indole-2,3′-[3*H*]pyrido[3,2-*f*][1,4]benzoxazine][6]) also opens to the merocyanine form(s) **2′** in fluoro alcohols. Compound **2′** comprises 70 mol% in HFP, 15 mol% in TFE, 9 mol% in FE, and 2 mol% in EtOH in the dark. A TFE-d_3 (5 atom% ^{1}H) solution containing **2** is also purple at equilibrium at room temperature, although it is only about 15% open form. A signal is observed between the hydroxy proton of TFE and the 2′-proton of **2′** (ring proton *ortho* to the oxygen) in the ^{1}H NOESY spectrum. Furthermore, the resonance of the hydroxy proton of TFE is deshielded (δ 5.4) in comparison to pure TFE (δ 5.2) as shown in Fig. 2. When the solution is irradiated with UV (300–400 nm) light, the resonance becomes more deshielded (Fig. 2). We infer that TFE interacts with **2′** *via* an H-bond to the oxygen with rapid exchange on the NMR time scale (500 MHz). Additionally, we note a signal between the *N*-methyl protons at the indole group and the imine proton for **2′** in the ^{1}H NOESY spectrum, while there are no signals between the imine proton and the geminal methyl protons, nor are there signals between the imine proton and the 2′-proton; thus, for **2′**, TTC is the only isomer in TFE. In a solution of **2** in HFP, which is 70% ring-opened, there are several cross peaks (^{1}H ROESY) indicating the presence of both the TTC and TTT isomers. The cross peaks are illustrated schematically in Fig. 3. There is also a cross peak between the solvent hydroxy proton and the open-form *N*-methyl protons, once again indicating a possible H-bond to the former oxazine ring oxygen. If, as implied in the ^{1}H NMR studies, the stability of the open forms is due to H-bonding, there should be additional manifestations of the H-bond on the properties and spectroscopy of the compounds.

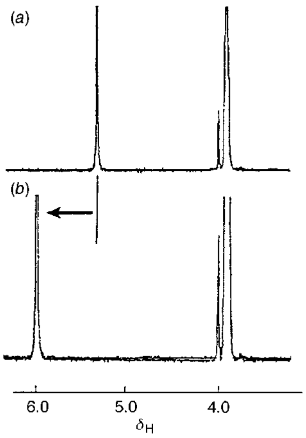

Fig. 2 ^{1}H NMR spectra (500 MHz) of the hydroxy proton of (*a*) TFE equilibrated in the dark, and (*b*) the same solution measured after irradiation with UV light. The TFE-d_3 solution contains **2**/**2′** (15 mM) and TFE (0.5 mM).

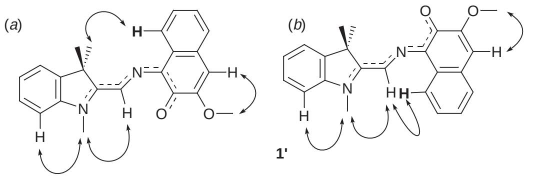

Fig. 1 (*a*) TTC and (*b*) TTT merocyanines **1′**. Cross peaks in the ^{1}H ROESY spectrum used to assign the structure are shown as curved arrows. The cross peaks of the bold H atoms are particularly diagnostic.

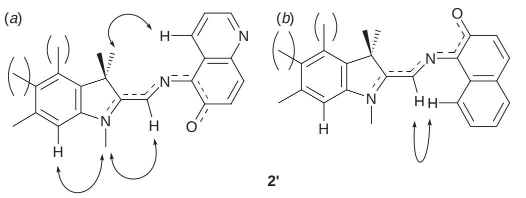

Fig. 3 (*a*) TTC and (*b*) TTT merocyanines **2′**. Cross peaks in the ^{1}H ROESY spectrum used to assign the structure are shown as curved arrows.

By perturbing a solution of **2**/**2′** in TFE with the appropriate wavelength range of light, excess **2** or **2′** can be formed. Both time courses can be analyzed as first order reactions within the temperature range of 15–40 °C (Fig. 4). Both activation energies are equal (25 ± 1 kcal mol^{-1} **2**→**2′**, 25 ± 1 kcal mol^{-1} **2′**→**2**), so the resulting difference is the enthalpy difference between **2** and **2′** which is 0 ± 1.4 kcal mol^{-1}. Typical values for similar molecules are *ca.* 4 kcal mol^{-1} in most solvents, from the non-polar benzene and toluene to the polar EtOH and MeCN.[7] The difference of 4 kcal mol^{-1} is consistent with the enthalpy of an H-bond in general[8] and with those between TFE and various acceptors in noncompetetive solvents[9] in particular.

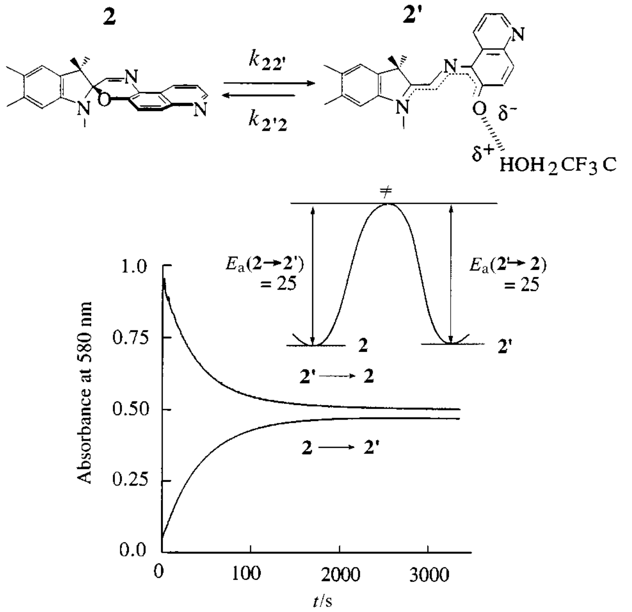

Fig. 4 Kinetics of the opening and closing reactions of **2**/**2′** in TFE (0.7 mM) at 22 °C. Activation energies are in kcal mol^{-1}.

If there is a specific H-bond formed as hypothesized, then there should be a shift in the λ_{max} of the long wavelength band of the merocyanine.[6] In common solvents, the long wavelength band of the merocyanine is weakly solvatochromic (*e.g.* λ_{max} in toluene, MeCN and MeOH for **2′** is 602 nm, EtOH, 605 nm, ethylene glycol and 3-methyloxazolidin-2-one, 610 nm). However, in the fluoro alcohols there is considerable solvatochromism (λ_{max} values: HFP, 534 nm; TFE, 582 nm; FE, 590 nm). The values of E_T(30) as a benchmark for the strength of hydrogen-bond donation and polarity of the fluoro alcohols are also in the order HFP > TFE > FE [E_T(30): 63.3, 59.8, 55.5 respectively].[4f] Furthermore, there is a good correlation between the energy of the long wavelength band of the merocyanine and the logarithm of the equilibrium constants (estimated as [**2′**]/[**2**] from the NMR data). Thus, changes in the energy of the ground state, through solvent H-bonding to the oxygen, influence the spectroscopy and the equilibrium consistently.

We have performed *ab initio* calculations[13,14] on all the solvent molecules and the solute **2′**. We also performed preliminary calculations on the H-bonded complexes at the semiempirical quantum level using PM3 parameterization. Full geometry optimizations of the complexes with the solvents HFP, TFE and FE were performed. The calculated H-bond distance between the O of the **2′** carbonyl and the H of the hydroxy hydrogen of the solvent are 1.7729, 1.818 and 1.820 Å for HFP, TFE and FE, respectively. The calculations support the observed order in the effectiveness of the fluoro alcohols in stabilizing the merocyanine form. Theory also shows very little change in the O–H bond distances in the fluoro alcohols (difference: complex-free solvent (Å) HFP: 0.014, TFE: 0.0163, FE: 0.0058).

Finally, we note that the behavior in the Lewis acid solvents differs dramatically from the behavior in the weak Brönsted acid, glacial acetic acid (AA). A sample of **2**/**2′** in AA, after a considerable time, yields a band at 420 nm. This solution is not photoactive. The band at 420 nm arises from protonated **2′** with TTT geometry [Fig. 3(*b*)].[1b] When a quantity of Et$_3$N equivalent to the AA is added to the solution, the band due to the protonated form disappears. There is no significant absorbance in the visible region. Illumination with UV light yields a transient absorption peak at 610 nm, which is characteristic of **2′** in polar solvents.

The Lewis acid Zn^{II} causes the ring opening reaction **2**→**2′**. The complex is stable, as is the solvate of HFP. The visible wavelength is 538 nm, between that of HFP and TFE solutions. Thus, the original hypothesis that Lewis acids of different sorts similarly influence the structure and properties of the photochromic species is confirmed.

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5 This shorthand nomenclature reflects the *transoid* or *cisoid* orientation about the partial double bonds between the former spiro carbon and the naphthalene ring.

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