Proton-Stabilized Photochemically Reversible E/Z Isomerization of Spiropyrans

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ABSTRACT: Spiropyrans undergo Cspiro−O bond breaking to their ring-open protonated E-merocyanine form upon protonation and irradiation via an intermediate protonated Z-merocyanine isomer. We show that the extent of acid-induced ring opening is controlled by matching both the concentration and strength of the acid used and with strong acids full ring opening to the Z-merocyanine isomer occurs spontaneously allowing its characterization by 1H NMR spectroscopy as well as UV/vis spectroscopy, and reversible switching between Z/E-isomerization by irradiation with UV and visible light. Under sufficiently acidic conditions, both E- and Z-isomers are thermally stable. Judicious choice of acid such that its pKa lies between that of the E- and Z-merocyanine forms enables thermally stable switching between spiropyran and E-merocyanine forms and hence pH gating between thermally irreversible and reversible photochromic switching.

INTRODUCTION

Smart systems built from molecular switches1 that respond to external triggers, such as light,2 electricity,3 heat,4,5 sound,6 and pH,7 through changes in molecular properties (color, polarity, shape, conductivity, reactivity, etc.) are highly desirable due to the possibility to tune these physical responses through structural (synthetic) modification.8,9 Building such molecular switches into materials can impart responsiveness at the macroscopic level, often amplifying the changes in physical properties ranging from sensing10 and surface properties11 to luminescence12,13 and electrochromism.14,15 Photochromes, including dithienylethene,16 azobenzenes,17,18 and spiropyrans,19 are among the most widely applied, due to their modularity and flexibility toward modification and the possibility to combine them with other responsive units, e.g., multiphotochromes.20 The combination of synthetic versatility, and the thermo- and acidochromism, shown by spiropyrans, in addition to their well-known photochromism reported first in 1952,21 has made this class among the most important in applications in smart materials and systems to date.

The photochromism of spiropyrans arises from a light driven interconversion between a “ring-closed” spiropyran (SP) structure and the zwitterionic “ring-open” merocyanine (MC) state, in which the C−O bond of the spirop motif is cleaved, and is stabilized by an accompanying Z/E-isomerization around the spiro- and pyran-bridging double bond (Scheme 1). The merocyanine “open form” can exist as any of several distinct isomers, denoted commonly by reference to the cis/trans orientation around each of the three bonds starting at the Cspiro−C bond, indicated in Scheme 1 by α, β, and γ. The preferred conformations and the complex photochromic pathways for several (neutral) spiropyrans have been studied using various ab initio models.24−29 The orientation of the β-bond affects the thermal stability of the merocyanine with regard to reversion to the spiropyran form. Although several colored isomers have been observed at cryogenic temperatures,30 the low thermal stability of the cis-β configurations (referred to as the Z-isomer) means that only the more stable trans-β configurations (E-isomer) are observed at ambient temperatures.31 Indeed, the TTC form, specifically, was shown by Ernsting and co-workers to be the thermally most stable isomer.32

Protonation of the phenol moiety of the merocyanine form impacts the chemistry of spiropyrans and indeed acidochromism has been reported for several spiropyran structures whereby addition of acid results in thermally induced conversion to the protonated merocyanine form (MCH+).33−46 However, the mechanism and nature of the intermediate species formed throughout these reports are not consistent, and several conflicting mechanistic scenarios have been proposed to date.
Both Fissi et al.\textsuperscript{45} and Wojtyk et al.\textsuperscript{33} for example, proposed that a rapid equilibrium between the nonprotonated and N-protonated spiropyran is established in the presence of trifluoroacetic acid, lying in favor of the protonated E-merocyanine form. The immediate conversion of the protonated E-merocyanine form upon protonation of a spiropyran impregnated poly(dimethylsiloxane) polymer films was noted by Nam and co-workers also, but with subsequent thermal reversion back to the spiropyran form.\textsuperscript{46} Later Genovese et al. reported that reversion to the ring-closed form could be induced by irradiation with visible light also.\textsuperscript{34} Remo\textsuperscript{́}n et al., on the other hand, proposed that, in aqueous media, N-protonation only occurs at pH below 0.5, and that the only protonated species present is the ring-open merocyanine form, which is in thermal equilibrium with the nonprotonated closed form.\textsuperscript{36} Later, Schmidt et al. noted the formation of the protonated E-merocyanine in ethanol upon addition of trifluoroacetic acid.\textsuperscript{37} Collectively, these reports indicate that ring opening to the stable protonated E-merocyanine occurs upon protonation. However, over two decades ago, Zhou and co-workers reported a species “Y” while investigating the pH dependence of the negative photochromism of a 6′,8′-dinitrospiropyran, for which the merocyanine form is most stable even when unprotonated.\textsuperscript{43} Species Y was assigned to the protonated form of species “X”, a transient spiropyran species, which has a broken C–O bond and a geometry intermediate to the perpendicular spiro and the planar merocyanine form, and a rapid equilibrium is established between species Y and the spiro form under sufficiently acidic conditions was established. In the same period, Roxburgh et al. reported the trifluoroacetic acid-induced thermal ring-opening of spiropyrans to their protonated E-isomer, which was proposed to be via either the unprotonated or protonated Z form.\textsuperscript{44} The proposed intermediacy of the protonated Z form was supported by Shiozaki subsequently, who proposed that protonation of spiropyran in ethanol with sulfuric acid, a stronger acid than the trifluoroacetic acid, generated the Z-merocyanine form, which could not only undergo subsequent thermal but also photochemical Z/E-isomerization (Scheme 2).\textsuperscript{38} Shiozaki’s interpretation of the changes observed by UV/vis absorption spectroscopy was supported by theoretical studies and is analogous to the acid-induced ring opening (C–O bond cleavage) observed for the related photochromic spirooxazines.\textsuperscript{47} The formation of the Z-MCH\textsuperscript{+} form has been proposed elsewhere as well\textsuperscript{48} and has been reported in gas-phase studies.\textsuperscript{49}

Here, we show through a combination of spectroscopy and theory that the observed pH-induced switching of both spiropyrans (SP) and nitrospiropyrans (NSP) in solution can be rapid and complete (Scheme 2) but is highly dependent on acid strength in nonaqueous solvents. The extent of reaction with acids follows the order of pK\textsubscript{a} values reported, including the intermediate pK\textsubscript{a} of HNO\textsubscript{3} in the middle, for which an excess amount is required to generate the desired response.\textsuperscript{50–52}
Furthermore, we show unambiguously that the initial step is cleavage of the C–O bond to form a relatively stable Z-isomer of the merocyanine that undergoes thermal as well as photochemically induced Z/E-isomerization to the more stable E-form. Overall, we show that fully reversible isomerization is retained upon acid/base switching provided that the acid used is stronger than the phenol moiety in at least the E-isomer. The demonstration of pH-induced switching between spiro and Z-merocyanine forms as well as photochemical E/Z switching opens new opportunities in the application of spiropyrans as molecular switches. It is especially relevant in applications where large local changes in pH can occur such as at electrodes, e.g., during cyclic voltammetry,25 which can affect the observed photochemistry profoundly.

It is notable that in most earlier studies of the pH dependence of spiropyrans, trifluoroacetic acid,33–35,37,39,40 as well as HCl,21,36,41,42 were the acids of choice employed. Notably, however, in studying pH-gated spiropyran photochromism, Shiozaki employed sulfuric acid.38 Here, we show that the choice of acid is crucial for fully understanding the acido-photochromism of spiropyrans. We show that addition of acid to SP and NSP induces a bathochromic shift, the extent of which is dependent on the strength of the acid used. With relatively weak acids, such as trifluoroacetic and HCl acid, in acetonic, acidochromism in SP is weak with only a minor bathochromic shift upon UV irradiation. For NSP, the changes are even less apparent due to its already red-shifted absorption induced by the electron-withdrawing nitro group, which rationalizes why the acidochromism of the spiro form has thus far gone essentially unnoticed. We show here that with stronger acids, protonation-induced changes are clear for both SP and NSP and that both show pH-gated photochromism to the protonated merocyanine forms.

Spontaneous ring opening to the Z-MCH+/Z-NMCH- states is observed upon addition of strong acid, with subsequent reversible photoinduced isomerization to the E-MCH+/E-NMCH- states. The higher acidity of the protonated Z-merocyanine form is demonstrated by adding an acid with a pKₐ intermediate of those of Z-MCH- and E-MCH-, enabling direct photochemical switching between the SP and thermally stable E-MCH- form at room temperature. Understanding the acid/base switching of spiropyrans and the requirement for matching of the pKₐ of the acid with that of the merocyanine forms, allows for stable access of a total of four photochromic states and opens up a wide range of possibilities for applications as functional units. Finally, although only the spiropyran form is thermally stable at room temperature in the absence of acid and addition of acid induces spontaneous ring opening to the Z-MCH- and E-MCH- forms, by using an acid with a pKₐ between that of the Z- and E-merocyanine isomers, reversible photochemical switching between thermally stable colorless SP and colored E-MCH- forms can be achieved at room temperature.

### EXPERIMENTAL SECTION

**Materials.** NMR and chemicals used for the synthesis of SP were purchased from Aldrich or TCI and were used without further purification. The synthesis of SP is described in the Supporting Information (SI) as well as characterization by NMR spectroscopy (1H, 13C APT, HSQC, HMB, COSY, and NOESY) of its protonated Z and E forms generated by trifluoromethanesulfonic acid and phosphoric acid, respectively. High-performance liquid chromatography grade acetonitrile was used for the spectroscopic studies.

**Physical Methods.** NMR spectra were obtained on a Bruker 600 NMR spectrometer. Chemical shifts (δ) are reported in parts per million and coupling constants in hertz. Integrations are reported, with multiplicities denoted as: s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet. Chemical shifts are reported with respect to tetramethylsilane and referenced to residual solvent (CD3OH) signals. UV/vis absorption spectra were recorded using an Analytik Jena Specord600 spectrometer. Quantum yields were determined as described in the SI, with calculations concerning the protonated photochromism were performed by determining a photostationary state (PSS) (λ_{exc} 365 nm) in the presence of strong 8% E-MCH- and 68.3% E-NMCH- by scaled subtraction. The absorption spectra immediately after protonation to the Z-forms and both those resulting from partial deprotonation at the PSS and direct protonation of the merocyanine forms were used for reference. Irradiation was carried out with light-emitting diodes (Thorlabs) at 365 nm (4.1 mW, M365F1), 455 nm (3200 mW, M455L3-C5), 565 nm (2.0 mW, M565F1), and 660 nm (14.5 mW, M660F1). For details of the theoretical calculations see in the SI.
of the ring opening was confirmed by monitoring absorbance at 375 nm only (i.e., monochromatic light source) where the SP form does not absorb but the Z-MCH form does absorb, before and after addition of acid. The change in absorbance at 375 nm was immediate and complete with the mixing time.

The red shift that manifests Z to E-isomerization is ascribed to the increase in electronic delocalization that accompanies increased planarity. Indeed, the maximum visible absorption of the TTC isomer of the (deprotonated) merocyanine shifts from 550 to 595 nm in the TTT isomer (Scheme 1).56,57 The protonated E-merocyanines are also obtained by addition of 1 equiv of a (strong) acid to E-MC and E-NMC formed by irradiation of SP and NSP at −30 °C (to limit thermal reversion, Figures S4 and 4, respectively). Subsequent irradiation at 365 nm re-establishes the PSS obtained with acid (vide supra) with reversion to the Z-isomers upon irradiation at 455 nm.

The acid/base dependence of the photochemistry of both spiropyrans is summarized in Schemes 3 and 4. The data presented here contradict earlier proposals that irradiation of the protonated E-merocyanine leads to the formation of the spiropyran form,55,54,36,46,58 based on the loss of visible absorption (i.e., decoloration). Instead, it is the protonated Z-merocyanine that was obtained. Indeed, this is the case that is apparent in the blue shifted shoulder due to the Z-(N)MCH+ form in spectra reported earlier.37

Figure 1. UV/vis absorption spectra of (top) SP and (bottom) NSP (62 μM in acetonitrile, black lines) upon addition of excess CF3CO2H (10 and 52 equiv, respectively, red lines) and upon subsequent irradiation at 365 nm (blue lines). Irradiation with visible light recovers the absorption spectrum prior to irradiation at 365 nm.

Figure 2. UV/vis absorption spectra of (top) SP and (bottom) NSP (62 μM in acetonitrile, black lines) upon addition of 1 equiv CF3SO3H (red lines). Irradiation at 365 nm induces a red shift to 420 nm (blue lines), which is reversed by irradiation at 455 nm (for E-MCH+ to Z-MCH+ see Figure 3).

Figure 3. UV/vis absorption of the E-MCH+ form (blue line, generated by irradiation at 365 nm, inset) over time, showing near complete reversion to the initial Z-MCH+ form upon continuous visible light irradiation (by the spectrometer, spectra at 100 s intervals, whereas no change in absorbance was observed over 200 s in the dark).


Although deprotonation of MCH+ at the photostationary state (PSS365nm) results in full recovery of the absorption spectrum of the ring-closed SP and NSP forms, when base is added stepwise substoichiometrically, the conversion of the Z-isomer is observed prior to that of the E-isomer (Figure S5). The order of recovery is consistent with the pK_a of the Z-isomer being less than that of the E-isomer, which is expected considering the contribution of ring closing to the acid/base equilibrium. Furthermore, at ~30 °C, a temperature, at which the E-MC isomers are thermally stable, the visible absorption of the MC form does not appear until the sufficient base has been added to deprotonate all of the Z-MCH+ present (Figure S6).

**Calculated Energies and Barriers for Ring Opening of SP and NSP.** The energies of the observed isomers were calculated using a density functional theory known to be suited for spiropyrans, as detailed in the SI.41 The calculated energies of unprotonated spiropyran forms relative to their merocyanine isomers are fully consistent with experimental data; i.e., that the ring-open form is thermally accessible from the NSP form. Interestingly, a comparison between the computed Raman spectra with those measured experimentally for the non-protonated SP and NSP forms (Figures S7 and S10) as well as for the protonated Z-MCH+ and E-MCH+ show a good qualitative match, which supports that the selected level of theory is well suited for our purposes.

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**Scheme 3. pH-Gated Photochromism of Spiropyrans and Nitrospiropyrans, in Absence and Presence of Strong Acids.**

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**Scheme 4. Computed Free-Energy Profiles for the Optimized Lowest Energy Conformers**

(a) SP and (b) NSP in the ring-closed spiropyran and ring-open merocyanine forms and the barriers to their interconversion. All energy differences given in kcal/mol.

The lowest energy MC form, the TTC, lies 3.2 kcal/mol higher than the ring-closed SP form and has a 17.5 kcal/mol barrier from the E to Z form before undergoing low-barrier ring closing. The lowest energy NMC form, on the other hand, is the TTC conformer, which is 0.8 kcal/mol lower in energy than the ring-closed form, though closely followed by the TTC (1.8 kcal/mol). Furthermore, the TTC form, which is the main species observed experimentally also for nitrospiropyrans,32,59−61 (with in acetonitrile one order of magnitude greater abundance than the TTC form),62 has a significantly higher barrier to conversion to the Z-NMC form (26.9 kcal/mol for direct conversion, 21.8 kcal/mol for conversion through the TTC form). These data are consistent with its observed thermal stability at room temperature. Notably, theory shows that even if the indolinic nitrogen is protonated, as proposed earlier,33,36 proton transfer coupled with Cspiro−O bond cleavage is barrierless and yields the thermally more stable Z-merocyanine form (Scheme S5).

The barriers are significantly higher than those of the unprotonated forms, ranging from 29.6 kcal/mol (Scheme 5a) to 39.4 kcal/mol (Scheme 5b), consistent with their experimentally observed thermal stability. The photochemical interconversion between the Z- and E-merocyanine forms thus enables controlled access over two distinct protonated states as shown, through the energetic entrapment of the respective isomers.

**Re-enabling Room Temperature Switching of SP.** The difference in the pK_a of the Z and E-merocyanine isomers additionally opens the possibility to gate the photochromism of SP with pH. In large excess, H_3PO_4 induces formation of Z-MCH+ (Figure S7), whereas near-stoichiometric amounts have essentially no effect on the absorption spectrum of SP.
Remarkably, in presence of equimolar phosphoric acid at room temperature solely the \( E^-\text{MCH}^+ \) isomer is generated both upon irradiation at 300 nm (Figure 5) and thermally over time (Figure S8), with full recovery to the unprotonated \( \text{SP} \) form upon subsequent irradiation at 455 nm. This effect is observed because the \( pK_a \) of \( \text{H}_3\text{PO}_4 \) lies between that of the \( E^-\text{and} Z^-\text{MCH}^+ \) isomers. Any \( \text{H}_2\text{PO}_4^- \) present will deprotonate \( Z^-\text{MCH}^+ \) spontaneously inducing ring closing, whereas any photo-generated \( E^-\text{MC} \) will undergo protonation by \( \text{H}_3\text{PO}_4 \) preventing thermal reversion and thus enables essentially direct photoconversion between \( \text{SP} \) and \( E^-\text{MC}^+ \) forms through the Le Chatelier principle (Scheme 6) despite that \( \text{SP}/E^-\text{MC} \) photochromism is thermally inhibited at room temperature. Furthermore, the thermal stability of the \( E^-\text{MC}^+ \) formed in the presence of near-stoichiometric amounts of \( \text{H}_3\text{PO}_4 \) allows for its characterization by NMR spectroscopy (\( ^1\text{H}, ^13\text{C APT, HSQC, HMBC, COSY, and NOESY} \)) as well as that of the \( Z^-\text{MC}^+ \) form generated by addition of \( \text{CF}_3\text{SO}_3\text{H} \) (see the SI).

**CONCLUSIONS**

In conclusion, we show through a combined experimental and theoretical study that the acidochromism of spiropyrans is highly dependent on the strength of the acid used in aprotic solvents, with acids, such as \( \text{CF}_3\text{CO}_2\text{H} \) and \( \text{HCl} \), used typically, being too weak to protonate the \( Z^-\text{(N)MC}^+ \) isomer. Fully pH-gated photochromism of simple spiropyrans is achieved with stronger acids (e.g., \( \text{CF}_3\text{SO}_3\text{H} \)), manifested in the two-state photoisomerization of \( Z^-\text{(N)MC}^+ / E^-\text{(N)MC}^+ \) and together with \( \text{SP}/E^-\text{MC} \) photoisomerization, leads to an overall four-state molecular switching cycle. In retrospect, the reactivity reported in the present study implies that in earlier studies the \( Z^-\text{(N)MC}^+ \) form may have been observed erroneously assigned as the expected ring-closed spiropyran form. The theoretically computed energies agree with the experimentally observed forms and moreover underline the increased stabilities of the \( Z^-\text{ and} E^- \) isomers through significantly higher thermal barriers than in the deprotonated states. Additionally, in contrast to conclusions drawn earlier regarding the protonation of spiropyran,

\[ \text{See caption of Scheme 3.} \]
phenolates. Hence, even if an acid is strong enough to protonate the indolic nitrogen, spontaneous ring opening to the Z-(N)
MCH' form would make such a protonation transient at most. Finally, by selecting an acid such that its pK_a lies between that of
the Z- and E-MCH' isomers (e.g., H_3PO_4 in the case of SP), enables gated photochromism and a unidirectional multistate
interconversion between spiropyran and merocyanine species at room temperature. The nitro group of NSP is electron
withdrawing in comparison with SP and as such stabilizes the merocyanine form both in the deprotonated form and as a
leaving group in the ring-opening process. As a counterpoise to these effects, however, the nitro group decreases the pK_a and
hence the strength of acid required to achieve thermal ring opening needs therefore to be greater. Overall, however, the nitro
group of NSP does not appear to affect the mechanisms involved in comparison with SP.

The pK_a-dependent control of the state of the photochrome opens new opportunities in the application of spiropyrans in
photocontrol of pH and in understanding the influence of local pH changes (e.g., at surfaces of electrodes) have on spiropyran-
based electrochemical devices.

### ASSOCIATED CONTENT

< Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.8b03528.

Details of synthesis and characterization of SP with NMR spectroscopic characterization (1H, 13C APT, HSQC, HMBC, COSY,
and NOESY) of both Z-MCH' and E-MCH'; actinometry; computational studies; experimental and calculated Raman spectra of the
SP/NSP forms and Z-MCH'/Z-NMCH' and E-MCH'/E-NMCH' forms; and additional UV/vis absorption spectral data (PDF)

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All authors have contributed and given approval to the final version of the manuscript.

#### Funding

Financial support was provided by The Netherlands Ministry of Education, Culture and Science (Gravity Program 024.001.035
to L.K. and W.R.B.), and Chinese Scholarship Council (J.C.). This work used computational resources of the CCIPL in Nantes
and the Genci-IDRIS.

#### Notes

The authors declare no competing financial interest.

### ABBREVIATIONS

SP, 1,3,3-trimethylbenzimidolopyrylspiropyran; NSP, 6'-nitro-1,3,3-trimethylbenzimidolopylspiropyran; MC, 1,3,3-trimethylbenzimidolopyrlymerocyanine; NMC, 6'-nitro-1,3,3-trimethylbenzimidolopyrlymerocyanine

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