Weak acid triggers the ring opening of an otherwise long-lived triangle terthiazole closed isomer†

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The stability of the colored cyclized form of a compound from the new class of photochromic triangle terthiazoles was found to be strongly decreased by the presence of trifluoroacetic acid (TFA) in acetonitrile at room temperature. The apparent first-order process rate constant of the observed bleaching is of the same order of magnitude as if the acid-free sample was heated to about 100 °C. Association constants with TFA were determined from the kinetics analysis and by NMR titration and were found to be moderate for the colored form and very weak for the colorless form. These results were interpreted considering the basicity of the molecules and the solvent effect on the acid strength. The structural consequences of the protonation on the ring-closed compound and on the entire ring-opening process were examined by DFT calculations. Protonated closed and open forms were found to be geometrically "closer" than their non-protonated parents and the altered bond-length alternation may explain the diminution of the activation barrier. The puzzling instability of the protonated terthiazole was compared to a related thermally stable imidazolium homologue. From structural DFT considerations, it was concluded that this different behavior may be explained in term of charge stabilization, the sulfur being less efficient than the nitrogen.

1. Introduction

Although believed as a simple transformation, photochromic switching is a typical non-equilibrium process[1] due *inter alia* to the presence of an incident light flux. This situation has to be taken into account for potential applications such as optical data storage.[2] Hence, the control of coloration kinetics rate and conversion remains a major issue in photochromism.[3] One approach relies on the availability of the dye in the material, taking benefits of the different chemical properties of the photoisomers to sequestrate one form of the photochromic dye using "dark" chemical equilibrium.[4] The second one, the direct action on the elementary steps of the coloration, implies a chemical approach of quantum yield optimization by tailoring the dye's substituents: a nice example can be found for the photo-bleaching (ring opening) in the diarylethene family using donor substituents to weaken the crucial bond.[5]

Another possibility is to by-pass, by a thermal pathway, the sole photochemical reaction in T-photochromes or one of the two processes in P photochromes. Although this seems to go against the Woodward–Hoffman (WH) rules, it has been commonly observed. For instance, in the case of T-photochromes, spirooxazines are well known to be in equilibrium with their open form at room temperature.[6] In the case of diarylethene compounds, when the two aryl moieties are strongly aromatic[7] or if the ethene subunit belongs to a weakly aromatic ring[8] spontaneous thermal reopening may occur. Yet the thermal bleaching is then an intrinsic (often unwanted) property, and it would be highly desirable to be able to control this thermal route. Chemical control of the ring opening is rather difficult since their active core is basically a hydrocarbon (*i.e.* the cyclohexadiene/hexatriene unit) thus having no "handles" to trigger a possible chemical activation. Nonetheless, it has been shown recently by several teams[9–12] that this could be achieved by using an additional redox path since a change in the number of electrons involved in the pericyclic reaction, a key feature of the WH rules, should dramatically affect the thermal activation barrier between the two open-shell isomers. Indeed, under oxidative conditions dithienylethenes, *via* their cation-radicals, can ring-close or -open according to the pattern of the subsituents.[12] However, the question of chemical control remains open for closed shell compounds for which the WH rules are valid.

From the observation that dithienylethenes (DTEs) carrying electron withdrawing substituents present some appreciable thermal bleaching,[13,14] the idea of using substituents able to switch electronically from donor to acceptor in order to operate the isomerization process has been an issue addressed by several teams.[15–17] Thus, a redox active substituent (ferrocene) was used to promote upon oxidation an internal

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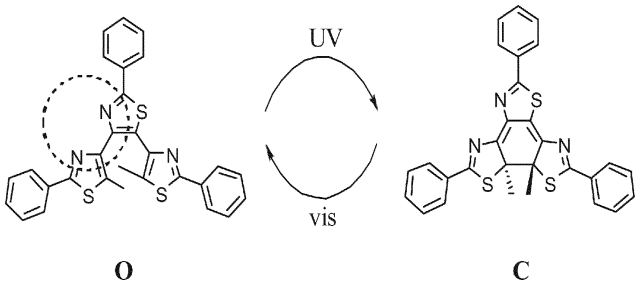
† Electronic supplementary information (ESI) available: ^{1}H NMR titration of the open form, 2D NMR spectra and ^{1}H assignments, details of the analyses for the kinetics and titration, DFT calculations (energies, distances, TD DFT UV-vis spectrum of the closed protonated form). See DOI: 10.1039/b822878g



Scheme 1 Photochromic ring-opening ring-closure of terthiazole (**O**: open; **C**: closed). The dashed line shows the α-diimine moiety.

charge transfer with the DTE unit, inducing the thermal ring opening reaction.[17] The conjugation of a pH-active substituent (anilinium/aniline acido-basic couple) to the DTE unit was found to be a very efficient way to trigger the thermal opening process.[16] However, in the latter study the switching requires the complete conversion of the substituent *via* protonation. Would it be possible to imagine a molecule in which only a weaker interaction, such as a hydrogen bond, would be sufficient to promote the thermal reaction?

Recently, one of us has proposed a new family of diarylethenes, the triangle terthiazoles (Scheme 1) for such a study.[18] In these heterocyclic analogues of *ortho*,*ortho*′-terphenyl, the weak resonance energy of the thiazole ring allows the ring-closed, blue colored form to be stable for years at room temperature.

Furthermore the presence of a chelating α-diimine moiety has spurred the study of its complexes with lanthanides.[19,20] Since the three basic nitrogen atoms are very close to the hexatriene/cyclohexadiene moiety, this prompted us to investigate the influence of a protic compound on the stability of the closed colored form. In the present work, we thought of using a moderate H donor: trifluoroacetic acid (TFA) in acetonitrile, and we wish to present here our preliminary results.

2. Experimental

General

The terthiazole was available from a previous study[18]

UV-vis kinetic traces were acquired on a HP8451 diode array detector equipped with a single monochromator at 25 °C.

Colored solutions were obtained by exposing a cuvette containing a 2.4×10^{-5} M solution of terthiazole to intense UV light (250 W high-pressure mercury lamp) in order to reach a photostationary state (OD_{max} *ca.* 0.24). Then the appropriate amount of trifluoroacetic acid (TFA) was added, the cuvette quickly shaken, and placed in the spectrophotometer in which continuous magnetic stirring was maintained. Kinetic follow up was achieved either by recording the entire absorption spectrum (in the range 250–750 nm) or by monitoring the absorbance at 580 nm (λ_{max} of the colored form). In the latter case, to avoid unwanted photobleaching due to the beam of the spectrophotometer, a high-pass filter (cutoff 500 nm) was placed before the cuvette.

NMR titrations were performed on a Bruker 300 MHz apparatus in CD_3CN by adding aliquots of a CD_3CN solution of neat trifluoroacetic acid. 2D-COSY and ^{19}F–^{1}H HOESY were recorded on a Bruker 400 MHz spectrometer.

DFT geometry optimizations of molecules were carried out with the Gaussian 03 package[21] employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang and Parr (B3LYP).[22] The 6-31G(d) basis sets were used for all atoms. The single-point energy calculation was also carried out at B3LYP /6-31G(d) level. The optimized structures in the gas phase were used to obtain single point energies in acetonitrile solvent, using the polarizable continuum model (PCM).

3. Results and discussion

3.1 Preliminary experiment

Upon addition of an excess of neat anhydrous trifluoroacetic acid, the deep blue color of an acetonitrile solution containing the mixture of isomers of the triangle terthiazole at the photostationary state faded away within minutes. The resulting solution was totally insensitive to light. However, the color of the solution was fully restored when the medium was treated with triethylamine, thus indicating that TFA does not destroy but rather greatly destabilizes the colored isomer and inhibits the photoisomerization.

3.2 Kinetics of the bleaching of the closed form by UV-visible absorption spectroscopy

After pre-irradiation, the amount of produced colored species was then monitored by UV-vis spectroscopy. Once TFA was added, the UV-visible absorption was monitored over various periods of time. Surprisingly, the first spectrum was found to be almost identical to that of the starting solution, especially in the visible region. Nonetheless bleaching was observed whatever the amount of TFA added (Fig. 1).

Bleaching kinetics was examined quantitatively by monitoring the decay of the absorbance of the closed isomer at 580 nm (Fig. 2).

A simple model to describe the early parts of the kinetics was adopted. It relies on the assumption that a fast

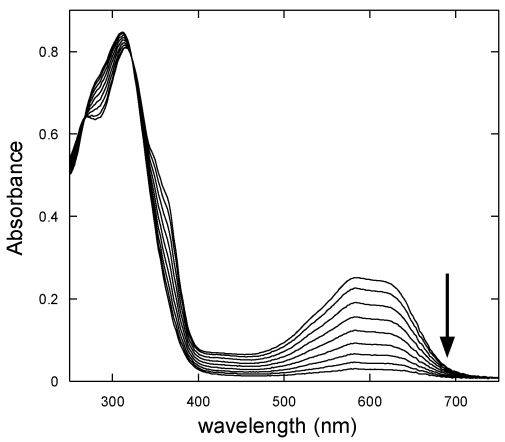


Fig. 1 Evolution of the UV-visible spectrum of a 2.4×10^{-5} M pre-irradiated solution of terthiazole in CH_3CN after addition of 66 equivalents of TFA at 25 °C. Initial concentration of the colored species was 1.75×10^{-5} M. Sampling interval: 150 s.

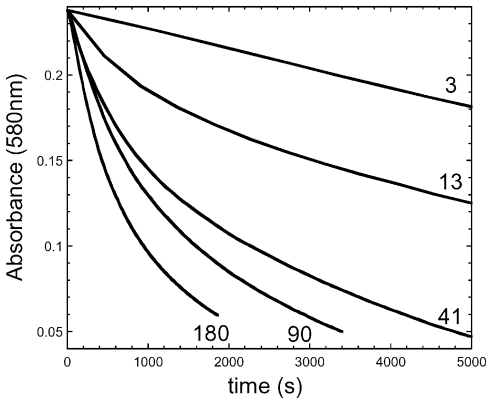


Fig. 2 Kinetic monitoring of the absorbance at 580 nm after addition of TFA at 25 °C. The number of equivalents of TFA added ranged from 3 to 180. For the sake of clarity, only some of the recorded curves have been plotted.

pre-equilibrium exists between free closed dye **C**, the acid TFA and a species {**C**.TFA} that could be either a protonated form $\mathbf{CH}^+$, an ion pair {$\mathbf{CH}^+$, $CF_3CO_2^-$} or a hydrogen-bonded complex {**C**.TFA} (see ESI†). The isomerization reactions were also limited to that involving the complexed closed dye {**C**.TFA} as the free **C** form is known to be thermally stable. Products of the reaction could either be free or "complexed" open **O** species. The parameters of the kinetic model to be determined were the association constant $K^{\mathbf{C}}_{eq}$ of the closed terthiazole **C** with TFA, and the rate constant k of the opening process.

$$\mathbf{C} + \mathrm{TFA} \rightleftharpoons \{\mathbf{C}.\mathrm{TFA}\}\text{: } (K^{\mathbf{C}}_{eq})\ K^{\mathbf{C}}_{eq} = [\{\mathbf{C}.\mathrm{TFA}\}]/[\mathbf{C}][\mathrm{TFA}];$$

$$\{\mathbf{C}.\mathrm{TFA}\} \rightarrow \mathbf{O} + \mathrm{TFA}\text{: } (k);\ v = \mathrm{d}[\mathbf{O}]/\mathrm{d}t = k[\{\mathbf{C}.\mathrm{TFA}\}];$$

Experimental data were found to fit very well (Fig. 3) with this model and values for $K^{\mathbf{C}}_{eq}$ and k were obtained from initial slope v_0 analysis: $K^{\mathbf{C}}_{eq} \approx 560\ \mathrm{M}^{-1}$ and $k \approx 1.9 \times 10^{-3}\ \mathrm{s}^{-1}$ *i.e.* a lifetime of less than 600 s. If we compare this result to those previously obtained for the thermal bleaching, the observation of a similar bleaching rate constant would require warming the terthiazole solution up to *ca.* 100 °C. The efficient destabilization of the closed isomer is also highlighted by the poor association constant since the amount of the {**C**.TFA} species varies from 5 to 40% when 16 to 180 equivalent of TFA are added.

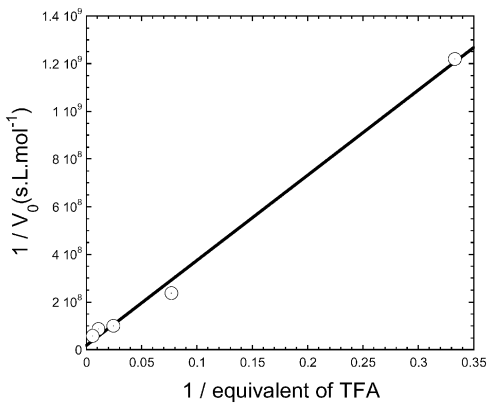


Fig. 3 Double reciprocal plot of initial slopes *vs.* equivalents of trifluoroacetic added: ε^{580}(closed) ≈14500 L mol^{-1} cm^{-1}), $[\mathbf{C}]_0 = 1.7 \times 10^{-5}$ M.

This remarkably effective simple model prompted us to investigate the behavior of the open isomer **O** with TFA, especially to examine if the coloration inhibition would be the result of a conformational control suppressing the conrotatory ring closure.[4]

3.3 NMR analysis of the interaction of the open O form with TFA

Due to the multiple nitrogen basic atoms, several structures can be assumed for the monoprotonated form, especially chelated ions (Fig. 4): one plausible structure retains the helical geometry and provides a possibility of chelating the proton by a five-membered ring chelate *via* the α-diimine moiety (structure a). The other plausible structure is obtained when the terthiazole, adopting a U-shaped geometry, binds a proton *via* its two distal thiazole rings forming a seven-membered ring chelate (structure b). In the latter conformation, the conrotatory pericyclic is impossible. We thus analyzed the NMR data in the light of these possible geometries.

Several ^{1}H NMR experiments were conducted at room temperature: a titration of the **O** form by TFA in CD_3CN and 2D-COSY and ^{19}F–^{1}H HOESY on a **O**–TFA mixture with a large excess of TFA (*ca.* 60 equivalents, see ESI†). As expected the equilibrium was fast enough so no distinct spectrum was building up upon addition of TFA, the interaction with the acid giving rise only to a drift of some of the chemical shifts (Fig. 5).

Aside the two singlets of the methyl groups (Me1 and Me2), the well resolved signals in the aromatic region, already present in the starting material spectrum and assigned to the *ortho* hydrogens (H_o1, H_o2 and H_o3), were used to qualitatively sort the three phenyl groups.

While the CH_3 hydrogens experienced an expected downfield shift upon TFA addition—although not with the same intensity (Fig. 6), the aromatic hydrogens proved to be either insensitive (H_o1) or even more shielded (H_o2 and H_o3). This difference was also found in the COSY spectrum in which only the two phenyl groups sensitive to TFA were found to be well resolved. In the ^{19}F–^{1}H HOESY NMR experiments it was established that the interaction of the TFA's trifluoromethyl group with the *ortho* hydrogens H_o1 of the "unsensitive" phenyl ring was weaker at short mixing time than with the

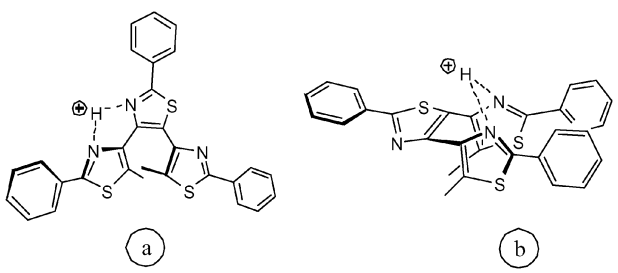


Fig. 4 Proposed conformers for chelated protonated open terthiazole, $\mathbf{OH}^+$: (a) helical, (b) U-shaped.

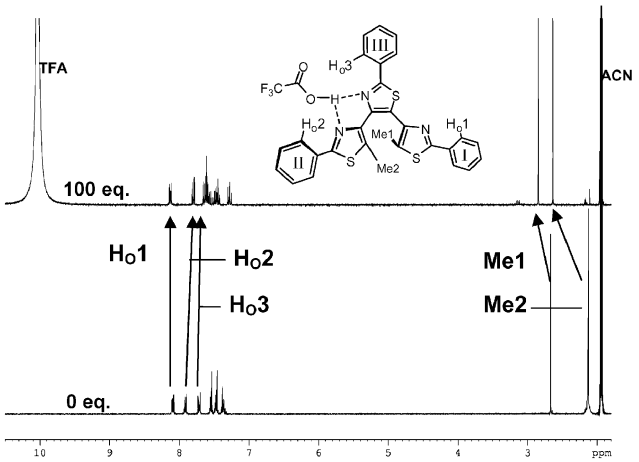


Fig. 5 ^{1}H NMR chemical shift variations upon addition of 100 equivalents of TFA in a 3×10^{-3} M solution of terthiazole in CD_3CN.

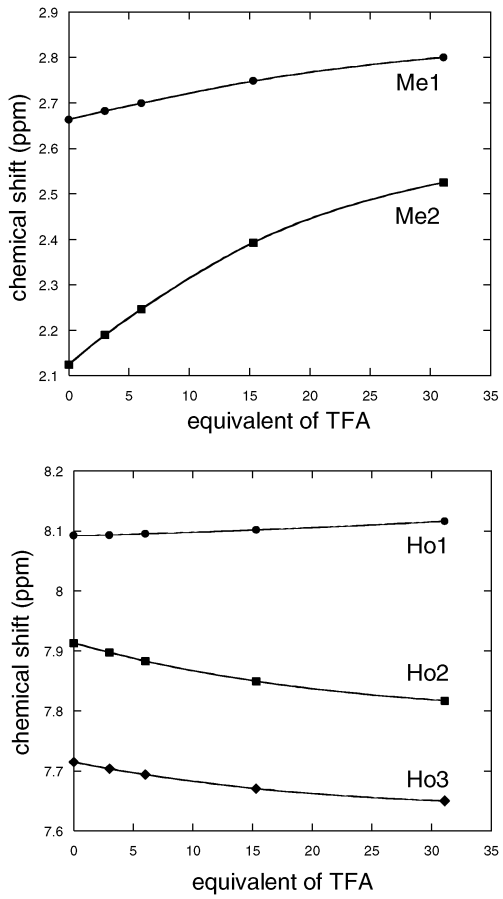


Fig. 6 Changes and assignation of the observed signals in the ^{1}H NMR spectrum of the open terthiazole **O** upon addition of TFA in CD_3CN at room temperature; [**O**] $\approx 3 \times 10^{-3}$ M.

rest of the molecule, especially when comparing to H_o2. The contrast in the behavior of the phenyl rings and in the magnitude of the shifts for the methyl signals were found to be more consistent with a helical structure and made possible the assignment of the hydrogens. Furthermore the HOESY experiment suggested that the major form of the complex was not ionized.

From the NMR titration, a value of $K^{\mathbf{O}}_{eq} \approx 4 \pm 2\ M^{-1}$ was obtained for the complexation equilibrium constant, showing a much weaker affinity of the open **O** isomer for TFA than the closed one **C**. More generally we were quite puzzled by the magnitude of the interaction between the both forms of the dye and trifluoroacetic acid in acetonitrile. Very few data are available in the literature to rationalize the observed behavior. Thiazole, the model heterocycle of the open isomer **O**, is indeed a weak base in water (2-phenylthiazole pK_a^w: 2.52)[23] and its incorporation into a bithiazole may not increase much the stability of the protonated form.‡ Upon transfer to acetonitrile, pK_a values are raised considerably and for pyridine it is moved from 5.2 in water to 12.6 in acetonitrile.[24] More interesting is the case of CF_3COOH whose pK_a is shifted from *ca.* 0.5 in water to up to 13 in acetonitrile[25] with the possibility to give the homoconjugated ions $\{(CF_3COO)_2H\}^-$.[26] These dramatic changes in the acid's behavior in acetonitrile can explain the very poor association constant observed for the open triangle terthiazole. For the ring-closed **C** compound, the estimation of its acido-basic properties was made by comparison to retinaldimine pigments. Presenting also a conjugated imine moiety, their pK_a^w values are estimated to be around 7 in aqueous solution,[27] thus higher than that of the thiazole. This is in agreement with the marked difference observed in association constant between the closed and open forms.

3.4 DFT calculations

The identity of the active species was still a problem, thus theoretical investigation (B3LYP/6-31G(d) level) of the compound's isomeric forms were undertaken. In a first step, energies of all possible monoprotonated species were calculated in gas phase in order to identify the protonation site on the closed isomer. Then, these optimized structures were used to get single point energies in acetonitrile solvent, using the polarizable continuum model (PCM). The most stable structures were found to be when protonation occurred on the central bridging thiazole. The prediction of the closed protonated molecule's UV-vis absorption spectrum in acetonitrile was made by TD-DFT (PCM) calculations (Fig. 7).

Remarkable features were noticed especially in the visible part: the band responsible for the color of the closed form was found to be strongly bathochromically shifted. No such modification of the UV-vis spectrum was, however observed, thus the main species in the solution should be an associated complex.

During the TFA induced ring opening process, the triangle terthiazole can exist as six different species in acetonitrile (Fig. 8). According to the results obtained experimentally and theoretically on both isomers, two species, the fully ionized $\mathbf{OH}^+$ and $\mathbf{CH}^+$, have certainly to be considered as very minor compounds but their participation to the

‡ One can compare to 2,2′-bipyridine (bpy): for the first protonation, pK_a^w(bpyH$^+$/bpy) ranges from 4.33 to 5.15 while for pyridine itself, pK_a (pyH$^+$/py) is about 5.2. See: P. Wiczling, M. J. Markuszewski and R. Kaliszan, *Anal. Chem.* 2004, **76**, 3069; E. Craven, C. Zhang, C. Janiak, G. Rheinwald and H. Lang, *Z. Anorg. Allg. Chem.* 2003, **629**, 2282; G. R. Newkome, K. J. Theriot and F. F. Fronczek, *Acta Crystallogr., Sect. C*, 1985, **41**, 1642.

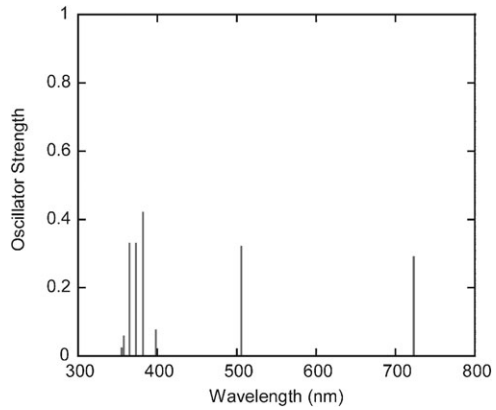


Fig. 7 TD DFT (PCM) calculated spectrum of the protonated closed form $\mathbf{CH}^+$ (no counter ion).

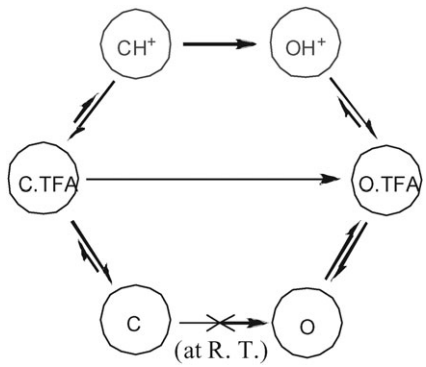
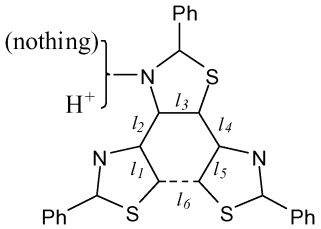


Fig. 8 The six possible terthiazole species involved in the ring opening process.

transformation cannot be excluded. Thus, seeking for a molecular explanation of the lowering of the activation energy for the thermal opening, we considered these species for structural changes considering that the distortions would be more striking when the proton transfer is complete.

Structural comparisons were done on the optimized geometries computed in the gas phase by DFT for the neutral **C** and **O** and protonated $\mathbf{CH}^+$ and $\mathbf{OH}^+$ forms, keeping the protonation site on the central bridging thiazole. We first focused on the "photoactive core". At first glance, bond length changes between the closed and open protonated forms were found to parallel their neutral counterparts: upon opening, double bonds tended to expand, while single bonds contracted. We then examined the magnitude of the changes by calculating the ratio of the global variation (closed to open: $\mathbf{C} - \mathbf{O}$) of the protonated *vs.* the neutral forms $\{[l_n(\mathbf{CH}^+) - l_n(\mathbf{OH}^+)]/[l_n(\mathbf{C}) - l_n(\mathbf{O})]\}$ (Table 1). Except for the single bond to be broken, all ratios were found to be slightly less than unity: although these values may not be meaningful for most of the bonds tested, it tends to that show that calculated protonated closed and open forms "resemble" each other more structurally than the neutral parent compounds. This is particularly clear for the bond l_3 the variation of which is the smallest upon moving from $\mathbf{CH}^+$ to $\mathbf{OH}^+$ (82%) for all bonds considered. Another interesting point was the impact of protonation on the bond length especially for the closed form, that was highlighted by calculating their relative variation

Table 1 Ratio of bond changes for the opening process for the protonated and neutral forms and relative bond length variation upon protonation for the photoactive core of the dye



Bond	$\frac{l_n(\mathbf{CH}^+) - l_n(\mathbf{OH}^+)}{l_n(\mathbf{C}) - l_n(\mathbf{O})} \cdot 100$	$\frac{l_n(\mathbf{CH}^+) - l_n(\mathbf{C})}{l_n(\mathbf{C})} \cdot 100$
l_1	94.8	−0.46
l_2	93.6	−0.64
l_3	82.8	−1.40
l_4	91.9	−0.01
l_5	98.3	0.33
l_6	100.7	0.43

$\{[l_n(\mathbf{CH}^+) - l_n(\mathbf{C})]/l_n(\mathbf{C})\}$. All bonds in direct relationship with the charged nitrogen tended to shorten including the double bond l_2, but the most important change is again for the bond l_3. Interestingly the bond to be broken (l_6) tends to stretched, facilitating the opening.

Clearly this bond is "on its way" to accompany the structural changes required by the ring opening.

A pictorial way to summarize these results can be done using the convenient Marcus curves representing the free energy of the reactant and product, and classically used to describe electron transfer reactions.[28] Schematically, in this framework, the use of a harmonic representation of the free energy allows one to derive the activation energy from two parameters, the free energy released (the exergonicity) and the intrinsic activation energy (or reorganization energy) that reflect the stiffness of the mode used as reaction coordinate and the overall change in molecular structure. As in the case of dissociative electron transfer one can assume that in the present case, despite the change in the total number of bonds, the quadratic representation of the free energy is roughly valid.[29] Then, the structural "proximity" between the open and closed forms is illustrated by a distance $|q^0_{\mathbf{C}} - q^0_{\mathbf{O}}|$ which in equilibrium geometries are larger for the neutral structures than for the protonated structures (Fig. 9), q defining a reaction coordinate describing the global rearrangement of the molecular skeleton (and among others the bond to be broken). Consequently the intrinsic activation energy (measured at the curves' crossing point for no exergonicity, *i.e.* $\Delta G^0 = 0$) is reduced. This interpretation is reminiscent to what has been suggested to explain the ring-opening or -closure of diarylethene cation radicals.[12]

3.5 Comparison with similar ter-hetarylenes

Eventually the remarkable effect of trifluoroacetic acid on the stability of the closed terthiazole photochrome has to be compared to the results obtained on a very close family of ter-heterocycles based on a combination of thiazole and

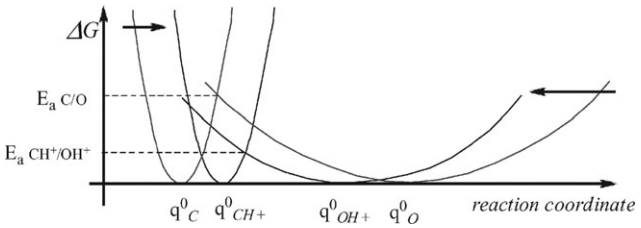


Fig. 9 Effect of the protonation on the Marcus curve-like representation of the reaction path at no exergonicity. Parabolas are non-symmetrical to take in account the bond changes upon ring opening (closed molecules are "stiffer" than the open ones). The change in equilibrium geometries upon protonation is given by the arrows and the intrinsic activation energy by the dotted lines.

imidazole. It has been indeed reported that N-alkylation of both nitrogens of the imidazole ring yielding a very electron deficient imidazolium did not affect the thermal stability of the ring-closed colored form, thus in sharp contrast with the present results.[30,31] For these molecules, the charge is believed to be strongly localized on the NCN moiety, and both nitrogens participate equally to the stabilization (Fig. 10).

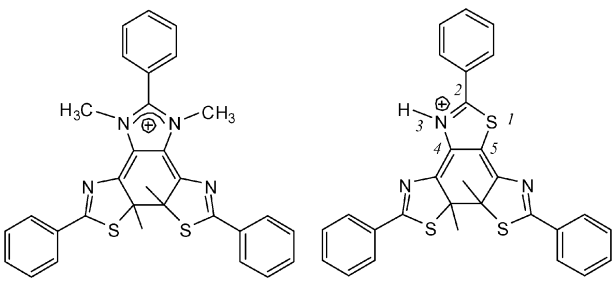


Fig. 10 Closed cationic forms of (left) a triangle bis-thiazolylimidazolium ([DTI_C]$^+$) (ref. 30) and (right) bis-thiazolylthiazolium (**CH**$^+$) (this work). Numbering of the heterocycle is indicated.

Geometrical changes were thus examined on the "thiazole"§ carrying the protonation site (see ESI†). This is of the part of the molecule where the bond lengths variations are the most important upon protonation. Interestingly the most affected ones are the C^2–N^3 and C^4–N^3 bonds in the immediate vicinity of the active site (+3.5% and −3.6%, respectively) while the C^2–S^1 bond is affected only by 1% indicating that its bond order is not changed much: the sulfur participates less actively to the charge stabilization than the other atoms.

4. Conclusion

The triangle terthiazole photochromic compound studied in this work presents thus a unique property, as its bleaching can be induced efficiently at room temperature with a protic compound, namely trifluoroacetic acid. In acetonitrile both isomers are very weak bases, but nonetheless the interaction is sufficient to promote efficient ring opening. The most satisfactory explanation is that complexation of the closed colored dye with TFA leads to an increase of the substituent's electron withdrawing effect that would affect the thermal activation barrier of the pericyclic reaction. The interplay between the charge stabilization and the electronic mechanism of the ring opening and the mechanical constraint applied to the reactive cyclohexadiene core play a pivotal role in the understanding of this thermal process and may explain why the behavior of such compounds is totally different from structurally very similar imidazolium containing dyes. The fact that the proton is the smallest of the Lewis acids may also explain the marked difference in stability with the already published lanthanide complexes of this ligand. Indeed the incoming H atom may not be chelated between the two nitrogens, so all the effects would then be localized on one part of the molecule, the central thiazole unit. So far, it would be tempting to consider that only hydrogen bonds are necessary to trigger the process. However while there is no spectroscopic evidence for the presence of fully protonated species, they may be present in trace amounts. A deeper kinetic analysis is in progress to refine the roles played by each species during the transformation.

§ Due to cyclization, it is no longer an aromatic thiazole ring.

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