

Electronic Supplementary Information **revised version**

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

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pages	schedule
S2:	I - NMR Titration of the open form by TFA in CD ₃ CN
S3:	II - Assignment of the aromatic protons of open form in the presence of TFA in CD ₃ CN (2D-COSY ¹ H)
S4:	III - ¹ H - ¹⁹ F HOESY (400 MHz, mixing time 0.5s) of open form in the presence of an excess of TFA (>60eq) in CD ₃ CN
S5:	IV - Bleaching kinetics of the closed isomer C in the presence of TFA via Initial Slope v ₀ analysis
S6:	V - Association constant from NMR titration of the open isomer by TFA in acetonitrile.
S8:	VI - DFT calculated energies in gas and acetonitrile phases
S9 :	VII - Bond lengths variation (in angstrom) by DFT Calculations
S10:	VIII - TD-DFT calculation of the UV-visible spectrum of the CH ⁺ species in liquid phase, no counter anion.

I- NMR Titration of the Open form by TFA in CD₃CN

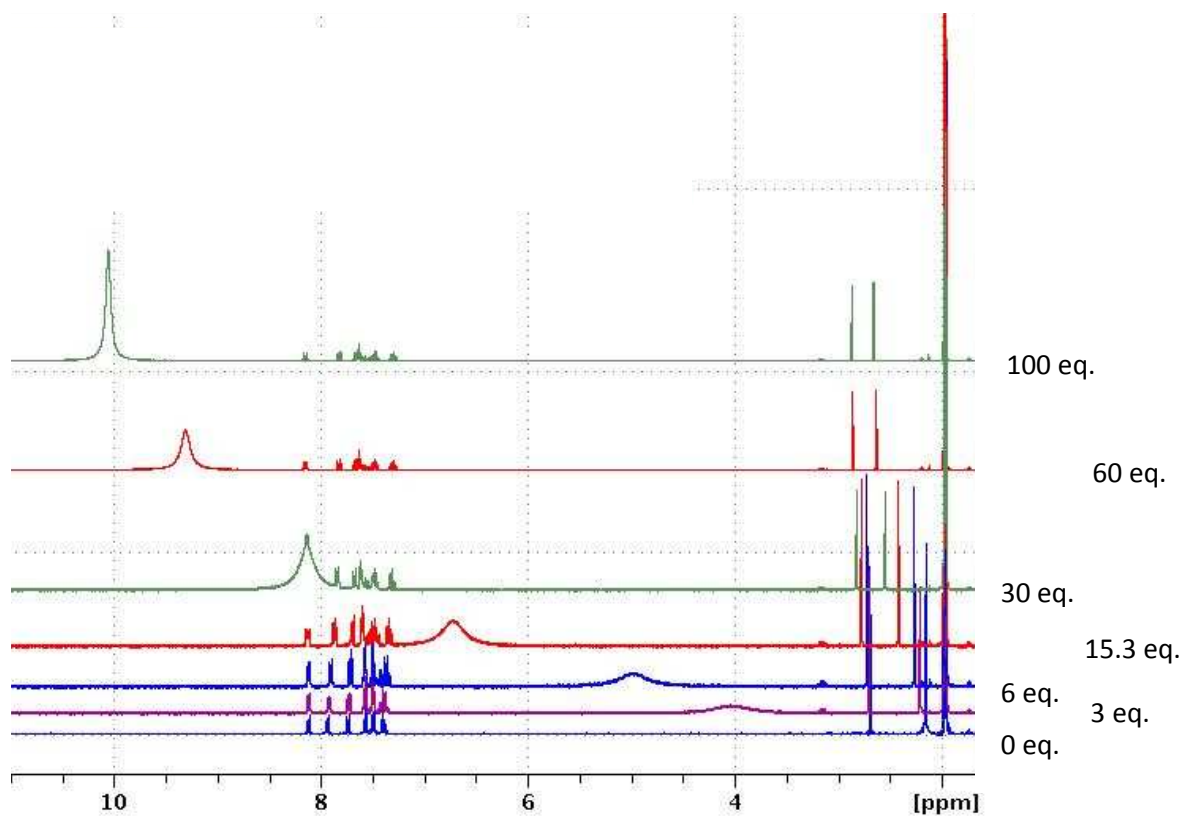


Fig S1 : NMR titration of Open triangle terthiazole by TFA ; [O] $\approx 3.10^{-3}$ M; [TFA] from $9e-3$ to 0.3M

II- Assignment of the aromatic protons of Open form in the presence of TFA in CD₃CN (2D-COSY ¹H)

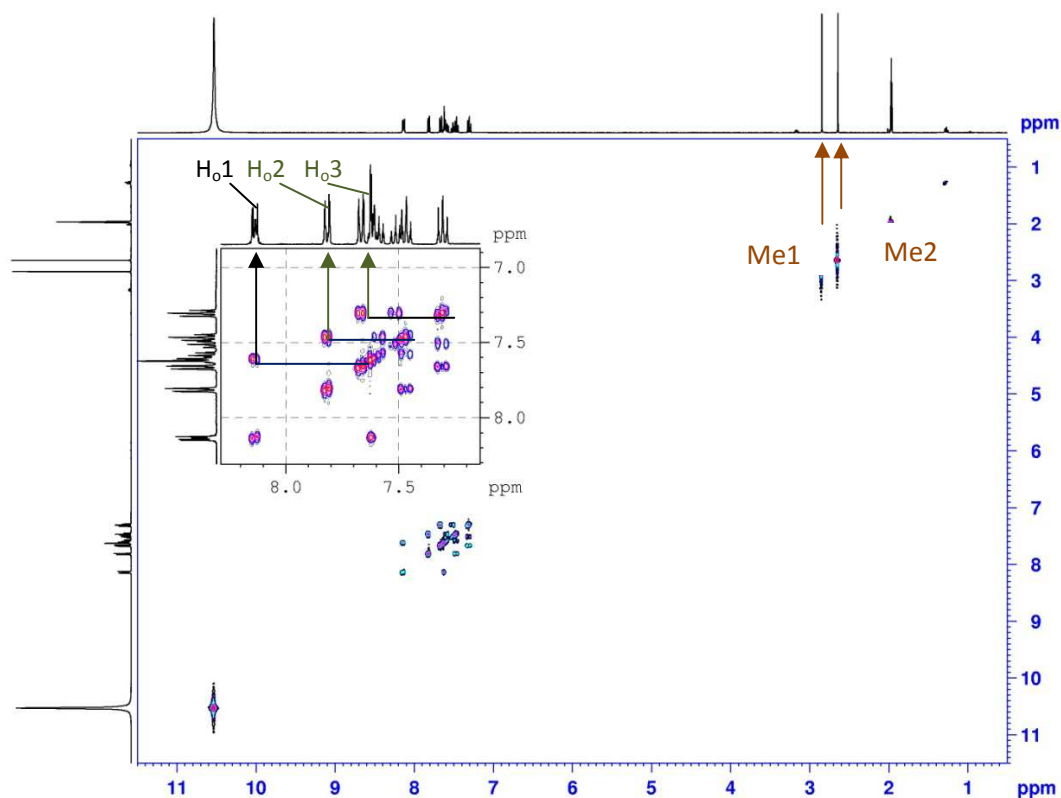
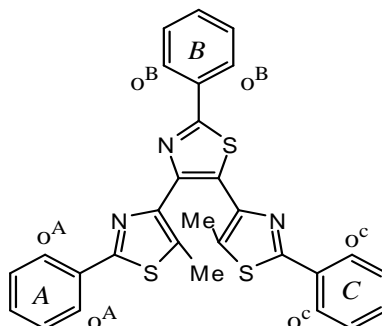


Fig S2: Open form 2D-COSY spectrum, Excess TFA (> 60 eq) in CD₃CN offset: expansion of the aromatic zone showing the correlation of the *ortho* phenyl hydrogen H_o1,2,3 to other signals. H_o1 is correlated to only one signal (3H) while H_o2 and 3 are correlated to two signals (integration resp. 2 and 1).



Scheme S3: 2D-COSY proton assignment : at this stage, no ambiguous assignment can be made to identify H_o1,2,3 and H_o^{A,B,C} as well as for Me1 and Me2

III- ^1H - ^{19}F HOESY (400 MHz, mixing time 0.5s) of Open form in the presence of an excess of TFA (>60eq)

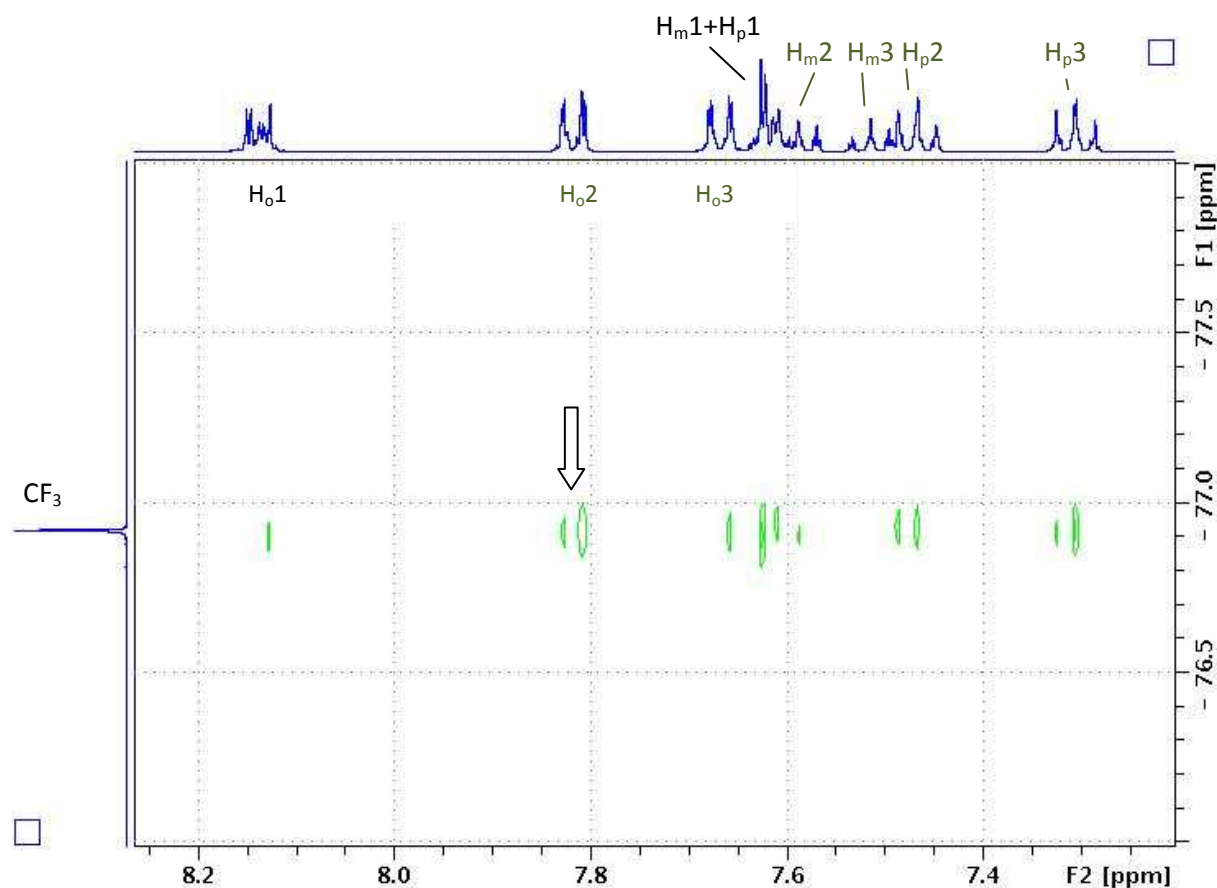
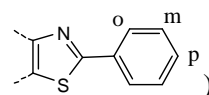
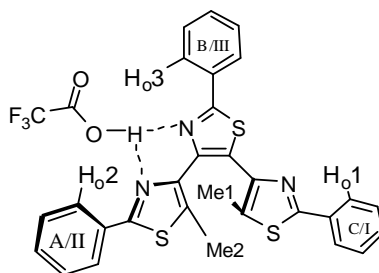


Fig S4: H-F HOESY Spectrum (0.5s) (Aromatic hydrogen labeling

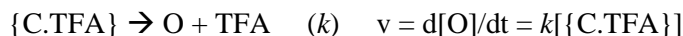
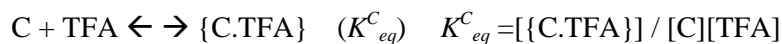


From the slightly higher intensity of the H₀₂ correlation spot, a putative assignment can be given as : ring I ≈ ring C, ring II ≈ ring A and ring III ≈ ring B. Methyl groups would then be Me1 ≈ Me(C), and Me2 ≈ Me(A).



IV- Bleaching kinetics of the closed isomer C in the presence of TFA via Initial Slope v_0 analysis

The kinetic scheme is the following:



with K_{eq}^C the association constant of the closed terthiazole C with TFA and k the rate constant of the opening process.

At the very beginning of the reaction, one can neglect the isomerization reaction so $[C] \approx ([C]_0 - [C.TFA])$. Keeping in mind that when $[TFA] \rightarrow \infty$; $v \rightarrow V_{max} = k[C]_0$ and taking in account that the trifluoroacetic acid is always in large excess so that $[TFA] \approx [TFA]_0$, then:

$$V_0 = V_{max} \frac{K_{eq}^C [TFA]}{K_{eq}^C [TFA] + 1} = V_{max} \frac{K_{eq}^C Eq [C]_0}{K_{eq}^C Eq [C]_0 + 1},$$

with $Eq = [TFA]_0 / [C]_0$ number of equivalent of acid added to the solution.

In double reciprocal, it becomes:

$$1/v = (1/V_{max}) (1 / (K_{eq}^C Eq [C]_0) + 1)$$

Thus a plot of $1/v_0$ vs. $1/Eq$ must give a straight line with $slope = (1 / (V_{max} K_{eq}^C [C]_0))$ and $intercept = 1/V_{max}$, from which one can extract the association constant $K_{eq}^C = (intercept/slope)/[C]_0$ and the rate constant $k = 1/(intercept)[C]_0$.

V- Association constant from NMR titration of the open isomer by TFA in ACN (acetonitrile).

An average chemical shift δ deriving from δ_O , $\delta_{\{O.TFA\}}$ and α , respectively the chemical shift of the free open dye O, the chemical shift and the fraction of complexed open dye {O.TFA} is introduced for each signal:

$$\delta = \alpha\delta_{\{O.TFA\}} + (1 - \alpha)\delta_O = \alpha(\delta_{\{O.TFA\}} - \delta_O) + \delta_O, \text{ so } 1/\alpha = (\delta_{\{O.TFA\}} - \delta_O) / (\delta - \delta_O)$$

Taking in account that the trifluoroacetic acid is always in large excess, the association constant can be rewritten as

$$[\{O.TFA\}]/([O]_0 - [\{O.TFA\}]) = K_{eq}^O [TFA]_0 = \alpha/(1 - \alpha), \text{ or } 1/\alpha = 1 + 1/K_{eq}^O [TFA]_0$$

Thus in a double reciprocal plot of $1/(\delta - \delta_O)$ v.s. $1/[TFA]_0$, one should obtain a straight line with (*slope*) = $1/(K_{eq}^O (\delta_{\{O.TFA\}} - \delta_O))$ and (*intercept*), $1/(\delta_{\{O.TFA\}} - \delta_O)$ since

$$(\delta_{\{O.TFA\}} - \delta_O) / (\delta - \delta_O) = 1 + 1/K_{eq}^O [TFA]_0,$$

the association constant K_{eq}^O being given by the ratio (*intercept*)/(*slope*). Four signals are easily followed during the titration and were considered for the association constant determination : H₀2, H₀3, Me1 and Me2.

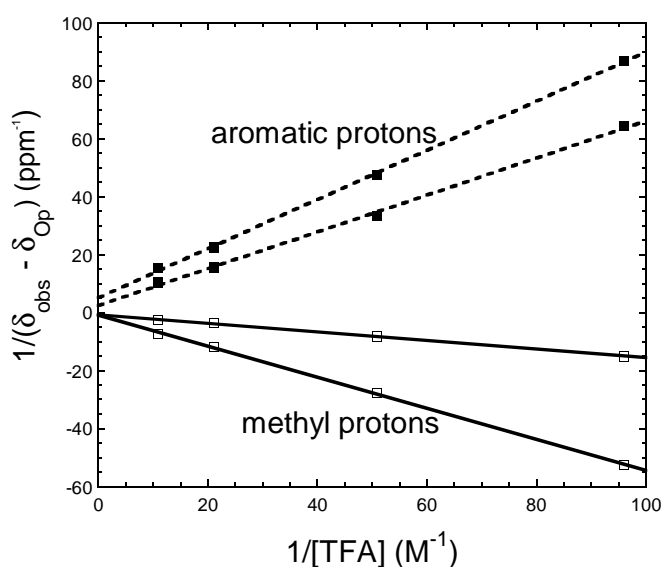


Figure S5: Linearization of the data according to the previous formula giving rise to K_{eq}^O estimation. $[O] \approx 3 \cdot 10^{-3} M$; $[TFA]$ from $1e-2$ to $0.1 M$. From top to bottom : “aromatic protons” : H₀2 & H₀3 and “methyl protons”: Me1 and Me2.

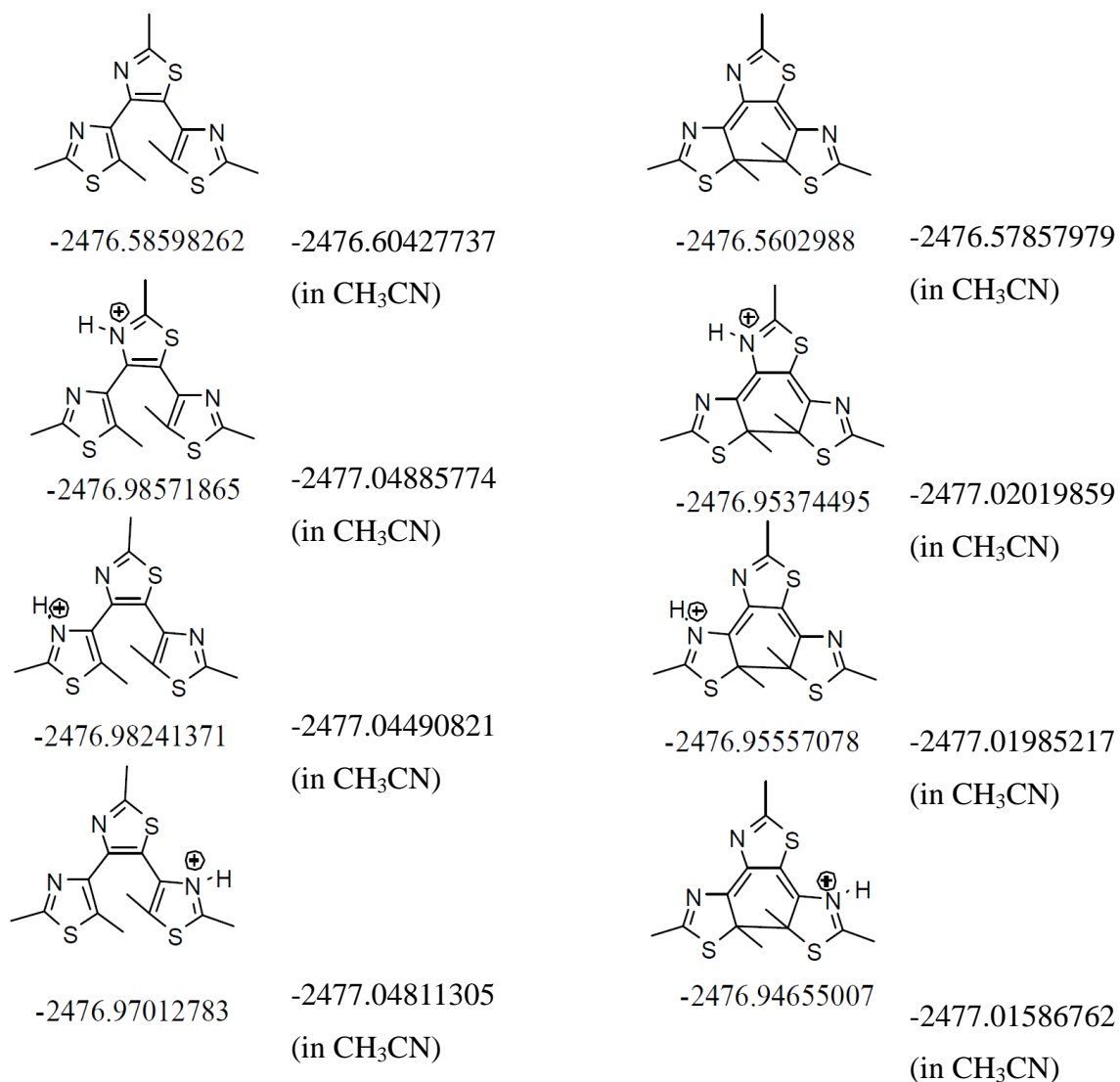
Proton	Intercept	slope	K_{eq}^O (M^{-1})
Me1	-0.885	-0.537	1.65
Me2	-0.689	-0.150	4.6
H _o 2	2.48	0.639	3.9
H _o 3	5.26	0.847	6.2

Table S1 : Analysis of the linearization for the 4 selected signals

An average value of $K_{eq}^O \approx 4 \pm 2 M^{-1}$ was adopted.

VI-DFT calculated energies in hartree for neutral and monoprotonated forms closed & open
 (phenyl groups not mentioned for clarity)

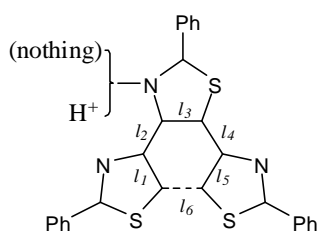
Energies calculated *in vacuo* and corrected for the effect of acetonitrile (CH₃CN), with a dielectric constant of 36.64, by using the polarizable continuum model (PCM) of solvation.



VII- Bond lengths variation (in angstrom) by DFT Calculations

See text for computational details.

A-Photoactive core (gas phase)

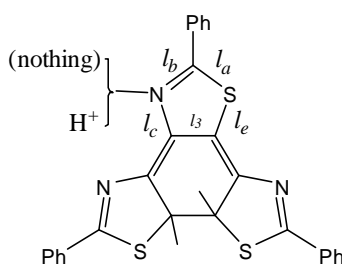


Bond	O	C	OH ⁺	CH ⁺	C-O	CH ⁺ -OH ⁺
l_1	1.37679	1.5456	1.37854	1.53857	0.16881	0.16003
l_2	1.47989	1.37396	1.46427	1.36513	-0.10593	-0.09914
l_3	1.38226	1.46193	1.37546	1.44146	0.07967	0.066
l_4	1.46631	1.35954	1.45749	1.35934	-0.10677	-0.09815
l_5	1.37931	1.54443	1.3872	1.54957	0.16512	0.16237
l_6	3.69934	1.54549	3.72035	1.5521	-2.15385	-2.16825

B- Weak dependence of bond lengths with solvent

medium	l_1	l_2	l_3	l_4	l_5	l_6
C (gas phase)	1.54560	1.37396	1.46193	1.35954	1.54443	1.54549
C (PCM)	1.54516	1.37396	1.46177	1.35873	1.54240	1.54619

C- Central “thiazole ring” of the closed compound



Bond	C	CH ⁺	CH ⁺ -C	(CH ⁺ -CH)/C (%)
l_a	1.7454	1.81098	0.06558	1,0
l_b	1.339	1.29328	-0.04572	3,5
l_c	1.39651	1.38244	-0.01407	-3,6
l_3	1.44146	1.46193	0.02047	1,1
l_e	1.77897	1.7594	-0.01957	-1,4

VIII- TD-DFT calculation of the UV-visible spectrum for the CH^+ species in liquid phase, no counter anion.

Excited State	λ [nm] (Oscillator Strength)	Assignment
1	723 (0.29)	HOMO > LUMO
2	506 (0.32)	HOMO > LUMO+1
3	398 (0.076)	HOMO-1 > LUMO
4	382 (0.42)	HOMO > LUMO+2
5	373 (0.33)	HOMO-2 > LUMO
6	365 (0.33)	HOMO-3 > LUMO
7	358 (0.058)	HOMO-4 > LUMO
8	355 (0.023)	HOMO-5 > LUMO

