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COMMUNICATION

Lewis acid enhanced switching of the 1,1-dicyanodihydroazulene/vinylheptafulvene photo/thermoswitch†‡

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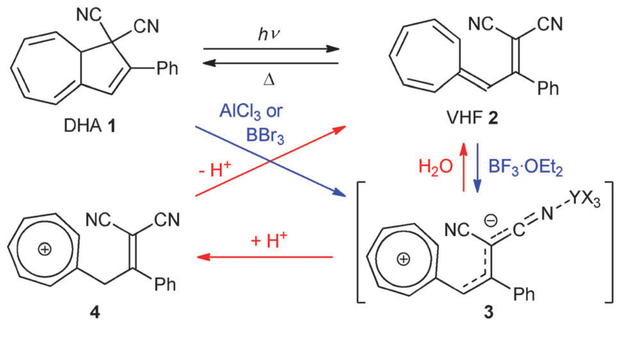
Mild Lewis acids enhance the rate of the thermal conversion of vinylheptafulvene (VHF) to dihydroazulene (DHA). In the absence of light, stronger Lewis acids promote the otherwise photoinduced DHA to VHF conversion.

Photoswitches have been used extensively for controlling the state of supramolecular systems and assemblies by means of light.[1] The most prevalent of these have been the azobenzenes and dithienylethenes, which can be interconverted between their two states by light of different wavelengths. Another system that has been less explored is the dihydroazulene/vinylheptafulvene photo/thermoswitch.[2] DHA **1** undergoes a photochemically induced ring-opening to VHF **2**, which reverts back to the DHA *via* a thermally induced ring-closure (Scheme 1). Previous work has focused on how functional groups directly attached to the carbon atoms in the five- and seven-membered rings of DHA influence the switching events.[2]

We became interested to elucidate the possibility of further tuning of the switching event *via* a reversible Lewis acid (LA) complexation to the available lone pairs of the cyano groups in **1** and **2**. It is well-known that nitriles can act as ligands for soft metal ions, and this has previously been employed for assembly of several complexes and three-dimensional arrays.[3] The usefulness of the nitrile group in supramolecular chemistry was further emphasised by the ability of nitrile-functionalised calixarenes to act as sensors for soft metal ions.[4] As the conversion of VHF to DHA is thought to proceed *via* a zwitterionic structure,[2c] in which the positive charge is localised on the seven-membered ring and the negative charge is stabilised by the two cyano groups, coordination of LA to the cyano groups of **2** is particularly attractive. Here we have studied the influence of zinc and silver ions, in addition to aluminium and boron halides, and counter-balancing effects of Lewis basic solvents. We note that LAs were previously used for triggering a photochromic spirooxazine switch[5] and photoisomerisation of cinnamic esters.[6]



Scheme 1 Conversions between dihydroazulene (DHA **1**) and vinylheptafulvene (VHF **2**). YX_3 = $AlCl_3$, BF_3, BBr_3.

The first objective was to study the effect of the LA on the VHF to DHA thermal back-reaction (TBR) in different solvents at 35 °C (Table S1, ESI‡). $ZnCl_2$ was chosen as the LA and it was brought into solution in different solvents as its etherate complex, $ZnCl_2{\cdot}(Et_2O)_2$ in Et_2O. First, 10 molar eq. of $ZnCl_2{\cdot}(Et_2O)_2$ was added to the solution of DHA **1**, which was then irradiated at its absorption maximum (*ca.* 357 nm depending on the solvent), resulting in quantitative conversion to VHF **2**. The TBR could be approximated to an exponential decay, thus the rate of the TBR could be defined by an apparent half-life ($t_{1/2}$) of compound **2**. In chlorinated solvents, CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl (DCE), a two-to-three fold increase in the rate of the TBR was observed when $ZnCl_2{\cdot}(Et_2O)_2$ was present. In contrast, solvents which contained atoms with accessible lone pairs (MeCN, Me_2CO, EtOAc, EtOH) showed no increase in the rate of the reaction (Table S1, ESI‡) as such Lewis bases outcompete the CN groups in coordinating to the $ZnCl_2$ (Scheme 2).

A second screening was conducted with different LAs, Brønsted acids, and salts in DCE at 25 °C (Table S2, ESI‡). The addition of acetic acid, $HBF_4{\cdot}Et_2O$, or an ionising salt ($[NBu_4]PF_6$) had little effect on $t_{1/2}$. Next, the influence of $ZnCl_2{\cdot}(Et_2O)_2$ was investigated to see if the amount of Et_2O added altered $t_{1/2}$. As expected, higher $ZnCl_2$ concentration (less Et_2O) increased the conversion rate; however, too little Et_2O caused $ZnCl_2$ to precipitate out of solution (Table 1). With 10 eq. of $ZnCl_2{\cdot}(Et_2O)_2$ (199 : 1, DCE : Et_2O) a $t_{1/2}$ of only 21 min was

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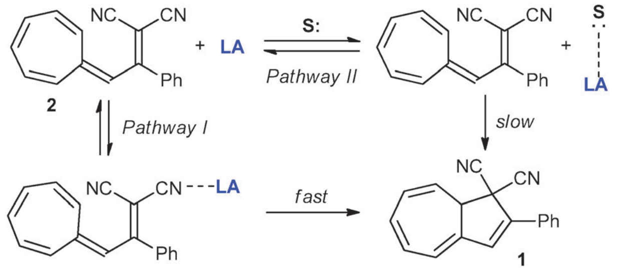
‡ Electronic supplementary information (ESI) available: Experimental procedures for the synthesis of compounds **2** to **5**. Copies of NMR and UV-Vis spectra and X-ray data CCDC 804840 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10804b



Scheme 2 Lewis acid induced enhancement of the thermal back reaction. LA = Lewis acid, S: = Lewis basic solvent.

Table 1 Apparent $t_{1/2}$ (min) of the TBR ($\mathbf{2} \rightarrow \mathbf{1}$, 2.63×10^{-5} M) with $ZnCl_2{\cdot}(Et_2O)_2$ at 25 °C

Lewis acid	Eq.	$t_{1/2}$/min	DCE : Et_2O[b]
	—	597	1 : 0
	—	598	49 : 1
$ZnCl_2{\cdot}(Et_2O)_2$ (9 : 1)[a]	10	316	27 : 1
$ZnCl_2{\cdot}(Et_2O)_2$ (49 : 1)[a]	10	98	147 : 1
$ZnCl_2{\cdot}(Et_2O)_2$ (199 : 1)[a]	10	21	597 : 1
$ZnCl_2{\cdot}(Et_2O)_2$ (199 : 1)[a]	25	25	240 : 1
$ZnCl_2{\cdot}(Et_2O)_2$ (199 : 1)[a]	0.1	352	59 700 : 1

[a] Ratio of CH_2ClCH_2Cl (DCE) : Et_2O in the $ZnCl_2{\cdot}(Et_2O)_2$ solution. [b] Solvent ratio in a cuvette.

obtained. An increased content of the Lewis base Et_2O promoted the right hand pathway shown in Scheme 2.

Silver ions were then examined. The addition of dry AgOTf to a solution of **1** induced a chemical reaction upon irradiation of a solution at 357 nm (**1** was not regenerated) and gave a precipitate (no chemical reaction was observed with **1** or **2** in the absence of light). The hydrated AgOTf gave cloudy solutions in DCE, while the etherate, presumably $[Ag(Et_2O)_3]OTf$,[7] was found not to cause a reaction or precipitation upon irradiation of **1** and **2**; also it seemed stable to air. However, the $[Ag(Et_2O)_3]^+$ gave an increase to the rate of TBR (Table 2), reducing $t_{1/2}$ from 597 to 71 min with 10 eq. and to as low as 9 min with 250 eq. Interestingly, the addition of 10 eq. $[Ag(Et_2O)_3]OTf$ or $ZnCl_2{\cdot}(Et_2O)_2$ in DCE : Et_2O 49 : 1 only showed a minor increase in the speed of the photoinduced ring-opening of **1** (Table S3, ESI‡).

The absorption is redshifted for the $[VHF–Ag]^+$ complex compared to VHF (λ_{max} shifts from 475 to 519 nm, Fig. 1) while a similar shift was not observed for the DHA absorption. Investigating the spectral shift as a function of increasing $[Ag^+]$ yielded an association constant in the order of 10^3 M^{-1} (Fig. S4, ESI‡).

Analysis of the rate of the TBR showed that the $ZnCl_2{\cdot}(Et_2O)_2$ or $[Ag(Et_2O)_3]OTf$ acted in a catalytic fashion. The equilibrium (Pathway I in Scheme 2) is formed much faster than either of the conversion rates. Thus, as the fast conversion of $[VHF–LA]^+$ to DHA proceeds, LA is released resulting in more $[VHF–LA]^+$ formed as the equilibrium adjusts, thereby making a greater fraction of the VHFs convert following the fast pathway. Although two parallel decays interwoven by the equilibrium should be in play, the data can be approximated to a single exponential decay, where $t_{1/2}$ of the $VHF/[VHF–LA]^+$ decreases as the LA concentration increases (Tables 1 and 2).

Table 2 Apparent $t_{\frac{1}{2}}$ (min) of the TBR ($\mathbf{2} \rightarrow \mathbf{1}$, 2.63×10^{-5} M) and VHF λ_{max} (nm) with eq. $AgOTf{\cdot}(Et_2O)_3$ at 25 °C

Eq. Ag(I)	0	0.1	0.5	1	10	25	100	150	250
Half-life	597	556	406	317	71	33	13	10	9
VHF λ_{max}	474	475	475	475	478	483	508	514	519

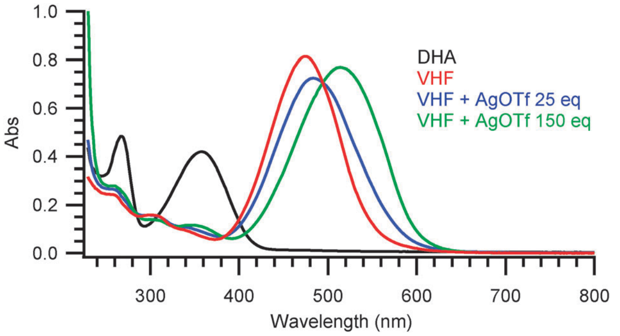


Fig. 1 UV-Vis absorption spectra (2.63×10^{-5} M) in DCE showing red-shift in VHF λ_{max} with increase of $AgOTf{\cdot}(Et_2O)_3$.

The $AlCl_3{\cdot}THF$ complex induced no effect on the rate of the TBR (possibly due to the high affinity of aluminium for the oxygen of THF). Yet, in the absence of THF ligands, $AlCl_3$ was found to react with the DHA (*vide infra*). $BF_3{\cdot}Et_2O$ did not react with DHA but reacted quickly with the red coloured VHF **2** (λ_{max} 474 nm) to form a colourless solution (λ_{max} 288 nm, Fig. 2). We anticipate formation of a tropylium species **4** by protonation of the suspected intermediate **3** (Scheme 1) on the γ carbon, relative to the two cyano groups. It was noticed that upon addition of ethanol, compound **4** reverted back to the red-coloured VHF, which then underwent the usual thermal conversion to the original DHA. NMR studies seemed to confirm formation of **4** with the characteristic downfield signals of the tropylium CH at δ_H 9.09–8.92 and δ_C 156.80, 156.10, 154.98 (CD_3CN). This is the suspected uncharacterised cationic intermediate that is to be formed in the synthesis of DHA,[2e] by hydride abstraction from 2-(cyclohepta-2,4,6-trienyl-1-phenylethylidene) malononitrile. The NMR experiment showed that the reaction was faster in CD_3CN than in CD_2Cl_2. Compound **4** was stable in an NMR tube (CD_3CN, CD_2Cl_2) for at least two weeks and was deprotonated to VHF **2** by Brønsted basic solvents (H_2O, EtOH, NEt_3).

Unexpectedly, treatment of a solution of DHA in CH_2Cl_2 with strong LAs, $AlCl_3$ or BBr_3, resulted in direct ring-opening in the absence of light within minutes. The $AlCl_3$ gave a

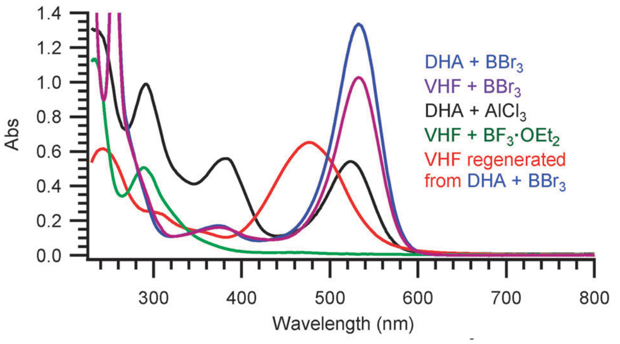


Fig. 2 UV-Vis absorption spectra (3.28×10^{-5} M) in DCE for various LAs added. Regeneration of VHF (red curve) occurs by addition of EtOH (also causing dilution of the sample).

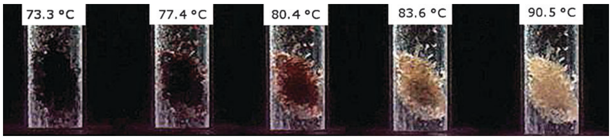
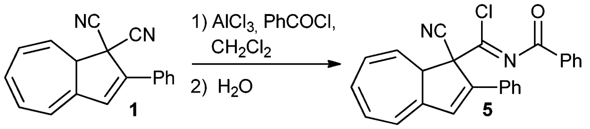


Fig. 3 Conversion of red **2** to yellow **1** coloured crystals (77–84 °C, starting temperature 65 °C; ramp rate 1 °C min^{-1}).

quantitative conversion of **1** to **2**, after treatment of the pink-coloured intermediate formed, presumably **3** (Scheme 1, Fig. 2), with water or ethanol; it is stoichiometric and not catalytic in its reactivity. It was higher yielding than BBr_3. In a control UV-Vis experiment, VHF gave similarly coloured reaction products (λ_{max} 524 and 533 nm for $AlCl_3$ and BBr_3, respectively, Fig. 2) which supports the ring-opening theory. The pink colour of the solutions faded with time. The reaction between DHA and $AlCl_3$ or BBr_3 was also followed by NMR, which indicated the presence of a tropylium ring in support of structure **3**. We found that treatment of DHA with $AlCl_3$ followed by water is a convenient way of converting DHA to VHF on a preparative scale in the absence of light. Although VHF derivatives have been isolated previously, it required prolonged and powerful irradiation of a saturated DHA solution in hexane (in which the TBR is slow).[2f] The VHF crystals lose their dark red colour as they degraded back to DHA at rt (40% in about one month; determined by ^1H NMR). Heating the crystals caused a change in their colour from dark red (**2**) to yellow (**1**) (Fig. 3).

The observation that the γ carbon of **3** gets protonated suggests that other electrophiles could be used to attack this position. Yet, treatment with $PhCOCl/AlCl_3$ gave an unexpected compound resulting from the addition of PhCOCl to one of the CN groups forming a carbimidoyl chloride (**5**) (Scheme 3). This reaction did not occur in the absence of $AlCl_3$ (rt, 1 week) or when PhCOCl was used in excess relative to $AlCl_3$. The X-ray crystal structure of this compound (Fig. 4) concurs with the other spectroscopic and microanalytical data. While this functional group is known in a few compounds in the literature,[8] to the best of our knowledge this appears to be the first crystal structure of a carbimidoyl chloride group.



Scheme 3 Conversion of one CN to a carbimidoyl chloride.

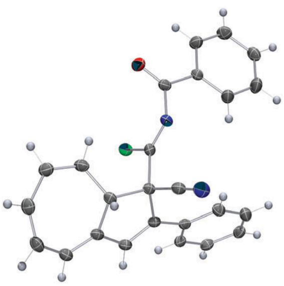


Fig. 4 Ortep diagram of carbimidoyl chloride compound **5**. Selected bond lengths are shown in Table S7 (ESI‡).

The compound was sensitive to acidic conditions and silica gel needed to be neutralised prior to chromatography. Irradiation resulted in conversion of the "DHA" (**5**) to a "VHF" form (λ_{max} shifts from 353 to 447 nm in cyclohexane) but the initial compound was not regenerated thermally. However, the "VHF" form decayed at a rate about 30 times faster than VHF **2** in cyclohexane.

In conclusion, the rate of the thermal back reaction of VHF to DHA was controlled by LAs such as $ZnCl_2{\cdot}(Et_2O)_2$ and $[Ag(Et_2O)_3]OTf$. The effect was counter-balanced by a Lewis basic solvent. The reversibility of the LA complexation to the cyano groups is particularly attractive for the future exploration of the DHA/VHF system in advanced multistate switches and supramolecular sensors with colour changes as read-out. Stronger LAs such as BBr_3 and $AlCl_3$ were found to chemically induce ring-opening of the DHA molecule in the absence of light, and subjecting DHA to PhCOCl and $AlCl_3$ provided a carbimidoyl chloride derivative. This functionality may be a scaffold for further functionalization and tuning of the system. It is also attractive to subject the cyano group(s) to even stronger coordinating metal-centres for a further enhancement of the TBR and rendering the system more resistant to Lewis basic solvents. This would potentially lead to more sensitive thermoswitches.

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