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Towards Solar Energy Storage in the Photochromic Dihydroazulene–Vinylheptafulvene System

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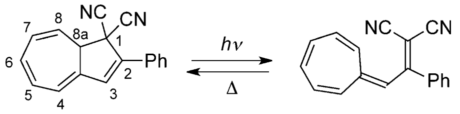
Abstract: One key challenge in the field of exploitation of solar energy is to store the energy and make it available on demand. One possibility is to use photochromic molecules that undergo light-induced isomerization to metastable isomers. Here we present efforts to develop solar thermal energy storage systems based on the dihydroazulene (DHA)/vinylheptafulvene (VHF) photo/thermoswitch. New DHA derivatives with one electron-withdrawing cyano group at position 1 and one or two phenyl substituents in the five-membered ring were prepared by using different synthetic routes. In particular, a diastereoselective reductive removal of one cyano group from DHAs incorporating two cyano groups at position 1 turned out to be most effective. Quantum chemical calculations reveal that the structural modifications provide two benefits relative to DHAs with two cyano groups at position 1: 1) The DHA–VHF energy difference is increased (i.e., higher energy capacity of metastable VHF isomer); 2) the Gibbs free energy of activation is increased for the energy-releasing VHF to DHA back-reaction. In fact, experimentally, these new derivatives were so reluctant to undergo the back-reaction at room temperature that they practically behaved as DHA to VHF one-way switches. Although lifetimes of years are at first attractive, which offers the ultimate control of energy release, for a real device it must of course be possible to trigger the back-reaction, which calls for further iterations in the future.

Introduction

According to the International Energy Agency (IEA), the sun could be the biggest source of energy by 2050, producing over a quarter of the world's electricity.[1] When it comes to the engineering of organic molecules for light-harvesting, most of the focus is on organic solar cells. However, the development of organic molecules for solar energy storage has attracted increasing interest in recent years.[2] Photochromic molecules that undergo light-induced isomerizations to higher-energy, metastable isomers present such targets, which would provide closed-cycle systems of energy harvesting, storage, and release. A particularly attractive property would be the release on-demand, with no environmentally unfriendly oxidation products involved.[2] The dihydroazulene/vinylheptafulvene pair **1**/**2** (DHA/VHF, Scheme 1) is a photo/thermo-switch system, which, if suitably functionalized, could be a candidate for a molecular solar thermal energy storage system.[3] DHA **1** is a yellow photochromic compound, which upon irradiation turns into the red VHF **2**. The back-reaction of this metastable, higher-energy isomer into DHA **1** is not light-induced but occurs instead thermally (thermal back-reaction, TBR). Its rate is solvent dependent and enhanced by treatment with mild Lewis acids.[4]



DHA **1** VHF **2**

Scheme 1. DHA–VHF isomerization. DHA numbering is also shown.

Two significant challenges for using photochromic molecules for energy storage are to reach a sufficiently high energy density and at the same time to halt the TBR. Boulatov et al.[2a] have estimated an upper limit for the energy density of photochromic molecules of 1 MJ kg^{-1}, which would be useful for real applications. Recent calculations show that the Gibbs free energy difference of the parent DHA/VHF **1**/**2** is 27.7 kJ mol^{-1} in vacuum, at the M06-2X/6-311+G(d) level, which corresponds to a Gibbs free energy density of only 0.11 MJ kg^{-1} (energy stored in VHF).[5] The parent system is thus far from optimum. Our calculations showed, however, that more than a doubling of the energy density could be obtained by removing one of the two cyano groups (DHA/VHF **3**/**4**, Figure 1). Thus, a Gibbs free energy difference between isomers **3** and **4** of 57.7 kJ mol^{-1} was obtained, corresponding to an energy density of 0.25 MJ kg^{-1}. At the same time, calculations showed

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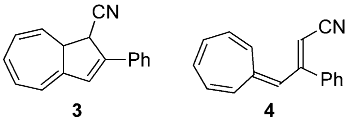
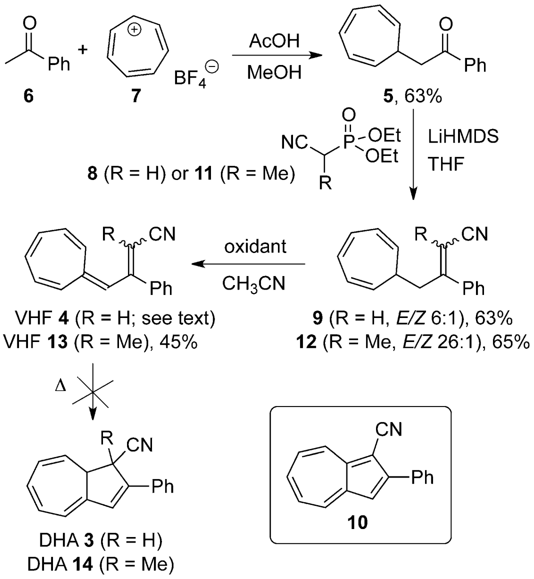


Figure 1. New DHA–VHF derivatives with only one cyano substituent at C1.

that the activation enthalpy of the TBR was increased from 92.3 kJ mol^{-1} (transition state from **2** to **1**) to 106.9 kJ mol^{-1} (transition state from **4** to **3**), in vacuum, at the PBE0/6-311+G(d) level, and the TBR would thus be considerably slowed down for this isomer. This is in line with previous findings that the TBR relies on the ability to stabilize a negative charge at C1.[6] The system is thereby attractive as it has the potential to store more energy without fast release. Few examples with substituents different from CN at C1 have been described, and information on their photochromic properties was not reported in detail.[7] However, a "monocyano-DHA" derivative bearing a 4,5-dihydro-1,3-thiazole ring had a very slow TBR.[8] For these reasons, we decided to develop a synthetic protocol for monocyano-DHA/VHF molecules. The overall objective is to elucidate whether this structural modification is useful for solar energy storage and hence if it would be beneficial to combine it with other structural modifications to reach ultimately the upper energy storage limit.



Scheme 2. Attempted synthesis of monocyano-DHAs from monocyano-VHF precursors. Oxidant system: i) $NOBF_4$, ii) pyridine, with R=H; or i) tritylium tetrafluoroborate, ii) NEt_3, with R=Me.

Results and Discussion

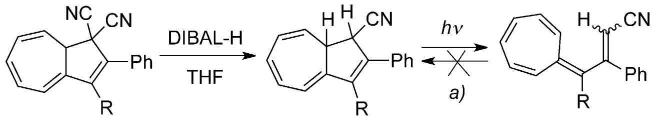
Synthesis

For the synthesis of monocyano-DHA **3**, two protocols were investigated: The first protocol employed the corresponding VHF **4** as a potential precursor and the second employed the easily obtainable DHA **1**. Although the second protocol was successful, the first one, in which the VHF had to be constructed from suitable precursors, was more problematic, as outlined in Scheme 2. The first intermediate **5** was prepared from acetophenone **6** and tropylium tetrafluoroborate **7**, following the procedure reported by Gobbi et al.[9] for the initial step to give **1**. Then, a Horner–Wadsworth–Emmons reaction of **5** with the ethyl phosphonate **8** in the presence of lithium bis(trimethylsilyl)amide (LiHMDS) in THF was performed, providing **9** as a 6:1 mixture of *E*/*Z* isomers in 63% yield. The subsequent oxidation/elimination of the VHF precursor **9** to VHF **4** was not straightforward. The standard procedure[10] with tritylium tetrafluoroborate as oxidizing agent and triethylamine as base in 1,2-dichloroethane heated at reflux showed evidence of decomposition and traces of azulene species, later assigned as **10**, whereas **4** was difficult to isolate from the byproducts. Reducing the amount of NEt_3 (from excess to stoichiometric), running the reaction at room temperature, and degassing the solution excluded the formation of azulene **10** and limited the decomposition. Replacement of tritylium tetrafluoroborate with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provoked complete decomposition. The use of nitrosyl tetrafluoroborate as hydride abstractor in MeCN followed by deprotonation with pyridine turned out to be the best conditions to obtain **4**, although isolation of a pure fraction was still not possible. It was identified later by ^{1}H NMR spectroscopic analysis of an irradiated solution of DHA **3**, obtained through the second protocol (see below). Besides, no traces of DHA **3** were detected upon heating **4** for up to 12 h.

To enhance the stability, we decided to replace the H at C1 with a methyl group by using the same synthetic strategy (Scheme 2). The methyl phosphonate **11** was used in a Horner–Wadsworth–Emmons reaction, providing the corresponding VHF precursor **12** in 65% yield (26:1 *E*/*Z* isomers, ratio evaluated by NMR analysis). The oxidation–elimination step with tritylium tetrafluoroborate and NEt_3, under strictly degassed conditions, now furnished monocyano-VHF **13** as a mixture of *E*/*Z* isomers in 45% yield with no traces of degradation compounds. Nevertheless, attempts to convert **13** into the corresponding DHA **14** by heating in 1,2-dichloroethane/toluene were not successful. Although **13** proved to be more stable than its analogue **4** and allowed full characterization of this product, decomposition in solution was detected after 12 h in an NMR tube.

The second protocol was then followed to prepare **3**. When a solution of DHA **1** in THF was treated with diisobutylaluminium hydride (DIBAL-H) at 0 °C in the dark, no aldehyde formation was detected. Instead, replacement of a cyano group with a hydride to give monocyano-DHA **3** occurred in 23% yield (Scheme 3). Small amounts of azulene were detected. We note that an analogous anomalous reductive decyanation of an α-sulfonitrile induced by $LiAlH_4$ was previously reported.[11]

The crude mixture was purified and only one pair of enantiomers of DHA **3** was detected. A large coupling constant (9.7 Hz) between H8a and H1 was measured in the ^{1}H NMR spectrum. From structures optimized at the B3LYP/6-311+G(d,p) level of theory of the four possible isomers combined with the Karplus Equation, we can assign the isomers to the



DHA **1** (R = H)
DHA **15** (R = Ph)

3 (R = H), 23%
16 (R = Ph),16%

4 (R = H)
17 (R = Ph)

Scheme 3. Direct synthesis of monocyano-DHAs by stereoselective reduction. a) TBR of VHF **17** to some extent at elevated temperature for a long period.

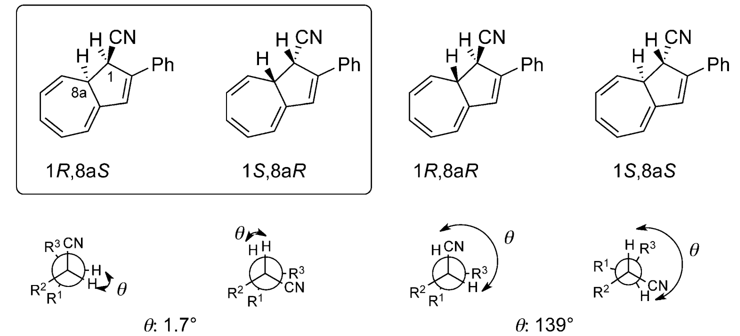


Figure 2. Possible DHA **3** diastereomers with corresponding Newman projection on C1–C8a and dihedral angle Θ. The enantiomeric pair in the box seemed to be formed only from the reaction shown in Scheme 3.

enantiomeric pair (1*R*,8a*S*) and (1*S*,8a*R*), in which the hydride was inserted from the same side of H8a, presumably for steric reasons (Figure 2).

Although the yield of the reaction was modest, it furnished **3** directly from **1** and can be prepared on large scale.[10] NMR experiments were performed to follow the ring opening of **3** to **4** upon irradiation and to confirm the structure of compound **4** obtained through the first protocol. Photolysis of the NMR sample showed a decrease of the characteristic signals, H1 and H8a at $\delta = 4.71$ and 3.33 ppm, and the increase of two new signals at $\delta = 6.05$ and 5.23 ppm, indicating protons linked to sp^2 carbons, H1 and H3 (see the Supporting Information). Hence, DHA **3** was readily opened upon irradiation to VHF **4**, but again this compound did not return to DHA upon heating.

With VHF **4** we have achieved a molecule for which the TBR seems to be completely prevented. To shed further light on the influence of having only one CN at C1, we decided to combine this structural motif with a VHF-like molecule, which is known to undergo an ultrafast ring-closure reaction. Daub and co-workers[12] have reported the 2,3-diphenyl-substituted DHA **15** (Scheme 3). The corresponding VHF undergoes a very fast TBR with a relaxation time τ of only 20 s in MeCN, which corresponds to a $t_{1/2}$ of 14 s (for **2** in MeCN, $t_{1/2} = 218$ min). Subjecting DHA **15** to a DIBAL-H reduction gave **16**, as a 6:1 mixture of diastereomers, in 16% yield. Coupling constants of 9.8 and 4.5 Hz between H8a and H1 were measured in the ^{1}H NMR spectrum of the major and the minor isomer, respectively. Based on the geometry-optimized structures reported in Figure 2, we assign the isomers with the large coupling constant to the 1*R*,8a*S*/1*S*,8a*R* enantiomeric pair and the others to the 1*R*,8a*R*/1*S*,8a*S* enantiomeric pair. Crystals of the major isomer of **16** were grown from dichloroethane/heptane and X-ray analysis confirmed that, in the major isomer, H1 and H8a lie on the same side of the ring (Figure 3). The dihedral angle Θ H1/C1/C8a/H8a is 2.9°, in agreement with the values extrapolated from the coupling constant and the two Ph rings are twisted out of co-planarity by 62.3°. Compound **16** readily underwent ring opening to VHF **17** upon irradiation. This VHF was also reluctant to undergo the TBR, but, in fact, photophysical studies seem to indicate that some conversion is nevertheless obtained after several hours at 70 °C in MeCN (see below).

From calculations at the CAM-B3LYP/6-311+G(d) level, the 1*R*,8a*R* diastereomer of **3** was found to be 6.02 kJ mol^{-1} lower in free energy than that of the 1*R*,8a*S* diastereomer in MeCN. Similarly, for the 1*R*,8a*R* diastereomer of **16** compared with the 1*R*,8a*S* one, a free energy difference of 4.44 kJ mol^{-1} was found in MeCN. This result indicates that the formation of the 1*R*,8a*S*/1*S*,8a*R* isomers as major products is due to kinetic control.

A final synthetic objective was to develop a more general method to introduce substituents straightforwardly at C1 from DHA **1**. Preliminary results have been obtained through a reductive decyanation reaction, followed by trapping of the carbanion with an electrophile following a protocol developed for derivatives of malononitrile.[13] Although the method is not yet optimized or generalized for "dicyano-DHAs", it allowed the synthesis and characterization of DHA **14** (Scheme 4). DHA **1** was treated with 3 molar equivalents of lithium naphthalenide (LN)[14] in THF at −78 °C and the intermediate was then quenched with methyliodide to give **14** in 21% yield. Photolysis gave VHF **13**, but no TBR was observed.

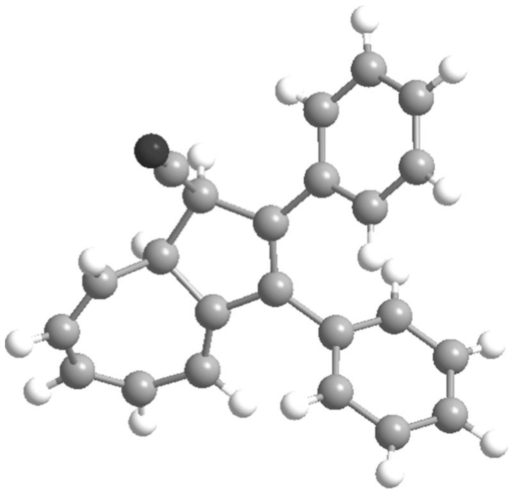
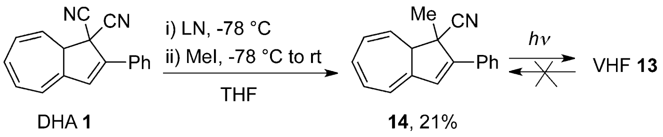


Figure 3. Molecular structure of **16** (major isomer) from X-ray crystallographic analysis.



Scheme 4. Direct synthesis of methylcyano DHA by reductive alkylation. LN = lithium naphthalenide.

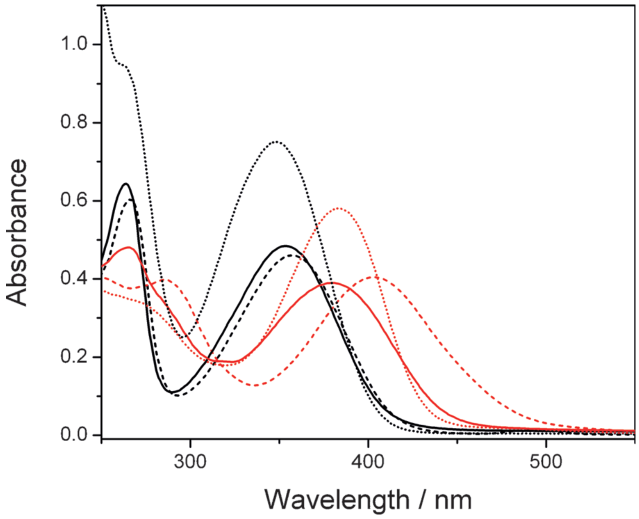


Figure 4. UV/Vis absorption spectra of DHA **3** (black) and VHF **4** (red) in MeCN (——, 2.6×10^{-5} M) and DCE (-----, 2.8×10^{-5} M) and of DHA **14** (black) and VHF **13** (red) in DCE (•••••, 4.7×10^{-5} M).

UV/Vis Spectroscopy and switching studies

The UV/Vis absorption spectra in MeCN (solid lines) and in dichloroethane (DCE, dashed lines) of DHA **3** and VHF **4** are shown in Figure 4. In MeCN, compound **3** shows two main peaks at 353 and 264 nm (S_1–S_0 and S_2–S_0 transitions). The peak at 353 nm is at the same wavelength as for DHA **1** in MeCN, thus the characteristic DHA absorption is not influenced by removal of one CN. This seems plausible as it is not in conjugation with the π-system. Irradiation of the sample with monochromatic light at 353 nm for 10 s intervals and for a total duration of 150 s resulted in complete conversion to VHF **4**, which has an absorption maximum at 379 nm. This absorption is significantly blueshifted relative to that of VHF **2** (λ_{max} 470 nm in MeCN), which is in accordance to it having one less cyano group in conjugation with the π-system. The possibility for **4** to undergo TBR was monitored for 24 h at 25 °C and at 60 °C in MeCN. No signs of ring closure and formation of DHA were detected, although after 24 h at 60 °C, small changes in the spectrum appeared and a decrease in the VHF absorption of roughly 4%, possibly due to decomposition.

Also in DCE, compound **3** was converted to **4** upon irradiation (Figure 4, dashed lines). In this solvent the absorption maxima of **3** and **4** are redshifted in comparison to those in MeCN, revealing a solvatochromic effect (in particular for **4**). Thus, λ_{max} for DHA **3** is at 358 nm and for VHF **4** at 403 nm. The strong solvatochromism of the VHF absorption signals significant charge delocalization in the ground-state structure, being stabilized by a polar solvent such as MeCN. The possibility for TBR was monitored in time at 25 and 60 °C, but again no signs of the ring-closure reaction were evidenced. Addition of silver triflate (10–200 equivalent) or $ZnCl_2$ in ethereal solution (200 equiv), was previously reported as successfully enhancing the TBR of **2** to **1**.[4] Yet, this addition did not promote the TBR of **4**. Furthermore, monitoring the spectrum at 60 °C in presence of Lewis acids revealed partial decomposition of **4**, to give an azulene, tentatively assigned to **10** (see the Supporting Information). The TBR was also investigated with VHF **13** in DCE, both by heating the sample and by addition of Lewis acids, but no TBR was evidenced.

The UV/Vis absorption spectrum of **16** shows an absorption maximum at 352 nm in DCE (Figure 5), whereas for DHA **15** a maximum at 340 nm in toluene was reported.[12] The absorption spectrum after irradiation of **16** at 365 nm showed new maxima at 276 and 329 nm and a shoulder at 383 nm. Thus, the spectrum of the generated monocyano-VHF **17** was quite different from that of VHF **4**. Yet, a similar behaviour was reported by Daub and co-workers for the corresponding VHF of **15**.[12] Attempts to induce the TBR of **17** upon heating at 50 °C in DCE and adding Lewis acids ($ZnCl_2$ and silver triflate) were not successful. For a solution of the VHF, complete decomposition to an azulene was recorded after 60 d in deoxygenated MeCN (see the Supporting Information). However, a partial TBR, seemingly with some decomposition also, was induced upon heating at 70 °C in MeCN for 72 h under strictly anaerobic conditions (see the Supporting Information). We cannot quantify the degree of conversion, but observed that the species generated, tentatively assigned to a DHA, was indeed light-sensitive, and upon irradiation it was returned into a VHF.

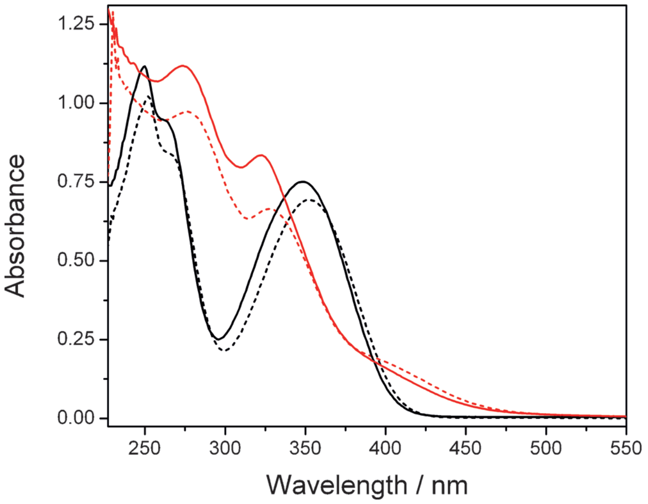


Figure 5. UV/Vis absorption spectra of DHA **16** (black) and VHF **17** (red) in MeCN (—— 6.5×10^{-5} M) and DCE (-----, 5.0×10^{-5} M).

Raman Spectroscopy

In Figure 6, the solid-state Raman spectra of DHAs **1**, **15**, and **16** are shown in the CN-stretching region. Both **1** and **15** have

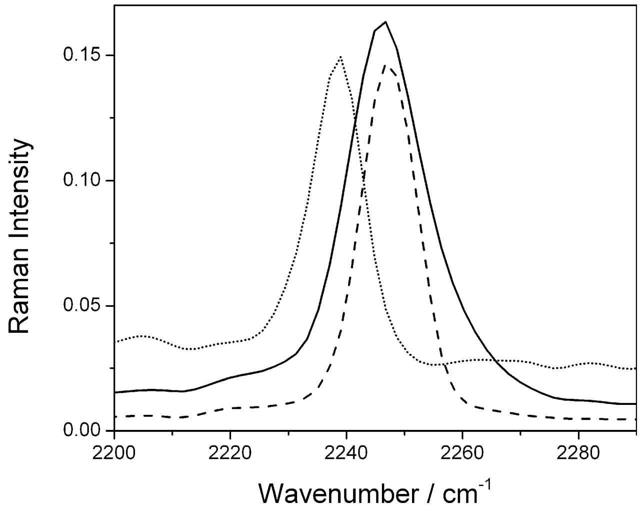


Figure 6. Raman spectra of solid state of **16** (•••••), **15** (——), and **1** (-----) in the CN-stretching region.

symmetric and asymmetric CN-stretching vibrations, but we were unable to distinguish them. The CN-stretching vibration in DHA **1** is observed at 2247 cm^{-1} with a full width at half maximum (FWHM) of 11 cm^{-1}. The harmonic symmetric and asymmetric CN-stretching vibrations in **1** are calculated to be within 6 cm^{-1} of each other, hence the band observed at 2247 cm^{-1} contains both CN-stretching vibrations. The band observed in the CN-stretching region for **15** at 2247 cm^{-1} has a FWHM of 17 cm^{-1}, which also contains both the symmetric and asymmetric CN-stretching vibrations that are calculated to be within 8 cm^{-1} of each other. The substitution of an additional Ph group to **1** has no effect on the frequency, however, the width of the band increases by about 6 cm^{-1} suggesting that the transitions are split slightly more in **15** than in **1**. The CN-stretching vibration in **16** is observed at 2238 cm^{-1} and is thus redshifted relative to the CN-stretching vibrations in **15** and **1**. The FWHM of the CN-stretching band in **16** is 11 cm^{-1} as for **1**.

Calculations: Thermodynamic and kinetic properties

To shed further light on the thermochemical properties and kinetics of the TBR of the 3-phenyl derivatives and hence the applicability for use as molecular heat batteries, a computational study was conducted and the results compared to energies recently calculated for the **1**/**2** and **3**/**4** pairs.[5] The storage Gibbs free energies and storage enthalpies, defined as the relative energies between the lowest-energy VHF and DHA conformations for DHAs **1**, **3**, **15**, and **16**, were calculated by using the CAM-B3LYP, M06-2X, and PBE0 functionals with the 6-311+G(d) basis set in vacuum, cyclohexane (CH), and MeCN (see the Supporting Information). Table 1 shows the reported data from M06-2X, the functional which previously was found most optimum.[5] For the VHFs of **15** and **16**, the s-*cis* conformations were lowest in energy (in agreement with the very fast ring closure of the VHF of **15**), whereas the s-*trans* conformations were most stable for the VHFs of **1** and **3** (corresponding to **2** and **4**, respectively). As the entropy changes for the VHF to DHA conversion are negative, the enthalpy changes become more negative (corresponding to larger heat releases) than the changes in Gibbs free energy.

Table 1. Energies for the VHF to DHA back-reaction based on the lowest-energy identified conformation of DHAs **1**, **3**, **15** and **16**, and of the corresponding VHFs.[a]

	2→1[5]		**4→3**[5]		"VHF of **15**"→ **15**		**17→16**	
	Δ*G*	Δ*H*	Δ*G*	Δ*H*	Δ*G*	Δ*H*	Δ*G*	Δ*H*
Vacuum	−27.7	−35.2	−57.7	−62.3	−51.4	−60.3	−71.9	−76.5
CH	−22.7	−30.7	−57.2	−62.4	−48.2	−56.2	−67.6	−77.4
MeCN	−15.7	−22.9	−58.5	−64.1	−45.5	−46.8	−64.9	−74.7

[a] All values are presented in kJ mol^{-1} at 298 K.

Removal of a cyano group significantly increased the storage capacity of DHA **3** compared with DHA **1**.[5] Similarly, a significant increase in the storage capacity (ignoring the increased molecular weight) is observed when including a phenyl group in position 3. Indeed, the effect is found to be additive with a Δ*G* of −71.9 kJ mol^{-1} for **16** in vacuum. The relative stability of **1** and **15** turned out to be slightly dependent on solvent, as the solvent polarity increases, the stability decreases. This effect is significantly lower for the monocyano derivatives **3** and **16**.

Barriers $\Delta G_{\mathrm{VHF}\rightarrow\mathrm{TS}}$ for the TBR from s-*cis*-VHF to the transition state are shown in Table 2 for the formation of DHAs **1**, **3**, **15**, and **16** in vacuum, CH, and MeCN. In vacuum a slight decrease in the barrier of **15** compared with **1** is observed. A similar effect is seen for **16** compared with **3**. Again, the dicyano derivatives **1** and **15** are observed to be significantly solvent dependent, with a decrease in the TBR barrier of almost 40 kJ mol^{-1} in the case of formation of **15** when changing from vacuum to MeCN for M06-2X. Conversion of the VHF of **15** has a low barrier in MeCN of 73.8 kJ mol^{-1}, in agreement with the experimental finding of ultrafast switching.[12] However, the barrier for the monocyano derivatives is seen to be almost unaffected by solvent polarity (**4**→**3** and **17**→**16**).

Table 2. Calculated back-reaction barrier $\Delta G_{\mathrm{VHF}\rightarrow\mathrm{TS}}$ for conversion of s-*cis* VHFs to the corresponding DHAs.[a]

	2→1[5]	**4→3**[5]	"VHF of **15**"→**15**	**17→16**
Vacuum	119.5	133.0	112.8	125.7
CH	115.0	128.6	113.4	125.4
MeCN	103.4	128.8	73.8	123.3

[a] All values are presented in kJ mol^{-1} at 298 K.

From the calculations alone for the relative Gibbs free energies and free energy of activation for the TBR, the DHA/VHF pair **16**/**17** shows attractive features for applications as a solar heat battery, with a high storage capacity and a large barrier for the TBR. The barrier corresponds to a half-life of >10 years at ambient temperature, but a half-life of about 160 h at 70 °C.

The calculations thus support our experimental results. Indeed, no TBR was evidenced at ambient temperature, but after 72 h at 70 °C, some conversion to a DHA did indeed seem to occur (likely with some degradation also).

Conclusion

The preparation of monocyano-VHF/DHA derivatives was accomplished, either by building up the molecules from simple precursors or by direct modification of the parent DHA **1** by reductive decyanation followed by treatment with an electrophile; only the latter method gave access to the DHAs. These monocyano-DHAs retained the ability to undergo ring opening to the VHF forms upon irradiation. Replacement of a cyano group with a hydrogen or methyl group inhibits, however, the back-reaction. High activation energy barriers were confirmed by calculations (lifetimes of years) and are in principle a desirable outcome, allowing for control of energy release, together with the fact that calculations show that the energy storage capacity is increased significantly by having only one cyano group instead of two such groups. Yet, an obvious challenge is to trigger the back-reaction in a suitable manner, which is the focus of future studies.

Experimental Section

General procedures

All reactions were carried out under an argon atmosphere, using HPLC-grade solvents. THF was distilled over Na/benzophenone. Acetonitrile was dried over activated 3 Å molecular sieves. All handling of DHAs was done in the dark, with flasks and columns wrapped in tin foil. TLC was carried out on commercially available precoated plates (Silica 60) with fluorescence indicator P254. Spectrophotometric measurements were carried out in a 1 cm path length cuvette at 25 °C, unless otherwise stated. Spectrophotometric analysis of the ring-opening reaction was conducted by irradiating a solution of DHA (conc. $2–7\times10^{-5}$ M) in a cuvette with a 150 W Xenon arc lamp, equipped with a monochromator (the chosen wavelength was the longest-wavelength absorption maximum) or by using a 365 nm lamp. The TBR was attempted by heating the sample in a cuvette in a Peltier unit in the UV/Vis spectrophotometer. NMR spectra were acquired on a 500 MHz Bruker instrument equipped with a cryoprobe. All chemical shift values in ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peak ($CDCl_3$ $\delta_H=7.26$ ppm, $\delta_C=77.16$ ppm, C_6D_6 $\delta_H=7.16$ ppm, C_6D_6 $\delta_C=128.06$ ppm, CD_3CN $\delta_H=1.94$ ppm, $\delta_C=118.26$ ppm). High-resolution mass spectrometry (HRMS) was performed by using either electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI); FT-ICR = Fourier transform ion cyclotron resonance. Tropylium tetrafluoroborate **7** and tritylium tetrafluoroborate were prepared following reported procedures[10] as was a solution of lithium naphthalenide (LN).[14] Raman spectra were recorded with a RFS 100 FT-Raman instrument (Bruker), fitted with a 1064 nm Nd:YAG laser. The spectra were recorded with a 4 cm^{-1} resolution, 1000 scans and 350 mW laser power. OriginPro 8.6 software was used to produce the plots. Single crystal structure was determined using a Bruker D8-Venture diffractometer using $Mo_{K\alpha}$ radiation. Data were reduced using Apex and solved using Olex2 v. 1.2. CCDC 1042291 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

2-(2,4,6-Cycloheptatriene-1-yl)-1-phenylethanone (5): Acetophenone **6** (8.90 g, 77.0 mmol) and acetic acid (2.4 mL) were added to a solution of **7** (12.0 g, 70.0 mmol) in MeOH (120 mL). The mixture was stirred under Ar for 6 h at RT. A second portion of **7** (4.0 g, 22.0 mmol) was added, and after stirring for an additional 8 h, a visible color change from light yellow to dark brown had occurred. Then, water (200 mL) was added and the mixture was extracted with Et_2O (3×100 mL). The combined organic layers were dried over Na_2SO_4 and the crude product was purified by dry column vacuum chromatography (SiO_2, CH_2Cl_2 in heptane, 5% steps from 0 to 75%, 20 mL fractions) to give the product **5** (10.13 g, 63%) as a dark-red oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.96$ (dd, $J=8.3$, 1.0 Hz, 2H), 7.57 (tt, $J=7.1$, 1.1 Hz, 1H), 7.47 (dd, $J=8.3$, 7.1 Hz, 2H), 6.66 (t, $J=2.9$ Hz, 2H), 6.24–6.19 (m, 2H), 5.30 (dd, $J=6.1$, 2.9 Hz, 2H), 3.35 (m, 2H), 2.51 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=198.86$, 137.10, 133.25, 131.15, 128.75, 128.22, 125.47, 125.31, 41.63, 34.91 ppm (5 carbon atoms missing due to overlap); HRMS (ES): m/z calcd for $C_{15}H_{14}ONa^+$: 233.09369 $[M+Na]^+$; found: 233.09372; elemental analysis calcd (%) for $C_{15}H_{14}O$: C 85.68, H: 6.71; found: C 85.35, H: 6.45.

***E/Z*-4-(Cyclohepta-2,4,6-triene-1-yl)-3-phenylbut-2-enenitrile (9)**: Lithium bis(trimethylsilyl)amide (LiHMDS, 1 M solution in toluene, 29.9 mL, 29.9 mmol) was added to a solution of **8** (5.29 g, 4.83 mL, 29.9 mmol) in dry THF (80 mL) under Ar at 0 °C. The mixture was stirred at 0 °C for 30 min, then a solution of **5** (5.78 g, 27.5 mmol) in THF (30 mL) was added. After stirring for 3 h at RT, water (200 mL) was added and the mixture was extracted with CH_2Cl_2 (2×100 mL). The organic phase was washed with water (100 mL) and dried over $MgSO_4$. The crude dark-red oil was purified by dry column vacuum chromatography (SiO_2, toluene in heptane, 5% steps, from 0 to 100%, R_f (*Z* isomer): 0.34, R_f (*E* isomer): 0.56 in toluene) to give **9** (6:1 *E/Z* mixture), as a yellow oil (4.0 g, 63%). A pure fraction of the *E* isomer was obtained as a yellow solid, which allowed its full characterization. M.p.: 71–72 °C (*E* isomer); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.50–7.30$ (m, 5H), 6.57 (t, $J=3.1$ Hz, 2H), 6.21–6.07 (m, 2H), 5.59 (s, 1H), 5.22 (dd, $J=5.8$, 3.2 Hz, 2H), 3.23 (d, $J=7.9$ Hz, 2H), 1.84 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=163.08$, 137.55, 131.09, 130.21, 129.03, 126.44, 125.62, 124.41, 117.56, 97.89, 37.79, 36.70 ppm (5 carbon atoms missing due to overlap); HRMS (MALDI, dithranol): m/z calcd for $C_{17}H_{16}N^+$: 234.12773 $[M+H]^+$, for $C_{17}H_{15}Na^+$: 256.10967 $[M+Na]^+$; found: 234.12785 $[M+H]^+$, 256.10983 $[M+Na]^+$; elemental analysis calcd (%) for $C_{17}H_{15}N$: C 87.52, H: 6.48, N 6.00; found: C 87.56, H: 6.31, N: 5.95.

4-(Cyclohepta-2,4,6-trien-1-ylidene)-3-phenylbut-2-enenitrile (4): A 0.582 M solution of $NOBF_4$ in dry MeCN (3.9 mL, 4.6 mmol) was slowly added at −20 °C to a solution of **9** (0.529 g, 2.3 mmol of 6:1 *E/Z* mixture) in dry MeCN (20 mL) under Ar, during which the solution changed color from light yellow to dark orange. The reaction mixture was stirred at −20 °C for 30 min, then it was diluted with dry CH_2Cl_2 (20 mL) and pyridine (0.18 mL, 4.6 mmol) was added. The reaction was stirred at −20 °C for 30 min and then poured into water. The crude mixture was extracted with CH_2Cl_2 (3×50 mL) and the organic phase washed with aq. HCl (1 M, 50 mL) and dried over Na_2SO_4. The crude residue was purified by dry column vacuum chromatography (SiO_2, EtOAc in heptane, 0.5% steps from 0 to 20%, 10 mL fractions, R_f (**4**): 0.43 in 20% EtOAc/Heptane) to give **4**

contaminated by decomposition products. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals from irradiation of a solution of **3**): $\delta = 6.35$ (ddd, $J = 11.9$, 2.4, 1.0 Hz, 1 H), 6.05 (s, 1 H), 6.03–5.97 (m, 1 H), 5.95–5.88 (m, 2 H), 5.73–5.67 (m, 1 H), 5.66–5.57 (m, 1 H), 5.23 ppm (d, $J = 1.0$ Hz, 1 H). ^{1}H NMR (500 MHz, CD_3CN): $\delta = 7.52$–7.35 (m, 5 H), 6.40–6.36 (m, 1 H), 6.09–5.99 (m, 1 H), 5.99–5.90 (m, 3 H), 5.82–5.79 (m, 1 H), 5.74–5.66 (m, 1 H), 5.50 ppm (s, 1 H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 159.51$, 147.03, 140.65, 138.95, 134.71, 133.64, 132.92, 131.00, 130.86, 130.72, 129.94 (2×CH), 128.34 (2×CH), 120.42, 118.80, 95.29 ppm.

2-Phenyl-1,8*a*-dihydroazulene-1-carbonitrile (3): To a solution of DHA **1** (256 mg, 1.0 mmol) in dry THF (25 mL) shielded from light, DIBAL-H (1 M solution in heptanes, 2 mL) was slowly added at 0 °C under Ar. The reaction mixture was stirred at 0 °C for 2 h, then aq. HCl (1 M, 50 mL) was added and the mixture stirred for 10 min at RT. The crude product was extracted with CH_2Cl_2 (2×100 mL) and the organic phase dried over Na_2SO_4. The crude residue was purified by flash column chromatography (SiO_2, 70 % toluene in heptane, R_f (**3**): 0.48 (20 % EtOAc/heptane)) to give **3** (60 mg, 26 %) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.59$–7.56 (m, 2 H, Ph), 7.44–7.40 (m, 2 H, Ph), 7.38–7.41 (m, 1 H, Ph), 6.74 (d, $J = 2.0$ Hz, 1 H, H-3), 6.51 (A part of ABMX system, $J_{AB} = 6.4$ Hz, $J_{AM} = 4.6$ Hz, 1 H, H-5 or H-6), 6.42 (B part of ABMX system, $J_{AB} = 6.4$ Hz, $J_{BX} = 4.7$ Hz, 1 H, H-6 or H-5), 6.26–6.21 (m, 2 H, H-4 and H-7), 5.80 (dd, $J = 9.8$, 3.9 Hz, 1 H, H-8), 4.71 (dd, $J = 9.8$, 2.0 Hz, 1 H, H-1), 3.33 ppm (ddt, $J = 9.8$, 3.9, 2.1 Hz 1 H, H-8a); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 143.83$, 143.04, 132.99, 130.99, 130.19, 129.94, 129.24, 129.04, 126.89, 126.03, 121.28, 118.51, 118.12, 41.66, 40.52 ppm (2 carbon atoms missing due to overlap); HRMS (MALDI, dithranol): m/z calcd for $C_{17}H_{14}N^+$: 232.11208 $[M+H]^+$, $C_{17}H_{13}NNa^+$: 254.09402 $[M+Na]^+$; found: 232.11229 $[M+H]^+$, 254.09430 $[M+Na]^+$; elemental analysis calcd (%) for $C_{17}H_{13}N$: C 88.28, H: 5.67, N 6.06; found: C 87.40, H: 5.42, N: 6.25.

2,3-Diphenyl-1,8*a*-dihydroazulene-1-carbonitrile (16): DIBAL-H (1 M solution in heptanes, 4.2 mL) was slowly added at 0 °C under Ar to a solution of DHA **15** (700 mg, 2.1 mmol) in dry THF (50 mL) shielded from the light. The reaction mixture was stirred at 0 °C for 2.5 h, then aq. HCl (1 M, 50 mL) was added and the mixture stirred for 10 min at RT. The crude product was extracted with CH_2Cl_2 (2×50 mL) and the organic phase dried over Na_2SO_4. The crude residue was purified by flash column chromatography under N_2 atm (SiO_2, 60 % toluene in heptane, R_f-**16**: 0.26) to give **16** (105 mg, 16 %) as a yellowish solid and 5:1 mixture of isomers (detected by ^{1}H NMR spectroscopy). A pure sample of the major isomer was isolated for full characterization. M.p. 212–215 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$–7.32 (m, 3 H), 7.23–7.20 (m, 3 H), 7.17–7.13 (m, 4 H), 6.50 (A part of ABMX system, $J_{AB} = 11.0$ Hz, $J_{AM} = 6.0$ Hz, 1 H, H-5), 6.45 (B part of ABMX system, $J_{AB} = 11.0$ Hz, $J_{BX} = 5.8$ Hz 1 H, H-6), 6.29 (ddd, $J = 9.9$, 5.8, 2.0 Hz, 1 H, H-7), 5.88 (d, $J = 6.0$ Hz, 1 H, H-4), 5.84 (dd, $J = 9.9$, 4.2 Hz, 1 H, H-8), 4.95 (d, $J = 9.8$ Hz, 1 H, H-1), 3.30 ppm (ddt, $J = 9.8$, 4.2, 2.0 Hz, 1 H, H-8a); ^{1}H NMR (500 MHz, $CDCl_3$, selected signals for the minor isomer): $\delta = 6.37$ (A part of ABX system, $J_{AB} = 11.0$ Hz, $J_{AX} = 6.0$ Hz, 1 H, H-6), 6.20 (ddd, $J = 10.0$, 6.0, 1.5 Hz, 1 H, H-7), 5.92 (d, $J = 6.7$ Hz, 1 H, H-4), 5.46 (dd, $J = 9.9$, 3.5 Hz, 1 H, H-8), 4.27 (d, $J = 4.5$ Hz, 1 H, H-1), 3.52 ppm (m, 1 H, H-8a); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 144.82$, 142.60, 139.65, 134.27, 133.63, 131.20, 129.99, 129.41, 129.18, 128.91, 128.51, 128.46, 128.37, 126.87, 125.44, 121.16, 118.44, 118.42, 42.18, 40.84 ppm (3 carbon atoms missing due to overlap); HRMS (ES): m/z calcd for $C_{23}H_{17}NNa^+$: 330.12532 $[M+Na]^+$; found: 330.12621; elemental analysis calcd (%) for $C_{23}H_{17}N$: C 89.87, H: 5.57, N 4.56; found: C 89.77, H: 5.66, N: 4.66.

4-(Cyclohepta-2,4,6-trien-1-yl)-2-methyl-3-phenylbut-2-enenitrile (12): Lithium bis(trimethylsilyl)amide (LiHMDS, 1 M solution in toluene, 6.3 mL, 6.3 mmol) was added to a solution of diethyl 2-cyanoethylphosphonate **11** (1.196 g, 6.3 mmol) in dry THF (20 mL) under Ar at 0 °C. The mixture was stirred at 0 °C for 30 min, then a solution of **5** (1.1957 g, 5.7 mmol) in THF (10 mL) was added. After stirring for 3 h at RT, water (50 mL) was added and the mixture extracted with CH_2Cl_2 (3×50 mL). The organic phase was washed with water (50 mL) and dried over $MgSO_4$. The crude dark-red oil was purified by flash column chromatography (SiO_2, 75 % toluene in heptane, $R_f = 0.42$) to give **12** as 26:1 *E/Z* mixture as a light-yellow oil (0.91 g, 65 %). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.30 (m, 3 H), 7.09–7.04 (m, 2 H), 6.61–6.58 (m, 2 H), 6.20–6.15 (m, 2 H), 5.22 (dd, $J = 5.6$, 3.6 Hz, 2 H), 3.13 (m, 2 H), 1.85 (s, 3 H), 1.64 ppm (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 157.02$, 137.66, 131.01, 128.66, 128.40, 127.43, 125.33, 124.76, 119.88, 107.87, 41.12, 37.25, 17.91 ppm (5 carbon atoms missing due to overlap); HRMS (MALDI, dithranol): m/z calcd for $C_{18}H_{18}N^+$: 248.14338 $[M+H]^+$, $C_{18}H_{17}NNa^+$: 270.12532 $[M+Na]^+$; found: 248.14335 $[M+H]^+$, 270.12529 $[M+Na]^+$.

4-(Cyclohepta-2,4,6-trien-1-ylidene)-2-methyl-3-phenylbut-2-enenitrile (13): Tritylium tetrafluoroborate (0.242 g, 0.733 mmol) was added to a solution of **12** (0.1648 g, 0.66 mmol) in dichloroethane (10 mL) under Ar, and the mixture was heated at 80 °C for 1 h. The mixture was cooled to 0 °C and diluted with toluene (10 mL). Then, NEt_3 (0.073 g, 0.0725 mmol) was added slowly over 30 min, at which point the color changed to dark red. After stirring at 0 °C for 1 h, the reaction was concentrated to dryness. The resulting dark-red residue was purified by flash column chromatography (SiO_2, 80 % toluene in heptane) under N_2 atm and using degassed solvents, giving **13** (73 mg, 45 %). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.44$–7.31 (m, 4 H), 7.19–7.14 (m, 1 H), 6.21 (dd, $J = 12.0$, 1.7 Hz, 1 H), 6.14 (s, 1 H), 5.95–5.75 (m, 3 H), 5.48–5.30 (m, 2 H), 1.84 ppm (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 153.89$, 144.06, 140.86, 137.52, 133.25, 132.67, 132.08, 129.16, 129.13, 129.04 (2xCH), 128.67 (2×CH), 128.57, 123.42, 120.63, 104.57, 17.97 ppm; HRMS (MALDI, dithranol): m/z calcd for $C_{18}H_{16}N^+$: 246.12773 $[M+H]^+$, $C_{18}H_{15}NNa^+$: 268.10967 $[M+Na]^+$, $C_{18}H_{15}NK^+$: 284.08361 $[M+K]^+$; found: 246.12792 $[M+H]^+$, 268.10991 $[M+Na]^+$, 284.08386 $[M+K]^+$.

2-Phenyl-1,8*a*-dihydroazulene-1-methyl-1-carbonitrile (14): A 0.66 M stock solution of LN (2 mL, 1.32 mmol) was added to a degassed solution of **1** (110 mg, 0.43 mmol) in dry THF (10 mL) under Ar at −78 °C. After 1 h at −78 °C, MeI (0.15 mL, 2.41 mmol) was added and the solution allowed to reach RT overnight. Then, aq. NH_4Cl (10 mL) was added. The mixture was diluted with Et_2O (10 mL) and the organic phase separated and dried over $NaSO_4$. The crude residue was purified by flash column chromatography under N_2 atm (SiO_2, 60 % toluene in heptane, R_f (**14**): 0.18) to give **14** (22 mg, 21 %) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.76$–7.72 (m, 2 H), 7.44–7.37 (m, 2 H), 7.38–7.32 (m, 1 H), 6.61 (s, 1 H), 6.54 (dd, $J = 11.2$, 6.2 Hz, 1 H, H-6 or H-5), 6.40 (dd, $J = 11.2$, 6.0 Hz, 1 H, H-5 or H-6), 6.23–6.18 (m, 2 H, H-7 and H-4), 5.79 (dd, $J = 9.9$, 4.0 Hz, 1 H, H-8), 2.91 (dt, $J = 4.0$, 2.0 Hz, 1 H, H-8a), 1.77 ppm (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.96$, 140.95, 133.17, 131.03, 129.77, 129.75, 128.98 (2×CH), 126.87 (2×CH), 126.50, 121.91, 121.87 (CN), 118.53, 52.66 (C-8a), 49.06 (C1), 27.28 ppm (Me). HRMS (ES): m/z calcd for $C_{18}H_{15}NNa^+$: 268.10967 $[M+Na]^+$; found: 268.11035.

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Keywords: electrocyclic reactions · energy conversion · molecular devices · photochromism · renewable resources · quantum chemistry

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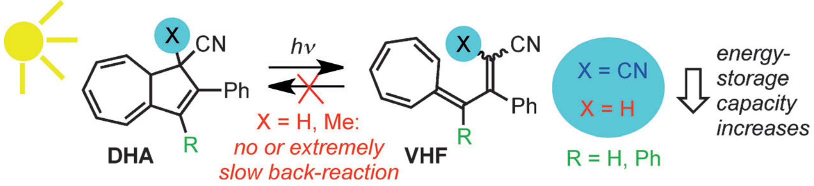

Renewable Resources

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Towards Solar Energy Storage in the Photochromic Dihydroazulene–Vinylheptafulvene System

Molecular solar thermal energy storage: Derivatives of the dihydroazulene (DHA)/vinylheptafulvene (VHF) photo/thermoswitch with only one cyano group at position 1 were prepared and investigated experimentally and theoretically. Compared to derivatives with two cyano groups, these compounds exhibit larger energy differences between DHA and VHF isomers and hence larger energy storage capacities, while the VHF to DHA back-reaction is on hold (see scheme).