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Molecular Solar Thermal Energy Storage Systems with Long Discharge Times Based on the Dihydroazulene/Vinylheptafulvene Couple

Josefine Mogensen,[a] Oliver Christensen,[a] Martin Drøhse Kilde,[a] Martin Abildgaard,[a] Lotte Metz,[a] Anders Kadziola,[a] Martyn Jevric,*[a],[b] Kurt V. Mikkelsen,*[a] and Mogens Brøndsted Nielsen*[a]

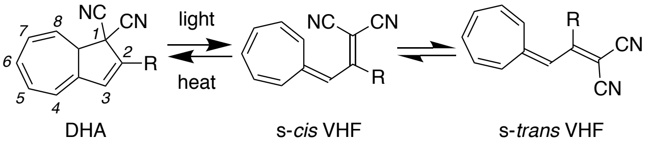
Abstract: Molecular solar thermal energy storage (MOST) systems based on photochromic molecules that undergo photoisomerization to high-energy isomers are attractive for storage of solar energy in a closed-energy cycle. One challenge is to control the discharge time of the high-energy isomer. Here we show that incorporation of a strong acceptor substituent in the seven-membered ring of the dihydroazulene/vinylheptafulvene (DHA/VHF) couple increases the half-life of the energy-releasing VHF-to-DHA back-reaction from hours to more than a day in a polar solvent. For some derivatives, the absorption maximum of the photo-active DHA is also significantly redshifted, thereby better matching the solar spectrum. Synthetic protocols and kinetics studies are presented together with a computational study of the energy densities of the systems and excitation spectra. The computations show that the increased lifetime of the high-energy isomer is counter-balanced by a lower energy storage capacity in vacuum than for the parent system, but a slightly higher energy density than for the parent system in a polar solvent.

Introduction

Photochromic molecules that upon irradiation undergo a conversion from a low-energy isomer to a high-energy isomer have attracted considerable interest in recent years as a potential way of storing solar energy.[1] One of several challenges is to achieve high-energy isomers that do not quickly return to the original isomer by a thermal relaxation. One candidate, when properly substituted, for molecular solar thermal energy storage (MOST) systems is the dihydroazulene/vinylheptafulvene (DHA/VHF) couple (Scheme 1) that was first reported by Daub and co-workers[2] and recently explored by us in the context of solar energy storage.[3] DHA **1** (R = Ph; see Figure 1) undergoes a photoisomerization to its corresponding VHF that in time returns to the DHA; in acetonitrile at 25 °C with a half-life of 218 min.[4] The s-*trans* conformer of VHF is usually the most stable and therefore mainly present in solution, while the s-*cis* conformer is the reactive one for the ring closure reaction. Photochromism has also been observed in polymeric films[5] and in crystals by reversible DHA – s-*cis*-VHF conversions.[6]

Removal of one of the two cyano groups at position C1 (DHA **2**; Figure 1) has a remarkable effect on the VHF half-life as the back-reaction is basically completely set on hold.[3b] This infinitely long energy storage time is in principle convenient if the back-reaction could in some way be triggered. We have found that some metal ions do promote the back-reaction of simple VHFs,[7] but in the case of the mono-cyano substituted VHF, decomposition occurred in time instead of the desired ring closure reaction.

Another approach is to attach substituent groups in the seven-membered ring of DHA. Indeed, structure-property relationships have shown that introduction of an aryl group with an electron-withdrawing substituent at position C7 of DHA causes a longer lifetime of the VHF.[8] Thus, the VHF of the *p*-cyanophenyl-substituted DHA **3** (Figure 1) has a half-life of 641 min in acetonitrile at 25 °C. We imagine, however, a more significant rate decrease of the thermal back-reaction by placing an electron-withdrawing cyano group directly at the DHA/VHF system without a bridging phenylene unit. Moreover, a strong dicyanomethylene acceptor could be advantageous for this purpose as well as for possibly inducing a redshift of the DHA absorption maximum, depending on its position on the seven-membered ring. For these reasons, we decided to target DHA derivatives **4**-**8** with an acceptor at either C6 or C7 of DHA. Here we present synthesis, optical and switching studies, as well as theoretical studies of these acceptor-functionalized DHAs/VHFs.



Scheme 1. Dihydroazulene/vinylheptafulvene (DHA/VHF) photo-/thermoswitch. Numbering of the DHA core is shown.

Results and Discussion

Synthesis and X-Ray Crystallography. A cyano group was introduced at position C7 via the protocol outlined in Scheme 2. First, DHA **1** was subjected to a well-established bromination-elimination protocol, providing the bromo-functionalized intermediate **9**.[9] We have previously shown that DHA derivatives can be cyanated by a Stille coupling[3d] and therefore **9** was treated with Bu_3SnCN and $Pd(PPh_3)_4$, which provided the target product **4**. The yield of **4** was rather low, and the toxicity of stannanes makes alternative protocols attractive. We attempted

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a Rosenmund-von Braun[10] reaction by treating the bromination-elimination product formed from **1** with CuCN in DMF at 120 °C, but after several attempts this reaction only gave an unidentified cyano-substituted DHA (different from the 7-substituted one) in a poor yield of 3%. Fully unsaturated azulenes were formed as side-products in the reaction due to elimination of HCN. Attempts of using $Zn(CN)_2$ and a Pd catalyst turned out unsuccessful, providing unidentified products. Cyanation of the DHA at position C7 is thus a rather challenging task, and the method using Bu_3SnCN and $Pd(PPh_3)_4$ is at present the most reliable.

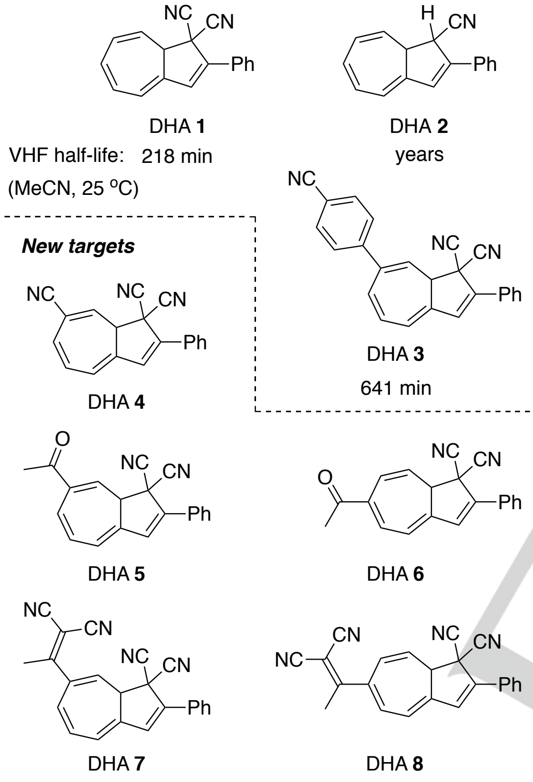
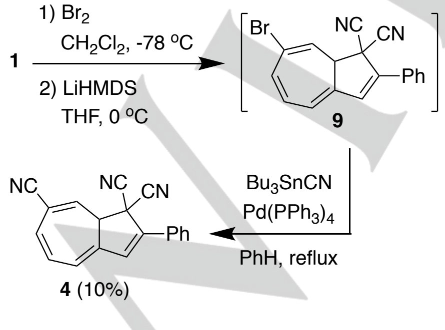


Figure 1. Selection of known and new acceptor-functionalized DHAs as well as DHA with only one cyano group at C1. For previously studied DHAs, the corresponding VHF half-lives in acetonitrile are listed.



Scheme 2. Synthesis of 7-cyano-substituted DHA **4**. LiHMDS = lithium hexamethyldisilazide.

Compound **4** could be crystallized from hot ethanol, and the structure was confirmed by X-ray crystallography (Figure 2). The VHF was obtained by irradiation of a solution of **4** in CD_3CN until complete conversion occurred using a long-wave UV lamp followed by removal of the solvent under a stream of N_2. The residue was then crystallized from CH_2Cl_2/heptane, and the structure is shown in Figure 2. The structure obtained from the investigated single crystal corresponds to the *E*-VHF isomer (in its s-*trans* conformation) where also *Z*-to-*E* isomerization at the exocyclic fulvene double bond has occurred (Figure 3). Such isomerization is known to occur thermally for VHF in polar solvents,[9] and it can also be induced by light.[11] Both isomers were indeed present in solution according to NMR spectroscopy.

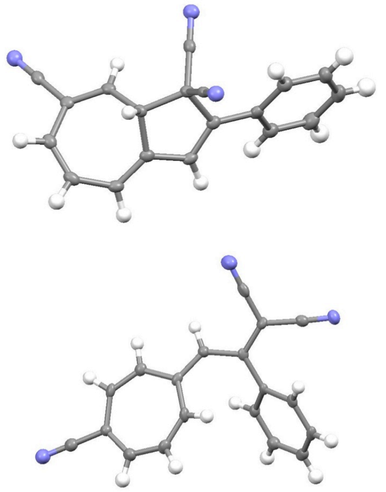


Figure 2. Molecular structures of DHA **4** (top; CCDC 1877316) and the corresponding *E*-VHF in the s-*trans* conformation (bottom; CCDC 1877315).

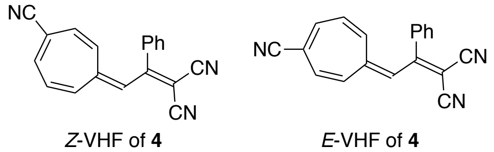
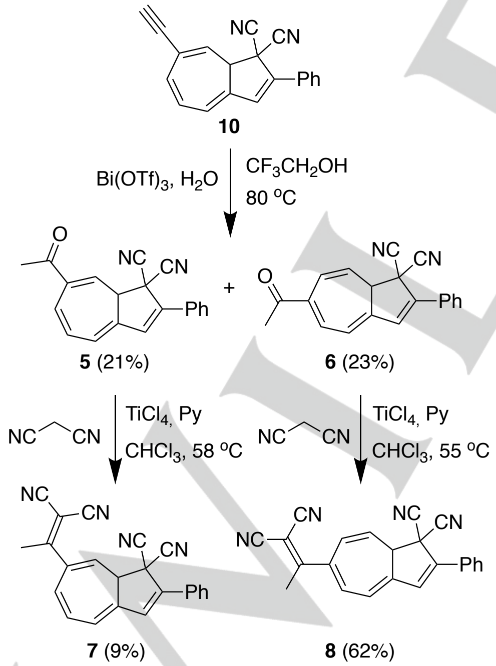


Figure 3. Structure of *Z*-VHF (s-*trans* conformer) that can be generated by ring-opening of **4** and its *E*-isomer (s-*trans* conformer) that is formed by rotation around the exocyclic fulvene bond.

Our next objective was to introduce acetyl groups at the seven-membered ring. We have previously found that *tert*-butyl thioethers can conveniently be converted into thioacetates under mild conditions by the action of acetyl chloride and bismuth(III) triflate.[12, 13] This reaction was found to be somewhat sensitive to the presence of a terminal alkyne that could be converted into a vinyl triflate. We imagined that related conditions could possibly be employed to convert the known[9b] 7-ethynyl-substituted DHA **10** into the product **5**. Moreover, Lui *et al.*[14] have found that terminal alkynes can be converted to acetyl groups by triflic acid in trifluoroethanol. Treating **10** with bismuth(III) triflate (0.2 equiv.) in trifluoroethanol (and a few drops of water) at elevated temperature provided an almost equal mixture of the 7- and 6-substituted isomers **5** and **6** in an overall good yield (Scheme 3). As the reaction mixture was shielded from light, the DHA must have opened thermally to the *Z*-VHF, which can then return to the original DHA or to the 6-substituted isomer via an *E*/*Z*-isomerization at the fulvene double bond.

To incorporate the dicyanovinyl group, a Knoevenagel condensation between **5** and malononitrile in toluene with ammonium acetate and glacial acetic acid was first attempted. Yet, after reflux for 24 hours, there was no sign of product formation. Another set of conditions with a buffer solution of glacial acetic acid and hexamethyldisilazane (HMDS) as solvent was then attempted, with stirring at 75 °C for 1-2 days. Under these conditions, the Knoevenagel reaction worked, but the conditions also resulted in elimination of HCN and formation of compound **11** with a fully unsaturated azulene core (Figure 4); this compound was isolated in a yield of 72%. Although not the purpose of this work, the synthetic route presents an interesting azulene functionalization methodology.[15] Next, we turned to a $TiCl_4$-catalyzed Knoevenagel condensation in chloroform at 55-60 °C with pyridine as base, and, gratifyingly, product **7** could now be isolated, albeit in low yield (9%) (together with unreacted starting material). The reaction conditions worked, however, significantly better on **6** as substrate that was successfully converted into product **8** in a yield of 62%. A shorter reaction time had to be used in the synthesis of **7** as decomposition of the product seemed to occur according to TLC analysis.



Scheme 3. Synthesis of acceptor-functionalized DHAs. Py = pyridine.

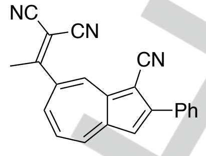


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Figure 4. Azulene product isolated after treatment of **5** with malononitrile in AcOH/HMDS at 75 °C.

UV-Vis Absorption and Switching Studies. The new acceptor-substituted DHAs were all photo-active and underwent photoisomerization (by irradiation at 365 nm) to their corresponding VHFs; yet, full conversion of **8** into its VHF was not accomplished (hence being less photo-active than **7**). Longest-wavelength absorption maxima in MeCN of the DHA and VHF forms are listed in Table 1 (ignoring some long-wavelength absorptions of the VHF of **7**), while the absorption spectra are shown in Figure 5. It transpires that the 6-substituted DHAs **6** and **8** both exhibit a redshifted absorption relative to their corresponding 7-substituted isomers (**5** and **7**). The 6-substituted isomers have the substituent group in linear conjugation with the largest part of the DHA core (C2-C6), while the substituent is only in linear conjugation with the C7-C8 double bond for the 7-substituted isomers. For the VHFs we cannot exclude some *E*/*Z* isomerization under the conditions as this may occur both thermally and photochemically as mentioned above and previously established for VHF derivatives.[9,11] Indeed, ^{1}H-NMR spectroscopic studies revealed formation of a pure VHF isomer upon irradiation in $CDCl_3$, but a mixture of VHF isomers in CD_3CN (see SI, Figures S5-S7).

Table 1. UV-Vis absorption maxima (λ_{max}), molar absorptivities (ε) in brackets, rate constants (k) and half-lives ($t_{1/2}$) for the VHF ring closure reactions at 25 °C in MeCN.

	DHA λ_{max} / nm (ε / 10^3 M^{-1} cm^{-1})	VHF λ_{max} / nm (ε / 10^3 M^{-1} cm^{-1})	k / 10^{-4} min^{-1}	$t_{1/2}$ / 10^3 min
4[a]	360 (14.6)	433 (26.9)	5.4	1.3
5[b]	358 (12.3)	454 (24.9)	6.4	1.1
6[b]	372 (18.1)	451 (24.2)	6.5	1.1
7[a]	337 (13.8)	451 (25.6)	4.4	1.6
8[a]	394 (19.4)	427-442[c]	4.2	1.7

[a] Rate constant determined by extrapolation to 25 °C from measurements at various temperatures. [b] Rate constant determined as an average of two measurements at 25 °C. [c] Mixture of DHA and VHF.

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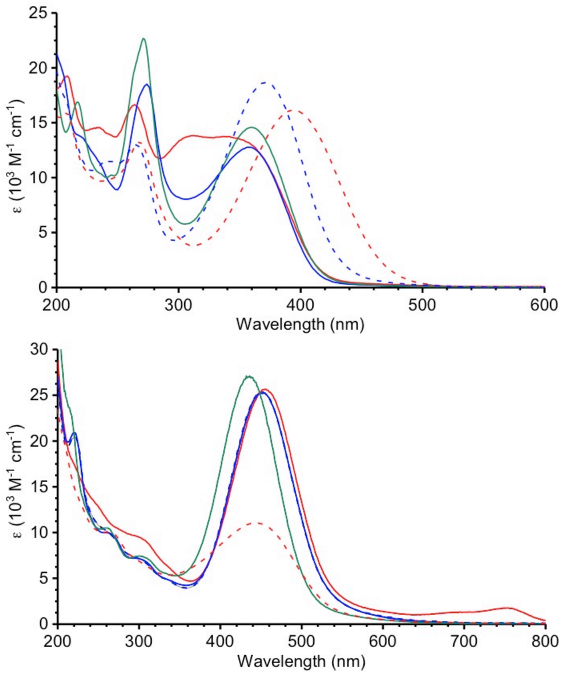

Figure 5. UV-Vis absorption spectra of DHAs **4** (green curve), **5** (blue solid curve), **6** (blue broken curve), **7** (red solid curve), and **8** (red broken curve; not full conversion) on top, and their corresponding VHFs at bottom (colors correspond to the DHA precursors). Solvent: MeCN.

The thermal VHF-to-DHA back-reactions were followed by UV-Vis absorption spectroscopy (first-order decay of VHF absorption) at various temperatures in MeCN (see SI), and the rate constants at 25 °C were determined by extrapolation for **4**, **7**, and **8**. For **5** and **6**, the rate constants were determined as an average of two measurements at 25 °C. The data are listed in Table 1. Only small differences are seen between the two VHF isomers generated from each DHA isomer. As mentioned above, we cannot exclude that both isomers are present due to isomerization by rotation around the exocyclic fulvene bond, but as the decays were well fitted by a single exponential function, the two VHF isomers undergo ring closures with similar rates. For all derivatives, a significant increase in the VHF half-life has been achieved in comparison to the VHFs of **1** and **3**. We also observe a clear trend in regard to the rate of ring closure and the character of the substituent: the half-life increases as the electron-withdrawing character increases in the progression C(O)Me, CN, CMe(C(CN)$_2$); the electron-withdrawing character can be represented by Hammett substituent constants: σ_p = 0.50 for C(O)Me, σ_p = 0.66 for CN, σ_p = 0.84 for CH(C(CN)$_2$).[16]

The redshifted absorption of **8** in combination with the increased VHF lifetime is particularly important in the context of MOST systems, while its small photoactivity is a drawback. One question remaining is how the functionalizations influence the energy densities. To answer this question, we subjected the compounds to a computational study.

Computations. *Energy densities.* For **1** an energy density of 0.11 MJ kg^{-1} was previously reported in vacuum; the number corresponds to the Gibbs free energy difference between DHA and VHF in its most stable s-*trans* conformation.[3e] The energy densities in MJ kg^{-1} for the new couples were calculated in vacuum and in solvents of different polarities using the DFT functional M06-2X and the basis set 6-311+G(d), and the results are listed in Table 2. Solvent effects were included using the integral equation formalism variant of the polarizable continuum model (IEFPCM). The unit MJ kg^{-1} was chosen to balance any increase in Gibbs free energy difference by an undesirable increase in molecular weight. In Figure 6, energy densities are plotted relative to that of the DHA/VHF couple **1** in the various media. First, as previously noted,[3a,e] we see from Table 2 that the energy density of **1** decreases when increasing the polarity of the solvent. This decrease is also observed for the new compounds, but to a less significant degree than for the parent system. In actual fact, while the energy densities of compounds **4**-**8** are all lower than that of **1** in vacuum, the energy densities of **4**, **5**, **6**, and **8** are all higher in dichloromethane, ethanol, and acetonitrile than that of **1**, albeit all these compounds have a higher molecular weight than **1**. The VHF of **1** has significant zwitterionic character on account of the electron-withdrawing cyano substituents at C1, and this form is stabilized in a polar solvent, thereby decreasing the DHA-VHF energy difference. By placing an electron-withdrawing substituent at the seven-membered ring, this electronic push-pull effect is to some extent counter-balanced, which would explain why the new derivatives do not experience the same unfavorable decrease in energy density when proceeding from vacuum to a polar medium. It should be emphasized that the energy differences are all very small, but at least the energy density in polar solvents is not compromised by the acceptor substitution.

Table 2. Absolute energy densities (MJ kg^{-1}) of the DHA/s-*trans* VHF couples (difference in Gibbs free energy of the two isomers) in various media.[a] Calculated using M06-2X/6-311+G(d) and IEFPCM.

	vacuum	CH	PhMe	CH$_2$Cl$_2$	EtOH	MeCN
1	0.108	0.088	0.085	0.068	0.062	0.061
4	0.097	0.088	0.087	0.076	0.072	0.071
5	0.098	0.083	0.080	0.076	0.071	0.072
6	0.102	0.091	0.104	0.081	0.078	0.077
7	0.085	0.074	0.075	0.059	0.055	0.055
8	0.096	0.085	0.084	0.076	0.073	0.074

[a] CH = cyclohexane.

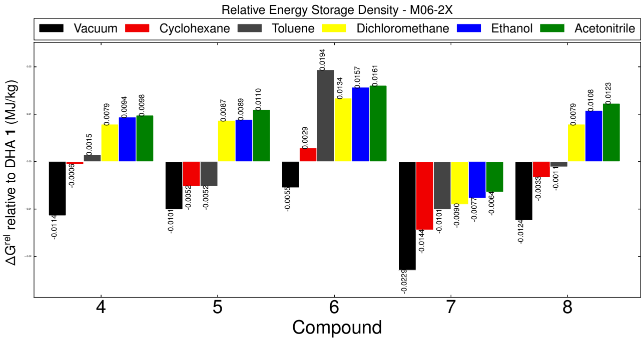

Figure 6. Calculated energy storage densities (Gibbs free energies) relative to the DHA/VHF system **1** in vacuum (black) and various solvents (shown in colors) (M06-2X/6-311+G(d); IEFPCM); from left to right, compounds **4**, **5**, **6**, **7**, and **8**.

Excitation spectra. The excitation spectra of DHAs and VHFs of **7** and **8** in MeCN were calculated at the CAM-B3LYP/6-311+G(d) level of theory using linear-response Time-Dependent Density Functional Theory (TD-DFT). Solvent effects were included using IEFPCM. The calculated absorption spectra are shown in Figure 7. The calculations reveal a significant redshift (41 nm) in the DHA absorption when proceeding from **7** (348 nm) to **8** (389 nm), in agreement with the experimental findings (where a redshift of 57 nm was observed). For the VHF of **7**, we find absorptions at 445 nm (s-*cis* conformer) and 450 nm (s-*trans* conformer), and for the VHF of **8**, absorptions at 441 nm (s-*cis* conformer) and 435 nm (s-*trans* conformer). The calculations thus support the small blueshift of the VHF of **8** relative to that of **7** that was inferred from the experimental studies, but with some ambiguity due to the lack of full DHA-to-VHF conversion.

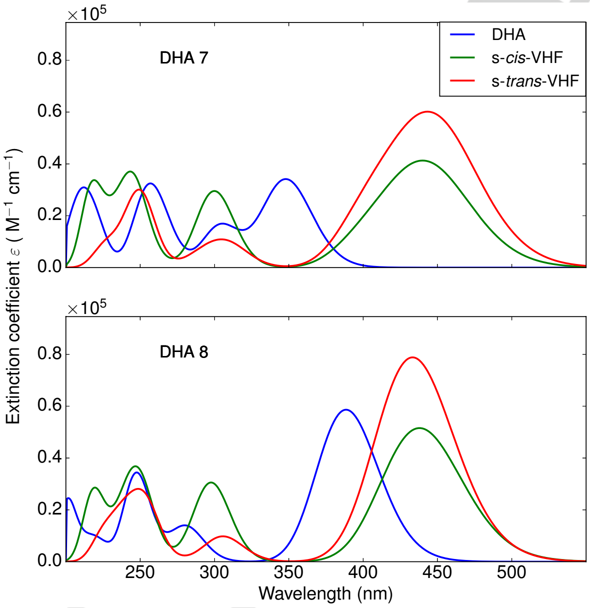

Figure 7. Calculated (TD-DFT) excitation spectra in MeCN for DHAs **7** (top) and **8** (bottom) and their corresponding s-*cis* and s-*trans* VHFs. Method: CAM-B3LYP/6-311+G(d). The spectra were calculated assuming Gaussian band shapes of the absorption peaks with a standard deviation of 0.4 eV.

Conclusions

In conclusion, a selection of acceptor-substituted DHAs was prepared using DHA **1** as starting material. Conveniently, the acetyl functionality could be introduced by hydrolysis of a terminal alkyne substituent. Knoevenagel condensation with malononitrile was more challenging, but ultimately we found good conditions that allowed synthesis of the 6-substituted derivative in good yield, while the 7-substituted derivative was obtained in rather low yield. Introduction of a cyano group directly at C7 was also rather challenging, but achieved by cyanation of a bromo-substituted precursor.

By attaching the acceptor substituent directly to the seven-membered ring rather than via a phenylene unit, we find that the rate of the VHF-to-DHA back-reaction drops significantly, which is of particular importance in the context of photochromic molecules for solar energy storage. The VHF-to-DHA conversion is in general fastest in polar solvents,[4] and the increase of the half-life to be on the timescale of a day in acetonitrile is therefore an important step towards MOST systems based on DHA/VHF. For derivatives with the substituent at position C6 of DHA, we find at the same time a convenient redshift in the characteristic DHA absorption. This redshift was also found from computations, which show that the CAM-B3LYP/6-311+G(d) level of theory provides excellent agreement with experimental DHA and VHF absorptions, and it is thus a convenient method for predicting absorptions of this couple.

Most of the new acceptor-substituted systems exhibit a slightly higher energy density (Gibbs free energy difference between DHA and s-*trans* VHF forms) than the parent system in polar solvents despite the increased molecular weights of these compounds. Thus, the acceptor substitution is not in disfavor of the energy storage capacity. It is clear, however, that the energy density of each of these systems is very small. It may be slightly increased by allowing for example two DHA units to share the same dicyanovinyl unit introduced in the seven-membered ring – thereby reducing the overall molecular weight per DHA unit. Yet, the structural modifications presented here should be combined with others that can more strongly increase the energy densities, such as for example our previous use of loss of aromaticity of benzo-fused DHAs upon DHA-to-VHF conversion.[3d,f]

Experimental Section

General Methods. All solvents and reagents were purchased from chemical suppliers and used as received. DHAs **1**[4] and **10**[9b] were prepared according to literature methods. All photochromic compounds were handled in the dark at all times except during light-induced ring opening. All glassware containing photochromic compounds was wrapped in tin foil. Thin layer chromatography (TLC) was performed in the dark, and carried out on commercially available pre-coated aluminum plates (silica 60) with fluorescence indicator. A color change from yellow to red or orange upon irradiation by UV light (365 nm) indicates the presence of DHA. Purification by flash column chromatography was performed on silica gel (40-63 μm). $CDCl_3$ for NMR spectoscopic studies was passed through activated aluminum oxide before use. NMR spectra were acquired on a Bruker 500 MHz instrument with cryoprobe; the ^1H

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NMR and ^{13}C NMR spectra are referenced to the residual solvent peak ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm). Infrared spectroscopy (IR) data were obtained on a Bruker Alpha FT-IR spectrometer equipped with a Platinum ATR single reflection diamond module (ATR = attenuated total reflectance); samples were loaded by evaporation from a suitable solvent. The most characteristic absorption due to functionalization in the seven-membered ring is listed for compounds **4**-**8**, while full spectra are listed in the SI. High Resolution Mass Spectrometry (HRMS) was performed on a MALDI-FT-IR instrument equipped with a 7 T magnet, using dithranol as matrix. Melting points are uncorrected. Elemental Analysis was performed at London Metropolitan University.

UV-Vis Absorption Spectroscopy and Switching Studies. All the UV-Vis experiments were performed in MeCN. The recorded absorption spectra of the pure DHAs and the absorption spectra resulting from the light-induced ring openings, using an UV lamp (365 nm), were performed in a 1-cm quartz cuvette at 25 °C until full conversion of the DHA was achieved (yet, complete conversion of DHA **8** was not achieved). The back-reactions for the VHFs of **5** and **6** were followed at 25 °C in 1-cm quartz cuvettes. After the ring openings of DHAs **4**, **7** and **8**, the solutions were transferred to glass ampules, which were then sealed, and the back reactions were followed at various elevated temperatures (see SI). All the absorption spectra were recorded in the wavelength range from 800 to 200 nm on a Varian Cary 50 UV-Vis Spectrophotometer.

Calculations. Density Functional Theory (DFT) calculations were performed using *Gaussian09*.[17] The DFT functionals used were M06-2X[18] and CAM-B3LYP[19], and solvents were modeled using the Integral Equation Formalism Polarizable Continuum Model (IEFPCM).[20] The DHA and VHF structures show a significant degree of conformational freedom. For this reason, a conformer search utilizing a genetic algorithm was performed to find the lowest energy conformers. The program OpenBabel version 2.4.1 was used to generate the conformers.[21] For each DHA/VHF structure, up to 500 conformers were generated and geometry-optimized using CAM-B3LYP/D95V level of theory.[22] Unique conformers were then selected based on having a unique geometry, (evaluated using the Kabsch algorithm with a threshold of 0.5 Å) and a unique dipole moment (requiring a difference of at least 0.1D between unique conformers).[23] Finally, for each group of conformers, the one with the lowest energy E_0 is given a Boltzmann factor of 1. The Boltzmann factor $F = \exp(-(E_0 - E_n)/k_BT)$) for every conformer in this group compared to the lowest-energy conformer was then calculated. If $F < 0.001$, the conformer was eliminated, as it has a low probability of appearing. The remaining unique, significant conformers were then optimized using the chosen functionals and the 6-311+G(d) basis set, both in vacuum and in the chosen solvents.

The excited states and oscillator strengths of the structures were obtained using linear-response Time-Dependent Density Functional Theory (TD-DFT). 15 electronic excitations were calculated for each structure, and the UV-VIS spectra were calculated assuming Gaussian band shapes of the absorption peaks with a standard deviation of σ = 0.4 eV.

2-Phenylazulene-1,1,7(8a*H*)-tricarbonitrile (4). To a stirring solution of DHA **1** (256 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) at -78 °C was added dropwise a solution of Br_2 (1.28 mL, 0.78 M in CH_2Cl_2, 1.00 mmol) and resulting reaction mixture stirred for a further 30 min. The solvent was removed under reduced pressure and the residue dissolved in dry THF (30 mL) and the vessel cooled in an ice bath. To this solution was added dropwise a solution of LiHMDS (1.1 mL, 1.0 M in toluene, 1.1 mmol), generating the bromide **9**, and the contents allowed to stir 2 h, where the ice bath was removed after the first hour. Saturated aqueous NH_4Cl (10 mL) was added followed by dilution with H_2O (50 mL) and Et_2O (50 mL). The phases were separated and the aqueous phase was extracted with Et_2O (50 mL). The combined organics were dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation. The crude material was dissolved in benzene (150 mL) and the solution sparged with argon. To this degassed solution was added Bu_3SnCN (354 mg, 1.12 mmol), $Pd(PPh_3)_4$ (122 mg, 0.11 mmol) and the resulting solution heated to reflux point for 16 h. The solvent was removed *in vacuo* and the residue subjected to flash column chromatography (EtOAc/toluene 1:49) to afford the title compound (29 mg, 10%) as an off-yellow colored solid. R_f = 0.46 (EtOAc/toluene 1:19). M.p. = 173 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.76-7.74 (m, 2H), 7.53-7.48 (m, 3H), 6.92 (s, 1H), 6.82 (ddd, *J* = 11.4, 6.4, 0.9 Hz, 1H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.49 (d, *J* = 4.9 Hz, 1H), 6.43 (dd, *J* = 6.4, 1.8 Hz, 1H), 3.83 (dd, *J* = 4.9, 1.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.83, 140.06, 134.63, 131.25, 131.06, 130.91, 129.78, 129.61, 127.41, 126.62, 120.75, 117.18, 114.28, 114.06, 112.20, 50.94, 44.75 ppm. IR: ν = 2223 cm^{-1} (C≡N – 7-membered ring). Analysis calcd (%) for $C_{19}H_{11}N_3$: C 81.12, H 3.94, N 14.94; found: C 80.85, H 3.69, N 14.87. X-ray crystals were obtained from an evaporating ethanol solution.

7-Acetyl-2-phenyl-1,1(8a*H*)-dicarbonitrile (5) and 6-Acetyl-2-phenyl-1,1(8a*H*)-dicarbonitrile (6). Compound **10** (48.5 mg, 0.17 mmol) was suspended in 2,2,2-trifluoroethanol (5 mL), after which 4 drops of H_2O and $Bi(OTf)_3$ (23 mg, 0.035 mmol) were added. The suspension was then stirred for 48 h at 80 °C. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with H_2O (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, EtOAc/toluene 1:19), which gave **5** (11 mg, 21%) as an orange solid and **6** (12 mg, 23%) as a yellow solid. Compound **5**: R_f = 0.50 (EtOAc/toluene 1:9). M.p. = 51-53 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.78-7.74 (m, 2H), 7.52-7.46 (m, 3H), 7.11 (d, *J* = 11.7 Hz, 1H), 6.92 (s, 1H), 6.76 (dd, *J* = 11.7, 6.2 Hz, 1H), 6.70 (d, *J* = 4.7 Hz, 1H), 6.38 (dd, *J* = 6.2, 1.6 Hz, 1H), 3.80 (dd, *J* = 4.7, 1.6 Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.91, 141.38, 139.44, 138.77, 132.58, 131.70, 130.59, 130.22, 129.51, 127.92, 126.63, 126.47, 121.23, 114.74, 112.81, 50.62, 45.03, 26.54 ppm. IR: ν = 1678 cm^{-1} (C=O). HRMS (MALDI+, FT-ICR, dithranol): *m/z* = 321.09976 $[M+Na^+]$, calcd for ($C_{20}H_{14}N_2ONa^+$): 321.09983. Compound **6**: R_f = 0.43 (EtOAc/toluene 1:9). M.p. = 165-167 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80-7.76 (m, 2H), 7.53-7.47 (m, 4H), 6.97 (s, 1H), 6.89 (dd, *J* = 10.5, 1.9 Hz, 1H), 6.50 (dd, *J* = 6.8, 1.9 Hz, 1H), 5.97 (dd, *J* = 10.5, 3.9 Hz, 1H), 3.74 (dt, *J* = 3.9, 1.9 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 197.76, 144.30, 143.81, 139.72, 136.39, 131.71, 130.98, 130.11, 129.57, 126.76, 125.84, 120.20, 119.60, 114.77, 112.44, 51.03, 45.19, 26.39 ppm. IR: ν = 1666 cm^{-1} (C=O). HRMS (MALDI+, FT-ICR, dithranol): *m/z* = 321.09980 $[M+Na^+]$, calcd for ($C_{20}H_{14}N_2ONa^+$): 321.09983.

7-(1,1-Dicyanoprop-1-en-2-yl)-2-phenylazulene-1,1(8a*H*)-dicarbonitrile (7). Compound **5** (91 mg, 0.30 mmol) was heated to 58 °C in $CHCl_3$ (50 mL), and malononitrile (233 mg, 3.53 mmol), pyridine (0.07 mL, 0.9 mmol), and titanium(IV)chloride (0.5 mL, 4.6 mmol) were added. After 2 h, additionally malononitrile (232 mg, 3.51 mmol), pyridine (0.07 mL, 0.9 mmol), and titanium(IV)chloride (0.5 mL, 4.6 mmol) were added, and the reaction mixture was heated for 2 more h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and poured on ice/water (150 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 100 mL), and the organic phases were combined, dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, EtOAc/ THF/heptane 7:30:63 -> 10:35:55), which gave **7** (10 mg, 9%) as an orange solid in addition to unreacted starting material (15 mg). R_f = 0.17 (EtOAc/THF/heptane 7:30:63). M.p. = 146-148 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.77-7.74 (m, 2H), 7.53-7.47 (m, 3H), 6.93 (s, 1H), 6.88 (dd, *J* = 11.4, 6.2 Hz, 1H), 6.46 (d, *J* = 11.4 Hz, 1H), 6.42 (dd, *J* = 6.2, 1.4 Hz, 1H), 6.06 (d, *J* = 4.8 Hz, 1H), 3.79 (dd, *J* = 4.8, 1.4 Hz, 1H), 2.49 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.43, 142.64, 141.20, 136.54, 134.98, 131.24, 130.89, 129.98, 129.57, 126.74, 126.60, 122.54, 120.60, 114.54, 112.49, 112.06, 111.82, 87.11, 50.78, 44.78, 24.06 ppm. IR: ν = 2230 cm^{-1} (C=C(**C≡N**)$_2$)). HRMS (MALDI+, FT-ICR, dithranol): *m/z* = 369.11125 [M+Na$^+$], calcd for ($C_{23}H_{14}N_4Na^+$): 369.11107.

6-(1,1-Dicyanoprop-1-en-2-yl)-2-phenylazulene-1,1(8a*H*)-dicarbonitrile (8). Compound **6** (51 mg, 0.17 mmol) was heated to 55 °C in $CHCl_3$ (25 mL), and malononitrile (126 mg, 1.91 mmol), pyridine (0.04 mL, 0.5 mmol), and titanium(IV)chloride (0.03 mL, 0.3 mmol) were added. After 4.5 h, additionally malononitrile (123 mg, 1.86 mmol), pyridine (0.04 mL, 0.5 mmol), and titanium(IV)chloride (0.03 mL, 0.3 mmol) were added, and the reaction mixture was heated overnight. The reaction mixture was diluted with CH_2Cl_2 (75 mL) and poured on ice/water (150 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 75 mL). The organic phases were combined, dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, EtOAc/toluene 1:9), which gave **8** (36 mg, 62%) as an orange solid. R_f = 0.43 (EtOAc/toluene 1:9). M.p. = 169-170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.54-7.49 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.97 (s, 1H), 6.49 (dd, *J* = 7.0, 1.7 Hz, 1H), 6.38 (d, *J* = 10.4 Hz, 1H), 6.03 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.82 (dt, *J* = 4.0, 1.7 Hz, 1H), 2.53 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.63, 144.51, 144.08, 138.14, 134.26, 131.43, 131.22, 129.91, 129.62, 126.83, 124.89, 121.52, 119.26, 114.46, 112.68, 112.52, 112.35, 85.32, 50.88, 45.13, 22.89 ppm. IR: ν = 2227 cm^{-1} (C=C(**C≡N**)$_2$)). HRMS (MALDI+, FT-ICR, dithranol): *m/z* = 369.11104 [M+Na$^+$], calcd for ($C_{23}H_{14}N_4Na^+$): 369.11107.

2-(1-(3-Cyano-2-phenylazulen-5-yl)ethylidene)malononitrile (11). Compound **5** (53 mg, 0.18 mmol) and malononitrile (106 mg, 1.60 mmol) were dissolved in glacial acetic acid (7 mL), after which a solution of HMDS (5 mL) and glacial acetic acid (13 mL) was added. The reaction mixture was then heated to 75 °C for 48 h. The reaction mixture was diluted with toluene (100 mL) and H_2O (100 mL), and the aqueous phase was further extracted with toluene (2 x 100 mL). The organic phases were combined, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, EtOAc/toluene 2:5), which gave **11** (41 mg, 72%) as a dark green solid. R_f = 0.16 (EtOAc/toluene 2:5). M.p. = 208 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (broad d, *J* = 1.9 Hz, 1H), 8.47 (dt, *J* = 9.7, 0.8 Hz, 1H), 8.09-8.06 (m, 2H), 7.76 (ddd, *J* = 10.4, 1.8, 0.9 Hz, 1H), 7.71 (s, 1H), 7.58-7.49 (m, 4H), 2.82 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.45, 154.40, 143.92, 142.14, 139.56, 136.84, 135.06, 133.55, 133.00, 130.42, 129.51, 128.92, 127.27, 119.74, 117.12, 112.10, 112.07, 98.44, 88.04, 25.42 ppm. HRMS (MALDI+, FT-ICR, dithranol) *m/z* = 342.10037 [M+Na$^+$], calcd for ($C_{22}H_{13}N_3Na^+$): 342.10072.

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Keywords: Conjugation • Cyanides • Electrocyclic reactions • Fused-ring systems • Photochromism

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Entry for the Table of Contents

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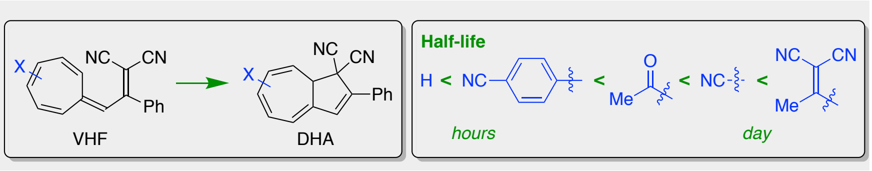

A selection of dihydroazulene (DHA) derivatives with an electron-withdrawing group in the seven-membered ring was prepared using a preformed DHA as precursor. The DHAs all underwent photoisomerizations to the corresponding vinylheptafulvenes (VHFs). The VHFs thermally returned to DHAs with half-lives that strongly depended on the electron-withdrawing character of the substituent.

Energy release*

Josefine Mogensen, Oliver Christensen, Martin Drøhse Kilde, Martin Abildgaard, Lotte Metz, Anders Kadziola, Martyn Jevric, Kurt V. Mikkelsen*, Mogens Brøndsted Nielsen**

Page No. – Page No.

Molecular Solar Thermal Energy Storage Systems with Long Discharge Times Based on the Dihydroazulene/Vinylheptafulvene