Long-Term Energy Storage Systems Based on the Dihydroazulene/Vinylheptafulvene Photo-/Thermoswitch

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The dihydroazulene/vinylheptafulvene (DHA/VHF) couple presents a photo-/thermoswitch that has attracted interest for the development of molecular solar thermal energy storage systems. Here we present the synthesis and optical properties as well as the switching properties of DHA derivatives incorporating alkyne and norbornadiene (NBD) substituents at position C2. The corresponding VHF isomers exhibited remarkably long lifetimes. Thus, the VHF-to-DHA back-reaction half-life for a derivative with a phenylethynyl substituent was 22 days in acetonitrile at room temperature, while the half-life of a VHF reference compound having a phenyl substituent is around 3.5 h under the same conditions. This finding is particularly attractive in the quest for long-term energy storage systems, considering limited enhancement of molecular weight and maintenance of good quantum yield photoisomerization. Moreover, from the thermal back-reaction of an NBD compound, used as a precursor for the DHA-NBD dyad, we estimated the radical-stabilizing influence of a $C(Me){=}C(CN)_2$ substituent.

Introduction

Molecular photoswitches have found significant interest as molecular solar thermal energy storage (MOST) systems.[1] One such system undergoes photoisomerization to a meta-stable, high-energy isomer that thermally will return to the original isomer accompanied by release of the energy as heat. A useful system should satisfy a large number of requirements, such as absorption within the solar spectrum, small overlap of absorption spectra of the two isomers, high quantum yield of photoisomerization, long lifetime of the meta-stable isomer, and a high energy difference between isomers.[1] Various photoswitches have been moved forward for this closed cycle of energy capture, storage, and release, including azobenzenes, norbornadienes, and dihydroazulenes.[1h]

We have in particular focused attention on derivatives of the dihydroazulene photoswitch DHA **1a** shown in Scheme 1; it undergoes a photoisomerization to the vinylheptafulvene isomer VHF **1b** that in time returns to **1a**.[1g,2] Most studied derivatives incorporate an aryl substituent at position C2 of DHA, and it was found that electron-donating or *ortho*-substituted aryl groups resulted in enhanced VHF lifetimes,[3] of particular relevance in the context of MOST design. While aryl substitution is synthetically convenient[4] and was shown to have a role in the stability of the system, early work by Daub and co-workers[5] has shown that placing instead a methyl group at C2 (DHA **2a**; Figure 1) enhances the corresponding VHF lifetime significantly.

We became interested to explore further the effect of different hybridization of the C2-substituent on the properties and stability of the photo-/thermoswitch couple, and specifically the influence of an acetylenic substituent as in the new DHA **3a** (Figure 1). Moreover, we will present synthesis and

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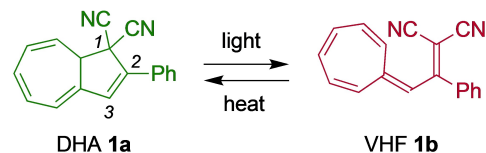Sino-Danish College (SDC)
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Scheme 1. Dihydroazulene (DHA)/vinylheptafulvene (VHF) isomerizations.
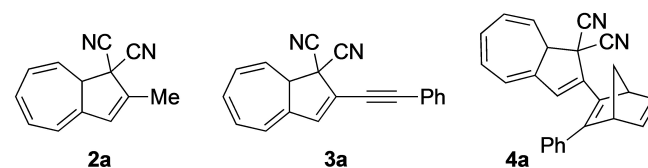
Figure 1. Known DHA **2a** and target molecules **3a** and **4a**.

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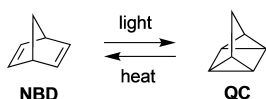
Scheme 2. Norbornadiene (NBD)/quadricyclane (QC) isomerizations.

properties of the DHA **4a** where a norbornadiene (NBD) substituent is directly connected at C2. The rationale here was to elucidate the influence of alkene *versus* aryl substitution and also to generate a dyad system comprised of two photoswitches, as NBD can photoisomerize to quadricyclane (QC) (Scheme 2). Indeed, in previous work we have studied multi-photochromic compounds, among them DHA-NBD dyads with the NBD unit located at the seven-membered ring or at the *meta/para* position of a C2 phenyl substituent on DHA (maintaining intact the reference scaffold of DHA **1a** with a phenyl ring on C2). DHA was photoactive in all the previous structures, while the photoactivity of the NBD unit was found to depend strongly on the connectivity between the two photoswitches.[6] We shall show here that a lack of NBD photoactivity was observed for **4a**, but, interestingly, the VHF-to-DHA back-reaction was found to be strongly retarded by the NBD substituent as it also was by the alkyne substituent of **3a**. Thus, in this work we demonstrate how moving away from aryl substitution at position C2 can have very beneficial implications for the VHF lifetime in the context of MOST systems.
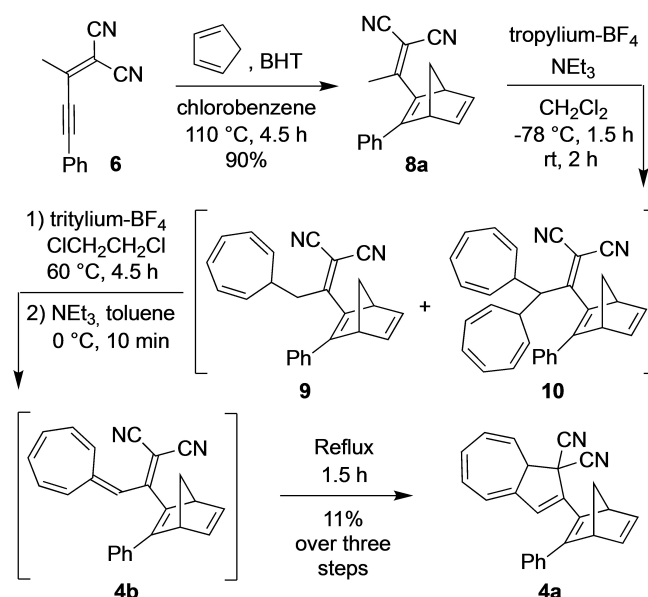
Results and Discussion

Synthesis. DHA **3a** was synthesized in a four-step procedure as shown in Scheme 3 starting from known 4-phenylbut-3-yn-2-one **5**, prepared according to a literature protocol.[7] A Knoevenagel condensation with malononitrile gave compound **6**, which was reacted with tropylium tetrafluoroborate and triethylamine to give the VHF precursor **7** as an intermediate that was not isolated, but in a subsequent step oxidized by the action of tritylium tetrafluoroborate followed by treatment with
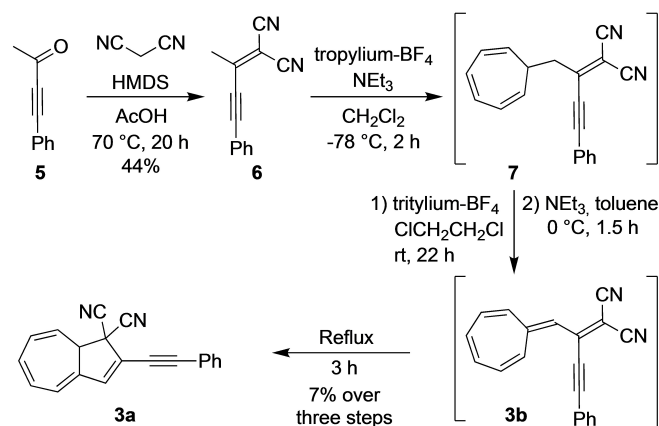
triethylamine to provide the VHF **3b**. Subjecting this compound to reflux resulted in ring closure to finally provide DHA **3a** in a yield of 21% containing minor impurities. Further chromatography followed by recrystallization resulted in a final yield of pure compound of 7%.

DHA **4a** was synthesized by assembling first the norbornadiene *core* and then the dihydroazulene (Scheme 4). First the key intermediate **6** from the above synthesis was reacted with cyclopentadiene in chlorobenzene at 110°C to furnish the NBD photoswitch **8a** in high yield.[8] This compound was then treated with triethylamine and tropylium tetrafluoroborate, providing a mixture of compounds **9** and **10** that was next treated with tritylium tetrafluoroborate and triethylamine. The resulting VHF **4b** was finally heated to generate the DHA **4a** in 11% yield over three steps.

Compound **3a** may in principle serve as a precursor for **4a** in a Diels-Alder reaction with cyclopentadiene. However, we did not explore this approach as in our experience it turned out rather challenging reacting a related DHA-based alkyne. Thus, using as dienophile a tolane with a cyano substituent at the *para* position of the one phenyl (thereby rendering the compound a better dienophile than **3a**) and a DHA at the *meta* position of the other phenyl provided only, assumingly, minor formation of the corresponding NBD product, after several hours of microwave heating. Besides, formation of by-products was particularly pronounced, resulting in tedious and unsuccessful purification attempts. The synthetic route described in Scheme 4 allowed the use of a more electron poor alkyne/dienophile in the cycloaddition step with cyclopentadiene, which hence occurred in few hours and in a high yield.

Scheme 3. Synthesis of alkynyl-substituted DHA. HMDS = hexamethyldisilazane; tropylium = C7H7+; tritylium = Ph3C+; rt = room temperature.

Scheme 4. Synthesis of NBD-substituted DHA. BHT = Butylated hydroxytoluene (2,6-di-*tert*-butyl-4-methylphenol).

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Table 1. Longest-wavelength absorptions, extinction coefficients, photoisomerization quantum yields (ϕ), and half-lives ($t_{1/2}$) for back-reactions.

System (Solvent)	λ_{max} (a) (ε [10^3 M^{-1} cm^{-1}]	ϕ [%]	λ_{max} (b) (ε [10^3 M^{-1} cm^{-1}]	$\Delta\lambda_{max}$[a]	$t_{1/2}$ 25 °C[b]	$t_{1/2}$ 50 °C[c]
3a/3b (MeCN)	363 (22.3) DHA	40	514 (30) VHF	151	22 d	696 min
4a/4b (PhMe)	387 (9.7) DHA	5	466 (17) VHF	79	5 d	286 min
8a/8b (PhMe)	368 (8.0) NBD	3	329 (4.7) QC	39	2.85 h	8.6 min

[a] Separation between DHA/VHF or NBD/QC absorption maxima. [b] Extrapolated from Arrhenius plot. [c] Measured.
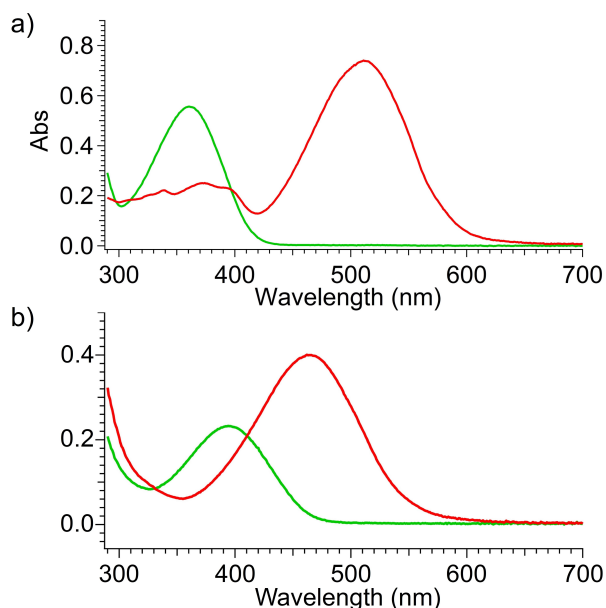

Figure 2. a) UV/Vis absorption spectra of DHA **3a** (green; 2.7 x 10^{-5} M) and VHF **3b** (red; resulting from irradiation of **3a** at 365 nm) in acetonitrile. b) UV/Vis absorption spectra of DHA **4a** (green; 2.5 x 10^{-5} M) and VHF **4b** (red; resulting from irradiation of **4a** at 365 nm) in toluene.
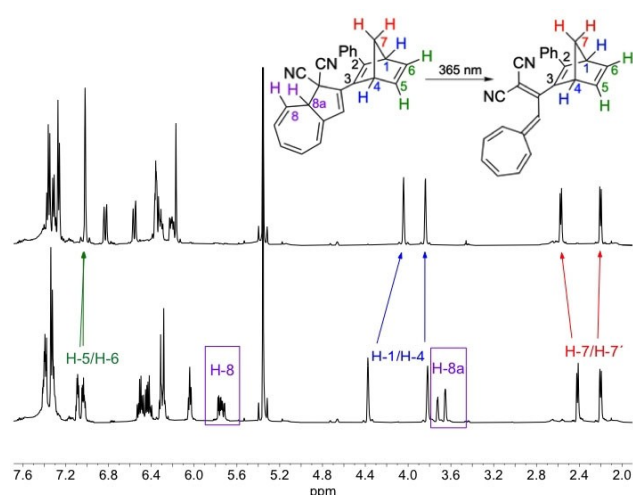

Figure 3. ^{1}H NMR spectra at 500 MHz in CD$_2$Cl$_2$ of NBD-DHA **4a** before (bottom) and after irradiation at 365 nm for 10 min (top; NBD-VHF **4b**). Diagnostic protons from the DHA *core* are evidenced by violet frames; these disappeared after irradiation, while typical NBD *core* protons shifted.

Optical and Switching Properties

With the three photoswitches **3a**, **4a** and **8a** in hand, the optical and switching properties were studied in detail by UV-Vis and NMR spectroscopies and compared to previously reported compounds, carefully chosen as references. Results are summarized in Table 1 and Figures 2–4.

DHA **3a** showed an absorption maximum at 363 nm in MeCN, which is redshifted by 10 nm in comparison to that of reference compound **1a**[4b] in the same solvent. Irradiation at 365 nm induced the ring-opening to the corresponding VHF **3b** (Figure 2a), which showed an absorption maximum at 514 nm, red-shifted by 44 nm in comparison to that of VHF **1b**.[4b] Hence a significantly larger separation between the characteristic DHA and VHF absorption maxima has been achieved for **3a/3b** (151 nm) in comparison to **1a/1b** (117 nm), which is an important aspect for developing useful MOST systems. The photoisomerization quantum yield for the DHA-to-VHF ring-opening was determined to 40% in MeCN, which is slightly reduced from the 55% reported for **1a**.[9] The kinetics of the thermal ring closure of VHF **3b** was determined at different temperatures; e.g., a half-life of 696 min was determined at 50 °C. From an Arrhenius plot, extrapolation provides a half-life at 25 °C of 22 days (see SI). For comparison, the half-life of VHF **1b** was previously determined to only 218 min in MeCN.[4b] Thus, the alkyne substituent has resulted in a more than 130-fold rise of the VHF lifetime. From a merely electronic point of view this is a somewhat surprising result inasmuch as an alkynyl substituent is more electron-withdrawing than a phenyl
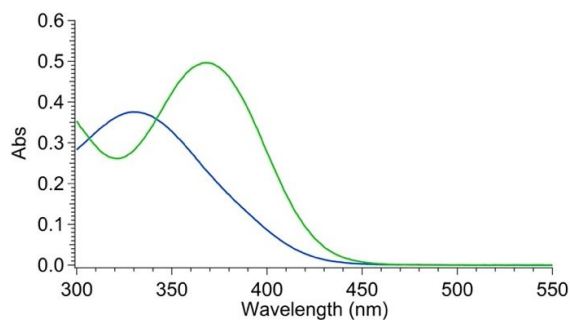

Figure 4. UV/Vis absorption spectra of NBD **8a** (green; 6.3 x 10^{-5} M) and corresponding QC **8b** (blue; resulting from irradiation of **8a** at 365 nm) in toluene.

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substituent. For aryl substituents at C2 it was previously established that the more electron-withdrawing, the faster VHF ring closure,[3a] which was explained by the involvement of a zwitterionic transition state. The acetylenic bridge present in **3b** should allow for co-planarity between the heptafulvene and phenyl rings, as indicated by the redshift in the longest-wavelength absorption maximum, which might explain a higher stability of the VHF form and therefore an enhanced lifetime. Overall, the quite small change in structure and molecular weight from **1a** to **3a** has brought two important MOST improvements: (i) long-lived VHF and (ii) reduced spectral overlap between the two isomers.

Compound **4a** was studied in toluene and showed an absorption maximum at 387 nm, red-shifted in comparison to those of **3a** and **1a**. Irradiation of the sample solution at 365 nm showed the formation of a new spectrum with a characteristic VHF absorption maximum red-shifted to 466 nm (Figure 2b). Clear isosbestic points (see SI) upon irradiation indicated the presence of only two species in solution. As **4a** is structurally a dyad, irradiation may lead to ring-opening of DHA to VHF and/or [2+2] cycloaddition of NBD to QC. NMR spectroscopic studies were performed in CD_2Cl_2 to identify the structure of the irradiated form and showed the exclusive presence of NBD-VHF **4b** (Figure 3, top spectrum). Indeed, by irradiation of **4a** at 365 nm (Figure 3, bottom spectrum), the protons of the DHA *core* disappeared (the most distinguishable signals, i.e. H-8a and H-8, are shown in violet frames in Figure 3), while the typical NBD *core* signals upon irradiation only shifted due to the resulting influence of the VHF moiety (indicated by arrows in Figure 3). If the NBD-to-QC photo-isomerization had occurred, signals in the aliphatic region should appear due to the presence of two new sp^3-CH on a QC *core*.[10] On the contrary, only a slight shift of the two NBD sp^2-CH at 7.1 ppm was detected, accompanied by a simplified multiplicity, which reasonably is connected to the loss of chirality of the VHF. No evidence of QC formation was detected even after further irradiation of the NMR sample at 254 nm.

The photoisomerization quantum yield for the DHA-to-VHF conversion of **4a** into **4b** was evaluated and resulted only in 5% in toluene, hence extremely reduced by the proximity of the NBD moiety. A small fluorescence was observed from this sample, which could justify the loss in quantum yield of photoisomerization. The thermal back-reaction from **4b** to **4a** was evaluated in toluene at 50, 60 and 70°C and then extrapolated to 25°C by an Arrhenius plot (see SI). The VHF **4b** half-life in toluene was 286 min at 50°C and 5 days at 25°C; hence significantly longer than for VHF **1b**. Irradiation of **4a** at wavelengths of 300 nm, which have previously shown to induce NBD-to-QC conversion, did not result in any further spectral changes in the case of **4b**. This finding on the directly connected NBD-DHA **4a** is in line with the lack of photoactivity previously observed for NBD-DHA dyads having a *para*-phenylene connectivity.[6] Moreover, lack of NBD photoactivity was previously observed for a dyad incorporating azobenzene[1j] as well as for diarylethene photoswitches containing an NBD bridge.[11]

Finally, we studied the NBD **8a** (see Figure 4 and SI). It exhibited an absorption maximum at 368 nm in toluene. Irradiation at 365 nm provided the QC isomer (**8b**) with a blue-shifted absorption maximum at 329 nm. The QC returned thermally to NBD with a half-life of 2.85 h at 25°C in toluene. This back-reaction is significantly shorter than for a comparable structure where the electron-withdrawing $C(Me)=C(CN)_2$ substituent is replaced by a CN substituent for which a half-life of 54 days in toluene has been reported.[12] Previously we established a correlation between the presence of a radical stabilizing group and the rate of the QC-to-NBD retro-cycloaddition;[13] the more stabilizing the substituent, the faster the back conversion (signaling a two-step, diradical-intermediate mechanism for the back-reaction), and the data found for **8b** are in line with those findings as the dicyanovinyl group should indeed be a good radical-stabilizing group. Therefore using the following empirical linear relationship between the rate constant k and the Creary[14] radical substituent value $\sigma_C{}^*$: $\ln(k/s^{-1}) = 3.01 \times \sigma_C{}^* - 15.8$, we obtain a Creary radical substituent value of $2.06 \sim 2.1$ for the $C(Me)=C(CN)_2$ substituent. For comparison, it is 0.47 for CN and 0.67 for $CH=CH_2$.[14]

Conclusion

In conclusion, two new DHA derivatives with alkyne and NBD substitution, respectively, at position C2 were prepared and characterized. The DHA-NBD dyad was constructed from a preformed NBD photoactive derivative containing phenyl and $C(Me)=C(CN)_2$ substituents on the two carbon atoms of one $C=C$ bond. From the kinetics of the corresponding QC's back-reaction to form NBD, we obtained an estimate of the Creary radical substituent value of 2.1 for the $C(Me)=C(CN)_2$ substituent, implying that this group is a very strong radical-stabilizing group (assuming the previously established[13] empirical relationship between the QC-to-NBD rate constant and the Creary constant to be valid also for strongly radical-stabilizing groups). In contrast, the NBD photoactivity was lost in the DHA-NBD dyad system that only underwent DHA-to-VHF photoisomerization.

For both DHA compounds, a larger spectral separation between the characteristic absorption maxima of DHA and VHF isomers was observed. Moreover, both exhibited significantly enhanced lifetimes of the meta-stable VHF form; in particular the alkyne substituent gave a remarkably long half-life of 22 days in the polar solvent acetonitrile, which is 130-fold longer than for the reference compound **1a**. This favorable structural modification is accompanied by only a small increase of molecular weight. By further functionalization of the phenyl-ethynyl substituent with either electron-donating or withdrawing groups on the phenyl or water-solubilizing groups, we may be able to improve MOST requirements even further.

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Experimental Section

General Methods – Synthesis and Experimental Characterizations

Solvents and reagents were purchased from Sigma-Aldrich and used without further purification. All handling of photochromic compounds was done in the dark, with flasks and columns wrapped in aluminum foil to exclude light, and isolated fractions were kept in the dark. Thin-layer chromatography (TLC) was carried out on commercially available precoated plates (Silica 60) with fluorescence indicator P254 and revealed with TLC lamp (365 and 254 nm). NMR spectra were acquired on a 500-MHz Bruker instrument equipped with a direct cryoprobe. All chemical shift values in ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peak (CDCl$_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm). High Resolution Mass spectrometry (HRMS) analysis was performed on an FT-ICR instrument (Fourier Transform Ion Cyclotron Resonance) using Electrospray Ionization (ESI). Melting points are uncorrected. Tropylium tetrafluoroborate and tritylium tetrafluoroborate were prepared according to literature protocols.[4b] UV-Vis absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer equipped with a Peltier heat exchange unit and were carried out in a 1-cm path length cuvette at 25 °C, unless otherwise stated. Photoswitching experiments were conducted by irradiating a solution of the compound (concentration range $2-7 \cdot 10^{-5}$ M) in the cuvette using a Thorlabs LED M365L2 for 365 nm, or Thorlabs LED M300 L4 for 300 nm. The thermal back-reaction was studied by heating the cuvette with the solution in a Peltier unit in the UV-Vis spectrophotometer. The photoisomerization quantum yields were measured using a high concentration regime (absorbance above 2 at wavelength of irradiation) using potassium ferrioxalate/tris(1,10-phenanthroline) as chemical actinometer; following a general literature protocol.[15] Compound **4a** was obtained as mixture of diastereoisomers, and TLC analysis performed with various eluent systems never showed any separation. All these compounds show partial splitting of signals in ^{13}C-NMR spectra.

2-(4-Phenylbut-3-yn-2-ylidene)malononitrile (6). A solution of malononitrile (2.41 g, 36.5 mmol) and ketone **5** (1.80 g, 12.5 mmol) in acetic acid (6.5 mL) was added to a solution of 1,1,1,3,3,3-hexamethyldisilazane (5.2 mL, 25 mmol) in acetic acid (12 mL). The reaction mixture was heated to 70 °C and allowed to stir overnight. After the reaction mixture had cooled to rt, water (100 mL) was added. The reaction mixture was extracted with CH$_2$Cl$_2$ (4× 100 mL), and the combined organic phases were washed with water (3×100 mL), dried over MgSO$_4$ and evaporated *in vacuo*. Repeated purification by flash column chromatography (SiO$_2$, 40–63 μm, 10–20% EtOAc/heptane) (SiO$_2$, 40–63 μm, 20% EtOAc/heptane) gave the product **6** (1.06 g, 5.51 mmol, 44%) as an orange solid. R_f = 0.34 (20% EtOAc/heptane). M.p.: 87–90 °C. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.61 (dd, J = 8.4, 1.3 Hz, 2H), 7.50 (tt, J = 7.3, 1.3 Hz, 1H), 7.42 (dd, J = 8.4, 7.3 Hz, 2H), 2.47 (s, 3H) ppm. ^{13}C-NMR (126 MHz, CDCl$_3$) δ 155.7, 133.2, 131.7, 129.0, 120.2, 112.5, 112.1, 112.0, 90.7, 87.2, 23.4 ppm. HRMS (ESP +) *m/z*: calc for C$_{13}$H$_9$N$_2$$^+$ [M + H$^+$] = 193.07602, found = 193.07631; calc for C$_{26}$H$_{17}$N$_4$$^+$ [2 M + H$^+$] = 385.14477, found = 385.14530.

2-(Ethynylbenzene)-1,8a-dihydroazulene-1,1-dicarbonitrile (3a). Compound **6** (196 mg g, 1.02 mol) was dissolved in CH$_2$Cl$_2$ (70 mL). Tropylium tetrafluoroborate (242 mg, 1.36 mmol) was crushed using a mortar and pestle and added to the solution, which was then cooled to −78 °C. Then Et$_3$N (0.2 mL, 1.43 mmol) was added, and the reaction mixture was stirred for 2 h at −78 °C, then allowed to warm to rt and concentrated *in vacuo*. The residue (compound **7**) was dissolved in 1,2-dichloroethane (60 mL), and tritylium tetrafluoroborate (701 mg, 2.12 mmol) was added. After 22 h, the

reaction mixture was cooled to 0 °C, diluted with toluene (50 mL), and then Et$_3$N (0.3 mL, 2.15 mmol) was added slowly over 15 min (to provide VHF **3b**). The reaction mixture was stirred at 0 °C for 1.5 h, then allowed to warm to rt and finally refluxed for 3 h before the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography twice (SiO$_2$, 1: 17.5% EtOAc/heptane; 2: 15% EtOAc/heptane) to obtain **3a** in 21% yield. The remaining compound was recrystallized from CH$_2$Cl$_2$/MeOH, yielding DHA **3a** as dark yellow crystals (21.2 mg, 0.076 mmol, 7% over three steps). R_f = 0.33 (15% EtOAc/heptane). M.p. 98–99 °C. ^{1}H-NMR (500 MHz, CDCl$_3$) δ = 7.58–7.56 (m, 2H), 7.42–7.36 (m, 3H), 6.68 (s, 1H), 6.57 (dd, J = 11.3, 6.3 Hz, 1H), 6.50 (dd, J = 11.3, 6.3 Hz, 1H), 6.33–6.29 (m, 2H), 5.74 (dd, J = 10.3, 3.9 Hz, 1H), 3.66 (ddd, J = 3.9, 2.0, 2.0 Hz, 1H) ppm. ^{13}C-NMR (126 MHz, CDCl$_3$) δ = 139.6, 138.3, 132.3, 131.8, 130.9, 129.9, 128.7, 127.9, 123.7, 122.2, 121.5, 119.7, 114.4, 112.2, 100.8, 81.4, 49.6, 48.6 ppm. HRMS (ESP +) *m/z*: calc for C$_{20}$H$_{12}$N$_2$Na$^+$ [M + Na$^+$] = 303.08927, found = 303.09016.

2-(1-(3-Phenylbicyclo[2.2.1]hepta-2,5-dien-2-yl)ethyliden)malononitrile (8a). Freshly distilled cyclopentadiene (3.0 mL, 36 mmol) was added to a solution of compound **6** (0.877 g, 4.56 mmol) and BHT (0.0044 g) in chlorobenzene (3.0 mL). The reaction mixture was heated in a sealed vial covered with aluminum foil using an oil bath at 110 °C for 4.5 h. Then the reaction mixture was directly loaded on a column and purified by flash column chromatography (SiO$_2$, 40–63 μm, toluene). Evaporation of the solvent *in vacuo* gave NBD **8a** (1.06 g, 4.11 mmol, 90%) as an orange oil. R_f = 0.33 (toluene). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.42–7.34 (m, 3H), 7.17–7.11 (m, 2H), 7.04 (dd, J = 5.1, 2.9 Hz, 1H), 6.92 (dd, J = 5.1, 3.2 Hz, 1H), 4.06–4.01 (m, 1H), 4.00–3.95 (m, 1H), 2.39 (dt, J = 6.8, 1.5 Hz, 1H), 2.20 (s, 3H), 2.19 (dt, J = 6.8, 1.4 Hz, 1H) ppm. ^{13}C-NMR (126 MHz, CDCl$_3$) δ 173.0, 166.1, 146.0, 143.4, 142.5, 135.9, 129.4, 129.1, 127.2, 113.3, 112.9, 83.0, 71.2, 57.9, 56.6, 22.4 ppm. HRMS (ESP +) *m/z*: calc for C$_{18}$H$_{14}$N$_2$Na$^+$ [M + Na$^+$] = 281.10492, found = 281.10515; calc for C$_{36}$H$_{28}$N$_4$Na$^+$ [2 M + Na$^+$] = 539.22062, found = 539.22163.

2-(3-Phenylbicyclo[2.2.1]hepta-2,5-dien-2-yl) azulene-1,1(8aH)-di-carbonitrile (4a). Tropylium tetrafluoroborate (0.346 g, 1.95 mmol) was added to a solution of **NBD 8a** (0.401 g, 1.55 mmol) in CH$_2$Cl$_2$ (40 mL) under nitrogen atmosphere. The reaction mixture was cooled on a dry ice-acetone bath, and Et$_3$N (0.25 mL, 1.8 mmol) was added dropwise over 5 min. After 1.5 h the reaction mixture was allowed to warm to rt and then stirred for 2 h. The reaction mixture was concentrated onto Celite and purified by flash column chromatography (SiO$_2$, 40–63 μm, toluene). Evaporation of the solvent *in vacuo* gave a yellow oil containing a mixture of **9** and **10** (0.476 g). R_f = 0.42, 0.47 (toluene). Compound **9**: ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.40–7.33 (m, 3H), 7.17–7.12 (m, 2H), 6.92–6.86 (m, 2H), 6.65–6.60 (m, 2H), 6.22–6.13 (m, 2H), 5.11–5.03 (m, 2H), 3.93 (s, 2H), 2.90 (dd, J = 7.9, 1.3 Hz, 2H), 2.37 (d, J = 6.7 Hz, 1H), 2.14 (d, J = 6.7 Hz, 1H), 1.79 (p, J = 7.0 Hz, 1H). Additional signals are due to the presence of **10**. HRMS (ESP +) on the mixture gave: compound **9**: *m/z*: calc for C$_{25}$H$_{20}$N$_2$Na$^+$ [M + Na$^+$] = 371.15187, found = 371.15361; compound **10**: *m/z*: calc for C$_{32}$H$_{26}$N$_2$Na$^+$ [M + Na$^+$] = 461.19882, found = 461.20043. The following reaction was carried out on half of the crude mixture of **9** and **10**: Tritylium tetrafluoroborate (0.254 g, 0.771 mmol) was added to a solution of compounds **9** and **10** (0.243 g) in 1,2-dichloroethane (40 mL) under a nitrogen atmosphere. The reaction mixture was heated to 60 °C for 3.5 h. Then an additional portion of tritylium tetrafluoroborate (0.126 g, 0.382 mmol) was added, and the reaction mixture was stirred at 60 °C for one more hour. The reaction mixture was diluted with toluene (20 mL), cooled in an ice bath, and Et$_3$N (0.13 mL, 0.93 mmol) was added. The reaction mixture was left stirring in the ice bath for 10 min, after which it was heated to reflux for 1.5 h. The reaction mixture was concentrated onto Celite and purified by

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flash column chromatography (SiO$_2$, 40–63 μm, 50% toluene/heptane). Evaporation *in vacuo* gave the **DHA-NBD 4a** as a mixture of diastereoisomers (A and B) as an orange oil (0.0306 g, 0.0883 mmol, 11%). $R_f = 0.32$ (yellow→red upon light exposure) (50% toluene/heptane). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.38–7.33 (m, isomer A and B, 2H × 2), 7.30–7.26 (m, isomer A and B, 3H × 2), 7.09–7.05 (m, isomer A and B, 1H × 2), 6.99–6.95 (m, isomer A and B, 1H × 2), 6.48–6.34 (m, isomer A and B, 2H × 2), 6.29–6.22 (m, isomer A and B, 2H × 2), 6.00–5.96 (m, isomer A and B, 1H × 2), 5.73 (dd, $J = 10.1$, 3.9 Hz, isomer A, 1H), 5.70 (dd, $J = 10.3$, 3.7 Hz, isomer B, 1H), 4.37–4.33 (m, isomer A and B, 1H × 2), 3.78–3.74 (m, isomer A and B, 1H × 2), 3.66 (dt, $J = 3.7$, 1.9 Hz, isomer B, 1H), 3.59 (dt, $J = 3.9$, 1.9 Hz, isomer A, 1H) 2.40–2.37 (m, 1H × 2), 2.19–2.16 (m, 1H × 2) ppm. ^{13}C-NMR (126 MHz, CDCl$_3$, isomer A and B) δ 160.73, 160.66, 143.5, 143.4, 142.00, 141.99, 140.2, 140.0, 139.8, 139.4, 137.8, 137.6, 137.41, 137.36, 132.2, 131.8, 131.3, 131.0, 130.2, 129.6, 128.92, 128.91, 128.1, 127.9, 127.7, 126.7, 126.6, 120.09, 120.07, 119.9, 119.6, 115.8, 115.6, 113.4, 113.3, 70.8, 58.4, 54.0, 53.9, 50.44, 50.40, 46.5, 46.4 ppm (3 signals missing, probably due to overlap). HRMS (ESP+) *m/z*: calc for C$_{25}$H$_{18}$N$_2$Na$^+$ [M+Na$^+$] = 369.13622, found = 369.13673.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Energy storage: Two dihydrazulene/vinylheptafulvene (DHA/VHF) photo-/thermoswitches with alkyne and norbornadiene substituents, respectively, at position C2 of DHA were prepared and studied for their optical and switching properties. The VHF form of these compounds exhibited remarkably long lifetimes, a key factor in the quest for long-term solar energy storage systems using photochromic molecules.
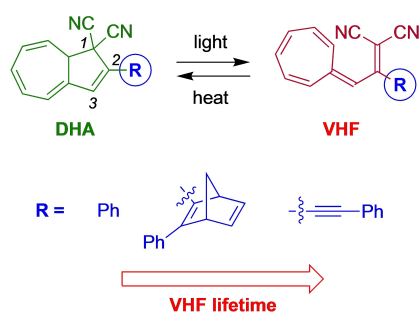
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Long-Term Energy Storage Systems Based on the Dihydroazulene/Vinylheptafulvene Photo-/Thermoswitch