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Energy Storage and Conversion

Aromaticity-Controlled Energy Storage Capacity of the Dihydroazulene-Vinylheptafulvene Photochromic System

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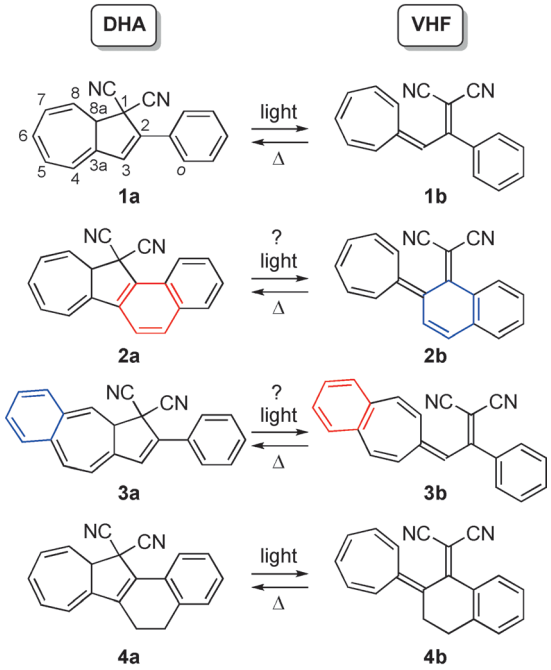
Abstract: Photochemical conversion of molecules into high-energy isomers that, after a stimulus, return to the original isomer presents a closed-cycle of light-harvesting, energy storage, and release. One challenge is to achieve a sufficiently high energy storage capacity. Here, we present efforts to tune the dihydroazulene/vinylheptafulvene (DHA/VHF) couple through loss/gain of aromaticity. Two derivatives were prepared, one with aromatic stabilization of DHA and the second of VHF. The consequences for the switching properties were elucidated. For the first type, sigmatropic rearrangements of DHA occurred upon irradiation. Formation of a VHF complex could be induced by a Lewis acid, but addition of H_2O resulted in immediate regeneration of DHA. For the second type, the VHF was too stable to convert into DHA. Calculations support the results and provide new targets. We predict that by removing one of the two CN groups at C-1 of the aromatic DHA, the heat storage capacity will be further increased, as will the life-time of the VHF. Calculations also reveal that a CN group at the fulvene ring retards the back-reaction, and we show synthetically that it can be introduced regioselectively.

Introduction

1,8a-Dihydroazulene-1,1-dicarbonitriles (DHAs) are photochromic molecules,[1] and this property was recently exploited for light-induced conductance switching in molecular electronics devices.[2] Thus, DHA **1a** is converted quantitatively into the isomeric vinylheptafulvene (VHF) **1b** upon irradiation (Scheme 1), which, in time, returns through a thermally induced back-reaction to the more stable DHA. Enhancing the energy difference between two isomers that are convertible by light in at least one direction has also attracted interest as a means of storing solar energy.[3] The DHA/VHF system is only photoactive in one direction (with a high quantum yield of 55% for **1a** in MeCN[4]), rendering it particularly attractive for this purpose. Energy storage by the *meta*-stable VHF **1b** corresponds, however, only to 27.7 kJ mol^{-1} or 0.11 MJ kg^{-1}.[5] This value is far from the optimum value of 1 MJ kg^{-1},[3c] which cor-



Scheme 1. Structures of the original DHA/VHF system **1a**/**1b** with atom numbering and new benzo-fused systems. Rings that change from aromatic (red color) to nonaromatic (blue color) are highlighted.

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responds to the energy difference of the unsubstituted norbornadiene–quadricyclane (NB/QC) system.[6] Unsubstituted norbornadiene is, however, characterized by a quantum yield of only 9% for the photoisomerization.[6]

The relative DHA/VHF stability can be tuned in several ways. For example, it is influenced by solvents because the more polar VHF is stabilized more in polar solvents, thereby reducing the energy difference.[5] Substitution can also change the relative stability; placing a phenyl group at C-3 or exchanging one of the cyano groups on C-1 with hydrogen leads to an approximate doubling of the DHA/VHF energy difference in vacuo.[5]

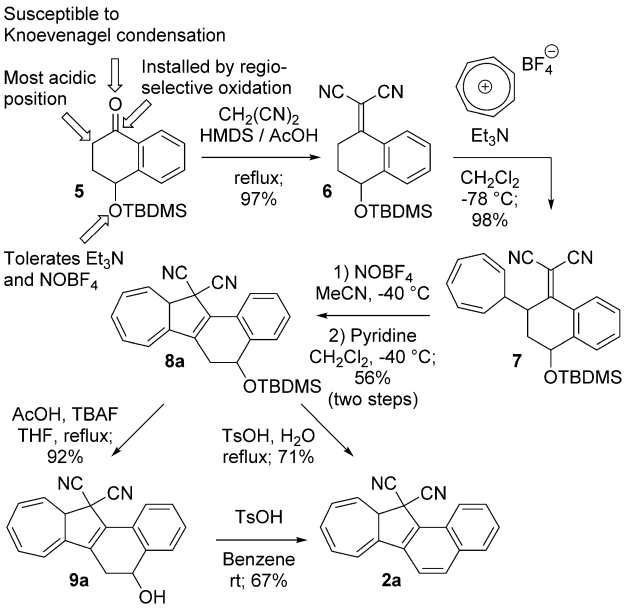
We became interested in exploring other ways of tuning the energy difference and here show that combining the DHA/VHF switching event with loss or gain in aromaticity can lead to dramatic changes in energy differences and implications for the switching properties. Previously, the properties of the metacyclophanediene–dihydropyrene photoswitch were strongly tuned by benzannulation.[7] Furthermore, Yang et al.[8] found that including the ethene bridge in dithienylethene photoswitches as part of an aromatic system significantly changes their stabilities relative to the non-benzenoid dihydrodithienobenzene isomers. We designed two derivatives of the DHA/VHF system in which a benzene ring fused to the DHA core would maintain its aromaticity when connected between position C-3 on the DHA and the *ortho*-position of the phenyl (**2a**; Scheme 1), but lose it when connected at the 6,7-position (**3a**). Ring-opening of DHA **2a** to VHF **2b** destroys the aromaticity of the fused ring, thereby presumably increasing the DHA/VHF energy difference. The opposite situation is the case for the **3a**/**3b** pair, and, in consequence, the DHA/VHF energy difference should be reduced. Here, we present a synthesis of these two compounds, the further functionalization of **2a**, and a detailed computational study of the energetics associated with the conversions in comparison to the couple **4a**/**4b** that was recently prepared[9] and to the NB/QC couple.

Results and Discussion

Synthesis

In an initial attempt to prepare DHA **2a**, we subjected the corresponding dihydronaphtho derivative **4a** to oxidation or radical bromination–elimination protocols, but none of these methods were successful. Instead, the synthesis of **2a** was achieved in six steps (Scheme 2) from the carefully chosen, known α-tetralone **5** starting material (after an optimization of its synthesis allowing preparation at 13 g scale without use of chromatography).

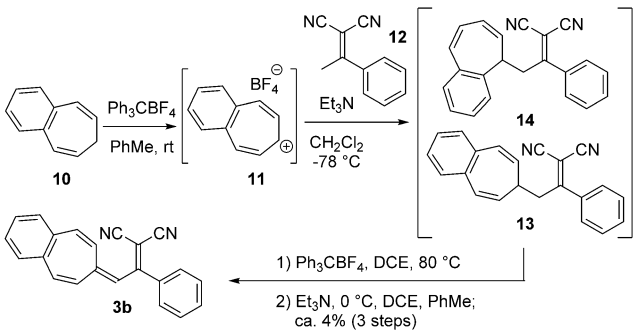
A Knoevenagel condensation with malononitrile using an AcOH/HMDS buffer gave **6** in 97% yield. Treatment of **6** with tropylium tetrafluoroborate in the presence of Et_3N gave **7** in 98% yield. A two-step oxidation using $NOBF_4$ followed by pyridine gave the VHF, which immediately underwent ring-closure to form **8a** in 56% yield. A desilylation was accomplished by treatment with tetrabutylammonium fluoride (TBAF) in the presence of AcOH (to avoid azulene formation[10]), affording alcohol **9a** in 92% yield. By treatment with TsOH in refluxing



Scheme 2. Synthesis of DHA **2a**. HMDS = hexamethyldisilazane. $NOBF_4$ = nitrosyl tetrafluoroborate. TBAF = tetrabutylammonium fluoride. TsOH = *p*-toluene sulfonic acid. TBDMS = *tert*-butyldimethylsilyl.

benzene, this compound was converted into the desired unsaturated DHA **2a** in 67% yield. Alternatively, the desilylation–elimination of **8a** could conveniently be achieved in one-pot by treatment with TsOH in refluxing benzene to furnish product **2a** in 71% yield.

The other target molecule, VHF **3b**, was obtained in three steps from the known[11] 7*H*-benzo[7]annulene **10** (Scheme 3). The benzotropylium species **11**[12] was formed by hydride abstraction using tritylium tetrafluoroborate and was then treated with **12**[13] in the presence of Et_3N to furnish **13** and its regioisomer **14**. The two isomers could be separated by chromatography and characterized for analytical purposes (see the Supporting Information). However, simply treating the mixture with tritylium tetrafluoroborate followed by Et_3N allowed us to isolate target molecule **3b** in an overall yield of ca. 4% after chromatographic purification. In another synthesis, we obtained the product **3b** in a yield of 19% from benzotropylium tetrafluoroborate **11**. The VHF corresponding to oxidation of **14** was not isolated during work-up; it thus seems that **14** ex-



Scheme 3. Synthesis of aromatic VHF **3b**. DCE = 1,2-dichloroethane.

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hibits some reluctance towards the oxidation. The structure of **3b** was confirmed by X-ray crystallographic analysis (see below). We then attempted to convert VHF **3b** into DHA **3a**. This conversion was, however, not successful, even by heating **3b** at 60 °C for 30 h in 1,2-dichloroethane (DCE). For comparison, the half-life of VHF **1b** was merely 9.4 min under the same conditions (see the Supporting Information).

Characterization by NMR spectroscopic and X-ray crystallographic analyses

The aromatic characteristics of the benzenoid rings of **2a** and **3b** were probed experimentally by ^{1}H NMR and ^{13}C NMR spectroscopies as well as by X-ray crystal structure analyses. The ^{1}H NMR chemical shifts of the two protons in the central benzene ring in **2a** were found in the aromatic region at $\delta = 7.94$ and 7.55 ppm and ^{13}C(H) resonances at $\delta = 133.22$ and 119.19 ppm. Likewise, the protons of the fused benzene ring in **3b** were found in the aromatic region (> 7.25 ppm, overlapping with the Ph resonances) and the ^{13}C resonances at $\delta >$ 120 ppm. The crystal structures (Figure 1) obtained from single-crystal structure determination offered additional support for the benzenoid characteristics; all carbon atoms in the naphthalene and benzene moieties of **2a** and **3b** were coplanar. The bond lengths of the naphthalene moiety of **2a** were similar to those found in naphthalene (see the Supporting Information). For **3b**, the bond lengths of the benzene ring were in the range 1.36–1.42 Å, hence close to the value of 1.39 Å in benzene.

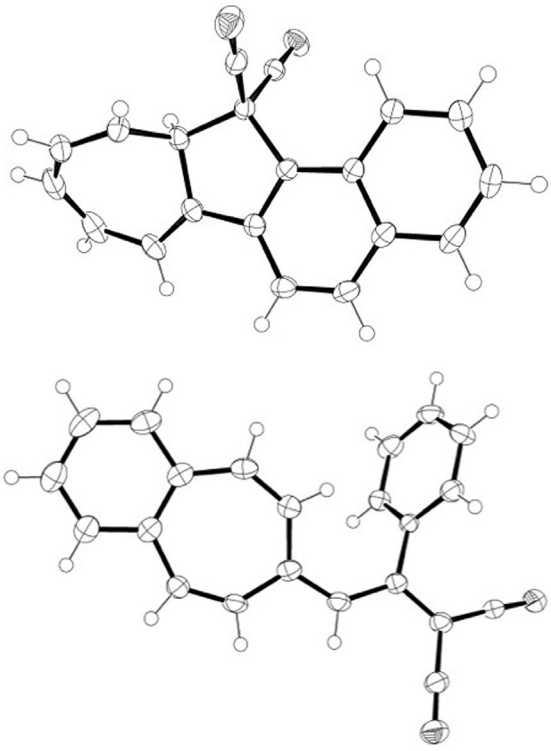
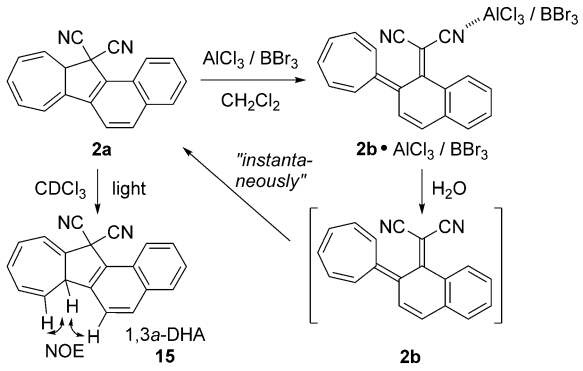


Figure 1. Molecular structures of **2a** (top; CCDC 1429767) and **3b** (bottom; CCDC 1421412) with displacement-ellipsoids of 50% for non-H atoms.

Optical and switching properties

The optical and switching properties of DHA **2a** were studied by using UV/Vis absorption spectroscopy. In both polar and nonpolar solvents, DHA **2a** exhibited a characteristic absorption at λ_{max} 342 nm in EtOH and cyclohexane. Unfortunately, neither in cyclohexane at 25 °C nor in (deoxygenated) EtOH at −100 °C did **2a** seem to undergo the desired photoisomerization upon irradiation at 365 nm. Instead of the appearance of the characteristic VHF absorption at 440–490 nm, the characteristic DHA absorption simply disappeared and new higher energy absorptions appeared. Thus, for **2a**, other light-induced reactions come into play, or, if in fact formed, an ultrafast conversion of VHF into DHA may occur. We consider that the VHF is simply too short-lived to be observed under the experimental conditions, even at low temperature (−60 to −100 °C) at which the quantum yield of ring-opening at the same time should be decreased.[4] To identify the product(s) formed, a sample of DHA **2a** in $CDCl_3$ was exposed to light at 365 nm for 60 h. By ^{1}H/^{1}H COSY and ^{1}H/^{1}H NOESY NMR spectroscopy, six different DHA structures were observed (see the Supporting Information), all products of sigmatropic rearrangements. Further irradiation resulted in formation of the corresponding 1,3*a*-DHA **15** (Scheme 4) along with one other isomer as major products.



Scheme 4. Light and Lewis acid (such as $AlCl_3$ or BBr_3) induced conversions of DHA **2a**.

Although formation of VHF could not be tracked by irradiation with light, treatment with Lewis acids (LA) successfully converted **2a** into the corresponding VHF·LA complex (**2b**·LA) (Scheme 4), the formation of which was monitored both by UV/Vis and NMR spectroscopies. Thus, addition of BBr_3 or $AlCl_3$ to a solution of **2a** in CH_2Cl_2 resulted in a redshift of the longest wavelength absorption maximum to 504 nm for VHF·BBr_3 and to 503 nm for VHF·$AlCl_3$ (Figure 2). Most importantly, the ^{1}H and ^{13}C NMR spectra of the VHF·$AlCl_3$ complex (see the Supporting Information) were very similar to those previously measured for the BBr_3 and $AlCl_3$ complex of **1b**.[14] Upon addition of water, the VHF·LA complex was broken up and then the VHF instantaneously returned to the DHA. We note that, while showing the characteristic DHA absorption peak, the initial ab-

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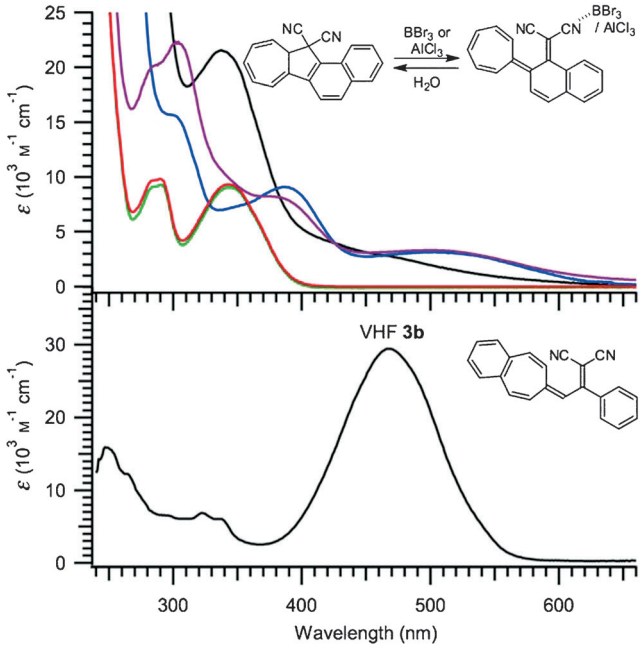


Figure 2. Top: UV/Vis absorption spectra in CH_2Cl_2 of DHA **2a** (red), VHF·BBr_3 complex (blue), VHF·$AlCl_3$ complex (purple), DHA generated from addition of water to BBr_3 complex (black), and DHA generated from addition of water to $AlCl_3$ complex followed by a liquid–liquid extraction (green). Bottom: UV/Vis absorption spectrum of VHF **3b** in DCE.

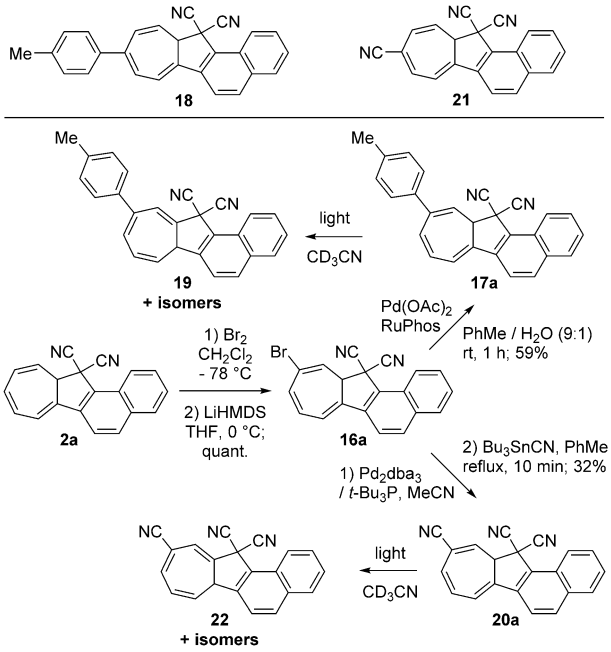
sorption spectrum obtained upon addition of water is not identical to that of DHA **2a**. However, after an aqueous work-up, the spectrum becomes identical to that of **2a**. The conversion between **2a** and **2b** is thus indeed reversible.

VHF **3b** was also studied by using UV/Vis absorption spectroscopy, showing a strong absorption at λ_{max} 468 nm in DCE (Figure 2). No sign of a thermally induced conversion into **3a** was observed, even by addition of Lewis acids, such as $ZnCl_2$, which has previously proven to catalyze the ring-closure reaction.[14] Clearly, the VHF seems to be too stable to undergo the ring-closure reaction as also suggested by calculations (see below). Thus, the aromatic character gained by the VHF reversed the relative DHA–VHF stability.

Further functionalization

Our next objective was to investigate the possibility of using **2a** as a substrate for a subsequent functionalization of the core, which is important for tuning of properties. In addition, we hoped that attachment of a substituent group in the seven-membered ring could shed light on whether a ring-opening does occur upon irradiation or not. Given that we have shown that pure 7-substituted DHAs partly isomerize into their 6-substituted derivatives—via the VHF—upon irradiation with light in polar solvents,[1e,10] we considered that it may be possible to probe whether the DHA does indeed rapidly form VHF by installation of a substituent at C-7 of the DHA core of **2a**: formation of any 6-substituted DHA would be evidence of a ring-opening/closure cycle.

By using a bromination–elimination–cross-coupling procedure,[10,15] we set out to prepare a DHA with a tolyl-substituent at C-7 of the DHA. Firstly, treatment of DHA **2a** with Br_2 in CH_2Cl_2 at −78 °C followed by LiHMDS in tetrahydrofuran (THF) at 0 °C almost quantitatively yielded the bromo-substituted DHA **16a** (Scheme 5). Treatment with tolyl boronic acid under our previously optimized Suzuki cross-coupling conditions



Scheme 5. Installation of "spectator group" to investigate whether light-induced ring-opening occurs.

(K_3PO_4, RuPhos, and $Pd(OAc)_2$)[15] gave the desired DHA **17a** in 59% yield (over three steps). With this tolyl-substituted DHA in hand, it was exposed to white light for 10 h in CD_3CN solution to investigate whether an isomerization into isomer **18** occurred. From $^1H/^1H$ COSY NMR spectroscopic analysis, it transpires that whereas DHA **17a** still undergoes the undesired sigmatropic rearrangements, formation of an intermediate VHF cannot be unambiguously established because an extremely complex NMR spectrum resulted from irradiation. In principle, a total of 12 DHA compounds can arise from a combination of ring-opening and ring-closure in combination with sigmatropic rearrangements. From the spectrum we were only able to unambiguously confirm the presence of the undesired compound **19** resulting from sigmatropic rearrangements (as well as several other isomers). Although this observation is not encouraging, it does not rule out the formation of VHF. Thus, we have previously established that the quantum yield of the ring-opening does not necessarily affect the degree of isomerization from the 7- to the 6-substituted isomer. Instead, we believe that the polarization of the VHF transition state does. Thus, a strongly electron-withdrawing substituent would place a larger partial positive charge on C-4 compared with that on C-8a (DHA core numbering) and could present a possible way

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to observe this isomerization. Thus, we set out to place a CN-group on C-7 by using a three-step palladium-insertion–transmetalation–cyanation procedure. Gratifyingly, treatment of **16a** with Pd_2dba_3/tBu_3P in CH_3CN followed by addition of Bu_3SnCN in toluene gave the cyano-substituted DHA **20a** in 32% yield (over three steps). This compound was then exposed to light at 366 nm in CD_3CN and CD_2Cl_2 solutions; however, again we could not unambiguously determine or rule out formation of the desired isomerized compound **21**. Instead, we again detect products from undesired sigmatropic rearrangements and formation of compound **22**. In all, although the new derivatives did not offer evidence for DHA to VHF photoactivity, we were pleased to see that the new polycyclic system could be regioselectively functionalized, and, as calculations show below, incorporation of a cyano group strongly increases the energy barrier for the VHF to DHA back-reaction, which is particularly relevant in a broader context of solar thermal energy storage systems, albeit the exact structure **20a** is not suited for this purpose.

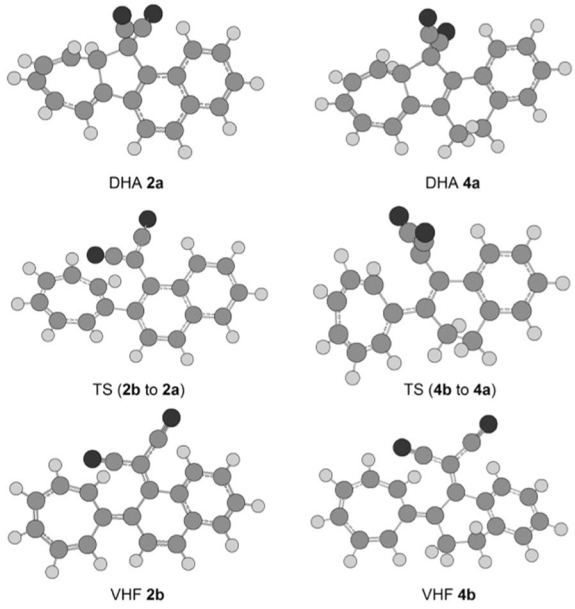

Figure 3. Optimized structures (M06-2X/6-311+G(d)) for the couples **2a**/**2b** and **4a**/**4b** and the transition state (TS) for each of the ring-closure reactions.

Calculations

To understand the thermodynamics and kinetics of the systems involving compounds **2**–**4**, they were subjected to a computational study. Structures were optimized (geometries shown in Figure 3) and energies calculated by using the M06-2X/6-311+G(d) method in vacuum and in three different solvents, cyclohexane (CH), dichloromethane (CH_2Cl_2), and acetonitrile (MeCN; for details, see the Supporting Information).[17] Gibbs free energies and enthalpies of the VHFs relative to those of the DHAs are listed in Table 1. The calculations show a remarkably high energy storage capacity of **2a**/**2b** of 0.38 MJ kg^{-1} (Gibbs free energy) in vacuum (but decreasing slightly with solvent polarity), which is almost four times that of the parent system **1a**/**1b** (0.11 MJ kg^{-1}).[5] Calculations were also performed for the cyano-substituted couple **20a**/**20b**, which gave

Table 1. Calculated Gibbs free energy, enthalpy differences for DHA/VHF couples (M06-2X/6-311+G(d); 298.15 K and 1 atm) and Gibbs free activation energies for VHF to DHA ring-closure reactions (M06-2X/6-311+G(d); 298.15 K and 1 atm).

	$\Delta G_{DHA\rightarrow VHF}$ (top) and $\Delta H_{DHA\rightarrow VHF}$ (bottom) [kJ mol^{-1}/MJ kg^{-1}]			
Couple[a]	Vacuum	CH	CH_2Cl_2	MeCN
2a/2b	107/0.38	103/0.37	94.3/0.34	90.3/0.32
	114/0.40	110/0.39	100.8/0.36	96.9/0.34
3a/3b[a]	−55.1/−0.18	−59.2/−0.19	−64.8/−0.21	−66.1/−0.22
	−47.2/−0.15	−50.9/−0.17	−55.1/−0.18	−56.3/≅0.18
4a/4b	58.5/0.21	56.0/0.20	51.7/0.18	51.0/0.18
	64.7/0.23	62.1/0.22	58.2/0.21	56.8/0.20
20a/20b	110/0.36	106/0.35	102/0.34	101/0.33
	116/0.38	114/0.37	110/0.36	108/0.35
23a/23b	131/0.51	131/0.51	131/0.51	131/0.51
	137/0.54	137/0.54	137/0.54	137/0.54
24a/24b	117/0.43	117/0.43	117/0.43	116/0.43
	125/0.46	124/0.46	124/0.46	123/0.46
NB/QC	65.5/0.71	66.0/0.72	66.7/0.72	66.9/0.73
	64.2/0.70	64.7/0.70	65.4/0.71	65.7/0.71
		$\Delta G_{VHF\rightarrow TS}$ [kJ mol^{-1}]		
Couple	Vacuum	CH	CH_2Cl_2	MeCN
2a/2b	33.5	24.0	17.4	17.1
3a/3b[b]	153	147	141	140
4a/4b	101	95.3	74.8	70.3
20a/20b	48.1	42.4	33.6	30.5
23a/23b	81.5	76.1	68.3	65.8
24a/24b	88.0	82.4	74.1	69.8

[a] VHF **3b** in its s-*trans* conformation. [b] VHF **3b** in its s-*cis* conformation.

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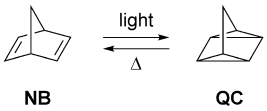
a similar value of 0.36 MJ kg^{-1} in vacuum. The high storage capacity is, however, counterbalanced by a low activation barrier of the VHF to DHA back-reaction. The ring-closure barrier heights are also listed in Table 1. Thus, the Gibbs free activation energy is only 33.5 kJ mol^{-1} in vacuum for the conversion of **2b** into **2a**, whereas it is 119.5 kJ mol^{-1} for the conversion of **1b**.[5] The low back-reaction barrier of **2b** agrees with the ultrafast conversion into **2a** observed experimentally when generating **2b** by a Lewis acid followed by treatment with water. Yet, the barrier is increased significantly for **20b** (48.1 kJ mol^{-1}), albeit still much lower than for the unlocked VHF **1b**. Thus, incorporation of the electron-withdrawing cyano group directly onto the seven-membered ring has a beneficial influence in regard to slowing down the back-reaction. Proceeding to **3a**/**3b**, we see that the situation is reversed. Now, the VHF is in fact more stable than the DHA and the activation energy for the back reaction is significantly higher than that of **1b**. Calculations on the couple **4a**/**4b** reveal that the locked structure itself contributes to increasing the energy storage capacity, which is almost doubled relative to that of the parent system **1a**/**1b**.

The loss/gain in aromaticity accompanying switching of the two benzenoid DHA/VHF systems was further corroborated by Nucleus Independent Chemical Shift (NICS) calculations.[18] NICS(0) values were calculated at the center of the added rings (colored rings in Scheme 1) using CAM-B3LYP/6-311+G(d). DHA **2a** has a negative NICS(0) value of −7.4 ppm, whereas the value turns positive (+1.1 ppm) in VHF **2b**. Oppositely, a more negative NICS value of VHF **3b** (−7.5 ppm) indicates gain of aromaticity relative to DHA **3a** (−2.5 ppm).

To benchmark our energy storage capacities against that of the norbornadiene/quadricyclane couple (NB/QC; Scheme 6), this isomer pair was also subjected to a computational study using the same level as for the DHA/VHF couples. The energies



Scheme 6. Isomerization between norbornadiene (NB) and quadricyclane (QC).

obtained in vacuum, CH, CH_2Cl_2, and MeCN are listed in Table 1. In vacuum, the Gibbs free storage energy is 0.71 MJ kg^{-1}, and the heat release for the back reaction is 0.70 MJ kg^{-1}. Accordingly, the couple **2a**/**2b** has a heat release that is about 57% of that of NB/QC (in vacuum). The latter couple likely represents the upper energy storage limit [MJ kg^{-1}] for photochromic molecules, and the obtained value for **2a**/**2b** is high considering the large molecular weight of this system.

We have previously seen that removing one cyano group in the parent system **1a**/**1b** can lead to both increased energy storage capacity and slower back-reaction.[5b] We therefore subjected compounds **23a**/**23b** and **24a**/**24b** (Figure 4) to a computational study; the results are included in Table 1. The

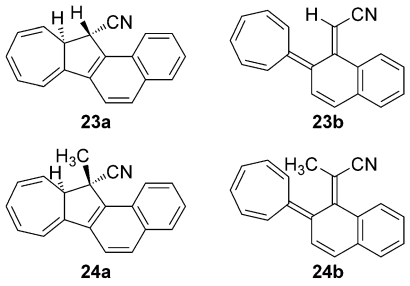


Figure 4. DHA/VHF couples with one cyano group substituted for a hydrogen and methyl, respectively.

numbers relate to the diastereoisomers shown in Figure 4; only small changes were obtained between the various isomers (see the Supporting Information, page S97). Indeed, substituting a cyano group for a hydrogen atom increases the energy storage capacity further (to +0.51 MJ kg^{-1}) and increases the activation energy for the VHF into DHA conversion from +33.5 to +81.5 kJ mol^{-1} (in vacuum). The heat release has now reached 77% of that of the NB/QC couple. By using instead a methyl substituent, the increase in the energy storage capacity is not as significant (+0.43 MJ kg^{-1}), but the activation energy for the back-reaction is conveniently increased further (+88.0 kJ mol^{-1}). It should still occur faster than the back-reaction of **4b** (+100.8 kJ mol^{-1}), for which we found previously an experimental half-life of only 13 ms in MeCN at room temperature.[9] Thus, further modifications are clearly required to slow down the ring-closure reaction further, but the calculations convincingly show how we can indeed fine-tune the properties by minor structural changes—by either removing a cyano group at C-1 or adding one at position C-7 of the DHA core. The modifications may be combined with suitable donor/acceptor functionalization in both the five- and seven-membered rings, which we have previously shown[16] is an important tool for tuning the rate of the VHF to DHA ring-closure reaction.

Conclusions

Efficient synthetic protocols for preparing two DHA-VHF systems were developed based on either loss or gain of aromaticity upon photoisomerization. Future work will seek to modify further the aromatic DHA structure to avoid light-induced sigmatropic rearrangements and to allow storage of the energy in the metastable VHF form for a sufficiently long time. Indeed, our computational study clearly predicts that benzannulation in combination with locking the VHF structure is a strong tool for increasing the energy storage capacity of the DHA/VHF system, providing a value of ca. 0.4 MJ kg^{-1}. Our calculations also show that by removing one cyano group at C-1, we will move further in the right direction, both increasing the energy storage capacity and slowing down the back reaction. However, the back reaction still needs to be retarded by other structural modifications because the calculated energy of activation remains too small. It is in this regard noteworthy that the new

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polycyclic DHA system can be regioselectively functionalized in the seven-membered ring, offering an important tool for tuning the molecular properties. In addition, although not solving the unwanted light-induced rearrangements, our trapping of the VHF species by complexation with a Lewis acid presents an alternative solution to preventing the fast back reaction. Ultimately, we hope that our iterative approach, combining synthesis and quantum-chemical calculations, will allow us to reach closed-cycle molecular energy storage systems that satisfy not only large storage energies but also controllable energy releases. The challenge is to make all the small structural variations work in concert.

Experimental Section

General procedures

All reactions were performed under an inert atmosphere by using either nitrogen with a gas-bubbler or argon with a balloon. All chemicals and solvents were used as received unless otherwise stated. *p*-Toluenesulfonic acid was dried by azeotropic distillation of water using benzene. Benzene and THF were distilled from a Na/benzophenone couple. Acetonitrile and CH_2Cl_2 were purified and dried using activated Al_2O_3 (drying-tower). $CDCl_3$ was purified by passing through activated Al_2O_3. Thin-layer chromatography (TLC) was carried out on commercially available pre-coated plates (silica 60) with fluorescence indicator. Chromatographic purifications were performed on silica (SiO_2) with a pore size of 60 Å and a particle size of 15–40 μm using the dry column vacuum chromatography method, as described previously[15,19] or 40–63 μm using flash column chromatography. Mass spectra were recorded with an ESP-MALDI-FT-ICR spectrometer equipped with a 7 T magnet (prior to the experiments, the instrument was calibrated with NaTFA cluster ions) or a MicrOTOF-QII spectrometer using ESP (calibrated with formic acid). All ^{1}H NMR and ^{13}C APT (attached proton test) NMR spectra were recorded with a 500 MHz instrument equipped with a (non-inverse) cryoprobe (500.1300/125.7578 MHz), with a Varian 300-MHz (300.0787 Hz) instrument with a penta-probe, or Bruker 500-MHz (499.9731/125.7183 MHz) instrument with a broad band-probe. All ^{1}H and ^{13}C chemical shifts are referenced to the residual solvent peak ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; [D$_6$]DMSO: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm; CD_3CN $\delta_H = 1.94$ ppm, $\delta_C = 1.32$ ppm). Elemental analyses were performed at the Department of Chemistry, University of Copenhagen or at London Metropolitan University. All spectroscopic measurements (including photolysis) were performed in a 1-cm path length quartz cuvette. UV/Vis absorption spectra were obtained by scanning the wavelength from 800 to 200 nm. Photoswitching experiments were performed with a 150 W xenon arc lamp equipped with a monochromator; the DHA absorption maximum (lowest energy absorption) for each individual species was chosen as the wavelength of irradiation (line width ±2.5 nm). The thermal back-reaction was performed by heating the sample (cuvette) with a Peltier unit in the UV/Vis spectrophotometer (temperature kept at 60 °C ±0.1 °C) or, at low temperature, in a cryostat (−100 °C to −60 °C ±0.1 °C). Photoswitching experiments of **1a**/**1b** and **3b** were performed in non-deoxygenated solvents as it has been shown that this does not significantly improve stability; experiment with **2a**/**2b** were performed in deoxygenated solvents to rule out oxidative degradation.

X-ray crystal structure analysis

CCDC 1429767 (**2a**) and 1421412 (**3b**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Naphtho[2,1-*a*]azulene-12,12(11a*H*)-dicarbonitrile (2a)

Method 1: To a solution of **8a** (98.9 mg, 240 μmol) in benzene (25 mL), TsOH·H_2O (4.7 mg, 27 μmol, 0.11 equiv) and water (ca. 0.01 mL, 0.05 mmol, 2 equiv) were added, and the mixture was heated to reflux for 2 h (Note: as the desilylation commences, the yellow color strengthens, but after the elimination of water, a decoloration is evident). The resulting slightly yellow solution was diluted with Et_2O (150 mL) and poured into saturated aqueous $NaHCO_3$ (50 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in vacuum. Purification by flash column chromatography (10% EtOAc/heptanes) gave **2a** (47.7 mg, 170 μmol, 71%) as a slightly yellow solid.

Method 2: To a solution of **9a** (95.4 mg, 0.320 mmol) in benzene (25 mL), TsOH·H_2O (6.1 mg, 32 μmol) was added and the reaction mixture was heated to reflux for 2 h. The resulting slightly yellow solution was diluted with Et_2O (150 mL) and poured into saturated aqueous $NaHCO_3$ (50 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (10% EtOAc/heptanes) gave **2a** (60.1 mg, 0.214 mmol, 67%) as a slightly yellow solid. TLC (10% EtOAc/heptanes): $R_f = 0.25$ (becomes brown upon treatment with vanillin and light heating). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.30$ (ddd, $J = 8.4$, 1.2, 0.9 Hz, 1H), 7.94 (d, $J = 8.6$ Hz, 1H), 7.93 (ddd, $J = 8.2$, 1.2, 0.9 Hz, 1H), 7.76 (ddd, $J = 8.4$, 8.1, 1.2 Hz, 1H), 7.62 (ddd, $J = 8.1$, 8.2, 1.2 Hz, 1H), 7.55 (d, $J = 8.6$ Hz, 1H), 6.79–6.71 (m, 2H), 6.67–6.59 (m, 1H), 6.37 (ddd, $J = 10.0$, 6.0, 1.9 Hz, 1H), 5.89 (dd, $J = 10.0$, 4.3 Hz, 1H), 3.82 ppm (dt, $J = 4.3$, 1.9 Hz, 1H) (not all spin-systems paired); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 137.59$, 135.03, 134.66, 133.22, 131.64, 131.55, 131.28, 129.60, 129.10, 128.57, 127.64, 127.61, 122.83, 119.45, 119.19, 117.55, 115.20, 113.24, 51.66, 42.10 ppm; HRMS (ESP$^+$ FT-ICR, added formic acid): *m/z* calcd for $[C_{20}H_{12}N_2Na]^+$ 303.08927 [MNa]$^+$; found 303.08990; $C_{20}H_{12}N_2$ (280.32): calcd C 85.69, H 4.31, N 9.99; found C 85.73, H 4.02, N 9.74.

2-(4-((*tert*-Butyldimethylsilyl)oxy)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (6)

To a mixture of **5** (6.30 g, 22.8 mmol) and malononitrile (3.91 g, 59.3 mmol, 2.6 equiv), AcOH (10.1 mL, 251 mmol, 11 equiv) and HMDS (5.3 mL, 25 mmol, 1.1 equiv) were added and the resulting dark-red to black reaction mixture was stirred and heated at reflux for 10 h. The reaction mixture was diluted with CH_2Cl_2 (400 mL), washed with water (3×100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuum. The crude residue was passed through a plug of silica (50% CH_2Cl_2/ petroleum spirit), which gave **6** (7.18 g, 22.1 mmol, 97%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.16$ (ddd, $J = 7.9$, 1.2, 0.6 Hz, 1H), 7.59 (ddd, $J = 7.5$, 7.6, 1.2 Hz, 1H), 7.51 (m, 1H), 7.44 (ddd, $J = 7.9$, 7.5, 1.3 Hz, 1H), 4.78 (dd, $J = 7.4$, 3.6 Hz, 1H), 3.26 (dt, $J = 18.4$, 6.3 Hz, 1H), 2.95 (ddd, $J = 18.4$, 7.3, 6.1 Hz, 1H), 2.18–1.86 (m, 2H), 0.91 (s, 9H), 0.15 (s, 3H), 0.06 ppm (s, 3H) (not all spin systems could be paired); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 171.87$, 144.44, 133.95, 129.15, 128.34, 127.97, 127.04, 113.81, 113.25, 80.69, 68.66, 30.35, 28.88, 25.85, 18.24, −4.39, −4.57 ppm; HRMS (MALDI$^+$ FT-ICR, dithranol): *m/z* calcd for $[C_{19}H_{24}N_2OSiNa]^+$ 347.15501 [M + Na$^+$]; found 347.15526.

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2-(4-((*tert*-Butyldimethylsilyl)oxy)-2-(cyclohepta-2,4,6-trien-1-yl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (7)

To a stirred suspension of **6** (1.14 g, 3.53 mmol) and mortared tropylium tetrafluoroborate (659 mg, 3.70 mmol, 1.05 equiv) in CH_2Cl_2 (250 mL) at −78 °C, Et_3N (0.52 mL, 3.7 mmol, 1.05 equiv) was added dropwise and the reaction mixture was stirred for 16 h while the temperature was allowed to slowly reach rt. The reaction mixture was poured into saturated aqueous NH_4Cl (100 mL) and the phases were separated. The organic phase was washed with saturated aqueous NH_4Cl (4×100 mL) and the combined aqueous phases were extracted with CH_2Cl_2 (100 mL). The organic extract was washed with saturated aqueous NH_4Cl (100 mL) and combined with the other organic phase. The combined organic phases were dried with $MgSO_4$, filtered and concentrated in vacuo, which gave a ca. 1:3 diastereomeric mixture of **7** (1.44 g, 3.47 mmol, 98%) as a light-yellow foam. A sample was purified for characterization by flash column chromatography (15% EtOAc/heptanes), which gave **7** as a colorless oil. TLC (20% EtOAc/heptanes): R_f = 0.51 and 0.56 ($UV_{254\,nm}$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (br d, J = 8.3 Hz, 1H [minor]), 7.73 (br d, J = 7.8 Hz, 1H [major]), 7.63–7.52 (m, 2H [major/minor]), 7.45–7.39 (m, 1H [major/minor]), 6.70–6.65 (m, 1H [major/minor]), 6.64–6.57 (m, 1H [major/minor]), 6.29–6.22 (m, 2H [major/minor]), 5.24 (dd, J = 9.5, 6.6 Hz, 1H [minor]), 5.20 (dd, J = 9.5, 6.7 Hz, 1H [major]), 5.14–5.08 (m, 1H [major/minor]), 4.89 (dd, J = 6.7, 4.4 Hz, 1H [minor]), 4.66–4.61 (m, 1H [major]), 3.70–3.64 (m, 1H [minor]), 3.47 (ddd, J = 9.3, 7.3, 5.4 Hz, 2H), 2.38–2.27 (m, 1H [major/minor]), 2.18 (dt, J = 13.6, 4.4 Hz, 1H [minor]), 2.11 (dt, J = 9.3, 6.7 Hz, 1H [major]), 1.87 (dt, J = 9.9, 6.6 Hz, 1H [minor]), 1.79 (ddd, J = 13.6, 8.3, 5.4 Hz, 1H [major]), 0.98 (s, 9H [major]), 0.88 (s, 9H [minor]), 0.21 (s, 3H [major]), 0.19 (s, 3H [major]), 0.13 (s, 3H [minor]), −0.02 (s, 3H [minor]) ppm (not all spin-systems paired); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.73 [minor], 175.66 [major], 143.05 [major], 142.91 [minor], 133.38 [major], 133.25 [minor], 131.62 [minor], 131.37 [major], 130.78, 130.07, 129.12, 128.63, 127.89 [minor], 127.84 [major], 127.53, 127.02, 126.99, 126.91, 126.86, 126.85, 125.73, 122.11 [minor], 122.11 [major], 122.00, 121.12, 113.47 [minor], 113.20 [major], 113.18 [minor], 112.81 [major], 83.53 [major], 82.12 [minor], 67.43 [minor], 66.39 [major], 44.28 [major], 42.60 [minor], 41.87 [minor], 39.80 [major], 35.56 [minor], 32.77 [major], 26.02 [major], 25.76 [minor], 18.33 [major], 18.06 [minor], −4.13 [major], −4.36 [minor], −4.59 [minor], −4.77 ppm [major] (one signal missing due to overlap, five minor aliphatic peaks dismissed as grease); HRMS (MALDI$^+$ FT-ICR, dithranol): m/z calcd for $[C_{26}H_{31}N_2OSi]^+$ 415.22002 $[M+H]^+$; found 415.22023.

5-((*tert*-Butyldimethylsilyl)oxy)-5,6-dihydronaphtho[2,1-*a*]azulene-12,12(11a*H*)-dicarbonitrile (8a)

To a stirred solution of **7** (1.23 g, 2.96 mmol) in anhydrous MeCN (150 mL) at −40 °C, $NOBF_4$ (719 mg, 6.16 mmol, 2.08 equiv) was added, and the reaction mixture was stirred for 2 h (full conversion according to TLC analysis). The resulting yellow reaction mixture was diluted with cold CH_2Cl_2 (150 mL) and at −40 °C, a solution of pyridine (0.50 mL, 6.2 mmol, 2.1 equiv) in CH_2Cl_2 (50 mL) was added. The temperature was allowed to slowly reach −20 °C over 2 h and the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The combined extracts were dried with Na_2SO_4, filtered, and concentrated in vacuum. Purification by dry column vacuum chromatography (0–100 $CHCl_3$/heptanes, 10% increments, 40 mL fractions) followed by flash column chromatography (10% EtOAc/heptanes) gave a ca. 1:3 diastereomeric mixture of **8a** (679 mg, 1.65 mmol, 56%) as a dark-yellow oil or low-melting solid. TLC (10% EtOAc/heptanes): R_f = 0.38 (two closely running spots, becomes brown upon treatment with vanillin and light heating). TLC (20% EtOAc/heptanes): R_f = 0.53 (yellow); m.p. 111–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 1H [major/minor]), 7.53–7.48 (m, 1H [major/minor]), 7.45–7.37 (m, 2H [major/minor]), 6.64 (dd, J = 11.3, 6.3 Hz, 1H [minor]), 6.60 (dd, J = 11.3, 6.3 Hz, 1H [major]), 6.52 (dd, J = 11.3, 6.2 Hz, 1H [minor]), 6.49 (dd, J = 11.3, 6.2 Hz, 1H [major]), 6.34–6.29 (m, 1H [major/minor]), 6.28 (br d, J = 6.2 Hz, 1H), 5.86 (dd, J = 10.2, 3.9 Hz, 1H [major]), 5.84 (dd, J = 10.2, 3.9 Hz, 1H [minor]), 5.03–4.97 (m, 1H), 3.82 (dt, J = 3.9, 2.0 Hz, 1H [major]), 3.76 (dt, J = 3.9, 2.0 Hz, 1H [minor]), 2.76–2.59 (m, 2H [major/minor]), 0.94 (s, 9H [minor]), 0.91 (s, 9H [major]), 0.14 (s, 3H [minor]), 0.13 (s, 3H [major]), 0.08 (s, 3H [minor]), 0.04 ppm (s, 3H [major]); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.71, 141.22, 139.45, 139.39, 138.87, 138.46, 133.68, 133.17, 131.19, 131.13, 131.09, 130.64, 129.76, 129.70, 127.88, 127.55, 127.55, 127.41, 126.54, 126.31, 123.37, 123.36, 119.92, 119.89, 118.50, 117.96, 115.07, 115.06, 112.86, 112.72, 68.66, 68.63, 51.41, 51.32, 42.84, 42.47, 31.66, 31.43, 25.95, 25.90, 18.25, 18.22, −4.32, −4.35, −4.61, −4.65 ppm; HRMS (ESP$^+$ FT-ICR, added formic acid): m/z calcd for $[C_{26}H_{28}N_2OSiNa]^+$ 435.18631 $[MNa]^+$; found 435.18712.

5-Hydroxy-5,6-dihydronaphtho[2,1-*a*]azulene-12,12(11a*H*)-dicarbonitrile (9a)

To a solution of **9a** (340 mg, 824 μmol) in THF (50 mL), AcOH (0.47 mL, 8.24 mmol, 10 equiv) and a 1 M solution of TBAF (1.65 mL, 1.65 mmol, 2 equiv) in THF were added successively and the reaction mixture was heated to reflux for 16 h. The reaction mixture was diluted with Et_2O (100 mL), washed with water (3× 50 mL) and saturated aqueous $NaHCO_3$ (50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuum. Purification by flash column chromatography (CH_2Cl_2) gave **9a** (226 mg, 0.758 mmol, 92%) as a yellow glass. M.p. 164–165 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (t, J = 7.7 Hz, 1H [major/minor]), 7.52–7.48 (m, 2H [major/minor]), 7.44–7.39 (m, 1H [major/minor]), 6.64–6.59 (m, 1H [major/minor]), 6.54–6.48 (m, 1H [major/minor]), 6.35–6.28 (m, 2H [major/minor]), 5.88 (dd, J = 10.2, 3.8 Hz, 1H [minor]), 5.83 (dd, J = 10.1, 3.9 Hz, 1H [major]), 4.98–4.94 (m, 1H [major/minor]), 3.82 (dt, J = 3.8, 1.9 Hz, 1H [minor]), 3.78 (dt, J = 3.9, 1.8 Hz, 1H [major]), 2.93–2.68 (m, 2H [major/minor]), 1.84 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.12 [minor], 140.93 [major], 138.77 [minor], 138.45 [major], 137.78 [minor], 137.55 [major], 132.63 [major], 132.43 [minor], 131.40 [major], 131.25 [minor], 130.94 [major], 130.78 [minor], 129.94 [minor], 129.90 [major], 129.59 [major], 129.53 [minor], 128.33 [major], 128.08 [minor], 127.90 [minor], 127.66 [major], 127.27 [major], 127.26 [minor], 123.79 [minor], 123.76 [major], 120.00 [minor], 119.67 [major], 118.93 [minor], 118.51 [major], 115.10 [major], 114.87 [minor], 112.78 [minor], 112.74 [major], 67.64 [minor], 67.45 [major], 51.26 [major], 51.19 [minor], 42.82 [minor], 42.58 [major], 30.58 [major], 30.43 [minor] ppm; HRMS (ESP$^+$ FT-ICR, added formic acid): m/z calcd for $[C_{20}H_{14}N_2ONa]^+$ 321.09983 $[MNa]^+$; found 321.10041.

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

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FULL PAPER

Energy Storage and Conversion

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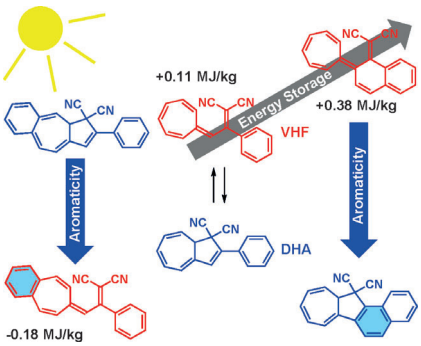
Aromaticity-Controlled Energy Storage Capacity of the Dihydroazulene-Vinylheptafulvene Photochromic System



Full of energy: An increase in the solar energy storage capacity of the dihydroazulene (DHA)–vinylheptafulvene (VHF) photo/thermoswitch is achieved by fusing a benzene ring to the DHA isomer (see figure). In contrast, the relative stability is interchanged by benzannulation of the VHF isomer.

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