Pure Appl. Chem., Vol. 82, No. 4, pp. 843–852, 2010.
doi:10.1351/PAC-CON-09-07-08

New routes to functionalized dihydroazulene photoswitches*

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Abstract: Molecular photoswiches are important for the development of advanced materials and molecular electronics devices. The dihydroazulene (DHA) is a particularly attractive molecule as it undergoes a light-induced ring opening to a vinylheptafulvene (VHF) isomer with altered optical properties. While functionalization of the five-membered ring of DHA has been possible for the last 25 years, this was not the case for the seven-membered ring. This article summarizes our synthetic efforts in achieving this goal. Incorporation of an alkyne at C-7 was accomplished by (i) regioselective bromination of DHA, followed by (ii) elimination of HBr, and (iii) Pd-catalyzed cross-coupling with triisopropylsilylacetylene. Light-induced ring opening of this DHA followed by thermal ring closure provided a mixture of 6- and 7-substituted DHAs with different absorption characteristics. The isomer ratio was controlled by the wavelength of irradiation and the solvent polarity. The dibromide formed in the initial step served as a precursor for a 3-bromo-functionalized azulene that was employed as a building block for acetylenic scaffolding. Incorporation of a dithiafulvene (DTF) unit at the five-membered ring of DHA resulted in a significant red-shift in the longest-wavelength absorption and consequently a lowering of the energy required for ring opening. Incorporation of a redox-active tetrathiafulvalene (TTF) unit allowed for redox-controlled photoswitching.

Keywords: acetylenic scaffolding; azulenes; cross-coupling; dihydroazulenes; redox-controlled photoswitching; tetrathiafulvalene; vinylheptafulvene.

INTRODUCTION

Molecular switches are systems possessing at least two reversibly interconvertible molecular states and are important within the field of molecular electronics and advanced molecular and supramolecular materials [1–3]. Azobenzenes and dithienylethenes are examples of photoswitches that have found such wide applications [4–8]. The exploitation of these molecules has benefitted from ready access to derivatives in which both rings are functionalized with suitable groups, such as electron donor and acceptor units (light-controlled push–pull chromophores), anchoring groups for adhesion to electrodes, or groups that provide liquid crystallinity.

Pure Appl. Chem.* **82, 757–1063 (2010). An issue of reviews and research papers based on lectures presented at the 13th International Symposium on Novel Aromatic Compounds (ISNA-13), 19–24 July 2009, Luxembourg City, Luxembourg on the theme of aromaticity.
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The dihydroazulene/vinylheptafulvene (DHA/VHF) system incorporating two cyano groups at C-1 represents another interesting two-state switch (Fig. 1). Thus, DHA undergoes a photochemically induced 10-electron retro-electrocyclization to VHF that in turn undergoes a thermally assisted ring closure back to DHA [9–11]. The initially formed s-*cis*-VHF is in equilibrium with the generally more stable s-*trans*-VHF. The large structural differences between the DHA and VHF isomers renders the system particularly attractive for molecular electronics. Thus, the conjugation pathway between a substituent at position 2 to one at position 6 changes from being linearly conjugated to cross-conjugated upon converting DHA to VHF (Fig. 1). Several studies [12] have revealed that π-electron delocalization is less efficient in a cross-conjugated molecule than in a linearly conjugated one, and, consequently, the single-molecule conductance is expected to be altered upon conversion of DHA to VHF. For exploitation of the DHA/VHF system as a light-controlled wire for molecular electronics, it is highly desirable to attach two handles to the system, one in each ring in order to allow it to span two electrodes. The pioneering work by Daub and co-workers [9–11] has allowed ready incorporation of a variety of aryl groups at the five-membered ring of DHA. The aryl group is conveniently included early in the synthesis before the final DHA is formed. The DHA/VHF system **1/2** (Fig. 1) presents one such example that has been investigated in detail [10].

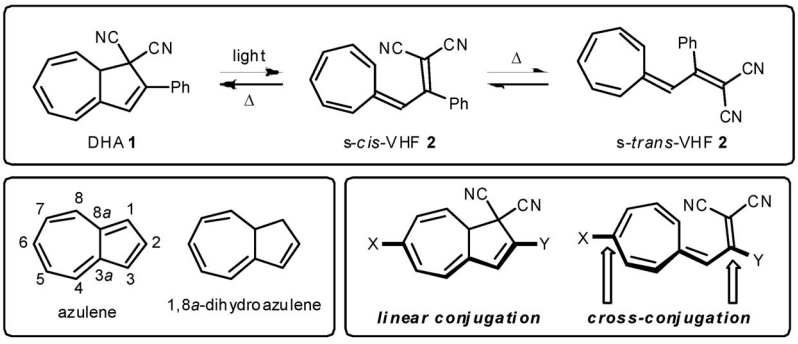


Fig. 1 DHA **1** can be opened by light to the VHF **2** [9–11]. This ring opening is accompanied by a change in conjugation across the molecule. Substituents Y and X at positions 2 and 6, respectively, are connected by a linear conjugation pathway in the DHA isomer, while the same trajectory has two cross-conjugated crossing points in the VHF isomer (indicated by the arrows).

Our focus was to develop new derivatives of **1** functionalized in the seven-membered ring. These derivatives should sustain the inherent DHA/VHF switching ability. In this respect, it deserves mention that the structure **3** in which both rings of DHA **1** are fused to a phenalene was previously reported by Sugihara et al. [13] (Fig. 2). Prinzbach and Herr [14] prepared DHA **4** incorporating ester substituents at C-4 and C-5. This compound was found to undergo a light-induced 1,3-sigmatropic shift to the isomer **5** rather than DHA/VHF switching.

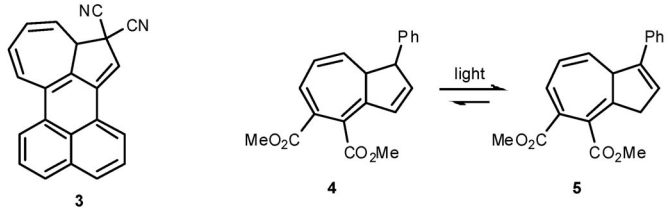


Fig. 2 Examples of DHAs substituted in the seven-membered ring [13,14]. The DHA-VHF isomerization was not reported for these compounds; instead compound **4** underwent a light-induced 1,3-sigmatropic shift.

In addition, we are interested in developing DHAs for multi-mode switching by incorporation of redox-active groups. Daub and co-workers [15–17] investigated redox-controlled switching of DHAs functionalized by ferrocene, anthraquinone, or heteroaryl groups in the five-membered ring. Interestingly, the neutral ferrocene-DHA conjugate was not photoactive, while instead the cation underwent ring opening upon irradiation [15]. In another approach, Diederich and co-workers [18] combined the DHA/VHF system with a *Z/E*-isomerizable tetraethynylethene and a proton sensitive aniline, providing a three-way chromophoric switch. We became interested in investigating the switching ability of DHAs incorporating dithiafulvene (DTF) and tetrathiafulvalene (TTF) electron donors (Fig. 3). TTF is oxidized in two reversible one-electron steps and has for this reason been widely explored in materials and supramolecular chemistry [19–22]. The resulting TTF dication consists of two aromatic 1,3-dithiolium rings. Each of these rings is characterized by a nucleus independent chemical shift index of $NICS(1)_{zz}$ = –23.96 ppm, and the rings are according to this parameter slightly less aromatic than the parent 1,3-dithiolium for which $NICS(1)_{zz}$ = –28.35 ppm [23]. Efficient synthetic protocols for preparing the acetylenic DTF and TTF derivatives **6** [24,25] and **7** [26] have been developed. These compounds are convenient building blocks for incorporating DTF and TTF into DHAs using transition-metal-catalyzed cross-coupling reactions.

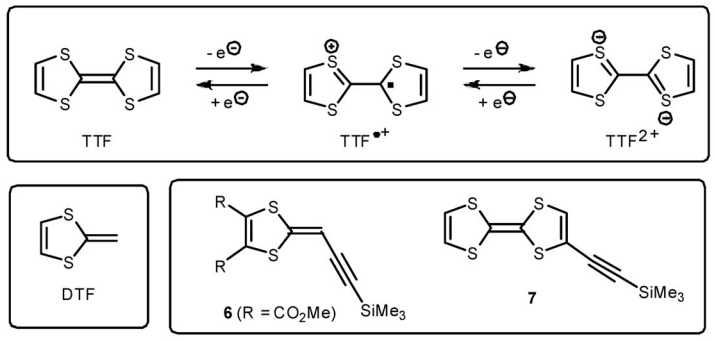


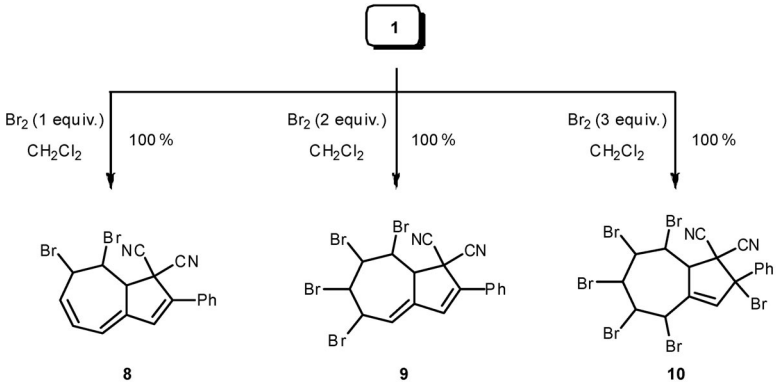
Fig. 3 TTF and DTF electron donors. TTF undergoes two reversible one-electron oxidations. Both the DTF and TTF can be functionalized with an acetylenic unit, and the resulting compounds (**6** and **7**) can be used as building blocks for acetylenic scaffolding [24–26].

CHEMISTRY OF THE SEVEN-MEMBERED RING OF DIHYDROAZULENE

Regioselective functionalization of the seven-membered ring

As a first objective, we set out to incorporate a substituent (a silyl-protected alkyne) in the seven-membered ring from the very beginning of the DHA synthesis. This approach turned out, however, to be unsuccessful. Instead, we decided to employ the readily accessible DHA **1** as a precursor to new DHAs. Thus, functionalization of DHA with a halide should allow for subsequent introduction of an alkyne via a Sonogashira cross-coupling reaction [27]. An alkyne substituent is a particularly attractive functional group as it offers the possibility for further acetylenic scaffolding [28–30].

Based on calculations, we envisioned that it should be possible to regioselectively brominate DHA **1** at positions 7 and 8. Thus, Br^+ adds preferably at C-8, generating a resonance-stabilized carbocation (rather than a cyclic bromonium ion). Indeed, treatment of **1** with one molar equivalent of bromine furnished quantitatively the dibromide **8** (Scheme 1) [31]. Furthermore, treatment with two molar equivalents of bromine selectively furnished the tetrabromide **9**, while treatment with three (or more) equivalents furnished the hexabromide **10** [32]. The identity of both **8** and **10** were confirmed by X-ray crystal structure analysis (Fig. 4).



Scheme 1 Regioselective brominations of DHA **1**.

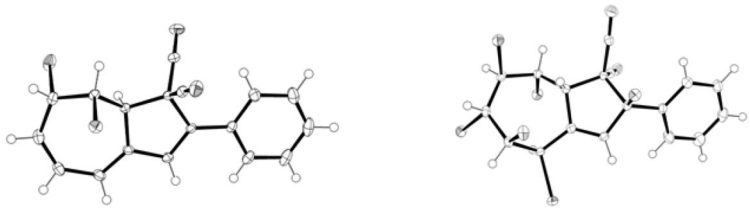
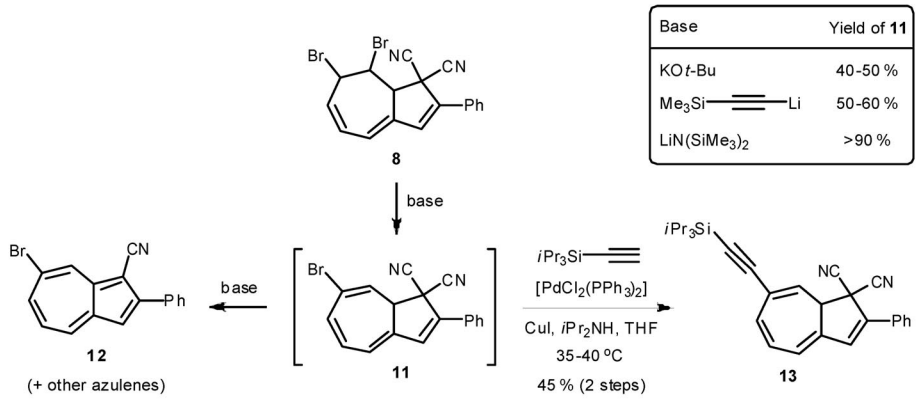


Fig. 4 X-ray crystal structures of **8** (left) and **10** (right) reproduced with permission from ref. [32]. Copyright © Wiley-VCH Verlag GmbH & Co. KGaA.

Elimination of HBr upon treatment with strong base turned out to be more difficult as azulenes were often formed as the major products. However, treating dibromide **8** with ca. 3 molar equivalents of lithium acetylide, generated from trimethylsilylacetylene and butyllithium, at low temperature produced selectively DHA **11** with a bromo-substituent at position 7 (Scheme 2) [32], presumably via an E1cB mechanism. Highest yields (50–60 %, based on ^{1}H NMR spectroscopic analysis) were obtained by adding lithium acetylide in three subsequent steps. Isolation of **11** was possible by column chromatography, but substantial decomposition could not be avoided. Both **1**, 1-cyano-2-phenylazulene as well as other azulenes were formed as by-products. Treatment with 1 molar equiv of $LiN(SiMe_3)_2$ gave, however, **11** in a yield of >90 % (according to ^{1}H NMR spectroscopy). Bases such as pyridine, DBU,



Scheme 2 Regioselective elimination followed by a Sonogashira cross-coupling reaction.

Et_3N or Hünig's base were all unable to generate the desired product, while 2.5 molar equiv of KO*t*-Bu (freshly sublimed) furnished **11** in a yield of 40–50 %. A larger excess of KO*t*-Bu (3.6 molar equiv) resulted in a mixture of azulenes from which the 7-bromoazulene **12** was isolated pure (9 %). Crude "bromo-DHA" **11** was subjected to a Sonogashira cross-coupling reaction with triisopropylsilylacetylene to furnish the acetylenic DHA **13** in an overall yield of 45 % (2 steps) after column chromatography (Scheme 2). The structure was confirmed by X-ray crystallography (Fig. 5).

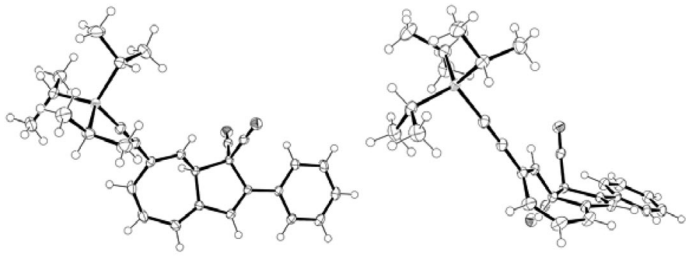


Fig. 5 X-ray crystal structure of **13** (two views shown) reproduced with permission from ref. [32]. Copyright © Wiley-VCH Verlag GmbH & Co. KGaA.

We have recently prepared a related compound with a trimethylsilylethynyl substituent at C-7. Preliminary experiments reveal that this compound is desilylated quantitatively with tetrabutyl ammonium fluoride in THF/MeOH in the presence of acetic acid. The acid is required in order to avoid elimination reactions furnishing azulenes.

Light–heat cycles: Generation of a new regioisomer

Compound **13** exhibited a longest-wavelength absorption maximum of 355 nm [32], which is similar to that of DHA **1** [10]. This similarity in absorption characteristics is explained by the lack of coplanarity between the alkyne unit and the major entity of the DHA unit, as revealed by the X-ray crystal structure (Fig. 5).

By irradiation of **13** in MeCN with 353-nm light, the DHA was converted to a VHF with a characteristic absorption at 477 nm (Fig. 6) [32]. The conversion was complete within the same time needed to convert DHA **1** into VHF **2**, which indicates that the quantum yield for converting **13** is similar to that of **1** ($\phi_{\text{DHA-VHF}} \sim 0.55$ [10]). The thermal VHF-DHA back-reaction proceeded somewhat slower, but more interestingly the resulting DHA absorption was red-shifted to 376 nm, indicating that a new DHA had formed. In order to identify the product formed after this light–heat cycle, the photolysis and thermal back-reaction were performed in CD_3CN, and the mixture was investigated by ^{1}H NMR spectroscopy. This study revealed that the two VHFs **14** and **15** (*Z*/*E*-isomers, Scheme 3) were formed during photolysis of **13** as judged by two sets of $i\text{Pr}_3$ resonances and overlapping resonances in the aromatic region. These two VHFs were thermally converted into DHAs **13** and **16** in a ratio of 1:2. The two DHAs are readily distinguished by ^{1}H NMR spectroscopy, and a ^{1}H-^{1}H COSY spectrum confirmed substitution at C-6 in compound **16**. Repeated ring-opening/closure cycles did not change the ratio between these two DHA regioisomers. The absorption maximum of **16** is estimated to ca. 381 nm by subtracting the absorption spectrum of **13** from that of the mixture of **13** and **16**. This red-shifted absorption is explained by a larger, coplanar conjugated system after moving the alkyne unit to C-6. As DHA **16** has a molar absorptivity at 430 nm that is significantly larger than that of DHA **13**, we reckoned that it should be possible to enhance the 7-isomer by irradiating the mixture at this wavelength. Indeed, this resulted in a ratio of regioisomers (**13**/**16**) of ca. 5.5:4.5 (after three light–heat cycles). In principle, additional cycles should ultimately change the ratio completely in favor of **13**. The isomerization reaction

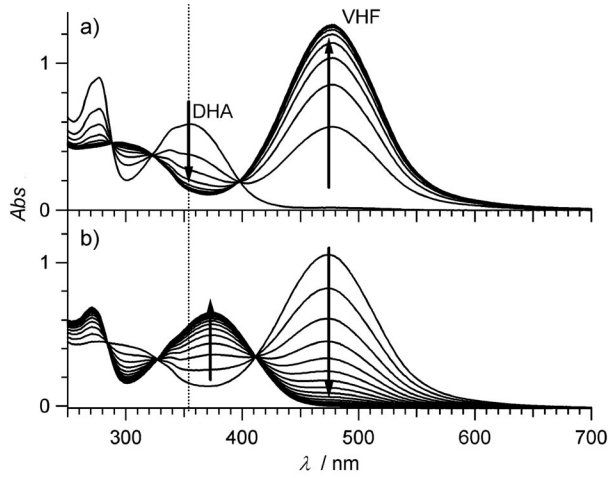
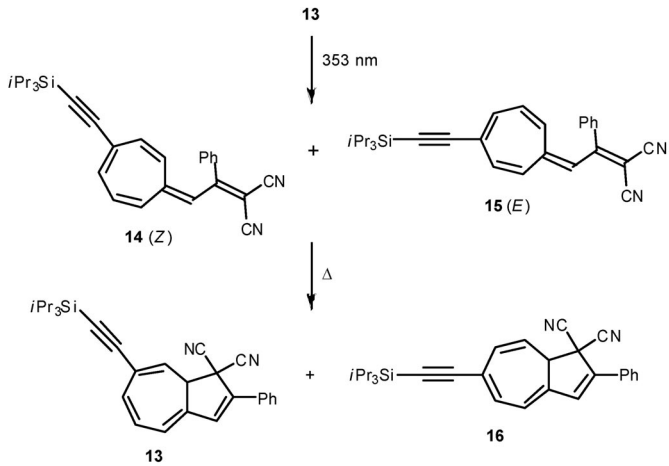


Fig. 6 (a) Irradiation of DHA **13** in MeCN with 353-nm light during 90 s (10-s steps). While the DHA absorption is decreasing, a new absorption band characteristic of VHF is emerging. (b) Thermal back-reaction of VHF into DHA monitored at 70 °C, 2-min steps. The DHA absorption is red-shifted after one cycle due to formation of the isomer **16** [32]. Copyright © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

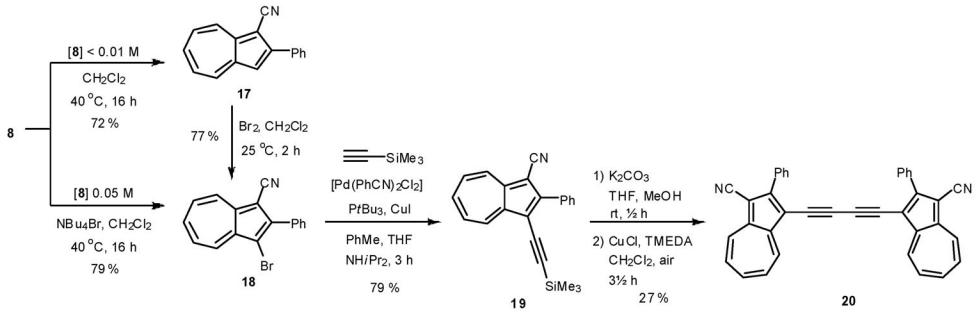


Scheme 3 Irradiation of DHA **13** provides two isomeric VHFs that are thermally converted to the original DHA and a regioisomer.

is also strongly solvent-dependent. Thus, subjecting **13** to light–heat cycles in cyclohexane did not result in formation of **16**, but regeneration of **13**. The isomerization presumably proceeds via a zwitterionic VHF that is characterized by free rotation about the exocyclic fulvene bond.

DHAs as precursors for functionalized azulenes

As mentioned above, 10π-aromatic azulene chromophores are readily formed from the dibromide **8**. In fact, when a 0.05-M solution of **8** in CH_2Cl_2 was left overnight at 40 °C, it was converted to a blue–violet mixture of the two azulenes **17** and **18** formed in a ratio of 4:7 and in a total yield of 61 % (Scheme 4) [31]. Heating **8** in the presence of one molar equivalent of bromide (Bu_4NBr) gave solely compound **18** in a yield of 79 %. Yet, running the reaction under more dilute conditions (0.009 M) and



Scheme 4 Synthesis of functionalized azulenes starting from the dibromide **8**.

in the absence of Bu_4NBr produced solely the cyanoazulene **17** in a yield of 72 %. While exploitation of 1-cyanoazulene as a precursor for 1-bromo-3-cyanoazulene was previously discarded [33], we found that treatment of azulene **17** with a small excess of Br_2 in CH_2Cl_2 resulted in clean conversion to the bromide **18** (Scheme 4) [31].

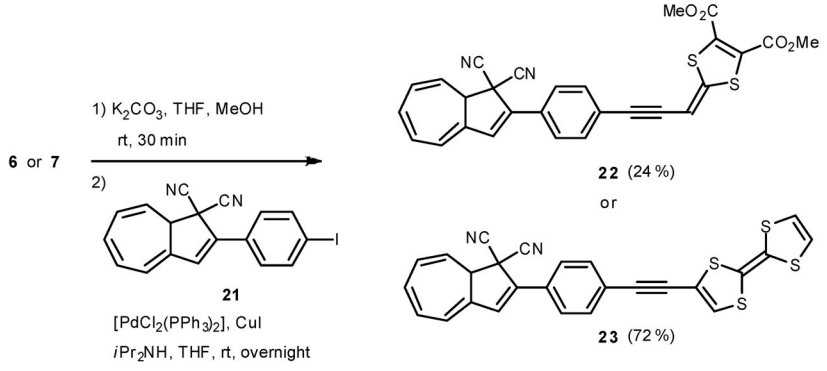
The bromide **18** was subjected to a Sonogashira cross-coupling reaction with trimethylsilylacetylene employing the catalyst system of Hundertmark et al. [34] (Scheme 4). The product **19** was desilylated with K_2CO_3 in MeOH/THF, and the terminal alkyne intermediate was then subjected to an oxidative homo-coupling reaction to give the azulene dimer **20** [31].

INCORPORATION OF REDOX-ACTIVE UNITS

Functionalization of the five-membered ring with DTF and TTF

TTF is a good electron donor, and the reversible switching between its three redox states has been exploited in a large selection of redox-controlled bi- or tri-stable molecular switches as elegantly demonstrated by Stoddart and co-workers [1]. The DTF unit also possesses electron donor capabilities, but is harder to oxidize. Despite this diminished donor strength, DTF has the potential of influencing more strongly the properties of a conjugated π-system via its direct attachment to the exocyclic fulvene carbon atom rather than to a ring carbon atom in the dithiole ring.

Sonogashira cross-coupling reactions between the DHA-iodide **21** [18] and each of the two alkynes **6** and **7** (after desilylation) provided DTF- and TTF-functionalized DHAs **22** [35] and **23** [36], respectively (Scheme 5). The yield of **22** was rather low, but we have often, for unknown reasons, experienced low yields when employing the terminal alkyne of **6** in cross-coupling reactions [37,38].



Scheme 5 Incorporation of redox-active DTF and TTF units.

Redox-controlled photoswitching

DTF-DHA **22** has its first absorption maximum at 407 nm [35], which corresponds to a red-shift of 57 nm relative to the parent phenyl-substituted DHA **1** (λ_{max} 350 nm [10]). Thus, the DTF donor unit exerts a strong influence on the DHA system. The neutral DTF-DHA underwent photoswitching at low energy with quantum yields of 1.8, 1.2, 0.7, 0.08, and 0.03 % for light at 360, 380, 400, 420, and 440 nm, respectively. Unfortunately, it was, however, not possible to oxidize the compound reversibly.

Instead, we turned to the TTF-DHA **23**. First, we note that its absorption is red-shifted by 23 nm relative to that of the parent Ph-substituted DHA, i.e., as expected a smaller red-shift than that experienced by **22** [36]. Irradiation at 375 nm resulted in ring opening (with a quantum yield of ca. 2 %), and the ring-opened VHF underwent smoothly thermal back-reaction to the DHA. Cyclic voltammetry (CV) of **23** in MeCN revealed two reversible TTF oxidations at half-wave potentials of +0.05 and +0.40 V vs. Fc^+/Fc and an irreversible DHA oxidation at +1.17 V vs. Fc^+/Fc. Despite the reversible behavior in the CV experiment, formation of the dication was only semi-reversible in the spectroelectrochemical experiment; thus, less than 50 % of the dication was returned to the radical cation upon reduction. Therefore, we limited the photoswitching studies to $\mathbf{23}^{\bullet+}$ in comparison to **23**. Interestingly, we found that after the same period of irradiation, considerably less of the DHA was converted to VHF for the cationic species than for the neutral one (Fig. 7). Thus, the efficiency of light-induced ring opening of $\mathbf{23}^{\bullet+}$ was diminished by more than a factor of 2 relative to that of neutral **23**. The switching was accompanied by a small decrease of the characteristic $TTF^{\bullet+}$ absorption band at ca. 621 nm, while high-energy bands characteristic for the neutral species were increasing in intensity. This observation may signal that light-induced electron transfer from the excited DHA (excitation energy of 3.3 eV) to the TTF radical cation is offering a de-excitation pathway that could account for the reduced photoswitching ability of $\mathbf{23}^{\bullet+}$. From the electrochemical data, this electron transfer is favorable by more than 2 eV. The true mechanism still needs, however, to be elucidated.

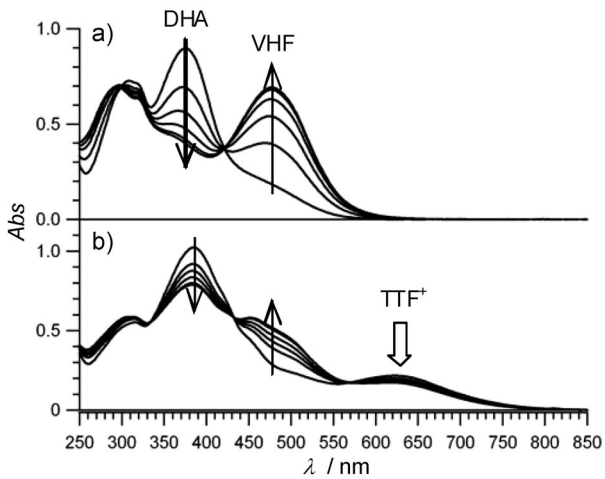


Fig. 7 UV–vis spectra recorded during irradiation of (a) **23** and (b) $\mathbf{23}^{\bullet+}$ at 375 nm in MeCN. The spectra were recorded over a period of 22 min (with intervals of 4 × 5 min, and then 2 min). The presence of 0.1 M Bu_4NPF_6 is required in the electrochemical formation of $\mathbf{23}^{\bullet+}$, but was for comparison also added to the solution of **23** for the spectra shown [36].

CONCLUSIONS

In conclusion, we have developed an efficient synthetic protocol for functionalizing the seven-membered ring of the DHA photoswitch with a silyl-protected alkyne unit. Subjection of this DHA to a light–heat cycle resulted in formation of a new DHA regioisomer exhibiting a red-shifted absorption maximum, and hence representing an additional photochromic state of the system. Current work is focused on employing the DHA as a module for further acetylenic scaffolding; by suitable functionalization we may tune the absorption characteristics of the two DHA regioisomers and move their absorption maxima further apart. In addition, we would like to employ the DHA/VHF system as a light-controlled switch for molecular electronics after incorporation of two suitable end-groups that can be adhered to electrodes. Functionalization of the seven-membered ring is the first step toward this goal. The synthetic protocol relies on ready access to the dibromide **8**, generated by regioselective bromination of DHA **1**, and this compound turned out as well to be a useful precursor for bromo-substituted azulenes. Tetra- and hexabromides were also readily prepared from **1**, and we are currently exploring the chemistry of these compounds; in particular, the possibility to control stepwise elimination reactions. Finally, we have developed an electrochemically controlled DHA/VHF switch incorporating a redox-active TTF unit. The photoswitching occured more than twice as efficiently for the neutral species as for the radical cation species. The wide applicability of TTF in both supramolecular and materials chemistry [19–22], in particular its ability to form charge-transfer complexes with electron acceptors, provides the scope for future development of such switches in a supramolecular context. Along with our control of the substitution pattern of the seven-membered ring, many structures await to be synthesized and investigated. There seems to be a lot of new chemistry to be discovered.

ACKNOWLEDGMENTS

The Danish Research Agency is gratefully acknowledged for supporting this work (Grants #2111-04-0018, #272-08-0540, #272-09-0043).

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