DOI: 10.1002/ejoc.200900041

Redox-Controlled Dihydroazulene-Vinylheptafulvene Photoswitch Incorporating Tetrathiafulvalene

Michael Åxman Petersen,[a] Asbjørn Sune Andersson,[a] Kristine Kilså,*[a] and Mogens Brøndsted Nielsen*[a]

Keywords: Dihydroazulene / Electrocyclic reactions / Photoswitches / Redox chemistry / Tetrathiafulvalene / Photochemistry

A derivative of dihydroazulene (DHA) incorporating the redox-active unit tetrathiafulvalene (TTF) was prepared and investigated for its ability to undergo light-induced conversion to the vinylheptafulvene (VHF) isomer. The absorption properties of the oxidized species were investigated by spectroelectrochemistry. Photoswitching was investigated as a function of the redox-state of the TTF unit, i.e., as neutral or as radical cation, and it was found that photoswitching occurred more than twice as efficiently for the neutral species as for the radical cation species, while the thermal back reaction was unaffected. In addition, we have found that the TTF–DHA conjugate is readily converted to an azulene–TTF donor–acceptor conjugate upon treatment with strong base.

Introduction

Molecular switches are systems that possess at least two reversibly interconvertible molecular states.[1] Photoresponsive systems are of particular interest because the use of light as an external stimulus for the interconversion of two states allows for rapid and clean processes.[2] The dihydroazulene/vinylheptafulvene (DHA/VHF) system, first reported by Daub[3] in 1984 represents such a photochromic system (Figure 1). The photochromism is based on two different types of electrocyclic reactions: a photochemically induced ring-opening reaction of DHA to the metastable VHF followed by a thermally assisted ring closure of VHF to DHA.[4] Multi-mode switching can be realized by incorporation of redox-active groups (as R in Figure 1). Thus, Daub and co-workers[5] investigated redox-controlled switching of DHAs functionalized by ferrocene, anthraquinone, or heteroaryl groups. Interestingly, the neutral ferrocene–DHA conjugate was not photoactive, while instead the cation underwent ring opening upon irradiation.[5a] In another approach, Diederich and co-workers[6] combined the DHA/VHF system with a (Z/E)-isomerizable tetraethynylethene and a proton-sensitive aniline, providing a three-way chromophoric switch.

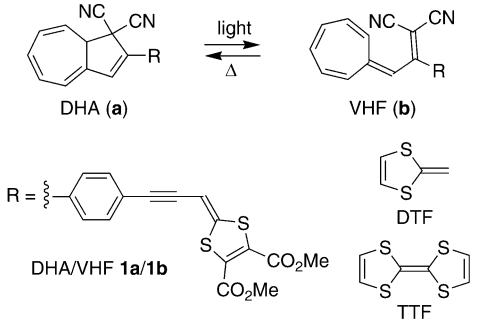


Figure 1. The dihydroazulene/vinylheptafulvene photochromic system.

We became interested in investigating the switching ability of DHAs incorporating the two-electron donor tetrathiafulvalene (TTF, Figure 1). In an earlier approach, we had incorporated the dithiafulvene (DTF) unit into a DHA/VHF switch (**1a**/**1b**),[7] which resulted in a significant redshift of the DHA absorption. However, redox-controlled switching was abandoned as the DTF unit underwent irreversible oxidation. The reversible electrochemistry of the parent TTF makes it a more attractive unit in DHA conjugates for multi-mode switching.[8]

Results and Discussion

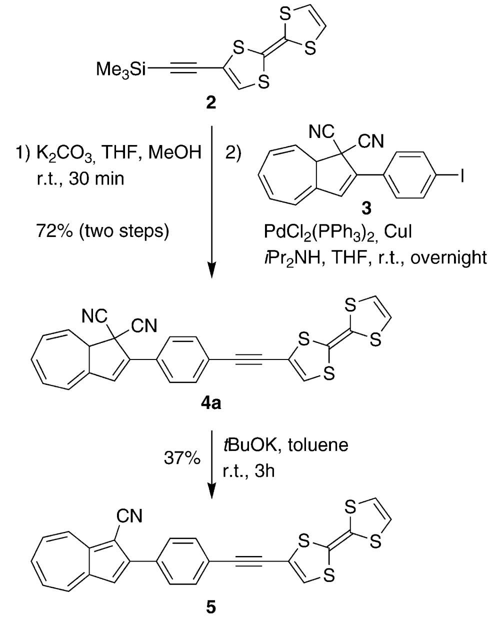
The TTF unit was attached to the DHA moiety according to Scheme 1. First, the ethynyl–TTF **2**[9] was desilylated using K_2CO_3 in MeOH/THF, and the resulting terminal alkyne was then subjected to a Pd-catalyzed cross-coupling reaction with the iodide **3**[6] to afford the TTF–DHA **4a** in a yield of 72%. Further, we note that treatment of **4a** with

---

[a] Department of Chemistry, University of Copenhagen,
Universitetsparken 5, 2100 Copenhagen Ø, Denmark
E-mail: kkj@nano.ku.dk
mbn@kiku.dk

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

a strong base (KO*t*Bu) results in the elimination of HCN to furnish azulene **5**, which is a strong chromophore with absorptions at λ_{max} 332, 387, and ca. 466 nm.



Scheme 1.

The frontier orbitals of **4a** were calculated at the B3LYP/6-31+G(d) level (after geometry optimization at this level) using the Gaussian 03 program package[10] and are shown in Figure 2. While the HOMO is mainly situated at the TTF unit, both the HOMO-1 and LUMO are delocalized over the DHA, the $C_6H_4C{\equiv}C$ linker, and some part of the TTF unit. The computations clearly indicate that the DHA and TTF units are not independent.

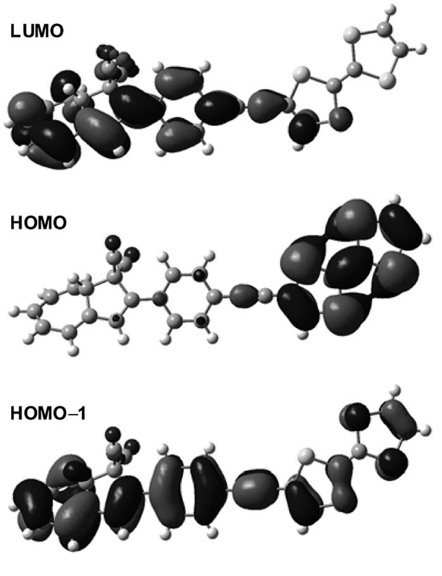


Figure 2. Frontier orbitals of **4a** [B3LYP/6-31+G(d)].

Compound **4a** exhibits an absorption at 373 nm in MeCN (Figure 3, a) characteristic for DHA compounds, but the absorption is red-shifted by 23 nm relative to that of the parent Ph-substituted DHA (1,1-dicyano-2-phenyl-1,8a-dihydroazulene).[11] This transition is presumably a HOMO-1 to LUMO transition for **4a** (Figure 2). Upon irradiating a sample of **4a** (thoroughly degassed with Ar to avoid oxygen, which is critical for the stability of the compound during irradiation) in MeCN with monochromatic light (λ = 375 nm; 150-W Xe arc lamp equipped with monochromator), the spectrum changes as revealed in Figure 3 (a). In parallel to the appearance of the VHF-band (λ_{max} = 477 nm), the intensity of the DHA absorption around 375 nm decreases, which is a clear indication that photochemical conversion of **4a** to **4b** is taking place. This conversion is accompanied by a color change of the solution from pale yellow to orange. In comparison to 1,1-dicyano-2-phenyl-1,8a-dihydroazulene, the VHF isomer is formed less efficiently from **4a**; thus, only about 10% of **4a** is converted during a period in which the Ph-substituted DHA is completely converted. The quantum yield for the conversion of **4a** is estimated to 2% based on the irradiation intensity and the known quantum yield of the Ph derivative (55%[11]); this small yield can be explained by the donor substitution at the DHA according to previous findings.[7,11] Repeated DHA–VHF cycles are accompanied by slight degradation. Thus, after four cycles, ca. 7–8% of **4a** is degraded. The broad absorption of **4a** at ca. 480 nm is presumably a charge-transfer transition from the TTF to the DHA unit (cf., the appearance of the HOMO and LUMO depicted in Figure 2).

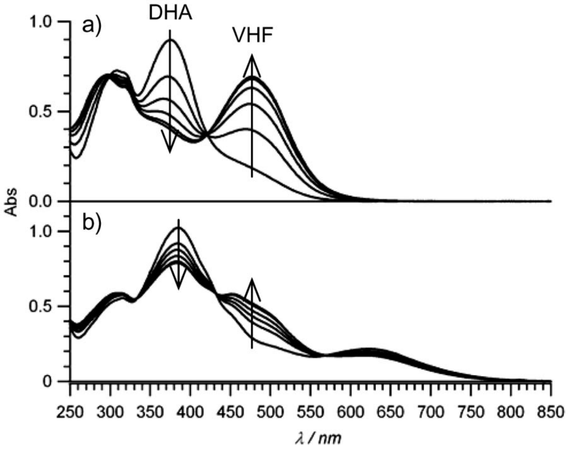


Figure 3. UV/Vis spectra recorded during irradiation of a) **4a** (2.7×10^{-5} M) and b) $\mathbf{4a}^{\cdot+}$ (3.0×10^{-5} M) at λ = 375 nm in MeCN. The spectra were recorded over a period of 22 min (with intervals of 4 × 5 min, and then 2 min). The presence of 0.1 M Bu_4NPF_6 is required in the electrochemical formation of $\mathbf{4a}^{\cdot+}$, but was for comparison also added to the solution of **4a** for the spectra shown. The irradiance was 1.5×10^{5} µW cm^{-2}.

The kinetics of the thermal back reaction **4b** → **4a** was studied in Ar-degassed MeCN (Figure 4). By exponential fitting of the decrease in the 477-nm absorption at 25 °C, the rate constant and half-life was determined to k = 9.5×10^{-5} s^{-1} and $t_{1/2}$ = 2.9 h. The ring closure is accordingly slightly faster than that for the Ph-substituted VHF (k = 7×10^{-5} s^{-1}).[11] The rate constants were determined at different temperatures, and from an Arrhenius plot (Figure 4) an activation energy of E_a = 80 ± 3 kJ mol^{-1} is obtained. The corresponding E_a values for the Ph- and DTF-substituted VHFs are 85[11] and 76 ± 4 kJ mol^{-1}[7], respectively.

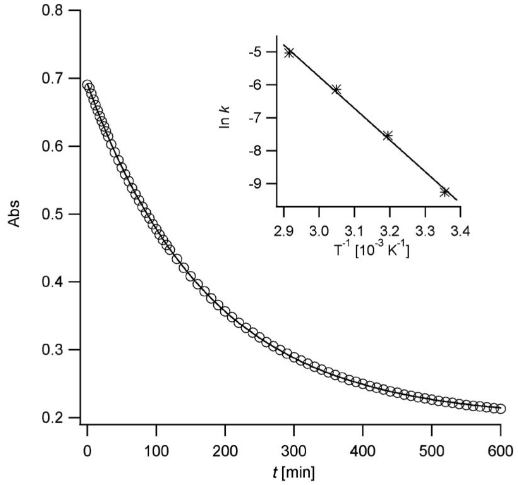


Figure 4. The time-dependent decrease of the absorption at 477 nm (circles) of **4b** (in MeCN at 25 °C) together with an exponential fit. The inset shows an Arrhenius plot for determining E_a of **4b** → **4a**.

Cyclic voltammetry of **4a** 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. The absorption spectra of the oxidized species (>90%) obtained by spectroelectrochemistry are shown in Figure 5. The broad absorption band of **4a**$^{\cdot+}$ at ca. 621 nm is characteristic for a TTF$^{\cdot+}$ species.[12] 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. Spectroelectrochemistry on ethynyl-TTF **2** showed the same behavior. We have therefore limited the photoswitching studies to **4a**$^{\cdot+}$ in comparison to **4a**. Interestingly, we find that after the same period of irradiation (22 min), considerably less of the DHA is converted to VHF for the cationic species than for the neutral one (Figure 3, b). Thus, the efficiency of light-induced ring opening of **4a**$^{\cdot+}$ is diminished by more than a factor of 2 relative to that of **4a**. The experiments were performed on solutions of similar absorbance and using the same irradiance. We note that the ring opening of **4a** is not significantly affected by the presence or absence of a counter electrolyte. As the molar absorptivities for **4a** and **4a**$^{\cdot+}$ are similar at 375 nm, the different photoswitching ability is most clearly seen by subtracting for each species the initial DHA absorption spectrum from the spectrum resulting after irradiation (Figure 6). The switching is accompanied by a small decrease of the TTF$^{\cdot+}$ absorption band at ca. 621 nm (Figure 3, b), while high-energy bands characteristic for the neutral species are 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 deexcitation pathway that could account for the reduced photoswitching ability of **4a**$^{\cdot+}$. From the electrochemical data, this electron transfer is favorable by more than 2 eV.

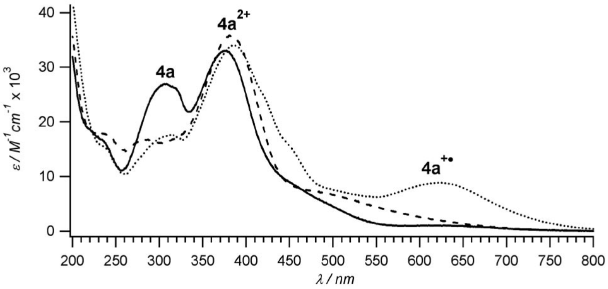


Figure 5. Spectroelectrochemistry of **4a** in MeCN (+ 0.1 M Bu_4NPF_6); oxidized species are in each case present in >90%.

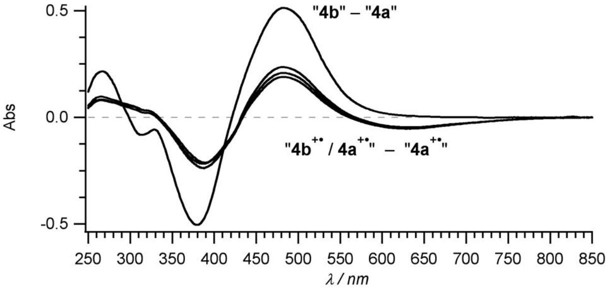


Figure 6. Difference spectra: plot of the absorption spectrum of **4a** (2.7×10^{-5} M) and **4a**$^{\cdot+}$ (3 independent experiments: 2.8/2.9/3.0×10^{-5} M) after irradiation for 22 min subtracted the initial DHA absorption spectrum in each case.

An Arrhenius plot provides an activation energy of E_a = 88 ± 2 kJ mol^{-1} for the thermal ring closure of **4b**$^{\cdot+}$. The experiment was performed in MeCN containing the counter electrolyte (0.1 M Bu_4NPF_6). When the ring closure of neutral **4b** is performed under the same conditions, a similar E_a of 89 ± 2 kJ mol^{-1} is obtained for this neutral species. Thus, the redox state does not seem to influence the thermal ring closure of the VHF unit.

Finally, we attempted chemical oxidation of **4a**, using either $NOSbF_6$[13] or $PhI(OAc)_2/HBF_4$.[14] While both these oxidizing agents did provide access to the radical cation species as judged from the absorption spectrum, the species decomposed within 10 min in the first case and during light excitation in the second.

In conclusion, we have developed an electrochemically controlled DHA/VHF switch based on TTF. The photoswitching occurs more than twice as efficiently for the neutral species as for the radical cation species, while the thermal back reaction is unaffected. The wide applicability of TTF in both supramolecular and materials chemistry,[15] 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. For example, preliminary experiments show that DHA **4a** forms an inclusion complex with cyclobis(paraquat-*p*-phenylene) characterized by a very broad charge-transfer absorption at ca. 812 nm.

Supporting Information (see also the footnote on the first page of this article): Syntheses of **4a** and **5**; spectral evolution upon irradiation of **4a** in comparison to 1,1-dicyano-2-phenyl-1,8a-dihydroazulene; voltammograms of **4a**, **5**, and 1,1-dicyano-2-phenyl-1,8a-dihydroazulene; spectroelectrochemistry of **2** and **5**; kinetics data for the thermal ring closure of **4b** and $\mathbf{4b}^{\cdot+}$.

Acknowledgments

The Danish Research Agency (grant #2111-04-0018) is gratefully acknowledged for supporting this work.

---

[1] V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405.

[2] a) H. Dürr, *Angew. Chem.* **1989**, *101*, 427; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 413; b) B. Feringa, W. F. Jager, B. de Lange, *Tetrahedron* **1993**, *49*, 8267; c) V. Balzani, F. Scandola in *Comprehensive Supramolecular Chemistry*, vol. 5 (Ed.: D. N. Reinhoudt), Pergamon-Elsevier, Oxford, **1996**, pp. 687–746; d) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77.

[3] J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem.* **1984**, *96*, 980; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 960.

[4] a) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.* **1986**, *119*, 2631; b) S. Gierisch, J. Daub, *Chem. Ber.* **1989**, *122*, 69; c) S. Gierisch, W. Bauer, T. Burgemeister, J. Daub, *Chem. Ber.* **1989**, *122*, 2341.

[5] a) J. Daub, S. Gierisch, J. Salbeck, *Tetrahedron Lett.* **1990**, *31*, 3113; b) J. Achatz, C. Fischer, J. Salbeck, J. Daub, *J. Chem. Soc., Chem. Commun.* **1991**, 504; c) H. Spreitzer, J. Daub, *Chem. Eur. J.* **1996**, *2*, 1150.

[6] a) L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem.* **1999**, *111*, 737; *Angew. Chem. Int. Ed.* **1999**, *38*, 674; b) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **2001**, *84*, 743.

[7] M. Å. Petersen, L. Zhu, S. H. Jensen, A. S. Andersson, A. Kadziola, K. Kilså, M. B. Nielsen, *Adv. Funct. Mater.* **2007**, *17*, 797.

[8] Some recent examples of TTF-based switches: a) Y. C. Zhou, D. Q. Zhang, L. Y. Zhu, Z. G. Shuai, D. B. Zhu, *J. Org. Chem.* **2006**, *71*, 2123; b) S. Nygaard, K. C.-F. Leung, I. Abrahamian, T. Ikeda, S. Saha, B. W. Laursen, S. Y. Kim, S. W. Hansen, P. C. Stein, A. H. Flood, J. F. Stoddart, J. O. Jeppesen, *J. Org. Chem.* **2007**, *129*, 960; c) Y. Feng, Q. Zhang, W. Tan, D. Zhang, Y. Tu, H. Ågren, H. Tian, *Chem. Phys. Lett.* **2008**, *455*, 256.

[9] T. Otsubo, Y. Kochi, A. Bitoh, F. Ogura, *Chem. Lett.* **1994**, 2047.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.03*, Gaussian, Inc., Wallingford, CT, **2004**.

[11] H. Görner, C. Fischer, S. Gierisch, J. Daub, *J. Phys. Chem.* **1993**, *97*, 4110.

[12] a) L. Huchet, S. Akoudad, E. Levillain, J. Roncali, A. Emge, P. Bäuerle, *J. Phys. Chem. B* **1998**, *102*, 7776; b) A. S. Andersson, K. Kilså, T. Hassenkam, J.-P. Gisselbrecht, C. Boudon, M. Gross, M. B. Nielsen, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 8451.

[13] J. Lyskawa, M. Sallé, J.-Y. Balandier, F. Le Derf, E. Levillain, M. Alain, P. Viel, S. Palacin, *Chem. Commun.* **2006**, 2233.

[14] M. Giffard, G. Mabon, E. Leclair, N. Mercier, M. Alain, A. Gorgues, P. Molinié, O. Neilands, P. Krief, V. Khodorkovsky, *J. Am. Chem. Soc.* **2001**, *123*, 3852.

[15] a) M. R. Bryce, *Adv. Mater.* **1999**, *11*, 11; b) M. B. Nielsen, C. Lomholt, J. Becher, *J. Chem. Soc. Rev.* **2000**, *29*, 153; c) M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589; d) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372; e) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433; f) N. Martín, L. Sánchez, M. A. Herranz, B. Illescas, D. M. Guldi, *Acc. Chem. Res.* **2007**, *40*, 1015.

Received: January 15, 2009