Multi-Mode Switching Based on Dihydroazulene/Vinylheptafulvene Photochromism: Synergism of Photochromism and Redox Switching in Heteroaryl-Functionalized Systems**

Hubert Spreitzer and Jörg Daub*

Abstract: The syntheses of the dihydroazulenes (DHAs) **DHA-a**–**DHA-f** containing covalently linked heteroaromatic subunits derived from dibenzodioxin, thianthrene, phenoxathiine, *N*-methylphenothiazine, *N*-methylphenoxazine, and *N*,*N*′-dimethylphenazine groups are described, and their spectroscopic and analytical data are reported. The dihydroazulene/vinylheptafulvene (DHA/VHF) photochromism (photochemical forward and thermal back reaction) depends with high sensitivity on the electronic properties of the functional groups. Whereas the dimethylphenazine derivative **DHA-f** is photochemically inactive towards rearrangement, all other DHAs (**DHA-a**–**DHA-e**) were found to isomerize to the corresponding vinylheptafulvene forms under irradiation. Cyclic voltammetry revealed that the DHA and the VHF forms have significantly different oxidation and reduction waves. The products of the oxidative one-electron transfer are characterized by UV/Vis/NIR spectroelectrochemistry. Those DHAs having weaker donor substituents (**DHA-a**–**DHA-c**) undergo oxidative dimerization whereas DHAs with stronger donating heterocyclic subunits (**DHA-d**–**DHA-f**) form stable radical cations.

Keywords
electrochromes · cyclic voltammetry · heterocycles · optical memory · photochromes

Introduction

Optical and electrochemical switching is expected to become increasingly important in future information-processing systems.[2] Therefore, the synergism of photochemical and electrochemical processes must be studied intensively on the molecular and supramolecular level. Multifunctional compounds such as, for example, functional dyes with photochromic and electrochromic properties provide the basis for dual-mode photo- and electrochemical switching. The modification of the molecular structure of the multifunctional compounds permits the tuning and optimization of the switching behavior.[3–5] The present paper reports on investigations of light-sensitive electron-transfer compounds composed of a photochromic dihydroazulene/vinylheptafulvene subunit and heteroaromatic groups sited at the C-2′ of the five-membered ring. They undergo facile oxidative redox switching and therefore enable photochromic behavior to be frozen by electron-transfer-induced oxidation (Scheme 1).[6]

Previous studies dealt with acceptor-type functional groups that were reduced to form radical anions and whose multi-mode switching was successfully studied by photomodulation amperometry.[3, 7] The present report is devoted to electron-rich heteroaromatic subunits that are susceptible to reversible oxidative electron transfer (radical cation formation). 9,10-Dihydroanthracenoid heteroaromatic subunits such as 1-dibenzodioxinyl, 1-thianthrenyl, 4-phenoxathiinyl, 3-phenothiazinyl, 3-phenoxazinyl, and 2-dimethylphenazinyl groups were selected for the model compounds with steadily decreasing oxidation potentials (Scheme 1).[8, 9] The half-wave oxidation potentials of the parent heteroaromatic compounds [$E_{1/2}$ vs. ferrocene/ferrocenium (FOC)] highlight the ease of oxidizability: dibenzodioxin (**1a**), +994 mV; thianthrene (**1b**), +834 mV; phenoxathiine (**1c**), +801 mV; *N*-methylphenothiazine (**1d**), +323 mV; *N*-methylphenoxazine (**1e**), +229 mV, and *N*,*N*′-dimethylphenazine (**1f**), −245 mV (see also Table 1). The reductive and oxidative electron-transfer chemistry of the functionalized **DHA-a**–**f**/**VHF-a**–**e** systems was determined by cyclic voltammetry and UV/Vis/NIR spectroelectrochemistry.

Results and Discussion

Synthesis: The **DHAs (a**–**f)** were synthesized following the protocol already described[10] (Scheme 2): the heterocyclic carbaldehydes **2** were converted to the corresponding dicyanovinylene compounds **3** by Knoevenagel condensation in high yields (70–93%). The [8+2] cycloaddition of **3** to 8-methoxyheptafulvene (8-MHF) **4**[11] gave the tetrahydroazulenes (THAs) **5** rather slowly. As already found in previous studies,[12] the time of reaction increases with increasing donor

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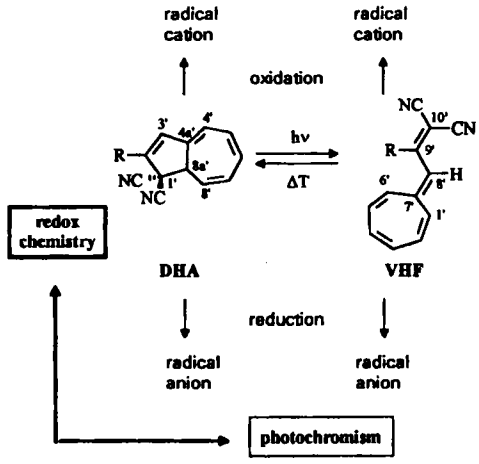
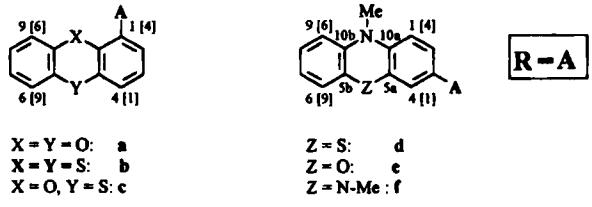
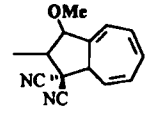




R=A	-A
1	-H
2	-CHO
3	$-CH=C(CN)_2$
5	

Scheme 1. Photochromic and redox behavior of the dihydroazulene/vinylheptafulvene subunit, and the various heteroaromatic groups used as substituents at the C-2′ of the five-membered ring.

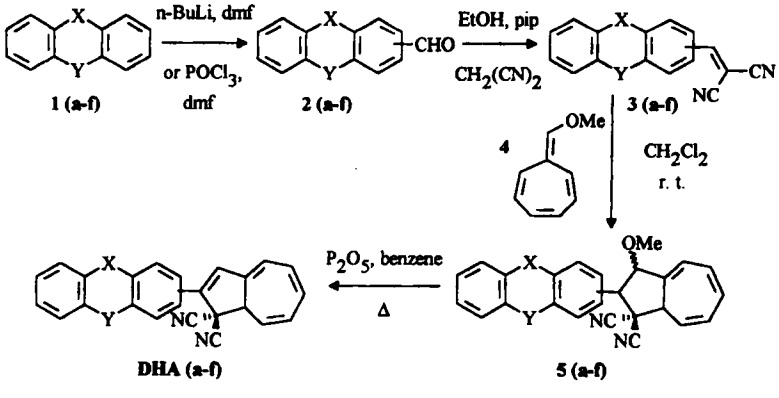
Table 1. Half-wave potentials and peak potentials (in mV vs. FOC) attributed a) to the radical cation formation of the heterocyclic subunits [$E_{1/2}$(het-ox)], b) to the irreversible wave of the oxidation of the DHA or VHF carbocyclic subunits [E_{pa}(ring-ox), E_{pc}(ring-ox)], and c) to the reduction of the DHA and VHF forms [E_{pc}(ring-red)]. Cyclic voltammetry in acetonitrile, 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP), ambient temperature, solvent: acetonitrile.

	$E_{1/2}$(het-ox)	E_{pa}(ring-ox)	E_{pc}(ring-ox)	E_{pc}(ring-red)
DHA-a	+1196	+1034	−232	−1942
VHF-a	+1199	+753		−1315
DHA-b	+1034	+990	−220	−1567/−2063
VHF-b	+1005	+765		−1339/−1678
DHA-c	+984	+926	−229	−1918
VHF-c	+1014	+751		−1330
DHA-d	+362	+965/+1054 [a]	−290	−2000
VHF-d	+391	+978/+1154 [a]		−1400
DHA-e	+286			−2000
VHF-e	+329			−1350
DHA-f	−144 [b]	+1485	−350	−2035
1a/3a	+994/+1153			
1b/3b	+834/+1022			
1c/3c	+801/+951			
1d/3d	+323 [c]/+495			
1e/3e	+229/+445			
1f/3f	−245 [d]/−10			

[a] Waves at +1054 and +1154 are tentatively assigned to the formation of dications. [b] Reversible formation of the dication at +547 mV. [c] Reversible formation of the dication at +1010 mV. [d] Reversible formation of the dication at +510 mV.

derivatives **5f** and **DHA-f** are extremely sensitive both to oxygen and acidic conditions. We were unable to purify **DHA-f** either by chromatography (SiO_2 or Al_2O_3) or by recrystallization (see experimental part).

The elimination of methanol from the THAs **5** by diphosphorous pentoxide (P_2O_5) furnished the dihydroazulenes **DHA-a–f**. Again, the yields of these reactions vary depending on the substituents:[13] **DHA-d–f** are formed in low yields (approximately 6%) whereas higher yields are obtained of **DHA-a** (51%), **DHA-b** (24%), and **DHA-c** (36%).



Scheme 2. Synthesis of **DHA-a–f**.

strength of the heterocyclic compounds; this parallels the lessening of the oxidation potentials (Table 1). Dibenzodioxin derivative **3a** requires 16 h to react to completion at room temperature. The cycloaddition of the dimethylphenazine derivative **3f** is still incomplete after five months. The dimethylphenazine

Photochromism: The photochemical and thermal interconversions between the DHA and VHF forms were studied in acetonitrile. With exception of **DHA-f** all dihydroazulenes show photochromic behavior at ambient temperature. In Table 2 the long-wavelength absorptions of the DHA forms and of the corresponding VHF forms are listed, including spectral data of the phenyl derivatives **DHA-Ph** and **VHF-Ph** for comparison.[10b] The evolution of the absorption bands of **VHF-c** from **DHA-c** is illustrated in Figure 1.

The long-wavelength absorption bands of the DHAs are sensitive probes for the electronic and steric effects of the functional groups. The dihydroazulene derivatives **DHA-d–f**, which are less sterically hindered owing to a C-2′–C-3 linkage and in which therefore both chromophores may adopt a planar configuration, display a bathochromic shift with increasing donor strength of the heterocyclic subunit (cf. **DHA-Ph**: 354, **DHA-d**: 410, and **DHA-f**: 471 nm). Those DHAs in which the heteroaromatic subunits are linked by C-2′–C-1(4) bonding absorb at shorter wavelength, as demonstrated, for example, by the thianthrene derivative **DHA-b**, which has the

Table 2. Characteristic absorption bands of **DHA/VHF-a-f**: λ_{max} [nm] (lg ε).

	a	b	c	d	e	f	Ph
λ_{max} (DHA-)	353 (4.03)	322 (3.80)	352 (4.15)	410 (4.25)	434 (4.30)	471 (3.95)	354 [a]
λ_{max} (VHF-)	478 (4.29)	479 (4.24)	476 (4.43)	465 (4.30)	469 (4.38)	-	471 [a]
$\Delta\lambda$ [b]	125	157	124	55	35		117

[a] Ref. [10b]. [b] λ_{max}(VHF) − λ_{max}(DHA) in nm.

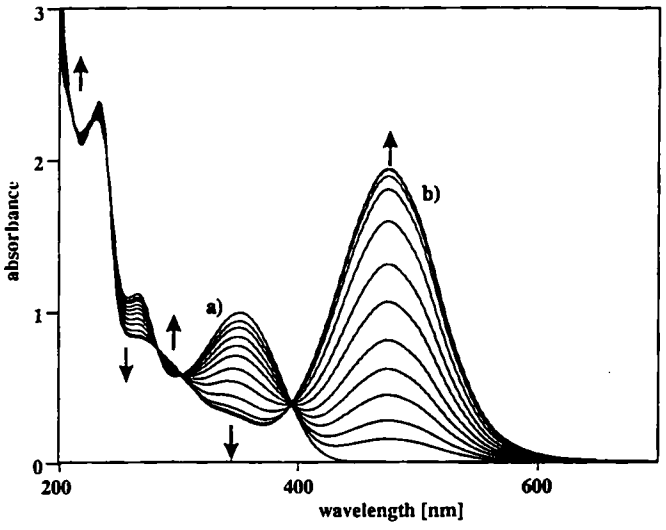


Fig. 1. Appearance of the long-wavelength absorption of **VHF-c** upon irradiation of **DHA-c** in CH_3CN, 20 °C. λ_{ir}: 260–390 nm.

strongest hypsochromic shift and absorbs at λ_{max} = 322 nm.[14] Compared with those of the dihydroazulenes, the absorption spectra of the vinylheptafulvenes are less dependent on the substituents at C-9′. They absorb in the range of 465 to 479 nm, in agreement with previous results.[12]

The photochemical rearrangement DHA → VHF is also clearly demonstrated by ^{13}C and ^{1}H NMR spectroscopy: the sp^3 hybridized carbons of the DHA substructure C-1′ (δ = 45–48) and C-8a′ (δ = 51) are transformed into the sp^2 hybridized carbons C-10′ (δ = 74–78) and C-6′ (δ = 134) of VHF. A significant shift is also observed for the proton resonances: DHA, 8a′-H (δ = 3.8) and VHF, 6′-H (δ = 5.7–6.2) (Table 3). It is also notable that the polarization of the π system of the "nonalternant" VHFs leads to a significant alternation of the ^{13}C chemical shifts obtained by ^{13}C NMR: C-10′ (δ = 74–78), C-9′ (δ = 163–168), C-8′ (δ = 119), and C-7′ (δ = 153–156).[15]

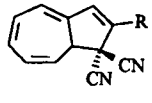
Table 3. Characteristic ^{1}H and ^{13}C NMR data of the dihydroazulenes and their corresponding vinylheptafulvene forms.

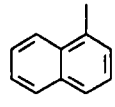
δ of the samples	DHA-a	DHA-b	DHA-c	DHA-d	DHA-e
DHA (C′-1′)	46.93	48.73	47.14	45.01	44.90
VHF (C′-10′)	78.04	77.53	77.95	74.55	73.81
DHA (C′-8a′)	51.16	50.67	50.88	51.12	51.17
VHF (C′-6′)	134.27	133.63	133.86	135.40	135.59
DHA (8a′-H)	3.80	3.82	3.81	3.76	3.76
VHF (6′-H)	6.18	5.71	5.97	6.05	6.15

There are two possible reasons for the absence of photochromism in **DHA-f**: either a fast thermal reverse reaction[16] or a competing photophysical process such as intersystem crossing or charge separation. Since even at −45° we were unable to detect the **VHF-f** form, a rapid thermal back-reaction must be excluded. Obviously the quantum yield of the photochemical reaction $\Phi_{DHA-f \rightarrow VHF-f}$ is low. Qualitatively, the rate constants of the photochemical transformations can be estimated from the half-lives of the photoreaction DHA → VHF. In Table 4 the quantum yields[17] and the experimentally determined half-lives are listed. It clearly follows that the photochemical pathway slows down with increasing donor strength of the substituents at C-2′ (**DHA-NO_2,DHA-Ph,DHA-OMe,DHA-NH_2**). In this context it is interesting to note that the ferrocene derivative **DHA-Fc** is found to be photochemically inert too.[3d] The donor strength of the ferrocenyl group lies in between that of the dimethylphenazine and the phenoxazine groups. In summary, the occurrence of DHA photoisomerization in solution is slight or even absent in compounds with strong donor as well as strong acceptor substituents.[14]

Table 4. Trends in the quantum yields of the photochemical isomerization ($\Phi_{DHA \rightarrow VHF}$) of the new compounds. $\Phi_{DHA \rightarrow VHF}$ values were taken from ref. [17] (CH_3CN; 24 °C). Half-lives ($t_{1/2}$): time in which 50% of DHA is converted into the corresponding VHF under standard conditions [CH_3CN; 5 °C; A(λ_{max}) = 0.5].

DHA	p-NO_2	Ph	p-OMe	p-NH_2	a	b	c	d	e
$t_{1/2}$	-	-	-	-	12 min	45 min	26 min	≈6 h	≈3 h
$\Phi_{DHA \rightarrow VHF}$	0.60	0.50	0.40	0.15	-		-	-	-



R	
p-NO_2-C_6H_4-	DHA-NO_2
C_6H_5-	DHA-Ph
p-CH_3O-C_6H_4-	DHA-OCH_3
p-H_2N-C_6H_4-	DHA-NH_2
	DHA-Fc
	DHA-Np

The rates of the thermal reverse reactions are within the scope of previously investigated vinylheptafulvenes and depend slightly on the electronic effects of the donor groups.[3] From the numbers given in Table 5 we conclude that steric effects are more important. The ring-closure reactions of the vinylheptafulvenes **VHF-a**, **VHF-b**, **VHF-c**, and **VHF-Np** are slower than those of **VHF-d**, **VHF-e**, and **VHF-Ph**. We believe that this is a result of the "*peri* interaction" in the *s-cis* stereoisomer

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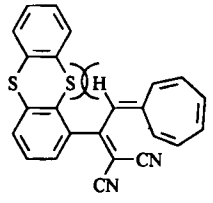
Table 5. Kinetic data for the cyclization of the VHFs. $t_{1/2}$ values are obtained by measuring the decrease of the long-wavelength absorption at the given λ_{meas} of the VHFs. $\Delta G^{\neq}$ values are calculated from Eyring plots (solvent: acetonitrile).

VHF form	a	b	c	d	e	Ph	Np
λ_{meas} (nm)	478	479	476	495	490	485	485
$t_{1/2}^{30\,°C}$ (min)	385	2074	443	118	121	77 (35 °C)	80 (65 °C)
$\Delta G^{\neq}_{303}$ (kJ mol^{-1})	100.5	104.8	100.9	97.5	97.5	98.1	108.0

(Scheme 3). In addition, the rates of the cyclizations of the heptafulvenes **VHF-a**, **VHF-b**, and **VHF-c** indicate that the thianthrene derivative **VHF-c** experiences a strong steric congestion caused by the sulfur atom. The 1-naphthyl derivative **VHF-Np** has by far the slowest rate of ring closure.[12]



s-cis-VHF-b

Scheme 3. The *peri* interaction in the *s-cis* stereoisomer of **VHF-b**.

Electrochemistry/spectroelectrochemistry: In order to determine the redox properties and the redox chemistry of the dihydroazulenes and the vinylheptafulvenes we have examined **DHA-a–f** and **VHF-a–e** by means of cyclic voltammetry and UV/Vis/NIR spectroelectrochemistry. The complexity of the reduction/oxidation processes is clear from Figure 2, which features the cyclovoltammograms of the dibenzodioxin derivative **DHA-a** before (solid trace) and after irradiation (broken line). The broken line is ascribed to the photoisomer **VHF-a**. In Table 1 the electrochemical data of **DHA-a–f** and **VHF-a–e** are listed. The oxidation potentials of the heterocyclic compounds **1** and **3** are included as models for the substructures of the DHAs and of VHFs, respectively.

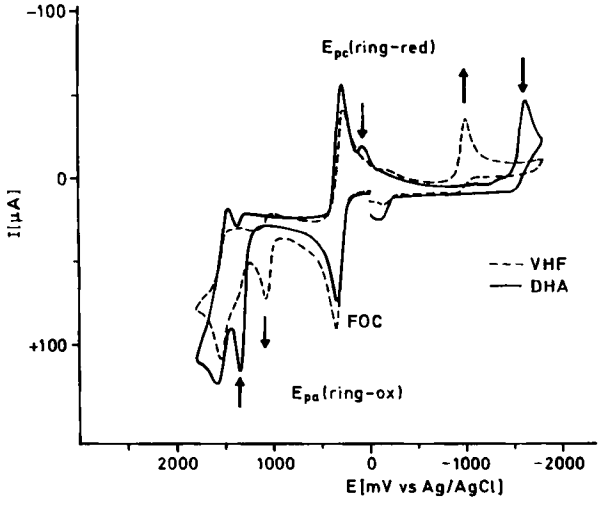


Fig. 2. Cyclic voltammograms of **DHA-a** before (unbroken line) and after (dashed line) irradiation (15 min) with daylight. Solvent: acetonitrile; $v = 250$ mVs^{-1}.

iii) the irreversible cathodic waves [E_{pc}(ring-red)], which we ascribe to the reduction of the dihydroazulene or vinylheptafulvene subunits. The assignments are further corroborated by more extended electrochemical and spectroelectrochemical measurements that will be described below.

Figure 3 shows the thin-layer cyclovoltammogram of **DHA-a**, which depicts two independent oxidation processes: i) an irreversible wave at $E_{pa} = 1034$ mV (vs. FOC) [$E_{pc} = -232$ mV (vs. FOC)] and ii) a reversible wave $E_{1/2}$(het-ox), which corresponds to the formation of the radical cation of the dibenzodioxin subunit. The irreversible wave represents a two-step pro-

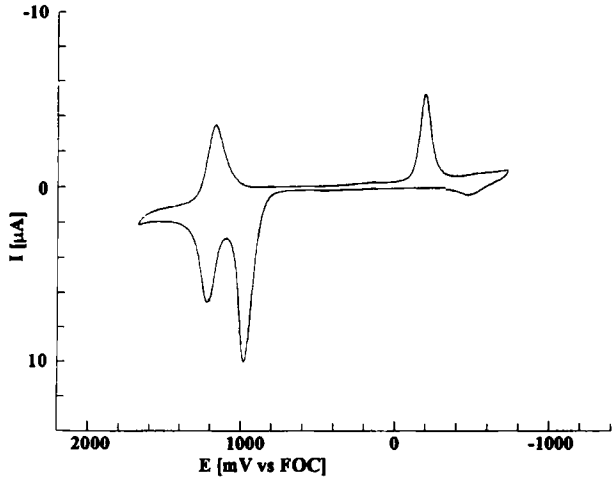
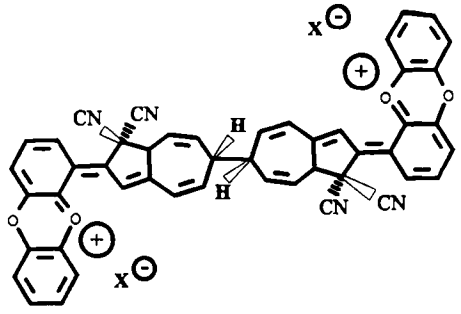


Fig. 3. Thin-layer cyclic voltammogram of **DHA-a** in CH_3CN; $v = 25$ mVs^{-1}.

cess pertaining to a one-electron oxidation of the dihydroazulene subunit followed by a chemical step (EC-type mechanism) that leads to a significant change of the molecular structure. Since polyenic radical cations have a preference for dimerization,[18] we propose the formation of a dimeric dication species as illustrated in Scheme 4. The chemical reversibility of this EC-type process is confirmed by multi-sweep thin-layer experiments.



Scheme 4. Dimeric dication of **DHA-a**.

For all DHA/VHF couples we observe three sections of *I*/*E* (current/potential) response: i) the anodic waves [$E_{1/2}$(het-ox)] for the oxidation of the heterocyclic substructures (reversible electrode process) of the DHA and VHF forms; ii) the waves [E_{pa}(ring-ox)/E_{pc}(ring-ox)], which imply the electrochemical oxidation (quasireversible or irreversible electrode process) of the dihydroazulene and vinylheptafulvene subunits, respectively;

Without exception, the heterocyclic subunits in the DHAs are oxidized at more positive potentials [$E_{1/2}$(het-ox)] compared with the parent heterocyclic compounds **1**. The largest gap exists for the dibenzodioxinyl and the thianthrenyl derivatives, whereas the potential differences of the phenothiazine **1-d** and **DHA-d** differ by less than 40 mV (strong localization of the radical cation).

It is interesting to note that the oxidation potentials [$E_{1/2}$(het-ox) and E_{pa}(ring-ox)] show a crossover within the series of compounds **DHA-a** to **DHA-f**. The reversible oxidative waves [$E_{1/2}$(het-ox)] of **DHA-d** and **DHA-f** appear at less positive potential compared with the irreversible ring-oxidation wave E_{pa}(ring-ox), whereas **DHA-a**, **DHA-b**, and **DHA-c** have a reversed sequence of potentials [$E_{1/2}$(het-ox) > E_p(ring-ox)]. In summary, the regiochemistry of the electrochemical oxidation can be systematically predetermined by the functional groups appended to the dihydroazulenes.

The interpretation that the irreversible oxidation wave [E_{pa}(ring-ox)] is caused by the formation of a dimeric dication species is further supported by spectroelectrochemical (SEC) measurements (Fig. 4, Fig. 5, Table 6). Figures 4 and 5 display the spectroelectrograms for the first oxidation waves of **DHA-a** and **DHA-e**. As expected from the significantly different oxidation potentials, the features of the spectra are also completely different, indicating varying regiochemistry of the oxidation processes. On electrochemical oxidation of **DHA-a** the absorption of the neutral form at $\lambda = 353$ nm decreases while a strong band at $\lambda = 438$ nm appears (Fig. 4). The evolving absorption is shifted too far into the short-wave region for a dibenzodioxinyl radical cation (cf. $\mathbf{1a}^{\bullet+}$ 660 nm, $\mathbf{3a}^{\bullet+}$ 662 nm), whereas the formation of a closed-shell dimeric dication species $(\mathbf{DHA\text{-}a})_2^{2+}$ is well supported. Compounds **DHA-b** and **DHA-c** exhibit the same spectral characteristic. On the other hand, the spectral feature shown in Figure 5 is in agreement with the formation of the radical cation $\mathbf{DHA\text{-}e}^{\bullet+}$ owing to the long-wavelength absorptions at $\lambda = 860$ and 545 nm. The possibility that $\mathbf{DHA\text{-}e}^{\bullet+}$ represents predominantly a localized *N*-methylphenoxazine radical cation is further supported by a comparison with the parent radical cation $\mathbf{1e}^{\bullet+}$, which has two absorption bands at 660 and 523 nm. The *N,N'*-dimethylphenazine derivative **DHA-f** and the phenothiazine derivative **DHA-d** behave accordingly. The long-wavelength absorption bands that appear during the electrochemical oxidation of **DHA-a–f** are summarized in Table 6.

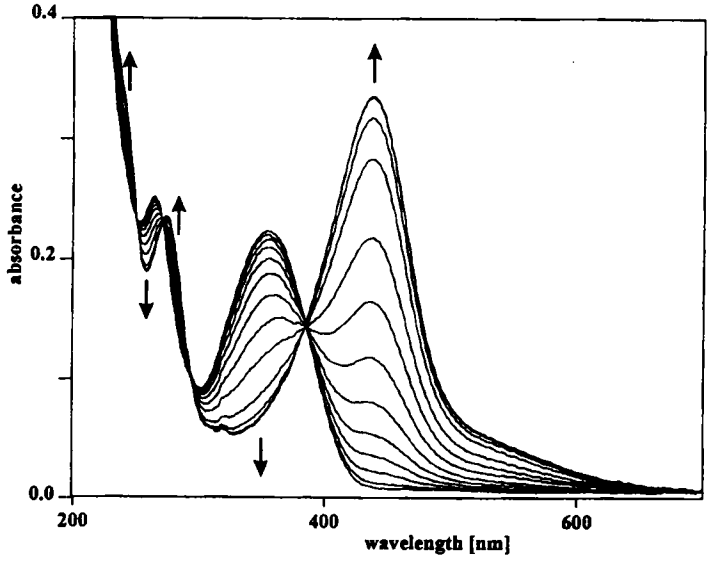


Fig. 4. Spectroelectrogram obtained by the oxidation of **DHA-a** to the dimeric dication (solvent: acetonitrile).

Table 6. Absorption spectra obtained by spectroelectrochemistry. λ (nm), w: weak, m: medium, s: strong absorption, sh: shoulder; solvent: acetonitrile.

	DHA-a	DHA-b	DHA-c	DHA-d	DHA-e	DHA-f
$DHA^{\bullet+}$	–	–	–	964 (sh, m), 732 (sh, m), 563 (s)	860 (m), 545 (s)	764 (w), 590 (sh, m), 534 (s)
$(DHA_2)^{2+}$	438 (s)	426 (m), 343 (m)	440 (s)	–	–	–
DHA^{2+}	–	–	–	–	–	741 (s), 424 (s)

The reductive part of the cyclic voltammogram (Fig. 2) is even more complex. The DHA forms undergo an irreversible reduction at about −2 V vs. FOC. Conversion of DHA to VHF leads to a cathodic peak at less negative potential (−1400 mV vs. FOC).[3b] It is also surprising to note that the irreversible waves for the oxidation of the VHF forms (**VHF-a–VHF-c**) appear at less positive potentials than the DHA isomers. This is obviously due to the fact that the heptafulvene substructure has strong electron-donor characteristics leading to a radical cation with tropylium ion-type substructure.[19]

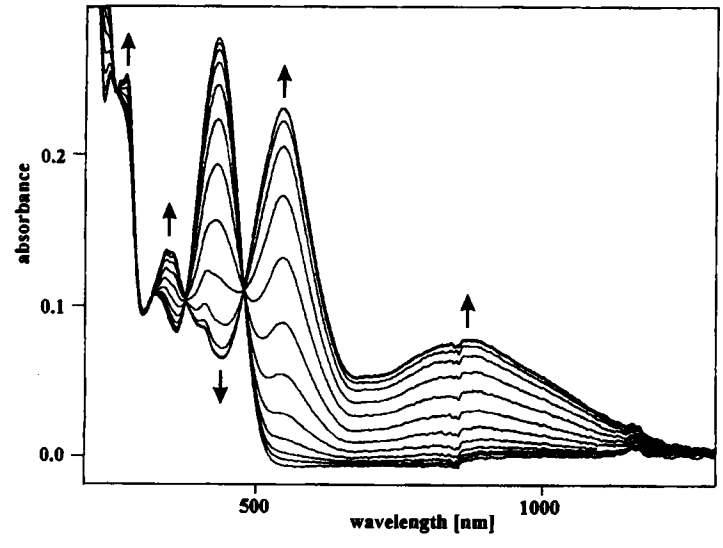


Fig. 5. Spectroelectrogram obtained by the oxidation of **DHA-e** to the radical cation $\mathbf{DHA\text{-}e}^{\bullet+}$ (solvent: CH_3CN).

Conclusions

The dihydroazulene/vinylheptafulvene photochromism satisfies the requirements for model systems for information storage and handling (write, read, and lock modes, Scheme 5) on the molecular level, since its structure can be efficiently modified in order to display multi-mode switching. In the present study we have shown that donor-substituted dihydroazulenes can be electrochemically transformed into oxidized species (radical cation or dication species) that suppress the photochromic switching. We have also proved that the original dihydroazulenes can be regained by reduction. The complete reaction sequence is reversible.

It has also been demonstrated that the functional groups at C'-2 of the DHA form control the chemoselectivity of the formation of the oxidation products. Either the formation of radical cations or the formation of dimeric species is favored by adjustment of the donor strength of the functional groups.

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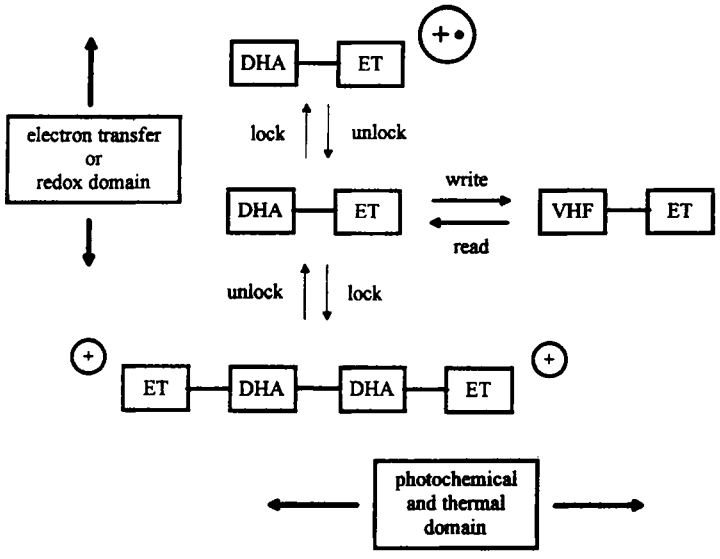

Scheme 5. Information storage in the dihydroazulene/vinylheptafulvene system.

Experimental Section

Methods: Melting points: uncorrected, Büchi SMP20 and Reichert Thermovar. UV/Vis: Perkin–Elmer Lambda 9 spectrophotometer. IR: Beckman Acculab 1. EIMS (70 eV): Varian CH-5. NMR: Bruker AC250 (24 °C) and ARX400 (21 °C) spectrometers at 250/400 and 63/101 MHz for ^1H and ^{13}C, respectively. Chemical shifts δ against TMS (^1H) or $CDCl_3$ (^{13}C) as internal standard. Kinetic measurements: the kinetic parameters were obtained by measuring the decrease of the VHF forms at the indicated wavelengths (Table 5). A spectrophotometer equipped with a spectrophotometrical cell kept at constant temperature was used.

Electrochemistry: A one-compartment cell (three-electrode configuration) was used with a platinum disc as working electrode, a platinum wire as counter electrode, and a pseudo-Ag/AgCl reference electrode. The electrochemical measurements were carried out under computer control. The potentiostat/galvanostat and the function generator were purchased from Amel (Milano, Italy) [19,21]. The reversible oxidation signal of ferrocene/ferrocenium (FOC) was used as internal reference. The solvents and the electrolyte (tetrabutylammoniumhexafluorophosphate, TBAHFP) were purified according to standard procedures [20]. All measurements were carried out under a nitrogen atmosphere and with the exclusion of light.

Spectroelectrochemistry: The solutions of the CV experiments were transferred by syringe to the spectroelectrochemical cell described previously [21]. The spectra were recorded with a Perkin–Elmer Lambda 9 spectrophotometer.

Synthesis: Solvents and reagents were used as purchased without further purification unless stated otherwise: THF was dried and stored over Na and benzophenone under N_2. DMF and CH_2Cl_2 were dried over P_2O_5; dioxane, EtOH, benzene, and Et_2O were dried with Na. The completion of the reactions was monitored by TLC.

10-Methyl-10H-phenothiazine-3-carboxaldehyde (2d), 4-phenoxathiinecarboxaldehyde (2c) and 10-methyl-10H-phenoxazine-3-carboxaldehyde (2e): see ref. [22].

5,10-Dihydro-5,10-dimethyl-2-phenazinecarboxaldehyde (2f) [23]: A solution of 5,10-dihydro-5,10-dimethylphenazine (**1f**) [24] (16.0 g, 76 mmol), freshly distilled $POCl_3$ (11.7 g, 75 mmol), and DMF (25 mL, ca. 4 equiv) in 230 mL dioxane (abs) was stirred at RT. The solution turned red and solidified after a while. Afterwards the reaction mixture was treated with 200 mL of a solution of NaOAc in water (20% w/w) and stirred overnight. The solvent was evaporated, the residue was treated with water and extracted several times with CH_2Cl_2. Purification by CC (column chromatography; SiO_2, solvent: CH_2Cl_2) afforded **2f** as cubic red crystals (12.1 g, 66%). M.p. 104 °C; IR (KBr): $\tilde{\nu}$ = 3070, 2970, 2900, 2820 (C–H), 1670 (C=O), 1600 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 432 (3.75), 354 (3.70), 287 (4.42), 238 (4.38), 215 nm (4.14); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.03 (s, 3H, N–CH_3-10), 3.08 (s, 3H, N–CH_3-5), 6.38 (d, $J_{4,3}$ = 8.0 Hz, 1H, 4-H), 6.41 (dd, $J_{9,7}$ = 1.5, $J_{9,8}$ = 7.6 Hz, 1H, 9-H), 6.45 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 6.74 (dt, $J_{7,6} = J_{7,8}$ = 7.6, $J_{7,9}$ = 1.5 Hz, 1H, 7-H), 6.78 (d, $J_{1,3}$ = 1.7 Hz, 1H, 1-H), 6.79 (dt, $J_{8,6}$ = 1.5, $J_{8,7} = J_{8,9}$ = 7.6 Hz, 1H, 8-H), 7.18 (dd, $J_{3,1}$ = 1.7, $J_{3,4}$ = 8.0 Hz, 1H, 3-H), 9.66 (s, 1H, CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 190.5 (CHO), 32.4, 32.0 (2CH_3), 145.2 (quat), 139.0 (quat), 137.8 (quat), 136.6 (quat), 130.5 (quat), 129.1 (tert), 122.8 (tert), 121.5 (tert), 111.7 (tert), 111.3 (tert), 110.6 (tert), 107.4 (tert). $C_{15}H_{14}N_2O$ (238.3): calcd. C 75.61, H 5.92, N 11.76; found C 75.62, H 5.91, N 11.68; MS: *m/z* (%) = 238 (86) [M^+], 223 (100) [$M^+ - CH_3$].

General procedure for the synthesis of dibenzo[b,e][1,4]dioxin-1-carboxaldehyde (2a) and 1-thianthrenecarboxaldehyde (2b) [25]: A solution of **1a** or **1b** (1 equiv) in dry THF under N_2 was treated with *n*BuLi (1 equiv in *n*-hexane) and stirred at 25 °C for one day. Afterwards the solution was cooled to −78 °C and treated with DMF (1 equiv). After four hours (temperature increased to 25 °C) the reaction mixture was poured into ice/water/2N HCl and extracted several times with CH_2Cl_2. The combined organic phases were evaporated and the residue was purified.

2a: Starting material was dibenzo[b,e][1,4]dioxin (**1a**) [26]. Purification by CC [SiO_2, solvents: i) petroleum ether to recover educt, ii) petroleum ether/CH_2Cl_2, 1:1] and recrystallization from *n*-hexane afforded the product as almost colorless needles (68%). M.p. 119 °C; IR (KBr): $\tilde{\nu}$ = 3060, 3040, 2960 (C–H), 1680 (C=O), 1620 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 353 (3.50), 292 (sh, 3.24), 257 (4.03), 218 nm (4.54); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.84–6.97 (m, 4H, 6-H, 7-H, 8-H, 9-H), 6.95 (t, $J_{3,2} = J_{3,4}$ = 7.9 Hz, 1H, 3-H), 7.04 (dd, $J_{4,2}$ = 1.7, $J_{4,3}$ = 8.0 Hz, 1H, 4-H), 7.41 (dd, $J_{2,3}$ = 7.8, $J_{2,4}$ = 1.7 Hz, 1H, 2-H), 10.41 (s, 1H, CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 187.5 (CHO), 124.0 (C-1), 144.9 (quat), 142.5 (quat), 141.6 (quat), 141.0 (quat), 124.7 (tert), 124.2 (tert), 123.4 (tert), 122.3 (tert), 121.8 (tert), 116.53 (tert), 116.51 (tert). $C_{13}H_8O_3$ (212.2): calcd. C 73.58, H 3.80; found C 73.54, H 3.79; MS: *m/z* (%) = 212 (100) [M^+], 211 (29) [$M^+ - H$].

2b: Starting material: thianthrene (**1b**). Purification by CC (SiO_2, petroleum ether/CH_2Cl_2, 1:1) and recrystallization from *n*-hexane afforded the product as a pale yellow microcrystalline powder (57%). M.p. 87–89 °C; IR (KBr): $\tilde{\nu}$ = 3060, 2860 (C-H), 1680 (C=O), 1570 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 339 (3.17), 288 (3.68), 261 (sh, 4.18), 248 nm (4.43); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.33 (m, 2H, 7-H, 8-H), 7.38 (t, $J_{3,2} = J_{3,4}$ = 7.7 Hz, 1H, 3-H), 7.49–7.57 (m, 2H, 6-H, 9-H), 7.71 (dd, $J_{4,2}$ = 1.4, $J_{4,3}$ = 7.7 Hz, 1H, 4-H), 7.83 (dd, $J_{2,3}$ = 7.7, $J_{2,4}$ = 1.4 Hz, 1H, 2-H), 10.57 (s, 1H, CHO); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 190.0 (CHO), 140.0 (C-10a), 137.7 (C-5a), 135.6, 134.0 (C-5b, C-10b), 134.8 (C-1), 133.7 (tert), 129.2 (tert), 128.9 (tert), 128.8 (tert), 128.4 (tert), 128.1 (tert), 127.4 (tert); $C_{13}H_8OS_2$ (244.3): calcd. C 63.91, H 3.30; found C 63.77, H 3.25; MS: *m/z* (%) = 244 (100) [M^+], 216 (27) [$M^+ - CO$], 215 (13) [$M^+ - CHO$].

General procedure for the synthesis for the dicyanovinyl derivatives: The appropriate heterocyclic carbaldehyde was dissolved in hot EtOH (abs) and treated with an equivalent amount of malonodinitrile and about 10 drops of piperidine. Immediately, the color of the solution deepened (in the case of the phenothiazine derivative from yellow to red) and after a few minutes the product began to precipitate. Precipitation was completed by cooling of the solution to −15 °C for about 1 h. The sample was used without further purification.

1-Dibenzo[b,e][1,4]dioxinmethylenepropanedinitrile (3a): Yield 88%, yellow needles. M.p. 144–146 °C; IR (KBr): $\tilde{\nu}$ = 3060, 3020 (C–H), 2220 (CN), 1580 cm^{-1} (C=C); UV (CH_3CN): λ_{max} (lgε) = 407 (3.45), 317 (4.24), 222 nm (4.54); ^1H NMR (250 MHz, $CDCl_3$): δ = 6.87–7.01 (m, 4H, 6-H, 7-H, 8-H, 9-H), 7.03 (t, $J_{3,2} = J_{3,4}$ = 7.7 Hz, 1H, 3-H), 7.08 (dd, $J_{4,2}$ = 2.0, $J_{4,3}$ = 8.1 Hz, 1H, 4-H), 7.80 (dd, $J_{2,3}$ = 7.5, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 8.18 (s, 1H, vinyl H); $C_{16}H_8N_2O_2$ (260.3): calcd. C 73.84, H 3.10, N 10.76; found C 73.81, H 3.09, N 10.75.

1-Thianthrenemethylenepropanedinitrile (3b): Obtained in 79% yield as yellow microcrystalline powder. M.p. 176–178 °C; IR (KBr): $\tilde{\nu}$ = 3060, 3025 (C–H), 2240 (CN), 1590 cm^{-1} (C=C); UV (CH_3CN): λ_{max} (lgε) = 400 (sh, 3.28), 328 (4.14), 284 (sh, 4.11), 255 (4.58), 235 nm (sh, 4.19); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.36 (m, 2H, 7-H, 8-H), 7.43 (t, $J_{3,2} = J_{3,4}$ = 7.9 Hz, 1H, 3-H), 7.51–7.56 (m, 2H, 6-H, 9-H), 7.72 (dd, $J_{4,2}$ = 1.2, $J_{4,3}$ = 7.7 Hz, 1H, 4-H), 8.03 (dd, $J_{2,3}$ = 7.9, $J_{2,4}$ = 1.2 Hz, 1H, 2-H), 8.50 (s, 1H, vinyl H); $C_{16}H_8N_2S_2$ (292.4): calcd. C 65.73, H 2.76, N 9.58; found C 65.63, H 2.98, N 9.66.

4-Phenoxathiinmethylenepropanedinitrile (3c): Yield 87%, orange needles. M.p. 144–146 °C; IR (KBr): $\tilde{\nu}$ = 3050 (C–H), 2235 (CN), 1580 cm^{-1} (C=C); UV (CH_3CN): λ_{max} (lgε) = 402 (3.23), 319 (4.20), 232 nm (4.37); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.18 (m, 4H, 2-H, 6-H, 8-H, 9-H), 7.21 (ddd, $J_{7,6}$ = 7.6, $J_{7,8}$ = 7.0, $J_{7,9}$ = 2.3 Hz, 1H, 7-H), 7.34 (dd, $J_{1,2}$ = 7.8, $J_{1,3}$ = 1.4 Hz, 1H, 1-H), 8.03 (dd, $J_{3,1}$ = 1.4, $J_{3,2}$ = 8.0 Hz, 1H, 3-H), 8.37 (s, 1H, vinyl H); $C_{16}H_8N_2OS$ (276.3): calcd. C 69.55, H 2.92, N 10.14; found C 69.43, H 3.11, N 10.18.

3-(10-Methyl-10H-phenothiazine)methylenepropanedinitrile (3d): Yield 93%, red microcrystalline powder. M.p. 202 °C; IR (KBr): $\tilde{\nu}$ = 3100, 2980, 2830 (C–H), 2220 (CN), 1600 (C=C), 1560 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 455 (4.14), 315 (4.25), 243 nm (4.16); ^1H NMR (250 MHz, $CDCl_3$): δ = 3.45 (s, 3H, N–CH_3), 6.82 (d, $J_{1,2}$ = 8.7 Hz, 1H, 1-H), 6.86 (dd, $J_{9,7}$ = 1.2, $J_{9,8}$ = 8.2 Hz, 1H, 9-H), 7.01 (dt, $J_{7,6} = J_{7,8}$ = 7.5, $J_{7,9}$ = 1.0 Hz, 1H, 7-H), 7.12 (dd, $J_{6,7}$ = 7.7, $J_{6,8}$ = 1.7 Hz, 1H, 6-H), 7.21 (ddd, $J_{8,6}$ = 1.7, $J_{8,7}$ = 7.3, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.50 (s, 1H, vinyl H), 7.60 (d, $J_{4,2}$ = 2.2 Hz, 1H, 4-H), 7.76 (dd, $J_{2,1}$ = 8.7, $J_{2,4}$ = 2.3 Hz, 1H, 2-H); $C_{17}H_{11}N_3S$ (289.4): calcd. C 70.57, H 3.83, N 14.52; found C 70.55, H 3.98, N 14.56; MS: *m/z* (%) = 289 (100) [M^+], 274 (27) [$M^+ - CH_3$].

3-(10-Methyl-10H-phenoxazine)methylenepropanedinitrile (3e): Yield 70%, green needles. M.p. 215 °C; IR (KBr): $\tilde{\nu}$ = 3060, 2920 (C–H), 2220 (CN), 1620 (C=C), 1570 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 486 (4.37), 305 (4.25), 276 (sh, 4.13),

228 (4.30), 211 nm (4.35); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta \approx 3.15$ (s, 3H, N-CH_3), 6.52 (d, $J_{1,2} = 9.1$ Hz, 1H, 1-H), 6.62 (dd, $J_{9,7} = 1.6$, $J_{9,8} = 7.8$ Hz, 1H, 9-H), 6.73 (dd, $J_{6,7} = 7.7$, $J_{6,8} = 1.8$ Hz, 1H, 6-H), 6.82 (dt, $J_{7,6} = J_{7,8} = 7.6$, $J_{7,9} = 1.6$ Hz, 1H, 7-H), 6.90 (ddd, $J_{8,6} = 1.7$, $J_{8,7} = 7.5$, $J_{8,9} = 7.7$ Hz, 1H, 8-H), 7.29-7.33 (m, 2H, 2-H, 4-H), 7.39 (s, 1H, vinyl H); $C_{17}H_{11}N_3O$ (273.3): calcd. C 74.71, H 4.06, N 15.38; found C 74.73, H 3.95, N 15.44; MS: m/z (%) = 273 (75) [M^+], 258 (100) [$M^+ - CH_3$].

2-(5,10-Dihydro-5,10-dimethylphenazine)methylenepropanedinitrile (3f): Yield 78%, blue microcrystalline powder. M.p. 213 °C; IR (KBr): $\tilde{\nu}$ = 3100, 2900, 2830 (C-H), 2220 (CN), 1610 (C=C), 1570 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 557 (4.16), 336 (4.43), 284 (sh, 3.95), 242 nm (4.43); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.04 (s, 3H, N-CH_3-10), 3.12 (s, 3H, N-CH_3-5), 6.31 (d, $J_{4,3} = 8.4$ Hz, 1H, 4-H), 6.44 (dd, $J_{9,7} = 1.4$, $J_{9,8} = 7.8$ Hz, 1H, 9-H), 6.49 (dd, $J_{6,7} = 7.8$, $J_{6,8} = 1.4$ Hz, 1H, 6-H), 6.75 (dt, $J_{7,6} = J_{7,8} = 7.7$, $J_{7,9} = 1.4$ Hz, 1H, 7-H), 6.83 (dt, $J_{8,6} = 1.4$, $J_{8,7} = J_{8,9} = 7.6$ Hz, 1H, 8-H), 7.00 (dd, $J_{3,1} = 2.0$, $J_{3,4} = 8.5$ Hz, 1H, 3-H), 7.09 (d, $J_{1,3} = 2.1$ Hz, 1H, 1-H), 7.34 (s, 1H, vinyl H); $C_{18}H_{14}N_4$ (286.3): calcd. C 75.50, H 4.92, N 19.57; found C 75.48, H 5.00, N 19.46.

[8+2] Cycloadditions with 8-methoxyheptafulvene (8-MHF) (4) [27]: A solution of the dicyanovinyl compound **3** (1 equiv), 8-MHF **4** (about 1.2-1.5 equiv) and a small amount of hydroquinone in an appropriate volume of dry CH_2Cl_2 was stirred under N_2 at RT until completion of the reaction (TLC monitoring). The solvent was subsequently evaporated and the crude product purified by CC.

2-(1-Dibenzo[b,e][1,4]dioxinyl)-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5a): Reaction time: 16 h. CC was carried out twice (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1) to afford the product (two diastereomers) as a colorless foamy powder (36%). M.p. 153-172 °C; IR (KBr): $\tilde{\nu}$ = 2940, 2840 (C-H), 1600 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 284 (3.74), 223 (4.59), 209 nm (sh, 4.51); ^{1}H NMR (only the data for the main diastereomer are given, 400 MHz, $CDCl_3$): δ = 3.46 (s, 3H, OMe), 3.51 (ddd, $J_{8a',3'} = 2.0$, $J_{8a',4'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 4.37 (d, $J_{2',3'} = 9.7$ Hz, 1H, 2'-H), 4.76 (ddd, $J_{3',2'} = 9.7$, $J_{3',4'} = 2.0$, $J_{3',8a'} = 2.0$ Hz, 1H, 3'-H), 5.47 (dd, $J_{8',7'} = 10.0$, $J_{8',8a'} = 3.9$ Hz, 1H, 8'-H), 6.26 (m, 1H, 7'-H), 6.42 (m, 1H, 4'-H), 6.57-6.64 (m, 2H, 5'-H, 6'-H), 6.85-6.97 (m, 5H, 4-H, 6-H, 7-H, 8-H, 9-H), 6.99 (t, $J_{3,2} = J_{3,4} = 7.9$ Hz, 1H, 3-H), 7.12 (dd, $J_{2,3} = 7.8$, $J_{2,4} = 1.5$ Hz, 1H, 2-H); $C_{25}H_{18}N_2O_3$ (394.4): calcd. C 76.12, H 4.60, N 7.10; found C 75.94, H 4.55, N 6.99.

2-(1-Thianthrenyl)-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5b): Reaction time: 16 h. CC (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1) yielded a yellow foamy powder (67%), which was used without further purification.

2-(4-Phenoxathiinyl)-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5c): Reaction time: 16 h. CC (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1) afforded a brown foamy powder (yield 67%), which was used without further purification.

2-[3-(10-Methyl-10H-phenothiazinyl)]-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5d): Reaction time: 21 d. CC (SiO_2; solvent: CH_2Cl_2) and crystallization from CH_2Cl_2/petroleum ether (1:1) afforded **5d** (one diastereoisomer) as colorless needles (63%). M.p. 188-190 °C; IR (KBr): $\tilde{\nu}$ = 3030, 2930, 2830 (C-H), 1600 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 303 (3.83), 253 nm (4.61); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.14 (ddd, $J_{8a',4'} = 2.0$, $J_{8a',7'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 3.17 (s, 3H, OMe), 3.40 (s, 3H, N-CH_3), 3.60 (d, $J_{2',3'} = 3.8$ Hz, 1H, 2'-H), 4.29 (d, $J_{3',2'} = 3.7$ Hz, 1H, 3'-H), 5.67 (dd, $J_{8',7'} = 9.7$, $J_{8',8a'} = 4.2$ Hz, 1H, 8'-H), 6.29 (ddd, $J_{7',6'} = 5.7$, $J_{7',8'} = 9.8$, $J_{7',8a'} = 1.8$ Hz, 1H, 7'-H), 6.32 (dd, $J_{4',5'} = 5.5$, $J_{4',8a'} = 1.7$ Hz, 1H, 4'-H), 6.59 (dd, $J_{6',5'} = 11.3$, $J_{6',7'} = 5.9$ Hz, 1H, 6'-H), 6.70 (dd, $J_{5',4'} = 5.8$, $J_{5',6'} = 11.3$ Hz, 1H, 5'-H), 6.83 (m, 1H, 9-H), 6.84 (d, $J_{1,2} = 8.3$ Hz, 1H, 1-H), 6.94 (dt, $J_{7,6} = J_{7,8} = 7.4$, $J_{7,9} = 0.8$ Hz, 1H, 7-H), 7.14 (dd, $J_{6,7} = 7.6$, $J_{6,8} = 1.5$ Hz, 1H, 6-H), 7.18 (ddd, $J_{8,6} = 1.5$, $J_{8,7} = 7.4$, $J_{8,9} = 8.1$ Hz, 1H, 8-H), 7.52 (d, $J_{4,2} = 2.1$ Hz, 1H, 4-H), 7.60 (dd, $J_{2,1} = 8.5$, $J_{2,4} = 2.1$ Hz, 1H, 2-H); $C_{26}H_{21}N_3OS$ (423.5): calcd. C 73.73, H 5.00, N 9.92; found C 73.32, H 5.03, N 9.87; MS: m/z (%) = 423 (91) [M^+], 289 (64) [M^+ - (8-MHF)], 274 (36) [M^+ - (8-MHF) - CH_3], 134 (100) [8-MHF].

2-[3-(10-Methyl-10H-phenoxazinyl)]-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5e): Reaction time: 35 d. CC (SiO_2; solvent: CH_2Cl_2) and precipitation from CH_2Cl_2/petroleum ether (1:1) yielded **5e** (one diastereoisomer) as colorless powder (58%). M.p. 138-140 °C; IR (KBr): $\tilde{\nu}$ = 3020, 2960, 2880 (C-H), 1620 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 321 (4.04), 237 (4.63), 210 nm (sh, 4.48); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06 (s, 3H, N-CH_3), 3.13 (ddd, $J_{8a',4'} = 2.0$, $J_{8a',7'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 3.18 (s, 3H, OMe), 3.53 (d, $J_{2',3'} = 3.8$ Hz, 1H, 2'-H), 4.29 (d, $J_{3',2'} = 3.8$ Hz, 1H, 3'-H), 5.67 (dd, $J_{8',7'} = 9.7$, $J_{8',8a'} = 4.1$ Hz, 1H, 8'-H), 6.29 (ddd, $J_{7',6'} = 5.8$, $J_{7',8'} = 9.8$, $J_{7',8a'} = 1.9$ Hz, 1H, 7'-H), 6.32 (dd, $J_{4',5'} = 6.4$, $J_{4',8a'} = 1.8$ Hz, 1H, 4'-H), 6.53 (m, 1H, 9-H), 6.53 (d, $J_{1,2} = 8.3$ Hz, 1H, 1-H), 6.59 (dd, $J_{6',5'} = 11.3$, $J_{6',7'} = 5.9$ Hz, 1H, 6'-H), 6.68-6.73 (m, 3H, 5'-H, 6-H, 7-H), 6.84 (ddd, $J_{8,6} = 1.1$, $J_{8,7} = 7.5$, $J_{8,9} = 8.2$ Hz, 1H, 8-H), 7.16 (d, $J_{4,2} = 2.1$ Hz, 1H, 4-H), 7.21 (dd, $J_{2,1} = 8.6$, $J_{2,4} = 2.1$ Hz, 1H, 2-H); $C_{26}H_{21}N_3O_2$ (407.5): calcd. C 76.64, H 5.19, N 10.31; found C 76.11, H 5.24, N 9.67; MS: m/z (%) = 407 (26) [M^+], 273 (94) [M^+ - (8-MHF)], 258 (60) [M^+ - (8-MHF) - CH_3], 134 (94) [8-MHF], 119 (100) [(8-MHF) - CH_3].

2-[2-(5,10-Dihydro-5,10-dimethylphenazinyl)]-1,2,3,8a-tetrahydro-3-methoxy-1,1-azulenedicarbonitrile (5f): Reaction time: 150 d. (Further equivalents of 8-MHF were added after 45 and 100 d; the reaction was not complete even after 150 d). It was rather difficult to purify the crude product because of fast decomposition during CC (either on SiO_2 or on Al_2O_3). The substance is unstable in solution in the presence of traces of acid or of oxygen [28]. Yield: 60% of a brown and foamy powder (only one diastereoisomer). M.p. 88-97 °C; IR (KBr): $\tilde{\nu}$ = 3020, 2950, 2920 (C-H), 1595 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 338 (3.95), 248 nm (4.66); ^{1}H NMR (400 MHz, C_6D_6): δ = 2.45 (s, 3H, N-CH_3-10), 2.77 (s, 3H, N-CH_3-5), 2.79 (s, 3H, OMe), 2.92 (ddd, $J_{8a',4'} = 2.0$, $J_{8a',7'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 2.94 (d, $J_{2',3'} = 3.9$ Hz, 1H, 2'-H), 3.69 (d, $J_{3',2'} = 4.0$ Hz, 1H, 3'-H), 5.62 (dd, $J_{8',7'} = 9.8$, $J_{8',8a'} = 3.9$ Hz, 1H, 8'-H), 5.66 (dd, $J_{4',5'} = 5.9$, $J_{4',8a'} = 1.5$ Hz, 1H, 4'-H), 5.78 (ddd, $J_{7',6'} = 5.8$, $J_{7',8'} = 9.8$, $J_{7',8a'} = 1.9$ Hz, 1H, 7'-H), 6.06 (d, $J_{4,3} = 8.1$ Hz, 1H, 4-H), 6.11 (dd, $J_{5',4'} = 5.9$, $J_{5',6'} = 11.4$ Hz, 1H, 5'-H), 6.14-6.16 (m, 2H, 6-H, 9-H), 6.23 (dd, $J_{6',5'} = 11.2$, $J_{6',7'} = 5.8$ Hz, 1H, 6'-H), 6.71-6.73 (m, 2H, 7-H, 8-H), 6.94 (d, $J_{1,3} = 1.5$ Hz, 1H, 1-H), 7.06 (brd, $J_{3,4} = 7.9$ Hz, 1H, 3-H); $C_{27}H_{24}N_4O$ (420.5): calcd. C 77.12, H 5.75, N 13.32; found C 76.54, H 5.87, N 10.48; MS: m/z (%) = 420 (9) [M^+], 286 (70) [M^+ - (8-MHF)], 271 (100) [M^+ - (8-MHF) - CH_3], 134 (16) [8-MHF].

MeOH elimination—synthesis of the DHAs: All operations were carried out under the exclusion of light. A solution of the THA **5** (1-3 g), ca. 10 g of P_2O_5 and 3 g of K_2CO_3 in dry benzene (ca. 200 mL) was refluxed until the reaction was complete. The hot reaction mixture was then filtered over silica gel, and the precipitate was washed several times with CH_2Cl_2. The solvent was removed from the combined organic phases. The crude product was purified by CC.

2-(1-Dibenzo[b,e][1,4]dioxinyl)-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-a): Reaction time: 3 h. CC (SiO_2; solvent: CH_2Cl_2) and recrystallization from methylcyclohexane afforded the product as pale yellow needles (yield 51%). M.p. 127-130 °C; IR (KBr): $\tilde{\nu}$ = 3070, 3030 (C-H), 1590 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 353 (4.03), 264 (4.10), 213 nm (4.43); ^{1}H NMR (400 MHz, $CDCl_3$; [a], [b], and [c] = tentative assignment): δ = 3.80 (ddd, $J_{8a',4'} = 2.0$, $J_{8a',7'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 5.79 (dd, $J_{8',7'} = 10.2$, $J_{8',8a'} = 3.8$ Hz, 1H, 8'-H), 6.31 (ddd, $J_{7',6'} = 6.1$, $J_{7',8'} = 10.2$, $J_{7',8a'} = 2.2$ Hz, 1H, 7'-H), 6.39 (dd, $J_{4',5'} = 6.3$, $J_{4',8a'} = 2.0$ Hz, 1H, 4'-H), 6.49 (dd, $J_{6',5'} = 11.2$, $J_{6',7'} = 6.1$ Hz, 1H, 6'-H), 6.59 (dd, $J_{5',4'} = 6.3$, $J_{5',6'} = 11.3$ Hz, 1H, 5'-H), 6.87-6.96 (m, 4H, 4-H, 6-H, 7-H, 8-H), 7.00 (dd, $J_{9,7} = 2.0$, $J_{9,8} = 7.3$ Hz, 1H, 9-H), 7.00 (t, $J_{3,2} = J_{3,4} = 8.0$ Hz, 1H, 3-H), 7.13 (s, 1H, 3'-H), 7.30 (dd, $J_{2,3} = 8.0$, $J_{2,4} = 1.5$ Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.96 [a] (C-5a), 141.74 [a] (C-5b), 141.29 [a] (C-10a), 140.84 [a] (C-10b), 138.69 (C-4a'), 137.17 (C-3'), 135.40 (C-2'), 130.93 (C-6'), 130.89 (C-5'), 127.57 (C-7'), 124.67 [b] (C-7), 124.09 [b] (C-8), 123.78 (C-3), 122.93 (C-2), 121.49 (C-4'), 119.91 (C-8'), 119.50 (C-1), 117.89 (C-4), 116.49 [c] (C-6), 116.35 [c] (C-9), 115.58, 112.92 (2CN), 51.16 (C-8a'), 46.93 (C-1'); $C_{24}H_{14}N_2O_2$ (362.4): calcd. C 79.55, H 3.89, N 7.73; found C 79.37, H 4.24, N 7.98; MS: m/z (%) = 362 (100) [M^+], 335 (49) [M^+ - HCN].

VHF-a: UV (CH_3CN): λ_{max} (lgε) = 478 (4.29), 278 (sh, 3.89), 210 nm (4.45); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (tdd, $J_{5',3'} = J_{5',1'} = 1.0$, $J_{5',4'} = 7.6$, $J_{5',6'} = 12.1$ Hz, 1H, 5'-H), 6.18 (brdd, $J_{6',4'} = 2.0$, $J_{6',5'} = 12.1$ Hz, 1H, 6'-H), 6.27 (m, 1H, 4'-H), 6.38 (m, 1H, 3'-H), 6.38 (s, 1H, 8'-H), 6.41 (ddd, $J_{2',1'} = 11.2$, $J_{2',3'} = 7.8$, $J_{2',4'} = 1.8$ Hz, 1H, 2'-H), 6.70 (m, 1H, 1'-H), 6.77 (dd, $J_{2,3} = 7.1$, $J_{2,4} = 2.2$ Hz, 1H, 2-H), 6.85 (m, 2H, 6-H, 9-H), 6.90 (m, 2H, 7-H, 8-H), 6.97 (dd, $J_{4,2} = 2.2$, $J_{4,3} = 8.1$ Hz, 1H, 4-H), 7.00 (dd, $J_{3,2} = 7.1$, $J_{3,4} = 8.1$ Hz, 1H, 3-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.90 (C-9'), 156.60 (C-7'), 143.20 [a] (C-5a), 142.26 (C-1'), 141.61 [a] (C-5b), 141.48 [a] (C-10a), 139.08 [a] (C-10b), 135.73 (C-3'), 135.19 (C-4'), 134.60 (C-2'), 134.38 (C-5'), 134.27 (C-6'), 124.80 (C-3), 124.45 [b] (C-7), 124.28 [b] (C-8), 123.42 (C-1), 123.24 (C-2), 118.95 (C-8'), 118.63 (C-4), 116.73 [c] (C-6), 116.34 [c] (C-9), 114.71, 114.32 (2CN), 78.04 (C-10').

2-(1-Thianthrenyl)-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-b): Reaction time: 4 h. CC (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1) afforded **DHA-b** as a pale yellow powder (24%). M.p. 140-142 °C; IR (KBr): $\tilde{\nu}$ = 3070, 3040 (C-H), 1550 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 322 (3.80), 253 nm (4.40); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (ddd, $J_{8a',4'} = 2.0$, $J_{8a',7'} = 2.0$, $J_{8a',8'} = 4.0$ Hz, 1H, 8a'-H), 5.85 (dd, $J_{8',7'} = 10.2$, $J_{8',8a'} = 3.8$ Hz, 1H, 8'-H), 6.36 (ddd, $J_{7',6'} = 5.4$, $J_{7',8'} = 10.2$, $J_{7',8a'} = 2.2$ Hz, 1H, 7'-H), 6.41 (dd, $J_{4',5'} = 6.2$, $J_{8a'} = 0.7$ Hz, 1H, 4'-H), 6.55 (dd, $J_{6',5'} = 11.2$, $J_{6',7'} = 6.0$ Hz, 1H, 6'-H), 6.63 (dd, $J_{5',4'} = 6.2$, $J_{5',6'} = 11.3$ Hz, 1H, 5'-H), 6.67 (s, 1H, 3'-H), 7.27 (m, 2H, 7-H, 8-H), 7.35 (t, $J_{3,2} = J_{3,4} = 7.7$ Hz, 1H, 3-H), 7.48 (m, 2H, 6-H, 9-H), 7.53 (dd, $J_{4,2} = 1.3$, $J_{4,3} = 7.7$ Hz, 1H, 4-H), 7.61 (dd, $J_{2,3} = 7.8$, $J_{2,4} = 1.3$ Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 139.86 (C-3'), 137.93 (C-4a'), 137.41 [a] (C-5a), 137.20 [a] (C-2'), 137.05 [a] (C-5b), 136.09 [a] (C-10a), 135.07 [a] (C-10b), 131.66 (C-1), 131.28 (C-6'), 130.79 (C-5'), 130.32 (C-2), 129.21 [b] (C-6), 128.58 [b] (C-9), 128.16 [c] (C-7), 128.08 [b] (C-4), 127.98 [c] (C-8), 127.64 (C-3), 127.64 (C-7'), 121.48 (C-4'), 119.76 (C-8'), 114.40, 112.08 (2CN), 50.67 (C-8a'), 48.73 (C-1'); $C_{24}H_{14}N_2S_2$ (394.5): calcd. C 73.07, H 3.58, N 7.10; found C 73.17, H 3.84, N 6.88; MS: m/z (%) = 394 (100) [M^+], 367 (28) [M^+ - HCN].

VHF-b: UV (CH_3CN): λ_{max} (lgε) = 479 (4.24), 254 nm (4.42); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (tdd, $J_{5',3'} = J_{1'} = 1.0$, $J_{5',4'} = 7.4$, $J_{5',6'} = 12.1$ Hz, 1H, 5'-H),

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5.71 (br dd, $J_{6',4'}$ = 1.0, $J_{6',5'}$ = 12.1 Hz, 1H, 6'-H), 6.13 (br ddd, $J_{4',2'}$ = 1.0, $J_{4',3'}$ = 10.7, $J_{4',5'}$ = 7.4 Hz, 1H, 4'-H), 6.37 (m, 1H, 3'-H), 6.42 (s, 1H, 8'-H), 6.44 (ddd, $J_{2',1'}$ = 11.6, $J_{2',3'}$ = 7.9, $J_{2',4'}$ = 1.2 Hz, 1H, 2'-H), 6.74 (br dd, $J_{1',2'}$ = 11.0, $J_{1',3'}$ = 1.4 Hz, 1H, 1'-H), 7.19 (dd, $J_{4,2}$ = 1.3, $J_{4,3}$ = 7.6 Hz, 1H, 4-H), 7.24 (m, 2H, 7-H, 8-H), 7.38 (m, 2H, 3-H, 9-H), 7.48 (m, 1H, 6-H), 7.61 (dd, $J_{2,3}$ = 7.8, $J_{2,4}$ = 1.3 Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.82 (C-9'), 153.52 (C-7'), 142.35 (C-1'), 138.42 [a] (C-1), 135.82 (C-3'), 135.69 [a] (C-5a), 135.45 (C-4'), 135.20 [a] (C-5b), 134.89 (C-2'), 134.59 (C-5'), 134.37 [a] (C-10a), 133.96 [a] (C-10b), 133.63 (C-6'), 130.38 (C-2), 129.14 [b] (C-9), 128.58 [b] (C-6), 128.51 (C-3), 128.09 [c] (C-7), 127.98 [c] (C-8), 127.24 (C-4), 118.63 (C-8'), 114.47, 114.24 (2CN), 77.53 (C-10').

2-(4-Phenoxathiinyl)-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-c): Reaction time: 2 h. CC (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1) and recrystallization from methylcyclohexane furnished **DHA-c** as a yellow powder (35%). M.p. 132–133 °C; IR (KBr): $\tilde{\nu}$ = 3060, 3020 (C–H), 1570 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 352 (4.15), 265 (4.20), 230 nm (4.51); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (ddd, $J_{8a',4'}$ = 2.0, $J_{8a',7'}$ = 2.0, $J_{8a',8'}$ = 4.0 Hz, 1H, 8a'-H), 5.81 (dd, $J_{8',7'}$ = 10.2, $J_{8',8a'}$ = 3.8 Hz, 1H, 8'-H), 6.32 (ddd, $J_{7',6'}$ = 6.1, $J_{7',8'}$ = 10.2, $J_{7',8a'}$ = 2.2 Hz, 1H, 7'-H), 6.43 (dd, $J_{4',5'}$ = 5.6, $J_{4',8a'}$ = 2.0 Hz, 1H, 4'-H), 6.51 (dd, $J_{6',5'}$ = 11.2, $J_{6',7'}$ = 6.1 Hz, 1H, 6'-H), 6.61 (dd, $J_{5',4'}$ = 6.3, $J_{5',6'}$ = 11.3 Hz, 1H, 5'-H), 7.04–7.17 (m, 5H, 2-H, 6-H, 7-H, 8-H, 9-H), 7.18 (dd, $J_{1,2}$ = 7.8, $J_{1,3}$ = 1.8 Hz, 1H, 1-H), 7.32 (s, 1H, 3'-H), 7.58 (dd, $J_{3,1}$ = 1.8, $J_{3,2}$ = 7.6 Hz, 1H, 3-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 151.56, 150.72 (C-5a, C-5b), 138.97 (C-4a'), 138.08 (C-3'), 135.11 (C-2'), 131.04 (C-6'), 130.87 (C-5'), 128.30 (C-1), 127.88 (C-9), 127.68 (C-7'), 126.84 (C-7), 126.82 (C-3), 125.35 [a] (C-2), 124.54 [a] (C-8), 122.09 [b] (C-4), 121.57 (C-4'), 120.88 [b], 120.22 [b] (C-10a, C-10b), 119.82 (C-8'), 117.98 (C-6), 115.36, 112.82 (2CN), 50.88 (C-8a'), 47.14 (C-1'); $C_{24}H_{14}N_2OS$ (378.5): calcd. C 76.17, H 3.73, N 7.40; found C 75.60, H 4.09, N 7.78; MS: m/z (%) = 378 (100) [M^+], 351 (32) [M^+ – HCN].

VHF-c: UV (CH_3CN): λ_{max} (lgε) = 476 (4.43), 283 (sh, 4.02), 232 nm (4.52); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (tdd, $J_{5',3'} = J_{5',1'}$ = 1.0, $J_{5',4'}$ = 7.7, $J_{5',6'}$ = 12.1 Hz, 1H, 5'-H), 5.97 (br dd, $J_{6',4'}$ = 1.7, $J_{6',5'}$ = 12.1 Hz, 1H, 6'-H), 6.11 (br ddd, $J_{4',2'}$ = 1.0, $J_{4',3'}$ = 10.6, $J_{4',5'}$ = 7.8 Hz, 1H, 4'-H), 6.32 (br ddd, $J_{3',1'}$ = 1.0, $J_{3',2'}$ = 8.0, $J_{3',4'}$ = 10.8 Hz, 1H, 3'-H), 6.40 (ddd, $J_{2',1'}$ = 11.5, $J_{2',3'}$ = 7.9, $J_{2',4'}$ = 1.1 Hz, 1H, 2'-H), 6.45 (s, 1H, 8'-H), 6.70 (br dd, $J_{1',2'}$ = 11.0, $J_{1',3'}$ = 1.7 Hz, 1H, 1'-H), 6.91 (dd, $J_{6,7}$ = 8.3, $J_{6,8}$ = 1.3 Hz, 1H, 6-H), 7.01 (ddd, $J_{8,6}$ = 1.4, $J_{8,7}$ = 7.2, $J_{8,9}$ = 7.8 Hz, 1H, 8-H), 7.05 (dd, $J_{3,1}$ = 1.6, $J_{3,2}$ = 7.6 Hz, 1H, 3-H), 7.09 (m, 2H, 7-H, 9-H), 7.15 (t, $J_{2,1} = J_{2,3}$ = 7.7 Hz, 1H, 2-H), 7.25 (dd, $J_{1,2}$ = 7.7, $J_{1,3}$ = 1.6 Hz, 1H, 1-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 164.01 (C-9'), 153.34 (C-7'), 151.62, 148.24 (C-5a, C-5b), 141.92 (C-1'), 135.62 (C-3'), 135.17 (C-4'), 134.45 (C-2'), 134.27 (C-5'), 133.86 (C-6'), 129.07 (C-1), 128.19 (C-9), 127.29 (C-3), 126.63 (C-7), 125.48 (C-2), 125.01 [a] (C-4), 124.99 (C-8), 122.95 [a], 119.27 [a] (C-10a, C-10b), 119.09 (C-8'), 117.96 (C-6), 114.69, 114.32 (2CN), 77.95 (C-10').

2-[3-(10-Methyl-10H-phenothiazinyl)]-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-d): Reaction time: 12 h. CC (SiO_2; solvent: CH_2Cl_2) and precipitation from CH_2Cl_2/petroleum ether (1:1) afforded **DHA-d** as an orange powder (6%). M.p. 143–144 °C; IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2880 (C–H), 1590 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 410 (4.25), 333 (sh, 3.99), 280 (4.25), 246 nm (4.29); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 3H, N–CH_3), 3.76 (ddd, $J_{8a',4'}$ = 1.9, $J_{8a',7'}$ = 1.9, $J_{8a',8'}$ = 3.9 Hz, 1H, 8a'-H), 5.80 (dd, $J_{8',7'}$ = 10.0, $J_{8',8a'}$ = 3.9 Hz, 1H, 8'-H), 6.30 (m, 2H, 4'-H, 7'-H), 6.44 (dd, $J_{6',5'}$ = 11.4, $J_{6',7'}$ = 6.4 Hz, 1H, 6'-H), 6.55 (dd, $J_{5',4'}$ = 6.3, $J_{5',6'}$ = 11.4 Hz, 1H, 5'-H), 6.75 (s, 1H, 3'-H), 6.84 (dd, $J_{9,7}$ = 1.1, $J_{9,8}$ = 8.3 Hz, 1H, 9-H), 6.87 (d, $J_{1,2}$ = 8.7 Hz, 1H, 1-H), 6.97 (dt, $J_{7,6} = J_{7,8}$ = 7.5, $J_{7,9}$ = 1.2 Hz, 1H, 7-H), 7.14 (dd, $J_{6,7}$ = 7.7, $J_{6,8}$ = 1.4 Hz, 1H, 6-H), 7.19 (ddd, $J_{8,6}$ = 1.5, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.43 (d, $J_{4,2}$ = 2.3 Hz, 1H, 4-H), 7.58 (dd, $J_{2,1}$ = 8.5, $J_{2,4}$ = 2.3 Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 147.16, 144.60 (C-10a, C-10b), 139.13 (C-2'), 138.83 (C-4a'), 130.95 (C-5'), 130.39 (C-6'), 130.35 (C-3'), 127.72 (C-8), 127.62 (C-7'), 127.24 (C-6), 125.55 (C-2), 124.70 (C-4), 124.70, 124.59 (C-5a, C-5b), 123.09 (C-7), 122.34 (C-3), 120.17 (C-4'), 119.26 (C-8'), 115.16 [a] (CN-1), 114.42 (C-9), 114.09 (C-1), 112.74 [a] (CN-2), 51.12 (C-8a'), 45.01 (C-1'), 35.46 (C–Me); $C_{25}H_{17}N_3S$ (391.5): calcd. C 76.70, H 4.38, N 10.73; found C 76.68, H 4.43, N 10.69; MS: m/z (%) = 391 (100) [M^+], 376 (17) [M^+ – CH_3].

VHF-d: UV (CH_3CN): λ_{max} (lgε) = 465 (4.30), 304 (4.10), 255 nm (4.44); ^{1}H NMR (400 MHz, $CDCl_3$, 5 °C): δ = 3.41 (s, 3H, CH_3), 6.01 (dd, $J_{5',4'}$ = 6.7, $J_{5',6'}$ = 12.1 Hz, 1H, 5'-H), 6.05 (br d, $J_{6',5'}$ = 12.1 Hz, 1H, 6'-H), 6.22 (s, 1H, 8'-H), 6.30 (m, 1H, 4'-H), 6.38 (m, 1H, 3'-H), 6.39 (dd, $J_{2',1'}$ = 13.2, $J_{2',3'}$ = 7.8 Hz, 1H, 2'-H), 6.67 (m, 1H, 1'-H), 6.84 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 6.85 (dd, $J_{9,7}$ = 1.0, $J_{9,8}$ = 8.2 Hz, 1H, 9-H), 6.99 (dt, $J_{7,6} = J_{7,8}$ = 7.5, $J_{7,9}$ = 1.1 Hz, 1H, 7-H), 7.12 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 7.16 (d, $J_{4,2}$ = 2.1 Hz, 1H, 4-H), 7.21 (ddd, $J_{8,6}$ = 1.5, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.29 (dd, $J_{2,1}$ = 8.4, $J_{2,4}$ = 2.1 Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 5 °C): δ = 167.67 (C-9'), 154.03 (C-7'), 148.55, 144.38 (C-10a, C-10b), 142.17 (C-1'), 135.40 (C-6'), 135.34 (C-3'), 134.99 (C-4'), 134.29 (C-2'), 133.60 (C-5'), 128.36 (C-2), 128.13 (C-3), 127.76 (C-8), 127.23 (C-6), 126.78 (C-4), 124.60 [a] (C-5a), 123.26 (C-7), 122.20 [a] (C-5b), 118.61 (C-8'), 115.60, 115.02 (2CN), 114.51 (C-9), 114.42 (C-1), 74.55 (C-10'), 35.55 (C–Me).

2-[3-(10-Methyl-10H-phenoxazinyl)]-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-e): Reaction time: 4 h. CC (SiO_2; solvent: CH_2Cl_2) and precipitation from CH_2Cl_2/petroleum ether (1:1) afforded **DHA-e** as orange-red powder (5%). M.p. 140 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3080, 3020, 2930, 2860 (C–H), 1625 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 434 (4.30), 324 (3.93), 258 (4.26), 213 nm (4.45); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H, N–CH_3), 3.76 (ddd, $J_{8a',4'}$ = 1.9, $J_{8a',7'}$ = 1.9, $J_{8a',8'}$ = 3.9 Hz, 1H, 8a'-H), 5.80 (dd, $J_{8',7'}$ = 10.3, $J_{8',8a'}$ = 3.8 Hz, 1H, 8'-H), 6.27 (m, 1H, 4'-H), 6.29 (ddd, $J_{7',6'}$ = 6.1, $J_{7',8'}$ = 10.2, $J_{7',8a'}$ = 2.2 Hz, 1H, 7'-H), 6.43 (dd, $J_{6',5'}$ = 11.1, $J_{6',7'}$ = 6.1 Hz, 1H, 6'-H), 6.55 (dd, $J_{5',4'}$ = 6.5, $J_{5',6'}$ = 11.3 Hz, 1H, 5'-H), 6.56 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H), 6.57 (dd, $J_{9,7}$ = 1.3, $J_{9,8}$ = 7.9 Hz, 1H, 9-H), 6.68 (s, 1H, 3'-H), 6.71 (dd, $J_{6,7}$ = 7.8, $J_{6,8}$ = 1.7 Hz, 1H, 6-H), 6.75 (dt, $J_{7,6} = J_{7,8}$ = 7.5, $J_{7,9}$ = 1.4 Hz, 1H, 7-H), 6.87 (ddd, $J_{8,6}$ = 1.8, $J_{8,7}$ = 7.2, $J_{8,9}$ = 7.9 Hz, 1H, 8-H), 6.98 (d, $J_{4,2}$ = 2.2 Hz, 1H, 4-H), 7.28 (dd, $J_{2,1}$ = 8.4, $J_{2,4}$ = 2.3 Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 145.71, 144.96 (C-5a, C-5b), 139.31 (C-2'), 139.08 (C-4a'), 136.58, 133.42 (C-10a, C-10b), 131.00 (C-5'), 130.12 (C-6'), 129.53 (C-3'), 127.61 (C-7'), 124.01 (C-8), 123.07 (C-3), 122.43 (C-2), 121.85 (C-7), 119.74 (C-4'), 119.22 (C-8'), 115.49 (C-6), 115.27, 112.85 (2CN), 112.57 (C-4), 111.85 (C-9), 111.34 (C-1), 51.17 (C-8a'), 44.90 (C-1'), 30.98 (C-Me); $C_{25}H_{17}N_3O$ (375.4): calcd. C 79.98, H 4.56, N 11.19; found C 79.57, H 4.90, N 10.74; MS: m/z (%) = 375 (100) [M^+], 360 (31) [M^+ – CH_3], 348 (12) [M^+ – HCN], 333 (20) [M^+ – HCN – CH_3].

VHF-e: UV (CH_3CN): λ_{max} (lgε) = 469 (4.38), 307 (4.15), 240 nm (4.53); ^{1}H NMR (400 MHz, $CDCl_3$, 5 °C): δ = 3.09 (s, 3H, CH_3), 6.07 (dd, $J_{5',4'}$ = 7.4, $J_{5',6'}$ = 12.1 Hz, 1H, 5'-H), 6.15 (dd, $J_{6',4'}$ = 2.2, $J_{6',5'}$ = 12.0 Hz, 1H, 6'-H), 6.19 (s, 1H, 8'-H), 6.30 (m, 1H, 4'-H), 6.36 (m, 2H, 2',3'-H), 6.54 (d, $J_{1,2}$ = 8.2 Hz, 1H, 1-H), 6.58 (dd, $J_{9,7}$ = 1.2, $J_{9,8}$ = 8.0 Hz, 1H, 9-H), 6.65 (m, 1H, 1'-H), 6.68 (dd, $J_{6,7}$ = 7.8, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 6.71 (d, $J_{4,2}$ = 2.1 Hz, 1H, 4-H), 6.76 (dt, $J_{7,6} = J_{7,8}$ = 7.7, $J_{7,9}$ = 1.3 Hz, 1H, 7-H), 6.88 (dt, $J_{8,6}$ = 1.5, $J_{8,7} = J_{8,9}$ = 7.7 Hz, 1H, 8-H), 7.01 (dd, $J_{2,1}$ = 8.3, $J_{2,4}$ = 2.1 Hz, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 5 °C): δ = 167.72 (C-9'), 153.85 (C-7'), 145.87, 144.85 (C-5a, C-5b), 142.03 (C-1'), 138.05 [a] (C-10a), 135.59 (C-6'), 135.12 (C-3'), 134.85 (C-4'), 134.01 (C-2'), 133.31 (C-5'), 133.19 [a] (C-10b), 126.43 (C-3), 125.32 (C-2), 124.10 (C-8), 122.09 (C-7), 118.70 (C-8'), 115.79 [b] (CN-1), 115.48 (C-6), 115.23 [b] (CN-2), 115.00 (C-4), 111.93 (C-9), 111.72 (C-1), 73.81 (C-10'), 31.01 (C–Me).

2-[2-(5,10-Dihydro-5,10-dimethylphenazinyl)]-1,8a-dihydro-1,1-azulenedicarbonitrile (DHA-f): Reaction time: 6 h. Dihydroazulene **(DHA-f)** is sensitive to acid and air. Fast filtration over SiO_2 and precipitation from CH_2Cl_2/petroleum ether (1:1) gave the product as a dark red powder (6%) [28]. M.p. 115 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3020, 2960, 2900 (C–H), 1610 cm^{-1} (Ar); UV (CH_3CN): λ_{max} (lgε) = 471 (3.95), 346 (4.19), 289 (4.12), 245 nm (4.49); ^{1}H NMR (400 MHz, C_6D_6): δ = 2.36 (s, 3H, N–CH_3-10), 2.50 (s, 3H, N–CH_3-5), 3.62 (ddd, $J_{8a',4'}$ = 1.8, $J_{8a',7'}$ = 1.8, $J_{8a',8'}$ = 3.6 Hz, 1H, 8a'-H), 5.75 (dd, $J_{9,7}$ = 1.3, $J_{9,8}$ = 6.5 Hz, 1H, 9-H), 5.82 (m, 3H, 4'-H, 7'-H, 8'-H), 5.99 (dd, $J_{6',5'}$ = 11.2, $J_{6',7'}$ = 5.8 Hz, 1H, 6'-H), 6.07 (s, 1H, 3'-H), 6.10 (m, 2H, 4-H, 6-H), 6.15 (dd, $J_{5',4'}$ = 6.5, $J_{5',6'}$ = 11.3 Hz, 1H, 5'-H), 6.33 (d, $J_{1,3}$ = 2.1 Hz, 1H, 1-H), 6.72 (m, 2H, 7-H, 8-H), 7.21 (dd, $J_{3,1}$ = 2.1, $J_{3,4}$ = 8.2 Hz, 1H, 3-H); $C_{26}H_{20}N_4$ (388.5): calcd. C 80.39, H 5.19, N 14.42; found C 79.46, H 6.16, N 12.97; MS: m/z (%) = 388 (100) [M^+], 373 (80) [M^+ – CH_3], 346 (25) [M^+ – HCN – CH_3], 331 (10) [M^+ – HCN – 2CH_3].

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[1] Preceeding publication: J. Daub, M. Beck, A. Knorr, H. Spreitzer, *Pure Appl. Chem.*, **1996**, *68*, 1399.

[2] a) *Molecular Electronics—Science and Technology, AIP Conference Proceedings 262* (Ed. A. Aviram), American Institute of Physics, New York, **1992**; b) A. Aviram, *J. Am. Chem. Soc.* **1988**, *110*, 5687–5692; c) B. L. Feringa, W. F. Jager, B. de Lange, *Tetrahedron* **1993**, *49*, 8267; d) J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304; e) *Photochemistry and Polymer Systems* (Eds.: J. M. Kelly, C. B. McArdle, M. J. de F. Maunder), Royal Society of Chemistry, Cambridge, **1993**.

[3] a) J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely, K. M. Rapp, *Angew. Chem.* **1989**, *101*, 1541; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1494; b) J. Daub, C. Fischer, J. Salbeck, K. Ulrich, *Adv. Mater.* **1990**, *2*, 366; c) J. Achatz, C. Fischer, J. Salbeck, J. Daub, *J. Chem. Soc. Chem. Commun.* **1991**, 504; d) J. Daub, S. Gierisch, J. Salbeck, *Tetrahedron Lett.* **1990**, *31*, 3113; e) J. Daub, C. Fischer, S. Gierisch, J. Sixt, *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 177; f) P. A. Bross, A. Mirlach, J. Salbeck, J. Daub, *DECHEMA Monogr.* **1990**, *121*, 375–382.

[4] a) T. Iyoda, T. Saika, K. Honda, T. Shimidzu, *Tetrahedron Lett.* **1989**, *30*, 5429; b) Z. F. Liu, K. Hashimoto, A. Fujishima, *Nature* **1990**, *347*, 658–660; c) A. A. Solov'ev, E. Y. Katz, V. A. Shuvalov, Y. E. Erokhin, *Bioelectrochem. Bioenerg.* **1991**, *26*, 29–41; d) Z. F. Liu, B. H. Loo, K. Hashimoto, A. Fujishima, *J. Electroanal. Chem.* **1991**, *297*, 133–144; e) T. Saika, T. Iyoda, K. Honda,

 © VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1996 0947-6539/96/0209-1157 $ 15.00+.25/0

T. Shimidzu, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1181; f) V. Goulle, A. Harriman, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1994**, 1034–1036; g) T. Saika, M. Irie, T. Shimidzu, *ibid.* **1994**, 2123–2124; h) M. Lion-Dagan, E. Katz, I. Willner, *J. Am. Chem. Soc.* **1994**, *116*, 7913–7914; i) M. Nakagawa, M. Rikukawa, M. Watanabe, K. Sanui, N. Ogata, *Chem. Lett.* **1994**, 1785–1788; j) S. H. Kawai, S. L. Gilat, R. Ponsinet, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 285–293; k) S. L. Gilat, S. H. Kawai, J.-M. Lehn, *ibid.* **1995**, *1*, 275–284.

[5] a) M. Campredon, G. Giusti, R. Guglielmetti, A. Samat, G. Gronchi, A. Alberti, M. Benaglia, *J. Chem. Soc. Perkin Trans. 2* **1993**, 2089–2094; b) J. F. Zhi, R. Baba, K. Hashimoto, A. Fujishima, *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 32–39; c) A. K. Newell, J. H. P. Utley, *J. Chem. Soc. Chem. Commun.* **1992**, 800.

[6] H. Spreitzer, Thesis, University of Regensburg, **1995**.

[7] J. Salbeck, V. M. Komissarov, V. I. Minkin, J. Daub, *Angew. Chem.* **1992**, 104, 1498; *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 1498.

[8] a) *Phenothiazines and 1,4-Benzothiazines—Chemical and Biochemical Aspects* (Ed.: R. R. Gupta), Elsevier, Amsterdam, **1988**; b) *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, **1984**.

[9] a) C. Bodea, I. Silberg, *Adv. Heterocycl. Chem.* 1968, *9*, 321–460; b) *Methoden Org. Chem. (Houben–Weyl), Vol. E9* (Ed.: E. Schaumann), Thieme, Stuttgart, **1995/96**.

[10] a) J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem.* **1984**, *96*, 980; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 960; b) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.* **1986**, *119*, 2631; c) S. Gierisch, J. Daub, *ibid.* **1989**, *122*, 69–75; d) S. Gierisch, W. Bauer, T. Burgemeister, J. Daub, *ibid.* **1989**, *122*, 2341.

[11] A. Hasenhündl, K. M. Rapp, J. Daub, *Chem. Lett.* **1979**, 597.

[12] S. Gierisch, Thesis, Regensburg University, **1989**.

[13] C. Fischer, J. Daub, *Chem. Ber.* **1993**, *126*, 1631.

[14] A comparable hypsochromic shift is also observed by the compounds with ortho-nitrophenyl at C-2: H. Görner, C. Fischer, J. Daub, *J. Photochem. Photobiol. A: Chem.* **1995**, *85*, 217–224.

[15] We anticipate that because of the push/pull stabilization of the VHF forms, the **DHA(a–e)/VHF(a–e)** interconversion leads to an off/on switching of second-order hyperpolarizability (ref. [3e]). Qualitatively, the significant positive solvatochromism is strong indication of an exalted second-order hyperpolarizability in VHF (ref. [18a]).

[16] S. Gierisch, J. Daub, *Chem. Ber.* **1989**, *122*, 69–75.

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

[18] a) J. Bindl, P. Seitz, U. Seitz, E. Salbeck, J. Salbeck, J. Daub, *Chem. Ber.* **1987**, *120*, 1747–1756; b) M. Baumgarten, K. Müllen, *Top. Curr. Chem.* **1994**, *169*, 1–103.

[19] Hubert Hirschlag, Diploma Thesis, Regensburg University, **1995**.

[20] *Recommended Methods for Purification of Solvents and Tests for Impurities* (Ed.: J. F. Coetze), Pergamon, Oxford, **1983**.

[21] a) J. Salbeck, I. Aurbach, J. Daub, *DECHEMA Monogr.* **1988**, *112*, 177; b) J. Salbeck, *J. Electroanal. Chem.* **1992**, *340*, 169; c) J. Salbeck, *Anal. Chem.* **1993**, *65*, 2169.

[22] H. Spreitzer, M. Scholz, G. Gescheidt, J. Daub, *Liebigs Ann.*, in press.

[23] See: a) V. D. Pokhodenko, V. G. Koshechko, A. N. Inozemtsev, *J. Chem. Soc. Chem. Commun.* **1985**, 72; b) K. Shindo, S. Ishikawa, T. Nozoe, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1158.

[24] H. Gilman, J. J. Dietrich, *J. Am. Chem. Soc.* **1957**, *79*, 6178.

[25] cf. a) H. Gilman, S. H. Eidt, *J. Am. Chem. Soc.* **1956**, *78*, 2633; b) B. D. Palmer, G. W. Rewcastle, G. J. Atwell, B. C. Baguley, W. A. Denny, *J. Med. Chem.* **1988**, *31*, 707; c) B. D. Palmer, M. Boyd, W. A. Denny, *J. Org. Chem.* **1990**, *55*, 438.

[26] H. H. Lee, W. A. Denny, *J. Chem. Soc. Perkin Trans. I.* **1990**, 1071.

[27] a) T. Knöchel, Thesis, Regensburg University, **1985**; b) J. Daub, G. Hirmer, L. Jakob, G. Maas, W. Pickl, E. Pirzer, K. M. Rapp, *Chem. Ber.* **1985**, *118*, 1836–1856.

[28] We were unable to obtain a pure sample. By spectroscopy, traces of by-products were detected. For the NMR spectra a freshly opened bottle of C_6D_6 (stored under argon) has to be used.

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