

OXIDATION STATE DEPENDENT LIGHT SENSITIVITY OF A FERROCENE/DIHYDROAZULENE CONJUGATE

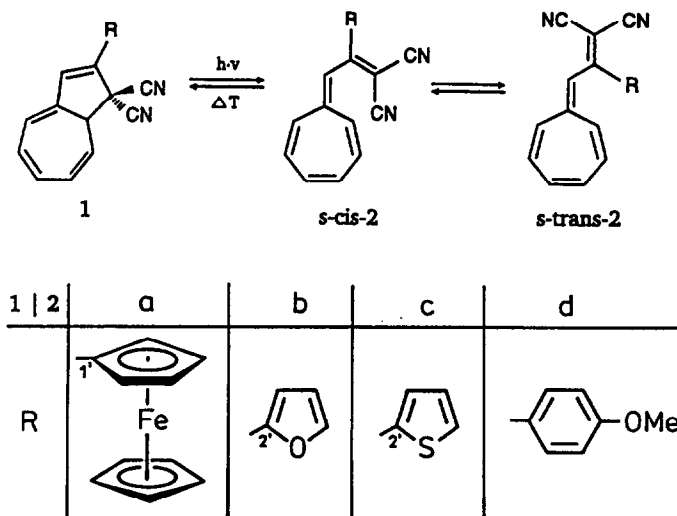
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Summary: *The synthesis of 1,8a-dihydro-2-ferrocenyl-1,1-azulenedicarbonitrile (1a) is described. Photochemical and electrochemical properties are investigated.*

In previous publications we reported on bichromophoric compounds containing covalently linked light-sensitive and redox-active structural units which were applied as media to modulate electric current by light pulses ¹). Light-sensitive substructure of these compounds is the photochromic dihydroazulene subunit which as shown by compound 1 rearranges under visible light irradiation to the extended conjugated vinylheptafulvene 2. Under thermal conditions 2 is reconverted to dihydroazulene ¹²). Hitherto, redox-activity was brought in by substituents like heteroaryl, aryl, polyazulenyl, or chinonyl groups ¹).

Scheme 1

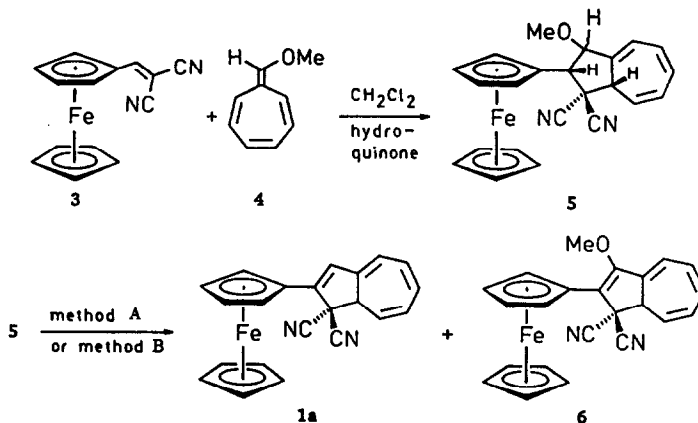


These investigations are now extended to the ferrocenyl substituted dihydroazulene 1a as a first example of electron-transfer active organometallic compounds which are expected to be even more suitable as switching media ³). The synthesis of 1a is shown in Scheme 2: [8+2]-cycloaddition of dicyanovinyl ferrocene 3 and 8-methoxyheptafulvene 4 at room temperature leads to a 55:45 mixture of diastereomeric tetrahydroazulenes 5 which were separated by column-chromatography

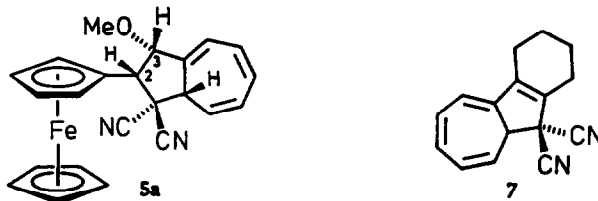
#Dedicated to Prof. F. Effenberger on occasion of his 60th birthday.

(silica gel, eluent dichloromethane/petroleum ether). At higher temperature the yield of cycloadduct **5** decreases due to cycloreversion of **5** supplying **3** again.

Scheme 2



The stereochemistry of the main product **5a** (mp 191°C) was assigned by $^1\text{H-NMR}$ in comparison to known compounds⁴). The elimination of methanol yielding dihydroazulene **1a** was performed either by phosphorous pentoxide in refluxing benzene (method A, yield 23%) or by absorption of **5** on silica gel and heating at 100°C for 1 h (method B, yield 33%)⁵). It is interesting to note that by method B the methoxy substituted dihydroazulene **6** was obtained as a by-product (ratio **1a** : **6** = 4 : 1).



Irradiation of **1a** with visible light (Osram HWLS 500 W) at room temperature gave no evidence for the formation of the ring-opened product **2a**. The same behaviour has been observed previously of the rotationally restricted compound **7**⁶). Under the same conditions, the furanyl and thienyl compounds **1b** and **1c** lead to stationary mixtures of **1b/2b** and **1c/2c**, respectively, while the p-methoxyphenyl derivative **1d** gave complete conversion to vinylheptafulvene **2d**⁷). It was also found that the rate ($10^4 k_{\text{obs}}$, sec^{-1}) of the thermal reverse-reaction $2 \rightarrow 1$ increases in the order: $k(2\text{d}) : k(2\text{c}) : k(2\text{b}) = 1.6 : 9.5 : 14.2$ ³). Therefore, the non-appearance of photochromism of **1a** at room temperature may result by a fast thermal reverse-reaction and/or by the specific photophysical properties of the ferrocene moiety (fast radiative decay or nonchemical nonradiative decay processes)⁹).

The cyclic voltammogram (Fig.1) of **1a** displays a reversible oxidation at +0.19 V vs ferrocene (FOC) which is clearly an indication to the Fe(II)/Fe(III) couple **1a**/**1a**⁺. Apparently, the dihydroazulene group in **1a** slightly stabilizes the ferrocene moiety relative to the parent compound, thus leading to a minor increase in the oxidation potential¹⁰).

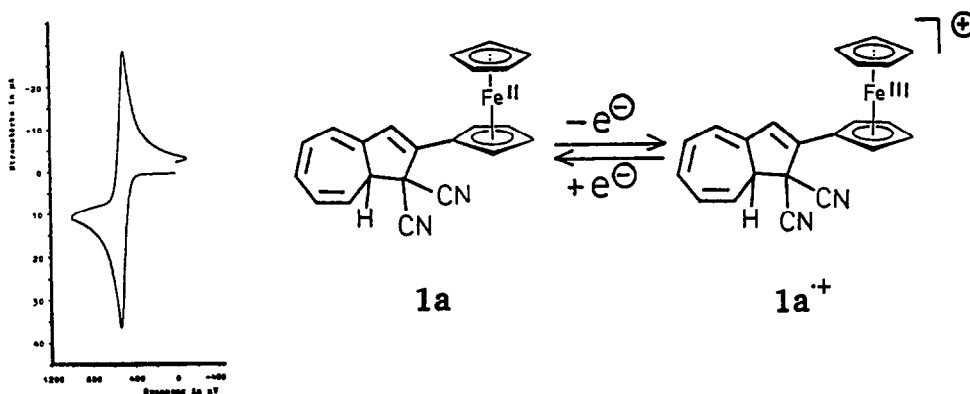


Figure 1: Cyclic voltammogram of **1a** (supporting electrolyte: 0.1M TBAHFP, in acetonitrile, Pt-electrode, sweep 250 mV/sec)

In contrast to **1a** itself the electrochemically generated ferrocenium derivative **1a**⁺ is photoactive: On irradiation with visible light the absorption of the dihydroazulene chromophore at $\lambda_{max} = 362$ nm decreases and a new absorption band corresponding to the heptafulvene chromophore and centered at $\lambda_{max} = 470$ nm appears⁸).

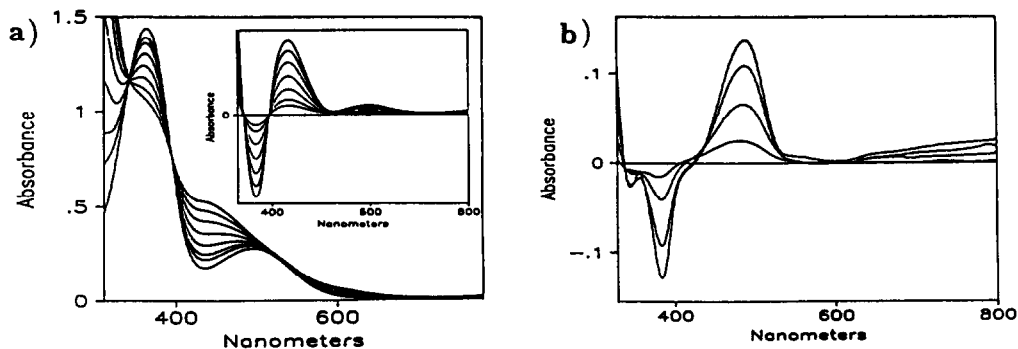


Figure 2: a) Spectra during chemical oxidation of **1a** with **8** in dichloromethane (inset difference spectra). b) Difference spectra obtained on irradiation of chemically generated **1a**⁺ with visible light in dichloromethane.

To confirm this oxidation-state-dependent photoreaction of **1a** the oxidation under chemical conditions was investigated. Titration of a solution of **1a** in dichloromethane with an equimolar concentrated solution of triphenylaminium hexachloroantimonate $[(C_6H_5)_3N^+/SbCl_6^-]$ **8** in dichloromethane leads exclusively to the formation of the ferrocenium ion **1a**⁺ as shown by isosbestic points at 344 nm and 395 nm and the typical absorption at 600 nm for the ferrocenium ion ¹¹⁾ (Fig.2a) . Again there appears a new absorption band at 489 nm in the difference spectra which is assigned to vinylheptafulvene **2a**⁺, on irradiating this solution with visible light (Fig. 2b).

Further studies aimed at examining the optoelectronic properties of **1a** and related compounds are in progress.

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References and Notes

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- 2) Latest publication on this subject: S.Gierisch, W.Bauer, T.Burgemeister, J.Daub, *Chem. Ber.* **122** (1989) 2341, and earlier papers cited therein.
- 3) S.Gierisch, Dissertation Universität Regensburg, 1989 (in part).
- 4) J.Daub, S.Gierisch, T.Knöchel, E.Salbeck, G.Maas, *Z. Naturforsch.* **41b** (1986) 1151.
- 5) Some physical and spectroscopic data: **1a**: mp 139-140°C, IR(KBr): 3100, 3020, 2250w (C≡N), 1590 cm⁻¹; ¹H-NMR (250 MHz, CDCl₃): 3.72 (mc; 1 H, 8a-H), 4.25 (s; 5 H, ferrocene-H), 4.52 und 4.72 (s; 2 H, ferrocene-H), 5.79 (dd, J = 10.1, 3.7 Hz; 1 H, 8-H), 6.20 (br d, J ≈ 5.8 Hz; 1 H, 4-H), 6.26 (mc; 1 H, 7-H), 6.42 (dd, J ≈ 11, 5.7 Hz; 1 H, 6-H), 6.51 (dd, J ≈ 11, ≈ 6 Hz; 1H, 5-H), 6.52 (s; 1 H, 3-H); UV (acetonitrile): λ_{max} (log_ε) = 243 (4.3), 272 (4.1), 362 (4.3), 492 (3.6); MS (12 eV):m/z = 364 (M⁺).
- 6) S.Gierisch, J. Daub, *Chem. Ber.* **122**(1989) 69.
- 7) Prepared according to the route in scheme 2; see l.c. ³⁾: **1b**, mp 91-92°C ; **1c**, mp 115-116°C. Synthesis of **1d**; see l.c. ⁸⁾.
- 8) J. Daub, S.Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.* **119** (1986) 2631.
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- 10) On the substituent dependency of the first oxidation potential in ferrocenes, see A. M. Al-Saeed, E.A. Seddon, K.R. Seddon, A.A. Shimran, S. Tompkins, M.C.Grossel, J.P. Knychala, J. *Organomet. Chem.* **347** (1988) C25.
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