

# Crown Ether-Bearing Dihydroazulenes<sup>[1]</sup>: Synthesis and Photochromism of a Benzo[15]crown-5 Derivative

Christian Fischer and Jörg Daub\*

Institut für Organische Chemie der Universität Regensburg,  
Universitätsstraße 31, W-8400 Regensburg

Received December 28, 1992

**Key Words:** Photochromism / Photoresponsive crown ether

Photosensitive crown ether **1** composed of 1,8a-dihydroazulene as a photodynamic unit and a benzo[15]crown-5 ether subgroup has been synthesized from C-7-substituted cycloheptatriene **8**, which has been obtained by nucleophilic addition of 4-acetylbenzo[15]crown-5 (**6**) to tropenylium tetrafluoroborate (**7**). Dehydrogenation of dicyanovinyl derivative **9** leads to heptafulvene **2** which thermally rearranges to dihydroazulene **1**. Attempts to synthesize **1** according to the

"[8 + 2]-cycloaddition route" have been unsuccessful. Crown ether **1** shows photochromic bistability with a photochemically driven forward and a thermal back reaction. The spectroscopic properties of **1** and the photochemical isomerization **1** → **2** have been shown to be almost insensitive to sodium iodide addition. The rate of the thermal back reaction **2** → **1** slightly is affected by sodium iodide addition.

Numerous approaches are currently pursued to design and synthesize molecular-based materials exhibiting photocontrolled sensor or photoregulation activity<sup>[2]</sup>. In principle, these supramolecular species<sup>[3]</sup> consist of three different subunits: (i) a unit for switching which preferentially is activated photochemically, (ii) a subgroup involved in metal-ion recognition, and (iii) functional groups to achieve aggregation by intermolecular interaction. Properties (i) and (ii) are found in photoresponsive crown ethers, a class of compounds which has already been studied to some extent<sup>[4]</sup>.

In previous studies we have shown that dihydroazulene (DHA)/vinylheptafulvene (VHF) photochromism can successfully be utilized in photocontrolled switching processes<sup>[5]</sup> which recommends this photodynamic system to be incorporated into photoresponsive materials for ion transport or sensor applications. The following study deals with the photolabile system **1/2** which assembles a photochromic dihydro-

droazulene/vinylheptafulvene subunit and a benzo[15]-crown-5 ether component covalently attached. Synthesis and the molecular rearrangement will be described (Scheme 1).

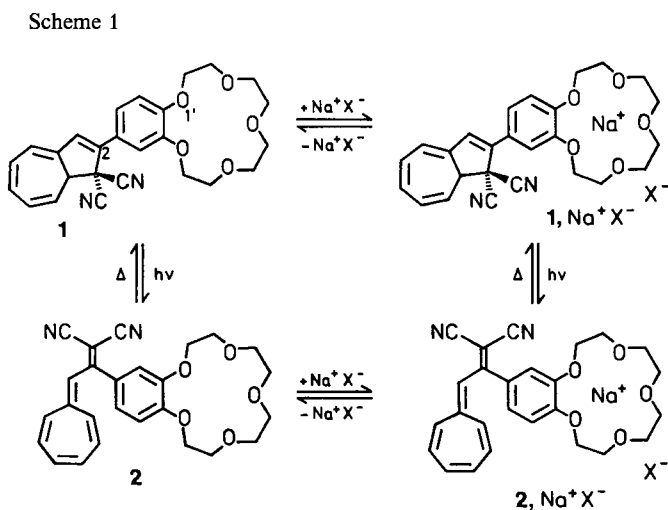
Benzo[15]crown-5 has been selected as ionophoric subunit since it is known that substituents at C-4 influence the binding constants for sodium ion complexation significantly<sup>[6]</sup>. Furthermore, by photochemical rearrangement **1** → **2** the acceptor strength of the hydrocarbon subunit increases.

## Synthesis

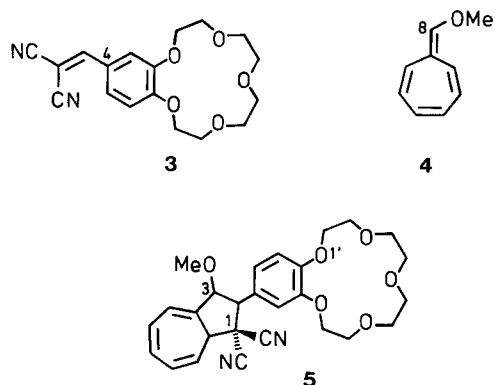
In a first approach the synthesis of dihydroazulene **1** has been attempted according to "[8 + 2]-cycloaddition route" utilizing the [8 + 2]-cycloaddition reaction of methylene-propanedinitrile **3** with 8-methoxyheptafulvene (**4**, 8-MHF)<sup>[7]</sup> and subsequent elimination of methanol<sup>[8]</sup>. Although successfully applied frequently it has turned out that donor-substituted aryl groups reduce the rate of cycloaddition significantly and even prevent elimination of methanol by irreversibly binding diphosphorous pentoxide at the electron-rich groups<sup>[9]</sup>.

This also applies to the present case as well: [8 + 2] cycloaddition of **3** to **4** with formation of tetrahydroazulene (THA) **5** proceeds rather sluggishly (reaction time 8 days, yield 48%), and subsequent elimination of methanol even fails completely.

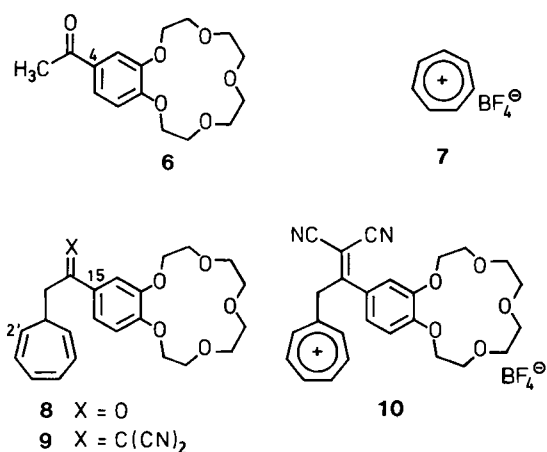
With more success the "vinylheptafulvene route" has been adopted<sup>[9]</sup>: The reaction of 4-acetylbenzo[15]crown-5 (**6**) with tropenylium tetrafluoroborate (**7**) affords cycloheptatriene **8**. The Knoevenagel condensation with malonodinitrile gives the dicyanovinyl derivative **9** which by hydride elimination and deprotonation yields vinylheptafulvene **2** via tropenylium derivative **10**. Thermally, **2** rearranges to di-



Scheme 2



Scheme 3



hydroazulene **1**. The structure assignment of **1** is based on spectroscopic data documented by a typical absorption band at 363 nm ( $\lg \epsilon = 4.3$ ).

Irradiation of dihydroazulene **1** with monochromatic light ( $\lambda = 366$  nm) causes rearrangement to **2**. The absorption band at 363 nm decreases and a new absorption at 474 nm appears (Figure 1) with isosbestic points at 398 and 314 nm. The addition of sodium iodide to a solution of **1** has no significant effect on the absorption spectra of **1/2** and does not impair the photochemical transformation [in acetonitrile,  $c(\text{NaI}) = 1.5 \cdot 10^{-5}$  M,  $c(\mathbf{1}) = 2.69 \cdot 10^{-5}$  M, at 25°C]. Long-wavelength bands of DHA **1** and VHF **2** are collected in Table 1 together with those of related compounds **11–14**<sup>[10]</sup>.

Vinylheptafulvene **2** reconverts clearly to dihydroazulene **1** under thermal conditions. Plotting  $\ln c(\mathbf{2})$  versus time at

Table 1. Long-wavelength absorption of **1**, **2**, **11–14** in acetonitrile [ $\lambda_{\text{max}}$  ( $\lg \epsilon$ ), in nm]

	$\lambda_{\text{max}}$ ( $\lg \epsilon$ )		$\lambda_{\text{max}}$ ( $\lg \epsilon$ )
<b>1</b>	363 (4.3)	<b>2</b>	474 (4.3)
<b>1 + NaI</b>	364 (4.3)	<b>2 + NaI</b>	473 (4.4)
<b>11</b>	365 (4.4)	<b>12</b>	467 (4.5)
<b>13</b>	364 (4.3)	<b>14</b>	473 (4.4)

different temperatures gives straight lines indicating first-order kinetics. To evaluate the sensitivity of the thermal back reaction to sodium iodide addition the thermal decay rates of the rearrangement **2**  $\rightarrow$  **1** have been determined at different temperatures (Table 2, Experimental). Half-lives ( $t_{1/2}$ ) at different temperatures have been found to decrease on sodium iodide addition (Table 2). The Arrhenius parameters also show that the exponential factor  $\ln A$  and energy of activation ( $E_a$ ) decrease if vinylheptafulvene **2** is thermally rearranged in the absence of sodium iodide [**2**  $\rightarrow$  **1**:  $E_a = 87.4$  kJ/mol;  $\ln A = 25$ , (**2** + NaI)  $\rightarrow$  (**1** + NaI):  $E_a = 103.6$  kJ/mol;  $\ln A = 32$ ].

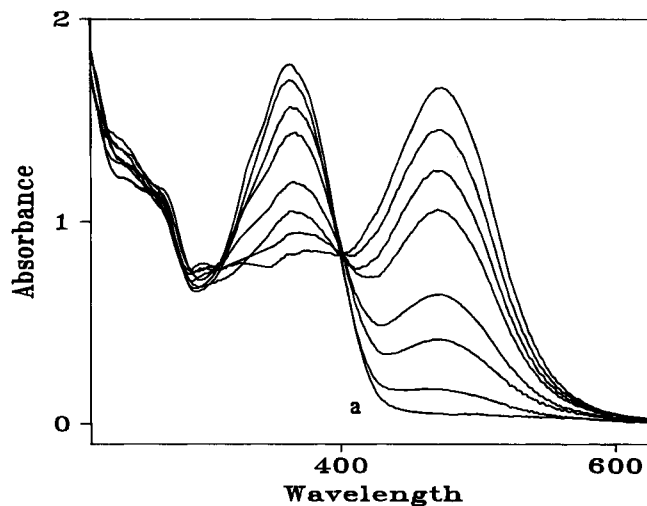
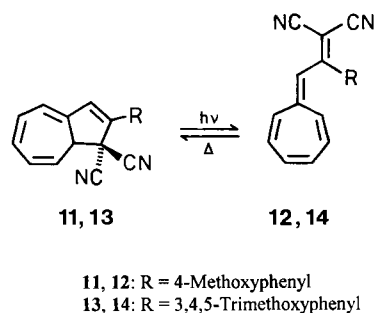


Figure 1. UV/Vis spectral changes caused by 366-nm irradiation of **1** in acetonitrile at 25°C. Time of irradiation: a) 0 s; final spectrum after 110 min

Scheme 4



## Discussion

Studies of Ungaro, El Haj, and Smid<sup>[6]</sup> indicate that the equilibrium constants ( $K$ ) of  $\text{Na}^+$  complexation of benzo[15]crown-5 ether strongly depend on the nature of the 4-substituent at the benzene ring. By conductometry in acetone at 25°C they have observed an almost 25-fold increase in the complexation constants in going from 4-amino to 4-nitro substitution leading to good Hammett plots. This finding is explained by a decrease in the donor strength of the ether oxygen in the 4-amino as compared to the 4-nitro compound which results in a decreased complexation in the 4-nitro derivative.

Since by the  $1 \rightarrow 2$  rearrangement the weaker donor group (dihydroazulene) is shifted to a stronger dicyanovinyl acceptor group we assume that  $1$  again should allow stronger  $\text{Na}^+$  complexation and therefore  $1/2$  should exhibit properties of a photochemically driven molecular switching system. The finding that thermal and photochemical  $1/2$  interconversions are not influenced by sodium iodide may be an indication that interconversions in Scheme 1 are mainly due to reactions proceeding via the uncomplexed species (pathways  $1 \rightleftharpoons 2$ ).

We thank Mrs. M. Feuerer and Mr. F. Gaßner for the support of this work. C. F. thanks the *Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie*, Frankfurt/Main, for a dissertation fellowship.

## Experimental

Melting points: uncorrected. — IR: Beckman Acculab 1. — UV/Vis: Shimadzu UV-210A. —  $^1\text{H}$  NMR: Bruker WM 250, Varian EM 360, Varian T-60; TMS as internal standard. — MS: Varian CH-5 and MAT 311A. — Column chromatography: Silica gel ICN Silitech 63–200. — Thin layer chromatography: Alumina foil Merck 60 F 254 (silica gel), layer thickness 0.2 mm. — [8 + 2]-Cycloaddition reactions were performed under nitrogen. — Elemental analyses: Mikroanalytisches Labor, Universität Regensburg.

Kinetic measurements were undertaken with a Shimadzu UV-210 spectrometer and low-temperature equipment. The rates were obtained by determining the decrease in the long-wavelength absorption of heptafulvene  $2$  (475 nm) (Table 2, Figure 2).

Table 2. Rates ( $k$  in s) of the thermal back reaction  $2 \rightarrow 1$  with  $[c(\text{NaI}) = 1.5 \cdot 10^{-4} \text{ M}]$  and without sodium iodide at different temperatures

$T/[\text{C}]$	Without sodium iodide		In the presence of sodium iodide	
	$\tau_{1/2}$ [min]	$\ln k$	$\tau_{1/2}$ [min]	$\ln k$
25	353	-10.3	219	-9.9
30	169	-9.6	113	-9.2
35	99	-9.1	53	-8.4
40	57	-8.5	29	-7.8
45	38	-8.1	16	-7.2

Precursor compounds: Benzo[15]crown-5<sup>[11]</sup>, 4-Formylbenzo[15]crown-5<sup>[12]</sup>, **4**<sup>[13]</sup>, **6**<sup>[14]</sup>, and **7**<sup>[15]</sup> were prepared as described.

*2-(2,4,6-Cycloheptatrien-1-yl)-1-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacylopentadecin-15-yl)ethanone* (**8**): A solution of 4.10 g (23.0 mmol) of tropenylium tetrafluoroborate (**7**) and 7.00 g (22.6 mmol) of **6** in 140 ml of methanol containing 1 ml of acetic acid is stirred at room temp. The color of the solution changes from white to red. After 4 h 80 ml of water is added, and the mixture is extracted with four portions of 100 ml of chloroform. The combined organic layers are washed with 100 ml of water and dried with  $\text{MgSO}_4$ . The solvent is removed and the resulting brown oil passed through a short silica gel column using dichloromethane as eluent. Evaporation of the solvent gave 4.00 g (89%) of **8** as a brownish oil. — IR (KBr):  $\tilde{\nu} = 3020 \text{ cm}^{-1}$ , 2930, 2870, 1705, 1670, 1590, 1510, 1425, 1355, 1270, 1140, 1050, 935, 705. —  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.50$  (m, 1H, methine H), 3.25 (d,  $J = 7 \text{ Hz}$ ; 2H, methylene H), 3.75 (s; 8H, methylene H at C-5, -6, -8, -9), 3.87 (m, 4H, methylene H at C-3, -11), 4.13 (m, 4H, methylene-H at C-2,

-12), 5.24 (m, 2H, 2', 7'-H), 6.00–6.35 (m; 2H, 3', 6'-H), 6.60 (m; 2H, 4', 5'-H), 6.81 (d,  $J = 9 \text{ Hz}$ ; 1H, 17-H), 7.47 (s, 1H, 14-H), 7.55 (d,  $J = 9 \text{ Hz}$ , 1H, 16-H).

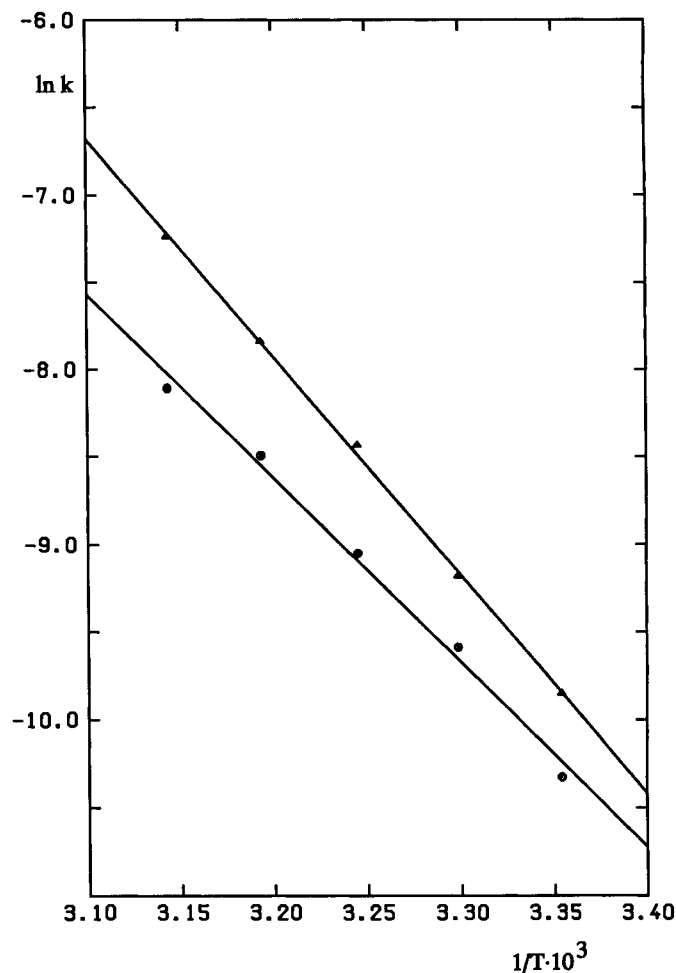


Figure 2. Arrhenius plot  $\ln k = f(1/T)$  ( $k$  in s,  $T$  in K) for the thermal back reaction  $2 \rightarrow 1$ : (○) without sodium iodide and (▲) in the presence of sodium iodide  $[c(\text{NaI}) = 1.5 \cdot 10^{-4} \text{ M}$  in acetonitrile

*[2-(2,4,6-Cycloheptatrien-1-yl)-1-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacylopentadecin-15-yl)ethylidene]propanedinitrile* (**9**): To 2.00 g (5.0 mmol) of **8** and 0.40 g (6.0 mmol) of malononitrile in 30 ml of dry benzene is added 6.7 g of ammonium acetate in 20 ml of acetic acid. Water is removed by azeotropic distillation. After refluxing for 16 h the solution is diluted with 15 ml of benzene, extracted 5 times with small portions of water, and the organic phase is dried with  $\text{MgSO}_4$ . After removal of the solvent by evaporation 1.99 g (89%) of a pale yellow powder is obtained. The solid is further purified by column chromatography on silica gel (dichloromethane/acetonitrile, 7:3). Recrystallization from petroleum ether (80–110°C) yields **9** as a yellow powder, m.p. 114–115°C. — IR (KBr):  $\tilde{\nu} = 3010 \text{ cm}^{-1}$ , 2920, 2860, 2210, 1585, 1545, 1510, 1445, 1420, 1335, 1300, 1270, 1140, 1040, 930, 840, 740, 695. —  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.97$  (m, 1H, methine H), 3.18 (d,  $J = 7.9 \text{ Hz}$ ; 2H, methylene H), 3.76 (br s; 8H, methylene H at C-5, -6, -8, -9), 3.89–3.94 (m, 4H, methylene H at C-3, -11), 4.14–4.18 (m, 4H, methylene H at C-2, -12), 5.14 (dd,  $J = 9.0/6.3 \text{ Hz}$ ; 2H, 2', 7'-H), 6.14–6.21 (m; 2H, 3', 6'-H), 6.60 (m; 2H, 4', 5'-H), 6.88 (d,  $J = 8.4 \text{ Hz}$ , 1H, 17-H), 6.99 (d,  $J = 2.2 \text{ Hz}$ , 1H, 14-

H), 7.07 (dd,  $J = 8.4/2.2$  Hz, 1H, 16-H). —  $C_{26}H_{28}N_2O_5$  (448.5): calcd. C 69.63, H 6.29, N 6.24; found C 69.83, H 6.23, N 6.23.

**Tropenylium Salt 10:** Under nitrogen a solution of 0.83 g (2.82 mmol) of trityl tetrafluoroborate in 17 ml of dry 1,2-dichloroethane is added dropwise to a solution of 1.25 g (2.79 mmol) of **9** in 5 ml of dry 1,2-dichloroethane within 30 min. The solution is stirred at 70°C for 1 h. After cooling to room temp. 200 ml of dry diethyl ether is added, and the mixture is stirred for another 0.5 h. Tropenylium salt **10** precipitates and is removed by filtration. Yield 0.36 g (24%) of **10** as dark red solid. — IR (KBr):  $\tilde{\nu} = 2940$   $cm^{-1}$ , 2880, 2210, 1595, 1510, 1340, 1250, 1125, 1050, 940, 820, 695.

**1,8a-Dihydro-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacylopentadecin-15-yl)-1,1-azulenedicarbonitrile (1):** To a solution of 0.36 g (0.67 mmol) of **10** in 20 ml of dry  $CH_2Cl_2$  0.23 g (2.34 mmol) of triethylamine is added at 0°C. The reaction mixture is diluted with 100 ml of  $CCl_4$  and filtered. After removal of the solvent from the filtrate 0.36 g of **2** is obtained as a red oil, which is taken up in 100 ml of benzene and the solution refluxed for 2 h. After removal of the solvent a brown solid results which is purified by column chromatography on silica gel (dichloromethane/acetonitrile, 7:3). Total yield of **1**: 0.245 g (82%) as an orange solid. Recrystallization from diethyl ether gives **1** as a yellow solid, m.p. 107–109°C. — IR (KBr):  $\tilde{\nu} = 2930$   $cm^{-1}$ , 2870, 1590, 1510, 1445, 1380, 1260, 1125, 1050, 930, 695. —  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta = 3.62$ – $3.68$  (m, 8H, methylene H at C-5, -6, -8, -9), 3.80–3.86 (m, 5H, methylene H at C-3, -11, 8a-H), 4.13–4.17 (m, 4H, methylene-H at C-2, -12), 5.78 (dd,  $J = 10.0/6.4$  Hz, 1H, 8-H), 6.29–6.34 (m, 1H, 7-H), 6.37 (br d,  $J \approx 6$  Hz, 1H, 4-H), 6.50 (dd,  $J = 11.2/5.9$  Hz, 1H, 6-H), 6.59 (dd,  $J = 11.2/6.3$  Hz, 1H, 5-H), 7.03 (d,  $J = 8.4$  Hz, 1H, 17-H), 7.04 (s, 1H, 3-H), 7.27 (d,  $J = 2.2$  Hz, 1H, 14-H), 7.40 (dd,  $J = 8.5/2.3$  Hz, 1H, 16-H). — MS (70 eV),  $m/z$  (%): 446 (15) [ $M^+$ ], 432 (5) [ $M - CH_2$ ], 358 (10) [ $M - 2 C_2H_4O$ ], 314 (43) [ $M - 3 C_2H_4O$ ], 300 (21) [ $M - 3 C_2H_4OCH_2$ ], 287 (26) [ $M - 3 C_2H_4OC_2H_5$ ], 258 (17) [ $M - 4 C_2H_4OCH_2$ ]. — UV/Vis (acetonitrile):  $\lambda_{max}$  (lg  $\epsilon$ ) = 216 nm (4.2), 363 (4.3).

**(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacylopentadecin-15-ylmethylene)propanedinitrile (3):** To 1.47 g (4.96 mmol) of 4'-formylbenzo[15]crown-5 and 0.36 g (5.45 mmol) of malononitrile in 19 ml of ethanol 3 drops of piperidine are added. The reaction mixture is stirred at room temp. The color of the solution changes immediately from white to yellow, and after 15 min a yellow solid precipitates. The solid is removed by filtration, washed with small portions of ethanol and hexane, and dried with  $CaCl_2$ . Yield 1.07 g (69%) of **3** as yellow crystals, m.p. 136–138°C. — IR (KBr):  $\tilde{\nu} = 3020$   $cm^{-1}$ , 2990, 2880, 2235, 1585, 1570, 1555, 1515, 1285. —  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta = 3.76$  (br s, 8H, methylene H at C-5, -6, -8, -9), 3.89–3.95 (m, 4H, methylene H at C-3, -11), 4.16–4.23 (m, 4H, methylene H at C-2, -12), 6.81 (d,  $J = 8.4$  Hz; 1H, 17-H), 7.35 (dd,  $J = 8.7/2.2$  Hz; 1H, 16-H), 7.61 (s; 1H, vinyl H), 7.65 (d,  $J = 2.2$  Hz, 1H, 14-H). — MS (70 eV),  $m/z$  (%): 344 (15) [ $M^+$ ], 212 (100) [ $M - 3 C_2H_4O$ ], 197 (36) [ $M - 3 C_2H_4O - CH_3$ ], 156 (21), 136 (52). —  $C_{18}H_{20}N_2O_5$  (344.4): calcd. C 62.78, H 5.85, N 8.13; found C 62.46, H 5.77, N 8.12.

**1,2,3,8a-Tetrahydro-3-methoxy-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacylopentadecin-15-yl)-1,1-azulenedicarbonitrile (Stereoisomeric Mixture) (5):** Under nitrogen 0.35 g (1.02 mmol) of **3** is added with stirring to a solution of 0.16 g (1.16 mmol) of 8-methoxyheptafulvene (**4**, 8-MHF)<sup>[16]</sup> in 25 ml of dry dichloromethane. Stirring is continued at room temp. for 8 d. Thereafter, the solution is passed through a short silica gel column using ethanol as the eluent. Evaporation of the solvent from the eluate yields 0.47 g of a yellow solid, which contains equal amounts of **3** and **5** as determined by NMR analysis. —  $^1H$  NMR (250 MHz,  $CDCl_3$ ): **5** (main stereoisomer, 70%):  $\delta = 3.14$  (m, 1H, 8a-H), 3.18 (s, 3H,  $OCH_3$ ), 3.62 (d,  $J = 3.8$  Hz, 1H, 2-H), 3.77 (br s, 8H, methylene H at C-5, -6, -8, -9), 3.91–3.95 (m, 4H, methylene H at C-3, -11), 4.17–4.23 (m, 4H, methylene H at C-2, -12), 4.32 (d,  $J = 3.6$  Hz, 1H, 3-H), 5.66 (dd,  $J = 9.8/4.1$  Hz, 1H, 8-H), 6.26–6.42 (m, 2H, 4-, 7-H), 6.52–6.79 (m, 2H, 5-, 6-H), 6.88 (d,  $J = 8.3$  Hz, 1H, 17-H), 7.21 (d,  $J = 1.9$  Hz, 1H, 14-H), 7.07 (m, 1H, 16-H). **5** (second stereoisomer, 30%), some characteristic signals:  $\delta = 3.20$  (s, 3H,  $OCH_3$ ), 5.50 (m, 1H, 8-H). **5** (third stereoisomer, trace), typical signal:  $\delta = 2.69$  (m, 1H, 8a-H).

- [1] Recent reports on dihydroazulene/vinylheptafulvene photochromism: [1a] J. Daub, C. Fischer, S. Gierisch, J. Sixt, *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 177. — [1b] H. Görner, C. Fischer, S. Gierisch, J. Daub, *J. Phys. Chem.*, in press.
- [2] [2a] S. Shinkai, O. Monabe, *Top. Curr. Chem.* **1984**, *121*, 67. — [2b] H. Bouas-Laurent, J.-P. Desvergne, F. Fages, P. Marsau in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds.: H. J. Schneider, H. Dürr), VCH, Weinheim, **1991**, p. 266.
- [3] [3a] J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89. — [3b] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood Series in Physical Chemistry, Ellis Horwood, New York, **1991**. — [3c] H. G. Löhr, F. Vögtle, *Acc. Chem. Res.* **1985**, *18*, 65. — [3d] F. Vögtle, *Supramolekulare Chemie*, B. G. Teubner, Stuttgart, **1992**.
- [4] [4a] M. Inouye, M. Ueno, T. Kitao, *J. Am. Chem. Soc.* **1990**, *112*, 8977. — [4b] T. Wolff, B. Klaußner, G. von Bünau, *Progr. Colloid Polym. Sci.* **1990**, *83*, 176.
- [5] [5a] J. Daub, C. Fischer, T. Knöchel, H. Kunkely, K. M. Rapp, J. Salbeck, *Angew. Chem.* **1989**, *101*, 1541; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1494. — [5b] J. Daub, C. Fischer, J. Salbeck, K. Ulrich, *Adv. Mater.* **1990**, *2*, 366. — [5c] J. Achatz, C. Fischer, J. Salbeck, J. Daub, *J. Chem. Soc., Chem. Commun.* **1991**, 504. — [5d] H. Dürr in *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**, chapter 11, p. 510.
- [6] R. Ungaro, B. El Haj, J. Smid, *J. Am. Chem. Soc.* **1976**, *98*, 5198.
- [7] J. Daub, *Chimia* **1987**, *41*, 52.
- [8] J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.* **1986**, *119*, 2631.
- [9] S. Gierisch, J. Daub, *Chem. Ber.* **1989**, *122*, 69.
- [10] Dissertation S. Gierisch, Universität Regensburg, **1989**.
- [11] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017.
- [12] F. Wada, H. Hirayama, K. Kikukawa, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1473.
- [13] W. Bauer, I. Betz, J. Daub, L. Jakob, W. Pickl, K. M. Rapp, *Chem. Ber.* **1983**, *116*, 1154.
- [14] W. W. Parish, P. E. Scott, C. W. Mc Causland, J. S. Bradshaw, *J. Org. Chem.* **1978**, *43*, 4577.
- [15] K. Conrow, *Organic Syntheses* **1973**, Coll. Vol. V, p. 1138.
- [16] W. Bauer, I. Betz, J. Daub, L. Jakob, W. Pickl, K. M. Rapp, *Chem. Ber.* **1983**, *116*, 1154.

[466/92]