56. On the Purported Structure of Cyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene

by **Rolf Gleiter***, **Hans Peter Schaaff**, **Hans Rodewald**, **Reiner Jahn**, and **Hermann Irngartinger**

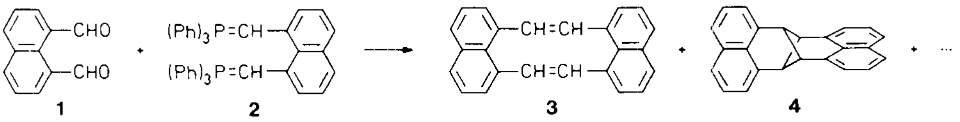
Institut für Organische Chemie der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg

(8. II. 87)

The reaction of the bis(sulfonium salt) **7** in a solution of Na_2CO_3 in H_2O/EtOH yielded three main products **8**–**10**. The spectroscopic data of **8** were identical to those which led *Mitchell* and *Sondheimer* to assign them to cyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene (**3**). Our investigations show, however, that the correct structural assignment leads to the structure of 7,7a-dihydrodibenzo[*de*,*mn*]naphthacene (**8**).

In connection with our spectroscopic studies on perpendicular π systems separated by a four-membered ring [1], we were interested to investigate 1,3:2,4-di(naphth-1′,8′-diyl)-cyclobutane (**4**) whose synthesis has been reported by *Mitchell* and *Sondheimer* as shown in *Scheme 1* [2]. Since the yield reported for **4** was very low (0.1 %), we presumed that it had been formed from cyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene (**3**) in a side reaction. Our aim, therefore, was directed to synthesize **3** in good yields and subsequently transfer it into **4** *via* a cycloaddition reaction. Our investigations did not lead to **3**, however, but to a hydrogenated derivative of dibenzo[*de*,*mn*]naphthacene (zethrene) whose spectroscopic properties are identical with those reported by *Mitchell* and *Sondheimer* for **3**.

Scheme 1



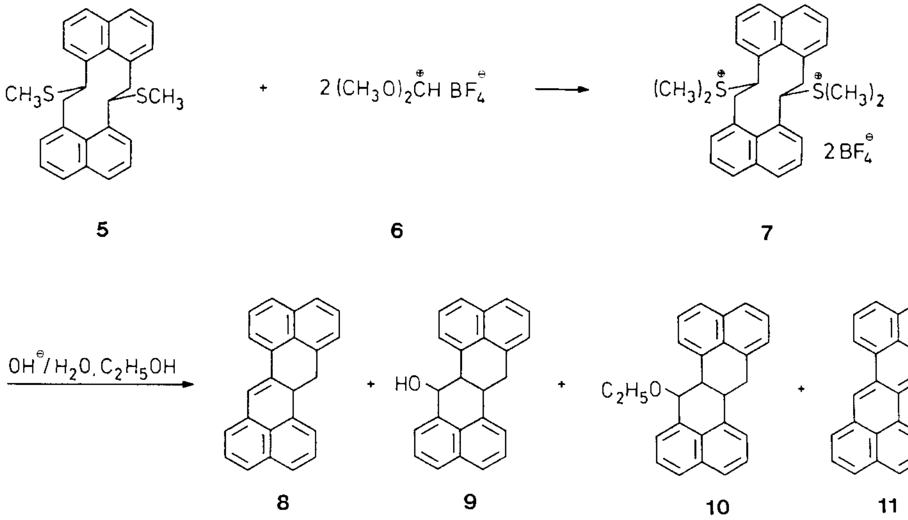
Synthesis and Structures. – Starting compound of our synthesis was the bisulfide **5** whose synthesis and structure will be reported in a separate paper [3]. With dimethoxycarbenium tetrafluoroborate (**6**), we obtained from **5** the bis(sulfonium salt) **7** (see *Scheme 2*). The reaction of **7** with a solution of Na_2CO_3 in H_2O/EtOH at 60° yielded, after chromatographic separation, the main products **8**–**10** in approximately equal amounts together with a small trace of dibenzo[*de*,*mn*]naphthacene (zethrene) (**11**).

A mass-spectroscopic analysis shows for the main product **8**, a *z*/*m* ratio of 304, a pure hydrocarbon, while the two other products with the *z*/*m* ratios of 322.135 and 350.167 contained oxygen.

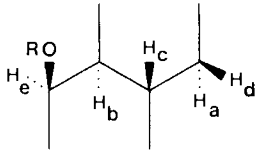
To elucidate the structures of **8**–**10** we will discuss their ^{1}H-NMR spectra *(Fig. 1)*.

The comparison of the ^{1}H-NMR spectra of **9** and **10** reveals a great similarity with respect to chemical shifts and coupling constants. The main difference is the appearance

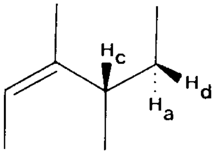
Scheme 2



of the signals of the Et group in the spectrum of **10** at 0.93 and 3.50 ppm. The most simple rationalization of this observation is the assumption of the same configuration of the protons H$_a$–H$_c$ as shown below in **a**. In both cases, proton H$_a$ shows a geminal and vicinal coupling to the protons H$_d$ and H$_c$, respectively. The coupling constants are: J(a,d) = 15.5 Hz and J(a,c) = 12.4 Hz. In agreement with the *Karplus-Conroy* rules [4], the coupling between H$_d$ and H$_c$ is small (J(c,d) = 4 Hz), whereas the coupling between H$_b$ and H$_c$ is large (J(b,c) = 12.4 Hz). The triplet of H$_c$ in both spectra is due to two identical couplings (J(a,c) = J(b,c)) with H$_a$ and H$_b$. The additional splitting of the triplet is due to the coupling with H$_d$. The coupling constants discussed for **9** and **10** support the configuration indicated above. A final confirmation is due to the X-ray analysis of **10** as discussed below.



a



b

The ^{1}H-NMR spectrum of **8**, recorded in CD_2Cl_2, shows again a *dd* at 3.65 ppm. Based on the two coupling constants (J = 5.1 Hz and J = 15 Hz) the corresponding proton should have the same configuration as H$_d$ in **9** and **10** with respect to H$_a$ and H$_c$. The signal at 4.52 ppm (*dd*) is assigned to proton H$_c$ because of the small coupling constant of J = 5.1 Hz (coupling with proton H$_d$) and the greater coupling constant of J = 13.3 Hz (coupling with proton H$_a$), in agreement with the *Karplus-Conroy* rules [4]. The chemical shift of H$_c$ is typical for an allylic, benzylic proton. The signal in the region from 3.44 to 3.58 ppm, a *m* consisting of three broadened absorption lines must be assigned to proton

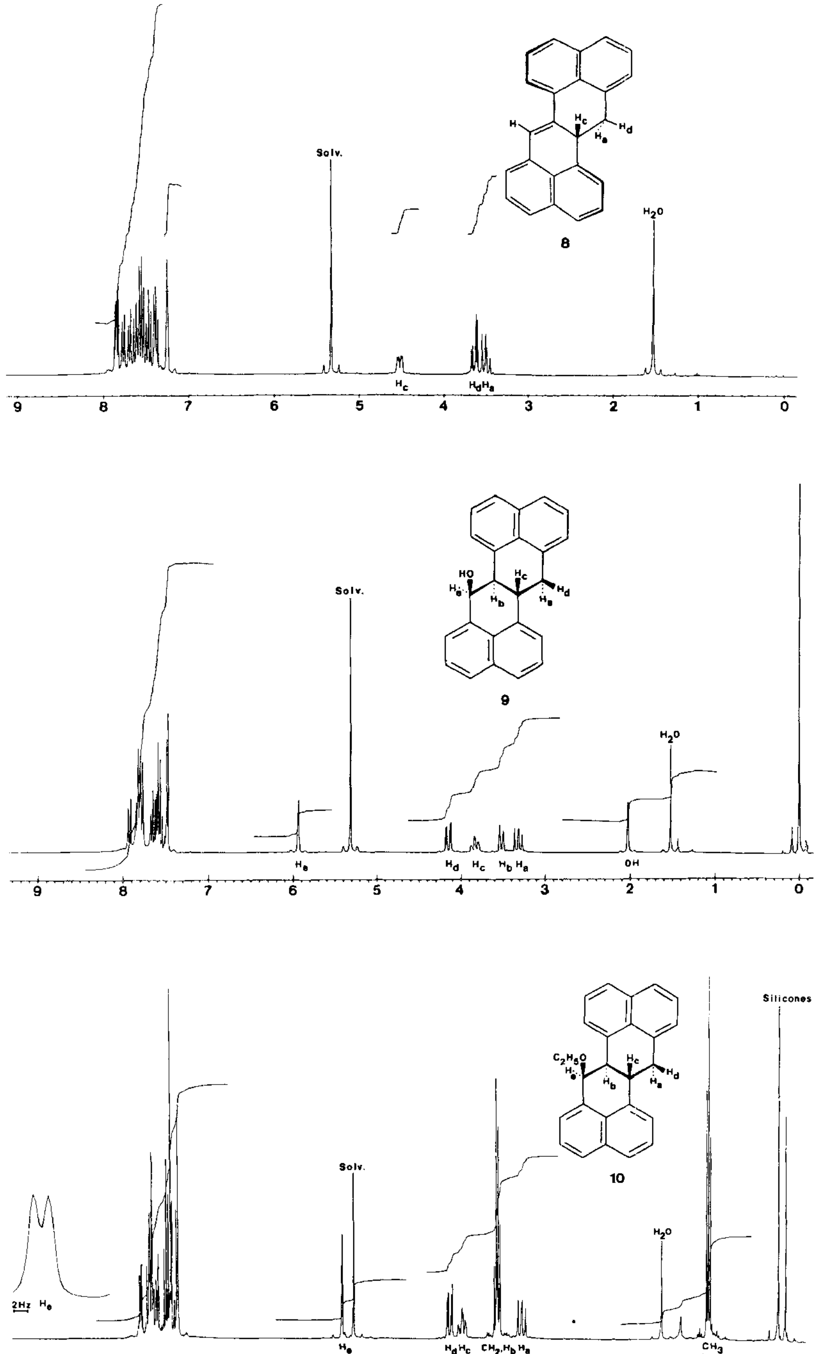


Fig. 1. *^1H-NMR spectra of* **8**–**10** *in CD_2Cl_2*

H_a. The appearance of this signal must be explained by its short distance to the neighboured signal of H_d and the similarity of the coupling constants observed at the signals of H_c (J = 13.3 Hz) and H_d (J = 15 Hz). This leads to the configuration shown in **b** above. The intensity of the signals in the aromatic region suggests 13 protons so that the signal of the olefinic, benzylic proton falls within the same region.

Special interest deserves the ^{1}H-NMR spectrum of **8** in C_6D_6 *(Fig. 2)*. Here, we find in the aliphatic region only two signal groups, a *d* (H_a, H_d) between 3.19 and 3.30 ppm and a *t* (H_c) between 4.03 and 4.33 ppm. A double-resonance experiment confirms the assignment discussed. The strong solvent dependance of the ^{1}H-NMR spectrum in the region between 3 and 5 ppm is in full accord with the findings of *Mitchell* and *Sondheimer* [2].

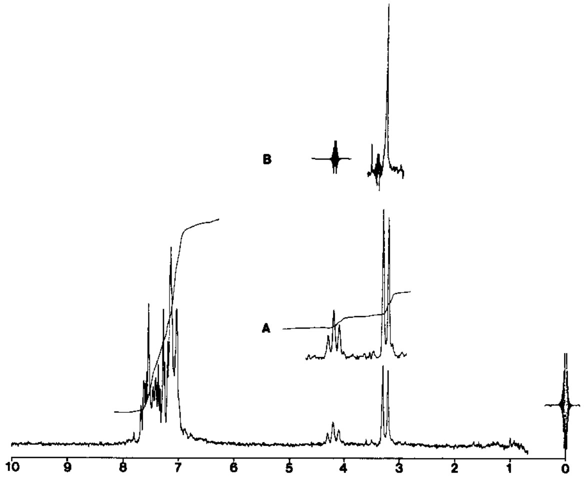
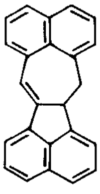


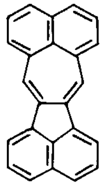
Fig. 2. *^{1}H-NMR spectrum of* **8** *in C_6D_6*. In *B*, the result of a double-resonance experiment on the signals enlarged in *A* is shown.

A further confirmation of the conformation **b** and thus the structure of **8** is given by the ^{13}C-NMR spectrum. Two signals at 40.09 and 42.79 ppm ($CDCl_3$) are assigned to a tertiary and secondary C-atom. In the region of 120–140 ppm, we find 21 ^{13}C signals out of 22 which are expected. Here, too, two signals coincide as experienced in the case of **7**. Furthermore, the IR and ^{1}H-NMR spectra of **8** are identical with those recorded by *Mitchell* and *Sondheimer* and erroneously assigned to structure **3**.

To assure further the structure of **8**, we have converted the alcohol **9** to **8** by reaction of **9** with TsCl in pyridine. The olefin **8** has been oxidized with DDQ to **11** [6]. These



12



13

results, together with the X-ray data of **10**, confirm the structure of **8** and exclude other isomers such as 6b,7-dihydronaphtho[1′,8′:4,5,6]cyclohept[1,2-*a*]acenaphthylene (**12**). The oxidation of **12** by DDQ should yield naphtho[1′,8′:4,5,6]cyclohept[1,2-*a*]-acenaphthylene (**13**) [7] but not **11**.

X-Ray Investigations of 10. – To assure the configuration of the central six-membered rings in **10**, we have carried out X-ray investigations on crystals of **10**. Our investigations reveal that in **10** both central six-membered rings are linked in *trans*-orientation (see *Fig. 3*) showing the half-chair conformation. The EtO group occupies an axial position on C(24). The naphthalene rings are almost parallel, the interplanar angle is found to be 8°.

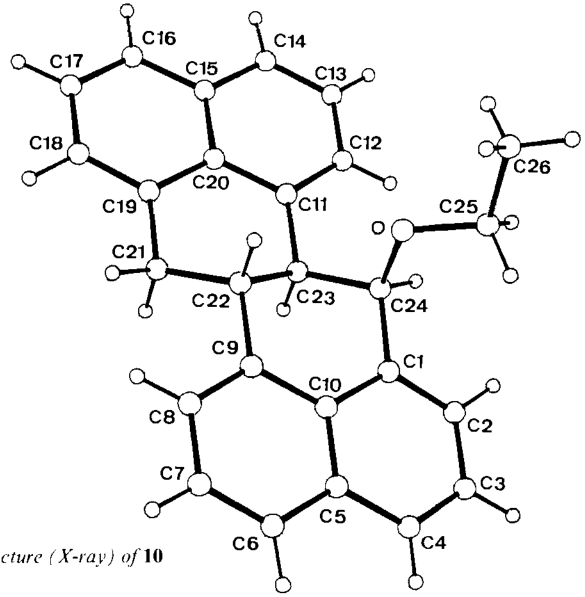


Fig. 3. *Molecular structure (X-ray) of* **10**

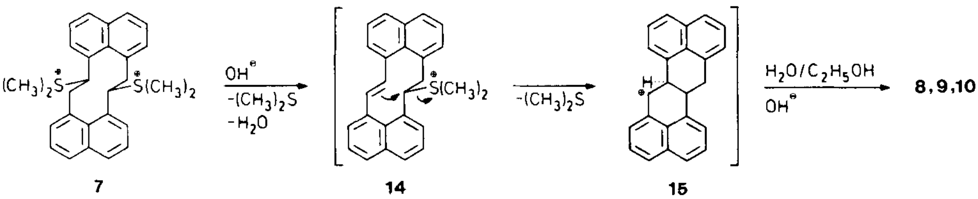
Table 1. *Interatomic Distances* [Å] *of* **10**. For the numbering of the atoms, see *Fig. 3*.

O–C(24)	1.435(2)	C(11)–C(20)	1.421(2)
O–C(25)	1.419(2)	C(11)–C(23)	1.527(3)
C(1)–C(24)	1.505(3)	C(12)–C(13)	1.401(3)
C(1)–C(2)	1.367(2)	C(13)–C(14)	1.356(3)
C(1)–C(10)	1.427(2)	C(14)–C(15)	1.409(3)
C(2)–C(3)	1.398(3)	C(15)–C(20)	1.426(3)
C(3)–C(4)	1.353(3)	C(15)–C(16)	1.412(3)
C(4)–C(5)	1.422(2)	C(16)–C(17)	1.350(3)
C(5)–C(10)	1.419(3)	C(17)–C(18)	1.400(3)
C(5)–C(6)	1.411(3)	C(18)–C(19)	1.362(3)
C(6)–C(7)	1.353(3)	C(19)–C(20)	1.421(3)
C(7)–C(8)	1.405(3)	C(19)–C(21)	1.508(3)
C(8)–C(9)	1.370(2)	C(21)–C(22)	1.521(3)
C(9)–C(10)	1.420(2)	C(22)–C(23)	1.536(2)
C(9)–C(22)	1.530(3)	C(23)–C(24)	1.519(2)
C(11)–C(12)	1.364(3)	C(25)–C(26)	1.488(3)

The bond C(22)–C(23) *(Fig. 3)* connecting both six-membered rings has a distance of 1.536 (2) Å (see *Table 1*).

Conclusions. – Based on the stereochemistry of **7** and the reaction products obtained when treating this compound with base, the following mechanism seems reasonable *(Scheme 3)*:

Scheme 3



The elimination of the first molecule of $(CH_3)_2S$ leads to the mono-olefin **14**. The double bond of **14** is ideally suited for a back side attack, when the second molecule of $(CH_3)_2S$ is eliminated. The resulting cation **15** yields either **9** or **10** by reaction with H_2O or EtOH, respectively, or will lead to **8** by an elimination mechanism.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *BASF AG*, for financial support. Thanks are due to Dr. *P. Kunzelmann*, Mrs. *M. Rimmler*, and Mrs. *G. Rissmann* for their help in separating the substances and recording their spectra. We thank Prof. *Mitchell* for providing us with copies of the IR, ^{1}H-NMR, and UV spectra from his dissertation, and to Prof. *H. J. Bestmann* for additional information on **13**.

Experimental Part

General. Methylation of **5** was carried out with dimethoxycarbenium tetrafluoroborate prepared according to *Borch* [5]. Also trimethyloxonium tetrafluoroborate under the same conditions gave excellent yields. Chromatography was carried out by MPLC (middle-pressure liquid chromatography) using a technical equipment from Fa. *Latek* and Fa. *Labomatic*. M.p. were measured on a *Tottoli* apparatus *(Büchi)* and on a *Bock-Monoskop M*, and are uncorrected. UV data were obtained using a *Varian Cary 17 D* spectrometer, the maxima of the bands are given in nm (log ε). IR spectra were recorded with a *Perkin Elmer 710 B* and on a *Bruker FT-IR IFS 85* instrument, the bands are characterized in cm^{-1}. NMR were taken with a *Varian EM390* (^{1}H-NMR at 90 MHz), a *Bruker AC200* (^{1}H-NMR at 200 MHz), and a *Bruker WH 300* (^{1}H-NMR at 300 MHz, ^{13}C-NMR at 75.46 MHz) spectrometer using TMS as internal standard (δ[ppm], J(Hz)). MS refer to data from a *Varian MAT 44* and from a *ZAB* instrument from *Vacuum Generators* (EI, 70 eV). Elemental analyses were performed at the Mikroanalytisches Labor der Chemischen Institute der Universität Heidelberg.

For the X-ray analysis, colourless crystals of **10** (from CH_2Cl_2/hexane) were used. Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ molecules in the unit cell (CH_2Cl_2/hexane). The cell dimensions are: $a = 10.870(2)$, $b = 13.491(2)$, $c = 12.942(2)$ Å, $\beta = 103.25(2)°$; $D_c = 1.26$ mg m^{-3}. The data were collected on a diffractometer (*Enraf-Nonius CAD4*, Mo$K\alpha$ radiation, graphite monochromator, θ–2θ scan, sin θ/λ = 0.66 Å^{-1}, with a crystal of the size 0.3 × 0.3 × 0.5 mm^3. Out of the 4451 independent reflections 2288 intensities have been classified as unobserved ($I(hkl) \geq 3\sigma(I(hkl))$). The structure was solved by direct methods (MULTAN). The refinement (F^2) of 332 variables in a full-matrix procedure with anisotropic thermal parameters for the C- and O-atoms and isotropic thermal parameters for the H-atoms converged to an R factor of 0.040. The atomic coordinates are given in *Table 2* [8]. All calculations have been carried out on a *PDP 11/44* computer with the *SDP* program system [9].

Table 2. *Atomic Coordinates and Thermal Parameters of* **10** (U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor)

Atom	x	y	z	$U_{eq} \times 10^3$
O	0.8259(1)	0.1862(1)	0.3942(1)	40(1)
C(1)	0.7719(2)	0.0857(1)	0.2338(1)	38(1)
C(2)	0.7332(2)	0.1319(1)	0.1379(1)	50(1)
C(3)	0.7746(2)	0.1003(2)	0.0487(1)	56(1)
C(4)	0.8564(2)	0.0236(2)	0.0569(1)	53(1)
C(5)	0.9016(2)	−0.0266(1)	0.1548(1)	42(1)
C(6)	0.9891(2)	−0.1052(1)	0.1654(1)	50(1)
C(7)	1.0279(2)	0.1524(1)	0.2595(2)	50(1)
C(8)	0.9779(2)	−0.1262(1)	0.3466(1)	42(1)
C(9)	0.8928(2)	−0.0504(1)	0.3410(1)	36(1)
C(10)	0.8559(2)	0.0030(1)	0.2443(1)	36(1)
C(11)	0.6648(2)	0.0671(1)	0.4983(1)	40(1)
C(12)	0.5920(2)	0.1495(2)	0.4976(2)	55(1)
C(13)	0.5448(2)	0.1766(2)	0.5857(2)	64(1)
C(14)	0.5702(2)	0.1204(2)	0.6749(2)	60(1)
C(15)	0.6446(2)	0.0342(1)	0.6807(1)	48(1)
C(16)	0.6713(2)	−0.0270(2)	0.7717(1)	62(1)
C(17)	0.7441(2)	−0.1086(2)	0.7754(2)	70(1)
C(18)	0.7933(2)	−0.1344(2)	0.6881(2)	63(1)
C(19)	0.7689(2)	−0.0792(1)	0.5976(1)	46(1)
C(20)	0.6928(2)	0.0072(1)	0.5910(1)	41(1)
C(21)	0.8206(2)	−0.1098(1)	0.5037(1)	48(1)
C(22)	0.8392(2)	−0.0212(1)	0.4362(1)	35(1)
C(23)	0.7146(2)	0.0363(1)	0.4019(1)	35(1)
C(24)	0.7324(2)	0.1224(1)	0.3311(1)	37(1)
C(25)	0.8325(2)	0.2814(1)	0.3491(2)	55(1)
C(26)	0.9120(2)	0.3467(1)	0.4306(2)	65(1)

anti-*7,15-Bis(dimethylsulfonio)-7,8,15,16-tetrahydrocyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene Bis(tetrafluoroborate)* (**7**). To 0.72 g (1.8 mmol) of **5** in 20 ml of dry CH_2Cl_2 were added 1 g (6.2 mmol) of $(MeO)_2CH \cdot BF_4$ [5] in 5 ml of dry CH_2Cl_2 within 15 min at −30° under Ar. After addition, the mixture was stirred for 4 h at r.t. Then, 20 ml of AcOEt were added and stirring continued for 30 min. The precipitated sulfonium salt **7** was filtered off, washed with AcOEt to yield 1 g (92%) of a nearly white powder. After recrystallization from $EtOH/H_2O$ 5:2, pink, sensitive-to-light crystals could be obtained: **7**, m.p. 209–212° dec. (from $EtOH/H_2O$ 5:2). IR (KBr): 3422*s* (H_2O), 3047*m*, 2954*m*, 2898*m*, 1601*m*, 1509*m*, 1471*m*, 1084*s*, 1061*s*, 1038*s*, 998*s*, 831*s*, 782*s*, 522*s*. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 8.27 (*d*, 2 H); 8.16 (*dd*, 4 H); 7.96 (*d*, 2 H); 7.88 (*t*, 2 H); 7.68 (*t*, 2 H); 5.64 (*d*, J = 9.3, 2 H); 5.37 (*d*, J = 18.6, 2 H); 4.68 (*dd*, J = 9.3, 18.6, 2 H). ^{13}C-NMR ((D_6)DMSO, 75.46 MHz): 135.74; 132.90; 132.60; 131.13; 129.63; 128.76; 126.67; 126.58; 58.24 (CHS); 43.95 (CH_2); 24.45 (CH_3S); 23.97 (CH_3S). Anal. calc. for $C_{28}H_{30}B_2F_8S_2$ (604.29): C 55.65, H 5.00, S 10.61; found: C 55.62, H 5.27.

*7,7a-Dihydrodibenzo[*de,mn*]naphthacene* (**8**), *7,7a,14,14a-Tetrahydro-7-hydroxydibenzo[*de,mn*]naphthacene* (**9**), *7-Ethoxy-7,7a,14,14a-tetrahydrodibenzo[*de,mn*]naphthacene* (**10**) *and Dibenzo[*de,mn*]naphthacene* (**11**; *Zethrene*). The reaction was carried out in a 1-l round-bottomed flask with three necks, dropping funnel, thermometer and magnetic stirring. The apparatus was flushed with Ar to remove most of the O_2 before dropping began. Under Ar, to 940 mg (1.56 mmol) of **7** were added 400 ml of a cold saturated soln. of Na_2CO_3 in $EtOH/H_2O$ 1:1 under stirring. The mixture was heated till the soln., which in course of time got clear, showed a sudden milky cloudiness at *ca.* 60°. At this temp. it was stirred for 15 min, cooled, and then extracted with CH_2Cl_2 until no strongly blue fluorescing product could be detected in the H_2O phase by an UV handlamp at wave-length of 366 nm. The org. layer was evaporated in the dark in vacuum at 30° till dryness. MPLC on reversed-phase material resulted in isolating of 4 compounds (in order of elution): **9** (60 mg), **10** (65 mg), **8** (70 mg), and a trace supposed to be **11** by UV characterization. Separation conditions: column 18.5 × 420 mm, 102 ml, packed with reversed-phase silica *C 18*, 35–70 µm (*Organogen*, Heidelberg); flow 20 ml/min; elution with MeOH; sample volume 0.5 ml (sample in CH_2Cl_2); detection by UV at 254 nm.

8: M.p. 170° dec. (red melt). t_R (MPLC) 13.4 min. UV (cyclohexane): 218 (4.92), 243 (4.54), 2.73 (sh, 3.81), 288 (sh, 3.75), 302 (sh, 3.81), 341 (sh, 4.12), 363 (4.24). IR (KBr): 3430*m* (H_2O), 3033*m*, 2925*m*, 1589*m*, 1500*w*, 1175*w*, 1036*w*, 1028*w*, 969*w*, 906*w*, 873*w*, 853*w*, 827*s*, 811*m*, 775*s*, 678*w*, 666*w*, 634*w*, 605*w*. ^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.91–7.20 (*m*, 13 H, arom. H, olef. H); 4.52 (*dd*, *J*(c,b) = 5.1, *J*(c,a) = 13.3, H_c); 3.65 (*dd*, *J*(b,c) = 5.1, *J*(b,a) = 15, H_b); 3.58–3.44 (*m*, H_a). ^{1}H-NMR (CD_2Cl_2, 90 MHz): 7.95–7.10 (*m*, 13 H, arom. H. olef. H); 4.67–4.37 (*m*, 1 H); 3.37–3.33 (*m*, 2 H). ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.93–7.15 (*m*); 4.6–4.35 (*m*); 3.59 (*s*); 3.50 (*d*, *J* = 3). ^{1}H-NMR (C_6D_6, 90 MHz): 7.73–6.90 (*m*, 13 H, arom. H, olef. H); 4.33–4.03 (*m*, 1 H); 3.30 (*s*, 1 H); 3.19 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75.46 MHz): 139.34; 137.69; 135.03; 133.62; 133.35; 131.97; 129.52; 128.17; 127.81; 126.76; 126.43; 126.37; 126.25; 125.89; 125.80; 125.74; 124.82; 124.18; 123.23; 121.82; 120.50; 42.79 (*t*, CH_2); 40.09 (*d*, CH). MS (166°): 305 (16.62, $M^{+\cdot} + 1$), 304 (67.45, $M^{+\cdot}$), 303 (64.42, $M^{+\cdot} - H$), 302 (45.63, $M^{+\cdot} - 2\,H$), 152 (27.18), 151 (100.00), 150 (87.26), 149 (41.98), 148 (11.94). Anal. calc. for $C_{24}H_{16}$ (304.39): C 94.70, H 5.30; found: C 94.52, H 5.19.

9: M.p. 258° dec. (red melt; from CH_2Cl_2). t_R (MPLC) 5.8 min. IR (KBr): 3561*m* (OH), 3462*m* (OH), 3040*w*, 2930*w*, 2877*w*, 1595*m*, 1505*m*, 1395*m*, 1219*m*, 1011*m*, 858*m*, 827*s*, 821*s*, 788*m*, 777*s*, 775*s*, 762*m*. ^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.98–7.42 (*m*, 12 arom. H); 5.94 (*m*, H_e); 4.15 (*dd*, *J*(d,c) = 4, *J*(d,a) = 15.5, H_d); 3.88 (*dt*, *J*(c,a) = *J*(c,b) = 12.4, *J*(c,d) = 4, H_c); 3.51 (*d*, *J*(b,c) = 12.4, *J*(b,e) ≈ 0, H_b); 3.31 (*dd*, *J*(a,d) = 15.5, *J*(a,c) = 12.4, H_a); 2.02 (*d*, *J* = 2.7, OH). MS (200°): 323 (2.80, $M^{+\cdot} + 1$), 322.1351 (11.57, $M^{+\cdot}$ ($C_{24}H_{18}O$, calc. 322.1358)); 305 (8.28), 304 (37.50, $M^{+\cdot} - H_2O$), 303 (62.66), 302 (100.00), 300 (14.53), 151 (41.45).

10: M.p. 161.5–163° (from CH_2Cl_2/hexane). t_R (MPLC) 9 min. IR (KBr): 3044*m*, 2965*m*, 2889*m*, 2862*m*, 1596*s*, 1582*m*, 1505*m*, 1452*w*, 1437*m*, 1396*m*, 1320*m*, 1220*m*, 1179*m*, 1173*m*, 1158*m*, 1119*s*, 1076*s*, 1032*m*, 1017*m*, 991*m*, 971*m*, 952*m*, 895*m*, 858*m*, 833*m*, 821*s*, 791*m*, 779*s*, 770*s*, 749*m*, 709*m*, 675*m*, 654*m*, 638*m*, 607*m*. ^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.95–7.40 (*m*, 12 arom. H); 5.44 (*d*, *J* = 2.2, H_e); 4.11 (*dd*, *J*(d,c) = 4, *J*(d,a) = 15.5, H_d); 3.95 (*dt*, *J*(c,a) = *J*(c,b) = 12.4, *J*(c,d) = 4, H_c); 3.58–3.45 (*m*, *J* = 7.1, CH_2, H_b); 3.22 (*dd*, *J*(a,d) = 15.5, *J*(a,c) = 12.4, H_a); 0.93 (*t*, *J* = 7.1, CH_3). MS (220°): 351 (2.16, $M^{+\cdot} + 1$), 350.1670 (7.32, $M^{+\cdot}$ ($C_{26}H_{22}O$, calc. 350.1671)); 305 (20.69), 304 (81.64, $M^{+\cdot} - C_2H_5OH$), 303 (80.75), 302 (100.00), 151 (41.10).

11: t_R (MPLC) 18.4 min. IR and UV of the red compound were identical with those reported for zethrene [6].

Conversion of **9** *to* **8**. To 40 mg (0.124 mmol) of **9** in 1 ml of dry pyridine under Ar was added 47 mg (0.248 mmol) of TsCl at 0°. The mixture was stored in a refrigerator at 5° for 68 h and then poured onto 5 g of ice. The precipitate was filtered off and washed with H_2O. Chromatography of the crude material (25 mg) on reversed phase afforded two fractions: 16 mg of **9** (identified by IR) and 3 mg of **8** (identified by IR).

Oxidation of **8** *to* **11**. To 50 mg (0.16 mmol) of **8** in 5 ml of benzene under Ar were added a soln. 37 mg (0.16 mmol) of DDQ in 5ml benzene at r.t. over a period of 5min. After stirring for 1 h, the mixture was filtered over 5 g of Al_2O_3 (*Brockmann*, Grade III). The Al_2O_3 was washed with benzene and the solvents evaporated at 40°. The crude product (31 mg) was recrystallized from toluene: **11**, m.p. 258–262°. UV, IR, and ^{1}H-NMR obtained were identical with those reported for zethrene [6].

REFERENCES

[1] R. Gleiter, T. Kobayashi, *Helv. Chim. Acta* **1971**, *54*, 1081; R. Gleiter, R. Haider, J. Spanget-Larsen, P. Bischof, *Tetrahedron Lett.* **1983**, *24*, 1149; J. Spanget-Larsen, R. Gleiter, R. Haider, *Helv. Chim. Acta* **1983**, *66*, 1441.

[2] R. H. Mitchell, F. Sondheimer, *J. Am. Chem. Soc.* **1968**, *90*, 530.

[3] R. Gleiter, H.-P. Schaaff, W. Götzmann, U. Huber-Patz, H. Rodewald, H. Irngartinger, to be published.

[4] M. Karplus, *J. Chem. Phys.* **1959**, *30*, 11; *J. Am. Chem. Soc.* **1963**, *85*, 2870; H. Conroy, *Adv. Org. Chem.* **1960**, *2*, 310; A. A. Bothner-By, *Adv. Magn. Reson.* **1965**, *1*, 195.

[5] R. F. Borch, *J. Org. Chem.* **1969**, *34*, 627.

[6] R. H. Mitchell, F. Sondheimer, *Tetrahedron* **1970**, *26*, 2141.

[7] H. J. Bestmann, D. Ruppert, *Angew. Chem.* **1968**, *80*, 668; *ibid. Int. Ed.* **1968**, *7*, 637.

[8] Further informations about the structural data may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany, giving the deposition number CSD 51797, the name of the authors and the journal numbers.

[9] B. A. Frenz and Ass., Inc., College Station, Texas, USA and Enraf-Nonius, Delft, Holland (1982).