

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

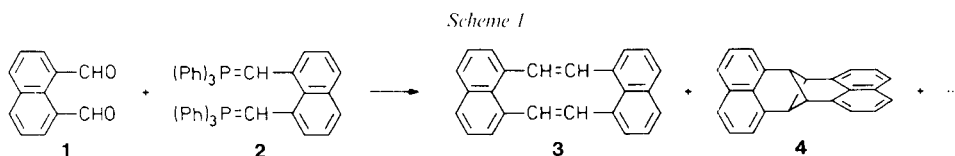
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(8. II. 87)

The reaction of the bis(sulfonium salt) **7** in a solution of Na_2CO_3 in $\text{H}_2\text{O}/\text{EtOH}$ 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**.

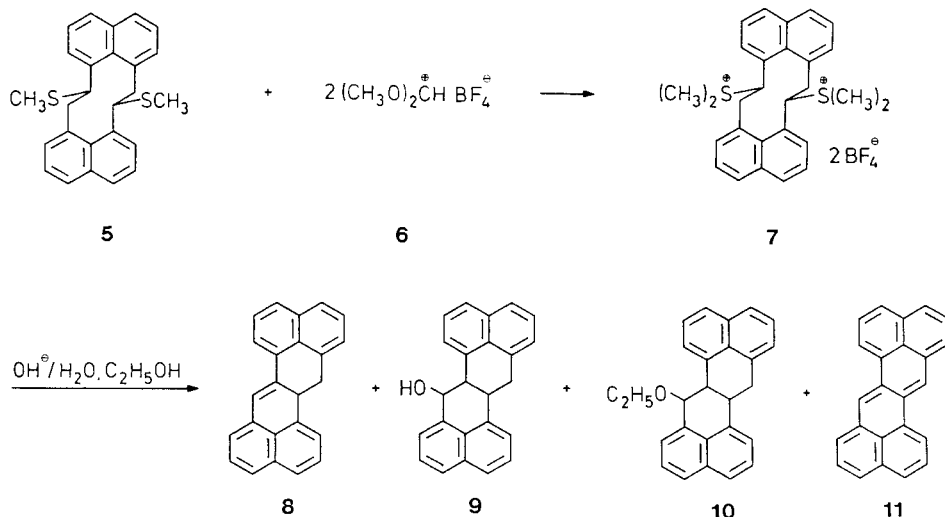
Synthesis and Structures. – Starting compound of our synthesis was the bisulfide **5** whose synthesis and structure will be reported in a separate paper [3]. With dimethoxycarbenium tetrafluoroborate (**6**), we obtained from **5** the bis(sulfonium salt) **7** (see *Scheme 2*). The reaction of **7** with a solution of Na_2CO_3 in $\text{H}_2\text{O}/\text{EtOH}$ 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.

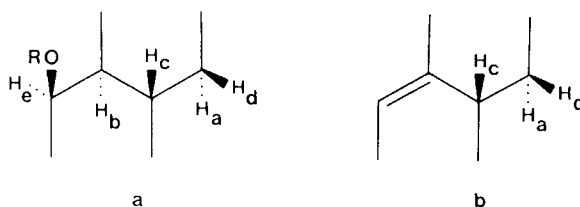
To elucidate the structures of **8–10** we will discuss their $^1\text{H-NMR}$ spectra (*Fig. 1*).

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

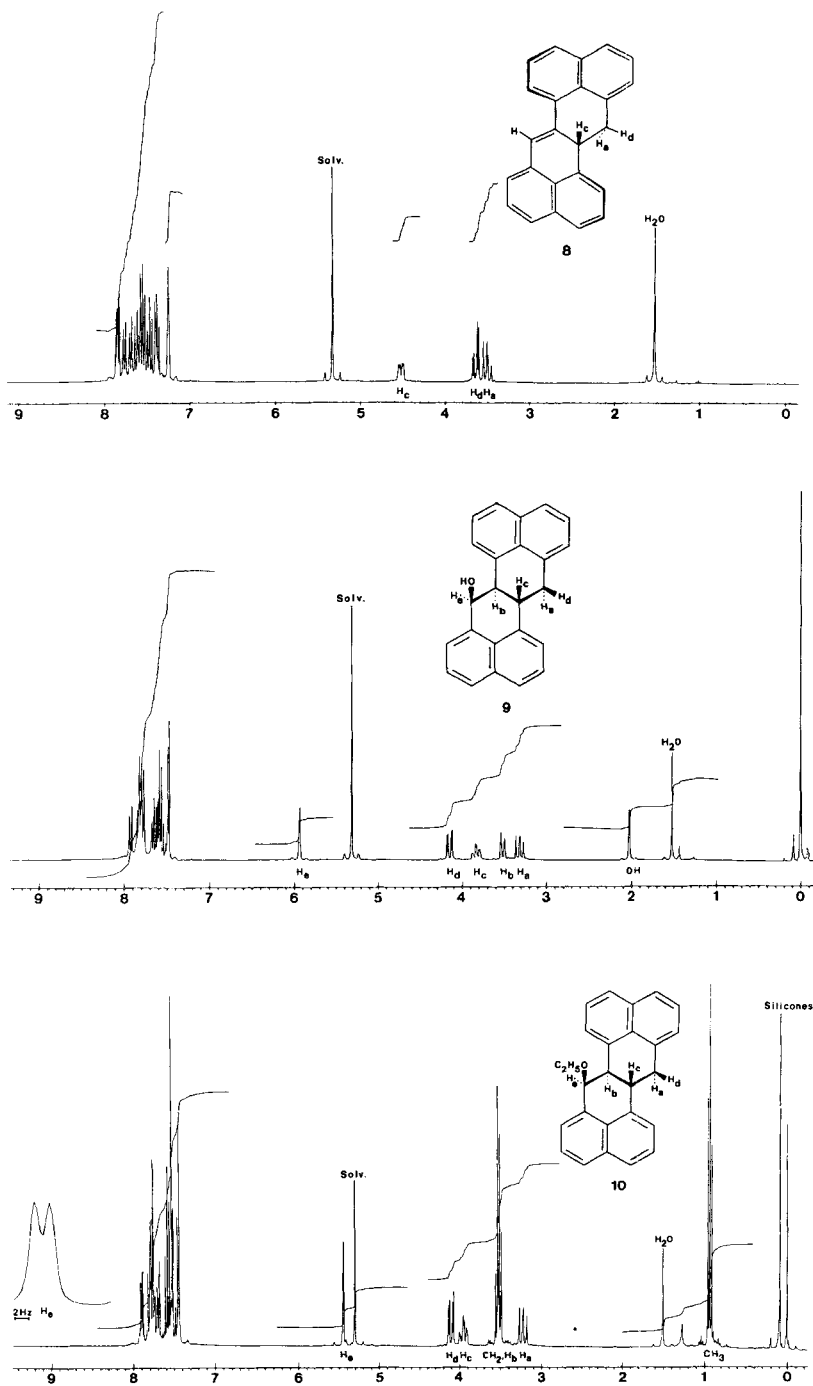
Scheme 2



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: $J(\text{a},\text{d}) = 15.5$ Hz and $J(\text{a},\text{c}) = 12.4$ Hz. In agreement with the *Karplus-Conroy* rules [4], the coupling between H_d and H_c is small ($J(\text{c},\text{d}) = 4$ Hz), whereas the coupling between H_b and H_c is large ($J(\text{b},\text{c}) = 12.4$ Hz). The triplet of H_c in both spectra is due to two identical couplings ($J(\text{a},\text{c}) = J(\text{b},\text{c})$) 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.



The ^1H -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 neighbored 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 ^1H -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 ^1H -NMR spectrum in the region between 3 and 5 ppm is in full accord with the findings of Mitchell and Sondheimer [2].

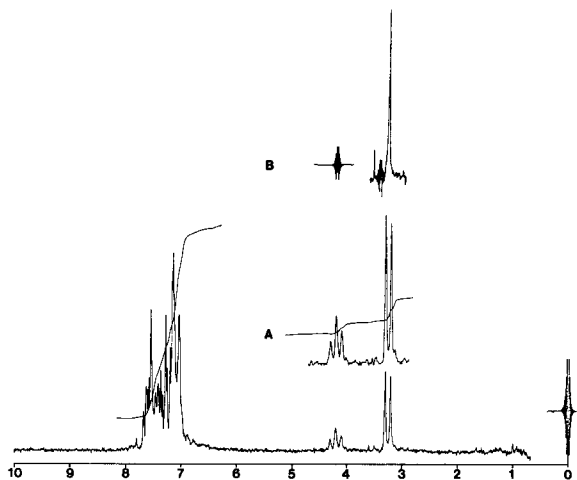
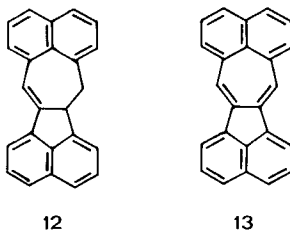


Fig. 2. ^1H -NMR spectrum of **8** in C_6D_6 . In B, the result of a double-resonance experiment on the signals enlarged in A is shown.

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 ^1H -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



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°.

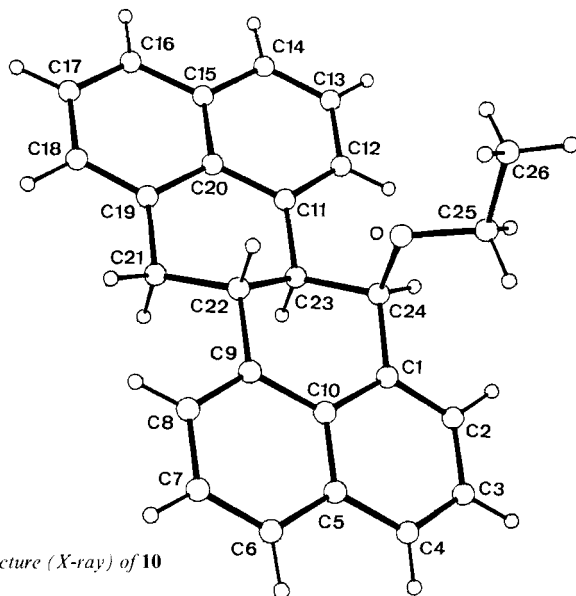


Fig. 3. Molecular structure (X-ray) of **10**

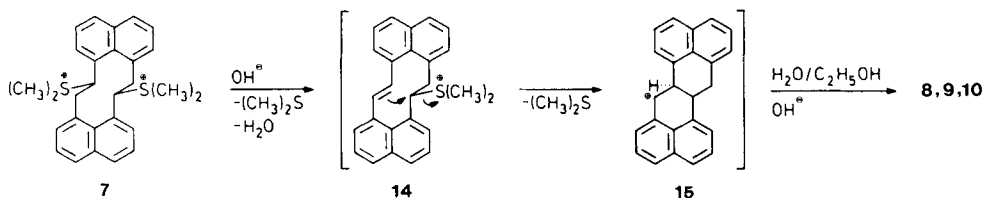
Table 1. Interatomic Distances [Å] of **10**. For the numbering of the atoms, see Fig. 3.

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 $(\text{CH}_3)_2\text{S}$ leads to the mono-olefin **14**. The double bond of **14** is ideally suited for a back side attack, when the second molecule of $(\text{CH}_3)_2\text{S}$ 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. Rimmeler, 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, ^1H -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 (^1H -NMR at 90 MHz), a Bruker AC200 (^1H -NMR at 200 MHz), and a Bruker WH 300 (^1H -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 $\text{CH}_2\text{Cl}_2/\text{hexane}$) were used. Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ molecules in the unit cell ($\text{CH}_2\text{Cl}_2/\text{hexane}$). The cell dimensions are: $a = 10.870(2)$, $b = 13.491(2)$, $c = 12.942(2)$ Å, $\beta = 103.25(2)^\circ$; $D_c = 1.26 \text{ mg m}^{-3}$. The data were collected on a diffractometer (Enraf-Nonius CAD4, MoK α radiation, graphite monochromator, θ - 2θ scan, $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$, with a crystal of the size $0.3 \times 0.3 \times 0.5 \text{ mm}^3$). 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	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} \times 10^3$
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(dimethylsulfonyl)-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 $(\text{MeO})_2\text{CH} \cdot \text{BF}_4$ [**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): 3422s (H_2O), 3047m, 2954m, 2898m, 1601m, 1509m, 1471m, 1084s, 1061s, 1038s, 998s, 831s, 782s, 522s. $^1\text{H-NMR}$ ($(\text{D}_6)\text{DMSO}$, 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). $^{13}\text{C-NMR}$ ($(\text{D}_6)\text{DMSO}$, 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 $\text{C}_{28}\text{H}_{30}\text{B}_2\text{F}_8\text{S}_2$ (604.29): C 55.65, H 5.00, S 10.61; found: C 55.62, H 5.27.

7,7a-Dihydrodibenzof[de,mn]naphthalene (**8**), 7,7a,14,14a-Tetrahydro-7-hydroxydibenzof[de,mn]naphthalene (**9**), 7-Ethoxy-7,7a,14,14a-tetrahydrodibenzof[de,mn]naphthalene (**10**) and Dibenzof[de,mn]naphthalene (**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): 3430m (H_2O), 3033m, 2925m, 1589m, 1500w, 1175w, 1036w, 1028w, 969w, 906w, 873w, 853w, 827s, 811m, 775s, 678w, 666w, 634w, 605w. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.91–7.20 (m, 13 H, arom. H, olef. H); 4.52 (dd, $J(\text{c},\text{b}) = 5.1$, $J(\text{c},\text{a}) = 13.3$, H_c); 3.65 (dd, $J(\text{b},\text{c}) = 5.1$, $J(\text{b},\text{a}) = 15$, H_b); 3.58 3.44 (m, H_a). $^1\text{H-NMR}$ (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). $^1\text{H-NMR}$ (CDCl_3 , 90 MHz): 7.93–7.15 (m); 4.6–4.35 (m); 3.59 (s); 3.50 (d, $J = 3$). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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, $M^{++} + 1$), 304 (67.45, M^{++}), 303 (64.42, $M^{++} - \text{H}$), 302 (45.63, $M^{++} - 2 \text{H}$), 152 (27.18), 151 (100.00), 150 (87.26), 149 (41.98), 148 (11.94). Anal. calc. for $\text{C}_{24}\text{H}_{16}$ (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): 3561m (OH), 3462m (OH), 3040w, 2930w, 2877w, 1595m, 1505m, 1395m, 1219m, 1011m, 858m, 827s, 821s, 788m, 777s, 775s, 762m. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.98–7.42 (m, 12 arom. H); 5.94 (m, H_c); 4.15 (dd, $J(\text{d},\text{c}) = 4$, $J(\text{d},\text{a}) = 15.5$, H_d); 3.88 (dt, $J(\text{c},\text{a}) = J(\text{c},\text{b}) = 12.4$, $J(\text{c},\text{d}) = 4$, H_c); 3.51 (d, $J(\text{b},\text{c}) = 12.4$, $J(\text{b},\text{e}) \approx 0$, H_b); 3.31 (dd, $J(\text{a},\text{d}) = 15.5$, $J(\text{a},\text{c}) = 12.4$, H_a); 2.02 (d, $J = 2.7$, OH). MS (200°): 323 (2.80, $M^{++} + 1$), 322.1351 (11.57, M^{++} ($\text{C}_{24}\text{H}_{18}\text{O}$, calc. 322.1358)); 305 (8.28), 304 (37.50, $M^{++} - \text{H}_2\text{O}$), 303 (62.66), 302 (100.00), 300 (14.53), 151 (41.45).

10: M.p. 161.5–163° (from $\text{CH}_2\text{Cl}_2/\text{hexane}$). t_R (MPLC) 9 min. IR (KBr): 3044m, 2965m, 2889m, 2862m, 1596s, 1582m, 1505m, 1452w, 1437m, 1396m, 1320m, 1220m, 1179m, 1173m, 1158m, 1119s, 1076s, 1032m, 1017m, 991m, 971m, 952m, 895m, 858m, 833m, 821s, 791m, 779s, 770s, 749m, 709m, 675m, 654m, 638m, 607m. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.95–7.40 (m, 12 arom. H); 5.44 (d, $J = 2.2$, H_c); 4.11 (dd, $J(\text{d},\text{c}) = 4$, $J(\text{d},\text{a}) = 15.5$, H_d); 3.95 (dt, $J(\text{c},\text{a}) = J(\text{c},\text{b}) = 12.4$, $J(\text{c},\text{d}) = 4$, H_c); 3.58–3.45 (m, $J = 7.1$, CH_2 , H_b); 3.22 (dd, $J(\text{a},\text{d}) = 15.5$, $J(\text{a},\text{c}) = 12.4$, H_a); 0.93 (t, $J = 7.1$, CH_3). MS (220°): 351 (2.16, $M^{++} + 1$), 350.1670 (7.32, M^{++} ($\text{C}_{26}\text{H}_{22}\text{O}$, calc. 350.1671)); 305 (20.69), 304 (81.64, $M^{++} - \text{C}_2\text{H}_5\text{OH}$), 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 5 ml benzene at r.t. over a period of 5 min. 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 $^1\text{H-NMR}$ obtained were identical with those reported for zethrene [6].

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