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107. Synthesis and Properties of 1,1-Dihalogenocycloprop[*b*]anthracenes[1])

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Summary

The synthesis of 1,1-difluoro-1*H*-cycloprop[*b*]anthracene (**3**) is described. The key step of the synthesis is the cycloaddition of 1,2-dichloro-3,3-difluorocyclopropene (**6**) to 2,3-dimethylidene-1,2,3,4-tetrahydronaphthalene (**5**). The ^{13}C-NMR. spectrum of **3** is assigned on the grounds of C,F-coupling constants, selective H-decoupling and the resulting residual C,H-coupling. The 1,1-dichloro derivative **4** was synthesized by the same route, but could not be isolated pure. Experiments for the reduction to 1*H*-cycloprop[*b*]anthracene (**2**) and for the ionization of **3** or **4** to the cation **16** failed.

Introduction. – Since their discovery in 1964 [2] the chemistry of cyclopropabenzenes has been extensively investigated [3]. This research is motivated by the desire to understand limits and consequences of strain and distortion imposed on the benzenoid framework. In addition, since cyclopropabenzenes are usually very unstable compounds, their preparation also represents a considerable synthetic challenge. Recent achievements in the field consist in the synthesis of both isomeric cyclobutacyclopropabenzenes [4] [5]. Extension to the arene homologues led to the discovery of several cyclopropanaphthalenes [6] including the shock-sensitive 1*H*,4*H*-dicyclopropa[*b,g*]naphthalene [7]. Contrary to the general expectation however, the synthesis of the still higher homologues, the cyclopropanthracenes, could not be achieved by straightforward extension of the methodology used for synthesis of cyclopropabenzenes or -naphthalenes.

Both *Garratt* [5] and *Billups* [8] investigated the *Billups* approach, *i.e.* bis-dehydrohalogenation of the dichlorocarbene adduct **1** of 1,4-dihydroanthracene with *t*-BuOK in dimethylsulfoxide, for the preparation of 1*H*-cycloprop[*b*]anthracene (**2**); however, only substituted anthracenes could be obtained. The failure of this procedure is not too surprising. Although it works particularly well for the

[1]) For a preliminary report, s. [1].

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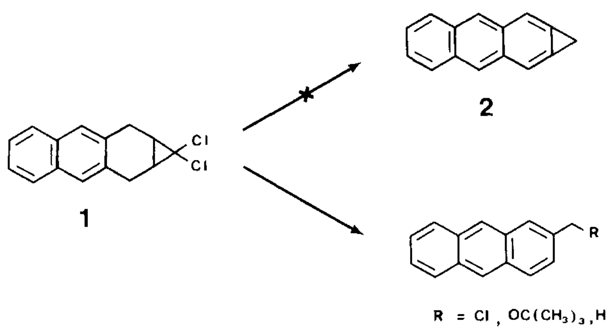
Scheme 1



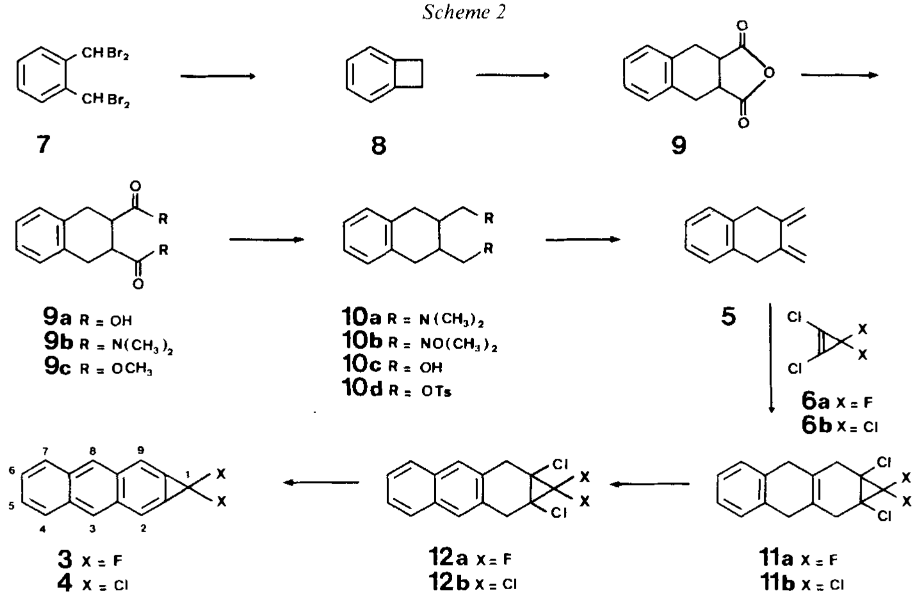
preparation of cyclopropabenzenes [9], its application to cyclopropa[*b*]naphthalenes leads to partial opening of the cyclopropane ring; success of the reaction requires careful control of the conditions and in particular a very large excess of base [10]. The difficulties encountered during the synthesis of 1*H*-cyclopropa[*b*]naphthalene with the *Billups* approach and the failure of the method for 1*H*-cycloprop[*b*]anthracene could be a consequence of bond fixation in cyclopropabenzenes [5], although no conclusive proof for this effect has yet been found.

This communication reports details on the synthesis and some properties of the 1,1-dihalogeno-1*H*-cycloprop[*b*]anthracenes **3** and **4**. The fact that these compounds have been isolated does not imply, however, that the parent hydrocarbon, 1*H*-cycloprop[*b*]anthracene (**2**), is stable at room temperature. Halogen substituents, in particular fluoride, seem to exert a stabilizing effect on cyclopropabenzenes; the high dipole moment of 3.54 D of 1,1-difluoro-1*H*-cyclopropabenzene [11] is indicative of profound charge redistribution upon fluoro substitution. This experimental observation is corroborated by MINDO/3 calculations which place a formal positive charge of +0.96 at C(1) [12] of difluorocyclopropabenzene.

Synthesis. – The approach used for the synthesis of the 1,1-dihalogeno-1*H*-cycloprop[*b*]anthracenes **3** and **4** is still another application of the *Vogel-Tobey* [13] synthesis of 1,1-difluoro-1*H*-cyclopropabenzenes, which has been previously applied to the preparation of difluoro- and dichloro-1*H*-cyclopropa[*b*]naphthalenes [14]. The C-framework was constructed by a cycloaddition of 2,3-dimethylidene-1,2,3,4-tetrahydronaphthalene (**5**) and the appropriate tetrahalogenocyclopropene (**6** and **6a**).

Diene **5** is available from *α,α,α',α'*-tetrabromo-*o*-xylene (**7**) *via* 1,2-dihydrocyclobutabenzene (**8**) [15] and *Diels-Alder* reaction with maleic anhydride [16]. The adduct **9** was hydrolyzed to the diacid **9a** which upon treatment with $(Me_2N)_3P$ afforded the diamide **9b** [17]. Reduction with $LiAlH_4$ followed by oxidation with H_2O_2 led to the *N*-oxide **10a**. The latter was pyrolyzed to the diene **5** in an overall yield of 7–8% starting from **7**. Although this yield is not yet satisfactory, it compares favorably with an alternative synthesis giving **5** in 3–5% yield from cyclobutanedicarboxylic acid [18]. A slightly different method for the preparation of diene **5** was investigated; the anhydride **9** was transformed to the diester **9c**, then to the bis-(*p*-toluenesulfonate) **10c** *via* diol **10b**. Base-induced elimination failed and afforded only 2,3-dimethylnaphthalene, which was also obtained in variable amounts as a side product during pyrolysis of the *N*-oxide **10a**.

Scheme 2



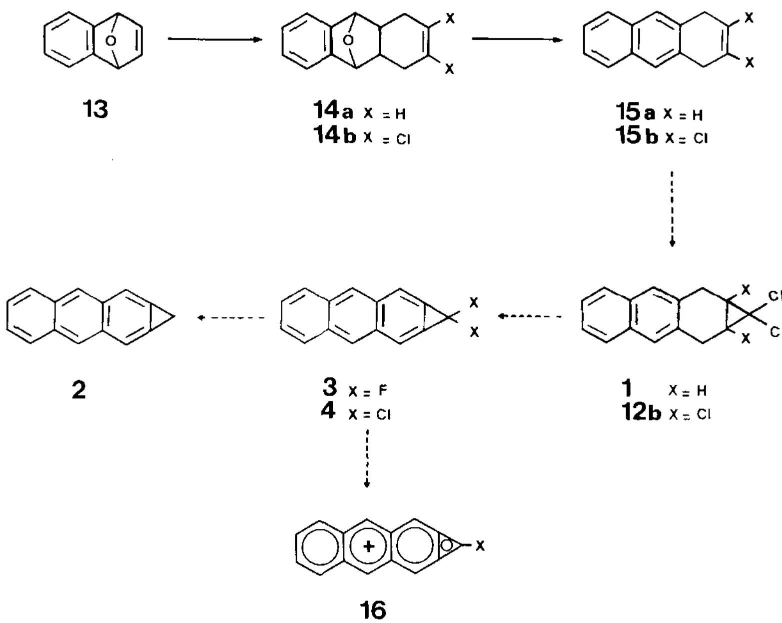
Cycloaddition of the tetrahalogenocyclopropenes **6a** and **6b** [19] to **5** proceeded between 25 and 45° in 2–6 days. The ^{19}F-NMR. spectrum of the adduct **11** shows an *AB*-pattern (J(F,F) = 153.8 Hz) typical for difluorocyclopropanes, with the *A*-part splitted into two quintuplets (^4J(H,F) = 4 Hz) at 31.59 ppm (F_{exo}) and the *B*-part at 18.38 ppm (F_{endo}). Attribution of the fluoro substituents to the *exo/endo*-positions was made in analogy to the attributions of *Tobey & Law* [20] for similar cycloadducts. The difluoro derivative **11a** underwent partial aromatization of the central ring under the conditions of the cycloaddition. Total conversion to **12a** and **12b** was effected by reaction with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). Finally, 1,1-difluoro-1*H*-cycloprop[*b*]anthracene (**3**) was obtained by bis-dehydrohalogenation of **12** with *t*-BuOK. Compound **3** is a yellow solid, m.p. 190–191° (dec.), and can be recrystallized from $CHCl_3$. Its spectral data are discussed below. In contrast, we were unable to isolate the dichloro derivative **4** in pure form. All attempts of purification resulted only in its destruction.

Since the above synthesis is long and the yields unsatisfactory some other approaches towards 1*H*-cycloprop[*b*]anthracenes were investigated *(Scheme 3)*. One attempt consisted in the aromatization of the dichlorocarbene adduct **1** of 1,4-dihydroanthracene, which was prepared by a sequence proposed by *Billups* [3b] (**13** → **14a** → **15a** → **1**). However, reaction of **1** with two mol-equiv. of *N*-bromosuccinimide (NBS), followed by treatment with base afforded non of the desired **4**.

Moreover, the dichlorodihydroanthracene derivative **15b** was synthesized by an analogous route starting with the *Diels-Alder* adduct **13** of benzyne and furane [21]. Reaction with 2,3-dichlorobutadiene [22] (→ **14b**) followed by aromatization gave the dichloro compound **15b**. However, it was not possible to obtain the tetrachloro derivative **12b** by addition of dichlorocarbene to **15b**, although all the conventional methods for generation of dichlorocarbene were tried.

It was also attempted to synthesize the parent hydrocarbon **2** by reduction of **4** with $LiAlH_4/AlCl_3$ [23], but no identifiable products were isolated from the reaction.

Scheme 3



Considerable effort was made to prepare the 1-fluorocycloprop[*b*]anthryl cation (**16**) by ionization of the difluoro compound **3**. However, all the methods tried, in particular those which had led to cyclopropaphenyl and cyclopropa[*b*]naphthyl cations (dissolution in $HFSO_3$) without difficulties [14] [24], failed completely. This difference in behavior of 1,1-dihalo-1*H*-cyclopropabenzenes and -[*b*]naphthalenes as compared to 1,1-dihalogeno-1*H*-cycloprop[*b*]anthracenes may be understood in qualitative terms on the grounds of molecular orbital considerations. The simple *Hückel* HMO model shows that the localization energy (a_μ^+) at C(1) decreases slightly in the series of the cyclopropaphenyl (1.65 β), cyclopropa[*b*]naphthyl (1.59 β) and cyclopropa[*b*]anthryl (1.57 β) cations. In contrast, the tendency to undergo protonation of the aromatic π-system increases strongly within the series in function of a_μ^- [25]. It is reasonable to assume that the dihalogenocycloprop[*b*]-anthracenes undergo protonation at C(3) and subsequent polymerization rather than ionization to cations.

Spectral properties of 1,1-dihalogeno-1*H*-cycloprop[*b*]anthracenes. – The ^{1}H-NMR. spectra of **3** and **4** have been published in the preliminary communication [1]. The spectrum of **3** shows a singlet at 8.75 ppm for the protons at C(3) and C(8) and a triplet (^4J(H,F) = 3.75 Hz) at 8.31 ppm for those at C(2) and C(9). The other protons give rise to an *AA'BB'*-system characteristic for naphthalene derivatives with multiplets at 8.10 and 7.58 ppm. In the dichloro derivative **4** the corresponding signals appear at 8.62 (*s*, H–C(3) and H–C(8)), 8.13 (*s*, H–C(2) and H–C(9)), 8.04 (*m*) and 7.52 (*m*). The fluoro substituents of **3** resonate at 77.6 ppm (*t*, ^4J(H,F) = 3.75 Hz), in good agreement with the 80.3 ppm reported for 1,1-difluoro-1*H*-cyclopropa[*b*]naphthalene [14] and 79.9 ppm for 1,1-difluoro-2,5-diphenyl-1*H*-cyclopropabenzene [26].

The ^{13}C-NMR. spectrum of **3** (see *Table 1* and *Fig. 1*) was assigned as follows: The signals of C(1), C(1a), C(9a), and C(2a), C(8a) were attributed on the grounds of their C,F-coupling constants of

Table. *^{13}C-NMR. of* **3** *and* **4** (chemical shifts in ppm, coupling constants in Hz)

	C(1)	C(1a), C(9a)	C(2), C(9)	C(2a), C(8a)	C(3), C(8)	C(3a), C(7a)	C(4), C(7)	C(5), C(6)
3[a])	103 *t* ^{1}J = 307.6	124.6 *t* ^{2}J = 19.5	115.9 *d*	136.8 *t* ^{4}J = 2.93	129.6 *d*	133.7 *s*	129 *d*	127.4 *d*
4[b])	–	–	113.1 *d*	135.2 *s*	128.7 *d*	132.6 *s*	128.1 *d*	126.5 *d*

[a]) In D_8-THF. [b]) In $CDCl_3$.

307.6, 19.5 and 2.93 Hz, respectively, with the assumption that $^{1}J(C,F) > {}^{2}J(C,F) > {}^{4}J(C,F)$. Proton decoupling showed that these signals are resonance lines of quaternary C-atoms. The line at 115.9 ppm was assigned to C(2), C(9); this signal is characteristic for all cyclopropa-arenes, and its position depends very little upon substitution and annelation [26]. The remaining quaternary C-atoms C(3a), C(7a) display a singlet upon partial H-decoupling, while the signals of C(3), C(8), C(4), C(7), and C(5), C(6) become doublets. These lines were identified by the magnitude of the residual C,H-coupling constants upon selective irradiation [27]. Residual C,H-coupling can be observed in the ^{13}C-NMR. spectrum if a magnetic field of frequency ν_2 is applied either at higher or lower field of the ^{1}H-NMR. spectrum. The residual coupling constant of proton H_i is large if the resonance line ν_i is far away from ν_2, because the degree of decoupling decreases with increasing $\Delta\nu = \nu_i - \nu_2$. Application of this method to the spectrum of **3** is represented schematically in *Figure 1*, where spectrum B (center) shows the

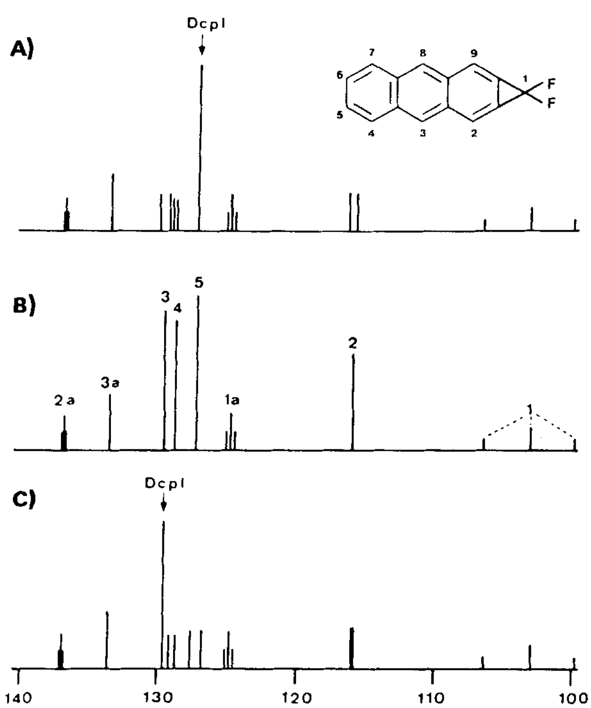


Fig. 1. *Selective H-decoupling in the ^{13}C-NMR. of* **3**. A) decoupling at 7.50 ppm; B) total H-decoupling; C) decoupling at 8.75 ppm.

resonance lines upon total H-decoupling. In spectrum A the protons at C(5) and C(6) at 7.50 ppm are decoupled and the ^{13}C-NMR. signal of C(5) and C(6) becomes a singlet. The residual C,H-coupling constants are 18 Hz for C(3) and C(8), 12 Hz for C(2) and C(9) and 6 Hz for C(4) and C(7), which corresponds to the ^{1}H-NMR. signals at 8.75, 8.39 and 8.10 ppm, respectively. Similarly (spectrum C), decoupling at low field (8.75 ppm) results in a singlet for the ^{13}C-NMR. signal of C(3) and C(8) with the residual coupling constants of 18 Hz for C(5) and C(6), 10 Hz for C(4) and C(7) and a small unresolved coupling constant for C(2) and C(9). The attributions are consistent.

The same procedure was applied to the NMR. spectra of the dichloro derivative **4**, although in this case some of the quaternary C-atoms could not be detected. The assignments are summarized in *Table 1*. They are based on the assumption that the protons at C(5) and C(6) resonate at higher field than those at C(4) and C(7), as it is the case in anthracene.

In the IR. spectrum of **3** we find two bands in the region characteristic for cyclopropabenzenes, one at 1635 cm^{-1} (*m*) and a slightly weaker one at 1649 cm^{-1}. The UV. spectrum of **3** *(Fig. 2)* shows the same pattern as anthracene; however, the bands are broader and those above 300 nm are shifted by about 20–30 nm to higher wavelength. The MS. of **3** is consistent with the proposed structure. Besides the parent ion at *m/z* 226 the peaks corresponding to loss of H [28], F and CF_2 are present.

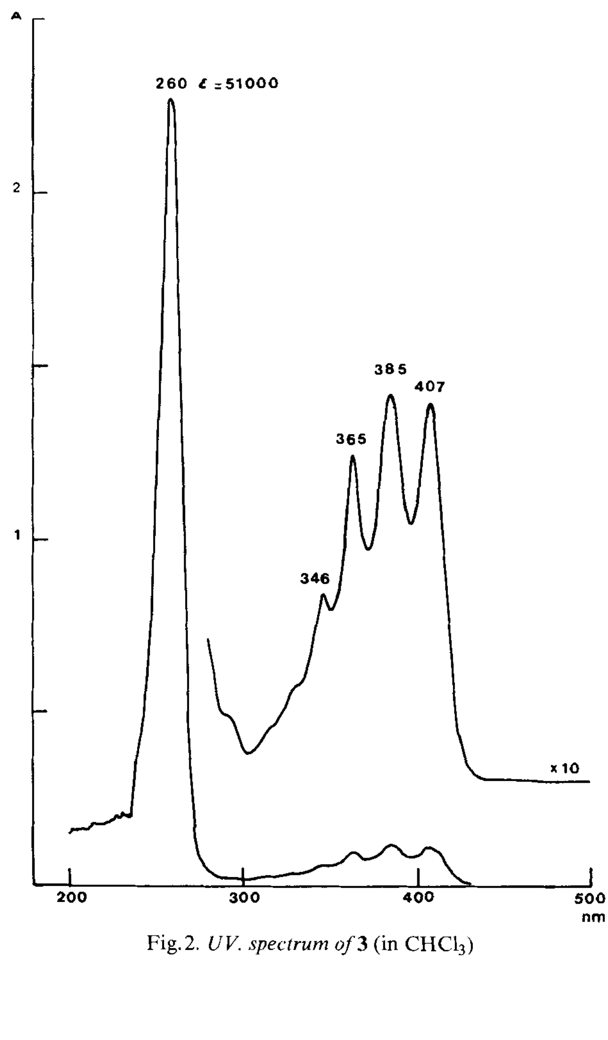


Fig. 2. *UV. spectrum of* **3** (in $CHCl_3$)

Conclusion. – The synthesis of the 1,1-dihalogeno-1*H*-cycloprop[*b*]anthracenes **3** and **4** should permit access to the unsubstituted 1*H*-cycloprop[*b*]anthracene (**2**) and to the cation **16**. However, a more efficient approach to **3** and **4** is required before extended experiments in these directions can be initiated.

Experimental Part

General remarks. UV. spectra were recorded on a *Uvikon-820* spectrophotometer with 1 cm quartz cells; λ_{max} (ε) in nm. – IR. spectra were recorded on a *Perkin-Elmer 257* or *Pye Unicam SP-1100* instrument; absorptions in wavenumbers (cm^{-1}); *s* = strong, *m* = medium, *w* = weak, and br. = broad. – ^{1}H-NMR. spectra were obtained at 360 MHz on a *Bruker WH-360* instrument, those at 100 MHz on a *Varian XL-100* and at 60 MHz on a *Varian T-60A* or *EM-360A* spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (= 0 ppm), the coupling constants ^{n}J in Hz; *s* = singlet, *d* = doublet, *qa* = quadruplet, *qi* = quintuplet, *m* = multiplet. ^{19}F-NMR. spectra were obtained at 94.1 MHz on a *Varian XL-100* instrument; chemical shifts relative to C_6F_6 (= 0 ppm). The ^{13}C-NMR. spectra were measured on a *Varian VXL-100* or *Bruker WH-360* spectrometer; chemical shifts relative to TMS (= 0 ppm). The mass spectra were obtained on *Varian SM-1* and *EM-600* instruments. The intensities of the peaks are expressed in % of the base peak (= 100%). When several isotopes of a given atom occur in the molecule, only the intensity of the peak corresponding to the lowest isotopic mass is given. The intensities of the other peaks are determined by the natural abundance of the various isotopes.

Synthesis of 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride (**9**). Maleic anhydride (12.4 g, 130 mmol) and 1,2-dihydrocyclobutabenzene (**8**) [15] (6.75 g, 64.5 mmol) were heated with 15 ml of mesitylene in a steel autoclave at 210° for 48 h. After cooling, excess maleic anhydride was dissolved in chloroform, and the crude product was separated by filtration. Recrystallization from ethyl acetate afforded **9** (8.4 g, 63%), m.p. 185–187° ([16]: 185°, 186.8–187.8°). 189°). – ^{1}H-NMR. (D_6-DMSO, 60 MHz): 7.15 (*s*, 4 H); 3.71 (*m*, 2 H); 2,96 (*m*, 4 H).

Synthesis of cis-*1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid* (**9a**). A suspension of **9** (10.0 g, 49.5 mmol) in 800 ml of water was heated to reflux for 2 h (total dissolution of **9**). Upon cooling the product precipitated; a second crop was obtained after concentration of the mother liquor: 9.76 g (89%) of **9a**, m.p. 193–195° (from H_2O) ([16]: 195°, 195.6–196.2°). – ^{1}H-NMR. (D_6-DMSO, 60 MHz): 7.05 (*s*, 4 H); 3.11 (*s*, 6 H).

Synthesis of cis-N,N,N′,N′-*tetramethyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxamide* (**9b**). To **9a** (10.3 g, 46.8 mmol) in 35 ml of boiling benzene was added under N_2 tris(dimethylamino)phosphine (9 ml, 47 mmol) dropwise by syringe. After 30 min, the solution was cooled to RT. and treated with 20 ml of sat. $NaHCO_3$-solution. The mixture was diluted with water, extracted with CH_2Cl_2, the organic phase dried and evaporated to afford 12.33 g (96%) of **9b**, m.p. 187–188° (from CH_2Cl_2). – IR. ($CHCl_3$): 16.20*s*. – ^{1}H-NMR. ($CDCl_3$, 60 MHz): 7.06 (*s*, 4 H); 3.4–2.8 (*m*, 18 H). – MS.: 274 (4, M^{+}), 230 (13), 229 (31), 202 (100), 201 (100), 200 (33), 158 (32), 157 (15), 130 (80), 129 (100), 129 (100), 128 (100), 72 (100).

Synthesis of dimethyl cis-*1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate* (**9c**). Anhydride **9** (2.80 g, 13.3 mmol) was heated in 80 ml of methanol containing 1.5 ml of conc. sulfuric acid at reflux for 15 h. The solution was then poured into water and extracted with ether. After evaporation of the solvent, the residue was recrystallized from petroleum ether (60–80°): 3.0 g (87%) of **9c**, m.p. 66–67° ([16]: 68–68.5°). – IR. ($CHCl_3$): 3010, 2980, 2930, 2890, 2830*m*, 1730*s*, 1435*s*, 1360*m*, 1240*s*, 1175*s*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 7.13 (*s*, 4 H); 3.70 (*s*, 6 H); 3.35–3.05 (*m*, 6 H). – MS.: 248 (7, M^{+}), 217 (9), 216 (9), 189 (5), 188 (38), 130 (13), 129 (100), 128 (34), 127 (10).

Synthesis of cis-N,N,N′,N′-*tetramethyl-1,2,3,4-tetrahydronaphthalene-2,3-bis(methylamine)* (**10a**). Diamide **9b** (12.3 g, 44.7 mmol) dissolved in 300 ml of dried THF was added dropwise to $LiAlH_4$ (2.32 g, 60.6 mmol) in 100 ml of anhydrous ether. The rate of addition was such that the solution was maintained at reflux. After addition, heating was continued for 1 h. The mixture was decomposed with H_2O and 15% NaOH-solution. Workup afforded **10a** (10 g, *ca.* 90%). A portion of the product was distilled at 108–110°/10^{-2} Torr. – IR. (liq.): 2920, 2800, 2740, 1440, 1250*w*, 1030, 740. – ^{1}H-NMR. (CCl_4, 60 MHz): 6.95 (*s*, 4 H); 2.67 (*m*, 4 H); 2.0–2.33 (*m*, 6 H); 2.15 (*s*, 12 H). – MS.: 246 (8, M^{+}), 188 (5), 143 (3), 129 (4), 58 (100).

Synthesis of cis-N,N,N',N'-*tetramethyl-1,2,3,4-tetrahydronaphthalene-2,3-bis(methylamine)* N,N'-*dioxide* (**10b**). Diamine **10a** (9.84 g, 40 mmol) in 50 ml of methanol was treated with 30% H_2O_2-solution (9.1 ml, 80 mmol) at 0°. After 2 and 5 additional hours new portions of H_2O_2 were added and stirring was continued for 18 h. A test with phenolphthaleine indicated the end of the reaction. Then, 10 mg of Pd-catalyst were added. Evolution of O_2 was complete after 16 h. After filtration, the solution was evaporated at 60°. The crude **10b** (10.5 g, 94%) was pyrolyzed without further purification.

Synthesis of cis-*1,2,3,4-tetrahydronaphthalene-2,3-dimethanol* (**10c**). To a solution of **9c** (2.97 g, 12 mmol) in 40 ml of ether was added dropwise at −5° a suspension of $LiAlH_4$ (630 mg, 16.5 mmol) in 20 ml of ether. After 16 h at 0°, the mixture was decomposed with 2N HCl. Workup of the organic phase gave **10c** (2.0 g, 87%), m.p. 95–96° (from benzene) ([29]: 100–101°). – IR. ($CHCl_3$): 3500–3100, 1035, 1020. – ^1H-NMR. ($CDCl_3$, 360 MHz): 7.10 (*m*, 4 H); 3.71 (*AB*-part of *ABM*-system, $^2J_{AB}=11.5$, $^3J_{AM}=4$, $^3J_{BM}=7.5$, H_A at 3.77, H_B at 3.64, 4 H); 2.30 (*m*, *M*-part of *ABM*- and *FGM*-system, 2 H); 3.53 (*s*, 2 H); 2.86 (*FG*-part of *FGM*-system, $^2J_{FG}=17.5$, $^3J_{FM}=7$, $^3J_{GM}=6$, H_F at 2.82, H_G at 2.89, 4 H). – MS.: 192 (absent, M^+), 174 (20), 156 (21), 144 (10), 143 (76), 142 (18), 141 (36), 130 (11), 129 (56), 128 (100), 127 (21), 116 (19), 115 (43), 91 (19), 78 (21), 77 (16).

Synthesis of cis-*1,2,3,4-tetrahydronaphthalene-2,3-dimethyl bis(*p*-toluenesulfonate)* (**10d**). *p*-Toluenesulfonyl chloride (5.72 g, 30 mmol) in 20 ml of pyridine was added dropwise at −10° to **10c** (1.52 g, 10 mmol) in 40 ml of pyridine. After 15 h at 0°, the mixture was poured on ice and extracted with CH_2Cl_2. After conventional workup, **10b** (3.29, 64%) was purified by recrystallization from CH_2Cl_2, m.p. 150–152°. – IR. ($CHCl_3$): 3000, 2900, 1600, 1490*w*, 1370*s*, 1180*w*, 1100, 970*w*. – ^1H-NMR. ($CDCl_3$, 360 MHz): 7.75 (*d*, 4 H); 7.34 (*d*, 4 H); 7.08 (*m*, 2 H); 6.95 (*m*, 2 H); 3.97 (*AB*-part of *ABM*-system, $^2J_{AB}=10$, $^3J_{AM}=7.5$, $^3J_{BM}=6$, H_A at 3.93, H_B at 4.02, 4 H); 2.84 (*G*-part of *FGM*-system, $^2J_{FG}=16.5$, $^3J_{GM}=5.5$, 2 H); 2.46 (*s*, 6 H); 2.5–2.35 (*m*, *F*- and *M*-part of *FGM*- and *ABM*-system, 4 H). – MS.: 500 (absent, M^+), 229 (11), 328 (41), 202 (21), 200 (14), 192 (12), 174 (14), 173 (28), 172 (15), 157 (19), 156 (100), 143 (73), 141 (35), 129 (15), 128 (17), 91 (21).

Synthesis of 2,3-dimethylidene-1,2,3,4-tetrahydronaphthalene (**5**). The *N*-oxide **10b** (2.5 g, 9 mmol) was pyrolyzed in a preheated oil bath at 170°/0.3 Torr. The pyrolysate was collected in a series of traps cooled to −78°. The liquid was dissolved in CH_2Cl_2, washed with H_2O, then with 5% hydrochloric acid, sat. $NaHCO_3$- and, finally, sat. NaCl-solution. The organic phase was dried with K_2CO_3 and evaporated. The remaining oil contained **5** (500 mg, 35%) [18] contaminated with varying amounts of 2,3-dimethylnaphthalene. It was used without further purification for the next step. – ^1H-NMR. (CCl_4, 60 MHz): 7.07 (*s*, 4 H); 5.33 (*m*, 2 H); 4.87 (*m*, 2 H); 3.50 (*t*, $^4J \simeq 1.5$, 4 H).

*Synthesis of 1a,9a-dichloro-1,1-difluoro-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop*[b]*anthracene* (**11a**). A solution of **5** (960 mg, 6.15 mmol) and 1,2-dichloro-2,3-difluorocyclopropene (**6**; 2.0 g, 13.8 mmol) [19] in 60 ml of CCl_4/CH_2Cl_2 1:1 was stirred with 1.1 g of $NaHCO_3$ at 45° during 6 d. The solvent was evaporated and the residue purified by column chromatography on silica gel using CH_2Cl_2 to afford a mixture of **11a** and 2,3-dimethylnaphthalene. The latter was separated by sublimation (70°/2 Torr). Pure **11a** (420 mg, 22%) was obtained by column chromatography and recrystallization from Et_2O, m.p. 142–143°. – IR. (CH_2Cl_2): 2850, 2800, 1580, 1415, 1210*s*, 1140*s*, 985*s*, 900*s*, 820*s*. – ^1H-NMR. ($CDCl_3$, 100 MHz): 7.14 (*s*, 4 H); 3.24 (*s*, 4 H); 2.92 (*d*, $^4J_{HF}=4$, 4 H). – ^{19}F-NMR. ($CDCl_3$, 94.1 MHz): 24.72 (centre of *AB*-system, $^2J(F,F)=153.8$, F_{exo} at 31.59 (*A*-part × *qi*, $^4J(F,H)=4$), F_{endo} at 18.38 (*B*-part)). – MS.: 300 (40, M^+), 265 (20), 229 (35), 178 (24), 128 (100).

*Synthesis of 1,1,1a,9a-tetrachloro-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop*[b]*anthracene* (**11b**). Diene **5** (500 mg, 1.6 mmol) was stirred with tetrachlorocyclopropene (430 mg, 2.4 mmol) and 200 mg of $NaHCO_3$ in 5 ml of CCl_4 for 4 h at RT. Workup as above gave **11b** (330 mg, 62%), m.p. 200–201° (from CH_2Cl_2). – ^1H-NMR. ($CDCl_3$, 60 MHz): 7.10 (*s*, 4 H); 3.23 (*s*, 4 H); 3.0 (*s*, 4 H).

*Synthesis of 1a,9a-Dichloro-1,1-difluoro-1a,2,9,9a-tetrahydro-1*H*-cycloprop*[b]*anthracene* (**12a**). Adduct **11a** (400 mg, 1.33 mmol) was dehydrogenated with DDQ (475 mg, 2.08 mmol) in 25 ml of CCl_4 during 20 h at RT. After evaporation of the solvent, the residue was purified by column chromatography (silica gel/CH_2Cl_2) and recrystallization from CH_2Cl_2 to give 350 mg of **12** (88%), m.p. 152–153°. – IR. ($CHCl_3$): 3010*w*, 2980*w*, 1600*w*, 1450*w*, 1425*w*, 1295*m*, 1120*m*, 1090*m*, 995*s*, 985*s*, 870*s*, 860*s*, 830*s*. – ^1H-NMR. ($CDCl_3$, 100 MHz): 7.78 (*m*, 2 H); 7.63 (*s*, 2 H); 7.46 (*m*, 2 H); 3.58 (*AB*-system, $^2J_{AB}=16.5$, H_A at 3.50 (*A*-part × *d*, $^4J(H,F_{exo})=3.5$), H_B at 3.66 (*B*-part × *d*, $^4J(H,F_{endo}) \simeq 1$), 4 H). – ^{19}F-NMR. ($CDCl_3$, 94.1 MHz): 29.13 (*AB*-system × *m*, $^2J_{AB}=152.6$, $^4J(F,H)=3.5$, F_{endo} at 24.99, F_{exo} at 33.99, 2 F). – MS.: 298 (36, M^+), 263 (67), 228 (42), 227 (51), 213 (23), 178 (100).

*Synthesis of 1,1,1a,9a-tetrachloro-1a,2,9,9a-tetrahydro-1*H*-cycloprop*[b]*anthracene* (**12b**). The procedure as above converted **11b** to **12b** in 95% yield, m.p. 220–222° (dec., from CH_2Cl_2). – IR. ($CHCl_3$): 3000*m*, 2920*m*, 1660*w*, 1600*w*, 1510*w*, 1440*m*, 950*m*, 910*m*, 880*s*, 860*s*. – ^{1}H-NMR. (CD_2Cl_2, 100 MHz): 7.78 (*m*, 2 H); 7.68 (*s*, 2 H); 7.45 (*m*, 2 H); 3.65 (*AB*-system, $^2J_{AB}$ = 16, H_A at 3.56, H_B at 3.75, 4 H). – MS.: 330 (73, M^+), 295 (88), 260 (57), 259 (100), 225 (81), 189 (54), 178 (38).

*Synthesis of 1,1-difluoro-1*H*-cycloprop*[b]*anthracene* (**3**). To a solution of **12a** (150 mg, 0.5 mmol) in 7 ml of anh. THF at −70° was added a solution of *t*-BuOK (125 mg, 1.1 mmol) in 5 ml of THF under N_2 during 45 min. The solution was stirred 2 h at −70°, warmed up to RT., evaporated at RT. and the residue extracted with ether. Evaporation of the ether gave crude, yellow **3** (110 mg, 96%). It was recrystallized from chloroform, m.p. 190–191°. – UV.: s. *Figure 2*. – IR. ($CHCl_3$): 3290*w*, 2800*w*, 1649*s*, 1635*s*, 1432*m*, 1178*s*, 1075*s*, 895*s*. – ^{1}H-NMR.: s. [1]. – ^{19}F-NMR. ($CDCl_3$, 94.1 MHz): 77.6 (*t*, ^4J(F,H) = 3.75, 2 F). – ^{13}C-NMR.: s. *Table 1*. – MS.: 227 (16), 226 (100, M^+), 225 (60), 207 (16), 176 (19), 150 (10), 126 (6).

*Synthesis of 1,1-dichloro-1*H*-cycloprop*[b]*anthracene* (**4**). The same procedure as above gave **4** from **12b** in *ca.* 70% yield, but **4** could not be separated from impurities. – ^{1}H- and ^{13}C-NMR.: s. [1] and *Table 1*.

Synthesis of 9,10-epoxy-1,4,4a,9,9a,10-hexahydroanthracene (**14a**). In a steel autoclave 1,4-epoxy-1,4-dihydronaphthalene [21] (**13**; 6.85 g, 47.5 mmol) and butadiene (13.5 g, 250 mmol) were heated at 140–145° during 15 h. After cooling, the mixture was dissolved in ether and evaporated. The residue was dissolved in methanol, insoluble material removed by filtration, the filtrate evaporated and the product recrystallized from cold pentane: 8.9 g (95%) of **14**, m.p. 64–66°. – IR. ($CHCl_3$): 3010*m*, 2980*m*, 2910*s*, 2820*s*, 1620*w*, 1450*m*, 1350*w*, 1280*w*, 1150*w*, 1010*w*, 990*s*, 950*s*, 910*s*, 850*s*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 7.25 (*m*, 2 H); 2.15 (*m*, 2 H); 5.96 (*m*, 2 H); 5.02 (*s*, 2 H); 2.53 (*m*, 2 H); 2.08 (*m*, 2 H); 1.95 (*m*, 2 H). – MS.: 198 (1, M^+), 180, 179, 178, 165, 131, 126, 120, 119 (< 1), 118 (100).

Synthesis of 2,3-dichloro-9,10-epoxy-1,4,4a,9,9a,10-hexahydroanthracene (**14b**). In 50 ml of benzene, 2,3-dichlorobutadiene (11 g, 90 mmol) [22], 1,4-epoxy-1,4-dihydronaphthalene (**13**; 7.3 g, 50 mmol) and 100 mg of hydroquinone were heated to reflux during 34 h. After evaporation of the solvent, the residue was recrystallized from methanol to give **14a** (8.1 g, 60%), m.p. 112–113°. – IR. ($CHCl_3$): 3010*m*, 2970*m*, 2930*m*, 3880*w*, 2830*w*, 1625*w*, 1450*m*, 1440*m*, 1350*w*, 1305*m*, 1280*w*, 1140*m*, 1070*m*, 1040*s*, 975*s*, 935*s*, 910*w*, 845*s*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 7.22 (*m*, 2 H); 7.16 (*m*, 2 H); 5.0 (*s*, 2 H); 2.70 (*AB*-part of *ABM*-system, $^2J_{AB}$ = 15, $^3J_{AM}$ = 8, $^3J_{BM}$ = 6, H_A at 2.59 H_B at 2.80, 4 H); 2.24 (*m*, *M*-part of *ABM*-system). – MS.: 266 (< 1, M^+), 248 (< 1), 231 (< 1), 230 (< 1), 213 (< 1), 212 (< 1), 178 (5), 152 (1), 118 (100).

Synthesis of 1,4-dihydroanthracene (**15a**). Oxide **14a** (8.0 g, 40 mmol) was boiled with 180 ml of methanol and 18 ml of conc. HCl-solution during 15 h. Upon cooling **15a** precipitated: 6.5 g (90%), m.p. (MeOH) 151–153° (from MeOH; [30]: 151°). – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 7.76 (*m*, 2 H); 7.64 (*s*, 2 H); 7.48 (*m*, 2 H); 6.06 (*m*, 2 H); 3.60 (*AB*-system, 4 H).

Synthesis of 2,3-dichloro-1,4-dihydroanthracene (**15b**). A solution of **15b** (3.3 g, 12.3 mmol) in 100 ml of ethanol and 20 ml of conc. HCl-solution was heated to reflux during 16 h. The product crystallized upon cooling: 2.87 g (93%) **15b**, m.p. 180–181° (from EtOH). – IR. (nujol): 1600*w*, 1380*m*, 1360*m*, 1290*w*, 1270*w*, 1150*w*, 1030*m*, 1010*w*, 960*m*, 930*s*, 900*m*, 860*s*, 750*s*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 7.75 (*m*, 2 H); 7.6 (*s*, 2 H); 7.43 (*m*, 2 H); 3.48 (*s*, 4 H). – MS.: 248 (18, M^+), 213 (89), 212 (19), 178 (100), 106 (23), 88 (48), 75 (19).

*Synthesis of 1,1-dichloro-1a,2,9,9a-tetrahydro-1*H*-cycloprop*[b]*anthracene* (**1**). To a solution of **15a** (1.8 g, 10 mmol) and CH_3ONa (1.98 g, 36 mmol) in 25 ml of petroleum ether was added dropwise at −10° ethyl trichloroacetate (6.2 g, 32 mmol). The solution was stirred below 0° for 2 h, and then at RT. for 15 h. The mixture was then poured on ice/water and extracted with CH_2Cl_2. After usual workup, the crude product was purified by column chromatography (SiO_2/CH_2Cl_2): 1.23 g (45%) **1**, m.p. 176–178° (from CCl_4). – IR. ($CHCl_3$): 3020*m*, 2990*m*, 2940*m*, 2890*m*, 2830*m*, 1600*m*, 1500*m*, 1460*w*, 1430*m*, 1350*m*, 1070*m*, 1015*w*, 975*m*, 950*w*, 940*w*, 920*w*, 870*s*, 835*s*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 7.77 (*m*, 2 H); 7.63 (*s*, 2 H); 7.43 (*m*, 2 H); 3.13 (*AB*-part of *ABM*-system, $^2J_{AB}$ = 17, H_A at 2.84, H_B at 3.42, 4 H); 2.12 (*m*, *M*-part of *ABM*-system). – MS.: 262 (32, M^+), 227 (4), 192 (100), 179 (61), 178 (71).

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