Für aussergewöhnliche Sorgfalt bei der Durchführung der präparativen Arbeiten danke ich Herrn *Hanspeter Lang*.

LITERATURVERZEICHNIS

[1] *G. Schetty*, Helv. *53*, 1437 (1970).
[2] *G. Schetty & E. Steiner*, Helv. *57*, 2149 (1974).
[3] *G. Schetty*, Chimia *18*, 244 (1964).

## 47. The Synthesis of 4b,5,12,12a-Tetrahydro-5,12-ethano-13*H*-indeno[2,3-*b*]anthracenes, 4b,5,10,10a-Tetrahydro-5,10-ethano-11*H*-indeno[2,3-*b*]naphthalenes and 1,2,3,4,4a,9a-Hexahydro-1,4-(*peri*-naphthaleno)-fluorenes

by **Walter Amrein**[1]) and **Kurt Schaffner**

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(15. X. 74)

*Summary.* The synthesis of *endo*- and *exo*-13-oxo-4b,5,12,12a-tetrahydro-5,12-ethano-indeno[2,3-*b*]anthracene (**23**; *Schemes 1 and 2*), *exo*- and *endo*-11-oxo-4b,5,10,10a-tetrahydro-5,10-ethano-indeno[2,3-*b*]naphthalene (**31**; *Scheme 3*), 1,2,3,4,4a,9a-hexahydro-1,4-(*peri*-naphthaleno)-fluoren-9-one (**36**; *Scheme 4*), and the corresponding hydrocarbons of the stereoisomeric ketone pairs **23** and **36**, is described.

In the accompanying paper [1] we report the results of an investigation into the intramolecular transfer of electronic excitation energy between indanone and naphthalene chromophores which are incorporated in conformationally relatively rigid carbon skeletons. We describe here the synthesis of the six ketones (*Schemes 1* and *2*: *endo*- and *exo*-**23**; *Scheme 3*: *endo*- and *exo*-**31**; *Scheme 4*: *endo*- and *exo*-**36**), and of some of the corresponding hydrocarbons (*endo*- and *exo*-**24**, *endo*- and *exo*-**37**) which served as the model compounds in this study.

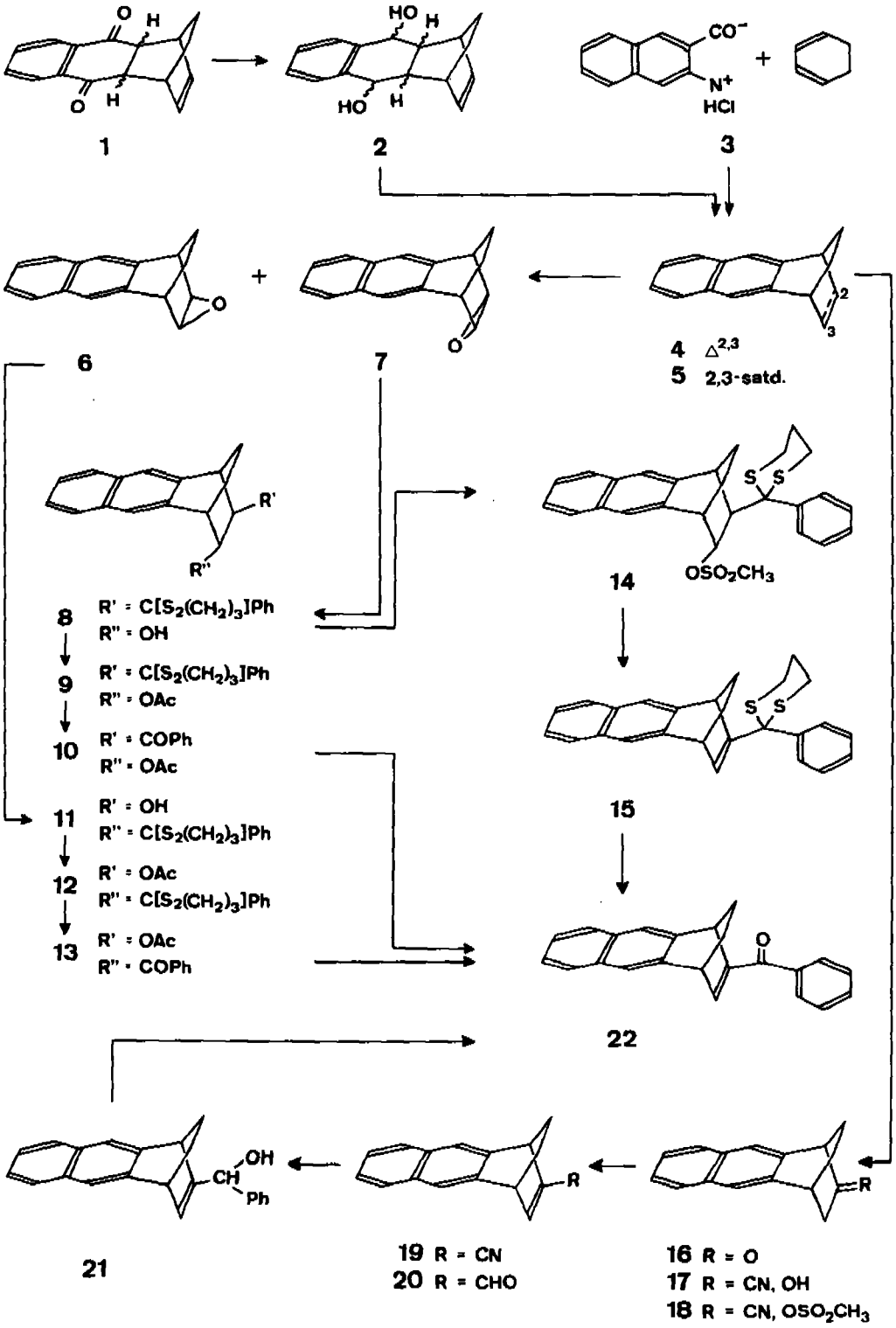
**The 4b,5,12,12a-tetrahydro-5,12-ethano-13*H*-indeno[2,3-*b*]anthracene system (23/24)** (*Schemes 1* and *2*). – 1,4-Bridged anthracenes are normally not accessible directly through cycloadditions onto the terminal aromatic ring [2]. For the construction of the carbon skeleton of compounds **23/24**, benzoylation of the double bond of 1,4-dihydro-1,4-ethanoanthracene (**4**) and subsequent cyclization of the key intermediate **22** was therefore chosen as an alternative route. Compound **4** can be prepared in good yield from the known diketone **1** [3] by sodium borohydride reduction to the diol **2** and dehydration with phosphorus oxychloride in pyridine[2]). Catalytic hydrogenation of **4** afforded 1,2,3,4-tetrahydro-1,4-ethanoanthracene (**5**).

A direct electrophilic benzoylation of the double bond of **4** is impeded by both the competing aromatic nucleophilicity and the proclivity for rearrangement of cationic intermediates of this system, and nucleophilic «acylation» using the anion

[1]) Part of the Doctoral Thesis by *W. Amrein* (ETH Zürich, 1974).

[2]) Addition of 2,3-dehydronaphthalene, prepared *in situ* by thermolysis of **3** [4], to 1,3-cyclohexadiene as a synthetic alternative gave only a low yield of **4**, which was difficult to purify from accompanying products.

*Scheme 1*


1
2
3
4 Δ2,3
5 2,3-satd.
6
7
8 R' = C[S2(CH2)3]Ph R'' = OH
9 R' = C[S2(CH2)3]Ph R'' = OAc
10 R' = COPh R'' = OAc
11 R' = OH R'' = C[S2(CH2)3]Ph
12 R' = OAc R'' = C[S2(CH2)3]Ph
13 R' = OAc R'' = COPh
14
15
22
16 R = O
17 R = CN, OH
18 R = CN, OSO2CH3
19 R = CN
20 R = CHO
21

of 2-phenyl-1,3-dithiane [5] was chosen instead. Oxidation of **4** with *m*-chlorobenzoic peracid furnished the *exo*- (**6**) and *endo*-epoxides (**7**) in a 3:2 ratio. The stereochemical assignment is based on the greater difference in NMR. chemical shifts of the methylene protons in the *exo*-epoxide ($\Delta\delta$ 1.0 *vs.* 0.4 in the *endo*-isomer) due to the anisotropy effect of the oxygen[3]). Both epoxides slowly reacted with 2-lithium-2-phenyl-1,3-dithiane to form the alcohols **8** and **11**.

A first attempt to convert the hydroxydithioacetals **8** and **11** to the unsaturated ketone **22** involved dehydration by way of mesylation and heating in collidine, followed by hydrolysis of the thioacetal. However, only the *endo*-isomer **8** furnished an isolable mesylate (**14**) which could be smoothly transformed to **22**. The mesylation of the *exo*-alcohol **11** led to a mixture containing none of the desired product, possibly as a consequence of decomposition and rearrangement of the mesylate at room temperature with anchimeric assistance by the naphthalene group. Moreover, the mercurolysis of **15** to **22** proceeded with poor yield.

A significant improvement in the transformation of both isomers **8** and **11** into **22** was achieved when the sequence of the two operations – restitution of the 2,3-double bond and ketone formation – was reversed. After protection of the hydroxyl groups by acetylation (→ **9** and **12**) in order to avoid retroaldol cleavage, the treatment with N-chlorosuccinimide and silver nitrate in acetonitrile [6], giving **10** and **13**, and treatment with potassium carbonate in *t*-butyl alcohol[4]) presented a satisfactory route to **22**. The total yield, involving eight steps starting from 1,4-naphthoquinone, was 7–8%.

In a previous synthetic approach to **22** the olefin **4** was converted to ketone **16** by oxidative hydroboration. When attempts to epoxidize the benzylidene derivative of **16** with hydrogen peroxide in alkali (in order to eventually effect a *Wharton* rearrangement [7] to alcohol **21**) failed, the benzoyl substituent of **22** was introduced *via* the unsaturated nitrile **19**. The cyanohydrin **17** was only obtained in a reasonable concentration, when **16** was treated in neat acetone cyanohydrin with simultaneous removal of acetone by molecular sieves from the otherwise unfavorable equilibrium. **17** could be trapped as the mesylate **18** in a non-separable mixture with starting material (**16**) when the solvent was stripped at low temperature in high vacuum, directly followed by treatment with methanesulfonyl chloride and triethylamine in methylene chloride at 0°. Heating of the mixture **16** + **18** to 130° in collidine afforded **19**, which could now be separated from the starting ketone. Optimal yields of **19** reached 90% of converted ketone, but a 1:1 ratio for **16**:**19** could not be improved. As reactions of the nitrile **19** with phenyllithium or phenylmagnesium bromide were not successful, low-temperature reduction with di-*i*-butyl aluminium hydride and mild hydrolysis of the intermediate *Schiff* base were chosen for the preparation of aldehyde **20**, which furnished alcohol **21** with phenyllithium and could be oxidized to **22** with pyridinium chromate in methylene chloride.

Initial experiments to cyclize **22** to the *endo*- and *exo*-ketones **23** failed when the conditions were employed which had been shown suitable for the *Nazarov* cyclization of 1-cyclohexenyl phenyl ketone by *Braude* [8] (phosphoric acid in formic acid) and

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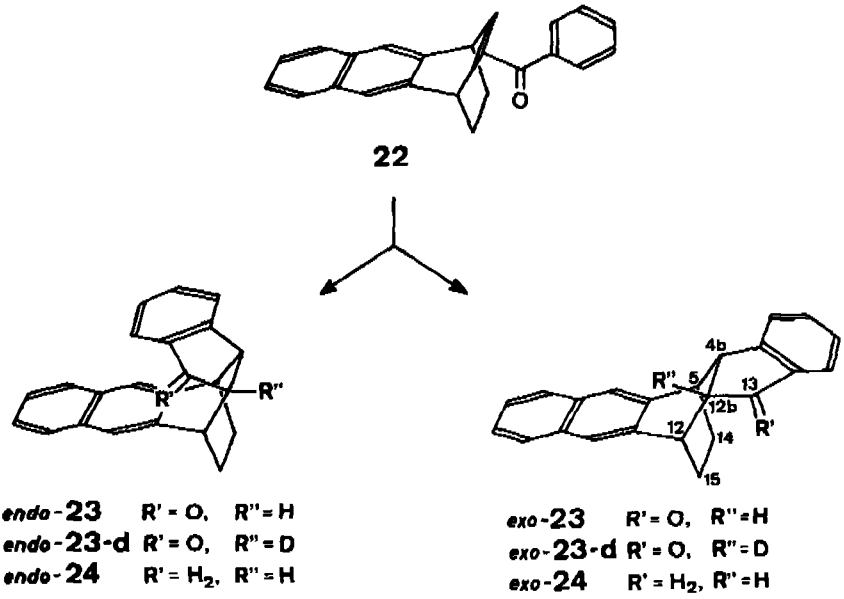
[3]) This stereochemical assignment is confirmed by chemical shift differences which are due to the anisotropic influence of the naphthalene group in subsequent *endo*/*exo* product pairs: the alcohol α-proton of the *exo*-compound **11** ($\Delta\delta$ 0.23) and the acetyl protons of the *endo*-acetates **9** ($\Delta\delta$ 0.27) and **10** ($\Delta\delta$ 0.42) show signals at higher field than those of the corresponding stereoisomers.

[4]) The use of ethanol as a solvent favored the formation the β-ethoxyketones.

*Scheme 2*




*House* [9] (conc. sulfuric acid)[5]). Similarly, **22** remained unchanged when conventionally treated with *Lewis* acids in aprotic media. Solely a combined application of boron trifluoride and tin tetrachloride in carbon disulfide proved successful to slowly convert **22**, in 90% yield, into a 7:1 mixture of *endo*- and *exo*-**23** which could be separated by chromatography. *Huang-Minlon* reduction of the two ketones, and in the case of *exo*-**23** preferably also reductive desulfurization of the dithioacetal derivative with *Raney* nickel, gave the hydrocarbons *endo*- and *exo*-**24**.

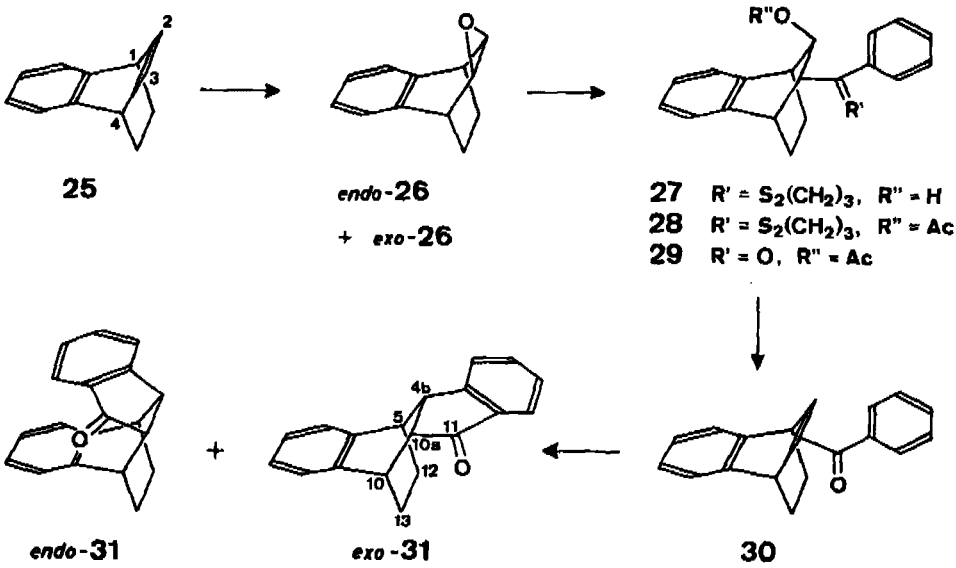
**The 4b,5,10,10a-tetrahydro-5,10-ethano-11*H*-indeno[2,3-*b*]naphthalene system (31)** (*Scheme 3*). – The synthesis of the stereoisomeric ketones *endo*- and *exo*-**31** followed the epoxide-benzoyl/acetoxy route which had proven the superior approach to the anthracene homologues **23**. The *endo*- and *exo*-epoxides **26** were prepared in a 3:1 ratio from the mixture of 1,4-dihydro-1,4-ethanonaphthalene (**25**) and 1,2,4a,8b-tetrahydrobiphenylene, which is obtained upon addition of benzyne to 1,3-cyclohexadiene [12], by *m*-chlorobenzoic peracid oxidation and subsequent chromatographic product separation. The anisotropic effect of the oxygen on the

[5]) UV. irradiation, another successful approach to the cyclization of 1-cyclohexenyl phenyl ketone [10], did not isomerize ketone **22** in the desired way, but rather led to a di-$\pi$-methane-type rearrangement [11]:


**22**

Similar photochemical results were also obtained with the ketones **30**, **33**, and **34**.

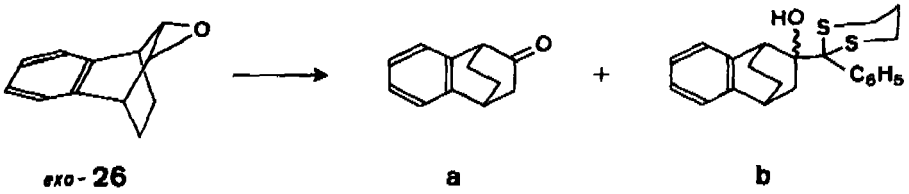
*Scheme 3*



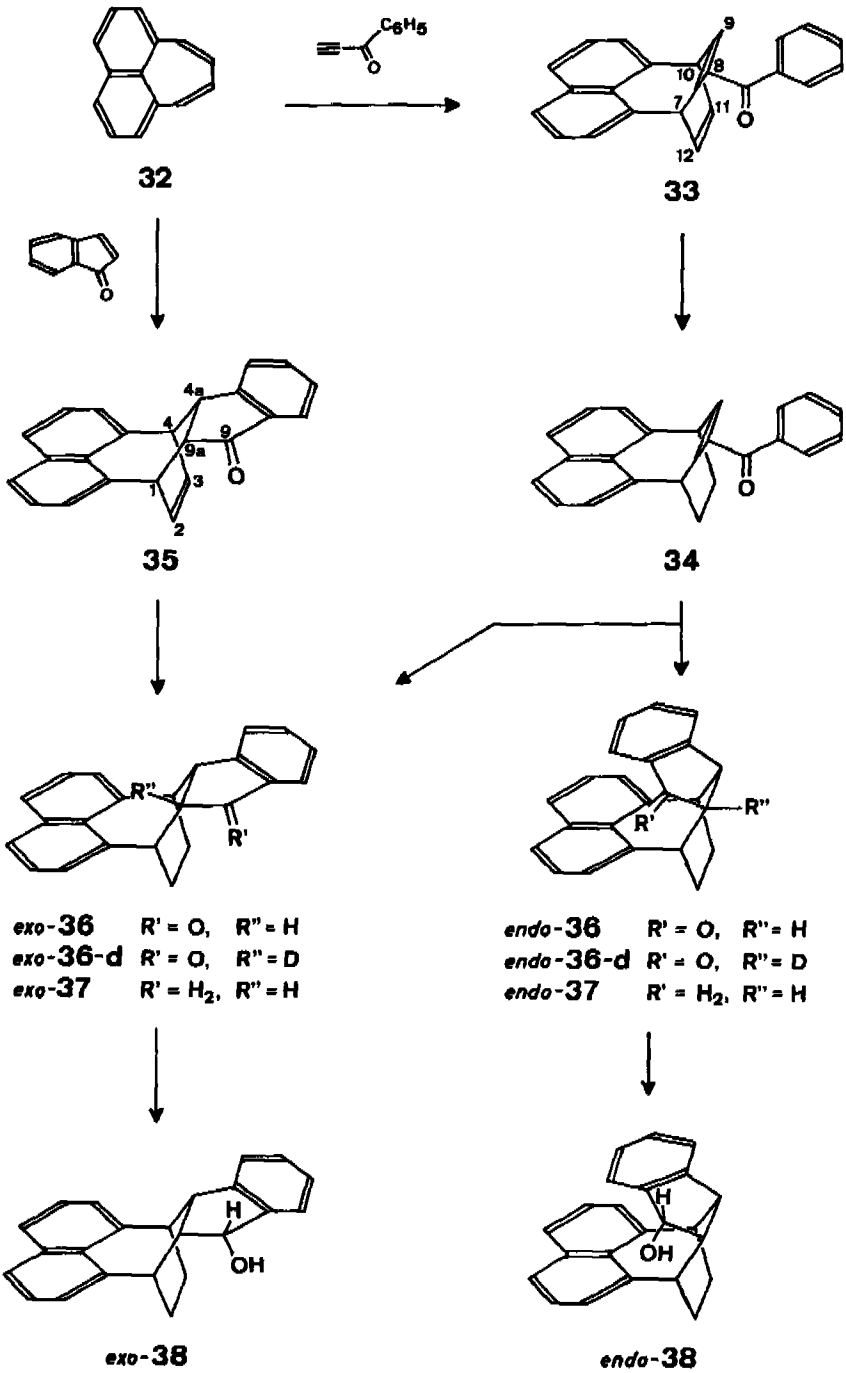

NMR. chemical proton shifts served again to assign the stereochemistry of the isomers **26**. In the *exo*-epoxide the *AA'BB'* shift difference of the methylene protons is about three times greater than in the *endo*-isomer, and the aromatic protons are approximately equivalent in *exo*-**26** but appear as an *AA'BB'* pattern in *endo*-**26**. Treatment of *endo*-**26** with 2-lithium-2-phenyl-1,3-dithiane, acetylation of the hydroxydithioacetal **27** to **28**, oxidative hydrolysis of the dithiane system to ketone **29** and $\beta$-elimination of acetic acid afforded **30** in a total yield of 15% based on the five-step sequence from **25**[6]).

The cyclization of **30**[5]) with boron trifluoride and tin tetrachloride in carbon disulfide gave a 73% yield of the ketones *endo*- and *exo*-**31** in a 7:1 ratio, when the reaction was stopped at an 86% conversion of starting material. The *exo* product **31**

[6]) Contrary to the case of the homologous sequence (**6** → **11**), the *exo*-epoxide **26** reacted differently when subjected to the conditions of the nucleophilic acylation, and thus proved useless in this synthesis. It rearranged to the ketone **a**, presumably as a result of an anchimeric assistance by the benzene ring, followed by base-catalyzed proton elimination from C(2) and restitution of the original carbon frame. Some of the intermediate lithium enolate of **a** reacted furthermore during the work-up with excess lithium-phenyl-dithiane prior to the complete hydrolytic decomposition of both and gave the hydroxy acetal **b** (*m.p.* 163–164°). However, numerous attempts to convert **b** into the unsaturated phenyl ketone **30** were unsuccessful.



*Scheme 4*


C6H5
O
32
33
9
10
8
7
11
12
O
O
4a
4
9a
9
3
1
2
O
35
34
O
R"
R'
R'
R"
exo-36 R' = O, R" = H
exo-36-d R' = O, R" = D
exo-37 R' = H2, R" = H
endo-36 R' = O, R" = H
endo-36-d R' = O, R" = D
endo-37 R' = H2, R" = H
H
OH
H
OH
exo-38
endo-38

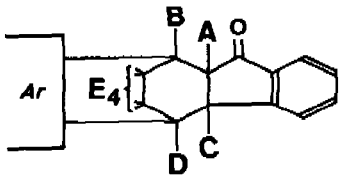
is unstable under the conditions of formation and its yield dropped significantly when the reaction was carried to completion.

**The 1,2,3,4,4a,9a-hexahydro-1,4-(*peri*-naphthaleno)-fluorene system (36/37)** (*Scheme 4*). – *Diels-Alder* additions across the diene moiety of cyclohepta[*de*]-naphthalene («pleiadiene», **32**)[7][8] provide for a convenient entry to the synthesis of *endo*- and *exo*-**36**/**37**. While the thermal addition of indenone [16] proved unsatisfactory owing to both the facile polymerization of the latter and the low reactivity of **32**, catalysis by boron trifluoride strongly increased the rate of addition, and product **35** was obtained in 58% yield. However, no stereoisomeric adduct could be found in the reaction mixture. The cycloaddition had occurred exclusively in the *endo* mode with respect to the diene partial structure, contrary to what might have been expected from an acid-catalyzed process. Catalytic hydrogenation of the 2,3-double bond gave quantitatively product *exo*-**36**.

A non-stereospecific construction of the (*peri*-naphthaleno)-hexahydrofluorene system – and thus an access to the still missing *exo*-isomer **36** – was achieved as follows: 1-phenylprop-2-yn-1-one [17] reacted slowly with **32** in a melt and yielded ketone **33**. The 11,12-double bond was selectively hydrogenated with tris(triphenylphosphine)-rhodium chloride. Cyclization of the resulting product **34** with boron trifluoride and tin tetrachloride in carbon disulfide afforded a 2:1 ratio of the ketones *endo*-**36** and *exo*-**36**, which again could be readily separated by chromatography[5]. The total yield of the three-step synthesis starting with «pleiadiene» was 33%. In the *Huang-Minlon* reduction of these ketones to the corresponding hydrocarbons **37**, the formation of the hydrazone intermediate from *endo*-**36** required drastic conditions. Desulfurization of the dithioacetal with *Raney* nickel proved a somewhat better procedure.

**The *endo/exo* assignment to the ketone pairs 23, 31, and 36.** – A detailed analysis of the NMR. methine and methylene proton signals revealed the geometry of the six ketones *endo*- and *exo*-**23**, -**31**, and -**36**. Confirmation of these stereochemical conclusions was finally obtained in an X-ray diffraction analysis of compound *endo*-**36** by *Dunand & Gerdil* [18].

In order to simplify the discussion of the NMR. data the following hydrogen atom designations (**A**–**E**), common to all three constitutions, are introduced:




The signals of the six spectra appear in four groups (see also Tables 1 and 2): *a*) a multiplet in the region $\delta$ 1.0–2.5 for the four **E** protons, *b*) a double doublet at around $\delta$ 3.0 for **A**, *c*) a complex system of partially overlapping signal groups within $\delta$ 3.5–4.0 for **B**, **C** and **D**, and *d*) a complex multiplet within $\delta$ 6.6–8.0 for the aromatic

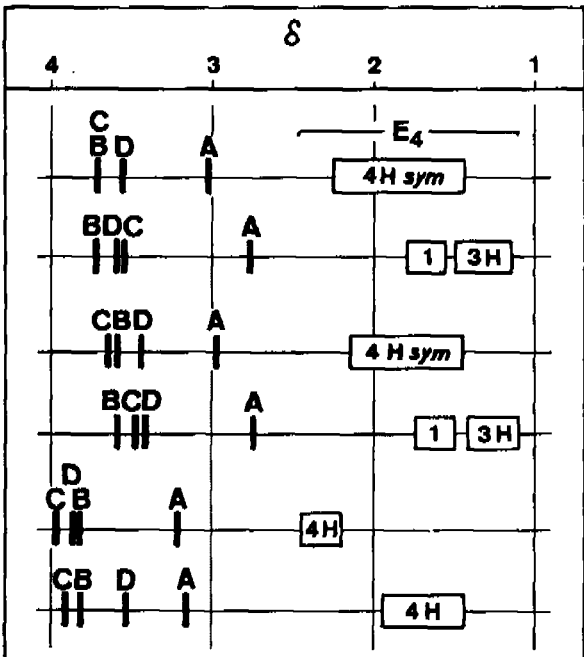
[7] 'Pleiadiene' (**32**) is readily available by the synthesis described by *Meinwald et al.* [13] and *Hartmann et al.* [14].

[8] *Cf.* [15] for the addition of maleic anhydride to **32**.

protons. For a reliable assignment of the signals in groups *b* and *c*, the *endo*- and *exo*-ketones **23** and **36** were monodeuteriated by base-catalyzed exchange of proton **A** (→ *endo*- and *exo*-**23-d**/**36-d**). The disappearance of the double doublet *b* in the deuteriated ketones identified this multiplet as well as the spin coupling constants $J_{AB}$ and $J_{AC}$ (by analogy also for the stereoisomers **31**). Experiments with the $Eu(fod)_3$ shift reagent on both the deuteriated and non-deuteriated ketones resolved the multiplet *c* into three separate one-proton signals. Spin decoupling by irradiation in the group *a* region further reduced the multiplicity of the signals *c*, already diminished in the absence of $J_{AB}$ and $J_{AC}$ in **23-d** and **36-d**, to a singlet for **B** and an *AB* system for **C** and **D** in the deuteriated ketones, and to a doublet for **B** and an *ABX* system for **C** and **D** (X = **A**) in the non-deuteriated compounds.

The chemical shifts of **A**–**D** and $J_{AB}$, $J_{AC}$ and $J_{CD}$ could thus be established (Table 1). Finally, confirmation of the assignments to **A**–**D** came forth with a neat correlation of the decreasing sensitivity towards the shift reagent with increasing distance between the hydrogens and the oxygen atom (**A** < **B** < **C** < **D**).

Table 1. *NMR. Chemical shifts of protons* **A**–**E** *and coupling constants* $J_{AB}$, $J_{AC}$ *and* $J_{CD}$ *in the* endo- *and* exo-*ketones* **23**, **31** *and* **36**

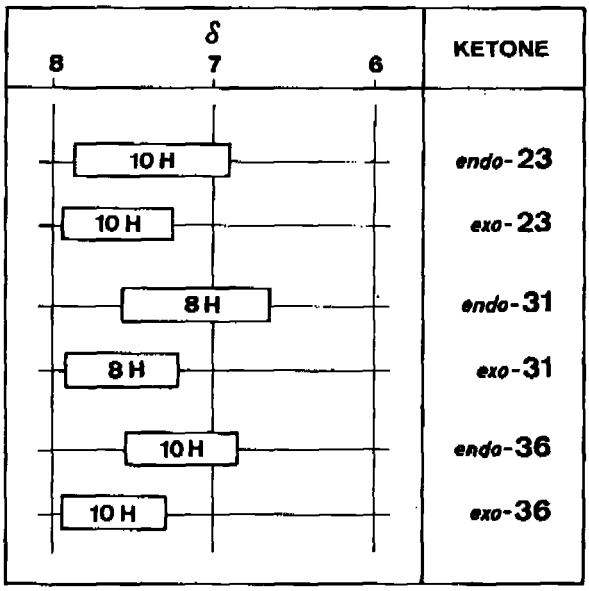



| KETONE | $J_{AB}$ | $J_{AC}$ | $J_{CD}$ |
|---|---|---|---|
| | | [Hz] | |
| *endo*-**23** | 3.5 | 7.8 | 3.0 |
| *exo*-**23** | 3.5 | 8.0 | 2.9 |
| *endo*-**31** | 3.2 | 7.6 | 2.9 |
| *exo*-**31** | 3.0 | 7.5 | 3.0 |
| *endo*-**36** | 5.9 | 7.8 | 5.5 |
| *exo*-**36** | 2.5 | 8.2 | 2.0 |

The symmetry of the bicyclo[2.2.2]octane frame in the *ortho*-aryl substituted compounds **23** and **31** constrains the bridgehead hydrogens **B** and **D** in the plane of the four carbon atoms C(**A**–**D**) and thus renders the coupling constants $J_{AB}$ and $J_{CD}$ insensitive to the *endo* and *exo* geometries. In the bicyclo[3.2.2]nonane skeleton of the *peri*-naphthaleno substituted ketones **36**, however, the C–**B** and C–**D** bonds at the bridgeheads are not co-axial but rather point away from the larger bridge (*i.e.*,

the naphthalene system). The vicinal C–A/C–B and C–C/C–D bonds accordingly occupy – in comparison with the former cases – conformations with a greater dihedral angle (approaching syn-clinal) in the *endo* geometry and a smaller angle (approaching syn-periplanar) in the *exo* geometry. These conformational differences are reflected in distinctly greater (5.9 and 5.5 Hz) and smaller values (2.5 and 2.0 Hz), respectively, for $J_{AB}$ and $J_{CD}$ in the stereoisomeric ketones **36** than in the *endo*- and *exo*-ketones **23** and **31**, where the corresponding values uniformely range within 2.9–3.5 Hz, and thus constitute evidence for the stereochemistry of ketones **36**.

Table 2. *NMR. Chemical shifts of the aromatic protons in the* endo- *and* exo-*ketones* **23**, **31** *and* **36**




The stereoisomeric constitutions of ketones **23** and **31** could be analyzed on the basis of shift differences arising from anisotropic shielding effects of the aromatic ring currents and the keto group, partially in correlation with the independently established geometric assignment of *endo*- and *exo*-**36**. In all three *endo*-ketones mutual shielding causes some of the aromatic protons to shift to higher field (relative to the *exo*-isomer; see Table 2). An analogous effect is expectedly noted for protons **E** in the *exo*-compounds (Table 1). In addition to the general shift of **E** to higher field in the latter cases, the proximity of the indanone, which is strongly asymmetric with respect to the $C_2$ axis of the remaining bicyclo[n.2.2] system, lowers the symmetry of the $E_4$ multiplet, particularly so in the more rigid *ortho*-aryl substituted ketones *exo*-**23** and -**31**. This effect increased in the experiments with the shift reagent, and the signal of the proton **E** situated nearest to the oxygen atom in *exo*-**23** and -**31** was shifted farthest downfield with $Eu(fod)_3$. Finally, **A** and **C** in **23** and **31** exhibit a further example of the aromatic anisotropy effect. They are more shielded in the *exo*-isomers and appear at higher field than in the *endo*-ketones.

Financial support for this work by the *Fonds National Suisse de la Recherche Scientifique* and *Firmenich* SA, Geneva, is gratefully acknowledged.

## Experimental Part

**General Remarks.** – The usual *work-up* of crude reaction mixtures involved extraction with ether or $CH_2Cl_2$, washing of the organic layer with $H_2O$ to the neutral point and drying over anhydrous $MgSO_4$. The solvent was then removed *in vacuo* in a rotary evaporator. – For *thin-layer chromatograms* (*TLC.*) *Merck* Fertigplatten $F_{254}$ (silicagel) were used. The spots were located by fluorescence and by treatment with conc. $H_2SO_4$ and heating. – *Preparative chromatography* was carried out, unless specified otherwise, on silicagel *Merck* (0.05–0.20 *mm*) in columns with decreasing diameter. – *Melting points* (m.p.) are not corrected. – *UV. spectra*: $\lambda_{max}$ in nm, $\varepsilon$ in parentheses. – *IR. spectra*: in $CCl_4$ unless specified otherwise; $\nu_{max}$ in $cm^{-1}$; s = strong, m = medium, and w = weak band intensity. – *NMR. spectra*: in $CDCl_3$ unless specified otherwise; 100 MHz; chemical shifts in $\delta$, and coupling constants ($J$) in Hz; br. = broad, *s* = singlet, *d* = doublet, *m* = other than first-order multiplet. – *Mass spectra* (MS): base peak in italics; relative peak intensity in parentheses.

**Synthesis of the 13-Oxo-4b,5,12,12a-tetrahydro-5,12-ethano-indeno[2,3-*b*] anthracenes (23)** (*Schemes 1 and 2*). – *1,4,4aξ,9ξ,9aξ,10ξ-Hexahydro-1,4-ethanoanthracene-9,10-diol* (**2**). 10 g 1,4,4aξ,9aξ-Tetrahydro-1,4-ethano-9,10-anthraquinone (**1**), m.p. 132–133°, prepared from 1,4-naphthoquinone and 1,3-cyclohexadiene [3], were dissolved in 100 ml MeOH, and 2,5 g $NaBH_4$ were added portionwise under an $N_2$ atmosphere and stirring. The mixture was kept at room temperature by external cooling. Slow addition of 500 ml $H_2O$ after 4 h precipitated 8,5 g (84%) **2**; m.p. 168–170°. – IR. ($CHCl_3$): 980 m, 1085 m, 2940 m, 3000 m, 3450 m (broad), 3850 m. – NMR.: 1.25–1.68/*AA'BB'*, two $H_2$—C; 2.18/br. *s*, H—C(4a and 9a); 2.75/*m*, H—C(1 and 4); 4.72/*m*, H—C(9 and 10); 6.37/AA'*XX'*, H—C(2 and 3); 7.30/*s*, H—C(5–8). – MS.: 242 ($C_{16}H_{18}O_2^+$, 9%), *224*, 195 (15%), 154 (24%).

*1,4-Dihydro-1,4-ethanoanthracene* (**4**). a) *Addition of 1,3-cyclohexadiene to 2,3-dehydronaphthalene*. 3.83 g 3-Amino-2-naphthoic acid [4] in 250 ml abs. EtOH were treated in an ice-bath with 10 ml conc. HCl and 5 ml isoamyl nitrite. After 1 h the product **3** (*3-diazo-2-naphthoate hydrochloride*) was precipated with 500 ml hexane, filtered off, washed with a small amount of abs. ether, and immediately suspended in 50 ml ethylene chloride which had been dried over molecular sieves. 5 ml 1,3-Cyclohexadiene and 5 ml propylene oxide were added and the mixture was refluxed for 3 h. The dark red solution was passed through a column of basic $Al_2O_3$ (act. I), and the column was washed out with $CH_2Cl_2$. Chromatography of the material contained in the combined filtrates on silicagel impregnated with 3% $AgNO_3$ yielded with hexane/benzene 4:1 1.08 g (23%) **4**; m.p. 112–114° (crystallized from hexane). – IR.: 700 s, 860 s, 885 s, 1610 w, 2950 m, 3045 m. – NMR. ($CCl_4$): 1.55/br. *s*, two $H_2$—C; 3.96/*m*, H—C(1 and 4); 6.51/AA'*XX'*, $J_{1,2}$ = 4, H—C(2 and 3); 7.47/*s*, H—C(9 and 10); 7.32 + 7.66/*AA'BB'*, H—C(5–8). – UV. (pentane): 231 (70000), 247 (3300), 256 (4570), 264.5 (5900), 247.5 (6150), 285 (4000), 304 (400), 317.5 (275). – MS.: 206 ($C_{16}H_{14}^+$, 11%), *178*, 165 (7%), 152 (9%).

b) *Dehydration of* **2**. 20 ml $POCl_3$ were added to a cooled solution of 5 g **2** in 40 ml pyridine. After stirring overnight, the mixture was poured onto $H_3PO_4$/ice. The precipitate was filtered off, thoroughly washed with $H_2O$ and taken up in $CH_2Cl_2$. Drying over $MgSO_4$ and filtration through neutral $Al_2O_3$ (act. I) gave 2.78 g (65%) **4**; m.p. 114–115° (crystallized from hexane). The two samples (a and b) were identified by mixed m.p. and comparison of IR., NMR., and MS.

*1,2,3,4-Tetrahydro-1,4-ethanoanthracene* (**5**). 500 mg **4** were hydrogenated in 20 ml ethyl acetate over 100 mg 10% Pd/C. Chromatography with benzene furnished 475 mg (94%) **5**; m.p. 112–113° (crystallized from hexane). – IR.: 861 m, 890 m, 1502 m, 1610 w, 2870 m, 2950 m, 3060 w. – NMR. ($CCl_4$): 1.26–2.15/*AA'BB'*-like br. *m*, four $H_2$—C; 3.12/br. *s*, H—C(1 and 4); 7.60/*s*, H—C(9 and 10); 7.32–7.95/*AA'BB'*, H—C(5–8). – UV. (isooctane): 227 (80500), 250 (2550), 259 (4000), 267 (5700), 277 (6250), 288 (4000), 303 (560), 313 (300), 317 (490). – MS.: 208 ($C_{16}H_{16}^+$, 61%), 180 (36%), *179*, 178 (31%), 165 (22%), 89 (23%).

exo-(**6**) *and* endo-*2,3-Epoxy-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**7**). 14.5 g *m*-Chloroperbenzoic acid (85%) were added at 0° to 9.85 g **4** in 200 ml $CH_2Cl_2$. The solution was stirred for 12 h at 3° and then filtered. The filtrate was diluted with ether and consecutively washed with aqueous solutions of NaI, $Na_2S_2O_3$, $NaHCO_3$, and NaCl. Chromatography with benzene/ethyl acetate 50:1 afforded a small amount of starting material, followed by separated fractions of **6**

and **7**. Crystallization of the two epoxides from hexane gave 1.95 g **6**, m.p. 186.5–188°, and 3.35 g **7**, m.p. 173–174°; total yield 50%.

**6**. – IR.: 845 m, 878 m, 940 m 1132 m, 1260 w, 1385 m, 1605 w, 2930 s, 3000 m, 3045 m. – NMR.: 1.20 + 2.15/*AA'BB'*, two $H_2$—C; 3.35–3.55/*m*, H—C(1–4); 7.40–7.85/*AA'BB'*, H—C(5–8); 7.66/*s*, H—C(9 and 10). – UV. (isooctane): 229 (65000), 248 (2860), 256 (4100), 265 (5430), 275 (5750), 285 (3700), 304 (440), 315 (215), 318 (380). – MS.: *222* ($C_{16}H_{14}O^{+}$), 193 (28%), 191 (27%), 179 (37%), 178 (83%), 165 (32%).

**7**. – IR.: 855 m, 880 m, 950 m, 1136 m, 1388 m, 1500 m, 1605 w, 2940 s, 3000 m, 3050 m. – NMR.: 1.46 + 1.85/*AA'BB'*, two $H_2$—C; 3.40–3.68/*m*, H—C(1–4); 7.30–7.85/*AA'BB'*, H—C(5–8); 7.51/*s*, H—C(9 and 10). – UV. (isooctane): 227 (61000), 249 (2860), 257 (4200), 266 (5850), 276 (6250), 289 (4150), 303 (518), 313 (260), 317 (350). – MS.: *222* ($C_{16}H_{14}O^{+}$), 193 (27%), 193 (27%), 191 (18%), 179 (19%), 178 (48%), 165 (27%).

*exo-2-Hydroxy*-endo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**11**). 4.2 g 2-Phenyl-1,3-dithiane [5] in 25 ml abs. tetrahydrofuran were treated at –40° under argon with 8.5 ml of a 2.5 M solution of BuLi in tetrahydrofuran. After 1 h 1.90 g **6** in 5 ml abs. tetrahydrofuran were dropped to the mixture which was then stirred for 10 days at 0°. Addition of $H_2O$, followed by the usual workup and chromatography with benzene/ethyl acetate 25:1 gave 2.84 g (75%) **11**; m.p. 162–163° (crystallization from hexane). – IR.: 700 m, 800 m, 1020 m, 1048 m, 1278 m, 1440 m, 1500 m, 1590 w, 1606 w, 2865 m, 2945 m, 3050 m, 3585 m. – NMR.: 0.8–2.6/*m*, five $H_2$—C and H—C(3); 3.04 + 3.23/2 *m*, H—C(1 and 4); 4.45/*m*, H—C(2); 7.25–8.18/*m*, eleven aromatic H. – MS.: 418 ($C_{26}H_{26}OS_2^{+}$, 48%), 196 (20%), *195*, 179 (18%), 121 (12%).

exo-*2-Acetoxy*-endo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**12**). Acetylation of 2.83 g **11** in 50 ml $Ac_2O$/pyridine 1:1 overnight at room temp. gave 3.08 g (100%) **12**; m.p. 239–240° (crystallization from $CH_3CN$). – IR.: 699 m, 904 s, 1018 m, 1204 m, 1230 s, 1438 m, 1480 m, 1605 w, 1740 s, 2940 m, 3050 m. – NMR.: 1.2–2.55/*m*, five $H_2$—C and H—C(3); 1.93/*s*, $H_3$—CCO; 3.28/*m*, H—C(4); 3.38/*m*, H—C(1); 5.31/*m*, double resonance with 3.38 → *d*, $J_{2,3} \approx 4.5$, H—C(2); 7.2–8.1/*m*, eleven aromatic H. – UV. (isooctane): 230 (84800), 262 (5150), 270 (6000), 280 (5800), 291 (3670), 307 (520), 321 (300). – MS.: 460 ($C_{28}H_{28}O_2S_2^{+}$, 27%), 400 (3%), 386 (2%), 356 (3%), 343 (6%), 326 (4%), 311 (3%), 293 (4%), 197 (10%), 196 (12%), *195*, 179 (18%).

exo-*2-Acetoxy*-endo-*3-benzoyl-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**13**) (for method, see [6]). An almost boiling solution of 3.08 g **12** in 100 ml $CH_3CN$ and 50 ml acetone was added portionwise to an ice-cooled mixture of 3.62 g N-chlorosuccinimide and 5.15 g $AgNO_3$ in 5 ml $H_2O$ and 25 ml $CH_3CN$ in such a way that the temperature did not rise above 10°. After stirring for 15 min at room temp. the reaction was stopped by the addition of 10 ml conc. aqueous $NaHSO_3$ solution. Dilution with much ether and repeated washing of the organic suspension with aqueous 15% $Na_2S_2O_3$ solution, followed by the usual work-up and chromatography with benzene/ethyl acetate 25:1 gave 1.15 g (46.5%) **13**; m.p. 140.5–142° (crystallization from hexane). – IR.: 693 s, 873 m, 888 m, 947 m, 1020 s, 1045 m, 1230 s, 1362 m, 1444 m, 1500 m, 1595 w, 1685 s, 1737 s, 2865 m, 2945 m, 3050 m. – NMR.: 1.36–1.86 + 2.1–2.4/*AA'BB'*, two $H_2$—C; 2.08/*s*, $H_3$—CCO; 3.38/*d*, $J_{3,4} = 2.5$, H—C(4); 3.52/*d*, $J_{1,2} = 3$, H—C(1); 3.75/*d* × *d*, $J_{2,3} \approx 3.5$, $J_{3,4} = 2.5$, H—C(3); 5.30/*d* × *d*, $J_{1,2} \approx 3$, $J_{2,3} = 3.5$, H—C(2); 7.2–8.0/*m*, eleven aromatic H. – UV. (isooctane): 225 (79600), 265 (7400), 275 (7200), 286 (4400), 304 (550), 314 (350), 318 (410), 330 (125), 360 (40). – MS.: *370* ($C_{25}H_{22}O_3^{+}$), 326 (16%), 282 (18%), 205 (12%), 180 (31%), 179 (57%), 178 (44%) 149 (13%), 105 (29%).

endo-*2-Hydroxy*-exo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**8**). 3.20 g **7** in 35 ml abs. tetrahydrofuran gave with 4.9 g 2-phenyl-1,3-dithiane and 10.2 ml 2.5 M BuLi solution (for procedure, see **6** → **11**; reaction time 2.5 days at 0°) product **8** in 95% yield; m.p. 168–169° (crystallized from hexane). – IR.: 698 m, 878 m, 1030 m, 1060 m, 1275 m, 1495 m, 1588 w, 1604 w, 2900 m, 2935 m, 3050 m, 3570 m. – NMR.: 0.80–2.80/*m*, five $H_2$—C and H—C(3); 2.88 + 3.02 + 4.68/3 *m*, H—C(1, 2 and 4); 7.20–8.15/*m*, eleven aromatic H. – MS.: 418 ($C_{26}H_{26}OS_2^{+}$, 17%), 196 (14%), *195*, 180 (12%), 179 (17%), 121 (3%).

endo-*2-Acetoxy*-exo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**9**). Acetylation of **8** (for procedure, see **11** → **12**) gave **9** in quantitative yield; m.p. 105–110°

(crystallization from hexane). – IR.: 700 m, 878 m, 1024 m, 1228 s, 1238 s, 1372 m, 1440 m, 1500 w, 1605 w, 1738 s, 2950 m, 3055 m. – NMR.: 1.1–2.8/*m*, five $H_2$—C and H—C(3); 1.66/*s*, $H_3$—CCO; 3.28/*m*, H—C(1 and 4); 5.60/*d* × *d*, $J_{1,2}$ = 3, $J_{2,3}$ = 5.5, H—C(2); 7.25–8.15/*m*, eleven aromatic H. – UV. (isooctane): 228 (110000), 247 (3900), 256 (5100), 266 (6350), 275 (6100), 287 (3700), 302 (560), 312 (260), 316 (480). – MS.: 460 ($C_{28}H_{28}O_2S_2^+$, 14%), 400 (12%), 356 (2%), 326 (5%), 298 (5%), 294 (7%), 293 (7%), 205 (3%), 197 (10%), 196 (14%), *195*, 180 (11%), 179 (22%).

endo-*2-Acetoxy*-exo-*3-benzoyl-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**10**). A solution of 4.60 g **9** in 50 ml $CH_3CN$ was rapidly dropped into a mixture of 5.65 g N-chlorosuccinimide, 8.05 g $AgNO_3$, 5 ml $H_2O$ and 10 ml $CH_3CN$, which was stirred at 0°. After 30 min the work-up and chromatography as described for **12** → **13** gave 1.25 g (34%) **10**; 170–171° (crystallized from hexane). – IR.: 684 m, 700 m, 885 m, 1022 m, 1215 m, 1232 s, 1362 m, 1445 m, 1593 w, 1680 s, 1737 s, 2885 m, 2945 m, 3050 m. – NMR.: 0.9–2.8/*m*, two $H_2$—C and H—C(3); 1.66/*s*, $H_3$—CCO; 3.30/*m*, H—C(1 and 4); 5.62/*d* × *d*, $J_{1,2}$ = 2.5, $J_{2,3}$ = 4.5, H—C(2); 7.25–8.15/*m*, eleven aromatic H. – MS.: 370 ($C_{25}H_{22}O_3^+$, 61%), 327 (13%), 310 (15%), 282 (27%), 222 (21%), 201 (28%), 191 (68%), 180 (67%), 179 (93%), 178 (88%), *149*, 135 (27%), 121 (42%), 105 (61%). – UV. (isooctane): 226 (80000), 266 (7900), 276 (7100), 286 (4300), 304 (600), 314 (360), 318 (500), 332 (140), 356 (50).

endo-*2-Methylsulfonyloxy*-exo-*3-(1'-phenyl-2', 6'-dithiacyclohexyl)-1, 2, 3, 4-tetrahydro-1, 4-ethanoanthracene* (**14**). 418 mg **8** were mesylated at room temperature with 0.12 ml $CH_3SO_2Cl$ and 0.25 ml $Et_3N$ in 4 ml $CH_2Cl_2$. The usual work-up and crystallization from hexane afforded 380 mg (77%) **14**; m.p. 137–138°. – IR.: 698 m, 900 m, 910 m, 940 s, 1170 s, 1178 m, 1278 m, 1340 s, 1440 m, 1500 m, 1590 w, 1605 w, 2900 m, 2950 m, 3055 m. – NMR.: 0.9–2.8/*m*, five $H_2$—C and H—C(3); 2.86/*s*, $H_3$—CS; 2.97/*m*, H—C(4); 3.74/*m*, H—C(1); 5.73/*d* × *d*, $J_{1,2} = J_{2,3}$ = 3.5, H—C(2); 7.15–8.15/*m*, eleven aromatic H. – MS.: 424 ($C_{26}H_{28}O_3S_3^+$, 2%), 400 (34%), 327 (24%), 326 (80%), 310 (5%), 295 (13%), 180 (48%), *179*, 178 (53%), 165 (18%), 108 (10%), 106 (14%), 96 (16%).

*2-(1'-Phenyl-2', 6'-dithiacyclohexyl)-1, 4-dihydro-1, 4-ethanoanthracene* (**15**). 124 mg **14** were heated overnight to 130° in 2 ml *sym*-collidine. The mixture was then taken up in ether and worked up. Chromatography with benzene gave 75 mg (75%) **15**; m.p. 162–163° after crystallization from hexane. – IR.: 692 m, 698 m, 878 m, 945 m, 1130 m, 1274 m, 1440 m, 1605 w, 2950 m, 3050 m. – NMR.: 1.20–200 + 2.46–2.95/2 *m*, five $H_2$—C; 4.09/br. *d*, $J_{3,4}$ = 6.5, H—C(4); 4.20/*m*, H—C(1); 6.66/*d* × *d*, $J_{1,3}$ = 2.5, $J_{3,4}$ = 6.5, H—C(3); 7.22–7.86/*m*, eleven aromatic H. – UV. (isooctane): 228 (57000), 256 (7000), 265 (7700), 275 (7200), 286 (4400), 304 (700), 314 (365), 319 (460). – MS.: 401 (30%), *400* ($C_{25}H_{24}S_2^+$), 372 (4%), 326 (18%), 298 (20%), 294 (23%), 293 (29%), 265 (17%), 179 (16%), 178 (7%), 165 (2%).

*1,2,3,4-Tetrahydro-1,4-ethanoanthracen-2-one* (**16**). 1.70 g **4**, 500 mg $LiBH_4$ and 1 ml $BF_3$ etherate in 100 ml abs. ether were cooled in an ice-bath and stirred for 6 h under argon before 2 ml 30% $H_2O_2$ were slowly added. After 30 min the alcohol intermediate was oxidized directly during 1 h by addition of *Collins* reagent [19] formed from 6 g $CrO_3$ and 10 ml pyridine in 150 ml $CH_2Cl_2$. The mixture was diluted with 500 ml hexane, filtered through celite and worked up. Chromatography with benzene/ethyl acetate 15:1 yielded 880 mg (48%) **16** which upon sublimation at 110°/0.01 Torr and crystallization from hexane melted at 134–135°. – IR. ($CHCl_3$): 890 m, 1098 m, 1105 m, 1317 m, 1405 m, 1500 m, 1610 w, 1725 s, 2860 m, 2940 m, 2990 m, 3030 m. – NMR.: 1.6–2.25/*m*, two $H_2$-C; 2.26 [H—C(*syn*-3)] + 2.46 [H—C(*anti*-3)] + 3.52 [H—C(4)]/*ABX*, $J_{3,3}$ = 18, $J_{anti\text{-}3,4}$ = 2.5, $J_{syn\text{-}3,4}$ = 3.2; 3.74/*m*, H—C(1); 7.34–7.88/*AA'BB'*, H—C(5–8); 7.65/*s*, H—C(9 and 10). – UV. (pentane): 230 (75000), 249 (2700), 259 (4100), 268 (5500), 277.5 (5900), 287 (3850), 308 (1200), 315 (720), 320 (1040). – MS.: 222 (*M*+, 87%), 194 (8%), *178*, 165 (35%).

$C_{16}H_{14}O$ (222.13) Calc. C 86.45 H 6.35% Found C 86.37 H 6.31%

*2,4-Dinitrophenylhydrazone of* **16**: m.p. 236–237° (crystallized from MeOH). – MS.: *402* ($C_{22}H_{18}O_4N_4^+$).

*3-Benzylidene derivative of* **16**: m.p. 198–198.5° (crystallized from MeOH). – UV. (isooctane): 229 (63500), 289 (21400), 321 (4750), 363 (680). – MS.: 310 (*M*+, 79%), *178*.

$C_{23}H_{18}O$ (294.17) Calc. C 89.00 H 5.85% Found C 88.93 H 5.92%

*2-Cyano-1,4-dihydro-1,4-ethanoanthracene* (**19**). Molecular sieves (5 Å, 1/16″) were added up to the surface of a solution of 150 mg **16** and a catalytic amount of KCN in 6 ml freshly distilled

acetone cyanohydrin. HCN was formed instantly with slight warming of the solution, which was acidified with 20 mg *p*-toluenesulfonic acid after 12 h and decanted. The molecular sieves were washed with $CCl_4$, and the combined solutions were stripped from solvents in a molecular distillation ($<60°/10^{-5}$ Torr). The residual oily mixture of **16** and *2-cyano-2-hydroxy-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**17**) was immediately mesylated at 0° with 300 µl $CH_3SO_2Cl$ and 1 ml $Et_3N$ in 10 ml $CH_2Cl_2$. The work-up gave a mixture of **16** and *2-cyano-2-methanesulfonyloxy-1,2,3,4-tetrahydro-1,4-ethanoanthracene* (**18**), which was directly pyrolyzed for 12 h at 130° in 4 ml collidine. Work-up and chromatography with benzene/ethyl acetate 15:1 afforded 65 mg starting material (**16**) and 78 mg (50%) **19**; m.p. 145–146° (crystallized from hexane). – IR.: 671 w, 872 s, 890 s, 952 m, 1138 m, 1445 m, 1500 m, 1610 m, 2220 s, 2875 m, 2970 m, 3060 m. – NMR.: 1.66/br. *s*, two $H_2$—C; 4.14/*d*, $J_{3,4} = 6.6$, H—C(4); 4.20/br. *s*, H—C(1); 7.33/*AMX*, $J_{1,3} = 1.8$, double resonance at 4.2 → br. *s*, H—C(3); 7.4–7.9/*m*, H—C(5–10). – UV. (isooctane). 223 (73000), 257 (10200), 265 (10600), 275 (8300), 286 (4700), 308 (320), 315 (207). – MS.: 231 ($M^+$, 29%), *203*, 190 (6%), 176 (6%), 149 (9%).

$C_{17}H_{13}N$ (231.13) Calc. C 88.28 H 5.67 N 6.06% Found C 88.13 H 5.72 N 5.96%

*1,4-Dihydro-1,4-ethanoanthracene-2-carbaldehyde* (**20**). 500 mg **19** in 50 ml abs. ether were reduced with 5 ml of *ca.* 1.5 M $(i\text{-Bu})_2$AlH solution in hexane at –78° under an argon atmosphere. After 3 h the solution was brought to 0°, 50 ml 1N acetate buffer (pH 5) were slowly added, and the mixture was vigorously stirred for 1 h. The work-up gave 550 mg of oily **20** which was homogeneous according to TLC. [IR.: 1685 s, 2705 m. – NMR. ($CCl_4$): 9.25/*s*, H—CO.] In view of its instability the product was directly converted to **21** and **22**.

*2-Benzoyl-1,4-dihydro-1,4-ethanoanthracene* (**22**). – a) *Elimination of AcOH from* **10** *and* **13**. Solutions of 1.2 g acetoxy-ketone in 30 ml *t*-BuOH/benzene 2:1 (freshly dried over molecular sieves) were refluxed with added 2.0 g $K_2CO_3$ (freshly dried at 200°) for 14 h with stirring under an argon atmosphere. Filtration and work-up of the filtrate yielded, after passing of the crude product through a short column of silicagel with benzene/ethyl acetate 25:1, 1.0 g (99%) **22**; m.p. 112–113° (crystallization from hexane). – IR.: 710 s, 910 m, 1132 m, 1245 m, 1265 s, 1300 m, 1337 m, 1450 m, 1600 s, 1645 s, 2870 m, 2960 m, 3050 m. – NMR.: 1.70/br. *s*, two $H_2$—C; 4.20/*d*, $J_{3,4} = 5.9$, H—C(4); 4.86/br. *s*, H—C(1); 7.19/*d* × *d*, $J_{1,3} = 1.8$, $J_{3,4} = 5.9$, double resonance at 4.20 and 4.86 → two different *d*, H—C(3); 7.28–7.90/*m*, eleven aromat. H. – UV. (isooctane): 230 (43700), 250 (16500), 261 (14000), 305 (715), 313 (325), 317 (320), 358 (70). – MS.: 310 ($C_{23}H_{18}O^+$, 44%), *282*, 206 (21%), 178 (25%), 105 (16%), 77 (6%).

b) *Conversion of* **20** *to benzyl alcohol* **21** *and oxidation*. 550 mg **20** were dissolved in 20 ml abs. ether and 20 ml abs. benzene and treated with 1.8 ml of a *ca.* 1.5 M $C_6H_5Li$ solution at 0° under an argon atmosphere. Addition of acetate buffer (pH 5) and work-up gave oily *2-(α-hydroxybenzyl)-1,4-dihydro-1,4-ethanoanthracene* (**21**), which was directly oxidized with 1.2 g $CrO_3$ in 2 ml pyridine and 30 ml $CH_2Cl_2$. The work-up and chromatography with benzene/ethyl acetate 15:1 afforded 274 mg **22**; m.p. 111–113°. The yield **20** → **22** was 41%. The two samples (a and b) proved identical on TLC., by mixed m.p., IR., NMR., and MS.

c) *From* **15**. Upon addition of 30 mg $HgCl_2$, 25 mg HgO and 0.1 ml $H_2O$ to a solution of 20 mg **15** in 2 ml MeOH and 2 ml acetone, the mixture was refluxed for 36 h, then taken up in ether and filtered through celite. The filtrate was washed with several portions of satd. aqueous $NH_4Cl$ solution. Chromatography with benzene/ethyl acetate 25:1 gave 3.1 mg (20%) **22** (identified by comparison of TLC. and IR. spectrum).

endo- *and* exo *13-Oxo-4b,5,12,12a-tetrahydro-5,12-ethano-indeno*[2,3-b]*anthracenes* (**23**). A solution of 500 mg **22** in 25 ml $CS_2$ was treated with 2 ml $BF_3$ etherate, refluxed for 1 h and, after addition of 4 ml $SnCl_4$ at room temp., refluxed again for 10 days with stirring under an argon atmosphere in the dark (TLC. control). The cooled reaction mixture was poured onto ice and 500 ml benzene/ether 1:1 were added. The work-up afforded 510 mg of a crude mixture which upon chromatography on 50 g silicagel with benzene separated into 40 mg **22**, 50 mg *exo*-**23**, and 384 mg *endo*-**23** (total yield of cyclized ketones 86.5%).

*endo*-**23**. – m.p. 241–243° (cryst. from $CH_2Cl_2$/hexane). – IR.: 700 m, 880 m, 888 m, 1122 m, 1282 m, 1470 m, 1500 m, 1605 m, 1710 s, 2860 m, 2940 m, 3050 m. – NMR.: 1.45–2.25/*AA'BB'XY*, two $H_2$—C; 3.02/*d* × *d*, $J_{5a,13a} = 7.8$, $J_{5a,6a} = 3.5$, H—C(5a); 3.56/*m*, $J_{13,13a} = 3$, H—C(13); 3.72/*m*, H—C(6 and 13a); 6.90–7.88/*m*, ten aromatic H. – UV. (isooctane): 206 (48400), 227 (90400),

239 (14400), 247 (12000), 269 (5200), 277 (5900), 293 (3900), 313 (223), 317 (309), 333 (26), 349 (27), 365 (19); (EtOH): 317 (500), 348 (7). – MS.: 310 ($C_{23}H_{18}O^+$, 73%), 252 (5%), 180 (26%), *179*, 178 (83%), 165 (16%), 155 (3%), 132 (4%).

*exo*-**23**. – m.p. 201.5–203° (cryst. from $CH_2Cl_2$/hexane). – IR.: 714 w, 866 w, 888 m, 950 w, 1040 w, 1284 m, 1461 m, 1500 m, 1603 m, 1710 s, 2875 m, 2945 m, 3055 m. – NMR.: 1.28/*m*, H–C(*syn*-15) and $H_2$–C(14); 1.66/*m*, H–C(*anti*-15); 2.78/*d* × *d*, $J_{5a,6}$ = 3.5, $J_{5a,13a}$ = 8, H–C(5a); 3.50/*m*, H–C(13a); 3.52/br. *s*, H–C(13); 3.72/*m*, H–C(6); 7.24–7.96/*m*, ten aromatic H. – UV (isooctane): 229 (110000), 238 (20000), 246 (15000), 257 (6900), 267 (8350), 276 (8850), 285 (6300), 295 (2900), 314 (250), 317 (400), 336 (86), 351 (80), 369 (30); (EtOH): 371 (500), 330 (125), 349 (55). – MS.: 310 ($C_{23}H_{18}O^+$, 44%), 252 (3%), 180 (14%), 179 (71%), *178*, 165 (8%), 155 (2%), 132 (3%).

endo- *and* exo-*13-Oxo-13a-deuterio-4b,5,12,12a-tetrahydro-5,12-ethano-indeno[2,3-b]anthracenes* (**23 d**). Solutions of *endo*- and *exo*-**23** in abs. dioxane (30 mg/5 ml) were each refluxed for 24 h under an argon atmosphere together with 2 ml $D_2O$ and 50 µl conc. NaOD in $D_2O$. The work-up of each solution with 20 ml benzene and 3 × 1.5 ml of $D_2O$ gave 25–28 mg ketone which were filtered in $CH_2Cl_2$ through neutral $Al_2O_3$ (act. IV, prepared with 10% $D_2O$) and recrystallized from hexane.

*endo*-**23-d**. – m.p. 240–241°. – NMR.: signal for H–C(5a) missing; bandwidths of *m* at 3.56 and 3.72 smaller than in *endo*-**23**. – MS.: *311* ($C_{23}H_{17}DO^+$), 310 (1.5%), 253 (5%), 179 (2%); $d_1 \geqslant 98\%$.

*exo*-**23-d**. – m.p. *202–203°*. – NMR.: signal for H–C(5a) missing; 3.50/br. *s*, H–C(13 and 13a); 3.70/*br. s*, H–C(6); other signals identical with *exo*-**23**. – MS.: 312 (14%), 311 ($C_{23}H_{17}DO^+$, 59%), 310 (2%), 253 (3%), 180 (18%), 179 (81%), *178*, 165 (9%), 133 (3%).

endo-*4b,5,12,12a-Tetrahydro-5,12-ethano-5*H*-indeno[2,3-b]anthracene* (**24**). A solution of 50 mg *endo*-**23**, 0.5 ml $(NH_2)_2$ hydrate, and 2 ml $(CH_2OH)_2$ in 3 ml abs. EtOH was refluxed for 14 h under an argon atmosphere. After cooling, 250 mg pulverized KOH were added and the volatile components removed while heating up to 190°. After 3 h under reflux conditions at *ca.* 200° the mixture was again cooled, diluted with $H_2O$ and worked up. Filtration through neutral $Al_2O_3$ (act. I) in $CH_2Cl_2$ and chromatography on a *Merck* silicagel column, size A, with benzene afforded 42 mg (88%) *endo*-**24**, m.p. 158–160° (cryst. from hexane). – IR.: 713 w, 875 m, 885 m, 950 m, *1262* m, 1440 m, 1488 m, 1610 w, *2880* m, *2920* m, *3020* m, *3050* m. – NMR.: *1.25–2.64/m*, H–C(5a) and $H_2$–C(14 and 15); 2.84–3.35 + 3.38/2 *m*, $H_2$–C(5) and H–C(6 and 13); 3.60–3.80/*m*, $J_{5a,13a}$ = 8, H–C(13a); 6.65–7.80/*m*, ten aromatic H. – UV. (isooctane): 228 (91000), 259 (4500), 268 (6500), 275 (6700), 288 (3600), 303 (560), 313 (280), 316.5 (470). – MS.: 296 ($C_{23}H_{20}^+$, 45%), 265 (3%), 181 (22%), *180*, 179 (40%), 178 (22%), 165 (22%), 115 (3%).

exo-*4b,5,12,12a-Tetrahydro-5,12-ethanol-5*H*-indeno[2,3-b]anthracene* (**24**). 35 mg *exo*-**23** were reduced, using the procedure described for the *endo*-isomer, to 27 mg (81%) *exo*-**24**, m.p. 177–180° (cryst. from hexane). – IR.: 680 m, 890 m, 950 m, 1485 m, 1504 w, 2880 m, 2940 m, 3040 m, 3080 m. – NMR.: 0.75–2.05/*m*, H–C(5a) and $H_2$–C(14 and 15); 2.52–3.60/*m*, $H_2$–C(5) and H–C(6, 13, and 13a); 7.15–7.98/*m*, ten aromatic H. – UV. (isooctane): 229 (108000), 249 (5800), 259 (7700), 267 (9950), 275 (9900), 287 (5100), 298 (2250), 303 (2000), 309 (1700), 317 (750). – MS.: 296 ($C_{23}H_{20}^+$, 36%), 265 (2.5%), 181 (17%), *180*, 179 (50%), 178 (23%), 165 (17%), 115 (2%).

**Synthesis of the 11-Oxo-4b,5,10,10a-tetrahydro-5,10-ethano-indeno[2,3-*b*]-naphthalenes (31)** (*Scheme 3*). – endo- *and* exo-*2,3-Epoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes* (**26**). A solution of 8 g of a 2:1 mixture of 1,4-dihydro-1,4-ethanonaphthalene (**25**) and 1,2,4a,8b-tetrahydrobiphenylene (prepared according to [12]; the mixture is difficult to separate preparatively) and 13 g 85% *m*-chloroperbenzoic acid in 250 ml $CH_2Cl_2$ was stirred at + 3° for 24 h (TLC. control). After filtration and work-up (see **4** → **6** + **7**) the crude material was chromatographed on 450 g silicagel with benzene/ethyl acetate 50:1, affording 1.40 g *exo*-**26**, 2.50 g 1,2,3,4,-4a,8b-hexahydro-1,2-epoxybiphenylene, and 3.90 g *endo*-**26**. Recrystallization of the two desired epoxides from pentane gave 1.10 g *exo*-**26** (m.p. 60–65°) and 2.95 g *endo*-**26**, (m.p. 44–50°). Estimated total yield based on **25**: 70%.

*exo*-**26**. – IR.: 650 m, 850 s, 930 m, 942 m, 1140 m, 1165 m, 1400 m, 1455 m, 1610 w, 2940 m, 3015 m, 3060 m. – NMR.: 1.05 + 2.04/2 *AA'BB'*-like *m*, two $H_2$–C; 3.32/br. *s*, H–C(1,4); 7.22/br. *s*, four aromatic H. – UV.: 213 (3750), 248 (210), 256 (330), 261 (480), 268 (520). – MS.: 172 ($C_{12}H_{12}O^+$, 77%), 144 (12%), 143 (46%), 142 (15%), 141 (33%), 129 (37%), *128*, 127 (14%), 116 (22%), 115 (30%), 91 (5%).

*endo*-**26**. – IR.: 650 m, 850 m, 950 m, 1030 m, 1140 m, 1234 m, 1312 m, 1405 m, 1460 m, 1620 w, 2860 m, 2940 m, 3010 m, 3065 m. – NMR.: 1.44 + 1.76/2 *AA'BB'*-like *m*, two $H_2$—C; 3.44/br. *s*, H—C(1–4); 7.04–7.36/*m*, four aromatic H. – UV.: 209 (2400), 254 (260), 261 (400), 268 (420). – MS.: *172* ($C_{12}H_{12}^+$), 144 (12%), 143 (90%), 142 (13%), 141 (39%), 129 (20%), 128 (95%), 127 (12%), 116 (27%), 115 (36%), 91 (5%).

endo-*2-Hydroxy*-exo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanonaphtha*lene (**27**). 7.8 g 2-Phenyl-1,3-dithiane [5] in 20 ml abs. tetrahydrofuran were treated at –40° under an argon atmosphere with 7.2 ml 2.5M BuLi solution. After 1 h a solution of 1.27 g *endo*-**26** in 5 ml abs. tetrahydrofuran was added. The mixture was stirred for 24 h at 0°, then hydrolyzed by consecutive addition of MeOH and ice. The usual work-up and crystallization from benzene gave 3.80 g **27**. Chromatography of the residue from the mother liquor with benzene/ethyl acetate 50:1 afforded another 1.80 g **27** (total yield 75%). Crystallization of the combined portions from hexane gave crystals of m.p. 175–177°. – IR.: 699 m, 892 m, 1030 m, 1260 s, 1440 m, 1460 m, 1480 m, 1590 w, 2900 m, 2960 m, 3040 m, 3570 m. – NMR.: 0.80–2.86/*m*, five $H_2$—C and H—C(3 and 4); 3.10/*m*, H—C(1); 4.63/*m*, H—C(2); 6.80–7.60 and 8.00–8.18/2 *m*, nine aromatic H. – UV. (isooctane): 215 (11000), 230 (3200), 255 (1150), 261 (1400), 268 (1300). – MS.: 368 ($C_{22}H_{24}OS_2^+$, 16%), 196 (15%), *195*, 163 (6%), 130 (16%), 129 (15%).

endo-*2-Acetoxy*-exo-*3-(1'-phenyl-2',6'-dithiacyclohexyl)-1,2,3,4-tetrahydro-1,4-ethanonaphthalene* (**28**). Acetylation of 5.50 g **27** in 100 ml $Ac_2O$/pyridine 1:1 at room temp. overnight yielded quantitatively **28** (6.1 g), m.p. 149.5–150° (cryst. from $CH_3CN$). – IR.: 700 m, 1023 m, 1225 m, 1240 s, 1373 m, 1440 m, 1481 m, 1590 w, 1733 s, 2900 m, 2940 m, 3040 m. – NMR.: 0.90–2.80/*m*, five $H_2$—C and H—C (3); 1.66/*s*, $H_3$—CCO; 3.05 3.24/*m*, H—C (1 and 4); 5.50/*d* × *d*, $J_{1,2} = 2.9$, $J_{2,3} = 5.1$, H—C(2); 6.88–7.49 and 7.95–8.09/*m*, nine aromatic H. – UV. (isooctane): 215 (11000), 230 (3700), 255 (1200), 261 (1500), 269 (1400). – MS.: 410 ($C_{24}H_{26}S_2O_2^+$, 24%), 350 (18%), 276 (10%), 198 (82%), 197 (20%), 196 (20%), *195*, 129 (9%).

endo-*2-Acetoxy*-exo-*3-benzoyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene* (**29**). A solution of 5.60 g **28** in 70 ml $CH_3CN$ was rapidly added at 0° to a mixture of 7.35 g N-chlorosuccinimide, 10.5 g $AgNO_3$, 10 ml $H_2O$, and 50 ml $CH_3CN$, which was stirred for 30 min and then worked up as described for **10**. Chromatography with benzene/ethyl acetate 25:1 afforded 2.30 g (53%) **29**. On standing in hexane the product formed crystals which melted at 55–60°. – IR.: 693 m, 900 m, 1024 m, 1235 s, 1445 m, 1460 m, 1480 m, 1595 m, 1682 s, 1734 s, 2945 m, 3020 m, 3060 w. – NMR.: 0.76–2.14/*m*, two $H_2$—C; 1.85/*s*, $H_3$—CCO; 3.20–3.43/*m*, H—C(1, 3 and 4); 5.56/*d* × *d*, $J_{1,2} - J_{2,3} = 3.0$, H—C(2); 7.18–7.56 and 7.91–8.06/2 *m*, nine aromatic H. – UV. (isooctane): 214 (8100), 240 (10100), 264 (1400), 268 (1550), 272 (1300), 278 (1100), 288 (700), 322 (125), 331 (110). – MS.: 320 ($C_{21}H_{20}O_3^+$, 29%), 277 (26%), 260 (35%), 192 (21%), *191*, 155 (83%), 149 (89%), 130 (58%), 105 (80%).

*2-Benzoyl-1,4-dihydro-1,4-ethanonaphthalene* (**30**). A solution of 1.7 g **29** in 50 ml abs. *t*-butyl alcohol/benzene 1:1 was stirred at reflux for 12 h together with 4.0 g $K_2CO_3$ (freshly dried at 200°) under an argon atmosphere. The mixture was then filtered and worked up. Chromatography with benzene/ethyl acetate 25:1 gave 1.02 g (74%) **30**, m.p. 89–90° after crystallization from hexane (780 mg). – IR.: 704 m, 912 m, 1138 m, 1258 m, 1290 m, 1456 m, 1473 m, 1598 m, 1607 m, 1646 s, 2870 m, 2955 m, 3020 m, 3060 m. – NMR.: 1.60/br. *s*, two $H_2$—C; 4.13/*d*, $J_{3,4} = 6.5$, H—C(4); 4.78/br. *s*, H—C(1); 7.16/*d*, $J_{3,4} = 6.5$, H—C(3); 7.06–7.70/*m*, nine aromatic H. – UV. (isooctane): 206 (18500), 243 (12500), 272 (5200), 348 (95). – MS.: 260 ($C_{19}H_{16}O^+$, 55%), *232*, 155 (68%), 127 (35%), 105 (59%), 77 (26%).

endo- *and* exo-*11-Oxo-4b,5,10,10a-tetrahydro-5,10-ethano-indeno*[*2,3*-b]*naphthalenes* (**31**). 1.0 g **30** in 15 ml $CS_2$ was treated with 2 ml $BF_3$ etherate and 4 ml $SnCl_4$ for 5 days as described for **22** → **23**. The reaction was monitored by TLC. (product *exo*-**31** is destroyed again when exposed too long to the conditions of formation). The work-up and chromatography with benzene/ethyl acetate 50:1 afforded 140 mg **30**, 72 mg *exo*-**31** and 504 mg *endo*-**31** (total yield of cyclized ketones 73%). Crystallization from hexane gave 54 mg *exo*-**31**, m.p. 132–133°, and 430 mg *endo*-**31**, m.p. 164–165°.

*endo*-**31**. – IR.: 712 m, 1057 m, 1155 m, 1288 m, 1464 m, 1484 m, 1608 m, 1714 s, 2875 m, 2945 m, 3030 m, 3080 m. – NMR.: 1.45–2.15/*m*, two $H_2$—C; 2.97/*d* × *d*, $J_{5a,6} = 3.2$, $J_{5a,11a} = 7.6$, H—C(5a); 3.46/*m*, decoupling by irradiation at 1.80 → *d*, $J_{11,11a} = 2.9$, H—C(11); 3.54–3.76/*m*,

H–C(5b and 11a); 6.63–7.58/*m*, eight aromatic H. – UV. (isooctane): 216 (8200), 239 (9800), 263 (970), 270 (1200), 284 (2160), 294 (2740), 320 (35), 332 (45), 346 (46), 365 (30), 382 (15). – MS.: 260 ($C_{19}H_{16}O^+$, 44%), 231 (3%), 215 (4%), 202 (6%), 133 (10%), *132*, 130 (68%), 129 (67%), 128 (17%), 115 (13%).

*exo*-**31**. – IR.: 703 m, 1047 m, 1288 m, 1467 m, 1485 m, 1608 m, 1716 s, 2280 m, 2955 m, 3030 m, 3080 m. – NMR.: 1.10–1.43/*m*, H–C (*syn*-13) and $H_2$–C(13); 1.48–1.75/*m*, H–C(*anti*-13); 2.74/*d* × *d*, $J_{5a,6} \approx 3.0$, $J_{5a,11a} = 7.5$, H–C(5a); 3.36–3.65/*m*, H–C(6, 11 and 11a); 7.22–7.91/*m*, eight aromatic H. – UV. (isooctane): 221 (9200), 238 (10200), 262 (1100), 269 (1300), 285 (2220), 295 (2640), 323 (55), 336 (65), 351 (50), 370 (25), 382 (15). – MS.: 260 ($C_{19}H_{16}O^+$, 20%), 231 (2%), 215 (2%), 202 (4%), 133 (10%), *132*, 130 (28%), 129 (43%), 128 (15%), 115 (8%).

**Synthesis of the 1,2,3,4,4a,9a-Hexahydro-1,4(*peri*-naphthaleno)-fluoren-9-ones 36** (*Scheme 4*). – *8-Benzoylbicyclo[3.2.2]nona*[de]*naphthalene* (**33**). A melt of 890 mg cyclohepta[*de*]-naphthalene (**32**) [13] [14] and 700 mg 1-phenylpropinone [17] was heated to 120° for 15 h and then chromatographed in benzene on 100 g silicagel. The eluted product gave on two crystallizations from hexane 1.05 g (68%) **33**; m.p. 125–127°. – IR.: 693 m, 890 m, 1000 m, 1240 m, 1264 s, 1333 m, 1346 m, 1442 m, 1593 m, 1605 m, 1640 s, 2940 m, 3050 m. – NMR.: 4.26/*d* × *d* × *d*, $J_{9,10} \approx 6.8$, $J_{10,11} = 6$, $J_{10,12} = 1.6$, H–C(10); 5.06/*d* × *d*, $J_{7,11} \approx 1.6$, $J_{7,12} \approx 6$, H–C(7); 6.52 + 6.66/*ABXY*, $J_{7,11} = 1.6$, $J_{7,12} \approx 6$, $J_{10,11} = 6$, $J_{10,12} = 1.6$, $J_{11,12} \approx 7.9$, H–C(11 and 12); 7.29/*m* (located by INDOR), H–C(9); 7.10–7.72/*m*, eleven aromatic H. – UV.: 222 (51700), 282 (6700), 302 (6000), 350 (350), *375* (110), 385 (onset of a non-structured band). – MS.: 308 ($C_{23}H_{16}O^+$, 28%), 204 (17%), *203*, 202 (33%), 105 (33%), 77 (12%).

*8-Benzoyl-11,12-dihydro[3.2.2]nona*[de]*naphthalene* (**34**). A solution of 800 mg **33** and 800 mg $[(C_6H_5)_3P]_3RhCl$ [20] in 80 ml abs. benzene was stirred vigorously for 24 h under a $H_2$ atmosphere in the dark and subsequently chromatographed on 100 g silicagel. Crystallization of the eluted product from hexane gave 685 mg (85%) **34**; m.p. 148–149°. – IR.: 709 m, 1120 m, 1178 m, 1240 m, 1263 m, 1444 m, 1595 m, 1646 s, 2860 m, 2940 m, 3055 m. – NMR.: 2.08–2.40/*m* (sym.), $H_2$–C(11 and 12); 3.87/*d* with additional fine coupling, $J_{9,10} = 7.5$, H–C(10); 4.62/*s* with additional fine coupling, H–C(7); 7.11/*d* × *d*, $J_{7,9} = 1.5$, $J_{9,10} = 7.5$, H–C(9); 7.20–7.74/*m*, eleven aromatic H. – UV.: 223 (48500), 273 (9250), 282 (8500), 303 (7200), 307 (7100), 319 (6000), 375 (165), 385 (onset of a non-structured band). – MS.: 311 (22%), *310* ($C_{23}H_{18}O^+$), 282 (62%), 254 (6%), 205 (71%), 178 (11%), 105 (26%), 77 (10%).

exo-*1,4,4a,9a-Tetrahydro-1,4*-(peri-*naphthaleno*)-*fluoren-9-one* (**35**). A solution of 600 mg **32** and 1 ml freshly prepared indenone [16] [b.p. 65–68°/0.02 Torr. IR.: 710 m, 1037 m, 1181 m, 1458 m, 1608 s, 1710 s, 3070 m. NMR. ($CCl_4$): 5.90 + 7.60/*AX*, $J = 6.5$, H–C(2 and 3, resp.); 6.96–7.54/*m*, four aromatic H] was treated with 0.5 ml $BF_3$ etherate and refluxed for 30 min. After cooling ice was added, the mixture worked up and the crude product freed from volatile components at 70–80°/0.05 Torr. Chromatography with benzene/ethyl acetate 25:1 gave 605 mg (58%) **35**. After treatment with charcoal and crystallization from MeOH the compound melted at 217–219°. – IR.: 718 m, 843 w, 1220 m, 1290 m, 1466 m, 1605 m, 1719 s, 2930 m, 3060 m. – NMR.: 3.30/*d* × *d*, $J_{1,9a} \approx 2$, $J_{4a,9a} = 7$, H–C(9a); 3.92–4.12/*ABXY*, $J_{3,4} = 5$, $J_{4a,9a} \approx 7$, H–C(4 and 4a); 4.24/*d* × *d* with additional fine coupling, $J_{1,2} = 6$, $J_{1,9a} = 2$, H–C(1); 5.94 + 6.15/*ABXY* $J_{1,2} \approx 6$, $J_{2,3} \approx 8.7$, $J_{3,4} \approx 5$, H–C(2 and 3); 7.16–7.82/*m*, ten aromatic H. – UV. (isooctane): 210 (39000), 227 (47000), 241 (11800), 284 (10500), 289 (12000), 302 (8000), 307 (6200), 318 (2000), 322 (1300), 332 (290), 364 (100), 383 (15). – MS.: 308 ($C_{23}H_{16}O^+$, 30%), 276 (2%), 230 (5%), 179 (15%), *178*, 165 (4%), 152 (16%).

endo- *and* exo-*1,2,3,4,4a,9a-Hexahydro-1,4*-(peri-*naphthaleno*)-*fluoren-9-ones* (**36**). – a) *Cyclization of* **34**. 500 mg **34** were cyclized as described for **22** → **23**. Chromatography with benzene gave 40 mg **34**, 97 mg *exo*-**36** and 161 mg *endo*-**36** (total yield of cyclized ketones 56%). Crystallization from hexane afforded 140 mg *endo*-**36**, m.p. 253–254°, and 70 mg *exo*-**36**, m.p. 172–173°.

*endo*-**36**. – IR.: 828 m, 1108 m, 1270 m, 1290 m, 1462 m, 1607 m, 1712 s, 2930 m, 3040 m, 3060 m. – NMR.: 2.20–2.45/*m*, $H_2$–C(2 and 3); 3.22/*d* × *d*, $J_{1,9a} = 5.9$, $J_{4a,9a} = 7.8$, H–C(9a); 3.64–4.06/*m*, decoupling by irradiation at 2.30 → *ABX*, $J_{4,4a} \approx 5.5$, $J_{4a,9a} = 7.8$, H–C(4 and 4a) + 3.85/*d*, $J_{1,9a} \approx 5.9$, H–C(1); 6.85–7.52/*m*, ten aromatic H. – UV. (isooctane): 210 (55000), 225 (62700), 247 (7770), 286 (8500), 301 (7900), 318 (910), 323 (720), 333 (115), 350 (59), 366

(30), 382 (10); (EtOH): 350 (85), 365 (onset of a non-structured band). – MS.: 311 (23%), *310* ($C_{23}H_{15}O^+$), 252 (5%), 179 (43%), 178 (33%), 165 (14%), 155 (5%), 152 (6%)[9].

*exo*-**36**. – IR.: 708 m, 828 w, 910 w, 1040 w, 1152 w, 1215 w, 1287 m, 1462 m, 1603 m, 1712 s, 2865 m, 2900 m, 2940 m, 3040 m, 3060 m. – NMR.: 1.45–1.95/*m*, $H_2$—C(2 and 3); 3.18/*d* × *d*, $J_{1,9a}$ = 2.5, $J_{4a,9a}$ = 8.2, H—C(9a); 3.54/*m*, $J_{4,4a}$ = 2, H—C(4); 3.79/*m*, H—C(1); 3.92/*d* with additional fine coupling, $J_{4a,9a}$ = 8.2, H—C(4a); 7.30–7.95/*m*, ten aromatic H. – UV. (isooctane): 210 (49000), 229 (77100), 247 (11000), 288 (11000), 301 (7900), 317 (1000), 321 (1140), 334 (155), 350 (110), 368 (46), 384 (12); (EtOH): 334 (352), 350 (140), 362 (40). – MS.: 311 (22%), 310 ($C_{23}H_{18}O^+$, 94%), 179 (63%), *178*.

b) *Hydrogenation of* **35**. 300 mg **35** in 20 ml ethyl acetate were hydrogenated for 2 h on 150 mg 10% Pd/C. Chromatography of the resulting product with benzene and two consecutive crystallizations from hexane afforded 172 mg *exo*-**36**; m.p. 172–173°. Crystallization of the combined mother liquors gave another 65 mg (total yield 82%) *exo*-**36** of a slightly lower m.p. (identification by mixed m.p., IR., NMR., MS., and TLC.).

endo-*9a-Deuterio-1,2,3,4,4a,9a-hexahydro-1,4-*(peri-*naphthaleno*)-*fluoren-9-one* (**36-d**) was prepared from *endo*-**36** as described for **23** → **23-d**; m.p. 253–254°. – NMR.: same as *endo*-**36**, except: signal for H—C(9a) missing; 3.64–4.06/*m*, decoupling by irradiation at 2.30 → 3.87 + 4.01/*A B*, $J_{4,4a}$ = 5.5, H—C(4 and 4a), and 3.85/*s*, H—C(1). – MS.: 312 (25%), *311* ($C_{23}H_{17}OD^+$), 310 (2%), 253 (41%), 179 (49%), 178 (34%), 165 (15%), 152 (8%).

endo-*1,2,3,4,4a,9a-Hexahydro-1,4-*(peri-*naphthaleno*)-*fluorene* (**37**). *Huang-Minlon* reduction of 50 mg *endo*-**36** (see **23** → **24**; the hydrazone formation required refluxing for 2 days) yielded, after filtration in benzene through silicagel and chromatography on a *Merck* silicagel column type A with cyclohexane/benzene 1:1, 35 mg *endo*-**37** which slowly crystallized from hexane at 0° (16.5 mg; 49%); m.p. 172–173°. – IR.: 720 w, 1395 m, 1460 m, 1480 m, 1595 w, 2870 m, 2935 m, 3040 m, 3060 m. – NMR.: 1.95–2.25/*m*, two $H_2$—C; 2.40–3.95/*m*, H—C(1, 4, 4a and 9a) and $H_2$—C(9); 6.60–7.55/*m*, ten aromatic H. – UV. (isooctane): 229 (42000), 268 (6000), 277 (7200), 290 (8400), 308 (3950), 318 (1340), 323 (1130). – MS.: 297 (25%), *296* ($C_{23}H_{20}^+$), 181 (17%), 180 (22%), 179 (37%), 165 (35%), 152 (8%), 116 (3.5%)[10].

exo-*9a-Deuterio-1,2,3,4,4a,9a-hexahydro-1,4-*(peri-*naphthaleno*)-*fluoren-9-one* (**36-d**) was prepared from *exo*-**36** as described for **23** → **23-d**; m.p. 172–173°. – NMR.: same as *exo*-**36**, except: signal for H—C(9a) missing; 3.54 + 3.79/2 narrow *m*, H—C(1 and 4); 3.90/*br. s*, H—C(4a). – MS.: 312 (25%), *311* ($C_{23}H_{17}OD^+$), 310 (2%), 252 (4%), 179 (48%), 178 (60%), 165 (10%), 152 (5%).

exo-*1,2,3,4,4a,9a-Hexahydro-1,4-*(peri-*naphthaleno*)-*fluorene* (**37**). *Huang-Minlon* reduction of 50 mg *exo*-**36** (see **23** → **24**) afforded after chromatography with benzene 38 mg (80%) *exo*-**37**; m.p. 115–117° after crystallization from MeOH (30 mg). – IR.: 713 w, 830 m, 1212 m, 1458 m, 1480 m, 1585 m, 1595 m, 2860 m, 2900 m, 2925 m, 3030 m, 3050 m. – NMR.: 1.70–2.25/*m*, $H_2$—C(2 and 3); 3.00–3.88/*m*, H—C(1, 4, 4a and 9a) and $H_2$—C(9); 7.18–7.88/*m*, ten aromatic H. – UV. (isooctane): 227 (43000), 269 (6200), 276 (8400), 289 (9200), 299 (6500), 306 (3150), 317 (990), 322 (1180). – MS.: 297 (25%), *296* ($C_{23}H_{20}^+$), 181 (15%), 180 (19%), 179 (38%), 165 (30%), 152 (9%), 116 (4%).

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[10] Compound *endo*-**37** could also be obtained by reductive desulfurization (with *Raney* nickel in EtOH at 70° for 15 min) of the dithioacetal prepared from *endo*-**36** (with 1,3-propanedithiol and *p*-toluenesulfonic acid in refluxing benzene for 5 days). Overall yield 37%.

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# 48. A Study of Intramolecular Energy Transfer in Conformationally Rigid Molecules with Stereoisomerically Oriented Donor and Acceptor Groups

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(3. XII. 74)

*Summary.* The indanone naphthalene compounds **1**, **3**, **5** and **7** exhibit, on both irradiation in the $^1L_b$ band (315 nm) and the $n \rightarrow \pi^*$ transition (> 340 nm) in EPA at 77° K, neither fluorescence from naphthalene nor phosphorescence from indanone, but exclusively phosphorescence from naphthalene, and quenching in liquid solution with 1,3-pentadiene results in triplet energy transfer from the naphthalene group only. The naphthalene phosphorescence exhibited by the ketones (**1**, **3**, **5**, **7**) has an enhanced quantum efficiency with respect to that on direct excitation of the corresponding hydrocarbons (**2**, **4**, **6**, **8**), and more strongly in the *exo* than in the *endo* orientation. In order to account for the energy wasting in the intramolecular triplet energy transfer in the *endo* compounds, a transfer route *via* a weak triplet donor-acceptor exciplex, specific to through-space interaction in the *endo* configuration (providing for additional radiationless T → S energy dissipation through vibrational coupling), competing with an efficient through-σ-bond exchange transfer mechanism operative in both configurations is proposed.

During the last 13 years numerous studies of the transfer of electronic energy between non-conjugated donor and acceptor chromophores within the same molecule have been published. The interest in this field is motivated by both photophysical

[1]) Part of the doctoral thesis of *W. A.*, ETH Zürich, 1974.