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CONFORMATIONAL STUDIES ON HELICENES—V[1]

ALTERATION OF THE CONFORMATION OF HELICENES BY ANNELATION OF BENZO GROUPS

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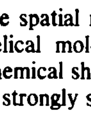
Abstract—Analysis of the NMR spectra of five heptahelicenes and some related compounds reveals that annelation of heptahelicene by one or more benzo groups results in a conformational change of the helix. The extent and direction of this change was deduced correctly from the NMR spectra by application only of the ring current theory and the influence of Van der Waals forces, as could be established from the X-ray analyses of heptahelicene and the tribenzo derivative **12**.

In a previous paper[2] we have shown that differences in the chemical shifts of corresponding protons in hexahelicene (**1**) and benzohexahelicenes may be ascribed for most protons to the shielding or deshielding effect of the additional benzo group. The argument did not serve, however, for the shift difference ($\Delta\delta$) found for the angular A protons in **1** and benzo[d]hexahelicene (**2**, phenanthro[4,3-g] chrysene). Its value ($\Delta\delta_{2,1} = 0.18$) appeared to be much larger than that for protons B-F ($\Delta\delta_{2,1} = 0.02$ to -0.01) and could not well be ascribed to a direct influence of the rather remote benzo group in **2**. Recently a similar large upfield shift was found[3] for the A proton in benzo[d]pentahelicene **3** ($\Delta\delta_{3,6} = 0.38$) relative to pentahelicene (**6**).



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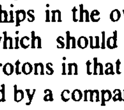

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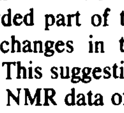
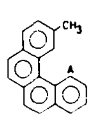


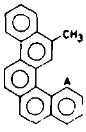
3

At the time we suggested that the shift difference for the A protons in **1** and **2** might be due to an alteration of the helix conformation as a consequence of the introduction of the benzo group. Such an alteration should change the spatial relationships in the overcrowded part of the helical molecule, which should cause changes in the chemical shifts of protons in that region. This suggestion is strongly supported by a comparison of NMR data of a series of compounds containing a [4]-, [5]-, [6]- and [7]-helicene (**4**, **6**, **1** and **8**) with those of the corresponding compounds **5**, **7**, **2** and **9**, which have only an additional benzo group in the same position relative to H_A (Table 1).



4

2-methylbenzo[c]phenanthrene



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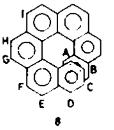
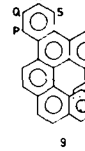
8-methylbenzo[c]chrysene



6

dibenzo[c,g]phenanthrene (pentahelicene)



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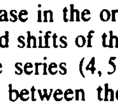
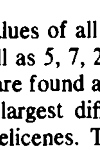
naphtho[1,2-a]triphenylene (benzo[f]pentahelicene)



8

dinaphtho[2,1-c;1',2'-g] phenanthrene (heptahelicene)



9

dinaphtho[2,1-c;1',2'-g] triphenylene '(benzo[l] heptahelicene)

It appears that, in general, the δ values of all protons decrease in the order 4, 6, 1, 8 as well as 5, 7, 2, 9. The upfield shifts of the A and B protons are found along the whole series (4, 5, 6, 7, 1, 2, 8, 9), the largest differences being between the penta- and hexahelicenes. Those of

Table 1. Chemical shifts and shift differences ($\Delta\delta$) in pairs of corresponding helicenes

compound / proton	4	5	$\Delta\delta_{5,4}$	6[b]	7	$\Delta\delta_{7,6}$	1	2	$\Delta\delta_{2,1}$	8	9	$\Delta\delta_{9,8}$
A	8.92	8.88	-0.04	8.34	8.20	-0.14	7.47	7.29	-0.18	7.01	6.69	-0.32
B	7.55[a]	7.60[a]	∼0.05	7.13	7.05	-0.08	6.53	6.54	0.01	6.27	6.26	-0.01
C	7.55[a]	7.60[a]	∼0.05	7.37	7.31	-0.06	7.08	7.06	-0.02	6.76	6.75	-0.01
D	7.87	7.88	0.01	7.78	7.73	-0.05	7.67	7.68	0.01	7.15	7.07	-0.08
E	7.70	7.74	0.04				7.77	7.80	0.03	7.35	7.23	-0.12
F	7.70	7.74	0.04				7.77	7.78	0.01	7.61	7.49	-0.12

[a] Centre of a multiplet of overlapping signals;

[b] Data from R.S. Mathews, D.W. Jones and K.D. Barthe, *Spectrochim. Acta* A27, 1185 (1971).

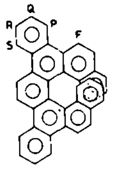
other protons (D, E and F) become only considerable at the end of the series. This general trend could be expected, as the region in which the terminal parts of the helix overlap increases. This intensifies shielding by opposite rings. Parallel with the increase of the overlapping area the $|\Delta\delta|$ value of the A protons gradually increases from 0.04 to 0.32. This effect is not observed for the other protons, with the exception of *E* anf *F* (and perhaps D) in **8** and **9** ($\Delta\delta = -0.12$, see below).

In the first paper of this series[2] we suggested that the supposed conformational change on addition of a benzo group to **1** might consist of a flattening of the triphenylenic part in **2**. According to a theory of Knauer,[4] the effect on δ_A might then be ascribed to a small reduction of the distance between C_A and $C_{A'}$ which intensifies a ring current supposed to be present in the central hole of the helix. However, in a subsequent paper[5] concerning alkyl substituted hexahelicenes, Knauer's theory did not appear tenable. A better interpretation of the NMR spectra of these compounds, and also of the remarkably large downfield shift ($\Delta\delta = +0.95$) of H_A in racemic- and the upfield shift ($\Delta\delta = -0.55$) in *meso*-diphenanthro[3,4-c;3',4'-l]chrysene[6] relative to hexahelicene appeared to be possible on the basis of Haigh's theory.[7] According to this theory the δ value of angular protons depends on two effects, which work in opposite directions on H_A of helicenes: an upfield shift as a consequence of shielding by opposite rings, and a downfield shift as a consequence of Van der Waals interactions in the overcrowded area. In a special case, the exact δ_A value will be determined by the relative importance of both effects. Lowered δ values can be caused either by increased shielding effects or by reduced Van der Waals interactions.

It seems to us that Haigh's theory is very well adapted for a consistent interpretation of the δ values given in Table 1, now that some general features of the structure of helical molecules have been established. X-ray analyses of hexahelicene[8] and some simple derivatives[9] have shown that the helical form is based on short distances of peripheral (1.28–1.36 Å) and long distances of inner bonds (1.42–1.45 Å). Another characteristic feature is the occurrence of short, non-bonding, intramolecular distances for C_A which are about equal to the Van der Waals distance (C_1–C_{16} = 3.21 Å in hexahelicene). Annelation with a benzene ring will enlarge the length of the peripheral bond involved. By this the ends of the molecule will shift slightly further over each other, but at the same time the distance between the terminals will increase slightly to relieve further crowding. Roughly speaking, the helix is slightly stretched in the direction of its axis, but the cross-section is slightly reduced. For H_A in hexahelicene, and the same is true for **6** and **8**, a further shift of the ends of the molecule over each other does not alter much of the shielding influence of opposite rings since the overlapping area is already very extensive for this proton. Stretching of the helix reduces, however, Van der Waals interactions of H_A which is situated in the most crowded area. The low δ_A value of benzohelicenes (**7**, **2**, **9**) must be due to the latter effect.

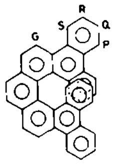
The peripherally bound protons (D, E, F) in heptahelicene do not experience steric hindrance. They move, however, into the shielding zones of opposite rings when the ends of the molecule become more overlapping. This explains the negative $\Delta\delta_{9,8}$ values found for these protons.

Using the known NMR spectrum of heptahelicene[10] and the general knowledge about the structure of hexahelicene from X-ray analysis[8,9] we tried to substantiate Haigh's theory and to give a further support to the conformational analysis of helicenes by NMR spectroscopy by analysing the NMR data of some new benzoheptahelicenes. We chose the symmetrically annelated benzo-, dibenzo-, and tribenzoheptahelicenes **9–12** because a symmetrical annelation pattern considerably simplifies the spectra, whereas annelation with more than one benzene ring should enlarge the supposed alteration of the helix conformation. The NMR data, together with those of heptahelicene (**8**), are given in Table 2. The spectra are represented in Fig. 1.



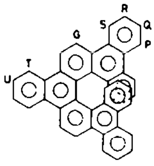
10

dinaphtho[2,1-f;1',2'-j]picene
(dibenzo[i,o]heptahelicene)



11

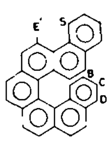
benzo[g]triphenyleno[2,1-c]chrysene
(dibenzo[f,r]heptahelicene)



12

benzo[f]triphenyleno[1,2-j]picene
(tribenzo[f,l,r]heptahelicene)

It is clear that the large upfield shift of H_A in **9**, relative to **8**, does not increase further on annelation of a second and third benzene ring. The δ_A values of **10–12** are even at a lower field than those of **9**. Comparison of **11** with **12** shows, however, that introduction of a third annelated benzo group in **11** has a similar, though somewhat smaller effect ($\Delta\delta$ −0.16), as annelation of a benzene ring with **8** ($\Delta\delta$ −0.32). This suggests that a similar conformational alteration occurs in both instances. The relatively high δ_A values in **10–12** can be ascribed to the low ring current in the central ring of the triphenylene moieties[11] (ring *c* in **10**, ring *b* in **11** and **12**). By this the shielding effect is reduced leading to higher δ_A values. The same effect is observed in the downfield shift of H_B in **10** relative to **8** and **9**. The low values of δ_B in **11** and **12** are mainly caused by the shielding effect of the benzo group annelated with ring *b*. The $\Delta\delta_B$ values relative to **8** (−0.37 and −0.35, respectively) are, however, much larger than for benzo[c]hexahelicene (**13**) relative to **1** ($\Delta\delta_B$ −0.15).[2] This might be an indication that annelation of a helicene with two or three benzene rings indeed causes larger conformational alterations than the introduction of only one benzo group.



13

benzo[c|hexahelicene

Table 2. Chemical shifts in ppm of protons in benzoheptahelicenes, measured in CS_2

compound / proton	8	9	10	11	12
A	7.01	6.69	6.75	6.94	6.78
B	6.27	6.26	6.36	5.90	5.92
C	6.76	6.75	6.79	6.73	6.72
D	7.15	7.07	7.15	7.83	7.84
E	7.35	7.23	7.39	-	-
F	7.61	7.49	8.34	-	-
G	7.83	7.89	-	8.48	8.66
H	7.85	8.60	-	7.96	8.76
I	7.90	-	8.86	7.90	-
P[a]		8.65	8.63	8.24	8.18
Q[a]		7.63	} 7.77	} 7.53	} 7.54
R[a]					
S[a]			8.74	8.47	8.53
T					8.77
U					7.74

[a] It deserves attention that P, Q, R, S in 9, 10 and 11 are not corresponding protons.

Several data concerning other protons point to the same direction: The chemical shift of the α_3 proton H_F in **10** is low (8.34) in comparison with α_3 protons in phenanthrene or triphenylene (8.50) which points to more shielding by an opposite ring in **10**; the same is valid for H_G in **11** (δ_G 8.48), and to a lesser degree in H_G of **12** (8.66) relative to the corresponding $\delta_{E'}$ in **13** (8.74). Similarly δ_S in **11** (8.47) and **12** (8.53) are lower than δ_S in **13** (8.61), and finally δ_P in **11** (8.24), already low in comparison with α_3 protons in triphenylene is further decreased in **12** (8.18). In all these cases the protons concerned, which are in the periphery of the overlapping area, are more shielded in the more annelated compound.

To check if translation of NMR data, in this way, into conformational characteristics is a reliable method,† an X-ray analysis has been made of two compounds (**8**[12] and **12**[13]) studied in this paper. Some data which seem to be important for our discussion are given in Table 3. Moreover, two projections of the compounds have been brought together in Figs. 2 and 3, in order to visualize the conformational differences.

The figures show that annelation indeed enlarges the peripheral bonds involved (C_5–C_6 and C_9–C_{10}). Apparently the other peripheral bonds (C_7–C_8) and the inner bonds, especially those opposite to the annelated ring (C_{23}–C_{25}), become also slightly longer but to a lesser degree. The resulting conformational change cannot be derived readily from distances between nonbonded carbon atoms in the overcrowded area. Shifting of C_1 parallel with as well as perpendicular to the opposite helix end occurs without significant variations of its distances to other atoms in the

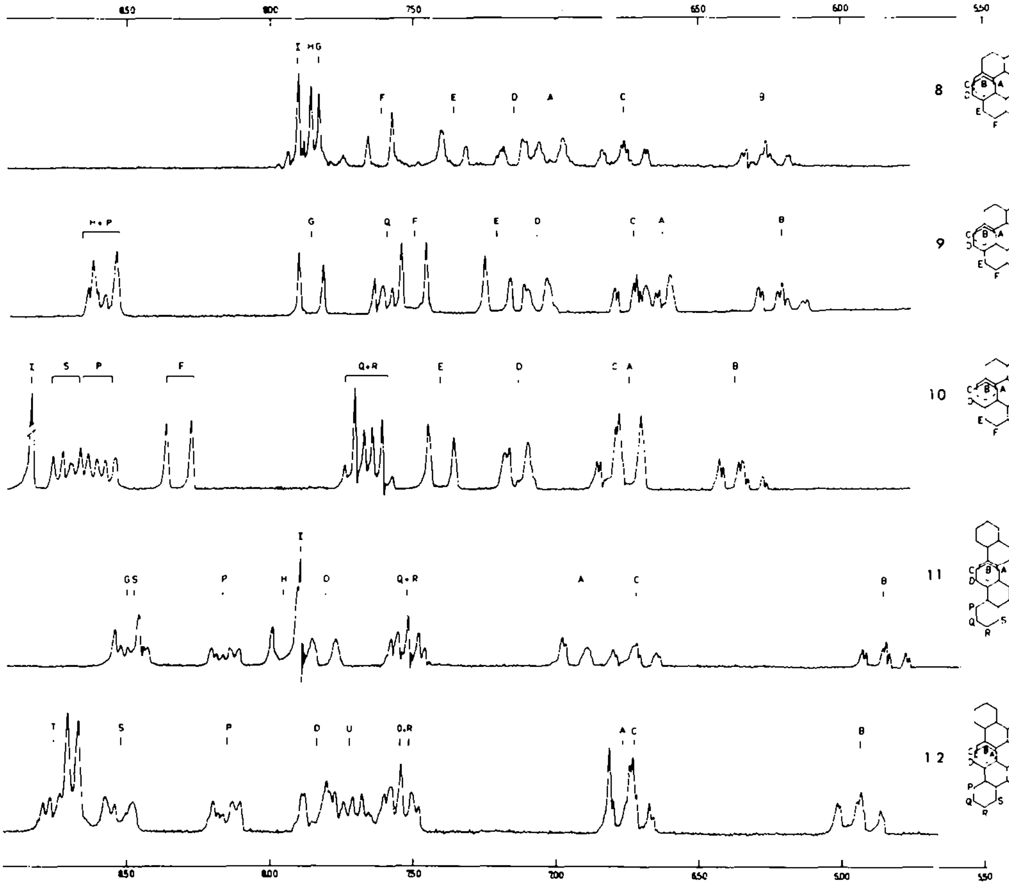


Fig. 1. NMR spectra of the heptahelicenes **8**, **10** and **11** in CS_2 solution, **9** and **12** in $AsCl_3$ solution.

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†Recently[1] from the NMR analysis of 1,16-dimethylhexahelicene we made certain conclusions about its conformation, which were also in accordance with the X-ray analysis.

Table 3. Bond distances and distances between non bonded atoms in heptahelicene (**8**) and tribenzoheptahelicene (**12**) in Å (numbering of atoms as given in Fig. 2)

Peripheral bonds	8	12
C_5-C_6	1.33	1.42
C_7-C_8	1.32	1.38
C_9-C_{10}	1.34	1.42
Inner bonds		
C_{18}-C_{19}	1.41	1.41
C_{19}-C_{21}	1.45	1.46
C_{21}-C_{23}	1.43	1.45
C_{23}-C_{25}	1.43	1.47
Non bonding distances		
C_1 -C_{21}	2.90	2.93
C_1 -C_{23}	3.05	3.02
C_1 -C_{25}	3.05	3.00
C_1 -C_{14}	4.16	4.15
C_1 -C_{18}	3.83	4.13
C_2 -C_{17}	5.25	5.87
C_3 -C_{16}	4.95	5.59
C_5 -C_{14}	6.35	5.83

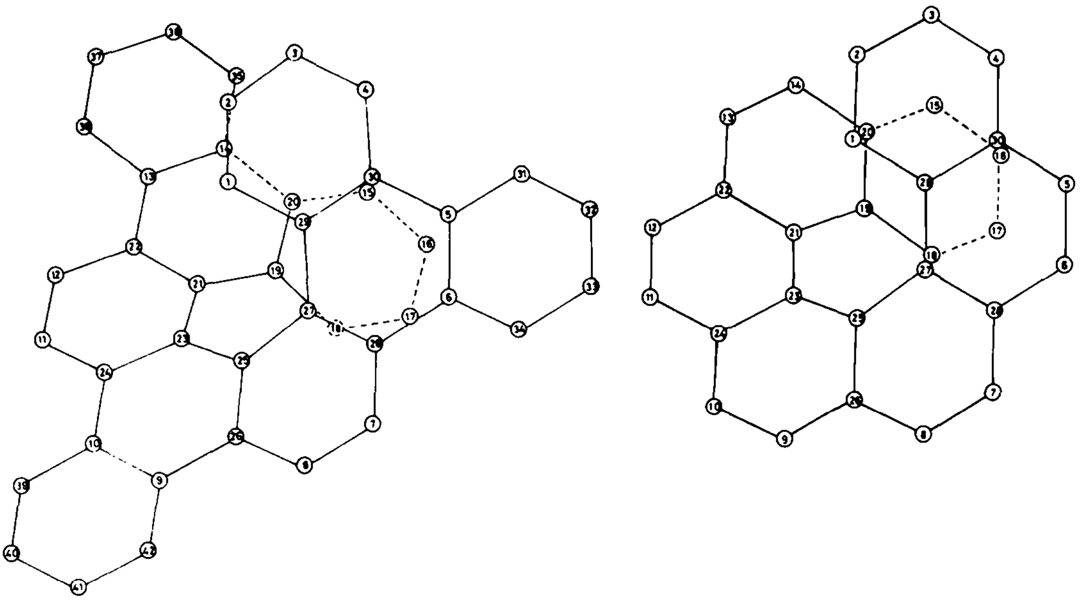


Fig. 2. Projections of heptahelicene (**8**) and tribenzoheptahelicene (**12**) on the mean square plane through a terminal ring.

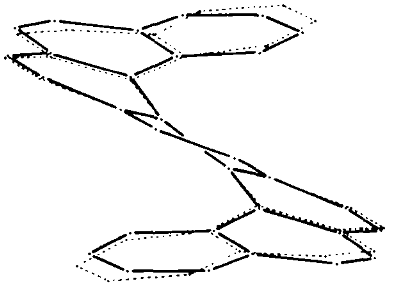


Fig. 3. Projection of heptahelicene (3) (—) and of the helical part of tribenzoheptahelicene (7) (. . .) on a plane through the axes of the helix.

overcrowded area. However, the data given for C_2–C_{17} and C_3–C_{16} clearly show that C_2 and C_3, which are already beyond C_{17} and C_{16} in **8**, are shifted farther away from these atoms in **12**, whereas the figures for C_5–C_{14} demonstrate that C_5 which is still before C_{14} in **8**, has approached this atom more in **12**. A more complete insight into the conformational change can be read off from the projections in Figs. 1 and 2.

The results entirely justify the estimation of conformational details in the structure of helicenes from NMR data when the analysis is based on ring currents and Haigh's theory.

EXPERIMENTAL

The NMR spectra were measured with a Varian HA-100 or XL-100 apparatus in CS_2 soln using 3% TMS as an internal reference. Because of the low solubility of the compounds, concentration effects could not be measured and δ values could not be extrapolated to infinite dilution. The spectra of **9** and **12** were traced by application of a time averaging computer. The frequencies were determined by the side-band technique. The accuracy is approximately 0.02 ppm for isolated absorptions and about 0.05 ppm for unresolved peaks. For the assignment of absorptions use was made of the analogy of spectra of related compounds and of decoupling experiments. For decoupling the compounds were dissolved in $AsCl_3$.

The UV spectra were recorded with a Beckman DK2A or a Cary 14 spectrophotometer, the mass spectra with a Varian MAT SM1B instrument.

Synthesis of the compounds

All new products were prepared *via* the following standard procedures. A suitable, methyl-substituted aromatic was converted into its bromomethyl derivative and then into the corresponding triphenylphosphonium salt. This was subjected to a Wittig reaction with a suitable aldehyde, and the resulting olefin was converted into a desired product by photodehydrocyclisation. Irradiations were carried out in benzene solutions. The solutions were boiled to remove air and while cooling a stream of oxygen free nitrogen was passed through the solutions for 30 minutes. An equivalent amount of iodine was added as an oxidant. As light source four Sylvania blacklite F8T5 fluorescent tubes were used. In cases where more cyclisation products arose the mixture was separated by column chromatography (Scheme 1).

1 - (2 - *Naphthyl*) - 2 - (8 - *benzo*[*c*]*chrysyl*)*ethylene* **15** was prepared starting with **5**;[14] *cis* **15** m.p. 170–171° (from MeOH); *m/e*: 430; UV λ_{max} (log ϵ) (MeOH) 357 (4.41), 320 (4.61), 298 (4.69), 287 (4.69), 2.77 (4.64). 267 (4.68), 257 (4.64), 249 (4.62), 223 (4.76). *trans* **15** m.p. 283–285° (from CCl_4); *m/e*: 430; UV (CH_2Cl_2, very slightly soluble.) λ_{max} 360, 323, 305, 294, 276, 241.

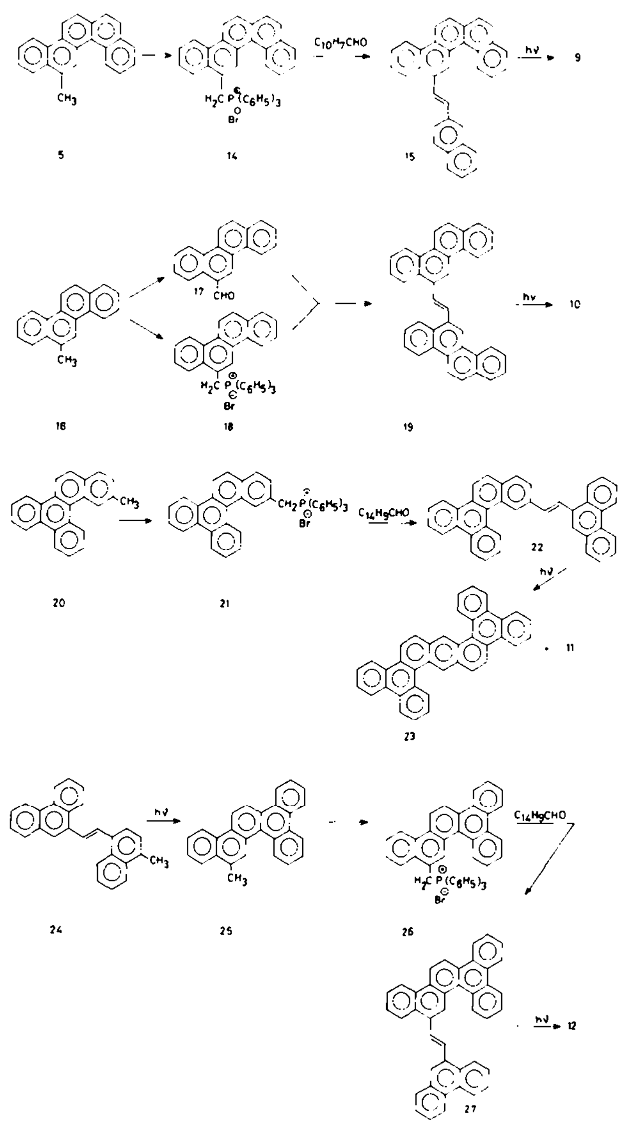
Benzo [l]*heptahelicene* **9**. Irradiation of a 3×10^{-4} molar solution of **15** gave 45% of **9**. m.p. 358–359°; *m/e*: 428; UV λ_{max} (log ϵ) (dioxane) [387 (3.80)], 340 (4.25), 312 (4.85), 277 (4.88).

Starting with **16**[14] both **17** and the salt **18** were prepared. The aldehyde was obtained by a Sommelet reaction in 40% yield. m.p. 163–164°.

1,2-*Di*(6-*chrysyl*)*ethylene* was prepared in 40% yield. *cis* **19** m.p. 260°; *m/e*: 480; UV λ_{max} (log ϵ) (CH_2Cl_2): 327 (4.30), 272 (5.04), 264 (5.00), 230 (4.73). *trans* **19** m.p. ~400°; *m/e*: 480; UV λ_{max} (log ϵ) (CH_2Cl_2) 370 (4.30), 329 (4.24), 313 (4.19), 272 (5.00), 262 (4.98), 230 (4.70).

Dibenzo[*i, o*]*heptahelicene* **10**. Irradiation of 10^{-3} molar **19** in benzene gave 50% of **10**. m.p. 338–340°; *m/e*: 478; UV λ_{max} (log ϵ) (CH_2Cl_2) [328 (4.55)], [308 (4.68)], 282 (4.93), 276 (4.91), [263 (4.81)], [250 (4.66)].

Starting with **20**[14] 1 - (9 - *phenanthryl*) - 2 - (3 - *benzo*[*c*]*triphenylenyl*)*ethylene* **22** was obtained. From the Wittig reaction only one isomer could be isolated. m.p. 255–258°; *m/e*: 480; UV λ_{max} (log ϵ) (CH_2Cl_2) 355 (4.36), 319 (4.54), 294 (4.72), 260 (4.83), 254 (4.85), 250 (4.84), [235 (4.65)]. Irradiation of this compound in benzene for 0.5 hr gave rise to about 60% of **23** and 20% of **11**. *Diphenanthro*[9,10-*a*; 9, 10-*h*]*anthracene* **23**, m.p. 332–335°; *m/e*: 478; UV λ_{max} (log ϵ) (CH_2Cl_2) 418 (3.94), 395



Scheme 1. Synthetic scheme for the preparation of benzoheptahelicenes.

(4.10), 372 (4.05), 337 (5.25), 318 (4.98), 305 (4.57), 269 (4.73), 255 (4.84).

Dibenzo[f, r]heptahelicene **11** m.p. 340–341°; *m/e*: 478; UV λ_{max} (log ϵ) (CH_2Cl_2) 358 (4.24), 345 (4.34), 333 (4.35), 282 (4.88), 274 (4.49), 241 (4.47).

1 - (9 - *Phenanthryl*) - 2 - [1 - (4 - *methylnaphthyl*)]*ethylene* **24** was prepared by a Wittig reaction from 9-phenanthraldehyde and the triphenylphosphonium salt of 1-bromomethyl-4-methylnaphthalene[15] in 50% yield. m.p. 155–156°; UV λ_{max} (log ϵ) (CH_2Cl_2) 343 (4.42), [302 (4.17)], 247 (4.80), 242 (4.80).

10-*Methylbenzo[f]picene* **25** was obtained in 80% yield by the photocyclization of **24**. m.p. 182–183°; *m/e*: 342; UV λ_{max} (log ϵ) (CH_2Cl_2) 384 (3.00), 366 (3.13), [336 (4.13)], [325 (4.47)], [316 (4.57)], 300 (4.97), 290 (4.85), [275 (4.67)].

Bromination of **25** with NBS gave in 60% yield the bromomethyl derivative (m.p. 180–186°). Treatment with triphenylphosphine gave the salt **26** in 70% (m.p. 297°). A Wittig reaction of **26** and 9-phenanthraldehyde in DMF with sidium methoxide as base gave in 80% 1 - (10 - *benzo[f]picyl*) - 2 - (9 - *phenanthryl*)*ethylene* **27**. m.p. 262, solidified at higher temperature and melted again at 272°; *m/e*: 530; UV λ_{max} (log ϵ) (CH_2Cl_2) 357 (4.43), 321 (4.75), 306 (4.79), 250 (4.94).

Tribenzo[f, l, r]heptahelicene **12** was obtained on irradiation of **28** in benzene for 1.5 hr in 90% yield. m.p. 375–380°; *m/e*: 528; UV λ_{max} (log ϵ) (CH_2Cl_2) 335 (4.61), 306 (4.91), 292 (4.98), 270 (4.84), 245 (4.73).

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