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THE STRUCTURE OF THE DIHYDROHEXAHELICENE FORMED BY THE IRRADIATION OF STYRYL BENZO [c] PHENANTHRENE UNDER ANAEROBIC CONDITIONS

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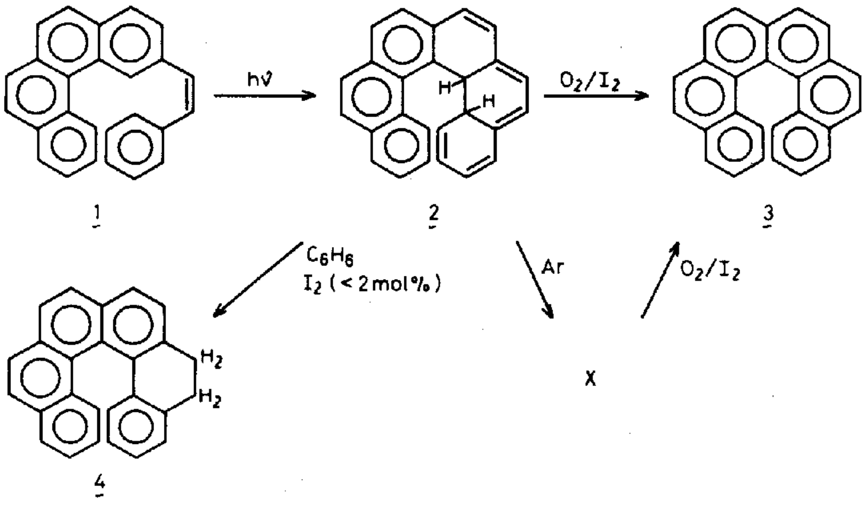
Abstract—According to Wismontski and Fischer irradiation under anaerobic conditions of 2-styryl benzo [c]phenanthrene (**1**) gives rise to an isolable dihydrohexahelicene which is easily oxidized into hexahelicene. Its structure obviously different from 5, 6-dihydrohexahelicene **4** was elucidated by the analysis of the 500 MHz-NMR spectrum. The structure and configuration: *trans*-**6a**, **16d**-dihydrohexahelicene with the **16d** hydrogen oriented inside the inner helix must be formed by a suprafacial 1.5-H shift of only one hydrogen from the primary formed photocyclization product **2**.

The photochemistry of 2-styrylbenzo [c]phenanthrene (1) in solution under *anaerobic* conditions has been the subject of two earlier reports in the literature. In the older article[1] it was shown that the primary photocyclization product of (1)—the 4a, 4b-dihydrophenanthrene derivative 2—isomerizes *via* a thermal and possibly also photochemical, intramolecular proton shift to another dihydrohexahelicene (X) which is easily oxidized by iodine to hexahelicene (3). The authors proposed the structure of 5,6-dihydrohexahelicene for X, mainly because of the occurence of a sharp singlet at 2.08 ppm in its NMR spectrum.

In a more recent paper[2] we reported that irradiation of 1 in benzene, under argon, and in the presence of a *small* amount of iodine (0.5–2 mol per cent) leads to a dihydrohexahelicene, which is *not* easily oxidized to 3. Analysis of the NMR spectrum demonstrated that the product was 5,6-dihydrohexahelicene (4). The difference in oxidizability and a comparison of the UV spectra of X and 4 showed that they are different compounds.

For the correct structure elucidation of X we attempted its isolation on a sufficiently large scale to trace the NMR spectrum. On irradiation of 1 in cyclohexane under argon in a spectrometer cuvet the rapid formation of X could be observed. Isolation of the compound in a larger-scale experiment, performed in a quartz or pyrex tube appeared, however, very laborious and difficult: The irradiation of one litre of a 5×10^{-3} molar solution of 1 at 350 nm in cyclohexane for 4 h, followed by evaporation of the solvent, gave a residue showing a complex NMR spectrum. Thin layer chromatography of the residue resulted in a diffuse pattern of several spots, among which a spot corresponding to hexahelicene. The difficulty in obtaining sufficiently pure X is partly due to its oxidizability, which requires extremely complete exclusion of oxygen from the solution and is a serious drawback during the chromatographic separation. Another factor seemed to be the photolability of X, which disappears completely on longer irradiation times. In view of the latter observation we repeated the large-scale experiment using a shorter irradiation time (0.5 h). The UV spectrum of the solution after 0.5 h irradiation was identical with the one given by Fischer[1] showing the presence of a large amount of X. Evaporation of the



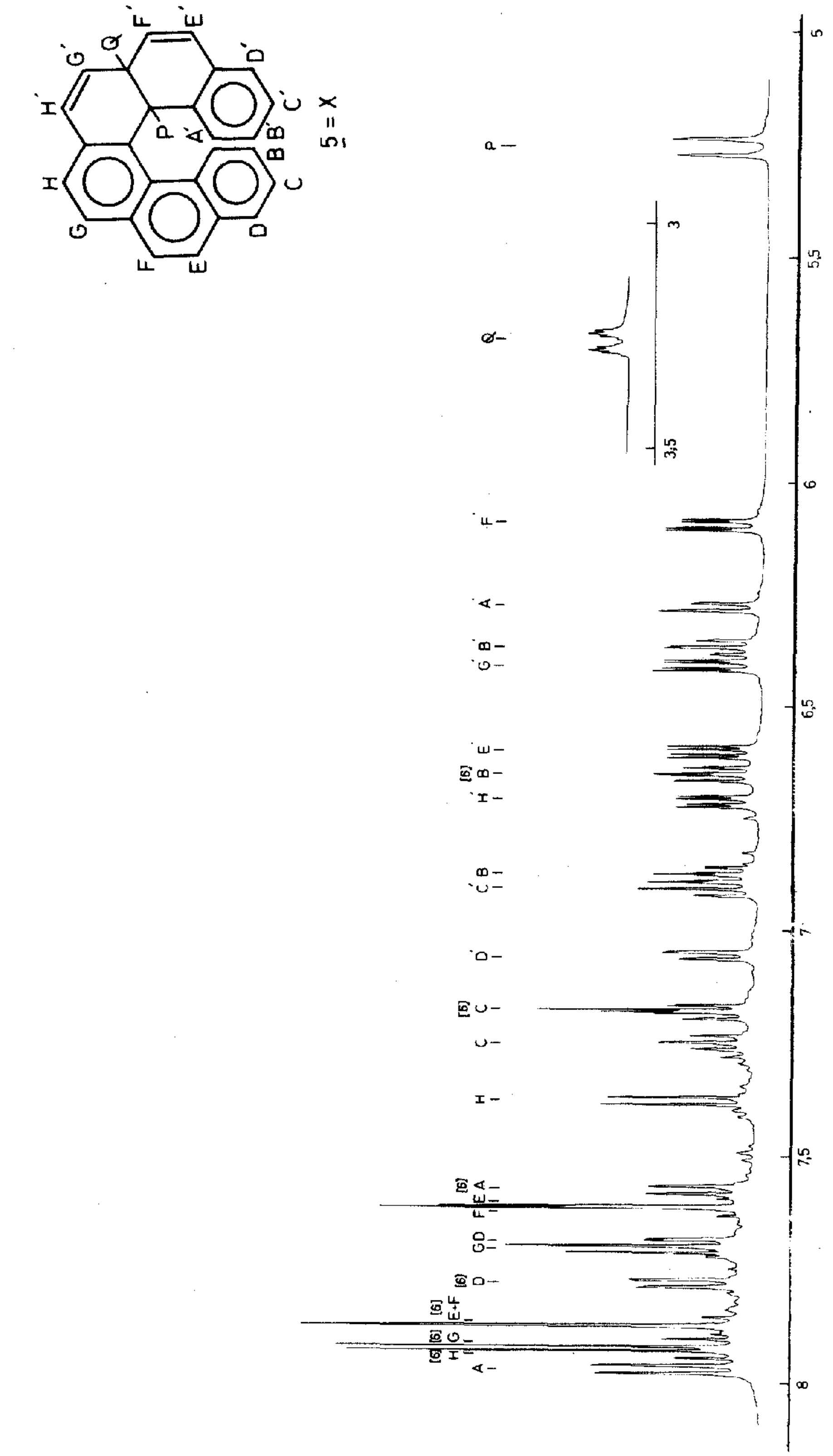


Fig. 1. 500 MHz spectrum of a mixture of *trans*-6a, 16d-dihydrohexahelicene **5** and hexahelicene **3** in $CDCl_3$. The hydrogens are assigned as given in the formula of **5**. Those of hexahelicene are given the symbol [6].

solvent gave a residue, whose NMR spectrum was traced without preceding separation. The spectrum contained a doublet at δ5.2, a double quintet at δ3.2 ppm and a complex aromatic pattern.[3] Thin layer chromatography of the sample on silicagel with hexane as the eluens resulted again in several small spots and a larger spot, which appeared to belong to hexahelicene.

A more useful result was obtained, when the residue was dissolved in a small amount of oxygen-free ethyl acetate, and subjected to fractional crystallization. In this way all starting material could be removed, leaving a sample which was mainly X, contaminated with only a small amount of 3.

Structure elucidation of X

Because of the complex NMR spectrum between δ6.5 and 8.0 ppm at 60 and 90 MHz the spectrum was also recorded at 500 MHz. This spectrum showed a large number of well resolved multiplets (Fig. 1). It contains two absorptions in the aliphatic region (δ3.2 and 5.2 ppm), each accounting for one proton. This excludes the occurrence of two methylene groups (as in 4); the aliphatic protons must be bound at tertiary C atoms.

By decoupling of all multiplets the coupled protons could easily be located (Table 1). It appeared that the aromatic part consisted of two sets of four coupled protons belonging to the terminal rings, and four sets of two coupled protons. Two of the latter sets are coupled with the aliphatic proton (Q) at higher field (δ3.2 ppm). All these couplings with Q are equal ($J = 2.6$ Hz). The coupling between the aliphatic protons J_{PQ} is large (17.75 Hz), indicating that they are present at adjacent carbon atoms. Occurence at two carbon atoms of the inner helix (as in 2) can be excluded because of the absence of an absorption in the visible spectrum at *ca* 500 nm and the difference in coupling with aromatic protons. (P shows only a very weak, long range coupling, $J = 0.4$ Hz). The only possibility is that P and Q are bound at the common C–C bond between the 6-membered rings II and III; because occurrence at the central band between the rings III and IV should lead to a symmetrical molecule, and occurrence at the common bond of rings I and II should be accompanied with a second, vicinal coupling of P. Therefore, we conclude that the structure of X must be that of 5, which is in accordance with all spectral data.

The values of $J_{QE'}$ and $J_{QH'}$ (2.6 Hz) are quite normal for an allylic system; $J_{QF'}$ and $J_{QG'}$ (also 2.6 Hz) are rather small for vicinal couplings; they point to dihedral angles QCCF′ and QCCG′ of *ca.* 90.[4,5] $J_{PQ} = 17.75$ points to axial positions for both protons. The small coupling of P concerns long-range coupling with E′ and H′.

The chemical shift of Q, calculated according to the Shoolery rules (3.1 ppm) agrees well with the observed value. The value, calculated for P(4.1 ppm) is much lower than is found (5.2 ppm), what must be due to deshielding by the opposite ring (VI); apparently P is located inside of the inner helix. This is evidenced by the strong NOE enlargement of the signal of proton A observed when P is irradiated.

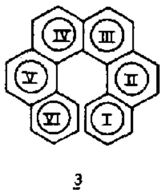
The olefinic protons (E′, F′, G′, H′) are at higher field than the aromatic protons (E, F, G, H) as expected. The assignment of F′ and G′ was done by their positive NOE effects on irradiation of Q. In the assignment of the two sets of two aromatic protons, the set having nearly equal δ-values was assumed to be E and F, because these protons correspond to H(9) and H(10) in the only phenanthrene moiety of 5. (G and H are much less equivalent.) The assignment of the two sets of four protons was based on the supposition that A′ must be at much higher field than A, because A′ is shielded by the opposite ring V and not deshielded by the adjacent ring II. The striking correspondence of the δ-values of protons in the terminal rings of 4 and 5 suggests a strong resemblence of the geometries of these compounds.

The presence of a small amount of 3 in the sample

Table 1. δ-Values of corresponding protons (ppm) in hexahelicene 3 and the dihydrohexahelicenes 4 and 5, measured in $CDCl_3$

protons	3^a	4^b	5 (X)
A'	7.58	6.26	6.28
B'	6.66	6.31	6.37
C'	7.19	6.80	6.91
D'	7.79	7.18	7.06
E'	7.87	2.95 (m)	6.60
F'	7.88		6.10
G'	7.92	7.44	6.41
H'	7.95	7.78	6.72
H	7.95	7.77	7.38
G	7.92	7.77	7.71
F	7.88	7.74	7.63
E	7.87	7.72	7.61
D	7.79	7.69	7.71
C	7.19	7.16	7.26
B	6.66	6.85	6.88
A	7.58	7.94	7.98
P			5.26
Q			3.26

a. Values from the spectrum at 500 MHz (Fig 1)
b. Ref. 2



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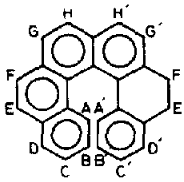

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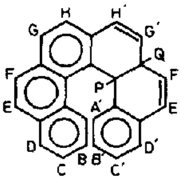
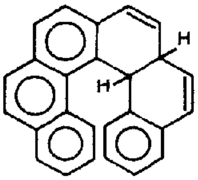


5 = X

used for NMR spectroscopy at 500 MHz revealed a detail, which has not been observed previously in spectra of hexahelicene, measured with lower resolution. Both pairs of coupled protons (EF and GH) occur as an AB pattern from which $J_{EF} = J_{GH} = 8.1$ Hz can be calculated. This agrees well with the calculated value (8.5 Hz)[6].

Now that the structure of X has been elucidated, the mechanism of its formation from **2** can be ascribed to a [1,5]-suprafacial H-shifts. In this way the *trans* configuration[7] of the aliphatic hydrogens in **2** is preserved. The reason that the hydrogen shift in **2** is completely restricted to one hydrogen, so that the isomeric dihydrohexahelicene **6** is not formed, might be due to the lower thermodynamic stability of **6** in comparison with **5**.



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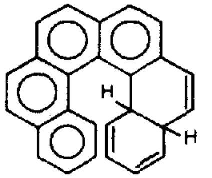

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EXPERIMENTAL

Irradiation was performed using four Sylvania F8T5 lamps with a maximum of emission at 350 nm. The lamps surrounded 50 ml pyrex tubes with a cyclohexane solution of **1**, C = 2–5 × 10^{-3} mol/l. The solutions were deaerated by bubbling pure Argon gas for 30 min. After irradiation for 0.5 hr the solvent was evaporated and the residue taken up in warm El-OAc. By cooling the first crop of crystals consists of **5**, contaminated with some hexahelicene.

The NMR spectra were recorded with a Bruker WM 500 spectrometer, interfaced with an Aspect 2000 computer, operating at 500.13 MHz at the Dutch national high frequency NMR facility at Nijmegen.

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