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SYNTHESIS OF 4-AZAHEXAHELICENE (1)
(benzo [c] phénanthro [1,2-f] quinoline)

R.H.Martin* and M.Deblecker.**
Service de Chimie Organique, Fac. Sc., Université Libre de Bruxelles
50, Av.F.D.Roosevelt - Bruxelles 5 - Belgique.

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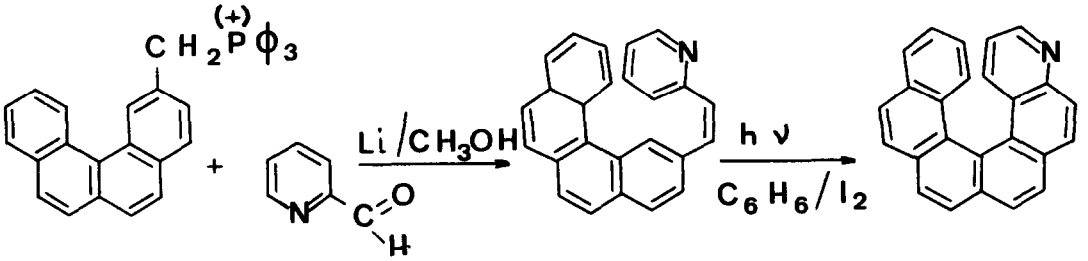
The photoinduced cyclodehydrogenation of 2-,3-, and 4-stilbazole, in dilute cyclohexane solutions, yields benzo [f] quinoline, benz [f] isoquinoline and benz [b] isoquinoline respectively (2,3); irradiation of 3- and 4-styrylisoquinoline gives the expected polycyclic aza-aromatic compounds (4). Recently Wynberg and Groen (5) have synthesised, by the same method, a hexa and a heptaheterohelicene containing thiophen rings. We have now applied this procedure to the synthesis of the first azahelicene known, namely 4-azahexahelicene.

4-azahexahelicene (IV) was obtained from the photoinduced cyclisation of 1-(2-benzo [c] phenanthryl)-2-(2-pyridyl)ethylene(III).



I II III IV

A Wittig reaction between I and II gave a cis-trans mixture of the expected 1,2-diarylethylene (III) (65 %). The cyclisation was carried out in benzene solution (250 mg in 750 ml) in the presence of iodine (4 mg), using a Hanovia 450W medium-pressure mercury lamp (Pyrex well) for 5 hours at room temperature. The cyclisation product was isolated by preparative TLC on silica-gel (benzene-ether 2/1) and recrystallised from benzene-alcohol, 45 mg (18 %) pale yellow crystals m.p 242-243°; found M.W.329 (m.s) C: 91,2 , H: 4,7 , N: 4,2 %; $C_{25}H_{15}N$ requires M.W.329; C: 91,2 , H: 4,6 , N: 4,2 %.

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* Author to whom enquiries should be addressed.

** Titulaire d'une bourse de Recherches de l'IRSIA.

The mass spectrum [molecular ion and fragment ion corresponding to azacoronene m/e= 301 (calc. 301)], the U.V. (Fig.2) and the N.M.R. (Fig.1; $CDCl_3$) spectra fully confirm the proposed structure. In particular, the observed chemical shifts and specific solvent effects ($CDCl_3$ - C_6D_6) are in complete agreement with expectations deduced from earlier work on polycondensed aza-aromatic systems (6).

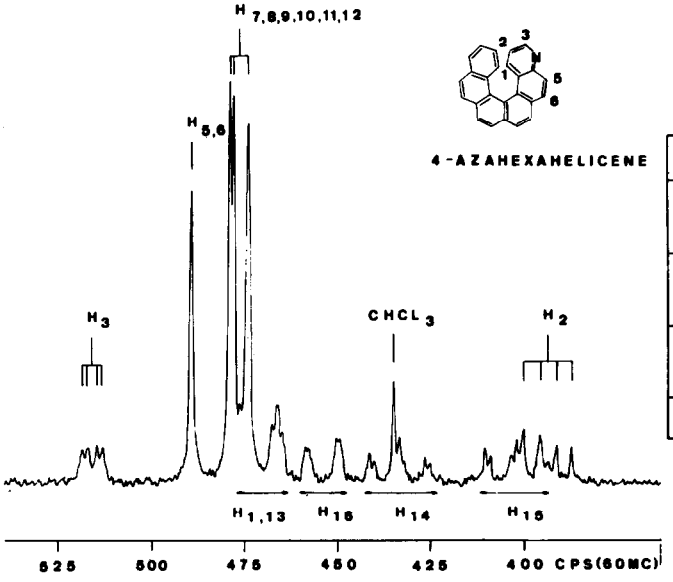

Fig.1

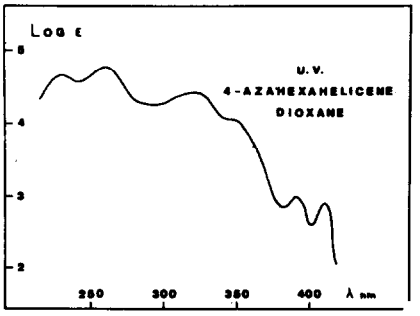

Fig.2

The spectral, optical and physico-chemical properties of 4-azahexahelicene will be reported later. Work towards the synthesis of isomeric azahexahelicenes and higher benzologues is under way.

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