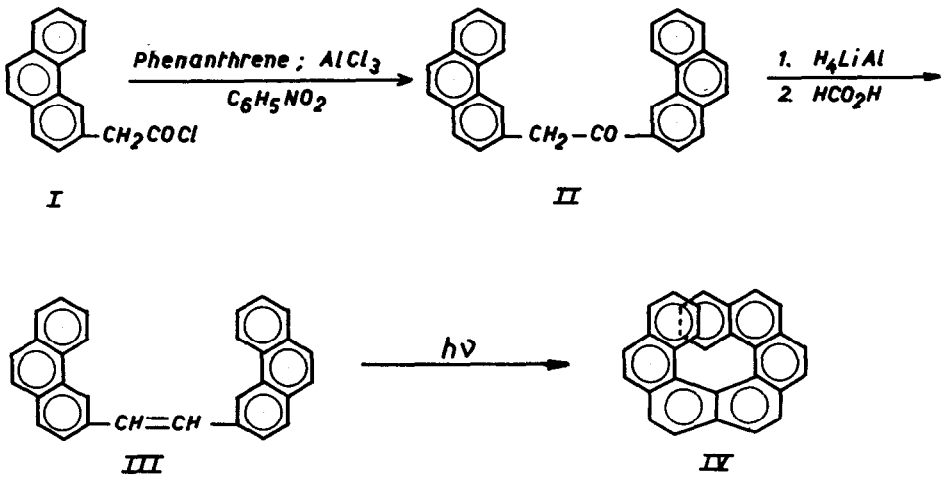
Tetrahedron Letters No.8, pp. 743-744, 1967. Pergamon Press Ltd. Printed in Great Britain.

SYNTHESIS OF HEPTAHELICENE (1)
BENZO[c]PHENANTHRO[4,3-g]PHENANTHRENE.

M.FLAMMANG-BARBIEUX*, J.NASIELSKI** and R.H.MARTIN.
Serv. de Chimie Organique Fac. Sc.,Université Libre de Bruxelles
50, Av. F.D. Roosevelt - Bruxelles 5, Belgique.

(Received 23 December 1966)

Heptahelicene (IV), a benzologue of hexahelicene (2), has been obtained by the photoinduced cyclisation of 1,2-bis(3-phenanthryl)ethylene (III).



I II III IV

Condensation of 3-phenanthrylacetyl chloride (I) with phenanthrene ($AlCl_3$, $C_6H_5NO_2$ at room temperature) gave a ketone (II) (m.p.182-183°), whose structure was established by N.M.R. spectroscopy [H_4, δ = 566c/s; H_2, δ = 495c/s (3)]. Reduction of II (H_4LiAl) followed by dehydration (HCO_2H) gave the expected diphenanthrylethylene (III), previously prepared via the thioaldehyde (4). The cyclisation was carried out in benzene solution (200 mg in 900 ml) in the presence of iodine, using a Hanovia 450 W medium-pressure mercury lamp (quartz well) for 8 hours at room temperature. The resulting mixture was chromatogra-

* Titulaire d'une bourse de recherche de l'IRSIA.
** Associé du FNRS.

phed on alumina (hexane) and the first fraction recrystallized from benzene-alcohol (25 mg, yellow crystals m.p.254-255°; Found : M.W.378 (mass spect.), C:95,4% , H:4,8% ; $C_{30}H_{18}$ requires M.W.378,44 ; C:95,2% , H:4,8%).

The N.M.R. (Fig.1) and the U.V. (Fig.2) spectra fully confirme the proposed structure.

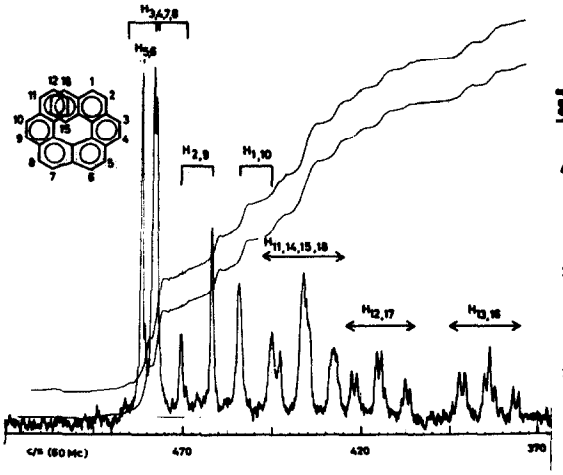


FIG. 1
N.M.R. spectrum of heptahelicene (7% in $CDCl_3$).

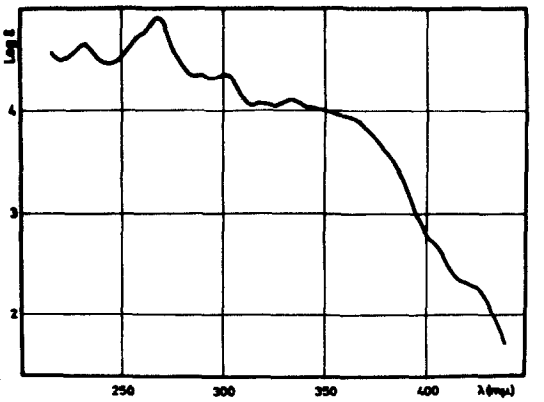


FIG. 2
U.V. spectrum (ethanol) of heptahelicene.

Work on the resolution of this new highly overcrowded hydrocarbon and on the synthesis of higher members of the helicene series is under way.

The authors are indebted to the "FNRS" and the "FRFC" for financial support.

REFERENCES.

(1) Part XXIV of "Synthesis in the field of polycyclic aromatic compounds". For part XXIII see F.Geerts-Evrard and R.H.Martin, Tetrahedron, Suppl.n°7, 287 (1966).

(2) M.S.Newman and D.J.Lednicer, J.Am.Chem.Soc., 78, 4765 (1956). - A new, non photoinduced synthesis of hexahelicene, worked out by D.Bogaert-Verhoogen, will be described shortly.

(3) R.H.Martin, N.Defay, F.Geerts-Evrard and H.P.Figeys, Bull.Soc.Chim.Belg., 73, 199 (1964).

(4) J.H.Wood, J.A.Bacon, A.W.Meibohm, W.H.Throckmorton and G.P.Turner, J.Am. Chem.Soc., 63, 1334 (1941).