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SYNTHESIS OF A DOUBLE HELICENE[1)]
RAC. AND *MESO* DIPHENANTHRO 3,4-c;3'4-l CHRYSENE

W.H. Laarhoven and Th.J.H.M. Cuppen
Department of Organic Chemistry, R.C. University, Nijmegen, The Netherlands

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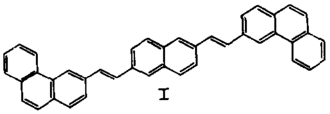
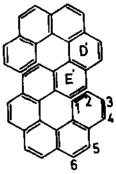
Photocyclization of 2,6-bis(3-phenanthrylethenyl) naphthalene (I) in benzene solution with added iodine affords among other products a double helicene (II).

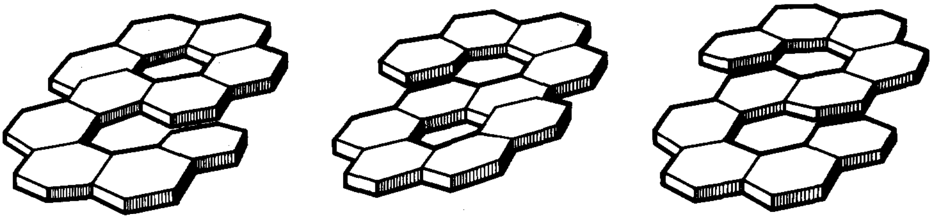


I



II

Three stereo isomers, *d*, *l* and *meso*, are possible for II as pictured in fig.I. It is likely that the *d* and *l* structures in the conformation as drawn, possess a strong deformation of the aromatic rings in the middle part of the molecule, whereas the *meso* form has a more regular structure.



d and l   meso

Fig.I The three possible structures of II

In fact two dehydrocyclization products (IIa and IIb) with identical U.V. and mass spectra (M=528) could be isolated.

IIa has mp.400-402° (from ethyl acetate).

IIb has mp.390° and is slightly soluble in most of the common organic solvents. Due to its low solubility the NMR spectrum of IIb (fig.II) could only be recorded in $AsCl_3$ solution by repeated scanning (36 times).

NMR spectra of IIa recorded in $CDCl_3$ (fig.II) and in $AsCl_3$ are very similar.

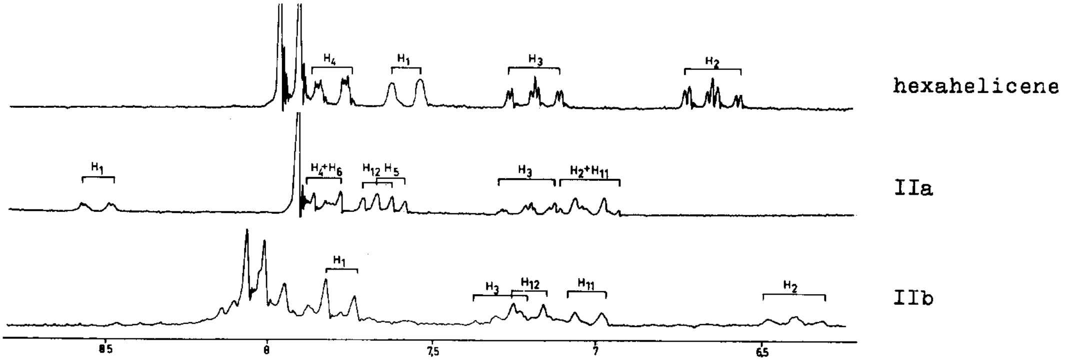


Fig.II NMR spectra of hexahelicene, IIa and IIb.

Comparison of the spectra of the isomers reveals some striking differences especially in the position of the protons H_1 and H_2.

As expected proton H_2 in IIb has an upfield shift with respect to the equivalent proton in hexahelicene, due to the ring current of the nearby benzene ring D'. However, H_2 in IIa has been shifted in a downfield direction.

Proton H_1 in IIa has a very large downfield shift with respect to hexahelicene ($\Delta\delta$=96 cps). Obviously, H_1 in IIa does not experience the anisotropy of ring E', as has been found in all helicenes up till now. The same is true to a minor degree for H_2 in IIa. Another feature of the spectrum of IIa is that protons H_5 and H_6 have different chemical shifts contrary to the corresponding protons in hexahelicene and IIb.

A structure which might explain these facts is drawn in fig.III. In this structure the deformation expected in the centre of the molecule is shifted to the ends. As the torsion in the d and l forms must be larger than in the meso form we suppose IIa to have the asymmetric form, while IIb is the meso compound. Details of the synthesis of the compounds and of physical measurements will be given elsewhere in the near future.

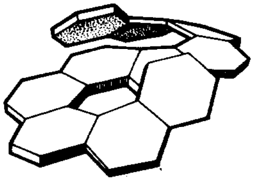


Fig.III The proposed structure of IIa.

1) Part IV of Photodehydrocyclizations of stilbene-like compounds.