Tetrahedron Vol. 28, pp 1823 to 1827. Pergamon Press 1972. Printed in Great Britain

CONFORMATIONAL STUDIES ON HEXAHELICENES—III

SYNTHESIS AND SPECTROSCOPIC DATA OF *MESO*- AND RAC.-2,2'-BIS HEXAHELICYL

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(*Received in the UK* 16 *November* 1971; *Accepted for publication* 2 *December* 1971)

Abstract 2,2'-Bis-hexahelicyl has been synthesized and separated into *meso* and racemic forms. Analysis of the NMR spectra of both forms in CS_2 as well as $AsCl_3$ revealed that the central biphenylic part of the *meso* compound is rather planar, whereas in the racemic compound both halves of the molecule have been twisted around the central bond.

FROM a previous study[1] it appeared that substitution of a t-butyl or a *p*-tolyl group in position 2 of hexahelicene does not lead to noticeable increase in steric hindrance.

It seemed to be of interest to know what kind of effects should be found on the introduction of a 2-substituent as large as a hexahelicyl residue. Therefore, we synthesized 2,2'-bis-hexahelicyl which consists of two dissymetric units giving rise to three stereoisomers (*meso*, D and L). It was to be expected that the *meso* and racemic forms should have quite different conformations.

RESULTS AND DISCUSSION

2,2'-Bis-hexahelicyl has been synthesized as represented in the scheme. The mixture of isomers was separated by chromatography. Details are given in the Experimental.

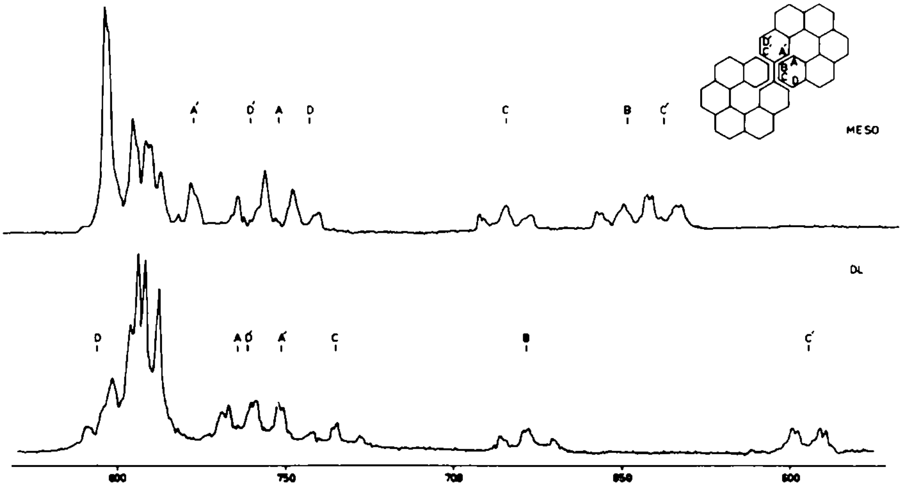
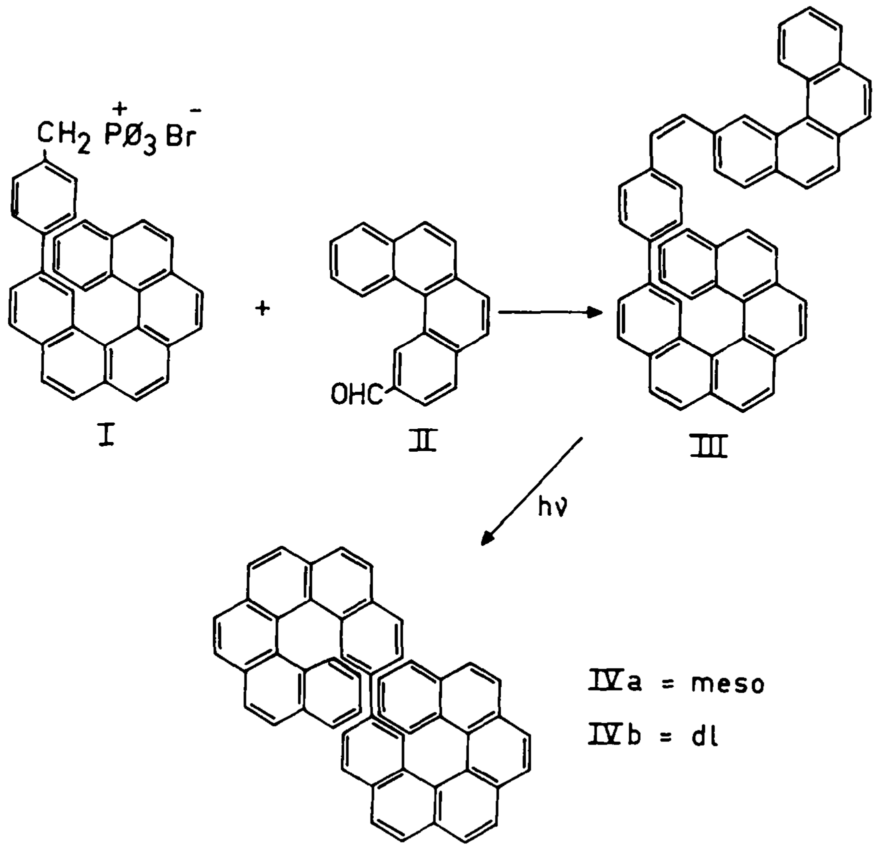


FIG 1. NMR spectra of *meso* and DL 2,2'-bishexahelicyl in $AsCl_3$ solution (100 Mc/s)



I

II

III

IVa = meso

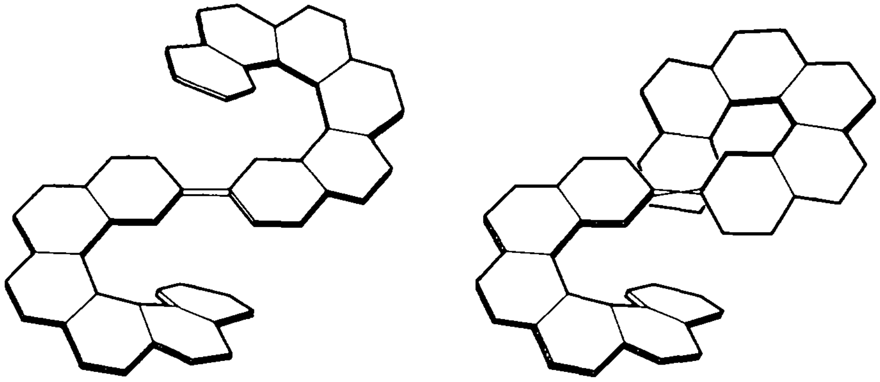
IVb = dl

The isomers could be distinguished by their m.p.s and solubilities. The isomer with the lower R_f-value (IVb) on silica (eluted with benzene) dissolved in CS_2, $CHCl_3$ and CCl_4, melted at 340–343°, solidified at 343° and melted again at 365°. The other isomer (IVa) had a higher R_f-value, did not dissolve in common organic solvents and melted at 360–365°. Apparently IVb is transformed into IVa on melting. From these properties we assigned the racemic configuration to the first isomer (IVb) and assumed the second one to be the *meso* compound (IVa).

The NMR spectrum of IVa was recorded in $AsCl_3$ solution, that of IVb in CS_2 solution and for a comparison with IVa also in $AsCl_3$. From a mixture of both isomers an NMR spectrum in CS_2 could be recorded. Subtraction of the relevant spectrum yielded a spectrum of IVa in CS_2. The spectra in $AsCl_3$ solution are given in Fig 1.

From decoupling experiments the positions of the protons A, B, C, D, A′, C′ and D′ (Fig 1) could be determined unambiguously in all spectra. Temperature dependence of the spectra was investigated by measurements at higher temperature (80°) on solutions of both compounds in $AsCl_3$, and at lower temperature (−80°) with a solution of IVb in CS_2.

Frequencies were estimated by the side-band technique. Concentration dependence of the spectra appeared to be very small.



Meso DL

FIG 2. Schematic models of the *meso* and DL form of 2,2′-bishexahelicyl

TABLE 1. CHEMICAL SHIFT IN PPM OF RING PROTONS A–D AND A′–D′ (SEE FIG 1) OF DL AND *meso* 2,2′-BISHEXAHELICYL IN $AsCl_3$ AND CS_2 SOLUTIONS

$AsCl_3$	DL			*meso*		
	δ_{0° (ppm)	$\delta_{0^\circ}-\delta_{80^\circ}$[a] (c/s)	Δ^c (c/s)	δ_{0° (ppm)	$\delta_{0^\circ}-\delta_{80^\circ}$[a] (c/s)	Δ^c (c/s)
A	7·65	(+5)	+8	7·54	(+3·5)	−3
B	6·78	(+5·5)	+8	6·49	(+4)	−21
C	7·35	(+7)	+9	6·85	(+6)	−41
D	8·05	(+7·5)	+14	7·45	(+7·5)	−41
A′	7·54	(0)	−3	7·78	(+9)	+21
C′	5·98	(−8)	−128	6·37	(+0·5)	−89
D′	7·63	(+2)	−23	7·61	(+3·3)	−25

CS_2	DL			*meso*		
	δ_{20° (ppm)	$\delta_{-80^\circ}-\delta_{20^\circ}$[b] (c/s)	Δ^c (c/s)	δ_{0° (ppm)		Δ^c (c/s)
A	7·57	(+2·5)	+10	7·40		−7
B	6·65	(+4)	+12	6·34		−19
C	7·22	(+8·5)	+14	6·67		−41
D	7·87	(+11·5)	+20	7·26		−40
A′	7·40	(−5·3)	−7	7·62		+15
C′	5·92	(−19)	−116	6·20		−88
D′	7·45	(+1·6)	−22	7·42		−25

[a] ($\delta_{0^\circ}-\delta_{80^\circ}$) is the difference in c/s between δ at 0° and δ at 80°.

[b] ($\delta_{-80^\circ}-\delta_{20^\circ}$) is the difference in c/s between δ at −80° and δ at 20°.

[c] Δ is the difference in c/s between δ of the DL or *meso* compound and the corresponding δ of hexahelicene for the same solvent

All relevant data are given in Table 1 together with the differences (Δ) in δ-values of of corresponding protons in IVa or b and hexahelicene.

In comparison with hexahelicene the signals of protons A–D at the unsubstituted rings of DL-bis-hexahelicyl are shifted downfield, whereas those of the *meso* form are shifted in opposite direction; the latter effect is the larger one. The variations may be ascribed to differences in ring current effects. In the *meso* form the unsubstituted terminal rings experience not only a ring current influence of the opposite ring of the same helix, but also that of the substituted ring of the other helix. The large shifts of the signals (especially for protons C and D) suggest that the influences of the substituted rings are additional. This suggests that the substituted rings are in one plane with the two helical parts of the molecule at opposite sides of this plane as is illustrated in Fig 2 (*meso*). This configuration explains why the proton signals C′ and D′ are also shifted upfield, as they undergo the ring current influence of the terminal ring in the other helix. The downfield shift of A′ is probably caused by a substitution effect as is also found in 2-*p*-tolylhexahelicene.[1]

In the racemic modification a large upfield shift is found for proton C′. As can be seen from models rotation of both halves of the molecule around the central bond over about 45° brings the proton C′ above the centre of the terminal ring of the other helix. In this configuration (illustrated in Fig 2, DL) D′ experiences a similar though smaller effect, but the orientation of protons A, B, C and D is such that no deshielding of any ring is possible.

By raising the temperature the frequencies of all protons, except A′ and C′ in the racemic form, increase. The rather small variations (<20 c/s over an interval of 160°) may be ascribed to less rigid conformations at higher temperatures, especially for the racemic form.

The differences in conformation between the isomers may be compared with those between biphenyl and *ortho* substituted biphenyl derivatives. The *meso* compound prefers a planar conformation in the central part as much as possible as does the unsubstituted biphenyl. Twisting enlarges steric interference between the two helices. In the DL compound a planar conformation is unfavourable, as in *ortho* substituted biphenyl derivatives. Twisting relieves the steric hindrance.

EXPERIMENTAL

UV spectra were recorded by a Cary 15 spectrophotometer, mass spectra by a Varian MS2B spectro meter and NMR spectra by a Varian HA100 apparatus.

The syntheses of 2-*p*-tolylhexahelicene and II have been described in the preceding paper. Bromination of 2-*p*-tolylhexahelicene with N-bromosuccinimide followed by treament with triphenylphosphine by known methods, yielded the phosphonium bromide (I). A Wittig reaction between I and II with $NaOCH_3$ as base in DMF yielded 81% of III; m.p. 168–172°; UV (*trans*) in MeOH: λ_{max} in nm (log ε): 345 (4·53); 321 (4·70); 313 (4·71); 284 (4·88): 244 (4·86); 323 (4·82).

Irradiation of III in benzene during 0·5 hr gave in 50% yield a mixture of racemic and *merso* IV. The isomers were separated by column chromatography and TLC on silica. The DL form was crystallized from CH_2Cl_2, yield 30%; m.p. 340–343°; *m/e* 654; UV in CH_2Cl_2; λ_{max} in nm (log ε); 414 (3·59); [357 (4·38)]; [336 (4·49)]; 323 (4·53); 272 (4·83). The *meso* form had m.p. 365°; *m/e* 654, UV in CH_2Cl_2; λ_{max} in nm (log ε); [416 (2·84)]; [355 (4·18)]; 323 (4·34); 277 (4·64).

When IVb was heated at 365°, the resulting material had an UV spectrum that was identical with that of IVa.

Acknowledgement—We thank Mr. J. M. F. Mous for recording the NMR spectra and Prof. dr. R. J. F. Nivard for his interest and discussions.

REFERENCE

[1] W. H. Laarhoven and R. G. M. Veldhuis, *Tetrahedron* **28**, 1811 (1972)