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STUDIES IN THE HELICENE SERIES.

Determination of the structure and of the dl configuration of a double helicene by INDOR and NOE experiments. Part XVIII[1)]

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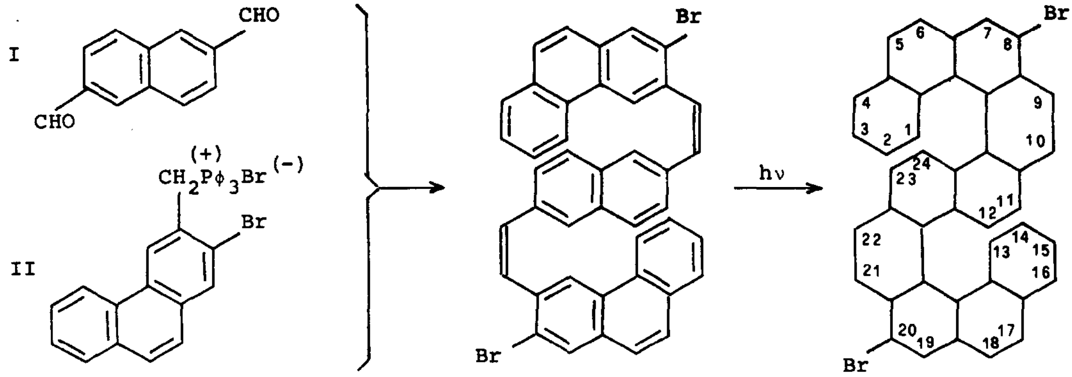
In the course of research on the synthesis of double helicenes, we have synthesised *dl* and *meso* 8,20-dibromo-bisphenanthro[4,3-a; 4',3'-j] chrysene (IV), the dibromo derivatives of the hydrocarbons (IV Br=H) previously prepared by Laarhoven and coll.[2)].

The bromine atoms were introduced to prevent the cyclisations taking *place on the β positions of the phenanthrene system.*



III IV

The synthesis of IV was carried out according to scheme 1. A double Wittig reaction (I: 140 mg; II: 970 mg[3)]; LiOEt: 150 mg) in refluxing benzene-ethanol (1:1) gave III (*cis* + *trans*) in 84% yield. M.S.: 688, 690 and 692 (1:2:1). A solution of III (135 mg) in toluene (750 ml) containing I_2 (4 mg)

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was irradiated at 60° for 20 min. (pyrex well, stirring) with a Hanovia 450 W medium pressure mercury lamp. Two cyclised products were isolated and purified by column chromatography (alumina/benzene): IVa (95 mg; 71%) m.p. 420-422°; M.S. 684, 686 and 688 (1:2:1); IVb (25 mg; 18%) m.p. 404-406°; M.S. 684, 686 and 688 (1:2:1).

Three structural isomers could result from a double photocyclisation, two of which are symmetrical from the NMR point of view. The U.V. (no abs.>430 nm) and NMR spectra fully exclude, respectively, the tetracene derivative and the non symmetrical isomer. The remaining structure IV can give rise to three stereoisomers (*meso* and *dl*). Analysis of the NMR spectra by INDOR[4,5] confirmed that the isolated products are indeed derivatives of IV.

In the case of IVa, the assignments are based on the following observations : 4-spin system H_1, H_2, H_3, H_4 : two examples are shown in Fig.1; H_9-H_{10}: the low field signals are assigned to H_9 on account of the strong *peri* deshielding effect of the bromine atoms; an analogous *ortho* effect is observed on H_7 (s); H_{11}-H_{12} : the proton at low field is considered to be H_{11} by analogy with the corresponding protons in the helicenes and in benzo[c]hexahelicene[6).

Examination of Table 1 shows a close analogy between the NMR spectrum of compound IVa and the NMR spectra of hexahelicene and benzo[c]hexahelicene, except for the low field shifts of H_1 and H_2 (0.84 and 0.63 ppm) in IVa.

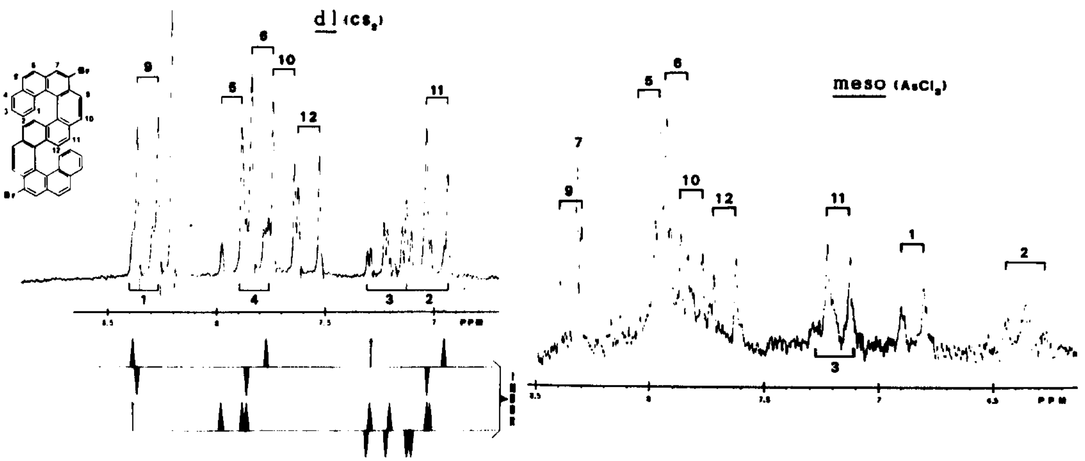

Fig.1 : NMR spectra (Brüker HX 90) of IVa (*dl*) in saturated CS_2 solution (260 scans) and of IVb (*meso*) in saturated $AsCl_3$ solution (308 scans).

The problem of the assignment of the configuration of IVa (*dl* or *meso*) was settled by the application of the NOE technique[7)].

Saturation of H_{14} (H_2) at 7.03 ppm in CS_2 solution, produced an increase of the integrated area of the signals corresponding to H_1 (H_{13}) + H_9 (H_{21}), relative to the singlet of H_7 (H_{19}) and to the 10 protons signals located in the middle of the spectrum (average of 6 integrations on a single run spectrum and integration of a 33 scans spectrum). The NOE effect on H_1 (H_{13}) was of the order of 25%. In a control experiment, the signals of H_7 (H_{19}) and of H_1 (H_{13}) + H_9 (H_{21}) were unaffected by saturation of H_{15} (H_3) at 7.22 ppm. These results clearly demonstrate that H_1 and H_{14} (H_{13} and H_2) are in close proximity. It follows that the observed low field shifts of these protons can be attributed to Van der Waals contact effects. Such a proximity exists only in the chiral configuration in which both ends of the twisted molecule are on the same side. The *dl* configuration of our isomer IVa (m.p.420-422°) is thus firmly established.

Table 1 : Chemical shifts in ppm (TMS=0).

	dl IVa		*meso* IVb	[6]helicene	benzo[c] hexahelicene*
	(CS_2)	($AsCl_3$)	($AsCl_3$)	(CS_2)	(CS_2)
H_1 - H_{13}	8.33	8.39	6.85	7.45	7.49
H_2 - H_{14}	7.05	7.13	6.36	6.53	6.42
H_3 - H_{15}	7.20	7.37	7.21	7.09	7.04
H_4 - H_{16}	7.83	7.97	7.78 ?	7.69	7.71
H_5 - H_{17}	7.92	8.05	8.00	7.81	7.84
H_6 - H_{18}	7.81	7.94	7.92	7.81	7.84
H_7 - H_{19}	8.21	8.35	8.35	7.88	7.92
H_8 - H_{20}	-	-	-	7.88	7.92
H_9 - H_{21}	8.31	8.40	8.38		7.93
H_{10} - H_{22}	7.69	7.84	7.84		7.93
H_{11} - H_{23}	6.99	7.14	7.19		6.85**
H_{12} - H_{24}	7.57	7.66	7.68		7.43***

dl IVa : $J_{5,6}$= 8.6 Hz, $J_{9,10}$= 8.6 Hz, $J_{11,12}$= 8.7 Hz.
meso IVb : $J_{5,6}$= 8.7 Hz, $J_{9,10}$= 8.6 Hz, $J_{11,12}$= 8.7 Hz
* Ref 6 : called benzo[m]hexahelicene, ** A' and *** B'

Because of the low solubility of the *meso* compound IVb (m.p.404-406°), its NMR spectrum was recorded in $AsCl_3$ solution and compared to the spectrum of *dl* IVa recorded in the same solvent. Both spectra show close analogies for the protons H_3 to H_{12} (Table 1). The $J_{9,10}$ and $J_{11,12}$ in IVb were confirmed by INDOR. On the other hand, H_1 and H_2 in IVb are shifted to higher fields, not only relative to H_1 and H_2 in IVa, but also by reference to the corresponding protons in benzo[c]hexahelicene (∿ 0.8 and 0.2 ppm). Similar high field shifts are observed in [11] 8), [12] 8) and [13] 9)helicene.

In their experiments, Laarhoven and coll.2) isolated both the *meso* and the *dl* unsubstituted isomers. These authors suggested that the high melting isomer (m.p.400-402°) has the *dl* configuration. That this isomer and the disubstituted *dl* derivative IVa have the same configuration is evident from the comparison of their NMR spectra (taking into account the low field shift of H_7 and H_9 due to the proximity of the bromine atoms in our compound). The same is true for the *meso* compounds. We have thus confirmed the assignment made by Laarhoven and coll., but the respective arguments used are contradictory. Our NMR assignments also differ to some extent.

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