RESOLUTION AND RACEMIZATION OF PENTAHELICENE

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All helicenes synthezised during recent times (1, 2) allow resolution into optical antipodes because of their screw-like conformation. Steric hindrance of the adjacent benzene rings prevents racemization of the helicenes being under investigation. Only hexahelicene racemizes at melting point temperature (3) . In pentahelicene (3.4.5.6-dibenzophenanthrene, I) steric hindrance is high enough to produce a·helical conformation (4). On the other hand, it is not obvious if the energy barrier separating the two antipodes of I is sufficient to allow resolution at room temperature.
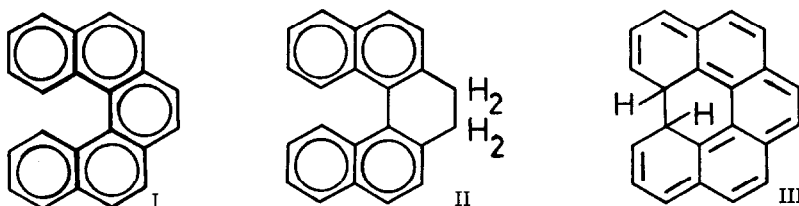
Resolution of pentahelicene (I) was achieved by the method of Newman and Lednitzer (3). An optically active complex was prepared by adding 670 mg of (+)-TAPA (5) to a solution of 625 mg of I in 30 ml acetic acid. After boiling and standing overnight 900 mg of dark purple-red crystals ($[\alpha]_D = -530^\circ$) were separated. Further addition of 65 mg of (+)-TAPA yielded 200 mg of the complex. -

(-)-I was separated from the complex by column chromatography (silica 0.05 - 0.8 mm, column 10 x 4 cm, solvent: petrolether + 5 % ether). The eluate was collected in an ice-cooled flask. The first fraction (300 ml) was rejected; the solvent of the following fractions

had been pumped off at temperatures $< 0^{\circ}$. Attempts on further purification were unsuccessful. (-)-I thus obtained shows the following data:

<u>Optical rotation</u> (in iso-octane, $26^{\circ}C$, apparatus: Zeiss-Kreispolarimeter $0,01^{\circ}$)

$[\alpha]_{578} = -1670^{\circ}$; $[\alpha]_{546} = -2025^{\circ}$; $[\alpha]_{436} = -4950^{\circ}$

<u>Circular dichroism</u> (in iso-octane, $25^{\circ}C$, apparatus: Dichrograph Société Jouan) *

λ nm	$\Delta\epsilon$ 1/cm · mole	λ nm	$\Delta\epsilon$ 1/cm · mole
396	+ 0.94	263	+ 76.02
376	+ 0.50	236	- 63.80
328	- 134.69	229	+ 25.05
309	- 299.08	207	+ 212.51
272	+ 73.87		

Investigation of racemization rate constants had been carried out in a thermostated 2 dm tube within a temperature region from 31 to $47^{\circ}C$. The kinetic data are given in the following table:

	E_a kcal/mole	log A	$\Delta H^{\ddagger}$ kcal/mole	$\Delta F^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
Pentahelicene (I)	23.5	12.4	22.9	24.1	- 4.1
9.10-Dihydro-pentahelicene (II)	30.8	13.4	30.0	29.9	+ 0.3

The activation data of I are compared with those of 9.10-dihydropentahelicene (6). The higher stability of II is obvious though molecular structure as well as conformation of I and II are comparable. Low optical stability has been described for the 9.10-dicarboxylic acid of I too the morphine salt of which showing fast mutarotation on standing in $CHCl_3$ (7).

The different behaviour of I and II may be explained assuming a cyclic intermediate III involved in the racemization of I. If this is true there must be a

* We are indepted to Dr. G. Snatzke for carrying out the c.d. measurements.

thermal equilibrium between the valence tautomers I and III. This may be
evidenced from results of photocyclization of I yielding 1.12-benzoperylene
(8). In this reaction a photochemical equilibrium I ⇌ III has been suggested.
As it is well known in the case of cis-stilbene photocyclization ring opening of
4 a, 4 b-dihydrophenanthrene (DHP) a cyclic intermediate of type III takes place
photochemically as well as thermally (9). An indirect evidence for the valence
tautomerism I ⇌ III may be seen from the following experiment: I had been
treated in boiling toluene (b. p. 111°C) for 16 hours in the presence of iodine
in the dark. Under these conditions 1.12-benzoperylene will be formated as
detected by u.v. spectrophotometry (yield: 4 %). - Thus, we suggest the
following mechanism for the racemization process:
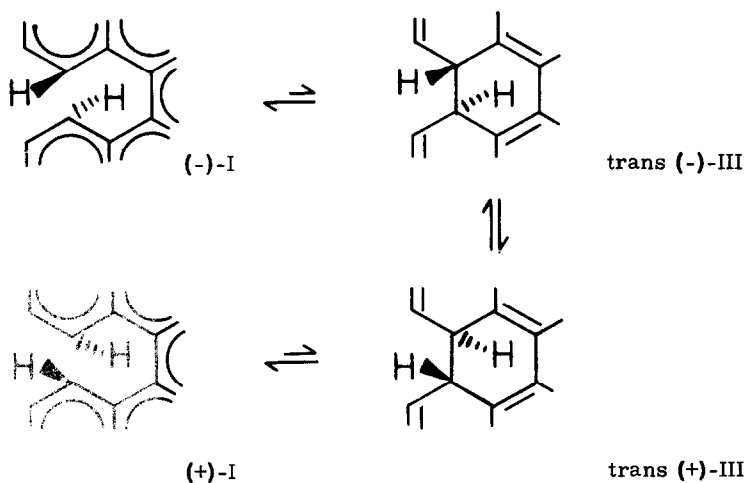
As trans-III is chiral too, the real racemization occurs during the change of
conformation of the 1'',4'-protons (denotation by Clar (10)). This step
involves splitting of a σ -bond as well as the thermal ring-opening of DHP (9).
In both cases negative values of $\Delta S^{\ddagger}$ had been observed (cf. table). Moreover,
$\Delta S^{\ddagger}$ and E$_a$ exactly hold the isokinetic relationship shown in the series of
DHP derivatives (9). In the case of II a ring-closed intermediate cannot be
expected. Therefore, racemization should proceed by inversion via a planar
conformation with remarkable in-plane distorsion of the aromatic skeleton. Such
a mechanism involves a rather high value of $\Delta H^{\ddagger}$ as compared with those of I
which indeed has been observed (cf. table).

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