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THERMAL RACEMISATION OF HEPTA-, OCTA-, AND NONAHELICENE

KINETIC RESULTS, REACTION PATH AND EXPERIMENTAL PROOFS THAT THE RACEMISATION OF HEXA- AND HEPTAHELICENE DOES NOT INVOLVE AN INTRAMOLECULAR DOUBLE DIELS–ALDER REACTION

R. H. MARTIN* and M. J. MARCHANT
Service de Chimie Organique, Fac.Sc., Université Libre de Bruxelles 50, Av. F. D. Roosevelt, B-1050
Bruxelles, Belgique

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Abstract—Kinetic results for the thermal racemisation in solution of hepta-, octa- and nonahelicene have been collected. A "conformational pathway" is suggested for these racemisations.

The thermal racemisation of hepta-, octa- and nonahelicene at the melt, was reported in a previous communication, together with the kinetic data for the racemisation of hexahelicene in naphthalene solution.[1] Furthermore, brief accounts or kinetic studies on the thermal racemisation of the following helicenes have been published: pentahelicene (kinetic results),[2] hexahelicene,[3] hexaheterohelicenes (kinetic results),[4] 2,2-bis hexahelicenyl[5] and diphenanthro [3,4-*c*; 3′,4′-1] chrysene.[6] However, no helicene in which the terminal rings facially overlap had been studied from this point of view prior to our work.

New kinetic results. A kinetic investigation of the thermal racemisation of hepta-, octa- and nonahelicene, in naphthalene solutions, has now been carried out. The procedure used for the resolution of the samples required in this work is described in the preceding communication (this issue of Tetrahedron). The initial optical rotation and the concentration of the solutions are shown in Table 1.

The racemisation and inversion rate constants ($k_r = 2k_i$) were deduced from the first-order plots (no concentration effect was detected). The results, including the half-life times of the optically active species are collected in Tables 2, 3 and 4.

Table 1

Helicene	Initial $[\alpha]_{579}^{25°}$ (CHCl$_3$)	Conc
hepta-	(+) 5577°	1%
octa-	(+) 6268°	1%
nona-	(+) 5473°	1·25%

In Table 5, the activation parameters are compared with those pertaining to the racemisation of pentahelicene[2] and hexahelicene.[1]

Our values, for hexa- to nonahelicene, have been optimised by least square variation.

Table 2. Racemisation of heptahelicene

t°C	T°K	k_r(min^{-1})	k_i(sec^{-1})	$t^{1/2}$(min)
239·3	512·46	9·33 10^{-4}	7·77 10^{-6}	743
256·5	529·66	3·43 10^{-3}	2·86 10^{-5}	202
286·2	559·36	2·67 10^{-2}	2·23 10^{-4}	26
286·8	559·96	2·94 10^{-2}	2·46 10^{-4}	23·5
295·0	568·16	5·15 10^{-2}	4·29 10^{-4}	13·4

Table 3. Racemisation of octahelicene

t°C	T°K	k_r(min^{-1})	k_i(sec^{-1})	$t^{1/2}$(min)
239·6	512·36	3·94 10^{-4}	3·29 10^{-6}	1761
240·0	513·16	4·78 10^{-4}	3·98 10^{-6}	1448
258·6	531·76	1·76 10^{-3}	1·46 10^{-5}	395
286·4	559·56	1·28 10^{-2}	1·07 10^{-4}	54
293·2	566·36	2·21 10^{-2}	1·84 10^{-4}	31

Table 4. Racemisation of nonahelicene

t°C	T°K	k_r(min^{-1})	k_i(sec^{-1})	$t^{1/2}$(min)
293·5	566·66	5·60 10-3	4·66 10^{-5}	123
296·0	569·16	5·98 10^{-3}	4·98 10^{-5}	116
305·0	578·16	1·00 10^{-2}	8·33 10^{-5}	70
305·5	578·66	1·11 10^{-2}	9·25 10^{-5}	63
335·8	608·96	7·40 10^{-2}	6·16 10^{-4}	7·4

Table 5

Helicene	$\Delta H^{\neq}$ Kcal M^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta G^{\neq}$ (27°C) Kcal M^{-1}	E_a^{*} (27°C) Kcal M^{-1}
penta[2]	22·9	−4·1	24·1	23·5
hexa	35·0	−4·2	36·2	35·6
hepta	40·5	−3·9	41·7	41·1
octa	41·0	−4·6	42·4	41·6
nona	41·7	−6·1	43·5	42·3

*From the relation $E_a = \Delta H^{\neq} + RT$

It is interesting to note that the $\Delta G^{\neq}$'s for hepta-, octa- and nonahelicene are very similar.

Reaction path. The unforeseen relative ease of thermal racemisation of the helicenes studied so far raises the problem of the reaction path of these racemisations. It should be pointed out, at this stage, that the helicenes are recovered in over 90% yields after the thermal racemisations. Thus, 93% pure nonahelicene was recovered after heating in naphthalene at 336° for 30 min.

With the results presently available, we will consider the following three hypotheses:

(1) bond breaking; (2) reaction path involving an intermediate resulting from an internal double Diels–Alder reaction; (3) "conformational pathway".

(1) Considering the kinetic results, we believe that complete bond breaking, involving a non-stabilised diradical, is very unlikely.

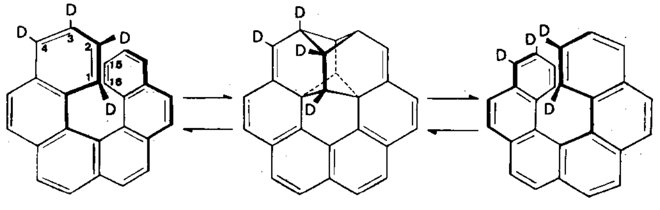
(2) Dr. J. Nasielski (Brussels) suggested to us that the thermal racemisations could involve intermediates resulting from internal double Diels–Alder reactions. These intermediates (e.g., 2) would give, by retro Diels–Alder reactions, either the M or the P configuration with equal probability in the case of the unsubstituted helicenes (for the justification of this restriction, *vide infra*).

An interesting case of *photoinduced* cyclisation between aromatic rings, equivalent to an internal double Diels–Alder reaction, has been observed by Wassermann and Keehn[7] in the [2,2] paracyclonaphthane series. The starting material is recovered by a thermal retro Diels–Alder reaction, on heating at 200°.

In the case of *dl* hexahelicene-1,2,3,4-d_4 (**1**), the double Diels–Alder reaction path would lead, after complete equilibration, to a 1:1* mixture of hexahelicene-1,2,3,4-d_4 (starting material) and hexahelicene-1, 2, 13, 14-d_4 (**3**). This follows from the fact that the double Diels-Alder reaction will produce a permutation of $D{-}C_1{-}C_2{-}D$ *vs* $H{-}C_{16}{-}C_{15}{-}H$ in the inversion process (Scheme 1). The presence of the new isomer **3** in the reaction product could easily be detected by ^{1}H-NMR spectroscopy.

A sample of *dl*-**1** dissolved in pure naphthalene (10% w/w), thoroughly degassed and sealed under reduced pressure ($5{\cdot}10^{-4}$ Torr) was heated at 286° for 70 minutes. After sublimation of the naphthalene and chromatography of the residue on alumina (benzene), the ^{1}H-NMR spectrum (Varian A60) of the recovered product was rigorously identical to the spectrum of the starting material. This experiment conclusively proves that an internal double Diels–Alder intermediate is not involved in the racemisation of hexahelicene.

A related experiment was performed on heptahelicene. In this hydrocarbon (**4**), the hypothetical double Diels–Alder reaction would occur between the first and the sixth ring involving $C_{1,2,3,14,14a,18a,18b \text{ and } 18f}$ or respectively $C_{18,17,16,5,4a,18f,18e \text{ and } 18a}$. A reaction between the two end rings of this hydrocarbon seems very unlikely in view of the fact that the cyclised product would be unduly strained. A number of such processes would cause a substituent located anywhere but in positions 1,2,17 and 18 to shift progressively right round the outer crown of the skeleton, except to positions 1, 2, 17 and 18, the first and second non-quaternary carbon atoms at each end of the helix. Thus, complete equilibration should give a mixture of seven monosubstituted isomers. In order to test this hypotheti-



1 (M) **2** **3** (P)

SCHEME 1

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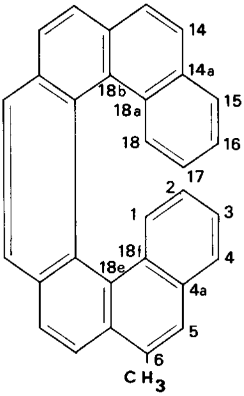
*The free energy of the two isomers must be quasi identical.

cal reaction path, a solution of *dl* 6-methylheptahelicene (**4**) in naphthalene (5% w/w), prepared as above, was heated for one hour at 305°.



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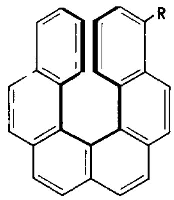
The helicene was recovered by sublimation of the naphthalene and purified by chromatography (alumina-benzene). The ^{1}H-NMR spectrum of the product, recorded on a Bruker 270 MHz spectrograph, is, in every respect, identical with the spectrum of the starting material; this excludes the occurrence of any migration of the substituent. In the reported experiment, no shift of the methyl group would result from a double Diels–Alder reaction involving the first and the last rings of 6-methylheptahelicene. However, the fact that we did not observe an internal double Diels–Alder reaction in the case of hexahelicene-1, 2, 3, 4-d_4, together with the strain argument, makes it very unlikely that such a process does indeed occur.

We thus conclude that the thermal racemisation of hexa- and heptahelicene does not involve an internal double Diels–Alder reaction.

In view of the great similarity between the kinetic data for hepta-, octa- and nonahelicene, we can safely extrapolate this conclusion to the thermal racemisation of octa- and nonahelicene.

(3) The last hypothesis, namely the reversible inversion of the helical structure (M $\rightleftharpoons$ P) by a "conformational pathway" (Scheme 2) is, in our opinion, the most reasonable one at the present time.

It is important to note that this process does not necessarily imply either a planar or a non planar achiral conformation *along* the reaction path. It must, however, be borne in mind that a three-dimensional non chiral conformation such as **5** (R=H) may well occur during the thermal racemisation of the unsubstituted helicenes (for R≠H, **5** is a chiral conformation!).*



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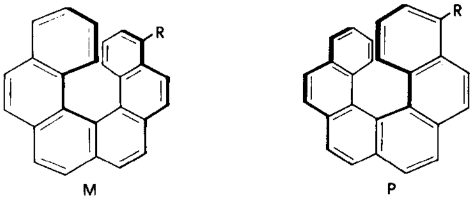

SCHEME 2

The "relatively low" potential barriers observed for the racemisation of the helicenes up to nonahelicene, can be justified in the "conformational process" by the fact that the necessary molecular deformations (bond torsion, bond bending, bond stretching, etc . . .) are spread over a large number of bonds.

We thus reach the important conclusion that the helicenes are in fact much more "flexible" than is generally believed. Space-filling models of (non planar) polycyclic aromatic hydrocarbons are undoubtedly largely responsible for this common misconception; as stressed by Mislow[9]: ". . . the model summarises and emphasises some aspects of the molecular properties and completely suppresses, in fact falsifies, others". Work on higher benzologues and substituted helicenes is in progress.

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*In 1968, Dougherty[8] stated that the thermal racemisation of [6] helicene "requires that the molecule twist through a symmetrical conformation", thus implying a conformational process for the racemisation of this hexacyclic helicene.