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RESOLUTION AND OPTICAL PROPERTIES ($[\alpha]_{max}$, ORD AND CD) OF HEPTA-, OCTA- AND NONAHELICENE

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—Hexa-, hepta-, octa- and nonahelicene give conglomerates from chloroform and 1,2-dichloroethane solutions. The partially resolved helicenes thus obtained are purified by repeated crystallisations, out of equilibrum conditions. The UV, ORD and CD curves of the pure enantiomers are shown in Figs 1, 2 and 3.

The resolution of [6] helicene, using an optically active π complexing agent (TAPA), was achieved by Newman *et al.*[1] in 1955. In the course of the last few years, brief accounts of the (partial) "spontaneous resolution" of [7] helicene[2] and heterohelicenes[3] have been published. An example of "induced resolution" by an optically active solvent (crystallisation of a heptaheterohelicene in (−) α-pinene) has been observed by Wynberg and Groen.[4]

In this communication, we wish to report the formation of conglomerates*[5] in the case of hexa-, hepta-, octa- and nonahelicene and the subsequent purification of the enantiomers by crystallisation, out of equilibrium conditions, of partially resolved supersaturated solutions.†

Relatively well resolved crystals were obtained from chloroform or, better, from 1,2-dichloroethane solutions. Crystallisations from CS_2 gave optically inactive crystals.

The complete separation of the enantiomers is performed as follows: approximately 0·1 g of the *dl*-helicene is dissolved, by heating, in an excess of 1,2-dichloroethane. The flask is partially closed so as to allow slow evaporation of the solvent at room temperature. When reasonably large crystals are formed, the mother liquor is decanted and the crystals are washed with methanol. The average weight of the individual crystals thus prepared is of the order of 1 to 5×10^{-3} g for heptahelicene and 10^{-4} g for octa- and nonahelicene. Larger crystals are usually poorly resolved, possibly on account of microtwinning.‡[6] Each individual crystal of the conglomerate is dissolved in chloroform and the sign of rotation is determined. The solutions showing the same sign are put together and evaporated

Table 1. $[\alpha]_{max}$ and m.p. of (levorotatory) hepta-, octa-, and nonahelicene

Helicene	$[\alpha]_{579}^{25°}$ ($CHCl_3$)	M.p. of the pure antipode	M.p. of the eutectic
hepta	(−) 5900° ± 200° ($c = 6 \times 10^{-2}$)	309–310°	254-355°[7]
octa	(−) 6900° ± 200° ($c = 4{\cdot}3 \times 10^{-2}$)	364–365°[a]	330–331°[2]
nona	(−) 8100° ± 200°[b] ($c = 6{\cdot}07 \times 10^{-2}$)	398–399°[a]	379–380°[a]

[a] M.p. corrected.

[b] The optical rotation of [9] helicene reported in Ref[8] and later quoted in Ref[9] should have read: $[\alpha]_D$ 15000° ± 5000° instead of (+) or (−) 15000°.

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*In the "spontaneous resolution by crystallisation" from a *dl* mixture, the crystals of the two enantiomers are formed in equal amounts and the solution remains optically inactive.

†When the crystals of the enantiomer in excess are collected, the solution, whose optical sign has changed, remains supersaturated with the other enantiomer.

‡It has been suggested that microtwinning occurs frequently in chiral space group such as $P2_1$ and $P2_12_12_1$. (*cf* p. 456, Ref 6).

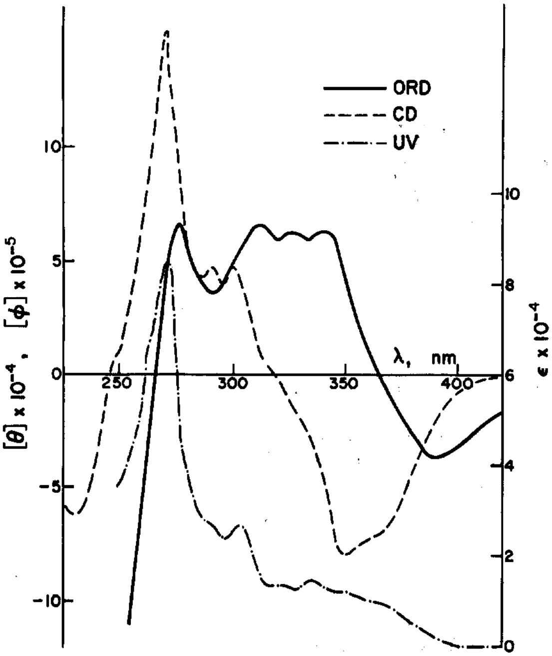

Fig 1. ORD, CD and UV spectra of optically pure (−) heptahelicene in CHCl$_3$.

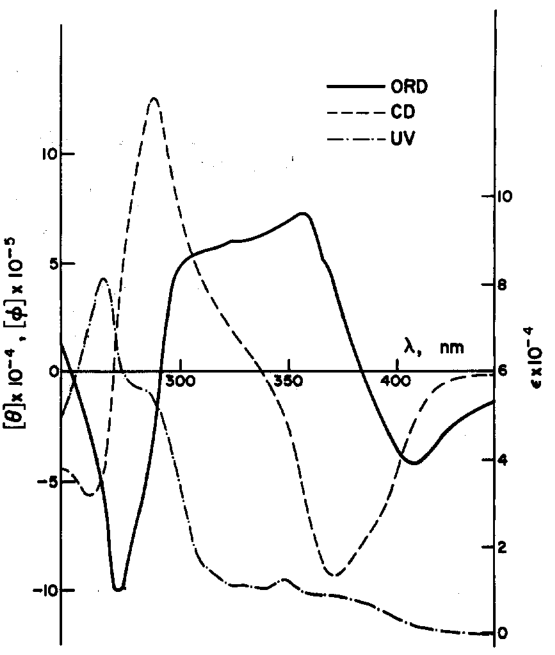

Fig 2. ORD, CD and UV spectra of optically pure (−) octahelicene in CHCl$_3$.

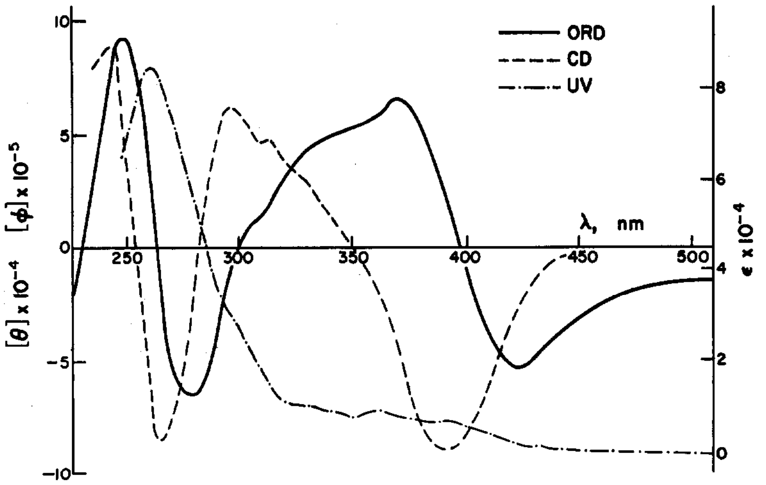

Fig 3. ORD, CD and UV spectra of optically pure (−) nonahelicene in CHCl$_3$.

to dryness. The residues are recrystallised quickly from supersaturated CHCl$_3$/MeOH solutions prepared by adding MeOH to saturated CHCl$_3$ solutions. The optical rotation of the solution is continuously controlled during the crystallisation. When the solution of the *levorotatory* fraction reaches its maximum dextrorotation (or *vice-versa*), the crystals are quickly removed by filtration. The mother liquor is then added to the *dextrorotatory* fraction, to which the same procedure is applied. By a number of such processes, the optical rotation of each fraction is strongly enhanced without loss of material. The purification of the enantiomers to constant m.p. and optical rotation is finally achieved by a few "classical" crystallisations. The results are collected in Table 1. At the request of a referee, we will now illustrate the evolution of a resolution by a specific example. It should however be borne in mind that so many factors are involved in this technique, that the following description is merely illustrative. The resolution of [8] helicene, which is not particularly easy, has been chosen for this purpose.

Specimens of *dextro* and *levo*-rotatory [8] helicene were obtained by "hand picking", $[\alpha]^{25^\circ}_{579}$: +747° and −761°.

The *dextro*-rotatory fraction showed the following $[\alpha]^{25^\circ}_{579}$ ($CHCl_3$) after n recrystallisations out of equilibrium ($CHCl_3$–MeOH) as described above: $n = 3$ +956°, $n = 7$ +2376°, $n = 10$ +3768°, $n = 16$ +4702°, $n = 17$ +5200°, $n = 19$ +6070°, $n = 20$ +6150°.

After four "normal" recrystallisations (at equilibrium) from pure $CHCl_3$-MeOH, the $[\alpha]^{25^\circ}_{579}$ ($CHCl_3$) reached a maximum value of +6900°. No further change was observed by recrystallisation from either $CHCl_3$-MeOH or C_6H_6-EtOH solutions.

The UV, ORD and CD curves of the pure levorotatory enantiomers are shown in Figs 1, 2 and 3.

The remarkable similarity between these curves and the curves of (−) pentahelicene (CD)[10] and (−) hexahelicene (ORD and CD)[11] establishes, without ambiguity, that the *levorotatory* helicenes, from penta- to nonahelicene, have the same, namely the left-handed (or M) helicity,[12] as was suggested earlier by Gestmann and Both.[12a]

A similar conclusion was reached by Wynberg *et al.* in the heterohelicene series.[13]

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