

¹³C NMR Differentiation of Diastereoisomeric Complexes of *cis*-Decalin with β -Cyclodextrin

Helena Dodziuk,*^a Jerzy Sitkowski,^a Lech Stefaniak,^a Janusz Jurczak^a and Danuta Sybilska^b

^a Institute of Organic Chemistry and ^b Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44, Poland

¹³C NMR spectra show chiral discrimination between two invertomers of *cis*-decalin complexed with β -cyclodextrin.

Chiral recognition by cyclodextrins (CDs) is still not well understood in spite of numerous successful practical applications and several proposed mechanisms for complex formation.¹ Especially intriguing seems to be the case of complexes formed by saturated hydrocarbons with cyclodextrins where

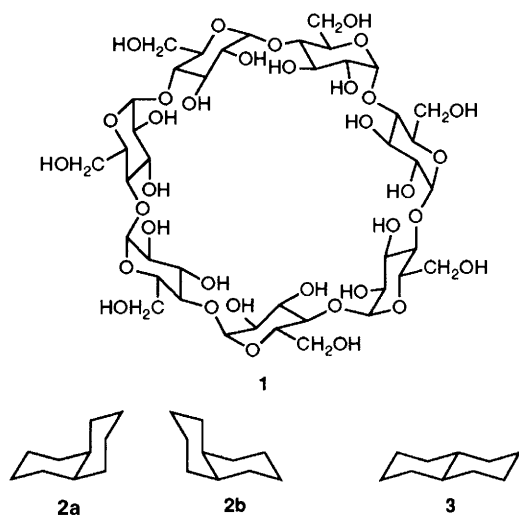
the only driving force for the very selective complex formation are weak but very numerous nonbonding interactions.

β -Cyclodextrin **1** was recently found to discriminate between the *cis*- and *trans*-decalin **2** and **3**, respectively, on a chromatographic column.² *cis*-Decalin is known to exist as a

Table 1 ^{13}C NMR signals of free decalin **2** and those of the complex **4** at various temperatures^a

T/K	393		303		233		223	
Substance	2	4	2	4	2	4	2	4
C-9, C-10	37.46	37.37	36.73	36.37	36.86	36.73 36.68	36.83	36.69 36.64
C-1	30.23	30.16			33.22	33.24 br ^b	33.19	33.26 33.24
C-4								
C-5					27.74	27.73 27.71	27.72	27.73 27.71
C-8								
C-2								
C-3	24.92	24.95			26.27	26.22 br ^b	26.23	26.20 br ^b
C-6					21.55	21.59 21.57	21.52	21.58 br ^b
C-7								

^a Experimental conditions: spectra were measured on Bruker AM-500 spectrometer operating at 125.76 MHz for ^{13}C NMR equipped with standard variable temperature unit. The standard conditions were: acquisition time 1.18 s, relaxation delay 2 s, pulse duration 3 μs (50° flip angle), number of scans 256 for each spectrum, conc. ca. 0.1 mol dm⁻³. ^b Broad.



mixture of enantiomers **2a** and **2b** interconverting by ring inversion.

A comparison of the ^1H NMR spectrum of decalin region of the crystalline complex³ dissolved in dimethylformamide and that of free decalin in the same solvent at room temperature exhibits some differences. In spite of their complexity, the comparison of the corresponding spectra at low temperatures clearly reveals the presence of the complex in solution and its prevalence at low temperatures.⁴ The decalin region in the low temperature ^1H NMR spectra is very complicated and not interpretable in terms of diastereoisomeric complexes formed by enantiomeric invertomers with β -CD as a host. In order to study chiral recognition in this case, ^{13}C NMR spectra of the complex **4** at temperatures varying from 393 to 223 K were recorded and compared with those of free decalin **2**. The ^{13}C NMR spectrum of the latter molecule at low temperature, with the inversion frozen, was reported as early as 1973.⁵ Three decalin signals were expected for the rapidly inverting molecule **2** while with inversion frozen the signals of carbon atoms other than the bridgehead ones, should be split in two resulting in five signals in the spectrum of free decalin at low temperature. Under the assumption of fast exchange on the NMR time scale between complexed and free decalin (the latter is present in a negligible amount in the mixture at low temperatures) the formation of diastereoisomeric complexes by two invertomers of **2** with β -CD should produce a splitting of the signals of all of the free decalin carbon atoms yielding ten signals. An inspection of the decalin regions of the spectra summarized in Table 1 reveals that: (i) owing to the slow inversion of six-membered rings in **2**, one broad signal of bridgehead carbon atoms appears in the spectra of the free guest **2** and of the complex **4** at 303 K, two other signals

exhibiting coalescence. (ii) Spectra of the complex and that of free decalin **2** at 393 K reveal three signals. The lack of the splitting expected for a mixture of the diastereoisomeric complexes of **2a** and **2b** with **1** at 303 and 393 K is believed to be due to (a) rapid exchange between free and complexed decalin and (b) to the shift of the equilibrium toward free decalin at the temperatures. (iii) In the spectra of the latter molecule at low temperatures the signals of the carbon atoms, other than the bridgehead ones, are split yielding five signals of equal intensity. (iv) In the spectrum of the complex **4** at 233 K three signals of *cis*-decalin carbon atoms are split into doublets and two others are significantly broadened. Such a splitting pattern is in accordance with the presence of two diastereoisomeric complexes formed by invertomers **2a** and **2b** with β -CD **1**. A slightly different splitting pattern also involving ten signals has been observed at 223 K. Understandably, the splitting of the bridgehead carbon atoms is the biggest and is seen first upon the temperature lowering. The almost equal intensity of the signals corresponding to diastereoisomeric complexes seems to indicate that the energy difference between them is small.

Diastereoisomeric complexes of some highly polar aromatic compounds with CDs were observed by means of ^1H NMR spectra and their application to optical purity measurements was proposed,⁶⁻⁸ but to our knowledge, no NMR manifestation of chiral recognition by CDs in ^{13}C NMR spectra has been reported.[†]

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[†] Note added in Proof: Chiral recognition by β -CD was also observed by ^{15}N NMR, R. Dyllick-Brezinger and J. D. Roberts, *J. Am. Chem. Soc.*, 1980, **102**, 1167.