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Structure of cyclodextrins and their complexes. Part 3. ^{1}H NMR spectra of diastereomeric complexes of *cis*-decalin with β-cyclodextrin[1]

Helena Dodziuk[a]; Jerzy Sitkowski[a]; Lech Stefaniak[a]; Janusz Jurczak[a]; Danuta Sybilska[b]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Kasprzaka 44, Poland [b] Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Kasprzaka 44, Poland

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Structure of cyclodextrins and their complexes. Part 3. ^{1}H NMR spectra of diastereomeric complexes of *cis*-decalin with *β*-cyclodextrin[1]

HELENA DODZIUK*[a], JERZY SITKOWSKI[a], LECH STEFANIAK[a], JANUSZ JURCZAK[a] and DANUTA SYBILSKA[b]

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, 01–224 Warsaw, Kasprzaka 44, Poland and* [b] *Institute of Physical Chemistry, Polish Academy of Sciences, 01–224 Warsaw, Kasprzaka 44, Poland*

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The complexation of *cis*-decalin with *β*-cyclodextrin yields complicated room- and low-temperature ^{1}H NMR spectra in the decalin region suggesting deformations of the invertomers of the guest molecule immersed in the cyclodextrin cavity.

Molecular and chiral recognition by cyclodextrins (CDs) still requires further studies in spite of their numerous successful practical applications, since the mechanism of their complex formation is not clear.[2] The study of relatively stable complexes[3] formed by saturated hydrocarbons with cyclodextrins seems of value for the clarification of the driving force for complex formation.

β-Cyclodextrin (**1**) was recently found to discriminate between *cis*- and *trans*-decalin, (**2**) and (**3**), respectively, on a chromatographic column.[3] *cis*-Decalin is known to exist as a mixture of (H9C9C10H10)P and (H9C9C10H10)M enantiomers,[4] (**2a**) and (**2b**), respectively, interconverting by ring inversion. Inversion freezing at 233 K allowed us to observe chiral discrimination of the *cis*-decalin enantiomers in the complex with *β*-CD in ^{13}C spectra.[1] The corresponding ^{1}H spectra at room and low temperature of free *cis*-decalin **2** and the complex will be reported in this note.

^{1}H NMR spectra in the decalin region of the crystalline complex[3] dissolved in dimethylformamide and those of free decalin in the same solvent at room and low temperature are presented in the Figure. The contradictory assignments of ^{1}H and ^{2}H free decalin spectra were given in refs. 5 and 6, thus, it merits further study.[7] A comparison of the spectra of the complex clearly reveals the presence of the complex in solution and its prevalence at low temperatures. Due to complicated equilibria between free and complexed host and guest (the latter present in solution as a mixture of invertomers), the decalin region in the ^{1}H spectra is very complicated and not interpretable in terms of diastereomeric complexes formed by enantiomeric invertomers with *β*-CD as a host.

The completely different appearance of the decalin signals of free and complexed species seems to indicate that immersion of the protons of the guest molecule into the CD cavity significantly changes their environment. The protons of two decalin enantiomers in the complex seem to behave in a different way at low temperature leading to a spectrum much richer in information than that of free **2**. This could imply deformation of the guest molecule invertomers upon the complex formation analogous to those found in substituted cyclohexanes[6] which, in principle, could be detected by the study of coupling constants (especially those through three bonds–^{3}J) in the system. Unfortunately, phase-sensitive COSY experiment for the complex yielded a picture too complicated to be interpretable.

Interestingly, heteronuclear COSY at 223 K yielded only one double cross peak at 1.64 and 1.65 ppm interrelating the signals of the C9, C10 carbon atoms (in diastereomeric complexes formed by the *cis*-decalin invertomers **2a** and **2b** with *β*-CD) with the H9 and H10 protons. This finding is in line with a few literature NMR observations of chiral discrimination by cyclodextrins.[1,8–10]

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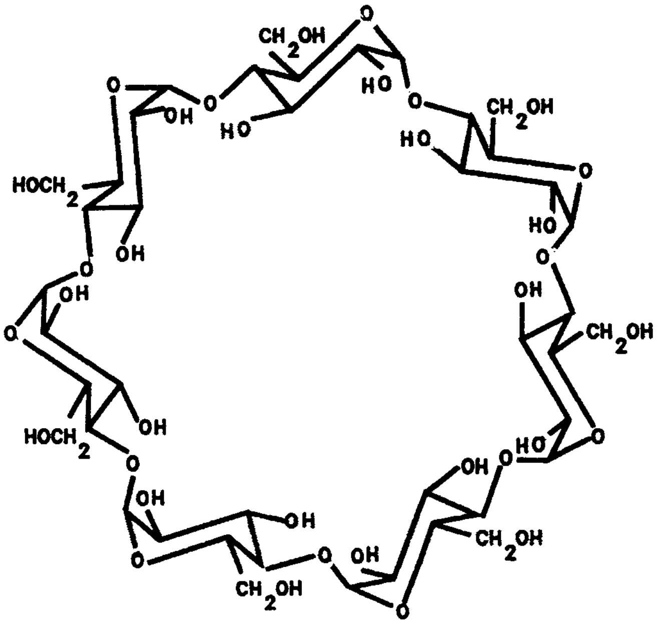
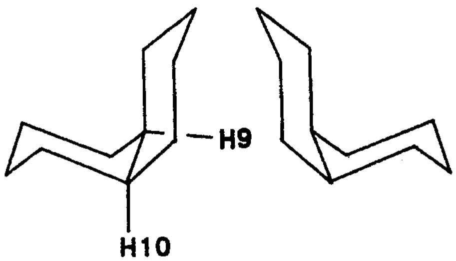
* To whom correspondence should be addressed.



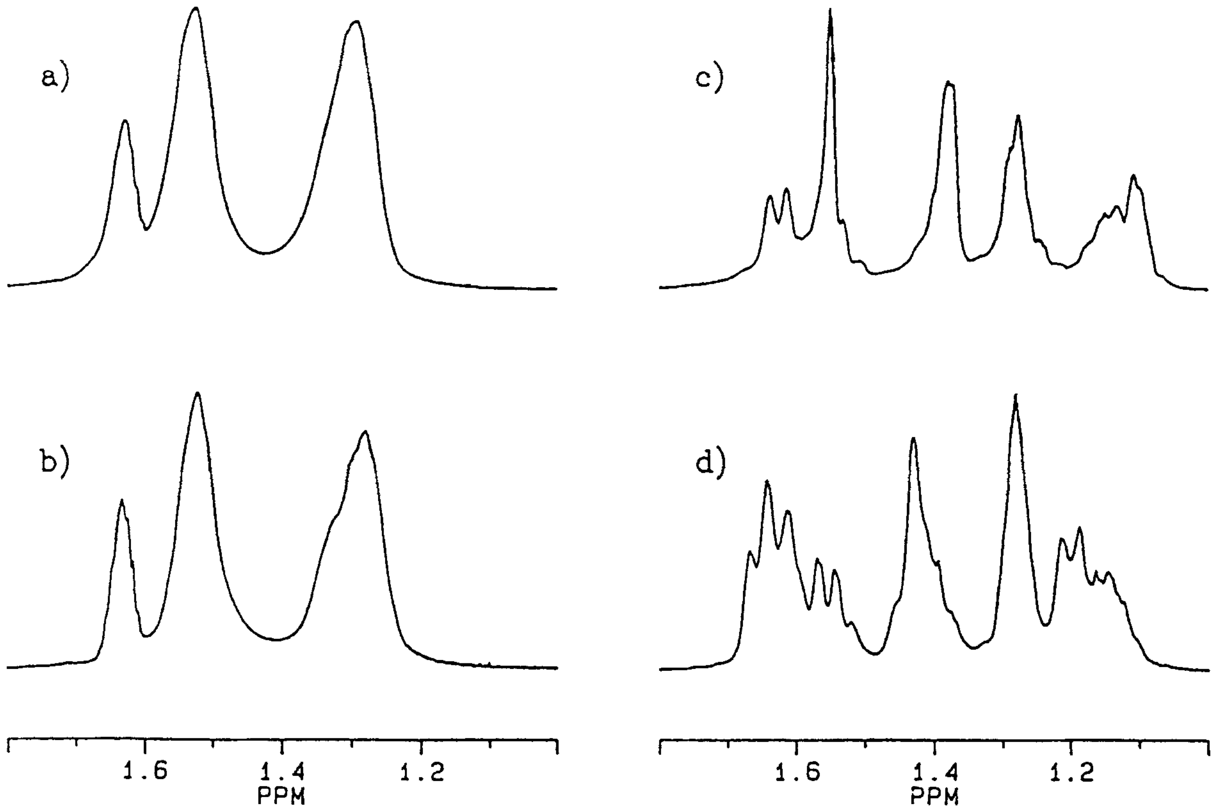
beta-cyclodextrin 1



2a 2b

cis-decalin

trans-decalin 3



^{1}H NMR spectra of the decalin region of (a) free *cis*-decalin and (b) the complex at room temperature and (c) free *cis*-decalin and the complex at 233 K.

EXPERIMENTAL

Spectra were measured on a Bruker AM-500 spectrometer operating at 500.13 MHz for ^{1}H NMR equipped with a standard variable temperature unit. The standard conditions were: acquisition time 6 sec, pulse duration 10 μsec (60° flip angle), number of scans 30 for each spectrum.

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6 Curtis, J.; Grant, D.M.; Pugmire, R.J.; *J. Am. Chem. Soc.* **1989**, *111*, 7711. Room temperature ^{2}H NMR spectrum of *cis*-decalin reported in this paper reveals five signals instead of the three expected by close similarity of proton and deuterium spectra. These signals have been interpreted in terms of separation of axial and equatorial deuterium signals at room temperature. The latter seems improbable in view of the low inversion barrier of cyclohexane rings in **2**, the study in ref. 5 and results obtained in our group to be published later.

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