

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

Structure of cyclodextrins and their complexes. Part 5.¹ The NMR observation of separate signals of host and guest pertaining to 1 : 1 and 1 : 2 complexes of acenaphthene with β -cyclodextrin

Helena Dodziuk^a; Jerzy Sitkowski^a; Lech Stefaniak^a; Danuta Sybilska^b; Janusz Jurczak^a

^a Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Kasprzaka, Poland ^b Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Kasprzaka, Poland

To cite this Article Dodziuk, Helena , Sitkowski, Jerzy , Stefaniak, Lech , Sybilska, Danuta and Jurczak, Janusz(1996) 'Structure of cyclodextrins and their complexes. Part 5.¹ The NMR observation of separate signals of host and guest pertaining to 1 : 1 and 1 : 2 complexes of acenaphthene with β -cyclodextrin', *Supramolecular Chemistry*, 7: 1, 33 – 35

To link to this Article: DOI: 10.1080/10610279608054993

URL: <http://dx.doi.org/10.1080/10610279608054993>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Structure of cyclodextrins and their complexes. Part 5.¹ The NMR observation of separate signals of host and guest pertaining to 1 : 1 and 1 : 2 complexes of acenaphthene with β -cyclodextrin

HELENA DODZIUK^a, JERZY SITKOWSKI^a, LECH STEFANIAK^a, DANUTA SYBILSKA^b and JANUSZ JURCZAK^a

^aInstitute of Organic Chemistry, ^bInstitute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44, Poland, e-mail dodziuk@ichf.edu.pl

(Received February 3, 1995)

In addition to usual shifted signals pertaining to the 1 : 1 complex, separate signals of a 1 : 2 complex of acenaphthene with β -cyclodextrin were observed in proton NMR spectra at low temperatures.

Hydrocarbons are the guests of choice for the study of driving forces of the complex formation with cyclodextrins, CDs. On the basis of chromatographic studies of molecules 1–3, we have recently found² that acenaphthene, 2, and 1,8-dimethylnaphthalene, 3, form unusually strong complexes with β -CD, 4. The stability constant of the complexes with 2 and 3 (ca. 500 M^{-1}) was approximately 100 times larger than the corresponding value for 1,3-dimethylnaphthalene, 1b. ¹H NMR spectra presented in this communication show atypical manifestations of the complex formation of 2 with 4, consisting in the appearance of separate signals of a 1 : 2 complex in which two CD molecules engage the guest.

The exchange rate between the free and complexed species is considered to be too fast to be observed on the NMR time scale.³ Thus, the typical behavior of the CD complexes manifests itself in shifts of the host and guest signals with no dynamic behavior and no new signals observed.⁴ To our knowledge, the only case when additional signals of the complex were reported in the literature refers to the rotaxane-type CD complexes.⁵ In contrast with the typical behavior, two groups of host and guest signals appear in the spectrum of the complex of 2

and 4 at low temperatures, presented in Figure 1g and 1h in comparison to the corresponding spectra of the free guest (Figure 1a) and that of the free host (Figure. 1b) measured at room temperature. The intensity of the additional signals observed at low temperatures was found to depend on the concentration of the host and guest. Therefore, the measurements of the guest signals were carried out with considerable excess of the host ($c_{\text{host}} = 0.116 \text{ M/L}$, $c_{\text{guest}} = 0.017 \text{ M/L}$) and vice versa ($c_{\text{host}} = 0.025 \text{ M/L}$, $c_{\text{guest}} = 0.170 \text{ M/L}$). By studying the shifts of the signals at 4.432 ppm for the host and of that at 6.789 ppm (the average of 6.796 and 6.782 ppm) for the guest as a function of the relative concentration of the host and guest, "Job curves"⁶ (exemplified in Figure 2) were obtained. The parabolic curves exhibit maxima for the 1 : 1 concentrations of the host and guest, clearly indicating the existence of the 1 : 1 complex in solution. By integrating, the additional signals at 7.021 ppm tentatively assigned to H2' (for the guest) and that at 6.289 ppm (for the host) were found to correspond to the 1 : 2 complex of 2 and 4, respectively. On the basis of its shape (poorly resolved doublet of doublets), the signal with the center at ca. 7.38 ppm was assigned to H3' protons. A considerable shift of this signal upon complexation (larger than 0.4 ppm) is larger than the usually observed shifts. It can be explained by the fact that the shifts reported in the literature refer to the average of free and 1 : 1 complexed species while the one discussed here corresponds to the pure 1 : 2 complex with the strongly interacting CD molecules. NOE experiment could pro-

*To whom correspondence should be addressed.

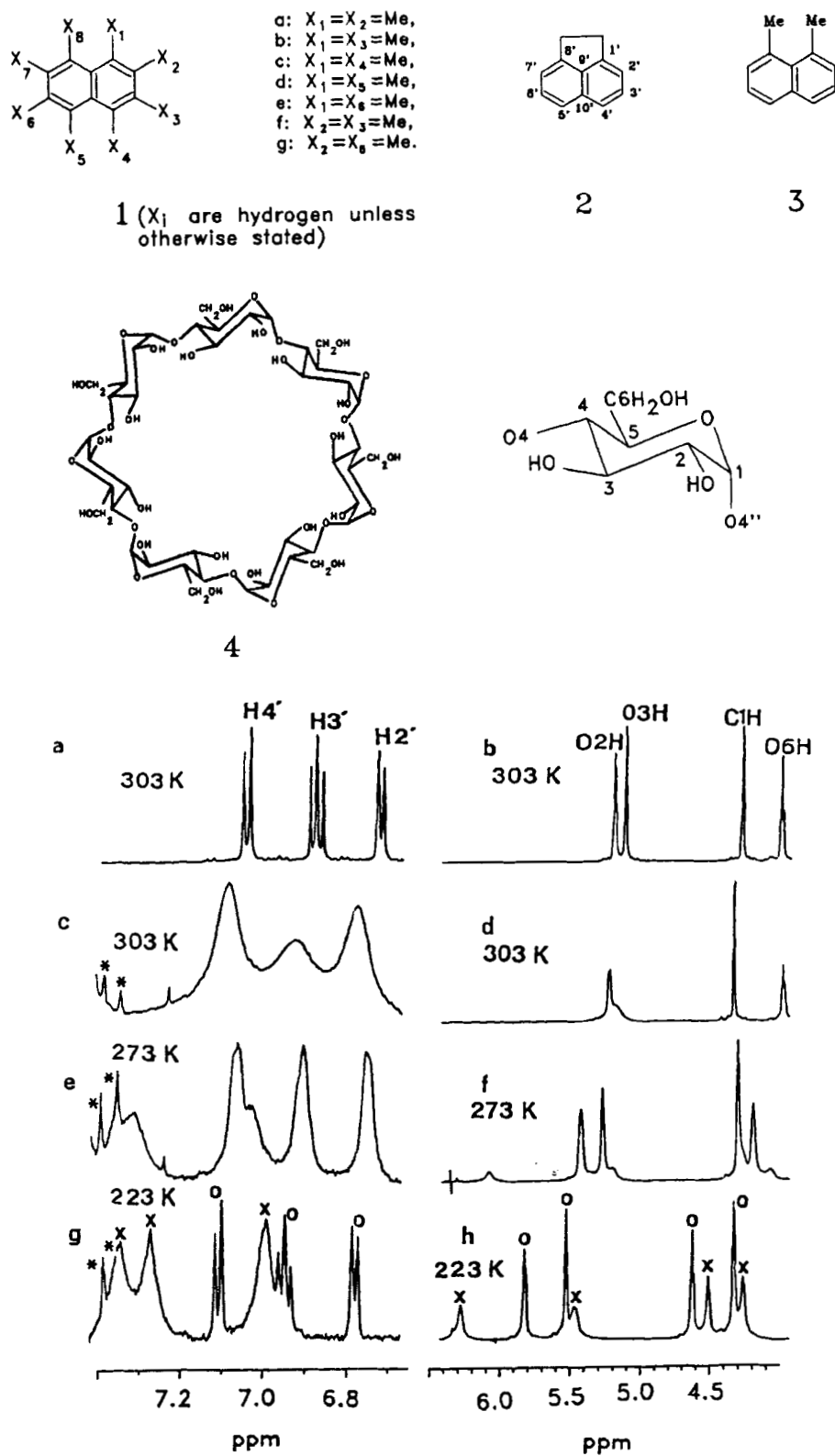


Figure 1 ^1H NMR spectra of acenaphthene, 2, and β -CD, 4, and their complex in DMF- d_7 solutions at various temperatures. (a) The region of aromatic protons of the free guest. (b) The region of the hydroxylic and anomeric protons of the host. (c-h) The corresponding spectral regions for the complex of 2 and 4. Note that the host region spectra (c, e, g) were recorded with an excess of the guest, while for the guest signals (spectra d, f, h) an excess of the host was used. The specific concentrations are given in the text. The "x" symbols denote signals pertaining to the 1 : 2 complex while the "o" ones refer to the average signals of the free species and 1 : 1 complex. The broad signal at ca. 7.32 ppm is obscured by the solvent signals.

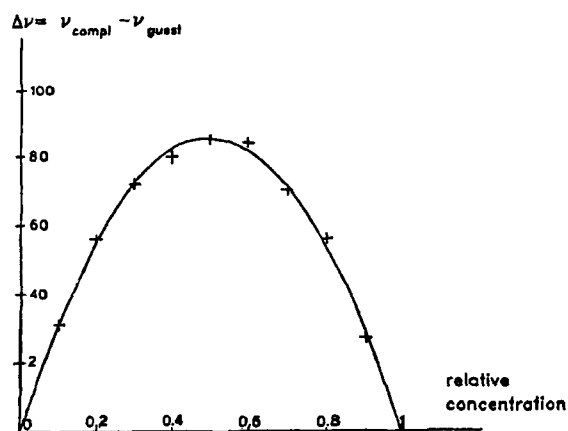


Figure 2 The "Job plot" for the H1 signal of the host at 303 K. Analogous plots have been obtained for the H4' guest signal at both 303 and 243K, as well as for the signal of the anomeric proton of β -CD at 243K.

vide the information on the position of the guest inside the cage formed by two CD molecules in the 1 : 2 complex. However, these proved unsuccessful, probably due to the high mobility of the guest (which is revealed by the breadth of the complex signals). Therefore, a tentative view of the latter complex is depicted in Figure 3. It should be stressed that our results are inconclusive as concerns the presence of the solvent molecule in both the 1 : 1 and 1 : 2 complexes. We were not able to solve this problem by an X-ray study since we were not able to obtain crystals of the complex of **2** and **4**.

The CD complexes with 1 : 2 stoichiometry were documented in the literature on the basis of thermochemical and photochemical measurements.⁷ To our knowledge, this is the first NMR observation of such a complex.

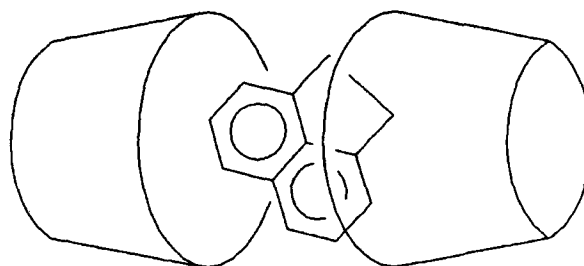


Figure 3 A schematic view of the 1 : 2 complex of **2** and **4**. Courtesy of VCH Publishers, New York.⁸

REFERENCES

- Former parts of the series: H. Dodziuk, J. Sitkowski, L. Stefaniak J. Jurczak, D. Sybilska, *J. Chem. Soc. Chem. Commun.*, (1992) 207; H. Dodziuk, J. Sitkowski, L. Stefaniak J. Jurczak, D. Sybilska, *Supramolecular Chemistry*, 3 (1993) 79; H. Dodziuk, K. Nowinski, *J. Mol. Struct. THEOCHEM*, **304** (1994) 61; H. Dodziuk, D. Sybilska, S. Miki, Z. Yoshida, J. Sitkowski, M. Asztemborska, A. Bielejewska, J. Kowalczyk, K. Duszczczyk, L. Stefaniak, *Tetrahedron*, **50** (1994) 3619.
- D. Sybilska, M. Asztemborska, A. Bielejewska, J. Kowalczyk, H. Dodziuk, K. Duszczczyk, H. Lamparczyk, P. Zarzycki, *Chromatographia*, **35** (1993) 637.
- Y. Kotake, E. G. Janzen, *J. Am. Chem. Soc.*, **110** (1988) 3699.
- a. Y. Yamamoto, Y. Inoue, *J. Carbohydr. Chem.*, **8** (1989) 29, Only papers of this group are reviewed there;
4b. F. Djedaini, F. Perly, "Nuclear Magnetic Resonance of Cyclodextrins, Derivatives, and Inclusion Compounds", Chapter 6 in "New Trends in Cyclodextrins and Derivatives", D. Duchene, Ed., Editions de Sante, Paris, France, 1991.
- H. Yonemura, M. Kasahara, H. Saito, H. Nakamura, T. Matsuo, *J. Phys. Chem.*, **96** (1992) 5765; M. Watanabe, H. Nakamura, T. Matsuo, *Bull. Chem. Soc. Jpn.*, **65** (1992) 164.
- P. Job, *Ann. Chim.*, **9** (1928) 113, see also ref. 4b.
- D. Jobe, R. E. Verall, R. Palepu, V. C. Reinsborough, *J. Phys. Chem.*, **92** (1988) 3582; K. Takahashi, *J. Chem. Soc., Chem. Commun.* (1991) 929; N. Sarkar, K. Das, D. Nath, K. Bhattacharyya, *Chem. Phys. Lett.*, **196** (1992) 491.
- H. Dodziuk, "Modern Conformational Analysis. Elucidating Novel Exciting Molecular Structures", VCH Publishers, New York, to appear in Fall 1995.