

Solvates of the Cyclohexatrylene Tetramer as Studied by Solid State ^{13}C NMR

N. E. BURLINSON* and J. A. RIPMEESTER**

Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada

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Abstract. The cyclohexatrylene tetramer was found to form well-defined solvates with chloroform and methylene chloride which were characterized by their solid state ^{13}C NMR spectra. Elemental analysis indicates the presence of two molecules of included solvent for every host molecule. Several distinct forms of the solvent-free tetramer were identified as well.

Key words: Cyclohexatrylene tetramer, solid state ^{13}C NMR.

1. Introduction

In a previous paper we investigated inclusion compound formation by cyclotrimeratrylene [1]. As the major structural feature responsible for the inclusion properties appears to be the presence of flexible methoxy groups on a large ring system [1,2] molecules such as the cyclohexatrylene tetramer might also be expected to form solvates or inclusion compounds.

In this study we use ^{13}C NMR to investigate solid inclusion compound formation by cyclotetraatrylene and report ^{13}C NMR spectra for the solvent-free material as well.

2. Experimental

Cyclotetraatrylene was the main by-product of the dehydration of veratryl alcohol to produce the cyclohexatrylene trimer [1,3]. Separation of the trimer and tetramer was facilitated by the limited solubility of the tetramer in solvents such as acetone. The tetramer was characterized by its ^1H NMR and mass spectrum [4].

The tetramer was obtained from the reaction as a feathery white solid which dissolved easily in chlorinated solvents such as methylene chloride and chloroform. The nature of the recrystallization product depended very much on the temperature of the solution. Evaporation of hot solutions of the tetramer in the two aforementioned solvents consistently yielded well-formed crystals, whereas cold solutions always deposited materials much like the original crude reaction product.

Results of an elemental analysis on the solvated crystals are shown in Table I. ^{13}C NMR solid state spectra were obtained on Bruker CXP-180 or CXP-200 NMR spectrometers.

* On a study leave from Dept. of U.S. Navy, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, MD 20910, U.S.A.

** On study leave from Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R9. Author for correspondence.

Table I. Elemental analysis of cycloveratrylene tetramer solvates

Solvent	Experimental		Calculated		
	%C	%H	%C	%H	
CHCl ₃	55.13	5.08	54.36	5.06	CTV · 2CHCl ₃
CH ₂ Cl ₂	60.80	5.82	59.22	5.77	CTV · 2CH ₂ Cl ₂

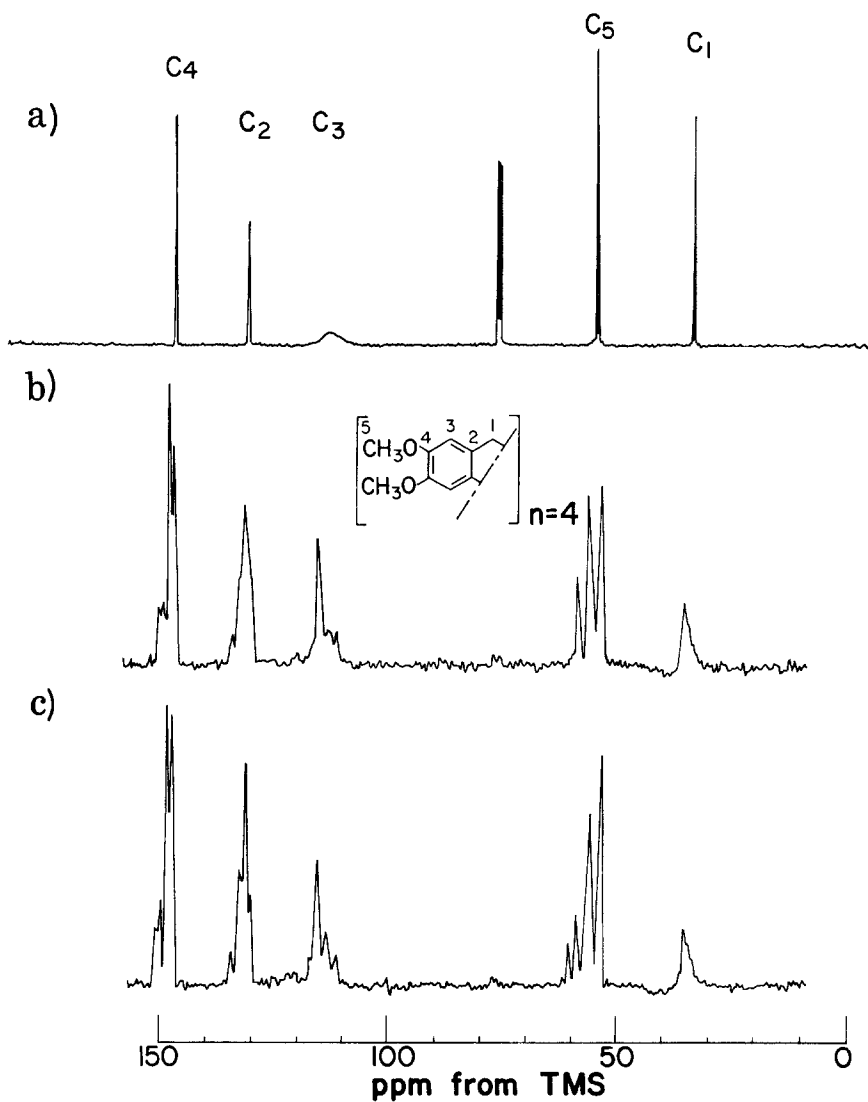


Fig. 1. (a) ¹³C NMR spectrum of the cycloveratrylene tetramer in CDCl₃ solution; (b) Solid state ¹³C NMR spectrum of the cycloveratrylene tetramer crude reaction product. (c) Same as (b) but heated at 150° C for several hours.

Experimental details have been given before [5], except that the first order sideband suppression technique of Hemminga and de Jager [6] was incorporated into the experiments. Solution NMR spectra were obtained on Bruker WP-80 and WH-400 NMR spectrometers.

3. Results and Discussion

Figure 1a shows the ^{13}C NMR spectrum of the cycloveratrylene tetramer in solution. A simple five-line spectrum results because of high symmetry of the dissolved molecule. The C_3 line is much broader than the other lines, and decreases in width with increasing temperature,

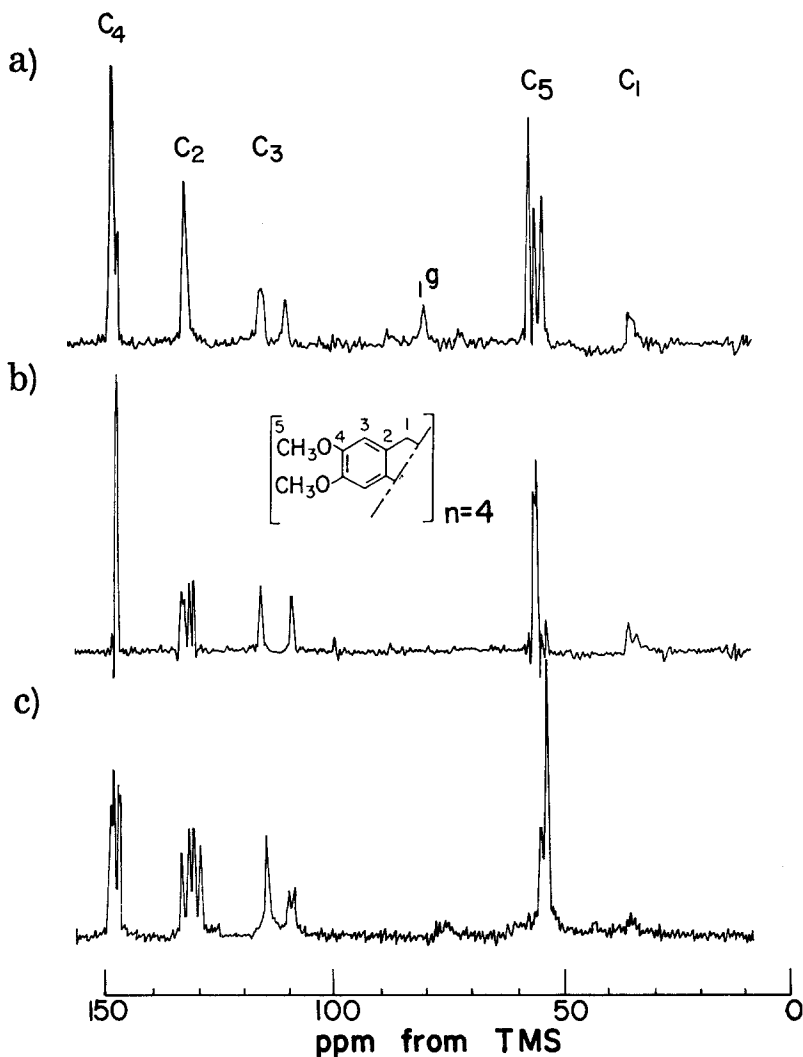


Fig. 2. Solid state ^{13}C NMR spectrum of cycloveratrylene tetramer. (a) Chloroform solvate, g = guest molecule resonance, (b) methylene chloride solvate; (c) shows (a) or (b) after heating at 130°C for several hours.

suggesting the presence of a chemical exchange process. A preliminary temperature dependent study of the ^1H NMR spectrum showed that all ^1H lines doubled at $\sim -30^\circ\text{C}$ (on the WP-90 spectrometer), so that the room temperature spectrum is indeed characteristic of rapidly interconverting conformers.

The solid tetramer as dried reaction product gives the spectrum shown in Figure 1b. Each carbon resonance is now characterized by a partially resolved multiplet, so that the molecule has lost its high symmetry characteristic of the dissolved state. The complex nature of the multiplets does not suggest any simple packing of the unit cell, and indeed the spectrum may well reflect the presence of several solid phases. Heating to 150°C for several hours induces several marked changes in the spectrum including a sharpening of the spectral features of the C_2 , C_3 , and C_4 lines, and the appearance of an extra line in the C_5 multiplet. This suggests that there may be some conformational mobility.

The crystalline material obtained by recrystallizing the tetramer from hot chloroform gave the ^{13}C NMR spectrum shown in Figure 2a. The spectrum of the host lattice is relatively simple, and probably reflects a unit cell where half of the tetramer is the asymmetric unit. The guest chloroform carbon is clearly visible at ~ 70 ppm. The spectrum of the solid tetramer containing methylene chloride as guest is shown in Figure 2b. The host lattice spectrum is again relatively simple, indicating a unit cell where half a molecule is the asymmetric unit. The methylene chloride carbon is not evident unfortunately. This may be because the carbon has partially averaged dipolar coupling with two chlorine nuclei in the methylene chloride molecule.

When either solvate is heated at 130°C for several hours, a guest-free material is obtained which gave the spectrum shown in Figure 2c. From the multiplicity of the C_2 and C_4 carbons, again the asymmetric unit is half a molecule. This form of the solid tetramer is quite different from that obtained as the original reaction product.

Other solvates of the cyclohexatriene tetramer could not be prepared in a consistent way. In one instance a form containing benzene was prepared which gave a ^{13}C spectrum very similar to the chloroform solvate, but it decomposed shortly after preparation. Several other solvents were tried as well, but consistent results were not obtained.

Only chloroform and methylene chloride gave well defined reasonably stable solvates. From the elemental analysis (Table I) it is evident that there are two solvent molecules for every host molecule, the small discrepancy arising from a loss of solvent. The exact nature of the solvates, i.e., whether these are clathrates or channel inclusions must await structural studies.

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