



# High pressure promoted exchange of guests from hemicarceplexes



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## ABSTRACT

Application of extremely high pressures on dimethylacetamide (DMA) hemicarceplexes promotes DMA extrusion and replacement with a solvent molecule at room temperature. Molecular dynamics study of decomplexation of hemicarcerands indicates that favored mechanistic process involves a single-step exchange of DMA with a solvent molecule.

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## 1. Introduction

Hemicarcerands designed by Cram<sup>1</sup> are a unique class of supramolecular host molecules, which could be regarded as a new type of reactive medium in which guest molecules are isolated from the environment and their physico-chemical properties are affected by hemicarcerand walls.<sup>2,3</sup> A number of guest molecules were encapsulated and studied within such containers.<sup>4</sup> A hemicarcerand/guest complex is termed a hemicarceplex when the residence time of a guest within the cavity of the host is such that the complex can be physically characterized.<sup>5</sup> Hemicarceplexes are prepared in a controlled manner by the replacement of template molecule by the addition of an appropriate guest after the container cavity has been formed with the aid of templating molecule (such as DMA or pyrazine).<sup>6</sup> The closely related carceplex is a variety of container molecule where the guest remains permanently incarcerated on synthesis. Prolonged heating in high boiling point solvents such as diphenyl ether is usually required for template removal and guest incarceration to empty container.

Guest could be also incarcerated by the aid of high pressure. Extremely high pressures were applied in several supramolecular studies<sup>7</sup> and in one case to hemicarcerands. Klärner reported that on heating at 110 °C under 11.5 kbar pressure for 3 days in CH<sub>3</sub>CN as

solvent, the hemicarceplex with two acetonitrile guests, (CH<sub>3</sub>CN)<sub>2</sub>@4<sup>8</sup> does not release CH<sub>3</sub>CN and a new complex is formed<sup>9</sup> assigned to incorporate three acetonitrile molecules, which reverts back to (CH<sub>3</sub>CN)<sub>2</sub>@4 within 1 h at atmospheric pressure at 55 °C. Related use of pressure to force encapsulation of small molecules in an open-cage fullerene derivative was reported by Komatsu, Murata<sup>10–12</sup> and Rubin.<sup>13</sup>

Our initial work with hemicarceplexes was focused on the developing a method for predictions of stability of these molecules using semiempirical calculations.<sup>14</sup> With the help of such a predictive computational tool, we were able to single out and encapsulate various guests in hemicarcerands **1–3** (Fig. 1). We report

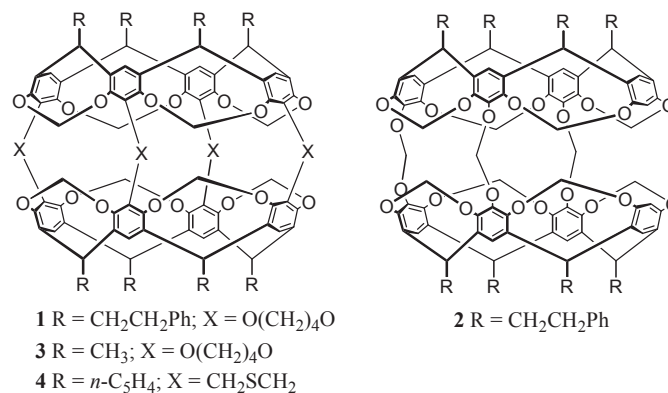


Fig. 1. Hemicarcerands **1–4**.

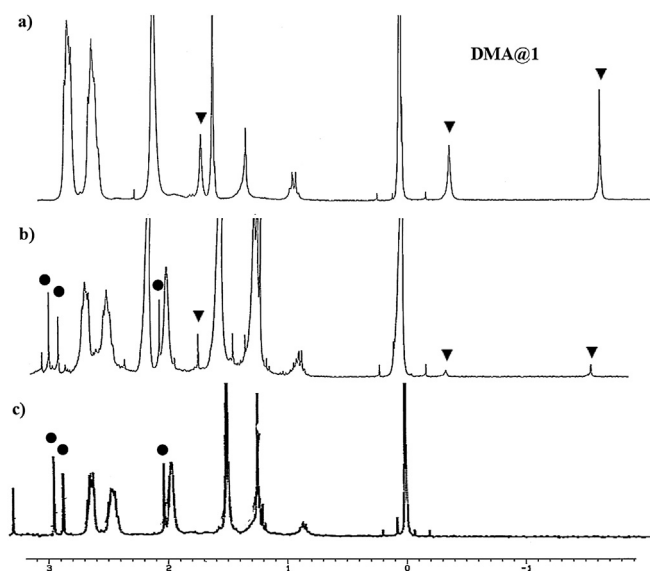
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herein results of host–guest studies of selected hemicarceplexes under high pressure.

## 2. Results and discussion

In order to study the pressure effects on complexation properties of prepared hemicarceplexes, we subjected **DMA@1**<sup>15</sup> under extremely high pressure of 14 kbar at room temperature. In such conditions, an interesting physical phenomenon was observed: when solution of **DMA@1** in CH<sub>2</sub>Cl<sub>2</sub> was pressurized, decomplexation of DMA occurred.

This result was proven by conducting high-pressure experiments in CD<sub>2</sub>Cl<sub>2</sub> at 14 kbar for 24 h at room temperature, followed by an immediate <sup>1</sup>H NMR analysis (Fig. 2). In such conditions, total removal of incarcerated DMA was achieved, as indicated by disappearance of the incarcerated guest resonances below tetramethylsilane (singlets at  $\delta$  –0.41 and –1.63).<sup>16</sup> At lower pressure (8 kbar), only partial extrusion of DMA was achieved after 24 h. Due to fast complexation/decomplexation of CH<sub>2</sub>Cl<sub>2</sub> at 25 °C<sup>15</sup> the true nature of the hemicarceplex after pressurization could not be determined (i.e., ‘empty’ **1** or the number of CH<sub>2</sub>Cl<sub>2</sub> molecules in **DCM<sub>n</sub>@1** hemicarceplex) by <sup>1</sup>H NMR spectroscopy. Formation of **DCM<sub>n</sub>@1** could be postulated from the chemical shift of inner OCH<sub>2</sub>O appearing at  $\delta$  4.11, which slightly differs in comparison with the literature value for ‘empty’ **1** ( $\delta$  4.30). However, elemental analysis confirmed the formation of ‘empty’ **1**, which was found to have incarcerated one molecule of water.<sup>15</sup> The ‘empty’ **1** could be effectively prepared from **DCM<sub>n</sub>@1** by drying in high vacuum or long standing. From these results it is evident that high pressure effectively promotes decomplexation of DMA. In fact, DMA was initially replaced by CH<sub>2</sub>Cl<sub>2</sub>, as we have later shown by MD studies. This result is at variance with the high stability of **DMA@1** at atmospheric pressure (decomplexation barrier of 23.5±1.5 kcal mol<sup>–1</sup>),<sup>15,17</sup> showing that the change of physical conditions (in this case applying high pressure) altered the behavior of the hemicarceplex. The opposite process, encapsulation of DMA in ‘empty’ **1** (DMA, 6 kbar, rt, 3 d), is much less efficient affording **DMA@1** in 10% yield, which could be explained in part by



**Fig. 2.** Partial <sup>1</sup>H NMR spectra (300 MHz, 25 °C) of solution of **DMA@1** in CD<sub>2</sub>Cl<sub>2</sub> before (a) or after pressurization (14 kbar) for 3 h, 25 °C (b) and 24 h, 25 °C (c). Spectra were recorded after the solution used in the experiment was exposed to atmospheric pressure. Signals assigned to protons of incarcerated and free DMA are indicated with ▼, and ●, respectively.

lower pressure applied in comparison to decomplexation experiment.

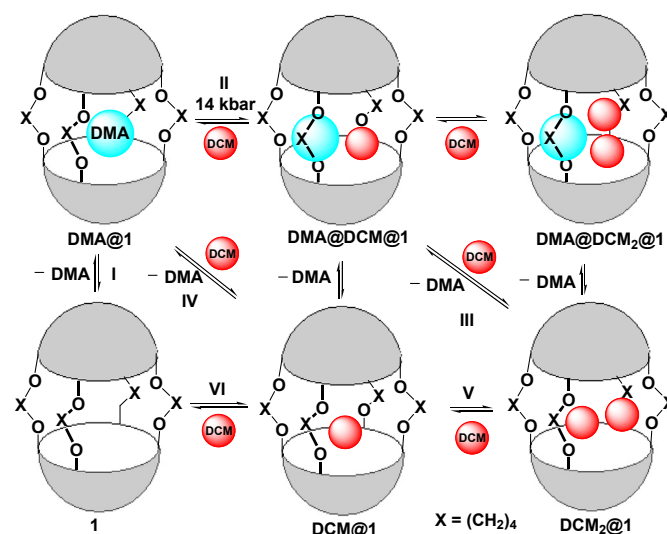
Although there is precedent work on the application of extremely high pressure on host/guest complexation, as far as we are aware, this is the first account on the decomplexation or guest exchange promoted by high pressure.

Further high-pressure decomplexation experiments of **DMA@1** revealed that other small solvent molecules could be used to extrude DMA (for details see [Supplementary data](#)). For instance, acetonitrile (6 kbar, 80 °C, 18 h) expels DMA, but no incarcerated MeCN was detected spectroscopically. Similarly, CH<sub>2</sub>Br<sub>2</sub> extrudes 65% of DMA upon pressurization (6 kbar, rt, 4 d). On the other hand, acetone (6 kbar, rt, 18 h) induced partial incarceration clearly evidenced by <sup>1</sup>H NMR spectroscopy (indicative peak resonance singlet at  $\delta$  –0.81). Additional pressurization for 4 days in acetone led to 95% DMA extrusion and replacement by acetone. In an analogous experiment, ethyl iodide (6 kbar, rt) was encapsulated after 7 days, and 65% of DMA was replaced by ethyl iodide (<sup>1</sup>H NMR peak resonance triplet at  $\delta$  –1.31).

Furthermore, an attempt to exchange DMA from **DMA@3** with *p*-dibromobenzene in CH<sub>2</sub>Cl<sub>2</sub> at 14 kbar (24 h, rt) stopped after DMA decomplexation (i.e., CH<sub>2</sub>Cl<sub>2</sub> complexation), and no incarceration of *p*-dibromobenzene could be spectroscopically detected. We assume that this observation is associated with the larger size of *p*-dibromobenzene guest in comparison with CH<sub>2</sub>Cl<sub>2</sub>.

Finally, high-pressure decomplexations of hemicarceplexes **DMA@2**<sup>18</sup> (3 d) and **furan@2** (24 h) were unsuccessful at 8 kbar in CH<sub>2</sub>Cl<sub>2</sub> (rt). These results can be explained by kinetic effects (i.e., increase of the barrier height) on complexation/decomplexation in the case of carcerand **2** (associated with smaller internal volume and smaller equatorial portals in comparison to **1** and **3**).

The reaction mechanism of host–guest incarceration in hemicarceplexes was previously studied computationally with molecular mechanics (AMBER)<sup>19</sup> and semiempirical methods (AM1)<sup>14</sup> where energetic barriers for guest complexation/decomplexation were calculated. Decomplexation observed experimentally is an unexpected result, since high pressure promotes condensation reactions and complexations, processes which have large negative volumes of activation.<sup>20</sup> The explanation of the process was sought computationally and possible mechanistic pathways are illustrated in [Scheme 1](#).



**Scheme 1.** Mechanism of high-pressure host–guest exchange in hemicarceplex **DMA@1**.

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