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NMR study of the reversible complexation of xenon by cucurbituril

Mustapha El Haouaj,[a] Michel Luhmer,[a] Young Ho Ko,[b] Kimoon Kim[b] and Kristin Bartik[a] *

[a] *Laboratoire de Chimie Organique E.P. (CP165/64), Université Libre de Bruxelles,*
50 Avenue F. D. Roosevelt, 1050 Bruxelles, Belgium. E-mail: kbartik@ulb.ac.be
[b] *National Creative Research Initiative Center for Smart Supramolecules and Department of*
Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and
Technology, San 31 Hyojadong, Pohang 790-784, South Korea

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The interaction of xenon with cucurbituril, a synthetic receptor, in aqueous solutions is investigated by ^{129}Xe and ^{1}H NMR spectroscopy. Xenon is reversibly trapped into the cavity to form a 1 : 1 host–guest complex. The exchange between the free and the complexed xenon is slow on the ^{129}Xe NMR chemical shift time scale but fast on the ^{1}H NMR chemical shift time scale. The apparent association constant of xenon for cucurbituril can be obtained from analysis of the ^{1}H spectra and is estimated to be around 200 M^{-1} at 298 K. Interestingly, even though no H-bonding or electrostatic interactions play a role in the stabilisation of the complex, its stability is comparable to the stability of cucurbituril complexes with certain aryl- and alkyl-ammonium ions.

Introduction

Xenon (Xe) is a highly polarisable, rather inert but hydrophobic atom which has a van der Waals radius of approximately 2 Å. Two xenon isotopes are easily accessible to NMR spectroscopy: ^{129}Xe ($I = 1/2$, natural abundance of 26.4%) and ^{131}Xe (3/2, 21.2%).[1] The NMR parameters of these isotopes are very sensitive to the environment of the xenon atom and considerable work has capitalised on their utility as probes of the structural and dynamic properties of host–guest complexes.[2,3]

Much of the Xe NMR work reported in the literature focuses on the use of ^{129}Xe chemical shifts to study microporous materials.[2,4] Few studies relate to xenon–host complexes in solution. Cram and co-workers have shown that xenon, like other gases, can be trapped by hemicarcerands[5] and they have proposed the term "constrictive binding" to describe the phenomenon where the guest must overcome steric constraints imposed by the host portals in order to enter and leave the host. Rebek and co-workers have captured xenon within the cavity of dimeric hosts which self-assemble in chloroform solution by complementary H-bonding.[6] In this case, the capture and release of the guest involves the breaking and re-formation of the dimeric host itself. We have shown that xenon can be complexed by α-cyclodextrin[7] and cryptophane-A[8] and that it is possible, using ^{129}Xe NMR, to obtain quantitative information concerning xenon complexation by host systems in solution. These studies have contributed to a deeper understanding of host–guest interactions in molecular host systems. They also provide good models for host–guest systems that do not owe their existance to H-bonding or electrostatic interactions.

In the present paper, we report a quantitative ^{1}H and ^{129}Xe NMR study of the reversible complexation of xenon by cucurbituril (CB) in aqueous solutions. CB is a cage compound of hexagonal symmetry which has a hollow core of approximately 5.5 Å diameter (Fig. 1).[9] The interior of the molecule is hydrophobic and is accessible from the exterior through two carbonyl-fringed portals of 4 Å diameter. Its easy synthesis and hollow structure make CB an attractive synthetic receptor. CB is soluble in strongly acidic solutions and also in neutral aqueous solutions in the presence of alkali metal ions.[10,11] Extensive studies have been undertaken on the host–guest interaction between CB and various alkyl- and aryl-ammonium ions in very acidic aqueous solutions.[12,13] Conclusive evidence for the formation of 1 : 1 complexes with internal complexation of the alkyl or aryl moiety has been obtained by NMR and UV spectroscopy. The successful inclusion is attributed to the hydrophobic forces which lead the hydrophobic alkyl or aryl moiety to enter the cavity with an associated gain of entropy, due to the "freeing" of the water molecules which solvate the hydrophobic groups of the guest and the host. The stabilisation of the complex is also attributed to the charge–dipole attraction between the ammonium cation and the dipoles associated with the carbonyl groups of the urea moieties in cucurbituril. The only studies undertaken on the inclusion of substances without an ammonium functionality are those reported by one of us (K. K.) which show that tetrahyrofuran (THF), cyclopentanone, furan and benzene form 1 : 1 complexes with CB in 0.2 M Na_2SO_4 aqueous solutions.[10] The results reported in this paper confirm once again the importance of London energies in the stabilisation of the host–guest complexes in solution.

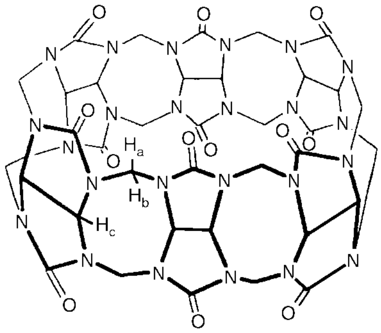

Fig. 1 Structure of cucurbituril (CB) with atom labelling.

Results and discussion

^{129}Xe and ^{1}H NMR spectra of a 2×10^{-2} M solution of cucurbituril (CB) in 0.2 M Na_2SO_4–D_2O (pH = 2.2) containing increasing amounts of xenon were recorded at 298 K on a AMX360 spectrometer. At first the ^{129}Xe spectrum exhibits a

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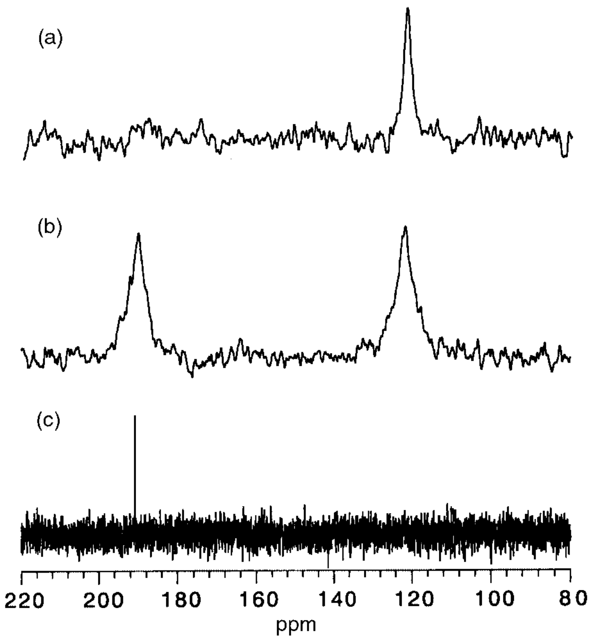

Fig. 2 ^{129}Xe NMR spectrum at 298 K of xenon dissolved in: (a) a solution of cucurbituril in 0.2 M Na_2SO_4–D_2O with $nXe/V_l = 0.05$ M; (b) a solution of cucurbituril in 0.2 M Na_2SO_4–D_2O with $nXe/V_l = 0.47$ M; (c) 0.2 M Na_2SO_4–D_2O. nXe is the total number of moles of xenon and V_l is the volume of the liquid phase in the sealed NMR tube.

single resonance line at 122 ± 0.5 ppm (Fig. 2a). As the amount of xenon is increased, a second resonance line appears at 190 ± 0.5 ppm (Fig. 2b) which corresponds to the position of the xenon resonance line in the solvent (Fig. 2c). This indicates that encapsulation of xenon in the CB cavity occurs, and that the exchange process is sufficiently slow on the xenon NMR chemical shift time scale to see the NMR resonance lines corresponding to both the complexed and the uncomplexed xenon. The linewidth of the resonance corresponding to the complexed xenon increases in a linear manner with the amount of dissolved xenon (from around 200 to about 800 Hz) while the linewidth of the resonance line of the uncomplexed xenon varies in a random manner between 450 and 600 Hz. The dependence of the linewidth of the complexed xenon on the xenon concentration indicates that the exchange process is more complex than the simple equilibrium: $CB + Xe \rightleftharpoons CB\text{–}Xe$. Indeed, for such a process in slow exchange it is expected that the linewidth of the bound xenon is independent of xenon concentration.[14] As in the previously reported study of xenon complexation by cryptophane-A[8] it is possible that an exchange process corresponding to the displacement of xenon by xenon also takes place ($CB\text{–}Xe + Xe^* \rightleftharpoons CB\text{–}Xe^* + Xe$). For such a process the linewidth of the complexed xenon is expected to be proportional to xenon concentration. Unfortunately, due to the poor signal-to-noise ratio of the xenon spectra we are not able to extract the xenon linewidths with the precision required for a quantitative analysis. Furthermore, it impossible to obtain the ^{129}Xe chemical shifts with a precision better than 0.5 ppm.

The long T_1 relaxation times of dissolved xenon[3,15] and the eventual difference in the T_1 of the uncomplexed and complexed xenon make it extremely difficult to determine, from integration of the xenon spectra, the analytical concentration of xenon in the solution and the ratio of the complexed to uncomplexed xenon. It is therefore impossible to determine with accuracy the affinity constant of CB for xenon from data in ^{129}Xe NMR spectra. We are, of course, considering the apparent affinity constant because it is highly unlikely that the internal cavity of CB is empty in the absence of dissolved xenon. It most likely contains water molecules, as observed by X-ray spectroscopy.[10] It must be emphasised that this problem is a general one in supramolecular chemistry. An empty cavity is probably very rare: solvent or gas molecules are certainly always encaged, but in the vast majority of cases it is difficult, if not impossible, to observe this complexation. It is possible to use a solvent which is too large to enter the cavity, but it remains impossible to avoid the complexation of gases such as N_2, O_2 or inert gases.

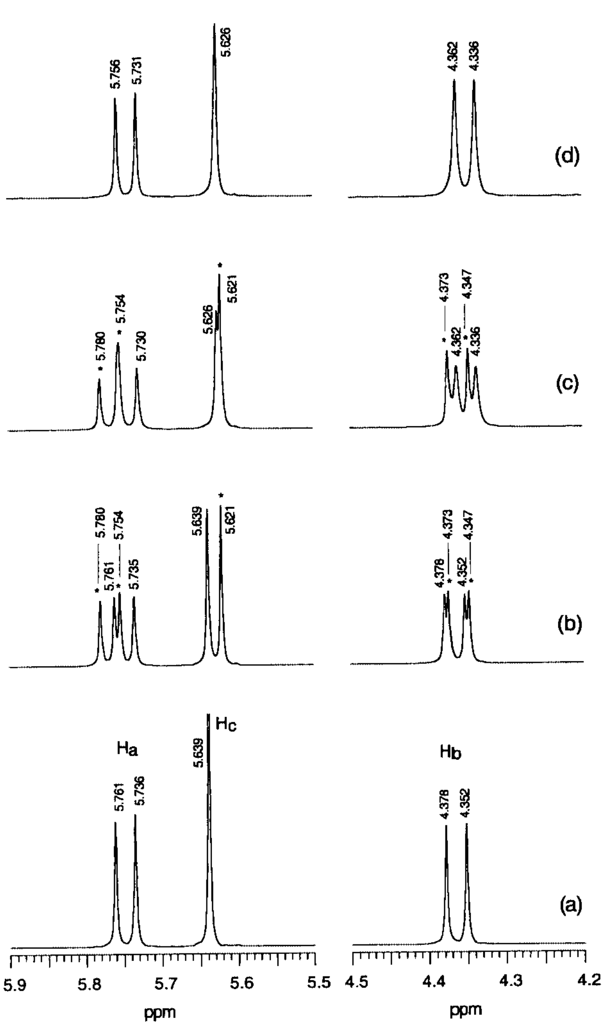

Fig. 3 ^{1}H-NMR spectrum at 298 K of cucurbituril in: (a) 0.2 M Na_2SO_4–D_2O; (b) 0.2 M Na_2SO_4–D_2O with [THF]/[CB] = 0.5; (c) 0.2 M Na_2SO_4–D_2O with [THF]/[CB] = 0.5 under 1 atm of xenon; (d) 0.2 M Na_2SO_4–D_2O under 1 atm of xenon. The signals which belong to the CB–THF complex are indicated by an asterisk (*).

The affinity constant characterising the CB–Xe complex can be determined from ^{1}H NMR data. The ^{1}H NMR spectrum of CB is shown in Fig. 3a. Assignments, confirmed by NOE experiments,† are indicated in the figure. The resonances shift upfield when xenon is added to the solution. The variation of the chemical shifts is shown in Fig. 4 as a function of the ratio nXe/V_l where nXe is the total number of moles of xenon in the sealed NMR tube and V_l is the volume of the liquid phase in the tube (this ratio is used because, as explained earlier, it is impossible to determine the analytical concentration of xenon in solution from data in the NMR spectra). Contrary to what is observed with ^{129}Xe NMR, the xenon exchange process is fast on the ^{1}H NMR chemical shift time scale. The observed chemical shifts (δ_{obs}) are therefore the weighted average of the chemical shifts of the cucurbituril protons when the cavity contains a xenon atom (δ_x) and when the cavity does not contain a xenon atom (δ_e), eqn. (1).

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† NOE experiments performed at 600 MHz and 45 °C, 2×10^{-2} M solution of CB in 0.2 M Na_2SO_4–D_2O. H_a irradiated: 15.5% enhancement on H_b; H_b irradiated: 15.8% enhancement on H_a and 10.7% enhancement on H_c; H_c irradiated: 5.2% enhancement on H_b.

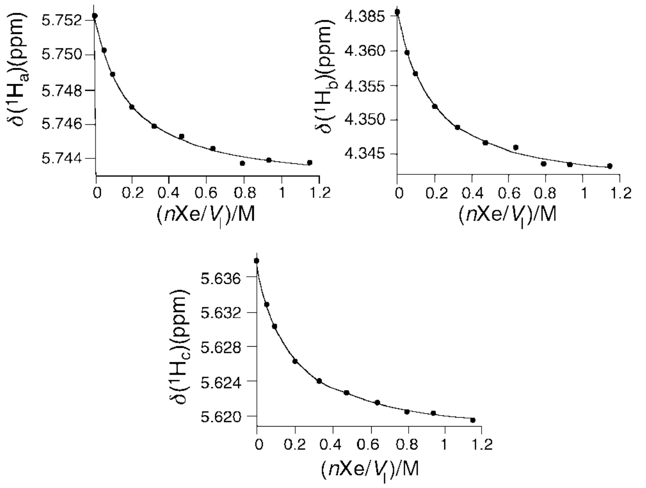

Fig. 4 Variation of the ^{1}H chemical shifts of the cucurbituril protons as a function of $n\mathrm{Xe}/V_l$. The curves correspond to the fitting of the model described in the text to the experimental data.

$$\delta_{\mathrm{obs}} = \delta_e + (\delta_x - \delta_e)\frac{[\mathrm{CB\text{–}Xe}]}{[\mathrm{CB}]_0} = \delta_e + (\delta_x - \delta_e)\frac{[\mathrm{Xe}]_{\mathrm{in}}}{[\mathrm{CB}]_0} \qquad (1)$$

If we assume that CB forms a 1 : 1 complex with xenon, the ratio of the concentration of the CB–Xe complex to the total concentration of CB in solution is equal to $[\mathrm{Xe}]_{\mathrm{in}}/[\mathrm{CB}]_0$, the ratio of the concentration of complexed xenon to the total CB concentration in solution.

The apparent equilibrium constant characterising the CB–xenon equilibrium is given by eqn. (2), where $[\mathrm{Xe}]_{\mathrm{out}}$ is the

$$K = \frac{[\mathrm{Xe}]_{\mathrm{in}}}{[\mathrm{CB}][\mathrm{Xe}]_{\mathrm{out}}} = \frac{[\mathrm{Xe}]_{\mathrm{in}}}{([\mathrm{CB}]_0 - [\mathrm{Xe}]_{\mathrm{in}})[\mathrm{Xe}]_{\mathrm{out}}} \qquad (2)$$

concentration of uncomplexed xenon. Assuming that $[\mathrm{Xe}]_{\mathrm{out}}$ corresponds to the solubility of xenon in the pure solvent, that xenon is a perfect gas and that Henry's law holds, it is possible to express, as detailed previously,[8] this concentration as a function of $n\mathrm{Xe}/V_l$ and $[\mathrm{Xe}]_{\mathrm{in}}$ [eqn. (3)], where V_l and V_g correspond, respectively, to the volumes of liquid and gas phases in the sealed NMR tube and $[\mathrm{Xe}]^\circ$ corresponds to the variation of the solubility of xenon in the solvent with pressure (M atm^{-1}). The variation of the solubility of xenon with pressure in a 0.2 M $\mathrm{Na_2SO_4}$ solution is not reported in the literature, but as a first approximation we can assume that it is equal to the variation of the solubility of xenon with pressure in water,[15] *i.e.* 4.3×10^{-3} M atm^{-1}. The presence of electrolytes in water is known to decrease the solubility of xenon, but only negligibly at these concentrations.[16]

$$[\mathrm{Xe}]_{\mathrm{out}} = g\left(\frac{n\mathrm{Xe}}{V_l} - [\mathrm{Xe}]_{\mathrm{in}}\right) \qquad (3)$$

$$\text{with } g = \frac{(V_l/V_g)\mathrm{H}}{1 + (V_l/V_g)\mathrm{H}} \text{ and } H = RT[\mathrm{Xe}]^\circ$$

Using expressions (1), (2) and (3) it is possible to express the variation of δ_{obs} with $n\mathrm{Xe}/V_l$ in terms of δ_x, δ_e and K. This expression was fitted to the experimental data (fitting shown in Fig. 4) and an average value 210 ± 15 M^{-1} was obtained for the affinity constant.

The apparent CB–Xe affinity constant can also be obtained *via* competition experiments with another guest for which the affinity constant is known, or for which it is easier to obtain the constant. THF is known to form a 1 : 1 complex with CB[10] and the ^{1}H spectra of a CB solution with different concentrations of THF were recorded. The THF exchange is slow on the ^{1}H NMR chemical shift time scale and the resonances of the bound THF are shifted approximately 0.8 ppm upfield with respect to those of the free THF. Two sets of signals are also observed for the CB protons. The region of the ^{1}H spectrum corresponding to the CB protons is shown in Fig. 3b for the solution where [THF]/[CB] = 0.5. One set of signals has the same chemical shifts as the resonances observed in the spectrum of CB in the absence of THF (Fig. 3a). The other set of signals must therefore correspond to the CB–THF complex. The apparent affinity constant characterising the CB–THF complex can be obtained by integrating the THF or the CB signals in the different spectra. The integration of these resonances yields a value of 1700 ± 50 M^{-1}. This value is different from the one that one of us reported previously, but the previous value turned out to be underestimated.[10]

For the competition experiments, xenon gas was bubbled into the solutions containing CB and THF. The $[\mathrm{THF}]_{\mathrm{in}} : [\mathrm{THF}]_{\mathrm{out}}$ ratio decreases when xenon is added to the solution, confirming that xenon does indeed compete with THF for the CB cavity. Two sets of signals are observed for the CB protons. Since CB–Xe and CB–THF complexes, as well as "empty" CB molecules, are simultaneously present in solution, one set must correspond to the CB–THF complex and, xenon complexation being fast on the ^{1}H NMR time scale, the other set must correspond to the average signal for "empty" CB and for the CB–Xe complex. The ^{1}H spectrum of the CB solution where [THF]/[CB] = 0.5 and into which xenon has been bubbled is shown in Fig. 3c. Fig. 3d is the ^{1}H spectrum of the CB solution, without THF, into which xenon gas has been bubbled. The fact that the chemical shift of the signals in this spectrum are identical to the unmarked signals in Fig. 3c confirms that these signals are indeed the average signal for "empty" CB and for the CB–Xe complex.

To determine the CB–Xe affinity constant, equilibria (4) and (5) must be considered.

$$\mathrm{CB} + \mathrm{Xe} \rightleftharpoons \mathrm{CB\text{–}Xe} \quad K1 \qquad (4)$$

$$\mathrm{CB} + \mathrm{THF} \rightleftharpoons \mathrm{CB\text{–}THF} \quad K2 \qquad (5)$$

It is possible to obtain an expression for $K1$ in terms of $[\mathrm{CB}]_0$, $K2$, $[\mathrm{THF}]_{\mathrm{in}}/[\mathrm{THF}]_{\mathrm{out}}$ and $[\mathrm{Xe}]_{\mathrm{out}}$. If we assume that $[\mathrm{Xe}]_{\mathrm{out}}$ corresponds to the solubility of xenon in the pure solvent (supposed here to be 4.3 mM, since it is at atmospheric pressure) we obtain an average value for $K1$ of 240 ± 20 M^{-1}. This value is identical, within experimental error, to the value obtained by analysing the variation of proton chemical shifts with xenon concentration.

The affinity constant of CB for xenon at 298 K is approximately one order of magnitude less than the affinity constant of CB for THF at the same temperature and in the same solvent. It is of the same order of magnitude as the affinity constant of CB for 4-methylbenzylamine in $\mathrm{CHOOH\text{–}H_2O}$ 50 : 50 (v/v) solutions at 298 K.[13] Generally speaking, in complexes that form reversibly, the observed equilibrium results from a compromise between host–solvent, guest–solvent and host–guest interactions. It is difficult to assess the importance of the various contributing factors affecting the affinity of ligands towards a host. In this case, since the solvent is water, hydrophobic forces must play a role. Indeed, xenon is hydrophobic, as clearly shown by the high negative dissolution entropy of xenon in water ($\Delta S^\circ = -140$ J mol^{-1} K^{-1} at 278 K).[17] Incidentally, it is interesting to remark that the free energy of dissolution of gaseous xenon in water is positive because of the negative entropy contribution; from the enthalpy point of view xenon "likes" water (ΔH° is negative).[17] The hydrophobicity of xenon is also clearly illustrated by the fact that the affinity constant of Xe for α-cyclodextrin at 298 K is one order of magnitude larger in aqueous solutions (20 M^{-1}) than in DMSO (2 M^{-1}).[7]

Van der Waals energies, especially the negative London energies, are often the dominant host–guest non-bonded interactions and the induction energies can generally be neglected.[18] The fact that the affinity constant of xenon for cucurbituril is one order of magnitude larger than the affinity constant of xenon for α-cyclodextrin in the same solvent (water) and at the same temperature (298 K) is a clear indication that the negative London energies play a role in stabilising the CB–Xe system. The London forces have also been shown to play an important role in the stabilisation of the cryptophane-A–xenon complex, which is characterised by an affinity constant (>3000 M^{-1}) which is, respectively, 5 and 20 times larger than the affinity constants which characterise the complexes of crytophane-A with $CHCl_3$ and CH_4.[8] Unfortunately, no other quantitative data has been reported in the literature for xenon–macrocycle complexes in solution.

The results reported in this work are a further illustration of the role of London energies in the stabilisation of host–guest complexes. Indeed, in systems where xenon is the guest, the stability of the complexes cannot be due to H-bonding, electrostatic interactions nor to charge transfers, which are sometimes, mistakenly, considered to be the most important non-bonded interactions.

Experimental

For the experiments undertaken as a function of xenon concentration, ^{129}Xe and ^{1}H NMR spectra were recorded at 298 K on a Bruker AMX360 spectrometer. ^{129}Xe spectra (nominal frequency 99.64 MHz) were recorded with a 30° pulse, a 5 s repetition time and a spectral width of 20000 Hz. Digital resolution was 0.61 Hz per point. The number of scans recorded varied from spectrum to spectrum, so as to obtain reasonable signal-to-noise ratios. The spectra were weighted with an exponential line-broadening corresponding to 10% of the natural linewidth of the narrowest signal. Chemical shifts are referenced to the frequency of pure xenon gas extrapolated to zero pressure. ^{1}H spectra were recorded using a 90° pulse, a 10 s repetition time, 64 scans and a spectral width of 1250 Hz. Digital resolution was 0.08 Hz per point after one level of zero filling. For the competition experiments ^{1}H NMR spectra were recorded at 298 K on a Varian UNITY 600 spectrometer using a 90° pulse, a 15 s repetition time, 64 scans and a spectral width of 7600 Hz. Digital resolution was 0.11 Hz per point after one level of zero filling.

Cucurbituril (CB) was synthesised according to procedures previously described in the literature.[12] Na_2SO_4, D_2O and tetrahydrofuran (THF) were purchased from Aldrich. Xenon gas at natural isotope abundance was purchased from Air Liquide.

Samples of CB in 0.2 M Na_2SO_4–D_2O were prepared at room temperature. For the measurements undertaken as a function of xenon concentration, samples of known volume (approximately 1.5 ml) of known concentration in CB (approximately 2×10^{-2} M) were placed in 10 mm high pressure NMR tubes of known volume (approximately 7 ml). Samples were then degassed by several freeze–thaw cycles on a vacuum line. Up to 10 atm of xenon gas were condensed into the samples. The total amount of xenon added was known precisely from the difference between the weight of the sample after xenon addition and the weight of the degassed sample. For the competition experiments, THF was added to samples of known concentration of CB (approximately 10^{-2} M). The samples were then placed in 5 mm J. Young valve NMR tubes. The precise [THF] : [CB] ratio was determined by integration in the proton NMR spectra. Xenon gas was bubbled into the solutions for approximately 15 minutes. Precautions were taken to reduce THF loss during bubbling (a cold ring was placed at the top of the NMR tube).

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