

ARTICLES

NMR Study of Complexation of Crown Ethers with [60]- and [70]Fullerenes

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[60]- and [70]fullerenes have been shown to form 1:1 molecular complexes with a series of crown ethers, namely, (i) 4'-nitrobenzo-15-crown-5 (**1**), (ii) dibenzo-24-crown-8 (**2**), (iii) dibenzo-30-crown-10 (**3**), (iv) benzo-15-crown-5 (**4**), and *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**5**) in CCl₄ medium by the NMR spectrometric method. Formation constants (*K*) of the complexes have been determined from the systematic variation of NMR chemical shifts of specific protons of the crown ethers in the presence of [60]fullerene and [70]fullerene. The magnitudes of *K* indicate that the crown ethers **2** and **3** form inclusion complexes with [60]fullerene but not with [70]fullerene.

1. Introduction

Following initial discovery,¹ research in fullerenes ([60]- and [70]fullerenes) has continuously expanded due to both fundamental interest and wide-ranging potential applications.^{2–4} Electrochemical methods have played an important role in the characterization of fullerene materials in solution^{5,6} and in the solid state.⁷ Notably, Echegoyen and co-workers detected⁸ stable [60]fullerene^{*n*–} and [70]fullerene^{*n*–} (*n* = 1–6), thereby supporting the theoretical prediction⁹ that [60]- and [70]fullerenes are able to accept at least six electrons upon reduction. Thus, high electron affinity of [60]- and [70]fullerenes make them efficient electron acceptors and they form electron donor–acceptor (EDA) complexes with various donors such as amines^{10,11} and olefins.^{12,13} Study of the formation of such complexes by [60]- and [70]fullerenes in solution and in the solid state is a field of current research.^{14–19}

Macrocyclic polyethers such as crown ethers²⁰ have received much attention in the past few years in both chemistry and biology.^{21–24} Research on crown ethers has been motivated by

their remarkable ability to complex alkali and alkaline earth metal cations.²⁵ The most important features of such cyclic polyether molecules which determine their binding strength are the number and type of donor atoms, dimension of the cavity, presence of substituents on the donor ring, and degree of ligand preorganization.²⁶ Thus, crown ethers can be treated as suitable hosts for suitable guest molecules. Despite a great number of studies on the complexation of crown ethers with many metal ions^{27,28} and in synthetic chemistry,²⁹ the electron donor–acceptor (EDA) interaction between crown ethers as donors and [60]- and [70]fullerenes as acceptors have so far received less attention. Very recently³⁰ charge-transfer bands of complexes of crown ethers with a series of acceptors (including [60]- and [70]fullerenes) have been reported. However, no measurement has been carried out to quantify the interaction between the fullerenes and crown ethers. Formation of host–guest (inclusion) complexes with calix[8]arene has been shown³¹ to be useful in the separation [60]- and [70]fullerenes from their mixture. This fact points to the importance of the study of complexation of fullerenes with host molecules in the development of methods of separation of targeted carbon clusters from soots. Since the formation constant (*K*) is an important parameter that measures the extent of inclusion in host–guest complexes, the object of

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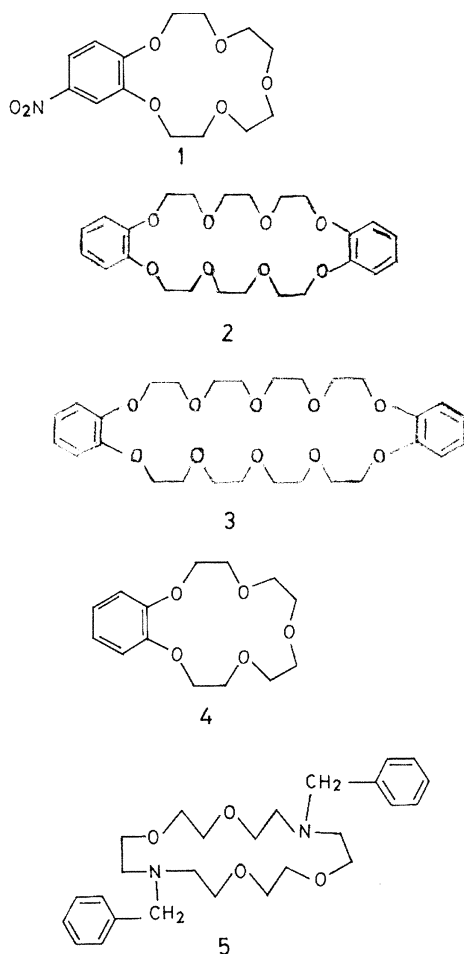


Figure 1. Structures of the crown ethers studied.

the present paper is to determine K of the complexes of [60]- and [70]fullerenes with a series of crown ethers (Figure 1), namely, (i) 4'-nitrobenzo-15-crown-5 (**1**), (ii) dibenzo-24-crown-8 (**2**), (iii) dibenzo-30-crown-10 (**3**), (iv) benzo-15-crown-5 (**4**), and *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**5**). The method of determination requires ¹H NMR chemical shift data and is based on a principle developed long ago by Mathur et al.³² and Hanna and Ashbaugh;³³ this method was recently used³⁴ for determination of K of molecular complexes of [60]fullerene with a series of methylbenzenes and pyridines.

2. Materials and Methods

[60]Fullerene was collected from Sigma. [70]Fullerene was collected from SES Research Corporation, USA. The crown ethers **1–5** were collected from Sigma. The solvent CCl₄ was of HPLC grade. ¹H NMR spectra of the donors and donor–[60]fullerene and donor–[70]fullerene mixtures in solutions of CCl₄ were recorded on a Bruker AC-200 (200 MHz) NMR spectrometer with CDCl₃ as an internal lock.

3. Results and Discussion

To determine the formation constant (K) of a molecular complex AB between the molecules of A and B



one requires knowledge of the equilibrium concentrations of the species A, B, and AB.

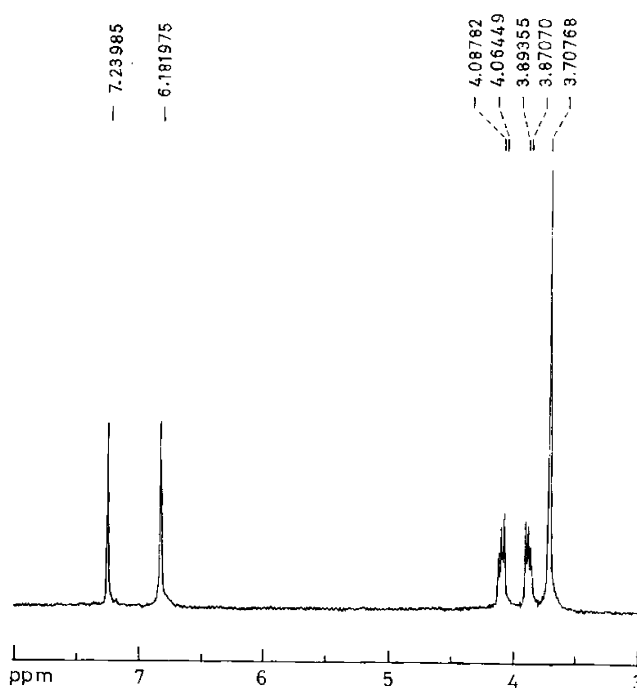


Figure 2. NMR spectrum of benzo-15-crown-5 in CCl₄ in the absence of [70]fullerene.

Both [60]- and [70]fullerenes have no protons, so the formation equilibria of [60]fullerene–crown ether and [70]fullerene–crown ether complexes have been studied in the present report on the basis of the following principle.

If we consider the signal of a particular proton in the molecule of B, then, owing to the rapid reversible equilibrium (eq 1) the observed chemical shift ($\delta_{\text{obs}}^{(B)}$) of the proton is the time-averaged shift of the same proton in the free B and in the complex; i.e.

$$\delta_{\text{obs}}^{(B)} = P_o \delta_o^{(B)} + P_c \delta_c^{(B)} \quad (2)$$

where P_o is the probability of finding the molecule B in the free state and P_c is the probability of finding it in the complexed state (c, i.e., AB); the latter is given by

$$P_c = [AB]/([AB] + [B]) \quad (3)$$

where the square brackets denote the concentration of the species enclosed. Again, if the initial concentration, $[A]_0$, of A is much less than that ($[B]_0$) of B, the formation constant (K) of the complex is given by

$$K = [AB]/[B]_0 ([A]_0 - [AB]) \quad (4)$$

A combination of eqs 2–4 gives

$$[B]_0 = \Delta_o [A]_0 (1/\Delta_{\text{obs}}) - 1/K \quad (5)$$

where $\Delta_{\text{obs}} = \delta_{\text{obs}}^{(B)} - \delta_o^{(B)}$ is the observed chemical shift of a B-proton in the equilibrium mixture of A and B relative to that in free B and $\Delta_o = \delta_c^{(B)} - \delta_o^{(B)}$ is the chemical shift of B-proton in the pure complex relative to that in the free B molecule. Thus a linear plot of $[B]_0$ against $1/\Delta_{\text{obs}}$ is expected, from the intercept and slope of which K and Δ_o respectively can be evaluated.

Variations of the methylene (–CH₂) proton signals in the ¹H NMR spectra of **4** in the absence and presence of [70]fullerene are shown in Figure 2 and Figure 3, respectively. It is found

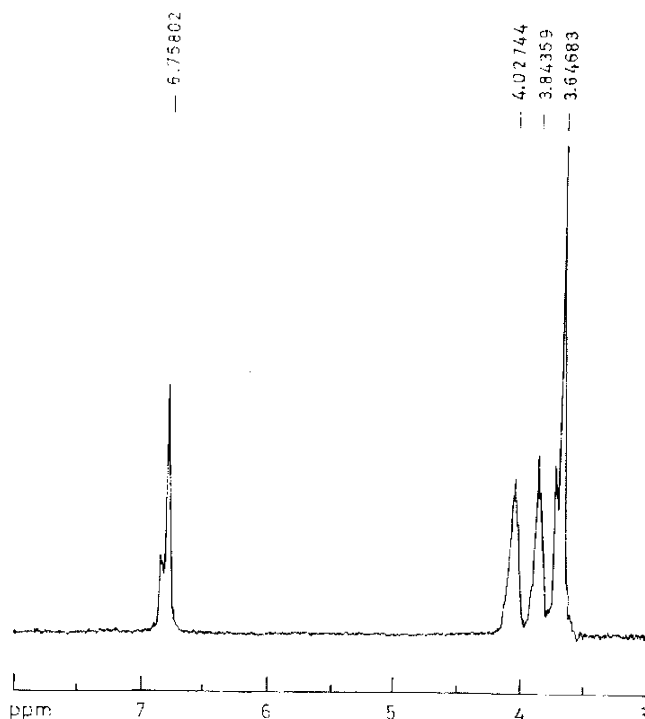


Figure 3. NMR spectrum of benzo-15-crown-5 ($2 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$) + [70]fullerene ($0.925 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$) in CCl_4 .

TABLE 1: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [60]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a

donor	$10^5[\text{A}]_0$, $\text{mol} \cdot \text{kg}^{-1}$	$10^3 \times \text{donor concn}$, $\text{mol} \cdot \text{kg}^{-1}$	Δ_{obs} , Hz
1	2.778	3.02	4.02
		5.19	3.04
		7.18	2.84
		7.90	2.55
		8.02	2.62
2	2.361	8.30	2.44
		2.25	4.09
		2.34	3.35
		2.40	4.12
		2.44	4.04
		2.65	3.77
		2.90	3.66
		4.35	2.45
		4.75	2.10
		5.96	1.66

^a Temperature = 298 K.

that signals of both methylene and aromatic protons are shifted upfield; the aromatic proton signal appears as a sharp singlet in the absence of [70]fullerene and splits in the presence of the latter. With a fixed concentration of [60]- and [70]fullerenes, the observed Δ decreases as the donor concentration increases. Similar features were observed with all the donors studied (Tables 1–6). The values of maximum Δ_{obs} in all the cases range from 0.904 to 11.90 Hz. Such values are much greater than that expected from the solvation effect (ca. 0.5 Hz). The values of Δ_{obs} are very similar in magnitude to those for usual molecular complexes (for example, complexes of TCNQ with a series of methylbenzenes³³ and of [60]fullerene with aromatic hydrocarbons and methylpyridines³⁴). In all the cases under the previous study, excellent linear plots in accordance with eq 5 were obtained, two such plots being shown in Figure 4.

Results of regression analysis and values of K and Δ_0 obtained therefrom are shown in Table 7. It is observed that high

TABLE 2: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [60]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a

donor	$10^5[\text{A}]_0$, $\text{mol} \cdot \text{kg}^{-1}$	$10^3 \times \text{donor concn}$, $\text{mol} \cdot \text{kg}^{-1}$	Δ_{obs} , Hz
3	4.722	0.979	6.25
		0.998	6.08
		1.14	5.08
		1.20	4.78
		1.90	3.33
		2.20	2.94
4	3.472	2.34	2.64
		2.80	4.28
		7.46	2.52
		8.39	2.42
		16.79	1.14
		18.90	1.12
		25.50	1.22
		26.10	1.26

^a Temperature = 298 K.

TABLE 3: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [60]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a

donor	$10^5[\text{A}]_0$, $\text{mol} \cdot \text{kg}^{-1}$	$10^3 \times \text{donor concn}$, $\text{mol} \cdot \text{kg}^{-1}$	Δ_{obs} , Hz
5	4.722	0.72	2.86
		1.90	2.55
		3.30	2.45
		3.70	2.23
		4.47	2.29
		5.12	1.99
		18.60	1.21
		31.04	0.83

^a Temperature = 298 K.

TABLE 4: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [70]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a

donor	$10^5[\text{A}]_0$, $\text{mol} \cdot \text{kg}^{-1}$	$10^3 \times \text{donor concn}$, $\text{mol} \cdot \text{kg}^{-1}$	Δ_{obs} , Hz
1	17.14	1.83	5.14
		4.30	2.71
		4.80	2.16
		6.15	2.22
		8.98	1.47
2	17.14	10.36	1.04
		1.09	5.00
		3.10	3.36
		3.79	2.99
		5.70	2.62
		6.00	2.44
		6.60	2.62
		6.70	2.26
		25.60	0.84

^a Temperature = 298 K.

formation constants (of the order of 10^3) characteristic of inclusion complexes^{18,35} are obtained only with the systems [60]fullerene•2 and [60]fullerene•3. For the other cases the present study indicates only molecular adduct formation (with much lower formation constants). The important finding is that the crowns 2 and 3 include [60]fullerene preferentially to [70]fullerene as revealed by their relative formation constants. This is presumably because the cavities of these two crown ethers are too small to include higher fullerenes. It may be mentioned at this point that a similar observation was made by Atwood et al. with *p*-Bu^t-calix[8]arene host, and they utilized this phenomenon to separate [60]- and [70]fullerenes from their

TABLE 5: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [70]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a

donor	$10^5[\text{A}]_0$, $\text{mol}\cdot\text{kg}^{-1}$	$10^3 \times$ donor concn, $\text{mol}\cdot\text{kg}^{-1}$	Δ_{obs} , Hz
3	2.747	1.46	11.90
		2.10	11.06
		2.79	9.71
		3.01	9.38
		3.60	8.47
4	0.925	13.20	3.64
		3.85	2.33
		5.60	1.96
		7.80	1.94
		10.40	1.77
		13.10	1.42
		16.30	1.19

^a Temperature = 298 K.**TABLE 6: NMR Chemical Shifts of Methylene ($-\text{CH}_2$) Protons in [70]Fullerene–Crown Ether Mixtures in CCl_4 Medium at Varying Concentrations of the Crown Ethers^a**

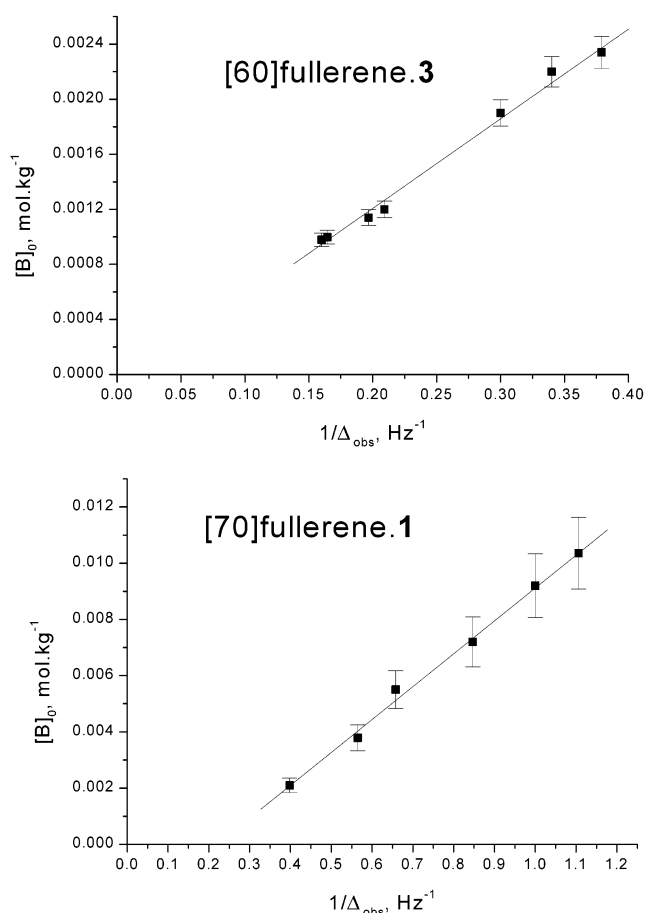
donor	$10^5[\text{A}]_0$, $\text{mol}\cdot\text{kg}^{-1}$	$10^3 \times$ donor concn, $\text{mol}\cdot\text{kg}^{-1}$	Δ_{obs} , Hz
5	2.747	2.10	2.51
		3.79	1.77
		5.50	1.52
		7.20	1.18
		9.20	1.01
		10.36	0.904

^a Temperature = 298 K.**TABLE 7: Formation Constants of the Complexes of [60]Fullerene and [70]Fullerene with Crown Ethers and Chemical Shifts of the Pure Complexes Relative to the Respective Crown Ethers^a**

crown ether	formation const, $\text{mol}^{-1}\cdot\text{kg}$		Δ_0 , Hz	
	[60]fullerene complex	[70]fullerene complex	[60]fullerene complex	[70]fullerene complex
1	177 ± 41	917 ± 430	1250 ± 132	85 ± 4
2	6289 ± 620	262 ± 24	436 ± 32	140 ± 4
3	8403 ± 476	282 ± 6	141 ± 5	2224 ± 22
4	641 ± 172	116 ± 30	635 ± 22	3302 ± 400
5	83 ± 4	389 ± 48	762 ± 20	427 ± 4

^a Temperature = 298 K.

mixture.³¹ Because of unfavorable cavity size, interaction of crowns **1** and **4** with fullerenes occurs through the benzene ring of the crowns. According to Taylor's rationale³⁶ for placing double bonds exocyclically with respect to the pentagons (in the valence-bond picture), there are five different types³⁷ of carbon atoms in [70]fullerene differing in electron density; this is supported by ^{13}C NMR data. This makes the polar cap region of [70]fullerene molecule relatively richer in electron density than the equator. On the other hand, the $-\text{NO}_2$ group attached to the benzene ring of crown **1** makes the ring electron deficient. Thus the interaction between this benzene ring and the polar end of [70]fullerene is much stronger than that in the case of [60]fullerene where there is no such irregularity in electron distribution. This explains the higher values of K for the complexes of crown **1** with [70]fullerene than that with [60]fullerene. This finding is in conformity with our previous observation with fullerene complexes of polynuclear aromatic hydrocarbons.¹⁹ However, the order is just the reverse in case of the two fullerene complexes of crown **4**. Formation constants

**Figure 4.** Plots of $[\text{B}]_0$ vs $1/\Delta_{\text{obs}}$ for [60]fullerene·**3** and [70]fullerene·**1** complexes.

of noninclusion complexes involve many energy terms (in particular, solvation) and it is not always possible to explain their order only in terms of electron accepting power of the concerned acceptors.

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