

Comparative Study of the Host–Guest Complexes of [60]- and [70]-Fullerenes with *N,N'*-Dibenzyl-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane in Different Solvents

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Charge-transfer absorption bands of the host–guest complexes of [60]- and [70]-fullerenes with the aza crown ether *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane (**1**) in π -donor solvents (toluene and *o*-xylene) and also in the nondonor solvent (CCl_4) have been detected. The CT absorption band of the [70]-fullerene–aza crown complex appears at a longer wavelength than that of the [60]-fullerene complex in each solvent, thereby indicating that [70]-fullerene has a higher electron affinity than [60]-fullerene. In analyzing these CT absorption bands, some other electron acceptors have also been used; this has led to the estimation of the hitherto undetermined vertical electron affinities of *N*-bromophthalimide and tetrachlorophthalimide and also the vertical ionization potential of the aza crown ether. Absorption spectrometric data established a 1(fullerene):2 (crown ether) stoichiometry of the complexes in solution having a crown ether concentration of $\sim 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$. By determining the formation constants at four different temperatures, the enthalpies and entropies of complexation have been determined. A plot of $T\Delta S_f^0$ against ΔH_f^0 shows that the extent of desolvation of the crown ether cavity due to the inclusion of the host fullerenes is very nearly equal for the two complexes. It has also been found that the formation constant of the $\text{C}_{70}\cdot\mathbf{1}$ complex is greater than that of the $\text{C}_{60}\cdot\mathbf{1}$ complex in each solvent at all four temperatures studied. This observation is on the order of the electron affinities of the two fullerenes (E_A of $\text{C}_{70} > E_A$ of C_{60}), which means that CT interaction plays an important role in the formation of the complexes.

Introduction

Crown ethers¹ have been found to have a wide application in biological fields,^{2,3} important chemical technology,^{4–11} and in the relatively recent field of supramolecular fullerene chemistry.^{12–20} For example, chiral recognition through host–guest complexation with crown ethers as hosts is a subject of very recent activity.^{21,22} Thus, molecular recognition of tryptophan enantiomers in an aqueous medium has recently been attempted through the synthesis of crown ether-tethered cyclodextrin hosts.²³ Crown ethers are also being used in the synthesis of rotaxanes, whose precursors are often host–guest complexes.^{24–26} The importance of aza crowns in photoinduced electron-transfer (PET) processes, which have a potential application in solar energy conversion, is revealed by a fairly recent synthesis (and PET study)²⁷ of an aza crown bridged [60]-fullerene–phthalocyanin conjugate. The phenomenon of host–guest (HG) complexation was shown²⁸ to be particularly useful in the purification of fullerenes from carbon soot. Aza crowns with suitable long-chain N substituents were shown^{29,30} to attain basketlike conformations and include [60]- and [70]-fullerenes in the baskets. There is evidence³¹ that HG complexation is accompanied by charge transfer (CT). With a lone pair of electrons on N, the aza crowns are potential electron donors, whereas fullerenes are known³² electron acceptors. Moreover, the desolvation of the host's cavity during complexation sometimes plays a significant role^{33,34} in determining the magnitude of the formation constant of the complex through the entropy effect, which, in turn, should depend on the nature of the solvent; in particular, aromatic (π donor) and aliphatic solvents should have distinct effects. The objective of the present

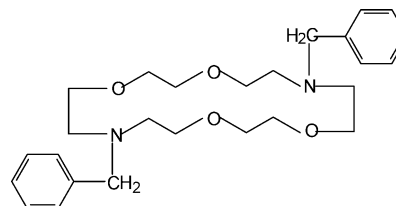


Figure 1. Structure of *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane (crown **1**).

paper is to detect CT interaction, if any, and the role of cavity desolvation during the HG complexation of [60]- and [70]-fullerenes with *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane (which will henceforth be called crown **1**, its structure being given in Figure 1).

Materials and Methods

[60]-Fullerene and crown **1** were purchased from Sigma. [70]-Fullerene was purchased from SES Research Corporation. The solvent CCl_4 (UV-spectroscopic grade) was distilled after drying it on CaCl_2 . Toluene and *o*-xylene (both of UV-spectroscopic grade) were double distilled after refluxing with metallic sodium for 1 h. All spectral measurements were done on a Shimadzu UV 1601 PC model spectrophotometer having a Peltier controlled thermobath.

Results and Discussion

Observation of CT Bands. In the present study, CT bands were observed in the case of complexes of crown **1** with (i) [60]-fullerene, (ii) [70]-fullerene, (iii) menadione, (iv) 2,3-dichloro-1,4-naphthoquinone, (v) *N*-bromophthalimide, and (vi)

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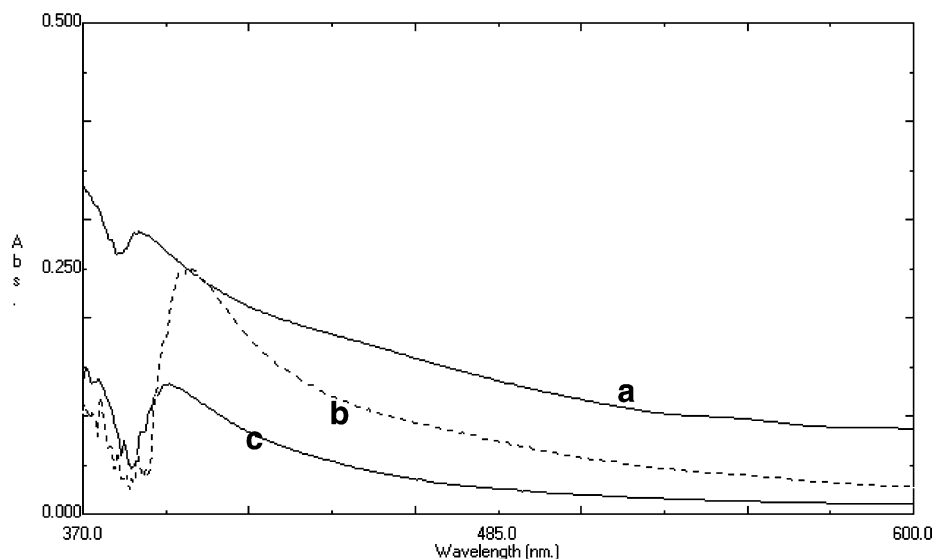


Figure 2. CT absorption band of C₇₀–crown **1** mixtures at three different solvents, (a) CCl₄, (b) *o*-xylene, and (c) toluene, against the solution of [70]-fullerene as the reference.

TABLE 1: CT Absorption Maxima and Transition Energies of Crown **1 Complexes**

acceptor	λ_{CT} nm	$h\nu_{CT}$	E_A^v	
			values in eV	ref
[70]-fullerene	385	3.220	2.59	35
[60]-fullerene	372	3.333	2.31	36
2,3-dichloro-1,4-naphthoquinone	455	2.725	2.38	37
menadione	491	2.525	2.18	38, 39
<i>N</i> -bromophthalimide	545	2.275	1.56	^a
tetrachlorophthalimide	346	3.583	1.93	^a

^a Determined in the present study.

tetrachlorophthalimide. To obtain CT bands, the spectrum of each of the solutions (in CCl₄) containing the crown **1** as the donor and an acceptor from the above list was recorded against the pristine acceptor reference solution. It is a common experience that CT bands in solution are detected only by taking a high concentration of donor compared to that of the acceptor. In the present case, [crown ether] $\approx 10^{-2}$ mol·dm⁻³, and concentrations of the acceptors were $\sim 10^{-3}$ to 10^{-5} mol·dm⁻³. The CT absorption bands of the [70]-fullerene–crown **1** mixture in three different solvents against the solution of [70]-fullerene at the same concentration as that in the mixture as a reference are shown in Figure 2. Crown **1** does not absorb above 300 nm; therefore, it does not interfere with the spectra while it locates the CT bands. The vertical electron affinities (E_A^v) of four of the acceptors under study are known,^{35–39} and they correlate well with the presently observed CT transition energies ($h\nu_{CT}$, Table 1) in accordance with the Mulliken⁴⁰ equation

$$h\nu_{CT} = I_D^v - C_1 + \frac{C_2}{I_D^v - C_1} \quad (1)$$

where I_D^v is the vertical ionization potential of the donor (crown **1**) and C_1 is given by the equation

$$C_1 = E_A^v + G_1 + G_0 \quad (2)$$

Here E_A^v is the vertical electron affinity of the acceptor; G_0 is the sum of several energy terms (such as dipole–dipole, van der Waals interaction, etc.) in the “no-bond” state, and G_1 is the sum of several energy terms in the “dative” state. In most

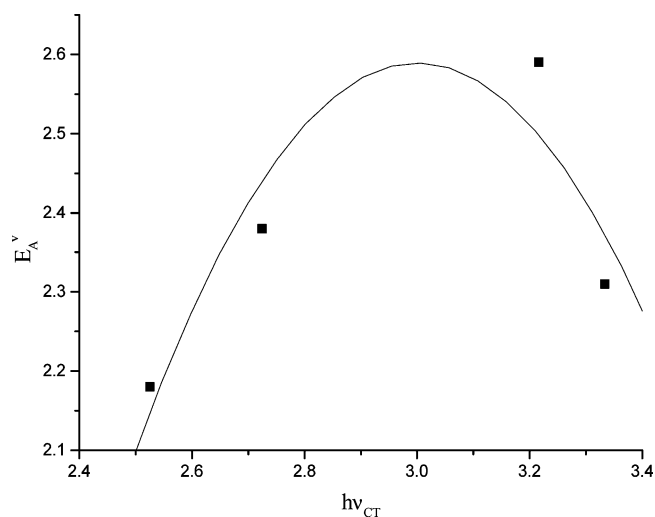


Figure 3. Parabolic plot to obtain the vertical electron affinity(E_A^v) of acceptors.

cases, G_0 is small and can be neglected, whereas G_1 is mainly the electrostatic energy of attraction between D^+ and A^- in the dative state. The term C_2 in eq 1 is related to the resonance energy of the interactions between the no-bond and the dative states. Equation 1 is obviously nonlinear (quadratic) with respect to C_1 (consequently, also with respect to E_A^v), and the following regression equation was obtained with the present experimental data.

$$E_A^v = -14.99700588 + 11.72206062 h\nu_{CT} - 1.95333646(h\nu_{CT})^2 \quad (3)$$

A parabolic plot (Figure 3) was obtained for E_A^v against $h\nu_{CT}$. By putting the values of $h\nu_{CT}$ of the complexes of *N*-bromophthalimide and tetrachlorophthalimide with crown **1** in eq 3, we determined the E_A^v values of these two acceptors; the values are given in the Table 1. The E_A^v of tetrachlorophthalimide (1.93 eV) is higher than that of *N*-bromophthalimide (1.56 eV), which is obviously due to the four electronegative chlorine atoms. Once the E_A^v values of the acceptors are known, the vertical ionization potential (I_D^v) of aza crown **1** is also obtained

TABLE 2: Absorbance Data for Crown 1–[60]-Fullerene Mixtures at Different Temperatures in CCl₄ against the Solvent as Reference

acceptor	10 ⁵ [acceptor] (mol dm ⁻³)	10 ² [crown 1] (mol dm ⁻³)	absorbance at 480 nm			
			298 K	303 K	308 K	313 K
[60]-fullerene	7.6104	1.244	0.2417	0.2305	0.2107	0.1862
		1.282	0.3125	0.3031	0.2854	0.2451
		1.440	0.2070	0.2000	0.1887	0.1842
		1.561	0.2438	0.2850	0.3047	0.2254
		1.682	0.2161	0.2188	0.2246	0.2295
		1.795	0.2286	0.2328	0.2373	0.2411
		1.840	0.2522	0.2531	0.2535	0.2540
		2.010	0.2286	0.2328	0.2373	0.2411

TABLE 3: Absorbance Data for Crown 1–[70]-Fullerene Mixtures at Different Temperatures in CCl₄ against the Solvent as Reference

acceptor	10 ⁵ [acceptor] (mol dm ⁻³)	10 ² [crown 1] (mol dm ⁻³)	absorbance at 380 nm			
			298 K	303 K	308 K	313 K
[70]-fullerene	6.57427	1.1463	2.1727	2.1423	2.1006	2.0658
		1.2368	2.1039	2.0876	2.0687	2.0389
		1.4027	2.1847	2.1423	2.1039	2.0718
		1.5008	2.1210	2.0941	2.0536	2.0245
		1.7195	2.1423	2.1315	2.1106	2.1107
		1.7421	2.1140	2.1039	2.0845	2.0813
		1.8326	2.1281	2.0973	2.0687	2.0447
		1.9231	2.2230	2.2054	2.1609	2.1460

TABLE 4: Absorbance Data for Crown 1–[60]-Fullerene Mixtures at Different Temperatures in Toluene against the Solvent as Reference

acceptor	10 ⁵ [acceptor] (mol dm ⁻³)	10 ² [crown 1] (mol dm ⁻³)	absorbance at 382 nm			
			298 K	303 K	308 K	313 K
[60]-fullerene	8.4175	1.2971	1.1885	1.1774	1.1669	1.1561
		1.5460	1.2102	1.1967	1.1791	1.1656
		1.7285	1.3138	1.3030	1.2795	1.1896
		2.0211	1.2679	1.2576	1.2417	1.2163
		2.0452	1.2329	1.2258	1.2178	1.2123
		2.0905	1.2690	1.2537	1.2283	1.1885
		2.1719	1.2779	1.2683	1.2526	1.2283
		2.2533	1.3020	1.2946	1.2831	1.2775

from the CT bands of the complexes as follows: A rearrangement of eq 1 yields

$$2C_1 + hv_{CT} = C_1 \left(\frac{C_1 + hv_{CT}}{I_D^v} \right) + \left(\frac{C_2}{I_D^v} \right) + I_D^v \quad (4)$$

By neglecting G_0 and taking the typical D–A distance in π -type EDA complexes to be 3.5 Å, we estimated the major part of G_1 to be $e^2/4\pi\epsilon_0 r = 4.13$ eV. Thus, C_1 is obtained from eq 2 for each of the acceptors. A plot of $2C_1 + hv_{CT}$ against $C_1(C_1 + hv_{CT})$ for a given donor and various acceptors should yield a slope of $1/I_D^v$ from which the value of I_D^v of the donor can be obtained. In the present case, with the experimental CT transition energies shown in Table 1, the plot is fairly linear (Figure 4), and the linear regression equation is

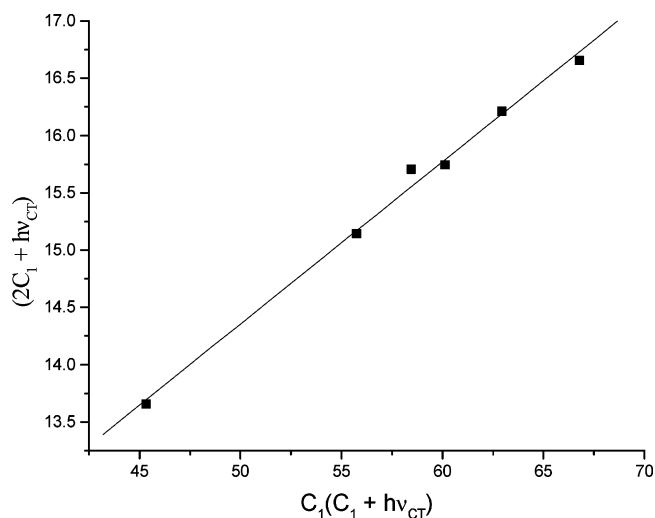
$$2C_1 + hv_{CT} = (0.1415 \pm 0.0056)[C_1(C_1 + hv_{CT})] + (7.2785 \pm 0.3284) \quad \text{corrln coeff} = 0.98 \quad (5)$$

The value of the I_D^v of crown 1 that is obtained from this correlation is 7.06 eV.

Determination of the Formation Constants (K). The absorbance data for mixtures of [60]-fullerene–crown 1 and [70]-fullerene–crown 1 at different temperatures in three different solvents are given in Tables 2–7.

Figure 5 shows a typical electronic absorption spectrum of [70]-fullerene (at the bottom) in an *o*-xylene medium against the solvent as reference. In the same figure, the absorption

spectra of mixtures containing a fixed concentration of [70]-fullerene and increasing concentrations of crown 1 at 298 K against the solvent as reference are shown. It is found that the absorbance value of any mixture is different from that of pure [70]-fullerene although no new peak is apparent. A portion of the spectra is expanded in the inset to clarify the change in absorbance upon the addition of crown 1 to a fixed concentration of [70]-fullerene. Because fullerenes usually have broad absorp-

**Figure 4.** Plot to determine the vertical ionization potential (I_D^v) of crown 1.

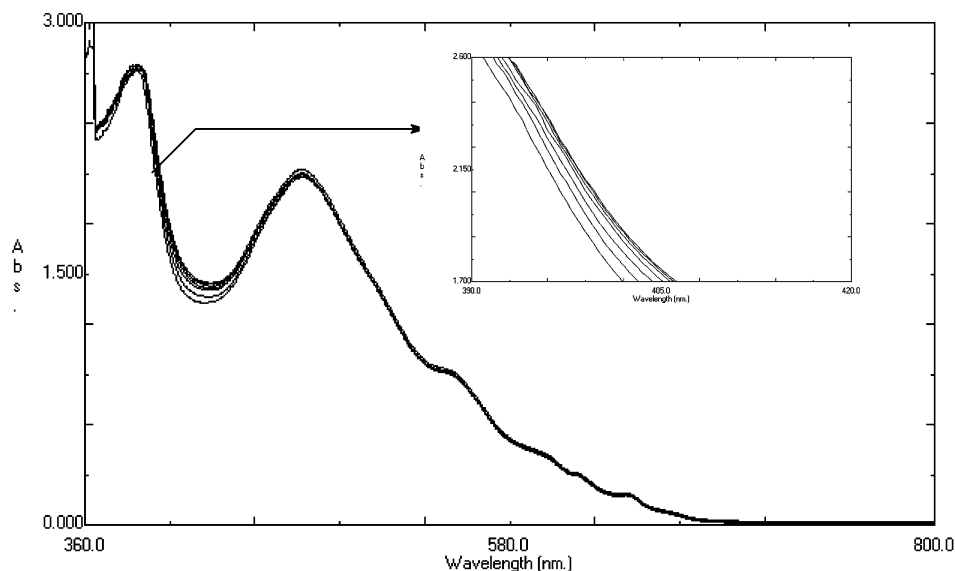


Figure 5. Absorption spectra of [70]-fullerene–crown **1** mixtures against the reference solvent (*o*-xylene) that contains a fixed concentration of [70]-fullerene, and the lowermost spectrum is of pure [70]-fullerene. (Inset) A portion of the spectra is expanded in the inset to clarify the change in absorbance upon the addition of crown **1** to a fixed concentration of [70]-fullerene.

TABLE 5: Absorbance Data for Crown 1–[70]-Fullerene Mixtures at Different Temperatures in Toluene against the Solvent as Reference

acceptor	$10^5[\text{acceptor}]$ (mol dm ⁻³)	$10^2[\text{crown } \mathbf{1}]$ (mol dm ⁻³)	absorbance at 394 nm			
			298 K	303 K	308 K	313 K
[70]-fullerene	7.48299	1.5083	1.8169	1.7985	1.7698	1.7637
		1.6817	1.8292	1.8187	1.7502	1.7346
		1.7345	1.7954	1.7369	1.7227	1.7130
		1.7466	1.7548	1.7776	1.7512	1.7200
		1.8099	1.7760	1.7651	1.7576	1.7456
		1.9155	1.8171	1.7887	1.7637	1.7500
		1.9532	1.8206	1.7952	1.7712	1.7560
		2.0437	1.7952	1.7838	1.7471	1.7325

TABLE 6: Absorbance Data for Crown 1–[60]-Fullerene Mixtures at Different Temperatures in *o*-Xylene against the Solvent as Reference

acceptor	$10^5[\text{acceptor}]$ (mol dm ⁻³)	$10^2[\text{crown } \mathbf{1}]$ (mol dm ⁻³)	absorbance at 384 nm			
			298 K	303 K	308 K	313 K
[60]-fullerene	12.5868	1.3952	1.8324	1.8031	1.7710	1.7542
		1.4404	1.8582	1.8582	1.8505	1.8544
		1.6139	1.9266	1.9025	1.8660	1.8395
		1.6893	1.8341	1.8358	1.8395	1.8431
		1.8175	1.8964	1.8737	1.8431	1.7965
		1.8778	1.8201	1.8270	1.8359	1.8431
		1.9608	1.8395	1.8450	1.8563	1.8798
		2.2474	1.9427	1.9176	1.8798	1.8376

TABLE 7: Absorbance Data for Crown 1–[70]-fullerene Mixtures at Different Temperatures in *o*-Xylene against the Solvent as Reference

acceptor	$10^5[\text{acceptor}]$ (mol dm ⁻³)	$10^2[\text{crown } \mathbf{1}]$ (mol dm ⁻³)	absorbance at 399 nm			
			298 K	303 K	308 K	313 K
[70]-fullerene	7.8125	1.3348	1.9695	1.9769	1.9794	1.9923
		1.4027	2.1042	2.0879	2.0569	2.0392
		1.5309	2.0297	2.1011	2.0659	2.0630
		1.6893	2.0977	2.1113	2.1113	2.1146
		1.7949	2.0361	2.0659	2.0394	2.0142
		1.8778	2.0376	2.0815	2.0481	2.0306
		1.9382	2.0630	2.0753	2.0691	2.0659
		2.1342	2.0194	2.0365	2.0540	2.0691

tion bands, the CT peak cannot be detected without masking the fullerene absorbance by taking the latter as reference, but if this is done, then the intensity of the peak is low. For this reason, the variation of the CT absorption intensity with a change in the donor concentration could not be employed to determine the stoichiometry and the formation constants (K) of the

complexes. Instead, it was observed that the intensities of the broad absorption bands of [60]- and [70]-fullerene (measured against the solvent as reference) were perturbed systematically with the addition of crown **1**. This phenomenon was utilized to determine the value of K by using the Benesi–Hildebrand⁴¹ equation. When the present experimental data were plotted

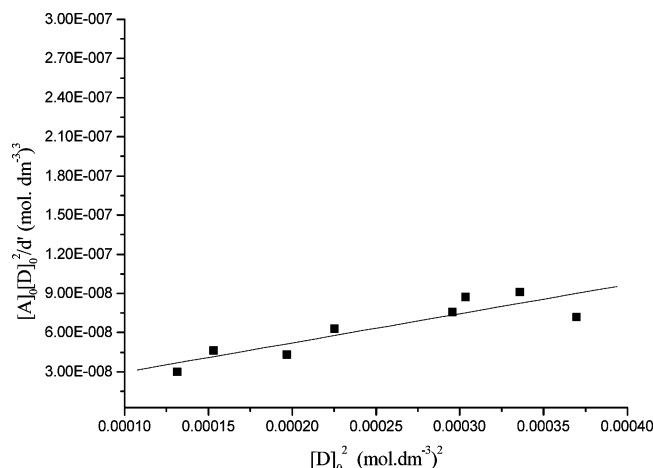


Figure 6. Benesi-Hildebrand plot for the [70]-fullerene complex in the CCl₄ medium at 298 K.

according to the B-H equation for 1:1 stoichiometry, a very wide scatter with a low correlation coefficient was observed. However, a modification of this equation to the form (eq 6) that is applicable to 1:2 (A/D) stoichiometry for cells with a 1-cm optical path length gave a good linear correlation as shown in Figure 6.

$$\frac{[A]_0[D]_0^2}{d'} = \frac{[D]_0^2}{\epsilon'} + \frac{1}{K\epsilon'} \quad (6)$$

with

$$d' = d - d_A^0 - d_D^0 \quad (7)$$

Here, $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor, respectively, d is the absorbance of the donor-acceptor mixture at the center of the respective perturbed broad peaks of C₆₀ and C₇₀ measured against the solvent as reference, and d_A^0 and d_D^0 are the absorbances of the acceptor and donor solutions with the same molar concentrations as in the mixture at the wavelength of measurement. The quantity $\epsilon' = \epsilon_c - \epsilon_A - 2\epsilon_D$ means the corrected molar absorptivity of the complex, and ϵ_A and ϵ_D are those of the acceptor and the donor, respectively, at the wavelength of measurement. K is the formation constant of the complex. Equation 6 is valid²² under the condition $[D]_0 \gg [A]_0$ for the 1:2 EDA complex. The experiments were carried out under this condition in CCl₄, toluene, and *o*-xylene media at a number of temperatures. The absorbance data that is shown in Tables 2–7 gave good linear plots according to eq 6 in all the cases. One typical case for the [70]-fullerene complex in the CCl₄ medium is shown in Figure 6. The formation constants for [60]- and [70]-fullerene complexes with crown **1** that were determined from such plots at four different temperatures are given in Tables 8 and 9.

Enthalpies (ΔH_f^0) and Entropies of Formation (ΔS_f^0) of the Complexes of [60]- and [70]-Fullerene with Crown **1.** The enthalpies (ΔH_f^0) and entropies of formation (ΔS_f^0) of the complexes have been determined by using eq 8. As measured, these terms will represent the net change in enthalpy and entropy for the solvated species.

$$\log K = \frac{-\Delta H_f^0}{2.303RT} + \text{constant} \quad (8)$$

The plots of $\log K$ versus $1/T$ for the complexes of [60]-fullerene

TABLE 8: Formation Constants (K) and Thermodynamic Parameters for Complexes of [60]-Fullerene with Aza Crown Ether in Three Different Solvents at Four Temperatures

solvent	temp	K (dm ⁶ mol ⁻²)	ΔH_f^0 (kcal mol ⁻¹)	ΔS_f^0 (cal K ⁻¹ mol ⁻¹)
CCl ₄	298	24500 ± 50	-23.6 ± 4.5	-58.5 ± 0.4
	303	19400 ± 50		
	308	9900 ± 50		
	313	3700 ± 50		
toluene	298	6100 ± 25	-7.2 ± 1.3	-6.7 ± 0.2
	303	5300 ± 25		
	308	4700 ± 50		
	313	3300 ± 50		
<i>o</i> -xylene	298	6000 ± 50	-6.0 ± 3.1	-2.8 ± 0.2
	303	4700 ± 25		
	308	3200 ± 50		
	313	4000 ± 50		

TABLE 9: Formation Constants (K) and Thermodynamic Parameters for Complexes of [70]-Fullerene with Aza Crown Ether in Three Different Solvents at Four Temperatures

solvent	temp	K (dm ⁶ mol ⁻²)	ΔH_f^0 (kcal mol ⁻¹)	ΔS_f^0 (cal K ⁻¹ mol ⁻¹)
CCl ₄	298	30000 ± 200	-14.2 ± 2.8	-27.0 ± 1.2
	303	22000 ± 200		
	308	18000 ± 100		
	313	9000 ± 50		
toluene	298	36000 ± 300	-6.6 ± 1.1	-1.2 ± 0.1
	303	26000 ± 400		
	308	24000 ± 300		
	313	21000 ± 400		
<i>o</i> -xylene	298	20800 ± 50	-15.3 ± 4.8	-31.2 ± 0.2
	303	19000 ± 300		
	308	7200 ± 50		
	313	7300 ± 50		

and [70]-fullerene with crown **1** in all three solvents are linear and have positive slopes.

The linear regression relations are as follows.

For C₆₀•**1** in CCl₄,

$$\log K = \frac{(5116.49 \pm 1018.54)}{RT} - (12.69 \pm 3.34) \quad \text{corrln coeff} = 0.96 \quad (9a)$$

For C₆₀•**1** in toluene,

$$\log K = \frac{(1565.89 \pm 280.00)}{RT} - (1.4519 \pm 0.9169) \quad \text{corrln coeff} = 0.97 \quad (9b)$$

For C₆₀•**1** in *o*-xylene,

$$\log K = \frac{(1306.99 \pm 683.94)}{RT} - (0.6401 \pm 2.2399) \quad \text{corrln coeff} = 0.80 \quad (9c)$$

For C₇₀•**1** in CCl₄,

$$\log K = \frac{(3091.88 \pm 618.63)}{RT} - (5.86 \pm 2.02) \quad \text{corrln coeff} = 0.96 \quad (9d)$$

For C₇₀•**1** in toluene,

$$\log K = \frac{(1424.81 \pm 229.55)}{RT} - (0.2496 \pm 0.7518) \quad \text{corrln coeff} = 0.98 \quad (9e)$$

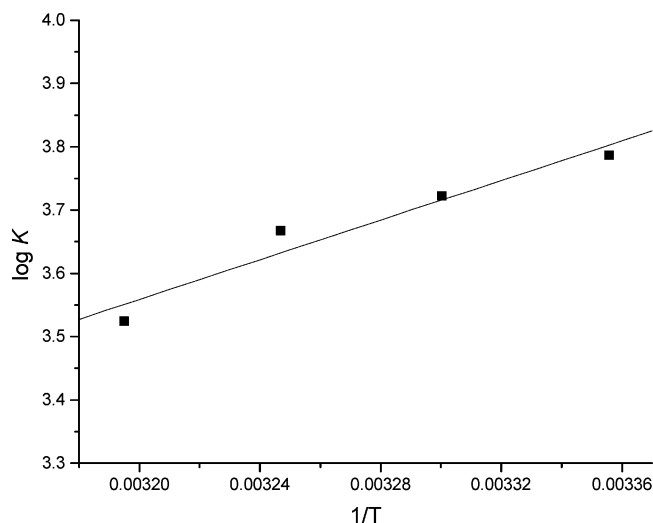


Figure 7. $\log K$ vs $1/T$ plot for the [60]-fullerene–crown **1** system at 298 K in the toluene medium.

For $C_{70}\cdot\mathbf{1}$ in *o*-xylene,

$$\log K = \frac{(3313.30 \pm 1049.59)}{RT} - (6.77 \pm 3.44) \quad \text{corrln coeff} = 0.94 \quad (9f)$$

One typical plot for the [60]-fullerene–crown **1** system at 298 K in the toluene medium is shown in Figure 7.

The positive slope in each case indicates that the complexation process is exothermic and thus driven by favorable enthalpy changes. The ΔH_f^0 and ΔS_f^0 values of the complexes in all three solvents are listed in Tables 8 and 9. It is observed that the ΔH_f^0 values of the $C_{60}\cdot\mathbf{1}$ and $C_{70}\cdot\mathbf{1}$ complexes are nearly the same as those in toluene medium, whereas the ΔS_f^0 value in this medium is higher in case of the $C_{60}\cdot\mathbf{1}$ complex. Again, in the *o*-xylene medium, both ΔH_f^0 and ΔS_f^0 are higher in magnitude for the $C_{70}\cdot\mathbf{1}$ complex. These apparently complicated relative orders of the thermodynamic parameters are difficult to explain because the aromatic π -donor solvent molecules also

have a tendency to form complexes with the fullerenes. An overall analysis can be made in terms of a relationship between $T\Delta S_f^0$ and ΔH_f^0 . In the present study, it is found that a linear relationship exists between $T\Delta S_f^0$ and ΔH_f^0 for both the complexes under study:

For $C_{60}\cdot\mathbf{1}$ complex at 298 K

$$T\Delta S_f^0 = (0.9423 \pm 0.0016)\Delta H_f^0 + (4804.3 \pm 23.5) \quad \text{corrln coeff} = 0.999 \quad (10a)$$

For $C_{70}\cdot\mathbf{1}$ complex at 298 K

$$T\Delta S_f^0 = (1.0217 \pm 0.0136)\Delta H_f^0 + (6394.5 \pm 171.5) \quad \text{corrln coeff} = 0.999 \quad (10b)$$

Linear relationships such as eqs 10a and 10b are commonly referred to as the “compensation effect” in host–guest complexation.^{33,34} The slopes and intercepts are very close to one another for the crown **1** complexes of the two fullerenes. The nearly equal (~ 5 to 6 kcal mol^{−1}) intercepts (i.e., the values of $T\Delta S_f^0$ when $\Delta H_f^0 \rightarrow 0$) represent the contribution to the free energy of complexation resulting from the desolvation of the host cavity during the inclusion of the fullerene balls. The value of the formation constant (K) is in the order $C_{70}\cdot\mathbf{1} > C_{60}\cdot\mathbf{1}$ in all of the solvents and at all of the temperatures studied. This is on the order of the electron affinities^{35,36} of the two fullerenes ($C_{70} > C_{60}$), which means that the CT interaction plays a major role in the formation of the complexes. Semiempirical PM3 calculations were carried out on the whole HG complexes, and the calculated heats of formation were in good agreement with the experimental findings. The theoretical $\Delta H_f^0 = -6.91$ kcal mol^{−1} for $C_{60}\cdot\mathbf{1}$ and -6.82 kcal mol^{−1} for $C_{70}\cdot\mathbf{1}$; the experimental $\Delta H_f^0 = -7.21$ kcal mol^{−1} for $C_{60}\cdot\mathbf{1}$ and -6.56 kcal mol^{−1} for $C_{70}\cdot\mathbf{1}$ in toluene. The geometry-optimized structures of the two complexes calculated by the PM3 method are shown in Figure 8. The inclusion of [70]-fullerene between two crown **1** molecules is clearly exhibited by the calculated structure.

Conclusions

Both [60]- and [70]-fullerene form 1:2 inclusion complexes with crown **1**. In a previous work,⁴² by NMR method, the

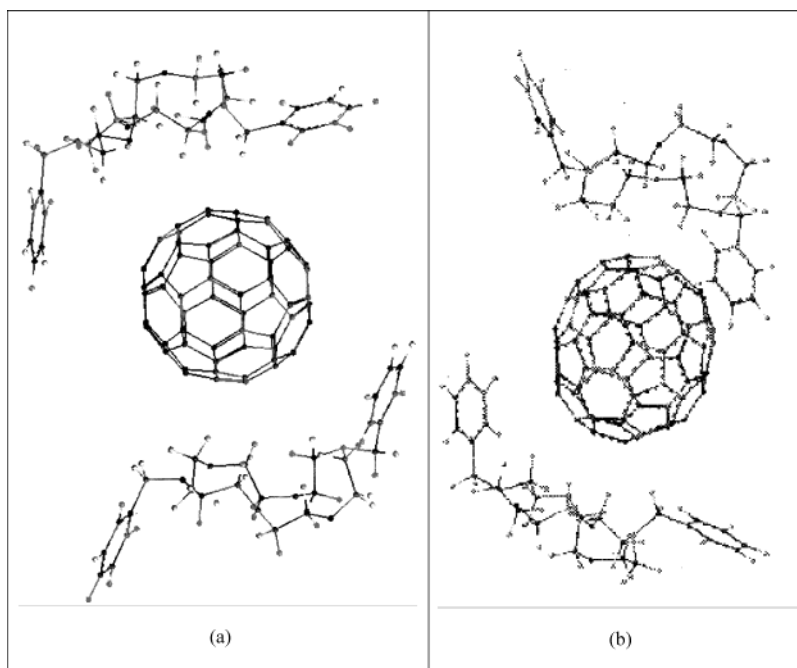


Figure 8. Energy-optimized structure of Crown **1** complexes of (a) [60]- and (b) [70]-fullerene as obtained by the PM3 method.

stoichiometry of the same two complexes was found to be 1:1; but, in that work the concentration of the crown ether was 10 times lower than that used in the present study. The concentration dependence of the stoichiometry of HG complexes is well known; for example, Haino et al.⁴³ showed that a [60]-fullerene-calix[5]arene complex is of 1:1 stoichiometry in solution but of 1(fullerene):2(calixarene) stoichiometry in the solid state, which means that as the concentration in solution increases the stoichiometry changes. In all three solvents, the formation constants of the crown **1** complexes are in the order $C_{70} \cdot \mathbf{1} > C_{60} \cdot \mathbf{1}$ at all temperatures studied. The complexes exhibit CT bands, with the absorption maxima being consistent with Mulliken's theory.⁴⁰ The CT transition energies of these complexes, together with those of some other acceptors, yield the vertical ionization potential (I_D^v) of crown **1** in solution and also the vertical electron affinities of *N*-bromophthalimide and tetrachlorophthalimide, which have hitherto remained undetermined. The free energy of complexation in the two cases involves a nearly equal contribution from the entropy effect but a higher contribution from the enthalpy effect ($T\Delta S_f^0 \leq \Delta H_f^0$).

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