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Study of Charge Transfer Interactions of a Resorcin[4]arene with [60]- and [70]Fullerenes by the Absorption Spectrometric Method

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The resorcin[4]arene host compound 2,8,14,20-tetrapentadecylpentacyclo [19.3.1.1.^{3,7}1.^{9,13}1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (**1**) has been shown to form charge-transfer complexes with a series of electron acceptors including [60]- and [70]fullerenes, and from the trends in CT transition energies the vertical ionization potential of **1** has been estimated (7.62 eV). By the UV−vis spectrophotometric method it has been shown that **1** forms an inclusion complex of 2(resorcinarene):1(fullerene) stoichiometry besides showing CT absoption bands. On the other hand, **1** does not include [70]fullerene and forms with it a simple CT type of molecular complex. This has been established by determining formation constants and enthalpies and entropies of complexation. It has been shown that inclusion of [60]fullerene is a predominantly entropy-driven process.

Introduction

Just as calix[*n*]arenes[1] are condensation products of phenol and aldehydes, resorcinarenes[2] are condensation products of resorcinol and aldehydes. The latter compounds are new cavitands finding interesting applications in molecular recognition.[3−8] With suitable modification, resorcin[4]arene cavitands have been shown to exhibit conformational switching upon protonation.[9] Very recently, some resorcin[4]arene-capped porphyrines have been synthesized and shown[10] to include water, methane, and benzene, and to inhibit the oxidation of Co(II) to Co(III). Study of inclusion phenomena with resorcinarenes is thus a field of recent interest. On the other hand, inclusion complexes of [60]- and [70]fullerenes as hosts are of current interest because of their potential application in photophysics,[11−15] superconductivity[16] ferromagnetism,[17] photo- and biomolecular chemistry,[18,19] and in the development of fullerene separation technology.[20,21] A good number of books and review articles[22−27] reveal the importance of such studies. In some inclusion complexes[28,29] of fullerenes with calix[n]arenes and crown ethers, charge-transfer (CT) absorption bands could be detected, from which significant information regarding the electron affinities of the fullerenes and ionization potentials of the host compounds could be extracted.[30,31] The compound **1** (Figure 1) i.e., 2,8,14,20-tetrapentadecylpentacyclo[19.3.1.1.^{3,7}1.^{9,13}1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol is a cavitand formed by condensation[32] of resorcinol with 1-hexadecanal. The purpose of the present work is to examine CT complexation of this resorcin[4]arene **1** with suitable electron acceptors including [60]- and [70]fullerenes and, in particular, to examine whether it forms an inclusion complex with both the fullerenes or with one fullerene in preference to the other.

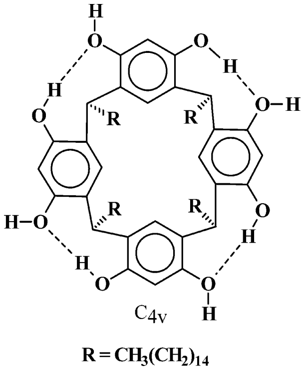

Figure 1. Structure of dicyclohexano-2,8,14,20-tetrapentadecylpentacyclo[19.3.1.1.^{3,7}1.^{9,13}1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19-(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (resorcinarene **1**).

Materials and Methods

[60]Fullerene was obtained from Sigma and [70]fullerene from SES Research Inc., Houston, TX. The acceptors *o*-chloranil, menadione, and 2,3-dichlo-1,4-naphthoquinone were obtained from Sigma and were used without further purification. The solvent, carbon tetrachloride, was of UV−spectroscopic grade. This was further purified by keeping it in fused calcium chloride for 24 h and then distilling just before use. All optical measurements were done on a UV 1601 PC model Shimadzu spectrophotometer fitted with a Peltier controlled thermo bath. The resorcin[4]arene **1** was prepared and purified by the method described in ref 32.

Results and Discussions

Charge-Transfer Complexation. The resorcinarene **1** is colored in CCl_4 solution and its absorption spectrum is shown in Figure 2(d). However, with only dialkoxy- and dialkyl-substituted benzene rings and no chromophoric groups, the compound **1** should not have color; the observed

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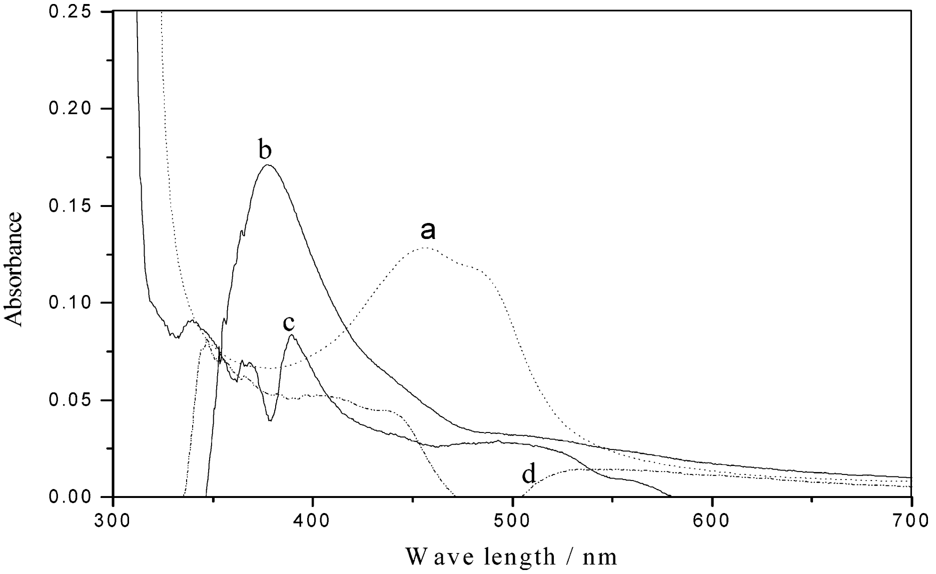

Figure 2. (a) Absorption spectrum of resorcinarene **1** (10^{-3} mol dm^{-3}) against the solvent CCl$_4$ as reference and CT absorption spectra of the complexes obtained by subtracting the absorbance due to resorcinarene from the actual spectra of mixtures containing compound **1** (10^{-3} mol dm^{-3}) and (b) 2,3-dichloro-1,4-naphthoquinone (10^{-4} mol dm^{-3}); (c) [70]Fullerene (10^{-5} mol dm^{-3}); (d) [60]fullerene (10^{-5} mol dm^{-3}) against the respective pristine acceptor solutions as reference.

TABLE 1: Charge Transfer Absorption Maxima (λ_{CT}), CT Transition Energy ($h\nu_{CT}$), Electron Affinity of the Acceptors (E_A^v), Vertical Ionization Potential (I_D^v) of Resorcin[4]arene 1 and Degree of Charge Transfer (α)

acceptor	λ_{CT} (nm)	$h\nu_{CT}$ (eV)	E_A^v (eV)	$10^3 \times \alpha$	I_D^v (eV)
o-chloranil	360	3.44	2.87	6.72	7.62 ± 0.04
[70]fullerene	390	3.18	2.59	6.40	
2,3-dichloro-1,4-naphthoquinone	378	3.28	2.38	6.22	
[60]fullerene	525	2.36	2.31	6.16	
menadione	364	3.41	2.18	6.03	

color and absorption bands in the visible range must be due to trace quantities of impurity, as has been discussed in detail by Strongin et al.[33] CT absorption bands of the complexes of **1** with the known electron acceptors, viz., [60]- and [70]fullerenes, menadione, *o*-chloranil, and 2,3-dichloro-1,4-naphthoquine could be detected by recording the spectra of mixtures containing **1** and the individual acceptors in the CCl$_4$ medium against the respective pristine acceptor solution as reference and then subtracting from it the absorbance due to **1**. Three such spectra are shown in Figure 2. In some cases multiple CT peaks were observed. In all cases the wavelengths at the CT peaks are different from the known λ_{mas} values of the component acceptors. The vertical ionization potential of compound **1** was determined from the trends in these CT transition energies as follows. For systems with multiple CT peaks, the longest wavelength peak was used for calculation.

The vertical electron affinities (E_A^v) of the first four acceptors mentioned above were obtained from literature[34−36] and that of the fifth one has been recently determined.[30] These E_A^v values correlate well with the presently observed CT transition energies ($h\nu_{CT}$, Table 1) in accordance with the Mulliken[37] equation

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

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

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

In eq 2, 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 involves several energy terms in the “dative” state. In most cases G_0 is small and can be neglected while 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 interaction between the “no-bond” and “dative” states. A rearrangement of eq 1 yields

$$2C_1 + h\nu_{CT} = \frac{C_1(C_1 + h\nu_{CT})}{I_D^v} + \left(\frac{C_2}{I_D^v} + I_D^v\right) \qquad (3)$$

Neglecting G_0 and taking the typical D−A distance in π-type EDA complexes to be 3.5 Å, the major part of G_1 is estimated to be $e^2/4\pi\epsilon_0 r = 4.13$ eV. Using these values C_1 is obtained from eq 2 for each of the acceptors. A plot of $2C_1 + h\nu_{CT}$ against $C_1(C_1 + h\nu_{CT})$ 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 3) and the linear regression equation is

$$2C_1 + h\nu_{CT} = (0.131 \pm 0.007)[C_1(C_1 + h\nu_{CT})] + (7.888 \pm 0.425);\ \text{correln. coefficient} = 0.99 \qquad (4)$$

From the slope, I_D^v of resorcinarene **1** is found to be 7.62 eV. In eq 4 the $h\nu_{CT}$ of the [60]fullerene complex, which is found to have 2:1 stoichiometry (as will be shown in the next sections) has also been included. Mulliken’s theory[37] is valid for 1:1 EDA complexes where the complex is regarded as a resonance hybrid of two structures (D,A) and (D$^+$,A$^-$); in the ground state the no-bond structure (D,A) predominates while in the excited state the ionic structure (D$^+$,A$^-$) contributes predominantly. The CT transition involves absorption of one photon and transfer of one

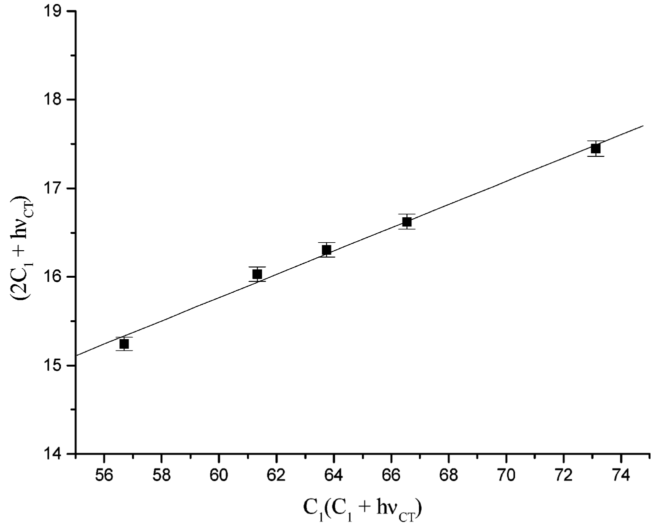

Figure 3. Plot for determination of vertical ionization potential of compound **1** according to eq 3.

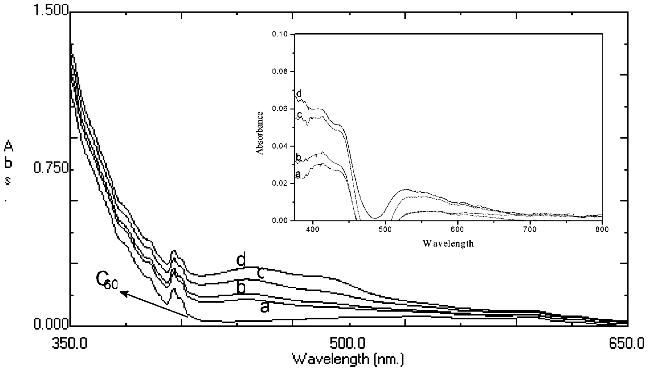

Figure 4. Absorption spectra of [60]fullerene (5.556×10^{-5} mol dm^{-3}, lowermost curve) and mixtures containing [60]fullerene (5.556×10^{-5} mol dm^{-3}) and compound **1** at concentrations (a) 3.125×10^{-3}, (b) 4.107×10^{-3}, (c) 6.071×10^{-3}, and (d) 8.095×10^{-3} mol dm^{-3} (progressively upward) all taken against solvent CCl_4 as reference. Inset: 375 to 800 nm range is the actual CT band of the complex at varying concentrations of **1** obtained by difference method.

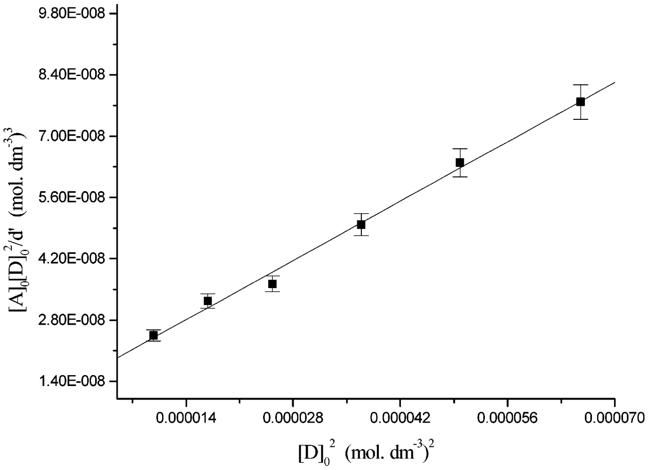

Figure 5. Benesi−Hildebrand plot for [60]fullerene−compound **1** complex at 313 K.

electron from D to A. If this mechanism of charge transfer is accepted for an EDA complex of 2D:1A stoichiometry then the complex may be modeled as involving one DA unit (formed by inclusion of A into D) as the acceptor and another D molecule as the donor. In this model eqs 1 to 3 remain approximately valid.

Degree of Charge Transfer (α). In a Mulliken two-state model,[37] the ground (ψ_g) and excited (ψ_{ex}) state wave functions of the CT complexes are described by a linear combination of dative ψ (D°,A°) and ionic ψ (D^+,A^-) states,

$$\psi_g = \sqrt{1-\alpha}\,\psi(D°,A°) + \sqrt{\alpha}\,\psi(D^+,A^-) \tag{5}$$

$$\psi_{ex} = \sqrt{1-\alpha}\,\psi(D^+,A^-) - \sqrt{\alpha}\,\psi(D°,A°) \tag{6}$$

where α is the degree of charge transfer. The function $\psi(D^+,A^-)$ differs from ψ(D°,A°) by the promotion of an electron from donor to the acceptor. In this case, α is given[37,38] by

$$\alpha = \frac{C_2}{2(I_D^v - E_A^v + C_1)^2 + C_2} \tag{7}$$

The values of α, calculated by using eq 7 and shown in Table 1, are small and indicate that very little charge transfer occurs in the ground state. However, as expected with a fixed donor, α increases with increase in the electron affinity of the acceptors (Table 1).

Molecular Complex Formation of the Resorcinarene 1 with [60]- and [70]Fullerenes. *Case 1. Complexation with [60]Fullerene.* Spectra of mixtures containing a fixed concentration of [60]fullerene (5.556×10^{-5} mol dm^{-3}) and varying concentrations of the resorcinarene **1** are given in Figure 4. The two substances have overlapping absorption bands in the visible region. To get rid of the absorbance due to resorcinarne and the uncomplexed [60]fullerene, i.e., to get the absorbance due to the complex only, we have constructed in the inset of Figure 4 the difference spectra (i.e, absorbance of mixture − the sum of the absorbances of **1** and [60]fullerene at concentration present in the mixture over the wavelength range scanned) are shown. Although the CT peak is at 525 nm, for calculation of the formation constant of the complex we selected the 406 nm fullerene peak because this shows the maximum spectral variation with change in concentration of **1** (vide inset of Figure 4). It is to be noted at this point that the impurity peak of resorcinarene **1** appears in the range 450−500 nm (as shown in Figure 2d). Hence while subtracting the resorcinarene absorption from those of the mixtures, a part of the difference spectrum in this range goes below the baseline, particularly when complex concentration is low. However at 406 nm (our selected wavelength for measurement of formation constant) the impurity absorption is not strong enough and so in the difference spectrum at 406 nm there is no absorbance below the baseline. Absorbance data of the mixtures at four different temperatures are shown in Table 2. Formation constants of CT complexes with 1:1 (donor/acceptor) stoichiometry, are usually determined by using the Benesi−Hildebrand[39] (B−H) equation which, for cells with 1 cm optical path length, is

$$\frac{[A]_0[D]_0}{d'} = \frac{[D]_0}{\epsilon'} + \frac{1}{K\epsilon'} \tag{8}$$

with

$$d' = d - d_A{}^0 - d_D{}^0 \tag{9}$$

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 some suitable wavelength (λ) against the

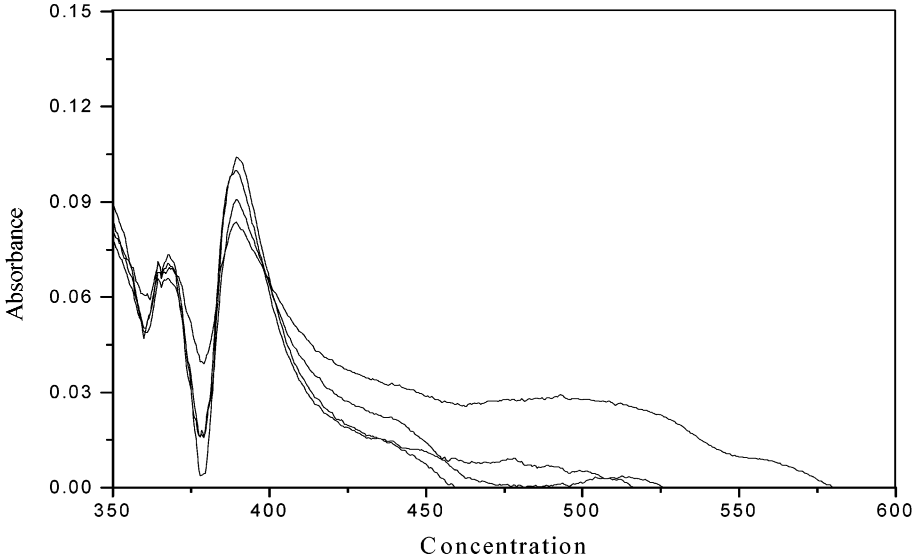

Figure 6. Variation of CT absorption spectra of mixtures containing [70]fullerene (3.271×10^{-5} mol dm^{-3}) and varying concentrations of **1**, obtained by the difference method. The progressively upward curves correspond to 2.917×10^{-3}, 4.375×10^{-3}, 6.042×10^{-3}, and 7.024×10^{-3} mol dm^{-3} of **1**.

solvent as reference, $d_A{}^0$ and $d_D{}^0$ are the absorbances of the acceptor and donor solutions with the same molar concentrations as in the mixture at the same wavelength (λ). The quantity $\epsilon' = \epsilon_c - \epsilon_A - \epsilon_D$ means the apparent molar absorptivity of the complex, ϵ_A and ϵ_D being those of the acceptor and the donor, respectively, at λ. K is the formation constant of the complex. Equation 8 is valid under the condition $[D]_0 \gg [A]_0$. If, however, the complex is of 2:1 (donor/acceptor) stoichiometry, the B−H equation is to be modified to

$$\frac{[A]_0[D]_0^2}{d'} = \frac{[D]_0^2}{\epsilon'} + \frac{1}{K\epsilon'} \qquad (10)$$

with

$$d' = d - d_A{}^0 - d_D{}^0 \qquad (11)$$

The quantity ϵ' now means $\epsilon_c - \epsilon_A - 2\epsilon_D$.

Experimental data shown in Table 2 show a very wide scatter and bad correlation when eq 8 was tried. But an excellent linear plot according to eq 10 was obtained at each of the temperatures studied. One such plot is shown in Figure 5. From the slopes and intercepts of such plots the formation constants were determined. The stoichiometry of the complex is therefore 2:1 (resorcin[4]arene/[60]fullerene).

Case 2. Complexation with [70]Fullerene. In this case, the spectra of mixtures containing **1** in varying concentrations and [70]fullerene (3.218×10^{-5} mol dm^{-3}) at a fixed concentration are very complex, but the difference spectra are simple. Figure 6 shows a number of such spectra where absorbance at the CT peak (390 nm) clearly increases with an increase in concentration of **1**, and two isosbestic points are distinctly visible. Absorbance data (Table 3) in this case fit excellently into eq 8, thereby showing that the stoichiometry in this case is 1:1. One typical B−H plot is shown in Figure 7.

Formation Constants, Enthalpies, and Entropies of Formation of the Fullerene Complexes of 1. Formation constants (K) of the fullerene complexes, as determined from the slopes and intercepts of the B−H plots at a number of temperatures, are shown in Table 4 where n in the unit of K is for a complex of n:1 stoichiometry. The high values of K in case of [60]fullerene complex at all the temperatures studied indicate that [60]fullerene is included in the cavity of **1**. In case of the [70]fullerene complex K is low which indicates that **1** does not include [70]fullerene. The values of ln$K$ for both the complexes

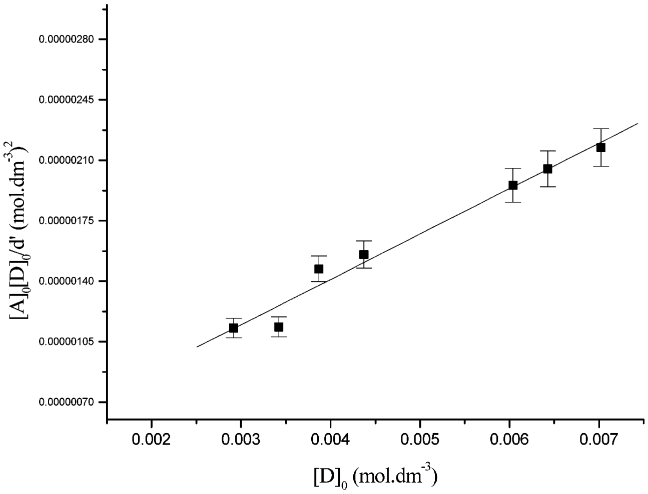

Figure 7. Benesi−Hildebrand plot for [70]fullerene−**1** complex at 303 K.

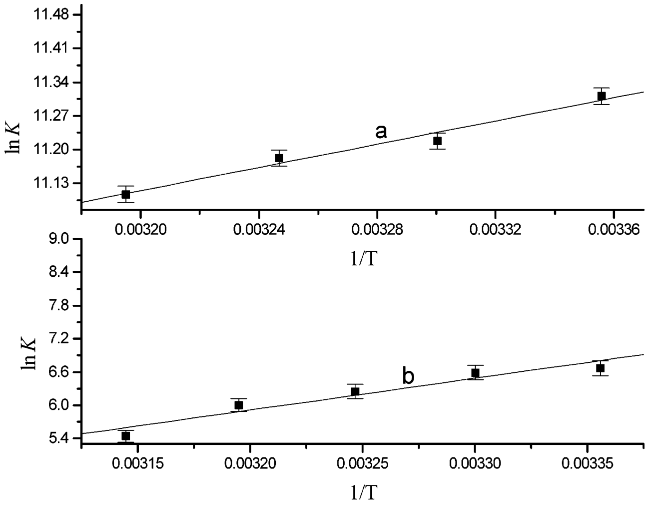

Figure 8. van't Hoff plots for complexes of compound **1** with (a) [60]fullerene and (b) [70]fullerene.

TABLE 2: Absorbance Data for Resorcinarene 1−[60]Fullerene Mixtures at Different Temperatures

acceptor	10^5[acceptor] (mol dm^{-3})	10^3[compound **1**] (mol dm^{-3})	corrected absorbance (d') at 406 nm			
			298 K	303 K	308 K	319 K
[60]fullerene	5.556	3.125	0.0285	0.0254	0.0227	0.0222
		4.107	0.0339	0.0311	0.0305	0.0290
		5.030	0.0461	0.0443	0.0408	0.0388
		6.071	0.0480	0.0471	0.0516	0.0411
		7.054	0.0503	0.0446	0.0435	0.0432
		8.095	0.0534	0.0516	0.0489	0.0468

TABLE 3: Absorbance Data for Resorcinarene 1−[70]Fullerene Mixtures at Different Temperatures

acceptor	10^5[acceptor] (mol dm^{-3})	10^3[compound **1**] (mol dm^{-3})	corrected absorbance at 390 nm				
			298 K	303 K	308 K	313 K	318 K
[70]fullerene	3.218	2.917	0.0922	0.0830	0.0740	0.0675	0.0572
		3.423	0.1061	0.0969	0.0891	0.0674	0.0569
		3.869	0.0953	0.0846	0.0773	0.0677	0.0577
		4.375	0.0963	0.0906	0.0786	0.0722	0.0613
		6.042	0.1119	0.0994	0.0895	0.0792	0.0733
		6.429	0.1105	0.1009	0.0941	0.0871	0.0795
		7.024	0.1120	0.1039	0.0967	0.0869	0.0811

TABLE 4: Formation Constants, Enthalpies, and Entropies of Formation of the Complexes of Resorcinarne 1 with [60]- and [70]Fullerenes

acceptor	temp (K)	formation constant (K) (mol^{-1} dm^3)^n	ϵ' (dm^3 mol^{-1} cm^{-1})	$\Delta H_f°$ (kJ mol^{-1})	$\Delta S_f°$ (J K^{-1} mol^{-1})
[60]fullerene	298	81679	1100 ± 10	−10.02 ± 1.10	60.36 ± 3.59
	303	74464			
	308	71835			
	313	66665			
[70]fullerene	298	789	3850 ± 15	−47.73 ± 7.64	−103.41± 24.80
	303	727			
	308	581			
	313	404			
	318	231			

exhibit excellent linear correlation with $1/T$ in accordance with the van't Hoff equation as shown in Figure 8. The regression equations are:

for [60]fullerene **1** complex

$$\ln K = (1205 \pm 130)/T + (7.26 \pm 0.43); \quad \text{correln. coefficient} = 0.99 \quad (12)$$

and for [70]fullerene **1** complex

$$\ln K = (5741 \pm 918)/T + (-12.46 \pm 2.98); \quad \text{correln. coefficient} = 0.96 \quad (13)$$

The enthalpies ($\Delta H_f°$) and entropies ($\Delta S_f°$) of formation of the complexes determined from eqs 12 and 13 are shown in Table 4. It is to be noted that $\Delta S_f°$ for the [60]fullerene complex is positive. When inclusion occurs, entropy tends to decrease due to the association of two molecules into one and, at the same time, many solvent molecules which were initially in the resorcinare cavity come out, leading to an increase in entropy. The resultant of these two during complexation with [60]-fullerene is positive, which means that there is a large extent of desolvation of the cavity during inclusion. [70]Fullerene, on the other hand, forms a noninclusion type of simple adduct, and hence the role of desolvation is much less important and $\Delta S_f°$ is negative due to simple molecular association.

Conclusion

The resorcin[4]arene **1** acts as a electron donor with vertical ionization potential of 7.62 eV and also as a host for [60]-fullerene guest. The compound **1** therefore has the ability to include [60]fullerene in preference to [70]fullerene, a fact which may possibly be utilized in purification of [60]fullerene from carbon soots.

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