

# Spectrophotometric Study of Complexation of Dicyclohexano-24-crown-8 with [60]- and [70]Fullerenes and Other Acceptors

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Molecular complex formation of dicyclohexano-24-crown-8 with electron acceptors such as [60]- and [70]-fullerenes, menadione (vitamin K<sub>3</sub>), and *o*- and *p*-chloranils have been studied in CCl<sub>4</sub> medium. Charge transfer (CT) absorption bands have been obtained in four cases which correlate well with the electron affinities of the acceptors. In the case of the [70]fullerene complex, an isosbestic point has been obtained. Entropies and enthalpies of formation of the [60]- and [70]fullerene complexes with the crown ether have been determined by estimating the formation constants spectrophotometrically at five different temperatures. It is observed that the crown ether under consideration does not form inclusion complexes with the fullerenes although the corresponding crown ether with a benzene ring instead of cyclohexane ring is known to include [60]fullerene in preference to [70]fullerene. The conformational flexibility of the cyclohexane ring affects the cavity size of the crown and thus hinders inclusion complex formation.

## 1. Introduction

Crown ethers<sup>1</sup> have found wide application in biological fields<sup>2,3</sup> and also in chemical technology.<sup>4–11</sup> On the other hand, host–guest complexation is a subject of current interest in the fields of supramolecular and fullerene chemistry.<sup>12–20</sup> For example, chiral recognition through host–guest complexation with crown ethers as hosts is a subject of very recent activity.<sup>21,22</sup> Thus, molecular recognition of tryptophan enantiomers in aqueous medium has been recently attempted through the synthesis of crown ether-tethered cyclodextrin hosts.<sup>23</sup> Crown ethers are also being used in the synthesis of rotaxanes whose precursors are often host–guest complexes.<sup>24,25</sup> In particular, dibenzo-24-crown-8 ethers have recently been used<sup>26</sup> for the synthesis of [3]rotaxanes. In a previous work<sup>27</sup> vertical ionization potentials of a number of crown ethers from CT bands of their molecular complexes have been reported. It has also been shown<sup>28</sup> that dibenzo-24-crown-8 forms an inclusion complex with [60]fullerene but a simple noninclusion type of molecular adduct with [70]fullerene. Such findings are of importance in developing methods of separation from fullerene mixtures.<sup>20</sup> But if the two benzene rings are replaced by two cyclohexane groups, then owing to greater conformational flexibility of cyclohexane the inclusion capacity of the crown ether host may either increase or decrease. The purpose of the present paper is to investigate this. The crown ether under the present investigation is, therefore, dicyclohexano-24-crown-8 (the structure of which is given in Figure 1, and henceforth in this paper it will be called “crown 1” for brevity). Host–guest complexes<sup>29</sup> sometimes exhibit charge-transfer bands<sup>30</sup> also. In this work a CT band was observed with the [70]fullerene complex. So it was felt necessary to examine the electron donor ability of crown 1, and for this purpose CT bands of crown 1 complexes with some more electron acceptors were determined and analyzed in light of Mulliken’s theory.<sup>31</sup> In many of our previous

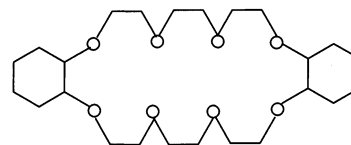


Figure 1. Structure of dicyclohexano-24-crown-8 (crown 1).

works<sup>28,30,32,33</sup> the acceptor was kept fixed and the donor varied and conclusions were drawn from some linearly rearranged form of the Mulliken equation. But this equation is not linear with respect to electron affinity of the acceptors in a study with a fixed donor. This point has been focused on in the first part of this work.

## 2. Experimental Section

[60]Fullerene was collected from Sigma, and [70]fullerene, from SES Research Inc., Houston, TX. *o*-Chloranil was collected from Sigma, and *p*-chloranil, from Fluka, Lausanne, Switzerland; they were further purified by sublimation just before use. The other chemicals, e.g. menadione (i.e., 2-methyl-1,4-naphthoquinone), 2,3-dichloro-1,4-naphthoquinone, and the crown ether 1, were collected 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.

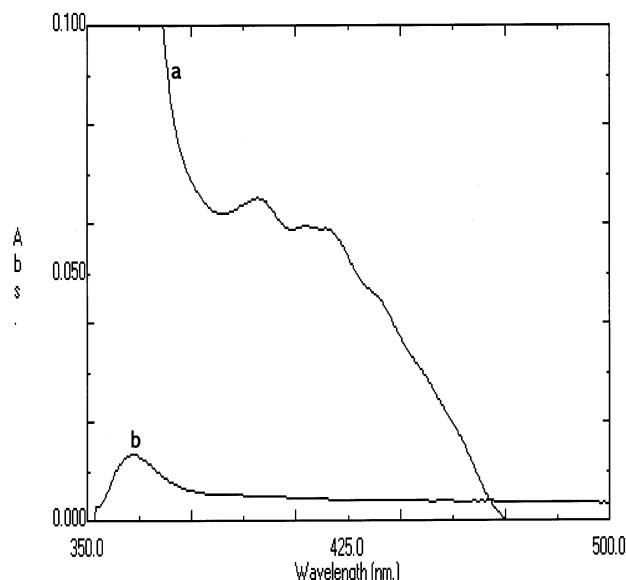
## 3. Results and Discussion

**3.1. Observation of CT Bands.** In this study CT bands were observed in case of complexes of dicyclohexano-24-crown-8 with (i) *o*-chloranil, (ii) *p*-chloranil, (iii) [70]fullerene, (iv) menadione, and (v) 2,3-dichloro-1,4-naphthoquinone. To obtain CT bands, the spectrum of each of the solutions (in CCl<sub>4</sub>) containing the crown ether 1 as donor and the acceptors i–v separately was recorded against the pristine acceptor solution as reference. It is a common experience that CT bands in

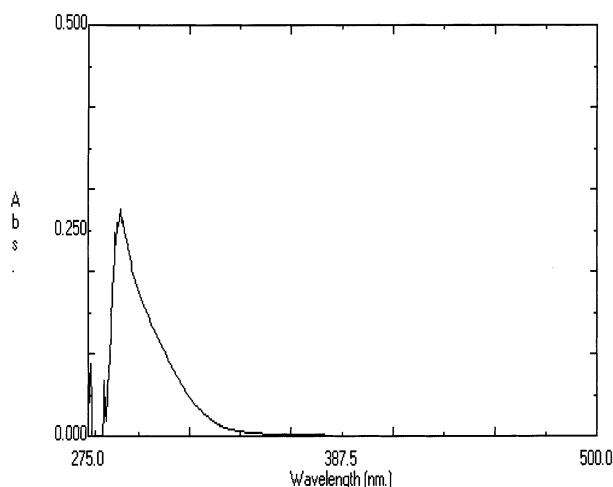
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**Figure 2.** Absorption spectrum of (a) menadione ( $1.045 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) against the solvent  $\text{CCl}_4$  as reference and (b) a mixture of menadione ( $1.045 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) + crown **1** ( $2.426 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) against the pristine menadione solution as reference.



**Figure 3.** Absorption spectrum of crown **1** ( $2.426 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) against the solvent  $\text{CCl}_4$  as reference.

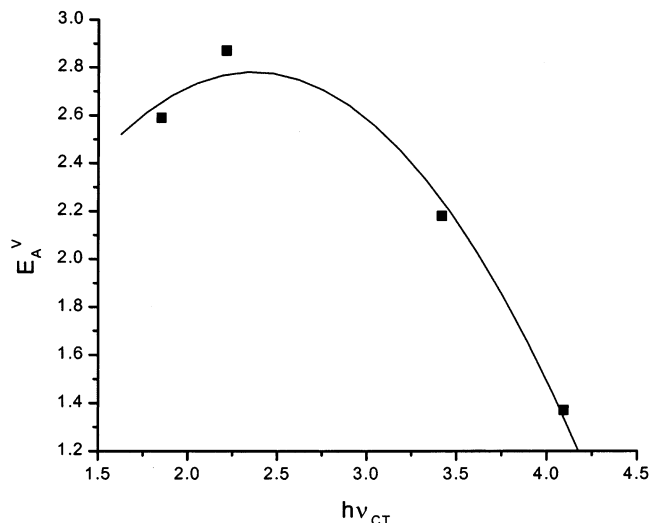
solution are detected only by taking a high concentration of donor compared to that of the acceptor. In the present case [crown ether]  $\approx 10^{-2}$  mol  $\cdot \text{dm}^{-3}$  and concentrations of the acceptors were  $\approx 10^{-3}$ – $10^{-5}$  mol  $\cdot \text{dm}^{-3}$ . One typical CT absorption band is shown in Figure 2, where the absorption band of the pristine acceptor solution is also shown. As shown in Figure 3, crown **1** does not absorb above 350 nm and so does not interfere while locating the CT bands. The vertical electron affinities ( $E_A^v$ ) of four of the acceptors under study are known,<sup>34–37</sup> and they correlate well with the presently observed CT transition energies ( $h\nu_{\text{CT}}$ , Table 1) in accordance with the Mulliken<sup>31</sup> equation:

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

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

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

where  $E_A^v$  is the vertical electron affinity of the acceptor,  $G_0$  is



**Figure 4.** Plot of  $E_A^v$  against  $h\nu_{\text{CT}}$  of complexes of crown **1** with acceptors of known electron affinity.

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

acceptor	$\lambda_{\text{CT}}$ , nm	$h\nu_{\text{CT}}$	$E_A^v$ , eV
[70]fullerene	670	1.851	2.59
<i>o</i> -chloranil	560	2.215	2.87
2,3-dichloro-1,4-naphthoquinone	379	3.274	
menadione	363	3.417	2.18
<i>p</i> -chloranil	303	4.093	1.37

the sum of several energy terms (like 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 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. 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:

$$E_A^v = 0.10439969 + 2.26587521h\nu_{\text{CT}} - 0.4797853(h\nu_{\text{CT}})^2 \quad (3)$$

A parabolic plot (Figure 4) was obtained for  $E_A^v$  against  $h\nu_{\text{CT}}$ . If the value of  $h\nu_{\text{CT}}$  of the complex of 2,3-dichloro-1,4-naphthoquinone with crown **1** is placed in eq 3,  $E_A^v$  of the acceptor ( $v$ ) is found to be 2.38 eV. This is reasonably higher than that of 1,4-naphthoquinone (2.12 eV<sup>36</sup>) and is obviously due to the electronegative chlorine atoms.

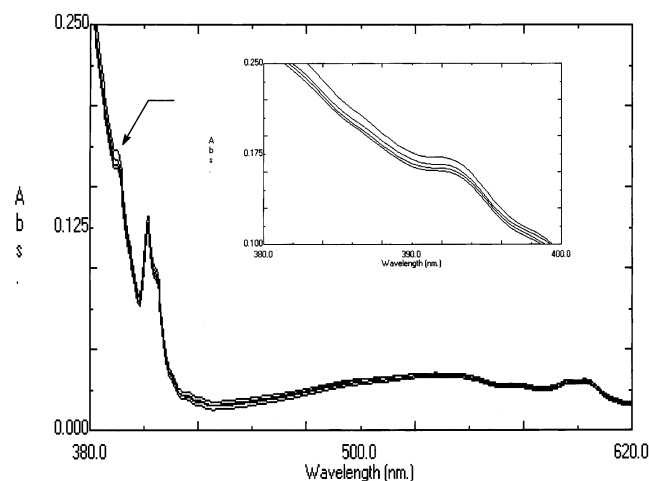
### 3.2. Spectrophotometric Study of Formation Equilibria of the Complexes of Crown 1 with [60]- and [70]Fullerenes.

The intensity in the visible portion of the absorption band, measured against the solvent as reference, decreases systematically with gradual addition of crown **1** (Figures 5 and 6). This indicates complex formation. An isosbestic point at  $\lambda = 375$  nm was obtained in case of the crown **1**–[70]fullerene complex (inset, Figure 6). Stoichiometry and formation constants of the complexes were determined by using the Benesi–Hildebrand<sup>38</sup> equation for cells with 1 cm optical path length

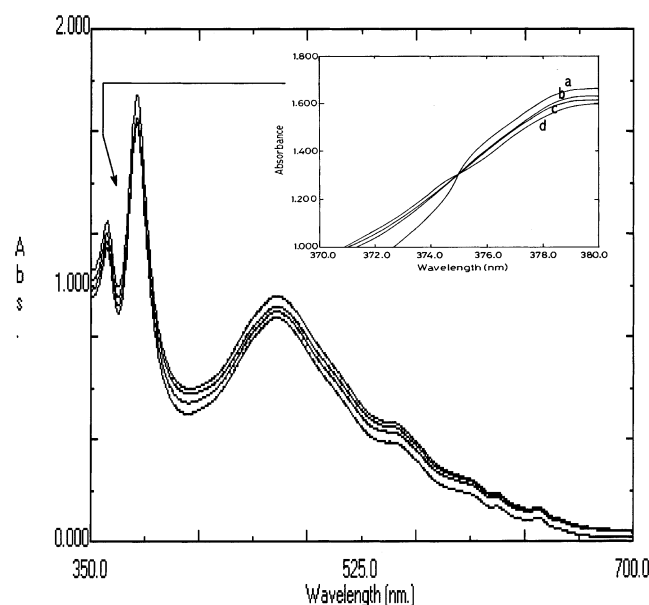
$$[A]_0[D]_0/d' = [D]_0/\epsilon' + 1/K\epsilon' \quad (4)$$

with

$$d' = d - d_A^0 - d_d^0 \quad (5)$$



**Figure 5.** Absorption spectra of [60]fullerene ( $3.968 \times 10^{-5} \text{ mol dm}^{-3}$ , uppermost curve) and mixtures containing [60]fullerene ( $3.968 \times 10^{-5} \text{ mol dm}^{-3}$ ) and crown **1** ( $5.507 \times 10^{-3}$ ,  $2.428 \times 10^{-2}$ , and  $3.188 \times 10^{-3} \text{ mol dm}^{-3}$  progressively downward) all taken against solvent  $\text{CCl}_4$  as reference. Inset: 380–400 nm range expanded for clarity.



**Figure 6.** Absorption spectra of [70]fullerene ( $3.271 \times 10^{-3} \text{ mol dm}^{-3}$ , uppermost curve) and mixtures containing [70]fullerene ( $3.271 \times 10^{-3} \text{ mol dm}^{-3}$ ) and crown **1** ( $1.616 \times 10^{-2}$ ,  $3.623 \times 10^{-2}$ , and  $4.312 \times 10^{-2} \text{ mol dm}^{-3}$  progressively downward) all taken against solvent  $\text{CCl}_4$  as reference. Inset: 370–380 nm range expanded to show an isosbestic point.

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  $\lambda$  against the solvent as reference, and  $d_A^0$  and  $d_D^0$  are the absorbances of the acceptor and donor solutions with same molar concentrations as in the mixture at the same wavelength (i.e.,  $\lambda$ ). The quantity  $\epsilon'$  means  $\epsilon_c - \epsilon_A - \epsilon_D$  where  $\epsilon_c$  is the molar absorptivity of the complex,  $\epsilon_A$  and  $\epsilon_D$  being those of the acceptor and the donor respectively at  $\lambda$ .  $K$  is the formation constant of the complex. Equation 4 is valid<sup>38</sup> under the condition  $[D]_0 \gg [A]_0$  for 1:1 donor–acceptor complexes. Absorbance data were taken at 392 and 471 nm respectively for the [60]- and [70]fullerene complexes because at these wavelengths the variation of absorbance with gradual addition of crown **1** was notable and the latter does not absorb appreciably at these two wavelengths. Experimental data are given in Tables 2 and 3. In all cases very good linear plots

**TABLE 2: Absorbance Data for Crown 1–[60]Fullerene Mixtures at Different Temperatures<sup>a</sup>**

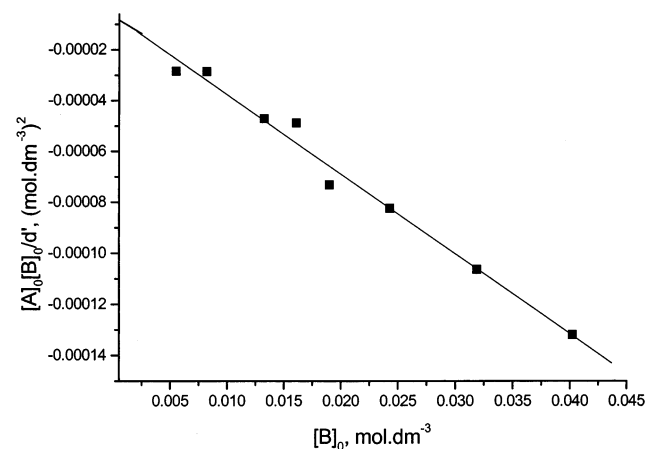
$10^2[\text{dicyclohexano-24-crown-8}], \text{ mol dm}^{-3}$	abs at 392 nm				
	288 K	296 K	304 K	312 K	319 K
0.551	0.1708	0.1701	0.1693	0.1672	0.1661
0.819	0.1698	0.1696	0.1656	0.1636	0.1635
1.326	0.1698	0.1691	0.1658	0.1619	0.1624
1.608	0.1725	0.1692	0.1639	0.1616	0.1599
1.898	0.1711	0.1686	0.1667	0.1639	0.1620
2.428	0.1701	0.1695	0.1644	0.1637	0.1633
3.188	0.1761	0.1686	0.1651	0.1619	0.1609
4.022	0.1706	0.1687	0.1649	0.1626	0.1611

<sup>a</sup>  $10^5[[60]\text{fullerene acceptor}] = 3.968 \text{ mol dm}^{-3}$ .

**TABLE 3: Absorbance Data for Crown 1–[70]Fullerene Mixtures at Different Temperatures<sup>a</sup>**

$10^2[\text{dicyclohexano-24-crown-8}], \text{ mol dm}^{-3}$	abs at 471 nm				
	293 K	298 K	303 K	308 K	313 K
0.00616	0.9011	0.8950	0.8896	0.8824	0.8770
0.01022	0.9318	0.9248	0.9188	0.9136	0.9072
0.01616	0.9365	0.9290	0.9231	0.9170	0.9124
0.03007	0.8965	0.8881	0.8820	0.8755	0.8695
0.03623	0.9209	0.9102	0.9011	0.8962	0.8901
0.04312	0.9004	0.8901	0.8824	0.8732	0.8685

<sup>a</sup>  $10^5[[70]\text{fullerene acceptor}] = 3.2708 \text{ mol dm}^{-3}$ .

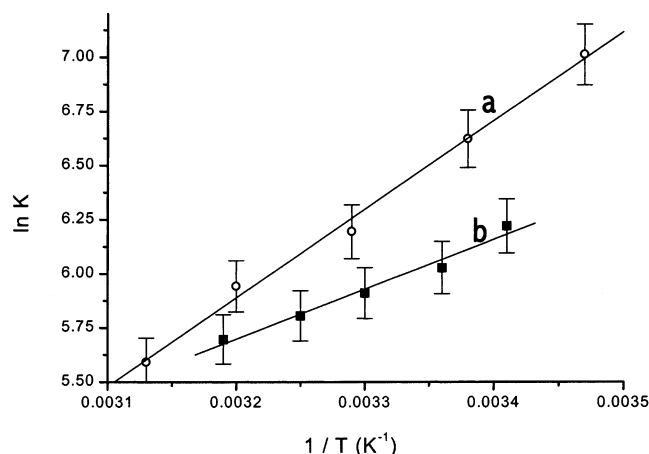


**Figure 7.** Benesi–Hildebrand plot for [60]fullerene–crown **1** complex at 304 K.

**TABLE 4: Formation Constants, Enthalpies, and Entropies of Formation of the Complexes of Dicyclohexano-24-crown-8 with [60]- and [70]Fullerenes**

acceptor	temp, K	formation const (K), $\text{mol}^{-1} \text{ dm}^3$	$\Delta H_f^\circ$ , $\text{kJ mol}^{-1}$	$\Delta S_f^\circ$ , $\text{J K}^{-1} \text{ mol}^{-1}$
[60]fullerene	288	1109	$-33.9 \pm 1.5$	$-59.7 \pm 4.4$
	296	752		
	304	490		
	312	381		
	319	268		
[70]fullerene	293	503	$-19.4 \pm 1.3$	$-14.7 \pm 4.4$
	298	415		
	303	369		
	308	332		
	313	298		

according to eq 4 are obtained, one typical case being shown in Figure 7. The correlation coefficients of all such plots were above 0.98. Values of  $K$  of the complexes obtained from such plots are shown in Table 4. The enthalpies of formation were obtained by using the van't Hoff equation. Plots of  $\ln K$  against  $1/T$  are shown in Figure 8. The regression equations were obtained for the two fullerene complexes under study.



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

For [60]fullerene complex

$$\ln K = (4081 \pm 177)/T + (-7.2 \pm 0.6) \quad (6)$$

For [70]fullerene complex

$$\ln K = (2335 \pm 159)/T + (-1.8 \pm 0.5) \quad (7)$$

In each case the |correlation coefficient| is 0.99.

#### IV. Conclusion

The study of charge-transfer bands of molecular complexes involving novel materials such as fullerenes is of current interest.<sup>39–43</sup> In this study CT bands of crown **1** complexes with a series of acceptors have been located, and using the full form of Mulliken's equation, the electron affinity of 2,3-dichloro-1,4-naphthoquinone has been determined; the estimated value has the right trend (higher than that of 1,4-naphthoquinone owing to electronegative chlorine atoms). While dibenzo-24-crown-8 forms inclusion complex<sup>28</sup> with [60]fullerene, the formation constant of the crown **1**–[60]fullerene complex is much lower in magnitude characteristic of noninclusion type of molecular adducts. This shows that replacement of the benzene ring by cyclohexane decreases the inclusion capacity of the crown ether. Since the cyclohexane ring has a much higher conformational flexibility than the benzene ring, it probably decreases the cavity size of the crown ether and thus makes it unable to include the fullerene balls. It is observed (Figure 8) that at any temperature the formation constant of the [60]fullerene complex is higher than that of the [70]fullerene complex although [70]fullerene is known<sup>32</sup> to have a higher electron affinity than [60]fullerene. This shows that it is not always possible to explain the order of *K* values of noninclusion type of CT complexes only in terms of electron affinities of the concerned acceptors probably because their formation involves many energy terms (in particular, solvation).

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