

# NMR Spectrometric Studies of Complexation of [60]Fullerene with Series of Anisoles

Sumanta Bhattacharya,<sup>\*,†</sup> Ajay K. Bauri,<sup>‡</sup> Subrata Chattopadhyay,<sup>‡</sup> and Manas Banerjee<sup>†</sup>

Department of Chemistry, The University of Burdwan, Golapbag, Burdwan - 713 104, India, and  
Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400 085, India

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Detailed <sup>1</sup>H and <sup>13</sup>C NMR spectrometric studies have been carried out to gain insight into the nature of molecular interactions of the electron donor–acceptor (EDA) complexes of [60]fullerene with a series of anisoles, namely, anisole, *m*-bromoanisole, and *p*-bromoanisole. [60]Fullerene has been shown to form 1:1 adducts with the above series of anisoles. Formation constants (*K*) for all the complexes have been determined from the systematic variation of the NMR chemical shifts of specific protons of the anisoles in the presence of [60]fullerene. The *K* values of [60]fullerene/anisole, [60]fullerene/*m*-bromoanisole, and [60]fullerene/*p*-bromoanisole complexes yield good estimates of the Hammett  $\rho$  constant for the complexation reaction. To the best of our knowledge, this paper reports for the first time a very fruitful technique by which the concentrations of EDA complexes can be estimated from systematic variations of the <sup>13</sup>C NMR signal.

## 1. Introduction

The past decade has seen tremendous development in [60]fullerene<sup>1</sup> chemistry, as an avalanche of research activity has been generated.<sup>2,3</sup> The peculiarities of the chemical behavior of the [60]fullerene molecule are determined by the large size, the high symmetry, and the spherical shape of the carbon cage, being rich in  $\pi$ -type electrons. Owing to high polarizability,<sup>4</sup> [60]fullerene forms many molecular complexes.<sup>5–11</sup> A modification of these complexes by doping through the gas phase,<sup>12</sup> using photoinduced charge transfer (CT),<sup>13</sup> or using field transistor technology<sup>14</sup> could provide novel materials with unusual conducting and magnetic properties.

The unusual temperature dependence of the solubility of [60]fullerene in a number of organic solvents<sup>15</sup> has attracted attention and stimulated research activities in different laboratories around the world. Though there are few reports on molecular interaction of [60]fullerene with benzenoid solvents,<sup>16,17</sup> a unified approach is long overdue and has not been reported so far. Our present investigations are directed toward the possible effects of the electron donor–acceptor (EDA) interaction of [60]fullerene with aromatic ether molecules such as anisoles. Though EDA interaction of [60]fullerene with various electron donors is well-documented,<sup>5–11,18,19</sup> no attention has been paid to its complexation with aromatic ethers such as anisoles, which are mainly being used as solvents in synthetic organic chemistry. The [60]fullerene/anisole interaction is also important for the interpretation of other spectroscopic data. Because the formation constant (*K*) is an important parameter which measures the extent of binding in molecular recognition, the object of the present paper is to determine *K* values of the complexes of [60]fullerene with a series of anisoles in CCl<sub>4</sub> solution by an NMR spectrometric method which is based on a principle developed long ago by Mathur et al.<sup>20</sup> and Hanna and Ashbaugh.<sup>21</sup> If the particular electronic subsystems of the donors and [60]fullerene<sup>22</sup> are taken into account, [60]fullerene/

anisole systems should provide an excellent paradigm for widening of the scope of the present investigations on molecular interactions of [60]fullerene with various other electron donors.

## 2. Materials and Methods

[60]Fullerene was obtained from Sigma, U.S.A. Anisole was collected from SRL, India. *m*-Bromoanisole was collected from Spectrochem, India. *p*-Bromoanisole was obtained from Lancaster, U.K. The solvent, CCl<sub>4</sub>, was UV spectroscopic grade. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the anisoles and anisole/[60]fullerene mixtures in solution of CCl<sub>4</sub> were recorded on a Bruker Ac - 200 (200 MHz) NMR spectrometer with CDCl<sub>3</sub> as an internal lock. Third parametric method (PM3) theoretical calculations were done using SPARTAN '02 and silicon graphics hardware.

## 3. Results and Discussions

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



one requires knowledge of the equilibrium concentrations of species A, B, and C. Now, [60]fullerene has no proton, and so, the formation equilibria of [60]fullerene/anisole complexes have been studied in the present report on the basis of the following principle.

This work is primarily concerned with the case where the rate of reaction is fast on the NMR time scale and only a time-averaged spectrum of the donor and the donor–acceptor complex is observed. In this case, the observed chemical shift of a particular proton in molecule B, owing to a rapid reversible equilibrium (1), is the time-averaged shift of the same proton in free B and in the complex

$$\delta_{\text{obs}}^{(B)} = P_0 \delta_0^{(B)} + P_C \delta_C^{(B)} \quad (2)$$

<sup>†</sup> The University of Burdwan.

<sup>‡</sup> Bhabha Atomic Research Centre.

where  $P_0$  and  $P_C$  are the probabilities of finding B molecules in the free and complexed forms, respectively.  $\delta_0^{(B)}$  and  $\delta_C^{(B)}$  are the chemical shifts of the same proton in pure B and in complex C.

Equation 2 can be explained as

$$\delta_{\text{obs}}^{(B)} = (1 - P_C)\delta_0^{(B)} + P_C\delta_C^{(B)}$$

or

$$\delta_{\text{obs}}^{(B)} - \delta_0^{(B)} = P_C(\delta_C^{(B)} - \delta_0^{(B)}) \quad (3)$$

Denoting  $\delta_{\text{obs}}^{(B)} - \delta_0^{(B)}$  as  $\Delta_{\text{obs}}$  (i.e., observed chemical shift of a B-proton in the equilibrium mixture of A and B relative to that in free B) and  $\delta_C^{(B)} - \delta_0^{(B)}$  as  $\Delta_0$  (i.e., chemical shift of B-proton in the pure complex relative to that in the free B molecule), we have

$$\Delta_{\text{obs}} = P_C\Delta_0 \quad (4)$$

Now,

$$P_C = [C]/([C] + [B]) = [C]/[B]_0 \quad (5)$$

where  $[C]$  and  $[B]$  are respective equilibrium concentrations of the complex and free B, and  $[B]_0$  is the initial concentration of B in the mixture before complexation. Combining eqs 4 and 5 gives

$$\Delta_{\text{obs}} = [C]\Delta_0/[B]_0 \quad (6)$$

Now, under the approximation  $[B]_0 \gg [A]_0$ , the formation constant ( $K$ ) can be written as

$$\begin{aligned} K &= [C]/[B][A] \\ &= [C]/\{([B]_0 - [C])([A]_0 - [C])\} \\ &= [C]/\{[B]_0([A]_0 - [C])\} \end{aligned}$$

because under the above approximation

$$[B]_0 - [C] \approx [B]_0$$

Hence

$$1/K = ([B]_0[A]_0/[C]) - [B]_0$$

$$1/K = [A]_0\Delta_0/\Delta_{\text{obs}} - [B]_0$$

So

$$[B]_0 = [A]_0(\Delta_0/\Delta_{\text{obs}}) - 1/K \quad (7)$$

Thus, a linear plot of  $[B]_0$  against  $1/\Delta_{\text{obs}}$  is expected, from which the intercept and slope of  $K$  and  $\Delta_0$ , respectively, can be evaluated. Variation of the methoxy proton signals in the  $^1\text{H}$  NMR spectra of anisole in the absence and presence of [60]fullerene are shown in Supporting Information Figures 1S, 2S, and 3S. With a fixed concentration of [60]fullerene, the observed  $\Delta$  decreases as donor concentration increases. Similar features were observed with *m*-bromoanisole and *p*-bromoanisole (Table 1). The values of maximum  $\Delta_{\text{obs}}$  in all the cases range from 6.30 to 115.92 Hz. Such values are much greater than that expected from solvation effects (ca 0.5 Hz). In all the cases under present study, excellent linear plots in accordance with eq 7 were obtained, one such plot being shown in Figure 1. The results of regression analysis are given as follows:

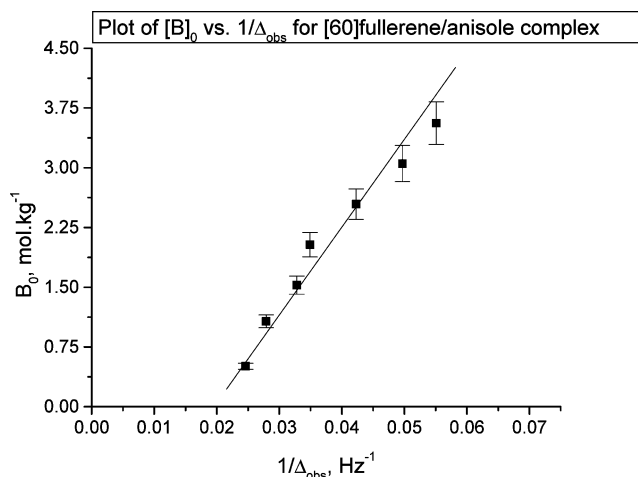


Figure 1. Plot of  $[B]_0$  vs.  $1/\Delta_{\text{obs}}$  for the [60]fullerene/anisole complex.

TABLE 1: NMR Chemical Shifts of Methoxy ( $-\text{OCH}_3$ ) Protons in [60]Fullerene/Anisole Mixtures in  $\text{CCl}_4$  Medium at Varying Concentrations of the Anisoles<sup>a</sup>

donor	$10^5 [A]_0$ $\text{mol}\cdot\text{kg}^{-1}$	concentration of the donor $\text{mol}\cdot\text{kg}^{-1}$	$\Delta_{\text{obs}}$ , Hz
anisole	7.407	0.763	40.56
		1.526	35.80
		2.289	30.46
		3.052	28.64
		3.815	23.64
		4.577	20.12
		5.340	18.12
<i>m</i> -bromoanisole	7.407	0.798	115.92
		1.597	113.54
		1.997	114.60
		2.396	109.92
		2.795	96.70
		3.195	94.90
<i>p</i> -bromoanisole	7.407	0.319	13.92
		0.958	10.68
		1.052	8.33
		2.236	6.30
		2.256	6.72

<sup>a</sup> Temperature = 298 K.

[60]fullerene/anisole system

$$[B]_0 = (95 \pm 7)/\Delta_{\text{obs}} - (1.6 \pm 0.3); \quad \text{correlation coefficient} = 0.99 \quad (8a)$$

[60]fullerene/3-bromoanisole system

$$[B]_0 = (590 \pm 170)/\Delta_{\text{obs}} - (4 \pm 1.6); \quad \text{correlation coefficient} = 0.90 \quad (8b)$$

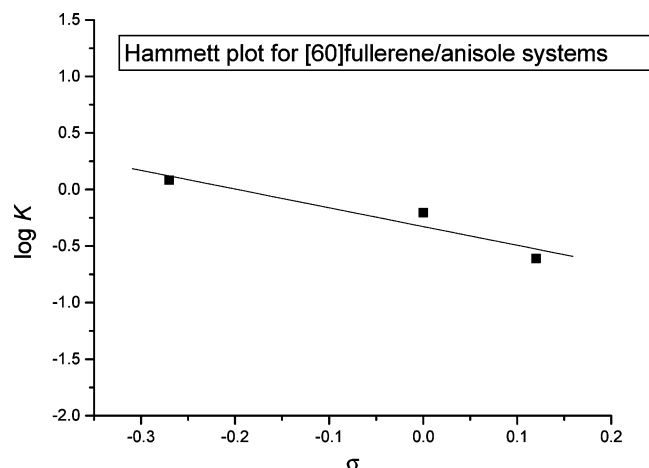
[60]fullerene/4-bromoanisole system

$$[B]_0 = (15 \pm 0.9)/\Delta_{\text{obs}} - (0.8 \pm 0.1); \quad \text{correlation coefficient} = 0.99 \quad (8c)$$

Values of  $K$  and  $\Delta_0$  obtained from above correlations are given in Table 2. The formation constants of the complexes of [60]fullerene with anisole, *m*-bromoanisole, and *p*-bromoanisole are in accordance with the Hammett<sup>23</sup> equation

$$\log K = (-1.65 \pm 0.55)\sigma - (0.3 \pm 0.1) \quad (9)$$

These linear free energy relationships are shown in Figure 2, where  $\sigma$  is the Hammett substituent constant for the Br group.



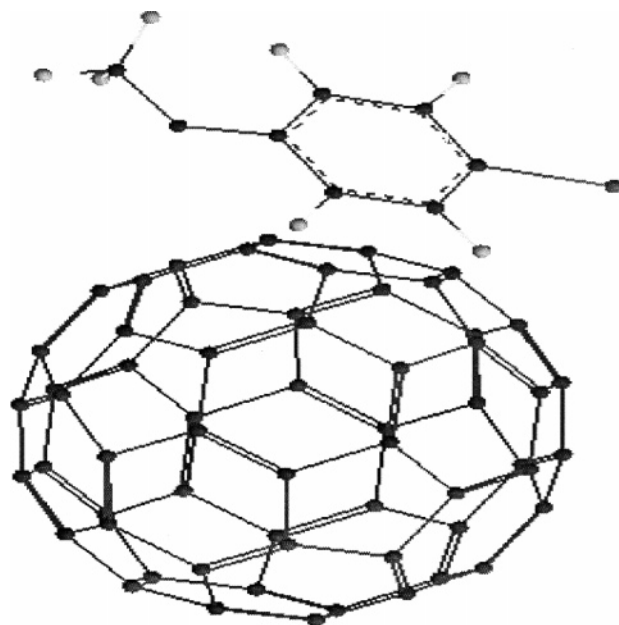
**Figure 2.** Hammett plot for complexes of anisole, *m*-bromoanisole, and *p*-bromoanisole with [60]fullerene as acceptor.

**TABLE 2: Formation Constants of the Complexes of [60]Fullerene with Anisole, *m*-Bromoanisole, and *p*-Bromoanisole and Chemical Shifts of the Pure Complexes Relative to the Respective Donors<sup>a</sup>**

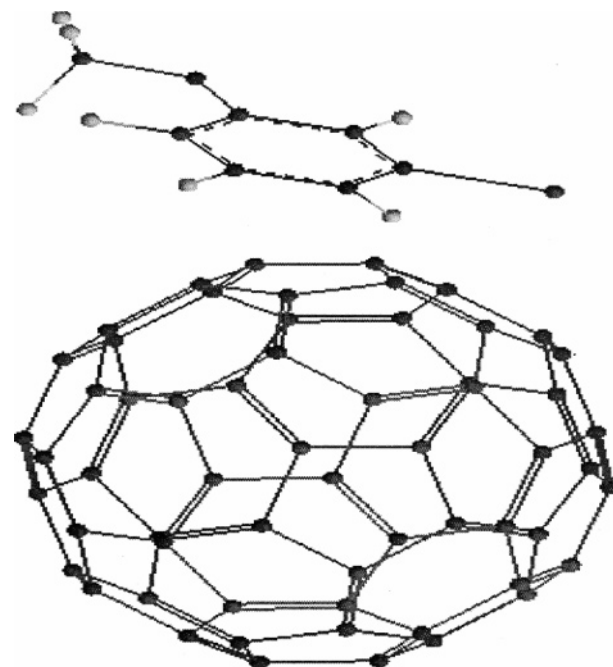
donor	formation constant kg·mol <sup>-1</sup>	10 <sup>3</sup> Δ <sub>0</sub> , Hz
anisole	0.625 ± 0.117	9.62 ± 0.7
<i>m</i> -bromoanisole	0.250 ± 0.100	59.74 ± 17.21
<i>p</i> -bromoanisole	1.250 ± 0.156	1.52 ± 0.09

<sup>a</sup> Temperature = 298 K.

The negative sign of the reaction constant,  $\rho$ , indicates that the complexation process is associative in nature (i.e., formation of the complexes) and the inductive effect of the Br group causes the accumulation of electron density on the carbon atom of the *m*- and *p*-bromoanisoles. Earlier reports on EDA complexes of 1,3,5-trinitrobenzene with methylpyridines<sup>24</sup> show that  $\Delta_0$  is solvent-dependent.  $\Delta_0$  values for the above complexes obey the following trend:  $\Delta_0(m\text{-bromoanisole}) > \Delta_0(\text{anisole}) > \Delta_0(p\text{-bromoanisole})$ . Thus, the *m*-bromoanisole molecule becomes highly solvated in the CCl<sub>4</sub> solution, and it cannot come close to the fullerene molecule to such an extent that an effective interaction could take place between [60]fullerene and the donor. For this reason, among all the donors under present study, *m*-bromoanisole forms a very weak complex with [60]fullerene, which is validated by the smaller value of the formation constant. The trends in the  $K$  values (Table 2) also suggest that [60]fullerene binds itself more strongly with *p*-bromoanisole compared to anisole and *m*-bromoanisole. Apart from the solvation effect, the main reason for the changes in the formation constant may be either a steric effect or the increase in polarizability of bromoanisoles relative to the parent compound (anisole). These features provide a certain amount of specificity of the donor–acceptor interaction of [60]fullerene. That is, the presence of the Br atom makes *p*-bromoanisole a much better donor than the parent compound. The observed decrease in the  $K$  value for the [60]fullerene/*m*-bromoanisole complex most certainly is a reflection of increased steric hindrance to a coplanar arrangement of the benzene ring in *m*-bromoanisole. In interpreting this observation, it has been assumed that the acceptor would interact strongly with the donor molecule only when the donor molecule arranges itself parallel to the  $\pi$ -belt region of the [60]fullerene sphere. In the case of *m*-bromoanisole, the Br atom in the meta position provides interference in the donor–acceptor interaction. It is presumed that under these circumstances the acceptor molecule is forced out of a favorable parallel orientation with respect to the donor ring, or if a parallel configuration is maintained, then

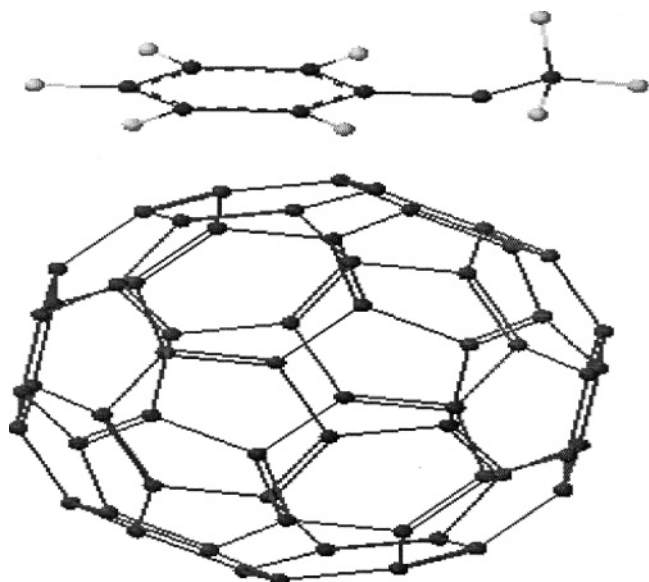


**Figure 3.** Stereoscopic view of (a) [60]fullerene/*p*-bromoanisole complex optimized by PM3 geometry.



**Figure 4.** Stereoscopic view of (a) [60]fullerene/*m*-bromoanisole complex optimized by PM3 geometry.

it is forced to lie so far away from the donor ring that effective interaction cannot occur to any extent. A geometry optimization by PM3 calculation also supports the above view. Thus, in the case of the [60]fullerene/*p*-bromoanisole complex, the donor–acceptor interaction occurs without any steric hindrance; both [60]fullerene and *p*-bromoanisole molecules approach quite closely to each other (see Figure 3), and they are oriented in the same way with their centers directly over each other.<sup>25</sup> In this geometry, some shortening of the interplanar distance from the normal van der Waals separation is also predicted as an accompaniment and the molecular orbitals of the donor and acceptor can effectively overlap. In contrast, a much looser association is predicted computationally for [60]fullerene/*m*-bromoanisole (see Figure 4) and [60]fullerene/anisole complexes (see Figure 5). For these two complexes, no such effective



**Figure 5.** Stereoscopic view of (a) [60]fullerene/anisole complex optimized by PM3 geometry.

**TABLE 3: PM3-Determined Heat of Formation ( $\Delta H_f^\circ$ ), Entropy of Formation ( $\Delta S_f^\circ$ ), and Free Energy of Formation ( $\Delta G_f^\circ$ ) Values for the Complexes of [60]Fullerene with Anisole, *m*-Bromoanisole, and *p*-Bromoanisole<sup>a</sup>**

complex	$\Delta H_f^\circ$ kJ mol <sup>-1</sup>	$\Delta S_f^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G_f^\circ$ kJ mol <sup>-1</sup>
[60]fullerene/anisole	-0.28	-14.0	3.43
[60]fullerene/ <i>m</i> -bromoanisole	0.73	-4.80	1.16
[60]fullerene/ <i>p</i> -bromoanisole	-0.75	-0.65	-0.55

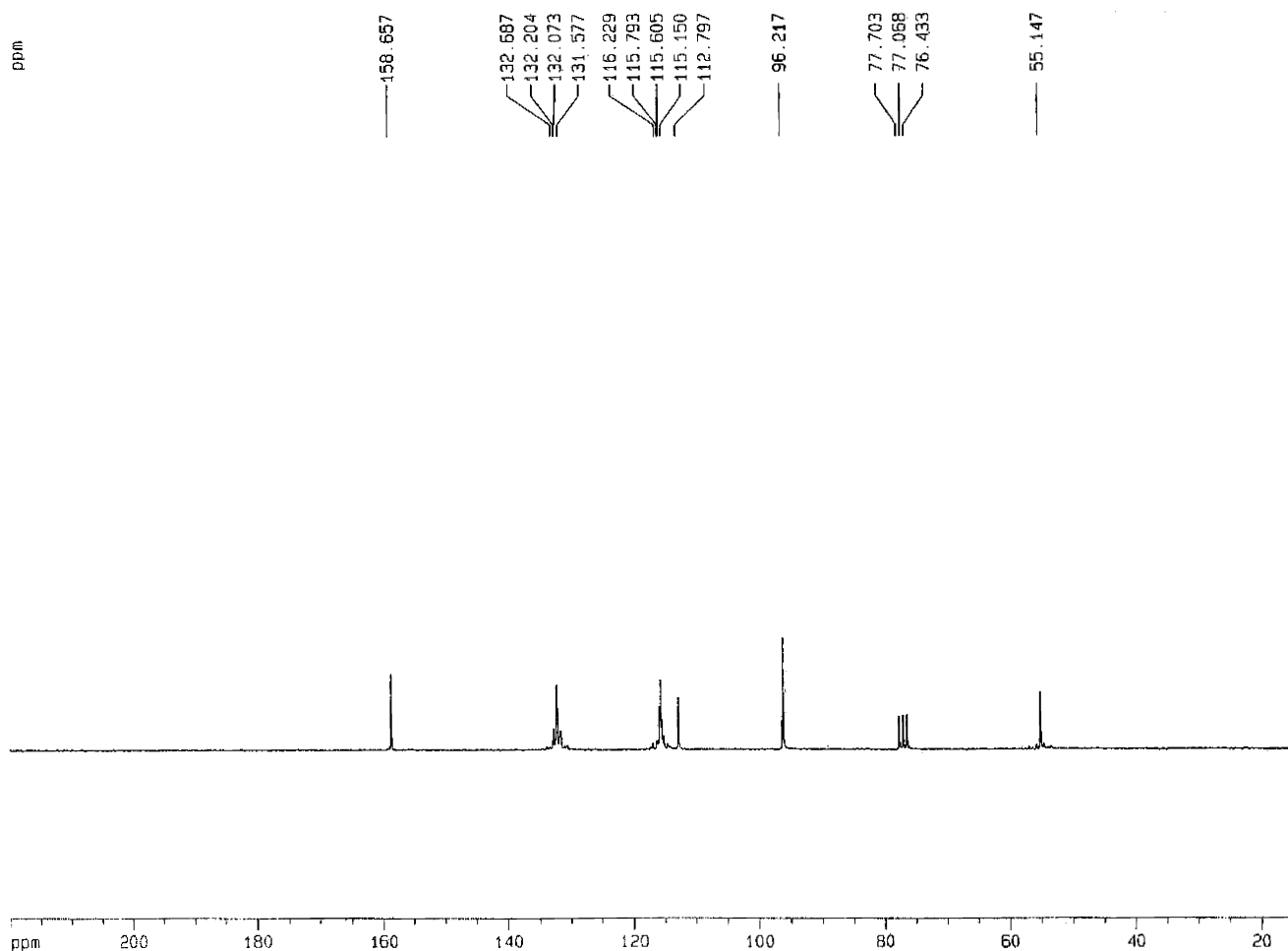
<sup>a</sup> Temperature = 298 K.

interaction between the benzene ring of the donor moiety and the  $\pi$ -belt region of [60]fullerene could take place because of steric inhibition. The effect of such steric hindrance can be found in polyaddition of ester to [60]fullerene.<sup>26</sup> Steric hindrance prevents the formation of the *cis*-1 product and may account for the low yields of the other two *cis* products. The importance of steric effects is also shown in the bromination and epoxidation of the double bond in the addend resulting from the reaction of [60]fullerene with cyclopentadiene. Both the bromine and oxygen atoms point away from the cage, and most notably, addition of bromine to the double bond occurs *cis* rather than *trans*.<sup>27</sup> Steric effects are also apparent in the reaction of peracid with [60]fullerene.<sup>28</sup> However, the charge-transfer interaction of 9,10-diphenylanthracene (DP) with [60]fullerene is caused by good steric compatibility of the DP molecule to the fullerene cage.<sup>29</sup> Theoretical heat of formation ( $\Delta H_f^\circ$ ) values also support the high *K* value observed in the case of the [60]fullerene/*p*-bromoanisole system, because it is empirically found that *K* and  $\Delta H_f^\circ$  usually follow the same trend at room temperature.<sup>30</sup> The  $\Delta H_f^\circ$  value is more negative in the case of the [60]fullerene/*p*-bromoanisole complex (Table 3) indicating that the above complexation process is enthalpy-favored. Korobov et al. have measured the  $\Delta H_f^\circ$  values for [60]fullerene/1,2-dichlorobenzene and [60]fullerene/1,3-dichlorobenzene complexes by differential scanning calorimetry.<sup>31</sup> The solution enthalpy of the [60]fullerene/*m*-bromoanisole system is less exothermic than that of the [60]fullerene/1,3-dichlorobenzene complex. A change in substituent groups in the benzene nucleus affects the formation equilibria between [60]fullerene and various solvents. Table 3 also reveals that, while complex formation is enthalpy-favored, it is also entropy-disfavored. Formation of the complexes,

therefore, results in a more ordered state, possibly because of freezing of the motional freedom of both the donor and acceptor molecules. From Table 3, it is quite clear that the  $\Delta S_f^\circ$  value is highest in the case of the [60]fullerene/*p*-bromoanisole complex. This is because, during the formation of the complex, solvent molecules around the donor moiety are displaced by a [60]fullerene molecule. It is proposed that under this circumstance, more solvent molecules are displaced from the solvent cage around the *p*-bromoanisole molecule during its complexation with the [60]fullerene molecule compared to two other donors. For this reason, there is a large entropy gain achieved for the [60]fullerene/*p*-bromoanisole complex. As a result of this, the [60]fullerene molecule can come close to the *p*-bromoanisole molecule, which is supported by a higher formation constant value for the [60]fullerene/*p*-bromoanisole complex. Apart from the  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$  values, the free energy of formation ( $\Delta G_f^\circ$ ) is a very useful tool in determining the binding strength of molecular complexes. Thus, a negative  $\Delta G_f^\circ$  value in the case of the [60]fullerene/*p*-bromoanisole complex also supports the strong association between the [60]fullerene and *p*-bromoanisole molecules. The results of the current study demonstrate a significant interaction of [60]fullerene with aromatic ethers, such as those often used as solvents, and suggest that the extent of binding should even greater for larger polynuclear aromatic hydrocarbon molecules like 1-methylnaphthalene ( $K = 0.08 \text{ M}^{-1}$ ).<sup>32</sup> The values of *K* for the complexes of anisole and bromoanisoles with [60]fullerene determined in the present work are much greater than those observed for the complexes of [60]fullerene with various aromatic anilines by Ichida et al.<sup>33</sup> The discrepancies in the formation constant values may be due to the difference in the donor concentration range. However, *K* values of [60]fullerene/anisole complexes are comparable to the results obtained by Sibley et al.<sup>34</sup> for their particular systems. Formation constants of the [60]fullerene/anisole, [60]fullerene/*m*-bromoanisole, and [60]fullerene/*p*-bromoanisole complexes, however, are much lower than those obtained for complexes of [60]fullerene with organometallic donors such as phosphine oxides reported in some of our very recent work.<sup>35</sup> Values of *K* for the complexes of [60]fullerene with tri-*n*-butylphosphine oxide, tri-*n*-octylphosphine oxide, and triphenylphosphine oxide are 760, 72, and 24 kg mol<sup>-1</sup>, respectively. Thus, these types of organometallic donors can serve as better donors in forming CT or EDA complexes with [60]fullerene. It has been observed that, with the same donor in a given solvent, the formation constant of a [60]fullerene complex is usually lower than that of a [70]fullerene complex. This is also observed in our present investigations. Thus, in CCl<sub>4</sub> medium,  $K = 0.67$  and 3.30 kg mol<sup>-1</sup> for complexes of [70]fullerene with *m*- and *p*-bromoanisole,<sup>36</sup> respectively, whereas for the corresponding [60]fullerene complexes,  $K = 0.250$  and 1.250 kg mol<sup>-1</sup>, respectively. The stronger interaction of [70]fullerene over [60]fullerene with *m*- and *p*-bromoanisole as shown by higher *K* values just reflects the larger number of unsaturated carbon-carbon bonds in [70]fullerene and is also due to higher electron affinity values of [70]fullerene compared to [60]fullerene.<sup>37</sup>

<sup>13</sup>C NMR spectra of [60]fullerene and donors (viz., anisole, *m*-bromoanisole, and *p*-bromoanisole) in the presence and absence of each other in CCl<sub>4</sub> medium were also recorded. Earlier reports suggest that pure [60]fullerene contains a single peak around 142.5 ppm.<sup>38,39</sup> But in [60]fullerene/anisole, [60]fullerene/*m*-bromoanisole and [60]fullerene/*p*-bromoanisole mixtures, the sole <sup>13</sup>C NMR peak of [60]fullerene suffers splitting and in each case an upfield displacement resulted due





**Figure 6.**  $^{13}\text{C}$  NMR spectrum of *p*-bromoanisole ( $2.256 \text{ mol}\cdot\text{kg}^{-1}$ ) + [60]fullerene ( $7.407 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ ) in  $\text{CCl}_4$  medium.

to complexation. One such case has been shown in Figure 6. The chemical shift of the isolated pure complex was estimated according to the method in the following section.

**3.1. Derivation of Working Formula for Determination of Chemical Shift for Pure Complex ( $\delta^{(C)}$ ) from  $^{13}\text{C}$  NMR Data.** Let us consider the formation equilibrium described in eq 1. If  $P_A$  and  $P_C$  are the probabilities of finding A molecules in the free and complexed forms, respectively, then the observed chemical shift of a particular carbon of A is given by

$$\delta_{\text{obs}}^{(A)} = P_A \cdot \delta^{(A)} + P_C \cdot \delta^{(C)} \quad (10)$$

where  $\delta^{(A)}$  and  $\delta^{(C)}$  are the chemical shifts of the same carbon in pure A and in the complex C. We can write the above equation as

$$\begin{aligned} \delta_{\text{obs}}^{(A)} &= P_A \cdot \delta^{(A)} + P_C \cdot \delta^{(C)} \\ &= (1 - P_C) \delta^{(A)} + P_C \cdot \delta^{(C)} \\ &= \delta^{(A)} + P_C (\delta^{(C)} - \delta^{(A)}) \end{aligned}$$

or

$$\delta_{\text{obs}}^{(A)} - \delta^{(A)} = P_C (\delta^{(C)} - \delta^{(A)}) \quad (11)$$

Denoting  $\delta_{\text{obs}}^{(A)} - \delta^{(A)}$  as  $\Delta_{\text{obs}}$  and  $\delta^{(C)} - \delta^{(A)}$  as  $\Delta^{(o)}$ , we have

$$\Delta_{\text{obs}} = P_C \Delta^{(o)} \quad (12)$$

Now

$$P_C = [C]/([C] + [A]) = [C]/[A]_0 \quad (13)$$

where [C] and [A] are respectively the equilibrium concentrations of the complex and free A, and  $[A]_0$  is the initial concentration of A in the mixture before complexation. Combining eqs 12 and 13 gives

$$\Delta_{\text{obs}} = [C] \Delta^{(o)} / [A]_0 \quad (14)$$

Now, under the approximation  $[B]_0 \gg [A]_0$ , the formation constant ( $K$ ) can be written as

$$\begin{aligned} K &= [C]/([B][A]) \\ &= [C]/\{([B]_0 - [C])([A]_0 - [C])\} \\ &= [C]/\{[B]_0([A]_0 - [C])\} \end{aligned}$$

because, under the above approximation,

$$[B]_0 - [C] \approx [B]_0$$

Hence,  $1/K = \Delta^{(o)}[B]_0/\Delta_{\text{obs}} - [B]_0$  (utilizing eq 14), or

$$B_0 = (\Delta^{(o)}[B]_0/\Delta_{\text{obs}}) - 1/K \quad (15)$$

This equation has been used for estimating the complexation-induced chemical shift of the  $^{13}\text{C}$  atom of the [60]fullerene in the pure complex. The derivation is analogous to that required

for the determination of  $K$  from the  $^1\text{H}$  chemical shift.<sup>40,41</sup> The only difference is that the probability  $P_C$  of finding A (i.e., [60]fullerene in the complexed state) is given by  $P_C = [\text{AB}]/[\text{A}]_0$ . Using the values of  $K$  (Table 2),  $[\text{B}]_0$ , and  $\Delta_{\text{obs}}$  for the  $^{13}\text{C}$  signal in eq 15, we have evaluated  $\Delta_0$  and thence  $\delta^{(C)}$  for the complexes of [60]fullerene with anisole, *m*-bromoanisole, and *p*-bromoanisole. Upfield shifts of 0.96, 1.26, and 3.654 ppm have been observed for [60]fullerene/*m*-bromoanisole, [60]fullerene/anisole, and [60]fullerene/*p*-bromoanisole complexes, respectively. This trend in  $\delta^{(C)}$  values corroborates very well with that of the formation constant values (i.e.,  $K_{[\text{60}]\text{fullerene}/m\text{-bromoanisole}} < K_{[\text{60}]\text{fullerene}/\text{anisole}} < K_{[\text{60}]\text{fullerene}/p\text{-bromoanisole}}$ ). We have also estimated the magnitude of concentration of [60]fullerene/anisole EDA complexes (i.e., [C]) at equilibrium mixtures using eq 14. The values of [C] for [60]fullerene/anisole, [60]fullerene/*m*-bromoanisole, and [60]fullerene/*p*-bromoanisole are  $5.05 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ ,  $4.16 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ , and  $5.47 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ , respectively. Such values of [C] also substantiated the trend in formation constant values (Table 2) for [60]fullerene/anisole systems.

#### 4. Conclusions

[60]Fullerene is shown to form 1:1 EDA complexes with the anisoles under present study, and NMR chemical shifts of specific protons can be suitably utilized to study the formation equilibria of the complexes. It has been observed that *p*-bromoanisole acts as a better donor in forming an EDA complex with [60]fullerene. Finally, the complexes have been shown to exhibit a Hammett-type linear free energy relationship.

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**Supporting Information Available:**  $^1\text{H}$  NMR spectra of Figures 1S (i.e.,  $^1\text{H}$  NMR spectrum of  $0.330 \text{ mol}\cdot\text{kg}^{-1}$  anisole in  $\text{CCl}_4$  in absence of [60]fullerene), 2S (i.e.,  $^1\text{H}$  NMR spectrum of mixture containing  $3.052 \text{ mol}\cdot\text{kg}^{-1}$  anisole and  $7.407 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$  [60]fullerene in  $\text{CCl}_4$ ), and 3S (i.e.,  $^1\text{H}$  NMR spectrum of mixture containing  $3.815 \text{ mol}\cdot\text{kg}^{-1}$  anisole and  $7.407 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$  [60]fullerene in  $\text{CCl}_4$ ) are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### References and Notes

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.
- (2) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075.
- (3) Lee, K.; Song, H.; Park, J. T. *Acc. Chem. Res.* **2003**, *36*, 78.
- (4) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.
- (5) Guldi, D. M. *Chem. Commun.* **2000**, 321.
- (6) Konarev, D. V.; Lyubovskaya, R. N. *Russ. Chem. Rev.* **1999**, *68*, 19.
- (7) Kesti, T.; Tkachenko, N.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *J. Photochem. Photobiol.* **2003**, 251.
- (8) Graja, A. *Pol. J. Chem.* **2002**, *76*, 167.
- (9) Konarev, D. V.; Lyubovskaya, R. N.; Drichko, N. V.; Semkin, V. N.; Graja, A. *Chem. Phys. Lett.* **1999**, *314*, 570.
- (10) Romanova, I. P.; Musina, E. I.; Nafikova, A. A.; Zverev, V. V.; Yakkvarov, D. G.; Sinyashin, O. G. *Russ. Chem. Bull.* **2003**, *52*, 1750.
- (11) Wang, M.-X.; Zhang, X.-H.; Zheng, Q.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838.
- (12) Otsuka, A.; Saito, G.; Hirate, S.; Pac, S.; Ishida, T.; Zakhidov, A. A.; Yakushi, K. *Mater. Res. Soc. Symp. Proc.* **1998**, *488*, 495.
- (13) Konarev, D. V.; Zerza, G.; Sharber, M.; Sariciftci, N. S.; Lyubovskaya, R. N. *Synth. Met.* **2001**, *121*, 1127.
- (14) Schön, J. H.; Kloc, Ch.; Siegrist, T.; Steigerwald, M.; Batlogg, B. *Nature (London)* **2001**, *413*, 831.
- (15) Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. *Nature (London)* **1993**, *362*, 140.
- (16) Doome, R. J.; Dermaut, S.; Fonseca, A.; Hammida, M.; Nagy, J. B. *Fullerene Sci. Technol.* **1997**, *5*, 1593.
- (17) Bhattacharya, S.; Banerjee, M.; Mukherjee, A. K. *Spectrochim. Acta, Part A* **2003**, *59*, 3147.
- (18) Bhattacharya, S.; Banerjee, S.; Chattopadhyay, S.; Banerjee, M. *Chem. Phys. Lett.* **2004**, *393*, 504.
- (19) Martin, A.; Sanchez, L.; Herranz, M. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648.
- (20) Mathur, R.; Becker, E. D.; Bradley, R. B.; Li, N. C. *J. Phys. Chem.* **1963**, *67*, 2190.
- (21) Hanna, M. W.; Ashbaugh, A. L. *J. Phys. Chem.* **1964**, *68*, 811.
- (22) Bhattacharya, S.; Bhattacharya, S. C.; Banerjee, M. *J. Phys. Chem. A* **2004**, *108*, 10783.
- (23) Hammett, L. P. *Chem. Rev.* **1953**, *53*, 191.
- (24) Foster, R. *Organic Charge-Transfer Complexes*, 2nd printing; Academic Press Inc.: London, 1969; Chapter 7, pp 192–198.
- (25) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811.
- (26) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437.
- (27) Meidine, M. F. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2125.
- (28) Ballenweg, S.; Gleiter, R.; Krätschmer, W. *J. Chem. Soc., Chem. Commun.* **1994**, 2269.
- (29) Bulusheva, L. G.; Okotrub, A. V.; Gusel'nikov, A. V.; Konarev, D. V.; Litvinov, A. L.; Lyubovskaya, R. N. *J. Mol. Struct.* **2003**, *648*, 183.
- (30) Connors, K. A. *Binding Constants: The Measurements of Molecular Complexes Stability*; Wiley: New York, 1987.
- (31) Korobov, M. V.; Mirakyan, A. L.; Avramenko, N. V.; Oloffson, G.; Smith, A. L.; Ruoff, R. S. *J. Phys. Chem. B* **1999**, *103*, 1339.
- (32) Scurlock, R. D.; Ogilby, P. R. *J. Photochem. Photobiol., A* **1995**, *91*, 21.
- (33) Ichida, M.; Sohda, T.; Nakamura, A. *Chem. Phys. Lett.* **1999**, *310*, 373.
- (34) Sibley, S. P.; Nguyen, Y. T.; Campbell, R. L.; Silber, H. B. *Spectrochim. Acta, Part A* **1997**, *53*, 679.
- (35) Bhattacharya, S.; Banerjee, S.; Nayak, S. K.; Chattopadhyay, S.; Mukherjee, A. K. *Spectrochim. Acta, Part A* **2004**, *60*, 1099.
- (36) Bhattacharya, S.; Bauri, A. K.; Chattopadhyay, S.; Banerjee, M. *Chem. Phys. Lett.* **2005**, *401*, 323.
- (37) Brink, C.; Andersen, L. H.; Hvelplund, P.; Mathyr, D.; Voldstad, J. D. *Chem. Phys. Lett.* **1995**, *233*, 52.
- (38) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.
- (39) Rao, C. N. R.; Pradeep, T.; Seshadri, R.; Nagarajan, R.; Narasimha Murthy, V.; Subbanna, G. N.; D'Souza, F.; Krishnan, V.; Nagannagowda, G. A.; Suryaprakash, N. R.; Khetrapal, C. L.; Bhat, S. V. *Indian J. Chem., Sect. A and B* **1992**, *31*, F5–F16.
- (40) Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, A. K. *J. Phys. Chem. A* **2001**, *105*, 9865.
- (41) Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, A. K. *J. Phys. Chem. B* **2003**, *107*, 11830.