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Study of Molecular Complex Formation between [60]Fullerene and Two Series of Donors by the NMR Method

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Formation of molecular complexes between [60]fullerene and (i) a series of aromatic hydrocarbons, namely, anthracene, acenaphthene, phenanthrene, pyrene, durene, pentamethylbenzene, and hexamethylbenzene, and (ii) a series of pyridines, namely, pyridine, 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine, and 2,4,6-collidine has been studied in CCl_4 medium by NMR method. [60]Fullerene has been shown to form 1:1 molecular adducts with the above series of compounds. Formation constants (K) of the above complexes have been determined from the systematic variation of NMR chemical shifts of specific protons of the donors in the presence of C_{60}. The K values of [60]fullerene complexes with pyridine, 3-picoline, and 4-picoline yield good estimates of the Hammett constant, ρ, for the complexation reaction.

Introduction

[60]Fullerene[1] and some of the C_{60}-based salts and complexes can be regarded as a novel class of materials in the fields of material science,[2,3] photophysical study,[4,5] organic chemistry,[6,7] and polymers.[8,9] The interest in such novel materials has especially increased after the discovery of their superconductivity[10] in C_{60} alkali metal salts, ferromagnetism,[11] and biological activity.[12,13] It has been theoretically predicted that the LUMO of C_{60} can accept six electrons,[14−16] and from electrochemical studies[17−20] reduction potentials corresponding to $[C_{60}]^{n-}$, $n =$ 3 to 6, have been determined. Thus, the high electron affinity of C_{60} makes it an efficient electron acceptor,[11] and it forms electron donor−acceptor (EDA) complexes with various electron donors such as amines,[21,22] olefins,[23] etc. Study of the formation of such complexes by C_{60} in solution and in solid state is a field of current research.[23−31] From NMR studies, the formation of molecular complexes with C_{60} with some η and π donors have recently been inferred,[32] but no quantitative analysis of the chemical shift values has been made for the determination of the formation constants (K) of the complexes. The method of determination of K from NMR data of EDA complexes was developed long ago by Hanna and Ashbaugh,[33] but to date there are no reports on application of this method for determination of K with C_{60} as acceptors. The object of the present paper is an attempt along this line. It has been shown in the present work that C_{60} forms 1:1 molecular complexes with (i) a series of aromatic hydrocarbons, namely, anthracene, acenaphthene, phenanthrene, pyrene, durene, pentamethylbenzene, and hexamethylbenzene, and (ii) a series of pyridines, namely, pyridine, 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine, and 2,4,6-collidine, from an analysis of ^1H NMR chemical shifts of the donor solutions in CCl_4 medium in the presence of C_{60}. Pyridine−C_{60} complex is of importance because a recent study[34] reports the synthesis of a water-soluble complex between [60]fullerene with cholesteryl group-bearing pullulan; the method of synthesis requires solution of C_{60} in pyridine (10% v/v), which indicates the possibility of the formation of a C_{60}−pyridine molecular complex. For this reason, it is felt necessary to study the interaction between C_{60} and pyridines (i.e., pyridines and methyl pyridines) in solution phase.

Materials and Methods

[60]Fullerene was obtained from Sigma. The aromatic hydrocarbons, viz., phenanthrene, acenaphthene, anthracene, pyrene, durene, pentamethylbenzene and hexamethylbenzene were purified by recrystallization from dry ethanol. Pyridine, 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine, and 2,4,6-collidine (commercial grade) were purified by repeated distillation with solid sodium hydroxide. HPLC-grade CCl_4 was used as solvent. ^1H NMR spectra of the donors and donor−C_{60} mixtures in solution of CCl_4 were recorded on a Bruker AC − 200 (200 MHz) NMR spectrometer with $CDCl_3$ as an internal lock.

Results and Discussions

C_{60} has no protons, and so the formation equilibria of C_{60}− aromatic hydrocarbon complexes have been studied in the present report on the basis of the following principle.

If we consider the signal of a particular proton in the donor moiety, then, owing to the rapid reversible equilibrium

$$D + A \Leftrightarrow DA \tag{1}$$

the observed chemical shift ($\delta_{obs}^{(D)}$) of the proton is the time-averaged shift of the same proton in the free donor and in the complex, i.e.,

$$\delta_{obs}^{(D)} = P_o\delta_o^{(D)} + P_c\delta_c^{(D)} \tag{2}$$

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

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$$P_c = [DA]/([DA] + [D]) \tag{3}$$

where each square bracket denotes the concentration of the species enclosed. Again, if the initial concentration of the acceptor, $[A]_o$, is much less than that ($[D]_o$) of the donor, the formation constant (K) of the complex is given by

$$K = [DA]/[D]_o([A]_o - [DA]) \tag{4}$$

A combination of eqs 2, 3, and 4 gives

$$[D]_o = \Delta_o[A]_o(1/\Delta_{obs}) - 1/K \tag{5}$$

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

Variation of the methyl proton signals in the ^{1}H NMR spectra of 2-picoline and HMB with gradual addition of C_{60} solution is shown in Figures 1 and 2. With a fixed concentration of C_{60}, the observed Δ decreases as the donor concentration increases. Similar features were observed with all the donors studied. Experimental data are given in Tables 1−5. The values of maximum Δ_{obs} in all the cases range from 2.907 to 28.88 Hz. Such values are very similar to those obtained by Hanna and Ashbaugh[33] in the range 7.1 to 13.7 Hz for TCNQ complexes with a series of methylbenzenes and are much greater than that expected from the solvation effect (ca. 0.5 Hz). In all the cases studied, excellent linear plots in accordance with eq 5 were obtained, two typical plots being shown in Figure 3. Results of regression analysis and values of K and Δ_0 obtained therefrom are shown in Table 5. Reliability of the values of K obtained by the NMR method is usually tested by plotting log K of a series of complexes with one electron acceptor against log K of the complexes of the same series of donors with another acceptor.[35] In the present case, the formation constants (determined by NMR method) of the complexes of durene, PMB, and HMB with two acceptors, viz., 1,3,5,-trinitrobenzene (TNB) and fluoranil, could be found in the literature,[35] and the corresponding log K values are found to show excellent linear correlation with the presently determined log K values of the C_{60} complexes:

$$\log K\,(C_{60}) = (-0.46 \pm 0.10)\log K\,(\text{TNB}) + (1.37 \pm 0.06);\ \text{correlation coefficient} = 0.97 \tag{6}$$

$$\log K\,(C_{60}) = (-0.36 \pm 0.08)\log K\,(\text{fluoranil}) + (1.47 \pm 0.07);\ \text{correlation coefficient} = 0.97 \tag{7}$$

The formation constants of the complexes of C_{60} with pyridine, 4-picoline, and 3-picoline are in accordance with the Hammett[36,37] equation:

$$\log K = (-1.00 \pm 0.003)\sigma + (1.28 \pm 0.0003) \tag{8}$$

while those of the complexes of TNB with the same series of pyridines[35] yield

$$\log K = (-1.00 \pm 0.003)\sigma + (0.146 \pm 0.050) \tag{9}$$

These linear free energy relationships are shown in Figure 4. In eqs 8 and 9, σ is Hammett substituent constant for the methyl group. As expected, the reaction constant ρ is the same (−1.00) in the two series of similar reactions (complexation). Moreover, the negative sign of this ρ indicates that the reaction (formation of the complex) is associative in nature and the inductive effect of the methyl group causes accumulation of electron density on the nitrogen atom of 3- and 4-picolines. For the other methylated pyridines, the formation constants of the complexes do not follow a regular trend because in all these cases the ortho position(s) is (are) occupied by methyl group(s), and this leads to considerable steric hindrance to complex formation. Such deviation from linear relationships owing to ortho substituents is well-known in case of reaction rate constants,[37] and this is the reason in Hammett theory that no σ parameter is available for ortho substituents. The formation constants of the complexes of C_{60} with aromatic hydrocarbons

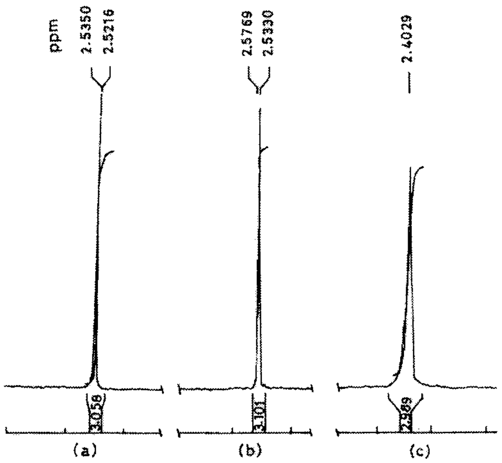

Figure 1. ^{1}H NMR spectrum (methyl proton signal) of (a) 2-picoline in CCl_4 in absence of C_{60}; (b) mixture of C_{60} (2.630×10^{-5} mol kg^{-1}) and 2-picoline (0.055 mol kg^{-1}); and (c) mixture of C_{60} (2.630×10^{-5} mol kg^{-1}) and 2-picoline (0.1374 mol kg^{-1}) in CCl_4.

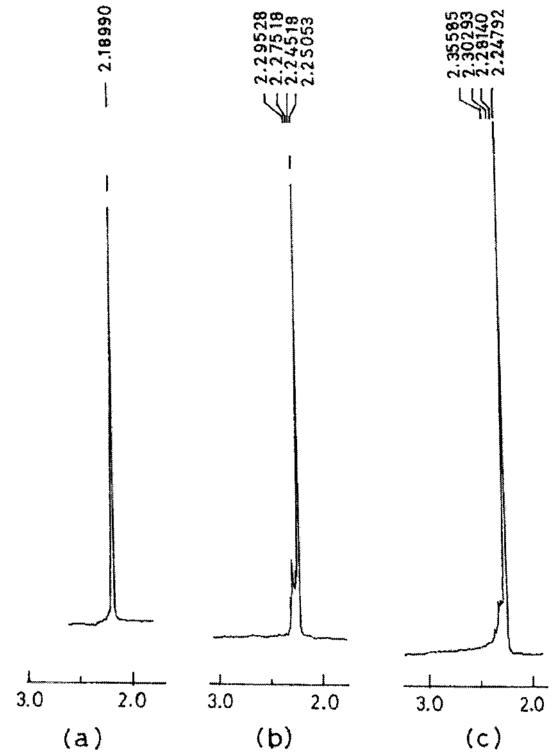

Figure 2. ^{1}H NMR spectra (methyl proton signal) of (a) HMB in CCl_4 in absence of C_{60}; (b) HMB (0.030 mol kg^{-1}) + C_{60} (2.312×10^{-5} mol kg^{-1}); (c) HMB (0.081 mol kg^{-1}) + C_{60} (2.312×10^{-5} mol kg^{-1}) in CCl_4.

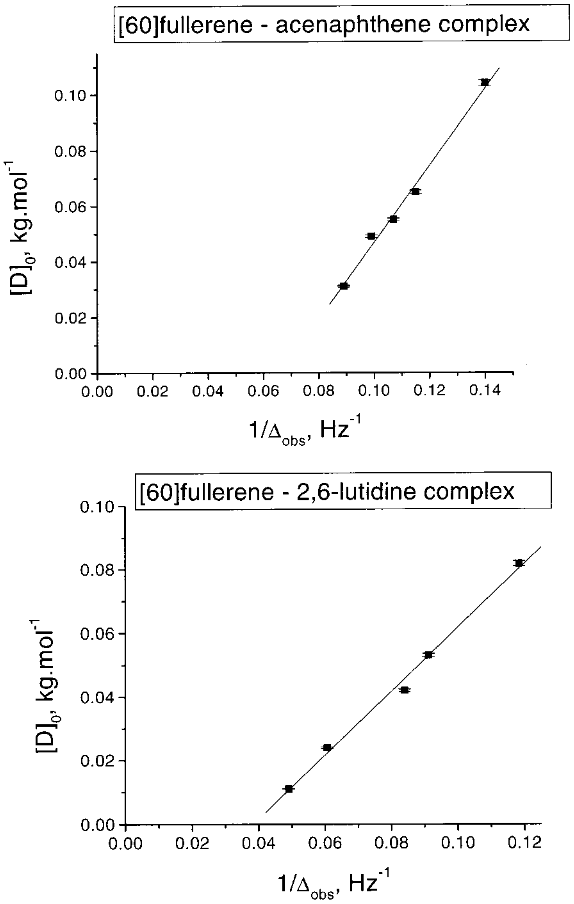

Figure 3. Plots of $[D]_0$ vs $1/\Delta_{obs}$ for the acenaphthene$-C_{60}$ (top panel) and 2,6-lutidine$-C_{60}$ (bottom panel) complex.

TABLE 1: NMR Chemical Shifts of Methyl Protons in Methylbenzene$-C_{60}$ Mixtures in CCl_4 Medium at Varying Concentrations of the Methylbenzenes[a]

donor	10^5 $[A]_0$, mol kg^{-1}	donor conc, mol kg^{-1}	Δ_{obs}, Hz
durene	2.311	0.025	6.25
		0.095	3.36
		0.126	2.48
		0.136	3.41
		0.214	2.13
PMB	2.762	0.035	4.22
		0.040	4.44
		0.087	2.92
		0.094	2.89
		0.605	2.74
HMB	2.312	0.030	17.15
		0.081	11.59
		0.159	8.12
		0.179	8.40

[a] Temp = 298 K.

obtained in the present work are slightly larger than those found from spectroscopic measurements[38] in toluene medium. This is presumably because toluene itself forms complexes with fullerenes,[39] but in the present case (CCl_4 medium) there is no such competition for complexation with the solvent. It is difficult to give a rationale for the observed trends in Δ_0 of the loose molecular complexes in solution. Earlier reports on EDA complexes of TNB with methylpyridines show that Δ_0 is solvent dependent and, in particular, the values for 2-picoline and 2,6-lutidine complexes are high in CCl_4 medium and could not be measured without error in CCl_4 medium. In the present case of C_{60} − 2-picoline complex a high value of Δ_0 is observed.

TABLE 2: NMR Chemical Shifts of Specific Protons in Polynuclear Aromatic Hydrocarbons (PAH)$-C_{60}$ Mixtures in CCl_4 Medium at Varying Concentrations of the PAH[a]

donor	10^5 $[A]_0$ mol kg^{-1}	donor conc mol kg^{-1}	Δ_{obs} Hz	protons observed
acenaphthene	3.715	0.031	11.23	-CH_2
		0.049	10.10	
		0.055	9.34	
		0.065	8.71	
		0.104	7.14	
anthracene	3.715	0.007	4.64	9,10
		0.018	3.85	
		0.025	3.29	
		0.026	3.22	
		0.034	2.98	
phenanthrene	3.856	0.007	2.91	α
		0.016	2.70	
		0.027	2.62	
		0.040	2.48	
		0.089	1.83	
pyrene	2.312	0.114	6.56	α
		0.168	5.21	
		0.135	6.10	
		0.186	4.81	

[a] Temp = 298 K.

TABLE 3: NMR Chemical Shifts of Specific Protons in Pyridine$-C_{60}$ Mixtures in CCl_4 Medium at Varying Concentrations of the Pyridines[a]

donor	10^5 [A] mol kg^{-1}	donor conc mol kg^{-1}	Δ_{obs} Hz	protons observed
pyridine	2.321	0.075	6.5	α
		0.085	6.1	
		0.1068	5.2	
		0.118	4.8	
3-methylpyridine	2.630	0.0896	5.65	methyl
		0.1115	3.84	
		0.1332	3.12	
		0.2847	1.98	
4-methylpyridine	3.896	0.022	6.42	methyl
		0.045	5.34	
		0.067	3.82	
		0.086	3.56	

[a] Temp = 298 K.

TABLE 4: NMR Chemical Shifts of Methyl Protons in Methylpyridine$-C_{60}$ Mixtures in CCl_4 Medium at Varying Concentration of the Methylpyridines[a]

donor	10^5 $[A]_0$ mol kg^{-1}	donor conc mol kg^{-1}	Δ_{obs} Hz
2-methylpyridine	2.630	0.055	26.02
		0.083	28.88
		0.1104	24.94
		0.1374	23.74
		0.1905	19.48
2,6-lutidine	7.014	0.038	16.48
		0.056	20.38
		0.084	10.96
		0.112	11.88
		0.129	8.44
2,4,6-collidine	9.018	0.052	10.50
		0.064	9.52
		0.077	8.62
		0.113	7.29

[a] Temp = 298 K.

Conclusion

The present study shows conclusively that C_{60} forms 1:1 molecular complexes with methylbenzenes, PAH, and meth-

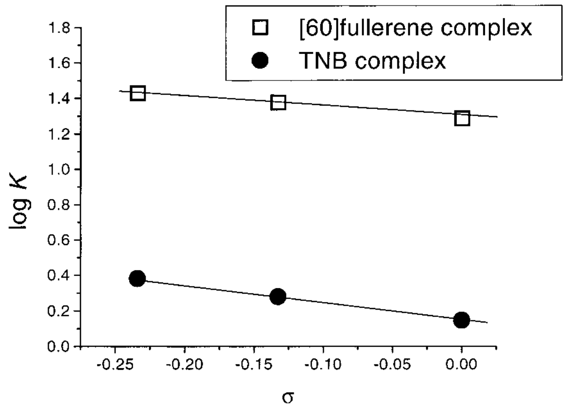

Figure 4. Hammett plot for complexes of pyridine, 3-picoline, and 4-picoline with C_{60} and TNB as acceptors.

TABLE 5: Formation Constants of the Molecular Complexes and Chemical Shifts of the Pure Complexes Relative to the Respective Donors[a]

donor	formation constants mol kg^{-1}	Δ_0 ppm
durene	17.2 ± 4.6	113.5 ± 17.5
PMB	13.3 ± 2.7	87.6 ± 10.3
HMB	11.8 ± 3.1	439.8 ± 47.8
anthracene	25.7 ± 2.9	180.4 ± 13.2
phenanthrene	6.9 ± 0.8	57.4 ± 6.4
pyrene	12.5 ± 2.5	278.1 ± 19.5
acenaphthene	11.4 ± 1.2	180.4 ± 13.2
pyridine	19.3 ± 3.4	176.4 ± 11.2
2-picoline	6.9 ± 1.2	1007.8 ± 116.1
3-picoline	23.7 ± 2.5	82.7 ± 11.9
4-picoline	26.8 ± 3.2	43.6 ± 1.6
2,6-lutidine	26.0 ± 2.6	71.4 ± 3.1
2,4,6-collidine	17.3 ± 2.3	51.8 ± 3.1

[a] Temp = 298 K.

ylpyridines, and NMR chemical shifts of specific protons can be suitably utilized to study the formation equilibria of the complexes.

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