PERKIN 2

Ground state EDA complex formation between [60]fullerene and a series of polynuclear aromatic hydrocarbons

Kakali Datta, Manas Banerjee, Bejoy K. Seal and Asok K. Mukherjee *

Department of Chemistry, University of Burdwan, Golapbag, Burdwan 713 104, India

Received (in Cambridge, UK) 7th September 1999, Accepted 24th November 1999

Formation constants of 1 : 1 adducts of [60]fullerene with naphthalene, phenanthrene, anthracene, pyrene and chrysene have been determined in CCl_4 medium. Ionisation potentials of donor molecules and charge transfer (CT) transition energies of the [60]fullerene adducts have been found to correlate in accordance with the Mulliken equation. From such correlation the electron affinity of [60]fullerene has been calculated to be 2.32 eV in solution. A good estimate for the sp^2C–sp^2C resonance integral β in benzenoid hydrocarbons has also been obtained from the observed CT transition energies.

Introduction

A great deal of experimental work has been done with [60]fullerene[1] in the fields of material science,[2–11] photophysical study[12–16] and organic chemistry.[17–22] Recently it has been reported[23] that C_{60} forms Diels–Alder adducts with anthracene and pentacene. Reports on the formation of ground state electron donor–acceptor (EDA) complexes involving C_{60} are relatively few.[14,24] Theoretically it has been predicted[25–27] that the LUMO of C_{60} can accept at least six electrons. Electrochemical studies in solution have yielded 3- to 5-electron reduction potentials.[24,28–30] With special solvent compositions Echegoyen *et al.*[31] and subsequently Diao *et al.*[32] have been able to observe a six-electron reduction potential corresponding to C_{60}^{6-}. Thus C_{60} is expected to behave as an acceptor in forming EDA complexes in solution. The object of the present paper is to study the formation of EDA complexes between C_{60} and a series of polynuclear aromatic hydrocarbons (PAH) and to obtain an estimate of the electron affinity of C_{60}.

Materials and methods

[60]Fullerene was obtained from Sigma. Naphthalene and phenanthrene were purified by sublimation. Anthracene from Sigma was used without further purification. Pyrene and chrysene were purified by recrystallisation from purified ethanol and benzene respectively in dark. The solvent, CCl_4, was purified by drying over fused $CaCl_2$ followed by distillation. Spectral measurements were done in a Shimadzu UV-2101PC model spectrophotometer fitted with TB-85 thermo-bath.

Results and discussion

Fig. 1 shows the electronic absorption spectrum of C_{60} in CCl_4 against the solvent as reference. The absorption spectra of two mixtures, one containing pyrene and C_{60} and the other containing naphthalene and C_{60} in CCl_4, are shown in the same figure. In the latter two cases, solution of C_{60} at the same concentration as that in the mixture was taken as reference and it was found that the broad, longest wavelength (540 nm) absorption band of C_{60}, attributable to its π–π* HOMO–LUMO transition,[24] was almost completely masked (because of the pristine [60]fullerene reference) while a new band due to the charge-transfer (CT) absorption of EDA complex appeared. A similar phenomenon was observed with each of the donors studied in the present work. In the case of naphthalene and phenanthrene, closely spaced double CT peaks were observed. Anthracene, pyrene and chrysene complexes showed broad absorption bands and λ_{max} in these cases were determined by subjecting the spectral data to a Gaussian curve fitting. The CT transition energies of the C_{60} complexes are given in Table 1 together with the Hückel energies of the highest occupied molecular orbitals (HOMO) of the PAH donors (taken from ref. 33); the AM1 ionisation potentials[34] (I_D) of the donors are also given in the same table. According to Mulliken's theory[35] the CT transition energies are related to the vertical ionisation potentials (I_D^v) of the donors by relation (1), where C_1 is given by eqn. (2). Here E_A^v is the

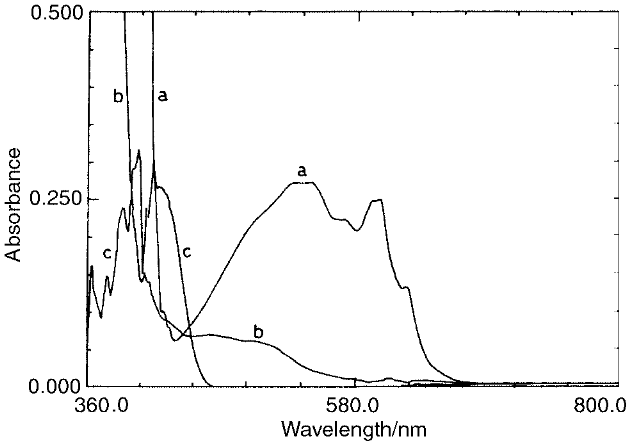

Fig. 1 Absorption spectra of C_{60} and two of its EDA complexes in CCl_4: (a) C_{60} (3.585×10^{-4} mol dm^{-3}) in CCl_4 against solvent as reference; (b) C_{60} (1.883×10^{-4} mol dm^{-3}) + pyrene (8.751×10^{-2} mol dm^{-3}); (c) C_{60} (3.585×10^{-4} mol dm^{-3}) + naphthalene (6.893×10^{-1} mol dm^{-3}) against the respective C_{60} solutions as reference.

Table 1 CT absorption maxima and transition energies of C_{60}–polynuclear aromatic hydrocarbon complexes and HOMO energies (in Hückel β unit) and AM1 ionisation potentials of the donors

Donor	λ_{CT}/nm[a]	$h\nu_{CT}$/eV	E_{HOMO}	I_D/eV
Naphthalene	413	3.008	0.618	8.711
Phenanthrene	413	3.008	0.605	8.617
Anthracene	511	2.431	0.414	8.123
Chrysene	472	2.632	0.520	8.371
Pyrene	454	2.737	0.445	8.131

[a] The longer wavelength in case of double peaks.

DOI: 10.1039/a907219e

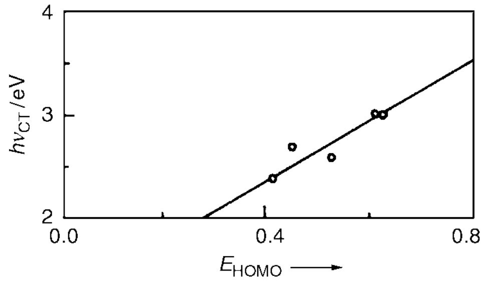

Fig. 2 Plot of $h\nu_{CT}$ against E_{HOMO} in β units.

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

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

vertical electron affinity of the acceptor, G_0 is 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 a number of energy terms in the 'dative' state. In most cases, G_0 is small and can be neglected while G_1 is largely the electrostatic energy of attraction between D^+ and A^-. The term C_2 in eqn. (1) is related to the resonance energy of interaction between the 'no-bond' and 'dative' forms in the ground and excited states and for a given acceptor it may be supposed constant.[35] A rearrangement of eqn. (1) yields eqn. (3).

$$2I_D^v - h\nu_{CT} = (1/C_1)\, I_D^v(I_D^v - h\nu_{CT}) + C_1 + (C_2/C_1) \quad (3)$$

The ground state I_D values calculated for the PAHs under study by the AM1 method may be taken as their I_D^v and with the observed transition energies we have obtained the correlation (4), with a correlation coefficient of 0.99. This confirms

$$2I_D^v - h\nu_{CT} = (0.1551 \pm 0.00991)\, I_D^v(I_D^v - h\nu_{CT}) + (6.6907 \pm 0.4717) \quad (4)$$

the CT nature of the transitions observed and yields $C_1 = 6.45$ eV. 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 as $e^2/4\pi\varepsilon_0 r = 4.13$ eV. Now using eqn. (2) the electron affinity of C_{60} in solution is found to be 2.32 eV. This is in fair agreement with the value 2.65 eV obtained in gas phase by Smalley *et al.*[36] which was later confirmed by Boltalina *et al.*[37] and Chen *et al.*[38] by mass spectrometric method and also by theoretical calculation (Apostol[39]).

A plot of $h\nu_{CT}$ against E_{HOMO} of the PAH donors (the Hückel energy of HOMO with α as the zero and β as the unit of energy) is also found to be linear (Fig. 2); the slope of this line must be equal to β, the resonance integral between two sp^2–C atoms, in accordance with the empirical McConnell–Ham–Platt equation,[40] where E_A is the electron affinity of the acceptor

$$\begin{aligned} h\nu_{CT} &= I_D - E_A + \Delta \\ &= -E_{HOMO}\,\beta + \text{constant} \end{aligned} \quad (5)$$

(C_{60}) and Δ is an energy term coming from solvation *etc.* which may be regarded as approximately constant for a given solvent and a series of structurally similar donors. In fact eqn. (5) is an approximate form of Mulliken's eqn. (1). The value of β obtained from the linear plot shown in Fig. 2 is −2.98 eV, which is in very good agreement with the value of −3.1 eV, obtained from the first four singlet–singlet transitions in benzene. All these observations definitely establish that C_{60} acts as an electron acceptor in forming EDA complexes with the polynuclear aromatic hydrocarbons studied. Stoichiometry and formation constants of the complexes were determined by using Benesi–Hildebrand[41] (B–H) and Rose–Drago[42] equations [eqns. (6) and (7)] respectively for cells with 1 cm optical length,

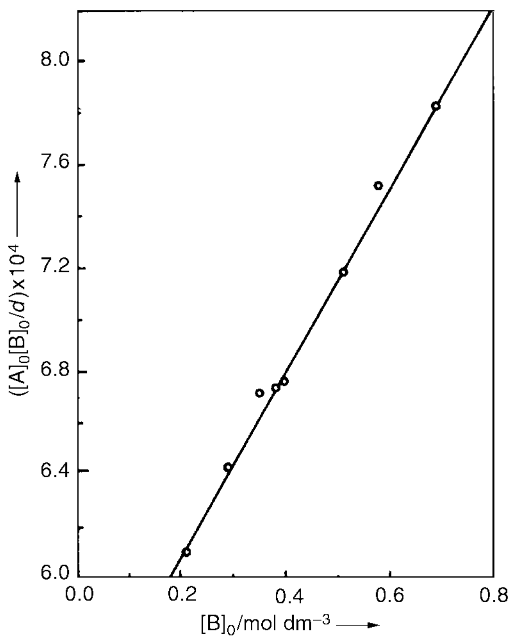

Fig. 3 Benesi–Hildebrand plot for C_{60}–naphthalene complex.

$$[A]_0[B]_0/d = [B]_0/\varepsilon' + 1/K\varepsilon' \quad (6)$$

$$[A]_0[B]_0/d = ([A]_0 + [B]_0)/\varepsilon' - d/\varepsilon'^2 + 1/K\varepsilon' \quad (7)$$

where $[A]_0$ and $[B]_0$ are the initial concentrations of the acceptor and donor respectively, d is the absorbance at the λ_{max} of the CT absorption band measured against the acceptor solutions, at the same molar concentration as that in the donor–acceptor mixture taken as reference. $\varepsilon' = \varepsilon_c - \varepsilon_A$, where ε_c is the molar absorptivity of the complex and ε_A is that of the acceptor, at the wavelength of measurement. K is the formation constant of the complex. Eqn. (6) is valid under the condition[41] $[B]_0 \gg [A]_0$ while eqn. (7) does not require such a condition; however, both are valid 1 : 1 (donor–acceptor) complexes. Absorbances at the maxima of the CT absorption bands at various concentrations of the components are shown in Table 2. Fig. 3 shows a typical B–H plot. K and ε' values for each system except the chrysene–fullerene complex were obtained by using eqn. (6). In the latter case eqn. (7) was solved iteratively to get the values of K and ε'. Owing to low solubility of chrysene in CCl_4, B–H condition could not be maintained in this case. Results are given in Table 2. C_{60} is thus shown to form ground state EDA complexes of 1 : 1 stoichiometry with each of the PAHs studied. Except for chrysene, the K values are of the order of the formation constants of typical π-type EDA complexes; for example,[43] K of the naphthalene–tetrachlorophthalic anhydride complex in CCl_4 medium at 301 K is 2.8 mol dm^{-3}. The relatively high K value for the chrysene–[60]fullerene complex may be attributed to the fact that the arrangement of hexagonal rings in chrysene molecules is similar to that in the belt region of the C_{60} surface, thereby leading to a good π-overlap. We also obtained a reasonable value of Hückel parameter β and the electron affinity of [60]fullerene from the present study.

Acknowledgements

K. D. thanks Burdwan University authorities for a senior fellowship. Financial assistance by the UGC, New Delhi, extended through the DSA project, is also gratefully acknowledged.

Table 2 Data for determination of stoichiometry, formation constants and molar absorptivities of the C_{60}–polynuclear aromatic hydrocarbon complexes

Donor	$10^4\,[A]_0$/mol dm^{-3}	$[B]_0$/mol dm^{-3}	Absorbance at λ_{CT}	K/dm^3 mol^{-1}	ε/dm^3 mol^{-1} cm^{-1}
Naphthalene	3.5853	0.20781	0.111	0.67 ± 0.01	2778
		0.29219	0.150		
		0.35104	0.172		
		0.38359	0.187		
		0.40373	0.198		
		0.51354	0.235		
		0.58307	0.258		
		0.68932	0.294		
Phenanthrene	1.6129	0.06134	0.052	1.67 ± 0.19	3333
		0.07593	0.059		
		0.13578	0.095		
		0.17468	0.124		
		0.19002	0.127		
		0.22368	0.148		
Anthracene	1.6414	1.2764×10^{-2}	0.012	10.24 ± 4.66	465
		1.6692×10^{-2}	0.010		
		2.8334×10^{-2}	0.014		
		3.8714×10^{-2}	0.024		
		5.9333×10^{-2}	0.030		
Chrysene	1.7450	2.4822×10^{-3}	0.003	65.5 ± 15.19	139
		5.5485×10^{-3}	0.006		
		9.7829×10^{-3}	0.007		
		10.6005×10^{-3}	0.012		
		11.9730×10^{-3}	0.013		
		13.3289×10^{-3}	0.010		
Pyrene	1.8827	3.7575×10^{-2}	0.039	6.8 ± 1.03	980
		4.7299×10^{-2}	0.056		
		4.7368×10^{-2}	0.041		
		5.3397×10^{-2}	0.049		
		6.9053×10^{-2}	0.059		
		8.0919×10^{-2}	0.076		
		8.7511×10^{-2}	0.068		

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
2 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. Glarum, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
3 K. Holczer, O. Klein, S. M. Huang, R. B. Kaner, K. J. Fu, R. L. Whetten and F. Diederich, *Science*, 1991, **252**, 1154.
4 T. Pradeep, G. U. Kulkarni, K. R. Kannan, N. Y. Vasanthacharya, T. N. Guru Row and C. N. R. Rao, *Ind. J. Chem.*, 1992, **31 A&B**, F17.
5 D. A. Loy and R. A. Assink, *J. Am. Chem. Soc.*, 1992, **114**, 3977.
6 H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537.
7 M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097.
8 N. Martin, L. Sanchez, B. Illescas and I. Perez, *Chem. Rev.*, 1998, **98**, 2527.
9 A. L. Balch and M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.
10 F. Diederich and M. Gomezlopez, *Chimica*, 1998, **52**, 551.
11 D. M. Guldi and P. V. Kamat, in *Fullerenes: Chemistry, Physics and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley, New York, in the press.
12 M. Maggini, G. Scorrano, M. Prato, G. Brusatin, P. Innocenzi, M. Guglielmi, A. Reiner, R. Signorini, M. Meneghett and R. Bozio, *Adv. Mater.*, 1995, **7**, 404.
13 F. A. Salzar, A. Fedorov, M. N. Berberan-Santos, *Chem. Phys. Lett.*, 1997, **271**, 361.
14 D. K. Palit, A. V. Sapre and J. P. Mittal, *Ind. J. Chem.*, 1992, **31 A&B**, F46.
15 J. P. Hare, H. W. Kroto and R. Taylor, *Chem. Phys. Lett.*, 1991, **177**, 374.
16 J. W. Arbogast, A. O. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 11.
17 R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagen, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl and R. E. Smalley, *J. Phys. Chem.*, 1990, **94**, 8634.
18 S. Chandrasekaran, *Ind. J. Chem.*, 1992, **31 A&B**, F36.
19 S. H. Hoke, J. Molstad, G. L. Payne, B. Khar, D. Ben-Amotz and R. G. Cooks, *Rapid Commun. Mass Spectrosc.*, 1991, **5**, 472.
20 C. J. Hawker, P. M. Saville and J. W. White, *J. Org. Chem.*, 1994, **59**, 3503.
21 X. Zhang and C. S. Foote, *J. Org. Chem.*, 1994, **59**, 5235.
22 I. Lamparth and A. Hirsch, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1727.
23 J. Mack and G. P. Miller, *Fullerene Sci. Technol.*, 1997, **5**, 607.
24 C. N. R. Rao, T. Pradeep, R. Seshadri, R. Nagarajan, V. Narasimha Murthy, G. N. Subbanna, F. D'Souza, V. Krishnan, G. A. Nagannagowda, N. R. Suryaprakash, C. L. Khetrapal and S. V. Bhat, *Ind. J. Chem.*, 1992, **31 A&B**, F5.
25 R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459.
26 (*a*) A. D. Haymet, *Chem. Phys. Lett.*, 1985, **122**, 421; (*b*) R. L. Disch and J. N. Schulman, *Chem. Phys. Lett.*, 1986, **125**, 465.
27 G. E. Scuseria, *Chem. Phys. Lett.*, 1991, **176**, 423.
28 P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 1050.
29 D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufler, L. P. F. Chibante and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364.
30 D. Dubois, K. M. Kadish, S. Flanagan and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 7773.
31 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.
32 G. Diao, L. Liand and Z. Zhang, *Talanta*, 1996, **43**, 1633.
33 C. A. Coulson, A. Streitwieser, M. D. Poole and J. I. Brauman, *Dictionary of π-electron calculation*, Pergamon Press, Oxford, 1965, pp. 35–57.
34 MOPAC version 6.0, Program # 137, QCPE, Indiana University, Bloomington, USA.
35 R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.
36 L. S. Wang, J. Conceicao, C. Changming and R. E. Smalley, *Chem. Phys. Lett.*, 1991, **182**, 5.

37 O. V. Boltalina, E. V. Dashkova and L. N. Sidorov, *Chem. Phys. Lett.*, 1996, **256**, 253.
38 G. Chen, R. G. Cooks, E. Corpuz and L. T. Scott, *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 619.
39 M. Apostol, *Fullerene Sci. Technol.*, 1997, **5**, 1627.
40 H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, 1953, **21**, 66.
41 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
42 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6183.
43 M. Chowdhury and S. Basu, *Trans. Faraday Soc.*, 1960, **56**, 335.

Paper a907219e