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A comparative study of molecular complexation of [60]- and [70]fullerenes with 1,3,5-tribromobenzene by UV–vis spectrophotometric method

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Abstract

By UV–vis spectrophotometric method it has been shown that 1,3,5-tribromobenzene (TBB) forms molecular complexes of 1:2 stoichiometry with [60]- and [70]fullerenes. An isosbestic point could be detected in case of the [70]fullerene complex. The formation constant of the [60]fullerene complex is higher than that of the [70]fullerene complex at each of the four temperatures under study. This is in opposite order of the electron affinities of the two fullerenes; moreover, no charge transfer band was observed in the spectra of either complex in solution. This indicates that van der Waals forces, rather than CT interactions, are responsible for complexation. The results reveal that the C-atoms at the pentagon vertices of [60]fullerene have greater polarizing power than those in [70]fullerene.

Keywords: Fullerene pentagon vertices; Polarizing power; Molecular complexation; van der Waals force

1. Introduction

A great deal of experimental work has been done with [60]- and [70]fullerenes [1–3] in the fields of material science [4–11], photophysical study [12–16], organic chemistry [17,18], superconductivity [19], ferromagnetism [20], photo- and biomolecular chemistry [21,22] and inclusion phenomena [23–26]. High electron affinity of [60]- and [70]fullerenes makes them efficient electron acceptors and they have been reported [27–30] to form charge transfer (CT) complexes with various donors in solution and also in the solid state. In both [60]- and [70]fullerenes, the pentagons are arranged at *meta* positions with respect to a central benzene ring. Again, according to Taylor's rationale [31], the most stable valence bond structure of the isolated pentagon fullerenes [32] must contain the C=C double bonds exocyclically with respect to the pentagons, as shown in Fig. 1. Electron density or polarizing power at the positions marked by small circles in Fig. 1 should be somewhat different for [60]fullerene from that in [70]fullerene. This has to be so because [70]fullerene is 'elongated' and its structure contains the two hemispherical halves of the [60]fullerene structure by an intervening phenanthrene belt. To test this aspect of the fullerene structures in the present work we have chosen to study the molecular interaction of these two fullerenes with 1,3,5-tribromo benzene, which is an aromatic molecule with polarizable Br atoms at *m*-positions with respect to one another.

2. Materials and methods

[60]Fullerene and 1,3,5-tribromobenzene (TBB) were collected from Sigma and [70]fullerene from SES Research Corporation, USA. The solvent CCl_4 (UV-spectroscopic grade) was distilled after drying it on fused $CaCl_2$. All spectral measurements were carried out on a Shimadzu UV 1601 PC model spectrophotometer fitted with a peltier controlled thermo-bath.

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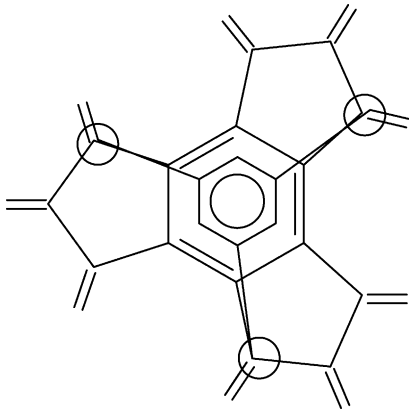

Fig. 1. Structure of a part of the molecular complex; the benzene ring of TBB is in an eclipsed position on one hexagonal ring of an IPR fullerene.

3. Results and discussions

3.1. Determination of formation constants (K)

The uppermost curve of Fig. 2 is the electronic absorption spectrum of [70]fullerene (at concentration 2.886×10^{-5} mol dm^{-3}) in CCl_4 medium against the solvent as reference. In the same figure are shown the absorption spectra of mixtures containing the same concentration of [70]fullerene and varying concentrations of TBB at 298 K against the solvent as reference. It is found that the intensity of the overall spectrum of the mixture decreases from that of pure [70]fullerene with gradual increase in concentration of TBB, although no new charge transfer peak is apparent. An isosbestic point is observed which is shown more clearly in Fig. 3 by expanding the 300–350 nm range. The spectrum of [60]fullerene in CCl_4 was also similarly perturbed with addition of TBB, but neither a CT absorption peak nor any isosbestic point was found. The appearance of isosbestic point in one case and the systematic perturbation of intensities of the fullerene absorption bands in both cases by addition of TBB are indicative of molecular complex formation. The formation constants (K) were determined at two widely different

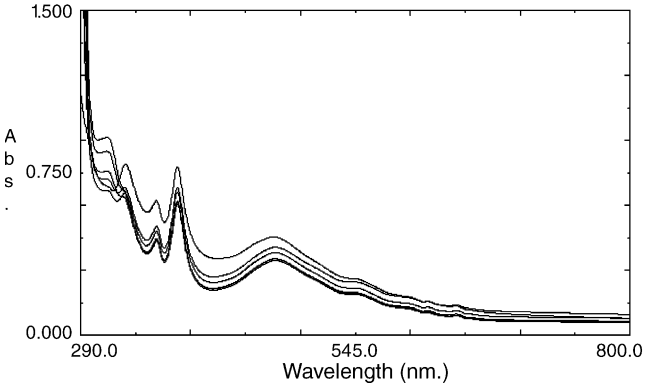

Fig. 2. Absorption spectra of [70]fullerene–1,3,5-tribromobenzene mixtures against the solvent (CCl_4) as reference containing a fixed concentration of [70]fullerene; the uppermost spectrum is of pure [70]fullerene.

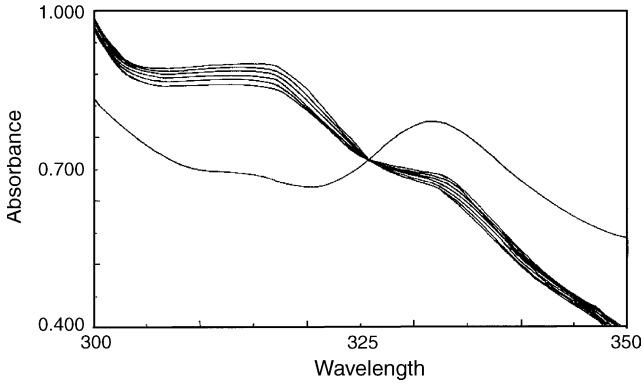

Fig. 3. Expansion of the 300–350 nm range of the first six spectra of Fig. 2 for showing the isosbestic point of [70]fullerene–TBB mixtures in CCl_4 medium. The isolated spectrum is due to pure [70]fullerene at the same concentration as that in the mixtures.

wavelengths in each case by using the Benesi–Hildebrand [33] equation. To eliminate the absorbance due to the uncomplexed components, the observed absorbance data were corrected by subtracting the absorbance due to the latter as follows:

If a 1:1 complex is formed according to the equilibrium,

$$A + D \leftrightharpoons AD \tag{1}$$

the observed absorbance (with a cell of 1 cm path length) is

$$\begin{aligned} d &= \varepsilon_A([A]_0 - c) + \varepsilon_D([D]_0 - c) + \varepsilon_C\, c \\ &= d_A^0 + d_D^0 + (\varepsilon_c - \varepsilon_A - \varepsilon_D)c \end{aligned} \tag{2}$$

or

$$d' = d - d_A^0 - d_d^0 = \varepsilon' \cdot c \tag{3}$$

Here $[A]_0$ and $[D]_0$ are the initial concentrations of A and D, respectively, in the mixture of A and D before complexation, d the absorbance of the mixture at some suitable wavelength in the respective perturbed absorption bands of C_{60} and C_{70} measured against the solvent as reference, d_A^0 and d_D^0 are the absorbances of A and D in solution with the same molar concentrations as in the mixture and at the wavelength of measurement. The quantity $\varepsilon' = \varepsilon_c - \varepsilon_A - \varepsilon_D$ means an effective molar absorptivity, ε_c the molar absorptivity of the complex, and ε_A and ε_D are those of A and D, respectively, at the wavelength of measurement. However, if the complex is of 1:2 stoichiometry ($A + 2D \leftrightharpoons AD_2$), the expression for d' remains the same and only ε' becomes $\varepsilon_c - \varepsilon_A - 2\varepsilon_D$. When the present experimental data were plotted according to the B–H [33] equation for 1:1 stiochiometry, a very wide scatter with low correlation coefficient was observed. However, a modification of the B–H equation to the form of Eq. (4), which is applicable to AD_2 type of molecular complexes, gave a good linear correlation with the present experimental data as shown in Fig. 4. The absorbance data for mixtures of [60]fullerene + TBB and [70]fullerene + TBB at four differ-