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Dispersion Interaction between Fluoranthene and Benzene in Cyclohexane

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The electronic absorption spectra of fluoranthene (abbreviated as FA) were measured in various solvents together with the polarization spectrum with the aid of the stretched polymer film technique. The electronic structure of FA is discussed in comparison with MO calculated results. The polarization directions of the electronic transitions of FA were determined. For instance, the 404 (very weak) and 360.3 nm bands are polarized along the shorter and the longer (C_2-) molecular axes, respectively. A weak van der Waals type FA–benzene complex formation was recognized in cyclohexane. The equilibrium constants for this complex formation were determined at various temperatures, e.g. $K = 0.147 \pm 0.03$ $\mathrm{dm^3{\cdot}mol^{-1}}$ at 298 K. The enthalpy, entropy, and free-energy changes are estimated to be $\Delta H^\circ = -5.9 \pm 1.2$ $\mathrm{kJ{\cdot}mol^{-1}}$ (-1.4 ± 0.3 $\mathrm{kcal{\cdot}mol^{-1}}$), $\Delta S^\circ_{298} = -36 \pm 1.0$ $\mathrm{J{\cdot}K^{-1}\ mol^{-1}}$ (-8.7 ± 0.24 $\mathrm{cal{\cdot}K^{-1}\ mol^{-1}}$), and $\Delta G^\circ_{298} = 4.7 \pm 0.4$ $\mathrm{kJ{\cdot}mol^{-1}}$ (1.1 ± 0.1 $\mathrm{kcal{\cdot}mol^{-1}}$). This ΔH° value is considerably small compared with the familiar hydrogen bonding energy, ca. -12 $\mathrm{kJ{\cdot}mol^{-1}}$($-3$ $\mathrm{kcal{\cdot}mol^{-1}}$).

It is well known that fluoranthene (abbreviated as FA) is one of the polycyclic aromatic hydrocarbons produced by the combustion of a fossil fuel.[1–5] A few papers have been published on the electronic and molecular structures of FA.[6–8] For instance, Michl et al. measured the electronic absorption and fluorescence spectra of FA in the rigid matrix of 3-methylpentane and discussed the nature of the electronic transitions.[6] Bhargavi et al. considered FA as a fragment of fullerene and calculated the bond orders for FA by the methods of VMC (Variational Monte Carlo) and PPP; they reported that the π bond orders (0.39) between the atoms linking benzene and naphthalene skeletons are considerably lower than those (0.51–0.71) in the aromatic rings.[7] This calculation is supported by an X-ray structural analysis.[8]

According to supersonic jet experiments, some polycyclic aromatic hydrocarbons form van der Waals molecular complexes with argon, methane, carbon dioxide, benzene, etc.[9] For instance, it is found that perylene forms 1 : 1 and 1 : 2 parallel-ring configuration molecular complexes with benzene, and the binding energy for the 1 : 1 benzene-perylene complex is experimentally determined to be 1950–2890 $\mathrm{cm^{-1}}$ (23.3–34.6 $\mathrm{kJ{\cdot}mol^{-1}}$). As described above, several papers have been published on the weak intermolecular interaction between nonpolar aromatic hydrocarbons from the viewpoint of the supersonic jet cool technique.[9,10] Furthermore, from measurements of the ionization potentials of benzene clusters, the binding energy in the benzene dimer is estimated to be 1.61 $\mathrm{kcal{\cdot}mol^{-1}}$.[11] However, it seems that investigations concerning van der Waals complex formations between neutral aromatic hydrocarbons in solutions at ambient temperature are very rare. Several ab initio calculations have been performed on van der Waals interacting systems between aromatic hydrocarbons, assuming several configurations, such as T-shaped and parallel-displaced.[12–17]

In the present investigation, we measured the electronic absorption spectra of FA in various solvents together with the polarization spectrum with the aid of the stretched polymer film technique. From the experimental data, the electronic structure of FA is discussed in comparison with results based on MO calculations. Furthermore, a weak van der Waals or dispersion force intermolecular interaction between FA and benzene in cyclohexane was considered.

Experimental

Commercially available FA (Aldrich Chem. Co. Inc.) was recrystallized twice from cyclohexane. Cyclohexane (Wako, S grade) used for the spectral measurements was distilled after removing impurities through a silica-gel column. Ethanol (Wako, S grade), benzene (Wako, Sp grade), and acetonitrile (Wako, Sp grade) were used as received. A polyethylene (PE) film containing FA was prepared by an already described method.[18]

Electronic absorption spectra in solutions were measured with a Shimadzu UV3100PC spectrophotometer. The polarized absorption spectrum was recorded on the above-mentioned spectrophotometer equipped with a Rochon-type polarizer.

MO Calculation

Hitherto, various kinds of semiempirical and ab initio MO methods have been developed.[19–25] However, for interpreting the electronic absorption spectra, there are few approximations that exceed the PPP method used here.[26–31] In the present PPP approximation including a variable β method,[32] two-center electron repulsion integrals were evaluated by the Nishimoto–Mataga[33] equations. The valence-state ionization potential and the electron affinity for the carbon atom were taken as 11.22 and 0.62 eV, respectively.[34] All singly electronic excited configurations were taken into account in the CI calculations. The geometry (C_{2v}), optimized by an ab initio calculation (6-31G*), was used for the present PPP MO calculation.

Results and Discussion

Electronic Absorption Spectra. The assignment of the electronic transitions may be a key to understanding the electronic properties; also, the electronic absorption spectra of FA in various media were measured (Fig. 1). FA shows electronic absorption bands at 404, 383, 359.5, 342.1, 323.9, and 309.3 nm in cyclohexane. While the 359.5 and 342.1 nm bands are unshifted in acetonitrile and ethanol, they are significantly red-shifted (ca. 2 nm) in benzene. This suggests the existence of a weak intermolecular interaction between FA and benzene molecules.

In order to know the polarization directions of the electronic transitions, the polarized absorption spectrum of FA was measured in a stretched PE film (Fig. 2). Here, $D_{\parallel}$ and $D_{\perp}$ are the optical densities measured with light beams polarized parallel and perpendicular to the stretching direction of the PE film, respectively. *Rd* is the ratio of the optical densities, $D_{\parallel}$ and $D_{\perp}$ ($Rd = D_{\parallel} / D_{\perp}$). FA shows the apparent absorption bands at 360.3, 343.6, 324.0, 310, 288.7, 283.3, 277.9, 273, 263.4, 259, 253, 246, 237.6, and 230 nm in the film. The band corresponding to the 404 nm shoulder observed in cyclohexane is apparently not observed in the PE film, but its existence is clearly recognized in the corresponding wavelength region based on the behavior of the *Rd* curve. The 324.0, 263.4, and 237.6 nm bands with lower *Rd* values are polarized along the shorter molecular axis (*y*), and the 360.3, 288.7, 283.3, 246, and 230 nm bands with higher values along the longer molecular axis (*z*). The 404 nm band observed in cyclohexane is considered to be polarized along the *y*-axis, since the *Rd* values in the wavelength region 370–410 nm decrease toward the longer wavelength side. The above experimental electronic transition data were compared with the MO calculated results given in Table 1. The longer molecular axis-polarized 360.3, 288.7, 246, and 230 nm bands are assigned as transitions from S_0 to S_2, S_4, S_7, and S_9, respectively. The shorter molecular-axis polarized 404 (in cyclohexane), 324.0, 263.4, and 237.6 nm bands are assigned as transitions from S_0 to S_1, S_3, S_6, and S_8, respectively. The 343.6 nm band is of vibronic nature, starting at 360.3 nm, the 310 nm band starting at 324.0 nm, the 283.3, 277.9, and 273 nm bands starting at 288.7 nm, and the 259 and 253 nm bands starting at 263.4 nm.

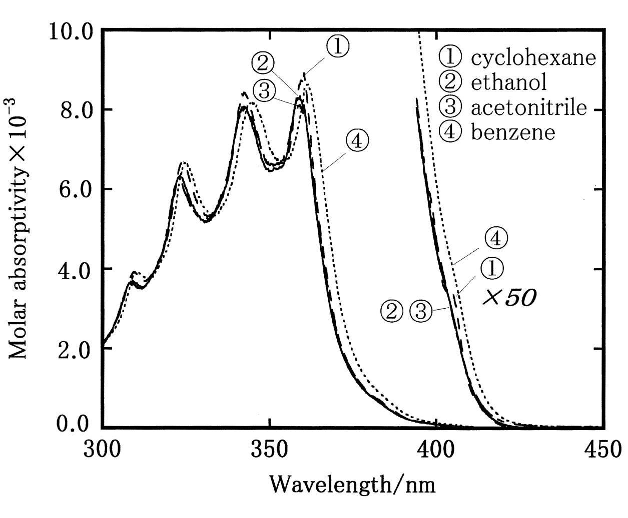


Fig. 1. Electronic absorption spectra of fluoranthene in cyclohexane (– – – –), ethanol (———), acetonitrile (– – – – –), and benzene (- - - - - -).

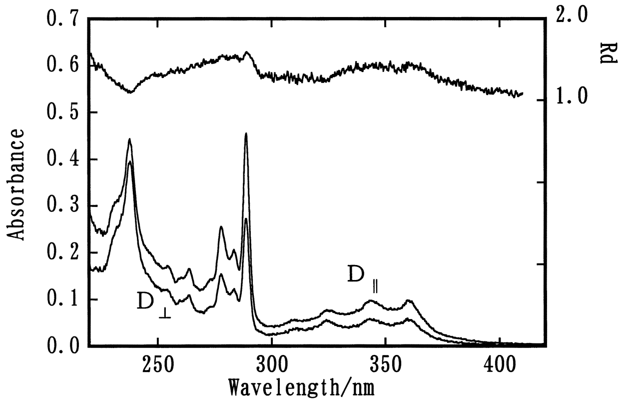


Fig. 2. Polarized absorption spectrum of fluoranthene in the stretched PE film at room temperature.

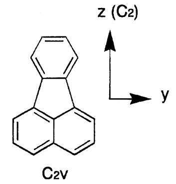
The excited-state wavefunctions of FA and the diagrammatic representations of MO's are shown in Fig. 3. The main contributors to Ψ_1 and Ψ_3 corresponding to the observed 404 and 324.0 nm bands are $\chi_{7,9}$, $\chi_{6,9}$, and $\chi_{8,10}$, i.e., the 404 and 324.0 nm electronic transitions are characterized by the intramolecular CT transition from the benzene skeleton to the naphthalene and its back CT. The main contributor to Ψ_2 is the LUMO ← HOMO transition delocalized on the whole molecule. The two intramolecular CT configurations interact so much that the resultant lower energy state is more stabilized than the LUMO ← HOMO transition state.

Dispersion Force Intermolecular Interactions. Generally, the lowest energy electronic bands of polycyclic aromatic hydrocarbons are red-shifted with an increase in the solvent polarity.[35] However, as described in the previous sections, the electronic absorption spectra of FA are almost independent on solvent polarities. Although benzene is a typical nonpolar solvent, the lowest energy absorption bands of FA are significantly red-shifted in benzene compared with those in other polar

Table 1. Comparison of the Calculated and Observed Results for the $S_n \leftarrow S_0$ Transitions of Fluoranthene

		Transition energy/nm		Intensity		Polarization direction[e)]	
		Calcd	Obsd[a)]	Calcd[b)]	Obsd[c)]	Calcd	Obsd
S_1	(B_2)	363.5	404[d)]	0.0094	0.01[d)]	y	y
S_2	(A_1)	352.5	360.3	0.3978	0.17	z	z
S_3	(B_2)	334.5	324.0	0.0416	0.17	y	y
S_4	(A_1)	292.6	288.7	0.2290	0.96	z	z
S_5	(A_1)	257.7	283.3	0.0082	0.38	z	z
S_6	(B_2)	250.8	263.4	0.0643	0.28	y	y
S_7	(A_1)	243.2	246	0.4512	0.30	z	z
S_8	(B_2)	242.7	237.6	1.0788	1.00	y	y
S_9	(A_1)	228.7	230	0.7845	0.74	z	z

a) In the PE film.
b) Oscillator strength.
c) Observed relative band height with respect to the 237.6 nm band.
d) Observed in cyclohexane.
e) See right figure.



$$\Psi_1 = 0.8773\chi_{7,9} - 0.4318\chi_{6,9} + \cdots$$

$$\Psi_2 = -0.9445\chi_{8,9} + \cdots$$

$$\Psi_3 = -0.6903\chi_{6,9} + 0.5299\chi_{8,10} - 0.3842\chi_{7,9} + \cdots$$

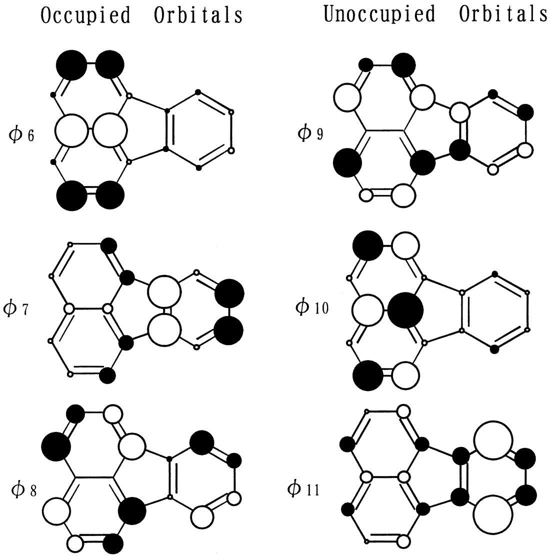


Fig. 3. Excited wavefunctions and diagrammatic representation of MO's of fluoranthene. Here, $\chi_{i,j}$ is a singly excited configuration wavefunction from the i'th occupied to the j'th unoccupied orbital.

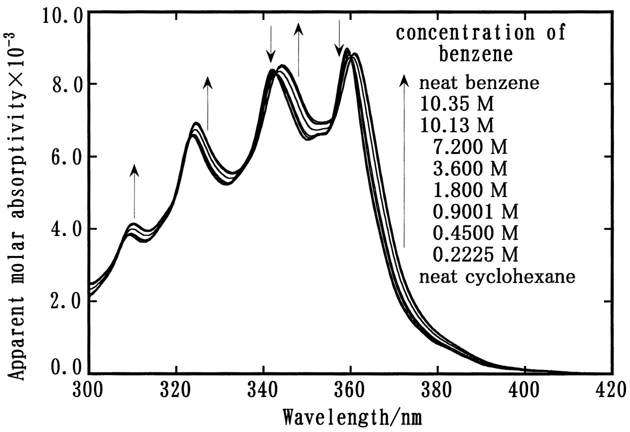


Fig. 4. Electronic absorption spectra of fluoranthene in cyclohexane–benzene mixed solvents at various concentration rarios.

and nonpolar solvents (ethanol, acetonitrile, and cyclohexane). This phenomenon contradicts with the above-mentioned general solvent effects, and may be induced by a specific solute (FA) –solvent (benzene) interaction. To confirm this speculation, the absorption spectra of FA have been measured in mixed solvents of benzene and cyclohexane with various mixing ratios. As can be seen from Fig. 4, the absorption spectrum of FA changes with the mixing ratio accompanying isosbestic points, indicating that the spectral changes are due to the following chemical equilibrium:

$$\text{FA} + \text{benzene} \overset{K}{\rightleftarrows} \text{FA} - \text{benzene}, \tag{1}$$

$$K = \frac{C_{\text{FA-benzene}}}{C_{\text{FA}} \times C_{\text{benzene}}}. \tag{2}$$

Here, FA–benzene stands for a molecular complex between FA and benzene. C_{FA}, C_{benzene}, and $C_{\text{FA-benzene}}$ mean the concentrations of FA, benzene, and FA–benzene, respectively, in the equilibrium state. From the absorption spectral changes shown in Fig. 4, the equilibrium constant can be estimated using an equation proposed by Rose and Drago,[36–38]

$$\frac{1}{K} = \frac{C_{\text{FA}}^{0} C_{\text{benzene}}^{0}}{A - A^{0}} \varepsilon_{\text{FA-benzene}} + \frac{A C_{\text{benzene}}^{0}}{A^{0} - A}. \tag{3}$$

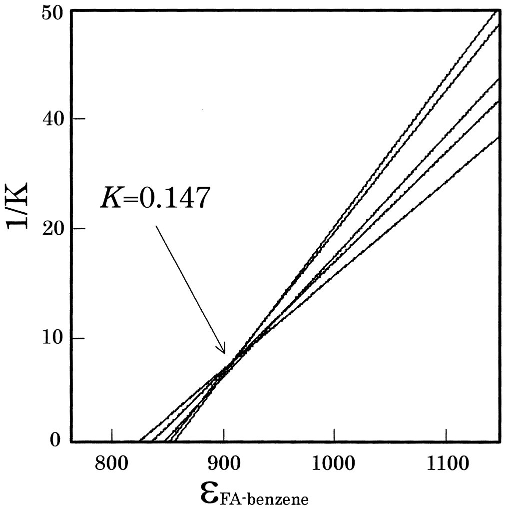


Fig. 5. $\varepsilon_{\text{FA–benzene}}$ vs $1/K$ plots at 298 K.

Here, A^0 and A are the optical densities of FA in neat cyclohexane and in a mixed solvent of cyclohexane and benzene, respectively. C_{FA}^0 and C_{benzene}^0 are the initial concentrations of FA and benzene, respectively. $\varepsilon_{\text{FA–benzene}}$ is the molar absorptivity of FA–benzene. Plots of $1/K$ vs $\varepsilon_{\text{FA–benzene}}$ result in straight lines for various concentrations of benzene, whose crossing point gives $\varepsilon_{\text{FA–benzene}}$ and $1/K$. The representative plots shown in Fig. 5 give straight lines and cross at approximately one point, which also indicates the formation of a 1:1 complex between FA and benzene. The equilibrium constant was estimated to be $K = 0.147 \pm 0.03$ dm^3·mol^{-1} (at 298 K).

In order to obtain the enthalpy and entropy changes for FA–benzene complex formation, the temperature dependence of the equilibrium constant was determined, i.e., the absorption spectra of FA were measured in cyclohexane containing various amounts of benzene at various temperatures (288–323 K, see Table 2). Plots of ln K against $1/T$ gave a straight line, whose slope yielded -5.9 ± 1.2 kJ·mol^{-1} (-1.4 ± 0.3 kcal·mol^{-1}) for the concerned enthalpy change ($\Delta H^\circ_{\text{FA–benzene}}$). It has been demonstrated from recent ab initio calculations that the main attractive force in non-polar aromatic, benzene, naphthalene etc. dimers is of a dispersion type.[15–17] This formation energy is thus considered to be a so-called London dispersion energy, and is considerably lower than the well-known hydrogen-bond formation energy ($\Delta H_{\text{H-bond}}$), e.g. $\Delta H_{\text{H-bond}} = -16$ kJ·mol^{-1} (-3.8 kcal·mol^{-1}) for the chloroform–*N*-methylacetamide hydrogen bond.[39] It is very rare to have experimentally obtained this kind of dispersion force interaction energy between two different nonpolar aromatic molecules. The binding energy, 23.3–34.6 kJ·mol^{-1} (5.6–8.3 kcal·mol^{-1}), obtained by the supersonic cool-jet method for the benzene-perylene complex is considerably lager than that obtained in the present experiment for the FA–benzene complex. This discrepancy is due to that the former binding or complex formation energy means ΔH_0 (= ΔU_0) in the nonequilibrium state, while the latter one, ΔH°_{300}, in the equilibrium state. Here, ΔH°_{300} means the complex formation energy at 300 K, and ΔH_0 at 0 K. The dimer formation energy for benzene was obtained from the ionization potentials of the benzene cluster to be 6.73 kJ·mol^{-1} (1.61 kcal·mol^{-1}), which also corresponds to ΔH_0 (= ΔU_0) in the nonequilibrium state.

Table 2. The Equilibrium Constants for FA–Benzene Molecular Complex Formation at Various Temperatures

Temperature /K	Equilibrium constant /dm^3·mol^{-1}
288	0.165
293	0.166
298	0.147
303	0.142
308	0.132
313	0.147
318	0.127
323	0.119

Two interaction models are considered for the intermolecular interaction between FA and benzene: (1) a T-type interaction, and (2) a parallel-displaced type interaction through π orbitals. Both the longer molecular axis polarized second (360.3 nm) and shorter axis polarized third (324.0 nm) electronic transitions of FA are shifted to the red by a complex formation with benzene, indicating that an undistorted T-type configuration is at least ruled out based on the transition–dipole interaction model. Thus, the present FA–benzene complex is considered to take a kind of parallel-type or a distorted T-type configuration.

It may be very interesting to estimate the entropy change for the complex formation concerned. The free energy and entropy changes at 298 K, $\Delta G^\circ_{\text{FA–benzene}}$ and $\Delta S^\circ_{\text{FA–benzen}}$, were calculated as 4.7 ± 0.4 kJ·mol^{-1} (1.1 ± 0.1 kcal·mol^{-1}) and -36 ± 1.0 J·K^{-1} mol^{-1} (-8.7 ± 0.24 cal·K^{-1} mol^{-1}) using the K and $\Delta H^\circ_{\text{FA–benzene}}$ values described above. The positive value of $\Delta G^\circ_{\text{FA–benzene}}$ shows that the intermolecular interaction between FA and benzene is considerably weak, and the large negative value of $\Delta S^\circ_{\text{FA–benzene}}$ implies that the entropy term plays an important role in the present complex formation.

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