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NMR and MO Studies on the Molecular Structure of a Fluoranthene-Benzene Complex

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Summary. Fluoranthene (*FA*) forms a 1:1 *van der Waals* complex with benzene in cyclohexane. The ^{1}H NMR spectrum of this complex shows that the *FA* moiety in the complex state has five kinds of hydrogen atoms and that the ^{1}H NMR peaks assigned to the protons attached to the naphthalene skeleton are largely shifted to higher magnetic field on complex formation with benzene. These observations indicate that the complex takes the structure of C_S symmetry, in which the benzene molecule mainly interacts with the π electronic system localized on the naphthalene moiety of *FA*. The present *ab initio* calculations reproduce well the ^{1}H NMR spectral shifts mentioned above and the experimentally predicted C_S structure of the complex. According to the PPP calculations for the electronic absorption spectral changes on the complex formation, the *FA*-benzene complex is considered to take a sandwich type structure.

Keywords. Weak intermolecular interaction; Fluoranthene-benzene molecular complex; MO calculations.

Introduction

A weak intermolecular interaction plays an important role in the primary processes of chemical reactions or in the stabilization of the three dimensional structure of proteins, *DNA*s, enzymes, *etc*. Up to date, *van der Waals* interactions between aromatic hydrocarbons have been studied mainly by means of a supersonic cool jet method [1–7]. For instance, *Even* and *Jortner* have measured laser-induced fluorescence excitation spectra for the systems of tetracene-benzene, fluorine-benzene, *etc*. under supersonic jet cooled conditions, and performed vibrational

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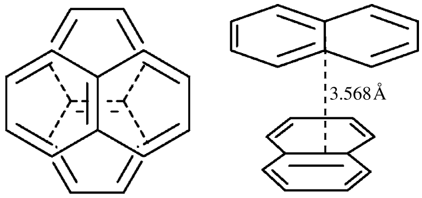
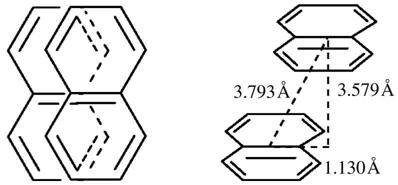


Crossed (Top view) Crossed (Side view)



Parallel-displaced (Top view) Parallel-displaced (Side view)

Scheme 1

analyses to recognize the formation of *van der Waals* complexes and to elucidate the nature of intermolecular interactions [2]. Many *ab initio* MO calculations have been performed for *van der Waals* complexes [8–13]. However, these calculations are mainly limited to structures in which identical molecules interact, such as benzene dimer, naphthalene dimmer, *etc.* [10, 12]. According to the *ab inito* calculations by *Gonzalez* and *Lim*, naphthalene dimer takes a crossed parallel or a parallel displaced structure (Scheme 1) [8].

It is known that naphthalene molecules interact with each other taking a parallel displaced arrangement in the crystalline state [14, 15]. In a previous paper, it is elucidated that *FA* forms a 1:1 *van der Waals* molecular complex with benzene in cyclohexane, and the thermodynamic quantities have been determined for the complex formation from the measurements of electronic absorption spectra. It is further elucidated that an undistorted symmetric T-type structure is ruled out from the observation that both the longer and shorter molecular axis polarized bands of *FA* are shifted to the red by the complex formation with benzene [16].

In the present paper, the structure of the *FA*-benzene complex has been elucidated from ^{1}H NMR signal shifts observed on the complex formation along with semiempirical and *ab inito* MO calculations.

Results and Discussion

^{1}H NMR Spectra

To obtain information on the geometry of the *FA*-benzene complex, ^{1}H NMR spectra have been measured. As for *FA* itself the assignment of ^{1}H NMR signals in chloroform-d has already been performed [17]. In the present study, the ^{1}H NMR spectrum of FA was measured in cyclohexane-d$_{12}$ to be able to observe the shifts in chemical shifts by complex formation with benzene, the cyclohexane being an

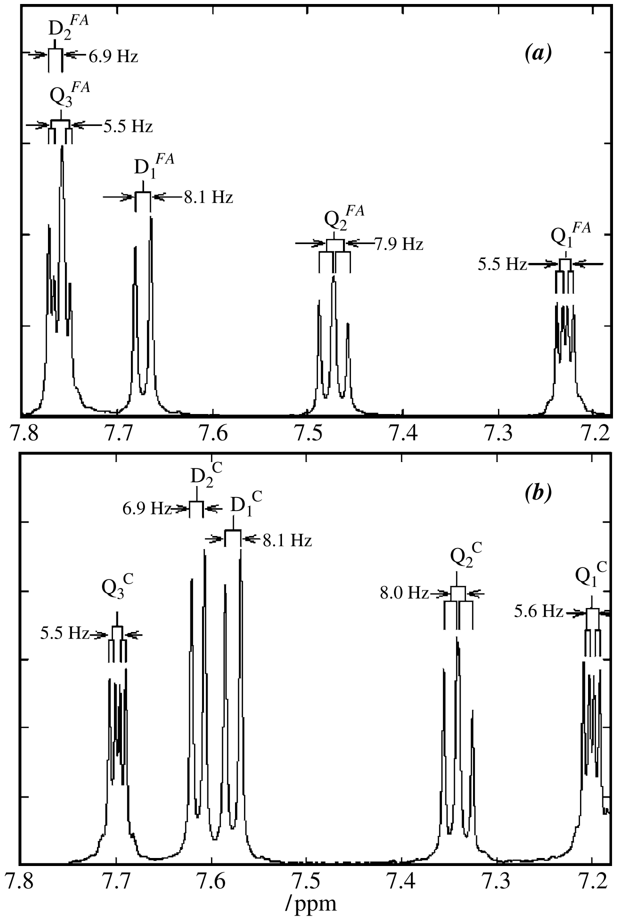


Fig. 1. The ^1H NMR spectra of *FA* in cyclohexane-d_{12} (a) and benzene-d_6 (b)

appropriate solvent for both the ^1H NMR and optical studies on the complex formation concerned. Figure 1 shows ^1H NMR spectra of FA measured in cyclohexane-d_{12} (a) and in benzene-d_6 (b). *FA* shows two doublet (D_1^{FA} (7.665 and 7.681 ppm) and D_2^{FA} (7.758 and 7.771 ppm)) and three quartet (Q_1^{FA} (7.221, 7.227, 7.232, and 7.238 ppm), Q_2^{FA} (7.458, 7.472, 7.473, and 7.488 ppm), and Q_3^{FA} (7.749, 7.755, 7.760, and 7.766 ppm)) ^1H NMR signals in cyclohexane, indicating that *FA* has five kinds of hydrogen atoms in accordance with the result of the single crystal X-ray analysis [18]. In order to assign the above ^1H NMR signals, an *ab initio* calculation (B3LYP/6-311++G(3df, 2pd)) was performed for FA (Fig. 2(a)); the calculated chemical shifts for protons are increased in the order: H_9 (8.6446 ppm), H_2 (8.9178 ppm), H_3 (9.1285 ppm), H_{10} (9.1791 ppm), and H_1 (9.2082 ppm). The observed Q_1^{FA}, Q_2^{FA}, D_1^{FA}, Q_3^{FA}, and D_2^{FA} are assigned to the calculated H_9, H_2, H_3, H_{10}, and H_1, respectively, from the comparison of the calculated and observed chemical shifts. The ^1H NMR spectrum of *FA* measured in benzene-d_6 also shows two doublet (D_1^C (7.569 and 7.585 ppm) and D_2^C (7.607 and 7.621 ppm)) and three quartet signals (Q_1^C (7.192, 7.198, 7.203, and 7.209 ppm), Q_2^C (7.326, 7.340, 7.342, and 7.356 ppm), and Q_3^C (7.689, 7.696, 7.700, and 7.707 ppm)) (Fig. 1(b)). These signals are assigned to the *FA*-benzene complex, whose formation was recognized in cyclohexane from the viewpoint of electronic absorption spectrum in our previous paper [16]. This ^{1}H NMR spectrum shows that the *FA* moiety in the complex has also five kinds of hydrogen atoms. This indicates that the *FA*-benzene complex has at least a symmetry of C_S. It is considered from comparison of J values between *FA* and *FA*-benzene complex that the observed ^{1}H NMR signals $Q_1{}^C$, $Q_2{}^C$, $D_1{}^C$, $D_2{}^C$, and $Q_3{}^C$ in benzene correspond to the signals $Q_1{}^{FA}$, $Q_2{}^{FA}$, $D_1{}^{FA}$, $D_2{}^{FA}$, and $Q_3{}^{FA}$, respectively, *i.e*., the signals $Q_1{}^C$, $Q_2{}^C$, $D_1{}^C$, $D_2{}^C$, and $Q_3{}^C$ are assigned to the protons $H_9{}^C$, $H_2{}^C$, $H_3{}^C$, $H_1{}^C$, and $H_{10}{}^C$ of *FA* in the complex. An *ab initio* calculation for the *FA*-benzene complex with C_S symmetry predicts that the ^{1}H NMR signals for protons of *FA* in the complex appear in the order of $H_9{}^C$ (8.6532 ppm), $H_2{}^C$ (8.7973 ppm), $H_1{}^C$ (8.8831 ppm), $H_3{}^C$ (8.9129 ppm), and $H_{10}{}^C$ (9.0781 ppm) (Fig. 2(b)), in which the optimized geometry given later was used. This calculated order is approximately in accordance with the above-mentioned experimental order except that the order of $H_1{}^C$ and $H_3{}^C$ is reversed. The observed $D_1{}^C$ and $D_2{}^C$ should be assigned to $H_3{}^C$ and $H_1{}^C$ judging from the observed J values. On the complex formation with benzene, $Q_1{}^{FA}$ and $Q_3{}^{FA}$ signals of *FA* are shifted towards higher magnetic field by 0.03 and 0.06 ppm, respectively, and $Q_2{}^{FA}$, $D_1{}^{FA}$, and $D_2{}^{FA}$ by 0.13, 0.10, and 0.15 ppm, respectively. That is, the observed $Q_2{}^{FA}$, $D_1{}^{FA}$, and $D_2{}^{FA}$ peaks, which are assigned

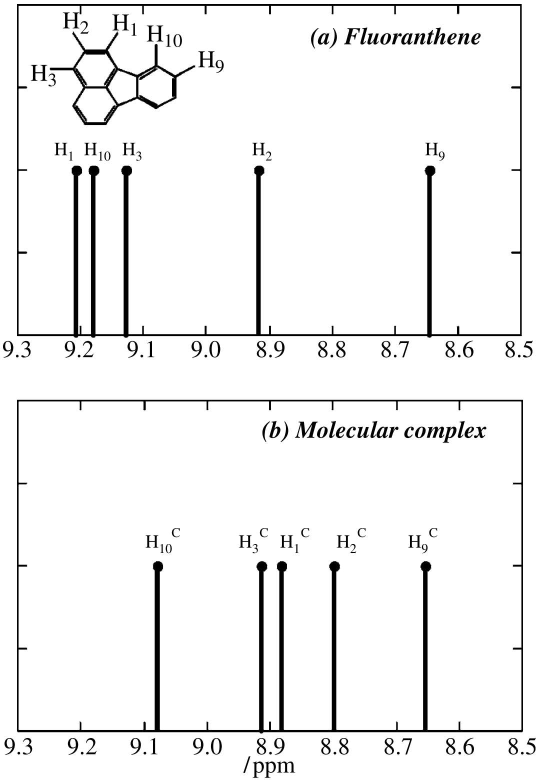


Fig. 2. The predicted ^{1}H NMR signals due to *ab initio* calculations for *FA* (a) and the *FA*-benzene complex (b)

to the hydrogen atoms attached to the naphthalene moiety of *FA*, are largely (by 0.1–0.15 ppm) shifted towards higher magnetic field upon complex formation. On the other hand, the observed Q_1^{FA} and Q_3^{FA} assigned to the hydrogen atoms of the benzene ring of *FA* show significantly smaller shifts (by 0.03–0.06 ppm). This means that the benzene molecule mainly interacts with the π electronic system localized on the naphthalene moiety of *FA*. The present *ab initio* calculations reproduce well the above-mentioned spectral behaviour as can be seen in Fig. 2.

Structure of the FA-Benzene Complex Predicted by ab Initio and Extended PPP Calculations

According to the ^{1}H NMR spectra described in the previous section, the *FA*-benzene complex has at least a symmetry C_S. Therefore, in the present *ab initio* calculations, two sandwich (S_1 and S_2) and four T-shaped (T_1, T_2, T_3, and T_4) structures with C_S symmetries were assumed to obtain the optimized geometry (Fig. 3). The procedure of the geometry optimization used in this approximation is as follows. (1) Optimization against x axis with a fixed interplanar distance of 3.8 Å between benzene and *FA* molecular planes for the sandwich geometry (with

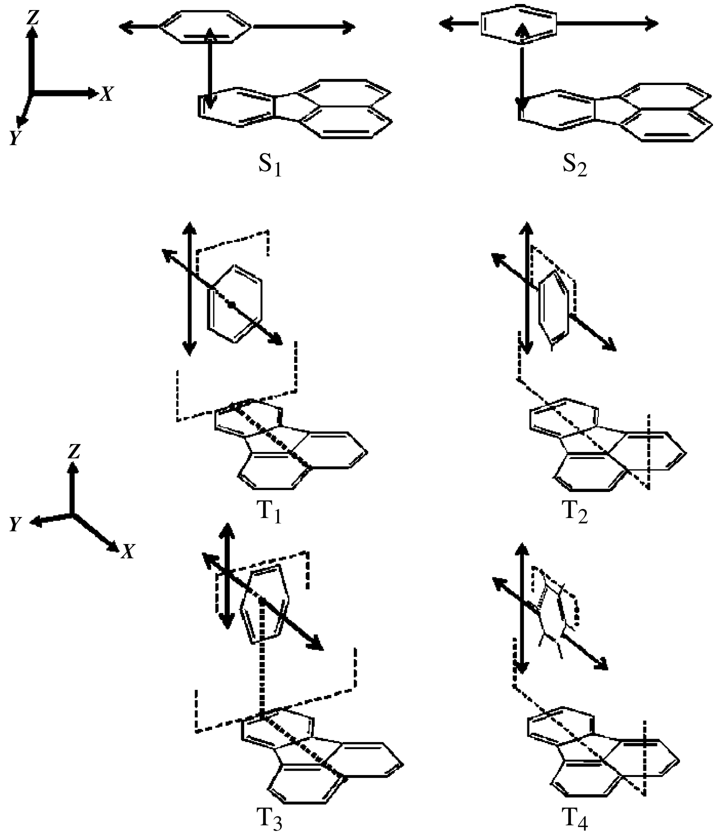
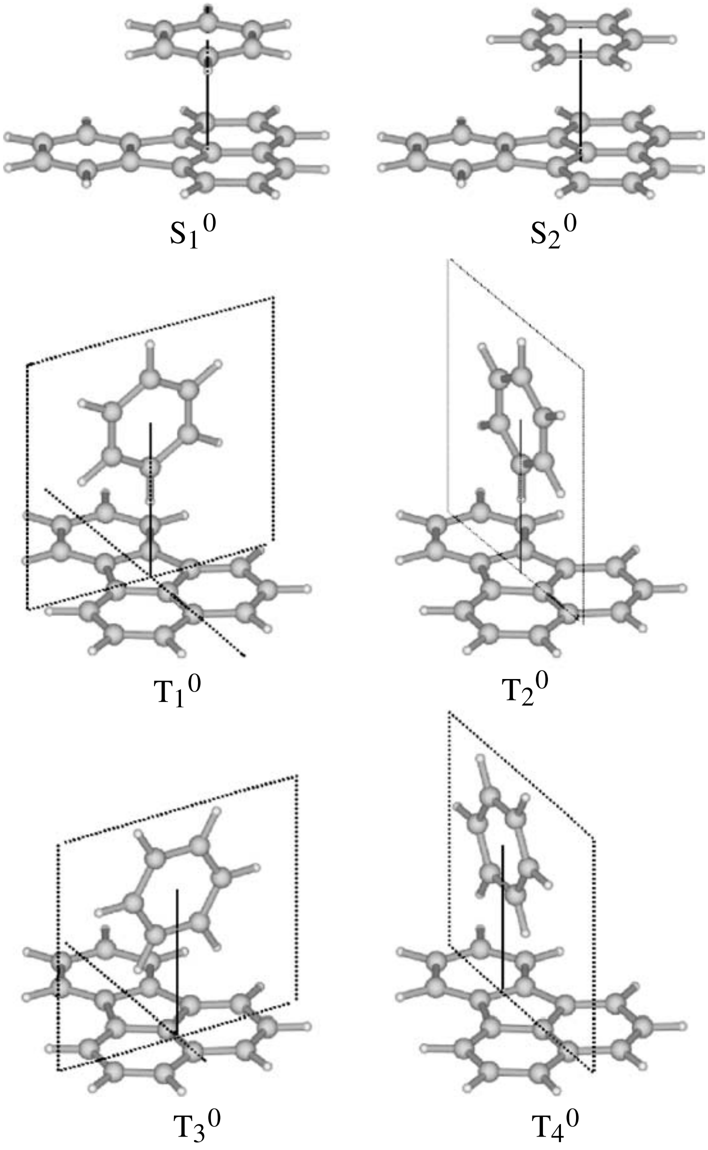


Fig. 3. The assumed structures used in the *ab initio* calculations for the *FA*-benzene system; for the meaning of the arrows, see text

the fixed distance of 2.54 Å between the plane of *FA* and the hydrogen atom of benzene for T-shaped geometries) [8]. (2) Using the optimized *x* value, optimization against *z* axis. (3) Optimization against *x* axis using the optimized *z* value obtained in (2). These geometry optimization procedures (1), (2), and (3) were continued until a self-consistent geometry was obtained.

The optimized geometries for the assumed six configurations with C_S symmetry are shown in Fig. 4, and their total and stabilization energies are listed in Table 1. As can be seen in this table, the most stable geometry is considered to be structure $S_2{}^0$ or $S_1{}^0$, the energy difference between structure $S_2{}^0$ and $S_1{}^0$ being negligibly small ($0.03\,\mathrm{kJ \cdot mol^{-1}}$), and the $S_2{}^0$ complex formation energy is calculated to be $34.6\,\mathrm{kJ \cdot mol^{-1}}$.



$S_1{}^0$ $S_2{}^0$

$T_1{}^0$ $T_2{}^0$

$T_3{}^0$ $T_4{}^0$

Fig. 4. The optimized *FA*-benzene complex structures obtained from the *ab initio* calculations

Table 1. The complex formation energies (ΔE) for the *FA*-benzene complex with various assumed structures calculated by MP2/6-31G(d) calculations

Structure	$\Delta E/\mathrm{kJ \cdot mol^{-1}}$[a]
$S_1{}^0$	−34.6
$S_2{}^0$	−34.6
$T_1{}^0$	−17.4
$T_2{}^0$	−19.4
$T_3{}^0$	−23.1
$T_4{}^0$	−22.9

[a] The calculated total energy before the complex formation is $-2.219118540 \times 10^6\,\mathrm{kJ \cdot mol^{-1}}$

In order to obtain more detailed structural information on the *FA*-benzene complex, extended PPP calculations were performed for the assumed complex structures in Fig. 4 and the results are shown in Table 2 along with those for *FA*. According to the observation, the $\pi\pi^*{}_2$ and $\pi\pi^*{}_3$ transitions of *FA* are both red shifted by about 2 nm on complex formation [16]. The calculated results for the four T-shaped structures cannot explain the observation; for instance, the calculated $\pi\pi^*{}_2$ transitions for the structures $T_1{}^0$ and $T_3{}^0$, and the $\pi\pi^*{}_3$ transition for the structures $T_2{}^0$ and $T_4{}^0$ are predicted to be unshifted in comparison with those of *FA* contradicting with the observation. These quantitative considerations support the previous prediction [16] that the undistorted symmetric T-shaped complexes are ruled out from the qualitative exciton model interpretation; in the T-shaped model only one of the longer and shorter molecular axis polarized transition moments can interact with the transition moment of benzene. The calculated $\pi\pi^*{}_2$ and $\pi\pi^*{}_3$ transitions for structure $S_1{}^0$ are red-shifted by 0.7 and 0.2 nm, and those for the structure $S_2{}^0$ by 1.1 and 0.6 nm in comparison with those of *FA*. While both calculated results for the structures $S_1{}^0$ and $S_2{}^0$ can qualitatively explain the observation, the latter is superior to the former in reproducing the observation more precisely.

It was also interesting to obtain the most stable geometry of the *FA*-benzene complex from the viewpoint of *ab initio* calculation using MP2/6-31G(d). The potential energy (E) curves were calculated for a geometry deformation from the C_S symmetry ($S_2{}^0$), *e.g.* for moving benzene in the three directions X_1, X_2, and X_3 (*cf.* Fig. 5) with the benzene plane parallel to *FA*'s one, *i.e.*, with the interplanar distance of 3.25 Å which is the optimized one for the C_S configuration, and it is reconfirmed from the viewpoint of *ab initio* calculation that the most stable geometry is of C_S. As a representative example, the potential curve for moving benzene in the X_2 direction is shown in Fig. 5. According to this figure, a small minimum is seen for the structure distorted from the C_S symmetry. This suggests the possibility that the *FA*-benzene complex takes an asymmetric structure. However, the existence of a *FA*-benzene complex with asymmetric structure is not admitted, *i.e.*, no ^{1}H NMR signals have been observed for the asymmetric species. This means that the energy separation between the two symmetric and asymmetric isomers is rather larger in the actual system than that obtained from the *ab initio* calculations. Next, a full optimization was performed in the vicinity of $S_2{}^0$ struc-

Table 2. The calculated transition energies for fluoranthene and various kinds of assumed structures of the *FA*-benzene complex

	Fluoranthene		S_1^0 geometry[a]		S_2^0 geometry	
	Transition energy/nm	Intensity	Transition energy/nm	Intensity	Transition energy/nm	Intensity
$\pi\pi^*{}_1$	364.3	0.008	364.3	0.007	364.5	0.008
$\pi\pi^*{}_2$	354.5	0.407	355.2	0.369	355.6	0.375
$\pi\pi^*{}_3$	333.3	0.061	333.5	0.055	333.9	0.057
$\pi\pi^*{}_4$	290.1	0.232	290.4	0.198	290.7	0.196

	T_1^0 geometry		T_2^0 geometry		T_3^0 geometry		T_4^0 geometry	
	Transition energy/nm	Intensity	Transition energy/nm	Intensity	Transition energy/nm	Intensity	Transition energy/nm	Intensity
$\pi\pi^*{}_1$	364.3	0.008	364.3	0.008	364.3	0.008	364.3	0.008
$\pi\pi^*{}_2$	354.5	0.407	354.7	0.385	354.5	0.407	354.8	0.389
$\pi\pi^*{}_3$	333.4	0.058	333.3	0.061	333.4	0.057	333.3	0.061
$\pi\pi^*{}_4$	290.1	0.232	290.2	0.214	290.1	0.233	290.2	0.218

[a] See Fig. 4

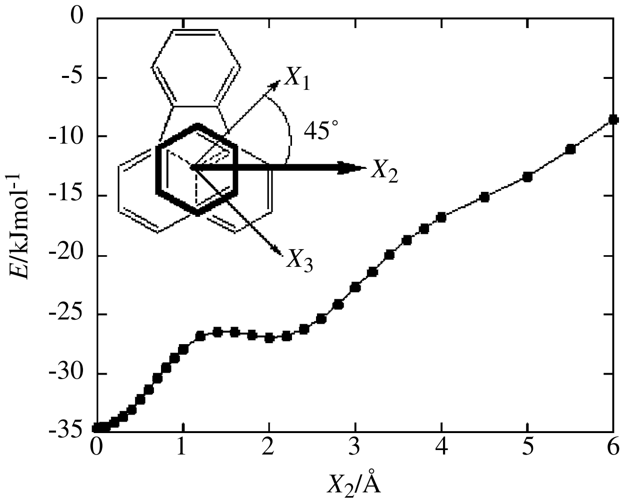


Fig. 5. The potential energy curve against X_2; E: The total energy for the interacting *FA*-benzene system with respect to that of the noninteractive system

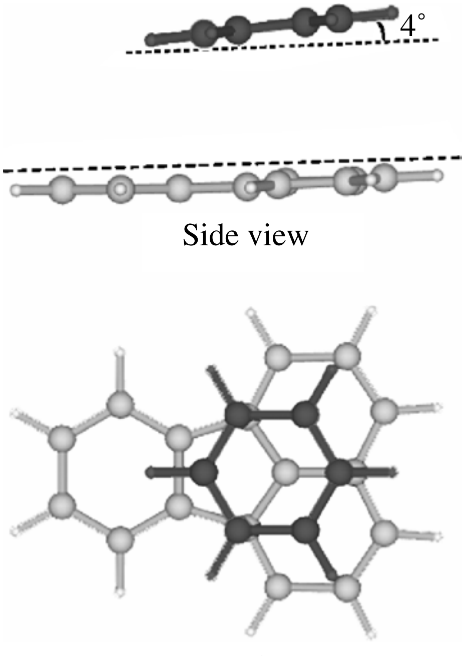


Fig. 6. The full optimized structure for the *FA*-benzene complex with the S_2 geometry

ture, and the result is shown in Fig. 6. As can be seen in this figure, the C_S symmetry is virtually maintained, and the two planes of *FA* and benzene slightly deviate from the complete parallel configuration, the dihedral angle being about 4°, the nearest neighbour interplanar distance is 3.22 Å, and the *FA* molecular plane is slightly bent inwardly in the complex. This slight structural deformation from S_2^0 can be neglected in the PPP calculations.

Experimental and MO Calculation

A commercially available *FA* (Aldrich) was recrystallized twice from cyclohexane (Wako). Cyclohexane-d_{12} and benzene-d_6 were used as received (Wako). ^{1}H NMR spectra were recorded on a JNM-ECP500 (JEOL).

For *ab initio* calculations a commercially available software (the Gaussian 98W) was used [19]. B3LYP/6-311++G(3df, 2pd) and MP2/6-31G(d) were employed for the assignment of NMR spectra and geometry optimization of the *FA*-benzene complex, respectively.

For the interpretations of the electronic absorption spectral shifts of *FA* on complex formation with benzene, an extended PPP method was employed using the geometries optimized by *ab initio* calculations [20–26]. The intermolecular interaction of *FA* with benzene is taken into account through the configuration interactions.

Acknowledgements

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References

[1] Kettley JC, Palmer TF, Simons JP (1985) J Phys Lett **115**: 40
[2] Even U, Jortner J (1983) J Chem Phys Part 2 **78**: 3445
[3] Haynam CA, Brumbaugh DV, Levy DH (1983) J Chem Phys **79**: 1581
[4] Doxtader MM, Mangle EA, Bhattacharya AK, Cohen SM, Topp MR (1986) Chem Phys **101**: 413
[5] Schwarts SA, Topp MR (1984) J Phys Chem **88**: 5673
[6] Saigusa H, Morohoshi M, Tsuchiya S (2001) J Phys Chem A **105**: 7334
[7] Law KS, Schauer M, Bernstein ER (1984) J Chem Phys **81**: 4871
[8] Gonzalez C, Lim EC (2000) J Phys Chem A **104**: 2953
[9] Hobza P, Spirko V, Selzle HL, Schlag EW (1998) J Phys Chem A **102**: 2501
[10] East ALL, Lim EC (2000) J Chem Phys **113**: 8981
[11] Meijer EJ, Sprik M (1996) J Chem Phys **105**: 8684
[12] Spirko V, Engkvist O, Soldan P, Selzle HL, Schlag EW, Hobza P (1999) J Chem Phys **111**: 572
[13] Gonzalez C, Lim EC (2001) J Phys Chem A **105**: 1904
[14] Abrahams SC, Robertson JM, White JG (1949) Acta Cryst **2**: 233
[15] Brock CP, Dunitz JD (1982) Acta cryst **B38**: 2218
[16] Enomoto S, Hasegawa M, Yoshinaga T, Hiratsuka H, Kobayashi M, Okubo J, Hoshi T (2002) Bull Chem Soc Jpn **75**: 689
[17] Laali KK, Okazaki T, Galembeck SE (2002) J Chem Soc Perkin Trans **2**: 621
[18] Hazell AC, Jones DW, Sowden JM (1977) Acta Crystallogr Sect B **33**: 1516
[19] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres

JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98, Gaussian Inc, Pittsburgh PA

[20] Pariser R, Parr RG (1953) J Chem Phys **21**: 466

[21] Pople JA (1953) Trans Faraday Soc **46**: 1375

[22] Hoshi T, Kobayashi M, Yoshino J, Komuro M, Tanizaki Y (1979) Ber Bunsen-Ges Phys Chem **83**: 821

[23] Kobayashi M, Maeda T, Hoshi T, Okubo J, Tanizaki Y (1989) J Soc Dyers Colour **105**: 362

[24] Nishimoto K, Forster LS (1965) Theor Chim Acta **3**: 407

[25] Mataga N, Nishimoto K (1957) Z Phys Chem Neue Folge **13**: 140

[26] Hoshi T, Yoshino J, Hayashi K (1973) Z Phys Chem Neue Folge **83**: 31