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Ab Initio Molecular Orbital Study of the Benzene–Chlorine Complex

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The geometrical structures and stabilization energies of benzene–chlorine complex were studied theoretically using an ab initio molecular orbital method. Full geometry optimization was carried out for four models ((**1**) [On Center (C_{6v} symmetry)], (**2**) [On Atom (C_s symmetry)], (**3**) [On Bond (C_s symmetry)] and (**4a,b**) [Resting (C_s symmetry)]) with restricted Hartree–Fock (RHF) and second-order Møller–Plesset perturbation (MP2) methods, MP2 (Frozen), and MP2 (Full), using various basis sets. The RHF method is not good enough to describe the molecular structure and interaction energy of the complex. The geometry obtained with the MP2/DZP+d method has good agreement with the X-ray crystal structure. An unusual basis set superposition error (BSSE) was found when the MP2 method with a frozen-core approximation was applied to evaluate the interaction energy. In the MP2 (Full) method, in which the inner-core wavefunctions was correlated, the reasonable stabilization energy is obtained. The BSSE-corrected interaction energies (ΔE(corr.)) of models(**1**), (**2**), and (**3**) are -6.63, -8.44, and -8.14 kJ mol^{-1}, respectively. The most stable structure of the benzene–chlorine complex was calculated to be model (**2**). Model (**3**) lies at only 0.3 kJ mol^{-1} higher energy than model (**2**) in the MP2(Full)/DZP+d calculation. The position of chlorine would be very flexible on the benzene ring, and the molecular structure of the complex is easily interchangeable between models (**2**) and (**3**).

Benzene–halogen complex is one of the typical and important Charge-Transfer (CT) complexes. There is a long history of theoretical studies concerning the structure of this complex.[1—5] Mulliken proposed a resting model for this complex in 1950.[2] This model was based on resonance and charge-transfer (CT) theories in order to interpret the experimental results of the benzene–halogen and several other complexes. Collin and D'Or[6] observed the infrared spectrum of the benzene–chlorine molecular complex in 1955, and suggested that the axis of the chlorine molecule is perpendicular to the benzene plane. Based on the experimental result of Collin and D'Or, Mulliken[7] also suggested the possibility of an oblique model or an unsymmetrical resting model, where one Cl atom might be above one CC bond, and the other Cl atom might be above the middle of the ring, or possibly outside the ring. Another model proposed by Ferguson[8] was like an axial model with C_{6v} symmetry based on his infrared spectrum study.

In 1958, Hassel and Strømme[9] reported on the X-ray crystal structure of the benzene–chlorine (1 : 1) complex as being at 183 K. They also examined the benzene–bromine (1 : 1) complex;[10] both the chlorine and bromine complexes had a similar geometry. The structure of the benzene–iodine complex has not yet been obtained. In the crystal of the benzene–chlorine complex, the chlorine molecule is located perpendicular to the benzene plane, and the intermolecular distance between the benzene and chlorine is 3.28 Å. The CC bond lengths of benzene do not change from those of a free benzene molecule. The bond distance of the chlorine molecule is also the same as that of the isolate free chlorine molecule.

The geometrical structure in the gas phase might be different from the structure in the crystal. Fredin and Nelander[11] reported that the chlorine molecule interacts mainly with one of the CC bonds by an experiment involving matrix-isolation technique. They have also suggested that the axial model of both the benzene–bromine and benzene–iodine complexes is more stable than the perpendicular to bond model, experimentally.

In 1975, Lucchese and Schaefer, III[12] reported on a theoretical study of the structures and stabilization energies of benzene–fluorine and benzene–chlorine complexes using the Hartree–Fock approximation. They optimized the geometry for an axial model by using the restricted Hartree–Fock (RHF) method with a minimal basis set. They found that the equilibrium distance from the center of the benzene ring to the nearest halogen atom is 4.18 Å, and that the binding energy relative to the infinitely separated molecules is only 0.26 kJ mol^{-1} (0.06 kcal mol^{-1}). Kochanski and Prissette[13] calculated the benzene–chlorine and benzene–iodine complexes for both the axial and "perpendicular-to-bond" (PB) models by the RHF method with double-zeta basis sets. In their report, the PB model is more stable in the benzene–chlorine complex, and the axial model is slightly more stable in the benzene–iodine complex.

Recently, De Almeida, and Craw[14] studied the structure of the benzene–chlorine monofluoride (C_6H_6–ClF) complex by RHF and the second-order Møller–Plesset perturbation (MP2) methods with split-valence basis sets augmenting the polarization functions. They found that the conformation of

the C_6H_6–ClF complex is closely related to the PB model, and that the ClF molecule is not perpendicular, but slants to the benzene plane.

In this study, we reexamined the geometrical structures of the benzene–chlorine complex using ab initio molecular orbital theory. The aim of this study was to determine the most stable structure of this complex and to compare the relative stabilization energies for various models theoretically. As mentioned above, it has been suggested both experimentally and theoretically that the geometrical structure of the benzene–chlorine complex in the gas phase is different from that in the crystal. Since only RHF calculations have been reported, we carried out a geometry optimization using the MP2 method, and evaluated the intermolecular interaction energies for this CT-complex.

Computational Procedure

Figure 1 shows the four possible geometrical models studied for the benzene–chlorine complex in this paper: i.e. model (**1**) [On Center (C_{6v} symmetry)], model (**2**) [On Atom (C_s symmetry)], model (**3**) [On Bond (C_s symmetry)] and models (**4a**) and (**4b**) [Resting (C_s symmetry)].

At first, in order to make a comparison with the experimental result concerning the geometrical parameters, various levels of calculation were examined for model (**1**), which is a stable structure in the crystal. The basis sets used were STO-3G, STO-6G, 3-21G, 4-31G, 6-31G, 6-31+G, 6-31G*, 6-31+G*, double-zeta (DZ) of Huzinaga[15] and Dunning,[16] DZ plus polarization functions (DZP) and DZP augmented with diffuse functions on all heavy atoms ($\zeta = 0.048$ for Cl and C) (DZP+d) on the RHF calculation, and DZ, DZ+d, DZP, and DZP+d at the MP2 method[17] with a frozen-core approximation. All of the geometrical parameters of model (**1**) were optimized by using the analytical energy-gradient method with both the RHF and MP2 methods.

In the next step, the geometries of models (**2**)—(**4**) were optimized using the RHF method with the STO-3G minimal basis set. Vibrational analyses were carried out in order to confirm whether the structures are located at the local minimum of the potential-energy surface. The most stable structure obtained above was re-optimized using the MP2 method with the frozen-core approximation (MP2(Frozen)) with the DZP+d basis set. In order to make a comparison with the stabilization energy in model (**1**), the MP2 calculation including inner-core orbitals (MP2(Full)) was performed at the optimized geometry of the MP2(Frozen) method. The stabilization energies of models (**1**), (**2**), and (**3**) were also evaluated in the MP2(Full) method with the DZP+d basis set at the optimized geometries obtained with the MP2(Frozen) method. The harmonic frequencies were calculated at the RHF level of theory due to the computational limitations.

The interaction energy corrected the basis set superposition error (BSSE) at the optimized geometries of CT complex was evaluated with the counterpoise method, as follows:[18]

$$\begin{aligned}\triangle E(\text{corr.}) = {} & E^{\text{C}}_{\text{DA}}(\chi_{\text{D}} \otimes \chi_{\text{A}}) - E^{\text{m}}_{\text{D}}(\chi_{\text{D}}) - E^{\text{m}}_{\text{A}}(\chi_{\text{A}}), \\ & +[E^{\text{C}}_{\text{D}}(\chi_{\text{D}}) - E^{\text{C}}_{\text{D}}(\chi_{\text{D}} \otimes \chi_{\text{A}}), + E^{\text{C}}_{\text{A}}(\chi_{\text{A}}) - E^{\text{C}}_{\text{A}}(\chi_{\text{D}} \otimes \chi_{\text{A}})],\end{aligned}$$

where χ_{D} and χ_{A} denote the basis functions on the donor and acceptor molecules. E^{C} and E^{m} are the energies calculated as the geometries of the complex and each isolated molecule. The non-corrected interaction energy ($\triangle E$(no corr.)) is defined as follows:

$$\triangle E(\text{no corr.}) = E^{\text{C}}_{\text{DA}}(\chi_{\text{D}} \otimes \chi_{\text{A}}) - E^{\text{m}}_{\text{D}}(\chi_{\text{D}}) - E^{\text{m}}_{\text{A}}(\chi_{\text{A}}).$$

All the calculations were carried out using the GAUSSIAN 92 program package[19] on an IBM RS6000 at Rikkyo University and on a computer system at the Institute for Molecular Science (IMS).

Results and Discussion

1. Geometry of Model (1). The X-ray crystal structure for the benzene–Cl_2 complex corresponds to the on-center model (1) (C_{6v} symmetry). In this complex, benzene acts as an electron donor and the Cl_2 molecule acts as an electron acceptor. We first examined the geometrical parameters, dipole moments and interaction energies of model (**1**) with the RHF and MP2 methods by using various basis sets. As shown later, the molecular geometry of model (**1**) is not a stable structure in the gas phase based on our calculation.

The basis set dependence for the structure and interaction energy of model (**1**) is shown in Table 1. The intermolecular distance between an electron donor and an electron acceptor generally indicates the intensity of a charge-transfer interaction. Although the distance between the benzene and chlorine (r(Bz–Cl)) was calculated to be in the 4.19—3.62 Å region by the RHF method, the MP2 method gives the

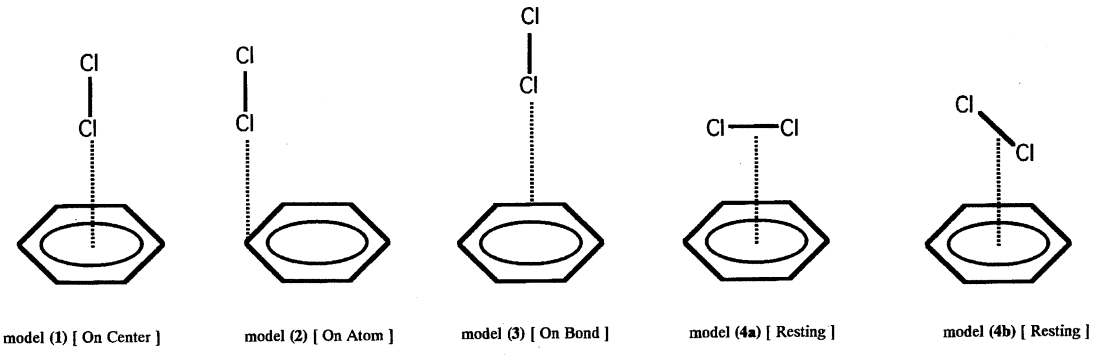

Fig. 1. Four geometrical models of benzene–chlorine complex calculated in this study.

Table 1. The Geometrical Parameters, Dipole Moments, and Stabilization Energies of Benzene–Chlorine Complex of Model (**1**) at C_{6v} Symmetry Calculated with Various Methods
Bond distances of isolated molecules are shown in parentheses.

Method/basis set	r(Bz–Cl)	r(Cl–Cl)	r(C–C)	r(C–H)	Bz–H[a)]	μ	$\triangle E$(no corr.)	$\triangle E$(corr.)
	Å	Å	Å	Å	deg.	Debye	kJ mol^{-1}	kJ mol^{-1}
RHF/STO-3G	4.012	2.063 (2.063)	1.387 (1.387)	1.083 (1.083)	179.99	0.055	−0.34	−0.26
RHF/STO-6G	4.187	2.060 (2.060)	1.386 (1.386)	1.079 (1.079)	179.99	0.049	−0.29	−0.24
RHF/3-21G	3.623	2.196 (2.193)	1.385 (1.385)	1.072 (1.072)	179.97	0.491	−4.04	−0.71
RHF/4-31G	3.748	2.179 (2.183)	1.384 (1.384)	1.072 (1.072)	179.98	0.316	−5.91	−3.78
RHF/6-31G	3.930	2.159 (2.157)	1.389 (1.388)	1.073 (1.073)	180.00	0.341	−2.36	−0.97
RHF/6-31+G	4.151	2.156 (2.155)	1.390 (1.390)	1.074 (1.074)	179.99	0.253	−2.91	−1.08
RHF/6-31G*	3.871	1.991 (1.990)	1.387 (1.386)	1.076 (1.076)	179.98	0.308	−2.97	−1.39
RHF/6-31+G*	4.154	1.994 (1.993)	1.388 (1.388)	1.076 (1.076)	179.99	0.213	−2.52	−1.39
RHF/DZ	4.068	2.187 (2.185)	1.396 (1.396)	1.073 (1.073)	180.00	0.248	−1.86	−1.18
RHF/DZ+d	4.007	2.178 (2.178)	1.396 (1.396)	1.073 (1.073)	179.99	0.305	−3.81	−1.13
RHF/DZP	3.971	2.004 (2.002)	1.391 (1.391)	1.076 (1.076)	179.96	0.221	−2.60	−1.81
RHF/DZP+d	4.002	2.004 (2.002)	1.391 (1.391)	1.077 (1.077)	179.96	0.275	−3.36	−1.71
MP2(Frozen)/DZ	3.469	2.252 (2.247)	1.426 (1.426)	1.095 (1.095)	180.14	0.439	−6.27	27.3
MP2(Frozen)/DZ+d	3.399	2.250 (2.249)	1.426 (1.426)	1.095 (1.095)	180.41	0.598	−13.86	24.9
MP2(Frozen)/DZP	3.254	2.026 (2.022)	1.406 (1.406)	1.091 (1.091)	180.08	0.382	−11.89	24.5
MP2(Frozen)/DZP+d	3.242	2.031 (2.025)	1.406 (1.405)	1.091 (1.091)	180.28	0.516	−18.59	21.6
MP2(Full)/DZP+d	3.234	2.030 (2.024)	1.402 (1.404)	1.091 (1.091)	180.30	0.519	−18.65	−6.53
Experimental[9)]	3.280	1.990	1.380					

a) Bz–H means the angle of mass center–C–H in benzene.

distance in the range from 3.47 to 3.23 Å. Including the electron correlation makes the intermolecular distance short, and turns out to give a large stabilization energy. A similar tendency has been reported for weak charge-transfer complexes, NH_3–Cl_2 and CH_3NH_2–Cl_2, where the intermolecular distances (NH_3–Cl_2: 2.599 Å, CH_3NH_2–Cl_2: 2.418 Å) with the MP2 (Frozen) method are substantially shorter than those (NH_3–Cl_2: 2.924 Å, CH_3NH_2–Cl_2: 2.885 Å) with the RHF method.[20)] Owing to the experimental result (3.28 Å) concerning the intermolecular distance for the benzene–chlorine complex, the Hartree–Fock level of calculation is not sufficient to represent the charge-transfer interaction, as well as for the amine–chlorine complexes.

As shown in Table 1, the intermolecular distance was found to be very close to the experimental value, when we included both the polarization and diffuse functions in the MP2 (Frozen) method. Comparing the contributions of the polarization functions and the diffuse functions to the intermolecular distance, the former is more effective than the latter to make the distance short, e.g. from 3.47 to 3.25 Å (adding the polarization function) and from 3.47 to 3.40 Å (adding the diffuse function). Usually, diffuse functions for anion species play an important role to accept electrons. In this complex, however, the effect of diffuse functions for the intermolecular distance is small, because the transferred electron charge from benzene to chlorine is extremely small.

It is interesting to see the angle of the mass center–carbon–hydrogen in the benzene molecule, which is shown as Bz–H in Table 1. After complex formation, the hydrogen atoms bend slightly upward to the benzene plane (maximum 0.04°) in the RHF method, although this out-of-plane bending angle is extremely small. In the optimized structure with the RHF method for the ethylene–chlorine complex,[21)] hydrogen atoms of ethylene were calculated to be down against the chlorine molecule; this out-of-plane angle is 0.36°. In the case of the benzene–Cl_2 complex, the RHF method does not seem to give a reasonable result, while the MP2 method describes the Bz–H angle appropriately.

Table 1 also lists the dipole moment of model (**1**). Although the experimental value has not yet been obtained, the first estimated value by Hanna[22)] with the semiempirical procedure was 0.50—0.64 D, which is a reasonable value compared with that of the dipole moment calculated with the MP2 level of theory. The RHF calculations tend to underestimate the dipole moment because of the long intermolecular distance. The amount of transferred charge from benzene to chlorine was evaluated to be about 0.03e C based on the dipole moment in this work, where $e = 1.602 \times 10^{-19}$ C.[23)] The value obtained from an MP2 calculation with DZP basis sets is slightly smaller than that with other basis sets. The amount of transferred charge from benzene to chlorine tends to be underestimated unless the diffuse functions which accept the electrons are added.

Based on the results of the present calculation, the RHF method is not sufficient to describe not only the geometry, but also the molecular property. We can conclude that the minimum requirement is an MP2 level calculation with the DZP+d basis set in order to make a comparison with the X-ray structure. It is noticeable that the molecular geometries of the benzene and Cl_2 parts in the complex are almost the same as the isolated structures. This means that the intermolecular interaction is very weak between benzene and Cl_2 in conjunction with the small dipole moment of this complex. Although such a complex has long been discussed as a CT complex, we may say that benzene–Cl_2 is likely to be a van der Waals complex.

2. Stabilization Energy and Basis Sets Superposition Error (BSSE) for Model (1). Table 1 also lists the stabilization energies of the complex formation for model (**1**); $\triangle E$(corr.) and $\triangle E$(no corr.) correspond to the energies with and without a correction of BSSE. The basis sets superposition error (BSSE) is important in calculating the interaction energy for a weakly bound complex. The value of $\triangle E$(no corr.) of the RHF method depends widely on the basis sets. The value $\triangle E$(no corr.), calculated with the MP2 method, is one order of magnitude larger than that with the RHF method. When the BSSE is corrected, although the value $\triangle E$(corr.) of the RHF method tends to converge to a value slightly less than 2 kJ mol^{-1} as the basis set is improved, 2 kJ mol^{-1} is too small due to the poor wavefunction. On the other hand, $\triangle E$(corr.) calculated with the MP2 method by the frozen-core approximation gives an extremely large positive value. This means that the complex is not stabilized from the isolated molecular systems. This result is very unlikely and must be caused by a defect in the calculating method.

It is well-known that the MP2 level of the theory overestimates BSSE, and that the inner-core wavefunctions have a large effect on the BSSE value. Since the inner-core wavefunctions are not correlated in the MP2(Frozen) method, BSSE is not exactly estimated. In the MP2(Full) method, in which the inner-core wavefunctions are correlated, $\triangle E$(corr.) shows a reasonable stabilization energy of -6.53 kJ mol^{-1}. In order to confirm this tendency, we calculated the stabilization energy for ethylene–chlorine and ethylene–chlorine monofluoride complexes with both the MP2(Frozen) and MP2(Full) methods using the DZP+d basis set. For the ethylene–chlorine complex, $\triangle E$(no corr.) and $\triangle E$(corr.) show -13.30 and 9.76 kJ mol^{-1} in the MP2(Frozen) method, and -13.28 and -6.89 kJ mol^{-1} in the MP2(Full) method, respectively. $\triangle E$(corr.) of the ethylene–chlorine system obtained with the MP2(Frozen) method indicates an unreasonable result, in which the complex formation is the endothermic process as well as in the case of the benzene–chlorine complex. On the other hand, $\triangle E$(corr.) for the ethylene–chlorine monofluoride complex shows -2.78 kJ mol^{-1} in the MP2(Frozen) method, and -16.41 kJ mol^{-1} in the MP2(Full) method. Since ClF is a stronger electron acceptor than Cl_2, the complex formation of the ethylene–chlorine monofluoride complex is calculated to be exothermic, even if the MP2(Frozen) method is utilized. Ethylene–chlorine has more than two-times less of an interaction energy than does the ethylene–chlorine monofluoride complex. Therefore, it is a common phenomenon in the weak π–σ^* complex that $\triangle E$(corr.) is not properly estimated when we use a frozen-core approximation, such as the MP2(Frozen) method.

In order to explore the effect of the basis set for BSSE, we examined the contribution of BSSE for two components, benzene and chlorine molecules. Figure 2 illustrates the basis set dependence of BSSE calculated with the RHF method. The largest BSSE is found for the 3-21G basis set. By improving the basis sets, the value of BSSE becomes small, except for the double-zeta basis set. The decrease in the BSSE value from 3-21G to 6-31G basis sets especially shows that an improvement of the inner-core wavefunctions is important for

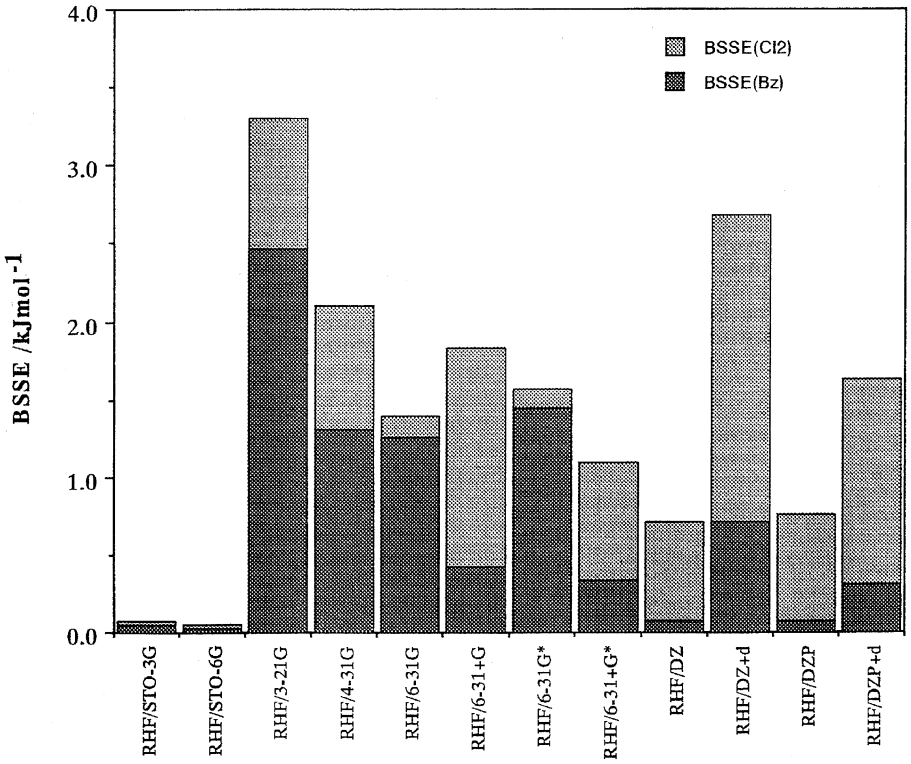

Fig. 2. Contribution of the basis set super position error (BSSE) with RHF method by using various basis sets in model (**1**). BSSE(Cl_2) means the contribution of BSSE in chlorine molecule and BSSE(Bz) indicates the one in benzene moiety.

BSSE. BSSEs for 3-21G, 4-31G, 6-31G, and 6-31G* basis sets contains a large component of benzene, while a large contribution of chlorine for BSSE is shown in the double-zeta basis sets. The contribution of chlorine for the BSSE becomes large by adding diffuse functions, e.g. 6-31G+ from 6-31G, 6-31+G* from 6-31+G*, DZ+d from DZ, and DZP+d from DZP.

Figure 3 shows the contribution of the benzene and chlorine parts for BSSE with the MP2 method. In the MP2(Frozen) method, chlorine's BSSE is very large compared to benzene's, and adding diffuse functions causes benzene's BSSE to be large as well as the RHF calculation. Although the diffuse function of an electron acceptor (chlorine) generally plays an important role in a charge-transfer complex, the effect of adding diffuse functions does not contribute to the stabilization in this system, but increases BSSE. From a comparison between the MP2(Frozen) and MP2(Full) methods, it is clear that a large BSSE value in the MP2(Frozen) method is caused by chlorine's BSSE, $E_A^C(\chi_D \otimes \chi_A)$, which includes a large contribution of the inner-core wavefunctions of benzene.

3. Stable Structure of the Benzene–Chlorine Complex. We carried out a full geometry optimization for all models using the RHF method with the STO-3G and DZP+d basis sets. As a result of a vibrational analysis for model (**1**) kept in the C_{6v} symmetry, we found two degenerate imaginary harmonic frequencies, $4.8i$ cm^{-1} (STO-3G) and $17.7i$ cm^{-1} (DZP+d) (E_1 mode). This means that the chlorine molecule leaves from the axial position to make the complex more stable. In both the STO-3G and DZP+d basis sets, the harmonic frequencies calculated for models of (**2**) and (**3**) were found to all be real, indicating that both models locate at the local energy minimum. The potential energy surfaces that both models (**4a**) and (**4b**) have no local minimum, because the benzene and chlorine molecules repel each other. When the geometrical parameters were re-optimized starting from model (**1**) without any symmetry restriction, the obtained optimized geometry essentially agreed with the stable structure of model (**2**), regardless of the starting geometry. Secondly, we also optimized the structures for models (**2**) and (**3**) by using the MP2(frozen) method with the DZP+d basis set.

Figure 4 shows the stable structures of models (**2**) and (**3**) at the MP2(Frozen)/DZP+d level of calculation. The intermolecular distances, 3.003 Å for model (**2**) and 3.014 Å for model (**3**), were calculated to be shorter than the value obtained for model (**1**) (3.242 Å). Although we must be careful concerning the stabilization energy by using the MP2(Frozen) method, as discussed in the previous section, the geometrical parameters obtained from the MP2(Frozen) method are almost identical to those with the MP2(Full) method. Consequently, the molecular structures are well described by the MP2(Frozen)/DZP+d method. In models (**2**) and (**3**), the chlorine molecular axis is tilted to 3.65° (**2**) and 2.07° (**3**) from the perpendicular axis of the benzene plane, and the chlorine molecule is located at the inside of the benzene ring. The Cl–Cl distances, 2.041 Å (**2**) and 2.040 Å (**3**), are slightly longer than the isolated chlorine molecule (2.015 Å). The chlorine–chlorine distance becomes long by forming a complex due to charge transfer to the lowest unoccupied molecular orbital (LUMO) of halogen. These geometrical

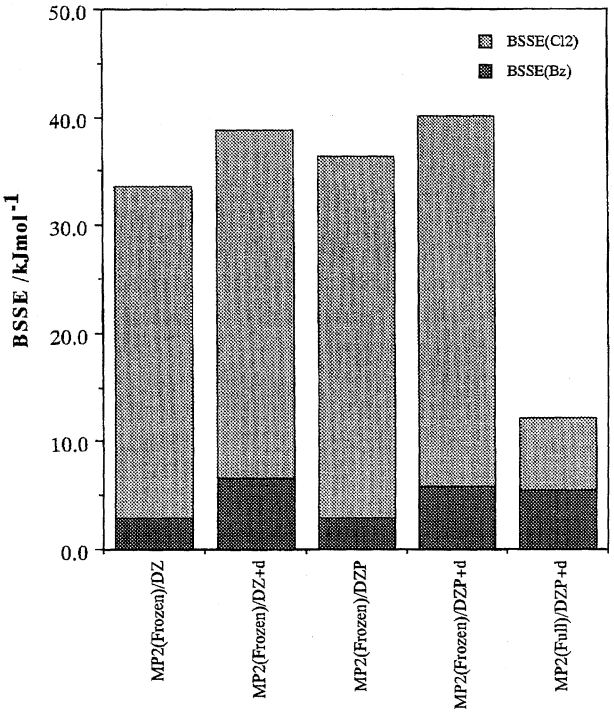

Fig. 3. Contribution of the basis set super position error (BSSE) with MP2 method by using various double-zeta basis sets in model (**1**). BSSE(Cl_2) means the contribution of BSSE in chlorine molecule and BSSE(Bz) indicates the one in benzene part.

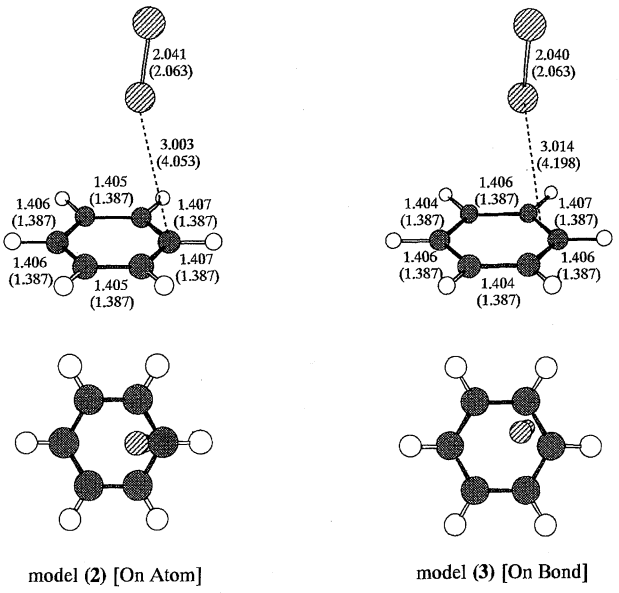

Fig. 4. Two stable structures for model (**2**) and model (**3**) of benzene–chlorine complex calculated with MP2(Frozen)/DZP+d method. The bond distances are shown in Å. The values in parenthesis are obtained with the RHF/STO-3G method.

Table 2. Stabilization Energy of Benzene–Chlorine Complex

	MP2(Frozen)/DZP+d	MP2(Full)/DZP+d//MP2(Frozen)/DZP+d		MP2(Full)/DZP+d
	$\triangle E$(no corr.)	$\triangle E$(no corr.)	$\triangle E$(corr.)	$\triangle E$(corr.)
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Model (1)	−18.59	−18.62	−6.63	−6.53
Model (2)	−20.24	−20.76	−8.44	
Model (3)	−19.95	−20.50	−8.14	

changes in models (**2**) and (**3**) are significantly larger than that in the case of model (**1**). Since the bond lengths of C–C and C–H of isolated benzene were calculated to be 1.405 and 1.091 Å, respectively, with the MP2/DZP+d method, the structures of the benzene moiety of models (**2**) and (**3**) were observed to be unchanged by complex formation.

Table 2 summarizes the stabilization energies of models (**2**) and (**3**) calculated by the MP2 method. As discussed concerning the unusual basis set superposition error (BSSE) in the previous section, we should use the MP2(Full) method to evaluate the stabilization energies with a BSSE correction. Instead of performing a full geometry optimization at the MP2(Full)/DZP+d level, we calculated $\triangle E$(corr.) of models (**2**) and (**3**) using the MP2(Full)/DZP+d method for the optimized geometries obtained with the MP2(Frozen)/DZP+d method due to computational limitations. As shown in Table 2, $\triangle E$(corr.) of model (**2**) is 0.3 kJ mol^{-1} less than that of model (**3**). Since this energy difference is very small, it is considered that both minimum structures for two models, (**2**) and (**3**), have essentially the same energy. The potential energy surface is eventually very flat for the location of a chlorine molecule on a benzene ring for any level of calculation. Furthermore, the geometrical difference is hardly detected as the "on atom" and "on bond" structures, because the chlorine molecule is located over the inside of the benzene ring in both models. The position of the chlorine molecule would be very flexible on the benzene ring, and the molecular structure of complex is easily interchangeable between models (**2**) and (**3**).

A matrix-isolation study by Fredin and Nelander[11] indicated that the chlorine molecule interacts mainly with one of the CC bonds. In ab initio calculations reported by Kochanski and Prissette,[13] "perpendicular to bond" configuration (PB), which we call model (**3**), is more stable than the "Axial" model (A), being our model (**1**) by using the RHF method with the double-zeta basis sets. They obtained stabilization energies for (**1**) and (**3**) to be −10.17 kJ mol^{-1} (−2.43 kcal mol^{-1}) and −11.97 kJ mol^{-1} (−2.86 kcal mol^{-1}), respectively, although they only optimized the molecular distance between the benzene and Cl_2, but no other geometrical parameters. The experimental value of the stabilization energy in the gas phase has not yet been obtained, although the stabilization energy in the solution phase has been reported to be −4.6 kJ mol^{-1} (−1.1 kcal mol^{-1}) by Lippert, Hanna and Trotter.[24] In our present study, it was clearly shown that model (**1**) is not a stable structure having two imaginary harmonic frequencies, and that the chlorine molecular axis turns out to be perpendicular to the benzene plane. The structure of the benzene–ClF complex with RHF calculations using the split-valence basis set with polarization functions, 4-31G and 6-31G**, has been reported by De Almeida and Craw.[14] In the benzene–ClF complex, the structure of model (**2**) was found to be most stable, and that the Cl–F axis is not perpendicular to the benzene plane, as well as the case shown in the benzene–chlorine complex. In the benzene–Br_2 and benzene–I_2 complexes, it is reported that the halogen molecule is located at the center of the benzene plane, both experimentally[25] and theoretically.[13] The charge-transfer interaction of the benzene–Cl_2 and benzene–ClF complexes are weaker than the benzene–Br_2 and benzene–I_2 complexes. The present calculation is consistent with such evidence.

Concluding Remarks

Through a comparison of the X-ray crystal structure and the geometry of the "on center" model (**1**), we can conclude that the MP2 level of a calculation with the DZP+d basis set is required to reproduce the experimental result. In order to obtain reasonable stabilization energies for the benzene–chlorine complex, MP2(Full) method must be used because an unusual BSSE is found in the MP2(Frozen) method. The result of a vibrational analysis shows that the "on center" model (**1**) does not locate at the energy minimum. Although the most stable structure was calculated to be the "on atom" model (**2**), the energy difference between the "on atom" (**2**) and the "on bond" (**3**) structures is very close, and the position of chlorine molecule is very flexible on the benzene ring. All of the results, such as the geometrical structures, dipole moments, and stabilization energies, presented in this paper indicate that the benzene–chlorine complex is a very weak charge-transfer complex.

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