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Benzene–Ethene Interactions as Studied by ab initio Calculations

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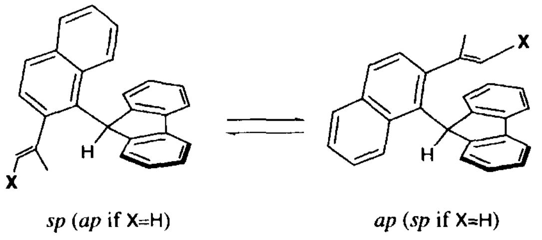
For a search for π–π* and/or CH–π interactions between benzene and ethene, ab initio calculations were carried out at HF/6-31G**, MP2/6-31G**, and B3LYP/6-31G** levels of theory. Thirteen configurations of benzene and ethene complexes were optimized by the energy gradient techniques, of which only two were real energy-minimum forms and the others were saddle points or conical points. The global minimum configuration is one in which one of the tilted ethene C–H groups interacts with the C–C π–bond of benzene (configuration F-1). A configuration, in which benzene and ethene planes are parallel, was not obtained as a minimum except for MP2 calculations. The intermolecular distances obtained by HF and B3LYP theories were longer than the sum of van der Waals radii, whereas those obtained by the MP2 method were close to the sum. Dipole moments were also obtained that suggest the existence of charge transfer interactions. It is concluded that the molecular interaction energy between benzene and ethene mainly consists of dispersion forces with minor contributions of CT interactions, while the configuration of the global minimum is determined by CH–π interactions. From the frequency analysis for the energy-minimum forms, the normal modes associated with the intermolecular CH–π interactions were obtained at low frequency regions.

Thermal equilibration of *sp* and *ap* rotamers of 1-(9-fluorenyl)-2-[(*E*)-2-halo-1-methylethenyl]naphthalene showed an increasing preference of the *ap*-isomer, as one descends the periodic table, in spite of the more congested situation in the *ap* than in the *sp* (Scheme 1).[1] This abnormal tendency was also correlated to an interesting structural feature, as revealed by X-ray structure analyses, that the atomic distances between the ethenyl carbon atoms and those in the fluorene moiety become small as we descend the periodic table.[1,2] These abnormal phenomena were taken as indications of the presence of intramolecular interactions between the etheno moiety and the fluorene, which could be π–π* interactions.[3—7]

However, the same situation may be manifested by other interactions, including CH–π interactions,[8—18] CH–halogen interactions,[19—21] and halogen–π interactions.[22,23] In order to shed light on the origin of such interesting observed trends, theoretical investigations should be helpful. Thus we decided to study the possible molecular interactions between benzene and ethene by the ab initio calculations as a prototype of interactions in *ap*-1-(9-fluorenyl)-2-[(*E*)-2-halo-1-methylethenyl]naphthalene.



Scheme 1.

Between benzene and ethene, we expect the presence of intermolecular interactions including dispersion forces, charge-transfer type interactions, π–π* and CH–π, electrostatic interactions, dipolar and/or quadrupolar, and exchange repulsion forces.

π–π* interactions are studied theoretically in the cases of benzene dimers[3—7] and between two ethene molecules.[5] Stacking of benzene molecules in crystals[24] is taken as evidence for the molecular π–π* as well as CH–π interactions.

CH–π interactions have also been studied both experimentally[8—15] and theoretically.[16—19] It is generally understood that the CH–π interactions can be taken as OH–π type interactions (π-donor and σ-XH acceptor) and are weaker than that of the normal hydrogen bond, whose energy is estimated to be ca. 5 kcal mol^{-1} (1 cal = 4.184 J): Probably the energy of CH–π interactions is less than 1 kcal mol^{-1}, when we consider the fact that the OH–π interaction energy is estimated to be 2.5 kcal mol^{-1} or less.[25—34] Experimental evidence suggests that the CH–π interaction energy is ca. 0.5 kcal mol^{-1}.[11]

We wish to report in this paper the results of our calculations together with discussion of the configurations of the molecular complexes. Applying the geometry optimization technique, we were able to detect possible configurations of the benzene–ethene complexes. We found two energy minima, one of which was the global minimum. Nature of the intermolecular interactions in the benzene-ethene complex will be discussed on the basis of CT interactions and dispersion forces. For confirmation of the presence of the CH–π interactions, a frequency analysis of the complexes was carried out. Six characteristic normal modes associated with the complex formation were obtained at the low frequency regions.

Calculations

Ab initio calculations were carried out with the use of Gaussian 94 program package.[35] The optimization was first carried out at the HF/6-31G** level of theory. Although the HF method is known to be the best method for calculation of one electron wave functions, molecular orbitals, it does not include the electron correlation energy, which should be important in intermolecular interactions. We thus performed calculations at the MP2/6-31G** level of theory, which is a method of molecular orbital calculations with perturbation theory. This should provide information both on the intramolecular electron correlation and on electronic dispersion energy. We also performed calculations by the B3LYP/6-31G** method which is one of the methods of calculation by Density Functional Theory and is widely used recently for calculations of large molecules. This method includes implicitly the electronic correlation energy via exchange-correlation functional.

The calculations were applied to 21 guessed configurations, the basis of selection of the guessed configurations being discussed in the Initially Guessed Configurations section. For the optimized structures, the amounts of charge transfer were calculated by applying population analysis.

To obtain the normal modes of vibration associated with the complex formation, the frequency analysis of complexes was carried out.

Basis set superposition errors were calculated with the use of the counterpoise method and the interaction energies obtained by the MP2 method were corrected.

Theoretical Considerations

Intermolecular Interaction Energies. Binding energy, or intermolecular interaction energy, of a complex $A\cdot B$, $\Delta E(A\cdot B)$, is calculated by

$$\Delta E(A\cdot B) = E(A\cdot B) - [E(A) + E(B)] \quad (1)$$

where $E(A\cdot B)$, $E(A)$, and $E(B)$ are the total electronic energy of a benzene–ethene complex, benzene, and ethene, respectively. The binding energy may be decomposed into the following interaction energies.

$$\Delta E(A\cdot B) = E_{\mathrm{disp}} + E_{\mathrm{CT}} + E_{\mathrm{EX}} + E_{\mathrm{ES}} + C, \quad (2)$$

where E_{disp}, E_{CT}, E_{EX}, E_{ES}, and C mean dispersion energy, charge transfer energy, exchange repulsion, electrostatic energy, and a correction term, respectively. For the molecular interactions between nonpolar molecules, the electrostatic interactions can be neglected. Therefore, E_{disp} and E_{CT} comprise the main portion of the building energy.

While E_{disp} can be obtained from the dynamical electron correlation expressed by induced-dipole-induced-dipole interactions, the correlation energy is obtained by the following equation:

$$E_{\mathrm{exact}} = E_{\mathrm{HF}} + \Delta E_{\mathrm{corr}}$$

$$\text{or} \quad \Delta E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}}, \quad (3)$$

where E_{exact} and E_{HF} mean the exact solution of the Schrödinger's equation of a molecule or a molecular complex and the energy of Hartree–Fock limit, respectively. Since we calculate many electron systems, neither E_{exact} nor E_{HF} is obtained. Therefore, we approximate them in the following ways.

Binding energy; ΔE^{X}, is expressed by

$$\Delta E^{\mathrm{X}}(A\cdot B) = E^{\mathrm{X}}(A\cdot B) - [E^{\mathrm{X}}(A) + E^{\mathrm{X}}(B)], \quad (4)$$

where superscript X indicates the level of theory, either MP2, B3LYP, or HF, whereas the electron correlation energy, $\Delta E^{\mathrm{X}}_{\mathrm{corr}}$, is expressed by Eq. 5:

$$\Delta E^{\mathrm{X}}_{\mathrm{corr}} = \Delta E^{\mathrm{X}} - \Delta E^{\mathrm{HF}}. \quad (5)$$

The correlation energy in interaction energy is calculated by

$$\Delta E^{\mathrm{X}}_{\mathrm{corr}} = E^{\mathrm{X}}(A\cdot B) - E^{\mathrm{HF}}(A\cdot B) - [E^{\mathrm{X}}(A) - E^{\mathrm{HF}}(A) + E^{\mathrm{X}}(B) - E^{\mathrm{HF}}(B)]. \quad (6)$$

Here, the basis set used for HF calculations must be the same as that used for X's.

Dipole Moments due to Charge Transfer Interactions. The charge transfer interactions can be described as[36]

$$E_{\mathrm{CT}} = b^2(I_{\mathrm{D}} - EA_{\mathrm{A}}), \quad (7)$$

where b^2, which is far less than unity, is the square of the coefficient of the wave function that describes the fully charge transferred state, and I_{D} and EA_{A} are the ionization potential of an electron donor and the electron affinity of an electron acceptor. Therefore, the energy of charge transfer interactions is approximately proportional to the amount of the charge transfer from a donor to an acceptor.

The dipole moment (D_{CT}) due to charge transfer interactions is approximately given by

$$D_{\mathrm{CT}} = 4.8 \times b^2 \times r \text{ (Debye)}, \quad (8)$$

where r is a distance, expressed in Å units, between the center of the positive charge in the donor and that of the negative charge in the acceptor (1 Debye $\approx 3.33564 \times 10^{-30}$ C m).

Initially Guessed Configurations

For the configurations with π–π* interactions, the initially guessed configurations were taken by considering the following points. Benzene dimers,[3—7] in which two benzene rings are parallel, do not completely overlap with each other, rather, the benzene rings overlap with shifted configurations to make interactions of π and π* orbitals favorable. For our benzene–ethene complex, this type of spatial arrangement would be a good starting point. We started from a configuration, in which the benzene plane and the ethene plane are parallel but the ethene plane is shifted slightly from the center of the benzene molecule, the ethene molecule sitting on one of the benzene edges (A-5). Finding that this structure was not an energy minimum, we shifted to five other configurations (A-1—A-4 and A-6) shown in Fig. 1.

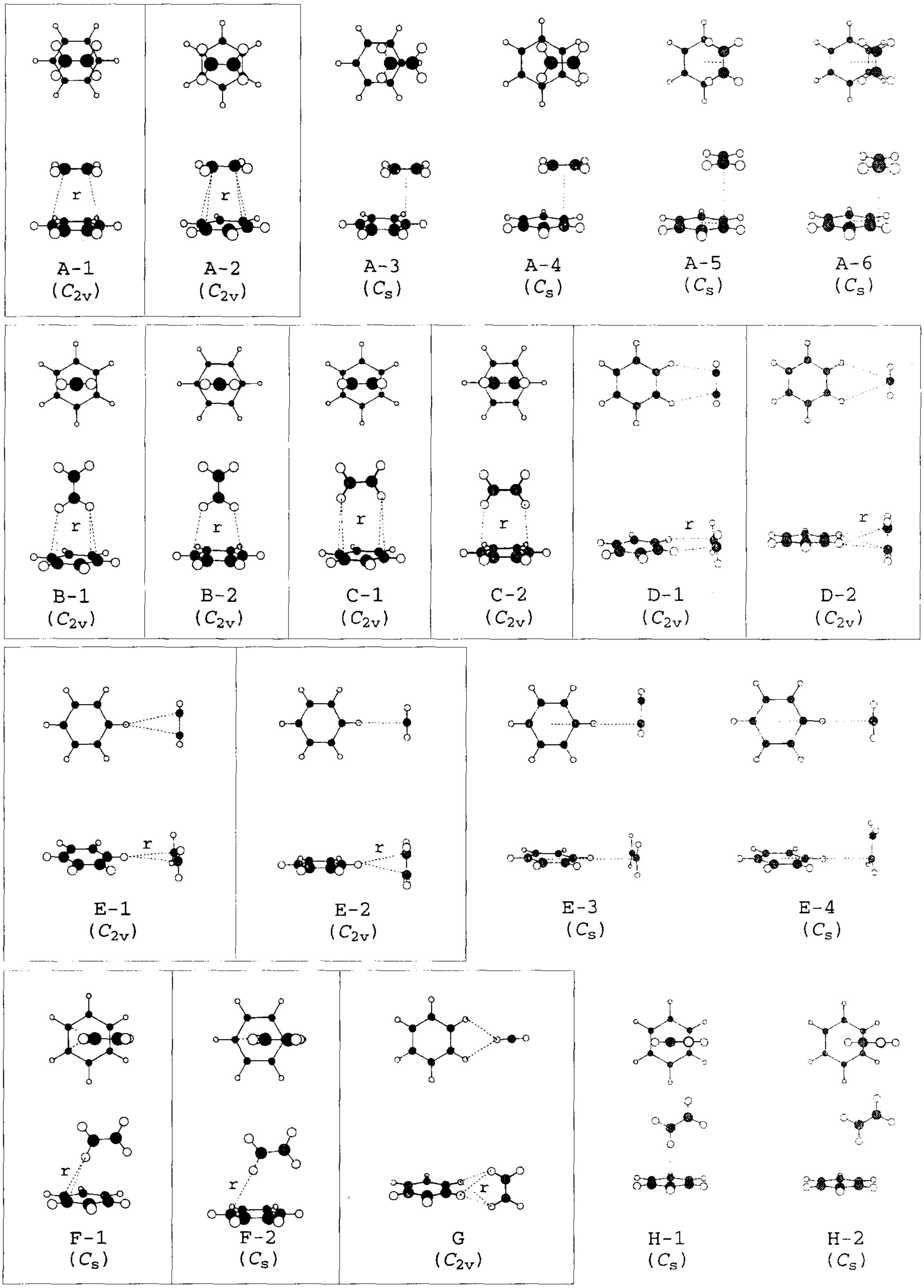


Fig. 1. Initially guessed and optimized configurations of benzene-ethene complexes. Geometry optimized configurations are shown in frames.

A-1 is the configuration in which the C–C axis of the ethene molecule eclipses the C1–C4 axis of benzene, whereas in A-2 the ethene axis bisects the benzene molecule, the C–C axis of ethene passing the centers of the opposing two C–C bonds of benzene. In A-3, the ethene molecule is shifted from A-1 to make the center of the C–C bond sitting upon the C–C bond of benzene, and, A-4, derived from A-2, is a configuration in which the center of the C–C bond of ethene is upon the center of a C–C bond of benzene. A-6 is derived from A-5 by shifting the ethene molecule further outside of the benzene molecule.

For the CH–π complexes, in both benzene dimers[3—7] and a benzene-ethyne complex,[12] many authors assume a priori that the most stable configurations are the ones, in which the C–H group of either ethyne or benzene directs to the center of the π-cloud: The C–H bond either directs toward the center of the benzene ring (H-1) or the center of one of the edges of the benzene ring (H-2). In the present case, both the C–H in the benzene ring and that in ethene can be the acceptor of electrons. We started from configurations H-1 and H-2.

The next is the complexes, in which two C–H groups of ethene interact with the benzene π-system. For the cases where the two hydrogens are connected to the C1 of ethene, we adopted two configurations, B-1 and B-2, both of which have C_{2v} symmetry: Both the C–C axis and the plane of ethene are orthogonal to the benzene plane. In B-1, the two C–H's of ethene direct toward the centers of the opposing two edges of benzene. In B-2, the two C–H's of ethene direct toward the carbons at 1 and 4 positions of the benzene ring.

In the case of interactions using two C–H groups, another possibility arises: This time, the two hydrogens are attached to different carbon atoms in ethene and the C–C axis of ethene is parallel to the benzene plane, whereas the ethene plane is orthogonal to the benzene ring (C's). In these configurations, we can also think of two configurations: One in which two CH's direct toward centers of the edges of the hexagon (C-1) and another in which two CH's direct toward C1 and C4 of the benzene molecule (C-2).

For the complexes in which ethene is a π-donor and benzene is a π-acceptor, the ethene molecule can take two positions relative to the benzene ring. The complex D-1 is that in which the C–C axis of ethene is within the plane of the benzene ring and the ethene plane is orthogonal to the benzene ring. Here, the two C–H groups of benzene interact with two carbon atoms in ethene. In D-2, the ethene molecule takes a position, in which both the C–C and the plane of ethene are orthogonal to the benzene plane and the two CH's of the benzene are at the middle point of the ethene C–C bond. Other types of complexes, E's, are ones in which only one CH of the benzene interacts with the ethene. According to the relative configurations of the benzene and the ethene, similarly to the complexes D's, E-1 and E-2 configurations can be guessed. We also calculated the cases in which one C–H group of benzene interacts with one carbon atom of ethene (E-3 and E-4).

Tilting the ethene molecule from C-1 produces configuration F-1 and tilting that from C-2 produces configuration F-2. By rotating the ethene plane vertically relative to that of benzene in complex C's, we obtain configurations F's. F-1 is one in which the ethene CH interacts with electrons of the π-bond between two of the carbon atoms of benzene and F-2 that interacting with one of the benzene carbons.

Configuration G can be obtained by rotating the ethene plane in complex D-2 horizontally relative to the benzene plane.

Results and Discussion

Optimized Configurations. The distances between the two molecules were optimized at the outset. Then the geometry optimization was carried out. Those configurations which changed the relative positions and directions of the component molecules were discarded. Of 21 guessed configurations, which are shown in Fig. 1, 8 changed into other configurations and the other 13 configurations were optimized.

The calculated total electronic energies and the binding

Table 1. Theoretical Total Electronic Energies and Binding Energies of Bezene–Ethene Complexes Calculated at Various Levels of Theory[a)]

Configuration	HF/6-31G**		B3LYP/6-31G**		MP2/6-31G**	
	T.E.[b)]/hartree	B.E.[b,c)]/kcal mol^{-1}	T.E./hartree	B.E./kcal mol^{-1}	T.E./hartree	B.E./kcal mol^{-1}
A-1	†	†	†	†	−309.8250100	−1.467
A-2	†	†	†	†	−309.8250179	−1.472
B-1	−308.7535334	−0.522	−310.8527478	−0.457	−309.8258117	−1.970
B-2	−308.7535330	−0.522	−310.8527411	−0.453	−309.8258106	−1.969
C-1	−308.7536235	−0.579	−310.8529138	−0.561	−309.8261877	−2.206
C-2	−308.7536214	−0.577	−310.8529090	−0.558	−309.8261784	−2.200
D-1	−308.7536126	−0.572	−310.8531199	−0.691	−309.8252846	−1.639
D-2	−308.7537366	−0.650	−310.8531103	−0.685	−309.8252813	−1.637
E-1	−308.7538043	−0.692	−310.8532615	−0.780	−309.8249527	−1.431
E-2	−308.7538115	−0.697	−310.8532710	−0.786	−309.8248820	−1.386
F-1	†	†	†	†	−309.8267436	−2.554
F-2	†	†	†	†	−309.8267175	−2.538
G	†	†	−310.8528204	−0.503	−309.8255681	−1.817

a) The total energies of benzene are −230.71386, −232.2582126, and −231.5053909 hartrees by HF, B3LYP, and MP2 methods respectively, whereas the corresponding values for ethene are −78.0388414, −78.5938066, and −78.3172819 hartrees. b) T.E. and B.E. stand for total electronic energies and binding energies, respectively. c) For obtaining the B.E., see text. †: These structures changed into other configurations during optimization.

energies of 13 optimized configurations are shown in Table 1. The configurations obtained as energy minima are also shown in Fig. 1.

The results compiled in Table 1 show that the binding energies of the complexes are dependent on the level of theory. We will first discuss the general tendency of the results obtained in reference to the characteristics of the theory and then each configuration of benzene-ethene complexes. After describing the features of the 13 configurations of benzene-ethene complexes, we will finally discuss the calculated results of normal modes to characterize them as true energy minima, saddle points, and/or conical points.

Characteristics of the Calculated Results. The HF and B3LYP methods give 0.5—0.8 kcal mol^{-1} binding energies, while the MP2 method gave 1.4—2.5 kcal mol^{-1} (Table 1), for the complexes. As Fig. 1 and Table 2 show, the H–C(π) distances in the complexes, calculated by the HF method, are 3.381—3.600 Å, which are far longer than the sum of the van der Waals radii of hydrogen (1.2 Å) and carbon (1.7 Å). The results obtained by B3LYP calculations are not much different from those obtained by the HF method. By contrast, the MP2 method afforded the H–C(π) distances of 2.9—3.1 Å, which are close to the sum of the van der Waals radii of the atoms concerned, while the interaction energies were 1.4—2.5 kcal mol^{-1}.

Thus the differences in binding energies, shown in Table 1, indicate that the dispersion forces are important in benzene-ethene interactions. The small distances, obtained by the MP2 method, between the molecules concerned (Table 2) are another indication of the importance of the dispersion forces.

Of interest is the result that the B3LYP method gives very small correlation energies for intermolecular interactions, whereas the MP2 methods give the larger values (Table 3). Even though the B3LYP method gives correlation energies of benzene and ethene as 968 and 348 kcal mol^{-1}, respectively, the intermolecular correlation energy is very small. This indicates that the MP2 method is superior to the B3LYP method when we discuss the intermolecular interaction. We propose to take the correlation energy obtained by the MP2 method as the dispersion energy.

Table 2. The Nearest Distances $r^{a)}$ (Å) in the Benzene–Ethene Complexes

Configuration	HF/6-31G**	B3LYP/6-31G**	MP2/6-31G**
	r/Å	r/Å	r/Å
A-1	†	†	3.535
A-2	†	†	3.567
B-1	3.600	3.432	3.072
B-2	3.552	3.376	3.017
C-1	3.566	3.387	3.005
C-2	3.504	3.313	2.932
D-1	3.416	3.145	2.935
D-2	3.533	3.362	3.119
E-1	3.383	3.171	2.961
E-2	3.381	3.167	2.969
F-1	†	†	2.883
F-2	†	†	2.866
G	†	2.653	2.509

a) The r represents the nearest C(π)···C(π) distances in π–π type complexes (A's), the nearest H···C(π) distances in CH–π type complexs (B's, C's, D's, E's, and F's) and the nearest CH···HC distance in the dispersion type complex (G). †: These strucutres changed into other configurations during optimization.

Table 3. Electron Correlation Energy Calculated from Eq. 5; $\Delta E_{\mathrm{corr}}^{\mathrm{MP2}}$ and $\Delta E_{\mathrm{corr}}^{\mathrm{B3LYP}}$

Configuration	$\Delta E_{\mathrm{corr}}^{\mathrm{B3LYP}}$	$\Delta E_{\mathrm{corr}}^{\mathrm{MP2}}$
	kcal mol^{-1}	kcal mol^{-1}
A-1		
A-2		
B-1	+0.065	−1.448
B-2	+0.069	−1.447
C-1	+0.018	−1.627
C-2	+0.019	−1.623
D-1	−0.119	−1.067
D-2	−0.035	−0.987
E-1	−0.088	−0.739
E-2	−0.089	−0.689
F-1		
F-2		
G		

Table 4. Dipole Moments of Benzene–Ethene Complexes Calculated at Various Levels of Theory

Configuration	HF/6-31G**	B3LYP/6-31G**	MP2/6-31G**
	μ/Debye	μ/Debye	μ/Debye
A-1	†	†	0.1243
A-2	†	†	0.1267
B-1	0.2708	0.2461	0.4610
B-2	0.2708	0.2479	0.4571
C-1	0.2350	0.2934	0.3818
C-2	0.2347	0.2965	0.3825
D-1	0.2507	0.3562	0.3748
D-2	0.2667	0.3445	0.3807
E-1	0.2879	0.3837	0.4264
E-2	0.2851	0.3787	0.4121
F-1	†	†	0.3922
F-2	†	†	0.3961
G	†	0.0410	0.0490

†: These structures changed into other configurations during optimization.

The calculated dipole moments are shown in Table 4. Since benzene and ethene do not have dipole moments, the present calculations show that there are charge transfer (CT) interactions between benzene and ethene. The amounts of charge-transfer, which are obtained by applying the population analyses, are given in Table 5. These results clearly show that there are charge-transfer interactions between benzene and ethene in every complex. As expected, when a π-donor is benzene in the CH–π complexes, the charge is transferred from benzene to ethene, and vice versa in the complexes when an ethene molecule acts as a π-donor in the CH–π interactions. The direction of the charge-transfer was inde-

Table 5. The Amounts of Charge Transfer[a)] [e][b)] in Benzene–Ethene Complexes Calculated at Various Levels of Theory

Configuration	HF/6-31G**	B3LYP/6-31G**	MP2/6-31G**
	$\Delta Q_{CT}/e$	$\Delta Q_{CT}/e$	$\Delta Q_{CT}/e$
A-1	†	†	+0.0063
A-2	†	†	+0.0063
B-1	+0.0056	+0.0091	+0.0132
B-2	+0.0056	+0.0092	+0.0132
C-1	+0.0068	+0.0115	+0.0147
C-2	+0.0068	+0.0116	+0.0146
D-1	−0.0061	−0.0125	−0.0104
D-2	−0.0072	−0.0122	−0.0128
E-1	−0.0089	−0.0148	−0.0151
E-2	−0.0089	−0.0147	−0.0147
F-1	†	†	+0.0113
F-2	†	†	+0.0113
G	†	−0.0033	−0.0033

a) The sum of atomic charges in benzene-moiety is shown. b) $e = 1.60\times10^{-19}$ C. †: These structures changed into other configurations during optimization.

pendent of the basis sets of calculation. However, the amount of the charge-transfer was dependent on the basis sets, the HF method giving relatively small values and the B3LYP and the MP2 methods giving about a doubled amount of charge-transfer relative to that obtained by the HF method. The reasons for the similar charge-transfers obtained by the two methods are intriguing: We believe this is due to calculation results of B3LYP that tends to calculate a shallow value of the orbital energy.

However, the binding energy as calculated by the MP2 method, ΔE^{MP2}, is not necessarily proportional to the amount of charge transfer, ΔQ_{CT}, nor to the dipole moments: The binding energy calculated by the MP2 method increases as the dispersion energy ΔE_{disp} increases, and as distances between the two molecules decrease (Tables 1, 2, and 3). This again speaks for the importance of the dispersion forces relative to charge transfer energy for the stabilization of the complexes.

Looking at Tables 4 and 5, we notice that calculated dipole moments do not necessarily obey the general rule mentioned in Eq. 8. This is because the distances between the negative charge and the positive one are dependent on the types of complexes. We must compare the dipole moments for configurations of similar distances of the charge centers. And the relationship is confirmed by doing so.

One might argue that the attractive force between benzene and ethene mainly consists of quadrupole interactions. However, attraction due to quadrupoles must be weak in hydrocarbons.[37] The role of quadrupole moments may be neglected.

Configurations of Complexes. For the π–π* interactions, the final optimized geometries were two, which are shown as A-1 and A-2 in Fig. 1. However neither of these forms are obtained as an energy-minimum form by the HF and B3LYP methods: The energy does not converge to a minimum. This will mean that the dispersion forces are important for the formation of complexes A-1 and A-2.

The binding energies in B-1 and B-2 configurations are obtained as ca. 0.5 kcal mol^{-1} both by the HF and the B3LYP methods, whereas that obtained by the MP2 method is ca. 2 kcal mol^{-1}. This again suggests that the dispersion forces are important in stabilizing these forms.

Binding energies in the C configurations are ca. 0.5 kcal mol^{-1}, as obtained by both the HF and the B3LYP methods, whereas they are ca. 2.2 kcal mol^{-1} according to the MP2 calculations.

For the configurations D's and E's, the binding energies obtained by the HF method are smaller than those obtained by the B3LYP method, which are smaller than those derived by the MP2 method by ca. 1 kcal mol^{-1}. This is a consequence of the importance of the dispersion force. The larger stabilization obtained by the B3LYP than by the HF method is attributed to a kind of the electronic correlation energy (Thomas–Fermi type correlation), which are taken into consideration in the former theory.

The stabilization of F's is again due to dispersion forces mainly, because both the HF and the B3LYP methods did not converge to a minimum at these configurations. We observe also a few charge-transfer interactions, which imply that there are CH–π interactions. There may also be a contribution to the stabilization due to π–π* overlap, because it is possible topologically to make overlapping of the π (or π*)-orbital of benzene with the π*(or π)-orbital of ethene.

As are discussed in the Frequency Analysis section, configuration F-2 gives an imaginary frequency, whereas F-1 gives all real frequencies. Thus, F-1 is a real minimum, while F-2 is a saddle point.

We wish to discuss the F-1 configuration in reference to configurations of other interactions, involving benzene, which are reported in the literature. Interestingly, in the configurations of H-donors in benzene-HX complexes, including HF,[38] HCl,[39] H_2O,[28—34] and NH_3,[40] the axis of H–X is not parallel to the benzene C_6 axis, but is tilted considerably.

This situation is reproduced in the F-1 configuration: The angle between the C–H bond and the C_6 axis of benzene is 24°. The feature implies that the nature of the CH–π interactions include the same characteristics as XH–benzene interactions, which, we believe, can be called "hydrogen-bond type" interactions.

As a model of a complex which is stabilized by dispersion forces, the complex G was obtained as an energy minimum by the B3LYP and the MP2 methods, while it was not a minimum by the HF method. In this complex, the benzene ring and the C–C axis of the ethene molecule are orthogonal with each other and the π-faces of benzene and ethene are orthogonal as well. Here the interaction between the π-system and the C–H group is not expected. In conformity with this expectation, the amount of charge transfer is very small in this configuration. The failure of the HF method in detecting G as an energy minimum is again attributed to the neglect of electronic correlation and dispersion forces. This configuration is found to be a real energy minimum

Table 6. Frequencies of Vibrational Modes due to Formation of the Benzene–Ethene Complexes in cm^{-1}

Configuration Mode	A-1	A-2	B-1	B-2	C-1	C-2	D-1	D-2	E-1	E-2	F-1	F-2	G
No. 1	−65	−63	−53	−51	−44	−45	−9	−8	−26	−21	14	−13	15
No. 2	−8	8	6	22	9	−13	17	15	−11	−8	53	52	38
No. 3	53	54	21	36	21	15	19	37	8	15	56	59	62
No. 4	58	59	49	50	70	70	48	52	39	18	72	71	71
No. 5	62	62	57	56	71	70	58	55	40	47	91	89	105
No. 6	65	65	67	67	80	73	60	58	52	51	97	94	115

by frequency analysis but is somewhat more unstable than configuration F-1.

Frequency Analysis. This was done by calculation on the optimized configurations at the MP2/6-31G** level. The results are shown in Table 6. The calculation produced 48 normal vibration modes, of which 30 modes are assigned to benzene, 12 to ethene, and the remaining 6 to the complexes which are formed by benzene–ethene interactions. The 6 modes of vibration should appear in a low frequency region of 10—100 cm^{-1}, because the binding energy is very small. However, many of the complexes show one or two imaginary frequencies, except F-1 and G. Thus the configurations F-1 and G are true energy minima, while the configurations A's, B's, C's, D's, and E's are saddle points or conical points. It is interesting to note that the energy differences between the energy-minimum states and the transition states (A's, B's, and C's), which correspond to the activation energy for configurational changes, are very small. The configurational changes should occur easily to result in favorable entropies of formation of benzene-ethene complexes. We should like to draw attention to a fixed configuration in F-1. This configuration should be determined by the CH–π interactions, because dispersion forces are not directional. This means that, in the molecular recognition, we cannot neglect the contribution of the CH–π interactions.

Vibrational Modes. The vibrational modes of complexes F-1 and G are shown in Fig. 2.

Configuration F-1 results in 6 modes of vibration. Mode 1 is rotation[41] of benzene around its C_6 axis (in-plane rotation) with simultaneous rocking of ethene around its axis which is orthogonal both to the ethene plane and its C–C axis. Mode 2 may be describes as the situation where the benzene molecule undergoes rocking around its C1–C4 axis while the ethene molecule undergoes rocking around its C–C axis. This type of vibration can have another mode due to the relative directions of the benzene and ethene motions: That mode is given by Mode 6. There is another mode of vibration, mode 3, where ethene rotates in its plane around an axis which is orthogonal to the ethene plane, while benzene rocks around its C1–C4 axis. Vibration Modes 4 and 5 are concerned with this in-plane rotation of the ethene molecule, while stretching vibration between CH(ethene) and the benzene ring takes place. This motion produces two modes of vibration owing to the relative directions of the rotation of the ethene molecules. The stretching vibration is clear evidence for the existence of CH–π interactions, which also determines the directional configuration of the complex.

Configuration G results in similar types of vibrations. Mode 1 is the combination of benzene-rocking and in-plane rotation of ethene. This type of vibration produces another mode by the relative directions of rocking and in-plane rotation: That is Mode 6. Mode 2 is the combination of in-plane rotation of benzene with rocking of ethene. Mode 5 is of the same type but different in relative directions of vibration. Mode 3 is the combination of rockings of benzene and ethene, which is not observed in configuration F-1. The final vibrational mode, 4, is stretching between the two molecules.

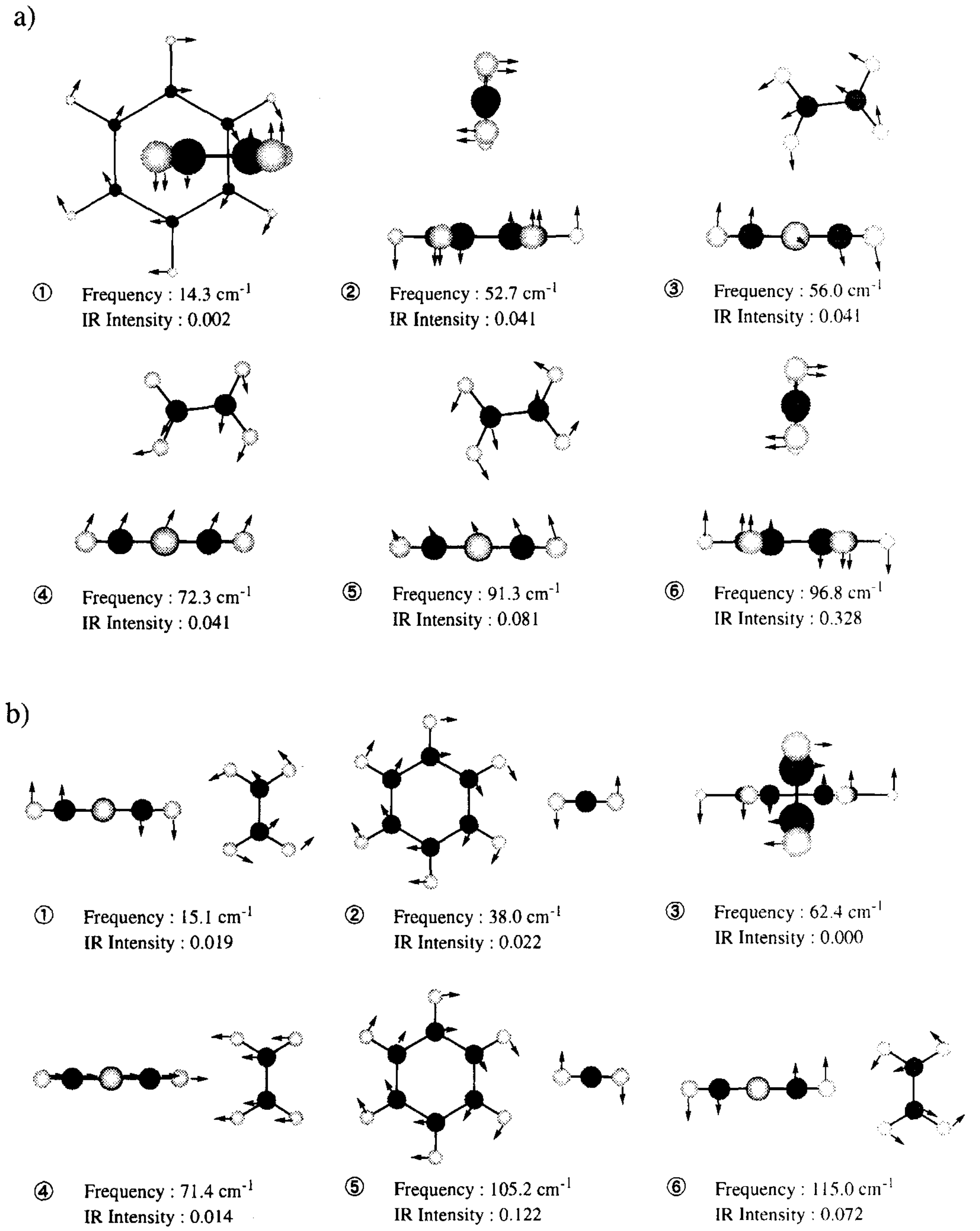
BSSE Corrections. The binding energy for the complexes which were calculated by the MP2 method, 1.4—2.5 kcal mol^{-1}, can be an overestimation, because this method tends to overestimate the intermolecular forces. The dispersion energy amounts to 1.9—4.4 kcal mol^{-1} (Table 3), which occupies a substantial portion of the calculated binding energies obtained by the MP2 method. Thus ΔE^{MP2}'s, were further corrected for Basis Set Superposition Errors (BSSE) by using the counterpoise method. The results were reasonable, affording 0.4—0.8 kcal mol^{-1} binding energies, as are compiled in Table 7. However, there are some problems in this calculation.

The configuration A-1 is calculated by the MP2 method to be stabilized by 1.467 kcal mol^{-1} while it becomes less

Table 7. MP2/6-31** Interaction Energies and BSSE for Benzene–Ethene Complexes

	ΔE^{MP2} a)	BSSE	ΔE^{MP2}+BSSE
Configuration	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
A-1	−1.467	1.975	+0.508
A-2	−1.472	1.984	+0.513
B-1	−1.970	1.234	−0.736
B-2	−1.969	1.234	−0.735
C-1	−2.206	1.358	−0.848
C-2	−2.200	1.352	−0.848
D-1	−1.639	1.052	−0.587
D-2	−1.637	1.261	−0.376
E-1	−1.431	0.903	−0.528
E-2	−1.386	0.904	−0.482
F-1	−2.554	1.767	−0.787
F-2	−2.538	1.742	−0.796
G	−1.817	1.415	−0.402

a) ΔE^{MP2} corresponds to the interaction energy before correction for BSSE.



a)

① Frequency : 14.3 cm^{-1}
IR Intensity : 0.002

② Frequency : 52.7 cm^{-1}
IR Intensity : 0.041

③ Frequency : 56.0 cm^{-1}
IR Intensity : 0.041

④ Frequency : 72.3 cm^{-1}
IR Intensity : 0.041

⑤ Frequency : 91.3 cm^{-1}
IR Intensity : 0.081

⑥ Frequency : 96.8 cm^{-1}
IR Intensity : 0.328

b)

① Frequency : 15.1 cm^{-1}
IR Intensity : 0.019

② Frequency : 38.0 cm^{-1}
IR Intensity : 0.022

③ Frequency : 62.4 cm^{-1}
IR Intensity : 0.000

④ Frequency : 71.4 cm^{-1}
IR Intensity : 0.014

⑤ Frequency : 105.2 cm^{-1}
IR Intensity : 0.122

⑥ Frequency : 115.0 cm^{-1}
IR Intensity : 0.072

Fig. 2. Lowest six frequencies, IR intensities and normal modes associated with intermolecular interaction : a) configuration F-1, b) configuration G.

stable than the system of independent benzene and ethene by 0.508 kcal mol^{-1} after the BSSE correction (Table 7). The situation was similar for A-2: Though this configuration is stabilized by 1.472 kcal mol^{-1} by the MP2 method, it becomes 0.513 kcal mol^{-1} less stable than the independent molecules after the BSSE correction. However, the amounts of electron-transfer and dipole moments were also calculated for complexes A-1 and A-2 by the MP2 method, though these amounts are smaller than other configurations, suggesting that these configurations A's are likely to be energy minima. Theoretical considerations would also predict that these configurations should be stable because of the π–π* overlap.

After BSSE corrections, the binding energies of C forms become ca. 0.85 kcal mol^{-1} to suggest that these configurations are the most stable among those studied. This is contradictory to the fact that these forms are a saddle point and a conical point, respectively, from frequency analyses.

These results question the reliability of BSSE. The BSSE is believed to be overestimated by the counterpoise method. However, this overestimation cannot account for the case of configurations C's. The overestimation may be corrected by using larger basis sets. Further calculations with larger basis sets to prove or disprove the presence of the π-π* interactions and to obtain better binding energies of A and C configurations are awaited in the future.

The binding energy in the configuration F-1 was ca. 0.8 kcal mol^{-1}, after BSSE corrections of the value obtained by the calculation at the MP2/6-31G** level, and was in good agreement with an experimental value of the CH–π interaction.[11] However, this agreement can be fortuitous and be due to cancellation of an overestimation of BSSE, which is derived by the counterpoise method, by an overestimation of binding energy by the MP2 method. By using a higher level of theory, a similar result may be obtained as a consequence of decreases both in overestimation of binding energy and in BSSE.

Conclusion

Benzene-ethene complexes are found to possess at least two energy minima, F-1, which is a displaced T form, and G, which is an edge-to-edge interacting form.

In the F-1 configuration, the binding energy was 2.554 kcal mol^{-1}. π–π^* interactions between the benzene and the ethene molecules may contribute to some extent, because topologically the overlap between the π of the benzene ring and the π^* orbital of ethene, or vice versa, is possible. Appearance of both dipole moment and stretching vibration for the configuration F-1 is firm evidence for the existence of the benzene-ethene complex.

The binding energy of configuration G was 1.814 kcal mol^{-1}. Thus this configuration is an energy minimum but is not a global minimum. However, it gives stretching mode of vibration by calculation, which gives a firm basis for the presence of this complex.

All the complexes of the T configuration, B-E, showed charge transfer from a π-electron donor to a CH electron-acceptor. Thus the stabilization due to CH–π interactions is manifested by dispersion forces and charge transfer interactions, where the dispersion forces play a dominant role. It should be pointed out that the configuration, which is the most stable, is similar to other XH–benzene complexes. We wish to emphasize the importance of the CT interactions in determining the configuration because the CT force is directional, while the dispersion force, which mainly contributes to the binding energy, is not directional. This also suggests that the CH–π interactions should play at least some roles in molecular recognition.

It was found that the B3LYP method is not suitable for calculating the CH–π intermolecular interactions, whereas the MP2 method gives satisfactory results. However, the values calculated by the MP2 method are larger than the expected values and experimentally observed ones. BSSE corrections may have to be used for obtaining reasonable values, though the BSSE itself has various problems.

Six vibrational modes due to complex formation were confirmed, the frequencies being at 10—100 cm^{-1}.

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References

1 M. Ōki, T. Hirose, K. Maeda, M. Yanagawa, Y. Kataoka, H. Kojima, N. Morita, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **70**, 859 (1997).

2 M. Ōki, T. Shionoiri, K. Otake, M. Ono, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **66**, 589 (1993).

3 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, **112**, 5525 (1990).

4 S. Hobza, H. L. Selzle, and E. W. Schlag, *J. Am. Chem. Soc.*, **116**, 3500 (1994).

5 S. Tsuzuki, T. Uchimaru, M. Mikami, and K. Tanabe, *Chem. Phys. Lett.*, **252**, 206 (1996).

6 C. Chipot, R. Jaffe, B. Maigret, D. A. Pearlman, and P. A. Kollman, *J. Am. Chem. Soc.*, **118**, 11217 (1996).

7 R. Jaffe and G. D. Smith, *J. Chem. Phys.*, **105**, 2780 (1996).

8 M. Nishio, M. Hirota, and Y. Umezawa, "The CH/π Interaction," Wiley-VCH, New York (1998).

9 Y. Kodama, K. Nishihata, S. Zushi, M. Nishio, J. Uzawa, K. Sakamoto, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **52**, 2661 (1979).

10 Y. Nakai, K. Inoue, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **62**, 2923 (1989).

11 S. Paliwal, S. Geib, and C. S. Wilcox, *J. Am. Chem. Soc.*, **116**, 4497 (1994).

12 T. Steiner, E. B. Starikov, A. M. Amado, and J. J. C. Yeixeira-Dias, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 1321.

13 D. R. Boyd, T. A. Evans, W. B. Jennings, J. F. Malone, W. O'Sullivan, and A. Smith, *Chem. Commun. (Cambridge)*, **1996**, 2269.

14 Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, and M. Nishio, *Bull. Chem. Soc. Jpn.*, **71**, 1207 (1998).

15 Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, and M. Nishio, *Tetrahedron*, **55**, 10047 (1999).

16 Y. Kodama, K. Nishihata, and M. Nishio, *Tetrahedron Lett.*, **24**, 2105 (1977).

17 T. Takagi, A. Tanaka, S. Matsuo, H. Maezaki, M. Tani, H. Fujiwara, and Y. Sasaki, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 1015.

18 S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Phys. Chem. A*, **103**, 8265 (1999).

19 C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1723 (1963).

20 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, **104**, 5063 (1982).

21 H. Hasegawa, K. Inukai, S. Kagoshima, T. Sugawara, T. Mochida, S. Sugiura, and Y. Iwasa, *Chem. Commun. (Cambridge)*, **1997**, 1377.

22 A. Irving, *Supramol. Chem.*, **8**, 267 (1997).

23 N. Hayashi, T. Mori, and K. Matsumoto, *Chem. Commun. (Cambridge)*, **1998**, 1905.

24 G. J. Piermarini, A. D. Mighell, C. E. Weir, and S. Block, *Science*, **165**, 1250 (1969).

25 M. Ōki, H. Iwamura, and Y. Urushibara, *Bull. Chem. Soc. Jpn.*, **31**, 770 (1958).

26 M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **33**, 717 (1960).

27 J. F. Malone, C. M. Murray, M. H. Charlton, R. Docherty, and A. J. Lavery, *J. Chem. Soc., Faraday Trans.*, **93**, 3429 (1997).

28 G. Karlström, P. Linse, A. Wallqvist, and B. Jönsson, *J. Am. Chem. Soc.*, **105**, 3777 (1983).

29 S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard, III, and G. A. Blake, *Science*, **257**, 942 (1992).

30 A. Gotch and T. S. Zwier, *J. Chem. Phys.*, **96**, 3388 (1992).

31 A. Courty, M. Mons, I. Dimicoli, F. Piuzzi, M.-P. Gaigeot, V. Brenner, P. d. Pujo, and P. Millié, *J. Phys. Chem. A*, **102**, 6590 (1998).

32 D. Feller, *J. Phys. Chem. A*, **103**, 7558 (1999).

33 S. K. Burley and G. A. Petsko, *FEBS Lett.*, **203**, 139 (1986).

34 P. Tarakeshwar, H. S. Choi, S. J. Lee, J. Y. Lee, K. S. Kim, T.-K. Ha, J. H. Jang, J. G. Lee, and H. Lee, *J. Chem. Phys.*, **111**, 5838 (1999).

35 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. C. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Lahan, V. G. Zakrzewski, J. W. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. T. Ayala, W. Chen, M. W. Wong, J. L.Anders, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, (1995).

36 R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

37 R. B. Doerksen and A. J. Thakkar, *J. Phys. Chem. A*, **103**, 10009 (1999).

38 F. A. Baiocchi, J. H. Williams, and W. Klemperer, *J. Phys. Chem.*, **87**, 2079 (1983).

39 W. G. Read, E. J. Campbell, and G. Henderson, *J. Chem. Phys.*, **78**, 3501 (1983).

40 D. A. Rodham, S. Suzuki, R. D. Suenram, F. J. Lovas, S. Dasgupta, W. A. Goddard III, and G. A. Blake, *Nature*, **362**, 735 (1993).

41 Although this is actually a reciprocal rotation, we call it "rotation" for the sake of simplicity.

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