Structures and Binding Energies of Benzene–Methane and Benzene–Benzene Complexes

An *ab initio* SCF/MP2 Study

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Ab initio SCF/MP2 potentials are calculated on benzene–methane and benzene–benzene complexes. Although no energy stabilization appears at the Hartree–Fock level, a small but non-negligible stabilization in energy is observed at the MP2 level in both complexes, indicating the importance of the dispersion energy. Besides the dispersion energy, the electrostatic interaction plays some role in determining the relative stabilities in several cases. The most stable structure of the benzene–methane complex adopts a C_{3v} symmetry with methane lying on the benzene C_6 axis and one hydrogen atom pointing towards benzene. The binding energy of this structure is -1.95 kcal mol^{-1} from MP2/MIDI-4** calculations and -1.09 kcal mol^{-1} from MP2/6-31G** calculations, where a p-polarization function is added only on the H atoms of methane. The benzene–methane complex is much less stable than the benzene–benzene complex.

Van der Waals interactions of aromatic systems have been of considerable interest because they often play an important role in determining molecular recognition,[1] diastereoselectivity[2] and crystal structures.[3] In this regard, weak complexes of benzene with small molecules have been attractive subjects of research as models of the van der Waals interactions of aromatic systems. For instance, benzene–water,[4–7] benzene–ammonia,[6–8] benzene–alkane[6,8,9] benzene–hydrogen halide[7,10,11] and benzene–benzene[4] complexes have been investigated experimentally and theoretically.

Of the various van der Waals interactions of aromatic systems, an attractive interaction between aromatic and alkyl groups was proposed about 15 years ago in an attempt to explain the structures of organic molecules,[12] and is called now the CH–π interaction. The conformations of transition-metal complexes have recently been interpreted in terms of this interaction.[3] An intermolecular interaction in the benzene–methane complex is considered a prototype model of this CH–π interaction. So far, a few experimental studies[8,9] and only one theoretical work[6] have been reported on this complex. In spite of those efforts, several issues remain to be resolved for the benzene–methane complex. For instance, its structure is still obscure; the structure proposed by experimentalists[8b] adopts a C_{3v} symmetry with methane lying on the benzene C_6 axis with three hydrogen atoms pointing towards the benzene, but this structure was calculated to be less stable than a C_{2v} structure with methane lying on the benzene C_6 axis and two hydrogen atoms pointing towards benzene.[6] Furthermore, it is also unclear which of dispersion, electrostatic and charge-transfer interactions plays a dominant role in the bonding of the benzene–methane complex. In this work, *ab initio* SCF/MP2 calculations and energy decomposition analysis are carried out on benzene–methane and benzene–benzene complexes. The aims of our work are (i) to estimate the strength of the CH–π interaction, (ii) to compare it with the π–π interaction of the benzene–benzene complex, (iii) to clarify the most stable structure of the benzene–methane complex and (iv) to elucidate the nature of the bonding in these complexes.

Computations

Ab initio SCF/MP2–MP4 calculations and energy decomposition analysis were carried out with the Gaussian 86[13] and

IMSPACK programs,†[14] respectively. In MP2–MP4 calculations, all the core orbitals were excluded from the active space. MIDI-4 basis sets[15] were employed in optimizing the intermolecular distances of the benzene–methane and benzene–benzene complexes. The binding energy of the benzene–methane complex was calculated by using MIDI-4* and MIDI-4** sets for benzene and methane, respectively, where MIDI-4** involves a d-polarization function ($\zeta = 0.60$) and a p-polarization function ($\zeta = 1.0$) on the carbon and hydrogen atoms, respectively, and MIDI-4* involves only the d-polarization function on the carbon atom. Some important structures of the benzene–methane complex were also calculated by using 6-31G* and 6-31G** basis sets for benzene and methane,[16] respectively, because these basis sets have been employed in many theoretical studies of the intermolecular interaction. The binding energy of the benzene–benzene complex was calculated with the MIDI-4 basis sets because of the large size of this complex. The basis set superposition error (BSSE) was corrected with the method proposed by Boys and Bernardi.[17]

Energy decomposition analysis (EDA) proposed by Morokuma[18] was applied to the investigation of the nature of the bonding of benzene–methane and benzene–benzene complexes. In this analysis, the binding energy (E_b) is divided into such terms as E_{es} (electrostatic), E_{ex} (exchange), E_{pl} (polarization), charge transfer (E_{ct}) and higher-order mixing (E_{mix}) terms;

$$E_b = E_t(A–B) - E_t(A) - E_t(B) \qquad (1)$$

$$= E_{es} + E_{ex} + E_{pl}(A) + E_{pl}(B)$$

$$+ E_{ct}(A \rightarrow B) + E_{ct}(B \rightarrow A) + E_{mix} \qquad (2)$$

where an A–B complex is considered to consist of two monomers, A and B. When A and B cause distortion upon complexation, we should consider the deformation energy (E_{def}) that arises from the distortion. Here, it was not necessary to consider E_{def} because geometries of benzene and methane were taken to be the same as in the isolated molecules (*vide infra*). From the definition given by eqn. (1) and (2), a negative value means stabilization in energy for all these terms.

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† Gaussian 70, and many other routines are involved.

Structures of the benzene–methane complexes examined in this work are shown in Scheme 1. These structures are classified into three groups: in the first, methane approaches benzene along the C_6 axis of benzene (see structures 1–3). In the second, methane approaches the edge of benzene, where the former lies on the molecular plane of the latter (see structures 4–6). In the third, methane approaches the apex of benzene (see structures 7 and 8). In all these eight structures, the highest symmetry was adopted: for instance, methane was placed on the C_6 axis of benzene in 1–3. Such an asymmetrical structure as 9 (Scheme 1) was not examined here because the symmetrical structure of 3 was reported to be more stable than the asymmetrical one, 9.[6] In the benzene–benzene complex, three kinds of structure were considered, as shown by 10–12 of Scheme 2. The apex-to-apex structure was not calculated here because this structure was reported to be significantly less stable than 10 and 11.[4c]

Scheme 1

Scheme 2
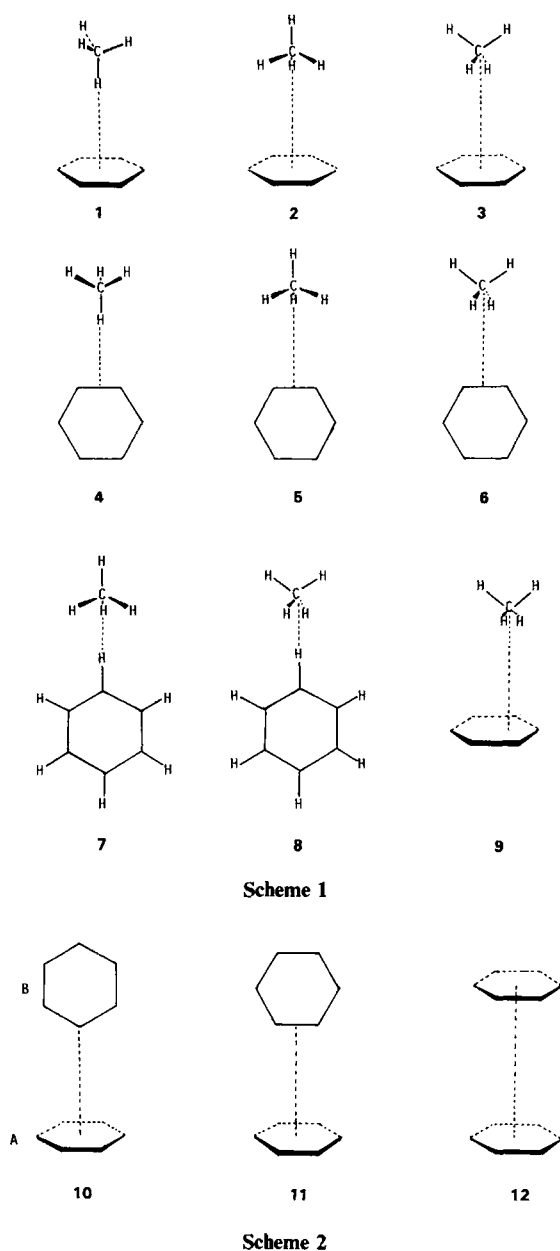
Potential-energy curves of these complexes were calculated as a function of R, the distance between the centres of mass of benzene and methane. In these calculations, the geometries of benzene and methane were fixed to their optimized structures

in the isolated molecules;† $R(C—C) = 1.3846$ Å and $R(C—H) = 1.0721$ Å for benzene, and $R(C—H) = 1.0829$ Å for methane.

Results and Discussion

First, the MP2–MP4 methods are compared in calculations on structures 1–3, to ascertain the reliability of the MP2 method, where the MIDI-4 basis set is used.‡ As shown in Table 1, their binding energies depend only slightly on the computational methods, and furthermore, differences in the binding energies of 1, 2 and 3 depend little on the computational methods. Therefore, the MP2 method is reliable for quantitative determination of the relative stabilities of this complex.

Potential-energy curves of the benzene–methane complex, 1, and the benzene–benzene complex, 10, are given in Fig. 1 as typical examples, where the MIDI-4 basis set is used. Several interesting features are found in these potential-energy curves; (1) no energy stabilization is observed at the HF level, (2) a small, but non-negligible, stabilization in energy appears upon introducing correlation effects with the MP2 method, suggesting the importance of the dispersion energy, and (3) BSSE correction reduces the binding energy by 15–40% and slightly lengthens the intermolecular distance. These features are found in all the structures of benzene–methane and benzene–benzene complexes (potential-energy curves of the other structures are omitted here).

Binding energies and intermolecular distances calculated with the MIDI-4 set are summarized in Table 2. For the benzene–methane complex, structure 1 is the most stable followed by structure 3. The binding energy of 1 is -0.57 kcal¶ mol^{-1} and that of 3 is -0.49 kcal mol^{-1} at the MP2 level after BSSE correction (note a negative value means stabilization; vide supra). The binding energies and relative stabilities will be discussed below in detail, based on calculations with better basis sets. Here, we are mainly concerned with the geometry and binding energy of the benzene–benzene

Table 1 Comparison of MP2–MP4 methods for calculating the binding energy (after BSSE correction)[a] of the benzene–methane complex, structures 1–3[b]

method	$E_b/kcal\ mol^{-1}$		
	1	2	3
MP2	−0.56	−0.48 (0.08)[c]	−0.36 (0.20)[c]
MP3	−0.49	−0.40 (0.09)	−0.30 (0.20)
MP4(DQ)	−0.42	−0.35 (0.08)	−0.25 (0.18)
MP4(SDQ)	−0.43	−0.34 (0.08)	−0.25 (0.18)

[a] MIDI-4 basis set is used. [b] See Scheme 1. The distance between the centres of mass of benzene and methane is rather arbitrarily taken to be 4.0 Å. [c] In parentheses are the differences in energy from structure 1.

† These values were optimized with the 3-21G basis set by using an energy-gradient technique. Because energy-gradient calculations are time-consuming, the 3-21G basis set was used only in the optimization of benzene and methane. Although the 3-21G basis set was first employed in calculating potential-energy curves, the binding energy calculated with this basis set exhibited a larger BSSE than that calculated with the MIDI-4 set. Therefore, detailed investigation was carried out with the MIDI-4 set.

‡ MP4/MIDI-4* and MP4/MIDI-4** calculations could not be performed owing to computational limitations.
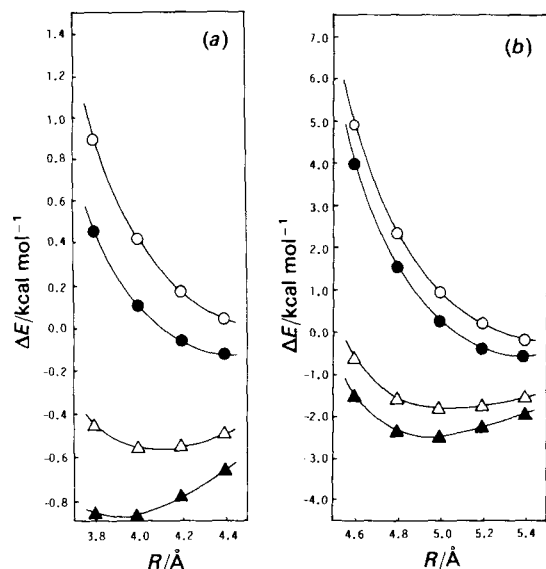
¶ 1 cal = 4.184 J.

Fig. 1 Potential-energy curves of (a) benzene–methane (structure 1, Scheme 1) and (b) benzene–benzene (structure 10, Scheme 2) complexes calculated with the MIDI-4 basis set. (○) HF (BSSE corrected); (●) HF; (△) MP2 (BSSE corrected); (▲) MP2. The basis set superposition error (BSSE) is corrected by the Boys' method. The standard energy (0) is taken at infinite separation of benzene and methane (or two benzenes)

complex and a comparison between benzene–benzene and benzene–methane complexes.

For the benzene–benzene complex, structure 12 is significantly less stable than 10 and 11, and the binding energy of 10 is -1.78 kcal mol^{-1} at the MP2 level after BSSE correction, which is almost the same degree as that of 11 (-1.59 kcal mol^{-1}), as reported by Karlström et al. (KLWJ).[4c] The binding energies of 10 and 11 before BSSE correction are similar in magnitude to those reported by KLWJ, while the basis sets used here differ from those of KLWJ. The most stable structure, 10, takes a T-shaped form in which an apex of one benzene approaches a face of the other benzene. This structure agrees well with the experimentally proposed structure.[4a,b] The electrostatic interaction favours this structure, as will be discussed later. Here, we should mention several conflicting claims about the structures;[19] recently, a C_{2h} slipped-parallel structure[4d] and a C_{2v} V-shaped structure[4e] have been proposed by different groups. Calculations on these two

Table 2 Binding energies[a] of benzene–methane and benzene–benzene complexes calculated at the MP2 level

structure[b]	before BSSE correction		after BSSE correction	
	R^c/Å	E_b/kcal mol^{-1}	R^c/Å	E_b/kcal mol^{-1}
1	3.19	-0.89	4.07	-0.57
2	3.86	-0.63	3.93	-0.36
3	3.87	-0.78	3.91	-0.49
4	5.52	-0.46	5.55	-0.34
5	5.18	-0.50	5.23	-0.39
6	5.17	-0.54	5.23	-0.41
7	5.49	-0.43	5.59	-0.31
8	5.60	-0.39	5.67	-0.28
10	4.94	-2.47	5.02	-1.78
11	5.05	-2.09	5.16	-1.59
12	3.91	-1.29	4.02	-0.49

[a] MIDI-4 is used. A negative value means stabilization relative to infinite separation. [b] See Schemes 1 and 2. [c] Distance between centres of mass of methane and benzene.

structures have not been performed in this work. Therefore, further calculations are necessary to determine theoretically the most stable structure of the benzene–benzene complex. Note that the benzene–benzene complex is much more stable than the benzene–methane complex; the binding energy of 10 is ca. three times greater than that of 1. The reason for this will be discussed later.

Effects of the polarization functions have been systematically examined for structure 1. As shown in Table 3, the binding energy at the MP2 level after BSSE correction is -0.84 kcal mol^{-1} when a d-polarization function is added on the carbon atoms of benzene, -1.30 kcal mol^{-1} when a d-function is added on the carbon atom of methane, -1.60 kcal mol^{-1} when a d-function is added on all the carbon atoms, and -1.81 kcal mol^{-1} when a d-function is added on all the carbon atoms and a p-function is added on the hydrogen atoms of methane. This result means that polarization functions are indispensable for quantitative estimation of the binding energy and that polarization functions on methane are more important than on benzene. We now consider the reason why the polarization functions improve the binding energy. There are several possible factors to be considered, as follows; polarization functions are expected to lead to better descriptions of the molecular multi-polar moment, charge-transfer interaction, polarization interaction and dispersion interaction. Only the last term improves the binding energy at the correlated level, while the others improve it at the HF level. As clearly shown in Table 3, the binding energy at the HF level is only slightly improved by polarization functions. However, the binding energy at the MP2 level increases significantly and systematically as the quality of the basis set is improved by addition of polarization functions. This result indicates that polarization functions are necessary to calculate correctly the dispersion energy.

All of the structures of the benzene–methane complex have been calculated by using MIDI-4** and MIDI-4* sets for methane and benzene, respectively. The most stable structure is 1 whose binding energy is -1.95 kcal mol^{-1}.† This value is in the range of experimentally estimated values (-1.5–2.0 kcal mol^{-1}).[8] The next stable structure is 3 whose binding energy is -1.78 kcal mol^{-1}. The least stable one is 4. Although the decreasing order of binding energies is slightly different for the MP2/MIDI-4 ($1 > 3 > 6 > 5 > 2 > 4 > 7 > 8$) and MP2/MIDI-4** ($1 > 3 > 2 > 6 > 5 > 8 \approx 7 > 4$) calculations, 1 is the most stable and 3 is the next in both calculations. The most stable structure, 1, adopts a C_{3v} symmetry with methane lying on the benzene C_6 axis and one hydrogen atom pointing towards benzene. The structure proposed by experimentalists takes a C_{3v} symmetry with methane lying on the benzene C_6 axis and three hydrogen atoms pointing towards benzene,[8b] which corresponds to 2. In this work, however, 2 is calculated

† The potential-energy curve of the benzene–methane complex (at the MP2 level after BSSE correction) was fitted by the following second-order function, $\Delta E_b = k(\Delta R)^2$, where ΔE_b and ΔR are deviations of E_b and intermolecular distance from the corresponding values of the equilibrium structure, respectively. The zero-point energy (ZPE) estimated from k is very small (ca. 6 cal mol^{-1}) and seems negligible in structure 1. This very small value is consistent with the very shallow potential-energy curve of the complex 1, as given in Fig. 1. Besides the above-examined stretching vibration, the ZPE is also influenced by intermolecular bending frequencies and the shifts in frequencies of the monomers on formation of the complex. This implies that the ZPE used here is an underestimation. However, the intermolecular bending frequencies and the frequency shifts in the monomers are considered to be small because the binding energies of these complexes are very small. Therefore, the calculated binding energy without ZPE correction is comparable with the experimental value.

Table 3 Effects of polarization functions on the binding energy (after BSSE correction)

structure	R^a	basis set methane	basis set benzene	E_b/kcal mol^{-1} HF	E_b/kcal mol^{-1} MP2
1	$(4.0)^b$	MIDI-4	MIDI-4	0.41	−0.56
1	$(4.0)^b$	MIDI-4	MIDI-4*	0.38	−0.80
1	$(4.0)^b$	MIDI-4*	MIDI-4	0.40	−1.30
1	$(4.0)^b$	MIDI-4*	MIDI-4*	0.37	−1.60
1	$(4.0)^b$	MIDI-4**	MIDI-4*	0.34	−1.80
1	4.07^c	MIDI-4**	MIDI-4*	0.24	−1.95
2	3.93^c	MIDI-4**	MIDI-4*	0.54	−1.61
3	3.91^c	MIDI-4**	MIDI-4*	0.53	−1.78
4	5.55^c	MIDI-4**	MIDI-4*	0.31	−1.31
5	5.23^c	MIDI-4**	MIDI-4*	0.23	−1.45
6	5.23^c	MIDI-4**	MIDI-4*	0.20	−1.51
7	5.59^c	MIDI-4**	MIDI-4*	0.12	−1.34
8	5.67^c	MIDI-4**	MIDI-4*	0.18	−1.35
1	3.82	6-31G**	6-31G*	0.66	−1.09
3	3.79	6-31G**	6-31G*	0.81	−0.68

^{a} Distance between centres of mass of benzene and methane. In parentheses, unoptimized distance; other values, optimized distance. ^{b} R is rather arbitrarily taken to be 4.0 Å. ^{c} Optimized value at the MP2 level (after BSSE correction) using MIDI-4 sets.

Table 4 Correlation energy^a at the distance giving the energy minimum^b

structure	$E_{(HF)}$	$E_{corr}{}^c$
1	$0.31 (0.24)^d$	$-0.88 (-2.19)^d$
2	0.54 (0.54)	−0.90 (−2.15)
3	0.53 (0.53)	−1.03 (−2.31)
4	0.31 (0.31)	−0.65 (−1.62)
5	0.24 (0.23)	−0.63 (−1.68)
6	0.21 (0.20)	−0.62 (−1.71)
7	0.12 (0.12)	−0.43 (−1.46)
8	0.19 (0.18)	−0.47 (−1.53)
10	0.85	−2.63
11	0.46	−2.05
12	3.05	−3.54

^{a} In kcal mol^{-1}. ^{b} At the MP2 level after BSSE correction. ^{c} $E^{(2)} = E(\text{MP2}) - E(\text{HF})$. ^{d} MIDI-4 set was used; in parentheses, MIDI-4** and MIDI-4* were used for methane and benzene, respectively.

to be less stable than 1 and 3 (see Tables 1–3). Also, 2 was calculated to be less stable than 3 by Bredas and Street (MP2/6-31G*).[6] Although the difference in binding energy between 1 and 3 is remarkably small, it increases upon improving the quality of the basis sets by adding polarization functions. To make sure that 1 is more stable than 3, these structures are calculated by using a different kind of basis set including polarization functions; i.e. 6-31G* for benzene and 6-31G** for methane. The binding energy of 1 is calculated to be −1.09 kcal mol^{-1} (Table 3), which is slightly smaller than the experimental value.[8] The binding energy of 3 is −0.68 kcal mol^{-1}. Thus, 1 is more stable than 3 by 0.41 kcal mol^{-1}. This difference between 1 and 3 is larger than that calculated by using the MIDI-4* basis set for benzene and the MIDI-4** set for methane. It can be concluded, therefore, that 1 is the most stable structure for the benzene–methane complex. Although 1 differs from the structure proposed by experimentalists[8b] only in the direction of the CH bond, the conclusion presented here is compatible with the experimental results, because of the difficulty in determining experimentally whether one CH bond of methane points towards benzene or not.

The correlation energy is estimated at the most stable intermolecular distance. As shown in Table 4, the correlation energy of the benzene–methane complex decreases in the order: first group (1–3) > second group (4–6) > third group (7 and 8), suggesting that the greatest binding energy of the first group results mainly from the greatest dispersion inter-

action. In the benzene–benzene complex, the greater stability of 10 than 11 arises from the greater dispersion energy, because the former is less stable than the latter at the HF level (Table 4). The greater stability of the benzene–benzene complex 10 than the benzene–methane complex 1 results from the greater dispersion energy of the former, again. Therefore, the dispersion energy plays a key role in determining the relative stabilities of the benzene–benzene and benzene–methane complexes. However, the most stable structure (1) of the benzene–methane complex receives the smallest dispersion energy in the first group (1–3). This means that the greater stability of 1 than 2 and 3 is determined at the HF level. Also in the benzene–benzene complex, the greater stability of 10 than 12 arises at the HF level.

Energy decomposition analysis (EDA) is carried out to clarify the factors determining the relative stabilities at the HF level, in which the MIDI-4 basis set is used.† 1 is compared with 2 at the intermolecular distance which yields the same E_{ex} values in 1 and 2, as shown in Table 5. Because the E_{ex} term arises from contact of electron clouds between two monomers, a comparison of two structures at the same E_{ex} value corresponds to a comparison of them at an intermolecular distance causing similar contact of two monomers.[20] Although E_{pl} and E_{ct} terms are almost the same in 1 and 2, the E_{es} term stabilizes 1 more than 2. A similar result is found in a comparison between 1 and 3. This implies that the electrostatic interaction favours 1 more than 2 and 3. The two

† Polarization functions hardly influence the interaction energy at the HF level, as shown in Tables 3 and 4. Thus, EDA was carried out with the MIDI-4 basis set, to use the same basis set in benzene–methane and benzene–benzene complexes.
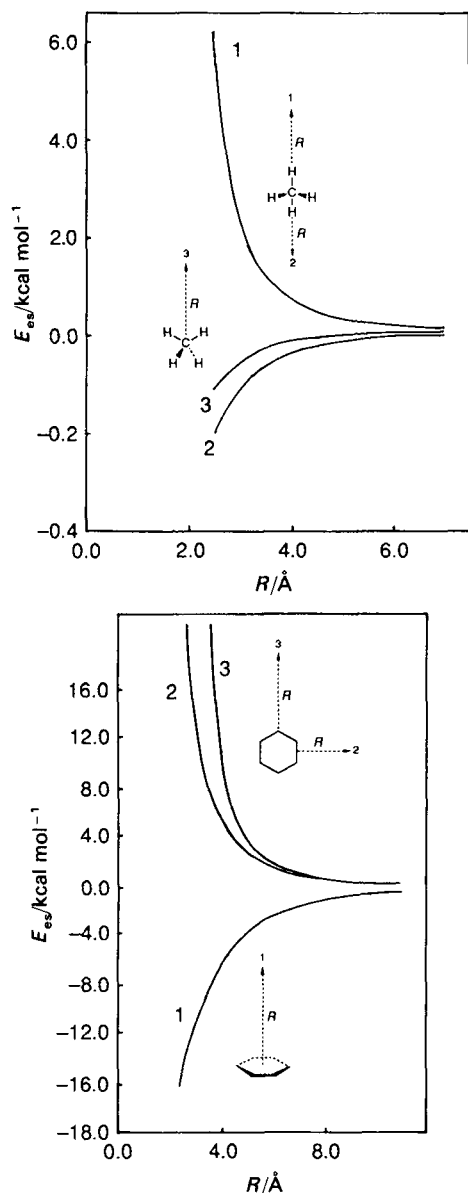
Table 5 Energy decomposition analysis of benzene–methane and benzene–benzene complexes^a (in kcal mol^{-1})

structure	R/Å	E_{es}	E_{ex}	$E_{pl}(A)^b$	$E_{pl}(B)^b$	$E_{ct}(B \to A)^b$	$E_{ct}(B \to A)^b$	E_{mix}
1	4.21^c	−0.20	0.35	0	−0.04	−0.15	−0.05	0
2	4.0	0.02	0.35	0	−0.03	−0.13	−0.04	0.02
1	4.10^c	−0.25	0.50	0	−0.04	−0.18	−0.05	0
3	4.0	−0.10	0.50	0	−0.04	−0.20	−0.04	0.03
10	5.0	−1.39	2.38	−0.03	−0.09	−0.53	−0.10	0.01
12	3.63^c	1.22	2.38	−0.07	−0.07	0.03	0.03	0.05

^{a} A negative value means stabilization. The MIDI-4 set was used. ^{b} For the benzene–methane complex, A is benzene and B is methane. For the benzene–benzene complex, see Scheme 2 for A and B. ^{c} The intermolecular distance is altered so as to equalize the E_{ex} of one structure with that of the other.

Fig. 2 Electrostatic potentials of methane and benzene calculated with the MIDI-4 basis set for directions 1-3

structures, 10 and 12, of the benzene–benzene complex are compared at an intermolecular distance yielding the same E_{es} value.† Again, the E_{es} term significantly favours 10 compared with 12. In this case, the E_{ct} term also contributes to the greater stability of 10 than 12.

Because the E_{es} term plays an important role in determining the relative stabilities in some cases, the electrostatic potentials of methane and benzene have been calculated.[2]‡ As shown in Fig. 2, benzene exhibits a negative potential in a direction perpendicular to its molecular plane and a positive one on its molecular plane. Methane exhibits a positive electrostatic potential along its C—H bond, but a negative one in the reverse direction. The negative potential is also found along a C_{2v} direction which bisects the HCH angle. In complex 1, the negative potential of benzene and the positive

† EDA of 11 was not carried out here because the greater stability of 10 than 11 results from the dispersion energy.

‡ MIDI-4 was used because polarization functions hardly influence the electrostatic potential around the equilibrium intermolecular distance.

potential of methane overlap each other, which is the best situation for electrostatic interaction. In complexes 2 and 3, on the other hand, the positive potentials of benzene and methane overlap each other, which is an unfavourable situation for electrostatic interaction. Consequently, 1 is the most stable in the first group of benzene–methane complexes, as shown by EDA. For benzene–benzene complexes, a similar situation is found; in 10, the negative electrostatic potential of one benzene overlaps with the positive one of the other benzene, which is favourable for electrostatic interactions. In 12, however, the positive electrostatic potential of one benzene overlaps with that of the other benzene, which is unfavourable for electrostatic interactions. Therefore, 10 is more stable than 12.

Conclusion

Eight structures for the benzene–methane complex and three structures for the benzene–benzene complex have been investigated at the MP2 level. The most stable structure, 1, of the benzene–methane complex adopts C_{3v} symmetry with the methane lying on the benzene C_6 axis and one hydrogen atom pointing towards benzene. Its binding energy at the MP2 level after BSSE correction is -0.57 kcal mol^{-1} with the MIDI-4 basis set. This value increases to -1.95 kcal mol^{-1} by adding a d-polarization function on all the carbon atoms and a p-function on the hydrogen atoms of methane. However, a smaller binding energy (-1.09 kcal mol^{-1}) is calculated at the MP2 level by using the 6-31G* basis set for benzene and the 6-31G** one for methane. Energy stabilization by complex formation is observed only at the correlated level, whereas no energy stabilization is calculated at the HF level. Therefore, the dispersion energy is of primary importance in the benzene–methane complex.

In the benzene–benzene complex, the apex-to-face structure, 10, is the most stable, in which the apex of one benzene approaches the face of the other. Again, no energy stabilization appears at the HF level, but a binding energy of -1.78 kcal mol^{-1} is calculated at the MP2 level by using the MIDI-4 set. Therefore, the dispersion energy is also important in the benzene–benzene complex. This binding energy is greater than that of the benzene–methane complex, mainly owing to the greater dispersion energy of the benzene–benzene complex.

Besides the dispersion energy, the electrostatic interaction is important in determining relative stabilities in some cases; for instance, 1 is more stable than 2 and 3 because of the greater electrostatic stabilization of 1, whereas the dispersion energy is smaller in 1 than in 2 and 3. Also in the benzene–benzene complex, the electrostatic interaction favours 10 more than 12, which is the main reason why 10 is more stable than 12.

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