

The role of C–H... π interaction in the stabilization of benzene and adamantane clusters[#]

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Abstract. In this investigation, a systematic attempt has been made to understand the interaction between adamantane and benzene using both *ab initio* and density functional theory methods. C–H... π type of interaction between C–H groups of adamantane and π cloud of benzene is found as the important attraction for complex formation. The study also reveals that the methylene (-CH₂) and methine (-CH) groups of adamantane interact with benzene resulting in different geometrical structures. And it is found that the former complex is stronger than the later. The diamondoid structure of adamantane enables it to interact with a maximum of four benzene molecules, each one along the four faces. The stability of the complex increases with increase in the number of benzene molecules. The energy decomposition analysis of adamantane-benzene complexes using DMA approach shows that the origin of the stability primarily arises from the dispersive interaction. The theory of atoms in molecules (AIM) supports the existence of weak interaction between the two systems. The electrostatic topography features provide clues for the mode of interaction of adamantane with benzene.

Keywords. Weak intermolecular interactions; adamantane-benzene clusters; C–H... π interaction; atoms in molecules.

1. Introduction

The concept of supramolecular chemistry is concerned with the organization and self-assembly of molecules and polymolecular systems which are held together by non-covalent interactions.¹ In contrast with the molecular chemistry, supramolecular chemistry aims to gain control over a variety of non-covalent interactions which orchestrate different supramolecular architectures. The concepts and perspectives of supramolecular chemistry are described in several authoritative books, monographs and reviews.¹ It is evident from numerous reports that both hydrogen bonding and van der Waals interactions are primarily responsible for the stability of supramolecular architectures.²

Numerous experimental and theoretical studies have been carried out on various small molecular clusters to probe hydrogen bonding and van der Waals interactions.³ Substantial advances in experimental techniques and molecular modelling in recent years have made it possible to obtain a finer level of understanding of the hydrogen bonding and weak interactions in diverse class of molecular clusters.⁴ Specifically, *ab initio* and

density functional theory (DFT) calculations at different levels of theoretical rigor have been carried out to explore the structure, stability, and strength of hydrogen bonded clusters and van der Waals complexes.⁵

The role of weak interactions involving π -aromatic rings has been widely observed in molecular clusters, organic/bioorganic systems and their supramolecular assemblies, as well as nanomaterials.⁶ The importance of π - π and X–H... π (X = O, N and C) interactions in these systems has been reported.⁶ Several experimental and computational investigations have been carried out to understand the structure, stability and spectra of these complexes.⁷ A systematic comparison of these interactions with the conventional hydrogen bonding has been made.⁸ It is well-known that the conventional hydrogen bond interaction (X–H...Y) involves two electron-withdrawing atoms (X, Y are usually nitrogen, oxygen, or fluorine), one being covalently bonded to hydrogen atom and the other bearing lone electron pairs non-covalently bonded to hydrogen atom. These complexes are characterized by a lengthening of the donor X–H bond and by a concomitant red shift in the X–H stretching frequency.⁹

In recent years, C–H... π interaction has received wide spread attention due to their importance in supramolecular chemistry and crystal engineering.¹⁰

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

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Hobza and co-workers have made seminal contribution to the understanding of this hydrogen bonding.¹¹ It is interesting to note that C–H... π interaction exhibits interesting spectral features when compared to the conventional hydrogen bonding. Specifically, in contrast to the features observed in conventional hydrogen bonds, this hydrogen bond is characterized by a shortening of the C–H bond and by a blue shift of the C–H stretching frequency.¹¹ Therefore, it is referred to as blue shifted hydrogen bond or improper hydrogen bond.¹¹ Hence it is of immense interest to explore the fascinating structural and geometrical features exhibited by the model weak complexes composed of C–H... π interaction.¹⁰ In this context, adamantane is a suitable molecule with two different C–H groups capable of interacting with π -aromatic rings.

Adamantane (C₁₀H₁₆) is a cycloalkane and also simplest diamondoid. Three cyclohexane rings arranged in armchair configuration forms a highly symmetric cage structure. It contains four bridge head methine hydrogens and twelve methylene hydrogen atoms. The synthesis of adamantane by Schleyer in 1957 transformed it from an elusive molecule to one of the staples of organic chemistry.¹² Adamantane and its derivatives have a broad range of chemical, polymer, and pharmaceutical applications.¹³ The scrutiny of the structure shows that this molecule can form fascinating structures through C–H... π type of interaction. Thus, a systematic attempt has been made to understand the nature of interaction between adamantane and benzene using electronic structure methods. The adamantane-benzene complexes are designated as AB_n (n = 1–4) in the remaining part of the text. The following points have been addressed in this study.

- (i) The structure and stability of AB_n (n = 1–4) clusters.
- (ii) To understand the mode of interaction of adamantane with benzene.
- (iii) To unravel the propensity of methine and methylene C–H groups of adamantane to participate in the C–H... π interaction.

In addition to the above-mentioned points the nature of interaction has also been characterized using the energy decomposition analysis and the Bader's theory of atoms in molecules (AIM).¹⁴

2. Computational methods

Since, the DFT based M05–2X functional yields reliable results for noncovalent interactions within 5Å,¹⁵

the geometry of all AB_n complexes were optimized at M05–2X/6–31+G** level of theory. Frequency calculations were carried out at the same level. The interaction energy (IE) of the various systems was calculated using both M05–2X and M06–2X methods using various basis sets. The geometries obtained from M05–2X were used for the calculation of IEs using M06–2X method. Further, to assess the performance of M05–2X, AB_n complexes were optimized using MP2/6–311+G** method and these geometries were used to calculate IE at MP2/aug-cc-pVDZ level. Basis set superposition error (BSSE) was corrected using supermolecule approach as suggested by Boys and Bernadi.¹⁶ All calculations were performed using Gaussian 09 suite of programs.¹⁷

2.1 Energy decomposition analysis

In addition to the calculation of the IEs, it is of immense interest to obtain information about the physical origin of the attractive interaction. To explore the nature of the interaction, IEs of the complexes were decomposed into the following terms

$$IE = E_{\text{electrostatic}} + E_{\text{exchange-repulsion}} + E_{\text{dispersion}}$$

The electrostatic interaction energy ($E_{\text{electrostatic}}$) was calculated using the interactions between distributed multipoles of interacting molecules using ORIENT package (version 3.2).¹⁸ Distributed multipoles up to hexadecapole on all atoms were obtained from the MP2/aug-cc-pVDZ wave functions using the GDMA program.¹⁹ To a first-order approximation, the contribution from the exchange-repulsion interaction can be calculated as the difference of the HF energy (IE calculated at HF/aug-cc-pVDZ) and the electrostatic interaction energy [$E_{\text{exchange-repulsion}} = (E_{\text{HF}} - E_{\text{electrostatic}})$]. In this decomposition analysis, the dispersion energy ($E_{\text{dispersion}}$) primarily corresponds to the correlation energy, which is the difference between the MP2 and HF intermolecular interaction energies ($E_{\text{corr}} = E_{\text{dispersion}} = E_{\text{MP2}} - E_{\text{HF}}$).

2.2 AIM theory

The Bader's theory of AIM was applied to characterize the weak interaction.¹⁴ The theory of AIM offers a rigorous way of partitioning any molecular system into atomic fragments by considering the gradient vector field of its electron density. Topological features such as bond critical points (BCPs) and paths of maximum electron density can be utilized to draw molecular

graphs. Full details of AIM theory can be found elsewhere.¹⁴ The wave functions generated from the M06-2X/6-31+G** level were used to generate the molecular graphs of AB_n complexes. The AIM calculations were carried out using AIM 2000 package.²⁰

3. Results

3.1 Adamantane-benzene complex

The optimized structures of different AB complex obtained from MP2/6-311+G** level are shown in figure 1. It can be seen that several modes of interactions are possible in adamantane-benzene complex due to diamondoid structure of adamantane. As discussed in the introduction, adamantane contains 12 methylene and four methine C-H groups. A set of three C-H's of the 12 methylene C-H groups (therefore 4 sets in complete), are parallel to each other. Furthermore, the dimensions of the region encompassing the three axial hydrogens are similar to that of the benzene ring. Thus, multiple C-H... π contacts are feasible through the methylene and methine hydrogens of adamantane. Analysis of the complexes of adamantane and benzene reveals that face-to-face and T-shaped modes are the possible types of interactions between them. In the first model, both molecules are parallel to each other with three methylene C-H groups directed toward the face of benzene. In the later, only one methine C-H group is directed towards the centre of the benzene ring.

In the face-to-face category, two different arrangements are available. The face-to-face mode of interaction: asymmetrical and symmetrical. These arrangements are referred as AB-1 and AB-2, respectively. The AB-2 has C_{3v} point group symmetry. In the C_{3v} sym-

metrical structure, the three methylene C-H bonds lie exactly perpendicular to the three carbon atoms of benzene. On the other hand, in the asymmetrical structure, one C-H group points towards the centre of the benzene ring, and the other two C-H groups lie outside the benzene ring. A similar observation has been seen in the case of cyclohexane-benzene complex.²¹ Similarly, two different arrangements are likely for the T-shaped conformation. In the first model, the methine C-H group interacts with the centre of the benzene. In the other case, two methylene C-H groups interact with benzene. These models are denoted as AB-3 and AB-4 in the remaining part of the text.

In all the complexes the CH... π contact is characterized by the CH... π distance (d) between the hydrogen atom of the C-H group and the nearest carbon atom in the benzene ring. It can be seen from figure 1 that the calculated d at MP2/6-311+G** method ranges from 2.252 to 2.770 Å. The same range as obtained from M05-2X/6-311+G** method varies from 2.45 to 3.107 Å. Examination of the results reveals that the values obtained from M05-2X method are marginally longer than that calculated from MP2 method. Similar findings were reported in the previous studies on comparison of M05-2X method with MP2 theory. However, these values are in good agreement with previous results on the interaction of saturated hydrocarbons with benzene²¹ and the C-H-X angle (α) is close to linearity. It is evident from the MP2 and M05-2X results that among all possible arrangements AB-3 has shortest intermolecular distance. It can be noted that the qualitative trend predicted by the M05-2X method is similar to that obtained from MP2 method. Further, optimization of geometries of larger complexes using MP2 theory is computationally demanding. Hence, M05-2X method was used to optimize the geometries of AB and AB_n ($n = 2-4$) complexes.

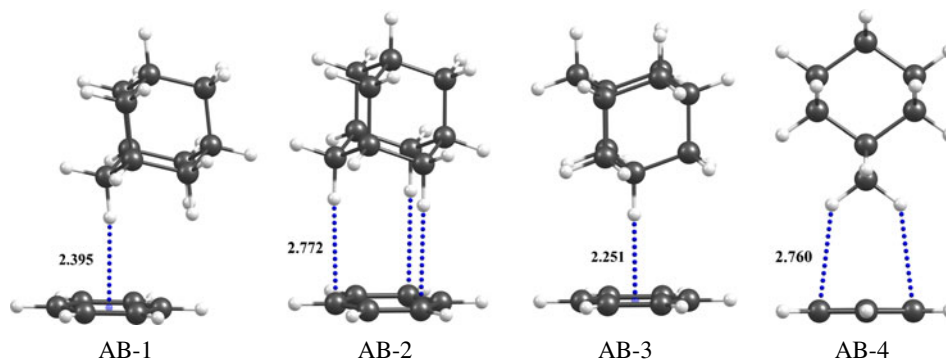


Figure 1. Optimized geometries of various adamantane-benzene complexes calculated at MP2/6-311+G** level of theory. The dotted line represents the CH... π hydrogen bond.

The optimized structures of AB and AB_n (n = 2–4) are shown in figure 2. Three different arrangements were obtained for AB₂ complexes. They are denoted as AB₂-1, AB₂-2 and AB₂-3 respectively. It can be seen that two faces of the adamantane interact with the benzene molecule. The AB₂-1 complex is similar to AB-1. In AB₂-1, two methylene C–H groups interact with the two benzene π -rings. The C–H... π distance is 2.660 Å and is identical for both sides. Due to the interaction of two benzene rings, the intermolecular distance, *d* is longer than that of AB-1. Likewise, AB₂-2 and AB₃-2 are similar to AB-2 and AB-3 complexes. The fourth mode of interaction which is similar to AB-4

was not considered due to its very weak nature. It can be seen from the figure 2 that in AB₃, three benzene molecules interact with the three faces of adamantane. These complexes are denoted as AB₃-1, AB₃-2, and AB₃-3. These are analogous to that of the respective AB and AB₂ complexes. Finally, a maximum of four benzene molecules can interact with the available four faces of adamantane. These complexes are represented as AB₄-1, AB₄-2, and AB₄-3. These structures were also similar to the corresponding AB, AB₂ and AB₃ complexes. Close scrutiny of geometrical parameters of AB_n (n = 2–4) complexes reveal that the *d* is marginally greater than that of the AB complexes.

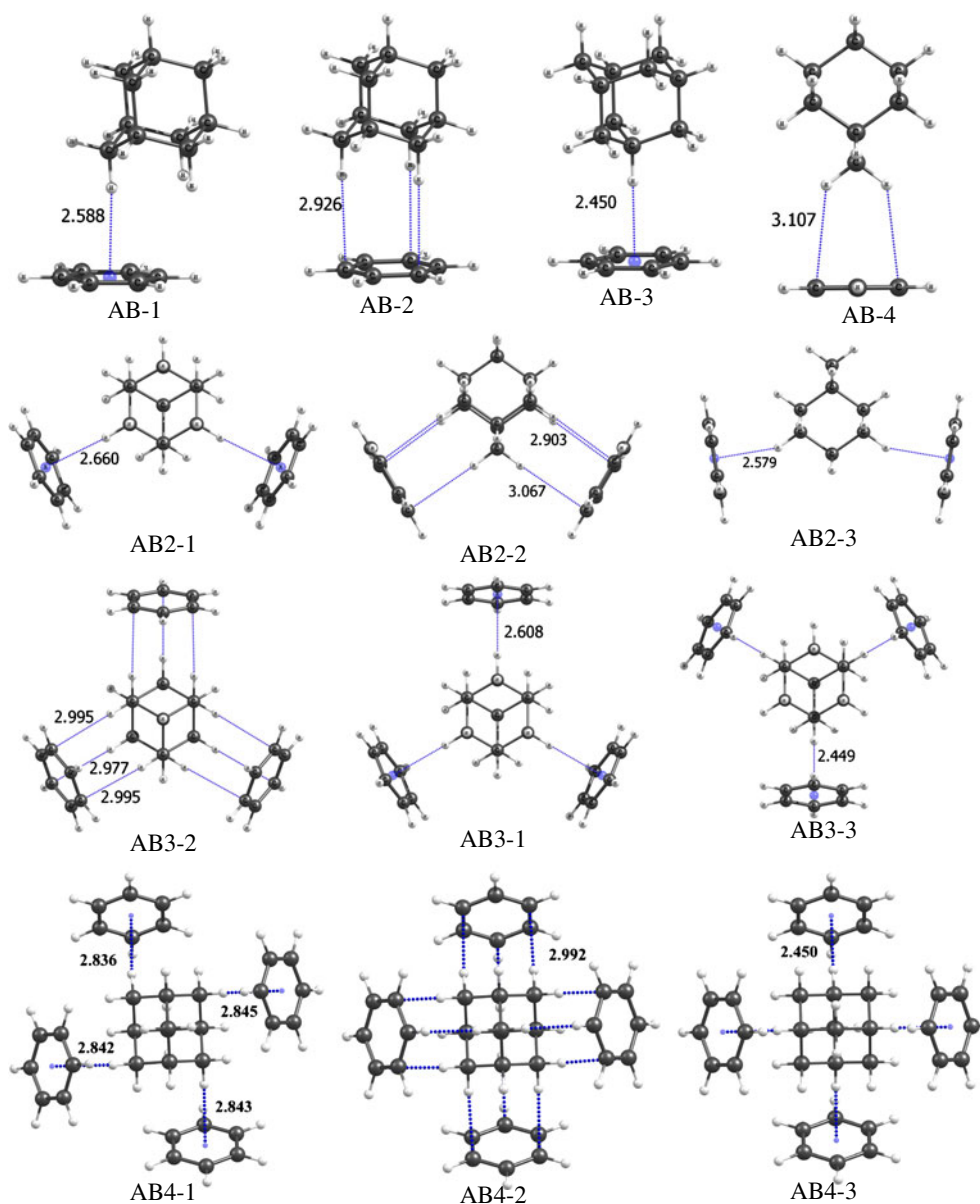


Figure 2. Optimized geometries of various adamantane-(benzene)_n complexes calculated at M05-2X/6-31+G** level of theory. The dotted line represents the CH... π hydrogen bond.

Table 1. Calculated Interaction Energies (IEs) and electron correlation energies of various adamantane–benzene complexes along with various contributions to IEs obtained from distributed multipole analysis (kcal/mol).

System	IEs	Various contributions to IEs		
	MP2/aug-cc-pVDZ	Electrostatic (E_{es}) ^a	Repulsion(E_{rep}) ^b	Correlation (E_{corr}) ^c
AB-1	−3.85	−2.24	5.41	−7.02
AB-2	−3.62	−2.59	5.76	−6.79
AB-3	−3.69	−1.31	5.67	−8.04
AB-4	−2.74	−1.45	4.76	−6.05

3.2 Interaction energies

The calculated BSSE corrected interaction energies (IEs) at MP2/6–311+G** level for adamantane–benzene complexes are listed in table 1. It can be seen that the calculated IEs of these complexes range from −2.74 to −3.86 kcal/mol. AB-1 complex with one C–H– π (methylene hydrogen) has the highest IE of −3.86 kcal/mol. The calculated IEs vary in the order IE(AB–1) > IE(AB–3) > IE(AB–2) > IE(AB–4). The calculated IEs using M05–2X and M06–2X methods are given in table 2. It can be noted that both M05–2X and M06–2X methods predict the same trend in the IEs yielded by the MP2 theory. The calculated IEs using M05–2X and M06–2X methods for AB_n (n = 2–4) complexes are given in table 3. The calculated range of IEs for AB₂, AB₃ and AB₄ at M05–2X level are −3.62 — −4.46, −5.24 — −6.47 and −6.66 — −8.00 kcal/mol, respectively. The single point calculations on these geometries using M06–2X method yields the range of IEs as −4.24 — −6.02, −6.07 — −8.54 and −7.77 — −10.12 kcal/mol for AB₂, AB₃ and AB₄, respectively. It can be seen that the IEs increases as the number of benzene unit increases.

3.3 Role of electrostatic and dispersion interactions

To understand the nature of interaction between adamantane and benzene molecules, the total IE was decomposed into several physically meaningful terms.

Table 3. Calculated Interaction Energies (IEs) of various adamantane–(benzene)_n complexes at various levels of theories (kcal/mol).

System	M05–2X/6–311++G**	M06–2X/6–311++G**
AB-1	−2.31	−3.02
AB-2	−1.99	−2.24
AB-3	−2.13	−2.79
AB2-1	−4.46	−5.76
AB2-2	−3.62	−4.24
AB2-3	−4.43	−6.02
AB3-1	−6.47	−8.54
AB3-2	−5.24	−6.07
AB3-3	−5.86	−7.84
AB4-1	−8.00	−9.81
AB4-2	−6.66	−7.77
AB4-3	−7.54	−10.12

The calculated IEs and its energy components are given in table 1. Similar findings have also been reported for the other complexes which are stabilized by the C–H... π interaction. In AB-1 complex, the contribution from dispersion energy is −7.02 kcal/mol. The electrostatic and repulsion energies are −2.24 and 5.41 kcal/mol, respectively. Although, the contributions from these interactions are different for other complexes, it is clear from the results that dispersion energy plays predominant role in the stabilization of the AB complexes. The difference in the electrostatic energy term may be attributed to the changes in the number of

Table 2. Calculated Interaction Energies (IEs) of various adamantane–benzene complexes at various levels of theories (kcal/mol).

System	M05–2X/aug-cc-pVDZ	M06–2X/aug-cc-pVDZ	MP2/aug-cc-pVDZ
AB-1	−2.20	−2.91	−3.85
AB-2	−1.82	−2.08	−3.62
AB-3	−2.15	−2.80	−3.69
AB-4	−1.32	−1.61	−2.74

C–H interaction with the π -ring. For example, the IE of AB-2 is similar to that of AB-3. However, the electrostatic contributions are different. In AB-2 complex, three C–H $^{\delta+}$ bonds interact with the π cloud whereas in AB-3 clusters, one C–H bond interacts with the aromatic ring. In both the cases exchange energy is repulsive in nature. In the case of AB-4 cluster, the two C–H bonds point towards π cloud in angular fashion and hence it is weak in nature as evident from the different contributions.

3.4 AIM analysis

The Bader's theory of atoms-in-molecule has been used to probe the hydrogen bonding and weak interactions in various systems.¹⁴ In this regard, Grabowski *et al.* have made significant contributions to the understanding of H-bonding in various systems using the theory of atoms in molecule.²² Parthasarathi *et al.* have shown that there is a linear relationship between the electron density and the Laplacian of the electron density values

Table 4. Calculated topological properties (a.u.) at the bond critical points of various adamantane–(benzene)_n complexes, obtained from M06–2X/6–31+G** level of theory^{a,b}.

	Label	$\rho(\rho_{\chi})$	$\nabla^2\rho(\rho_{\chi})$	G_c	V_c	H_c	G_c/V_c
AB-1	1	0.006	0.004	0.004	0.003	0.007	1.188
	2	0.006	0.004	0.004	0.003	0.007	1.165
	3	0.004	0.002	0.002	0.002	0.004	1.215
	4	0.004	0.002	0.002	0.002	0.004	1.215
AB-2	1	0.005	0.003	0.003	0.002	0.005	1.201
AB-3		0.007	0.005	0.005	0.004	0.008	1.194
AB2-1	1	0.004	0.003	0.002	0.002	0.004	1.21
	2	0.006	0.004	0.003	0.003	0.006	1.192
	3	0.004	0.002	0.002	0.002	0.004	1.218
	4	0.004	0.002	0.002	0.002	0.004	1.213
	5	0.005	0.004	0.003	0.003	0.006	1.189
	6	0.004	0.003	0.002	0.002	0.004	1.213
AB2-2	1	0.005	0.003	0.003	0.002	0.005	1.202
	2	0.004	0.003	0.002	0.002	0.004	1.206
AB2-3	1	0.006	0.005	0.004	0.003	0.007	1.186
AB3-1	1	0.004	0.003	0.002	0.002	0.004	1.211
	2	0.005	0.004	0.003	0.003	0.006	1.172
	3	0.004	0.002	0.002	0.002	0.004	1.217
	4	0.006	0.004	0.004	0.003	0.007	1.167
	5	0.004	0.003	0.002	0.002	0.004	1.216
	6	0.004	0.002	0.002	0.002	0.004	1.226
	7	0.004	0.002	0.002	0.002	0.004	1.221
	8	0.005	0.004	0.003	0.003	0.006	1.187
	9	0.005	0.004	0.003	0.003	0.006	1.186
	10	0.004	0.003	0.002	0.002	0.004	1.212
AB3-2	1	0.005	0.003	0.002	0.002	0.004	1.205
	2	0.005	0.003	0.002	0.002	0.005	1.205
AB3-3	1	0.007	0.005	0.005	0.004	0.008	1.192
AB4-1	1	0.004	0.002	0.002	0.002	0.004	1.223
	2	0.004	0.002	0.002	0.002	0.004	1.215
	3	0.004	0.003	0.003	0.002	0.005	1.187
	4	0.004	0.002	0.002	0.002	0.004	1.22
	5	0.004	0.002	0.002	0.002	0.004	1.218
	6	0.004	0.003	0.003	0.002	0.005	1.19
	7	0.004	0.002	0.002	0.002	0.003	1.224
	8	0.004	0.002	0.002	0.002	0.003	1.224
	9	0.004	0.003	0.002	0.002	0.004	1.174
	10	0.004	0.003	0.002	0.002	0.005	1.187
AB4-2	1	0.005	0.003	0.002	0.002	0.004	1.205
AB4-3	1	0.007	0.005	0.005	0.004	0.008	1.191

^aLabelling are shown in figure 3, ^ball values in *a.u.*

at the HBCP and the strength of H-bond and that there is a smooth change in the nature of interaction from van der Waals to classical H-bonding to strong H-bonding.²³

Further, it is an useful tool to quantify the strength of the interaction in terms of $\rho(r_c)$, $\nabla^2\rho(r_c)$, and ϵ values at the H-bonding bond critical points (HBCPs).²⁴ Hence, a detailed AIM analysis was carried out on various AB and AB_n (where n = 2–4) complexes. The calculated topological parameters are listed in the table 4. The calculated ranges of $\rho(r_c)$ and $\nabla^2\rho(r_c)$ values are 0.004 to 0.007 a.u. and 0.002 to 0.005 a.u., respectively.

These values are in the range stipulated by Ran *et al.* for saturated hydrocarbon-benzene interactions.²¹

The molecular graphs of various AB and AB_n (where n = 2–4) clusters are shown in figure 3 along with the labelling of bond paths. For each CH... π interaction, there exists a bond path linking the H atom of the adamantane with the carbon atom of the benzene. In figure 3, BCPs (bond critical points), RCPs (ring critical points) and CCPs (cage critical points) are represented as red, yellow and green circles, respectively. Similar topological features are found in other complexes. The AIM topological features of these complexes are similar

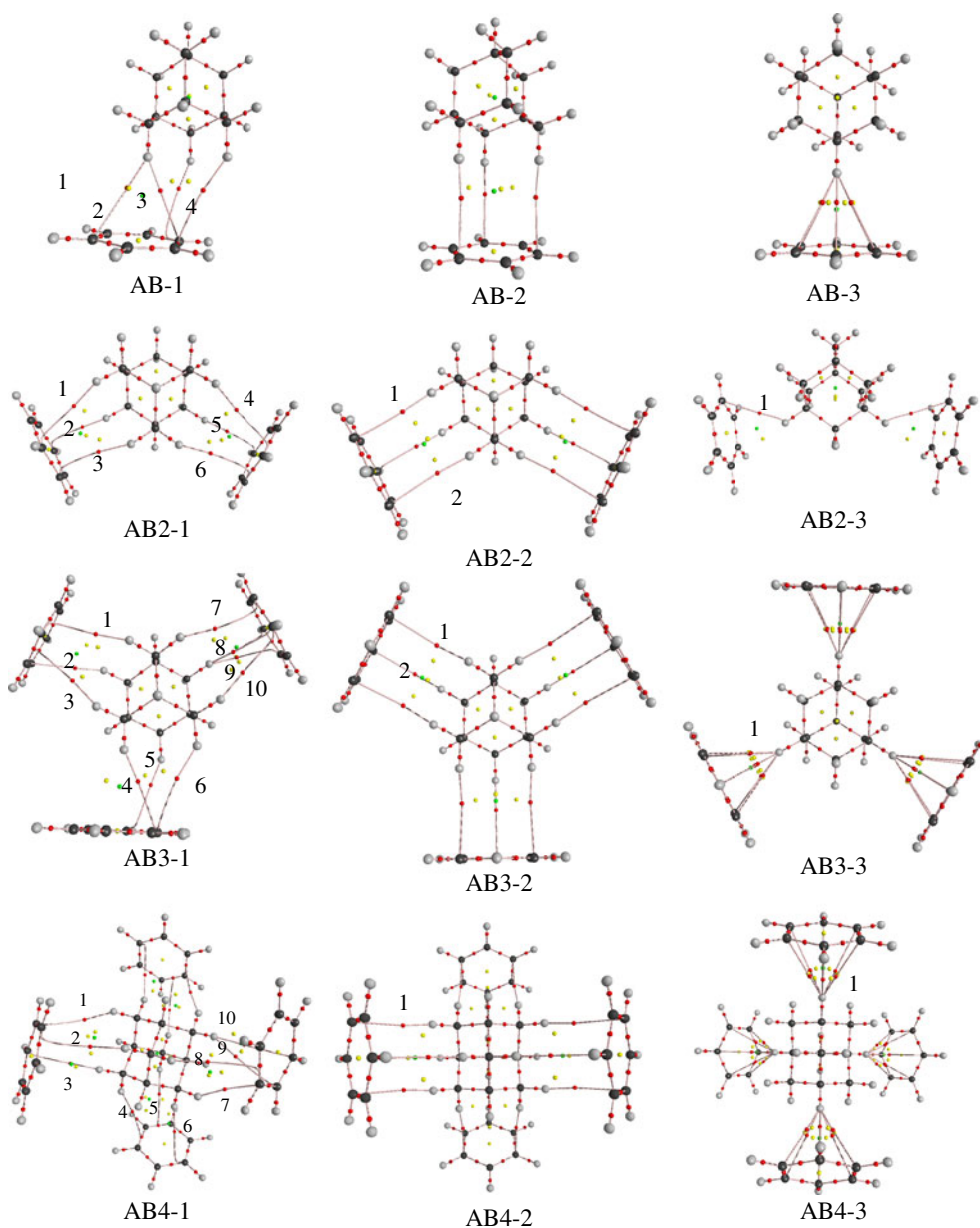


Figure 3. Molecular graphs of the various adamantane-(benzene)_n complexes.

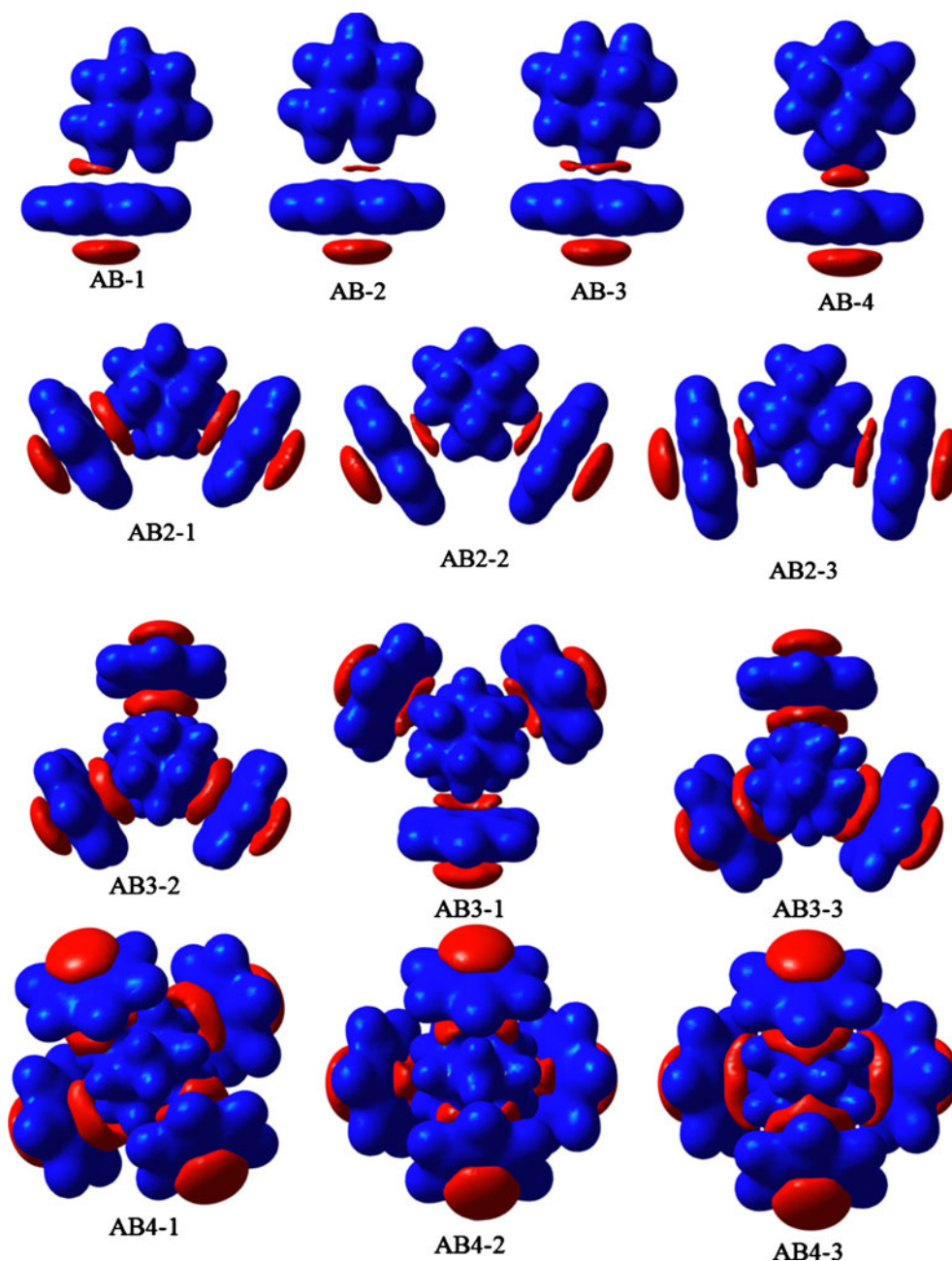


Figure 4. Molecular electrostatic potential maps of (isosurface value = 0.02 a.u.) of adamantane–(benzene)_n complexes calculated at M05–2X/6–31+G** level of calculation. Negative and positive potential are represented by red and blue colours, respectively.

to that of T-shaped benzene dimer wherein CH... π interaction stabilizes the T-shaped geometry.²⁵

The interatomic and intermolecular interactions are also studied in terms of local electron energy density (H_C) and its components, the local kinetic electron energy density (G_C) and local potential electron energy density (V_C) at the BCPs. The relation between these energetic parameters is given in Equation 1.

$$H_C = G_C + V_C. \quad (1)$$

Further, from virial theorem that

$$\frac{1}{4} \nabla^2 \rho_C = 2G_C + V_C. \quad (2)$$

The balance between the local kinetic electron energy density (G_C) and the local potential electron energy density (V_C) reveals the nature of the interaction. If the ratio, $-G_C/V_C$, is greater than one then the nature of the interaction is purely noncovalent. It can be seen for the AB_n complexes, positive values of H_C at BCP, and

the ratio of the kinetic electron energy density (G_C) and the potential electron energy density (V_C) are in the range from 1.165 to 1.226 which also further confirmed the existence of weak H-bond interaction between the two systems.

3.5 MESP analysis

Molecular electrostatic potential (MESP) analysis is an important tool for investigating the reactivity of a molecular system.²⁶ It gives an idea about the regions of electron localization in the molecule and therefore about the probable sites of electrophilic and nucleophilic attacks. The power of MESP in delineating non-covalent interaction has been well documented.²⁷ The MESP topographies of various adamantane-benzene complexes are shown in figure 4. Owing to the changes in the electrostatic potential features of the two interacting systems, their interaction patterns are also different.

4. Discussion

The intermolecular interactions in AB_n ($n = 1-4$) clusters were studied by using various electronic structure methods and were characterized by employing different tools such as energy decomposition analysis, MESP isosurfaces and the theory of AIM. Energy decomposition analysis reveals that the nature of interaction between adamantane and benzene is predominately dispersive in nature. The interplay of electrostatic interaction in the stabilization of various possible modes of interaction is evident from the energy decomposition analysis. It is also worth to note that the stability of the complex increases with the increase in the number of benzene molecules. The enhancement in the electron density at the BCPs between adamantane and benzene reassures the same findings. The results obtained from MESP analysis support similar observation, i.e. the MESP isosurface values increase from AB to AB_4 .

5. Conclusion

In summary, evidences show that adamantane favourably interact with benzene by forming C–H... π interaction. It is evident from the geometrical parameters and energetics that methine and methylene C–H groups of adamantane interact differently with benzene. Specifically, the strength of interaction of

methylene C–H group with benzene is stronger than that of methine C–H group. The four faces of the adamantane can interact simultaneously with four benzene rings. It is interesting to observe that the stability of the complexes increases with increase in the number of benzene molecules. The energy decomposition analysis of adamantane-benzene complexes using DMA approach shows that the origin of the stability primarily arises from the dispersive interaction. The theory of atoms in molecules (AIM) supports the existence of weak interaction between the two systems. The electrostatic topography features provide clues for the mode of interaction of adamantane with benzene.

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