Ab initio determination of the C₆H₆···CS₂ cluster stabilization energy

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Abstract

The benzene–carbon disulfide 1:1 complex has been investigated by means of ab initio methods. The electronic structure and the relative orientational molecular preferences in this system could be determined. The complex geometry was optimized using a DZ2P basis set (double \( \xi \) plus double polarization basis). Energy corrections for electronic correlation using the second-order Möller-Plesset perturbation theory (MP2) as well as for the basis set superposition error (BSSE) were applied. Calculations conducted to four minimum energy configurations between that proposed initially. The T-shaped structure, where the C₁ rotation axis coincides with the benzene C₆-axis, and the sandwich one, where the CS₂ is slipped over the benzene C₂-axis, passing between a C–C benzene bond were the most stable. The stabilization energy for these configurations was determined to be 0.519 and 0.541 kcal/mol, respectively. The results indicate the existence of weakly bound complexes between benzene and carbon disulfide for all the structures studied. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the last 20 years, van der Waals complexes have been the subject of many studies and some reviews [1,2], where theoretical and experimental advances have been reported for several systems. A large number of weakly bounded dimer [3], as well as simple heterodimers and those containing hydrocarbons [4,5] are related in the literature. Molecular complexes or clusters containing benzene can be classified as a kind of van der Waals complex [1,2]. They have attracted much interest as it has been suggested that interactions between aromatic moieties could play a key role in the conformation of chemical systems, as for instance, those observed in molecular biology [6–9].

Due to the lack of unambiguous experimental results for most of the benzene containing complexes, theoretical calculations have been performed [1,2]. Accurate values for the properties of different benzene clusters, for instance benzene···Ar, benzene···N₂, as well as for benzene dimer, have been obtained by means of non-empirical ab initio methods [1,2,8,9].

For the system containing benzene (C₆H₆) and carbon disulfide (CS₂), an early study gives the most provable C₆H₆···CS₂ structures based on semi-empirical calculation [10]. This theoretical work indicates a charge transfer from benzene to CS₂ for the most stable configuration.
Experimentally, the formation of transient clusters in liquid mixtures of \( \text{C}_6\text{H}_6 \) and \( \text{CS}_2 \) has been studied by means of far infrared studies [6,7]. Evidences of relatively strong intermolecular interaction in the mixtures are pointed out [7]. In addition, a few experimental works have suggested that the formation of gels of atatic polystyrene (aPS) in \( \text{CS}_2 \) may be due to complexation of sulfur atoms of \( \text{CS}_2 \) with the phenyl units on the polymer [11–14]. Gelation should occur when the two sulfurs can interact with phenyls of different polystyrene chains [14]. Although prototypical, the system, \( \text{C}_6\text{H}_6 \cdots \text{CS}_2 \) can constitute a reasonable reduced model, in relation to the intermolecular forces aging between the phenyls in aPS and the solvent \( \text{CS}_2 \).

The aim of the present work is to study the interaction of benzene–carbon disulfide 1:1 molecular complexes (\( \text{C}_6\text{H}_6 \cdots \text{CS}_2 \)), which can be related to van der Waals molecules, since it corresponds to a complex formed between two stable neutral monomers. An exact description of the system structure is required in order to reproduce all its properties, including geometry and stabilization energy. Therefore, in the present contribution, we have investigated through theoretical treatment probable \( \text{C}_6\text{H}_6 \cdots \text{CS}_2 \) structures with relation to their stability. The intermolecular interaction energy magnitude was established, and an idea about the interaction energy nature is pointed out.

### 2. Computational procedure

Calculations were performed with the CAD-PAC 5.2 program included on an Unichem3.1 package, employing a Cray-Supercomputer YMP-2E. A standard Dunning–Huzinaga DZ basis set \([12s8p1d,9s5p,4s]/[6s4p1d,4s2p,2s]\) was used [15,16]. Taking the non-polar character of both molecules in the cluster into account, it is reasonable to suggest dispersion energy as the major contribution to the intermolecular interaction. In this case, polarization functions are required in the basis set as well as consideration of correlation effects. Two polarization functions were added to the basis set for carbon (d functions with 1.6 and 0.4 exponents), hydrogen (p functions with 1.2 and 0.5 exponents) and sulfur (d functions with 0.67 and 0.23 exponents) in order to reproduce the quadrupole moment and the polarizability of the benzene and \( \text{CS}_2 \). The number of basis function totaled 274 in each case.

The determination of geometry of weakly bonded complex is not an easy task. The major difficulty arises from the significant influence of basis set superposition error (BSSE) in the interaction energy that could result in false minimum optimization in potential energy surface (PES). As no optimization procedure can be realized, including correction to BSSE, a set of proposed high probability regions of PES must be explored. The proposed structures were optimized at the Hartree–Fock level using the previously described DZ2P basis set. The geometry of all investigated \( \text{C}_6\text{H}_6 \cdots \text{CS}_2 \) complexes were fully optimized under the restriction of maintenance of the symmetry. For all the calculations reported herein, 16 GB of disc space and about \( 2 \times 10^5 \) CPU s were used. In order to include electronic correlation effects, the second order Möller-Plesset perturbation theory (MP2) was applied to each configuration, giving good estimates of the electronic correlation effects. Higher order MP theory could not be used because of the size of the clusters, as well as the basis set applied.

The interaction energy (\( \Delta E \)) of the \( \text{C}_6\text{H}_6 \cdots \text{CS}_2 \) clusters was evaluated as the difference between the total energy (\( E_{\text{C}_6\text{H}_6 \cdots \text{CS}_2} \)) of the optimized complexes and the benzene and carbon disulfide energies, \( E_{\text{C}_6\text{H}_6} \) and \( E_{\text{CS}_2} \), respectively. Taking the MP2 interaction correction energy \( E_{\text{COR}} \) into account, \( \Delta E \) becomes:

\[
\Delta E = \Delta E^{\text{SCF}} + \Delta E^{\text{COR}}.
\]

The basis set inconsistency, which arises because the basis function on one molecule adds flexibility to the basis set on the other molecule in the proposed structure [2], was taken into account. In order to correct BSSE, the counterpoise method was used, in which the molecular energies for benzene and carbon disulfide are calculated in the full heterodimer basis [2]. This method has been applied as the only accurate approach for such
a necessary correction [8]. Both interaction energy components $\Delta E^{\text{SCF}}$ and $\Delta E^{\text{COR}}$ were corrected for BSSE, and the overall BSSE was given by the sum of the SCF and COR parts.

Initially, a set of different configurations of the $1:1$ molecular $C_6H_6\cdots CS_2$ complexes was tested, but they converged to one of the four cluster structures given in Fig. 1: (a) the $C_\infty$ rotation axis of CS$_2$ lies along the $C_6$ axis of benzene. (b) The $C_\infty$ of CS$_2$ lies parallel to the plane of benzene and the $C_2$ axis of CS$_2$ coincides with the benzene-$C_6$ passing between the carbon–carbon atoms. (c) The CS$_2$ molecule is slipped over the $C_6H_6$ $C_2$-axis, passing between the carbon atoms, the carbon atom lies exactly above the $C$–$C$ bond of the benzene molecule. (d) The $C_\infty$ of CS$_2$ lies parallel to the plane of benzene where the $C_2$ axis of CS$_2$ coincides with the benzene-$C_6$, differently as in (b), and passes through the carbon–carbon benzene atoms.

A detailed potential energy surface investigation of the $C_6H_6\cdots CS_2$ clusters was not the aim of this work. The reason is that the calculation of points other than the minimal energy geometrical structure in each case should signify extremely high computational times.

3. Results and discussion

The optimized proposed configurations are depicted in Fig. 1a–d. The isolated optimized carbon disulfide and benzene structures are shown in Fig. 1e and f, respectively.

In the $C_6H_6\cdots CS_2$ clusters, the changes observed in the benzene bond lengths and angles have no experimental significance and can be considered equal to the isolated system. A bond length of 1.388 Å for the $C$–$C$ bonds, as well as 1.075 Å for the $C$–$H$ bonds in the aromatic

Fig. 1. Optimized proposed configurations of the $C_6H_6\cdots CS_2$ cluster structures (a–d) and the isolated CS$_2$ and $C_6H_6$ moieties (e and f).
molecule was calculated in all the cases. Table 1 gives the internal coordinates for carbon disulfide in the optimized structures. In the structures a and c (Fig. 1) the C–S bond lengths in CS₂ have their value modified in relation to the isolate moiety (structure e in Fig. 1). In both structures, a value of 1.540 Å for the C–S bond was found, whereas for the C–S₀ bond a length of 1.545 Å was obtained. The distance between the nearest sulfur atom and benzene ring plane in each structure was determined as being 3.9, 4.9, 4.0 and 4.9 Å for the structures a–d in Fig. 1, respectively. These results give the idea that, in the case of structures where a sulfur atom is placed through the benzene C₆ axis (a and c), the proposed geometry can be better stabilized. Shorter intermolecular distances are obtained, whereas different carbon–sulfur bond lengths in CS₂ can be related to relatively strong electronic interaction between benzene ring and the sulfur atom.

In the heterodimers b–d, where the carbon disulfide stays parallel to the benzene ring, a distortion of the S–C–S₀ angle could be expected. In fact, the S–C–S₀ angle becomes 179.80°, 179.82° and 179.79° in those structures. It is worth mentioning, for the T-shaped structure (Fig. 1a), the hydrogen atoms in the benzene are found to be out of the plane of the ring. They have been slightly attracted by the sulfur in the CS₂.

Total energies (E) for the four C₆H₆···CS₂ cluster configurations, as well as for the isolated C₆H₆ and CS₂ molecules are summarized in Table 2. The obtained cluster interaction energies, ΔE⁰ and ΔE¹COR, are given in Table 3, where the values corrected for BSSE can also be seen. At this point, some conclusions could be made.

According to the cluster interaction energies given in Table 3, the most stable configurations are given by a and c in Fig. 1. Considering room temperature, the Boltzmann distribution indicates the most probable configuration to be that of structure c in Fig. 1. It is easily understood by analysis of the cluster symmetry. Using ΔE corrected for correlation energy effects and BSSE, we have determined a distribution of 40.5% for the structure c, 6.9% for a, whereas for structure b and d, the distribution was 26.3%.

### Table 1

Internal coordinates for the CS₂ in the structures a–e, respectively, in Å and degrees

<table>
<thead>
<tr>
<th>Structures</th>
<th>Distances</th>
<th>Angle</th>
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<tbody>
<tr>
<td>C–S</td>
<td>C–S₀</td>
<td>S–C–S₀</td>
</tr>
<tr>
<td>a</td>
<td>1.540</td>
<td>1.545</td>
</tr>
<tr>
<td>b</td>
<td>1.540</td>
<td>1.542</td>
</tr>
<tr>
<td>c</td>
<td>1.540</td>
<td>1.544</td>
</tr>
<tr>
<td>d</td>
<td>1.542</td>
<td>1.542</td>
</tr>
<tr>
<td>e</td>
<td>1.542</td>
<td>1.542</td>
</tr>
</tbody>
</table>

### Table 2

Total energies, E⁰ and E¹COR (Hartree), for the 1:1 benzene–carbon disulfide cluster structures a–c, as well as for the isolated benzene and carbon disulfide molecules e and f depicted in Fig. 1

<table>
<thead>
<tr>
<th>Structures</th>
<th>E⁰</th>
<th>E¹COR</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-1063.645647</td>
<td>-1065.223591</td>
</tr>
<tr>
<td>b</td>
<td>-1063.644921</td>
<td>-1065.221483</td>
</tr>
<tr>
<td>c</td>
<td>-1063.644972</td>
<td>-1065.222780</td>
</tr>
<tr>
<td>d</td>
<td>-1063.644920</td>
<td>-1065.221476</td>
</tr>
<tr>
<td>e</td>
<td>-832.897103</td>
<td>-833.550397</td>
</tr>
<tr>
<td>f</td>
<td>-230.747773</td>
<td>-231.166919</td>
</tr>
</tbody>
</table>

### Table 3

Interaction energies, ΔE⁰ and ΔE¹COR (kcal/mol) with and without the correction for the BSSE for the 1:1 benzene–carbon disulfide cluster structures a–d depicted in Fig. 1

<table>
<thead>
<tr>
<th>Structures</th>
<th>ΔE Without correction for BSSE</th>
<th>Corrected for BSSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE⁰</td>
<td>ΔE¹COR</td>
</tr>
<tr>
<td>a</td>
<td>0.483</td>
<td>2.511</td>
</tr>
<tr>
<td>b</td>
<td>0.028</td>
<td>1.188</td>
</tr>
<tr>
<td>c</td>
<td>0.060</td>
<td>2.002</td>
</tr>
<tr>
<td>d</td>
<td>0.027</td>
<td>1.184</td>
</tr>
</tbody>
</table>
The interaction energy for the most stable C₆H₆···CS₂ configuration (structure c in Fig. 1) was 0.541 kcal/mol, corresponding to 188.87 cm⁻¹. The obtained ΔE values are compatible with those obtained for different benzene clusters in the literature, with a similar basis set at the MP2 level as, e.g., benzene···Ne (78 cm⁻¹) [2] and benzene···He (63 cm⁻¹) [2]. For benzene···N₂, the interaction energy depends strongly on the studied geometry [2]. Only values of ΔE for the sandwich symmetry are published at the MP2/DZ2P level, with ΔE = 577 cm⁻¹. In the case of the benzene dimer, for the most stable structures, namely the T-shaped, the parallelly-displaced and the sandwich one, the values of ΔE at the MP2/DZ2P level are given as 735.58, 794.58, and 297.79 cm⁻¹, respectively [2].

It is interesting to mention, at this point, the capability of aPS, which contains phenyl rings, to form physical gels in presence of CS₂. It has been shown that CS₂ promotes aPS gelation at the highest temperature, and, if the entanglements of the coils are necessary for gelation, an additional factor, which stabilizes the contacts between chains, is also required. The complete thermal reversibility of the gel temperature is another surprising feature in this system. The studies suggest that CS₂ and aPS build a polymer–solvent complex or a stoichiometric compound [11–14]. Without the solvent, physical links cannot be created. Experiments demonstrated that a part of the polymer chains are stiffened upon gelation [17]. We believe the situation is favored by the interaction between CS₂ and the phenyl rings of the atatic polystyrene, with a similar energy magnitude to those present in this work for the C₆H₆···CS₂ system.

The calculated electronic density of benzene and carbon disulfide in the clusters and of the isolated molecules, as well as the obtained dipole moment (μ) of the C₆H₆···CS₂ structures are given in Table 4. Analysis of the electronic density indicates the existence of electrostatic interaction between the molecular moieties. A charge transfer from benzene to carbon disulfide was observed for the structure a in Fig. 1. For the structure b–d a charge localization over the benzene molecule was observed. The charge transfer in this case occurs from carbon disulfide to benzene. For structure c, given in this work as the most stable, the charge coming from the CS₂ moiety is twice that of the structures a, b and d. The CS₂ localization in this case, where the molecule is slipped over the benzene C₂-axis passing between the carbon atoms, seems to favor the charge transfer, as expected according to the electron localization in the benzene and carbon disulfide molecules. The obtained intermolecular distances in structures a and c, smaller than those in b and d, can be also justified by taking the observed charge transfer behavior into account.

At this stage, it is reasonable to make some considerations about the character of the calculated C₆H₆···CS₂ energy interaction. Ab initio calculations do not explain the basic mechanism of the intermolecular interaction, but, as known, the energy interaction can be represented as [18]:

\[
\Delta E = E_{\text{electrostatic}} + E_{\text{induction}} + E_{\text{dispersion}} + E_{\text{repulsion}}.
\]

Table 4

<table>
<thead>
<tr>
<th>Structures</th>
<th>μ (Debye)</th>
<th>Electronic density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CS₂</td>
</tr>
<tr>
<td>a</td>
<td>0.47</td>
<td>-1.3</td>
</tr>
<tr>
<td>b</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>c</td>
<td>0.18</td>
<td>2.3</td>
</tr>
<tr>
<td>d</td>
<td>0.08</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Essentially, in bimolecular clusters involving electrons π, the π–π interactions should be controlled by electrostatic interactions. There are comments in the literature [18] suggesting the major energetic contributions to E total as coming from other factors. Mostly, interactions between two π-systems occur when the unfavorable contributions, e.g. π-electron repulsion, can be outweighed by attractive interactions between π-electrons and the σ-molecular framework [18]. In fact, the atomic properties in the intermolecular contact may control the strength of interactions.

According to the results in Table 3, in the C₆H₆···CS₂ cluster structure a, the interaction energy should be determined by major contributions.
of dispersion and induction, since applying MP2, a procedure that takes in account induction and dispersion effects, $\Delta E_{\text{SCF}+\text{COR}}$ is strongly increased. For the structure c, similar effects can be observed in the $\Delta E_{\text{SCF}+\text{COR}}$, when compared to $\Delta E_{\text{SCF}}$. Structures b and d, however, are only slightly affected by the MP2 treatment. This fact may signify that the electrostatic energy plays a significant role in the cluster stabilization in these cases.

This behavior can be better understood by analyzing the cluster geometry according to the $\pi$-electron localization in each case. In structures b and d, they are a face-to-face $\pi$-geometry, but the CS$_2$ carbon atom induces a $\pi$-deficient region ($\delta^+$) in interaction with the $\pi$-framework of the benzene ($\delta^-$). The result favors the attractive interactions, with electrostatic character. For the structures a and c, another way, a repulsive interaction may be predominant, since a “contact” between two regions with a high electronic density, around the sulfur atom and the benzene $\pi$ electrons respectively, has been induced by the cluster geometry. Therefore, the electrostatic repulsion to $\pi$-overlap dominates the interaction in the structures b and d, given lower values of $\Delta E$ than in a and c. The attractive electrostatic interaction between the partially positive charged carbon atom in CS$_2$ and the benzene $\pi$-framework may contribute for the geometry stabilization in a and c.

Similar to the benzene dimer [9], in the C$_6$H$_6$···CS$_2$ complex, quadrupole–quadrupole interactions are responsible for most of electrostatic interactions, and such contributions cannot be evaluated explicitly by the calculations performed in this work. However, some considerations can be made by analysis of the $\Delta E$ values corrected for BSSE in Table 3. While $\Delta E_{\text{SCF}}$ is related to quadrupole–quadrupole interactions, $\Delta E_{\text{SCF}+\text{COR}}$ shows that the interaction energy has been influenced by van der Waals forces. In this way, the predominant forces stabilizing structures a and c seem to be of the van der Waals kind, and they are more important in structure a, where they are twice the quadrupole. For structures b and d, quadrupolar interactions determine the cluster geometry.

The results given above indicate the existence of weakly bound complexes between benzene and carbon disulfide. The structure where the C$_\infty$ rotation axis of CS$_2$ lies along the C$_6$ axis of benzene is stabilized mainly by van der Waals interactions. In the other cases, where the C$_\infty$ of CS$_2$ lies parallel to the plane of benzene, electrostatic interactions play a dominant role in the cluster stabilization.

The obtained magnitude for benzene–carbon disulfide energy interaction lies between those previously calculated for clusters of benzene–noble gases, benzene–nitrogen as well as benzene homodimer.

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