

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/229112755>

MP2 ab initio calculations of the hexafluorobenzene—benzene and —monofluorobenzene complexes

ARTICLE *in* CHEMICAL PHYSICS LETTERS · FEBRUARY 1997

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(96)01450-9

CITATIONS

38

READS

12

4 AUTHORS, INCLUDING:



Fernando Colmenares

Universidad Nacional Autónoma de...

14 PUBLICATIONS 106 CITATIONS

SEE PROFILE



Miguel Costas

Universidad Nacional Autónoma de...

105 PUBLICATIONS 2,066 CITATIONS

SEE PROFILE

MP2 ab initio calculations of the hexafluorobenzene–benzene and –monofluorobenzene complexes

J. Hernández-Trujillo ^a, F. Colmenares ^a, G. Cuevas ^b, M. Costas ^a

^a *Departamento de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, México D.F. 04510, Mexico*

^b *Instituto de Química, Universidad Nacional Autónoma de México, Apdo. Postal 70-123, México D.F. 04510, Mexico*

Received 24 October 1996; in final form 3 December 1996

Abstract

Interaction energies for the C_6F_6 – C_6H_6 and C_6F_6 – C_6H_5F supermolecules have been investigated through pseudopotential SCF-MP2 calculations. For both systems, a minimum in the interaction energy curve was found. For C_6F_6 – C_6H_6 this is in agreement with experimental evidence for the formation of a complex, while for C_6F_6 – C_6H_5F the calculated interaction energy suggests the existence of this less symmetric complex. Well defined minima were obtained for the interaction energy curves only after the inclusion of electron correlation. However, the difference between the stabilization energies of the two complexes is determined by the electrostatic contribution.

1. Introduction

Weak interactions between aromatic molecules have been studied at both the theoretical and experimental levels. One of the most interesting systems is that formed by benzene and hexafluorobenzene. For this mixture, it has been shown that there is an associated species (complex) between these molecules in the solid state. This C_6F_6 – C_6H_6 complex has been characterized using several experimental techniques. The solid–liquid phase diagram [1] gives clear evidence of the 1:1 complex formation in the solid state. A detailed X-ray study [2] of C_6D_6 + C_6F_6 in the 1:1 mixture has shown that the data are best explained by a crystal structure consisting of molecular pairs of C_6D_6 and C_6F_6 packed in a face-to-face manner with an intermolecular distance of 3.52 and 3.71 Å for the separation amongst dimers, which are stacked in infinite columns. This packing differs markedly from that found in the pure

solids, where the aromatic rings are oriented perpendicular to each other [3,4]. The relatively weak nature of the C_6F_6 – C_6H_6 interaction has been revealed by magic angle D and ¹³C NMR solid-state studies [5]. It appears that the existence of a C_6F_6 – C_6H_6 complex in the solid state has been shown conclusively. In the liquid state, the existence of this complex has been suggested on the basis on thermodynamic evidence [6–8]. A detailed neutron and x-ray diffraction study [9] of the C_6F_6 – C_6H_6 mixtures indicated the existence of the complex in the liquid state, and suggested a reorientation from the mutually perpendicular geometry in the pure components to a nearly parallel alignment of the molecules in the 1:1 complex with 3.7 Å for the intermolecular distance. This supports the hypothesis of complex persistence in the liquid phase.

The molecular configuration of the C_6F_6 – C_6H_6 complex has been less studied at the theoretical level. A simple electrostatic model [9–11] indicates

that (i) the dimer is formed mainly through quadrupole–quadrupole interactions and (ii) the most stable molecular arrangement is that where both aromatic rings are parallel to each other. On the other hand, it is well known that SCF calculations fail to describe properly many weak interacting systems [12,13]. In particular, this has been found for the benzene dimer, for which only at the all-electron SCF-MP2 level of calculation does the interaction energy [14] agree with that obtained in jet cooling experiments [15,16]. Therefore, the inclusion of electron correlation could play an important role in the study of the type of systems considered in this work. However, at the present time, these highly computer-demanding all-electron calculations can not be readily performed. In this context, it is important to mention that several types of density functional theory (DFT) calculations, which represent a viable computational alternative, fail to produce the expected minimum in the potential energy curve for the C_6F_6 – C_6H_6 and C_6H_6 – C_6H_6 dimers [17]. This conclusion has also been reached for the benzene–benzene dimer [18]. These DFT failures are in agreement with reports [19,20] which indicate that the present density functionals are not able to describe weak interactions properly. Pseudopotential methods have not been used to study this kind of dimeric aromatic system; when substituted benzenes are included, this approach is an attractive alternative, since the detailed treatment of only the valence electron space allows going beyond SCF. In order to study the C_6F_6 – C_6H_6 intermolecular interaction, i.e. the stability of the dimer, closed-shell ab initio pseudopotential calculations including electron correlation at the MP2 level of theory have been carried out. For comparison, ab initio calculations on the C_6F_6 – C_6H_5F complex are reported. All calculations were done using the Gaussian 92 program [21] on a Cray Y-MP4 supercomputer.

2. Basis sets and pseudopotentials

The pseudopotentials and basis sets used here for the different atoms were chosen considering the feasibility of the calculation. For carbon and fluorine atoms the averaged relativistic effective potentials and basis set proposed by Pacios and Christiansen

[22] were used. The (4s4p) primitive gaussian basis sets that include only the 2s and 2p subshells in the valence space, were contracted to a [2s2p] double-zeta type basis sets. For the carbon atom, d-type polarization functions [23] were included as suggested by Pacios et al. [24]. For each monomer, experimental molecular distances and angles were used [25–27] and only singlet states were considered. Polarization functions for fluorine atoms are not included and hence for the C_6F_6 – $C_6H_{6-n}F_n$ ($n = 0, 1$) supermolecule calculations, polarization functions were added only to carbon atoms.

3. Results and discussion

For the calculation of the intermolecular interaction energies $\Delta E = E_{\text{dimer}} - \sum E_{\text{monomer}}$, several molecular arrangements for each complex were chosen. In Fig. 1 the different molecular arrangements considered are presented. In all cases, the calculations were performed including the standard counterpoise correction [28], and only singlet states were considered. In addition, the molecular geometry for each fragment was frozen at experimental values. The calculated interaction energies for C_6F_6 – C_6H_6 in the different molecular arrangements reveal that the face–face, and the mutually perpendicular structures are attractive and repulsive, respectively. The MP2 interaction energies for the eclipsed structures are presented in Fig. 2 and Fig. 3; for the face–face staggered orientations the energy at the minimum of the eclipsed geometry is not significantly lower (less than 0.05 kcal). For the two dimers in Fig. 2 and Fig. 3, relative minima with respect to the free fragments are found. Also, for comparison, corresponding SCF interaction energies calculated with the same pseudopotentials and basis sets are presented.

For the C_6F_6 – C_6H_6 complex, the presence of a minimum in the interaction energy curve is in agreement with the experimental evidence for the formation of a complex; also, the face–face molecular arrangement found here as the most stable one agrees with the available solid and liquid state experimental results. The minimum in the potential energy curve at the MP2 level in Fig. 2 is located at 3.7 Å, in excellent agreement with the experimental 3.5 and 3.7 Å intermolecular separation for the complex in

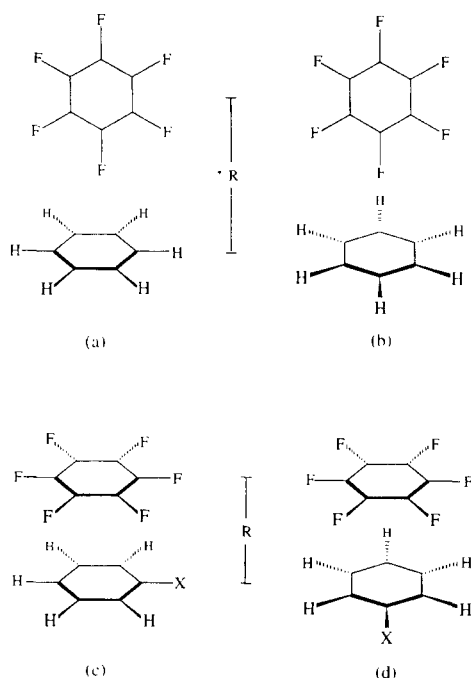


Fig. 1. Molecular arrangements considered in the $C_6F_6-C_6H_6-nF_n$ ($n = 0, 1$) supermolecule calculations: (a) perpendicular eclipsed, (b) perpendicular staggered, (c) face-face eclipsed and (d) face-face staggered. For (c) and (d), $X = H$ or F ; R is the distance between the centres of mass.

the solid [2] and liquid [9] states, respectively. These results suggest that the MP2 interaction energy value obtained (-4.33 kcal/mol) could be reliable. Unfortunately, there is no experimental value to compare with this calculated depth of the potential energy well. However, it can be stated that the $C_6F_6-C_6H_6$ interaction is of a weak nature. The flat curve obtained at the SCF level gives a minimum that is not reliable since this small interaction energy can well lie in the sensitivity limit of the method; moreover, this minimum occurs at an intermolecular distance which is too large compared with the experimental values. The situation for the $C_6F_6-C_6H_5F$ complex in Fig. 3 is similar to that for $C_6F_6-C_6H_6$; here, a minimum is also obtained at the MP2 level at a slightly larger distance (3.75 Å) with a smaller interaction energy (-3.49 kcal mol $^{-1}$). Again, the SCF calculations produced a small depth for the potential well occurring at a larger distance than for the MP2 calculations.

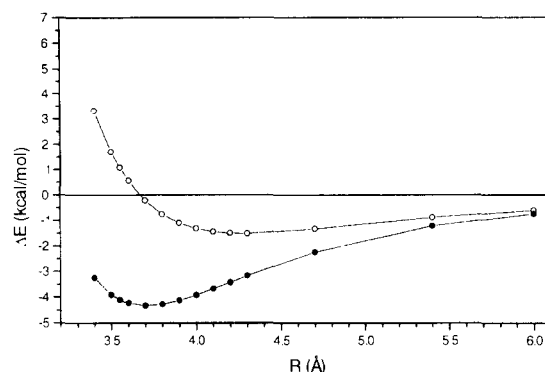


Fig. 2. Interaction energy for the $C_6F_6-C_6H_6$ complex at the eclipsed face-face orientation at different distances between the centres of mass: (—○—) SCF and (—●—) MP2. The interaction energy at the minimum is -4.33 kcal/mol occurring at 3.7 Å.

It is interesting to analyse the contributions to the total interaction energy $\Delta E = \Delta E^{SCF} + \Delta E^{CORR}$. The values for ΔE^{SCF} and ΔE^{CORR} for the two complexes obtained at the MP2 equilibrium geometry are given in Table 1. According to these values (i) it is the inclusion of the electron correlation i.e. the dispersion interaction between uncorrelated monomers [28], that produces a well defined minimum in the interaction energy curves; in other words, if the interaction were purely electrostatic, the SCF results should have already provided a proper description of the complexes, and (ii) it is ΔE^{SCF} , which is responsible for the difference in total interaction energy between the two studied systems. It appears that if

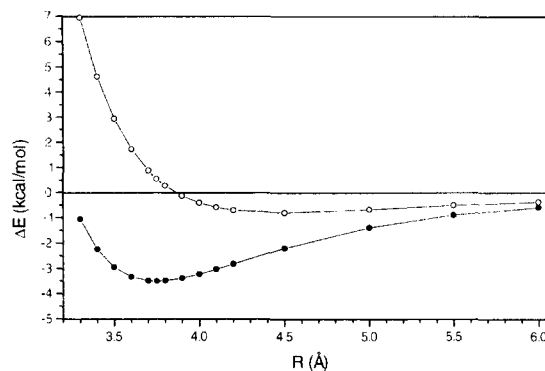


Fig. 3. Interaction energy for the $C_6F_6-C_6H_5F$ complex at the eclipsed face-face orientation at different distances between the centres of mass: (—○—) SCF and (—●—) MP2. The interaction energy at the minimum is -3.49 kcal/mol occurring at 3.75 Å.

Table 1

SCF and electron correlation contributions to the total interaction energy for the $C_6H_6-C_6F_6$ and $C_6H_5F-C_6F_6$ complexes^a

Complex	ΔE^{SCF}	ΔE^{CORR}
$C_6H_6-C_6F_6$	-0.22	-4.11
$C_6H_5F-C_6F_6$	+0.57	-4.06

^a Energy contributions (kcal/mol) calculated at the equilibrium geometry at the MP2 level.

one wishes to achieve a qualitative comparison between the stabilization energies of the two complexes, it is enough to estimate the corresponding electrostatic contribution. For this reason, the simple electrostatic model [9–11] agrees with the MP2 results; in this simple model, since the quadrupole moment of C_6H_6 is more negative than that of C_6H_5F , the $C_6H_6-C_6F_6$ interaction is stronger than the $C_6F_6-C_6H_5F$ one, as found here. This same trend is observed in the interaction enthalpies obtained through heat capacity measurements [29] in the liquid state. Although an ab initio interaction energy can not be compared with thermodynamic data in a straightforward way, the common trend might indicate that the results here could well characterize, at the microscopic level, the macroscopic thermodynamic results.

4. Conclusions

Using SCF-MP2 ab initio calculations, a minimum in the interaction energy curve was found for the systems $C_6F_6-C_6H_6$ and $C_6F_6-C_6H_5F$. For $C_6F_6-C_6H_6$ this is in agreement with experimental evidence for the formation of a complex between these two aromatic molecules; the minimum in the potential energy curve is located at 3.7 Å in excellent agreement with experiment and with an interaction energy of -4.33 kcal/mol which, as expected, corresponds to a weak interaction. For $C_6F_6-C_6H_5F$ our results indicate that the complex must exist, in agreement with recent experimental evidence [29]. The MP2 interaction energies were compared against the corresponding SCF values using the same pseudopotentials and basis set. From this comparison, it appears that the inclusion of electron correlation is essential to obtain a well defined minimum in the

interaction energy curve. On the other hand, it is the electrostatic contribution which determines the difference in stability between the different complexes. Clearly, generalization of this statement to other complexes formed between aromatic molecules requires further work.

Acknowledgements

We gratefully acknowledge the financial support of the Consejo Nacional de Ciencia y Tecnología (grant E-3904) and Proyecto de Super Computo UNAM-CRAY (grant SC-101294). JHT thanks financial support from Fundación UNAM and CONACYT. We extend our appreciation to Rebecca Silveston for her interest in this work in its early stages.

References

- [1] W.A. Duncan and F.L. Swinton, *Trans. Faraday Soc.* 62 (1966) 1082.
- [2] J.S.W. Overell and G.S. Pawley, *Acta Cryst.* B38 (1982) 1966.
- [3] E.G. Cox, D.W.J. Cruickshank and J.A.S. Smith, *Proc. Roy. Soc.* 247 (1958) 1.
- [4] N. Boden, P.P. Davis, C.H. Stam and G.A. Wesselink, *Mol. Phys.* 25 (1973) 81.
- [5] M.J. Duer, *J. Chem. Soc. Faraday Trans.* 89 (1993) 823.
- [6] A.K. Masood, A.M. North, R.A. Pethrick, M. Towland and F.L.J. Swinton, *J. Chem. Thermodyn.* 9 (1977) 133.
- [7] D.V. Fenby and R.L. Scott, *J. Phys. Chem.* 71 (1967) 4103.
- [8] W.A. Duncan, J.P. Sheridan and F.L. Swinton, *Trans. Faraday Soc.* 62 (1966) 1090.
- [9] E. Bartsch, H. Bertagnolli and P. Chieux, *Ber. Bunsenges. Phys. Chem.* 90 (1986) 34.
- [10] N.M.D. Brown and F.L. Swinton, *J. Chem. Soc. Chem. Commun.* (1974) 770.
- [11] J. Hernández-Trujillo, M. Costas and A. Vela, *J. Chem. Soc. Faraday Trans.* 89 (1993) 2441.
- [12] R.G. Gordon and Y.S. Kim, *J. Chem. Phys.* 56 (1972) 3122.
- [13] A.D. Buckingham, P.W. Fowler and J.M. Hutson, *Chem. Rev.* 88 (1988) 963.
- [14] P. Hobza, H.L. Selzle and W.W. Schlag, *J. Am. Chem. Soc.* 116 (1994) 3500.
- [15] T. Ebata, M. Hamakado, S. Moriyama, Y. Morioka and M. Ito, *Chem. Phys. Lett.* 199 (1992) 33.
- [16] W. Scherzer, O. Krätzschmar, H.L. Selzle and W. Schlag, *Z. Naturforsch.*, 47a (1992) 1248.
- [17] This laboratory, unpublished results.

- [18] E.J. Meijer and M. Sprik, *J. Chem. Phys.* 105 (1996) 8684.
- [19] S. Kristyán and P. Pulay, *Chem. Phys. Lett.* 229 (1994) 175
- [20] J.M. Pérez-Jordá and A.D. Becke, *Chem. Phys. Lett.* 233 (1995) 134.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, *Gaussian 92/DFT Revision F.3* (Gaussian, Inc., Pittsburgh, PA).
- [22] L. Fernández Pacios and P.A. Christiansen, *J. Chem. Phys.* 82 (1985) 2664
- [23] P.C. Hariharan and J.A. Pople, *Theoret. Chim. Acta* 28 (1973) 213.
- [24] L. Fernández Pacios and P.C. Gómez, *Int. J. Quantum Chem.* 49 (1994) 817.
- [25] K. Tamagawa, T. Iijima and M. Kimura, *J. Mol. Struct.* 30 (1976) 243.
- [26] A. Almenningen, O. Bastiansen, R. Seip and H.M. Seip, *Acta Chem. Scand.* 18 (1964) 2115.
- [27] L. Nygaard, I. Bojensen, T. Pedersen and J. Rastrup-Andersen, *J. Mol. Struct.* 2 (1968) 209.
- [28] J.H. van Lenthe, J.G.C.M. van Duijneveldt-van de Rijdt and F.B. van Duijneveldt, in: *Advances in Chemical Physics*, vol. LXIX, ed. K.P. Lawley (John Wiley, 1987) p. 521.
- [29] S. Pérez-Casas and M. Costas, unpublished results.