

Direct Measurement of the Stability of the Supramolecular Synthron $C_6H_6 \cdot C_6F_6$ Wim Vanspeybroeck,[†] Wouter A. Herrebout,[†] Benjamin J. van der Veken,^{*,†} Jan Lundell,[#] and Robin N. Perutz[‡]

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The 1:1 complex between benzene and hexafluorobenzene has been studied in liquid krypton. Molecular dynamics simulations on the solutions predict that the lifetime of the complex varies between 33(20) ps at 126 K and 17(5) ps at 158 K, long enough to allow detection of the complex by infrared spectroscopy. Infrared spectroscopy in the 125–165 K temperature range of solutions in liquid krypton containing hexafluorobenzene and benzene, benzene- d_1 , *sym*-benzene- d_3 , or benzene- d_6 reveal the presence of bands due to the complex. From an analysis of the spectra as a function of temperature, the complexation enthalpy in solution was determined to be $-6.0(2)$ kJ mol⁻¹. The liquid-phase complexation enthalpy was transformed into a gas-phase value of -12.3 kJ mol⁻¹ by correcting for the solvent influences using free energy perturbation theory Monte Carlo simulations of the solutions. Ab initio calculations, at the MP2/6-31G(d) level, predict a complexation energy of -16.8 kJ mol⁻¹ and show that the complex has C_s symmetry with the two aromatic rings slightly shifted and tilted away from 6-fold symmetry. A critical comparison of the ab initio frequencies with experimentally observed complex bands confirms literature data on the failure of the out-of-plane force field for benzene at the ab initio level employed.

Introduction

The interest in the complex between benzene and hexafluorobenzene is connected with the need for a better understanding of the intermolecular interactions between aromatic compounds, which are of great importance in many biochemical systems and in supramolecular chemistry.^{1–9} As a consequence, ever since the early work of Patrick and Prosser in 1960,¹⁰ this adduct has been the subject of intense research, involving a variety of experimental techniques.

Clear evidence for an attractive interaction between C_6H_6 and C_6F_6 was reported by Duncan and Swinton.¹¹ These authors studied the phase diagram of the binary system C_6H_6/C_6F_6 and found that the melting point of the 1:1 mixture is considerably higher than those of the pure components. More recently, the phase behavior of C_6H_6/C_6F_6 mixtures was studied by Monte Carlo simulations, which point at a cooperative effect enhancing the stability of the 1:1 solid.¹² Three solid-state phase transitions were detected for this solid, equimolar compound.^{13,14} The structures of the different phases have been investigated using X-ray and neutron diffraction.^{15,16} These studies show that in each of the phases the molecules are stacked in columns of alternating C_6H_6 and C_6F_6 molecules with the molecular planes parallel to each other. Molecular beam electric deflection studies¹⁷ have shown that in the $(C_6H_6)_2$ and $(C_6F_6)_2$ isolated dimers the molecular planes are oriented perpendicular to each other in a so-called T-structure, whereas in the $C_6H_6 \cdot C_6F_6$ complex the molecular planes are very nearly parallel. Similar results were obtained in the liquid phase by using neutron diffraction.¹⁸

The geometries of $(C_6H_6)_2$, $(C_6F_6)_2$, and $C_6H_6 \cdot C_6F_6$ were interpreted by considering the electrostatic quadrupole–quadrupole interaction between the aromatic monomers.¹⁹ The quadrupole moments of benzene and hexafluorobenzene are approximately equal in magnitude but have opposite signs,²⁰ owing to the presence of the six electronegative fluorine atoms in C_6F_6 . On the basis of these quadrupoles, electrostatic theory predicts a structure in agreement with the experimentally observed one. This suggests that the quadrupole–quadrupole interaction is the dominant structure-determining factor.

The $C_6H_6 \cdot C_6F_6$ adduct has also been studied using quantum mechanical calculations.^{21–23} With the geometry of the complex constrained to C_{6v} symmetry to simplify the calculations, pseudopotential-SCF-MP2 calculations²³ predict that the distance between the parallel aromatic rings equals 3.7 Å and that the dissociation energy has a value of $\Delta E = -18.13$ kJ mol⁻¹. Calculations at the MP2 = full/6-31G(d,p) and the MP2 = full/6-31G(d)(0.25) level, again for a fixed C_{6v} geometry, resulted in a van der Waals distance of 3.6 Å and a dissociation energy of -15.5 and -15.7 kJ mol⁻¹, respectively.^{21,22}

Despite the intense research attention for $C_6H_6 \cdot C_6F_6$, very few experimental data on the interaction energy between the monomers are available in the literature. The enthalpy of formation at 273 K of the solid complex from the solid monomers was estimated at $+1$ kJ mol⁻¹ using data from differential scanning calorimetry,¹³ suggesting that the complex must owe its stability to entropic contributions. More recently, aromatic–aromatic interactions were studied through room temperature heat capacity measurements.²⁴ The systems investigated include solutions of benzene and hexafluorobenzene in liquid *n*-heptane. The authors were able to derive an estimate of the association enthalpy for $C_6H_6 \cdot C_6F_6$ equaling $-9.1(9)$ kJ mol⁻¹. Because of the different environments in which the

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complex was investigated, it is rather difficult to compare these two enthalpies. Moreover, the indirect way in which they were measured may well have introduced some hidden uncertainty. To get a clearer picture of the interaction energy, therefore, in this study, we have set out to determine the complexation enthalpy in a more direct spectroscopic way. To this end, the formation of the complex in liquid krypton, in the temperature range between 126 and 158 K, was investigated theoretically by molecular dynamics simulation and experimentally using infrared spectroscopy. From a temperature-dependent study of the infrared spectra, the standard complexation enthalpy in liquid krypton was determined. This quantity was subsequently transformed into a vapor-phase enthalpy by correcting for the solvent influences using Monte Carlo simulations of the liquid phase. Also, a number of ab initio calculations on monomers and complex were performed.

Experimental Section

The infrared spectra were recorded on a Bruker 66v vacuum interferometer equipped with a globar source, a Ge/KBr beam splitter, and a liquid nitrogen cooled MCT detector. The spectra were obtained with a resolution of 0.5 cm^{-1} from interferograms averaged over 200 or 500 scans, apodized using the Blackmann–Harris 3-term, and Fourier transformed using a zero filling factor of 4. Areas of absorption bands were determined from least-squares band fitting procedures using Voigt functions.

The solutions were investigated in a brass cell of 1 cm path length, equipped with silicon windows, that is suspended in a vacuum shroud. The cell is cooled with boiling liquid nitrogen and is connected to a manifold for filling and evacuation. Solutions were prepared by first condensing the monomers in the cooled cell, followed by condensation of the solvent gas krypton. The latter process causes strong turbulence, so no extra mixing is required.

The solvent gases, argon and krypton, were supplied by l'Air Liquide and had stated purities of 99.9999% and 99.9995%, respectively. Hexafluorobenzene, benzene, benzene- d_6 , benzene- d_1 , and benzene-1,3,5- d_3 were obtained from Aldrich with a purity of 98% or higher. All samples were used without further purification.

The molecular dynamics calculations were executed with the software package Moldy.²⁵ Monte Carlo simulations were performed using a modified version of Boss 4.1.²⁶ Ab initio calculations were made with Gaussian 98.²⁷

Results

Molecular Dynamics Calculations. The literature ab initio interaction energies between benzene and hexafluorobenzene are of a magnitude from which it could be anticipated that the complex should be observable in typical cryosolutions.²⁸ The latter are no exception to the rule that the complexation enthalpy in solution is smaller than that in vacuo. This is due to solvation: upon formation of the complex in solution, part of the solvation shell must be removed to allow contact between the monomers. This gives a reduction in stability, which, despite the weakly interacting solvents used, can be significant for the type of weak complexes studied here. For $\text{C}_6\text{H}_6\cdot\text{C}_6\text{F}_6$, the area over which the monomers are in contact is considerable, which means that an important fraction of the solvation shell must be removed. It cannot be assumed a priori that this does not reduce the stability, and therefore its concentration, to such an extent that the complex can no longer be observed using cryospectroscopy. Because a reduction in stability corresponds to a decrease in the average lifetime of the complex, the feasibility

of a cryosolution infrared study was investigated by calculating this lifetime using molecular dynamics simulation.

The time correlation function that determines the profile of a typical infrared band is characterized by a relaxation time on the order of 1–2 ps. Hence, if the vibrational transitions of a weak complex are not to escape detection as a consequence of excessive broadening, the average lifetime of the species should not be smaller than a few picoseconds. The system investigated consisted of a cubic box containing one molecule of C_6H_6 , one molecule of C_6F_6 , and 198 krypton atoms. Simulations were carried out at 126, 142, and 158 K. All simulations were run in the NVT ensemble, while the temperature was controlled explicitly by using a Nosé–Hoover thermostat.²⁹ The solvent–solvent and solute–solvent interactions were described using Lennard-Jones atom–atom potentials. The interactions between C_6H_6 and C_6F_6 were modeled using a combination of Lennard-Jones atom–atom potentials and charge–charge interactions. The parameters of the Lennard-Jones potentials and the atomic charges were taken from the OPLS-AA force field.³⁰

The critical characteristic in the simulation is the interaction potential between benzene and hexafluorobenzene. For the potential used here, the well depth for the approach with parallel rings, at a ring separation of 3.6 Å, equals -21.7 kJ mol^{-1} . This value is somewhat higher than the ab initio complexation energies in the literature, which range from -15 to -18 kJ mol^{-1} . However, the interaction potential has to reflect the situation at temperatures in the 126–158 K interval. This requires zero-point and thermal corrections to be applied to the ab initio energy, which increase its value by several kilojoules per mole, bringing it closer to the above OPLS-AA value. Moreover, as will be pointed out below, the literature ab initio energies may not be fully reliable. Therefore, we have preferred to use the potential as derived.

For all solutions studied, a trajectory of 30×10^6 time steps was calculated, using a time step of $0.5 \times 10^{-3}\text{ ps}$. During each calculation, the distance between the centers of mass, r_{CM} , of the two aromatic molecules in the box was registered. This procedure eventually yields a plot of r_{CM} as a function of time. Typical plots for a solution in liquid krypton are shown in Figure 1. It can be seen that at certain moments the intermolecular distance drops rapidly to values below 4.0 Å, after which the two molecules remain trapped for a while in an attractive interaction. This signals that a complex is being formed. An r_{CM} value of around 4.0 Å can only be reached when the aromatic rings are parallel, or very nearly so. Thus, the molecular dynamics calculations show that the complex has a structure in agreement with the experimental data discussed in the Introduction. It can be seen that after some time the intermolecular separation suddenly rapidly increases, corresponding to dissociation of the complex.

By choosing a value for the limiting distance below which complex formation may be assumed, the average lifetime of the complex can be defined as the average time the molecules spend at center-of-mass separations smaller than that limiting distance. This distance was taken to be the position of the first minimum in the radial distribution function, which describes the probability distribution of the r_{CM} distances. The limiting distances derived from the simulations are given in Table 1, and they are indicated in Figure 1 by solid horizontal lines. The average lifetimes derived using these distances are also given in Table 1. In line with expectation, it can be seen that the lifetime decreases from 33(20) ps at 126 K to 17(5) ps at 158 K. It is clear, however, that in all cases the lifetimes are much larger than the relaxation time of 1–2 ps that determines the

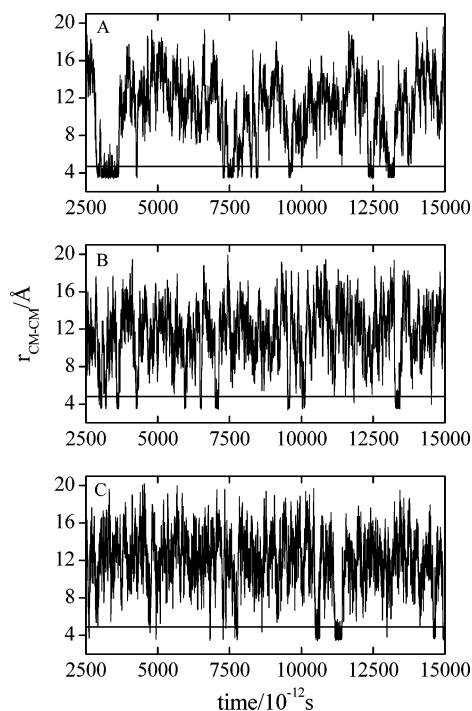


Figure 1. The center of mass/center of mass intermolecular benzene–hexafluorobenzene distance as function of time calculated by molecular dynamics simulation for solutions in liquid krypton at (A) 126, (B) 142, and (C) 158 K.

TABLE 1: Limiting Distances between Benzene and Hexafluorobenzene^a and Average Lifetimes for the 1:1 Complex in Liquid Krypton

| <i>T</i> (K) | limiting distance (Å) | lifetime (ps) |
|--------------|-----------------------|---------------|
| 126 | 4.7 | 33(20) |
| 142 | 4.8 | 20(11) |
| 158 | 4.9 | 17(5) |

^a Derived from the radial distribution functions, see text.

width of a typical infrared band. Hence, these simulations predict that lifetime broadening is not the limiting factor for the detection of the complex in solution.

Vibrational Spectra. The monomers C_6H_6 , C_6D_6 , and C_6F_6 have D_{6h} symmetry, for which one a_{2u} and three e_{1u} normal coordinates give rise to infrared active fundamentals. This limited number of allowed fundamentals evidently limits the number of complex bands that can be expected. Supporting evidence for the formation of complexes was, therefore, collected by also studying solutions of the partially deuterated benzenes C_6H_5D and *sym*- $C_6H_3D_3$. The latter is of symmetry D_{3h} with three a_2'' and seven e' normal coordinates giving rise to infrared active fundamentals, while the former belongs to the C_{2v} point group and has 11 a_1 , 6 b_1 , and 10 b_2 normal coordinates that are active. The infrared spectra of the monomers have been described in the literature and require no further comments.³¹ In what follows, we will identify transitions with the symmetry and the Herzberg number of the corresponding monomer mode.

Various aspects of the vibrational spectra of $C_6H_6 \cdot C_6F_6$ have been published in the literature. Measurements in the liquid phase above the melting point of the equimolar solid gave no indication for the presence of bands due to a complex.³² Solid-state infrared and Raman spectra of the solid equimolar compound have been compared with the solid-state monomer spectra.³² The authors concluded that the complexation shifts

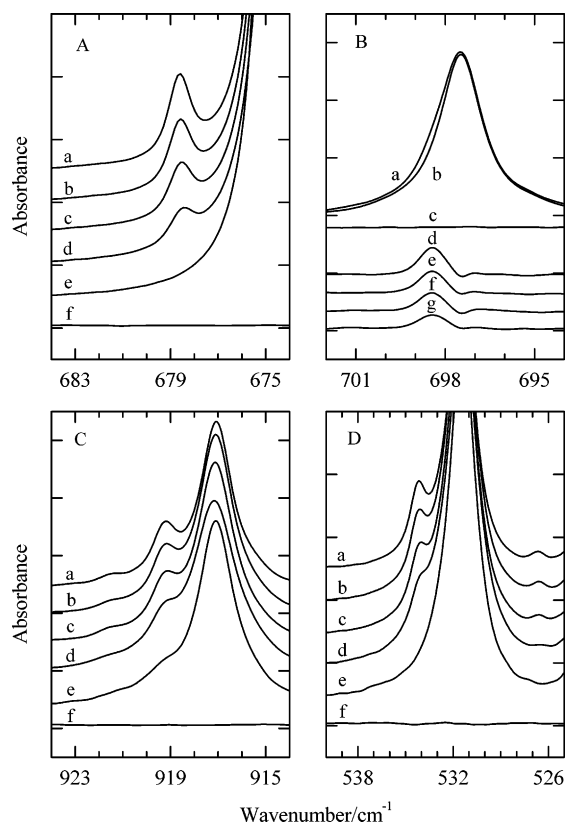


Figure 2. Details of the infrared spectra of benzene/hexafluorobenzene solutions in liquid krypton: (A) benzene- d_0 /hexafluorobenzene mixture at (a) 127, (b) 132, (c) 138, and (d) 148 K and (e) benzene monomer solution and (f) hexafluorobenzene monomer solution; (B) (a) benzene- d_1 /hexafluorobenzene mixture, (b) benzene monomer solution, (c) hexafluorobenzene monomer solution, and isolated complex band obtained by subtracting monomer contribution from the spectrum of the mixture at (d) 129, (e) 134, (f) 138, and (g) 144 K; (C, D) the $\nu_{15}(a_2'')$ and $\nu_{17}(a_2'')$ regions of a *sym*-benzene- d_3 /hexafluorobenzene mixture at (a) 135, (b) 140, (c) 144, and (d) 154 K and of (e) a *sym*-benzene- d_3 monomer solution and (f) a hexafluorobenzene monomer solution.

of the internal monomer modes are very small. Because of the crystal field influences, however, the small differences that they observed between the solid-state spectra are of little use in our study of the complexation shifts in solution. More recent vibrational studies^{33,34} have concentrated on specific aspects of the solid-state spectra and similarly offer little guidance for the present study.

Infrared spectra of mixed solutions in liquid krypton, typically containing mole fractions between 3×10^{-5} and 2×10^{-4} of an isotopomer of benzene and between 1×10^{-4} and 4×10^{-4} of hexafluorobenzene, were compared with those of single monomer solutions under identical conditions of concentration and temperature. The appearance of new bands was taken as evidence for the formation of complexes in the mixed solutions. This is illustrated in Figure 2. Traces a–d in Figure 2A show spectra in the region of the out-of-plane mode $\nu_{11}(a_{2u})$ of C_6H_6 recorded from a C_6H_6/C_6F_6 mixture at temperatures between 127 K (trace a) and 148 K (trace d). Compared with the spectra of the single monomer solutions in traces e (C_6H_6) and f (C_6F_6), a new band is present at 678.6 cm^{-1} the intensity of which rapidly increases with decreasing temperature. This behavior is typical for a band due to a complex, and the band is therefore assigned as due to $C_6H_6 \cdot C_6F_6$. A similar band was found on the high-frequency side of $\nu_{11}(a_{2u})$ of C_6D_6 at 499.9 cm^{-1} . The complexation shifts of these bands are $+3.9$ and $+3.3 \text{ cm}^{-1}$, respectively.

For the complex of C_6H_5D with C_6F_6 , three complex bands have been identified, all localized in the C_6H_5D moiety, at 780.4 cm^{-1} ($\nu_{17}(b_1)$), 698.4 cm^{-1} ($\nu_{18}(b_1)$), and 610.2 cm^{-1} ($\nu_{19}(b_1)$). It is clear that in each case an out-of-plane monomer mode is involved. The 698.4 cm^{-1} complex band is shifted by less than 1 cm^{-1} from its position in the monomer and was detected after the monomer contribution was subtracted out, as is illustrated in Figure 2B. For ν_{17} and ν_{19} , the complexation shifts are $+3.0\text{ cm}^{-1}$, and they give rise to spectral patterns as in Figure 2A with the complex band clearly resolved from the monomer band.

In the spectra of mixtures of C_6F_6 and *sym*- $C_6H_3D_3$, complex bands were observed at 919.2 cm^{-1} ($\nu_{15}(a_2'')$), at 698.4 cm^{-1} ($\nu_{16}(a_2'')$), and at 534.2 cm^{-1} ($\nu_{17}(a_2'')$). Also for this isotopomer, the observed complex bands are due to out-of-plane modes of the benzene moiety. The regions of ν_{15} and ν_{17} are illustrated in Figure 2, panels C and D, respectively. The weak complex band at 526.6 cm^{-1} in Figure 2D belongs to the monomer band at 523 cm^{-1} , the onset of which can be seen in the figure. This band is assigned to *m*- $C_6H_4D_2$, which was present in the *sym*- $C_6H_3D_3$ sample as an isotopic impurity.

Relative Stability. By using the band areas of the absorption bands of monomers and complex as integrated intensities, the standard complexation enthalpy $\Delta_{LKr}H^\circ$ can be derived from a temperature-dependent study. To this end, use is made of the modified Van't Hoff equation:

$$\ln \frac{I_{A \cdot B}}{I_A I_B} = - \frac{(\Delta_{LKr}H^\circ + Rb)}{R} \frac{1}{T} + c$$

in which I_A , I_B , and $I_{A \cdot B}$ are the integrated intensities of the monomer and complex absorption bands, R is the universal gas constant, b is a correction for the thermal expansion of the solvent,^{35,36} and c is a constant. The equation shows that a plot of $\ln(I_{A \cdot B}/(I_A I_B))$ against the reciprocal temperature $1/T$ must be a straight line, from the slope of which $\Delta_{LKr}H^\circ$ can be calculated.

Band areas were determined from least-squares band fittings. The monomer bands used in this study are 2488 cm^{-1} (C_6F_6), 1955 cm^{-1} (C_6H_6), 778 cm^{-1} (C_6H_5D), 532 cm^{-1} (*sym*- $C_6H_3D_3$), and 497 cm^{-1} (C_6D_6). A different procedure was followed to determine the integrated intensities of the complex bands. It is clear from Figure 2 that the intensity of the absorption bands associated with complex formation is small compared to the intensity of the monomer bands and that all observed complex bands are strongly overlapped by the corresponding monomer band. This makes an accurate determination of the band area of the complex bands rather difficult. Therefore, to improve the quality of the data on the complexes, their spectral bands were isolated by subtracting out the monomer contributions using appropriately rescaled spectra of single monomer solutions that were recorded at the same temperatures. Subsequently, the band areas of the isolated bands were obtained from least-squares band fittings. The complex bands used for the analysis are 678.6 cm^{-1} (C_6H_6), 780.4 cm^{-1} (C_6H_5D), 534.2 cm^{-1} (*sym*- $C_6H_3D_3$), and 499.9 cm^{-1} (C_6D_6).

For each of the four mixtures investigated, a temperature study in the 125–165 K range was carried out and a Van't Hoff plot was constructed. The plots are given in Figure 3 for the mixtures C_6F_6/C_6D_6 (a), $C_6F_6/sym\text{-}C_6H_3D_3$ (b), C_6F_6/C_6H_5D (c), and C_6F_6/C_6H_6 (d). The values for $\Delta_{LKr}H^\circ$ derived from the linear regression lines are $-9(1)$, $-6.7(5)$, $-7.8(6)$, and $-5.5(2)\text{ kJ mol}^{-1}$, respectively. We propose to use the average of these values, weighted by the inverse of the uncertainties, $-6.0(2)\text{ kJ mol}^{-1}$, as the standard complexation enthalpy for $C_6H_6 \cdot C_6F_6$ at 145 K in liquid krypton.

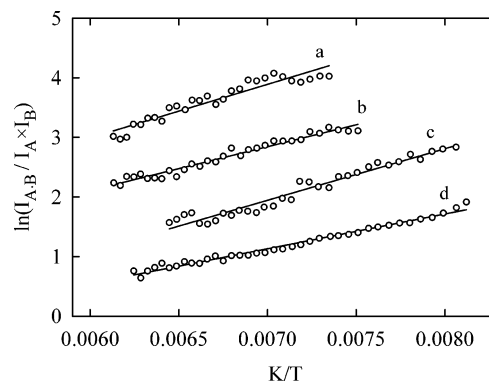


Figure 3. Van't Hoff plots for the benzene/hexafluorobenzene complexation equilibrium in liquid krypton.

Monte Carlo Simulations. It was anticipated above that for weak complexes, the solvent does have a significant influence on the standard complexation enthalpy. To gain insight into the stability of the complex in vacuo, therefore, the experimental complexation enthalpy was approximately corrected for solvent influences using free energy perturbation theory Monte Carlo simulations.³⁷ In this approximation, the solvation Gibbs energy, $\Delta_{sol}G^\circ$, of a species is calculated from the change in intermolecular interaction energy when a solute molecule is introduced in the solvent, without considering the influence of the solvent on the internal energies of the solute. From the temperature variation of $\Delta_{sol}G^\circ$, the solvation entropy is calculated using $\Delta_{sol}S^\circ = -(\partial \Delta_{sol}G^\circ / \partial T)_p$, and the solvation enthalpy is derived from $\Delta_{sol}H^\circ = \Delta_{sol}G^\circ + T\Delta_{sol}S^\circ$.

The solvation quantities were calculated for both monomers and for the complex. Each Monte Carlo simulation was run in the *NPT* ensemble using the standard procedure with periodic boundary conditions and a spherical cut off. The central box used in the calculations contained one solute molecule and 260 solvent atoms. The intermolecular potentials used to describe the solute–solvent and solvent–solvent interactions consisted of a sum of Lennard-Jones and electrostatic terms in which the polarization of the krypton atoms is accounted for using a first-order correction.³⁷ The different parameters defining the Lennard-Jones potentials and the partial charges used to mimic the quadrupoles of C_6H_6 and C_6F_6 are the same as those used in the MD calculations. The simulations were carried out at 12 equidistant temperatures between -94 and $-149\text{ }^\circ\text{C}$. The pressure was kept constant at 28 bar, that is, equal to the vapor pressure of krypton at 179 K, the highest temperature used in the calculations. The Gibbs energy of solvation is calculated using the formula

$$\Delta G_{01} = G_1 - G_0 = -kT \ln \langle e^{-(H_1 - H_0)/(kT)} \rangle$$

in which the angle brackets indicate averaging over the ensemble and H_0 and H_1 are the Hamiltonians describing the unperturbed system (pure solvent) and the perturbed system (one solute molecule dissolved), respectively.³⁸ Figure 4 shows the plots of the obtained $\Delta_{sol}G^\circ$ as a function of T for C_6H_6 (a), C_6F_6 (b), and $C_6H_6 \cdot C_6F_6$ (c). All plots are quite linear in the temperature range studied. The linear regression lines are shown in solid. From the slope and the intercept of these regression lines, the entropy and the enthalpy of solvation, $\Delta_{sol}S^\circ$ and $\Delta_{sol}H^\circ$, were calculated. The results are given in Table 2.

The solvation entropies in Table 2 are negative, which must be due to the loss of translational degrees of freedom of solvent atoms when they are captured in the solvation shell of the solute molecule. It may be remarked that the sum of the solvation

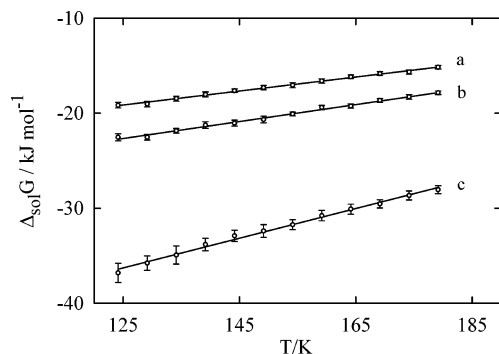


Figure 4. Solvation Gibbs energies as function of temperature as obtained from free energy perturbation Monte Carlo simulations for (a) benzene, (b) hexafluorobenzene, and (c) the benzene/hexafluorobenzene complex.

TABLE 2: Monte Carlo Solvation Enthalpies and Entropies

| | $\Delta_{\text{sol}}H^\circ$ (kJ mol ⁻¹) | $\Delta_{\text{sol}}S^\circ$ (J K ⁻¹ mol ⁻¹) |
|-------------------------------|---|--|
| C ₆ H ₆ | -28.4(3) | -73(2) |
| C ₆ F ₆ | -33.8(4) | -89(2) |
| sum of monomers | -62.2(5) | -162(3) |
| 1:1 complex | -55.9(6) | -156(4) |

entropies of the monomers, $-162(3) \text{ J K}^{-1} \text{ mol}^{-1}$, is higher than that of the complex, $-156(4) \text{ J K}^{-1} \text{ mol}^{-1}$. The reason for this is the loss of solvation upon formation of the complex. This requires that the solvent atoms on one face of either monomer are removed. In a naive model, this would mean that some 50% of the solvation is lost, which should lead to a decrease in solvation entropy by the same amount. The data in Table 2 show that the effect is present but to a much smaller extent. A detailed analysis of the failure of the naive model was not pursued.

Table 2 also indicates that the solvation enthalpies are nonnegligible. More importantly, however, is the fact that the sum of the solvent stabilizations of the monomers, $-62.2(5) \text{ kJ mol}^{-1}$, is bigger than the solvation stabilization of the complex, $-55.9(6) \text{ kJ mol}^{-1}$. The difference, $6.3(8) \text{ kJ mol}^{-1}$, is of the same order as the experimental complexation enthalpy in liquid krypton, $-6.0(2) \text{ kJ mol}^{-1}$. It follows that the complex is significantly less stable in solution than in the gas phase. By correcting the solution enthalpy with the solvation enthalpies, we obtained the gas-phase enthalpy, $\Delta_{\text{gas}}H^\circ$, of $-12.3(8) \text{ kJ mol}^{-1}$.

Ab Initio Calculations. Previous theoretical calculations^{21–23} on $C_6H_6 \cdot C_6F_6$ have reported both MP2 ab initio and DFT optimized structures and complexation energies of the complex but have not included vibrational frequencies. Because these are of some interest for our study, we have explored the possibilities for calculating them. However, calculations on benzene and its complexes are faced with considerable difficulties. It has been suggested that the dispersion energy is very important for the present type of complex,²¹ so it is unlikely that DFT calculations would lead to reliable complexation energies, while ab initio methods involving electron correlation should give better energies. This is borne out by the literature data on $C_6H_6 \cdot C_6F_6$,^{21,23} which show that the B3LYP DFT complexation energy using the 6-31G(d,p) basis set equals a mere -4.4 kJ mol^{-1} before BSSE correction, while the MP2 calculation with the same basis set leads to a value of $-11.2 \text{ kJ mol}^{-1}$ after BSSE correction. Unfortunately, MP2 calculations using basis sets of the above quality are known to reproduce the frequencies of the out-of-plane vibrations of benzene very poorly, which has been related to the finer characteristics of the π -electron system in unsaturated and aromatic com-

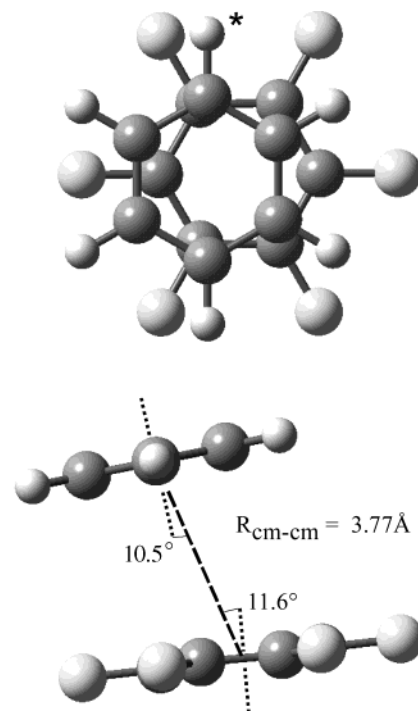


Figure 5. The MP2/6-31G(d) equilibrium geometry for $C_6H_6 \cdot C_6F_6$. The dashed line connects the centers of mass of the two rings, while the dotted lines are the respective 6-fold axes. The asterisk indicates the position of the deuterium atom in the isomer of $C_6H_5D \cdot C_6F_6$ discussed in the text.

pounds.^{39–42} MP2 calculations with more elaborate basis sets have led to the conclusion that even with the TZ2P+f basis set, one of these frequencies has not converged.⁴⁰ Computational requirements with very extended basis being prohibitive, we have limited ourselves to a critical analysis of MP2 calculations using basis sets of 6-31G quality. At the early stages, calculations were made using the 6-31G(d), 6-31G(d,p), and 6-31+G(d,p) basis sets, optimizing the structure under the restriction of C_{6v} symmetry of the complex, as in previous studies. The optimized structures invariably produced two negative vibrational eigenvalues, signaling that the structures obtained were not a local minimum. Therefore, the symmetry restriction was removed. Convergence of the calculations then proved difficult and slow, requiring the VERYTIGHT convergence criterium. To reduce the required CPU time, therefore, only the 6-31G(d) basis was used, taking into account BSSE corrections explicitly during both geometry optimization and force field calculation. In this way, a structure with all positive vibrational eigenvalues was obtained.

The resulting complex, shown in Figure 5, has C_s symmetry. Starting from a complex with C_{6v} symmetry with C–H and C–F bonds staggered, we obtained the converged structure by shifting the centers of mass of the monomers in opposite directions and perpendicular to the 6-fold axis in a symmetry plane that passes through two opposing C–F bonds and at the same time slightly tilting the benzene ring around the monomer 2-fold axis, which is perpendicular to the shift plane. As indicated in Figure 5, in the resulting structure, the centers of mass of the two rings are 3.77 Å apart, and the slight tilt is apparent from the different angles between the line connecting the centers of mass and the respective monomer 6-fold axes.

The complexation energy obtained here equals $-29.4 \text{ kJ mol}^{-1}$, close to previous MP2 values.^{21–23} The BSSE correction is considerable, reducing the complexation energy to $-16.8 \text{ kJ mol}^{-1}$.

Vibrational frequencies were calculated in the harmonic approximation. It is clear from the above that complex bands were observed for out-of-plane C_6H_6 modes only. In line with this, the calculated complexation shifts for in-plane modes of C_6H_6 and for all modes of C_6F_6 are very small. For the out-of-plane C_6H_6 modes, however, the predictions disagree with observations. The d_1 isotopomer of benzene serves neatly to demonstrate the problems. For ν_{17} of this monomer, the predicted frequency, 755.6 cm^{-1} , is not too unrealistic because the vapor-phase value is 777.8 cm^{-1} .³¹ The situation for ν_{18} and ν_{19} is dramatically worse with the MP2 values underestimating the respective vapor-phase frequencies by 87.8 and 101.1 cm^{-1} . Also, the predicted relative intensities are poor: if ν_{17} is assigned a relative intensity of 1 in both experiment and calculation, ν_{18} and ν_{19} are predicted with relative intensities of 1.4 and 8×10^{-5} , while the observed ratios are 0.87 and 3.4. Upon complexation, for the isomer with the deuterium in the position as indicated by the asterisk in Figure 5, the MP2 calculations predict shifts of 0.0 cm^{-1} (ν_{17}), $+0.1\text{ cm}^{-1}$ (ν_{18}), and -30.1 cm^{-1} (ν_{19}) with similar values for the other isomers. For ν_{19} , the experimental data discussed in a previous paragraph show that the predicted direction of the complexation shift is wrong and that its absolute value is off by an order of magnitude. Because the above out-of-plane modes belong to the same symmetry species, the results for ν_{17} and ν_{18} cannot be taken to be independent of those for ν_{19} . Consequently, it must be concluded that the present MP2 frequencies are of little diagnostic value for any of the out-of-plane modes.

Discussion

The molecular dynamics calculations predict that the lifetime of the complex in liquid krypton is sufficiently long to allow observation of the complex by infrared spectroscopy. In line with this, a number of bands have been identified in the experimental spectra that indicate the formation of a complex. There is little doubt that the complex is formed between benzene and hexafluorobenzene, because no features ascribable to homodimers could be detected in the single-monomer solutions. The premise used to justify the molecular dynamics calculations is confirmed a posteriori by the free energy perturbation calculations, which show that there is a considerable solvent effect on the stability of the complex. In this context, it would be interesting to expand the present experimental results with the complexation enthalpy in an even more inert solvent such as liquid argon. The solubility of the monomers, especially of benzene, however, is rather limited, and attempts to observe the complex in that solvent have failed up to now.

The complexation enthalpy determined here must be compared with the result recently derived from heat capacity measurements of mixed benzene/hexafluorobenzene solutions in *n*-heptane.²⁴ In that study, with measurements at 298.15 K, a value of $-9.1(9)\text{ kJ mol}^{-1}$ was found. This value is significantly more negative than our value in LKr, $-6.0(2)\text{ kJ mol}^{-1}$, at 145 K. To be useful, however, the comparison must be made with enthalpies that were obtained at the same temperature. Because in both experiments enthalpies were derived for solutions, correcting their values to the same temperature is far from straightforward. However, some insight can be gained by calculating the temperature evolution of the enthalpy for the gas-phase complexation, using statistical thermodynamics. For this, we have treated the translations and rotations classically, that is, their contributions are taken to be $RT/2$ per degree of freedom, which for the treatment of the rotations is justified by the relatively large masses of the

monomers and the complex. It is further straightforward to show from the experimental frequencies that the contributions of the internal modes of the monomers to the vibrational enthalpy are very small and can be neglected. This evidently is due to the magnitude of the complexation shifts that are invariably small. Hence, the vibrational contributions to the correction for ΔH° find their origin in the low-frequency van der Waals modes, which were calculated in the $4\text{--}60\text{ cm}^{-1}$ range. If these values are used, it is predicted that the complexation enthalpy at 298.15 K should be less negative by 2.44 kJ mol^{-1} than that at 145 K. In view of the above criticism of the ab initio calculations, however, the accuracy of the harmonic van der Waals frequencies and, consequently, the above change in ΔH° may be questioned. The upper and lower limits of this change were, therefore, estimated in the following way. If it is assumed that all van der Waals modes have vanishingly small frequencies, the upper limit to the correction of ΔH° is calculated to be 2.49 kJ mol^{-1} . For the other extreme, taking into account the weakness of the complex and the important masses of the monomers, it may safely be assumed that the van der Waals modes will have frequencies well below 200 cm^{-1} . If it is assumed that these modes all have a frequency of 200 cm^{-1} , the lower limit to the temperature correction is calculated. It is found to be 1.75 kJ mol^{-1} . It follows that the gas-phase complexation enthalpy must be less negative at 298.15 K by a value between 1.75 and 2.49 kJ mol^{-1} than at 145 K. Using the gas-phase correction as a reasonable approach for the non-solvent-related contributions reduces the $\Delta_{\text{LKr}}H^\circ$ at 298.15 K to a value between -4.3 and -3.5 kJ mol^{-1} , significantly different from the $-9.1(9)\text{ kJ mol}^{-1}$ derived for the liquid *n*-heptane solution.²⁴ Assuming that both methods measure the same thermodynamic characteristic of the complex, the difference must be due to solvent effects. It then follows from the above data that the difference in solvent effect between LKr and liquid *n*-heptane is very high, which is not entirely unrealistic in light of the importance of the solvent effect for the present equilibrium. Definitive insight into this could maybe come from accurate simulations of the solvent effects in liquid *n*-heptane, which may be relatively complicated when the four internal rotation degrees of freedom in this solvent have to be accounted for.

The relaxed structure obtained from the ab initio calculations has a symmetry that is lower than the one assumed in all previous calculations. It is noteworthy that this structure resembles the way in which subsequent benzene and hexafluorobenzene molecules are stacked in the crystalline solid. Yet, at present it cannot be assured that this structure is correct. This is a consequence of what was referred to above, that is, that the failure of the out-of-plane force field is linked with the fact that the π bonds in the aromatic rings are not properly described at the 6-31G(d) level.^{40,41} Because the aromatic rings are parallel in the complex, it cannot be excluded that an improved description of the π bonds by a more expanded basis set would significantly influence both the converged structure and the calculated complexation energy. It follows that insight into the finer details of the structure of the complex awaits either an accurate determination of the structure in the vapor phase or an ab initio calculation at a more sophisticated level. A consequence for the present study is that there is no reliable theoretical value for the complexation energy with which to compare our experimental data.

Conclusions

In this paper, results are reported of a spectroscopic study of the van der Waals complex between benzene and hexafluoro-

benzene formed in liquid krypton solutions. Molecular dynamics simulations have shown that the average lifetime of the complex varies between 33(20) ps at 126 K and 17(5) ps at 158 K, long enough for the complex to be detectable using infrared spectroscopy. Ab initio calculations at the MP2/6-31G(d) level result in a structure with C_s symmetry with the two aromatic rings slightly shifted and tilted with a BSSE-corrected complexation energy of $-16.8 \text{ kJ mol}^{-1}$. The vibrational frequencies of monomers and complexes were predicted at the same level. In the infrared spectra of solutions in liquid krypton of hexafluorobenzene and benzene, benzene-*d*₀, *sym*-benzene-*d*₃, or benzene-*d*₆, a limited number of new bands have been detected, and these bands have been assigned to the 1:1 complex C₆H₆·C₆F₆. In all cases, these vibrations involve out-of-plane motions of the benzene moiety. Detailed comparison reveals flaws in the out-of-plane ab initio frequencies, in line with earlier reports in the literature. Using spectra from a temperature-dependent infrared study, we determined the complexation enthalpy in liquid krypton to be $-6.0(2) \text{ kJ mol}^{-1}$. Free energy perturbation Monte Carlo simulations were used to transform this into a vapor-phase complexation enthalpy equal to $-12.3(8) \text{ kJ mol}^{-1}$.

In conclusion, it is clear that our measurements suggest that the interaction energy of arenes with fluorinated arenes in solution is substantially smaller than that of a typical hydrogen bond and would not be expected to result in persistent structural features in solution.

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