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Structure and Properties of Benzene-Containing Molecular Clusters: Nonempirical *ab Initio* Calculations and Experiments

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I. Introduction

Benzene-containing molecular clusters are attractive subjects of research because they model the interaction of aromatic π-systems. The significance of the interaction of aromatic π-systems in chemistry, physics, and biology is immense. This interaction controls such diverse phenomena as the tertiary structure of proteins, the porphyrin aggregation, the packing of aromatic molecules in crystals, the vertical base–base interaction in DNA, and the intercalation of drugs into DNA.

The calculation of molecular clusters containing such large molecules is one of the challenging tasks of the chemistry. It was (and sometimes still is) believed that such clusters are too large to achieve meaningful results that are comparable to those obtained for three—or four—atomic clusters. In the present review we demonstrate that even for as extended clusters as the benzene-containing complexes the theory can provide accurate values for the properties of different clusters. The significance of the theoretical treatment of these clusters is emphasized by the fact that despite an enormous progress in various experimental techniques the unambiguous structural description of such cluster is still impractical.

Because quantum theory is deductive it can provide the experimentalist with a unique chance to "see" the molecular complex prior to any experiment being performed or even designed. This is extremely important if, for example, theory predicts the intermolecular frequencies in the far infrared region the intended experiments should be able to scan that spectral region. Without this information the experimentalist could spend a lot of time searching unsuccessfully for these frequencies in inappropriate spectral regions. Seemingly, only close cooperation between experiment and theory could shed more light into molecular clusters of larger molecules, to elucidate the nature of their bonding and to describe completely their various properties. We here wish to demonstrate that theory and experiment for these large molecular clusters give very concordant results and, in fact, lend necessary support to each other. As a practical example, the assignments of the soft modes obtained for these clusters by the new zero electron kinetic energy (ZEKE) spectroscopy would have been impossible without these ab initio calculations.

II. Generation of a Consistent Set of Various Properties of a Molecular Cluster

Theory can provide a complete and consistent set of various properties of the cluster under study. This is realized in a sequence of steps:

(i) First there is a detailed investigation of the potential energy surface (PES). The aim is to localize not only all the minima but also all the saddle points. Further, regions far from minima should also be investigated. This is the most tedious step of the whole study and several dozens of points on the PES are required even for symmetrical clusters. The task is even more difficult because the gradient techniques for localization of stationary points can not be used. The reason is that the interaction energy at any point of the PES should be corrected for the basis set superposition error (BSSE). At the present time, only the classical function counterpoise procedure of Boys and Bernardi[1] can be applied without any limitations (see later).

As a result of this step the geometrical structure of the minima and saddle points is obtained. Fur-

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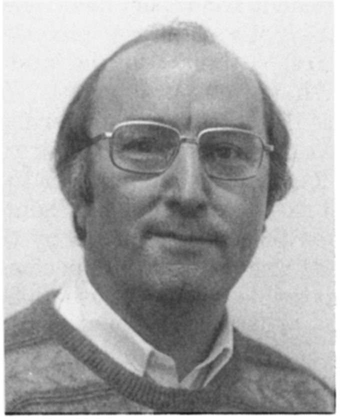
Pavel Hobza was born in 1946 in Přerov, Czechoslovakia, and graduated from Czech Technical University in 1969. In 1974 he received his Ph.D. (with Professor R. Zahradník) and in 1988 the D.Sc. degree; after 1989 he became Associate Professor of Charles University in Prague. Since 1989 he has been employed at the Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague. After postdoctoral study with Professor C. Sandorfy at the Université de Montréal, Montréal, he spent several periods as a visiting professor and a visiting scientist at Universite de Montréal, Montréal, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, and Technische Universität München, Garching. In 1992 he received his Deutsche-Forschung-Gemeinschaft Gastprofessur (Technische Universität München, Garching). Dr. Hobza has authored or coauthored about 150 papers and two books. These works deal mainly with molecular interactions and their role in physical chemistry and biodisciplines.



Heinrich L. Selzle was born in 1944 in Dachau, Germany. He studied physics at the Technical University of Munich where he received the degree of Dipl. Phys. in 1969. He then started his doctoral work at the Institut of Physical Chemistry where he received his Dr.rer.nat. (with Professor H. Gerischer) in 1971. After this he went as a postdoc with Professor E. W. Schlag to the Northwestern University, Evanston, and then returned to the Institut of Physical Chemistry at the Technical University of Munich. Dr. Selzle works experimentally in the field of molecular clusters. The experiments are mainly concerned with the study of the structure of these clusters and the weak interactions in the excited state.

ther, the one-electron properties (dipole moment, quadrupole moment, polarizability, etc.) are generated for these structures.

(ii) Second, higher level calculations on the global minimum are performed. Reasonable geometry characteristics and the majority of the one-electron properties have already obtained at the lower theoretical level. However, the interaction energy is more sensitive to the quality of the calculation. A much higher theoretical level is required in order to obtain accurate values for the interaction energy.

Edward W. Schlag was born in 1932 in Los Angles, CA, and obtained his Ph.D. in 1958 with B. S. Rabinovitch at the University of Washington in Seattle. In 1988 he obtained an honorary degree from the Hebrew University in Jerusalem. He was Professor of Chemistry at Northwestern University from 1960 to 1971. Since 1971 he has been Professor of Physical Chemistry and Director of the Institute of Physical Chemistry of Munich. He has been a member of the Bavarian Academy of Sciences since 1978 and is a Fellow of the American Physical Society. He has authored and coauthored some 270 papers and two books and chaired 9 international conferences in chemical physics. His fields of research involve spectroscopy and dynamics—principally multiphoton mass spectrometry, radiationless processes, cluster research, unimolecular reactions, electron transfer and ionization mechanisms, and most recently ZEKE photoelectron spectrometry.

(iii) Third, the PES is fit to an empirical potential. Probably the most important property of a molecular cluster is the respective intermolecular potential. The majority of the potentials presently used have been obtained empirically using various experimental characteristics such as virial, viscosity, and transport coefficients or heats of adsorption. The accuracy of these potentials is clearly not sufficient. For small clusters more accurate potentials can be obtained by fitting spectroscopic and scattering data but generation of experimental values is not easy. For larger clusters this approach is not possible within the limits of the existing computational methods, but there seems to be a rather promising procedure. In this the parameters of a potential are iteratively fitted to reproduce as close as possible selected thermodynamic characteristics which are evaluated in Monte Carlo or molecular dynamics simulations. An alternative to the empirical potentials are potentials derived from quantum chemical calculations. The main advantage of the latter procedure is the fact that it can be applied to any type of molecular cluster.

The analytic potential should be sufficiently flexible and should contain a manageable number of adjustable parameters. Various parts of the PES have different degrees of importance for the evaluation of different properties. If the aim is to determine vibrational frequencies then the analytic potential should be accurate in the region around the global minimum (supposing that other possible minima are considerably higher in energy). On the other hand, the potentials which are to be used more generally, e.g. for computer experiments, should also describe reasonably both short-range and long-range parts of the PES.

An analytic form of the intermolecular potential results from this step.

(iv) The fourth step involves utilization of the found intermolecular potential. Any theoretical treatment of the internal dynamics of the molecular cluster requires an analytic representation of the intermolecular potential.

The vibrational energy levels of the cluster could be obtained by solving the vibrational Schrödinger equation provided the intermolecular potential is available. In this way anharmonic vibrational frequencies can be generated. The use of the harmonic approximation is rather limited for the evaluation of vibrational frequencies of molecular clusters. This is especially true for flexible or floppy clusters. The calculation of intermolecular vibrational frequencies is very important because the intermolecular motions directly probe the intermolecular potential.

The structure of higher clusters ($X\cdots Y_n$) at temperature T is determined by molecular dynamics (MD); the knowledge of the respective intermolecular potentials is inevitable. By performing the MD calculations the thermodynamic characteristics of the cluster formation can also be obtained. It should be mentioned here that the thermodynamic characteristics belong to the most important cluster characteristics.

From this step, anharmonic vibrational frequencies, the structure of higher clusters at a temperature T, as well as thermodynamic characteristics of the cluster formation result.

III. Calculation of the Interaction Energy

Two theoretical methods can be used to calculate the interaction energy (ΔE). The supermolecular variation method determines ΔE as the difference between the energy of the cluster and the energies of the isolated systems. The perturbational method computes ΔE directly as a sum of physically distinct contributions arising from electrostatic, induction, dispersion, and exchange interactions. Both methods have advantages and drawbacks. The supermolecular approach is theoretically able to provide an interaction energy at any accuracy, however, only if a sufficiently large basis set and a sufficiently high level of correlation is used. The advantage of this approach is that it is simple and straightforward and standard quantum chemical codes can be used. Further, the knowledge of the wave function of the cluster enables one to determine its various physical properties. The drawback of the supermolecular method is the fact that the resulting interaction energy is subject to the BSSE. Since the perturbational ΔE is obtained directly (and not as the energy difference) it is free from the BSSE. Further, since the perturbational calculation is only limited to the intermolecular part of the interaction energy, the respective computational demands are lower than in the case of comparable supermolecular calculations. This allows one to use a larger basis set for perturbational calculation than in the variation supermolecular case. Nevertheless it is the supermolecular approach which nowadays is used almost exclusively. The perturbation approach, in the form of the symmetry-adapted perturbation theory (SAPT),[2] is used for highly accurate calculations which provide benchmarks for supermolecular calculations.

In the following parts the supermolecular method will be used for the evaluation of the interaction energy and other properties of a molecular cluster. Recent applications of SAPT can be found in ref 2.

The interaction energy of the complex is evaluated as the sum of the SCF interaction energy (ΔE^{SCF}) and the correlation interaction energy (ΔE^{COR})

$$\Delta E = \Delta E^{\mathrm{SCF}} + \Delta E^{\mathrm{COR}} \qquad (1)$$

Various procedures can be used for the evaluation of ΔE^{COR}; among the size-consistent (see later) methods the Møller–Plesset theory is presently in common use. If the theory is performed up to the fourth order it covers a substantial part of correlation energy.[3] The second-order MP theory (MP2), which can easily be applied even to large clusters, gives surprisingly good estimates of ΔE^{COR}. This is partly due to the compensation of third- and fourth-order contributions (see ref 3).

More accurate values of ΔE^{COR} result from the use of the coupled-cluster (CC) method, standardly including the single and double substitutions (CCSD). For higher accuracy inclusion of triple substitution is necessary either in the form of full CCSDT or on the simplified level (CCSD + T(CCSD)). Let us only mention here that the MP4 and CCSD + T(CCSD) stabilization energies are usually very similar. The MP4 and CCSD + T(CCSD) stabilization energy for the water dimer,[4] evaluated at the region of the van der Waals (vdW) minimum and at long distance region (O—O distances 3.0 and 4.8 Å) equal to −4.382, −4.368, and −1.147, −1.170 kcal/mol, respectively.

It is very difficult to reach the basis set limit in the correlation energy treatment and a slow convergence with extension of the basis set results. A powerful way to accelerate this convergency was developed in the laboratory of Kutzelnigg[5] and is based on use of special two-particle functions which depend explicitly on the interelectronic distance r_{12}. The MP2 and CCSD schemes which have linear terms in the interelectronic coordinates were developed;[5] these methods are abbreviated as MP2-R12 or CCSD-R12.

The interaction energy of complexes studied in this review was mainly determined as follows:

$$\Delta E = \Delta E^{\mathrm{SCF}} + \Delta E^{\mathrm{MP2}} \qquad (2)$$

The first term in eq 2 roughly corresponds to the sum of the perturbations arising from Coulomb, induction, and exchange–repulsion contributions, the second term consists of the second-order dispersion energy, the intermolecular correction to the Coulomb energy, the exchange terms related to both contributions, and the second-order deformation correlation terms.

A. Inconsistencies in the Evaluation of Variational Interaction Energy

As already mentioned, the ΔE is determined as the difference between the energy of the supersystem and the sum of the energies of the subsystems. This requires that all the energies are evaluated in a consistent way. This is not a trivial problem and two types of inconsistencies arise, the size inconsistency and the basis set inconsistency (see, e.g. our previous review, ref 3).

The first inconsistency is well understood theoretically and managed, and the simplest way to avoid it is to use no size-inconsistent methods for the evaluation of the interaction energy. Most of the quantum chemical methods are size consistent (SCF; CI-SDQ; CC; MPn, n = 2, 3, 4, etc.) and only some of them are size inconsistent (e.g. CI-D, CI-SD).

The second inconsistency, namely the basis set inconsistency leads to the BSSE. The problem of the BSSE, first recognized in the late 1960s,[6] led Boys and Bernardi to the introduction of the function counterpoise method.[1] The idea is very simple: the same basis set is used for the subsystem as for the supersystem. Because the BSSE is geometry dependent it is necessary to evaluate it for each mutual distance and orientation of the subsystems. Further, only size-consistent methods can be used. A first application[7] of the function counterpoise method was misleading since it resulted in the conclusion that the method gives overcorrected values. It was shown later[8] that this overestimation was due to the use of the STO-3G basis set and not due to the nature of the counterpoise method. Since then the problem of overcorrection has been subject of debate and the respective literature is immense. Recently, convincing evidence[9] from Warsaw, Utrecht, and other laboratories was accumulated showing the validity of the original (full) function counterpoise method. This conclusion was based on formal as well as on numerical (SAPT) results. From the studies mentioned we can also learn that a promising technique of a chemical Hamiltonian,[10] aiming to eliminate the BSSE from the very beginning, failed. The results obtained with these techniques were found[9] to be *inconsistent with the SAPT interaction energies*. This has an unpleasant consequence because these techniques represented the only chance to use the gradient optimization procedures for the localization of stationary points on the PES of molecular clusters.

Both interaction energy components, ΔE^{SCF} and ΔE^{COR}, should be corrected for the BSSE and the overall BSSE is given as the sum of SCF and COR parts.

A frequently raised objection against the use of the function counterpoise procedure concerns the convergency of the BSSE. It is argued that the BSSE does not converge with the increase of the basis set. This is especially true for the beyond-HF BSSE. The problem is connected with the presence of the diffuse polarization functions which are essential for the proper description of the beyond-HF stabilization energy. Provided the diffuse polarization functions are not "compensated" by polarization functions localized at the nuclei the BSSE remains rather large even for extended basis sets. If, however, really extended basis sets with several sets of polarization functions are used, only a negligible BSSE results (see later). In this case the function counterpoise procedure can be neglected. However, using basis sets of common size (like TZ+2P) the BSSE should be eliminated. Provided that a meaningful basis set is used, the stabilization energy corrected by the BSSE, is always closer to the respective basis set limit than the uncorrected values.

All the interaction energies presented in this review were determined with inclusion of the BSSE.

B. Basis Set

The aim of classical quantum chemistry is to attain the "chemical accuracy", i.e. not to differ by more than 0.001 hartree from the accurate value. One millihartree is about 0.6 kcal/mol which is comparable to the stabilization energy of many molecular clusters. Clearly, for molecular clusters an even higher accuracy is required. This is an extremely tedious task and the choice of the basis set is one of the most important steps. The following are several hints how to prepare the basis set for the particular cluster.

(i) Unless the basis set is really "extended" there is no chance to use a universal basis set and the basis set should be tailored to the cluster studied.

(ii) Avoid the use of split-valence basis sets. With present computers one is not saving substantial computational time when passing from a split valence to a full double-ζ basis set. On the other hand the use of split-valence basis sets could result in some strange results not typical for the basis sets of this size (see later).

(iii) The presence of polarization functions is inevitable and these functions should be diffuse. This means that not energy-optimized but dispersion-energy-optimized polarization functions are to be used. The basis set, however, should be balanced, i.e. it is not advisable to have only one set of diffuse polarization functions. If possible two or more sets of polarization functions are to be used.

For the accurate calculations the presence of higher polarization functions is required (i.e., e.g. f functions on first-period atoms).

(iv) The presence of diffuse functions could be important and should be tested.

(v) The presence of bond functions (or functions localized at dummy atoms) accelerates the convergence of the correlation interaction energy. The addition of a bond function is more effective for the convergence of the dispersion energy than the addition of higher angular momentum polarization functions.[11a] Promising results with bond functions were obtained in the group of van Duijneveldt[11b] and also recently by Tao et al.[11c]

(vi) The quality of the basis set could be tested against one-electron properties of the subsystem, like dipole moment, quadrupole moment or polarizability. If, for example, the basis set failed to give reasonable values of the quadrupole moment and the polarizability of benzene, this basis set should not be used for calculations of the benzene containing clusters.

(vii) Keep in mind that the basis set should not only describe properly the region of the energy minimum but also the long-range and short-range regions of the PES.

(viii) The basis set library of Dunning and coworkers[12] (correlation consistent and augmented correlation consistent basis sets) which fulfills all the requirements mentioned could be considered as one suitable basis set.

C. Nature of Stationary Points

Does the stationary point found correspond to the minimum or to a saddle point? To answer this question unambiguously it is necessary to calculate the second derivatives of the energy with respect to all the coordinates. Because the subsystems are kept rigid during the optimization for the present clusters it is necessary to consider "only" the six intermolecular degrees of freedom. The evaluation of the second derivatives of the potential energy represents the routine problem of computational quantum chemistry. Therefore it may seem surprising to state that such calculations for the present clusters are extremely tedious. It must be kept in mind that the second derivatives should be calculated at the same level as used for the optimization, i.e. in the present case MP2 with an extended basis set. From these evident reasons it is impossible to lower the theoretical level (going either to a smaller basis set or to the Hartree–Fock level). The character of a stationary point was therefore determined in the following way. The geometrical structure of any stationary point is determined completely by six intermolecular degrees of freedom. If the change of each of them leads to an energy increase the stationary point in question corresponds to a minimum. If, on the other hand, a change of any of them leads to an energy decrease than this point does not correspond to a minimum. The choice of the intermolecular degrees of freedom is arbitrary; in all cases we have taken the three translations (Δx, Δy, Δz) and the three rotations (around local axis x, y, z).

D. The Role of Zero-Point Energy

To compare any calculated result with the respective experimental one the effect of the zero-point energy (ZPE) should be considered. This is straightforward in the case of the interaction energy. Introducing the ΔZPE we are passing from the interaction energy to the interaction enthalpy (ΔH) at 0 K. The absolute value of ΔH is smaller than that of ΔE.

To include the effect of the ZPE to the geometry the vibrational averaging of the intermolecular distance should be performed. The ZPE increases the intermolecular distance.

IV. Calculation of Vibrational Frequencies

The intermolecular vibrational frequencies of any molecular cluster are clearly anharmonic, and it is therefore useless to evaluate them within the harmonic approach. This is even more so for benzene-containing clusters studied in the present review.

The anharmonic vibrational levels for various intermolecular motions were obtained for several benzene-containing clusters by solving the vibrational Schrödinger equation, i.e. by diagonalizing the vibration Hamiltonian (for example, for the benzene··Ar it was the Hougen–Bunker–Johns Hamiltonian[13]). The diagonalization of the Hamiltonian was done numerically in the one-dimensional case and variationally in the more-dimensional case. The basis set in the latter case was constructed as the product of the respective one-dimensional functions.

V. Evaluation of the Experimental Techniques Yielding Information on the Benzene-Containing Clusters

The experimental study of benzene-containing clusters was stimulated by the fact that in early experiments by Janda et al.[14] it was found that the benzene dimer is a polar complex. The experimental technique used was the electric deflection of the benzene dimer out of a molecular beam which was formed via an adiabatic expansion of benzene in Argon into the vacuum. The finding of a permanent dipole moment for the benzene dimer was very important for the discussion of the structure of gas phase clusters and from these experiments a structure for the benzene dimer similar to the nearest-neighbor geometry in the solid was conjectured.

The weak binding energy of molecular clusters, where the dominant contribution to the stabilization arises from the dispersion energy and higher order electric moments (electrostatic energy), is also the reason that now, in general, all experiments are performed in seeded supersonic jets. For the study of benzene-containing clusters, the benzene molecules are seeded in noble gases, particularly in helium or argon, and the clusters are formed during the isentropic expansion into the vacuum. For clusters of benzene other than with itself or with atoms of the driving gas, a proper mixture seeded in a noble gas is coexpanded. This supersonic expansion leads to a low internal temperature of the clusters and these are stabilized in local minima of the PES. The resulting low temperature of a few Kelvin for the rotational degree of freedom strongly simplifies the absorption spectra to the first electronic excited state[15] and allows for rotational resolution in the case of single molecules.[15–17] This strong cooling is also observed for clusters and here also rotational resolution can be obtained, which in the case of the benzene··Ar complex resulted in the first determination of the structure of this complex.[18] In these experiments the benzene molecule in the cluster was excited to the first electronic excited state and the fluoresence was detected. Information about clusters so far was obtained from spectral shifts,[19,20] and the cluster size was deduced from the pressure dependence[21] or in the case of clusters with noble gas atoms from additivity rules giving a fixed increment for the red shift when adding one more noble gas atom.[21–24] These rules are not strict and for pure benzene clusters a red shift of about 40 cm^{-1} was found for the dimer, but about 120 cm^{-1} was found for the trimer,[25] and a smaller red shift of 146 cm^{-1} was found for the pentamer compared to the red shift of 161 cm^{-1} of the tetramer.[26] The spectral shifts thus give only a first hint useful for the determination of the size or structure of a cluster. For the exact size determination mass spectroscopy has to be included. For this purpose we have combined the supersonic jet experiment with a high-resolution reflectron time of flight (RETOF) mass spectrometer. The clusters are resonantly excited to the first electronic excited state from where they are ionized with a second photon just slightly above the ionization threshold to avoid contamination of the spectra from fragmentation of higher clusters.[27] This resonance-enhanced multiphoton ionization (REMPI) permits not only the separation of the spectra of the individual clusters[28,29] but also allows for isotopic substitution which then reveals additional structural information.[30,31] The addition of high-resolution methods with sub-Doppler resolution is able to completely resolve the rotational band structure even for vdW complexes and thus gives rise to a high precision structural information as in the case of the benzene$\cdot\cdot$Ar complex.[32]

The spectra obtained from resonance-enhanced two-color photoionization so far have in common that the first excitation step starts from the vibrationless ground state of the cluster and structural information from excited vdW modes are only available for the electronic excited state. Vibrational spectroscopy of the ground state like IR absorption is not feasible in the supersonic jet experiment due to the low density in the jet and short possible interaction length with the light. One promising technique for obtaining ground-state vibrational spectra is given by the method of "stimulated emission pumping" (SEP) which is used in fluorescence dip or in ion dip spectroscopy. Here with a first laser a resonant intermediate state is excited and subsequently probed by measuring the total fluorescence or ion yield efficiency from multiphoton ionization (MUPI). With a second tunable laser, transitions to the ground state of the cluster are induced and the fluorescence signal or ion yield will be reduced giving rise to dips in the spectra. The ion dip spectroscopy here has the advantage of simultaneously giving mass and spectral information. From these measurements not only intramolecular ground-state vibrations in clusters can be determined,[33-35] but also as in the case of benzene clusters[36] intermolecular vibrations which then can be compared to results from calculated intermolecular potentials. Another important method is stimulated Raman spectroscopy combined with mass-detected REMPI. Here Venturo and Felker found two Raman bands below 10 cm^{-1} as well as higher intermolecular frequencies in the range of about 50 cm^{-1} for the benzene dimer.[37]

A major problem in cluster spectroscopy is given by the fact that even though the mass can be identified, this does not uniquely identify the cluster, since the cluster can be formed in more than one conformational isomer. A clear example here is given by the benzene$\cdot\cdot$$Ar_2$ complex where two stable structures, the (1|1) with the two Argon atoms on opposite sides and the (0|2) with the two Argon atoms on the same side were proposed from partially resolved rotational and different ionization threshold spectra.[38] The (1|1) structure has been confirmed by Weber and Neusser by Doppler-free high-resolution spectroscopy.[39] We have now applied the technique of mass-selected spectral hole burning in the gas phase to this cluster, a technique analogous to the one which was first developed for solid-state spectroscopy to identify different electronic and vibrational states below the inhomogeneous broadened bands.[40] In this type of experiment a common ground state of a specific conformational isomer is depopulated with a first laser which is tuned to a strong transition from this ground state to an excited state. A further absorption of a photon of the same laser ionizes the cluster, and a scan with a second laser after some delay will find a reduced intensity in the spectrum for all transitions which have this ground state in common. This method of persistent hole burning was first applied by Lipert and Colson[41] to clusters of phenol with water and phenol with ethanol, but no conformational isomers were found. Wittmeyer and Topp studied mass-unselected clusters of perylene, where they found different conformational isomers from the observation of fluorescence dips.[42] In our experiment we can demonstrate this technique of hole-burning spectroscopy in the gas phase with simultaneous mass detection which in addition uniquely identifies the cluster stoichiometry. Here we found for the benzene$\cdot\cdot$$Ar_2$ complex that two different conformational isomers are formed in the jet expansion[43] and we can uniquely identify the contributions of these two isomers to the spectrum.

We have also applied this method to the benzene dimer. Here different experimental techniques have been applied before, but there was still some controversy about the structure. Felker et al. have applied stimulated Raman spectroscopy using the ν_1 vibration of the ground state and found evidence for two symmetrically inequivalent positions in the dimer.[44,45] Arunan and Gutowsky were able to measure the rotational spectrum of the benzene dimer in the ground state and found a symmetric top dimer in a microwave experiment.[46] Both measurements showed that at least one isomer with two nonequivalent benzene molecules exists. Both methods have in common that only structures which are sensitive to the corresponding spectroscopy, i.e. a distinct change of an intramolecular mode in the cluster in the first case or the presence of a dipole moment in the second case will be detected. Both properties are a function of the dimer structure and thus are blind to possible other structures. The method of persistent hole burning in the gas phase is not limited by this fact, if an allowed transition in the monomer is used. We, therefore, used the S_1 6^1_0 transition for the hole-burning experiment. Here two different conformational isomers are discovered in the supersonic jet expansion,[47a] one of them corresponding to the T-shaped structure found in the other experiments. A third structure also found at the mass of the benzene dimer in the hole-burning experiment corresponds to the benzene$_2$$\cdot\cdot$water cluster.[47b] This cluster completely fragments after ionization and can be uniquely identified from measurements with isotopic substituted water.[47c] From measurements of isotopic substituted benzene the contributions of the absorption of the individual molecules in the nonequivalent positions could also be determined. It is interesting to note that for the S_1 0^0_0 transition like in the experiments discussed before only the T-shape is found, and here only the absorption into one of half of the dimer is observed, which has an environment of lowered symmetry in the cluster. This arises from the fact that in this case only for one molecule the restriction from the symmetry is removed, and the forbidden 0−0 transition in this special conforma-

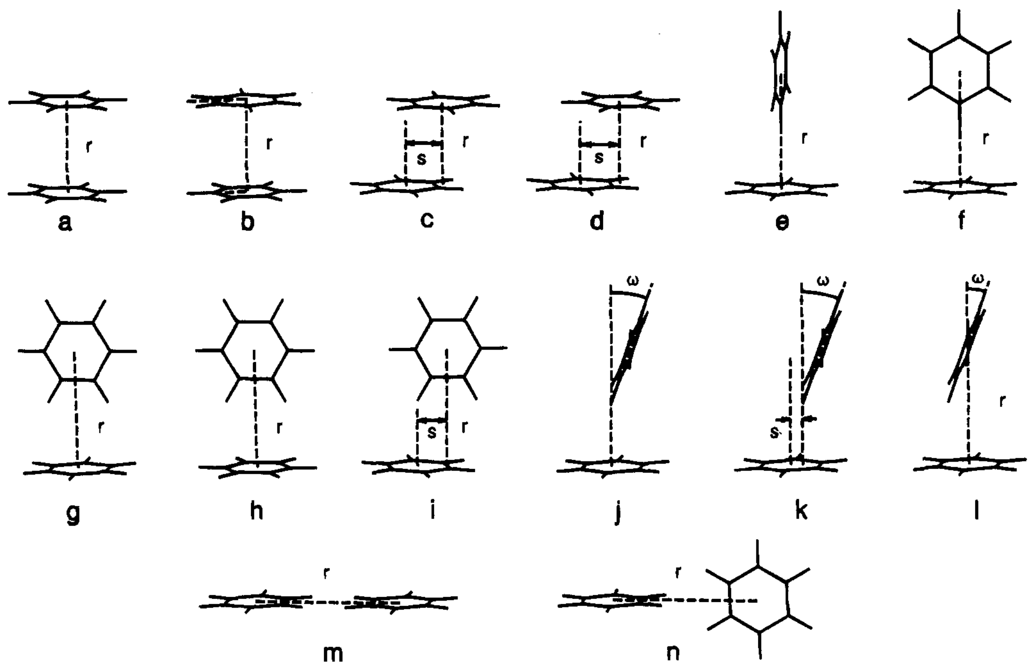


Figure 1. Structures of the benzene dimer.

tional isomer is now weakly allowed. The technique of persistent spectral hole burning in the gas phase has proven to be a very powerful method for studying different conformational isomers of different ground states which correspond to local minima in the PES of the cluster.

The experiments thus show that more than one conformational isomers of the cluster may be observed. Those are stable at low temperatures and their rigidity can be seen from the rotational analysis of high-resolution spectra.[32,39] At higher temperatures these structures are no longer rigid and can cross the energy barriers and exchange positions. The knowledge of the accurate PES is here also very important. This enables one to simulate the kinetics with molecular dynamics calculations and interpret the higher temperature spectra.

VI. Clusters Investigated

This study is concerned with benzene···X molecular clusters, where X is an atom (He, Ne, Ar, Kr, Xe), a diatomic (N_2), or a polyatomic molecule (benzene).

A. Benzene Dimer

The structures of the benzene dimer considered in this review are summarized in Figure 1.

1. Literature Survey on Experimental and Theoretical Studies

The benzene dimer was originally believed to have a parallel-sandwich structure but the experimental results[14] from the laboratory of Klemperer showed a dipole moment for the dimer which clearly excludes this structure. It was later suggested[48] in the same laboratory that the molecules are located in perpendicular planes forming a T-shaped structure. This conclusion, however, does not prove that only the T-shaped structure exists; in the respective microwave experiments, only the structures with a dipole moment are active, and hence only these are observed. Provided one particular structure of the dimer does not possess a permanent dipole moment, then this structure could not be detected in these experiments. The dimer was studied in the present laboratory[49,30] and from the splitting of the 0−0 transition of the homoisotopic dimers $(C_6H_6)_2$ and $(C_6D_6)_2$ it was concluded that the dihedral angle between the planes of the two molecules is not 90° but rather 70−90°. Karlström and coauthors[50] published as early as 1983 a high-quality ab initio CI study on the dimer and found the T-shape structure to be more stable than the parallel-sandwich or planar structure; other structures were, however, not investigated. Calculations by Williams[51] for the conformation of clusters of benzene molecules employing an exp-6-1 pairwise potential lead to a "herringbone" structure for the dimer. Schauer and Bernstein[52] then studied the benzene dimer also with an empirical potential. The simple exp-6 potential (not containing electrostatic term) predicted the parallel-sandwich as the only structure, the potential augmented by an electrostatic quadrupole term predicted again only one structure, but now the parallel-displaced C_{2h} one. Utilizing a point charge electrostatic term instead of the quadrupole electrostatic one, two energetically similar structures resulted[52]—the "herringbone" and the T-shaped ones. van de Waal utilized[53] the empirical atom−atom potential with point charges for the electrostatic term. If the point charges were smaller than 0.13 e a parallel-displaced structure resulted; when increasing the charge to about 0.17 e a T-shaped structure was also found.

In another study employing the empirical Fraga potential nine different dimer structures were investigated;[54] here the parallel-displaced and T-shaped structures were found to be the most stable. Fraga[55] proposed his potential (in the form of a transferable atom−atom potential) on the basis of fits to ab initio

Table 1. Calculated Properties of Benzene, Hartree–Fock Energy (E), Quadrupole Moment (Q), and Dipole Polarizability (α) (All Values are in Atomic Units)

no.	basis set[a]	exponents of diffuse and polarization functions	$-E$	$-Q_{zz}$	α_{xx}	α_{zz}	α
1	MINI-1		228.89533	5.97	54.2	8.0	38.8
2	MIDI-1		229.32605	6.69	66.7	22.6	52.0
3	MIDI-1+s(C) +p(C)	C: 0.04, 0.05	229.34341	7.52	73.8	38.5	62.0
4	3-21G		229.41618	7.43	67.3	14.4	49.7
5	MIDI-4		230.15831	8.57	72.9	21.7	55.9
6	6-31G*	C: 0.25	230.64075	6.25	72.6	30.5	58.6
7	6-316**	C: 0.25; H: 0.15	230.64968	5.67	76.8	33.0	62.2
8	6-31+G*	sp: 0.056; C: 0.25	230.65274	7.21	78.2	43.8	66.7
9	DZ		230.64065	7.39	69.7	24.1	54.5
10	DZ+2P[b]	C: 1.6, 0.4	230.72703	7.59	72.3	32.8	59.1
11	DZ+2P	C: 1.6, 0.4; H: 2.0, 0.5	230.74560	7.38	73.0	33.5	59.8
12	DZ+2P;2f	X:[c] 1.6, 0.4	230.74888	7.27	73.9	33.6	60.5
13	DZ+2P+s(C) +s(H);2f	C: 0.0511, H: 0.0592	230.74993	7.07	76.2	41.6	64.7
14	DZ+2P+s(C)+p(C)+s(H);2f	C: 0.0382	230.75083	7.18	78.3	44.2	66.9
15	DZ+2P+s(C)+p(C)+s(H);3f	X:[c] 2.4, 0.8, 0.267	230.75274	7.12	78.9	44.4	67.4
16	DZ+2P+s(C)+p(C)+s(H);4f	X:[c] 3.2, 1.6, 0.4, 0.2	230.75301	7.08	79.2	44.5	67.7
17	DZ+2P+s(C)+p(C)+f(C)+s(H)[d]	C: 0.8	230.76179	7.13	77.7	43.6	66.3
	experimental			7.4 ± 0.5[e]			69.6[f]

[a] References to the basis sets could be found in ref 60. [b] Polarization functions on C only. [c] Dummy atom at the center of mass. [d] Only one set of p-polarization functions on H with exponent equal to 1.0. [e] Reference 61. [f] Reference 62.

results. Čársky and coauthors[56] using ab initio SCF calculations with dispersion energy demonstrated that the T-shape structure is more stable than the parallel-sandwich one. In addition it was shown[56] that a distortion from the T-shape structure (by wagging of one ring) is associated only with a marginal change in energy.

Experimental results obtained[57] with mass-selective, ionization-detected stimulated Raman spectroscopy were consistent with a T-shaped structure. The same structure resulted[46] from rotationally resolved spectra of microwave experiments; the distance between centers of benzene molecules was shown to be 4.96 Å. In this paper[46] some evidence was also mentioned that a still lower energy state of the dimer could exist.

Surprising new results were obtained[47a] in this laboratory by a new way of mass-selected hole-burning experiments in the gas phase. The observed spectra are consistent with the existence of at least two different ground-state dimer structures. On the basis of these experiments, however, it is not possible to deduce the structure and stabilization energy of the single conformational isomers.

Again with the Fraga potential Sánchez-Marín et al. reinvestigated[58] the benzene dimer, but now 10 benzene dimer structures were studied and the nature of all the stationary points was determined. In the case of a model with one-center charges, the only minimum corresponds to the T-shaped structure. However, if a three-center charge model was utilized two minima (parallel-displaced and T-shaped) resulted. The former structure was found to be more stable than the latter one (−860 versus −802 cm^{-1}).

The experimental investigations discussed above concern the geometrical structure of the dimer or only the mere existence of the dimer. Experimental determination of the stabilization energy is more involved. The only experimental information on the stabilization energy of the dimer comes from measurements[59] of the ionization and appearance potential. The resulting value of 565 cm^{-1} includes the zero-point energy and therefore corresponds to the stabilization enthalpy.

The benzene dimer was repeatedly studied theoretically in this laboratory, using ab initio methods.[60]

2. Selection of the Basis Set

The basis sets considered are described in Table 1. In the same table the Hartree–Fock energies for the benzene molecule (here the experimental geometry used was CC = 1.406 Å and CH = 1.08 Å) are presented as well as the quadrupole moment and polarizability (for experimental values see ref 61). Let us recall that these one-electron properties are decisive for the evaluation of the quality of basis set. The total interaction energy of the benzene dimer consists mainly of an electrostatic quadrupole–quadrupole term, a dispersion term (proportional to product of polarizabilities) and, of course, the exchange-repulsion energy. From Table 1 it is clear that all the minimal and split-valence basis sets (with exception of basis sets 3 and 4) do not provide correct values of the quadrupole moment. This is surprisingly true also for the split-valence basis set augmented by polarization functions (basis sets 6 and 7). Only after adding the sp diffusion functions (i.e. basis set 8) did a reasonable quadrupole moment result. On the other hand already the DZ basis set gives correct values for the quadrupole moment. The quadrupole moment is not changed upon extending the DZ basis set by diffuse and polarization functions (i.e. basis sets 10–17). The SCF interaction energy (governed by the electrostatic quadrupole–quadrupole term) will thus be already well described at the DZ level.

The quadrupole moments presented in Table 1 were obtained from the SCF density matrix. By passing to the MP2 density matrix the quadrupole moments are reduced. With basis sets 8, 9, and 10 the following values of Q (in au) were obtained:

−6.41, −6.40, and −7.11. For the largest basis set, for which we were able to evaluate the correlation energy correction, namely for basis set 10, the reduction equals to about 7%. Similar or smaller reductions can also be expected for larger basis sets.

The polarizability is more sensitive to the quality of the basis set than the quadrupole moment. In this case there is almost no difference between the split-valence and the DZ basis set. From the table it is clear that if a basis set does not contain polarization functions (basis sets 1−5), a too small value for the polarizability results. These polarization functions should be diffuse; if standard (i.e. energy optimized) polarization functions are added (basis sets 6 and 7), again a too small polarizability results. Polarization functions on the hydrogen atom are not critical; passing from basis set 10 to 11 results only in a marginal polarizability increase. This pass, however, is more important in the case of the 6-31G* basis set, where it brings considerable improvement of the polarizability. This, however, is due to the unbalanced character of this basis set. From the table it is further seen that it is the vertical component of the polarizability which is especially sensitive to the quality of the basis sets. This is important; if sandwich complexes are being studied, then the vertical polarizability is decisive.

The addition of two sets of f functions localized at the center of the benzene to the basis set 10 brings almost no improvement; notice, however, the deepening of the total energy. On the other hand, if diffuse s and p functions were added to all the carbon atoms (basis sets 13 and 14), a significant improvement of the polarizability resulted. See also the results obtained with the small basis set 3! Addition of further sets of f functions (basis sets 15 and 16) brings no improvement of the polarizability which gives evidence on saturation of the basis set. The polarizability evaluated with basis set 16 is rather close to the experimental value. By evaluating the various basis sets tested it can be concluded that only extended basis sets provide a polarizability within a 15% limit to the experimental value. The values presented in Table 1 were obtained again on the SCF level. The inclusion of the correlation energy in this case has a smaller effect than it has in the case of computing the quadrupole moment. The following MP2 polarizabilities (in au) were obtained with basis sets 8, 9, and 10: 67.8, 58.9, and 58.6.

It is worth mentioning that the polarizability evaluated with the medium basis set 8 is rather close to that calculated with much the larger basis set 15. Whereas the former basis set has only one set of polarization functions on the carbon atoms, the latter basis set has two sets of polarization functions on all the atoms. It is the presence of diffuse sp shell and of diffuse d functions which is responsible for the surprisingly good total polarizability as well as the respective perpendicular component. The total energy calculated with basis set 15, however, is considerably lower than that obtained with basis set 8. Here one has to be warned: Basis set 8 gives a high-quality polarizability and also provides good values for ΔE^{COR}. Due to the good quadrupole moment, a reasonable electrostatic energy also results. But other characteristics evaluated with this basis set may not be correct. This basis set is therefore not reliable enough and should be used only with caution. Besides this basis set the more reliable basis sets 10 and 11 were therefore also used. Basis sets 10 and 11 represent a compromise between accuracy and economy. Basis sets 8, 10, and 11 have 255, 288, and 360 orbitals, respectively, for the benzene dimer (6d functions).

3. Structures and Stabilization Energies

Altogether 14 structures (cf. Figure 1) of the benzene dimer were investigated. Is there any chance to rationalize this tedious and time-consuming search for an optimal structure? In the previous parts the important role of the quadrupole moment of benzene was mentioned several times. The quadrupole−quadrupole term represents the first nonvanishing term in the electrostatic energy. The only other attractive contribution comes from the London dispersion energy (the quadrupole-induced dipole term is almost negligible). The quadrupole−quadrupole term is proportional to r^{-5} (where r is the distance between centers of molecules), while the dispersion energy decreases more rapidly with the distance (as r^{-6}). Furthermore, dispersion energy is known[3] to be less structure dependent. It is therefore useful to investigate the PES of the electrostatic quadrupole−quadrupole interaction. Using the expression for linear quadrupoles only two stable structures were found. In the first one the quadrupoles are perpendicular while in the second one they are parallel but mutually displaced. This means either the T-shaped structures **e**−**i** and **n** or parallel-displaced structures **c** and **d**. The interaction of two quadrupoles is repulsive for structures **a** and **m**. To reach quadrupole−quadrupole stabilization the top molecule in structure **a** should either be rotated by 90 degrees (forming the T-shaped structure) or displaced (forming the parallel-displaced structure).[62] The pilot investigation of the PES was performed with the small basis set 3 and can be summarized as follows:

(i) The T-shaped structure **e** was found to be most stable. The rotation of the subsystems around the intermolecular C_2 axis was free (stabilization energies of structures **e** and **f** were the same).

(ii) The other T-shaped structues **g** and **h** were less stable.

(iii) The parallel-sandwich structure **a** was considerably less stable; when the top molecule is displaced (i.e. passing to structure **c**) the stabilization energy increases. The rotation of subsystem around the C_6 axis was free (stabilization energies of structures **a** and **b** were the same).

(iv) Rotating the proton donor molecule in the T-shaped structure (i.e. passing from structure **e** to **l**) leads to a decrease of the stabilization energy. On the other hand the wagging motion around the lowest hydrogen in the T-shaped structure (structure **j**) is practically nonhindered.

(v) The distortion of the T-shaped structure by shifting the proton donor molecule (i.e. passing to the structure **k**) is associated with a decrease of the stabilization energy.

Table 2. Optimal Geometries and Interaction Energies for Selected Structures of the Benzene Dimer

structure[a]	basis set[b]	r (Å)[a]	s (Å)[a]	ΔE (kcal/mol)
a	DZ+2P[c]	3.9		−0.853
d	6-31+G*	3.5[d]	1.6	−3.517
	DZ+2P[c]	3.5[d]	1.6	−1.978
	DZ+2P	3.5[d]	1.6	−2.276
e	6-31+G*	5.0		−2.642
	DZ+2P[c]	5.0		−1.893
	DZ+2P	5.0		−2.107
i	DZ+2P[c]	4.9	1.2	−1.921
	DZ+2P		1.2	−2.101
n	DZ+2P[c]	6.2		−0.682
	DZ+2P	6.2		−0.890

[a] Cf. Figure 1. [b] Cf. Table 1. [c] Polarization functions on C only. [d] Distance of centers of mass is 3.85 Å.

(vi) The rotation of the top molecule in structure **c** by 30° (i.e. passing to the structure **d**) leads to a small increase of the stabilization energy.

(vii) Rotating the top molecule in structure **g** by 30°, i.e. passing to structure **h**, is connected with destabilization.

(viii) No stabilization was found for the planar structure **m**.

All results mentioned should be taken with care due to the quality of the basis set used. On the basis of these conclusion as well as on those obtained from the study of the quadrupole−quadrupole PES it was possible to find the critical structures which then were investigated using larger basis sets. The following structures were studied with the larger basis set 8, 10, and 11: **a**, **d**, **e**, **i**, and **n**. The respective optimal geometries and interaction energies are summarized in Table 2. From the structures given in Table 2 the parallel-sandwich structure **a** clearly does not fulfill the condition for being a minimum. Either rotating or displacing the top molecule leads to stabilization. For the remaining structures the change of any of the six intermolecular degrees of freedom (see above) results in destabilization. This means structures **d**, **e**, **i**, and **n** correspond to minima on the PES.

The most stable structure corresponds surprisingly to the parallel-displaced structure **d**. The T-shaped structure **e** and displaced T-shaped structure **i** are less stable. The energy difference among these isomers, however, are rather small; this was found with the most reliable DZ+2P basis set. These differences in the stabilization energy evaluated at the 6-31+G* level are considerably larger. Also the absolute values of the stabilization energy determined with this basis set are overestimated: the values obtained with DZ+2P basis sets are smaller by 36% (structure **d**) and by 20% (structure **e**). It clearly reflects the unbalanced character of the 6-31+G* basis set, and all the results obtained with this basis set should be verified with a more reliable basis set (see also the warning at the end of part VI.2).

From Table 2 it is evident that the geometry of the minima is not changed when using different basis sets. This is not surprising because the effect on the geometry of the molecular clusters is not too sensitive to the theoretical level applied.

From the four minima found the T-shaped (**e**), T-shaped displaced (**i**), and parallel-displaced (**d**) structures possess a dipole moment. For the former two structures it is considerably higher than for the latter one (0.537, 0.443, and 0.004 D; HF/6-31+G* level). The T-shaped structure (**h**) has a center of inversion and, therefore, does not have a dipole moment. The experimental dipole moment for the benzene dimer is not available.

4. Energy Barriers Among the Most Stable Minima

It was shown in the previous paragraph that there exist four minima on the PES; three of them, the T-shaped (**e**), displaced T-shaped (**i**), and parallel-displaced (**d**), are very close in stabilization energy. To be able to distinguish these structures experimentally the energy barriers among them should be high enough. Let us first consider the T-shaped structure (**e**) and the displaced T-shaped structure (**i**). The wagging motion around the lowest hydrogen (i.e. the one pointing to the center of the second benzene molecule) converts the former structure to the latter one. Due to the symmetry there are in fact two displaced T-shaped structures separated by the T-shaped structure **e**. The wagging motion described is connected with the decrease of the stabilization energy. The respective energy barrier was estimated from the energy of the "transition" structure, defined as the structure being between both structures considered. The MP2 calculations lead to a very low barrier of less than 20 cm^{-1}. The two structures differ not only in their stabilization energy but more important in symmetry. The T-shaped structure possesses a symmetry axis given by the 6-fold rotation axis of the benzene molecule of the top. No barrier for the motion around this axis of the benzene molecule forming the stem was found in the calculations which allows a free internal rotation of this dimer. This free internal rotation is unique for the perfect T-shaped structure, and the low rotational constants increases the density of energetically available states at low temperatures.

The wagging motion converting the T-shaped structure to the displaced T-shaped one is basically one dimensional, whereas the respective motion converting the T-shaped structure to the parallel-displaced one is more dimensional. Besides the wagging motion the displacement of the upper molecule and its approach toward the lower molecule must be considered. The more-dimensional problem brings clearly the difficulties with the optimization of the transition structure. The pilot calculations have shown that this barrier is also rather low. This displaced sandwich structure also lacks the possibility of a free internal rotation which reduces the energetically available states at low temperatures compared to the T-shaped structure.

5. Accuracy of Calculated Stabilization Energy

For the benzene dimer no benchmark calculations as for benzene···Ne or benzene···Ar (see later) exist. To estimate the accuracy of the calculated stabilization energy two points are to be discussed: (i) the effect of the truncation of the basis set; and (ii) the effect of higher correlation energy contributions.

(i) For reasons of economy basis sets considerably larger than DZ+2P could not be used to investigate the PES of the benzene dimer which contains several low-symmetry stationary points. Such basis sets could be used for the evaluation of one-electron properties, the quadrupole moment, and the polarizability. The accuracy of the calculated stabilization energy then could be deduced from the accuracy of these one-electron properties. From Table 1 it is clear that DZ+2P basis set gives a rather accurate value of the quadrupole moment but the respective polarizability is still underestimated. Passing to the larger basis sets the dipole polarizability increases by about 10%. Because the dispersion energy is proportional to the square of the polarizabilities we may expect that utilizing the DZ+2P basis set the stabilization energy of the benzene dimer will be underestimated at least by 20%. (Higher polarizabilities and higher terms of dispersion energy will be represented even worse by these basis sets; the 20% underestimation should be therefore considered as the very lower limit.)

(ii) An estimation of the role of higher correlation energy contributions is very complicated. From the literature it is known[3,63a] that for small complexes the MP3 and MP4 contributions compensate; this was confirmed also by us in the case of the benzene···He cluster (see later). The question arises whether a similar compensation[63b] exists also in the case of larger complexes and in particular in the case of the benzene dimer. The unambiguous answer could be given only by performing the MP4 (or equivalent) calculations for various structures of the dimer with at least a basis set of DZ+2P quality.

Finally, the effect of relaxation of the subsystem geometry will be mentioned. By keeping the subsystem geometry frozen, the relaxation of the subsystem geometry upon dimer formation is neglected. As shown by us[60] by performing the dimer gradient optimization (a small basis set was used) this effect is negligible and increases the stabilization energy only marginally (by about 0.01 kcal/mol).

6. Comparison with Experiments in the Gas Phase and in the Solid State

An experimental geometry in the gas phase is available only for the T-shaped structure[46] with a distance of the centers of mass of 4.96 Å between the two benzene molecules. It was further shown[57] that in the T-shaped dimer the (top) subsystem rotates freely about its C_6 axis. The optimal theoretical distance for the T-shaped structure equals 5.0 Å, the internal rotation was found to be free. The experiments in this laboratory[47a] with the mass-selected hole-burning spectroscopy showed the existence of at least two stable benzene dimer isomers and the most prominent feature in the spectrum was assigned to the T-shaped structure. The other isomer is found to increase in intensity only at strong cooling conditions, i.e. at very low temperatures, and represents probably the displaced sandwich structure. The weaker signal could be explained by the lower symmetry and the absence of a free internal rotation, which reduces the energetically available states. For vibrational temperatures which lead to excitation above the barriers for interconversion between the different isomers, the structure is no longer different and could be described as the T-shape with large amplitude wagging vibrations. Therefore the other (displaced) structure is found only at very low temperatures where it cannot cross the barrier and thus represents a stable isomer.

Conclusions from the previous paragraph were derived for the isolated benzene dimer which corresponds to the gas-phase conditions. The situation in the liquid or solid phase may be entirely different. The question is: What is the mutual orientation of the benzene molecules in the solid benzene? From neutron diffraction experiments[64] it is found that the solid is formed from parallel-displaced and T-shaped orientations of the aromatic rings. Other evidence on the orientation of the benzene rings originate surprisingly from the protein crystal structures. Geometries of aromatic residues in proteins were analyzed[65] using the high-resolution crystal structures. It was found[65] that a specific geometric aromatic interaction dominates and occurs most frequently. The interaction appeared with a significantly higher frequency than was expected from a random distribution. A total of 220 phenylalanine–phenylalanine interactions found in the crystal structures of proteins exhibits high occurrences of T-shaped and parallel-displaced structures and almost no occurrences of sandwich and planar structures. We may conclude this paragraph by noting that the most stable structures predicted by theoretical calculations are found in the gas phase and are also those found to predominate in solid benzene or in crystalline proteins.

The experimentally determined stabilization enthalpy[59] of the dimer is about 1.6 ± 0.2 kcal/mol. The optimal theoretical stabilization energy is 2.3 kcal/mol and after adding the ZPE, one obtains a stabilization enthalpy of 2.0 kcal/mol. This value is not too far from the experiment; it was shown, however, that the theoretical value is underestimated by about 20% thus producing a stabilization enthalpy of 2.4 kcal/mol. As we are not able to estimate the higher correlation energy contributions for the present cluster we cannot accurately reproduce the experimental value derived from ionization and appearance potentials.[59] On the other hand our estimated value agrees nicely with the stabilization enthalpy of 2.3 kcal/mol obtained[66] by evaluating different bulk properties of benzene determined by Monte Carlo simulations.

B. Benzene···Ar

Among the benzene···rare gas atoms complexes the benzene···Ar complex has a special position and will be therefore discussed separately. This complex namely represents the first system for which a consistent set of various properties was generated (see section II). Further, various cluster properties were evaluated experimentally.

1. Investigation of the PES

Five different structures of the complex (cf. Figure 2) were studied.[67] The structures **A**–**C** are of sandwich type while the structures **D** and **E** are planar.

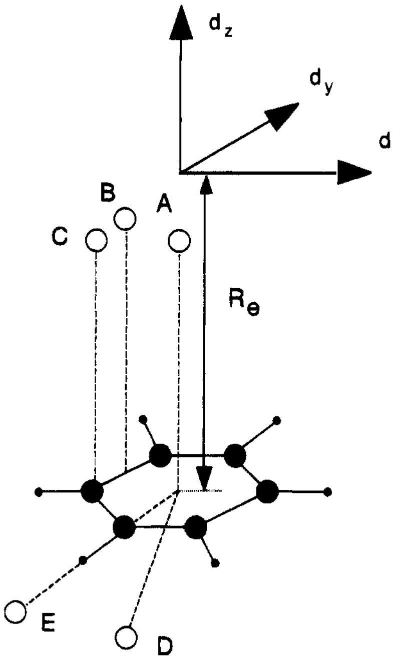


Figure 2. Structures of the benzene···Ar complex.

Table 3. Optimal Geometries and Interaction Energies for Different Structures of the Benzene···Ar Complex Studied at the MP2/6-31+G*/7s4p2d Level

structure[a]	A	B	C	D	E
R (Å)[a]	3.6	3.7	3.7	5.2	6.0
$-\Delta E$ (cm^{-1})	351	261	245	147	80

[a] Cf. Figure 2.

The calculations were performed at the MP2/6-31+G*/7s4p2d level. Stabilization energies and optimal geometries for these structures are summarized in Table 3. Clearly, the C_{6v} structure **A** is the most stable; displacing the Ar from the C_6 axis leads to a stabilization energy decrease. The sandwich structures are considerably more stable than the planar ones. On the other hand, the planar structures are surprisingly stable; stabilization was found even in the case of structure **E**. The prediction of the stabilization for the planar structures is important for any processes where Ar jumps from one side of the benzene to the other side. The optimal intermolecular distance found with 6-31+G*/7s4p2d1f basis set was 3.53 Å; performing the vibrational averaging of the intermolecular distance we received a theoretical R_0 value of 3.58 Å, which nicely agrees with the experimental value of 3.58 Å.[68] However, extended calculations[69a] (at the basis set limit of the MP2 method) give a slightly smaller intermolecular distance of 3.4 Å (cf. Table 4).

2. More Accurate Calculations for the Global Minimum

The C_{6v} structure of the complex was studied at higher theoretical levels, the respective characteristics are summarized in Table 4. Evidently, small basis sets underestimate the stabilization energy. Even rather large basis sets having two sets of f functions on Ar cover only about 70% of the one-particle basis set limit (MP2-R12 calculations). Higher correlation contributions are repulsive; the CCSD(T) stabilization energies are smaller than the respective MP2 values (see Table 4). For the five basis sets used the CCSD(T) stabilization energy amounts to 50, 60, 52, 64, and 60% of the MP2 stabilization energy. In all these cases the contribution to the stabilization energy originating from the triple excitation leads to more stabilization and is rather important. For the basis sets given in Table 4 this triple excitation term is equal to 60, 77, 90, 87, and 122 cm^{-1}, respectively.

Table 4. Higher Level Calculations on the C_{6v} Structure of the Benzene···Ar Complex

basis set	R (A)	$-\Delta E$ (cm^{-1}) MP2	$-\Delta E$ (cm^{-1}) CCSD (T)
6-31+G*/7s4p2d	3.6[a]	351	
3s2p1d/2s/4s3p2d	3.5	294	147
6-31+G*/7s4p2d1f	3.5[a]	429	
4s2p2d/2s2p/7s4p2d1f	3.5[a]	396	
4s2p2d/2s/5s4p2d1f	3.5	366	221
cc-pVDZ/aug-cc-pVTZ[69a]	3.4	338	176
4s2p2d/2s2p/7s4p3d2f	3.5[a]	417	
4s3p2d/2s1p/5s4p3d2f	3.5	428	274
4s3p2d1f/2s1p/6s5p3d2f1g[69b]	3.4	507	337
8s5p4d3f/4s3p/15s10p5d5f[69a,b]	3.4[a]	553	
experiment	3.58[68]	340[70,c] 359[71,c]	

[a] Optimized value. [b] MP2-R12. [c] Experimental stabilization enthalpy (without ZPE correction).

The results discussed above are warning—only higher level calculations covering triple excitations performed with extended basis sets possess reasonably accurate stabilization energies. From the Table 4 it is evident that the CCSD(T) stabilization energy evaluated with the largest basis set is still too small. Namely the respective MP2 stabilization energy is underestimated (with respect to the MP2-R12 value) by about 9%. Extrapolating the CCSD(T) value from ref 69b one obtains a stabilization energy of 376 cm^{-1}. Correcting this value by the ΔZPE results in a stabilization enthalpy of about 330 cm^{-1} which agrees well with both experimental values, 340 cm^{-1} (ref 70, an upper limit) and 359 cm^{-1} (ref 71).

3. Fitting the PES to an Empirical Potential

Any theoretical treatment of the internal dynamics of the complex investigated (and of any complex) requires an analytic representation of the relevant section of its PES. The analytic potential should fulfill two conditions: (i) it should be sufficiently flexible and (ii) it should contain a manageable number of adjustable parameters. It must be considered that various parts of the PES have different levels of importance for evaluation of different properties. If the aim is the determination of fundamental vibrational frequencies, then the analytic potential should be accurate in the region around the global minimum (other minima are supposed to be higher in energy). On the other hand, the potential which is to be used more generally, e.g. for computer experiments, should moreover describe also the short-range and long-range parts of the PES as well as regions around less stable minima. It is almost impossible to generate one universal potential; therefore two types of potentials were fitted[73] to the benzene···Ar PES. The first potential, the global potential (eq 3) tries to mimic all the parts of the PES

Table 5. The Parameters of the Global- and Morse-type Potentials

Global potential		Morse-type potential	
C_1 (Å)	2.808	D_e (cm^{-1})	425.0
C_2 (Å)	3.685	R_e (Å)	3.553
C_3 (cm^{-1} Å^6)	0.361	a (A^{-1})	1.48
C_4 (Å)	2.71	k_{xx} (cm^{-1} Å^{-2})	74.0
N	13.31	k_{xxz} (cm^{-1} Å^{-2})	−79.0
M	6.0	k_{zz} (cm^{-1})	405.0

and is therefore generally applicable. The second one is basically the Morse-type potential (eq 4). Due to its complexity, its use is limited to the evaluation of the vibrational spectrum.

A global potential was considered in the form

$$V = V^{\mathrm{REP}} + V^{\mathrm{DISP}} \tag{3}$$

$$V^{\mathrm{REP}} = a_1\{\Sigma_{i=1}^{6}(C_1/r_{\mathrm{H}i})^N + \Sigma_{i=1}^{6}(C_2/r_{ci})^N\} \tag{3a}$$

$$V^{\mathrm{DISP}} = a_2C_3\{-a_3\Sigma_{i=1}^{6}(1/r_{\mathrm{H}i})^M(1 - C_4/r_{\mathrm{H}i}) - a_4\Sigma_{i=1}^{6}(1/r_{ci})^M\} \tag{3b}$$

The form of this potential was certainly dictated by the nature of the forces acting between subsystems. For example, in the case of polar subsystems, it would be necessary to consider also the electrostatic r^{-1} term. The meaning of the single terms is following: $r_{\mathrm{H}i}$ and r_{ci} are the distances H···Ar and C···Ar, the constants a_1, a_2, a_3, and a_4 are equal to 83.5936, 8065.714, 41.35496, and 118.2612 cm^{-1}, respectively. C_1, C_2, C_3, C_4, N, and M are adjustable constants and their values are given in Table 5.

First, the repulsive and dispersion terms were adjusted separately. Fitting the repulsive term was straightforward,[73] while fitting the attractive term was more complicated. It was only after a damping $(1 - C_4/r_{\mathrm{H}i})$ was added that a meaningful fit resulted. The role of the damping function is to reduce[74] the dispersion energy for structures with short distances between the benzene atoms and the Ar atom; it was enough to consider only the hydrogen atoms of the benzene molecule. Besides a separate fitting of the repulsive and attractive terms also a simultaneous fitting of both terms was performed; this parameter set was used in subsequent calculations and is presented in Table 5.

The parameters of the Morse-type potential have been fitted to the points containing energies which are important for a correct evaluation of the low-lying vibrational states of the "intermolecular" motions. Adequate accuracy has been achieved with the following representation:

$$V = k_{xx}(d_x^{\,2} + d_y^{\,2}) + k_{xxz}w(d_x^{\,2} + d_y^{\,2}) + k_{zz}\,w^2 - D_e \tag{4}$$

where D_e is the dissociation energy of the complex and

$$w = 1 - \exp(-ad_z) \tag{4a}$$

The resulting parameters are presented also in Table 5. The Morse-type potential was fitted to the sandwich structures only. This potential mimics the ab initio energies for these structures very well (R_e = 3.553 Å, D_e = 425 cm^{-1}). On the other hand the global potential is rather successful for structures **B**, **C**, **D**, and **E**. For the structure **A** it underestimates the ab initio values by about 10% (R_e = 3.560 Å, D_e = 393 cm^{-1}). With the present form of the global potential we were not able to reach a better agreement for all the structures considered. A detailed comparison of ab initio values and values obtained from both potentials could be found in ref 73. The widely used benzene··Ar potential is of 6−12 Lennard-Jones type which was parameterized[75] using the heat of adsorption of Ar on graphite. The agreement between the ab initio interaction energy values and the values obtained from this potential is less satisfactory than using ab initio global and Morse potentials (cf. ref 73).

It must be mentioned that it is not easy to verify the quality of the potential. Besides the direct comparison with ab initio values (which are believed to be reasonably accurate) only an indirect way (e.g via evaluation of vibrational frequencies) exists. The latter will be described in the next section.

4. Utilization of the Intermolecular Potential Found

a. Vibrational Frequencies. The benzene··Ar complex has 33 vibrational degrees of freedom. A complete dynamical study represents therefore a considerable numerical task. The dynamical problem can be fairly accurately separated into two subproblems, one pertaining to the high-frequency modes of benzene and the other to the three low-frequency modes associated with complexation.

The vibrational energy levels for the three intermolecular degrees of freedom were obtained[73] variationally by diagonalizing the vibration Hamiltonian

$$\mathbf{H} = {}^1\!/_2\Sigma_{\alpha\beta}P_\alpha\mu_{\alpha\beta}P_\beta + V(d_x,d_y,d_z) \tag{5}$$

$$\alpha,\beta = x, y, z \tag{5a}$$

as a matrix of basis set functions expressed as products $\Pi_j\Phi_j(v_j)$. The functions $\Phi_j(v_j)$ were obtained numerically by solving the corresponding uncoupled one-dimensional Schrödinger equation:

$$({}^1\!/_2P_\alpha\mu_{\alpha\alpha}P_\alpha + V(d_\alpha))\Phi_\alpha = E\Phi_\alpha \qquad \alpha = x, y, z \tag{6}$$

In eqs 5 and 6, P_α (α = x, y, z) are the momenta conjugate to the vibrational coordinate, and the components $\mu_{\alpha\beta}$ of the inverse moment of inertia have the form of a power series (see ref 73).

The calculated and experimental frequencies are summarized in Table 6. Besides the ab initio potentials the empirical 6−12 Lennard-Jones potential was also used in the calculations. First the experimental results from Menapace et al.[76] and Weber et al.[32,77] will be discussed. Both experiments agree as to the vibrational bands at about 40 and 31 cm^{-1} and assigned them as intermolecular stretch (ν_z) and the first overtone of the intermolecular bend (ν_x, ν_y) vibration; for notation see Figure 2. The third band at about 62 cm^{-1} is assigned either as the third overtone of the intermolecular bend ($4\nu_x$, $4\nu_y$) or the first overtone of the intermolecular stretching ($2\nu_z$)

Table 6. Experimental and Theoretical Vibrational Frequencies[a] of the Benzene··Ar (in cm^{-1}) Complex

	experiment		intermolecular potential		
vibrational assignment	ref 76	refs 77 and 32	global	Morse	6-12 Lennard-Jones
ν_X, ν_Y			23.6 (25.0)	28.9 (29.8)	20.6 (21.8)
ν_z	39.7	40.1	35.3 (44.5)	39.1 (44.9)	31.6 (42.2)
$2\nu_X$, $2\nu_Y$	30.9	31.5	45.7	57.4	39.9
$\nu_X + \nu_Y$			52.9	61.5	48.8
$\nu_X + \nu_Z$, $\nu_Y + \nu_Z$			53.6	62.9	47.0
$2\nu_Z$		62.9	64.7	72.9	57.1
$4\nu_X$, $4\nu_Y$	61.8				

[a] The values in parentheses were obtained from one-dimensional approach.

vibration. The latter assignment is consistent with a rather large anharmonicity of more than 15 cm^{-1}.

The best theoretical results are expected to be those which correspond to the Morse-type potential. The theoretical intermolecular stretching mode agrees nicely with both experimental values. The theoretical bending mode agrees again nicely with the experimental value found for the band at 31 cm^{-1} and is thus assigned to the fundamental of this mode. This was in disagreement with the original assignment to the overtone of a bending mode[76] and led to a new discussion of the spectra. Consequently we feel that this agreement for the stretching and bending modes casts doubt on the assignment of the 63 cm^{-1} absorption as being the $2\nu_z$ transition. A more definitive assignment of this absorption to one of the four $2\nu_\alpha$ and $\nu_\alpha + \nu_z$ ($\alpha = x, y$) transitions would require an evaluation of the electric dipole moment. The theoretical calculations determined the $2\nu_z$ transition at 72.9 cm^{-1} which is consistent with a rather small anharmonicity (about 5 cm^{-1}). The results obtained with the global potential do not differ appreciably from the previous one and they favor this assignment, too. A less convincing support of our new assignment is provided by the 6−12 Lennard-Jones potential. However, it should be remebered that this potential has been derived[75] from heats of adsorption of rare gases on graphite.

The most important conclusion concerns the mixing among single modes; this mixing is so strong that any attempts to describe the higher overtones by means of single-mode labels is meaningless. Consequently, the single-mode labeling as used in Table 6 is only tentative and should be viewed with caution.

From the values of Table 6 it is further evident that the harmonic approach should be used with care. The same is true also for the one-dimensional anharmonic approach. The one-dimensional anharmonic stretching frequency evaluated with the 6−12 Lennard-Jones potential agrees fairly well with experimental value and therefore it could be believed that the 6−12 Lennard-Jones potential is sufficiently accurate. Performing, however, the full three-dimensional calculations we find that the stretching frequency is now far from the experimental value. This clearly indicates that the 6−12 Lennard-Jones potential should be used with caution for the benzene··Ar complex.

The results presented in Table 6 were obtained without taking the overall rotation into account. Van der Avoird used[78] the same analytic potential for the evaluation of intermolecular vibrational frequencies of the benzene··Ar but a more general form of the rovibrational Hamiltonian. This permit the inclusion of the overall rotations and also their Coriolis coupling with the intermolecular vibrations. The final assignment, taking selection rules and rotational structure into account, agrees with that of Table 6 in the case of the fundamental stretching and bending modes. The band at 63 cm^{-1} was assigned to be the bending mode overtone and not the combination mode.

On the basis of the theoretical studies[73,78] a new assignment of experimental peaks was made[79] which fully agrees with that suggested theoretically.

b. Molecular Dynamic Simulations. The structure of larger benzene··Ar$_n$ clusters at a temperature T could be determined with molecular dynamics (MD) simulations, provided the benzene··Ar and Ar··Ar potentials are available. The benzene··Ar$_2$ cluster was studied[80a] by constant energy molecular dynamics simulation. Two isomers of the cluster exist. The global minimum corresponds to the (1|1) isomer (having both argon atoms on opposite sides of benzene; D_{6h}), while the (2|0) isomer (here both argon atoms are localized on one side of benzene) is higher in energy. For the benzene··Ar the ab initio "global" potential, discussed above, was used while the Ar··Ar interaction was described by the empirical 6−12 Lennard-Jones potential. The MD simulations were performed with rigid benzene, the time step was equal to 2.5 fs. To find the relative abundances of different isomers very long MD runs (100−400 ns) must be performed.

The relative population of the (2|0) and (1|1) isomers found[80a] is almost constant at the temperature interval studied, i.e. between 27 and 37 K, and is equal to 64%:36%. This means that the population of (2|0) isomer, at the temperature interval investigated, is larger than that of (1|1) isomer. The preference of the energetically less favorable (2|0) structure is due to the entropy term. While there is only one isomer for (1|1) structure there are 12 equivalent (2|0) isomers (six on each side of benzene). The more ordered (1|1) structure possesses a lower entropy than the less ordered (2|0) structure. For temperatures below 27 K there are no interconversions between the (2|0) and (1|1) isomers; the cluster stays in the original structure on a long time scale. Temperatures above 37 K could not be reached because the clusters dissociate. This means the highest temperature for which the cluster exists for at least 5 ps is close to 40 K. A very similar relative population (62%:38%) was surprisingly reached with the empirical 6−12 Lennard-Jones potential; the temperature interval studied was 24−32 K. The MD simulations are thus less sensitive to the quality of the intermolecular potential than the intermolecular vibrational frequencies.

The MD calculations confirmed the experimental findings[38,39,43] that the benzene··Ar$_2$ possesses two isomers.

The situation with benzene··Ar$_n$ (n = 3−5) clusters[80b] is similar. Also here the population of the energetically less favorable isomer is higher. Contrary to the benzene··Ar$_2$ cluster the one-sided

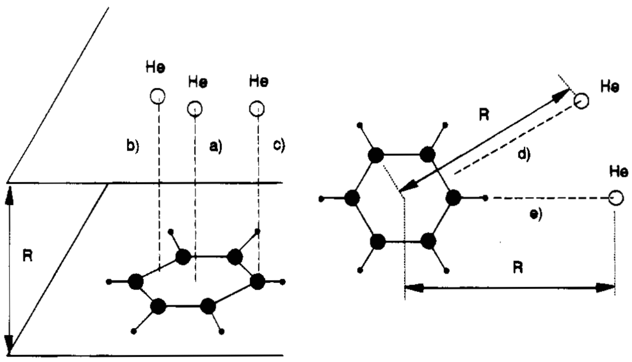


Figure 3. Structures of the benzene···He complex.

Table 7. Optimal Geometries and Interaction Energies for Different Structures of Benzene···He Complex Studied at the MP2/6-31+G*/7s4p2d Level[a]

structure[b]	a	b	c	d	e
R (Å)	3.3	3.6	3.6	5.0	5.5
$-\Delta E$ (cm^{-1})	64(63)	33	30	27	13

[a] The number in parentheses corresponds to the MP2/DZ+2P/7s4p3d2f level. [b] Cf. Figure 3.

isomers are found to be energetically more favorable for all the clusters studied. Hence, the entropy term is more favorable for all the two-side structures. With the benzene···Ar$_n$ (n = 3−5) clusters, the isomers were also generated as having the argon in the second shell. Promotion of an argon atom to the second shell is always connected with destabilization. The abundance of these isomers is considerably smaller. The temperature for dissociation increases with the increasing number of argon atoms in the cluster.

The MD simulations in combination with an accurate potential could not only give the structures at higher temperatures but primarily thermodynamic characteristics of the clusters. In the case of all the benzene···Ar$_n$ (n = 3−5) clusters it was shown that the population of energetically less favorable isomers is higher; this is evidently due to the entropy term.

C. Benzene···X (X = He, Ne, Kr, Xe)

1. Structure, Geometry, and Stabilization Energy

In the case of benzene···He the whole PES, similar to the case of benzene···Ar, was studied.[81] For the remaining complexes only the C_{6v} structure was considered.[81] This structure corresponds to the global minimum for all the benzene···rare gas complexes.

For all the complexes the same procedure as in the case of benzene···Ar was adopted, i.e. the "all electrons" basis set for the noble gas was used. These calculations do not take into account the relativistic effects which are important for heavy elements. It was shown[82] that relativistic effects are important only for complexes with Xe; in the case of Kr-containing complexes, the effects were less important. Neglecting the relativistic effects made[82] the (Xe)$_2$ dimer less stable by about 20%.

The benzene···He structures studied are visualized in Figure 3, and the respective intermolecular distances and stabilization energies are given in Table 7. The C_{6v} structure **a** is clearly again the most stable structure. Comparing the present complex with the benzene···Ar we find that the stabilization energy of the latter complex is considerably higher. Contrary to this the intermolecular distances differ considerably less: 3.326 Å (benzene···He) and 3.526 Å (benzene···Ar). Further, the PES of both complexes are different. Whereas the sandwich structures of the C_6H_6···Ar are clearly preferred over the planar ones, the **b** and **c** sandwich structures of the benzene···He are comparable in stabilization with the planar structure **d**. This means the PES of the benzene···He is more isotropic then that of the benzene···Ar. This difference will be reflected in a different behavior of both complexes, e.g. in the their different rovibrational energy structures.

Table 8. Optimal Geometries and Interaction Energies for C_{6v} Structure of Benzene···X (X = Ne, Kr, Xe) Complexes Studied at the MP2 Level with Various Basis Sets

basis set	X	R (Å)	$-\Delta E$ (cm^{-1})
6-31+G*/5s4p2d1f	Ne	3.5	99
DZ+2P/5s4p2d1f		3.5	78
8s5p4d3f/4s3p/ 11s3p5d4f[a]		3.3	154
6-31+G*/4s3p3d1f	Kr	3.7	485
DZ+2P/4s3p3d1f		3.7	393
6-31+G*/5s4p4d1f	Xe	3.9	601

[a] MP2−R12 (ref 69a).

The calculated[81] intermolecular distance 3.33 Å could be compared with the experimental value[17] of 3.17 ± 0.37 Å; because of a large experimental error the theoretical value is more reliable. The calculated intermolecular distances for benzene···Ne and benzene···Kr complexes, 3.50 and 3.71 Å, agree fairly well with the corresponding experimental values[68] of 3.460 ± 0.001 and 3.677 ± 0.002 Å.

The stabilization energy of the benzene···He complex is not changed dramatically when enlarging the basis sets. The addition of f functions to the He atom increased[81] the stabilization energy to 67 cm^{-1}; enlarging both the benzene and He basis sets resulted in a slight decrease of the respective stabilization energy to 63 cm^{-1}. For the benzene···He the MP4 stabilization energy was also calculated. By using the 6-31+G*/7s4p2d basis set the following energy contributions (in cm^{-1}) were found:[81] SCF (46.9), MP2 (−110.6), MP3 (5.5), MP4-SDQ (3.8), and MP4-T (−9.8). The resulting MP2 and MP4 interaction energies are very close (−63.7 and −64.2 cm^{-1}) which is due to the compensation of MP3 and MP4 contributions. From the total differential cross-section measurements the isotropic potential for the benzene···He was fitted;[83] the respective well depth amounts to 25 cm^{-1}. The ΔZPE for this complex is about 30 cm^{-1} (ref 81); hence the experimental stabilization energy is about 55 cm^{-1}. The agreement with the theory here is also reasonable.

Replacing the split-valence basis set of benzene by the larger DZ+2P set leads for benzene···Ne and benzene···Kr (similarly as for benzene···AR and benzene···He) to a decrease of the stabilization energy (cf. Table 8). From Table 8 we can learn, however, that the one-particle basis set limit of the MP2 procedure[69a] is as large as 154 cm^{-1}; the stabilization energy increase (in comparsion with the DZ+2P/

5s4p2d1f level) is dramatic, nearly 100%. The optimum intermolecular distance is reduced to 3.3 Å. The MP2-R12 stabilization energy agrees with the experimental value of 151 cm^{-1}.[71] Such a close agreement is somewhat surprising since the higher correlation energy contributions are usually repulsive. The 3s2p1d/2s1p/9s5p3d2f CCSD(T) calculations have shown[69a] that the respective stabilization energy is by about 20% smaller than the MP2 value. Due to the fact that the basis set used is not large enough it is not possible[69a] to make a definitive decision about the magnitude of the CCSD(T) and MP2 stabilization energies. It could only be concluded that for this cluster (similarly as for the benzene··Ar cluster) the MP2 stabilization energy is overestimated.

2. Intermolecular Vibrational Frequencies

For the present complexes only the stretching vibration modes were considered. Stretching energy levels were evaluated[81] performing one-dimensional calculations using the following Hamiltonian:

$$\mathbf{H} = -\hbar^2/2[(m_x + m_b)/m_x m_b \, d^2/dr^2] + V(r) \quad (7)$$

where m_x are the masses of the noble gas atoms, m_b is the mass of benzene, r is the stretching coordinate, and $V(r)$ is the stretching potential approximated by means of the empirical function fitted to the MP2 interaction energies. The resulting one-dimensional anharmonic and harmonic (in parentheses) frequencies (in cm^{-1}) for the benzene··X (X = He, Ne, Ar, Kr, Xe) complexes are the following: 31 (51), 24 (29), 44 (47), 38 (40), 37 (39). It is evident that benzene··Ar, benzene··Kr, and benzene··Xe complexes possess an harmonic-oscillator-like energy pattern. The opposite is true for benzene··He, the respective stretching potential supports only two bound states. The benzene··Ne potential, despite its apparent flatness, supports eight bound states. Hence, the only complex which cannot be treated by the standard rotation–vibration theory is the benzene··He complex.

D. Benzene··N_2

The benzene··N_2 complex differs from the benzene··noble gas complexes mainly in the fact that here (similar to the benzene dimer) the quadrupole–quadrupole electrostatic interaction plays a role. We have seen above that this interaction was responsible for the determination of the structure of the benzene dimer. The PES of the titled complex was therefore studied[84] carefully. The structures considered are visualized in Figure 4, and the respective stabilization energies are given in Table 9. The sandwich structure **a** is the most stable; the rotation of the nitrogen molecule around the C_6 axis (i.e. passing to the structure **b**) is free. Both results agree with the respective experimental findings.[85] The experimental equilibrium distance[85] is 3.50 Å; this value cannot be compared directly with the theoretical MP2 values from Table 9 because the experimental value corresponds to R_0 and not to the R_e value. Performing the vibrational averaging of the intermolecular distance we obtained[84] an R_0 value of 3.46 Å. Clearly, the agreement between the theoretical and the experimental distance is reasonable.

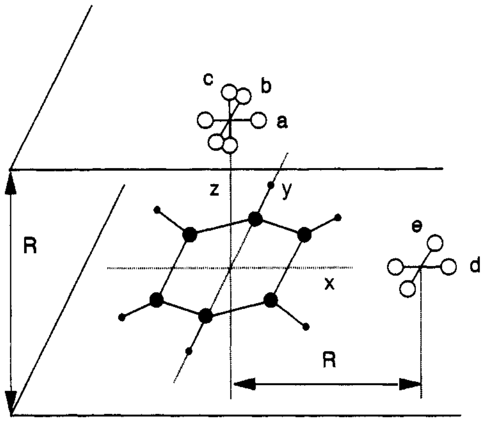


Figure 4. Structures of the benzene··N_2 complex.

Table 9. Optimal Geometries and Interaction Energies for Different Structures of Benzene··N_2 Complex Studied at the MP2/6-31+G*,5s4p2d Level[a]

structure[b]	a	b	c	d	e
R (Å)	3.4	3.4	3.8	5.0	5.5
$-\Delta E$ (cm^{-1})	591(577)	591	298	197	214

[a] The numbers in parentheses correspond to the MP2/DZ+2P,5s4p3d level. [b] Cf. Figure 4.

The other rotation of nitrogen molecule leading to the C_{6v} structure **c**, on the other hand, is hindered. The respective barrier is rather high, about 300 cm^{-1}. Let us remind the reader that for the benzene dimer the relative stabilization of the sandwich and T-shaped structures was just opposite; the T-shaped structure was considerably more stable than the sandwich one. The different behavior of the benzene··N_2 complex is easily explained on the basis of the quadrupole–quadrupole electrostatic interaction. The angular parts of this term are the same for both complexes but the scalar product of the quadrupole moments is different; it is positive in the case of the benzene dimer but it is negative for benzene··N_2 (quadrupoles of benzene and nitrogen molecule have opposite signs). Hence, the sandwich structure of the benzene dimer is destabilized by the quadrupole electrostatic term and the T-shaped structure is stabilized; the opposite is true for the benzene··N_2 complex.

The stabilization energy of the benzene··N_2 complex is only slightly changed when passing to larger basis sets on the benzene as well as on the nitrogen molecule (from 591 to 577 cm^{-1}). The zero-point energy of the complex is estimated (see later) to be 79 cm^{-1}, i.e., the theoretical interaction enthalpy at 0 K is about −500 cm^{-1}. This value has to be compared with the experimental value of 323 ± 24 cm^{-1} (ref 86). Similarly as for the benzene dimer and benzene··Ar complex, the MP2 stabilization energy is larger than the experimental value obtained from appearance potentials.[86]

The benzene··N_2 complex has 36 vibrational degrees of freedom; 31 high-frequency modes belong to benzene and N_2; and five low-frequency modes are intermolecular. By using empirical potentials it was shown[87] that the intermolecular stretch and torsion (around the y axis, cf. Figure 4) vibrations are energetically higher than the remaining bending and torsion modes. We have therefore decided to investigate in a first approach only the stretching and torsional (around the y axis) vibrations. Stretching and torsional energy levels were evaluated performing two-dimensional calculations using the following Hamiltonian

$$\mathbf{H} = {}^1\!/_2\mu_{RR}P_R^{\,2} + {}^1\!/_2\mu_{\alpha\alpha}P_\alpha^{\,2} + V(R,\alpha) \qquad (8)$$

The calculation was performed variationally in the product basis set of the respective one-dimensional wave functions. The form of the inverse moment of inertia and the interaction potential fitted to the ab initio data can be found in ref 84.

The calculated stretching and torsional vibrations were[84] found to be 57 and 73 cm^{-1}, respectively. From the experiment[88] only two vibrational modes were assigned, a stretching and a bending mode (46 and 27 cm^{-1}). The agreement between the theoretical and the experimental stretching frequency is reasonable. It must be kept in mind that taking the coupling with the remaining modes into account a further lowering of the stretching frequency is to be expected, i.e. the agreement with the experiment will be even better.

E. Final Evaluation of the Theoretical and Experimental Properties of Benzene···X Clusters

(i) The structures of all the clusters are successfully predicted already by the MP2 theory and in all cases they fully agree with the experiment. It is worthwhile to mention here that the optimal structures of the benzene dimer and benzene···N_2, which are very different, parallel-displaced and T-shaped for the former complex and sandwich for the latter one, are interpreted already using the quadrupole–quadrupole electrostatic term.

(ii) The most stable structures for the benzene dimer predicted theoretically were found in the gas phase, in solid benzene, as well as in the phenylalanine protein crystals.

(iii) The intermolecular distances evaluated at the MP2 level with medium basis sets agree with the experimental results. This is due to the fortuitous compensation of errors because the MP2-R12 method gives[69a] shorter intermolecular distances for the benzene···Ne and benzene···Ar complexes.

Intermolecular distances for benzene···N_2 and benzene···noble gas atom complexes are rather similar. This seems surprising in the case of benzene···He. Originally we expected a considerably smaller intermolecular distance for this complex. Evidently, it is the intermolecular exchange–repulsion which is responsible for those rather uniform intermolecular distances.

The difference between the calculated R_e and R_o is quite small, less than 0.1 Å.

(iv) The dipole moments of benzene···N_2 and benzene···noble gas atoms are small and similar. The agreement with the experimental value[89] for the benzene···Ar complex is reasonable. Under all circumstances electrons are transferred toward the benzene ring. The dipole moment of the T-shaped benzene dimer is slightly larger.

(v) The calculated stabilization energy (MP2 with medium basis sets) for the benzene dimer differs little from the experimental value obtained from ionization and appearance potentials and it is slightly smaller than the value obtained by evaluating different bulk properties determined by Monte Carlo calculations. As we are not able, at present, to estimate the higher correlation energy contributions we cannot evaluate the accuracy of the theoretical and experimental stabilization energies. For the benzene···Ar complex the MP2-R12 stabilization energy is considerably higher than the experimental value; when performing the calculations on CCSD(T) level the agreement with the experimental stabilization energy becomes very good. The role of higher correlation energy contributions seems to be not so important for benzene···Ne and benzene···He clusters and here the agreement between the experimental and the MP2 stabilization energies is reasonable.

(vi) The calculation of the intermolecular vibrational frequencies is topical because they are in fact the only observables. Measurements of these frequencies represent a difficult task and the complete set of intermolecular frequencies exists (among the complexes studied) only for the benzene···Ar complex. The agreement between theory and experiment (after reassignment) for this complex is very good and it is believed that similarly accurate frequencies could also be evaluated for other complexes. A warning should be given here—it is impossible to make any decision about suitability of a theoretical procedure on the basis of the comparison of only a single vibrational mode. As shown above the coupling between the modes is strong and affects the vibrational energies considerably.

(vii) The intermolecular potential represents without doubt the most important property of the complex. It could be compared with the experiment only indirectly via evaluated vibrational frequencies. We believe we have demonstrated that ab initio potentials represent a more accurate alternative to the, until now, standardly used empirical potentials whose parameters were obtained by fitting various experimental properties.

VII. Prospects

The main conclusion of the present review is the fact that today neither experiment nor theory is able to generate a complete and exhaustive set of various properties of the benzene-containing clusters; the same is true in the case of similar and larger clusters. The prospects in this field are expected to be seen (and highly needed) along the following lines:

(i) The interaction energy for complexes of the size of benzene dimer should be evaluated considerably more accurately, taking higher electron excitations into account. One of the promising approaches is the CCSD(T) procedure. The basis sets considered should be much larger than the basis sets used up to now; they must include several sets of the first and second polarization functions. The ultimate goal would be to utilize the one-particle basis set limits of the CCSD(T) (or equivalent) method.

(ii) The procedure described in i, due to its complexity, could not be applied for a detailed description of the potential energy surface. Here some compromise should be found (e.g. the use of bond functions as described in III.B.v) which enables one to describe the PES as completely and accurately as possible. The results of the procedure discussed above will serve as a benchmark.

(iii) Very promising results were obtained recently for neutral and ionic atomic clusters and ionic molecular clusters using the density functional theory with local spin-density and local density approximations.[90] The density functional theory fails, however, completely for molecular clusters where the dominant stabilization originates from the dispersion energy;[91] the benzene··Ar cluster being the typical example. The only chance to recover the dynamic correlation (its dispersion part is crucial for the molecular clusters mentioned) is via sophisticated nonlocal corrections to the local spin-density level energy. The problem still remains as to construct the nonlocal functionals.

(iv) An analytical potential function should be fitted to the PES evaluated in ii; it would be desirable to find a universal sophisticated function suitable for various purposes.

(v) It is not adequate to discuss various molecular clusters in terms of ΔE; the transfer to ΔG is inevitable. The molecular dynamics supported by the analytical potential developed in iv will provide the desired quantities.

(vi) Another possibility to treat the large molecular clusters (especially those important in biochemical and biological processes) cannot involve just the use of an intermolecular potential but must involve the introduction of methods of different type, e.g. methods of the physics of the continuum.

(vii) Even closer cooperation between theory and experiment will be inevitable to determine and interpret the various properties of molecular clusters as well as to elucidate the different processes connected with the formation and dissociation of molecular clusters in chemistry, physics, and especially biology. Theory here becomes an essential tool for the interpretation of cluster experiments.

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