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LETTERS

Anti-Hydrogen Bond in the Benzene Dimer and Other Carbon Proton Donor Complexes

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A new type of bonding, termed anti-hydrogen bond, is identified in the benzene dimer and other carbon proton donor complexes from correlated ab initio computations. Gradient optimization of the benzene dimer at the MP2/6-31G* and MP2/6-31G** levels shows a shortening of the C−H bond of the proton donor and a blue-shift of the corresponding C−H stretching frequency. The harmonic C−H stretching vibrational frequency shift agrees well with that evaluated for various anharmonic approaches. The blue-shift of the C−H stretching frequency was also found in the case of benzene complexes with other carbon proton donors, CH_4 and $CHCl_3$. The anti-H-bonds are expected to be very significant for the structure and dynamics of biomolecules.

Introduction

The hydrogen bond (H-bond), i.e., the bond between an electron-deficient hydrogen and a region of high electron density, is of key importance in biomolecules. H-bonds determine, for instance, the structure and biological activity of peptides, proteins, DNA, and many other systems. Most frequently, H-bonds are of the X−H···Y type, where X and Y are electronegative elements (like F, O, and N) and Y possess one or two electron lone pairs. The formation of an H-bond generally results in an elongation of the X−H bond and a broadening of the X−H stretching potential, which then causes red-shifts of the X−H stretching frequencies.

The concept of H-bonding has recently been extended to the X−H···π-type bonding, where π represents the delocalized π-electrons of an aromatic system. Such O−H···π H-bonds were found by analysis of fully rotationally resolved spectra of the HOH···benzene cluster;[1,2] a spectral manifestation of this H-bond was reported in ref 3. Other evidence of formation of this type of an H-bond has been reported recently by Brutschy and co-workers,[4] who detected a substantial red-shift of the O−H stretching fundamental frequency in the CH_3OH···benzene complex. Speculation about a similar kind of bond, such as a C−H···π type, has been stimulated by experimental[5] and theoretical[6,7] evidence from the T-shaped equilibrium structure of the benzene dimer. The T-shaped arrangement of aromatic rings, which is believed to be stabilized by the adjoining H-bonds, is rather common in a biological environment (e.g., it is believed to be responsible for the structure of phenylalanine[8]) and is as such of some interest.

Results and Discussion

To obtain a deeper insight and a correct theoretical description of the proposed C−H···π H-bonding, highly accurate model

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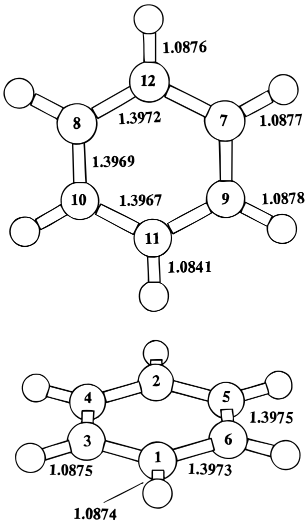

Figure 1. Structure of the optimized benzene dimer having the C_{2v} symmetry; C−C and C−H bond lengths (in Å) are visualized. All the valence angles in the proton acceptor amount to 120°, the angles in the proton donor differ from 120° by less than 0.3°. The proton donor is planar while hydrogens of the proton acceptor are slightly nonplanar (the respective dihedral angles differ from planarity by less than 0.3°). All the valence angles in the optimized benzene (D_{6h}) amount to 120°; the C−C and C−H bond lengths are 1.3967 and 1.0874 Å, respectively.

calculations on the T-shaped structure of the benzene dimer (cf. Figure 1) were carried out; this structure corresponds to the global minimum of the dimer.[6,7] Here the interest lies also in the changes of intramolecular geometries upon complex formation, and hence it is necessary to optimize all intermolecular and intramolecular degrees of freedom simultaneously by using gradient optimization. The gradient optimization was performed without inclusion of counterpoise corrections because until now no routine method exists that covers these corrections in the course of the optimization. The counterpoise corrections were added to the optimized geometry of the complex. For the future we plan to perform optimizations that will include these corrections during the gradient optimization. This type of calculation (gradient optimization) is in contrast to our previous studies on the benzene dimer[6,7] where the subsystems were held rigid and only intermolecular degrees were optimized by a step-by-step procedure; here the BSSE was taken into account. First, we have optimized the T-shaped geometry using a correlated ab initio method. The correlation energy, which dominantly stabilizes the dimer, was evaluated by the second-order Møller−Plesset perturbation theory (MP2) using the 6-31G* basis set (polarization d-functions were included on all the carbons). To our surprise, the C(11)−H bond of the proton donor becomes shorter (by about 0.003 Å) than all other dimer C−H bonds and the C−H bonds of the isolated benzene (cf. Figure 1 and Table 1). Extending the basis set by including polarization p-functions for the hydrogen atoms (6-31G**) has led to exactly the same result. Harmonic vibrational frequencies of the dimer were evaluated at both MP2/6-31G* and MP2/6-31G** levels. Contrary to expectation, the proton donor C(11)−H stretching frequency did not exhibit a red-shift typical for H-bond formation, but a significant blue-shift of about 50 cm^{-1} (see Table 2). Clearly, the C(11)−H bond involved in the T-shaped equilibrium structure of the benzene dimer exhibits features just opposite to those observed for normal H-bonds. We call this phenomenon the anti-hydrogen bond and propose the following interpretation. Attraction of two benzenes in the T-shaped structure is due to the dispersion and electrostatic quadrupole−quadrupole interactions. Accordingly, the attraction is proportional to the higher powers of the reciprocal distance r of the centers of mass of the benzene molecules (r^{-6} and r^{-5} for the dispersion and electrostatic interactions, respectively). To minimize the intermolecular distance and thus optimize the attraction, it is advantageous to compress the C(11)−H bond. Forces causing shortening of the C(11)−H bond are responsible for making the C(11)−H stretching potential deeper and narrower and thus allow for a blue-shift of the respective stretching frequency.

TABLE 1: Stabilization Energies (Δ*E*), Mulliken Charges on Isolated Proton Donor Hydrogens (*q*(H)), and Change of the X−H Bond Length (Δ*r*) of the Proton Donor in Various Benzene-Containing Complexes Determined at the MP2/6-31G* Level; Values in Parentheses Correspond to the MP2/6-31G Level**

complex	symmetry	q(H)	ΔE (kcal/mol)[a,b]	Δr (Å)[c]
$(C_6H_6)_2$[d]	C_{2v}	0.20 (0.15)	1.1	−0.0033 (−0.0033)
$C_6H_6\cdots CH_4$[e]	C_{3v}	0.17 (0.12)	0.3	−0.0008 (−0.0009)
$C_6H_6\cdots HCCl_3$	C_{3v}	0.30 (0.30)	3.2	−0.0025 (−0.0023)
$C_6H_6\cdots HCN$[f]	C_{6v}	0.32 (0.27)	3.2	+0.0018 (+0.0017)

[a] Corrected for basis set superposition error and relaxation energy. [b] Stabilization energy is underestimated owing to the lack of diffuse polarization functions; present theoretical procedures give, however, more reliable intramolecular characteristics. [c] Negative (−) values mean shortening of the C−H bond while positive (+) values elongation of that bond. [d] Cf. Figure 1. [e] MP2 calculations with 6-31G* basis set on benzene and 6-31+G[2d,p] basis set[12] on CH_4 give q(H) and Δr of 0.16 and −0.0020 Å, respectively. [f] MP2 calculations with 6-31G* basis set on benzene and 6-31+G [2d,p] basis set[12] on HCN give q(H) and Δr of 0.44 and +0.0023 Å, respectively.

TABLE 2: Harmonic C−H Stretching Frequences (*ν*) and Intensities (*I*) of Various Carbon Proton Donors in the Isolated State and in Benzene-Containing Complexes Calculated at the MP2/6-31G* Level; Values in Parentheses Correspond to the MP2/6-31G Level**

	ν(C−H);[a] I(C−H)[b]		
proton donor	isolated state	donor···C_6H_6	$\Delta\nu$[a,c]
C_6H_6	3250 (3283);[d] 1.5	3299 (3325); 0	+49 (+42)
CH_4[e]	3248 (3279); 6.4	3263 (3294); 21.3	+15 (+15)
$CHCl_3$	3242 (3255); 39	3297 (3307); 0.3	+55 (+52)
HCN[f]	3513 (3533); 216	3497 (3515); 66	−16 (−18)

[a] In cm^{-1}. [b] In km/mol. [c] Positive (+) values mean blue-shift characteristic for anti-H-bond, while negative (−) values indicate red-shift characteristic for H-bonding. [d] Symmetric C−H frequency. [e] MP2 calculations with 6-31G* basis set on benzene and 6-31+G [2d,p] basis set[12] on CH_4 give the following values of ν(C−H) in the isolated state and in the donor···C_6H_6 complex: 3246, 3272 cm^{-1}, which gives a blue-shift of 26 cm^{-1}. [f] MP2 calculations with 6-31G* basis set on benzene and 6-31+G [2d,p] basis set[12] on HCN gives following values of ν(C−H) in the isolated state and in the donor···C_6H_6 complex: 3444, 3423 cm^{-1}, which gives a red-shift of 21 cm^{-1}.

From the point of view of a direct experimental detection of the proposed anti-H-bond, the most important manifestation is provided by the blue-shift of the pertinent C−H stretching frequency in the infrared spectral region. Spectral manifestation of the tiny bond shortening is much less explicit and its detection would always require a very tedious spectral analysis of extremely complex rotational or rotational−vibrational highly resolved spectra. Characterization of the anti-H-bond in terms of the discussed blue-shift appears to be very suitable also from the point of view of theory. The C−H stretching potential is very deep and fairly parabolic at its minimum. Thus, the C−H fundamental (observable) frequency may be expected to coincide reasonably with its harmonic approximant. But still, the C−H motion, as well as other vibrational motions, is anharmonic, and this may cast doubt on the “harmonic” results. Thus, to

TABLE 3: C−H Stretching Fundamental Frequencies of the Monomer and T-Shaped Dimer of Benzene (in cm^{-1}) Calculated at Harmonic and Various Anharmonic Levels[a] Using the MP2/6-31G* Method

	harmonic	anh 1	anh 2	anh 3	anh 3a
monomer	3250	3018	3018	3084	3111
dimer	3298	3086	3072	3140	3168
shift	48	68	54	56	57

[a] For explanation of various anharmonic levels, see text.

obtain an unequivocal answer, we should go beyond the limits of the harmonic approximation. To make the results tractable, some significant simplifications must be adopted.

The simplest way for estimating the role of anharmonicity consists of treating the C−H bonds as independent oscillators and freezing all the remaining vibrational motions both in the monomer and dimer molecules. The required C−H stretching fundamental frequencies are easily obtained as differences of the first-excited- and ground-state energies of the corresponding one-dimensional Schrödinger equations. This simple model provides an even more profound blue-shift than the harmonic approximation as seen in Table 3 (anh 1). However, the C−H stretchings are not isolated, and their couplings with other motions should be of some consequence. The most important coupling should arise between the C(11)−H and the intermolecular benzene···benzene stretching motions. To account for this coupling, as in our recent study,[9] a nonrigid benzene···benzene reference configuration is introduced. This consists of a rigid C_6H_5 (donor) fragment moving against a rigid (acceptor) benzene molecule while preserving the C_{2v} symmetry (T-shape) of the equilibrium configuration (see Figure 1). The donating hydrogen is moving along the molecular symmetry axis; the fragments are rigid at their equilibrium geometries. Similarly as in the case of the one-dimensional problem, the potential energy function was determined by fitting the pointwise evaluated ab initio energies to an analytic function, and the kinetic energy operator was constructed using the Hougen−Bunker−Johns procedure.[10] The corresponding two-dimensional (2-D) Schrödinger equation was solved variationally using basis set functions expressed as products of the eigenfunctions of the one-dimensional C−H and benzene···benzene (uncoupled) stretching problems. As anticipated, the coupling of the C−H and benzene···benzene motions moves the value of the blue-shift back to its harmonic estimate (see anh 2 in Table 3).

In addition, the coupling considered by the above 2-D model is not the only one that contributes to the value of the resulting frequency shift, and the close agreement of the 2-D and harmonic results does not prove quantitative accuracy of the harmonic theory. Unfortunately, a complete and quantitative theoretical study of the benzene···benzene complex, including the ab initio evaluation of the multidimensional potential energy surface and the solution of the complete vibrational problem, is a rather prohibitive task. However, if we assume that there is no major difference between the coupling conditions among the high-frequency motions in the monomer and dimer molecules and if we take into account the large difference between the energy contents of these motions and the low-frequency intermolecular motions, then we may find it legitimate to separate the C−H motion from the remaining motions using the adiabatic separation. In the simplest version of this approach we neglect all the nonadiabatic couplings and transform the problem essentially to an ab initio optimization of the dimer structures for a selected set of the C−H distances. The resulting energies and geometries provide an effective potential and kinetic energy functions that in turn allow for the evaluation of the C−H stretching energies by solving the corresponding two-dimensional Schrödinger equation. This procedure as seen in Table 3 (anh 3) leads to practically the same blue-shift as in the previous 2-D calculation. Interestingly, a very similar blue-shift was also obtained with the kinetic energy operator approximated by means of the Wilson's G matrix (anh 3a in Table 3). The most elaborated model including the anharmonic effects (anh 3) is in agreement with the previous calculations (anh 1, anh 2) indicating thus promising adequacy of the harmonic model.

The direct experimental detection of the blue-shift in the benzene dimer, which is missing, represents a rather complicated task (see ref 11).

Is the formation of an anti-H-bond limited to the benzene dimer or does it occur also in other carbon proton donor···benzene complexes? We studied the complexes of benzene with other proton donors, CH_4, $CHCl_3$, and HCN. Hydrogens in these systems bear smaller or larger positive charge than those of the benzene molecule (cf. Table 1). For the CH_4···benzene and Cl_3CH···benzene complexes, the MP2/6-31G* and MP2/6-31G** optimization resulted again in a shortening of the C−H bond length (see Table 1). Only for a strong proton donor like HCN is an elongation of the C−H bond length of the proton donor (cf. Table 1) found. Harmonic vibrational analysis indicate a blue-shift of the C−H stretching frequency of the proton donors in the CH_4···benzene and Cl_3CH···benzene complexes and a red-shift in the HCN···benzene complex (Table 2). Evidently, the change of the C−H bond length in the proton donor is connected with the spectral shift of the respective C−H stretching frequency.

The evaluation of X−H stretching frequencies is sensitive to the quality of the basis set used. The harmonic vibrational analysis of benzene···X (X = CH_4 and CCl_3H) was therefore performed again at the MP2 level with the larger basis set recommended in ref 12; benzene was described by a 6-31G* basis set while proton donors by a larger 6-31+G[2d,p] basis set (for exponents of polarization functions, see ref 12). The experimentally observed red-shift of the water O−H stretching frequencies of the benzene···HOH complex of ref 3 was reproduced almost exactly in ref 12 by harmonic calculations using the basis sets mentioned. From Tables 1 and 2 it is evident that the lower level results for both complexes investigated were fully confirmed.

From the values of the stabilization energies of various benzene-containing complexes (Table 1) and their spectral shifts (Table 2), it is evident that the spectral shift does not correlate with the stabilization energy.

Apart from the frequency shift, the H-bonding manifests itself in molecular spectra also by profound intensity changes. To get an insight into these phenomena in the complexes studied, we have evaluated the pertinent intensities within the framework of the "double-harmonic" approximation. Intensities of the C−H stretching frequency in the benzene dimer, benzene···CH_4, benzene···$CHCl_3$, and benzene···HCN complexes, and in the corresponding isolated C−H proton donors, are presented in Table 2. As we see, there is a qualitative difference in the behavior of different complexes in dependence on the electric properties of the C−H proton donor. While the standard H-bonding (benzene···HCN) leads, as expected, to a sizable increase of the pertinent intensity, the anti-H-bonding is accompanied by a rather small intensity change. Of course, while we are able to disregard the role of the mechanical anharmonicity in the intensity shift evaluation, we do not know yet if this is possible in the case of the electrical anharmonicity. Thus, to get a more conclusive insight, we plan to evaluate the intensity changes beyond the limits of the harmonic approximation.

Conclusion

Three of four carbon proton donors studied here do not form a standard H-bond with the benzene π-system as would be characterized by a red-shift of the C−H proton donor stretching vibration frequency. In contrast a significant blue-shift was detected in these C−H proton donor complexes. The new type of bond characterized by this blue-shift is termed an anti-H-bond.

It seems that the anti-H-bond concept is of a general nature and is significant not only in molecular clusters but also in biomolecules. We do expect that any interaction between an alkyl group and aromatic ring in proteins leads to this type of a bond. We have already found one example.[13] The C−H bond in the methyl group of *n*-propylbenzene (global minimum−gauche structure) is contracted owing to the significant dispersion attraction between the methyl group and the aromatic ring (MP2/6-31+G* calculations). The anti-H-bond concept is certainly not limited to C−H···π contacts. We have shown recently[14] that the C−H···O contact in the adenine···thymine base pair, which is speculated to be the third H-bond of the pair,[15] also exhibits anti-H-bond character.

The anti-H-bond effect that leads to C−H bond shortening appears to be of general importance in internal interactions in biomolecules and can be seen as evidence for the dispersion nature of this interaction. This is in contrast to normal H-bond interactions, which are dipolar in nature and result in a X−H bond lengthening.

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(11) Experimentally the anti-H-bond should be observable as a strong blue-shift of the C−H stretching frequency in the benzene dimer. The isolated benzene dimer is only stable at very low temperatures and can be prepared in supersonic jet experiments. The low concentration under these conditions does allow for direct IR absorption measurements; hence, other experimental techniques have to be applied. Depletion spectroscopy is one, where a strong laser is tuned to the absorption band of this C−H stretching frequency. The absorbed photons will dissociate the dimer and lead to a reduced signal in a subsequent resonance-enhanced multiphoton ionization experiment. At the present, no strong tunable IR lasers at this wavelength range of 3 μm are available, as commercial OPO systems here only extend to 2.6 μm. Other hole-burning techniques such as stimulated Raman spectroscopy with ion detection or stimulated emission pumping of the benzene dimer could give information on the ground-state frequencies but have not yet been employed to study this effect. The shortening of the C−H bond in the isolated dimer cannot be measured directly, as microwave spectra only allow for the determination of the center-of-mass distance between the two benzene rings. Here information should be obtained from solid benzene, but the benzene solid structure is of more herringbone structure, and not a T-shape one. The bond length can be obtained from neutron scattering experiments, as X-ray studies are not sensitive to the hydrogen atoms. We have carefully checked the literature, but to our best knowledge there is no relevant paper available giving any information on the shortening of the C−H bond in the benzene dimer. The same is true for matrix IR experiments.

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