Intermolecular Interactions in *p*-Chlorobenzoic Acid Dimers

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The molecular structure of the parallel orientation of the *p*-chlorobenzoic acid dimer has been studied at the second-order Møller−Plesset level using split-valence-quality basis sets augmented by polarization functions. In the obtained dimer structure, the Cl atoms are located behind the carboxyl groups of the neighboring monomer, while in crystalline copper and nickel *p*-chlorobenzoate complexes, the Cl atoms and the benzene nuclei form a parallel displaced umbrella structure with the Cl atoms mutually above the center of the respective benzene ring. The interaction energy for the parallel *p*-chlorobenzoic acid dimer complex is calculated at the second-order Møller−Plesset level to be 5.1 kcal mol^{-1}. The intermolecular attraction is mainly due to dispersion effects between the aromatic rings. The obtained distance between the benzene nuclei of 343 pm is in agreement with the experimental values of 341.6 and 366.6 pm measured for nickel and copper *p*-chlorobenzoate complexes, respectively. At the second-order Møller−Plesset level, the umbrella structure is found to be bound by 2.6 kcal mol^{-1}, as compared to infinite separations, with a chlorine−ring distance of 364 pm. However, at the second-order Møller−Plesset level, the umbrella structure is not a local minimum.

I. Introduction

Nonbonding molecular-stacking interactions are of fundamental importance in many biological[1] and supramolecular complexes.[2] In our laboratory, $Mtn_2(ZbzO)_2$ type complexes have recently been studied experimentally.[3,4] M denotes Cu^{II} or Ni^{II}, tn 1,3-diaminopropane, and ZbzO a substituted benzoate anion. An early discovery was that *trans*-di(*p*-chlorobenzoate-*O*)di(1,3-diaminopropane-*N*,*N′*)copper(II) and *trans*-di(*m*-chlorobenzoato-*O*)di(1,3-diaminopropane-*N*,*N′*)copper(II) form an umbrella configuration, which means that the benzoate anions are parallel displaced with the Cl atoms located mutually above the center of the benzene rings and interacting with them.[5] Similar packing systems were also found for the *m*- and *p*-bromobenzoate[6] and *m*- and *p*-iodobenzoate analogues.[6,7] It also was found that the replacement of the central copper(II) with nickel(II) did not affect the umbrella configuration. Little is known about the strength of this stacking interaction. However, it was recently argued that the stacking-interaction energy in some picrate complexes must be of strength comparable to the difference between hydroxide and water coordinate bond energies.[8] The experimental distance between the chlorine atom and the least-squares plane formed by the carbon atoms in the aromatic ring of the *p*-chlorobenzoate molecule in *trans*-di(*p*-chlorobenzoato-*O*)di(1,3-diaminopropane-*N*,*N′*)nickel(II) is 341.56(10) pm;[4] see Figure 1. The values are about the same size as the sum of the van der Waals radii of 365 pm for chlorine and the aromatic ring. The corresponding distance for the copper(II) analogue is 366.6(2) pm.[9]

The van der Waals interaction between aromatic molecules has been a subject for many experimental[10−12] and theoretical studies.[13−18] For a recent review of closed-shell interactions, see ref 19. The benzene dimer, which is the simplest prototype system possessing this kind of van der Waals interaction, has been studied at complete active space self-consistent-field (CASSCF),[15] second-order Møller−Plesset perturbation (MP2),[16] and coupled-cluster (CCSD(T))[17] levels. Chipot et al.[18] have studied the parallel complex of the toluene dimer at MP2 level. In their study they found that the distance between the toluene molecules is 10 pm smaller than for the corresponding benzene dimer. This can partly be explained by the presence of dipole−dipole interactions, but the decrease in ring−ring distance was mainly attributed to increased dispersion effects. For the same reason, one may expect that the ring−ring distance in the *p*-chlorobenzoic acid (PCBA) dimer is shorter than for the benzene dimer.

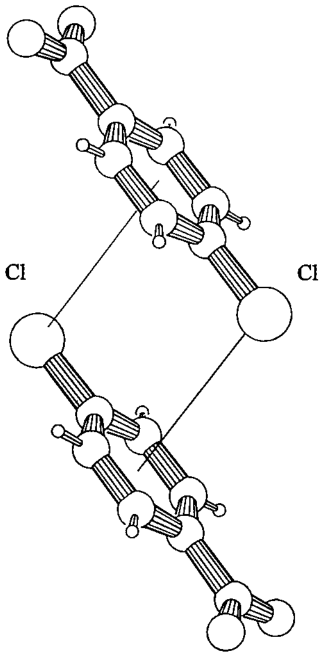

Figure 1. *p*-Chlorobenzoate stacking in *trans*-di(*p*-chlorobenzoato-O)di(1,3-diaminopropane-*N*,*N′*)copper(II) crystals. For clarity only the anions are shown.

The benzene−Cl_2 complex was experimentally observed forty years ago.[20] Several structures with one of the chlorine atoms located at the center of the benzene ring (as in the umbrella

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structure) have been suggested.[20,21] However, in a very recent ab initio study on the benzene−chlorine complex Matsuzawa and Osamura[22] found that the energetically favored structure is the perpendicular structure with the chlorine located above a carbon atom.

Hobza et al.[13,14] studied the stacking of nucleic acid−base pairs at ab initio level including electron correlation effects and obtained interaction energies of 6−12 kcal mol^{-1}. They also found that the stabilization of the DNA base-pair complexes was mainly due to electron correlation effects.

In an early paper dealing with *p*-benzoquinone−hydroquinone, pyridine−pyrrole, and pyridine−phenol stacking, the stacking interaction was studied at the Hartree−Fock level in combination with a London type expression for the dispersion energy.[23] As expected, the Hartree−Fock contribution was found to be repulsive, while the stabilization of the stacking came exclusively from the dispersion energy.[23] In their study of the face-to-face interaction between polycyclic aromatic hydrocarbons and nitrated benzenes, Heard and Boyd[24] claimed that interaction energies was dependent on the quadrupole moment, and apparently for these complexes dispersion effects do not contribute significantly to the binding energy.

To get a better insight into the stacking interaction between the *p*-chlorobenzoate molecules in $\mathrm{Mtn_2(ZbzO)_2}$, we performed ab initio calculations on PCBA dimers and thus replaced the metal atoms with hydrogens and omitted the tn ligands. We chose the acid form since the anion dimer is probably unbound due to the Coulomb repulsion between the monomers, and the size of the metal complex would be too large for MP2 calculations. Initially, we optimized the structure of the PCBA dimer at the second-order Møller−Plesset perturbation level. A more reliable dimer structure was then estimated by manually correcting the energies for basis set superposition errors. To check the applicability of computationally less expensive density functional methods, we also optimized dimer structures at density functional levels. However, since current density functionals are not capable of describing dispersion effects,[25−31] second-order Møller−Plesset calculations should be the preferable method.

II. Computational Methods

The molecular structure of the parallel oriented *p*-chlorobenzoic acid (PCBA) dimer was fully optimized at the second-order Møller−Plesset (MP2) level using the resolution of the identity approach (RI-MP2). In the RI-MP2 approach, the two-electron integrals are approximated by expanding the transition density in atom-centered auxiliary basis sets,[32−34] and computational savings of 1 order of magnitude can be achieved without any significant loss of accuracy as compared to conventional MP2 calculations.

The resolution of the identity second-order Møller−Plesset approach can briefly be described as follows. For a closed-shell restricted Hartree−Fock reference wave function the Møller−Plesset (MP2) energy can be written as

$$E_{\mathrm{MP2}} = \sum_{ijab} t_{ij}^{ab} (ia|jb) \tag{1}$$

with

$$t_{ij}^{ab} = \frac{2(ia|jb) - (ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{2}$$

where $(ia|jb)$ is the electrostatic interaction energy between the transition densities $i(r)a(r)$ and $j(r)b(r)$; ϵ are the orbital energies. The labels a, b refer to virtual orbitals, while the i, j orbitals are occupied. In the RI-MP2 approximation,[32−34] the two-electron integrals $(ia|jb)$ are approximated by

$$(ib|ja) = \sum_P B_{ia}^P B_{jb}^P \tag{3}$$

with

$$B_{ia}^P = \sum_Q (ia|Q) V_{QP}^{-1/2} \tag{4}$$

P and Q label auxiliary basis functions and

$$V_{PQ} = \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, Q(r_1) \, P(r_2) r_{12}^{-1} \tag{5}$$

As in the traditional MP2 approach, the gradient with respect to external perturbations such as changes in the molecular structure can be calculated analytically. The analytical gradient at the RI-MP2 level as used in this work has recently been derived and implemented by Weigend and Häser.[34]

Density functional theory (DFT) calculations were performed using the resolution of the identity approximation (RI-DFT)[35] as implemented in TURBOMOLE.[36] Several functionals such as the Vosko−Wilk−Nusair (VWN) local density approximation with Slater exchange terms (S-VWN), the Becke exchange functional combined with the VWN correlation functional and the Perdew correlation correction (B-P),[37−39] the Becke exchange functional combined with the Lee−Yang−Parr correlation functional (B-LYP),[40] and the Becke three-parameter functional[41] combined with the Lee−Yang−Parr correlation functional (B3-LYP) were used.

All interaction energies have been corrected for basis set superposition errors (BSSE) by applying the counterpoise method of Boys and Bernardi.[42] For weakly bonded systems the structure obtained using analytical gradients may significantly differ from the structure obtained when the energies are corrected for basis set superposition errors. Since the optimized BSSE-corrected structure for the dimer has to be found manually in at least a six-dimensional space, the task is not trivial. To estimate the final BSSE-corrected structures, we performed a set of calculations in which all degrees of freedom except one are fixed. Thus only the distance between the molecules is varied. The fixed structural parameters are chosen to be those of the MP2 optimization.

III. Basis Sets

In this study, we employ split-valence-quality basis sets augmented with polarization functions (SVP). The sp part of the basis sets (s part for hydrogen) is optimized for atoms at the self-consistent-field (SCF) level.[43−45] The exponents of the polarization functions are 0.8, 0.8, 1.2, and 0.65 for H, C, O, and Cl, respectively. In the RI-MP2 calculations, $1s_{\mathrm{C}}$, $1s_{\mathrm{O}}$, $1s_{\mathrm{Cl}}$, $2s_{\mathrm{Cl}}$, and $2p_{\mathrm{Cl}}$ shells are uncorrelated, resulting in 104 correlated electrons in 310 active orbitals, formally yielding about 100 million amplitudes. Different auxiliary basis sets are used in the RI-MP2 and RI-DFT calculations. In the RI-MP2 calculations, the auxiliary basis sets are constructed by decontracting the standard triple-zeta-quality basis sets[43,44] and augmenting them with higher angular-momentum functions. The RI-MP2 auxiliary basis set for H consists of 5s2p1d contracted to 3s2p1d (5s2p1d/3s2p1d). For C, and O we used 11s6p2d1f/6s4p2d1f auxiliary basis sets and for Cl 14s9p2d1f/6s5p2d1f. The optimized auxiliary basis sets used in the RI-DFT calculations[43]

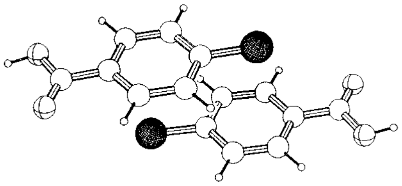

Figure 2. Stereoscopic view of the umbrella structure of the *p*-chlorobenzoic acid dimer as obtained in the S-VWN LDA calculation.

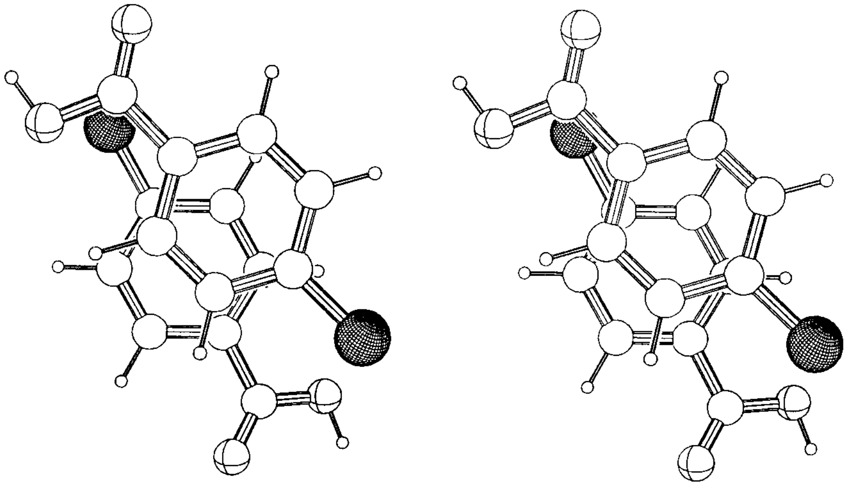

Figure 3. Stereoscopic view of the optimized parallel structure of the *p*-chlorobenzoic acid dimer as obtained in the MP2 calculation.

consist of 4s2p/2s1p for H and of 8s3p3d1f/6s3p3d1f for C and O. For Cl we used a 12s6p5d1f1g/5s3p2d1f1g auxiliary basis set.

IV. Results

A. Parallel Dimer Structure. In the MP2 optimization of the structure of the *p*-chlorobenzoic acid (PCBA) dimer, the initial structure was chosen to be the experimental umbrella structure; see Figure 2. In the optimization, the chlorines moved toward the carboxyl groups, yielding a sandwich complex with approximatively 50% overlap of the benzene rings. The obtained average distance between the slightly canted benzene rings is 315 pm, which is about 50 pm smaller than for the sandwich complex of the benzene dimer calculated at the MP2 level using the same basis sets. The MP2 structure of the parallel PCBA dimer is shown in Figure 3. The complex is almost parallel since the angle between the least-squares planes defined by the benzene rings is about 4°. The chlorines are located behind the hydroxyl oxygen (353 and 348 pm) and the carboxyl carbon (356 and 330 pm), forming a slightly nonsymmetric structure.

To check the applicability of density functional (DFT) methods, we performed single-point DFT calculations using several functionals and the optimized MP2 structure. All DFT calculations on the parallel complex using functionals including gradient corrections as well as the HF calculation provided repulsive interaction energies for the MP2 structure. The parallel complex was bound only at the S-VWN local density approximation (LDA) level with an interaction energy of 5.0 kcal mol^{-1}, while at the MP2 level the interaction energy is 3.4 kcal mol^{-1}. The attraction between the PCBA molecules is mainly due to dispersion effects between the benzene rings. Electrostatic interaction (in first-order dipole−dipole interaction) is not sufficient for the binding since the dimer is unbound at SCF and gradient-corrected DFT levels. The interaction energies given in Table 1 are calculated at different levels of theory using the MP2 structure.

TABLE 1: BSSE-Corrected Interaction Energies (in kcal mol^{-1}) for the Parallel PCBA Complex Calculated at Different Levels of Theory. The Dimer Distance (*R*) Is Given in pm

complex	method	structure	*R*	$E_{\text{interaction}}$	conformation
$(ClC_6H_4COOH)_2$	MP2	MP2	315	3.4	parallel
$(ClC_6H_4COOH)_2$	SCF	MP2	315	−10.6	parallel
$(ClC_6H_4COOH)_2$	B-P	MP2	315	−7.9	parallel
$(ClC_6H_4COOH)_2$	B-LYP	MP2	315	−10.4	parallel
$(ClC_6H_4COOH)_2$	S-VWN	MP2	315	5.0	parallel
$(ClC_6H_4COOH)_2$	B3-LYP	MP2	315	−8.1	parallel
$(ClC_6H_4COOH)_2$	MP2	BSSE-MP2[a]	343	5.1	parallel
$(ClC_6H_4COOH)_2$	SCF	BSSE-MP2[a]	343	−3.7	parallel

[a] BSSE corrected structure; see text.

Since the chlorine prefers to be oriented behind the carboxyl group, one may suspect that there is an interaction between the back of the carboxyl group and the chlorine. To check that, we performed MP2 calculations on the $HCOOH{\cdot}ClHCCH_2$ complex as a model case. The initial structure for the $HCOOH{\cdot}ClHCCH_2$ complex was taken from the acid-chlorine part of the PCBA dimer. The MP2 calculation shows that there is no significant interaction between the chlorine atom and the back of the carboxyl group. In the optimization, the vinyl-chloride formic-acid complex reoriented and formed a weak hydrogen bond between the chlorine atom and the hydroxyl group. This hydrogen bond conformation is not relevant for the parallel complex of the PCBA dimer.

Since van der Waals interaction is weak and basis set superposition errors are large as compared to the interaction energy, the actual distances between the monomer cannot be obtained directly using analytical gradients. In this work, the counterpoise-corrected minimum for the parallel complex is estimated by calculating the energy, corrected for basis set superposition errors, as function of the distance between the benzene rings. The ring−ring distance for the BSSE-corrected structure of the PCBA dimer became 343 pm. The BSSE correction is thus 28 pm. The interaction energy increased to

TABLE 2: BSSE-Corrected Interaction Energies (in kcal mol^{-1}) for the Sandwich Complex of the Benzene Dimer Calculated at the MP2 Level As Compared to Literature Values. The Dimer Distance (*R*) Is Given in pm

complex	method	structure	R	$E_{\text{interaction}}$	reference
$(C_6H_6)_2$	MP2	MP2[a]	363	0.7	PW[b]
$(C_6H_6)_2$	MP2	BSSE-MP2	400	1.2	PW[b]
$(C_6H_6)_2$	MP2	BSSE-MP2	390	2.2	17
$(C_6H_6)_2$	MP2	BSSE-MP2	380	2.1	46
$(C_6H_6)_2$	MP2	BSSE-MP2	371	1.3	18
$(C_6H_6)_2$	CCSD(T)	BSSE-CCSD(T)	410	1.0	17

[a] The structure is not corrected for BSSE. [b] Present work.

TABLE 3: BSSE-Corrected Interaction Energies (in kcal mol^{-1}) for the Umbrella Structure of the PCBA Dimer Calculated at Different Levels of Theory. The Dimer Distance (*R*) Is Given in pm

complex	method	structure	R	$E_{\text{interaction}}$	conformation
$(ClC_6H_4COOH)_2$	S-VWN	S-VWN	322	3.1	umbrella
$(ClC_6H_4COOH)_2$	MP2	S-VWN	322	0.8	umbrella
$(ClC_6H_4COOH)_2$	SCF	S-VWN	322	−9.4	umbrella
$(ClC_6H_4COOH)_2$	B-P	S-VWN	322	−6.9	umbrella
$(ClC_6H_4COOH)_2$	B-LYP	S-VWN	322	−9.0	umbrella
$(ClC_6H_4COOH)_2$	B3-LYP	S-VWN	322	−7.3	umbrella
$(ClC_6H_4COOH)_2$	S-VWN	BSSE-S-VWN[a]	332	3.3	umbrella
$(ClC_6H_4COOH)_2$	MP2	BSSE-MP2[b,c]	364	2.6	umbrella
$(ClC_6H_4COOH)_2$	SCF	BSSE-MP2[b]	364	−2.8	umbrella
$(ClC_6H_4COOH)_2$	S-VWN	S-VWN[d]	322	7.0	umbrella
$(ClC_6H_4COOH)_2$	DMol VWN	DMol VWN[d]	305	5.0	umbrella

[a] BSSE-corrected structure at the S-VWN level; see text. [b] BSSE-corrected structure at the MP2 level; see text. [c] Not a local minimum. [d] Uncorrected for BSSE.

5.1 kcal mol^{-1}. The same procedure for the sandwich complex of the benzene dimer shifted the minimum from 363 pm to 400 pm, which agrees with literature values.[16,17] In Table 2, one sees that the present basis sets are capable of giving a qualitative description of the benzene dimer. A larger basis set would give a stronger benzene−benzene interaction.[46] However, at the coupled cluster singles and doubles level with a perturbative treatment for triple excitations (CCSD(T)), the interaction energy is approximately half the MP2 value.[17]

B. Umbrella Dimer Structure. Since the LDA interaction energy for the optimized MP2 structure was positive, we performed structure optimization at the LDA level using the S-VWN functional with the umbrella structure as a starting geometry. The umbrella structure turned out to be a local minimum at the S-VWN LDA level with an interaction energy of 3.1 kcal mol^{-1}. However, interaction energies obtained in single-point SCF calculations and at gradient-corrected DFT levels (B-P, B-LYP, B3-LYP) using the S-VWN LDA structure are negative. At these levels of theory the umbrella structure is unbound. At the MP2 level, the interaction energy using the S-VWN LDA umbrella structure is positive; see Table 3. The binding energy is only 0.8 kcal mol^{-1} as compared to infinite separations. At the MP2 level we did not find any local minimum for the umbrella structure. In a reoptimization of the molecular structure starting from the S-VWN LDA structure the chlorine part moved downhill toward the back of the carboxyl group of the other monomer.

The local density approximation (LDA) without any gradient corrections is known to overestimate the binding energies.[26,47] DFT methods that include gradient corrections usually provide more accurate results, but at the gradient-corrected density functional level we were not able to obtain an attractive interaction between the PCBA molecules. We also performed DFT calculations using the S-VWN functional and standard doubly numerical basis sets augmented by polarization functions (DNP) as implemented in the DMol program.[48,49] In the DMol calculation, a relatively strongly bound dimer with umbrella structure was obtained. However, since the LDA method usually overestimates the binding energies[26,47] and no BSSE corrections are possible with the DMol program package,[48,49] we consider the DMol LDA result unreliable.

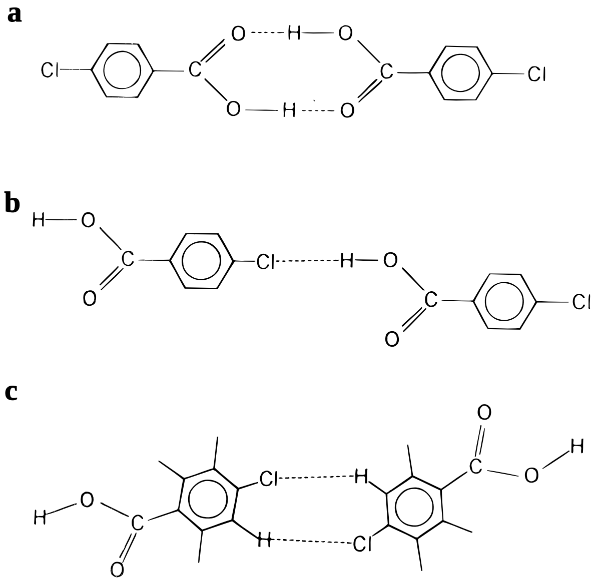

Figure 4. Three other *p*-chlorobenzoic acid dimer structures considered.

BSSE-corrected umbrella structures were estimated at both the S-VWN and MP2 levels. Since the BSSE errors are somewhat smaller at the DFT level than at the MP2 level, the BSSE correction to the molecular structure at the S-VWN level is only 13 pm, while at the MP2 level it is 43 pm. For the BSSE-corrected structure, the chlorine−ring distance at the S-VWN level is 332 pm with an interaction energy of 3.3 kcal mol^{-1}, while the corresponding values as obtained at the MP2 level are 364 pm and 2.6 kcal mol^{-1}, respectively. The S-VWN and MP2 interaction energies for the umbrella structure are thus approximately half of the corresponding energies for the parallel complex. Note that the chlorine−ring distance calculated at the S-VWN level is 30 pm shorter than the distance obtained at the MP2 level, while the MP2 distance is in agreement with the experimental stacking distances of 341.6 pm[4] and 366.6 pm[9] for nickel and copper *p*-chlorobenzoate complexes, respectively.

Close to the minimum the correlation energies for both the umbrella and the parallel complex of the PCBA dimer are fitted by a simpgle Cr^{-n} with n equal to 5.1 For the benzene dimer the exponent is found to be somewhat larger, or 5.5. Since the PCBA dimers are unbound at the SCF level and the correlation energies behave approximately like the London dispersion energy ($n = 6$), one may conclude that the interaction between tne PCBA molecules in both the umbrella and the parallel complex is mainly due to dispersion and not electrostatic interaction.

C. Other Considered Dimer Structures. Three other PCBA dimers but no perpendicular structures were considered; see Figure 4. Their structures were optimized at the B-LYP level. The strongest interaction energy was obtained for ClC_6H_4-$COOH{\cdot}HOOCC_6H_4Cl$, which forms two strong hydrogen bonds between the carboxyl groups (Figure 4a). As in $HCOOH{\cdot}ClHCCH_2$, there is a weak hydrogen bond between the carboxyl group and the chlorine in the $HOOCC_6H_4Cl{\cdot}HOOCC_6H_4Cl$

TABLE 4: BSSE-Corrected Interaction Energies (in kcal mol^{-1}) for Hydrogen Bond PCBA Dimers As Compared to the Hydrogen Bond Vinyl Chloride−Formic Acid Complex Calculated at Different Levels of Theory

complex	method	structure	$E_{\mathrm{interaction}}$	conformation
$Cl_6H_4COOH\cdot HOOCC_6H_4Cl$	B-LYP	B-LYP	21.3	$-COOH\cdot HOOC-$
$HOOCH_4C_6Cl\cdot ClC_6H_4COOH$	B-LYP	B-LYP	<0	$-Cl\cdot H-C_6H_{3-}$
$HOOCC_6H_4Cl\cdot HOOCC_6H_4Cl$	B-LYP	B-LYP	2.9	$-COOH\cdot Cl-$
$HCOOH\cdot ClHCCH_2$	MP2	MP2	3.3	$-COOH\cdot Cl-$
$HCOOH\cdot ClHCCH_2$	SCF	MP2	2.8	$-COOH\cdot Cl-$
$HCOOH\cdot ClHCCH_2$	B-LYP	MP2	2.7	$-COOH\cdot Cl-$

TABLE 5: Typical BSSE Energy Corrections to Interaction Energies (in kcal mol^{-1}) Calculated at Different Levels of Theory

complex	method	structure	ΔE (BSSE)	conformation
$(ClC_6H_4COOH)_2$	MP2	MP2	−8.7	parallel
$(ClC_6H_4COOH)_2$	SCF	MP2	−3.8	parallel
$(ClC_6H_4COOH)_2$	B-LYP	MP2	−4.9	parallel
$(ClC_6H_4COOH)_2$	S-VWN	S-VWN	−3.9	umbrella
$(ClC_6H_4COOH)_2$	MP2	S-VWN	−6.4	umbrella
$(ClC_6H_4COOH)_2$	SCF	S-VWN	−3.1	umbrella
$ClC_6H_4COOH\cdot HOOCC_6H_4Cl$	B-LYP	B-LYP	−3.3	$-COOH\cdot HOOC-$
$HOOCC_6H_4Cl\cdot HOOCC_6H_4Cl$	B-LYP	B-LYP	−3.3	$-COOH\cdot Cl-$
$(C_6H_6)_2$	MP2	MP2	−2.7	sandwich
$HCOOH\cdot ClHCCH_2$	MP2	MP2	−3.4	$-COOH\cdot Cl-$
$HCOOH\cdot ClHCCH_2$	SCF	MP2	−1.9	$-COOH\cdot Cl-$

complex (Figure 4b). The interaction energy of the $HOOCC_6H_4Cl\cdot HOOCC_6H_4Cl$ complex calculated at the B-LYP level is 2.9 kcal mol^{-1}. For $HCOOH\cdot ClHCCH_2$, the B-LYP interaction energy is 2.7 kcal mol^{-1}, and at the MP2 level we obtained 3.3 kcal mol^{-1}; see Table 4. Since the binding energies at the SCF, B-LYP, and MP2 levels agree, electrostatic interactions play a significant role for the binding of the $-COOH\cdot Cl-$ complexes. Furthermore, the distance between the hydrogen of the hydroxyl group and the chlorine is 243 pm, which is significantly shorter than the distance between the chlorine and the carboxyl group in the parallel PCBA complex. The last complex we considered was $HOOCH_4C_6Cl\cdot ClC_6H_4COOH$ (Figure 4c). At the B-LYP DFT level this complex was found to be unbound. Typical basis set superposition corrections are listed in Table 5.

V. Summary

The MP2 optimization of the parallel PCBA dimer complex yielded a structure with the chlorine atoms located behind the carboxyl group of the other monomer. The complex is of sandwich type with approximatley 50% overlap of the benzene rings, and the binding energy is calculated at the MP2 level to be 5.1 kcal mol^{-1}. Experimentally, umbrella structures with the chlorines located above the center of the benzene rings have been found.[5] At the MP2 level, we found no local minimum for the umbrella structure. However, the binding energy for the umbrella structure compared to infinite separations of the PCBA molecules is 2.6 kcal mol^{-1}. This is probably enough to cause a stacking with umbrella conformation in crystals since the parallel complex cannot exist in infinite three-dimensional structures. Neither the parallel nor the umbrella structures are bound at SCF or gradient-corrected DFT levels (B-P, B-LYP, B3-LYP), which indicates that the interaction is dominated by dispersion effects and that electrostatic interaction is of secondary importance. The most stable PCBA dimer is, as expected, the complex with the carboxyl groups connected to each other forming two hydrogen bonds. The binding energy of this complex is calculated at the B-LYP level to be 21.3 kcal mol^{-1}, which is 4 times larger than the binding energy of the parallel PCBA complex or almost 1 order of magnitude larger than the binding energy of the umbrella complex.

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