On the Nature of Bonding in Lone Pair···π-Electron Complexes: CCSD(T)/Complete Basis Set Limit Calculations

Jiong Ran[†] and Pavel Hobza*[,†,‡]

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic, and Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

Abstract: The nature of the stabilization in lone pair···π-electron complexes was investigated using the highly accurate CCSD(T) method based on the complete basis set limit, as well as the DFT-SAPT perturabative method. Specifically, we studied various structures of benzene···water, benzene···dimethylether, and 1,2,4,5-tetracyanobenzene···water complexes. The lone pair···π-electron interactions between an unsubstituted aromatic ring and a water molecule are repulsive in the whole range of vertical distances. Partial stabilization results by rotating the water molecule by 90° (with the water and aromatic ring being localized in parallel planes) or by decreasing the negative charge at oxygen and simultaneously increasing the polarizability of the system, which provides stabilization even for genuine lone pair···π-electron interactions. In these cases, a substantial part of the stabilization stems from dispersion energy. Substituting an aromatic ring by electron-withdrawing cyano groups represents the most powerful way to achieve a substantial stabilization of genuine lone pair···π-electron interactions. This stabilization is comparable to quite strong H-bonding, originating in electrostatic and, to a slightly lesser degree, dispersion energies.

Introduction

The world of noncovalent interactions has become much broader in recent years, and new types of noncovalent bonding have appeared. In addition to classical (red-shifted) H-bonding, also improper blue-shifted H-bonding has been described, and the family of H-bonding interactions has been further extended by dihydrogen bonds.[1] Dihydrogen bonding (attractive interactions between two hydrogen atoms, one bearing positive and one bearing negative charge) was first detected in crystalline structures, and the same is true of other interactions between halogens and electronegative elements that also initially seemed very strange. The latter interaction

was later called halogen bonding[2] and was explained as an interaction between the positive σ-hole at the top of negatively charged halogens and negatively charged electronegative elements. Again, from the crystalline structures, two other very unusual interaction types have appeared recently, namely, lone pair···π and anion···π interactions. Anion···π interactions were recently investigated by Kim et al.[3] In both cases, negatively charged elements are found at the top of the aromatic system, and thus, a water···benzene complex becomes the prototype of the lone pair···π interaction. Lone pair···π interactions have been found in different protein crystalline structures,[4−6] and despite the fact that the exact position of the hydrogens is not known, it is expected that lone pair···π and not X−H···π interactions are present.

Confirming the presence of lone pair···π interactions is thus an important task, which the analysis of crystalline structures, however, evidently cannot achieve. On the other hand, quantum chemical calculations could prove favorable because they not

* To whom correspondence should be addressed. E-mail: pavel.hobza@uochb.cas.cz.
† Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems.
‡ Palacký University.

Bonding in Lone Pair⋯π-Electron Complexes

J. Chem. Theory Comput., Vol. 5, No. 4, 2009 **1181**

only provide sufficiently accurate energies and structures but also can shed light on the nature of the respective interactions. To investigate the nature of the bonding in lone pair⋯π complexes, it is necessary to determine the interaction energy as accurately as possible. Accurate stabilization energies of various types of noncovalent complexes, including the present ones, can be obtained only at the CCSD(T) level using the complete basis set (CBS) limit.[7] The MP2 method, even if performed at the CBS limit, cannot be used here, as it is known to overestimate the dispersion energy,[7] which might be critical for the complexes under consideration. The application of other recently introduced methods such as SCS-MP2[8] and its variants including SCS (MI)-MP2[9] or various DFT-D[10,11] approaches is limited in this case, because their good performances are based on parametrization toward a suitable data set of accurate energies (e.g., ref 12), which, however, does not contain the present stabilization motif. CCSD(T)/CBS values represent the benchmark data with a high accuracy, expected to be higher than 5% from the unknown exact values.[1] To understand the nature of the bonding of lone pair⋯π interactions, we need to know their energy components as well as their accurate stabilization energies. These values can be determined on the basis of perturbative SAPT[13] calculations.

To explain the stabilization in lone pair⋯π complexes, we decided to investigate water⋯benzene, dimethylether⋯benzene, and water⋯1,2,4,5-tetracyanobenzene complexes.

Methods

The structures of water, dimethylether, benzene, and 1,2,4,5-tetracyanobenzene were optimized without any constraints at the MP2 level using the cc-pVTZ basis set. This level provides accurate geometries of isolated systems.[14]

To understand the nature of lone pair⋯π interactions, we investigated different arrangements of benzene⋯water, benzene⋯dimethylether, and 1,2,4,5-tetracyanobenzene⋯water complexes (cf. Figure 1). In structures **1**, **4**, and **5**, the π-aromatic rings of benzene and 1,2,4,5-tetracyanobenzene interact exclusively with the lone electron pairs of water or dimethylether, whereas in structures **3** and **7**, the dominant stabilization feature is the O−H⋯π H-bond. In the cases of structures **2** and **6**, the π-aromatic rings interact with both the lone electron pairs and protons of water. The vertical distance (from O to the center of the aromatic ring) in all of the complexes investigated was optimized by the step-by-step method using the CCSD(T)/CBS energies. Gradient optimization at this level is impractical, and if based on another computational method, it can yield completely misleading structures.

The CCSD(T)/CBS binding energies were determined as a sum of the MP2/CBS energies and a CCSD(T) correction term.[15] This method takes advantage of the fact that the CCSD(T) and MP2 methods exhibit approximately the same basis set dependence.[16] The extrapolations based on the aug-cc-pVDZ and aug-cc-pVTZ basis sets were performed using the method of Halkier et al.[17] Because of the different dependences on the basis set, the Hartree−Fock energies and MP2 correlation energies were extrapolated separately. The CCSD(T) correction term [ΔCCSD(T)], defined as

$$\Delta CCSD(T) = (\Delta E_{CCSD(T)} - \Delta E_{MP2})|_{basis} \qquad (1)$$

was then added to the MP2/CBS interaction energy. The correction term is generally obtained with a relatively small or medium-sized basis set, and in this case, we used the aug-cc-pVDZ basis set. One of the reasons for the success of this technique is the fact that the ΔCCSD(T) correction term converges much more quickly, as a function of the basis set size, than the CCSD(T) or MP2 interaction energies themselves.

All interaction energies were corrected for the basis set superposition error using the counterpoise method of Boys and Bernardi,[18] and the frozen-core approximation was systematically used throughout this work.

The CCSD(T)/CBS energies represent benchmark data but do not provide any information about the energy components that can be used to analyze the nature of the stabilization. Therefore, we also used the DFT-SAPT calculations[19,20] performed with the aug-cc-pVDZ basis set. This method allows for the separation of interaction energies into physically well-defined components, such as those arising from the electrostatic, induction, dispersion, and exchange terms. The DFT-SAPT interaction energy (E^{int}) is given by the equation
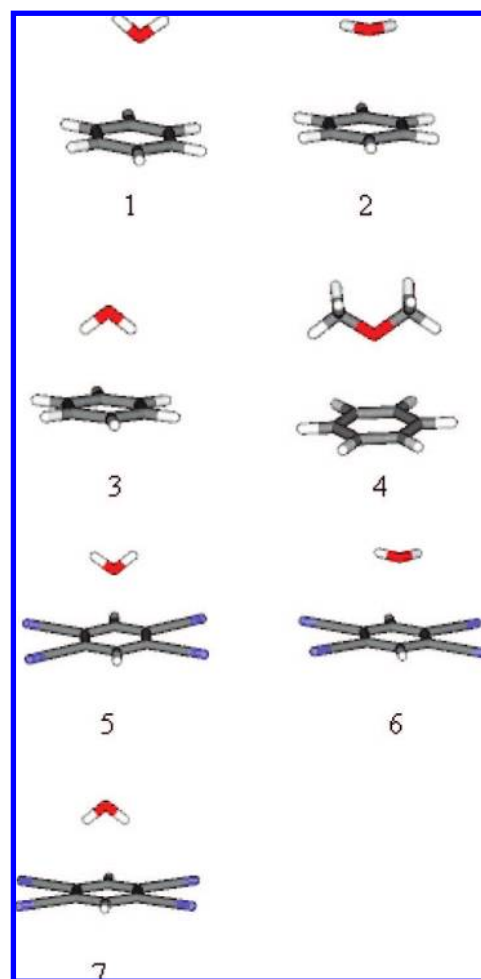

Figure 1. Various structures of the benzene⋯water (**1−3**), benzene⋯dimethylether (**4**), and 1,2,4,5-tetracyanobenzene⋯water (**5−7**) complexes.

$$E^{\text{int}} = E^{(1)}_{\text{el}} + E^{(1)}_{\text{ex}} + E^{(2)}_{\text{ind}} + E^{(2)}_{\text{ex-ind}} + E^{(2)}_{\text{disp}} +$$
$$E^{(2)}_{\text{ex-disp}} + \delta(\text{HF}) \quad (2)$$

where the individual terms describe the electrostatic, exchange-repulsion, induction, exchange-induction, dispersion, and exchange-dispersion terms. The last term is a Hartree−Fock correction for higher-order contributions to the interaction energy. Throughout the study, the exchange-induction and exchange-dispersion terms will be included in the parent induction and dispersion terms. The DFT-SAPT interaction energies calculated with the aug-cc-pVDZ basis sets are known to be slightly underestimated with respect to mainly the dispersion energy.[19] The SAPT/aug-cc-pVTZ energy was estimated by enlarging the dispersion energy by 15% while keeping the other terms at the aug-cc-pVDZ values. Finally, Halkier et al.'s extrapolation scheme[17] was used to extrapolate the DFT-SAPT CBS energy from calculated aug-cc-pVDY and estimated aug-cc-pVTY values. All calculations were performed with the Gaussian 03[21] and MOLPRO[22] programs.

Results and Discussion

Table 1 lists the interaction energies of structures **2**−**6** (cf. Figure 1) at their minimum distances using various methods. Structures **1** and **7** are not included because no energy minima were detected in their potential energy curves. Table 2 lists the CCSD(T)/CBS interaction energies for all structures for selected distances from 2.2 to 15 Å. Table 3 reports the DFT-SAPT energies for structures **2**−**6** (structures **1** and **7** are omitted for the same reason as in Table 1). Tables S1 and S2 in the Supporting Information include all interaction energies determined by various methods for all structures considered and the Cartesian coordinates of complexes **1**−**7** at the MP2/cc-pVTZ level, respectively.

Overall, the CCSD(T)/CBS energies are consistent with the DFT-SAPT/CBS results. The energy differences are less than 5%. The only exception is structure **4**, where the energy difference is higher (17%) and can be explained by the much higher positive CCSD(T) correction term.

Benzene···Water Complexes. First, the genuine lone pair···π interactions (structure **1**) in the title complex were investigated. Figure 2 and Tables 2 and S1 (Supporting Information) show the dependence of the CCSD(T)/CBS and various MP2 interaction energies on the vertical distance. Evidently, neither of the curves exhibits an energy minimum (at negative energies), and only repulsion results. As the distance increases, the interaction energy becomes less repulsive, and with the exception of long distances, the CCSD(T) correction term is also repulsive. These results tell us clearly that there is no stabilization between the lone electron pairs and the aromatic ring. We do not know how to explain the existence of a small repulsion peak around 4.0−4.5 Å. It might be due to the extrapolation procedure or to the interaction of higher multipoles.

The only way to gain some stabilization in this complex is to change the orientation of the lone pair donor, specifically for which structures **2** and **3** were studied. In addition to the lone pair···π interaction, structure **2** is also expected to be

Table 1. Calculated Intermolecular Distances (R in Å) and Interaction Energies (kcal/mol) for the Energy Minima of the Different Lone Pair···π Complexes[a]

complex	R	MP2/a VDZ	MP2/a VTZ	MP2/CBS	ΔCCSD (T)	CCSD (T)/CBS
2	3.4	−0.375	−0.601	−0.696	0.060	−0.636
3	3.3	−2.837	−3.218	−3.378	0.129	−3.249
4	3.2	−0.873	−1.086	−1.176	0.354	−0.822
5	3.0	−4.853	−5.015	−5.083	0.171	−4.912
6	3.3	−2.453	−2.585	−2.641	0.009	−2.632

[a] Compare Figure 1; structures **1** and **7** have no energy minima.

Table 2. Calculated Interaction Energies (kcal/mol) at Various Distances (R in Å) for Various Structures of the Lone Pair···π Complexes at the CCSD(T)/CBS Level

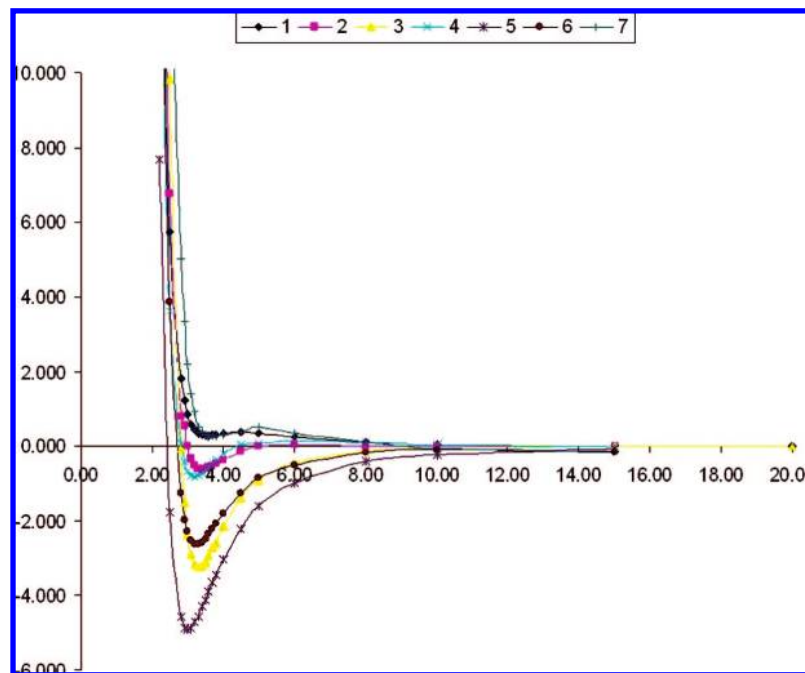| R	complexes						
	1[a]	**2**	**3**	**4**	**5**	**6**	**7**
2.20	16.400	21.386	36.706	15.472	7.693	18.064	43.173
2.50	5.729	6.756	9.833	3.633	−1.755	3.846	15.691
2.80	1.829	0.791	−0.053	0.073	−4.574	−1.244	5.029
2.90	1.237	0.542	−1.486	−0.400	−4.883	−1.960	3.334
3.00	0.845	0.010	−2.392	−0.667	−4.912	−2.271	2.174
3.10	0.591	−0.320	−2.911	−0.791	−4.866	−2.514	1.402
3.20	0.436	−0.512	−3.171	−0.822	−4.696	−2.618	0.914
3.30	0.346	−0.606	−3.249	−0.794	−4.558	−2.632	0.509
3.40	0.300	−0.636	−3.208	−0.729	−4.307	−2.577	0.370
3.50	0.283	−0.626	−3.087	−0.645	−4.121	−2.483	0.317
3.60	0.284	−0.587	−2.924	−0.551	−3.888	−2.364	0.242
3.70	0.296	−0.525	−2.732	−0.456	−3.662	−2.228	0.278
3.80	0.312	−0.477	−2.586	−0.367	−3.440	−2.089	0.294
4.00	0.343	−0.355	−2.142	−0.207	−3.031	−1.814	0.303
4.50	0.371	−0.136	−1.390	0.043	−2.215	−1.243	0.395
5.00	0.337	0.010	−0.909	0.131	−1.609	−0.862	0.500
6.00	0.236	0.029	−0.430	0.140	−0.969	−0.509	0.333
8.00	0.103	0.020	−0.138	0.092	−0.417	−0.179	0.096
10.00	0.048	0.008	−0.058	0.036	−0.226	−0.111	−0.081
15.00	0.011	0.001	−0.012	0.008	−0.057	−0.154	−0.147

[a] Compare Figure 1.

stabilized by O−H···π H-bonding, which is of electrostatic origin. The respective energy curve (cf. Figure 2) exhibits a non-negligible minimum of 0.64 kcal/mol at a vertical separation of 3.4 Å. The MP2/CBS interaction energy is stabilizing, and the CCSD(T) correction term is small and repulsive. Note the significant basis set dependence of the MP2 interaction energy. Analyzing the energy components (cf. Table 3), we found that stabilization in this structure originates predominantly in dispersion energy, with the induction term being less important. Here, the slightly repulsive electrostatic term should be noted. All of these data confirm the fact that the stabilization of this lone pair···π interaction originates from dispersion and only to a lesser degree from induction and charge transfer, which is included in the induction energy term. Repulsive electrostatic energy showed no evidence of H-bonding.

Further rotation of the water molecule leads to a H-bonded structure (structure **3**) that is characterized by a large stabilization of more than 3 kcal/mol. The energy minimum is localized at 3.3 Å, and also here, the MP2 interaction energy is stabilizing, and the CCSD(T) correction term is repulsive. This structure contains two O−H···π H-bonds, and there is no evidence of a lone pair···π interaction. These findings are confirmed by the DFT-SAPT calculations. Table 3 shows a large attractive electrostatic term, a rather small induction term, and a surprisingly large dispersion energy.

Bonding in Lone Pair···π-Electron Complexes

J. Chem. Theory Comput., Vol. 5, No. 4, 2009 **1183**

Table 3. Calculated[a] DFT-SAPT Interaction Energies (kcal/mol) for the Lone Pair···π Complexes at Each Minimum Distance

structure[b]	$E^{(1)}_{el}$	$E^{(1)}_{ex}$	$E^{(1)}$	$E^{(2)}_{ind}$	$E^{(2)}_{disp}$[c]	$E^{(2)}$[c]	δ(HF)	E (kcal/mol)[c,d]
2	0.033	1.758	1.791	−0.229	−1.753 (−2.015)	−1.981 (−2.244)	−0.046	−0.237 (−0.499, −0.609)
3	−3.080	3.980	0.900	−0.507	−2.868 (−3.298)	−3.375 (−3.805)	−0.304	−2.779 (−3.209, −3.390)
4	0.637	2.727	3.364	−0.275	−3.277 (−3.768)	−3.552 (−4.043)	−0.113	−0.301 (−0.792, −0.999)
5	−4.417	3.541	−0.876	−0.566	−2.883 (−3.315)	−3.449 (−3.881)	−0.195	−4.520 (−4.952, −5.134)
6	−1.656	2.152	0.496	−0.365	−2.218 (−2.551)	−2.583 (−2.916)	−0.064	−2.151 (−2.484, −2.624)

[a] DFT-SAPT (PBE0AC/aug-cc-pVDZ basis set). [b] Compare Figure 1; structures **1** and **7** have no energy minima. [c] Values in parentheses were estimated using the aug-cc-pVTZ basis set. [d] Second values in parentheses were extrapolated from energies calculated using the aug-cc-pVDZ basis set and energies estimated using the aug-cc-pVTZ basis set.

Figure 2. Calculated potential energy plot for the various lone pair···π complexes (see Figure 1 for compound numbers) at the CCSD(T)/CBS level. The *X* and *Y* axes show distance (Å) and the interaction energy (kcal/mol), respectively.

The latter term is almost as attractive as the electrostatic energy, and if we consider the estimated aug-cc-pVTZ value, it is even larger. It must be mentioned that this structure is different from the standard H-bonded structure, where just one hydrogen interacts with the aromatic ring. Consequently, the distance between the centers of mass of the two subsystems is smaller in the present structure, which makes the dispersion energy larger. Nevertheless, in all H-bonded complexes of the aromatic system with water, the dispersion energy should be of comparable importance to the electrostatic energy.

Benzene···Dimethylether Complex. We have seen that the approach of water and benzene (structure **1**) is connected with repulsion only. By substituting hydrogens in water with methyl groups (passing from water to dimethylether), the situation is changed. Analyzing the charge at oxygen, we found that it is less negative in dimethylether than in water, which indicates that the electrostatic repulsion term might be smaller in the dimethylether···benzene complex than in the water···benzene complex. Further, the polarizability of dimethylether is higher than that of water, which implies a larger dispersion energy stabilization in the dimethylether··· benzene complex. Tables 1, 2, and S1 (Supporting Information) and Figure 2 suggest the existence of a rather deep

minimum (0.82 kcal/mol) localized at 3.2 Å. In this case, the MP2 interaction energy is attractive, and the CCSD(T) correction term repulsive. In contrast to the previous cases, the latter term is considerably larger. The DFT-SAPT analysis (Table 3) undoubtedly clarifies the origin of stabilization. As in the previous cases, it is the dispersion energy that is almost completely responsible for the stabilization of the complex. The induction energy, which includes charge transfer, is more than 1 order of magnitude smaller than the dispersion energy. The negligible role of charge transfer is also reflected in the rather small value of the δ(HF) term (see Table 3). In agreement with the above-mentioned facts, the electrostatic energy is repulsive.

We can summarize that, when polarizability of the lone pair acceptor is increased and its negative partial charge on the interacting site is decreased, the lone pair···π interactions become attractive. Evidently, upon larger substitution, the attraction can be substantially larger. The attraction originates, however, unambiguously from the London dispersion energy.

1,2,4,5-Tetracyanobenzene···Water Complexes. Upon substitution of the hydrogens at positions 1, 2, 4, and 5 of benzene with electron-withdrawing cyano groups, the π-electron clouds above the ring become less negative. The elec-

trostatic potentials of benzene and 1,2,4,5-tetracyanobenzene are entirely different (not shown). Whereas the former contains a significant negative region above the ring, the latter does not have any negative region but has only a positive one. Consequently, interactions with proton donors (H-bonding) should be suppressed, whereas interactions with proton acceptors (electron donors) should be magnified. In both cases, we considered the stacking approach, which was fully confirmed in Tables 1, 2, and S1 (Supporting Information) and Figure 2. Structure **5** exhibits a very deep energy minimum of about 5 kcal/mol at a rather short distance of 3.0 Å. Notice the relatively large (positive) value of the CCSD(T) correction term. Rotating the water molecule by 180°, i.e., when water approaches benzene by its hydrogens (structure **7**), the situation is reversed, and practically no minimum in the potential energy curve is detected. We do not know how to explain the small attraction beyond 10 Å. This might be due to the extrapolation method used or to interactions of higher multipoles. The approach of water and 1,2,4,5-tetracyanobenzene localized in parallel planes (structure **6**) is characterized by a relatively deep energy minimum of 2.63 kcal/mol at a rather large vertical separation of 3.3 Å. The DFT-SAPT analysis shows a very large attractive electrostatic energy for structure **5**. This energy is considerably less attractive for structure **6**. Induction energy is largest for structure **5**, and the same is true for dispersion energy. The largest values of dispersion and induction energies for structure **5** are certainly also related to its very short vertical distance (3.0 and 3.3 Å in structures **5** and **6**, respectively). The electrostatic and dispersion energies in complex **5** are similar, which resembles the situation in complex **3** (see above).

Substituting benzene with electron-withdrawing groups evidently represents the most powerful way to stabilize the lone pair···π-electron complexes. The respective stabilization can be substantial, even comparable to a rather strong H-bonding.

Conclusions

(i) The lone pair···π-electron interactions between an unsubstituted aromatic ring and a water molecule are repulsive for the whole range of vertical distances. Partial stabilization results when the water molecule is rotated by 90° (with the water and the aromatic ring located in parallel planes). In this structural arrangement, there is no H-bonding, and the dominant stabilization comes from dispersion energy.

(ii) Decreasing the negative charge at oxygen and increasing the polarizability of the system provides stabilization even for genuine lone pair···π electron interactions. Also in this case, the substantial part of the stabilization stems from dispersion energy.

(iii) Substituting an aromatic ring by electron-withdrawing groups represents the most powerful way to achieve a substantial stabilization of genuine lone pair···π-electron interactions. This stabilization, which is comparable to a rather strong H-bonding, originates in electrostatic and, to a slightly lesser degree, dispersion energy.

Supporting Information Available: Intermolecular distances (R in Å) and interaction energies (kcal/mol) for the lone pair···π complexes obtained with various methods (Table S1), as well as Cartesian coordinates of complexes 1−7 (monomers optimized at the MP2/cc-pVTZ level) (Table S2) are available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348. (b) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253. (c) Hobza, P.; Müller-Dethlefs, K. *Chem. Rev.* **2000**, *100*, 143. (d) Hobza, P.; Zahradník, R.; Müller-Dethlefs, K. *Collect. Czech. Chem. Commun.* **2006**, *71*, 443.

(2) Aufinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 16789.

(3) Kim, D. Y.; Singh, N. J.; Kim, K. S. *J. Chem. Theory Comput.* **2008**, *4*, 1401.

(4) Steiner, T. *Biophys. Chem.* **2002**, *95*, 195.

(5) Sarkhel, S.; Rich, A.; Egli, M. *J. Am. Chem. Soc.* **2003**, *125*, 8998.

(6) Egli, M.; Sarkhel, S. *Acc. Chem. Res.* **2007**, *40*, 197.

(7) Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985.

(8) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 141102.

(9) Distasio, R. A.; Head-Gordon, M. *Mol. Phys.* **2007**, *105*, 1073.

(10) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463.

(11) Jurečka, P.; Černý, J.; Hobza, P.; Salahub, D. *J. Comput. Chem.* **2007**, *28*, 555.

(12) Řezáč, J.; Jurečka, P.; Riley, K. E.; Černý, J.; Valdes, H.; Pluháčková, K.; Berka, K.; Řezáč, T.; Pitoňák, M.; Vondrášek, J.; Hobza, P. *Collect. Czech. Chem. Commun.* **2008**, *73*, 1261.

(13) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.

(14) Dabkowska, I.; Jurečka, P.; Hobza, P. *J. Chem. Phys.* **2005**, *122*, 204322.

(15) Jurečka, P.; Hobza, P. *J. Am. Chem. Soc.* **2003**, *125*, 15608.

(16) Jurečka, P.; Hobza, P. *Chem. Phys. Lett.* **2002**, *365*, 89.

(17) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(18) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(19) Hesselman, A.; Jansen, G.; Schutz, M. *J. Chem. Phys.* **2005**, *122*, 14103.

(20) Hesselman, A.; Jansen, G.; Schutz, M. *J. Am. Chem. Soc.* **2006**, *128*, 11730.

Bonding in Lone Pair···π-Electron Complexes

J. Chem. Theory Comput., Vol. 5, No. 4, 2009 **1185**

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al.Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Revision C.02. Gaussian, Inc.: Wallingford CT, 2004.

(22) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO*, version 2006.1; University College Cardiff Consultants Limited: Cardiff, U.K., 2006.

CT900036Y