Molecular modeling of the weakly bounded dimers of some phenothiazine derivatives

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Abstract. The intermolecular π-π stacking interaction between some phenothiazine derivatives has been investigated using the Hartree-Fock (HF) and the local second order Møller-Plesset perturbation theory (LMP2) methods. Two different conformations (parallel and antiparallel stacking) of ethyl-phenothiazine and the parallel stacking of thio-methyl-phenothiazine were investigated. In all three cases the HF results show nearly unbounded dimers, while at LMP2 level they become stable structures, mainly due to the presence of large dispersion forces. The intermolecular optimal distances were also calculated by both methods the values obtained by HF being significantly larger as compared with those obtained by LMP2. Considering the LMP2 geometry, the HF contribution in the intermolecular interaction energy gives positive values acting as a repulsion forces and slacking the dimer interaction. This effect is compensated by the large contribution of the dispersion component which finally keeps together the binary stacking structures. These results show the major role of the dispersion effects in stabilizing stacking structures of the aromatic rings and the feasibility of self-assembling in molecular two-dimensional supra-structures.

1. Introduction

In the last two decades, it is becoming more and more unambiguous that non-covalent interactions are crucial for determining the structures and properties of the supramolecular and biomolecular systems. Despite the fact that parallel-displaced π-π stacking interactions have been recognized to be an important force in stabilizing the double helical structure of DNA and the tertiary structure of proteins, very few features are known about their roles in self-assembled monolayers of other large π molecules such as aromatic thiols [1]. In the class of aromatic thiols we are interested in several molecular species from the phenothiazine family which are potentials candidates for establishing π-π stacking interactions. The final target is to bring some insight for an optimal design of molecular systems able to self-assemble on gold atomically flat surfaces by sulfur bonds.

The phenothiazine (PT) derivatives have been selected due to their wide applicability. Due to their properties, PT derivatives are interesting candidates for the obtaining new materials (e.g. via mercapto or thioacetate derivatives) by deposition as self-assembled monolayers (SAMs) on Au(111) surface. Some recent publications revealed special properties for the aggregates obtained by the deposition of phenothiazine units on gold nanoparticules via mercapto derivatives [2].

The main goal of the paper is to use the local expansion of second order Møller-Plesset perturbation theory (LMP2) method for checking the stability and for optimizing the geometry of several dimers containing PT derivatives. The paper is organized as follows: the first two chapters

present the molecular systems and the computational methods. The results are presented and discussed in the chapter 3 while the conclusions and the references follow in the ending part of the paper.

2. Molecular systems and computational methods

The optimized geometry structures of two (parallel and antiparallel) stacking configurations of the ethyl-phenothiazine (EPT) and the parallel stacking configuration of the thio-methyl-phenothiazine (TMPT) were carried out using the Hartree-Fock (HF) and the local expansion of second order Møller-Plesset perturbation theory (LMP2) methods [3-6]. The investigation techniques were implemented in the MOLPRO program package suite [7] considering the cc-pVDZ basis set. Local correlation methods are, by construction, free from the basis set superposition errors (BSSE) and in this way the LMP2 method is a suitable method for the calculation of intermolecular interactions. Two of the most important advantages of the method are that potentially expensive counterpoise (CP) corrections are avoided and the dispersion effects, which are crucial for stacking interaction of the aromatic rings, are also included. Further reductions in the computational cost are provided by combining LMP2 with the density fitting (DF) approximation of electron repulsion integrals in a method denoted DF-LMP2 [8,9].

3. Results and discussion

The main results of our work are presented in a condensed way in table 1 and are shown graphically in the figure 1. Our results consist mainly in the intermolecular interaction energies as well as in some relevant inter-atomic distances. The quantitative estimations has bee done for ΔE^{LMP2} – the total LMP2 energy, ΔE^{HF} – the HF component and ΔE^{disp} – the dispersion component, values obtained for LMP2 geometry and ΔE^{HF} – the HF energy value obtained for HF geometry. Concerning the geometrical aspects of our molecular systems the most important have been considered to be the distances between S atoms d^{S-S}, N atoms d^{N-N} or S–N atoms d^{S-N}, each of them obtained for both LMP2 and HF geometries. In case of EPT both the parallel and antiparallel dimers were investigated. As our final purpose is to use the affinity between the sulfur and gold as a tool for self-assembling TMPT molecules on atomically flat Au(111) surfaces, in the TMPT case only the parallel dimer was investigated.

Figure 1 shows the parallel and antiparallel EPT dimer geometry considering two different viewing directions, as well as the TMPT parallel conformation. As concerning the color code the gray is assigned to carbon, the yellow to sulfur, and the dark and light blue to nitrogen and to hydrogen respectively.

All investigated geometry show bonded dimer structures at LMP2 level, the strongest bonding being obtained in case of TMPT dimmer. A little bit smaller is the bonding energy of parallel EPT dimer, while the weakest bonding is found for the antiparallel EPT dimer. In order to find out the contribution of electron correlation to the intermolecular interaction energy, the HF values were also calculated at the given LMP2 geometry. In a very surprising manner the obtained results show positive values which means that the HF counterpart of LMP2 energy has a repulsive character (more than 6.0 kcal/mol in all three cases) and only the correlation correction stabilize the dimer geometry. This fact presents a very important handicap because about 50% of the correlation correction is required to compensate the HF repulsion: -8.667 kcal/mol *versus* +7.416 for parallel EPT dimer, -7.600 kcal/mol *versus* +8.849 for antiparallel EPT dimer and -10.250 kcal/mol *versus* +6.042 for parallel TMPT dimer. Additionally, it is well-known that in case of aromatic rings the most part of the electron correlation contribution of the intermolecular interaction energy is given by the dispersion effects [30]. They seem to have a crucial role also in our case, because the major part of the correlation effects is given by these dispersion contributions: -13.906 kcal./mol for parallel EPT dimer, -14.198 kcal/mol for antiparallel EPT dimer and -14.173 kcal/mol for TMPT dimer, respectively. As regarding the basis set dependency, it was confirmed that the double-zeta split valence basis set (cc-pVDZ) gives a slightly large intermolecular energy [10,11]. Taking into account the relative large number of atoms contained in the investigated molecular systems our feeling is that we are near the upper limit of

applicability for the MP2 method implemented in Molpro. Moreover, using basis sets completed with diffuse functions the amount of interaction energy will be further a little bit reduced [10]. Getting so strange behavior of HF component we have performed the geometry optimization at HF level in order to check whether the HF geometry show a bonded structure or not. We have found negligible negative intermolecular interaction energies for all three molecular systems: -0.168 kcal/mol for parallel EPT dimer, -0.367 kcal/mol for antiparallel EPT dimer and -1.217 kcal/mol for parallel TMPT dimer.

In the last case the HF energy has a slightly larger negative value, attributed to the H–S attractive interaction of the thiol groups.

Table1. The total intermolecular interaction energies, (the HF and the dispersion components) and several relevant atomic distances (see figures) for EPT parallel and antiparallel dimers of and for the TMPT parallel dimer respectively.

Parameter	Value	Method	Parameter	Value	Method	Parameter	Value	Method
EPT-parallel			EPT-antiparallel			TMPT-parallel		
ΔE^{LMP2}	-8.667	DF-LMP2	ΔE^{LMP2}	-7.600	DF-LMP2	ΔE^{LMP2}	-10.250	DF-LMP2
ΔE^{HF}	+7.416	DF-LMP2	ΔE^{HF}	+8.849	DF-LMP2	ΔE^{HF}	+6.042	DF-LMP2
ΔE^{HF}	-0.168	DF-HF	ΔE^{HF}	-0.367	DF-HF	ΔE^{HF}	-1.217	DF-HF
ΔE^{disp}	-13.906	DF-LMP2	ΔE^{disp}	-14.198	DF-LMP2	ΔE^{disp}	-14.173	DF-LMP2
d^{S-S}	3.891	DF-LMP2	d^{S1-N2}	3.704	DF-LMP2	d^{S-S}	3.867	DF-LMP2
d^{S-S}	5.129	DF-HF	d^{S1-N2}	5.007	DF-HF	d^{S-S}	5.367	DF-HF
d^{N-N}	4.054	DF-LMP2	d^{N1-S2}	3.925	DF-LMP2	d^{N-N}	4.114	DF-LMP2
d^{N-N}	5.426	DF-HF	d^{N1-S2}	5.523	DF-HF	d^{N-N}	5.436	DF-HF
						$d^{S'-S'}$	4.594	DF-LMP2
						$d^{S'-S'}$	5.412	DF-HF

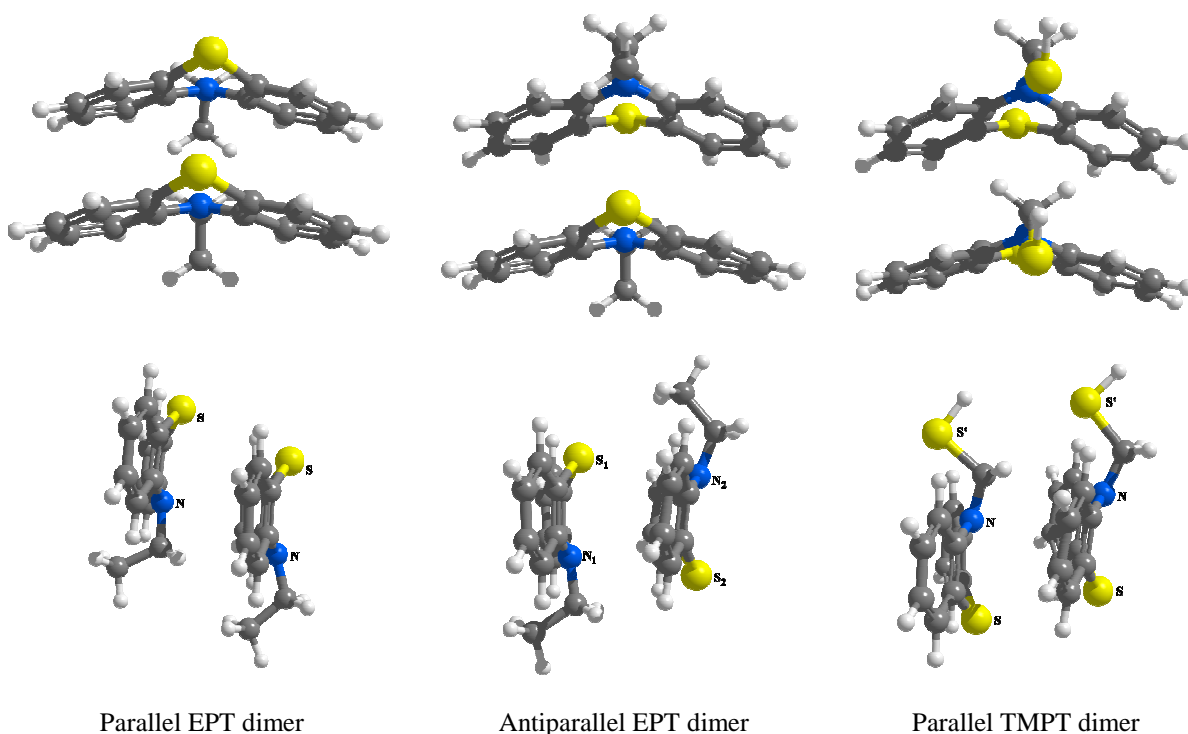Parallel EPT dimer   Antiparallel EPT dimer   Parallel TMPT dimer

Figure 1. The geometry structures of parallel and antiparallel EPT and parallel TMPT.

The phenothiazine molecule has a three-ring structure in which two benzene rings are joined by a sulfur and nitrogen atom at nonadjacent positions, due to the "umbrella" form of the N orbitals. The angles between the planes of the benzene rings vary between 140°-150°, for different parallel or antiparallel dimers. This special non-planar configuration of the – let it call "V" shape – allows a more stable dimer structure as compared to the planar case. The monomers degrees of freedom for the relative displacement are reduced to the line defined by the S and N atoms, since in the perpendicular directions the spatial shift is much more difficult.

Analyzing the results described previously one observes that the calculated values of inter-atomic distances S–S and N–N are correlated with the energy values. Namely, if in LMP2 geometry they are about 3.8 Å and 4.0 Å, respectively; in case of HF geometry they become longer with about 1.2 Å and 1.4 Å, respectively (see figure 1). This fact is due to the strong attractive character of the dispersive interaction given by the electron correlation. The superposition of benzene rings for different types of monomers presents also some particularities. While, for EPT and TMPT parallel structures, one of the benzene rings is markedly shifted relative to the corresponding benzene ring from the other monomer, for antiparallel conformation they remain almost unshifted (see figure 1) but presenting a small planar angle ($\approx 7°$) between the rings.

4. Conclusions

The intermolecular π-π stacking interaction between some phenothiazine derivatives has been investigated using the Hartree-Fock and the local second order Møller-Plesset perturbation theory methods combined with the density fitting approximation of electron repulsion integrals and considering the cc-pVDZ basis set. Two hypothetical parallel and antiparallel stacking conformations of ethyl-phenothiazine and the parallel stacking conformation of thio-methyl-phenothiazine were investigated. In all cases the stacking structures joint together in a characteristic "V" form. The results show that the dispersion effects have a crucial role in stabilizing stacking structures of the aromatic rings and consequently our prediction is that the process of self-assembling in molecular supra-structures (such as monolayers for example) having as the basic unit some phenothiazine derivatives might occur with a high probability.

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