Study of the interaction between aniline and CH_3CN, CH_3Cl and CH_3F.

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Abstract

A computational study of dimers formed by aniline and one CH_3X molecule, X being CN, Cl or F, was carried out to elucidate the main characteristics of the interacting systems. Two different structures were found for each of the dimers, depending on the relative location of the CH_3X molecule with respect to the amino hydrogen atoms. The most stable minimum for both acetonitrile and methyl chloride corresponds to structures where the CH_3X molecule is located with its methyl group over the aromatic ring establishing a C-H···π contact and simultaneously interacting with the amino group with a N-H···X contact. In methyl fluoride complex, however, no significant interaction takes place with the aromatic ring in the most stable structure. In this case, the interaction takes places with the amino group forming a five member cycle with N-H···F and C-H···N contacts.

As regards interaction energies, the stronger complex is formed with acetonitrile, with an interaction energy amounting to -6.4 kcal/mol. Methyl chloride and methyl fluoride form complexes with interaction energies amounting to -4.1 and -4.2 kcal/mol, respectively, though the structural arrangements are quite different for both structures.

The results of the SAPT(DFT) analysis indicate that in most complexes the leading contribution to the stabilization of the complex is dispersion, though the electrostatic contribution is almost as important. However, in methyl fluoride most stable complex the larger attractive term is of electrostatic nature.

Introduction

Intermolecular interactions involving aromatic rings are important processes in both chemical and biological recognition. Their understanding is essential for the rational designs of drugs and other new functional materials. On the basis of these intermolecular interactions, not only theoretical design but also experimental realization of novel functional receptors has become possible.[1-6] Therefore, the study of the fundamental intermolecular interactions and new types of interactions is important for aiding the design of new materials as well as for understanding cluster formation. In particular, novel types of interaction involving aromatic rings have been an important subject in the past decade. In this regard, if the interaction involves the aromatic system, it is usually one of the following three types: cation···π, π···π or X-H···π.[5, 6] This last kind of interaction has been the subject of much interest as it implies a hydrogen bond where the aromatic ring acts as acceptor.[2, 5, 6]

Also, numerous studies have been undertaken on a variety of small molecular clusters to probe solvation phenomena, as solvation effects play an important role in defining structural and functional aspects of biological macromolecules. In particular, studying small clusters allows exploring the nature of the transition between clusters in the gas phase and solvated bulk systems. Usually these microsolvation studies deal with protic solvents, especially water, so the most important characteristics of the interaction between the solvent and the solute are described by the presence of hydrogen bonds.[7, 8] Studies devoted to non-protic solvents are much more scarce.

The three CH_3X molecules considered in this work are non-protic, though they exhibit different polarity. Thus, acetonitrile presents a dipole moment of 3.92 D, whereas methyl chloride and methyl fluoride have dipole moments of 1.87 and 1.85 D, respectively. In our recent study on phenol complexes we have shown that only in the case of the acetonitrile complex a typical hydrogen bonded structure is observed. For all other cases the most stable structures correspond to arrangements where both hydrogen bond and C-H···π contacts are present, with an important dispersive component.[9] It can be expected that aniline, the simplest amine with an aromatic ring, will behave in a quite similar manner, with structures presenting hydrogen bonds involving the amino group but also π contacts. Therefore, in the present work we extend our studies to the interaction in clusters containing one aniline molecule and one CH_3X molecule (X=CN, F, Cl). The procedure used to study the clusters is described in detail in the following section and the results obtained in subsequent ones.

Computational details and procedure

Starting structures were constructed attending to chemical intuition, trying to represent the possible X-H⋯π and N-H⋯X favorable contacts. Several initial structures were therefore fully optimized by using the MP2 method together with the 6-31+G* basis set, being afterwards refined at the MP2/aug-cc-pVDZ level.

After locating the stationary points of the potential energy surface of each cluster and having characterized them as minima by performing a vibrational analysis, the interaction energies were calculated by means of the counterpoise method to avoid basis set superposition error.[10, 11] Thus, the interaction energy results from subtracting the energies of the fragments that constitute the clusters employing the geometry and the whole basis set of the cluster

$$\Delta E_{\text{int}} = E_{ij}(ij...) - \sum_i E_i^{clus.}(ij...)$$

As the geometry of the molecules changes when the cluster is formed, and additional contribution describing this effect must be included, obtained as the energy difference between the molecules in the cluster geometry and in isolation.

$$E_{def} = \sum_i \left(E_i^{clus.}(i) - E_i^{isol.}(i) \right)$$

The total complexation energy results from adding these two contributions, though deformation effects are usually small and negligible for most clusters, and in the discussion we will not consider them.

To estimate the basis set effects, interaction energies were also computed by employing the larger aug-cc-pVTZ basis set. In this case, we have taken advantage of the resolution of the identity (RI) approach to reduce the computational cost, by employing suitable fitting basis sets as provided in Turbomole.[12-14] Finally, the interaction energies of complexes were obtained at CCSD(T)/aug-cc-pVDZ level. Also, an estimation of the CCSD(T)/aug-cc-pVTZ was performed by assuming that the effect of enlarging the basis set can be estimated with the MP2 method. Thus the CCSD(T)/aug-cc-pVTZ was obtained as:

$$\Delta E_{CCSD(T)}^{AVTZ} = \Delta E_{CCSD(T)}^{AVDZ} + (\Delta E_{MP2}^{AVTZ} - \Delta E_{MP2}^{AVDZ})$$

Supermolecule method gives a plain number as result, so a perturbational analysis was carried out to have more insight into the nature of the interaction. A Symmetry Adapted Perturbation Theory (SAPT) analysis was performed to compute the different contributions to the interaction energy.[15] The calculations were carried out by employing the SAPT(DFT) approach,[16-18] which has been shown to provide reasonable estimation of interaction energy contributions at a lower computational cost than ordinary SAPT. The total interaction energy is expressed as a combination of different terms as:

$$\Delta E_{\text{int}} = E_{exchange} + E_{electrostatic} + E_{induction} + E_{dispersion} + \delta_{HF}$$

corresponding to repulsion, electrostatic, induction and dispersion contributions to the interaction energy. The δ_{HF} term recovers contributions at higher order estimated at the HF level. These calculations were performed by using the SAPT2006 code[16] of Szalewicz and coworkers interfaced to Dalton 2.0 package.[17] All other calculations were performed with Gaussian03.[19]
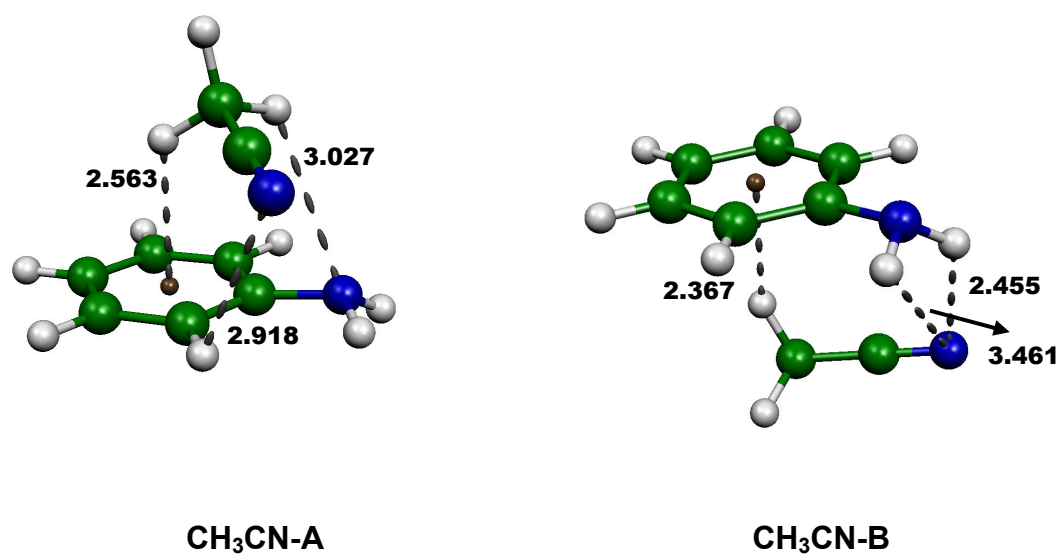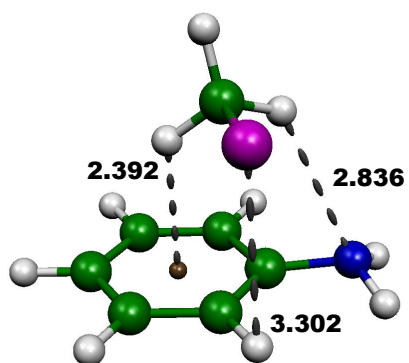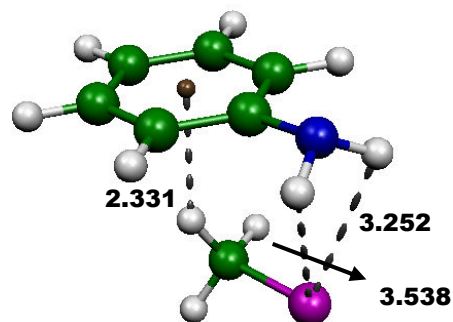
CH₃CN-A   **CH₃CN-B**

Figure 1. Minimum energy structures located for the clusters with one CH₃CN molecule at the MP2/aug-cc-pVDZ level. Distances in Å.

Results

Figure 1 shows the structures of the clusters formed by aniline and acetonitrile. Two different structures were located. In one of them, CH₃CN-A, acetonitrile interacts with the aromatic ring by means of the methyl group, simultaneously establishing a C-H···N contact at about 3 Å. In the CH₃CN-B structure acetonitrile molecule is located in such a way that again interacts with the aromatic ring (on the other side) but also with the amino group, exhibiting two N-H···N contacts, though one of them presents a so long distance (3.542 Å) that its contribution to the stabilization of the cluster must be marginal.
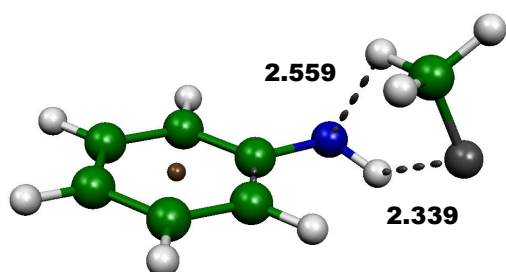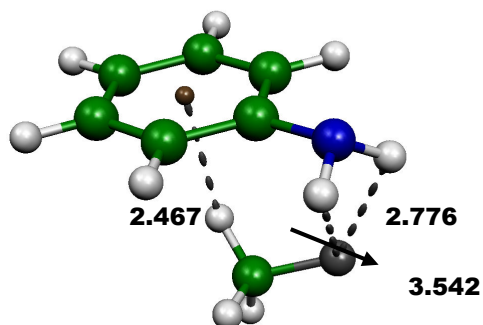
CH₃Cl-A

CH₃Cl-B

Figure 2. Minimum energy structures located for the clusters with one CH₃Cl molecule at the MP2/aug-cc-pVDZ level. Distances in Å.

CH₃F-A

CH₃F-B

Figure 3. Minimum energy structures located for the clusters with one CH₃F molecule at the MP2/aug-cc-pVDZ level. Distances in Å.

The same structural patterns are observed for the methyl chloride complexes shown in Figure 2, though in this case distances to the aromatic ring are somewhat shorter than with acetonitrile. In the case of methyl fluoride, as shown in Figure 3, a similar CH_3F-B structure is found in accordance with the other two studied systems. However, structure CH_3F-A shows a different pattern, with the methyl fluoride molecule interacting exclusively with the amino group, with no interactions with the aromatic ring. This is a similar structure to that found in phenol complexes.[9]

Table 1. Interaction energies (kcal/mol) for the clusters studied in this work obtained at the MP2/aug-cc-pVDZ level.

	ΔE	E_{def}	$\Delta E_{complex.}$	ΔE_{ZPE}	S(cal/mol K)
CH$_3$CN-A	-6.00	0.36	-5.64	-4.65	-31.45
CH$_3$CN-B	-7.03	0.25	-6.78	-5.68	-31.88
CH$_3$Cl-A	-4.22	0.14	-4.08	-3.09	-27.70
CH$_3$Cl-B	-4.48	0.08	-4.40	-3.51	-25.42
CH$_3$F-A	-3.90	0.18	-3.72	-2.77	-27.62
CH$_3$F-B	-3.56	0.19	-3.37	-2.44	-27.82

Table 1 lists the interaction energy obtained for each of the clusters studied together with other energetic information as obtained at the MP2/aug-cc-pVDZ level of calculation. First, it can be observed that deformation effects are negligible for all structures studied. In fact, only small changes on the torsion angle of the amino group with respect to the ring plane were observed, the rest of the geometrical parameters being unaffected by complexation. Also, zero point energy corrections are similar for both structures of each CH_3X molecule, as it is the case of the entropy. Thus, we will discuss electronic energies since the observed trends are the same.

For acetonitrile complexes, CH$_3$CN-B structure is about 1 kcal/mol more stable than CH$_3$CN-A, probably due to the stronger N-H···N contact. This is also the case in methyl chloride complexes, though the energy difference between structures is reduced to 0.26 kcal/mol. In the case of methyl fluoride, however, the stability sequence is reversed, being CH$_3$F-A the most stable one. However, this is a consequence of the different structural arrangement of CH$_3$F-A, which only interacts with the amino group exhibiting N-H···F and C-H···N contacts.

Table 2. Interaction energies (kcal/mol) for the clusters with one CH$_3$X molecule computed with different methods.

	MP2/AVDZ[a]	CCSD(T)/AVDZ[a]	MP2/AVTZ[a]	CCSD(T)/AVTZ[a,b]
CH$_3$CN-A	-6.00	-4.51	-6.78	-5.28
CH$_3$CN-B	-7.03	-5.44	-7.96	-6.38
CH$_3$Cl-A	-4.22	-3.02	-4.91	-3.72
CH$_3$Cl-B	-4.48	-3.32	-5.22	-4.07
CH$_3$F-A	-3.90	-3.70	-4.35	-4.15
CH$_3$F-B	-3.56	-2.93	-4.14	-3.51

[a] AVDZ and AVTZ stand for the aug-cc-pVDZ and the aug-cc-pVTZ basis sets, respectively.

[b] Estimated as indicated in the text.

Table 2 summarizes the effect of employing a larger basis set or a better treatment of electron correlation. As expected MP2 tends to overestimate interaction energies when compared to CCSD(T), whereas increasing the size of the basis set results in extra stabilization. Our best estimations correspond to the CCSD(T)/aug-cc-pVTZ level, which confirms the trends observed at the MP2 level of calculation. So, aniline is predicted to form the strongest dimer with acetonitrile, the interaction energy amounting to -6.4 kcal/mol. Methyl chloride and methyl fluoride form complexes of similar strength (about -4.1 kcal/mol) though presenting different structural arrangements.

Figures 4 to 6 present the results obtained from the energy decomposition analysis as obtained with SAPT(DFT). The figures show the interaction energy decomposed in electrostatic, induction and dispersion contributions. The exchange term (repulsion) is also shown with its sign changed, so the comparison with the attractive contributions is facilitated. Finally a δ_{HF} term is also including reflecting contribution from higher order terms as computed at the Hartree-Fock level.

It can be observed from Figure 4 that even for acetonitrile the most attractive contribution corresponds to dispersion, though electrostatic contribution exhibits a similar value. This is so for the most stable CH_3CN-B complex, since for the CH_3CN-A structure dispersion term is even more dominant. This is a consequence of the lack of N-H···N contact in CH_3CN-A so the interaction is mainly dispersive, though, taking into account the large dipole moment of acetonitrile, the electrostatic contribution is still important.
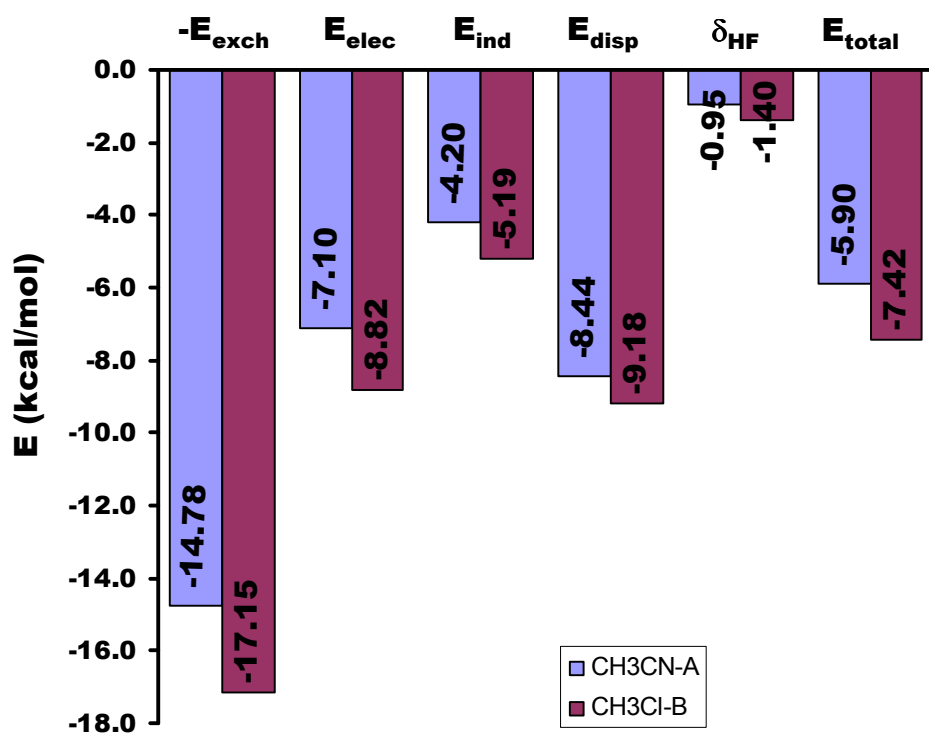

Figure 4. SAPT(DFT) decomposition analysis of the interaction energy for the clusters formed by aniline and acetonitrile.
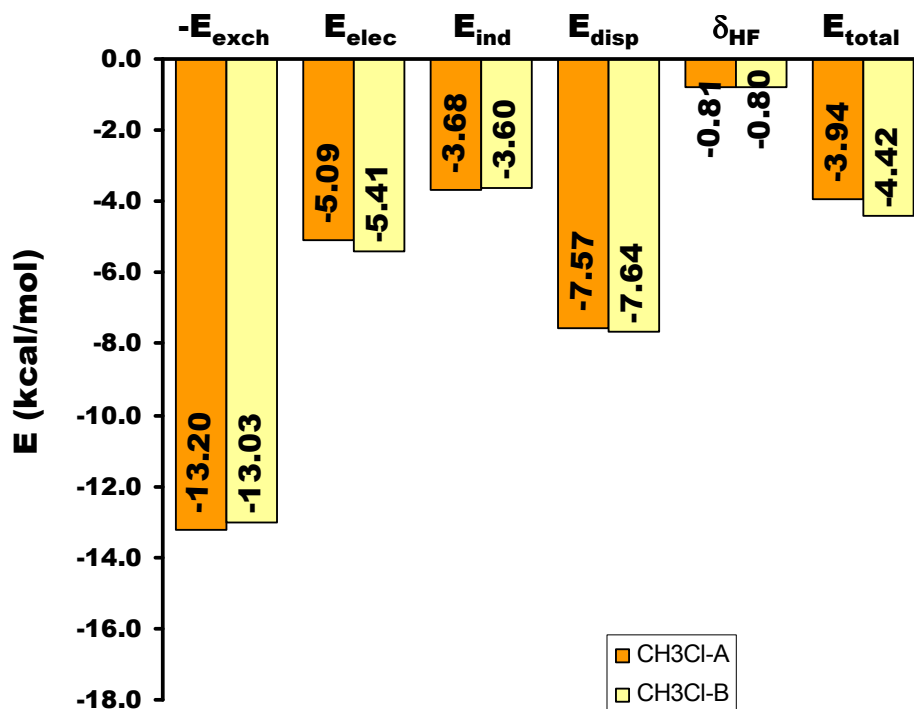
Figure 5. SAPT(DFT) decomposition analysis of the interaction energy for the clusters formed by aniline and methyl chloride.
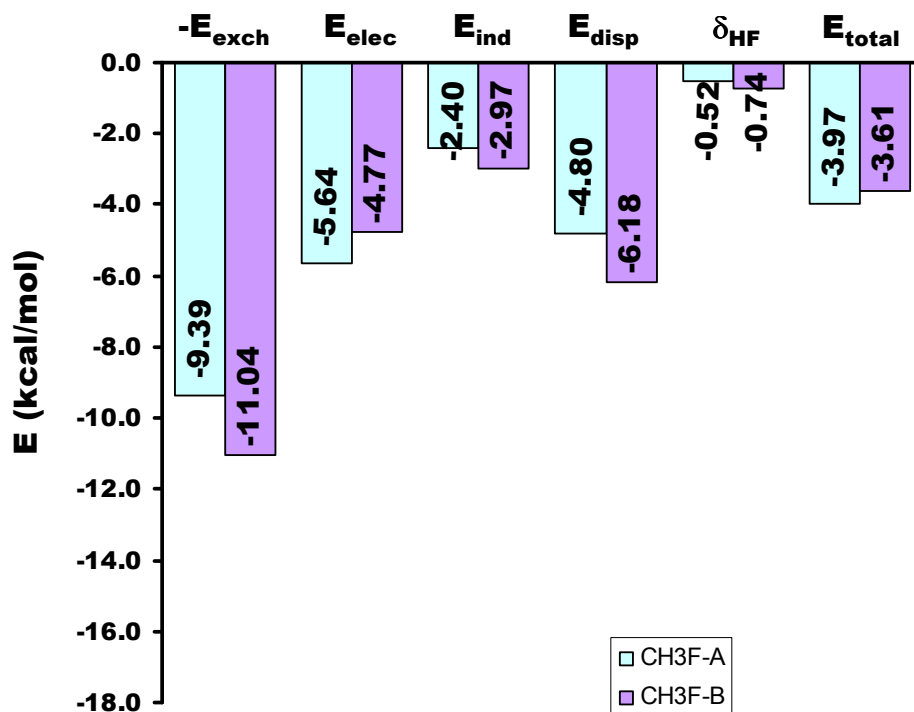

Figure 6. SAPT(DFT) decomposition analysis of the interaction energy for the clusters formed by aniline and methyl fluoride.

In the case of methyl chloride complex, the behaviour is similar, but dispersion contribution is even more dominant for both CH_3Cl-A and CH_3Cl-B structures, since both the electrostatic and the induction contributions are significantly smaller than in the acetonitrile complexes, reflecting the lower polarity of methyl chloride.

Finally, methyl fluoride complexes, exhibit a different pattern. Whereas CH_3F-B dimer presents a similar behaviour to that observed for methyl chloride complex (dispersion dominating the interaction, with even smaller electrostatic and induction contributions) the interaction in CH_3F-A is dominated by the electrostatic contribution, as a consequence of the different structural pattern shown by this complex. In CH_3F-A complex two hydrogen bonding contacts are shown and as a consequence the interaction is dominated by the electrostatic contribution, though dispersion is still important.

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