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REGULAR ARTICLE

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 or two CH_3X molecules, 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 NH_2 hydrogen atoms. The most stable complex is formed with acetonitrile, with a complexation energy amounting to −27.0 kJ/mol. Methyl chloride and methyl fluoride form complexes with complexation energies amounting to −18.1 and −17.5 kJ/mol, respectively, though the structural arrangement is quite different for both structures. In most complexes, the leading contribution to the stabilization of the complex is dispersion, though the electrostatic contribution is almost as important. Three different minima were obtained for clusters containing two CH_3X molecules depending on the side they occupy with respect to the phenyl ring. The complexation energies for these structures amount to −58.5, −38.6 and −36.3 kJ/mol for acetonitrile, methyl chloride and methyl fluoride, respectively.

Keywords Intermolecular interactions · Ab initio calculations · CH···π interaction · Aniline heterodimers · Dispersion

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1 Introduction

Intermolecular interactions involving aromatic rings are important processes in both chemical and biological recognition. Their understanding is essential for the rational design 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 [1–4]. Therefore, the study of the fundamental intermolecular 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 [2, 4].

Cation···π interactions have proven of importance on different aspects of molecular recognition and stability in biological systems. Cation···π contacts can be found on almost any protein due to the presence of amino acids containing aromatic residues in their side chain, together with other amino acids that present cationic groups, usually depending on the pH of the medium. These cation···π interactions are usually very strong in the gas phase, but much weaker in the presence of solvent, though there is some controversy about the real contribution of the cation···π interactions in real systems [2, 5].

On the other hand, $\pi\cdots\pi$ contacts are essentially weak and dispersive in nature, which makes them quite difficult to describe. Different studies have dealt with these types of interactions, mainly centered in the study of benzene dimer but also dedicated to stacking interactions on larger systems [2, 4, 6].

X-H$\cdots\pi$ interactions have also been the subject of many previous works, since these types of contact implies a hydrogen bond with the participation of an aromatic cloud. Thus, O–H$\cdots\pi$ and N–H$\cdots\pi$ have been the frequently studied, but there are also other possibilities as the C–H$\cdots\pi$ interaction [2–4]. These contacts are more dispersive than typical hydrogen bonds and need rigorous method to be described in detail.

Also, 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 [7, 8]. 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 [7–10]. Studies devoted to non-protic solvents are much scarcer but show that in the microsolvation of aromatic molecules by aprotic solvents, the pattern of interaction cannot relay on hydrogen-bonded structures but on other interactions involving the aromatic ring. Therefore, a subtle balance between different contributions to the interaction energy is expected in these systems, with dispersive contributions playing a major role [11–17].

In the present work, a computational study on the interaction between aniline and three aprotic molecules, namely acetonitrile, methyl fluoride and methyl chloride, was performed. These molecules are similar but present 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 [18]. In our recent work on the interaction of these molecules with phenol, we have shown that only for acetonitrile, a typical hydrogen-bonded structure is observed, whereas in all other cases, the most stable structures correspond to arrangements where both hydrogen bonds and C–H$\cdots\pi$ contacts are present, with an important dispersive component [11]. 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. In any case, aniline has a more basic character than phenol, so a smaller tendency to act as donor in hydrogen bonds can be expected.

Therefore, in the present work, we extend our studies to the interaction in clusters containing one aniline molecule and up to two CH_3X molecules (X = CN, F, Cl). The results will allow revealing the differences in the interaction with molecules with different polarity and tendency to form hydrogen bonds, whereas the comparison with the results obtained for trimers will give information about the stepwise solvation on these systems.

2 Computational details and procedure

Starting structures were constructed attending to chemical intuition, trying to represent the possible X-H$\cdots\pi$ and N–H$\cdots$X favorable contacts. Several initial structures were therefore fully optimized using the MP2 method together with the aug-cc-pVDZ basis set.

After locating the stationary points of the potential energy surface of each cluster and having characterized them as minima by performing a vibrational analysis at the MP2/aug-cc-pVDZ level, the interaction energies were calculated by means of the counterpoise method to avoid basis set superposition error [19–21]. 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. Thus,

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

where terms in parentheses indicate the basis set employed and superscripts the geometry used in the calculation.

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

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

The total complexation energy results from adding these two contributions, though deformation effects are usually small and negligible for many clusters.

$$\Delta E_{\text{compl.}} = \Delta E_{\text{int}} + E_{\text{def}}$$

In the case of clusters containing two CH_3X molecules, a more detailed analysis of the interaction energy is performed by determining the energy contributions for each pair of molecules. The three-body contribution is obtained as the difference between the interaction energy of the trimer and the sum of all the pair interaction energies [22–24].

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 [25–27]. Finally, as MP2 method has been reported to produce overestimated interaction energies in clusters containing aromatic molecules, the interaction energies of complexes were also obtained for the dimers at the CCSD(T)/aug-cc-pVDZ level [4, 21].

The interaction energy at the basis set limit was estimated by extrapolating the results obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets [28, 29]. Thus, the MP2 correlation energy at complete basis is obtained as:

$$\Delta E^{\mathrm{CBS}}_{\mathrm{corr,MP2}} = \frac{X^3}{X^3-(X-1)^3}\Delta E^{\mathrm{pVXZ}}_{\mathrm{corr,\,MP2}} - \frac{(X-1)^3}{X^3-(X-1)^3}\Delta E^{pV(X-1)Z}_{\mathrm{corr,\,MP2}}\ ;\ X=3$$

and the MP2 interaction energy at the basis set limit is obtained as:

$$\Delta E^{\mathrm{CBS}}_{\mathrm{MP2}} = \Delta E^{\mathrm{pVTZ}}_{\mathrm{HF}} + \Delta E^{\mathrm{CBS}}_{\mathrm{corr,\,MP2}}$$

Finally, the MP2 results are corrected using the CCSD(T) results obtained with the aug-cc-pVDZ basis set to estimate CCSD(T) interaction energies at the complete basis set limit: [21]

$$\Delta E^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} = \Delta E^{\mathrm{CBS}}_{\mathrm{MP2}} + (\Delta E^{\mathrm{AVDZ}}_{\mathrm{CCSD(T)}} - \Delta E^{\mathrm{AVDZ}}_{\mathrm{MP2}})$$

Supermolecule method gives a plain number as result, so a perturbational analysis was carried out for dimers 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 [30]. The calculations were carried out by employing the SAPT(DFT) approach, which has been shown to provide reasonable estimations of interaction energy contributions at a lower computational cost than ordinary SAPT [30–32]. The total interaction energy is expressed as a combination of different terms as:

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

corresponding to repulsion, electrostatic, induction and dispersion contributions to the interaction energy. The δ_{HF} term recovers contributions at higher orders estimated at the HF level. SAPT(DFT) calculations were performed using the PBE0 functional together with the aug-cc-pVDZ basis set at the MP2/aug-cc-pVDZ optimized geometries of the clusters. The SAPT2006 code of Szalewicz and coworkers [31] interfaced to Dalton 2.0 package [33] was used to perform the calculations. All other calculations were performed with Gaussian03 [34] except the RI-MP2 calculations that were done with Turbomole [25].

3 Results

3.1 Aniline ··· CH_3X complexes

Figure 1 shows the structures of the clusters formed by aniline and one CH_3X molecule as obtained at the MP2/aug-cc-pVDZ level. Two minima were found for any of the molecules studied in this work. In the case of acetonitrile complexes, one of these structures (**CN1-A**) presents one C–H···N contact at about 3.0 Å and a C–H···π contact at 2.6 Å from the center of the ring. The other minimum found for this complex (**CN1-B**) presents different characteristics, since the amino group acts as a hydrogen donor, establishing a N–H···N contact at about 2.5 Å, together with a C–H···π contact at 2.4 Å. The structures correspond to situations where the acetonitrile molecule is located on one or another side of the phenyl ring, thus interacting with the NH_2 group as hydrogen donor or acceptor. These structures are similar to those found in phenol–acetonitrile complexes [11], but it is worth noting that no structure showing a typical hydrogen bond has been located for aniline.

The same structural patterns are observed for the methyl chloride complexes shown in Fig. 1, though in this case distances to the aromatic ring are somewhat shorter than with acetonitrile. Also, in structure **Cl1-B**, the chlorine atom is located almost at the same distance from the two amino hydrogens.

In the case of methyl fluoride, structure **F1-B** presents similar characteristics as the other two systems studied. However, structure **F1-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, due to the tendency of fluorine atom to participate in hydrogen bonds and thus establishing a contact with the N–H group at 2.3 Å [11]. Also, as a consequence of the small size of the molecule, the methyl group interacts preferentially with the nitrogen lone pair instead than with the more distant phenyl ring.

Table 1 lists the complexation energies obtained for each of the clusters studied together with other energetic information as obtained at the MP2/aug-cc-pVDZ level of calculation. It can be observed that deformation effects are small for all structures studied.

For acetonitrile complexes, structure **CN1-B** is about 5 kJ/mol more stable than **CN1-A**, probably due to the presence of a N–H···N contact. This is also the case in methyl chloride complexes, though the energy difference between structures is reduced to 1.3 kJ/mol. In methyl fluoride clusters, however, the stability sequence is reversed, being **F1-A** the most stable one. This is a consequence of the different structural arrangement of **F1-A**, where methyl fluoride molecule only interacts with the

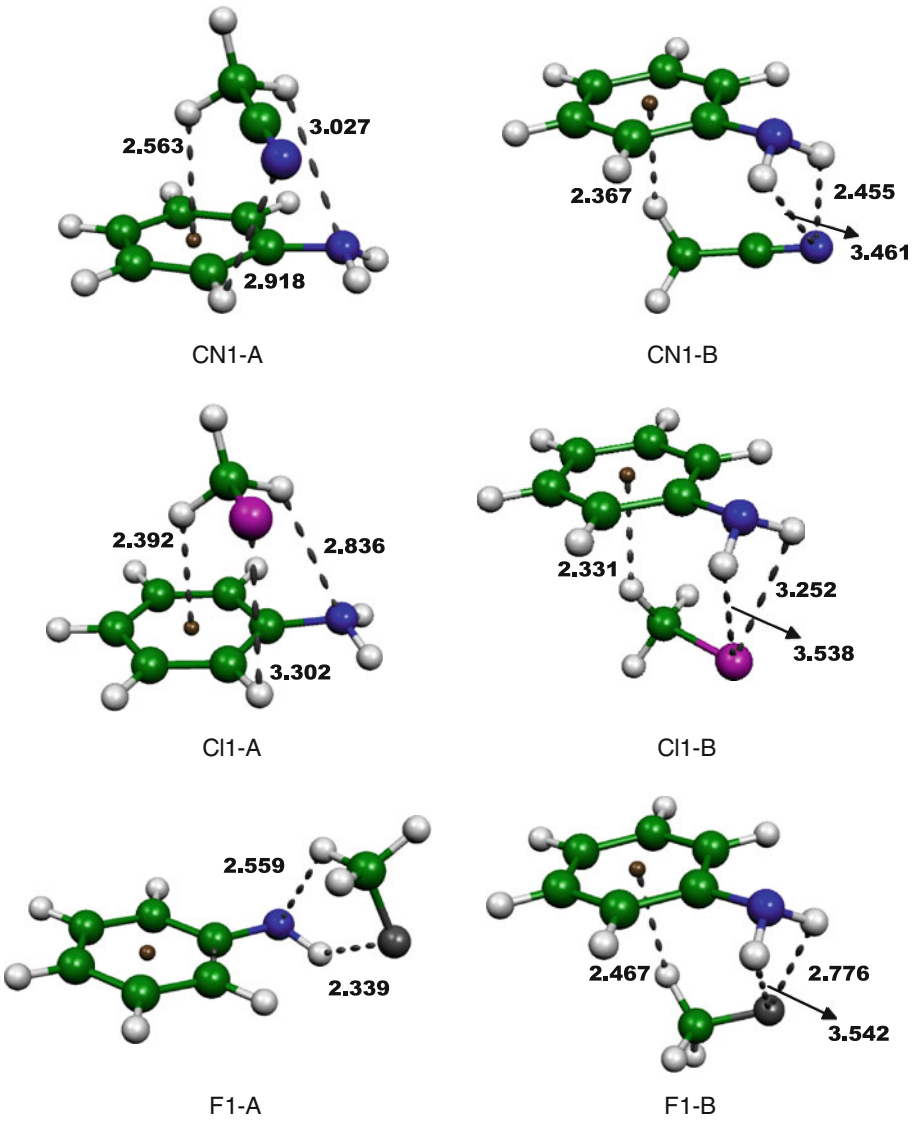

Fig. 1 Minimum energy structures located for the clusters with one CH_3X molecule at the MP2/aug-cc-pVDZ level. Distances in Å

Table 1 Complexation energies (kJ/mol) for the clusters with one CH_3X molecule obtained at the MP2/aug-cc-pVDZ level

	ΔE_{compl}	E_{def}	D_0	ΔS^0 (J/mol K)
CN1-A	−23.6	1.5	−19.5	−131.6
CN1-B	−28.4	1.0	−23.8	−133.4
Cl1-A	−17.1	0.6	−12.9	−115.9
Cl1-B	−18.4	0.3	−14.7	−106.4
F1-A	−15.6	0.8	−11.6	−115.6
F1-B	−14.1	0.8	−10.2	−116.4

Inclusion of zero-point energies gives D_0 values

amino group exhibiting N–H···F and C–H···N contacts. Therefore, in all complexes, aniline tends to act as a hydrogen donor in the most stable structures. In acetonitrile and methyl chloride clusters, this implies that the molecules are located in the side of the phenyl ring opposite to the lone pair of the amino group. In methyl fluoride complexes, aniline is able to act as hydrogen donor with the methyl fluoride molecule located in the same side as the nitrogen lone pair, thus allowing a second C–H···N contact contributing to the stabilization of the complex. Comparing the clusters formed with the different CH_3X molecules, it can be seen that acetonitrile presents the stronger interaction, followed by methyl chloride and methyl fluoride. In the case of acetonitrile, this could be a consequence of its larger dipole moment, but the differences between methyl chloride and methyl fluoride must be due to other phenomena, since both molecules have almost equal dipole moments.

When zero-point energy corrections are included, no changes are observed in the order of stability of the complexes studied. Also, the entropies for complex formation are of course negative as corresponds to a dimerization process but show no important differences between the structures found for each CH_3X molecule. Only for methyl

chloride, a larger difference is observed, slightly favoring the formation of **Cl1-B**.

Table 2 summarizes the effect of employing a larger basis set or a better treatment of electron correlation on the complexation energies. As expected, MP2 complexation energies are more negative than the corresponding CCSD(T) ones obtained with the same basis. When the basis set is enlarged, all clusters show larger complexation energies, but the increment is not large, amounting to about 4 kJ/mol for acetonitrile complexes and 2–3 kJ/mol for methyl chloride and methyl fluoride clusters. With the results obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, values for the complexation energy at the complete basis set limit were obtained as explained in computational details. The values thus obtained for the CCSD(T)/CBS limit are pretty similar to those obtained at the MP2/aug-cc-pVDZ level. The energy differences among different structures are very similar, with the exception of structure **F1-A**, which now presents a similar stability to that observed in methyl chloride complexes. This is due to the fact that **F1-A** is the structure with the smallest change when passing from MP2 to CCSD(T) results (the structure where MP2 performs better, though this is probably because **F1-A** is the only structure where no CH$\cdots\pi$ contact is established). Thus, at the CCSD(T)/CBS level, complexes formed by methyl chloride and methyl fluoride are almost isoenergetic, whereas those formed with acetonitrile are more stable by 9 kJ/mol.

Figure 2 presents 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 included reflecting contributions from higher order terms as computed at the Hartree–Fock level [31, 32].

Table 2 Complexation energies (kJ/mol) for the clusters with one CH_3X molecule obtained with different methods

	MP2/AVDZ[a]	CCSD(T)/AVDZ[a]	MP2/AVTZ[a]	CCSD(T)/CBS[a,b]
CN1-A	−23.6	−17.4	−26.9	−22.1
CN1-B	−28.4	−21.8	−32.3	−27.0
Cl1-A	−17.1	−12.0	−19.9	−16.3
Cl1-B	−18.4	−13.6	−21.5	−18.1
F1-A	−15.5	−14.7	−17.4	−17.5
F1-B	−14.1	−11.5	−16.5	−15.0

[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

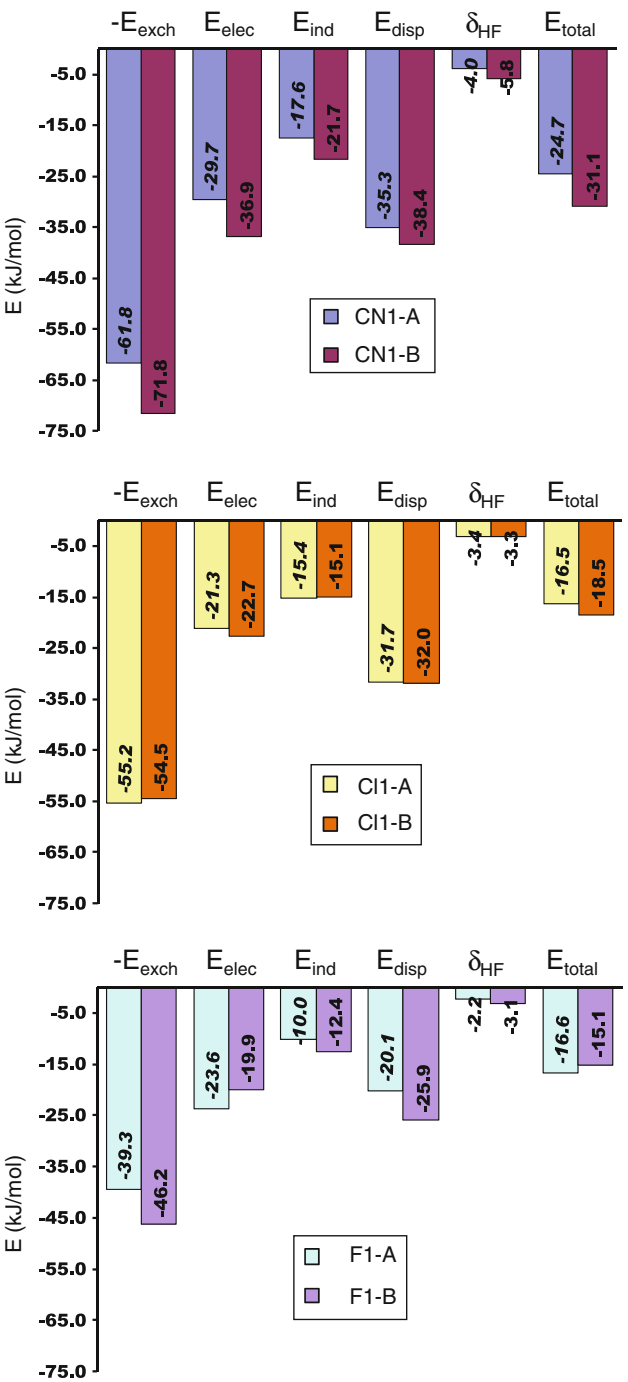

Fig. 2 SAPT(DFT) decomposition analysis of the interaction energy for the clusters formed by aniline and one CH_3X molecule

It can be observed from Fig. 2 that all contributions to the interaction energy are relevant. In structure **CN1-A**, there are two leading attractive contributions due to dispersion and electrostatic. For this complex, the contribution of dispersion is even larger than the electrostatic one, in accordance with the results obtained for phenol complexes [11]. In structure **CN1-B**, the situation is similar, with even

larger (though more similar) contributions from both dispersion and electrostatic, but also induction. These larger contributions are due to the contact N–H···N and to the shorter distances observed in the cluster.

In methyl chloride complexes, the energy partitioning is similar, but with larger differences between electrostatic and dispersion contributions. The larger size of the chlorine atom produces larger contributions from dispersion, whereas the smaller dipole moment produces a reduction in the electrostatic contribution. Also, differences between structures **Cl1-A** and **Cl1-B** are much smaller than those observed for acetonitrile complexes. **Cl1-B** structure is mainly favored by slightly more attractive electrostatic contributions.

Finally, methyl fluoride complexes exhibit a different pattern. Whereas the **F1-B** dimer presents a similar behavior to that observed for methyl chloride complex (dispersion dominating the interaction, with even smaller electrostatic and induction contributions), the interaction in **F1-A** is dominated by the electrostatic contribution, as a consequence of the different structural pattern shown by this complex. In **F1-A** complex, two hydrogen bonding contacts are established and, as a consequence, the interaction is dominated by the electrostatic contribution, though dispersion is still important.

Therefore, in acetonitrile complexes, all attractive contributions favor **CN1-B**, in methyl chloride electrostatic contributions make **Cl1-B** more stable, and structure **F1-A** is favored mainly by electrostatics, which overcomes the more favorable dispersion contribution of **F1-B**, but also for a smaller repulsion term.

3.2 Aniline ··· $(CH_3X)_2$ complexes

Figure 3 shows the minima found for the clusters formed by aniline and two CH_3X molecules, as obtained at the MP2/aug-cc-pVDZ level of calculation. It can be seen that for each CH_3X molecule, three different minima were

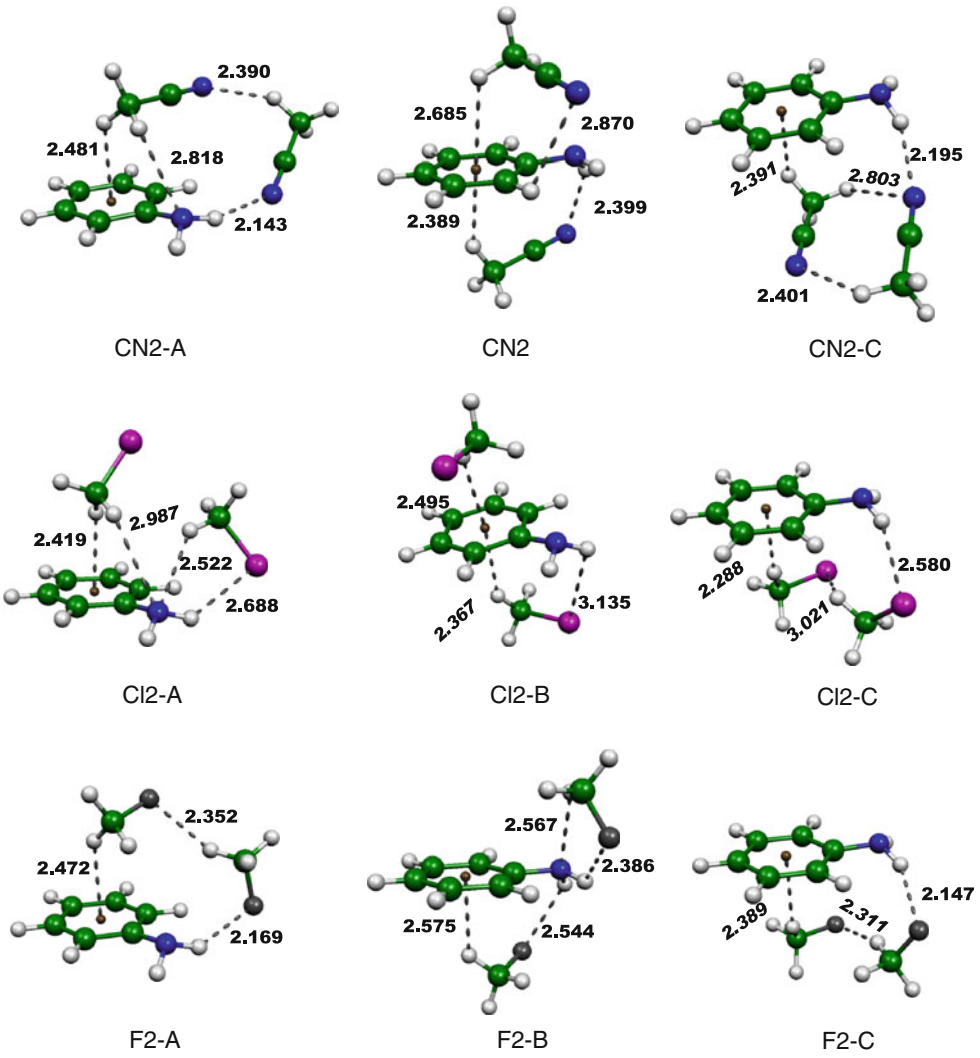

Fig. 3 Minimum energy structures located for the clusters with two CH_3X molecules at the MP2/aug-cc-pVDZ level. Distances in Å

found, depending on the location of the molecules with respect to the plane of the aromatic ring of aniline. Thus, in structures **A**, both CH_3X molecules are located on the same side as the nitrogen lone pair, establishing a chain of head-to-tail contacts forming a cyclic pattern. This is evident for complexes formed with acetonitrile or methyl fluoride, whereas for methyl chloride, there is a smaller tendency of chlorine atom to interact with the methyl group of the other molecule, so distances are much longer, and the two CH_3Cl molecules interact almost independently with aniline.

Structures **B** are the combination of the two minima found for the complexes with one CH_3X molecule, each molecule on a different side of the ring. Finally, in structures **C**, both molecules occupy the same side of the phenyl ring, opposite to the nitrogen lone pair. In these structures, both methyl chloride and methyl fluoride establish NH···X, CH···X and CH···π contacts defining a cyclic pattern as in structures **A**. In the case of **CN2-C**, both molecules of acetonitrile tend to orientate in an antiparallel way, as observed in acetonitrile dimer, so structure **CN2-C** resembles an acetonitrile dimer interacting with aniline [35, 36].

Table 3 shows the complexation energies obtained for the trimers formed by aniline and two CH_3X molecules as obtained at the MP2/aug-cc-pVDZ level. In the case of acetonitrile clusters, the most stable structure is **CN2-A,** probably due to the sequence of attractive contacts between acetonitrile molecules and aniline. This structure is only slightly more attractive than **CN2-C**, indicating that there is no clear preference for the side of the aniline ring occupied by the acetonitrile molecules. The least stable structure is **CN2-B**, where acetonitrile molecules cannot interact because they are in different sides of the phenyl ring.

In the case of methyl chloride clusters, all structures present very similar complexation energies, which differ by less than 2 kJ/mol, being **Cl2-C** the least stable structure. This behavior is a consequence of the weak interaction between methyl chloride molecules, favoring the interaction between methyl chloride and aniline over the interaction between methyl chloride molecules. Methyl fluoride clusters present a similar behavior to that observed in methyl chloride.

Again, inclusion of zero-point energies does not change the tendencies already observed, and there are also small differences on complexation entropies, though **Cl2-B** and **F2-B** are slightly favored over the other structures. The values obtained at the CCSD(T)/CBS level listed in Table 4 do not show significant changes with respect to those obtained at the MP2/aug-cc-pVDZ level. Thus, our best estimation for the cluster formed with acetonitrile indicates a complexation energy of −58.5 kJ/mol, whereas values of −38.6 and −36.3 kJ/mol are obtained for methyl chloride and methyl fluoride, respectively.

Table 5 shows the decomposition of the interaction energy of the trimers by pairs of molecules. In **CN2-A**, the three pair interactions contribute significantly to the stabilization of the cluster. It is worth noting that the interaction is stronger for the acetonitrile molecule that interacts with the π cloud than for the acetonitrile interacting with the NH_2 group. Also, the interaction between acetonitrile molecules contributes with −15.7 kJ/mol. In **CN2-C**, the situation is similar, with the three pairs contributing with stabilizing interactions. The interaction between acetonitrile molecules is stronger in this structure since they adopt an orientation similar to that found for acetonitrile dimer [35, 36]. Finally, in **CN2-B**, the behavior is totally different. There are two stabilizing contributions from the interaction of acetonitrile with aniline, whereas acetonitrile molecules almost do not interact. Also, except in **CN2-A**,

Table 3 Complexation energies (kJ/mol) for the clusters with two CH_3X molecules obtained at the MP2/aug-cc-pVDZ level

	ΔE_{compl}	E_{def}	D_0	ΔS^0 (J/mol K)
CN2-A	−59.0	1.6	−50.6	−258.9
CN2-B	−53.1	2.6	−44.9	−262.5
CN2-C	−58.3	1.3	−50.1	−264.5
Cl2-A	−36.7	0.8	−29.0	−239.3
Cl2-B	−35.7	1.1	−28.2	−227.4
Cl2-C	−35.1	0.5	−27.2	−242.3
F2-A	−32.6	1.0	−24.1	−244.6
F2-B	−30.3	2.2	−22.3	−237.4
F2-C	−31.1	0.7	−22.6	−251.8

Inclusion of zero-point energies gives D_0 values

Table 4 Complexation energies (kJ/mol) for the clusters with two CH_3X molecules computed with different methods

	MP2/AVDZ[a]	CCSD(T)/AVDZ[a]	MP2/AVTZ[a]	CCSD(T)/CBS[a,b]
CN2-A	−59.0	−49.9	−65.1	−58.5
CN2-B	−53.1	−40.3	−60.0	−50.2
CN2-C	−58.3	−48.5	−64.8	−57.8
Cl2-A	−36.7	−29.8	−42.7	−38.6
Cl2-B	−35.7	−25.7	−41.6	−34.3
Cl2-C	−35.1	−26.9	−42.1	−36.9
F2-A	−32.6	−29.8	−37.0	−36.3
F2-B	−30.3	−26.7	−34.6	−33.1
F2-C	−31.1	−27.8	−35.7	−34.6

[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 5 Pair energy decomposition (kJ/mol) of the clusters formed by aniline and two CH_3X molecules[a]

	ΔE_{AB}	ΔE_{AC}	ΔE_{BC}	Enopair
CN2-A	−16.8	−23.6	−15.7	−4.5
CN2-B	−30.0	−25.9	−0.3	0.7
CN2-C	−17.0	−17.6	−23.9	−1.0
Cl2-A	−17.4	−15.0	−3.8	−1.3
Cl2-B	−19.1	−17.9	−0.2	0.3
Cl2-C	−15.4	−18.4	−1.4	−0.6
F2-A	−15.5	−12.6	−3.9	−1.7
F2-B	−16.4	−15.8	−0.5	0.3
F2-C	−14.7	−14.0	−2.1	−0.9

[a] **A** is aniline, **B** is the CH_3X molecule, which establish a N–H···X contact. See Fig. 3

the contribution from three-body effects is almost negligible.

In the case of methyl chloride and methyl fluoride complexes, the behavior is similar, but in this case, the interaction between CH_3X molecules is much weaker, contributing less than −4 kJ/mol in any of the clusters, being the origin of the smaller energy difference with respect to **B** structures, where CH_3X molecules do not interact significantly. The reason of this behavior could be found in the different interaction energies for CH_3X dimers, which amount at the MP2/aug-cc-pVDZ level to −25.2, −9.1 and −8.6 kJ/mol for acetonitrile, methyl chloride and methyl fluoride, respectively. The reason could be the larger dipole moment of acetonitrile leading to stronger electrostatic interactions.

3.3 Frequencies

Table 6 shows the calculated frequency shifts induced by complexation for the N–H stretching normal modes of aniline. In the clusters formed with one CH_3X molecule, only **B** structures exhibit significant red shifts amounting to $-25\ cm^{-1}$ for acetonitrile and to about $-12\ cm^{-1}$ for methyl chloride or methyl fluoride. These shifts are a consequence of the interactions with the amino group of aniline, which are not present in **A** structures, which presents no significant shifts. In any case, these shifts are smaller than other observed in typical hydrogen bonds and even smaller than those observed in similar phenol clusters [11]. So, in aniline clusters, the interaction is established preferentially with the aromatic ring, affecting only marginally to the amino group.

In clusters formed with two CH_3X molecules, several larger shifts are observed, especially in structures **B**, where the amino group is blocked by the two CH_3X molecules. In any case, only for acetonitrile, a typical cooperative effect

Table 6 Calculated frequency shifts (cm^{-1}) and relative intensities for the N–H stretching normal modes with respect to isolated aniline

	NH asymmetric		NH symmetric	
	$\Delta\upsilon$	I/I_0	$\Delta\upsilon$	I/I_0
CN1-A	1.7	1.2	−3.2	1.4
CN1-B	−26.4	1.4	−24.2	2.3
Cl1-A	−0.9	1.1	−3.2	1.2
Cl1-B	−13.0	1.0	−7.3	1.2
F1-A	−0.4	1.8	−5.3	1.8
F1-B	−11.5	1.1	−7.2	1.3
CN2-A	−16.6	4.8	−43.3	13.1
CN2-B	−33.2	2.0	−37.6	2.8
CN2-C	−20.2	4.3	−34.4	9.5
Cl1-A	−13.2	2.3	−19.5	2.6
Cl1-B	−16.7	1.1	−13.6	1.3
Cl1-C	−9.7	3.0	−13.4	4.3
F2-A	−7.4	2.7	−13.2	3.3
F2-B	−18.3	2.1	−17.1	1.6
F2-C	−2.0	3.0	−5.5	3.0

Values for isolated aniline (intensity in parentheses): asymmetric stretching: 3,660.0 (15.8); symmetric stretching: 3,545.7 (13.0)

is observed for the NH symmetric stretching mode in structure **CN2-A**, with a red shift of $-43\ cm^{-1}$ and a significant increment in intensity. The rest of the structures considered exhibit significant shifts of similar magnitude in all cases, but with marginal increments in intensity.

4 Conclusions

Intermolecular interactions for clusters formed by aniline with acetonitrile, methyl chloride and methyl fluoride were computationally studied. Two different minima were located for clusters formed by aniline and one CH_3X molecule. 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. Our best estimations of the complexation energies of these complexes amount to −27.0 kJ/mol for the acetonitrile complex and to −18.1 and −17.5 kJ/mol for complexes formed with methyl chloride and methyl fluoride, respectively.

The SAPT(DFT) energy decomposition indicates that in most complexes, the dispersion contribution is dominant though accompanied by significant electrostatic interactions. Only for methyl fluoride, a cluster is found with a

dominant electrostatic contribution, though this is due to the different spatial arrangement of the molecules in this complex. The final order of stability is a consequence of a subtle balance of the different contributions, which favor one or another minimum.

Three different minima were found in clusters containing two CH_3X molecules, depending on whether both molecules are on the same side of the ring as the nitrogen lone pair, both on the opposite side or one on each side of the ring. Energetically, there is little difference for the molecules to be on one or another side of the ring, leading to structures with similar complexation energies, though the most stable one corresponds in all cases to the minimum with both molecules on the same side of the ring as the nitrogen lone pair. In these structures, molecules form a cyclic pattern by establishing N–H···X, C–H···X and C–H···π contacts.

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