

The aniline–argon van der Waals complex: ab initio second-order Møller–Plesset study of the potential energy surface in the ground electronic state

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Abstract

The potential energy surface of the aniline–argon (An–Ar) complex in the ground electronic state has been investigated by ab initio calculations using second-order Møller–Plesset (MP2) theory. The basis sets for the aromatic molecule and for the argon atom were cc-pvdz and aug-cc-pvtz, respectively. The structure in which the argon atom is opposite to the amino hydrogens (*anti* conformer) is found to be more stable than the structure in which the argon atom and the amino hydrogens are on the same side of the ring (*syn* conformer). The calculated binding energies for the two conformers are 407 and 393 cm^{−1}, respectively. The introduction of diffuse orbitals for the aniline molecule using an aug-cc-pvdz basis set does not affect the relative stability of the two conformers. The calculated intermolecular distance, structure and rotational constants of the An–Ar complex reproduce satisfactorily the experimental data. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Van der Waals complexes between aromatic ring and rare-gas atom represent very interesting models of π -interaction. Similar interactions occur in several biological phenomena such as in the tertiary structure of proteins, the vertical base–base interaction in DNA and the intercalation of drugs into DNA, as well as in chemical phenomena such as solvation, cluster growth and matrix shifts in vibrational and electronic spectra. A lot of work has been dedicated to the study of van der Waals molecules from both experimental [1] and theoretical [2–4]

points of view. Experimentally, the combination of laser spectroscopy with molecular jet expansions allows accurate studies of complexes in the gas phase. Spectroscopic techniques like resonance-enhanced multiphoton ionization (REMPI) [5–7], laser-induced fluorescence (LIF) [8–11] or microwave (MW) spectroscopy [12–15], among others [16,17], have been used.

The theoretical description of these systems is challenging. Recently, these systems have been studied by ab initio calculations. Due to the very small stabilization energy the choice of an adequate theoretical level is not trivial. In benzene–rare gas complexes [18–21] the intermolecular interaction potential is dominated by correlation effects while in the

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cases of benzene dimer (Bz_2) [22] and benzene– N_2 ($\text{Bz}-\text{N}_2$) [23] the equilibrium structures are stabilized by electrostatic quadrupole–quadrupole terms. The theoretical treatment of these weak interactions requires post-Hartree–Fock procedures such as configurational interaction or Møller–Plesset (MP) perturbation theory. Thus, one of the most interesting aspects at present is to compare theoretical with experimental results in order to verify the accuracy of the *ab initio* calculations for the properties of different complexes.

To this purpose benzene complexes have been extensively studied. Different positions of the rare-gas atom have been considered and their binding energies have been estimated in the ground state to determine the most stable structure. It was demonstrated that in benzene complexes [18–21] the rare-gas atom lies on the C_6 axis, and that in non-symmetric benzene derivatives [24] it remains close to the original position above the ring center. But, it is interesting to note that since these complexes contain a planar symmetric aromatic molecule, there are no differences between the two sides of the ring.

Aniline has been studied in both the ground and the first electronic states [25–28] and it is well known that the amino group has a pyramidal structure in the ground state. Experimentally, the inversion angle of the amino group is $\sim 43^\circ$ [27]. So, the two sides of the aniline ring are non-equivalent and different van der Waals complexes are possible. The complex with rare-gas on the side of the ring opposite to the amino hydrogens is labeled the *anti* conformer while the complex with rare-gas and the amino hydrogens on the same side of the ring is labeled the *syn* conformer.

The aniline–argon ($\text{An}-\text{Ar}$) complex has been studied experimentally in this [9] and in other laboratories [5–8,11–13], yielding information about the structure, rotational constants and intermolecular vibrational frequencies in both ground and first excited electronic states. Despite this work, there are still some doubts about the equilibrium position of the rare-gas atom with respect to both sides of the aniline ring.

Several authors [5–7,26] have constructed the potential energy surface of this complex using 6-12 Lennard-Jones potential reproducing satisfactorily some experimental data, such as the intermolecular

distance and the intermolecular vibrational frequencies. These authors predict the *syn* conformer as the most stable structure of the complex in the ground electronic state. Other authors [8], on the other hand, claim the opposite. These observed a small increment in the intermolecular distance for the deuterated- ND_2 complex with respect to the normal isotopomer. This indicates that the position of the argon atom is opposite to the amino hydrogens but, due to the vibrational averaging of the rare-gas atom, this result is not conclusive. Therefore, they have also investigated the inversion barrier of the complex and reproduced the experimental transitions of the inversion coordinate using a Baughman's model [29] in order to estimate the difference in the binding energies between the two conformers. They concluded that the *anti* conformer is more stable than the *syn* one in the ground electronic state, although the tunneling between the two conformers is not completely quenched. Storm et al. [12] have also reached the same conclusion from the analysis of the moments of inertia of this cluster and of the ^{15}N -isotopomer from the MW spectrum in the ground state.

Thus, the aim of this paper is to shed light on the equilibrium structure of the $\text{An}-\text{Ar}$ complex and to estimate the binding energy from *ab initio* MP2 calculations. We have studied both conformers of the complex. The theoretical results such as, equilibrium intermolecular distances, rotational constants and structures, are compared to the existing experimental data in the ground electronic state.

2. Computational details

The interaction energy of the $\text{An}-\text{Ar}$ complex was evaluated as the sum of the self-consistent field (SCF) interaction energy and the correlation interaction energy by second-order Møller–Plesset perturbation theory (MP2). It has been demonstrated that this method provides a reliable estimate of the van der Waals interaction [2,3]. The effect of higher correlation contributions (third and fourth) has been investigated for several small complexes [3]. It was found that the MP2 and MP4 interaction energies are almost identical: in the case of $\text{Bz}-\text{He}$, e.g., they differ by $< 1\%$ [18]. The interaction energy derived from direct MP2 calculations is subject to the basis

set superposition error (BSSE) and we correct it using the counterpoise method of Boys and Bernardi [30], as usually done in this type of work.

The basis set plays a very important role for obtaining accurate results, and much of the previous work has shown that high-quality basis sets are necessary for describing van der Waals complexes. Hobza et al. [3] and Klopper et al. [31] have made a complete MP2 study of the intermolecular distance and of the interaction energy of the Bz–Ar complex with different basis sets. With the cc-pvdz basis set of Dunning [32–34] for the benzene molecule and the aug-cc-pvtz for the argon atom the computed energy agrees with the experimental interaction energy, while the intermolecular distance is underestimated by only 5% [3,31]. Given the close similarity between the Bz–Ar and the An–Ar complexes, we have used the previous basis set as a starting point to study the potential energy surface of the An–Ar cluster. Further, we have also used an augmented aug-cc-pvdz basis set for the aniline molecule in order to understand the effect of the basis set size.

Finally, all the calculations have been carried out on a Silicon Graphics IRIX 2000, at the University of Málaga, using the Gaussian 94 program revision E.2 [35].

3. Results and discussion

The structure of the complex has been optimized by simultaneously adjusting all the geometrical parameters. Table 1 shows the experimental and calculated structure of aniline isolated or as a complex with argon atom and Fig. 1 shows the labeled atoms and the inversion angle (ϕ) of the amino group. This is defined as the angle between the ring and the NH₂ planes. We have also defined the γ parameter as the angle between the ring plane and the CN bond. The benzene ring, in the optimized aniline structure, is almost perfectly planar while the nitrogen atom lies out of the ring plane by an angle $\gamma = 3^\circ$. This calculated structure agrees with the experimental one obtained from the analysis of the MW spectrum [25]. Further, the experimental inversion angle (43°) is well reproduced by the ab initio calculation (47°). On the other hand, if we compare the aniline with the two An–Ar optimized structures, it can be noticed

Table 1

Experimental and calculated geometry of aniline in the ground state for the isolated molecule and for the two conformers of An–Ar complex

	Experimental ^a	Calculated		
	An	An ^c	An–Ar ^d	
			<i>syn</i>	<i>anti</i>
<i>Distances (Å):</i>				
N–H	1.001	1.019	1.019	1.019
C ₁ –N	1.402	1.411	1.410	1.410
C ₁ –C ₂	1.397	1.411	1.411	1.411
C ₂ –C ₃	1.394	1.403	1.402	1.403
C ₃ –C ₄	1.396	1.405	1.405	1.405
C ₂ –H ₂	1.082	1.096	1.096	1.096
C ₃ –H ₃	1.083	1.095	1.095	1.095
C ₄ –H ₄	1.080	1.094	1.094	1.094
<i>Angles (°):</i>				
HNH	113.1	108.5	108.5	108.5
C ₆ C ₁ C ₂	119.4	118.6	118.5	118.5
C ₃ C ₄ C ₅	118.9	119.1	119.1	119.1
C ₁ C ₂ C ₃	120.1	120.6	120.6	120.6
C ₂ C ₃ C ₄	120.7	120.5	120.5	120.5
H ₂ C ₂ C ₃	120.1	120.0	120.0	120.0
H ₃ C ₃ C ₂	119.4	119.3	119.3	119.3
ϕ	43 ^b	47	–47	45
γ	0.6	3	–2	5

^aRef. [25].

^bRef. [27].

^cMP2 cc-pvdz values.

^dMP2 cc-pvdz/aug-cc-pvtz values.

that the changes of the aniline geometry are almost negligible. Thus, the aniline structure was kept fixed in all calculations.

The MP2 energies obtained without BSSE correction indicate that the *anti* conformer is more stable than the *syn* one by only 15 cm^{–1}. Following the previous works [5,6,8,9] we have taken the principal inertia axes of each complex as the reference frame for describing the motion of the argon atom around the aniline molecule. The inset of Fig. 1 shows the principal inertia axes of the *anti* conformer and the corresponding cartesian reference frame. From the analysis of the optimized structures, we have observed that the two conformers differ in the positions of the center of mass (COM) along the *x*-axis. The amine substitution of Bz moves the COM ~ 0.5 Å toward the nitrogen atom. The same displacement is

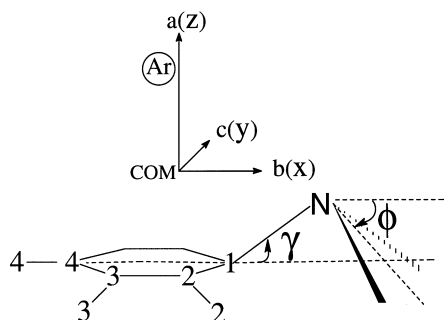


Fig. 1. Schematic representation of the *anti* An-Ar complex showing the atomic labels, the definition of the γ and ϕ angles, the principal axes of inertia and the cartesian reference frame. Distances and angles have been adjusted for a better representation. The XZ plane is the symmetric plane of the aniline molecule.

found for the *anti* conformer of the An-Ar complex, whereas the COM in the *syn* conformer is positioned at 0.4 Å. Thus, the position of the argon in the *anti* conformer is displaced by 0.1 Å toward the nitrogen with respect to the *syn* one. The y-positions of the COM are at zero for both conformers while the z-position of the COM in the *anti* conformer is slightly closer to the ring plane than in the case of the *syn* conformer, by only 0.005 Å. Thus, we take the COM of the *anti* conformer as the reference frame for representing the potential energy surface (PES) like a function of the argon position along the three axes in all the figures below, and the displacement between the two COMs has been taken into account.

In order to find the equilibrium structure of the complex we have calculated the MP2 BSSE corrected PES along the z-axis for both conformers. Fig. 2 shows the potential curves. The equilibrium distance for both cases was found at 2.685 Å from the COM of the respective complex. The plane of the ring for the *anti* conformer is displaced by -0.864 Å from the COM. Thus, the distance between the argon atom and the ring is 3.549 Å in the *anti* conformer. Due to the displacement of the COM of the two conformers, the intermolecular distance becomes slightly larger in the *syn* conformer, 3.554 Å. These results agree with the experimental value, 3.50 Å, obtained from the analysis of the LIF spectrum [8,9] and they are very similar to those found in analogous aromatic complexes [2,3,5–11].

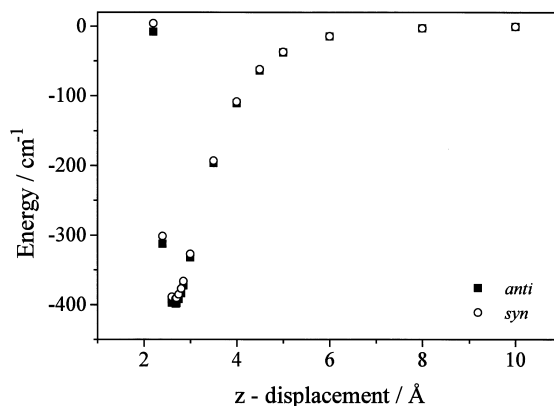


Fig. 2. Calculated PES as a function of the argon position along the z-axis for the two conformers of the An-Ar complex in the ground electronic state. The displacements are referred to the COM of the *anti* conformer.

Due to symmetry reasons, the y-equilibrium position of the argon atom is zero. Fig. 3 shows the PES as a function of the argon position along the y-axis for both conformers. Although there are no great differences between them, it can be seen that the *anti* conformer is slightly more stable than the *syn* one at shorter displacements.

Finally, the PES as a function of the argon position along the x-axis has been mapped. In this case, the function is asymmetric due to the interaction

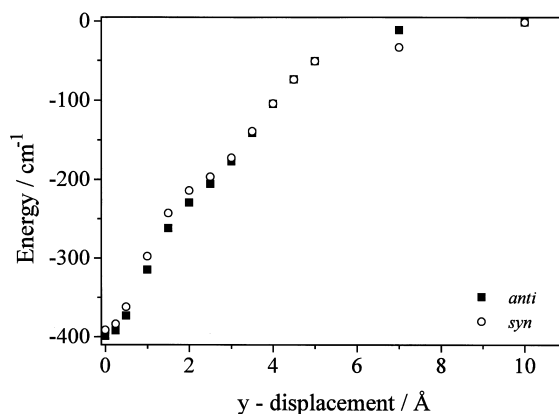


Fig. 3. Calculated PES as a function of the argon position along the y-axis for the two conformers of the An-Ar complex. The argon atom is positioned at the equilibrium distance $z = 2.69$ Å from the COM in both cases and at the optimized distances $x = 0.07$ Å for the *anti* conformer and $x = -0.19$ Å for the *syn* one.

between the argon atom and the amino group (Fig. 4). For x -displacements less than 1.5 Å the *anti* conformer is slightly more stable than the *syn* one while the opposite holds for displacements larger than 1.5 Å. A remarkable difference can be noticed between the *anti* and *syn* curves near $x = 2.5$ Å. In this position the *anti* conformer is less stable than the *syn* one by 40 cm⁻¹. This difference is due to the repulsion between the argon atom and the lone pair of the nitrogen atom. We have also studied the PES for both conformers as a function of position along the x -axis at increased and decreased z distance (compared to the equilibrium z distance) in order to obtain more information about the anisotropy introduced by the amino group. We move the position of the argon atom $z = \pm 0.4$ Å with respect to the intermolecular equilibrium distance. This displacement corresponds to 10% of the intermolecular distance and it is four times the vibrational average of the argon atom along this axis in the ground state [5,6,9]. Such displacements are large enough to point out the differences between the two PES along this axis. As expected, the asymmetry disappears for the increased z displacement while at decreased z distance (Fig. 5) the electrostatic repulsion between the nitrogen at $x = 2.5$ Å and the argon atom for the *anti* conformer becomes much more important than for the *syn* one.

The x -position of the argon atom which gives the lowest energy is localized in both cases between

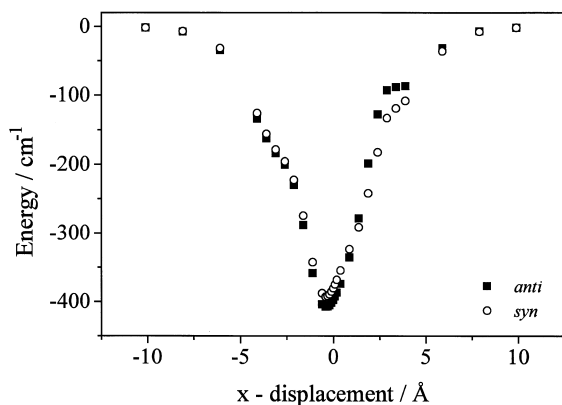


Fig. 4. Calculated PES as a function of the argon position along the x -axis for the two conformers of the An-Ar complex. The argon atom is positioned in both cases at the equilibrium distance $z = 2.69$ Å and at $y = 0.0$ Å from the COM.

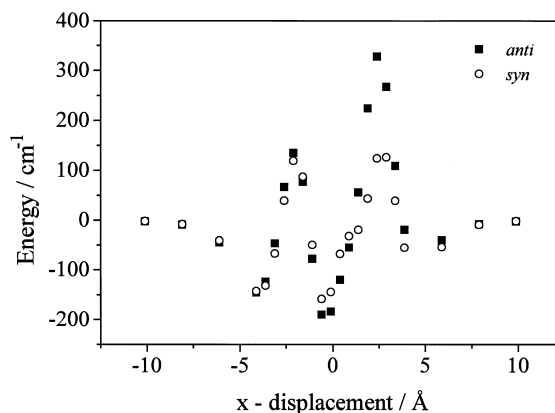


Fig. 5. Calculated PES as a function of the argon position along the x -axis for the two conformers of the An-Ar complex. The argon atom is positioned in both cases at $z = 2.29$ Å (0.4 Å below the equilibrium position) and at $y = 0.0$ Å from the COM.

$x = -0.3$ and $x = -0.2$ Å from the COM of the respective complex (see Fig. 4). Thus as the COM is shifted by $\sim +0.4$ Å from the center of the aniline ring, in both conformers the rare-gas atom is displaced away from the center of the aromatic ring toward the nitrogen. Similar behaviour is found in others complexes which incorporate a single nitrogen atom in the aromatic system, e.g., the complexes of pyridine [15] and pyrrole [36] with argon.

The BSSE corrected binding energies for the *anti* and *syn* conformers amount to 407 and 393 cm⁻¹, respectively. Thus, in view of this result the *anti* conformer is more stable than the *syn* one but the difference between the binding energies is only 14 cm⁻¹. This value is similar to that obtained without BSSE correction. Moreover, this result agrees with the experimental data obtained from both the analysis of the MW spectrum of the ¹⁵N-isotopomer [12] and the analysis of the LIF spectra of An-Ar and its deuterated derivatives [8]. In the latter work, the authors have used different approaches to distinguish the two sides of the complex. They determined the amino hydrogen positions with respect to the COM of the complex by comparing the rotational constants of An(ND₂)-Ar and An-Ar complexes using the Kraitchman's equations [37]. They concluded that the hydrogen atoms are displaced from the aromatic plane in direction opposite to the argon atom. On the other hand, they estimated the binding energy differ-

ence between the two conformers by a model [29] which reproduced the experimental transitions of the inversion coordinate corresponding to the amino group. They determined a difference in the binding energy of $\sim 20 \text{ cm}^{-1}$ in agreement with our ab initio value. Finally, in order to identify what is responsible for the localization of the argon atom in the *anti* conformer, they made a comparison of the vibrationally averaged structures between An–Ar and $\text{NH}_3\text{--Ar}$ [38,39] complexes. The authors concluded that the preference for the *anti* conformer is due to a combination between the attraction of the nitrogen lone pair and the repulsion of the NH bonds with the argon atom. The ab initio calculations indicate that the effect of the stabilization of the *anti* conformer is governed by the attraction between the argon atom and the nitrogen lone pair. In the *anti* conformer, e.g., the *x*-position of the COM is more displaced toward the nitrogen atom (0.1 \AA) than in the *syn* conformer. Furthermore, in the *anti* conformer the nitrogen is out of the ring plane by 5° while this angle becomes -2° in the *syn* conformer and the intermolecular distance in the *anti* conformer is slightly shorter (3.549 \AA) than in the *syn* one (3.554 \AA). We have calculated the energy for both conformers by constraining the nitrogen in the ring plane in order to find the contribution due to the repulsion between the argon atom and the amino hydrogens. The binding energy difference becomes 4 cm^{-1} and then, the repulsion between the argon atom and the amino hydrogens does not control the position of the argon in the complex. Thus, the ab initio calculations have enabled us to identify that the most stable structure for the An–Ar complex is imposed by the slight displacement of the nitrogen out of the ring plane, while from the analysis of the experimental data it is not possible to distinguish whether the nitrogen atom or the amino hydrogens control the conformation of the complex. In view of this result it should be taken into account the displacement of the nitrogen in any model which studies the inversion motion of the amino group. Parneix et al. [40], e.g., found the *syn* conformer as the most stable structure in the ground state without considering this circumstance.

The calculated rotational constants for both conformers at the equilibrium structure are compared with the experimental data obtained from the analy-

sis of the LIF spectrum [9] in Table 2. The agreement between the calculated and the experimental values is satisfactory for both conformers if the vibrational averaging [5,6,9] along the three axes is taken into account. Therefore the equilibrium structure of the complex cannot be deduced from the rotational constants. In fact, Consalvo et al. [13] have shown that there are different structures of the complex, two-*anti* and two-*syn* orientations, all compatible with the moments of inertia. This ambiguity is related to the large-amplitude vibrational motion (LAM) of the argon atom along the three axes. For instance, if we take a binding energy range of 10 cm^{-1} around the equilibrium position for both conformers, the displacement range of the argon atom is $\sim \pm 0.1 \text{ \AA}$ along the *z*-axis and $\pm 0.25 \text{ \AA}$ along the *y*-axis. Due to the asymmetric PES along the *x*-axes, the displacement range is 0.20 \AA toward the nitrogen and 0.3 \AA away from it. This indicates that the LAM along the *x*- and *y*-axes are bigger than along the *z*-axis, i.e., the motion of the argon atom in a plane parallel to the ring is easier than in the perpendicular direction. Moreover, the PES is slightly more attractive along the *x*-axis direction toward the nitrogen than along the *y*-axis. These results agree with experiments. Sinclair and Pratt [8] determined the coordinates of the argon atom from the changes in the rotational constants that occur between the aniline and the An–Ar complex. The measured values were comparable to the values of LAM and they determined that the PES is more attractive in the *x*-direction.

Finally, we have followed the same procedure with the augmented aug-cc-pvdz and aug-cc-pvtz

Table 2

Experimental rotational constants of An–Ar complex and the calculated values derived from the equilibrium structure of the two conformers

	Experimental ^{a,b}	Calculated ^c	
		<i>anti</i>	<i>syn</i>
<i>A</i> (cm^{-1})	0.060029(8)	0.058908	0.059371
<i>B</i> (cm^{-1})	0.038265(23)	0.037918	0.037326
<i>C</i> (cm^{-1})	0.031023(23)	0.030701	0.030433

^aNumbers in parentheses represent the standard deviation of the parameter in units of the last quoted decimal place.

^bRef. [9].

^cMP2 cc-pvdz/aug-cc-pvtz values.

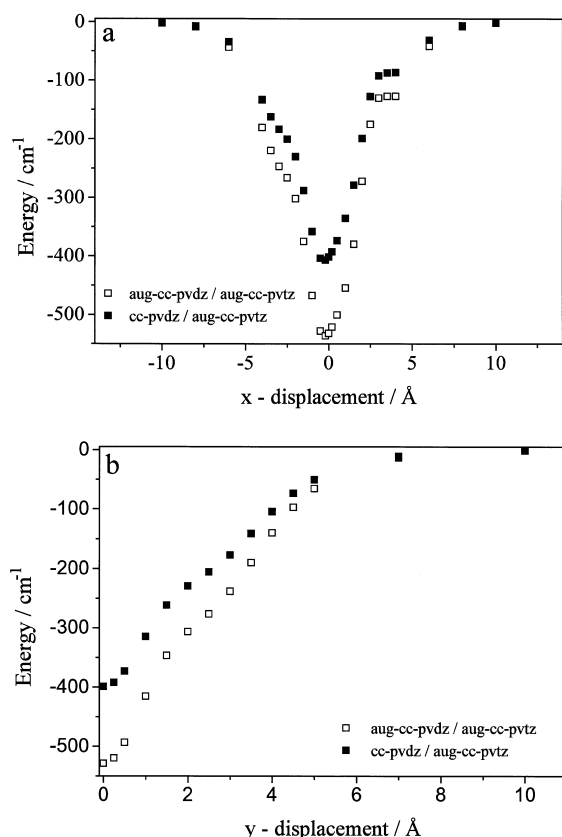


Fig. 6. Comparison between the PESs calculated with cc-pvdz/aug-cc-pvtz and aug-cc-pvdz/aug-cc-pvtz basis sets as a function of the argon position along the (a) x - and (b) y -axes for the *anti* conformer of the An–Ar complex.

basis set for the aniline molecule and argon atom, respectively, in order to investigate the dependence of the results on the basis set size. In this case the intermolecular distance for the *anti* and the *syn* conformer is 3.449 and 3.454 Å, respectively. The position of the argon atom along the x - and y -axes does not change with respect to the values obtained with the smaller basis set. The PES as a function of the argon position along the x - and y -axes for the *anti* conformer are represented in Fig. 6a and b, respectively. These do not show qualitative differences with the previous ones, since both basis set have similar profiles and they only differ by the depth of the minimum. However, the binding energy difference between the two conformers, is still 14 cm^{-1} . This result might be important for future

work, since it shows that the results obtained with the augmented basis set do not justify the increased computational cost. In fact, the energies calculated with the cc-pvdz/aug-cc-pvtz basis set differ from those obtained with the augmented basis set by a factor 1.3. In this case, the binding energy of the *anti* conformer is 537 cm^{-1} and we believe that this energy is overestimated as has been shown for the Bz–Ar complex [31].

Although the *ab initio* calculations probe only the stationary structure while the experiments probe the vibrating complex, both types of data indicate that the *anti* and *syn* conformers have similar binding energies and that the argon atom and the nitrogen of the amino group appear preferentially on the same side of the ring.

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