Pure Rotational Spectrum and Model Calculations of Anisole−Ammonia[†]

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Received: March 25, 2009; Revised Manuscript Received: April 29, 2009

The rotational spectra of two isotopologues of the anisole−ammonia molecular complex have been measured with the pulsed-jet Fourier transform microwave technique. The obtained rotational and quadrupole coupling constants provide an unequivocal conformational assignment. The NH_3 group lies out of the plane of the aromatic ring and it is bonded to anisole via three weak, $N-H\cdots O$, $C_{Me}-H\cdots N$, and $N-H\cdots\pi$ contacts.

Introduction

Gas-phase spectroscopic studies of molecular complexes provide a wealth of information about challenging problems involving the role of intra- and intermolecular interactions. Hydrogen bonding plays a major role in determining the structure and function of chemical systems of interest in molecular biology; in addition, interactions involving aromatic molecules are especially important in analyzing, e.g., DNA nucleotide bases.

Precise and detailed information on this kind of interaction have been obtained from the study of hydrogen-bonded molecular complexes. Many of the investigated complexes are constituted by one or more molecules of solvent (typically water) linked to organic or biomolecules. Water participates in several kinds of hydrogen bonds, acting either as a proton acceptor or as a proton donor. The most common hydrogen bonds in these systems are of the type $O-H_w\cdots O$, $O-H\cdots O_w$, $O-H_w\cdots N$, and $N-H\cdots O_w$,[1−4] where the subscript indicates an atom belonging to the water molecule. They are moderately strong, in the range 15−25 $kJ\cdot mol^{-1}$.

Less information is available on molecular complexes where ammonia is solvating organic molecules. In most of its complexes with organic molecules, ammonia acts exclusively as a proton acceptor, as indicated by the rotational spectra of $F_3CH\cdots NH_3$,[5] $CH_3OH\cdots NH_3$,[6] pyrrole$\cdots NH_3$,[7] and *tert*-butanol$\cdots NH_3$.[8]

However, in some interesting cases, ammonia has been found to have both hydrogen-bond donor/acceptor behavior, such as in 7-hydroxyquinoline−ammonia complexes, where ammonia acts as a protic wire,[9] or the case of the adducts of NH_3 with the conformers of glycidol where a strong $O-H\cdots N$ and a weaker $N-H\cdots O$ hydrogen bond link the two subunits.[10]

In the case of the benzene−ammonia complex, the ammonia molecule behaves as a proton donor interacting with the π-electron cloud of the benzene ring.[11]

Anisole possesses two sites that can act as proton acceptors, the oxygen lone pairs and the aromatic π system. In the case of the interaction with water, water shifts from the π system to the oxygen when going from benzene−water[12] to anisole−water.[13,14] It is interesting to check whether this happens also in the case of ammonia. For this reason, we decided to investigate the pulsed-jet Fourier transform microwave (FTMW) spectrum of ANI−NH_3.

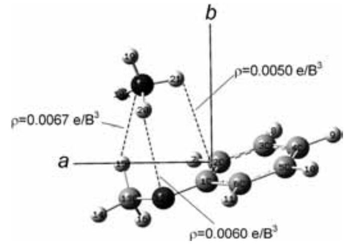

Figure 1. Shape of the most stable conformer of ANI−NH_3 with the atom numbering. The three weak interactions linking the monomers are indicated, with the corresponding (ab initio) minimum electronic densities; see below.

Rotationally resolved electronic spectra have already shown that, in the case of anisole−ammonia (ANI−NH_3), the NH_3 moiety is located out of the plane of the aromatic ring,[15] but the experimental data were not sufficient to establish the orientation of the ammonia group. However, theoretical calculations suggest the ammonia molecule to interact, via the nitrogen lone pair, with one of the hydrogen atoms of the anisole methyl group, whereas one of the ammonia hydrogen atoms is pointing toward the π-electron cloud of the phenyl ring.[15,16] The sketch of this configuration is reported in Figure 1, where an additional $N-H\cdots O$ contact, which will be supported by the present study, is shown.

Pure rotational spectroscopy provides inertia data that exactly locate the position of the atoms involved in the adduct, giving univocal structural assignment. In particular, in the case of ANI−NH_3, the values of the moments of inertia of normal and isotopically substituted species can be related to the intermolecular parameters describing the relative position of the two monomers, and the quadrupole coupling constants can be associated with the orientation of the ammonia molecule within the complex.

Experimental Details

A gaseous mixture of 0.5% anhydrous ammonia (99.99% pure, supplied by Sigma-Aldrich) diluted in helium was passed over a sample of anisole (≥99%, supplied by Fluka and used without further purification) at room temperature and expanded through a solenoid valve (General Valve series 9) into the Fabry−Perot resonator chamber. The backing pressure was kept at 4 bar to reach a concentration of about 0.1% of anisole in the gas mixture prior to the expansion.

The same experimental procedure was adopted in the case of the isotopic substituted species with ^{15}N (98% enriched, supplied by Sigma-Aldrich).

[†] Part of the "Vincenzo Aquilanti Festschrift".

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10.1021/jp9026964

The microwave spectra of ANI−NH$_3$ and ANI−^{15}NH$_3$ have been recorded in the frequency range 6−18 GHz using a COBRA version[17] of a Balle−Flygare-type[18] molecular beam Fourier transform microwave spectrometer already described elsewhere,[19] recently updated with the FTMW++ set of programs.[20]

The estimated accuracy of the measured frequency was about 2 kHz and the resolution of the hyperfine components was 7 kHz.

Theoretical Calculations. Already several sets of theoretical calculations are available on ANI−NH$_3$. They include molecular mechanics, B3LYP/6-311++G(d,p),[15] and MP2$_{CP}$/6-311+G(d,p)[16] approaches. However, in the case of some molecular adducts, such as triazine−H$_2$O[21] and glycidol−NH$_3$,[10] we found it useful to preliminarily explore the conformational space by using a model potential and to analyze the minima that were found thereafter by accurate ab initio calculations. We applied this procedure also to ANI−NH$_3$.

a. Model Potential Calculations. We used the model implemented in the GDMA[22] and ORIENT[23] programs, developed by Stone and co-workers.

The model is based on the idea that the dominant contribution to interaction energy comes from the electrostatic term modeled by using the distributed multipole analysis (DMA) of electron charge distribution,[24] and the resulting attractive electrostatic term is counterbalanced by an isotropic atom−atom six-exponential repulsion−dispersion term.

The repulsion and dispersion parameters used in the calculations are those determined by Mirsky.[25] The dispersion term includes one of the Tang−Toennies dumping functions to suppress the singularity as the interatomic distance tends to zero.[26] The electrostatic interactions involve distributed multipoles of bare anisole and ammonia molecules calculated up to hexadecapole, both at the nuclei and at the center of each bond, from the ab initio (MP2/6-311++G**) wave functions.

Within these preliminary calculations, the structures of ammonia and anisole were frozen and any structural relaxation upon complexation was neglected.

The conformational research allowed the localization of the 15 local minima shown in Figure 2 with the corresponding interaction energies D_e, in the range 9−16 kJ·mol^{-1}.

We observe that the binding energies of conformers II and III, both with NH$_3$ acting as a proton donor toward the ether oxygen, are very similar to each other. However, conformer III was never considered in the previous theoretical reports.

For the six most stable conformers ($D_e \approx 13-16$ kJ·mol^{-1}) we also calculated the dissociation energy values corrected for the harmonic zero-point energy contribution obtaining $D_0(\mathrm{I}) = 11.09 > D_0(\mathrm{V}) = 9.64 > D_0(\mathrm{III}) = 9.63 > D_0(\mathrm{II}) = 9.33 > D_0(\mathrm{VI}) = 8.69 > D_0(\mathrm{IV}) = 8.44$ kJ·mol^{-1}. The zero-point energy contributions change considerably the stabilization energy order of the various conformers.

b. Ab Initio Calculations. The data obtained with the model potential calculations were refined for the six more stable conformers of ANI−NH$_3$ with full geometry optimization on the MP2 counterpoise corrected PES (MP2$_{CP}$(full))/6-311++G** level of calculation.[27,28] Only four stationary points were found since species IV and VI appeared not to be minima and relaxed to species I and V, respectively. The results are summarized in Table 1.

They agree with the previous investigations,[15,16] in finding species I as the global minimum. However, we located a new conformation (III), which escaped the previous calculations, and which appears to be the second most stable species. Probably, this is a merit of the preliminary fast and global "scanning" with ORIENT.

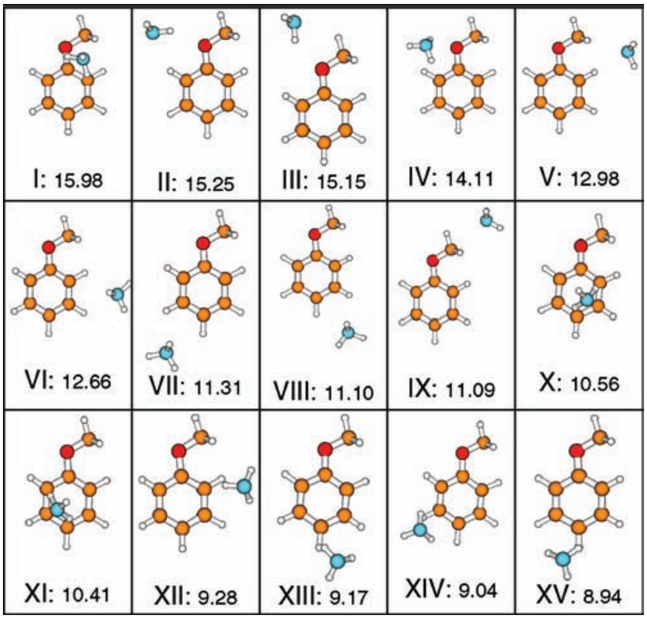
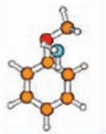
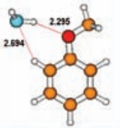
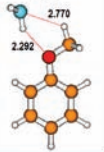
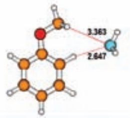


Figure 2. Predicted shapes and dissociation energies (kJ·mol^{-1}) of the 15 plausible conformers of ANI−NH$_3$—numbered from I to XV in order stability—obtained using the Stone model potential (see text for details).

TABLE 1: MP2$_{CP}$(full)/6-311++G Structures, Energies, and Spectroscopic Constants of the Four Most Stable Conformers of ANI−NH$_3$**

	I	II	III	V
				
$-E$ / E$_h$ [a]	402.434918	402.434219	402.434546	402.433444
ZPE/ E$_h$ [b]	0.168123	0.168387	0.168320	0.167585
$-E_0$ / E$_h$ [c]	402.266796	402.265832	402.266226	402.265859
D_e / kJ mol^{-1} [d]	12.80	10.96	11.92	8.93
D_0 / kJ mol^{-1} [e]	9.02	6.49	7.52	6.56
A/MHz	2138	2206	3304	2014
B/MHz	1090	1038	792	996
C/MHz	997	711	644	672
μ_a / D	0.12	0.70	0.49	-3.20
μ_b / D	0.56	2.52	-0.03	-1.57
μ_c / D	0.06	0.00	0.00	0.00
χ_{aa} / MHz	0.08	-0.43	1.18	-1.58
χ_{bb} / MHz	1.67	-1.79	-3.39	-0.49
χ_{cc} / MHz	-1.75	2.22	2.21	2.06

[a] Absolute energy. [b] Zero-point corrections. [c] Zero-point energies. [d] Dissociation energies. [e] Zero-point corrected dissociation energies.

We report a summary of all available theoretical calculations in a table in the Supporting Information.

Rotational Spectra. According to the values of the rotational constants of ref 15, the calculated dipole moment components, and the relative intensities of the predicted rotational transitions in the spectrometer frequency range, the first search has been targeted to the low J, μ_b R-type transitions. The set of transitions $(J+1)_{1,J+1} \leftarrow J_{0,J}$, with J in the range 3−5, it has been easily identified. Subsequently, more μ_b and the weaker μ_c R-type transitions were measured. No μ_a type transitions have been detected. This is in agreement with the MP2$_{CP}$(full)/6-311++G** calculated dipole moment components for species

TABLE 2: Spectroscopic Parameters (S Reduction, I^r Representation) for the ^{14}N and ^{15}N Isotopomers of ANI−NH$_3$

	ANI−^{14}NH$_3$	ANI−^{15}NH$_3$
A/MHz	2132.9433(8)[a]	2087.5873(7)
B/MHz	1091.7811(4)	1082.7776(4)
C/MHz	1000.7962(3)	983.5337(3)
D_J/kHz[b]	0.861(6)	0.903(5)
D_{JK}/kHz	2.32(4)	1.95(2)
D_K/kHz	1.62(5)	2.08(6)
d_1/kHz	−0.146(4)	−0.167(4)
d_2/kHz	0.036(4)	0.036(3)
χ_{aa}/MHz	−0.063(6)	
χ_{bb}/MHz	1.096(5)	
χ_{cc}/MHz	−1.033(5)	
σ/kHz	2	1
N[c]	46	26

[a] Error in parentheses in units of the last digit. [b] The MP2$_{CP}$(full)/6-311++G** values of D_J, $D_{J,K}$, and D_K are 0.90, 2.58, and 1.53 kHz, respectively. [c] Number of lines in the fit.

TABLE 3: r_s Coordinates of the N Atom Are Compared to the r_e (Ab Initio) and r_{FIT} Values

	$\lvert r_s \rvert$	r_e[b]	r_{FIT}[c]
a/Å	1.935(1)[a]	1.960	1.922
b/Å	2.286(1)	2.242	2.310
c/Å	0.28(1)	−0.502	−0.287

[a] Error in parentheses in units of the last digit. [b] MP2$_{CP}$(full)/6-311++G** values. [c] From the structure of Table 4.

TABLE 4: Structural Parameters of the Observed Conformer of ANI−^{14}NH$_3$ from the MP2$_{CP}$(full)/6-311++G Calculations, Except the Parameters Given in Bold**

bond lengths/Å		valence angles/deg		dihedral angles/deg	
C2C1	1.4014				
C3C2	1.4019	C3C2C1	119.4		
C4C3	1.3953	C4C3C2	121.0	C4C3C2C1	0.4
C5C4	1.4013	C5C4C3	119.2	C5C4C3C2	−0.4
C6C5	1.3932	C6C5C4	120.4	C6C5C4C3	0.1
H7C2	1.0832	H7C2C1	121.2	H7C2C1C6	179.4
H8C3	1.0864	H8C3C2	118.9	H8C3C2C1	−179.9
H9C4	1.0854	H9C4C5	120.4	H9C4C5C6	179.8
H10C5	1.0863	H10C5C6	119.4	H10C5C6C1	180.0
H11C6	1.0859	H11C6C5	121.4	H11C6C5C4	−179.7
O12C1	1.3632	O12C1C6	115.6	O12C1C6C5	179.2
C13O12	1.4234	C13O12C1	116.6	C13O12C1C6	176.2
H14C13	1.0892	H14C13O12	105.6	H14C13O12C1	−177.3
H15C13	1.0937	H15C13O12	110.9	H15C13O12H14	−118.6
H16C13	1.0954	H16C13O12	110.8	H16C13O12H14	118.4
N17O12	3.3299	N17O12C1	79.4	N17O12C1C2	**76.8**[a]
X18N17	1.	X18N17O12	**74.8**[a]	X18N17−O12C1	**−117.9**[a]
H19N17	1.0133	H19N17X18	111.7	H19N17X18O12	154.2
H20N17	1.0142	H20N17X18	111.7	H20N17X18H19	−120.4
H21N17	1.0139	H21N17X18	111.7	H21N17X18H19	120.3

[a] These three angles have been adjusted to reproduce the experimental values of the N r_s coordinates and the ^{14}N quadrupole coupling constants. Their ab initio values are N17O12C1C2 = 74.2, X18N17O12 = 79.4, and X18N17−O12C1 = −114.7, respectively.

TABLE 5: Values of the Rotational and Quadrupole Coupling Constants of ANI−NH$_3$, Calculated According to the Structure of Table 4

A/MHz	2110	χ_{aa}/MHz	−0.065
B/MHz	1090	χ_{bb}/MHz	1.092
C/MHz	1000	χ_{cc}/MHz	−1.027

I, which are $\mu_a = -0.02$; $\mu_b = 0.72$; $\mu_c = 0.05$ D, respectively, after the structural corrections mentioned ahead.

The measured transitions, exhibiting the hyperfine structure due to the interaction between the ^{14}N nuclear spin and the rotational angular momentum, were fitted with Pickett's SPFIT program.[29] The Hamiltonian $\mathbf{H} = \mathbf{H}_R^{(S)} + \mathbf{H}_Q$ was used, with Watson's semirigid rotor Hamiltonian[30] $\mathbf{H}_R^{(S)}$ set up in the symmetric (S) reduction and I^r representation. $\mathbf{H}_Q$ is the nuclear quadrupole coupling term. The Hamiltonian was constructed in the coupled basis set $\mathbf{F} = \mathbf{I} + \mathbf{J}$ and diagonalized. The determined spectroscopic constants are given in Table 1.

Subsequently, the rotational spectrum of ANI−^{15}NH$_3$ was assigned and measured. The fitting of the rotational lines was performed with the Hamiltonian described above, but omitting the $\mathbf{H}_Q$ term.

All measured transitions are collected in a table in the Supporting Information.

No line splitting ascribed to an internal rotation motion has been observed, probably because the NH$_3$ moiety undergoes an almost free internal rotation.

Structural Analysis. The structural parameters defining the position and orientation of NH$_3$ with respect to ANI can be obtained from the six rotational constants, from the set of quadrupole coupling constants, and from the r_s coordinates[31] of the nitrogen atom in the principal axis systems of ANI−^{14}NH$_3$. The r_s coordinates are reported in Table 3, and there compared to the ab initio values (r_e) and the values obtained with the refined structure discussed ahead (r_0).

The rotational constants in the ground state (A_{00}, etc.) are likely modified, with respect to the "rigid" values (A_r, etc.), according to equations of the type

$$A_{00} = A_r + W_{00}^{(2)} F \rho_a^2, \text{ etc.} \qquad (1)$$

where $W_{00}^{(n)}$ are the Herschbach's barrier-dependent perturbation sums relative to the A sublevels of the ground state[32] and $\rho_g = \lambda_g I_\alpha / I_g$ ($g = a, b, c$).

The r_s coordinates should be reliable data to determine the position of the N atom in the complex because, according to the nature of the analysis, the vibrational effects, similar in ANI−^{14}NH$_3$ and ANI−^{15}NH$_3$, should be largely removed. Quadrupole coupling constants, whose values depend on the direction cosines of the quadrupole tensor and the principal axes, appear as reliable data to determine the orientation of NH$_3$ in the complex. For this reason, we adjusted the corresponding structural parameters, to reproduce the N r_s coordinates and the χ_{gg} ($g = a, b, c$) values.

The final geometry we propose is given in Table 4, where all structural parameters are from the MP2$_{CP}$(full)/6-311++G** calculations, except the parameters given in bold figures.

From the structure of Table 4, we derived the lengths of the three weak H bonds that link ammonia to anisole, that is, N17···H15 = 2.860 Å, H20···O12 = 2.782 Å, and H21···π = 3.022 Å, respectively. There π represents the mid point of the C1−C2 bond. The shortest length of the N17···H15 (N−H···O) interaction would suggest it to be the strongest one. However, the calculated values of the electronic densities at the three "bonds", 0.0067, 0.0060, and 0.0050 au, respectively, hint at the N17···H15 linkage being the most important one.

Finally, in Table 5, we report the values of the rotational constants and the quadrupole coupling constants calculated using the structure of Table 4, whereas the calculated r_s coordinates are already reported in Table 3.

One can see that the discrepancies are very small for the r_s coordinates and χ_{gg} values, whereas the rotational constants are poorly reproduced, according to the corrections related to eq 1.

Conclusions

From the pure rotational spectra of ANI$-^{14}NH_3$ and ANI$-^{15}NH_3$ we could univocally determine the position and orientation of the NH_3 moiety in the complex, based on the N atom r_s coordinates and the values of ^{14}N quadrupole coupling constants. The rotational constants are not precisely reproduced by the proposed model, according to the effects on the inertia caused by the almost free internal rotation of the NH_3 group.

In addition, the theoretical calculations allowed for the discovery of another—considerably stable—conformer, not mentioned in the previous theoretical studies.

The obtained results outline, once again, that pulsed-jet FTMW spectroscopy is a unique tool in giving precise information on the structure of complex molecular adducts, such as ANI$-NH_3$. In this case, contrary to ANI$-H_2O$, the forces governing the molecular conformation are very weak, and the energy differences between the various molecular shapes are very subtle.

It might appear surprising that only one conformer has been observed, but it is not unusual for different conformers separated by low interconversion barriers to relax into the global minimum. It has been shown, indeed, that for barriers smaller than $2kT$ (ca. 420 cm^{-1} in our case), such a relaxation takes place in cases of a single degree of freedom for conformational relaxation.[33]

Acknowledgment. This research was funded by the University of Bologna.

Supporting Information Available: Completion of ref 27. Tables of transition frequencies and scheme with a summary of the dissociation energies of the most stable conformers as obtained with various theoretical models. This information is available free of charge via the Internet at http://pubs.acs.org.

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JP9026964