Free jet rotational spectrum and *ab initio* calculations of acetanilide

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Acetanilide has been investigated by free jet millimeter wave absorption spectroscopy. The rotational spectrum of the conformer with the methyl group *anti* to the phenyl group has been assigned. Several rotational transitions of the A sublevel of the ground torsional state have been measured for both normal and N–D isotopic species. All the atoms of the peptidic group and the carbon of the methyl group are coplanar to the ring. The V_3 barrier to the methyl group internal rotation has been obtained from the effective pseudo defect of inertia. The results of MP2 and B3LYP/6-31G* *ab initio* calculations are in agreement with the experimental data, but indicate two additional stable high energy conformers.

Introduction

The peptidic group, –CO–NH–, is very common in nature and generally adopts a planar configuration. Precise information on the planarity or lack of it and on the large amplitude motions related to this group can be obtained by using rotationally resolved spectroscopy, but only a few molecules containing the peptidic group have been studied with this technique because it requires the sample under investigation to be in the gas phase. The simplest molecule containing this group is formamide. Its planarity has been discussed for a long time: its rotational spectrum was first interpreted in terms of a planar structure,[1] but later on in terms of a non-planar structure.[2] Finally, by combining microwave (MW) and infrared data, Hirota *et al.* showed that the molecule is essentially planar.[3] Planar 'peptidic-like' structures of the –CO–NH– moiety were found also in methyl hydrazinocarboxylate[4] and *N*-methylformamide[5] through their MW spectra. The results obtained from the rotational spectrum and *ab initio* calculations of another simple derivative of formamide, *N*-methoxyformamide, were reported a few years ago:[6] in this case, the –CO–NH– group was found to be non-planar, the CO–NH dihedral angle being about 22°.

N-Phenylamides are also characterised by the –CO–NH– functional group. Their conformations have been generally indicated as *trans* and *cis* (but *anti* and *syn* would probably be more correct), depending on the position, with respect to the phenyl group, of the H or CH$_3$ attached to the CO group. The gas phase conformations and relative stabilities of *anti* and *syn* (or *synoid*) isomers of some of them have been determined recently from vibrationally resolved electronic spectra obtained by resonant two-photon ionization in a supersonic expansion.[7,8] Both the *anti* and *synoid* conformers of formanilide were identified (abundancies 93.5 and 6.5%, respectively). The abundance of the *anti* species decreased in *N*-methylformanilide (that is, when replacing the amidic hydrogen with a methyl group), while only the *anti* species was found in acetanilide (that is, when replacing the formyl hydrogen of formanilide with a methyl group). Acetanilide (AA, see Fig. 1) is exclusively *anti* in the solid phase as well, as shown by the reported X-ray[9] and neutron diffraction[10] crystal structures. The *anti* conformation is the only one with a planar arrangement of the heavy atoms and, thus, will be labelled *planar* (see Fig. 1) here, in contrast with plausible stable conformers with a non-planar arrangement, such as the *perpendicular* and *twisted* arrangements, also shown in Fig. 1.

AA plays an important role in microsomal electron transport: the attack of molecular O$_2$ under the action of the enzyme microsomal aromatic hydroxylase inserts a single oxygen atom in the *para* position, giving *p*-hydroxyacetanilide.[11]

Since rotational spectra give precise information on structural aspects, conformations, and sometimes on the potential energy surfaces of the large amplitude motions, we decided to investigate the millimeter wave free jet absorption spectrum of AA. According to the results found in the literature, only the spectrum of the *planar* form was expected to be observed in our experiments.

Experimental

A sample of AA was purchased from Aldrich and used without further purification. The ND isotopic species was prepared by direct proton/deuterium exchange *via* mixing of AA with heavy water in molecular excess.

The microwave spectra were recorded in the frequency range 60–78 GHz with a free jet millimeter wave absorption spectrometer described elsewhere.[12,13] To obtain a suitable concentration of the sample in the carrier gas, it was necessary to warm it up: the sample, seeded in argon at a stagnation pressure of *ca.* 300 kPa at 130 °C, was expanded adiabatically to about 50 mPa through a 0.35 mm diameter nozzle.

Rotational spectrum

Due to the high molecular weight and to the doubling of all transitions in A and E component lines arising from the almost free rotation of the methyl group (low barrier V_3), the
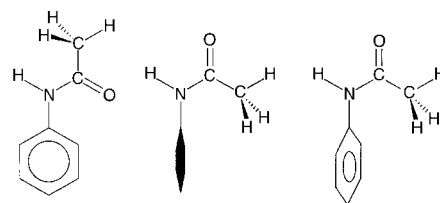

Fig. 1 The most stable conformers of AA. The conformer labelled as planar is the observed one.

Table 1 Experimental transition frequencies of AA (MHz)

Doubly overlapped R-type transitions[a]			Doubly overlapped Q-type transitions[a]			R-type resolved transitions		
$J'(K'_a)$–$J''(K''_a)$	NH	ND	$J'(K'_a)$–$J''(K''_a)$	NH	ND	$J'(K'_aK'_c)$–$J''(K''_aK''_c)$	NH	ND
9(9)–8(8)	64 918.27	63 578.75	11(11)–11(10)	64 240.93	62 646.07	18(7,12)–17(6,11)	65 538.00	64 450.54
10(9)–9(8)	66 352.93	65 007.93	12(11)–12(10)	64 238.56	—	18(7,11)–17(6,12)	65 538.47	64 451.09
10(10)–9(9)	72 471.00	70 974.20	12(12)–12(11)	70 358.79	68 611.99	19(7,13)–18(6,12)	66 953.85	65 859.93
11(9)–10(8)	67 787.24	66 436.91	13(11)–13(10)	64 235.80	62 640.65	19(7,12)–18(6,13)	66 954.86	65 861.07
11(10)–10(9)	73 905.68	72 403.30	13(12)–13(11)	70 356.46	68 609.88	20(7,14)–19(6,13)	68 365.15	67 264.51
12(8)–11(7)	63 102.23	61 898.20	14(11)–14(10)	64 232.09	62 636.94	20(7,13)–19(6,14)	68 367.02	67 266.66
12(9)–11(8)	69 221.56	67 865.81	14(12)–14(11)	70 353.77	68 606.85	21(6,16)–20(5,15)	63 486.62	62 516.66
12(10)–11(9)	75 340.07	73 832.35	15(11)–15(10)	64 227.68	62 632.19	21(6,15)–20(5,16)	63 564.32	62 608.21
13(8)–12(7)	64 535.33	63 325.78	15(12)–15(11)	70 350.47	68 603.39	21(7,15)–20(6,14)	69 771.36	68 663.45
13(9)–12(8)	70 655.37	69 294.16	16(11)–16(10)	70 346.36	62 626.77	21(7,14)–20(6,15)	69 774.78	68 667.56
14(8)–13(7)	65 967.54	64 752.50	16(12)–16(11)	70 346.36	68 599.13	22(6,17)–21(5,16)	64 831.27	63 847.70
14(9)–13(8)	72 088.93	70 722.15	17(11)–17(10)	64 215.97	62 619.96	22(6,16)–21(5,17)	64 956.61	63 995.20
15(8)–14(7)	67 398.70	66 178.15	17(12)–17(11)	70 341.50	68 594.09	22(7,16)–21(6,15)	71 171.21	—
15(9)–14(8)	73 521.75	72 149 51	18(11)–18(10)	64 208.38	62 611.93	22(7,15)–21(6,16)	71 177.24	—
16(7)–15(6)[b]	62 695.49	—	18(12)–18(11)	70 335.71	68 587.98	23(6,18)–22(5,17)	66 150.93	—
16(8)–15(7)	68 828.66	67 602.37	19(11)–19(10)	64 199.44	62 602.58	23(7,17)–22(6,16)	72 563.80	—
17(7)–16(6)[b]	64 118.48	63 037.24	19(12)–19(11)	70 328.91	68 580.83	23(7,16)–22(6,17)	72 574.24	—
17(8)–16(7)	70 257.11	69 025.05	20(11)–20(10)	64 189.04	—			
18(8)–17(7)	71 683.71	70 445.92	20(12)–20(11)	70 320.97	—			
			21(11)–21(10)	64 177.05	—			
			21(12)–21(11)	70 311.88	—			
			22(12)–22(11)	70 301.40	—			

[a] Because of the near prolate degeneracy, only K_a is indicated in the notation of the levels. [b] Broadened because of a small asymmetry splitting: not included in the fit.

rotational spectrum of AA contains many lines, even when jet cooled. Nevertheless, some μ_b–R-type lines, doubly overlapped due to the near prolate degeneracy, and with relatively low quantum numbers J, could be identified. Later, several single μ_b–R-type lines and two μ_b–Q-branches were measured. Only the A component lines were assigned, because the E components, which do not follow a semirigid rotor pattern, are very difficult to locate in the spectrum. In the same way, the spectrum of the N–D isotopic species has been assigned. The measured transitions are reported in Table 1. They have been fitted with Watson's quartic reduced Hamiltonian[14] (I^r repre-

Table 2 Spectroscopic constants for AA

	NH	ND
A/MHz	3776.614(4)[a]	3697.969(4)[a]
B/MHz	783.520(3)	781.655(4)
C/MHz	649.666(4)	646.051(6)
Δ_J/Hz	14(2)	17(2)
Δ_{JK}/Hz	55(4)	41(4)
Δ_K/Hz	490(21)	476(24)
N^b	58	45
J_{max}	22	19
σ/MHz	0.05	0.05
Δ_c/uÅ$^{2 c}$	−0.923	−0.955

[a] Errors in parentheses are expressed in units of the last digit. [b] Number of transitions in the fit. [c] Inertial defect.

sentation and A reduction), giving the effective rotational and centrifugal distortion constants shown in Table 2. No ^{14}N quadrupole coupling effects were observed.

Conformation and structure

The rotational constants of Table 2 match the model values obtained for the *planar* form, in agreement with the results of Manea *et al.*[7] In addition, the substitution coordinates[15] of the amino hydrogen (H_N), $|a| = 1.229(3)$, $|b| = 1.685(2)$ and $|c| = 0.14(3)$ Å, indicate the existence of a plane of symmetry, which includes the H_N atom. The value 0.14 Å is indeed compatible with the effect of low energy torsions on a planar structure. The H_N coordinates calculated with various *ab initio* geometries (see next section) of the *planar* form are in agreement with the experimental values. For example, the B3LYP/6-31G* method gives $|a| = 1.225$, $|b| = 1.686$ and $|c| = 0.0$ Å. The corresponding calculated rotational constants are 3692.5, 778.3 and 645.46 MHz, respectively, in relatively good agreement with the experimental values in Table 2. We should, however, note that the *ab initio* geometries correspond to equilibrium values, while the ground state rotational constants are related to an r_0 structure.

Finally the defect of inertial Δ_c, reported in Table 2, also suggests the heavy atoms to be all coplanar. Δ_c ($= I_c - I_a - I_b$) represents a measure of the non-planarity and is zero for a planar rigid molecule. In the case of AA, it should be, within the rigid approximation, −3.18 u Å^2, the value corresponding to two methylic hydrogens out of the plane; its

Table 3 Calculated energies and main structural parameters of the three conformers of AA with the B3LYP and MP2 methods (6-31G* basis set)

	B3LYP			MP2		
	planar	*perpendicular*	*twisted*	*planar*	*perpendicular*	*twisted*
E_{conf}/kJ mol$^{-1 a}$	0.0	17.6	12.8	0.0	9.7	8.1
C_2C_1–NC/°	0.0	90.0	−139.0	0.0	90.0	−123.7
C_1N–CO/°	0.0	180.0	178.0	0.0	180.0	175.1
HN–CO/°	180.0	0.0	6.9	180.0	0.0	7.7

[a] E_{conf} is the energy relative to the *planar* conformer.

lower value is imputable to a very low methyl group V_3 barrier, as explained in a following section.

Ab initio calculations indicating two additional stable high energy conformers

MP2/6-31G* *ab initio* calculations on AA indicate the *perpendicular* conformer in Fig. 1 to be a stable species.[7] The energy of this conformer relative to the *planar* species was found to be so low, however, that its electronic spectrum, in contrast with the experimental data,[7] should have been observed.

We ran density functional calculations (6-31G*), more suitable than the MP2 method in reproducing, for this kind of molecular system, the energy difference between conformers. We found that the conformational energy of the *perpendicular* conformer was indeed higher than the MP2 value, in agreement with the failure to observe its spectra. We also found that the conformer with a planar frame and with the methyl group *syn* to the ring is a stationary point, but as a transition state. When starting from a slightly distorted (no symmetry) *syn* geometry, the calculations converged to a third stable conformer with a distorted geometry, the *twisted* conformer in Fig. 1. The *twisted* species was found from both MP2 and B3LYP calculations. The energies and the dihedral angles which guide the conformational equilibrium are reported in Table 3. The energies of the less stable conformers are higher, in better agreement with the experimental observations,[7] with the DFT approach.

All the calculations were performed using the GAUSSIAN-94[16] program.

Methyl group internal rotation

The unusually low value of the Δ_c parameter found for the *planar* conformer is indicative of an exceptionally low V_3 barrier to methyl group internal rotation. In fact, rotational constants are effective quantities which include "pseudo" contributions due to the methyl group internal rotation, according to the equations

$$A_{00} = A_r + W_{00}^{(2)} F \rho_a^2$$
$$B_{00} = B_r + W_{00}^{(2)} F \rho_b^2$$
$$C_{00} = C_r \qquad (1)$$

derived in ref. 17, A_r, B_r and C_r are the rotational constants in the limit of the very high barrier. $W_{00}^{(n)}$ are the Hersbach's barrier-dependent perturbation sums relative to the A sublevels of the ground state[18] and $\rho_g = \lambda_g I_\alpha / I_g I_\alpha$ and I_g (g = a, b, c) are the moment of inertia of the top (methyl group) and the principal moments of inertia, respectively.

The value of the pseudo-inertia defect ($\Delta_c = I_c - I_a - I_b$) obtained from the effective rotational constants will always be smaller (absolute values) than its value in the case of an infinite barrier ($ca. -3.18$ u Å^2, corresponding to two out-of-plane methyl hydrogens). At low barriers, this effect becomes significant and allows a rather accurate determination of the barrier height by means of eqn. (1). It is worth noting that the V_3 values obtained in this way were always lower than those obtained from a fitting of the A–E splittings, probably due to the fact that, in eqn. (1), the contributions from out-of-plane vibrations other than the methyl torsion are ignored. In fact, if the V_3 values obtained for thioacetic acid,[19] methyl thiol formate[20] and acetic acid[21] are used, the values of the pseudo-inertia defect calculated by means of eqn. (1) are smaller than their pseudo-rigid rotor effective value by about 0.2 u Å^2.

On this basis, when eqn. (1) was used here to determine the V_3 barrier for both isotopic species of AA, 0.2 u Å^2 was added to each of the effective pseudo-inertia defects reported in Table 2. The resulting s and V_3 values are gathered in Table 4,

Table 4 Internal rotation parameters of AA

F/GHz^a	161.4
$\rho_a{}^a$	0.0207
$\rho_b{}^a$	0.0024
$\rho_c{}^a$	0.0
s	4.1(1)
Δ_0/cm^{-1}	3.1
V_3/kJ mol^{-1}	0.59(5)

^{a} Fixed to the value obtained from the structure.

along with the parameters related to the geometry which have been used in the calculations. Also, Δ_0, the estimated vibrational spacing between the ground state A and E sublevels, is reported in Table 4. The spacing is relatively large, *ca.* 3 cm^{-1}, as suggested in ref. 7.

This V_3 barrier is one of the lowest so far determined experimentally. For a few molecules, lower V_3 barriers have been determined: among them methyl isocyanate (CH_3NCO),[22] acetamide (CH_3CONH_2)[23] and *trans* methyl nitrite (CH_3ONO)[24] (350, 295 and 120 J mol^{-1}, respectively).

Conclusions

Ab initio calculations and the rotational spectrum of AA confirmed that the *planar* conformer with the CH_3 group *anti* to the ring is the most stable, in agreement with the reports of other experimental investigations.[7–10] The CO–NH group adopts a planar 'peptide-like' conformation, as in the case of formamide,[3] methyl hydrazinocarboxylate,[4] N-methylformamide[5] and formanilide.[7,8]

B3LYP rather than MP2 calculations seem to be suitable for the description of the potential energy surfaces, and therein the conformational equilibrium, of the C_2C_1–NC and C_1N–CO torsions.

A very low V_3 barrier has been obtained from the pseudo defect of inertia.

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