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# Conformations and Relative Stabilities of the *Cis* and *Trans* Isomers in a Series of Isolated *N*-Phenylamides

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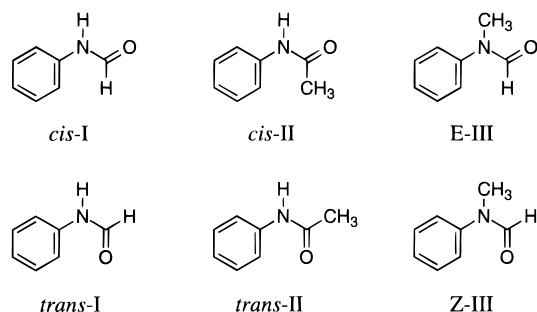
Received August 12, 1996<sup>⊗</sup>

**Abstract:** The gas-phase conformations of a series of isolated *N*-phenylamides have been determined from vibrationally resolved electronic spectra obtained by resonant two-photon ionization in a supersonic jet expansion. Both the *cis* and *trans* isomers of formanilide were identified, with the *cis* isomer in 6.5% abundance. The spectral features displayed by this isomer are consistent with a nonplanar geometry which undergoes a large change in the phenyl torsional angle following electronic excitation. The more abundant *trans* isomer of formanilide adopts a planar structure and is stabilized by 2.5 kcal/mol with respect to the *cis* isomer. In the excited electronic state the relative stabilities of the two isomers are reversed. Acetanilide, in contrast, is found exclusively as the *trans* isomer, also having a planar structure. *N*-Methyl substitution causes a reversal of the relative isomer stabilities found in formanilide and leads to an isomer distribution consisting of approximately 90% *E* and 10% *Z* in *N*-methylformanilide. These experimental observations are compared to previous condensed phase structural determinations as well as to the relative energies and structures predicted from *ab initio* Hartree–Fock geometry optimizations.

## Introduction

The investigation of isomer distributions in amides has received considerable attention due to their influence on the structures of peptides and proteins. The key structural aspect of amides is the stiff, nearly planar structure about the C–N bond due to its partial double bond character. Restricted rotation about this bond over a fairly high energy barrier, typically 15–20 kcal/mol,<sup>1</sup> leads to two geometrical isomers. Extensive NMR investigations by LaPlanche and Rogers<sup>2</sup> on a series of *N*-monosubstituted alkylamides in solution found the *trans* conformation, where *trans* refers to the relative orientation of the substituents on the amide nitrogen and carbonyl carbon, to be the preferred geometry. *N*-Alkylacetamides were found almost exclusively as the *trans* isomer whereas *N*-alkylformamides exhibited a small population of the *cis* isomer.

Replacement of the *N*-alkyl substituent of a secondary amide by a phenyl group increases the stability of the *cis* isomer.<sup>3</sup> Further stabilization of the isomer in which the carbonyl substituent and phenyl ring adopt a *cis* arrangement occurs with *N*-methylation of these compounds.<sup>1,4–6</sup> Three representative *N*-phenylamides, widely studied in solution by NMR spectroscopy, are the two secondary amides formanilide (**I**), and acetanilide (**II**), and the tertiary amide *N*-methylformanilide (**III**). These studies have clearly shown that formanilide exists as a mixture of approximately 50% *cis* and 50% *trans* isomers at room temperature and moderate concentrations in chloroform,<sup>1,3,7</sup> while *N*-methylformanilide is found in 95% abundance as the *E* isomer.<sup>5</sup> The effects of substitution at the carbonyl carbon have been investigated in acetanilide which is found



almost entirely as the *trans* isomer, in an estimated 99.9% abundance.<sup>4</sup> Steric interactions have generally been invoked to explain these observed isomer ratios,<sup>5</sup> although shortcomings with this reasoning have been noted in the case of some simple *N*-alkylamides.<sup>2</sup>

Several complexities are encountered in the interpretation of these NMR results due to solute–solvent interactions and self-association of the solute. Bourn *et al.*<sup>3</sup> have noted that the *cis/trans* isomer ratio in formanilide is concentration dependent and increases from 27% to 55% *cis* as the mol fraction of the solvated amide decreases from 0.525 to 0.015. This was taken as strong evidence for self-association of the solute through hydrogen bonding. The persistence of the self-association with dilution in the case of the *cis* isomer was attributed to a molecular geometry which is amenable to the formation of two hydrogen bonds between two amides in a cyclic arrangement.<sup>3</sup> Multiple hydrogen bonds can only be formed in the case of the *trans* isomer as linear chain structures.

The near-UV absorbing chromophore in these systems permits electronic spectroscopy to be used as an additional tool for structural determination. Two advantages of this approach are that information about both the ground and excited electronic states may be extracted and that the studies may be readily carried out in the gas phase under the essentially isolated conditions of a supersonic jet expansion. The extreme cooling of the vibrational and rotational degrees of freedom during the expansion is required to obtain vibronically resolved spectra from which structural conclusions can be drawn. Equally

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, February 1, 1997.

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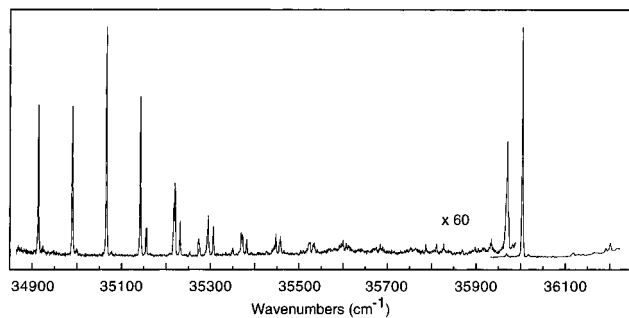
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**Figure 1.** Resonant two-photon ionization spectrum of formanilide seeded in a He expansion. The lower wavenumber region is shown multiplied by a factor of 60.

important, the absence of solvent and solute interactions under these conditions permits the intrinsic equilibrium geometries and relative energies to be determined which can be used in comparison with previous solution results to determine the contribution of the solvation process to the isomer stabilities and conformations. Thus the current study undertakes a reinvestigation of the isomer distributions and conformational preferences of the same three widely studied *N*-phenylamides, **I–III**, under the completely isolated conditions of a supersonic molecular beam.

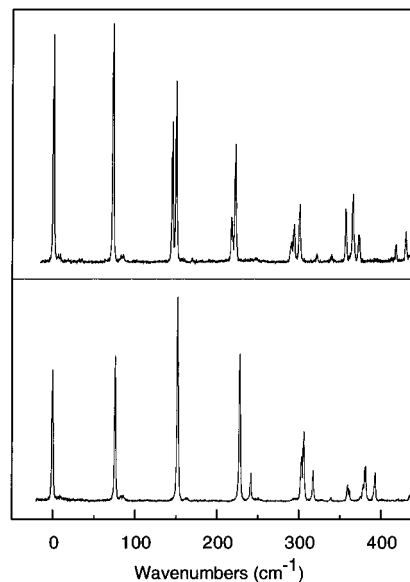
### Experimental Section

The supersonic molecular beam apparatus used in these experiments consists of two differentially pumped chambers. The first chamber is maintained at a background pressure of approximately  $1 \times 10^{-3}$  Torr by a 9-in. oil vapor booster pump, while a pressure of  $2 \times 10^{-7}$  Torr is attained in the second chamber by a liquid nitrogen trapped 6-in. oil diffusion pump. The samples, seeded in either He or Ar carrier gas, are heated to 85–100 °C and expanded in the first chamber from a 1-mm pulsed nozzle, then skimmed by a 1-mm skimmer. The resulting molecular beam enters the second chamber and is crossed at right angles with an unfocused laser beam from a tunable, frequency doubled, Nd:YAG pumped dye laser. Molecular ions are produced by sequential absorption of two photons in the ionization region of a linear time-of-flight mass spectrometer<sup>8</sup> and the mass selected ion signal is recorded as a function of excitation wavelength with a gated integrator.

Formanilide and acetanilide were purchased from Eastman Chemicals and used without further purification. Formanilide-*d*<sub>5</sub> was synthesized from aniline-*d*<sub>7</sub> by reaction with formic acetic anhydride. This mixed anhydride, an efficient formylating agent,<sup>9</sup> was prepared by heating formic acid with acetic anhydride to 60° over a 2-h period under a dry atmosphere. The aniline was then added and the reaction was allowed to proceed at 0° for 15 min, with stirring. Vacuum evaporation was used to remove all volatile compounds and gave a solid product in 95% yield. *N*-Methylformanilide was purchased from Aldrich and purified for traces of *N*-methylaniline by repeatedly washing with hexanes/ethyl acetate on a silica gel column. The purity of all compounds was checked by <sup>1</sup>H NMR and GC-MS.

### Results

The resonance enhanced two-photon ionization spectrum of formanilide is shown in Figure 1. The spectrum was recorded using He as the carrier gas at a stagnation pressure of 4.6 atm and the intensity of the ion signal was normalized for variations in the laser power. This normalization was accomplished by dividing the raw ion signal by the simultaneously monitored laser power raised to the 1.5th power. This particular power dependence was experimentally determined by monitoring the change in the intensity of several vibronic peaks over a range of laser intensities.



**Figure 2.** Resonant two-photon ionization spectrum of formanilide (lower panel) and formanilide-*d*<sub>5</sub> (upper panel) in the region of the *cis* isomer. The horizontal axis is labeled in wavenumbers relative to the electronic origins of each species which are 34913.6 and 35063.3 cm<sup>-1</sup> for the *d*<sub>0</sub> and *d*<sub>5</sub> isotopomers, respectively.

**Table 1.** Torsional Energies and Relative Intensities in the *S*<sub>1</sub> State of *cis*-Formanilide

<i>v</i> '	torsional spacing (cm <sup>-1</sup> )	torsional energy (cm <sup>-1</sup> )	relative intensity	calcd relative intensity <sup>a</sup>
0	0.0	0.0	0.46	0.35
1	76.1	76.1	0.61	0.76
2	76.2	152.3	1.00	0.88
3	75.7	228.0	0.70	0.72
4	78.2	306.2	0.46	0.47
5	75.1	381.3	0.23	0.26
6	77.4	458.7	0.15	0.12

<sup>a</sup> Calculated with the parameters  $\Delta\tau = 25^\circ$ ,  $\nu_e/\nu_g = 1.17$ .

A strong electronic origin transition is clearly identified at 36004.6 cm<sup>-1</sup>. There is little vibronic structure associated with this transition. When the lower wavenumber region of the spectrum is magnified by a factor of 60, an additional set of vibronic transitions is observed. These originate at 34913.6 cm<sup>-1</sup> and consist primarily of a fairly harmonic progression in a vibrational mode having a frequency of 76 cm<sup>-1</sup>. Scans further to the red reveal no additional features. The two spectral regions are attributed to the two possible geometric isomers of formanilide, labeled for now as isomers A and B, with isomer A having the 34913.6-cm<sup>-1</sup> origin and isomer B having the 36004.6-cm<sup>-1</sup> origin. Areas under the peaks in the two spectral regions were integrated in order to determine the relative populations of the two isomers and resulted in a ratio of 6.5% A to 94% B. The integration was performed over the entire Franck-Condon envelope of the A isomer region since the oscillator strength for this species is clearly distributed over a large number of vibronic transitions. When the spectrum was recorded using 2 atm of Ar as the carrier gas the same integrated intensities were obtained.

The lower panel of Figure 2 shows an expanded view of the normalized photoionization spectrum of formanilide in the region corresponding to the A isomer. The 76-cm<sup>-1</sup> vibrational progression is tentatively assigned to the torsional motion of the phenyl ring. Table 1 lists the torsional spacings, energies, and relative peak intensities of the first seven members of this progression. To confirm the assignment of this mode the spectrum of phenyl-deuterated formanilide was investigated. The upper panel of Figure 2 displays the same region of the

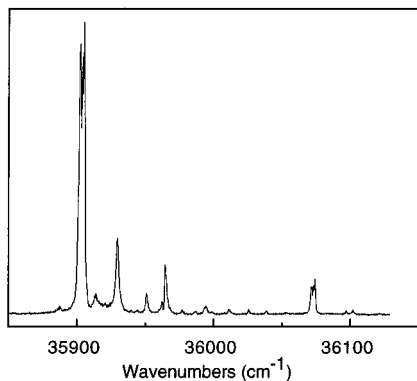
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**Table 2.** Torsional Energies and Relative Intensities in the  $S_1$  State of *cis*-Formanilide- $d_5$ 

$v'$	torsional spacing ( $\text{cm}^{-1}$ )	torsional energy ( $\text{cm}^{-1}$ )	relative intensity	calcd relative intensity <sup>a</sup>
0	0.0	0.0	0.96	0.96
1	72.5	72.5	1.00	1.01
2	72.5	145.0	0.59	0.57
3	72.1	217.1	0.19	0.23
4	72.9	290.0	0.09	

<sup>a</sup> Calculated with the parameters  $\Delta\tau = 16^\circ$ ,  $\nu_o/\nu_g = 1.08$ .

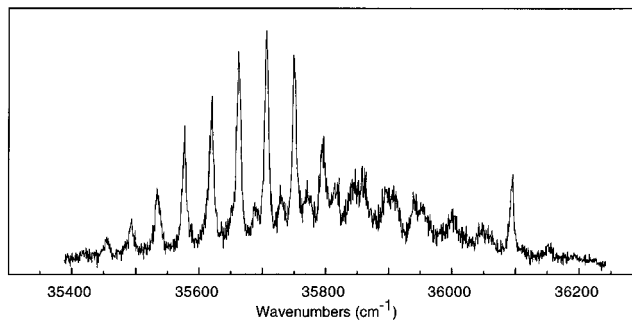
**Figure 3.** Resonant two-photon ionization spectrum of acetanilide seeded in a He expansion.

normalized spectrum of formanilide- $d_5$ . The frequency axis in Figure 2 is labeled relative to the electronic origins of each of the two compounds. In formanilide- $d_5$ , this transition is located at  $35063.3 \text{ cm}^{-1}$ , which corresponds to a blue-shift of  $150 \text{ cm}^{-1}$ , due to the changes in the zero-point vibrational energies of the ground and excited electronic states upon deuteration. A similar  $164\text{-cm}^{-1}$  blue-shift is also observed for the origin of the deuterated B isomer.

The upper spectrum in Figure 2 shows the expected drop in the vibrational frequency of the torsion fundamental, from  $76.1$  to  $72.5 \text{ cm}^{-1}$ , due to the increased effective mass upon phenyl deuteration. In addition a splitting of the torsional peaks is observed starting with the first torsional overtone which is not apparent in the spectrum of the undeuterated compound. The lower wavenumber member of the first split peak has a frequency spacing of  $72.5 \text{ cm}^{-1}$  from the torsion fundamental making clear its assignment as the torsional overtone. The second feature, at  $149.4 \text{ cm}^{-1}$  from the origin and  $76.9 \text{ cm}^{-1}$  from the torsion fundamental, is assigned to a second active vibration which undergoes a slightly different shift upon deuteration. First and second overtones of this second vibration are found at  $300.2$  and  $450.3 \text{ cm}^{-1}$ . Torsional progressions in combination with each of these account for the rest of the lines in the spectrum. Table 2 lists the torsional energies and spacings for this isotopomer as well as the observed line intensities.

The photoionization spectrum of acetanilide recorded using a He expansion at a stagnation pressure of  $1.7 \text{ atm}$  is displayed in Figure 3. A strong split origin transition at  $35902.4$  and  $35905.1 \text{ cm}^{-1}$  is followed by a set of vibrational features at  $27.1$ ,  $48.6$ ,  $62.1$ , and  $92.1 \text{ cm}^{-1}$ . The split origin and very low frequency vibrations are quite characteristic of transitions involving activity in a methyl torsional mode. Scans over a broad spectral region at high sensitivity show no additional features at lower wavenumbers and only peaks at higher wavenumbers which would appear to be weakly active vibrational transitions associated with the previously identified origin. Thus there is no evidence for a second populated ground state isomer in acetanilide.

The photoionization spectrum of the tertiary amide *N*-methylformanilide was also investigated and is shown in Figure

**Figure 4.** Resonant two-photon ionization spectrum of *N*-methylformanilide seeded in a He expansion.

4. The vibronic features are considerably broader in this spectrum than in the other amides, and a substantial underlying background is present. As in formanilide, the low-wavenumber region of the spectrum shows a progression in a low-frequency mode, although here much more extended and having a smaller frequency of  $42 \text{ cm}^{-1}$ , which peaks at  $35454.6 \text{ cm}^{-1}$ . This progression appears to originate at the actual electronic origin is made difficult by the underlying background on which these relatively broad and weak peaks sit. At  $36095.6 \text{ cm}^{-1}$  a moderately intense isolated feature is found which is not associated with a vibrational progression and is therefore assigned to the origin of a second isomer. Integration of the peak areas in the two spectral regions gives a population ratio of approximately 90% isomer A (lower wavenumber region) and 10% isomer B (single peak at  $36095.6 \text{ cm}^{-1}$ ), although these numbers can only be considered a rough estimate due to the large linewidths and underlying background in the spectrum.

## Discussion

The spectral assignments in this series of amides have been made in conjunction with Hartree–Fock *ab initio* geometry optimizations.<sup>10</sup> These calculations were performed with both 3-21G and 6-31G\* basis sets on both geometrical isomers of all compounds. The relative energies and detailed geometries of the two isomers, particularly the dihedral angle between the phenyl ring and the amide plane, were used in making assignments. A summary of these theoretical results is given in the last four columns of Table 3.

**A. Formanilide.** The existence of two ground state geometrical isomers in formanilide is clearly revealed by the electronic spectrum shown in Figure 1. Isomer A absorbs at lower wavenumbers and has a much smaller ground state population than isomer B, as indicated by the relative integrated intensities. It is therefore the less stable of the two isomers. The electronic transition that occurs in isomer A is nonvertical in at least one low-frequency normal coordinate while the same electronic transition in isomer B involves very little change in geometry. Both of these observations, when compared to the calculated energies and structures, provide compelling evidence for the assignment of isomer A to the *cis* isomer and isomer B to the *trans* isomer. Hartree–Fock calculations with either the 3-21G or 6-31G\* basis sets predict a more stable *trans* isomer for formanilide having a planar structure, as opposed to a nonplanar *cis* isomer in which the phenyl ring is twisted considerably out of the plane of the amide group. The nonplanarity of the *cis* isomer in its ground electronic state makes it likely to show vibronic activity along the phenyl torsional mode in its electronic spectrum, since the electronic forces favoring maximum conjugation will almost certainly differ in the two electronic states. Since the *trans* isomer is

**Table 3.** Summary of Experimental Data and *ab Initio* Calculations

amide	isomer origins (cm <sup>-1</sup> )	isomer ratios (%)	calcd phenyl torsional angle (deg)		calcd $E_{cis} - E_{trans}$ or $E_E - E_Z$ (kcal/mol)		
			3-21G	6-31G*	3-21G	6-31G*	
formanilide	34913.6 ( <i>cis</i> )	6.5 <sup>a</sup>	33	42	}	2.4	0.3
	36004.6 ( <i>trans</i> )	94 <sup>a</sup>	0	0			
acetanilide	( <i>cis</i> )	0 <sup>b</sup>	90	90	}	4.5	2.1
	35902.4 ( <i>trans</i> )	100 <sup>b</sup>	0	0			
<i>N</i> -methyl- formanilide	35454.6 ( <i>E</i> )	~90 <sup>a</sup>	45	54	}	-1.1	-2.8
	36095.6 ( <i>Z</i> )	~10 <sup>a</sup>	0	51			

<sup>a</sup> At 373 K. <sup>b</sup> At 358 K.

already calculated to be planar in its ground electronic state, any increase in the electronic forces will not produce a change in the torsional angle. While the calculated values for the relative energies and torsional angles vary with the basis set used, the trends are clear and support this assignment.

**(1) Relative Populations and Energy Differences of the *Cis* and *Trans* Isomers.** The *cis/trans* isomer ratio of 6.5/94 was obtained experimentally by integrating the peak areas of the *cis* and *trans* regions in the photoionization spectrum, Figure 1. An assumption in this procedure is that the signal intensities are directly related by the same proportionality constant to the concentrations of the two species in the expansion. This is only true if the oscillator strengths for the two electronic transitions are the same even though one isomer appears to have substantially better conjugation between the phenyl and amide moieties. To investigate the validity of this assumption, semiempirical CI calculations,<sup>10</sup> using the AM1 Hamiltonian, were performed on both isomers of formanilide. The oscillator strengths for the  $S_1 \leftarrow S_0$  transitions in the two isomers were predicted to differ by less than 1%. The origin of this result is clear on examining the nature of the molecular orbitals actually involved in the electronic transition. Two singly excited configurations were found to make the dominant contribution to the  $S_1$  state: HOMO-1→LUMO and HOMO→LUMO+1. While both the HOMO and LUMO  $\pi$  orbitals extend over the phenyl and amide groups, the HOMO-1 and LUMO+1 are essentially benzene localized  $\pi$  orbitals. Thus the oscillator strength is derived only from that portion of each molecular orbital which is found on the benzene ring.

The relative populations of the *cis* and *trans* isomers can be used to determine the energy difference  $E_{cis} - E_{trans}$  from the Boltzmann distribution law. The degeneracy factor for the *cis* isomer was taken as twice that of the *trans* isomer due to its nonplanarity and therefore two equivalent energy minima along the potential surface for rotation about the phenyl–nitrogen bond. A temperature corresponding to the nozzle and reservoir temperature, 373 K, was also used. These values result in an energy difference,  $E_{cis} - E_{trans}$ , of 2.5 kcal/mol. Energy differences of 2.4 and 0.3 kcal/mol were calculated with the 3-21G and 6-31G\* basis sets, respectively.

The use of the nozzle temperature in a Boltzmann distribution for molecules in a supersonic expansion, where rotational temperatures are on the order of 5 K, requires some justification since it implies that the equilibrium distribution of isomers does not change on cooling. When the dependence of the relative abundances of the two isomers in the expansion on the nature of the carrier gas was investigated by repeating the experiment using argon, the percentage of the *cis* isomer was unchanged, indicating that no additional relaxation of the higher energy isomer had occurred. This result is readily understood in light of the work by Ruoff *et al.*<sup>11</sup> on the relaxation of conformational isomers in seeded supersonic expansions. The authors observed

substantial conformer relaxation in the presence of Ar when the barrier to conformer interconversion was less than 1 kcal/mol and no conformer relaxation when the barrier exceeded 1 kcal/mol. Since the barriers for hindered rotation about an amide bond are on the order of 15–20 kcal/mol,<sup>1</sup> no relaxation would be expected.

The strongest supporting argument for the lack of relaxation is provided by dynamic NMR studies in solution. At a coalescence temperature of 349 K, an estimate for the rate constant for isomer interconversion of 55 s<sup>-1</sup> was determined,<sup>12</sup> corresponding to a 0.018 s lifetime for the *cis* and *trans* species. More recent measurements, based on lineshape analysis,<sup>7</sup> have yielded values for both the spin–lattice and spin–spin relaxation times in formanilide on the order of 2–4 s at a lower temperature of 295 K. Extrapolation of these values to the nozzle temperature of 373 K produces a lifetime estimate on the order of several milliseconds. Molecules seeded in the heated He supersonic expansion have a flow velocity approaching  $2 \times 10^5$  cm/s and in the current experimental setup are optically probed approximately 10 cm or 50  $\mu$ s after leaving the reservoir. This implies that there is insufficient time for any appreciable relaxation of the conformational distribution to occur.

Rationalizing which of the two isomers of formanilide should be energetically favored is not trivial since both structures would appear to have comparable steric crowding between either the carbonyl oxygen or the formyl hydrogen and the *ortho* phenyl hydrogen, based on the similarity of the oxygen and hydrogen van der Waals radii.<sup>13</sup> However, the *ab initio* geometry optimizations lend some insight into this question. The optimized geometries of both the *trans* and *cis* isomers, as calculated with a 6-31G\* basis, are shown as structures **IV** and **V** in Figure 5. From these it appears that key factors in the stability of the *trans* isomer are the bond angles about the carbonyl carbon. In both isomers the N–C<sub>carbonyl</sub>–O bond angle is considerably larger than 120° and the N–C<sub>carbonyl</sub>–H bond angle is considerably less than 120°. This tends to increase the distance between the *ortho* phenyl hydrogen and the oxygen in the *trans* isomer and decrease the distance between the *ortho* phenyl hydrogen and the formyl hydrogen in the *cis* isomer. Similar values have been found for the carbonyl bond angles in both formamide<sup>14</sup> and *N*-methylformamide<sup>15</sup> based on microwave spectroscopic data.

A geometry optimization carried out on the *cis* isomer constrained to be planar yielded structure **VI** in Figure 5. This produces a 2.099-Å separation between the formyl and *ortho* phenyl hydrogens and a calculated energy 0.75 kcal/mol greater than for the nonplanar structure **V**. When the planar constraint is removed, the phenyl ring is calculated to adopt a 42° torsional

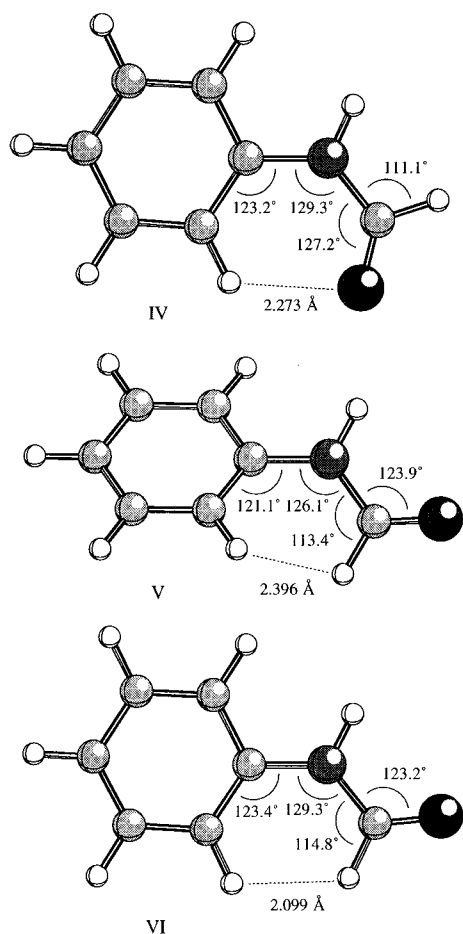
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**Figure 5.** Calculated structures for *trans*-formanilide (**IV**), *cis*-formanilide (**V**), and *cis*-formanilide constrained to a planar geometry (**VI**). The optimized geometry of *cis*-formanilide displays a 42° angle between the phenyl ring and the amide plane.

angle with respect to the amide plane which results in a 2.396-Å separation between the two crowded hydrogens. This change in torsional angle is also accompanied by decreases in the  $C_{\text{phenyl}}-C_{\text{phenyl}}-N$ ,  $C_{\text{phenyl}}-N-C_{\text{carbonyl}}$ , and  $N-C_{\text{carbonyl}}-H$  bond angles of 2.3, 3.2, and 1.4°, respectively, as illustrated in Figure 5. These bond angle changes alone would cause a decrease in the hydrogen atom separation, indicating their strained nature in the planar structure. The optimized geometry of the *trans* isomer, structure **IV**, displays a 2.273-Å separation between the carbonyl oxygen and the *ortho* phenyl hydrogen. This is achieved with  $C_{\text{phenyl}}-C_{\text{phenyl}}-N$  and  $C_{\text{phenyl}}-N-C_{\text{carbonyl}}$  bond angles of 123.2 and 129.3°, respectively, that are nearly identical to those in the planar constrained *cis* structure along with a substantial increase in the  $N-C_{\text{carbonyl}}-O$  bond angle, in comparison to the *cis* structures, to 127.2°. These distortions all act together to increase the separation between the carbonyl oxygen and the *ortho* phenyl hydrogen.

These observations suggest that while steric crowding in the *cis* isomer is relieved by phenyl torsion, the mechanism for steric relief in the *trans* isomer involves bond angle distortion. Even so, the *trans* isomer is still calculated to have a fairly short 2.273-Å oxygen-hydrogen separation which is less than the sum of the hydrogen and oxygen van der Waals radii.<sup>13</sup> Such a close contact is often taken as indicative of hydrogen bond formation although in this case it would involve a weak  $C-H\cdots O$  interaction. These types of interactions have been shown statistically significant by Taylor and Kennard<sup>16</sup> in a large sample of crystal structures which had previously been determined using neutron diffraction. The origin for the  $C-H\cdots O$  interaction was attributed primarily to van der Waals and

electrostatic forces. Since typical van der Waals interactions were estimated to be repulsive at the short contacts observed, the primary stabilization was assigned to the electrostatic interaction.<sup>16</sup> Judging from the distorted bond angles calculated for the *trans* isomer of formanilide, the net interaction between the hydrogen and oxygen atoms is not attractive at the calculated separation. Nevertheless a weak electrostatic interaction may counteract some of the van der Waals repulsion energy and help stabilize the planar structure.

**(2) Relative Energies of the *Cis* and *Trans* Isomers in the Excited State.** With the relative energy difference between the *cis* and *trans* isomers determined to be 2.5 kcal/mol in the ground electronic state, the assignment of the two isomer origins in Figure 1 can be used to relate the isomer energies in the excited electronic state. The 1091-cm<sup>-1</sup> red-shift observed for the *cis* isomer origin corresponds to a 3.1 kcal/mol relative stabilization of this isomer upon electronic excitation. Thus in the electronically excited state of formanilide the relative stabilities of the two isomers are reversed and the *cis* isomer is 0.6 kcal/mol more stable. Part of this stabilization arises from a structural change in the *cis* isomer, as seen from the nonvertical nature of the electronic transition. If the value for the ground state energy differences is taken from the 6-31G\* calculations, 0.3 kcal/mol, an even larger value, 2.8 kcal/mol, is found for the relative stabilization of the *cis* isomer in the excited state.

**(3) Relative Orientation of the Phenyl and Amide Groups.** The extended progression observed in the ionization spectrum of the *cis* isomer of formanilide appears to arise from the phenyl torsional mode. Since the spacings between adjacent members of the progression are nearly equal the excited state torsional potential is essentially quadratic over the region sampled by the lowest observed levels. The intensity distribution in this progression is sensitive to the nature of the ground state potential as well, particularly the location of the ground state minimum relative to the excited state minimum. These intensities were analyzed using the approximation that both the ground and excited state torsions could be treated as displaced harmonic oscillators. The overlap integrals between the ground state vibrationless level and various excited state levels were evaluated in terms of two parameters:  $\nu_e/\nu_g$ , the ratio of the frequencies of the excited and ground state oscillators, and  $\Delta\tau$ , the angular displacement between the two potential minima.<sup>17</sup> These parameters were then optimized in a nonlinear least-squares procedure to best fit the observed relative intensities.

Analysis of the torsional intensities in the undeuterated compound, Table 1, yields values of 1.17 for  $\nu_e/\nu_g$  and 25° for  $\Delta\tau$ . To determine  $\Delta\tau$  the value of the rotational constant, or effective mass, for hindered rotation in the ground electronic state was needed and was estimated at 1.33 cm<sup>-1</sup>, based on the ground state geometry given by the *ab initio* 6-31G\* calculation.<sup>18</sup> Columns four and five of Table 1 display both the results of this analysis and the experimental intensities in the torsional progression. Substantial discrepancy is clearly seen between experimental and best fit values for the earlier members of this progression.

The origin for the discrepancy is revealed by the spectrum of the phenyl deuterated isotopomer formanilide-*d*<sub>5</sub>. Deuteration of the phenyl ring reduces the rotational constant for hindered rotation to 1.25 cm<sup>-1</sup>. Other vibrations which involve substantial amounts of motion of the phenyl hydrogens will also be shifted in frequency. The spectrum of formanilide-*d*<sub>5</sub>, upper panel of Figure 2, clearly shows a second vibration at 149.4 cm<sup>-1</sup> lying slightly higher in frequency than the torsional

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overtone at  $145.0\text{ cm}^{-1}$ . In the undeuterated species these two peaks, at  $152.3\text{ cm}^{-1}$ , and all subsequent members of the torsional progression, are overlapped, leading to distorted intensities. A possible assignment for this second active vibration is to a mode involving bending primarily about the amide nitrogen which appears in the *ab initio* Hartree–Fock calculations with a 6-31G\* basis to have a harmonic frequency of  $156.4\text{ cm}^{-1}$ . Deuteration of the phenyl ring results in a substantially smaller relative frequency shift for this mode than for torsion.

When the Franck–Condon analysis was repeated for the deuterated species, considerably better fit to experiment was obtained as is evident from the values in the last two columns of Table 2. Here a  $\nu_s/\nu_g$  ratio of 1.08 was determined along with a value of  $16^\circ$  for  $\Delta\tau$ . Since the sign of  $\Delta\tau$  is not required for the Franck–Condon analysis, two possible changes in torsional angle are consistent with the fit. In looking at the molecular orbitals involved in the electronic transition it appears that the bond between the amide nitrogen and the phenyl carbon takes on more double bond character in the first excited state, as does the phenyl carbon to vinyl carbon bond in many phenyl polyenes, such as styrene.<sup>19</sup> This implies a smaller equilibrium torsional angle on excitation, which in combination with the  $42^\circ$  angle calculated for the ground state at the 6-31G\* level yields a value of  $26^\circ$  for the excited state. Activity in the second vibrational mode would be consistent with an increase in the  $C_{\text{phenyl}}\text{--N--}C_{\text{carbonyl}}$  bond angle which would help accommodate a smaller phenyl torsional angle.

**(4) Comparison to Solution.** The abundance of the *cis* isomer in isolated formanilide is significantly different from that found in solution studies. The nearly equal isomer abundances found at typical concentrations used for NMR studies<sup>1,3,4</sup> appear to arise from substantial solute–solute hydrogen bonding interactions. At lower concentrations, where self-association is still considerable, these interactions preferentially stabilize the *cis* isomer due to a molecular geometry which is amenable to the formation of two hydrogen bonds between two amide molecules in a dimeric ring structure.

Clear experimental evidence for self-association through hydrogen bonding in formanilide has been observed by Suzuki *et al.* using IR spectroscopy over a range of much lower solute concentrations than in the NMR studies.<sup>20</sup> Absorptions for both free and associated *cis* and *trans* isomers were assigned based on the characteristic shift of the N–H stretch upon hydrogen bond formation. When monitored as a function of concentration, an increased abundance of associated *cis*-formanilide relative to associated *trans*-formanilide was observed upon dilution and was attributed to the additional stabilization derived from a dimeric hydrogen-bonded structure with two hydrogen bonds. At the lowest concentrations studied, 0.0008 M in carbon tetrachloride, the free amide species were dominant and an energy difference,  $E_{\text{cis}} - E_{\text{trans}}$ , for the unassociated species of  $620 \pm 60\text{ cal/mol}$  was derived by monitoring the intensity ratio of the N–H stretching bands over a range of temperatures. This value for the energy difference would yield an isomer distribution of approximately 55% *trans* and 45% *cis* at the nozzle temperature used in the present experiments.

While these IR measurements were carried out at a concentration roughly 600 times smaller than used in the NMR studies, a supersonic expansion environment can be viewed as an extrapolation to infinite dilution. Not only is solute self-association eliminated but any solute–solvent interactions are also completely absent under isolated conditions. Isomer ratios

measured in this environment reflect solely the intrinsic energy difference between the two isomers and are found to differ considerably from the earlier IR investigations. This difference must indicate a preferential stabilization of the *cis* isomer or destabilization of the *trans* isomer in solution.

**B. Acetanilide.** The electronic spectrum of acetanilide, Figure 3, is clearly indicative of a strongly vertical transition. The split origin and complex low-frequency vibronic activity arise from methyl torsion and the presence of two populated methyl rotor states of *A* and *E* symmetry in the ground electronic state. Both remain essentially equally populated, even after cooling, due to nuclear spin considerations. Much of this structure can be adequately fit to a three-fold symmetric periodic potential employing  $\cos(3\tau)$  and  $\cos(6\tau)$  terms, but since the splitting of the *A* and *E* levels in the ground electronic state is unknown, the fit is not definitive. However, no characteristic features associated with phenyl torsion are observed, indicating that the phenyl torsional angle is the same in the ground and excited states. The obvious explanation for this is that the molecule has  $C_s$  symmetry in both states and that the torsional angle is zero. If this is the case, the observed isomer must be *trans*-acetanilide due to the very large steric interaction between the methyl group and the *ortho* phenyl hydrogen that would be present in a planar *cis* isomer.

Confirmation of this assignment is made by *ab initio* calculations with both 3-21G and 6-31G\* basis sets. While the *trans* isomer is predicted to have a planar  $C_s$  structure, the optimized geometry of the *cis* isomer is found to have the phenyl ring perpendicular to the plane of the amide group, indicating large steric interactions between the methyl and *ortho* phenyl hydrogens. The *trans* isomer is calculated to be the more stable, although the energy difference between the two isomers varies with the size of the basis set. A value of 2.1 kcal/mol for  $E_{\text{cis}} - E_{\text{trans}}$  is given by the 6-31G\* calculation which would yield a 9% abundance of the *cis* isomer in the heated nozzle. Scans over a broad wavelength range, however, show no evidence for a second isomer, suggesting a larger energy difference. The small peak observed at  $36073\text{ cm}^{-1}$  has the same pattern of methyl torsion splitting as does the *trans* isomer origin and is therefore assigned to a weakly Franck–Condon active mode of the *trans* isomer rather than to the origin of the *cis* isomer. With the smaller 3-21G basis set an energy difference of 4.5 kcal/mol is predicted, leading to an isomer ratio of 0.4% *cis* to 99.6% *trans* which is more consistent with the observations.

Acetanilide has also been found from NMR studies to be present in solution almost exclusively as the *trans* isomer,<sup>4</sup> where it adopts a nearly planar conformation.<sup>21</sup> The IR spectrum shows a dominant band associated with the free *trans* isomer and a very weak peak for the free *cis* isomer.<sup>20</sup> No strong band corresponding to an associated hydrogen-bonded structure was found even at higher concentrations. The crystal structure obtained from both X-ray<sup>22</sup> and neutron<sup>23</sup> diffraction similarly contains the *trans* isomer of acetanilide but in contrast with the current finding for the isolated molecule yields a structure in which the phenyl torsional angle has a value of  $17^\circ$ .

Interestingly, the calculated structure for *trans*-acetanilide reveals a close contact between the carbonyl oxygen and the *ortho* phenyl hydrogen of 2.245 Å, quite similar to the value calculated in *trans*-formanilide. This is also evident from the neutron diffraction study where oxygen–hydrogen separations of 2.232 and 2.257 Å were observed at 15 and 298 K, respectively, and the possibility of a weak C–H $\cdots$ O hydrogen bond was noted.<sup>23</sup> The crystal structure also reveals values for

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the  $C_{\text{phenyl}}-C_{\text{phenyl}}-N$ ,  $C_{\text{phenyl}}-N-C_{\text{carbonyl}}$ , and  $N-C_{\text{carbonyl}}-O$  bond angles of 123.5, 127.3, and 123.5°, respectively, which are close to the calculated values of 123.8, 129.4, and 124.4°. In the calculated structure of the *cis* isomer, having a 90° phenyl torsion angle, values very near 120° are found for the  $C_{\text{phenyl}}-C_{\text{phenyl}}-N$  and  $N-C_{\text{carbonyl}}-O$  bond angles. Comparison of these would again lead to the conclusion that the interaction between the carbonyl oxygen and *ortho* phenyl hydrogen in the *trans* isomer is not attractive at this separation, but is perhaps reduced in its repulsive value by a weak hydrogen bonding interaction. The resulting decrease in the steric destabilization leads to a conformation having coplanar phenyl and amide groups with maximum conjugation.

**C. *N*-Methylformanilide.** Assignment of the A and B isomers in *N*-methylformanilide is facilitated, as with form-anilide, by comparison to *ab initio* Hartree-Fock calculations. Experimentally, isomer A, absorbing at lower wavenumbers, must be the more stable due to its much larger integrated transition intensity. The calculations predict a more stable *E* isomer with both a 3-21G and 6-31G\* basis, although the magnitude of the energy difference does vary. This leads to assignment of isomer A to the *E* isomer and of isomer B to the *Z* isomer. The numerical value for the integrated spectral intensities yields an approximate 90% abundance for the *E* isomer which corresponds to an energy difference,  $E_E - E_Z$ , of -1.1 kcal/mol, in complete agreement with the 3-21G basis set calculation. Calculations with the larger basis set result in a larger energy difference of -2.8 kcal/mol. However, the experimental values contain considerable uncertainty due to the poorly resolved nature of the vibronic transitions and the underlying background observed in the spectrum and make comparison to the calculated values difficult. Since the *E* isomer is observed to have the lower energy electronic origin transition, it will have an even larger relative stabilization in the electronically excited state.

The electronic transition in the *E* isomer is highly nonvertical in a low-frequency mode which by analogy to form-anilide is assigned to phenyl torsion. Its activity signals a large change in the equilibrium torsional angle following electronic excitation. This would suggest a nonplanar structure in the ground electronic state and a more planar structure in the excited electronic state. A detailed Franck-Condon analysis is hampered by the difficulty in determining accurate values for the intensities of each member of the torsional progression and so has not been attempted. Additionally, the lowest vibronic feature that is evident in Figure 4 at 35454.6  $\text{cm}^{-1}$  may not actually be the electronic origin due to the very small Franck-Condon factors associated with such a large geometry change. An accurate fit to the entire torsion progression could, in principle, provide the assignment for this lowest observed peak. In contrast, the electronic transition in the *Z* isomer appears quite vertical, as in the corresponding *trans* isomer of form-anilide, and is therefore consistent with a 0° torsional angle in both electronic states.

These structural conclusions are less well supported by the *ab initio* geometry optimizations than in the case of form-anilide. While the calculations using a 3-21G basis set are consistent, predicting the *Z* isomer to adopt a  $C_s$  symmetry structure, with a 0° torsional angle, and the *E* isomer to have a 45° torsional angle, different conclusions would be drawn from use of the 6-31G\* calculations. In these, both isomers are found to have torsional angles near 50° and therefore both would be expected to show torsional activity in their electronic spectra. The *Z*

isomer with a 0° torsional angle would have the carbonyl oxygen and *ortho* phenyl hydrogen in close proximity, possibly stabilized in part by a weak hydrogen-bonding interaction. When 6-31G\* geometry optimizations were carried out on the *Z* isomer constrained to have  $C_s$  symmetry a structure with an oxygen-hydrogen separation of 2.119 Å was obtained with an energy 1.0 kcal/mol above the nonplanar minimum. This very short separation appears to be a consequence of the calculated value of the  $C_{\text{phenyl}}-N-C_{\text{carbonyl}}$  bond angle of 124.7° which is considerably smaller than the 129.3° value calculated for the *trans* isomer of form-anilide. An incorrect value in this bond angle in the direction of a smaller angle might produce an oxygen-hydrogen separation too small for the associated repulsive interaction to be stabilized by the enhanced conjugation obtained from a small torsional angle. Thus the calculated optimized geometries appear to be quite sensitive to a number of structural parameters.

In solution, *N*-methylformanilide has been found as two isomers with the *E* isomer in 95% abundance, independent of the solvent or concentration.<sup>5</sup> The greater stability of the *E* isomer was explained in terms of the *trans* arrangement of the bulkier substituents, phenyl and oxygen. The present calculations suggest that the explanation is not so simple. An estimate of 40° for the phenyl torsional angle was also made based on the observed chemical shift difference of the formyl proton in the two isomers.<sup>5</sup> Such an analysis would appear to require similar torsional angles in both the *E* and *Z* isomers and would therefore not be consistent with the current gas-phase results.

## Conclusion

The relative stabilities of the *cis* and *trans* isomers of form-anilide under isolated conditions are significantly different than in solution. While this study has derived an intrinsic energy difference of 2.5 kcal/mol in favor of the *trans* isomer, NMR studies at typical solute concentrations find nearly equal abundances of the two isomers, primarily due to solute-solute hydrogen bonding. Even at lower concentrations where association is negligible, IR spectroscopy finds evidence for only a 0.6 kcal/mol relative stabilization of the *trans* isomer in  $\text{CCl}_4$ . Electronic excitation results in a reversal of the relative isomer stabilities with the *cis* isomer at least 0.6 kcal/mol more stable. Isomer ratios derived for isolated acetanilide and *N*-methylform-anilide are much more representative of those seen in solution.

The phenylamide *Z* and *trans* isomers have a coplanar arrangement of the phenyl ring and amide group while the *E* and *cis* isomers have substantial phenyl torsional angles. *Ab initio* geometry optimizations suggest that the equilibrium conformations are determined by a number of structural parameters such as the valence bond angles about the carbonyl oxygen and amide nitrogen. Coplanarity of the phenyl ring and the amide group requires a fairly close contact between the carbonyl oxygen and *ortho* phenyl hydrogen. Although the net interaction between these two atoms does not appear attractive, the repulsion may be reduced by the electrostatic component of a weak  $C-H\cdots O$  hydrogen-bonding interaction. This additional stabilization appears to play an important role in permitting the adoption of a conformation having maximum conjugation between the phenyl and amide groups.

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