Role of Conjugation in the Stabilities and Rotational Barriers of Formamide and Thioformamide. An ab Initio Valence-Bond Study

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Abstract: The validity of the traditional resonance model for the amide and thioamide functional groups is examined by calculating the planar and rotated conformations of formamide and thioformamide with and without allowing for the delocalization of the nitrogen's lone pair. The vertical delocalization energies are found to be quite significant, in support of the traditional view that resonance is an important feature of the electronic structure of amides and thioamides. The rotational barriers are however not solely due to conjugation; they also partly arise from the preferred orientation of the nitrogen's lone pair as perpendicular to the molecular plane, even in the absence of conjugation. The resonance stabilization of the planar conformers is responsible for about one-half of the rotational barrier of formamide and two-thirds of that of thioformamide. The larger rotational barrier of thioformamide is therefore due to a greater importance of conjugation effects relative to formamide.

Introduction

The amide functional group plays a fundamental role in biology, as a basic building block of proteins and enzymes. It is characterized by some specific properties like coplanarity of the groups attached to the nitrogen atom, substantial rotational barrier, and kinetic stability toward nucleophilic attack or hydrolysis. All these properties are readily rationalized with the most popular concept of amide resonance, whose most general definition is the ability of the nitrogen atom to delocalize its lone pair over the whole C,N,O π system so as to gain stabilization. This delocalization of the π electrons implies that the planar amide group has to be represented by a set of resonance structures, among which three (**1**−**3**) are usually considered as important, although six structures can, in all rigor, be drawn for a system of four electrons in three orbitals. While
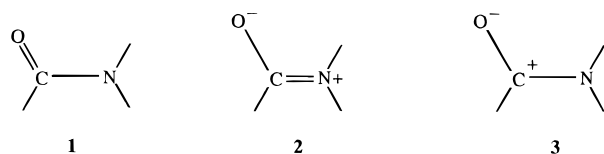
earlier textbooks explicitly include only **1** and **2** in the amide resonance scheme,[1,2] more recent textbooks[3] also include **3** in order to account for the polarity of the C=O bond, and finally the long-bond structure **4** has also been added by Harcourt[4] on the basis of valence bond (VB) calculations performed in minimal basis set. Be it as it may, what matters in the resonance model is that the delocalization implies the planarity of the nitrogen group, and is disrupted when the C−N bond is twisted as in **5**, leading to a net destabilization that explains the

significant rotational barrier. Other properties of the amide group, like the shortened C−N distance, reduced C=O stretching frequency, and reduced nitrogen basicity are also satisfactorily explained by the resonance model that implies contribution of structure **2** to the ground state of the planar form.

Regardless of the success, the simple resonance picture has been challenged by Wiberg et al.[5,6] on the basis of theoretical population analyses using the "atoms-in-molecules" (AIM) method.[7] These authors found the electron population at nitrogen to be *larger* in the planar conformer than in the twisted form **5**, in obvious disagreement with the resonance model. They explained the rotational barrier by the larger ionic character of the C−N linkage in the planar conformer, resulting in a stronger and shorter bond and in a net stabilization relative to the twisted form. Wiberg and Rablen later put less emphasis on the AIM population analysis, that they found to be inconsistent with other methods of estimating net atomic charges,[8] but concluded from examination of charge density difference plots that oxygen is only a spectator during the rotation of the C−N bond, in agreement with the rather small change in C−O bond distance as compared to the C−N lengthening accompanying the rotation. These authors argued[8,9] in favor of a resonance model involving the three resonance structures **1**−**3** for formamide, while the classical two-structure (**1** and **2**) model was found to be adequate for thioformamide. At variance with this latter statement, Laidig and Cameron[10] found the resonance model to be inadequate for both formamide and thioformamide, on the basis of integrated

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Fermi correlations and AIM population analyses, and explained the rotational barrier in terms of stabilizations/destabilizations related to hybridization changes. As a far-reaching consequence of this analysis, these authors propose that (thio)amides be viewed as special cases of amines, somewhat at variance with the widespread feeling that amides form a peculiar functional group on their own.

This challenging of the resonance picture stirred up a lot of controversy, both from theoreticians and experimentalists. The AIM method for deriving charge distributions was at the heart of the debate, and was questioned by Perrin,[11] whose arguments were later challenged by Laidig[12] and Gatti.[13] Yamada[14] studied the experimental ^{17}O, ^{13}N, and ^{15}C chemical shifts in a series of twisted amides and observed a decrease of the densities at carbon and oxygen and an increase at nitrogen on going from planar to more and more twisted forms, in agreement with the classical resonance model. Brown et al.[15] reported some ^{13}C and ^{15}N NMR data in support of the resonance model, while other physicochemical data indicated that other factors can modify or offset the resonance effects.

It is to be noted that all the arguments that have been invoked in favor or in opposition to the resonance model are somewhat indirect, since they deal with charge distributions, Fermi correlation, or bond length changes upon C$-$N rotation while the crucial quantity that is attached to the model is the delocalization energy, especially to account for the much discussed rotational barrier. This prompted us to probe the validity of the resonance model by bringing some new elements of a different kind, by means of an ab initio valence-bond (VB) method that allows to turn the delocalization on or off, at will, in a conjugated molecule. By this method, it is possible to *directly* measure the stabilization brought by the delocalization of the nitrogen lone pair in planar amide, by comparing the energy of the fully delocalized ground state to that of an adiabatic state in which the lone pair is constrained to remain strictly localized on the nitrogen atom. Doing this for both the planar and the twisted forms allows the contribution of resonance to the rotational barrier and, more generally, to the properties associated to the special stability of the planar form to be estimated. With the help of this technique, that will be applied to formamide and thioformamide as model systems, the aim of this paper is to study the properties of amide resonance in a quantitative way and to answer the following questions: (i) How much does the delocalization of the nitrogen's lone pair over the carbonyl or thiocarbonyl group stabilize the planar forms of amides relative to the twisted forms? (ii) Does the resonance model fully account for the rotational barrier of amides? (iii) Are the large C$-$N shortening and weak C$-$O lengthening upon rotation compatible with a resonance model? (iv) Why is the rotational barrier of thioformamide larger than that of formamide?

Theoretical Methods

As the main criticism against the classical view of amide resonance arises from the work of Laidig and Cameron,[10] we have used a basis set and a level of theory as coherent as possible with their Hartree$-$Fock/6-311++G** calculations. Thus, the wave functions for both the ground states and the localized states are of the single-determinant

type. The ground states with the delocalization turned on, designated by the generic term Φ_{del}, are calculated at the Hartree$-$Fock level, with no restriction on the optimization of the orbitals. The diabatic states with the delocalization turned off, Φ_{loc}, are calculated the same way but with the additional constraint that the nitrogen's lone pair is prevented, throughout its optimization, to delocalize over the entire molecule but must remain purely localized on the nitrogen atom. The latter calculations, which deal with wave functions made of nonorthogonal orbitals, use the VBSCF method of van Lenthe and Balint-Kurti,[17] later implemented by Verbeek[18] in the TURTLE[19] program. Note that in the localized diabatic states, all orbitals except the localized lone pair are free to delocalize over the whole molecule, so that the inductive effects and the polarities of the various bonds, including the C$-$O π bond, are fully allowed for in the present calculations.

For an unambiguous definition of the localized states, the latter are restricted to conformations in which the nitrogen group remains sp^2-hybridized, i.e., not pyramidalized. Such conformations are called sp^2-0° for the unrotated conformers (Figure 1a) and sp^2-90° for the rotated ones (Figure 1b). The effects of pyramidalization, leading to the fully relaxed sp^3-0° and sp^3-90° conformations, are estimated in a second step.

All calculations use the standard 6-311G** basis set. The geometry optimizations of the delocalized ground states were carried out through a standard gradient technique with the GAUSSIAN92 program.[20] Because no gradient routine was available for the VBSCF method, we optimized each geometric parameters of the localized diabatic states one by one, by an iterative procedure.

Results and Discussion

Geometries of the Delocalized Ground States. The geometries of the planar, sp^2-90°, and sp^3-90° conformers of thioformamide and formamide, as optimized at the Hartree$-$Fock level, are displayed in Figure 1. The geometries for the thioformamides are in excellent agreement with those reported by Laidig and Cameron,[10] calculated at the same level of theory but with a slightly larger basis set, showing that the description of such neutral organic molecules does not require the use of diffuse orbitals. The changes of bond lengths upon rotation around the C$-$N bond are considerable, 0.099 Å for the C$-$N bond and -0.037 Å for the C$-$S bond. The geometries of the formamides are also in good agreement with both the Hartree$-$Fock and MP2 geometries calculated in 6-31G* basis set by Wiberg and Breneman.[6] Upon rotation, the C$-$N bond lengthening is of the same order of magnitude, 0.078 Å, as in the thioformamide case, but the C$-$O bond shortening is surprisingly small, -0.01 Å. This feature of the formamide rotation has been noted by several authors and sometimes used as an argument against the importance of resonance stabilization in amides.[6] Note that for both formamide and thioformamide, the C$-$N bond is smaller in the sp^2-90° (Figure 1b) than in the sp^3-90° conformer (Figure 1c), by 0.020$-$0.022 Å. Thus, the C$-$N lengthening upon rotation is not entirely due to loss of conjugation but partly arises from a change of hybridization at the nitrogen atom, as sp^3 hybrids are generally known to form longer bonds than sp^2.

Geometries of the Localized Diabatic States. The geometries of the diabatic states of formamide and thioformamide,

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(a)

C-H = 1.094 (1.091)
N-H1 = 0.994 (0.992)
N-H2 = 0.991 (0.990)
O-C-H = 122.3 (123.3)
C-N-H1 = 119.2 (118.8)
C-N-H2 = 121.5 (121.2)

C-H = 1.081 (1.079)
N-H1 = 0.995 (0.989)
N-H2 = 0.993 (0.989)
S-C-H = 120.2 (121.4)
C-N-H1 = 119.7 (119.2)
C-N-H2 = 121.4 (120.5)

(b)

C-H = 1.093 (1.087)
N-H = 0.990 (0.992)
O-C-H = 120.0 (121.9)
C-N-H = 118.8 (118.8)

C-H = 1.083 (1.076)
N-H = 0.990 (0.991)
S-C-H = 118.2 (120.6)
C-N-H = 120.4 (120.2)

(c)

C-H = 1.090
N-H = 1.004
O-C-H = 121.5
C-N-H = 105.7

C-H = 1.080
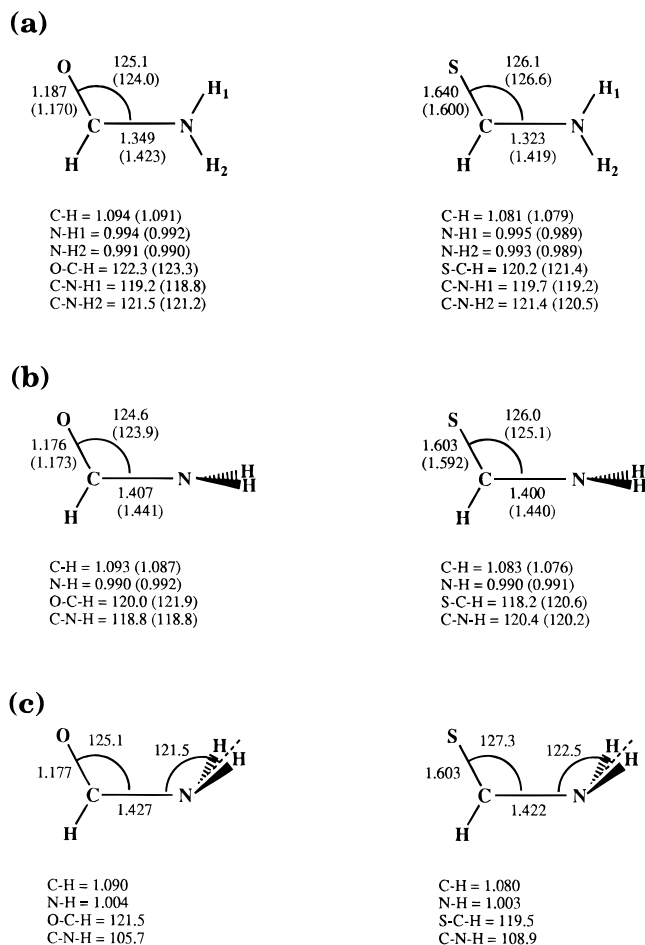N-H = 1.003
S-C-H = 119.5
C-N-H = 108.9

Figure 1. Geometries of the delocalized states and, in parentheses, of the localized states of formamide and thioformamide: (a) planar conformers, referred to as sp^2-90°; (b) sp^2-90°-rotated conformers; and (c) sp^3-90°-rotated conformers.

with the nitrogen's lone pair constrained to be a strictly localized atomic orbital of 2p type, are displayed in Figure 1, parts a and b, for the sp^2-0° and sp^2-90° conformers. It first appears that there are little differences between the C−O, C−S, and C−N bond lengths of the planar conformers in their lone-pair-localized diabatic states (Figure 1a, values in parentheses) and those of the pyramidal-twisted conformers in their ground states (Figure 1c), thus supporting the idea that the rotation around the C−N bond and the concomitant variations of bond lengths are mainly a matter of localization−delocalization. Interestingly, turning off the delocalization in formamide leads to a large increase of the C−N bond but to a very small decrease of the C−O bond. Some asymmetry between bond-length variations upon loss of conjugation is not abnormal and was already found[21] in the formate ion: the bond with the largest force constant simply undergoes the smallest variation. However, in the formamide case the C−O variation is so small that an alternative explanation is required, and might be linked to the polarity of the C−O bond. If the C=O bond were not polar, turning off the delocalization would lead to disappearance of **2** to the benefit of **1**, and a significant C−O shortening would result. If on the other hand the loss of conjugation mainly corresponds to a transfer from **2** to the polar structure **3**, no change is expected in the bond length of the C−O linkage which remains essentially a single bond. Thus, the small C−O shortening upon loss of conjugation is an argument in favor of Wiberg's proposal[8,9] that formamide resonance involves three VB structures (**1**−**3**) rather

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than only two. By contrast, the significant C=S shortening accompanying loss of conjugation in thioformamide suggests that the two-structure resonance model is more adequate for thioformamide. Another indication that the two species should be differently described in terms of resonance structures is the C−N bond length being shorter in thioformamide than in formamide in their planar ground states (Figure 1), by 0.026 Å, while the same bond lengths are exactly similar in the corresponding diabatic localized states. To summarize: examination of the geometric consequences of turning off the delocalization of the nitrogen's lone pair suggests that the C−N linkage has more double bond character in thioformamide than in formamide, while the reverse is true for the C−O(S) linkage.

For both formamide and thioformamide, the sp^2-90° conformations exhibit somewhat longer C−N bonds and shorter C−O(S) bonds in the localized diabatic states as compared to the ground states, indicative of a slight delocalization of the nitrogen's lone pair in the latter, due to hyperconjugation.

Delocalization Energies. The energy difference between the delocalized ground state Φ_{del} and the localized diabatic state Φ_{loc} of a conformer represents the delocalization energy (DE), which is called "vertical" if the localized state is calculated with the same geometry as the ground state, or "adiabatic" if both localized and ground states are calculated in their respective optimized geometries. The vertical delocalization energies,

$$DE = E(\Phi_{loc}) - E(\Phi_{del}) \tag{1}$$

displayed in Table 1, allow the importance of π-electron resonance in the description of amides vs thioamides to be appreciated. The values for the planar conformations of formamide and thioformamide are considerable, 27.3 and 37.6 kcal/mol, showing that the nitrogen's lone pair is strongly delocalized in both molecules. Note that the two values are significantly different, another indication that resonance effects are even more important in thioformamide than in formamide. By contrast, the vertical delocalization energies of the sp^2-90° conformations of both molecules are rather similar, 12.4 and 10.8 kcal/mol, respectively, and significantly smaller than in the planar conformations. These values reflect the importance of hyperconjugation in the σ frame and show that the nitrogen's lone pair, while being not involved in a conjugated π system, remains slightly delocalized in the twisted conformations.

The delocalization energies of the pyramidalized twisted forms (sp^3-90°) cannot be calculated directly, and one may wonder whether they differ from the sp^2-90° calculated values. Should it be so, the stabilization brought by pyramidalization would differ from the normal value of 6 kcal/mol for the inversion barrier of primary amines.[3] This however is not the case, as the pyramidalization of the sp^2-90° to sp^3-90° ground states, as calculated at the Hartree−Fock level, brings stabilizations of 6.7 and 6.8 kcal/mol, respectively, for formamide and thioformamide. It can therefore be concluded that the delocalization energies of the sp^2-90° forms apply to the pyramidal twisted forms as well.

Let us now consider the adiabatic delocalization energies, which are more directly related to the overall stabilization that resonance brings to the planar conformations relative to the twisted ones and to the role of resonance in the rotational barrier. Geometrical relaxation stabilizes the planar localized diabatic state of formamide by 3.1 kcal/mol, leading to an adiabatic DE of 24.2 kcal/mol for the sp^2-0° conformation of formamide. This conformation however does not correspond to the fully relaxed unrotated localized state, which should be pyramidalized in the absence of any π conjugation, and therefore further stabilized by 6.7 kcal/mol to get the final adiabatic DE of the unrotated

Table 1. Absolute Energies (in hartrees) for the Ground States (Φ_{del}) and Localized Diabatic States (Φ_{loc}) of Formamide and Thioformamide[a]

	Φ_{del}	Φ_{loc} (vertical)[b]	vertical DE	Φ_{loc} (optimized)[c]
formamide				
planar or sp^2-0° (a)	−168.982 29 (0)	−168.938 85 (27.3)	(27.3)	−168.943 74 (24.2)
sp^2-90° (b)	−168.946 71 (22.3)	−168.929 46 (33.1)	(10.8)	−168.930 43 (32.5)
sp^3-90° (c)	−168.957 39 (15.6)			−168.941 11 (25.8)[d]
sp^3-0°				−168.954 42 (17.5)[d]
thioformamide				
planar or sp^2-0° (a)	−491.618 98 (0)	−491.559 06 (37.6)	(37.6)	−491.567 97 (32.0)
sp^2-90° (b)	−491.574 75 (27.8)	−491.554 98 (40.2)	(12.4)	−491.556 35 (39.3)
sp^3-90° (c)	−491.585 54 (21.0)			−491.567 14 (32.5)[d]
sp^3-0°				−491.578 76 (25.2)[d]

[a] The relative energies, in kcal/mol, are indicated in parentheses. The labels (a), (b) and (c) refer to the conformations displayed in Figure 1. [b] Calculated with the geometry of Φ_{del}. [c] Calculated in its own optimized geometry. [d] Estimated by taking the energy difference between the sp^2-90° and sp^3-90° ground states as the pyramidalization energy.

Table 2. Mulliken and NPA Net Charges for the Ground States (Φ_{del}) and Localized Diabatic States (Φ_{loc}) of Formamide and Thioformamide[a]

	Φ_{del}	Φ_{loc} (vertical)[b]	Φ_{loc} (optimized)[c]
planar formamide			
NH$_2$	−0.027 (−0.092)	−0.074 (−0.143)	−0.116 (−0.176)
CH	0.485 (0.776)	0.506 (0.794)	0.523 (0.807)
O	−0.457 (−0.684)	−0.432 (−0.651)	−0.407 (−0.631)
sp^2-90° formamide			
NH$_2$	−0.117 (−0.206)	−0.121 (−0.211)	−0.141 (−0.224)
CH	0.455 (0.779)	0.457 (0.778)	0.471 (0.788)
O	−0.338 (−0.572)	−0.336 (−0.567)	−0.330 (−0.564)
sp^3-90° formamide			
NH$_2$	−0.077 (−0.197)		
CH	0.437 (0.796)		
O	−0.360 (−0.599)		
planar thioformamide			
NH$_2$	0.095 (0.002)	0.022 (−0.091)	−0.030 (−0.118)
CH	0.152 (0.252)	0.161 (0.272)	0.156 (0.221)
S	−0.246 (−0.254)	−0.183 (−0.181)	−0.126 (−0.102)
sp^2-90° thioformamide			
NH$_2$	−0.051 (−0.168)	−0.058 (−0.175)	−0.075 (−0.182)
CH	0.097 (0.170)	0.100 (0.168)	0.104 (0.158)
S	−0.046 (−0.003)	−0.042 (0.007)	−0.029 (0.023)
sp^3-90° thioformamide			
NH$_2$	−0.008 (−0.152)		
CH	0.085 (0.192)		
S	−0.076 (−0.040)		

[a] NPA values are indicated in parentheses. [b] Calculated with the geometry of Φ_{del}. [c] Calculated in its own optimized geometry.

formamide, 17.5 kcal/mol. The same calculation leads to a value of 25.2 kcal/mol for the adiabatic DE of unrotated thioformamide.

For the rotated forms, on the other hand, the adiabatic DEs differ very little from the vertical DEs. Still assuming that the delocalization energy is nearly independent of pyramidalization in the twisted forms, the adiabatic delocalization energies amount to 10.2 and 11.5 kcal/mol, respectively, for twisted formamide and thioformamide in both their pyramidalized and unpyramidalized conformations.

Comparison of the adiabatic DEs for the unrotated and rotated forms shows that the delocalization of the nitrogen's lone pair stabilizes the unrotated conformation more than the rotated one by 7.3 kcal/mol for the formamide case vs 13.7 kcal/mol for thioformamide. These numbers, which represent the contributions of resonance stabilization to the rotational barriers, may appear relatively small. They however well reflect the balance of two opposite effects, which characterize amide resonance: a stabilization due to π-electron delocalization, and a destabilization due to the concomitant loss of pyramidalization at the nitrogen center. Be it as it may, resonance effects clearly appear to play a greater role in thioformamide than in formamide.

Rotational Barriers. Our calculated rotational barrier of thioformamide is 21.0 kcal/mol, corrected to 20.2 kcal/mol by using the zero-point-energy (ZPE) correction of Laidig and

Cameron,[10] in satisfactory agreement with the G2 value of 18.0 kcal/mol,[8] an indication that electron correlation is not crucial for the present discussion. The rotational barrier of formamide is smaller than that of thioformamide, 15.6 kcal/mol at the Hartree−Fock level, close to the values 15.7 (Hartree−Fock) and 16.7 kcal/mol (MP2) reported by Wiberg and Breneman.[6] After ZPE correction,[10] our computed rotational barrier for formamide amounts to 15.4 kcal/mol vs 16.0 at the G2 level.[8]

As a rough estimate, resonance accounts for about one-half of the rotational barrier of formamide (7.3 vs 15.6 kcal/mol) and for two-thirds of that of thioformamide (13.7 vs 21.0 kcal/mol). This means that the rotation of the localized diabatic states is not free, despite the complete lack of double-bond character of the C−N linkage, and indeed it appears from Table 1 that *the localized (unpyramidalized) conformations of formamide and thioformamide have significant rotational barriers,* respectively 8.3 and 7.3 kcal/mol. As a tentative explanation, the nitrogen's lone pair is probably stabilized by the neighborhood of an electron-deficient carbon, even in the absence of conjugation. The lone pair then orients itself in the direction corresponding to the minimum of electron density at the carbon atom, i.e. along an axis perpendicular to the molecular plane. Be it as it may, it is clear that conjugation contributes only partly, though significantly, to the rotational barriers of amides.

Population Analysis. It is interesting to visualize the effect of amide resonance in terms of charge transfer from the NH_2 group to the carbonyl (thiocarbonyl) group as the delocalization is turned on, and this can be done through a compared population analysis of the localized and delocalized planar conformations. Note that some compared charge analyses have already been performed on the planar and 90°-rotated ground states of formamide and thioformamide;[8] however, we emphasize that the net charges on rotated amides are rather different from those of the planar localized diabatic states (see Table 2), due to the significant effect of rotation and pyramidalization, and are, therefore, of limited help to understand the nature of amide resonance in the planar forms.

Both Mulliken and NPA[22] methods of population analysis have been used. Although NPA net charges are generally larger than Mulliken ones in absolute values, both set of values give rather similar charge transfers from the vertical localized states to the delocalized ground states. In thioformamide, the NH_2 group loses about 0.08 electrons (0.073 and 0.093 electrons according to Mulliken and NPA analyses, respectively) that are mainly donated to the sulfur atom as the delocalization is turned on, in agreement with a simple description of the conjugated molecule in terms of VB structures **1** and **2**. In formamide, the charge transfer is slightly smaller, about 0.05 electrons that are donated to both the oxygen and the CH group. This is consistent with a description of the localized state of formamide in terms of **1** and **3**, with the further participation of **2** in the delocalized state.

Taking the geometry-optimized (sp^2-0°) localized states (Table 2, third column) as references leads to bigger but qualitatively similar charge transfers. Both NPA and Mulliken charge analyses point to a larger importance of resonance in thioformamide than in formamide. By comparison, the charge transfers from the localized to the delocalized states are negligible in the twisted forms.

Conclusion

With the help of ab initio VB calculations, we have directly measured the stabilization that delocalization of the nitrogen's lone pairs brings to planar conformations and 90°-rotated conformations of formamide and thioformamide, and the contribution of this resonance stabilization to the rotational barrier around the C−N bond. The large delocalization energies

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of both species in their most stable conformation demonstrate that conjugation of the π electrons is an important feature of the electronic structure of amides and thioamides and that the nitrogen's lone pair is significantly delocalized over the (thio)-carbonyl group. According to both vertical and adiabatic calculated delocalization energies, conjugation is even more important in thioformamide than in formamide.

The contribution of resonance stabilization to the C−N rotational barrier, estimated as that quantity by which the planar conformation is stabilized by delocalization relative to the fully relaxed 90°-rotated conformer, amounts to 7.3 and 13.7 kcal/mol, respectively, for formamide and thioamide. In both cases, resonance stabilization, although significant, does not account for the whole rotational barrier that is also due, in part, to an effect that is not related to conjugation and that we tentatively intrepreted as the preference of the nitrogen's lone pair for a direction perpendicular to the molecular plane, following the minimum of electron density at the carbon atom. As a result, π-electron conjugation is responsible for about one-half of the rotational barrier of formamide and two thirds of that of thioformamide. The larger rotational barrier of thioformamide is therefore due to a greater importance of conjugation effects relative to formamide.

As a whole, our results support the traditional resonance model for amides and the concomitant explanation for their high rotational barriers, although other effects contribute to the barriers. Both geometrical considerations and net charge analyses of the localized and delocalized states agree on the conclusion that the early two-structure resonance model is adequate for thioformamide but insufficient for formamide, unless the C−O linkage in **1** is considered as a polar bond. If not, the extended three-structure model (**1**−**3**) is more adequate for formamide, following the proposals of Wiberg and Rablen.[8,9] In this scheme, the proposal that the density at the oxygen atom is hardly affected by rotation around the C−N bond[6,8] is not contradictory with the importance of conjugation. However regardless of the resonance model retained, the importance of conjugation in amides and their resulting C−N double-bond character confirm the idea that these molecules are not only some particular cases of amines but definitely form a specific functional group on their own.

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