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Why Does Thioformamide Have a Larger Rotational Barrier Than Formamide?

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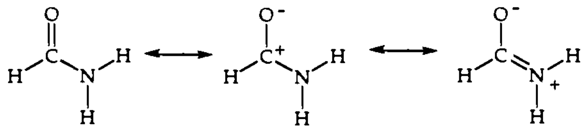
Abstract: The C−N rotational barrier for thioformamide is known to be larger than that for formamide. The origin of this barrier has been examined with the aid of ab initio molecular orbital calculations. The larger barrier is reproduced, and it is found that the amino group of thioformamide is less "floppy" than that of ordinary amides. In addition, the change in charge density at sulfur on rotation of the amino group in thioformamide is much greater than that at oxygen in formamide. It is concluded that the traditional picture of amide "resonance" is more appropriate for thioamides than for amides. The small difference in electronegativity between carbon and sulfur and the larger size of sulfur are the major factors that allow charge transfer from nitrogen to sulfur in thioamides. The effect of replacing the carbonyl oxygen of formamide by =NH, =PH, =CH_2, and =SiH_2 also was examined. The energies associated with group separation reactions were divided into π components (the rotational barriers) and σ components. The latter were found to increase with increasing electronegativity of the substituent, indicating that they resulted from internal Coulombic stabilization. The π components were about the same for the corresponding first and second row C=Y groups where Y is the terminal atom or group of the double bond, and they increased with increasing electronegativity of Y.

1. Introduction

The rotational barrier in formamide appears to be fairly well-understood.[1,2] The electronegative oxygen leads to polarization of the C=O bond in the sense $C^+{=}O^-$ for both the σ and π systems. In the planar form, the nitrogen assumes sp^2 hybridization (the H−N−H bond angle is 119°) and places its lone pair in a p orbital that can interact with the electron deficient carbon. This stabilization is lost on a 90° rotation about the C−N bond. The oxygen is essentially a spectator during the rotation since its electron population changes by only 0.057 e. This may be seen in a plot of the difference in charge density between planar formamide and the 90° rotated formamide transition state with the lone pair *anti* to the carbonyl oxygen (Figure 1, upper left). Here, decreases in charge density on going from the planar to the rotated form are indicated by dashed contours and increases by solid contours. For clarity, only the changes associated with the carbonyl oxygen are shown. There is a π component in the planar form that is lost on rotation and a σ component that appears in the rotated form. Integration gives the π change as 0.088 e and the σ change as 0.031 e leading to a net change of only 0.057 e.[3] These charge shifts may be compared with those for vinylamine (Figure 1) which gives a larger shift (0.066 e) but has a rotational barrier only one-third as large as that for formamide. Therefore, the major contributor to the barrier cannot be charge transfer to the oxygen but rather is charge transfer between nitrogen and carbon.[1]

This indicates that the π component of the stabilization of the planar amide should be represented by three resonance structures, of which the latter two are of major importance for the rotational barrier. In addition, there is an important σ component that is not represented in the conventional resonance formalism.[2]



The positive charge at carbon is an important feature of the chemistry at the carbonyl group and leads to an increased sensitivity of the strength of RCO−X bonds to increasing electronegativity of X as compared to CH_3−X bonds and the marked destabilization of the carbonyl group when it is attached to substituents bearing a positive charge at the attached atom (e.g. CF_3, NO_2, SiH_3 groups).[2]

2. Thioamides

The interactions in thioformamide must be quite different than those in formamide.[4] Sulfur has an electronegativity close to that for carbon,[5] and so the C=S bond should not be strongly polarized. Correspondingly, one might expect that the C=S carbon would be considerably less electron deficient. Despite this, it is known that the rotational barrier in thioformamide is somewhat larger than for formamide.[6] This phenomenon is in accord with an earlier observation that electron donating substituents interact more strongly with the thiocarbonyl group

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

[1] Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831.

[2] Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

[3] The relatively small π charge transfer from N to oxygen in an amide is also predicted by frontier orbital (FMO) theory. Here, the C−O π orbital will have its largest coefficient at O, and conversely, the π^* orbital will have its largest coefficient at carbon. Thus, π-charge transfer from nitrogen will go mainly to C. However, FMO theory does not recognize the important role of σ-charge transfer in the reverse direction, nor the effect of the change in electronegativity of N as a result of rotation about the C−N bond.

[4] After this paper was submitted, a related paper dealing with thioamides appeared: Ou, M.-C.; Tsai, M.-S.; Chu, S.-Y. *J. Mol. Struct.* **1994**, *310*, 247. They also concluded, based on a population analysis, that there was more charge transfer from N to S in a thioamide than from N to O in an amide.

[5] Pauling, L. *The Nature of the Chemical Bond,* 3rd ed.; Cornell University: Ithaca, NY, 1960; p 88.

[6] Sandström, J. *J. Phys. Chem.* **1967**, *71*, 2318. Neuman, R. C., Jr.; Young, L. B. *J. Phys. Chem.* **1965**, *69*, 2570. Loewenstein, A.; Melera, A.; Rigny, P.; Walter, W. *J. Phys. Chem.* **1964**, *68*, 1597. Stewart, W. E.; Siddall, T. H., III *Chem. Rev.* **1970**, *70*, 517.

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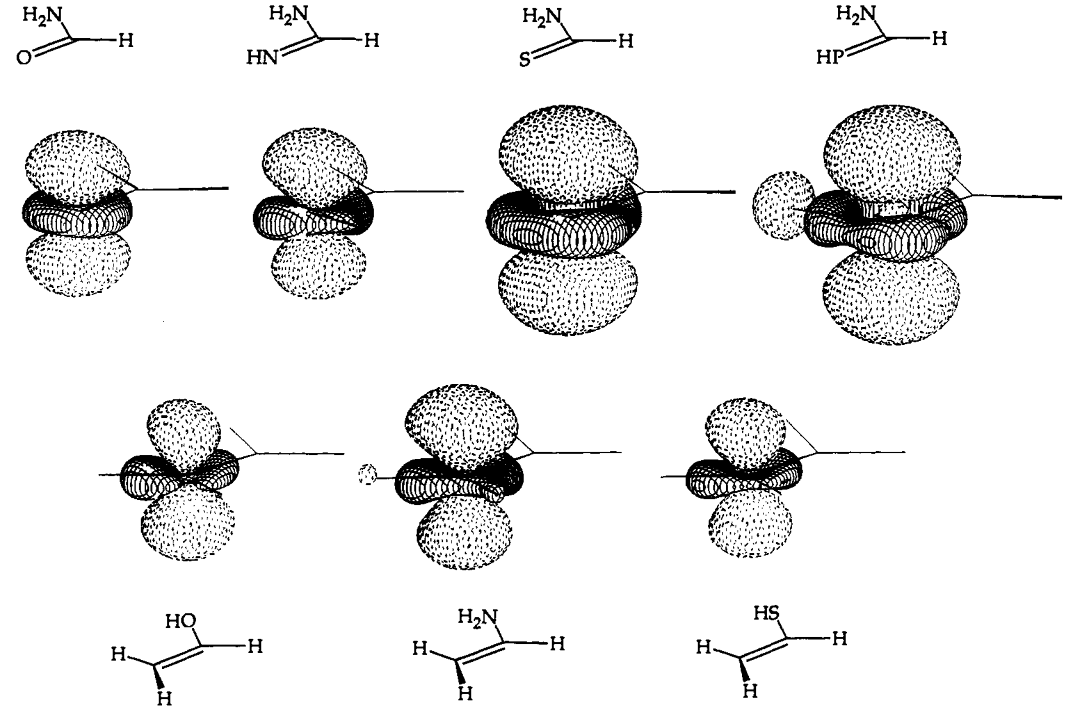

Figure 1. Charge density difference plots for the Y= groups (rotated-planar) for formamide, formamidine, thioformamide and the phosphorus analog of formamidine (upper row) and for the terminal methylene groups of vinyl alcohol, vinylamine, and vinylthiol (lower row). The contour level is 2 × 10^{-3} e/au^3.

than with the carbonyl group[7] and with the high dipole moments which have been measured for thioamides.[8] What is the origin of this barrier?

We have attempted to gain information on this question by carrying out ab initio MO calculations. Some calculations have been reported, but they have been at relatively low theoretical levels.[9] Here, geometry optimizations were carried out at the MP2/6-31+G* level of theory which usually leads to quite good structural parameters.[10] Diffuse functions were included in order to treat the lone pairs properly.[11] The energies are given in Table 1 and some key structural features are listed in Table 2. Currently, the best practical level of theory is the G2 model developed by Pople et al.[12] which is effectively QCISD(T)/6-311+G(3df, 2p) plus the zero-point energy and a higher level correction. The G2 energies also are given in Table 1. The calculated rotational barrier for the thioamide is larger than that for formamide, in good agreement with the experimental observations.

In calculating the zero-point energy of thioformamide, it was found that the NH_2 out-of-plane bending vibration had a considerably higher frequency than that for formamide. The bending potentials for the two molecules were examined and are shown in Figure 2. It is clear that the bending mode for the thioamide is different and stiffer than that for the amide.

Table 1. Energies of Formamide and Thioformamide

Total Energies, H^a

compound	MP2/6-31+G*	ZPE^b	G2	μ
formamide, planar	−169.42187	27.4	−169.64548	4.14
formamide, ts^c	−169.39425	27.2	−169.61993	1.34
formamide, ts^d	−169.39042			
thioformamide, planar	−492.00586	26.6	−492.23362	4.32
thioformamide, ts^c	−491.97462	25.8	−492.20488	0.95
thioformamide, ts^d	−491.97209			
formaldehyde	−114.18466	16.4	−114.33888	2.58
thioformaldehyde	−436.77488	15.0	−436.93369	1.68
formic acid, *Z*	−189.26744	20.8	−189.51630	1.39
formic acid, ts	−189.24477	19.5	−189.49804	3.02
thioformic acid, *Z*	−511.84349	19.4	−511.09731	1.09
thioformic acid, ts	−511.82076	18.0	−511.07789	2.29
formyl fluoride	−213.24812	13.0	−213.24812	2.04
thioformyl fluoride	−535.81918	11.4	−536.09908	1.47

Rotational Barriers, kcal/mol^e

compound	MP2	G2
formamide	17.3	16.0
thioformamide	18.8	18.0
formic acid	12.9	11.5
thioformic acid	12.9	12.3

[a] All electrons were included in the electron correlation. [b] HF/6-31G* frequencies scaled by 0.893. [c] Lower energy transition state having the lone pair *anti* to the carbonyl group. [d] Higher energy transition state having the lone pair *syn* to the carbonyl group. [e] The values include the change in zero-point energy.

One of the ways in which the interaction of the C=S group with substituents may be examined makes use of group separation reactions[13] as shown in Table 3. Here, the formyl and thioformyl series are compared with NH_2, OH, and F as the substituents. The energy changes based on the G2 energies are given as $\Delta H_{\mathrm{react}}$. The rotational barriers are commonly taken as a measure of the π interaction and are given as ΔH_{π}. The π interaction for fluorine was taken as zero in accord with our earlier observations concerning acetyl compounds.[2] As noted previously, the rotational barriers are smaller than the overall

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(7) Lüttringhaus, A.; Grohmann, J. *Z. Naturforsch.* **1955**, *10B*, 365. Lüttringhaus, A.; Mecke, R.; Mecke, R.; Grohmann, J. *Elektronentheorie den Homöpolaren Bindung*; Akademie-Verlag: Berlin, 1956.

(8) Lee, C. M.; Kumler, W. D. *J. Org. Chem.* **1962**, *27*, 2052. Jensen, K. A. *Acta Chem. Scand.* **1963**, *17*, 551.

(9) Lim, K. T.; Francl, M. M. *J. Phys. Chem.* **1987**, *91*, 2716.

(10) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(11) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(12) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(13) Hehre, W. J.; Ditchfield, R.; Radom, L; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. Besides the energies given in the tables, the following G2 energies were used in calculating the group separation energies: ethane, −79.630 90; methyl fluoride, −139.554 21; methanol, −115.534 89; methylamine, −95.666 91 (from ref 12); acetaldehyde, −153.576 83; propene, −117.645 02; $CH_3CH{=}NH$, −133.697 70; $CH_3CH{=}PH$, −419.9212.

Table 2. Bond Lengths, Å

compound	C−O(S)	C−N
formamide, planar	1.2286	1.3602
formamide, ts	1.2195	1.4404
thioformamide, planar	1.6225	1.3507
thioformamide, ts	1.6191	1.4368
formic acid, planar	1.2154	1.3523
formic acid, ts	1.2080	1.3821
thioformic acid, planar	1.6177	1.3468
thioformic acid, ts	1.6093	1.3800
formyl fluoride	1.1940	1.3650
thioformyl fluoride	1.5943	1.3606
formaldehyde	1.2237	
thioformaldehyde	1.6170	

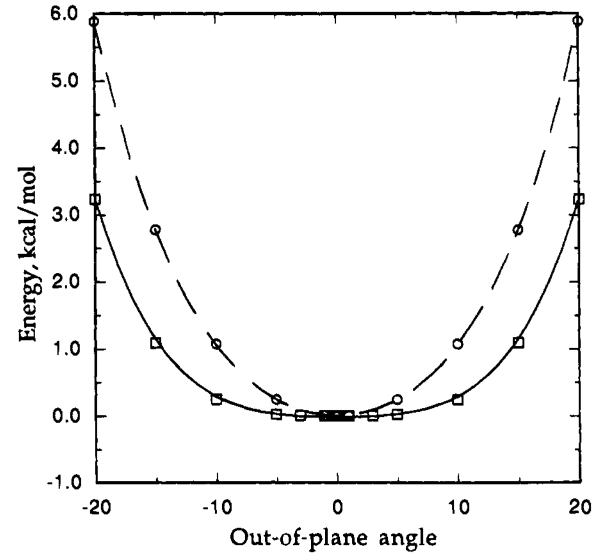


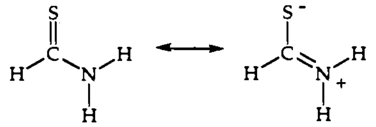
Figure 2. Out-of-plane bending potentials for the amino groups of formamide (solid line) and thioformamide (dashed line).

energy changes. We have shown in the acetyl series that the difference (given as ΔH_σ) is due to the electronegativity of the substituent.[2] As it withdraws charge density from the carbonyl carbon via the σ bond, it increases the carbon's positive charge and increases the internal Coulombic attraction of the carbon for the negatively charged carbonyl oxygen. In accord with this proposal, the C=O bond lengths are known to decrease as the electronegativity of the substituent increases.[14]

It may be seen that the ΔH_σ terms are much smaller in the thiocarbonyl series. The C=S bond has relatively little polarization, and as a result, an increase in the positive charge at the carbon will not lead to much of a stabilizing attractive interaction with the sulfur. In this connection, it is interesting to note the quite small energy change for the group transfer reaction of thioformyl fluoride as compared to formyl fluoride.

In order to gain further information on the differences between the formyl and thioformyl compounds, the change in charge density on rotating the amino group in thioformamide was examined in the same fashion as for formamide and is shown in Figure 1. The scales for the plots are the same, and it can be seen that much more charge is transferred to and from sulfur than was found with the oxygen of formamide. Integration of the charge density showed a π change of 0.162 e and a σ change of 0.046 e, with a net change of 0.116 e. The changes in charge are summarized in Table 4. Thioformamide gives about twice the charge transfer that was found with formamide, and vinylamine gives an intermediate value.

It can be seen that the changes found on rotating about the C−N bond of thioformamide are closer to one's expectations from the simple amide resonance picture than are those for formamide:



There is a considerable transfer of π charge to the sulfur in the planar form, and the NH_2 resists out-of-plane bending distortions that would decrease the interaction in the dipolar canonical structure. Thus, it is the thioamides that best correspond to this picture, and the amides are significantly different.

Why is charge transfer from N to S important in thioamides whereas charge transfer from N to O is not very important in amides? There appear to be at least two important factors. The sulfur in the C=S bond has a relatively small charge whereas the oxygen of the C=O group has a relatively large negative charge, and consequently, the energetic cost of further polarization is quite large.[15] However, charge cannot be the only factor. The electronegativity of sulfur is close to that of carbon, and so one might expect similar amounts of charge transfer in vinylamine and thioformamide. However, this is not the case, and considerably more charge transfer is found with the thioamide. Thus, there is an important difference between first and second row substituents which makes sulfur able to accommodate additional charge transfer. It is likely that the large size of sulfur plays an important role. From a purely classical electrostatic point of view, it requires less energy to place a given quantity of charge on a large atom than on a small one.

It is important to distinguish between charge transfer to the terminal atom of the double bond during C−N bond rotation and the magnitude of the barrier. Charge transfer increases in the order formamide, vinylamine, thioformamide. The barriers, however, increase in the order vinylamine, formamide, thioformamide. Charge transfer from nitrogen to carbon in formamide is a major extra factor that contributes to the barrier.

3. Imino and Phosphimino Derivatives

Despite the importance of carbonyl polarization in determining the rotational barrier in formamide, a similar barrier was found with thioformamide which has much less polarization in its C=S bond. This is in contrast to vinylamine which also has an unpolarized double bond but has a low barrier to rotation. In order to gain additional information concerning the interactions in these compounds, it seemed desirable to further examine the role of the electronegativity of the atom double bonded to carbon in formamide analogs.[16]

Of the second row elements having lone pairs, P, S, and Cl, only S is a "conjugating" substituent. With PH_2 as the substituent it has been found that the planar forms of

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(14) The experimental C=O bond lengths in acetamide, acetic acid, acetyl chloride, and acetyl fluoride are 1.220, 1.209, 1.192, and 1.181 Å, respectively. (*Landolt-Börnstein, New Series*, Group II; Springer Verlag: Berlin, 1976; Vols. 7 and 15, 1982.) Calculated C=O bond lengths are given in ref 2. See also Wang, Q.-P.; Bennet, A. J.; Brown, R. S.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1991**, *113*, 5757, for a comparison of C=O bond lengths with the Hammett σ constants for the substituents.

(15) The carbonyl group does become further polarized when it is place in a polar medium in which the energetic cost of polarization is decreased: Wiberg, K. B.; Rablen, P. R. Unpublished results.

(16) Other recent studies of imino derivatives: Haefelinger, G.; Krygowski, M.; Kuske, F. K. H. *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 1480. Poirer, R. A.; Majlessi, D.; Zielinski, T. J. *J. Comput. Chem.* **1986**, *7*, 464. Bond, D.; Schleyer, P. v. R. *J. Org. Chem.* **1990**, *55*, 1003. Wang, X. C.; Nichols, J.; Feyereisen, M.; Gutowski, M.; Boatz, J.; Haymet, A. D. J.; Simons, J. *J. Phys. Chem.* **1991**, *95*, 10419. Aray, Y.; Murgich, J. *J. Chem. Phys.* **1992**, *97*, 9154. Wong, M.-W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

Table 3. Calculated (G2) Energy Changes

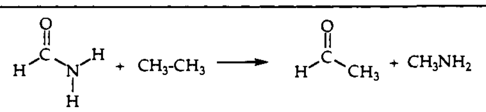
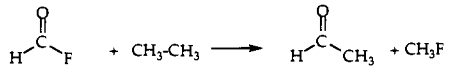
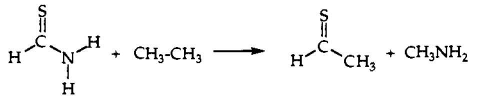
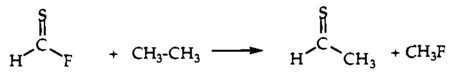
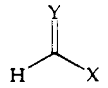
	ΔH_{react}	ΔH_{π}	ΔH_{σ}
 $HC(=O)NH_2 + CH_3\text{-}CH_3 \rightarrow HC(=O)CH_3 + CH_3NH_2$	+20.5	+16.0	+4.5
 $HC(=O)OH + CH_3\text{-}CH_3 \rightarrow HC(=O)CH_3 + CH_3OH$	+22.3	+11.5	+10.8
 $HC(=O)F + CH_3\text{-}CH_3 \rightarrow HC(=O)CH_3 + CH_3F$	+15.0	0.0	+15.0
 $HC(=S)NH_2 + CH_3\text{-}CH_3 \rightarrow HC(=S)CH_3 + CH_3NH_2$	+18.4	+18.0	+0.4
 $HC(=S)OH + CH_3\text{-}CH_3 \rightarrow HC(=S)CH_3 + CH_3OH$	+15.7	+12.3	+3.5
 $HC(=S)F + CH_3\text{-}CH_3 \rightarrow HC(=S)CH_3 + CH_3F$	+4.7	0.0	+4.7

Table 4. Charge Shifts for Group Y on Rotation about the C−X Bond, MP2/6-31+G*

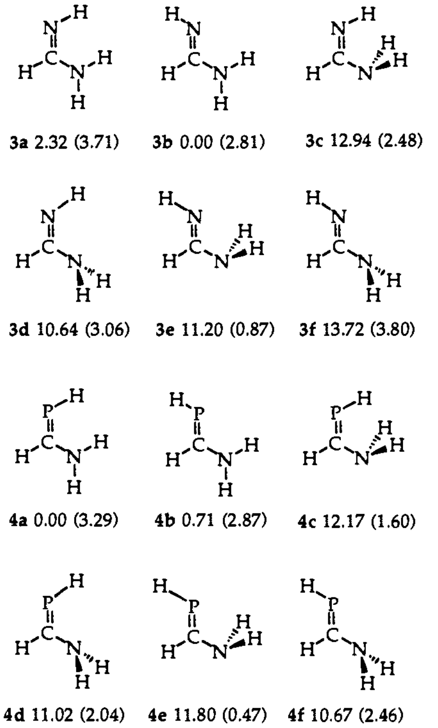


Y	X	π, e	σ, e	net, e
O	NH_2	−0.088	0.031	−0.057
NH	NH_2	−0.079	0.026	−0.053
S	NH_2	−0.162	0.046	−0.116
PH	NH_2	−0.151	0.052	−0.099
SiH_2	NH_2	−0.116	0.002	−0.114
CH_2	NH_2	−0.089	0.023	−0.066
O	OH	−0.058	0.016	−0.042
S	OH	−0.086	0.030	−0.056
CH_2	OH	−0.052	0.016	−0.036
CH_2	SH	−0.052	0.016	−0.036

$CH_2{=}CH{-}PH_2$[2,17] and CH_3COPH_2[2] are transition states, but with SH, the corresponding compounds are minima. With P, the lone pair is in an orbital with high s character, and the other bonds are made with orbitals that are mainly p as shown by the 95° bond angles at P in phosphine. The same would be true with S, but here, there is an additional lone pair that will be in an orbital with high p character and will be able to interact with a p orbital on an adjacent center. Chlorine does not act as a conjugating substituent because of its high electronegativity that leads to essentially no basicity for the lone pair electrons.

In contrast to the cases in which the lone pair participates in conjugation, it should be possible to have P as the acceptor of charge if a PH group were to replace the carbonyl oxygen in an amide. Therefore, we have examined these compounds, and for a suitable comparison, we have also examined the corresponding imino compounds. In these cases, there are additional conformations to be examined since the hydrogen attached to P or N could either be *syn* or *anti* to the amino nitrogen. The energies were first calculated at the MP2/6-31+G* level, and the relative energies are shown in Figure 3. The G2 energies of the lower energy ground state rotamers and of the corresponding transition states for rotation about a C−N bond also were obtained and are given in Table 5.

These compounds may conveniently be compared with formamide and thioformamide by using group separation reactions (Table 6). With formamidine, all three terms are much smaller than those for formamide. This must result from two related factors. The smaller electronegativity of nitrogen as compared to oxygen, and the consequent smaller polarization of its bond to carbon, weakens the electrostatic σ component. It also reduces the ability of the π system to accept charge from the amino nitrogen lone pair, thus reducing the rotational barrier and the π component of the stabilization energy. The phosphorus analog also has smaller energy terms than those found with thioformamide. Phosphorus is electropositive with respect to carbon and therefore would be less receptive to charge donation from nitrogen than is sulfur. As a result, one would expect less charge transfer and smaller π stabilization energies with these compounds. Furthermore, the polarization of the C=P bond is reversed compared to the C=O bond, and so electrostatic factors will *destabilize* negatively charged substituents such as the amino group in the σ component. As a result, one would predict slightly unfavorable σ energies; in fact they are essentially zero.



3a 2.32 (3.71) **3b** 0.00 (2.81) **3c** 12.94 (2.48)

3d 10.64 (3.06) **3e** 11.20 (0.87) **3f** 13.72 (3.80)

4a 0.00 (3.29) **4b** 0.71 (2.87) **4c** 12.17 (1.60)

4d 11.02 (2.04) **4e** 11.80 (0.47) **4f** 10.67 (2.46)

Figure 3. Geometries and relative energies of amidine conformers and their phosphorus analogs.

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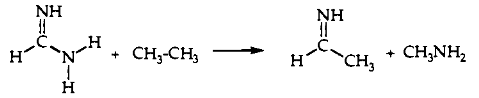
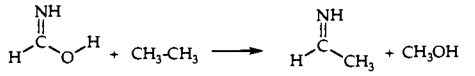
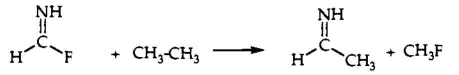
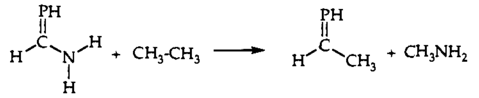
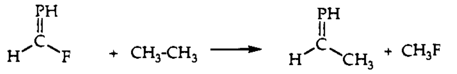
(17) Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399.

Table 5. Calculated Energies of =NH and =PH Analogs of Formamide

compound	conf[a,c]	MP2/6-31+G*	ZPE	μ	G2
$HC(=NH)NH_2$	gs, NH *syn* (**3a**)	−149.54963	35.2	3.71	
	gs, NH *anti* (**3b**)	−149.55358	35.3	2.81	−149.75456
	ts, NH *syn*, lp down (**3c**)	−149.53207	34.8	2.48	
	ts, NH *syn*, lp up (**3d**)	−149.53587	34.9	3.06	
	ts, NH *anti*, lp down (**3e**)	−149.53507	34.9	0.89	−149.73831
	ts, NH *anti*, lp up (**3f**)	−149.53079	34.8	3.80	
$HC(=PH)NH_2$	gs, PH *syn* (**4a**)	−435.75211	31.1	3.29	−435.97431
	gs, PH *anti* (**4b**)	−435.75148	31.3	2.87	
	ts, PH *syn*, lp down (**4c**)	−435.73264	31.0	1.60	
	ts, PH *syn*, lp up (**4d**)	−435.73434	30.9	2.04	−435.95640
	ts, PH *anti*, lp down (**4e**)	−435.73324	31.0	0.47	
	ts, PH *anti*, lp up (**4f**)	−435.73489	30.9	2.46	
$HC(=NH)OH$	gs, NH *syn*, OH *anti*	−169.39218	27.8	3.05	
	gs, NH *syn*, OH *syn*	−169.39232	28.0	2.24	
	gs, NH *anti*,OH *syn*	−169.39921	28.2	1.29	−169.62677
	gs, NH *anti*, OH *anti*	−169.38847	27.8	4.27	
	ts, NH *anti*	−169.38009	27.2	3.17	−169.61153
$HC(=PH)OH$	gs, PH *syn*, OH *anti*	−455.58523	23.9	2.63	
	gs, PH *syn*, OH *syn*	−455.58894	24.2	1.29	−455.83516
	gs, PH *anti*, OH *syn*	−455.58863	24.3	0.04	
	gs, PH *anti*, OH *anti*	−455.58442	23.9	3.49	
	ts, PH *syn*	−455.57612	23.2	1.75	−455.82497
$HC(=NH)F$	gs, NH *syn*	−193.38134	20.4	0.51	−193.63532
	gs, NH *anti*	−193.37832	20.4	3.28	
$HC(=PH)F$	gs, PH *syn*	−479.57033	16.5	0.61	
	gs, PH *anti*	−479.57044	16.5	1.96	−479.84327
$HC(=SiH_2)NH_2$	gs	−384.46641	35.2	1.86	−384.67884
	ts, lp *syn*	−384.45893	35.0	0.91	−384.67044
	ts, lp *anti*	−384.45570	34.9	1.98	−384.66788
$HC(=SiH_2)OH$	gs, *Z*[b]	−404.30138	27.6	1.62	−404.54040
	E[b]	−404.29972	27.1	1.60	−404.53995
	ts	−404.29607	27.1	1.94	−404.53568
$HC(=SiH_2)CH_3$	gs	−368.44457	41.5	0.26	−368.63665
$HC(=SiH_2)F$	gs	−428.28767	20.2	2.13	−428.55180
CH_3SiH_3	gs (C_{3v})	−330.50514	40.9	0.69	−330.65782
$HC(=SiH_2)SiH_3$	gs (C_s)	−619.45307	38.2	1.53	−619.67184

[a] *Syn* and *anti*, up and down are with respect to the other heteroatom. [b] The energies are given for the C_s structures. The true minima are slightly distorted, have C_1 symmetry, and are 0.03 to 0.06 kcal/mol lower in energy at the G2/MP2 level. [c] Entries in parentheses for $HC(=NH)NH_2$ and $HC(=PH)NH_2$ refer to Figure 3. gs refers to ground state and ts refers to transition state.

Table 6. Calculated (G2) Energy Changes

	ΔH_{react}	ΔH_{π}	ΔH_{σ}
	+13.1	+10.2	+2.9
	+15.6	+9.6	+6.0
	+9.0	0.0	+9.0
	+10.7	+11.2	−0.5
	+6.2	+6.4	−0.2
	−0.8	0.0	−0.8

The extent of charge transfer was calculated via integration of charge density difference maps as was done for formamide and thioformamide (Table 4). Again, almost twice as much charge transfer was found with the =PH derivative as compared to =NH; the amount of transfer to =PH is just slightly less than that to =S. Thus, there is a fundamental difference between first and second row substituents at the double bond.

In order to complete this series of substituents at the double bond, we also have examined the compounds in which the carbonyl oxygen has been replaced by CH_2 or SiH_2. Since silicon is significantly electropositive with respect to carbon, one might find some interesting differences between the two groups of compounds. The energies are included in Table 5, and the group separation reactions are summarized in Table 8. The latter are smaller for the silyl compounds than for the vinyl derivatives and become negative with fluorosilaethene. With the silyl compounds, the rotational barriers are larger than the group separation energies, making the ΔH_{σ} terms negative. This

Table 7. σ and π Components of the Group Transfer Energies, kcal/mol

Y	$X = NH_2$	$X = OH$	$X = F$
	σ Components		
O	+4.5	+10.8	+15.0
NH	+2.9	+6.0	+9.0
CH_2	+1.3	+2.3	+2.4
S	+0.4	+3.5	+4.7
PH	−0.5	−0.2	−0.8
SiH_2	−1.4	−3.1	−5.1
	π Components		
O	+16.0	+11.5	0.0
NH	+10.2	+9.6	0.0
CH_2	+5.1	+4.0	0.0
S	+18.0	+12.3	0.0
PH	+11.2	+6.4	0.0
SiH_2	+5.3	+3.0	0.0

is a result of the repulsion between the positively charged carbon of the carbonyl group and the positively charged silicon of the substituent.

The σ and π components of the group transfer energies are of some interest. They are summarized in Table 7. It can be seen that the σ components correlate well with the electronegativity of the substituents Y and X; the greater the electronegativity, the larger the value of ΔH_σ. This is reasonable in terms of the Coulombic interactions since they will be largest when the difference in charge between the central atom and the terminal atoms is large.

In the cases considered above, stabilization was observed when the central carbon had a positive charge and the attached groups had a negative charge. However, the effect also should be observed when the polarities are reversed. Carbon−silicon bonds are polarized $C^- - Si^+$, and therefore the energy of $HC(=SiH_2)SiH_3$ was calculated and its group separation energy with ethane was derived (Tables 5 and 8). It was found to be endothermic showing that the compound is stabilized. This stands in contrast to $HC(=SiH_2)F$ where the central carbon would be essentially neutral and the group separation reaction is exothermic. These interactions are similar to those we have previously noted in considering the stabilization of CF_4.[18] Here, the stability of polyfluorinated alkanes was attributed to the Coulombic interaction between the strongly positively charged carbons and the negatively charged attached fluorines. Similar stabilization was found with $C(SiH_3)_4$ despite its reversed polarity, and no stabilization was found with FCH_2SiH_3 where the central carbon is essentially neutral.

The π components operate differently. They decrease as the electronegativity of X increases since this leads to a reduction of the lone pair energies making them less available for a π interaction. They are larger with the second row Y substituents than with the first row for the reasons summarized above and in accord with the charge density integrations. The net result is that the π-energies are remarkably similar for O and S, for NH and PH, and for SiH_2 and CH_2, despite the large electronegativity differences in each of these pairs. The greater electronegativity of the first row elements as compared to the second row, and the greater ability of the second row atoms to accept charge apparently balance to yield this similarity in total π-interaction energies.

4. Charge Distributions and Bond Orders

Whereas the changes in charge distribution on rotation about the C−N bond can readily be examined for the terminal atom of the double bond (Figure 1), it has proven much more difficult to examine the charge shifts between the C and N. One way to try to examine these shifts makes use of atomic charges derived from the ab initio calculations. We have recently provided a detailed comparison among six different methods for deriving these charges.[19] Although the values were different between these several methods, the direction of charge shifts were generally the same when substituents were changed. The main case in which important differences were found was amides.

The charges calculated using the atoms in molecules (AIM) approach of Bader,[20] the natural population analysis (NPA) of Weinhold and Reed,[21] and the proatom based method of Hirshfeld[22] were obtained for formamide, thioformamide, and the =NH, =PH, $=CH_2$, and $=SiH_2$ analogs. There are some systematic differences in the way in which the methods handle C−H and N−H bonds.[19] This is not of interest in the present context, and therefore the data are presented for the groups in the molecules rather than for the individual atoms (Table 9).

Despite the differences in the calculated charges, perhaps the changes in charge on rotation about a C−N bond will be similar among the procedures. This is explored in Table 10. It can be seen that the changes for the terminal atom of the double bond are in the same direction and of similar magnitude for all of the procedures. Also, they agree that the changes are larger for S than for O and for PH than for NH. However, there is not agreement concerning the shift in charge density between C and N. The AIM charges suggest a significant shift in charge density from nitrogen to carbon in each case, whereas the shift at carbon is in the opposite direction with the NPA and Hirshfeld charges. It is not surprising that the AIM charges are different. Here, the charges assigned to carbon and nitrogen are in large measure determined by the location of the boundary between them (the zero-flux surface). The position of the boundary is strongly affected by the difference in electronegativity between the two atoms forming the bond. On going from the planar to the 90°-rotated form of an amide, the hybridization at nitrogen changes from approximately sp^2 to one having much less s character in order to be able to place the noninteracting lone pair in an orbital with as much s character as possible, leading to 106° H−N−H bond angles. Thus, the nitrogen is less electronegative in the transition state than in the ground state, and the boundary moves toward the nitrogen and away from carbon on going to the transition state. As a result, the electron population assigned to nitrogen decreases.

The Hirshfeld method does not partition the charge density in a manner that involves a surface that can move as the electronic structure of a molecule varies, and this will lead to a difference in the way the charges are assigned. The NPA method is also more constrained with respect to changes in atom sizes than is AIM. So, the difference among the methods is not a question of which is correct but rather results from a difference in interpretation concerning the nature of the bond.

What does the molecule "think" happens during rotation about a C−N bond? Here, we must again return to charge density difference maps because they alone can show the details of the changes in charge density. In preparation of such maps, one difficulty derives from the changes in charge density associated with the atoms being moved, which are the amino hydrogens in the present case. We have used methylamine as an example

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(18) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

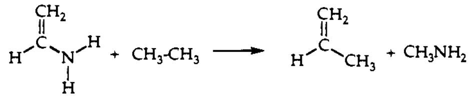
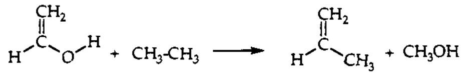
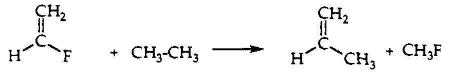
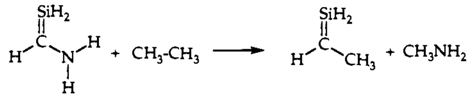
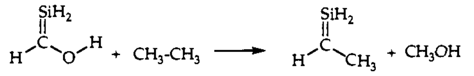
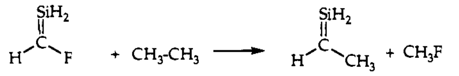
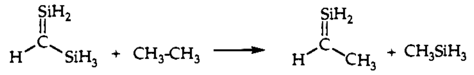
(19) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

(20) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*; Clarendon Press: Oxford, 1990. Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

(21) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem . Rev.* **1988**, *88*, 899.

(22) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129. Cf. Ritchie, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1829. Ritchie, J. P.; Bachrach, S. M. *J. Comput. Chem.* **1987**, *8*, 499. Davidson, E. R.; Chakravorty, S. *Theor. Chim. Acta* **1992**, *83*, 319.

Table 8. Calculated (G2) Energy Changes

	$\Delta H_{\mathrm{react}}$	ΔH_{π}	ΔH_{σ}
 $H_2C{=}CH{-}NH_2 + CH_3{-}CH_3 \longrightarrow H_2C{=}CH{-}CH_3 + CH_3NH_2$	+6.1	+5.1	+1.3
 $H_2C{=}CH{-}OH + CH_3{-}CH_3 \longrightarrow H_2C{=}CH{-}CH_3 + CH_3OH$	+6.3	+4.0	+2.3
 $H_2C{=}CH{-}F + CH_3{-}CH_3 \longrightarrow H_2C{=}CH{-}CH_3 + CH_3F$	+2.4	0.0	+2.4
 $H_2Si{=}CH{-}NH_2 + CH_3{-}CH_3 \longrightarrow H_2Si{=}CH{-}CH_3 + CH_3NH_2$	+3.9	+5.3	−1.4
 $H_2Si{=}CH{-}OH + CH_3{-}CH_3 \longrightarrow H_2Si{=}CH{-}CH_3 + CH_3OH$	−0.1	+3.0	−3.1
 $H_2Si{=}CH{-}F + CH_3{-}CH_3 \longrightarrow H_2Si{=}CH{-}CH_3 + CH_3F$	−5.1	0.0	−5.1
 $H_2Si{=}CH{-}SiH_3 + CH_3{-}CH_3 \longrightarrow H_2Si{=}CH{-}CH_3 + CH_3SiH_3$	+5.2	0.0	+5.2

of "normal" amino hydrogens in an attempt to minimize this problem. From the 3D charge density distribution of the transition state structure of formamide we have subtracted the charge density corresponding to a methylamine in which the atomic coordinates of the amino group, the carbon, and one of the methyl hydrogens exactly match those of the amino group, carbonyl carbon, and aldehydic proton of formamide. From the ground state of formamide we have subtracted the charge distribution of a similar methylamine with the atomic coordinates matching those of planar formamide. The two unconstrained hydrogens in the former case were held fixed in the latter. The final charge density difference was then obtained as the difference between these two modified formamide charge density distributions.

In this procedure, the charge density due to the methyl group of methylamine exactly cancels between the two modified amide rotamer charge distributions, and the amino hydrogens are largely canceled. Thus, the final difference density shows how the electronic structure in the vicinity of the C—N bond changes in response to rotation about this bond with little interference from the changing positions of the hydrogen atoms. The resultant 3D plots are shown in Figure 4 for both formamide and thioformamide.

The σ and π systems reflect opposite charge shifts at almost all points in space, in accord with much of our other experience. This is a result of electron repulsion. Thus, if π electrons move in one direction, the σ electrons will tend to move in the opposite direction in order to minimize the repulsion between the two groups of electrons.

As noted above, the changes in charge density at O and S are relatively simple. The change at nitrogen shows the depletion of π charge density in the planar form corresponding to charge transfer to carbon in the amide or to sulfur in the thioamide. In contrast to these atoms, the changes near the carbon are quite complex. On the O or S side, the carbon shows an increase in π-like charge density, whereas on the NH_2 side it shows a decrease in π-like charge density. In view of the complex nature of the interactions at carbon, it is not surprising that different methods of assigning electron populations at this atom lead to differing results.

The decrease in the π-region on the amino side of the carbon is consistent with the loss of nitrogen lone pair donation to this region on rotation away from the planar form. The increase on the other side is perhaps related to the C=O polarization. If the terminal oxygen or sulfur has additional π charge density in the ground state, it comes partially at the expense of the other end of the C=O or C=S bond. Thus, on rotation, the carbon may recover some of this charge density.

The regions in the plot for the thioamide are uniformly larger than those for the amide. This is most pronounced in the C=O and C=S regions but is also reflected in a larger deformation in the NH_2 regions for thioformamide than for formamide, in agreement with the larger barrier for the former. Qualitatively, the C—N regions have the same structure in the two compounds.

It is interesting to note that with formic acid and thioformic acid, in contrast to the amino-substituted compounds, the directions of the charge shifts for all three population methods are the same, and in the case of formic acid, all are relatively small. A difference between nitrogen and oxygen is that the latter has two lone pairs. This may minimize the need for net rehybridization during rotation about the C—O bonds. All methods agree that the charge shift to sulfur is greater than that to oxygen, in agreement with the larger barrier to C—N rotation in thioamides than in amides.

Bonding in the amides may conveniently be examined using the covalent bond orders calculated via the procedure developed by Cioslowski and Mixon (Table 11).[23] It must be remembered that they are covalent bond orders, and therefore, they will change when the charges at the atoms involved undergo changes. The total bond order would be the sum of the covalent and ionic components, but it is not as yet possible to give a value to the ionic component.

In most cases, the C=Y covalent bond order increases on going to the transition state for C—X bond rotation, and correspondingly, the C—X bond order decreases. This is in agreement with the additional polarization of the C=Y bond in the planar form and with the partial double bond character imparted to the C—X bond.

In the planar form, the nitrogen of the amides is sp^2 hybridized and uses more s character in its bond to carbon than in the rotated form where the hybridization is closer to p. This would tend to make the nitrogen more electronegative in the planar form, making the C—N bond more polar and decreasing the bond order. However, the opposite is observed so that the

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[23] Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

Table 9. Group Charges

compound	group	AIM	NPA	Hirshfeld
HC(=O)NH$_2$, planar	CH	+1.607	+0.637	+0.232
	O	−1.191	−0.601	−0.331
	NH$_2$	−0.415	−0.036	+0.100
HC(=O)NH$_2$, ts	CH	+1.448	+0.684	+0.280
	O	−1.136	−0.512	−0.262
	NH$_2$	−0.313	−0.171	−0.017
HC(=S)NH$_2$, planar	CH	+0.165	+0.056	+0.153
	S	+0.221	−0.090	−0.288
	NH$_2$	−0.385	+0.033	+0.137
HC(=S)NH$_2$, ts	CH	−0.102	+0.047	+0.169
	S	+0.398	+0.096	−0.149
	NH$_2$	−0.297	−0.142	−0.017
HC(=NH)NH$_2$, gs	CH	+1.287	+0.419	+0.171
	NH	−0.977	−0.366	−0.223
	NH$_2$	−0.409	−0.053	+0.052
HC(=NH)NH$_2$, ts	CH	+1.177	+0.431	+0.191
	NH	−0.850	−0.283	−0.161
	NH$_2$	−0.329	−0.147	−0.028
HC(=PH)NH$_2$, gs	CH	−0.227	−0.149	+0.071
	PH	+0.619	+0.171	−0.152
	NH$_2$	−0.391	−0.022	+0.083
HC(=PH)NH$_2$, ts	CH	−0.500	−0.218	+0.048
	PH	+0.828	+0.370	−0.027
	NH$_2$	−0.329	−0.153	−0.021
HC(=O)OH, *Z*	CH	+1.740	+0.786	+0.307
	O	−1.184	−0.573	−0.290
	OH	−0.554	−0.213	−0.017
HC(=O)OH, ts	CH	+1.692	+0.781	+0.307
	O	−1.137	−0.506	−0.249
	OH	−0.558	−0.275	−0.058
HC(=S)OH, *Z*	CH	+0.198	+0.193	+0.205
	S	+0.338	−0.020	−0.203
	OH	−0.536	−0.173	−0.002
HC(=S)OH, ts	CH	+0.096	+0.156	+0.191
	S	+0.452	+0.097	−0.141
	OH	−0.550	−0.253	−0.050
HC(=NH)OH, gs	CH	+1.452	+0.575	+0.221
	NH	−0.886	−0.363	−0.178
	OH	−0.570	−0.212	−0.043
HC(=NH)OH, ts	CH	+1.411	+0.541	+0.215
	NH	−0.835	−0.282	−0.152
	OH	−0.572	−0.259	−0.063
HC(=PH)OH, gs	CH	−0.146	−0.007	+0.114
	PH	+0.686	+0.202	−0.091
	OH	−0.540	−0.195	−0.023
HC(=PH)OH, ts	CH	−0.246	−0.054	+0.094
	PH	+0.796	+0.310	−0.031
	OH	−0.552	−0.260	−0.063
HC(=NH)F	CH	+1.502	+0.674	+0.281
	NH	−0.838	−0.290	−0.125
	F	−0.663	−0.384	−0.156
HC(=PH)F	CH	−0.163	+0.063	+0.137
	PH	+0.815	+0.306	−0.003
	F	−0.655	−0.369	−0.134
CH$_3$CH=NH	NH	−0.840	−0.279	−0.166
	CH	+0.758	+0.271	+0.128
	CH$_3$	+0.083	+0.009	+0.038
CH$_3$CH=PH	PH	+0.790	+0.389	−0.046
	CH	−0.865	−0.353	+0.011
	CH$_3$	+0.077	+0.009	+0.037

Table 10. Shift on Rotation, Planar-Rotated

	group	AIM	NPA	Hirshfeld
HC(=O)NH$_2$	CH	+0.159	−0.047	−0.049
	O	−0.055	−0.089	−0.069
	NH$_2$	−0.102	+0.135	+0.117
HC(=S)NH$_2$	CH	+0.267	+0.009	−0.016
	S	−0.177	−0.186	−0.139
	NH$_2$	−0.088	+0.175	+0.154
HC(=NH)NH$_2$	CH	+0.111	−0.012	−0.019
	NH	−0.027	−0.083	−0.062
	NH$_2$	−0.080	+0.094	+0.080
HC(=PH)NH$_2$	CH	+0.273	+0.069	−0.023
	PH	−0.209	−0.199	−0.125
	NH$_2$	−0.062	+0.131	+0.104
HC(=O)OH	CH	+0.048	+0.005	0.000
	O	−0.047	−0.067	−0.041
	OH	+0.004	+0.062	+0.041
HC(=S)OH	CH	+0.102	+0.037	+0.014
	S	−0.114	−0.117	−0.062
	OH	+0.014	+0.080	+0.048
HC(=NH)OH	CH	+0.041	+0.034	+0.006
	NH	−0.051	−0.081	−0.026
	OH	+0.002	+0.047	+0.020
HC(=PH)OH	CH	+0.100	+0.047	+0.020
	PH	−0.110	−0.112	−0.060
	OH	+0.012	+0.065	+0.040

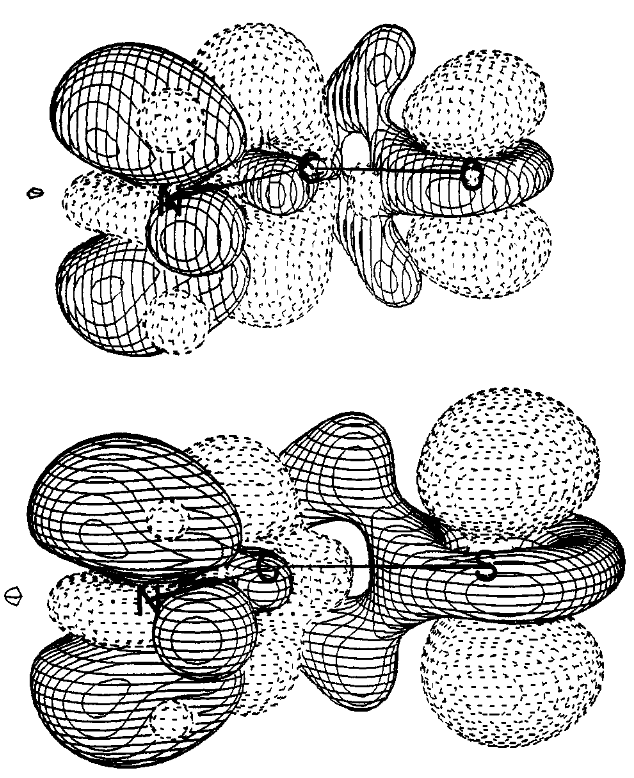

Figure 4. Charge density difference plots for formamide (rotated-planar) (upper) and thioformamide (lower) showing the changes that occur at the central carbon and the nitrogen.

influence of the lone pair π interaction with the carbon, which increases the bond order, is apparently dominant.

With the compounds having C=NH or C=PH bonds, the covalent bond orders are uniformly 1.5−1.6, and they change relatively little on rotation about the C−X bonds. It is interesting to note that whereas the bond order increases slightly for the C=NH derivatives, it decreased slightly for the C=PH compounds. This is despite relatively similar rotational barriers in the two series.

5. Calculations

All ab initio calculations were performed using a development version of Gaussian 93,[24] and NPA charges[21] were obtained using the built-in capabilities of this program. Charge densities were calculated, subtracted, and visualized using the CASGEN package of programs written at Yale. The difference density plots illustrating the effects of bond rotation were obtained at the MP2(fc)/6-31+G* level of theory, with partially modified geometries for the transition states. The ground state for each molecule was optimized at the MP2(fc)/6-31+G* level with respect to all degrees of freedom. The torsional transition state was then calculated at the ground state geometry, with only the atoms of the rotating group permitted to move. For instance, in the case of formamide, only the N−H bond lengths, the C−N bond length and the HNC bond angles were optimized, while the formyl group remained frozen at the ground state geometry.

Table 11. Covalent Bond Orders, MP2/6-31+G*

	C=Y	C−X	Δ(C=Y)	Δ(C−X)
HC(=O)NH$_2$, planar	1.271	1.019		
HC(=O)NH$_2$ ts	1.369	0.901	0.098	−0.118
H$_2$C=O[a]	1.453			
HC(=S)NH$_2$, planar	1.874	1.183		
HC(=S)NH$_2$, ts	1.993	1.046	0.119	−0.137
H$_2$C=S[a]	2.017			
HC(=NH)NH$_2$, gs	1.513	1.005		
HC(=NH)NH$_2$, ts	1.554	0.953	0.041	−0.052
H$_3$CCH=NH	1.590			
HC(=PH)NH$_2$, gs	1.556	1.118		
HC(=PH)NH$_2$, ts	1.537	1.056	−0.019	−0.062
H$_3$CCH=PH	1.558			
HC(=O)OH, gs	1.286	0.861		
HC(=O)OH, ts	1.336	0.806	0.050	−0.055
HC(=S)OH, gs	1.948	1.006		
HC(=S)OH, ts	1.989	0.926	0.041	−0.080
HC(=NH)OH, gs	1.505	0.860		
HC(=NH)OH, ts	1.530	0.807	0.025	−0.053
HC(=PH)OH, gs	1.563	0.978		
HC(=PH)OH, ts	1.548	0.932	−0.015	−0.046
HC(=NH)F	1.563	0.734		
HC(=PH)F	1.539	0.842		

[a] For H$_2$CS the bond critical point is 1.876 Å from the C and 1.180 Å from the S indicating that C is somewhat more electronegative than S. For H$_2$CO the bond critical point is 1.551 Å from the O and 0.762 Å from the C indicating that C is much less electronegative than O.

With formic acid, only the O−H and C−O bond lengths, the HOC bond angle, and the HOCO torsional angle were allowed to vary. The small energetic cost of these geometric restraints compared to the magnitude of the rotational barrier justifies this procedure. It is necessary so as to avoid large shifts in charge density resulting only from the movement of nearby nuclei, rather than from the transmission of electronic changes in more remote parts of the molecule.

Difference densities were "edited" prior to visualization to remove the large changes occurring in the immediate vicinity of the moving atoms using a program BLBZER, also written at Yale. The difference density was "erased" (set to zero) for all points in a three-dimensional grid which could be reached from a particular starting point without crossing any contours representing a difference density less than 0.001 90. The nuclear coordinates of the moving hydrogen atoms were used as starting coordinates, and in some cases additional origins were required as well.

Integration of the charge density in the regions shown in the difference density plots was accomplished using a program BLBINT (written at Yale) and a methodology described previously.[25] The difference density was summed for all points in a three-dimensional grid which could be reached from a particular starting point without crossing any contours representing a difference density less than a given cutoff value. The starting point was generally chosen as the nuclear coordinates of a given atom for the σ region and one bohr above or below the atom for the π regions. This procedure was carried out separately for the σ and π regions of each compound using a standard series of cutoff values.[26] The results were then plotted against the cutoff value, and a quadratic equation was fit to the set of points corresponding to each region (σ or π) of each compound. The final integrations reported are the y-intercepts of the fitted polynomials; i.e., they represent an extrapolation of the calculated values to a hypothetical contour cutoff value of zero.

AIM charges were obtained using the PROAIM package,[27] and bond orders were calculated using a modified version of the program BONDER.[28] Hirshfeld charges were calculated using a program HIRSHD written at Yale, using proatoms defined in the manner described previously by us[19] and by others.[29]

6. Conclusions

Thioformamide is characterized by having a larger rotational barrier and a stiffer out-of-plane amino wagging potential than formamide. This is accompanied by considerably more charge transfer from nitrogen to sulfur in the thioamide than from nitrogen to oxygen in amides. The difference arises from the large charge transfer from carbon to oxygen in a carbonyl group and the small charge transfer in a thiocarbonyl group. In the amides, the carbonyl carbon is electron deficient, and the nitrogen lone pair interacts with the carbon leading to C−N double bond character. In the thioamide, the carbon is not electron deficient, and the uncharged and large sulfur may accept charge density from the nitrogen.

In the molecules of the type HC(=Y)X, the intramolecular stabilizing interactions are of two types. If both X and Y are electronegative (or electropositive) with respect to carbon, the resulting charge distribution will lead to internal Coulombic interactions that result in stabilization. The larger the difference in electronegativity between the substituents and carbon, the larger the stabilization. Little stabilization is found when one of the substituents is electronegative and the other is electropositive. The second type is a π interaction which is related to the rotational barrier. This is favored by relatively weakly bound (i.e., basic) lone pair electrons.

The amount of charge transfer to the terminal atom of the double bond and the magnitude of the rotational barrier in compounds of the type HC(=Y)X are not well correlated. The amount of charge transfer increases by a factor of 2 if Y is a second row element rather than first row but varies relatively little along a given period. The rotational barriers change drastically along a period as the electronegativity of Y varies but are relatively similar between the first and second rows. However, both the magnitudes of the barriers and the quantity of charge transfer are greater for X = NH$_2$ than for X = OH.

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[26] The standard contour cutoff values were 0.005 00, 0.004 50, 0.004 00, 0.003 50, 0.003 00, 0.002 50, 0.002 00, 0.001 75, 0.001 50, 0.001 25, 0.001 00, 0.000 80, 0.000 60, and 0.000 40 electrons per cubic bohr. However, not all of these values could be used with all of the compounds. As the cutoff value declines, eventually the regions of interest become contiguous with other, unrelated regions of the difference density grid. This is evidenced by a discontinuity in the integration value as the contour is gradually lowered and indicates that the value is no longer meaningful in the intended manner. This is the reason why one must extrapolate to an effective zero contour rather than perform a direct calculation with an exact zero contour. For each compound, all the cutoff values in the list given above which maintained the integrity of the region of interest were used.

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