Supporting Information for

## Importance of Electronic Delocalization on the C-N Bond Rotation in HCX(NH<sub>2</sub>) (X=O, NH, CH<sub>2</sub>, S and Se)

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## S1. Natural atomic orbital population analysis.

We have used Weinhold's natural atomic orbital (NAO) population analysis, which is not very sensitive to the choice of basis sets, to evaluate atomic charges for the adiabatic and diabatic states for the series of compounds, HC(=X)NH<sub>2</sub>, where X = O, S, Se, NH, and CH<sub>2</sub>. The population on the  $\pi$  AOs (P<sub>n</sub>) as well as the overall partial charge (q<sub>overall</sub>) for various atoms are given in Table S1. In the present BLW localization scheme, the NAO charge population of the nitrogen p<sub>n</sub> orbital in the diabatic states should be two. However, since partial atomic charge is not a physical observable, there is always some arbitrariness in a population analysis scheme, which can lead to slight deviation from the integer number. We note that the deviation from a total population of two in the BLW wavefunction (Table S1) is relatively small (about 0.03 e), suggesting that the BLW method is appropriate for the present analysis.

The NAO populations of the delocalized wave functions from HF calculations listed in Table S1 reveal that in the four planar structures, the  $\pi$  charges are shifted from nitrogen to the C=X group with X being S, Se, C or N. It is interesting to note that there is a nearly equal sharing of the gain in charge density by C and X in this series. The exception is for formamide, in which the carbon and oxygen shares are 64% and 36%, respectively. Furthermore, Glendening and Hrabal suggested that the higher polarizability of the heavier chalcogen facilitates the reverse  $\pi^*_{CX}$  polarization, leading to enhanced delocalization from the nitrogen lone pair to the carbonyl group. This is consistent with the NAO population results in Table S1 at the nitrogen atom for the planar structure **A**, which shows a decrease in population in order of increasing resonance energy (Table S1): HCONH<sub>2</sub> (1.810 e) > HCSNH<sub>2</sub> (1.726 e) > HCSeNH<sub>2</sub> (1.707 e). For the 90° rotamers, because  $\pi$  conjugation is absent, the computed nitrogen lone pair populations are close to two both from the HF and BLW calculations. The difference in charge

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population between the HF and BLW wave functions is due to the existence of a negative hyperconjugation in the HF calculation, which is turned off is the BLW calculation.

## S2. Geometrical valations.

The electronically delocalized and localized structures are determined respectively by the Hartree-Fock and block-localized wavefunction method. As defined in the text, the delocalized and localized structures for the planar configuration are **A** and **B**, and they are **C** and **D** for the 90° rotamer. The pyramidal transition structure is denoted as **E**, which was only determined at the Hartree-Fock level. All geometry optimizations described in this section are carried out using the 6-31G(d) basis set. A further note on the optimization details is that in the BLW optimization, only the C=X and the C-N bond lengths are optimized with the remaining structural parameters fixed at the corresponding HF values. Listed in Table S2 are the optimal C=X and C-N bond lengths in HCXNH<sub>2</sub> (X = O, S, Se, NH and CH<sub>2</sub>).

The comparison between bond lengths in **A** and **B** reveals that  $\pi$  conjugation results in the shortening of the CN bond and the lengthening of the CX bond, reflecting the enhancement of the CN bond order and weakening of the C=X bond order. Due to the high force constant in the CX double bond, the variation of the CX bond is less pronounced than that of the CN bond when the  $\pi$  conjugation is turned off. This has been noted by Fogarasi and Szalay,<sup>11</sup> who compared experimental and theoretical results. Specifically, our results reveal that the resonance in the planar formamide shortens the CO bond by 0.017Å and lengthens the CN bond by 0.069Å. Consequently, the small change in the carbonyl bond distance as a result of the C-N bond can not provide a good indication of the resonance effect in formamide. On the other hand, the CN bond has larger variations following the electronic delocalization between the amino group and the carbonyl group. In fact, the CN bond distance is well correlated with the magnitude of the

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electronic delocalization. Specifically, selenoformamide has the greatest conjugation effect of the five molecules considered, which also corresponds to the largest CN bond shortening of 0.099Å. For the weakly conjugated vinylamine, the variation of the bond lengths between **a** and **b** is the smallest with a decrease of 0.063Å in the CN bond length.

For the strictly localized structure **b**, the CN bond length corresponds to a pure  $C(sp^2)$ - $N(sp^2)$  single bond. Interestingly, the bond lengths in the localized forms of formamide, thioformamide and selenoformamide are all essentially the same. Although the variation of the CN bond length in the formamide, formamidine and vinylamine series is small, it may be related directly to the "steric" repulsion between atom X and the amino group, specifically between the two CX bond  $\pi$  electrons and the nitrogen lone pair. This can be verified by the energy term  $\Delta E_2$ , which is noticeably different in the HCXNH<sub>2</sub> (X=O, NH and CH<sub>2</sub>) series, compared with the modest changes in the X=O, S and Se series. The positive  $\Delta E_2$ 's demonstrate that the repulsive interaction between the nitrogen lone pair and the adjacent CH and CX  $\sigma$  bonds in the twisted structures is greater than the repulsion between the N lone pair and the CX  $\pi$  bond. The overall "steric" effect upon rotation around the C-N bond results from the competition between the above two factors. Thus, the higher the CX  $\pi$  bond polarization, the lower the repulsion between the  $\pi$  bond and the nitrogen lone pair in the planar localized structure and consequently, the higher the "steric" effect, upon rotation. For the series of X=O, NH and CH<sub>2</sub>,  $\Delta E_2$  decreases remarkably from 12.0 kcal/mol to 3.9 kcal/mol in the order of O > NH > CH<sub>2</sub>, in accord with the single CN bond lengths in **b**. Due to the relief of the repulsion between the  $\pi$  electrons on the CX bond and the amino group in the twisted structure c, the CX bond lengths shorten in thioformamide and selenoformamide, where the CX bond force constants are lower than in the

other systems. The variation of the **b**-**c** bond lengths again highlights the sensitivity of the central bond length to the "steric" effect. The CX bond lengths in the localized twisted HCXNH<sub>2</sub> **c** are always shorter than those in H<sub>2</sub>CX (which are 1.184Å, 1.598Å, 1.725Å, 1.251Å and 1.317Å for X=O, S, Se, NH and CH<sub>2</sub> optimized at the same HF/6-31G(d) level, respectively). These findings support Wiberg's statement<sup>7</sup> that the substituents attached to the carbonyl group withdraw charge density from the carbonyl carbon inductively via the  $\sigma$  bond and increase the carbon positive charge as well as the internal Coulombic attraction of the carbon for the negatively charged carbonyl oxygen. An ultimate example is provided by the acetyl fluoride. The HF/6-31G(d) C=O bond length (1.164Å) in acetyl fluoride is even shorter than that in formaldehyde (1.184Å), even though the fluoride lone pairs, delocalize over the entire molecule, should have lengthened the C=O bond. Our BLW calculations give a C=O bond length 1.155Å in the strictly localized acetyl fluoride,<sup>30</sup> which proves that the induction effect of fluorine is effective in shortening the CO bond.

The 90°-twisted structures benefit from hyperconjugation between the  $\pi$  electrons on the CX bond and the amine group (Type **A** in Fig.2) as well as the negative hyperconjugation from the nitrogen lone pair to the CHX fragment (Type **B** in Fig.2). Hence, if both effects are not "turned off", a shorter CN bond in the localized diabatic states will result, as suggested by the comparison between the present work and that of Lauvergnat and Hiberty.<sup>14</sup> By turning off only the negative N(donor)→CX hyperconjugation (**B**), Lauvergnat and Hiberty found that the CN bond lengths in the localized twisted structures of formamide and thioformamide are 1.441Å and 1.440Å, respectively, which are shorter than our results 1.459Å and 1.460Å. The other optimal bond lengths are in reasonable agreement (the discrepancies are less than 0.006Å).

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The hyperconjugation effects in the twisted structure also shorten the CN bond distance, and slightly lengthen the CX separation, although the changes are smaller than that in the planar structures. Our calculations show that such hyperconjugation effects are significant in all five systems ( $\Delta E_3$  in Table 5). In HCXNH<sub>2</sub> (X=O, S and Se), the hyperconjugation stabilization is about half of the conjugation energy in the corresponding planar structure, while in vinylamine or formamidine the hyperconjugation energy is more than half the conjugation energy. The charge redistribution accompanying the hyperconjugation interaction counterbalances the effect of  $\pi$  conjugation, reducing the magnitude of partial charge on the carbonyl oxygen. Thus, population analyses alone may not give conclusive information about the conjugation effect.

The nitrogen atom tends to be pyramidal in all twisted structures. Apart from vinylamine, the pyramidalization of the nitrogen atom stabilizes the staggered structures by c.a. 7.0 kcal/mol, higher than the inversion barrier 5.8 kcal/mol in NH<sub>3</sub> determined experimentally.<sup>31</sup> This suggests that the pyramidalization in HCXNH<sub>2</sub> not only stabilizes the lone nitrogen pair of electrons, but also decreases the repulsion between the lone pair and the adjacent HCX fragment. This repulsion is absent in NH<sub>3</sub>. The relative low pyramidalization energy in vinylamine may have the same origin as for  $\Delta E_2$ , e.g., the unpolarized C=C  $\pi$  bond is more repulsive towards the NH<sub>2</sub> group than the other cases. This is shown by the ∠CNH angle in the twisted HCXNH<sub>2</sub> structure **e**. In the optimal twisted vinylamine, the ∠CNH angle is 111.1°, larger than in the other twisted systems (108.5°, 109.0°, 109.2° and 109.0° for formamide, formamidine, thioformamide, and selenoformamide, respectively). The pyramidalization also corresponds to the change of the hybridization of nitrogen from sp<sup>2</sup> to sp<sup>3</sup>, which lengthens the CN bond but influences the CX separation negligibly. The lengthening of the CN bond is almost the same (about 0.024Å) for the five systems.

Concluding this section, we note that the rotational barrier about the C-N bond is not a direct measure of the  $\pi$  interactions. However, the resonance energy is similar in magnitude to the rotational barrier because of a fortuitous cancellation of the "steric", hyperconjugation and relaxation energy terms. Furthermore, the extremely low rotational barrier in vinylamine can not be fully attributed to the resonance energy in its planar conformation. In fact, compared with formamide and thioformamide, the very low steric effect ( $\Delta E_2$ ) in vinylamine, which is directly related to the negligible polarization of the C=C bond, is responsible for half of the low overall rotational barrier in vinylamine.

Table S1. Computed Weinhold natural atomic orbital population (P) and partial charges (q) from the delocalized state ( $\Psi^{HF}$ ) And the localized state  $(\Psi^{BLW})$ . Units are given in electrons.

	Planar ge $\psi^{\mathrm{HF}}$	Planar ge	Q	metry 2	<b>I</b> BLW		6	°-twisted	geometr $\Psi$	y d	Perp.	geom. e
	1	÷		÷		l	Ť		÷			
		$P(\pi)$	qtotal	$P(\pi)$	$\mathbf{q}_{\mathrm{total}}$		$P(\pi)$	qtotal	$P(\pi)$	qtotal	$P(\pi)$	qtotal
	z	1.810	-0.928	1.971	-1.054		1.960	-1.045	1.989	-1.065	-	-0.998
$\mathbf{H}_2$	C	0.676	+0.673	0.572	+0.765		0.669	+0.673	0.655	+0.701	0.649	+0.674
	0	1.514	-0.703	1.456	-0.664		1.349	-0.589	1.350	-0.589	1.380	-0.616
	Z	1.726	-0.842	1.967	-1.032		1.963	-1.009	1.992	-1.029	/	-0.955
$\mathbf{I}_2$	U	0.756	+0.013	0.628	+0.125		0.830	-0.056	0.814	-0.036	0.797	-0.053
	S	3.518	-0.235	3.406	-0.142		3.188	+0.019	3.191	+0.025	3.235	-0.020
	Z	1.707	-0.833	1.965	-1.038		1.962	-1.008	1.993	-1.029	-	-0.955
$H_2$	U	0.744	-0.036	0.611	+0.082		0.848	-0.127	0.832	-0.106	0.811	-0.123
	Se	9.549	-0.203	9.424	-0.098		9.169	+0.084	9.173	+0.091	 9.223	+0.042
	Z	1.838	-0.912	1.974	-1.018		1.959	-1.002	1.990	-1.022	/	-0.960
$NH_2$	C	0.800	+0.381	0.725	+0.445		0.843	+0.341	0.832	+0.364	0.817	+0.347
	Z	1.362	-0.815	1.301	-0.771		1.169	-0.665	1.172	-0.669	1.204	-0.706

-0.939	72 +0.003	41 -0.454
	0.0	1.0
-1.002	+0.017	-0.432
1.992	0.986	1.016
-0.985	-0.000	-0.420
1.966	0.995	1.009
-0.992	+0.105	-0.542
1.978	0.869	1.153
-0.908	+0.065	-0.583
1.868	0.920	1.212
Z	U	U
	HCCH <sub>2</sub> NH <sub>2</sub>	

	a	b	с	d	e
Х	R <sub>CX</sub> R <sub>CN</sub>				
0	1.193 1.349	1.176 1.418	1.175 1.459	1.182 1.405	1.183 1.427
S	1.641 1.324	1.602 1.417	1.590 1.460	1.604 1.399	1.606 1.422
Se	1.778 1.318	1.727 1.417	1.712 1.460	1.733 1.397	1.734 1.421
NH	1.258 1.356	1.241 1.424	1.243 1.455	1.250 1.400	1.248 1.425
$CH_2$	1.325 1.371	1.312 1.434	1.312 1.464	1.318 1.409	1.316 1.428

**Table S2.** Optimal CX and CN bond lengths (Å) in delocalized and localized structures with the 6-31G(d) basis set