Molecular Hardness, Polarizability and Valency Variation of Formamide and Thioformamide on Internal Rotation: A Density Functional Study

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The variations of hardness, polarizability, and valency of formamide and thioformamide on internal rotation are studied through calculations using the Kohn−Sham version of spin-polarized density functional theory. It is observed that a minimum energy structure is associated with maximum hardness and maximum molecular valency. Also the calculated C−N bond order is found to be larger in thioformamide in the energetically more stable planar structure which is consistent with its higher rotational barrier. The observation that the preferable protonation site is at the oxygen (sulfur) atom and not the nitrogen atom in formamide (thioformamide) is explained through the calculated Fukui reactivity indices.

1. Introduction

The concepts of electronegativity[1] and hardness[2] are two important concepts that have been used extensively over the years for rationalization and prediction of various aspects of chemical binding and reactivity of molecules. Defined respectively as the first[3] and second[4] derivatives of energy (E) with respect to the number of electrons (N), these two parameters essentially determine the response of an atom or molecule to the change in the number of electrons at fixed external potential. Polarizability of a species, on the other hand, is determined by the response due to the change in external fields at fixed N. Interconnection[5,6] between these two different response functions have now been established and efficient schemes[6] for simultaneous calculation of polarizability and hardness parameters have been proposed. The inverse relation of hardness and polarizability, in fact, has been known,[7,8] and recently, maximum hardness[9] and minimum polarizability[10,11] have been associated with greater stability of a species.

Recently, there have been two important developments in this area. The concept of electronegativity has been provided[12] with a rigorous foundation using the framework of density functional theory[13] (DFT) and a new quantitative definition[4] of hardness[2] has been proposed. This second parameter has since been proved to be very useful in any electronegativity based approach.[5,6,14,15] Although the qualitative concepts of hard and soft acids and bases have existed almost for 30 years, it is the quantification of these concepts that has rejuvenated[5,6,14−19] this area of research.

In recent years, the concept of hardness has attracted renewed attention for the study of chemical reactions after the discovery of the principle of maximum hardness[9] and it has been shown[16−19] that the hardness profile along a reaction path passes through a minimum near or at the transition state for various types of reactions such as inversion, exchange, deformation, and isomerization. Along the lines of maximum hardness, there is already indication for a principle of maximum molecular valency.[18] For example, recent studies have shown[18] that the molecular valency reaches its minimum value at the transition state for isomerization type of reactions and maximum value at the equilibrium configuration for normal modes of vibrations and internal rotations. The correspondence between the variations of hardness, polarizability, molecular valency and various energy components has also recently been investigated as a function of the reaction coordinate or the bond distortion in simple molecules.[10,18−21] Interesting correlations between electronegativity, hardness, polarizability and size have also been shown[7,8] to exist. Recently, a local version of the hard and soft acid and base (HSAB) principle has been postulated,[22] and in conjunction with the Fukui function, has been applied to chemical reactivity.

Internal rotation in biologically important molecules like amides has been of considerable current interest and an investigation through the variation of hardness, polarizability and valency is likely to provide much insight.

The amide group is a very important functional group in proteins and the hindered rotation about the C−N bond of amides is central to different conformations of peptides and proteins and is intimately linked with many of the associated biological activities. One of the most popular explanations of the hindered rotation has been provided by the so-called resonance model which ascribes the stabilization of the planar structure of the amides to an effective electron delocalization from the nitrogen to the oxygen atom and the consequent partial double bond character of the C−N bond accounts for the barrier to internal rotation around this bond. Formamide and thioformamide, being the simplest amides, have been subjected to several investigations[23−27] recently, and an attempt has been made to correlate the calculated rotational barriers with the charge transfer between different atoms in planar and rotated conformations.

Although the calculated rotational barriers in these amides have been reported with reasonable accuracy, the explanation through the resonance model has been subjected to criticism, particularly after the studies of internal rotation in thioformamide,[25−27] obtained by replacing the oxygen atom of formamide by the less electronegative sulfur atom. While the resonance model predicts higher barrier for the amide due to higher electronegativity of the oxygen atom and hence higher charge transfer and higher bond order of the C−N bond, experimental as well as calculated results predict larger barrier for thioamide

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in comparison to the amide. This as well as several other controversies regarding the resonance model have prompted several theoretical investigations in the recent past on the origin of rotational barrier in these two compounds. Recently, Laidig and Cameron[27] have proposed a Fermi hole model as a measure of electron delocalization in an attempt to provide insight into this problem.

In all these proposed models as well as various other interpretive aspects, the partial atomic charges and several other quantities that are known to play important role[28] are intimately linked with the concept of electronegativity, hardness, etc. Thus, in the present work, our aim has been to study the variation of calculated molecular hardness, polarizability, and valency as well as bond order and also the atomic Fukui indices during internal rotation and to explain the observed larger rotational barrier in thioformamide. Another aspect that we have considered is the protonation of the two amides. The protonation site as well as the relative magnitudes of the associated energy changes in these two molecules are rationalized in terms of the Fukui reactivity indices calculated here. For the present studies, we have employed density functional theory, which has been well-known as a versatile tool not only for the investigation of electronic structure[13] of atoms, molecules, and solids but also for providing foundation[29] to many widely used chemical concepts.

2. Theory and Computational Method

In DFT, the energy of a many-electron system is expressed as a functional of the single particle electron density $\rho(\boldsymbol{r})$, viz.

$$E[\rho] = \int d\mathbf{r}\, \upsilon(\mathbf{r})\, \rho(\mathbf{r}) + F[\rho] \tag{1}$$

and for a fixed external potential $\upsilon(\boldsymbol{r})$, the energy functional $E[\rho]$ assumes a minimum value for the true density. Here $F[\rho]$ is a universal functional of density, but due to lack of knowledge of its exact form, one has to introduce approximations for practical calculations. In the Kohn−Sham[30] version for density calculation scheme, $F[\rho]$ is expressed as a sum of three components, of which the classical electrostatic contribution is expressed exactly in terms of density, a noninteracting kinetic energy functional is also evaluated exactly and only the remaining exchange−correlation (XC) energy component is approximated. In the spin-polarized version of DFT, the up and down-spin electron densities $\rho_\alpha(\boldsymbol{r})$ and $\rho_\beta(\boldsymbol{r})$, where $\rho(\boldsymbol{r}) = \rho_\alpha(\boldsymbol{r}) + \rho_\beta(\boldsymbol{r})$, are the basic variables and the energy functional is minimum for true values of these two density components.

For an N-electron system, the energy minimization leads to the Kohn−Sham equations[30] for the spin orbitals (with $i = 1$ to N) given by (atomic units are used throughout)

$$\left[-\frac{1}{2}\nabla^2 + \upsilon^{\sigma}_{\mathrm{eff}}(\mathbf{r},[\rho_\alpha,\rho_\beta])\right]\psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r}) \tag{2}$$

where $\rho_\sigma(\mathbf{r}) = \sum_i n_{i\sigma}\rho_{i\sigma}(\mathbf{r})$ and $\rho_{i\sigma}(\mathbf{r}) = |\psi_{i\sigma}(\mathbf{r})|^2$ with the occupation numbers $n_{i\sigma}$ satisfying $\sum_i n_{i\sigma} = N_\sigma$, where N_σ (for $\sigma = \alpha$ or β) denotes the number of up- or down-spin electrons. Here, the spin-dependent Kohn−Sham effective potential is given by

$$\upsilon^{\sigma}_{\mathrm{eff}}(\mathbf{r},[\rho_\alpha,\rho_\beta]) = \upsilon(\mathbf{r}) + \int \frac{d\mathbf{r}'\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu^{\sigma}_{\mathrm{XC}}(\mathbf{r};\,[\rho_\alpha,\rho_\beta]) \tag{3}$$

where the XC potential, $\mu^{\sigma}_{\mathrm{XC}}$ is given by the functional derivative $[\delta E_{\mathrm{XC}}[\rho_\alpha,\rho_\beta]/\delta\rho_\sigma(\mathbf{r})]$ of the XC energy functional $E_{\mathrm{XC}}[\rho_\alpha,\rho_\beta]$. The total energy is evaluated using the expression

$$E = \sum_\sigma \sum_i \epsilon_{i\sigma} - \frac{1}{2}\int\int \frac{d\mathbf{r}\, d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{XC}}[\rho_\alpha,\rho_\beta] - \sum_\sigma \int d\mathbf{r}\mu^{\sigma}_{\mathrm{XC}}(\mathbf{r})\rho_\sigma(\mathbf{r}) \tag{4}$$

where the XC energy functional $E_{\mathrm{XC}}[\rho_\alpha,\rho_\beta]$ is usually obtained by using local spin-density approximation[31] (LSD) or LSD with some nonlocal corrections (e.g., involving density gradients).

The electronegativity and hardness parameters which are defined in terms of the first and second derivatives of energy as $\chi = -(\partial E/\partial N)$ and $\eta = (^1/_2)(\partial^2 E/\partial N^2)$ respectively, and are conventionally obtained from the experimental values of the ionization potential (I) and the electron affinity (A) through the finite difference approximations given by

$$\chi = \frac{1}{2}(I + A) \tag{5}$$

$$\eta = \frac{1}{2}(I - A) \tag{6}$$

can now be obtained by evaluating the energy derivatives from the calculated total energies of any atom or molecule and its positive and stable negative ions. This however involves multiple calculations requiring solution of the Kohn−Sham equations for more than one value of N for a particular atom or molecule. Alternatively, one can also use the finite difference formulas with I and A approximated by suitable eigenvalues from a single Kohn−Sham calculation for the neutral species alone. The electronegativity and hardness parameters can thus be approximated in terms of the eigenvalues corresponding to the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) as

$$\chi = -\frac{1}{2}(\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}}) \tag{7}$$

$$\eta = -\frac{1}{2}(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) \tag{8}$$

While these two derivatives have played important role in the theory of chemical binding, DFT has also introduced other derivatives which are highly useful for explaining chemical reactivity. Thus, besides the partial atomic charges which are widely used for predicting reactivity, there are also other new reactivity indices, such as the Fukui function defined by Parr and Yang[32] as

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta\upsilon(\mathbf{r})}\right] = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_{\upsilon} \tag{9}$$

There is a derivative discontinuity associated with this quantity, as a consequence of which one can define the three quantities $f^{+}(\mathbf{r})$, $f^{-}(\mathbf{r})$, and $f^{0}(\mathbf{r})$ as the right, left, and average derivatives, respectively. Within the finite difference approximation, these quantities are given by

$$f^{+}(\mathbf{r}) = [\rho_{\mathrm{N}+1}(\mathbf{r}) - \rho_{\mathrm{N}}(\mathbf{r})] \tag{10}$$

$$f^{-}(\mathbf{r}) = [\rho_{N}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \tag{11}$$

$$f^{0}(\mathbf{r}) = \frac{1}{2}[\rho_{\mathrm{N}+1}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \tag{12}$$

where $\rho_N(\mathbf{r})$, $\rho_{N+1}(\mathbf{r})$, and $\rho_{N-1}(\mathbf{r})$ denote the electron densities

TABLE 1: Calculated Values of Total Energy, Hardness, Electronegativity, Polarizability, and Molecular Valency of Planar, *cis*- and *trans*-Formamide, and Thioformamide (All Quantities Are in Atomic Units except Those Indicated Otherwise)

	formamide			thioformamide		
properties	planar	*cis*	*trans*	planar	*cis*	*trans*
total energy[a]						
E_M	−169.8752	−169.8457	−169.8425	−492.7876	−492.7520	−492.7489
E_{M^+}	−169.4979	−169.4703	−169.4671	−492.4699	−492.4183	−492.4152
E_{M^-}	−169.7517	−169.7818	−169.7672	−492.7377	−492.7541	−492.7419
hardness (eV)	6.945	5.977	5.195	5.000	4.510	4.634
electronegativity (eV)	3.586	4.238	4.082	3.643	4.568	4.444
valency	6.328	6.175	6.175	6.121	5.967	5.939
polarizability[b]						
α	21.52	20.66	21.18	34.90	32.91	33.24
$\alpha_\perp$	12.23	15.94	16.01	17.18	20.87	20.82

[a] E_M, E_{M^+}, and E_{M^-} denote the total energies of the neutral molecule M and its positive (M^+) and negative (M^-) ions, respectively. [b] α and $\alpha_\perp$ denote respectively the average polarizability and its out-of-plane component.

of the neutral molecule and its negative and positive ions respectively. It may be noted that the symbols f^+ and f^- used here refer to increase and decrease of the number of electrons, respectively. This has been the standard convention for defining the Fukui function in the literature[13,32] although the subscripts "+" and "−" usually refer to loss and gain of electrons (increase and decrease of positive charge), respectively. While the position-dependent Fukui function provides a detailed picture, one can obtain an averaged information from the corresponding condensed Fukui functions on each atom employed by Yang and Mortier[33] as well as Lee et al.[34] by considering the charges on individual atoms. Thus the condensed Fukui function[33−35] on atom A is given by

$$f_A^+ = [q_A(N+1) - q_A(N)] \tag{13}$$

$$f_A^- = [q_A(N) - q_A(N-1)] \tag{14}$$

$$f_A^0 = \frac{1}{2}[q_A(N+1) - q_A(N-1)] \tag{15}$$

where $q_A(N)$ represents the gross charge on atom A in the molecule containing N electrons, and $[q_A(N+1)$ and $q_A(N-1)]$ denote the same for its negative and positive ions, respectively. These can be further approximated as

$$f_A^+ \approx q_A^{\mathrm{LUMO}}(N) \tag{16}$$

$$f^-{}_A \approx q_A^{\mathrm{HOMO}}(N) \tag{17}$$

$$f^0{}_A \approx \frac{1}{2}[q_A^{\mathrm{LUMO}}(N) + q_A^{\mathrm{HOMO}}(\mathrm{N})] \tag{18}$$

where $q_A^{\mathrm{LUMO}}(N)$ and $q_A^{\mathrm{HOMO}}(N)$ denote the gross charges on atom A contributed by the LUMO and HOMO of the N-electron neutral molecule.

The other quantity of interest is the molecular valency V_M defined as

$$V_M = \frac{1}{2}\sum_A V_A \tag{19}$$

where V_A, the valency of the atom A in the molecule, is essentially the diagonal element of the bond order matrix.

The polarizability can be calculated by solving the Kohn−Sham equations for the atom or molecule in the presence of different values of uniform external fields and considering the expansion of the calculated field-dependent dipole moment as

$$m_i(\mathbf{F}) = m_i + \sum_j \alpha_{ij} F_j + \frac{1}{2}\sum_{j,k} \beta_{ijk} F_j F_k \tag{20}$$

where m_i, α_{ij}, and β_{ijk} denote, respectively, components of the permanent dipole moment, dipole polarizability, and the first dipole hyperpolarizability, respectively. The polarizability components α_{ij} can easily be obtained from least-squares fits of the calculated dipole moments to a polynomial in the field variable.

All the calculations in this work have been done using the Gaussian density functional program deMon[36] where the Kohn−Sham molecular orbitals are expanded in a basis of Gaussian type orbitals. The Perdew−Wang-91 exchange correlation potential[37] and the DZVP orbital basis set[38] have been used. Fine grid option of deMon has been used for density calculation, and the default field step size of 0.0005 au alongwith a polynomial fit of the field-dependent dipole moment has been employed for polarizability calculation.

3. Results and Discussion

We have calculated several molecular and atom-in-molecule properties of formamide and thioformamide molecules for planar as well as nonplanar conformations using geometries taken from the recent literature.[23,27] We have also carried out calculations for the positive and negative ions of these conformers for both the amides using the respective geometries for the neutral molecules. The calculated total energies for the neutral molecules as well as their positive and negative ions are reported in Table 1. It is observed that the rotational barrier (with respect to the planar conformer) in formamide and thioformamide as calculated here are 18.5 and 22.3 kcal/mol, respectively, and the corresponding values from other ab initio calculations[23,27] reported earlier are 16.0 and 22.6 kcal/mol, respectively. The experimental value[39] of the barrier for formamide is 18.4 kcal/mol and the present calculated result is in excellent agreement with this. The calculated values of electronegativity, hardness, and molecular valency are also reported in Table 1. From the values of these quantities, it is evident that the energetically most stable conformer (planar form) is associated with maximum hardness and maximum molecular valency and thus the principle of maximum hardness[9] as well as the maximum molecular valency principle[18] are found to be obeyed in both formamide and thioformamide. The molecular electronegativity values are found to be minimum for the lowest energy conformations in both the amides. The lower hardness for thioamide as compared to the amide is consistent with the fact that sulfur is more soft than oxygen. However, although oxygen is more electronegative than sulfur, the molecular electronegativity of formamide is less than that of thioformamide. This is

TABLE 2: Calculated Values of Bond Order of Planar, *cis*- and *trans*-Formamide and Thioformamide

	formamide			thioformamide		
bond	planar	*cis*	*trans*	planar	*cis*	*trans*
C−N	1.2708	1.1028	1.0759	1.3602	1.1387	1.1140
C═O/S	2.0761	2.2222	2.2215	1.7917	2.0251	2.0170
C−H	0.9197	0.9196	0.9206	0.8995	0.8947	0.9001
N−H	0.9255	0.9321	0.9353	0.9180	0.9319	0.9321
N−H	0.9330	0.9321	0.9360	0.9225	0.9316	0.9327
N−O/S	0.1042	0.0	0.0	0.1451	0.0	0.0

TABLE 3: Calculated Values of Partial Atomic Charges in Planar, *cis*- and *trans*-Formamide and Thioformamide

	formamide			thioformamide		
atom	planar	*cis*	*trans*	planar	*cis*	*trans*
C	0.095	0.065	0.051	−0.201	−0.228	−0.231
N	−0.367	−0.449	−0.420	−0.305	−0.418	−0.415
O/S	−0.287	−0.191	−0.167	−0.166	−0.017	0.020
H	0.081	0.118	0.092	0.177	0.197	0.172
H	0.242	0.229	0.222	0.256	0.234	0.227
H	0.236	0.229	0.222	0.239	0.231	0.226

a direct consequence of higher charge separation in the case of formamide. The average molecular polarizabilities as well as the perpendicular (out of plane) components are also reported in Table 1. Unlike the previous studies,[10,11] energetically most stable structure is not found to be associated with a minimum polarizability. However, the out of plane component (perpendicular component $\alpha_\perp$) of the polarizability α is found to be minimum for the energetically most stable structure. The calculated values of bond orders are reported in Table 2. The C−N bond order, which plays an important role in the internal rotation in amides, is found to be larger for the planar amide and thioamide as compared to the nonplanar structures. This is a consequence of the change of hybridization of the nitrogen atom from near sp^3 to near sp^2, as one moves from nonplanar to planar structure and the consequent possibility of formation of a partial π bond between carbon and nitrogen atoms with the help of the extra *p*-orbital of the N atom. This increase in the C−N bond order is thus accompanied by a reduction of the C−O/S bond order for the planar structure.

While the above discussion is pertinent to the individual structures of formamide and thioformamide, we now compare the relative values of different parameters for these two molecules. Thus, the C−N bond order in thioformamide is higher than that in formamide. The partial atomic charge at the N atom in thioformamide is consequently less than the same in formamide. The calculated valency of N is also larger in thioformamide. The quantity ΔV_M representing the difference between the total molecular valency of the planar structure and that of the nonplanar forms is also higher for thioformamide. The change in the C−N bond order in going from the planar to a nonplanar structure is also more for thioformamide. All these observations are in support of a higher rotational barrier in thioformamide for internal rotation from planar to the nonplanar form.

We have also calculated the gross atomic populations and the atomic Fukui reactivity indices for all the atoms in the two molecules formamide and thioformamide and these values are reported in Tables 3 and 4, respectively. From the gross atomic populations at N and O(S) atoms, one expects that the protonation should take place at the nitrogen atom for both the amides, since the N atom is more negatively charged. But the experimentally observed preferred protonation site is the oxygen (sulfur) atom in amide (thioamide). We, however, invoke the density functional version of the frontier orbital theory[32] and predict that preferable protonation should be favored at the oxygen (sulfur) atom in amide (thioamide), since the calculated atomic Fukui indices for the electrophillic attack, i.e., the values of f^-, are more at these atoms (see Table 4). A comparison of the relative values of f^- at the oxygen and sulfur atoms in amide and thioamide, respectively, further suggests that the proton affinity of thioamide should be more than that of formamide although oxygen is more electronegative than sulfur and the gross atomic population is also more at the oxygen atom in amide as compared to the sulfur atom in thioamide. The reported calculated values[40] of the proton affinities for protonation at the oxygen and sulfur atoms in formamide and thioformamide are 209.5 and 212.3 kcal/mol, respectively, and the present prediction agrees with the observed trend.

The same reasoning based on the Fukui reactivity index can be useful in understanding the internal rotation in amide and thioamide. The HOMO contribution to the gross atomic population, i.e., the Fukui index at the sulfur atom of thioamide is higher than that of the oxygen atom in formamide. Considering the same argument as used in the resonance model but using the charges corresponding to HOMO alone, it is clear that sulfur attracts more frontier orbital electron density from nitrogen via carbon in thioamide as compared to the oxygen atom in amide and this contributes to the higher C−N bond order and higher rotational barrier in thioformamide.

4. Concluding Remarks

The prediction and understanding of changes in energy and other properties of molecules due to systematic variations in their structures provide interesting challenges in chemistry. The present work has been concerned with a density functional

TABLE 4: Calculated Values of Atomic Fukui Indices in Planar, *cis*- and *trans*-Formamide and Thioformamide

		formamide			thioformamide		
atom		planar	*cis*	*trans*	planar	*cis*	*trans*
C	f^+	0.599[a] (0.450)[b]	0.596 (0.380)	0.621 (0.460)	0.504 (0.212)	0.505 (0.201)	0.496 (0.210)
	f^-	0.062 (0.128)	0.051 (0.141)	0.076 (0.127)	0.045 (0.100)	0.041 (0.097)	0.042 (0.090)
N	f^+	0.128 (0.033)	0.021 (0.041)	0.012 (0.010)	0.167 (0.086)	0.013 (0.045)	0.012 (0.020)
	f^-	0.043 (0.091)	0.477 (0.270)	0.357 (0.233)	0.009 (0.061)	0.146 (0.150)	0.023 (0.084)
O/S	f^+	0.258 (0.195)	0.313 (0.244)	0.328 (0.239)	0.318 (0.462)	0.431 (0.526)	0.455 (0.536)
	f^-	0.767 (0.429)	0.441 (0.300)	0.415 (0.270)	0.898 (0.631)	0.798 (0.559)	0.892 (0.571)
H	f^+	0.010 (0.130)	0.009 (0.136)	0.009 (0.144)	0.007 (0.084)	0.006 (0.093)	0.006 (0.095)
	f^-	0.108 (0.188)	0.021 (0.116)	0.142 (0.192)	0.034 (0.093)	0.013 (0.074)	0.037 (0.120)
H	f^+	0.003 (0.095)	0.031 (0.102)	0.016 (0.075)	0.006 (0.074)	0.023 (0.067)	0.017 (0.070)
	f^-	0.010 (0.075)	0.006 (0.087)	0.005 (0.089)	0.007 (0.044)	0.002 (0.059)	0.003 (0.068)
H	f^+	0.003 (0.098)	0.032 (0.097)	0.016 (0.073)	0.003 (0.082)	0.023 (0.068)	0.016 (0.069)
	f^-	0.012 (0.089)	0.006 (0.087)	0.006 (0.089)	0.008 (0.072)	0.002 (0.061)	0.003 (0.068)

[a] Calculated values obtained by using eqs 16 and 17. [b] The bracketed quantities refer to values calculated by using eqs 13 and 14.

investigation of the barrier to internal rotation about the C−N bond in formamide and thioformamide and also the preferred protonation sites in these molecules. It is observed that the energetically most stable structure (planar form) is associated with maximum hardness and maximum molecular valency for both the amides. Larger rotational barrier in thioamide is explained in terms of the C−N bond order, which is found to be higher in the case of thioamide. Another observation is that the energetically preferred protonation site is the oxygen (sulfur) atom in amide (thioamide) and not the nitrogen atom. This trend is well interpreted through the calculated atomic Fukui reactivity indices of the neutral molecule alone (but not by the gross atomic population). Although oxygen is more electronegative than sulfur, the proton affinity (basicity) of thioamide is more than that of amide. This is also explained by the calculated atomic Fukui indices at the oxygen and sulfur atoms in amide and thioamide, respectively. Rationalization of larger rotational barrier in thioamide is also analysed in the light of a modified amide resonance model by considering the charges corresponding to the HOMO alone, i.e., by using the atomic Fukui indices at sulfur and oxygen atoms.

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