J. Am. Chem. Soc. **1995,** *117,* 4401−4402

Rotational Barriers Originate from Energy Changes in Individual Atoms

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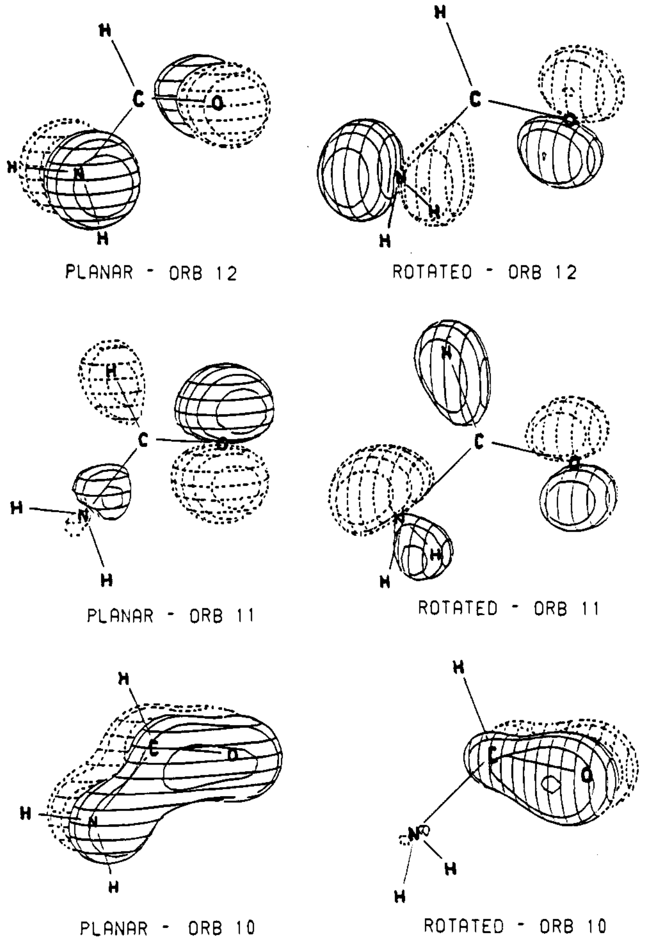
Received June 21, 1994

For many years, practicing organic chemists have successfully rationalized the properties of large molecules in terms of local phenomena. This is reflected in Lewis dot structures, Benson's group additivity method for molecular enthalpies,[1] and similar schemes applied to entropy and to ultraviolet and infrared spectroscopy. The basis for these examples is that most forces between atoms in a molecule are significant only over a range comparable to a bond length. A particularly interesting case is the paper by Wiberg and Breneman on the internal rotation barrier in formamide.[2] Here we verify and extend the Wiberg and Breneman contention that all the interactions leading to the formamide rotational barrier can be incorporated into properties of the C−N bond itself. We employ the recently introduced energy index for atom A, EI_A, the average one-electron valence energy of atom A in the molecule,[3] and show that $\Delta EI_C + \Delta EI_N$ is proportinal to the barrier height and quantifies the dominant role of nitrogen lone pair stabilization found by Wiberg and Breneman. We carry the local model of internal rotation further by determining $\Delta EI_C + \Delta EI_N$ for ethane, methylamine, and methanol (X = C, N, O) and demonstrate that the relative magnitudes of all four barriers are quantitatively obtained. The simplicity of the method used to compute the barriers leads to an equally simple explanation of their origin. A review of rotational barriers—values, calculations, and models—is given in ref 4.



PLANAR - ORB 12 ROTATED - ORB 12

PLANAR - ORB 11 ROTATED - ORB 11

PLANAR - ORB 10 ROTATED - ORB 10

Figure 1. Molecular orbitals of the three highest occupied levels for the planar and 90° rotated conformations in formamide.

As obtained by Wiberg and Breneman the calculated effect of rotation around the C−N bond in formamide from the planar to the 90° configuration is an increase in C−N bond length from 1.36 to 1.44 Å that is large compared to the decrease in the C−O bond length (1.19−1.18 Å). This geometrical change suggests that the effect of rotation around the C−N bond is restricted to the bonding in C and N. It maybe noted that such a suggestion is in sharp contrast to the Lewis dot resonance structures customarily used to explain the near planarity and high rotational barrier of formamide: the double bond character of the C−N bond is traded with the double bond character of the C−O bond. Because rotational barriers can generally be predicted accurately within the Hartree−Fock approximation and because of the resulting simplification in the interpretation, we carried out all of our calculations *ab initio* at the restricted SCF MO level with the 6-31G* basis set. Results for our local one-electron energies in the planar and 90° rotated configuration at their optimized geometries are given in Table 1. The sum of the changes on C and N alone approximates the total energy change upon rotation. Both the direction and order of the magnitude are correct. The sum is $^4/_3$ the total energy change, but this factor is the same for the other rotational barriers reported here. Given that the overestimate is systematic, the rotational barrier in formamide is thus explained solely on the basis of the change in energy for the carbon and nitrogen bond in formamide. Importantly, only the nitrogen atom, and not the carbon, shows a significant change in energy upon rotation. This unique change results from the stabilization of the lone pair on the nitrogen when formamide is in the planar geometry. The change in stabilization energy from planar to the 90° rotated configuration can be viewed very simply in terms familiar to physical organic chemists: the rotational barrier results from change in hybridization from the planar sp^2 to the rotated sp^3. As discussed previously,[3] EI_N is the *in situ* electronegativity of nitrogen (which is in energy units) and changes upon change in hybridization. A conventional molecular orbital analysis (given below) verifies this simple picture.

Only the three highest occupied molecular orbitals need be considered: two oxygen pairs of electrons and one nitrogen pair. Any pair that can form a π bond is restricted to the A'' irreducible representation (π symmetry), and in the planar conformation, the only occupied MOs of this symmetry are 10 and 12. Thus, the sp^2 nitrogen lone pair is to be found in these orbitals. As seen in Figure 1, it is nearly equally split between each of these MOs. An oxygen π lone pair is also nearly equally split between these MOs. MO 11 in the planar conformation is A' (σ symmetry), and as seen in Figure 1, it is predominately an oxygen σ lone pair.

Upon rotation around the C−N bond, the orbitals undergo several important changes. The nitrogen lone pair is changed into σ symmetry and goes from sp^2 to sp^3 hybridization; it can then interact with the oxygen σ lone pair. MO 12 in the rotated conformation is A', and therefore MOs 11 and 12 of the rotated conformation can be understood as a linear combination of a σ oxygen lone pair which has not changed dramatically upon rotation and a nitrogen σ lone pair which has. MO 10 of the planar conformation has an energy of −0.57 hartrees, while MOs 11 and 12 of the rotated conformation have energies of −0.47

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0002-7863/95/1517-4401$09.00/0

Table 1. Energy Contributions of the Atoms to Rotational Barriers in Formamide, Ethane, Methylamine, and Methanol (Hartrees) Compared to Calculated and Experimental Values

conf	EI_A	EI_B	$\Delta EI_A + \Delta EI_B$	ΔE (calcd)[a]	ΔE (exptl)
$CHONH_2$					
rot	C, −0.825 27	N, −0.745 28			
	(O, −0.779 56)[b]	(H, −0.761 94)			
	(H, −0.662 05)	(H, −0.761 94)			
planar	C, −0.824 37	N, −0.781 61			
	(O, −0.734 71)	(H, −0.794 54)			
	(H, −0.653 37)	(H, −0.808 18)			
Σ^c =	−0.000 90 +	0.036 33 =	0.035 43	0.025 01	0.030 12[d]
C_2H_6					
ecl	C, −0.664 44	C, −0.664 44			
	(H, −0.617 22)	(H, −0.617 22)			
sta	C, −0.667 62	C, −0.667 62			
	(H, −0.616 03)	(H, −0.616 03)			
Σ =	0.003 18 +	0.003 18 =	0.006 36	0.004 76	0.004 66[e]
CH_3NH_2					
ecl	C, −0.691 60	N, −0.694 90			
	(H, −0.611 86)	(H, −0.725 56)			
	(H, −0.625 85)	(H, −0.725 56)			
	(H, −0.625 85)				
sta	C, −0.693 37	N, −0.698 10			
	(H, −0.609 83)	(H, −0.722 16)			
	(H, −0.625 06)	(H, −0.722 16)			
	(H, −0.625 06)				
Σ =	0.001 77 +	0.003 20 =	0.004 97	0.003 81	0.003 12[f]
CH_3OH					
ecl	C, −0.718 37	O, −0.771 74			
	(H, −0.641 41)	(H, −0.832 64)			
	(H, −0.628 83)				
	(H, −0.628 83)				
sta	C, −0.719 13	O, −0.773 72			
	(H, −0.640 71)	(H, −0.827 44)			
	(H, −0.628 13)				
	(H, −0.628 13)				
Σ =	0.000 76 +	0.001 98 =	0.002 74	0.002 16	0.001 71[g]

[a] Total energy difference of ground state and rotated conformations (fully optimized) by RHF method (formamide, 6-31G*; others, 6-31G**). [b] The values of EI_A and EI_B given in parentheses throughout the table are included for completeness only. They are not included in the $\Delta EI_A + \Delta EI_B$ summation. [c] Sum equal to the differences of EI_As of column 2 plus differences of EI_Bs of column 3. [d] Kamei, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2269. [e] Weiss, S.; Leroi, G. *J. Chem. Phys.* **1968**, *48*, 962. [f] Lide, D. R., Jr. *J. Chem. Phys.* **1957**, *27*, 343. [g] Ivash, E. V.; Dennison, D. M. *J. Chem. Phys.* **1953**, *21*, 1804.

and −0.43 hartrees, respectively: the part of the nitrogen lone pair in the planar MO 10 has obviously been destabilized. The oxygen π electrons from planar MOs 10 and 12 form the CO π bond in MO 10 of the rotated conformation and are thus obviously stabilized as well, but a *quantitative* accounting of MO one-electron energies *cannot* be carried out because of the failure of Walsh's rules to rationalize rotational barriers.[5] This failure is manifest in the one-electron energies of MOs 10, 11, and 12 in the planar versus the 90° rotated configuration, which are respectively −0.571 58, −0.528 38; −0.428 62, −0.465 94; and −0.414 91, −0.433 46 hartrees. Use of EI_N and EI_C, the average energies of the valence electrons on atoms N and C, overcome this problem. Thus, the barrier is found explicable in terms of individual atoms, the simplest possible model of barrier origin. Note also that the finding that the barrier was almost solely due to change in EI_N is verified in the orbital plots of MOs 10, 11, and 12: in MOs 11 and 12, there is no contribution from carbon, while in MO 10, the charge density around C is very similar for the planar and 90° rotated configuration.

The barriers in ethane, methylamine, and methanol are a classic testing ground for rotational barrier theories, and the data in Table 1 show that their magnitudes, including the approximate 3:2:1 rule, are reproduced by $\Delta EI_C + \Delta EI_X$, X = C, N, and O. Because their smaller heights are an order of magnitude less than that for formamide, the change in C−X bond length is quite small, but MP2/6-31G** geometry optimization calculations by Bader *et al.*[6] show that the largest geometrical changes occur in the bond around which rotation is made. Again, an analysis of the MO changes parallels the $\Delta EI_C + \Delta EI_X$ interpretation, and for these molecules the local energy picture is more readily grasped if we first describe the ethane barrier in terms of its MO changes. The very small C−C bond length change between the eclipsed and staggered configurations found by Bader *et al.*[6] (approximately 0.01 Å) is compatible with the long-known fact that the ethane barrier is explicable in terms of rigid rotation and therefore eliminates one potentially complicating feature. We also note that rotation *cannot* alter the σ orbital, and therefore we need only be concerned with the two pairs of doubly degenerate π-like orbitals. One pair forms a bonding interaction, the other, an antibonding interaction. These follow the general rule that the overlap-determined destabilization of the antibonding orbitals is always greater than the overlap stabilization of the bonding π orbitals, and it follows at once that the reduced overlap repulsion in the staggered configuration gives rise to the barrier. Reduced repulsive interaction is directly correlated with increased stability of EI_C. Therefore, ΔEI_C, the change in the carbon *in situ* electronegativity, is proportional to the ethane barrier.[7]

An understanding of successive reduction in barrier height—ethane > methylamine > methanol—is once again quantitatively attributable to *in situ* electronegativity changes in a role complimentary to that in ethane. As the electronegativities of C and X become increasingly different, the MOs become more localized on C and X. Thus, e.g., in methanol the carbon and oxygen orbitals have quite different radial dependence (the oxygen electron density is closer to its nucleus), therefore reduced π overlap repulsion, therefore smaller $\Delta EI_C + \Delta EI_O$.

In summary, many properties in molecules can be explained in terms of local interactions, and we have shown that the recently developed energy index, EI_A, the *in situ* electronegativity of atom A, quantitatively describes the rotational barrier around A−B by $\Delta EI_A + \Delta EI_B$. In formamide, the barrier comes from breaking a partial AB π bond and can be viewed as the energy rise due to the change in hybridization from sp^2 to sp^3 of the nitrogen. The large unique change in C−N bond length during rotation is a manifestation of the local nature of the barrier origin and its large magnitude. In ethane, methylamine, and methanol, the barrier arises from breaking a partial C−X π antibond (X = C, N, and O) and can be quantified by the increase in C and X electronegativity accompanying reduced π overlap repulsion for the staggered configuration, with a concomitant increase in electronegativity difference between C and X. The use of the energy index has given a particularly simple explanations and quantification of the four molecules most often cited as the prototypical set of rotational barriers.

Acknowledgment. The authors wish to thank Geo-centers, U.S. Army ARDEC, and the ACS/PRF for financial support.

JA9419728

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