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Energy Barriers to Internal Rotation: Hyperconjugation and Electrostatic Description

Nina Sadlej-Sosnowska

National Institute of Public Health, 30/34 Chełmska Street, 00-725 Warsaw, Poland

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Analysis of internal rotation around single bonds was aimed at answering the following question: Is the hyperconjugation always a driving force for molecular shape and conformational preferences? For hydroxydiazenium *N*-oxide, one of the molecules investigated here, the answer appeared to be negative. As a consequence, there arose another question: What are the forces that hinder internal rotations around single bonds? To provide the answer to the latter, the individual repulsive and attractive terms to the potential energy changes accompanying internal rotation were calculated. Density functional theory was applied as it allows for the separate determination of the Coulomb repulsion, exchange, and correlation to the electron−electron interaction. Calculations were performed for ethane, biphenyl, 2,2′-difluorobiphenyl, formic acid, and hydroxydiazenium *N*-oxide. It has been found that both attractive and repulsive interactions are diminished near the barrier top but the attraction attenuates to a higher degree than the repulsion does. This holds true even for the molecules that are sterically crowded near the top. It has been shown that the exchange and correlation contributions are lower by factors of 10 and 100, respectively, than the electrostatic interactions.

Introduction

Overall molecular shape is determined by forces that hinder internal rotations around the single bonds. As the rotation is not free, the potential energy surface of even relatively small molecule can possess a great number of local minima, corresponding to the same number of stable conformers differing in energy and geometric properties.[1] Hindered rotation was first experimentally found for ethane,[2] and since then, ethane has been the most frequently studied prototype molecule for internal rotation investigation since it is the simplest molecule containing a carbon−carbon single bond. The structural preferences in ethane and other molecules have been attributed to steric effects, interpreted as the repulsion of electrons in different bonds and on different atoms, drawn closer to each other in the course of rotation of the molecule.[3−5] For ethane, it was claimed that the barrier is "caused" by eclipsed C−H bond repulsion. Recently, investigations by Weinhold[6−9] and others[10−16] aroused awareness of hyperconjugative interactions between filled and empty orbitals in the energy profiles accompanying internal rotations. The idea of the hyperconjugative interactions belongs to the natural bonding orbital (NBO) analysis of the molecular wave functions.[17] In the analysis, the wave functions are expanded in terms of localized and orthogonal molecular orbitals. These hyperconjugative orbital interactions involve partial electron transfer from nearly doubly occupied bonding orbitals to antibonding, nearly vacant ones and result in delocalization of the electron density from the one which would have been expected on the basis of classical Lewis formulas.[18]

In several papers devoted to the origin of internal rotation and based on the NBO theory results, hyperconjugative orbital interactions have sometimes been opposed to electrostatic interactions. The latter were claimed to be of minor importance. Comparison of the steric repulsive interactions with the hyperconjugation-induced ones[8−11,15] also results in the comparison of the electrostatic and the hyperconjugation terms of the total energy changes accompanying internal rotation. However, one should bear in mind that the aforementioned electrostatic and hyperconjugative energy changes belong to two different distributions of the total energy. In terms of the NBO treatment of the MO wave functions, it is possible to separate "Lewis" and "non-Lewis" (i.e. delocalization) contributions to the total energy:[7]

$$E = E_{\mathrm{Lewis}} + E_{\mathrm{deloc}} \tag{1}$$

Thus, the rotation barriers about any single bond may be decomposed as

$$\Delta E = \Delta E_{\mathrm{Lewis}} + \Delta E_{\mathrm{deloc}} \tag{2}$$

Another energy distribution is offered in Hartree−Fock (H−F) methodology or density functional theory (DFT). In H−F theory, the energy is given as[19]

$$E = V_{\mathrm{nn}} + \langle hP\rangle + 1/2\langle PJ(P)\rangle - 1/2\langle PK(P)\rangle \tag{3}$$

where V_{nn} stands for the nuclear repulsion energy, P stands for the density matrix, $\langle hP\rangle$ is the one electron kinetic plus potential energy (core energy), $1/2\langle PJ(P)\rangle$ is the classical Coulomb repulsion of electrons, and $-1/2\langle PK(P)\rangle$ is the exchange energy. The Coulomb repulsion energy is calculated by treating the motions of individual electrons as influenced by a "static Coulomb field" generated by all other electrons. Exchange energy term involves electron−electron interactions and has the effect of reducing the size of the Coulomb term. For a given molecule, H−F calculations (with the use of Gaussian 98 program) produce E, V_{nn}, electron kinetic energy, and V_{ne}, electron−nuclear attraction energy. Currently there are no means of reporting Coulomb and exchange energies separately.

On the other hand, in the density functional theory, DFT, the energy partition can be presented as[19]

$$E = V_{\mathrm{nn}} + \langle hP\rangle + 1/2\langle PJ(P)\rangle + E_{\mathrm{x}} + E_{\mathrm{c}} \tag{4}$$

where E_{x} stands for the exchange energy and E_{c} for the correlation energy.

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Electron correlation accounts for coupling of electron motions and leads to a lessening of the electron−electron repulsion energy, just as the exchange energy does.

Calculations performed in this work were carried out in the framework of DFT not only because it allows one to determine the correlation energy but also because it has an option to report Coulomb and exchange terms separately. Therefore, the rotation barrier, ΔE, between structures of different geometry, e.g. Z (trans) and E (cis) isomers of formic acid, can be decomposed as

$$\Delta E = \Delta V_{\mathrm{nn}} + \Delta\langle \mathrm{hP}\rangle + 1/2\Delta\langle PJ(P)\rangle + \Delta E_{\mathrm{x}} + \Delta E_{\mathrm{c}} \quad (5)$$

The last three terms correspond to electron−electron interaction, V_{ee}. So eq 5 is equivalent to

$$\Delta E = \Delta V_{\mathrm{nn}} + \Delta\langle \mathrm{hP}\rangle + \Delta V_{\mathrm{ee}} \quad (6)$$

or

$$\Delta E = \Delta V_{\mathrm{nn}} + \Delta V_{\mathrm{en}} + \Delta V_{\mathrm{ee}} + \Delta E_{\mathrm{k}} \quad (7)$$

It can be seen that the last equation describes the total energy change as a sum of the potential and kinetic (ΔE_{k}) contributions.

Equations 5−7 present an alternative way to eq 2 for treating rotation barriers. One can guess that the five terms of eq 5 are dispersed into both terms of eq 2, and vice versa. The energy distribution can be performed according to the first or to the second approach. Therefore, it is not correct to compare and oppose the hyperconjugative and the electrostatic contributions to energetic barriers, e.g. state that the latter are of minor importance—both are valid within the limits of different distributions. In terms of the theory of atoms in molecules, the electrostatic effects were found to be sufficient to explain the occurrence of barriers to rotation for such molecules as C_2H_6, CH_3OH, and CH_3NH_2.[20] Another calculation of the rotation barrier in acetaldehyde on the HF and MP2 levels yielded the same outcome: an increase in total potential energy, despite the electron and nuclear repulsion energies decrease in rotation toward the top of the barrier.[21]

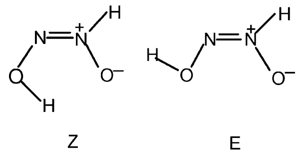
Definition of major barrier sources in other molecules which may rotate around C−C, C−OH, and N−OH single bonds has been the goal of this study. Each individual energy component will be treated according to the philosophy expressed in eq 2 or to the distribution offered by eqs 5−7. Both approaches to the rotation barriers will be confronted.

Calculations

A reliable determination of the energy variation accompanying the conformational change requires relaxation of all other molecular coordinates.[22] That is why the geometry optimization has been carried out with all internal degrees of freedom allowed to adjust themselves during the rotation around one selected bond except for a fixed dihedral angle scanned at regular intervals.

Energies of all structures were calculated at the B3LYP/6-311++G** level. In the case of formic acid, the calculations were also repeated using the B3PW91 and MPW1PW91 DFT functionals to make sure that the effects observed do not depend on the functional used. As the results obtained were much the same, other calculations proceeded using the B3LYP. Natural bond orbital (NBO) calculations have been carried out using NBO 4.0 interfaced to Gaussian 98.[23]

CHART 1



Results

The molecules chosen for the internal rotation investigation were ethane, biphenyl, 2,2′-difluorobiphenyl, formic acid, and hydroxydiazenium *N*-oxide. Ethane was chosen because the major part of studies on internal rotation was made with this molecule as a model specimen.[3,6−9,11,20] Biphenyl molecules, similarly to ethane, can rotate around a single C−C bond. However, a steric hindrance appears upon the rotation when they approach planar transition states.[24] Due to the latter, the basic conformation of both molecules is twisted: the gas-phase electron diffraction value of the dihedral angle between the planes of two aromatic rings is 44.4° for biphenyl[25] and 60° for 2,2′-difluorobiphenyl.[26] Formic acid and hydroxydiazenium *N*-oxide, in turn, were taken as the examples of polar molecules possessing free electron pairs and significant dipole moments. Internal rotation in the first involves C−O, while in the second it involves N−O bond. Barrier energetics in lone-pair molecules containing an oxygen atom has been previously investigated.[10,12,14,21,27−31] It has been shown that, in the course of the rotation around single bonds between atoms possessing free electron pairs, the latter play an active role in the process.

Free rotation in formic acid[14,30] and in hydroxydiazenium *N*-oxide[31] has been previously investigated, yet individual contributions to the energy were not addressed. Both molecules can exist not only as the lowest energy Z conformers but also as E conformers of higher energy. Because the Z and E conformers of hydroxydiazenium *N*-oxide molecule are less known than other molecules investigated here, they are shown in Chart 1.

Contribution of the Lewis and Delocalization Energies to the Barrier. The first approach in the investigation of energetic consequences of the rotation around single bonds has been treated in terms of delocalization of electron density (eq 2). Results of the rotation around the C−C single bond were reported previously,[2−11,20,21,24] and the plots of $\Delta E_{\mathrm{Lewis}}$ and $\Delta E_{\mathrm{deloc}}$ vs corresponding dihedral angle are given only for formic acid and hydroxydiazenium *N*-oxide (Figures 1a and 2a). The energy increments are calculated with respect to the most stable *Z* conformer (dihedral angle equaling 0).

In the case of formic acid, the values for Z and E conformers and for the transition state rotamer are given in Table 1. As both E_{Lewis} and E_{deloc} are negative, the maximum of $\Delta E_{\mathrm{deloc}}$ at the transition state in Figure 1a is equivalent to the least span of hyperconjugation. For what follows, it can be stated that hyperconjugation favors the stable conformations. On the other hand, a minimum of $\Delta E_{\mathrm{Lewis}}$ in the same figure carries the information that the top barrier rotamer would have the lowest energy of all rotamers with full occupation of the bonding orbitals (corresponding rigorously to Lewis formulas). However, for the E conformer, $\Delta E_{\mathrm{Lewis}}$ and $\Delta E_{\mathrm{deloc}}$ are both positive and cooperate in increasing the energy of E to an extent greater than in the case of Z conformer. In Figure 1b the relative total energy plot is confronted with the curve displaying the “% non-Lewis”, e.g. the percentage of electrons that cannot be described by the

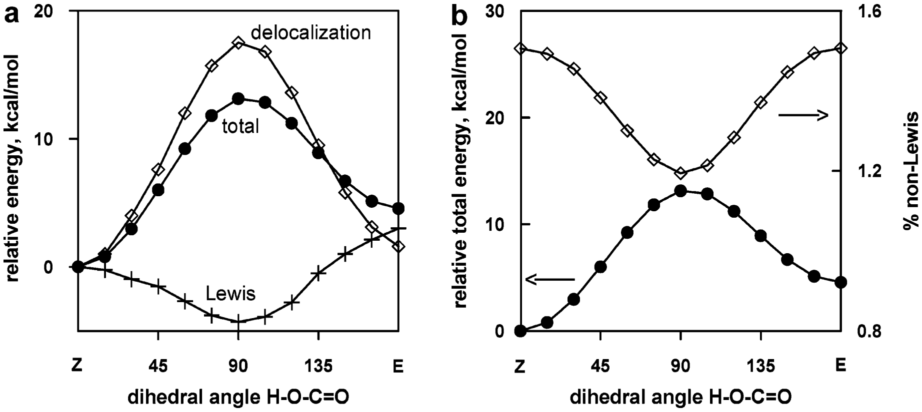


Figure 1. (a) Dependence of the relative total energy of formic acid molecule and its $\Delta E_{\mathrm{Lewis}}$ and $\Delta E_{\mathrm{deloc}}$ parts on the OH rotation angle. (b) Relationship between the relative total energy of formic acid molecule and the percentage of electron density (% non-Lewis) which cannot be accounted for by the classical Lewis formula.

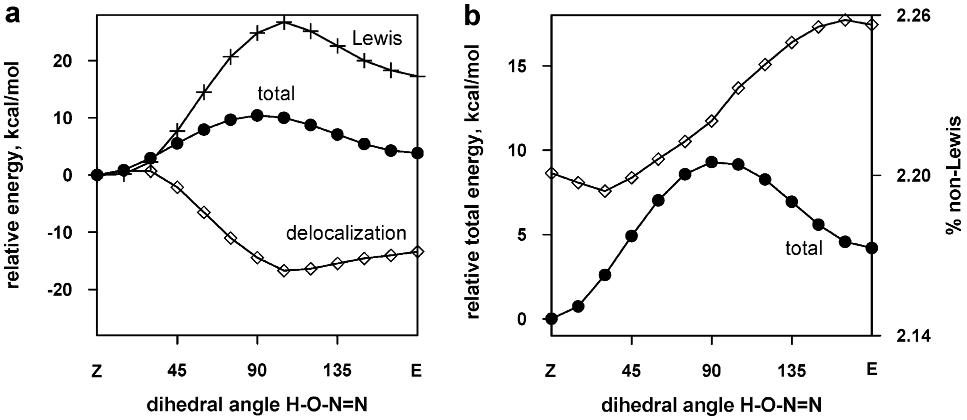


Figure 2. (a) Same dependence as in Figure 1a for hydroxydiazenium *N*-oxide. (b) Same dependence as in Figure 1b for hydroxydiazenium *N*-oxide.

TABLE 1: Contributions of Lewis Energy ($\Delta E_{\mathrm{Lewis}}$) Due to the Localized Electron Density and the Hyperconjugation Energy ($\Delta E_{\mathrm{Deloc}}$) Due to the Delocalized Electron Density to Barrier for Rotation around the C−OH Bond in Formic Acid[a]

structure	E_{rel} (kcal/mol)	E_{Lewis} (au)	$\Delta E_{\mathrm{Lewis}}$ (kcal/mol)	E_{deloc} (au)	$\Delta E_{\mathrm{deloc}}$ (kcal/mol)
Z	0	−189.541 87	0	−0.285 81	0
top	13.13	−189.548 74	−4.31	−0.258 03	17.43
E	4.56	−189.537 08	3.01	−0.283 32	1.56

[a] B3LYP/6-311++G** geometries. Experimental data on geometry of *Z* (trans) and *E* (cis) conformers were reported by: Bjarnov, E.; Hocking, W. H. *Z. Naturforsch.* **1978**, *A33*, 610.

TABLE 2: Contributions of Lewis Energy ($\Delta E_{\mathrm{Lewis}}$) Due to the Localized Electron Density and the Hyperconjugation Energy ($\Delta E_{\mathrm{Deloc}}$) Due to the Delocalized Electron Density to Barrier for Rotation around the N−OH Bond in Hydroxydiazenium *N*-Oxide[a]

structure	E_{rel} (kcal/mol)	E_{Lewis} (kcal/mol)	$\Delta E_{\mathrm{Lewis}}$ (kcal/mol)	E_{deloc} (kcal/mol)	$\Delta E_{\mathrm{deloc}}$ (kcal/mol)
Z	0	−296.187	0	−0.47200	0
top	10.38	−310.638	24.83	−0.49503	−14.45
E	3.82	−309.583	17.22	−0.49335	−13.40

[a] B3LYP/6-311++G** geometries.

classical Lewis structure. It can be seen that the two plots mirror each other in a nearly ideal manner. This result remains in agreement with findings of Weinhold[9] and Goodman,[11] who confirmed that hyperconjugation (i.e. electron delocalization from bonding to antibonding orbitals in the framework of NBO theory) is mainly responsible for the rotation barrier in ethane. In other words, in formic acid, like in ethane, the “Lewis-like” structures would exhibit energetic preferences opposite from those when hyperconjugation, i.e., delocalization of electron density, is taken into account.

We expected that the results obtained for another small polar molecule, hydroxydiazenium *N*-oxide, would be qualitatively similar. However, to our surprise it has turned out that, for the latter molecule, the relation between total and delocalization energies is quite different (see the last columns in Tables 1 and 2). Figure 2a,b displays the same functions of the rotation angle H−O−N═N in that molecule as Figure 1a,b does for H−O−C═O in formic acid. This figure shows that the hyperconjugative stabilization is the largest for the NNOH dihedral angle of 105°, near the maximum of total energy, occurring at 90° (perpendicular arrangement of the OH bond vs the NNO plane). For hydroxydiazenium *N*-oxide, it is the Lewis energy which is decisive for the energetic preferences; its minima correspond to conformers Z and E. The maximum of $\Delta E_{\mathrm{Lewis}}$ near the barrier top shows that the corresponding rotamer would be of highest energy and the energetic order of the three rotamers would be the same if the rotamers' electron densities corresponded exactly to the Lewis formula.

Our result provides evidence of the adverse energy effects due to charge rearrangements associated with hydroxyl internal rotation in the COOH or NNOH groups. Whereas in formic acid $\Delta E_{\mathrm{deloc}}$ is responsible for E and Z conformers displaying lower energy than the top (perpendicular) structure, in hydroxydiazenium *N*-oxide, with the delocalization energy being the

TABLE 3: Electrostatic Contributions to Energy of the Staggered and Eclipsed Ethane Calculated at the B3LYP/6-311++G Level**[a]

structure	E_{rel} (cal/mol)	V_{nn} (au)	ΔV_{nn} (kcal/mol)	V_{en} (au)	ΔV_{en} (kcal/mol)	V_{ee} (au)	ΔV_{ee} (kcal/mol)
staggered	0	42.164 40	0	−268.556 42	0	67.139 16	0
eclipsed	2.70	41.997 27	−104.87	−268.225 90	207.40	66.983 74	−97.52

[a] The top entries in Tables 3−7 represent the lowest energy conformers; the next ones, transition states.

TABLE 4: Electrostatic Contributions to Energy of the Twisted and Plane Biphenyl Molecule Calculated at the B3LYP/6-311++G Level**

structure	E_{rel} (kcal/mol)	V_{nn} (au)	ΔV_{nn} (kcal/mol)	V_{en} (au)	ΔV_{en} (kcal/mol)	V_{ee} (au)	ΔV_{ee} (kcal/mol)
twisted	0	599.455 87	0	−2273.418 87	0	749.272 36	0
plane	2.10	598.747 92	−444.24	−2271.932 95	932.41	748.494 86	−487.89

TABLE 5: Electrostatic Contributions to Energy of the Twisted and Plane 2,2′-Difluorobiphenyl Molecule Calculated at the B3LYP/6-311++G Level**

structure	E_{rel} (kcal/mol)	V_{nn} (au)	ΔV_{nn} (kcal/mol)	V_{en} (au)	ΔV_{en} (kcal/mol)	V_{ee} (au)	ΔV_{ee} (kcal/mol)
twisted	0	828.099 41	0	−3205.195 84	0	1055.779 24	0
plane	10.79	822.543 04	−3486.62	−3194.040 53	6999.96	1050.200 36	−3500.75

TABLE 6: Electrostatic Contributions to the Energy of the Z and E Conformers and Transition State Rotamer of Formic Acid Calculated at the B3LYP/6-311++G Level**

structure	E_{rel} (kcal/mol)	V_{nn} (au)	ΔV_{nn} (kcal/mol)	V_{en} (au)	ΔV_{en} (kcal/mol)	V_{ee} (au)	ΔV_{ee} (kcal/mol)
Z	0	70.331 11	0	−587.391 08	0	138.172 56	0
top	13.13	69.691 49	−402.37	−586.161 58	771.51	137.621 87	−345.56
E	4.56	70.121 97	−126.59	−587.004 66	242.48	137.999 79	−108.41

TABLE 7: Electrostatic Contributions to the Energy of the Z and E Conformers and Transition State Rotamer of Hydroxydiazenium *N*-Oxide Calculated at the B3LYP/ 6-311++G Level**

structure	E_{rel} (kcal/mol)	V_{nn} (au)	ΔV_{nn} (kcal/mol)	V_{en} (au)	ΔV_{en} (kcal/mol)	V_{ee} (au)	ΔV_{ee} (kcal/mol)
Z	0	125.806 51	0	−865.874 42	0	218.610 33	0
top	10.38	123.401 28	−1509.28	−861.306 76	2866.21	216.487 19	−1332.27
E	3.82	123.861 29	−1220.62	−862.319 08	2230.98	217.018 59	−998.82

sole term taken into consideration, the energetic ordering should be $E_{\mathrm{top}} < E_{\mathrm{cis}} < E_{\mathrm{trans}}$, exactly opposite to the calculated energy order.

Contribution of Different Potential Energy Terms to the Barrier. The second approach to the investigation of energy barriers is based on the energy partition offered by eqs 4−6. Tables 3−7 present the contributions of the electron−electron (V_{ee}) repulsion, nuclear−nuclear (V_{nn}) repulsion, and electron−nuclear (V_{en}) attraction terms to total potential energy of the molecules under investigation. The most stable structures are mentioned in the first rows of each table. The second rows show the rotamers of the highest energies. Table 6 and 7 present also (in the third rows) the properties of the second stable conformers.

Data in the above-mentioned tables illustrate the fact that both repulsive terms, V_{ee} and V_{nn}, are the largest in the most stable conformation and that they decrease by hundreds to thousands kcal/mol when going to the barrier top. More detailed results for the energy as a function of the rotation angle for formic acid (rotation of OH around the C−O bond), and for hydroxydiazenium *N*-oxide (rotation of OH around the N−O bond) are shown in Figures 3 and 4. The figures display increments of the total energy and of the potential energy components, calculated as a function of the rotation angle of the O−H bond vs the plane spanned by other atoms. Energy values at maxima and minima are shown in Tables 6 and 7. It is worth noticing how different are the energy scales for the total energy and its components. By virtue of the virial theorem, the total potential energy (which is not shown in Figures 3 and 4) is twice as large as total energy and runs parallel to it. Therefore, it is evident that the repulsive interactions strongly favor the conformations being at the energy barrier top, being weaker than those in the stable conformations. The contribution deciding the real energetic preferences is made by the attractive forces which produce the energetic effect larger than the sum of both repulsive terms. Since the attraction term, V_{ne}, is negative, the highest value of ΔV_{ne} at the top of the curve indicates the lowest absolute value of V_{ne} at that point. In other words, the attractive forces are weakened. For ethane, the absolute value of the negative V_{en} energy is lower by 207.4 kcal/mol at the barrier top (eclipsed form) than at the most stable staggered structure. For formic acid, it is lower by 771.5 and 529 kcal/mol at the barrier top than in the Z and E conformations, respectively. In 2,2′-difluorobiphenyl, the corresponding decrease is as large as 7000 kcal/mol. The attraction term increments, ΔV_{ne}, are larger

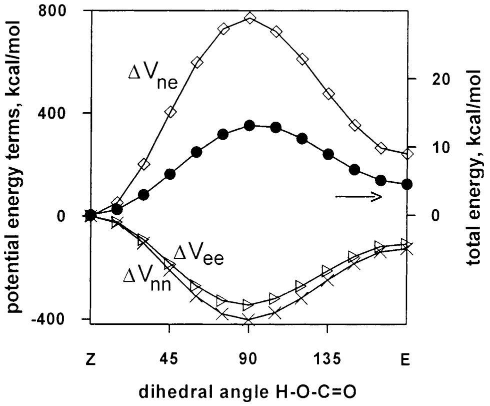


Figure 3. Dependence of attractive (ΔV_{ne}) and repulsive (ΔV_{nn} and ΔV_{ee}) energy increments on the H−O rotation angle in the formic acid molecule. $\Delta V_{\mathrm{ne}} > 0$ means that on going to the barrier top, the negative attraction is weaker than in the stable (Z, E) conformations. Positive V_{nn} and V_{ee} are also weaker at the top (see Table 6).

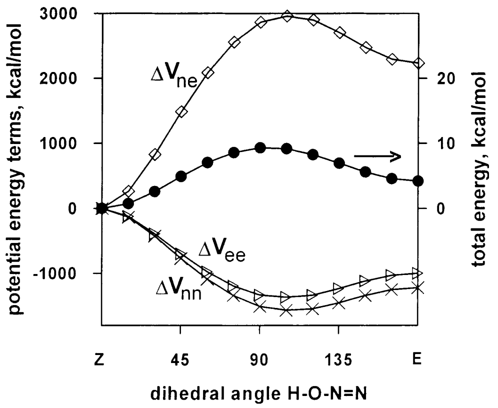


Figure 4. Same plots as in Figure 3 for hydroxydiazenium *N*-oxide.

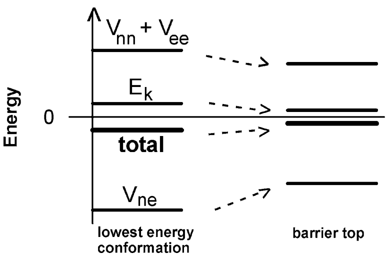


Figure 5. Relative contributions of the changes in the attractive, repulsive, and kinetic energies to the rotation barrier.

than the sums of both repulsive terms increments, ΔV_{nn} and ΔV_{ee}. Energy differences between the structures at the top of the energy barrier and the most stable ones, ΔV_{ne}, ΔV_{ee}, and ΔV_{nn}, attain fairly high values (Tables 3−7), yet the ratio of the corresponding terms is very near 1. This is possible because the respective two values, subtracted or divided, are very significant.

The interplay between the repulsive and attractive forces causes the conformations mentioned in the top lines of Tables 3−7 to be the most stable ones. The effect is opposite to what could have been expected when taking into consideration only the repulsive forces.

The sum of the potential ($\Delta V = \Delta V_{nn} + \Delta V_{ne} + \Delta V_{ee}$) and kinetic ($\Delta E_k = -\Delta V/2$ in virtue of the virial theorem) energy increments should equal the calculated barrier height for all molecules and the Z − E energy difference, in the case of formic acid and hydroxydiazenium *N*-oxide. It is so inasmuch as it is allowed by the accuracy resulting from the subtraction of very large individual energy terms and by the fact that the factor in virial theorem differs somewhat from 2.

Data in Tables 3−7 and Figures 3 and 4 provide evidence that all electrostatic interactions decrease at the barrier top and nearly balance one another when all the energy contributions are figured up to the total energy value, due to the opposite signs of the attractive and repulsion interaction. For what follows, the total energy change associated with the internal rotation is much smaller (2−3 orders of magnitude) than the separate potential energy terms. A diagram representation of the relative contributions of the changes in the attractive, repulsive, and kinetic energies to the barrier is shown in Figure 5. This diagram is valid for all the five molecules reported here as well as for a few others not described here (e.g. for the allyl radical).

Tables 3−7 present total electronic interaction energies V_{ee} which are composed, within the theoretical model, of three terms: Coulomb repulsion energy E_{coul}; exchange energy E_x; correlation energy E_c. Without a doubt, it is interesting to inquire what the contributions of the individual terms to electron−electron interaction are and how they change when geometry of the molecules changes during the rotation.

TABLE 8: Coulomb, Exchange, and Correlation Energies Given as Percent of the Total Electron−Electron Repulsion Energy[a]

molecule	E_{coul} (%)	E_x (%)	E_c (%)
ethane	115.8	−14.7	−1.1
biphenyl	107.5	−7.0	−0.5
2,2-difluorobiphenyl	106.8(9)	−6.4(5)	−0.4
formic acid	113.7	−12.9	−0.8
hydroxydiazenium *N*-oxide	111.7(8)	−11.0(1)	−0.7

[a] The values are calculated for the lowest energy conformer and at the barrier top (in parentheses). The latter are given only if they differ from the stable conformer at least by 0.1%.

TABLE 9: Total Electron−Electron Interaction, Exchange, and Correlation Energy Changes (ΔV_{ee}, ΔE_x, and ΔE_c) on Rotation with Respect to the Total Energy Difference ΔE[a]

molecule	$\Delta V_{ee}/\Delta E$	$\Delta E_x/\Delta E$	$\Delta E_c/\Delta E$	ΔE (kcal/mol)
ethane	−36.1	0.29	0.03	2.70
biphenyl	−232.4	−0.96	−0.30	2.10
2,2-difluorobiphenyl	−324.4	0.13	−0.12	10.79
formic acid	−26.3	0.25	0.04	13.13
hydroxydiazenium *N*-oxide	−128.3	0.59	0.16	10.38

[a] The differences are calculated for the lowest energy conformer and at the barrier top.

The answer to the first question is given in Table 8, which displays the dissection of the total electron−electron interaction into the Coulomb, exchange, and correlation energies. Presented data show that the Coulomb term is the most important of the three and the contribution of correlation to the electron−electron interaction is small. The answer to the second question is the following: For the highest energy rotamers, the contributions of E_{coul}, E_x, and E_c values are nearly the same as for the most stable structures and differ at the most by 0.1% (Table 8).

Finally, Table 9 presents the total electron−electron interaction, the exchange, and correlation energy differences with respect to the total barrier energy. It can be seen that the contribution of ΔE_x and ΔE_c to the energy barrier may attain 10%. At the same time, the electrostatic contributions are about a factor of several dozens to several hundred larger than the barrier height.

Discussion

The inference that the repulsive forces are not responsible for the observed energetic consequences of the C−OH and N−OH rotation is in agreement with the results of Badenhoop and Weinhold on the steric analysis of the internal rotation barrier.[8] They conclude that for ethane and ethane-like molecules (CH_3OH, CH_3NH_2) the exchange energy difference between the staggered and eclipsed forms predicts a counterintuitive eclipsed minimum. However, they use the "exchange energy" term for the electron−electron interaction V_{ee}.. Most frequently,[19,32] the main part of this interaction is named electron−electron Coulomb repulsion, V_{ee}, and only a minor contribution E_x is termed the exchange energy. It should be noted however that the "exchange" is not a physical process. It is due to the expression of the molecular wave function in terms of the atomic wave functions. The Hellmann−Feynman theorem of quantum mechanics states that if exact wave functions are used, the total energy may be exactly calculated by the direct evaluation of the classical electrostatic contributions.[33] In the correlated methods, there is also an even smaller element, called E_c (eq 4). For the reason that the electrostatic contributions cancel each other out in great measure, this small-scale term (Table 8) constitutes a noticeable contribution to the barrier height. The contribution (at the B3LYP/6-311++G** level) is 3% (ethane), 4% (formic acid), and 16% (hydroxydiazenium *N*-oxide) of the total barrier. As for biphenyls, the contribution is negative: −30 and −12%, respectively. The numbers do not constitute a consistent set. On the other hand, the electron repulsion contribution, including exchange energy, equals $-36\Delta E$ and $-26\Delta E$ for small and simple molecules, ethane and formic acid. It is larger for the negatively charged hydroxydiazenium *N*-oxide ($-128\Delta E$) and for biphenyls ($-232\Delta E$ and $-324\Delta E$, respectively). The minus sign means that the electron−electron repulsion is lower at the barrier top.

For the rotation around C−C, C−OH, and N−OH single bonds the electrostatic point of view provides us with a homogeneous interpretation: Rotamer energy is the lower, the stronger is the electrostatic attraction of negative energy within the molecule as a whole, accompanied by the increased repulsive interactions. It was previously stated that in a few molecules the only barrier-forming term is an increase in the nuclear−electron attraction energy.[10] However, it has to be taken into account that the attractive energy is negative and the positive value of ΔV_{ne} is equivalent to the physical lowering of the attraction at the barrier.

Such molecules as biphenyls are especially interesting, since according to atoms in molecule (AIM) results[24] the rotation through the barrier involving a planar transition state is sterically hindered there. We emphasize that even in this case the electron−electron and nuclear−nuclear repulsion, calculated for the entire molecule, is lower in the planar transition state than in the lowest energy twisted state (Tables 4 and 5). Yet it is possible that, in the sterically crowded molecules, the repulsive terms between the individual atoms may be larger at the barrier top than someplace else.

Conclusions

Calculations performed for hydroxydiazenium *N*-oxide led us to conclude that for hydroxydiazenium *N*-oxide hyperconjugation acts against the most stable Z planar conformation and, to a lesser extent, against the E conformation. In other words, steric attraction but not hyperconjugation seems to be decisive in this case. Hyperconjugation does not provide a unique measure of the energetic preferences connected with the internal rotation around the single bonds. It may either favor the most stable configuration or, on the contrary, promote the rotamer of the highest energy. In the latter case, it is the Lewis energy term which determines the rotamer energy sequence.

On the other hand, the proposed quantitative picture of the internal rotation barrier provides a rationale for the conformational preferences in terms of elementary electrostatic forces. The information obtained by concentrating on the individual potential energy components consistently explains the rotamers energetics. The repulsive interactions favor the energetic preference opposite to that calculated or measured (e.g. eclipsed and not staggered ethane molecule, planar and not twisted structure of biphenyls). However, the increased repulsion for the most stable configurations (known from experiments) is more than compensated by the negative attraction term, the total calculated energy being at its lowest.

By and large, both descriptions remain in accordance with the statement that energy changes accompanying free rotation are due to rearrangement of the electron density, which influences all terms in eqs 2 and 5.

References and Notes

(1) Sadlej-Sosnowska, N.; Dobrowolski, J. Cz.; Oziminski, W. P.; Mazurek, A. P. *J. Phys. Chem. A* **2002**, *106*, 10554.

(2) (a) Ebert, L. *Leipziger Vorträge*; S. Hirzel Verlag: Leipzig, Germany, 1929; p 74. (b) Wagner, C. *Z. Phys. Chem. Abt. B* **1931**, *14*, 166; *Chem. Abstr.* **1932**, *26*, 9. (c) Eucken, A.; Weigert, K. *Z. Phys. Chem. Abt. B* **1933**, *23*, 265; *Chem. Abstr.* **1934**, *28*, 962^3. (d) Kemp, J. D.; Pitzer, K. S. *J. Chem. Phys.* **1936**, *4*, 749. References 2a−c are cited as indicated by a reviewer after: Schreiner, P. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3579.

(3) Sovers, O. J.; Kern, C. W.; Pitzer, R. M.; Karplus, M. J. *J. Chem. Phys.* **1968**, *49*, 2592.

(4) Lowe, J. P. *Science* **1973**, *179*, 527.

(5) Pitzer, R. M. *Acc. Chem. Res.* **1983**, *16*, 207.

(6) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700.

(7) Reed, A. E.; Weinhold, F. *Isr. J. Chem.* **1991**, *31*, 277.

(8) Badenhoop, J. K.; Weinhold, F. *Int. J. Quantum Chem.* **1999**, *72*, 269.

(9) Weinhold, F. *Nature* **2001**, *411*, 539.

(10) Pophristic, V.; Goodman L.; Guchhait N. *J. Phys. Chem. A* **1997**, *101*, 4290.

(11) Pophristic, V.; Goodman, L. *Nature* **2001**, *411*, 565.

(12) Pophristic, V.; Goodman L. *J. Phys. Chem A* **2002**, *106*, 1642.

(13) Salzner, U.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1993**, *115*, 10231.

(14) Musso, G. F.; Magnasco, V. *Mol. Phys.* **1984**, *53*, 615.

(15) Nakai, H.; Kawai, M. *Chem. Phys. Lett.* **1999**, *307*, 272.

(16) Nakai, H.; Kawamura, Y. *Chem. Phys. Lett.* **2000**, *318*, 298.

(17) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(18) The terms delocalization and hyperconjugation are used interchangeably further on.

(19) Frisch, A.; Frisch, M. J. *Gaussian 98 User's Reference*, 2nd ed.; Gaussian Inc.: Carnegie Office Park, Bldg. 6, Pittsburgh, PA 15106; p 71.

(20) Bader, R. F.; Cheeseman, J. R.; Laidig, K. E.; Wiberg, K. B.; Breneman, C. *J. Am. Chem. Soc.* **1990**, *112*, 6530.

(21) Goodman, L.; Kundu, T.; Leszczyński, J. *J. Am. Chem. Soc.* **1995**, *117*, 2082.

(22) Hehre, W. J.; Radom, L.; von Ragué Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley & Sons: New York, 1986; p 262.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1992**, *114*, 4382.

(25) Alkmenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct. (THEOCHEM)* **1985**, *128*, 59.

(26) Bastiansen, O.; Smedvik, L. *Acta Chem. Scand.* **1954**, *8*. 1593.

(27) Goodman, L.; Pophristic, V. *Chem. Phys. Lett.* **1996**, *259*, 287.

(28) Ozkabak, A. G.; Goodman, L. *J. Chem. Phys.* **1992**, *96*, 5958.

(29) Guo, D.; Goodman, L. *J. Chem. Phys.* **1996**, *100*, 12540.

(30) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.

(31) Taylor, D. K.; Bytheway, I.; Barton, D. H. R.; Bayse, C. A.; Hall, M. B. *J. Org. Chem.* **1995**, *60*, 435.

(32) Hehre, W. J.; Jianguo, Y.; Klunzinger, P. E.; Liang L. *A Brief Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction, Inc.: Irvine, CA, 1998.

(33) Rigby, M.; Smith, E. B.; Wakeham, W. A.; Maitland, G. C. *The Forces Between Molecules*; Clarendon Press: Oxford, U.K., 1986.