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On the Tilt and Asymmetry of Methyl Groups in Asymmetric Environments

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Abstract: An interpretation of the tilt and asymmetry of methyl groups in asymmetric environments is sought by means of ab initio calculations on a variety of geometry-optimized conformations of methylamine, nitrosomethane, methanol, and methylborine. Constraining parts of the molecules to nonequilibrium geometries and allowing the remainder to seek the minimum energy structure provides additional data beyond that available from the stable form. Localized orbitals and Mulliken population analyses are used in examination of the electronic structures. The methyl tilt can be interpreted as a combination of bond-bond repulsions between the C–H and X–H bonds and between the X–H bonds and the lone pair. Both are important, although the C–H···X–H interaction is dominant. The observed asymmetric differences in the C–H bond lengths are also discussed.

The C_{3v} symmetry of a methyl group need not be preserved in any compound in which it is attached to an asymmetric group. Relatively little experimental information exists on the extent to which such distortion occurs, but some data have become available.

As a first approximation, the methyl group may be treated as a rigid, symmetric rotor and the angle which the symmetry axis of the group makes with the C–X direction used as a structural parameter to be determined experimentally. This angle is known as the methyl tilt. Most cases that have been studied involve an atom X with one or more lone pairs of electrons, in which case the tilt has been determined to fall in the range from 2 to 4° and to be invariably directed toward the lone pair. Some compounds in which this has been observed are shown in Table I.

In some cases, the full asymmetry of the methyl group has been explored experimentally. This has been possible in some studies by microwave spectroscopy,[2] and a recent series of infrared studies[3] has indicated that the methyl C–H bond trans to a lone pair on the substituent atom X is generally longer than the other two. The differences in C–H bond distances are on the order of 0.01 Å and the angular asymmetries within the methyl group range up to 3.5°.

Several ab initio calculations on methanol,[4-6] methylamine,[6-8] methyl mercaptan,[6] and dimethylamine[9] have shown that experimentally measured methyl tilts are very well reproduced within the LCAO-MO-SCF approximation. It may at first seem surprising that such minor structural features may be predicted with high accuracy, but the major sources of error in the Hartree–Fock method, finite basis sets and neglect of electron correlation, are of minimal importance here. The difference in electron correlation produced by tilting a methyl group a few degrees is certainly insignificant. The energy optimization used in the SCF iteration weighs most heavily the electron distribution near the nuclei, so that properties such as the dipole moment which are sensitive to the charge density at large distances from the nucleus require a large basis set for accurate determination. The angular geometry of molecules, however, is most sensitive to the charge density in the bonding region near the central atom, and it appears that an extremely close approximation to the Hartree–Fock limit is not required. In spite of the several studies on methyl group tilt, few attempts have been made to analyze the behavior in terms of localized orbitals and coulomb or exchange effects as has been done, for example, with rotational barriers.[10]

The purpose of this paper is to seek a simple model which explains the methyl group asymmetries. In structural chemistry, such explanations are usually constructed by examining data on known, stable substances and seeking correlations which have predictive power. Molecular orbital calculations have introduced a powerful new tool for such purposes in that structures which are artificially constrained in some desired manner may also be examined. In effect, one may distort the molecule in a selected way and then, by energy optimization of the remaining geometrical parameters, see how the rest of the molecule responds to this distortion. The test of the "bent bond explanation" for the methyl tilt in methylamine discussed below provides a particularly straightforward illustration of this procedure.

Details of the Calculations

Several series of geometry-optimized ab initio calculations have been made on methylamine staggered, eclipsed, and in two conformations with the amine planar; nitrosomethane staggered and eclipsed; methanol staggered and eclipsed; and methylborine with the borine planar, eclipsed, and staggered. The conformations examined are sketched in Figure 1.

All calculations were made by solving the Roothaan LCAO-MO-SCF equations[11] using a basis set of Gaussian atomic orbitals. A set with 7s and 3p functions on the heavy atoms and 4s on the hydrogens was contracted to 4s and 2p on the heavy atoms and 2s on hydrogen. The exponents and contraction coefficients were those of Roos and Siegbahn[12] for carbon, oxygen, and nitrogen and Huzinaga's exponents[13] scaled with 1.25 for hydrogen. The calculations were performed with the program MOLPRO, written by Pulay and Meyer. The program uses Gaussian lobe functions to approximate the p functions. All geometries were optimized using the gradient method of Pulay[14] and the force field for methylamine found by Pulay and Török.[7] The gradient method calculates analytically the forces acting on the atoms as functions of the internal parameters and greatly facilitates the geometry optimization. Geometries were optimized until the predicted changes in the angles were less than 0.2° and the

Table I. Experimental Methyl Group Tilts

Compd	Tilt angle, deg	Compd	Tilt angle, deg
CH_3OH	3.3[a]	CH_3SH	3.8[d,e]
CH_3NH_2	3.5[b]	$(CH_3)_2S$	2.8[f]
$(CH_3)_2NH$	3.4[c]	CH_3NO	2.5[g]
$(CH_3)_2O$	2.5[a]		

[a] Reference 18. [b] K. Tabake and T. Kojima, *J. Phys. Soc. Jpn.*, **30,** 1145 (1971). [c] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48,** 5058 (1968). [d] K. T. Hecht and C. M. Dennison, *ibid.*, **26,** 98 (1957). [e] T. Kajima and T. Nisikawa, *J. Phys. Soc. Jpn.*, **12,** 680 (1957). [f] L. Pierce and M. Hagashi, *J. Chem. Phys.*, **35,** 479 (1961). [g] Reference 17.

predicted changes in the bond distances less than 0.002 Å. Use of the calculated force field for methylamine speeded the convergence toward the minimum geometry without altering the final result. Previous calculations[9,15] show that the basis set and method used reproduce with high accuracy the known methyl group asymmetries.

The canonical molecular orbitals resulting from the calculation were transformed into localized orbitals using Boys[16] localization criterion that

$$\sum_{i=0}^{n} \langle \phi_i\phi_i | r_{12}^2 | \phi_i\phi_i \rangle$$

shall be minimized, where n is the number of occupied orbitals ϕ_i. Such localized orbitals provide a useful approximation to the chemist's common discussion of lone pairs, bonding electrons, etc.

Results

The results of all the geometry optimizations are shown in Table II. The methyl tilt in the following discussion is defined as one-third the value of the CH_3 rocking parameter, $\frac{1}{3}(2\alpha_1 - \alpha_2 - \alpha_3)$, where α_1 is the unique X-C-H angle and α_2 and α_3 are the two equal, symmetric X-C-H angles. The features which are of significance for an understanding of the methyl group tilt and asymmetry are discussed separately here.

(a) Methylamine with Amine Nonplanar Staggered and Eclipsed (Figure 1, a_1 and a_2). The minimum energy geometries agree well with those found in the ab initio calculations by Paine and Allen.[8] A large asymmetric distortion appears in the stable, staggered conformation, but both the tilt and bond length asymmetry vanish in the eclipsed conformation. The C-N bond length is unchanged, but there is significant alteration of the geometry of the amine group, the C-N-H angles increasing from 113.7 to 115.4° and the H-N-H angle opening from 110.6 to 112.2° in passing from the staggered to the eclipsed conformation. The angle increases indicate that in a localized orbital picture the nitrogen becomes more sp^2 hybridized and the lone pair acquires more p character. However, even in the staggered form the amine group is considerably distorted from sp^3 hybridization, so that here also the lone pair must have large p character. The difference in the C-H bond lengths obtained from infrared frequencies[3] is 0.008 Å with the unique C-H being longer, identical with that calculated here.

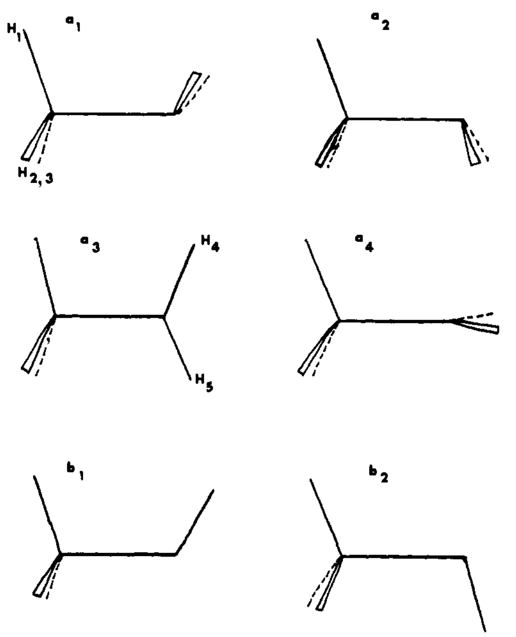

Figure 1. Conformations examined: (a) methylamine and methylborine; (b) nitrosomethane and methanol.

(b) Methylamine with C-N-H Angles Reduced (Figure 1, a_1 and a_2). One interpretation of methyl group tilts involves a bent C-X bond. The lone pair is said to repel the bonding electrons causing the bond to be bent so that the methyl group axis is then collinear with the carbon end of the bent C-X bond. Localized orbital calculations[9] indicate that the C-X bonding orbital is indeed bent in the right direction by the right amount to account for the methyl tilt. Discussion of "causation" in consideration of molecular structures is treacherous, since the word does not have its usual meaning, no time sequence being involved. The actual meaning of this explanation is that the nuclei and electrons seek a potential energy minimum that turns out to simultaneously exhibit three features: a lone pair

Table II. Energies and Optimized Structures of Compounds Examined[a]

	CH_3NH_2				CH_3BH_2		CH_3OH		CH_3NO	
	a_1	a_2	a_3	a_4	a_3	a_4	b_1	b_2	b_1	b_2
C-X	1.472	1.472	1.448	1.450	1.582	1.579	1.439	1.441	1.502	1.505
$C-H_1$	1.089	1.085	1.083	1.090	1.085	1.094	1.086	1.079	1.080	1.076
$C-H_2$	1.081	1.086	1.088	1.081	1.092	1.088	1.082	1.085	1.081	1.082
$X-H_4$	1.005	1.001	0.990	0.992	1.189	1.191	0.965	0.967	1.207[b]	1.207[b]
$X-H_5$	1.005	1.001	0.993	0.992	1.194	1.191				
$\angle XCH_1$	113.7	111.0	108.8	113.8	114.0	108.5	112.3	106.0	110.5	107.7
$\angle XCH_2$	108.6	111.0	112.6	110.1	110.1	112.9	109.0	111.9	107.2	108.9
$\angle H_2CH_3$	107.7	107.6	107.7	107.0	105.5	109.2	108.8	109.1	109.0	109.8
$\angle H_1CH_2$	108.4	108.1	107.4	107.9	108.3	111.8	108.8	108.9	111.5	111.1
$\angle CXH_4$	113.7	115.4	121.0	120.9	122.1	120.9	111.6	110.8	113.6[c]	113.1[c]
$\angle HXH$	110.6	112.2	118.2	118.2	118.1	118.2				
Tilt	3.4	0.0	2.5	2.5	2.6	2.9	2.2	3.9	2.2	0.8
Energy	−95.07655	−95.07329	−95.07258	−95.07259	−65.37226	−65.37226	−114.86000	−114.86236	−168.56150	−168.55986

[a] Energies in hartrees, bond lengths in Å, angles in deg. For configurations and numbering of atoms, see Figure 1. [b] N═O. [c] ∠CNO.

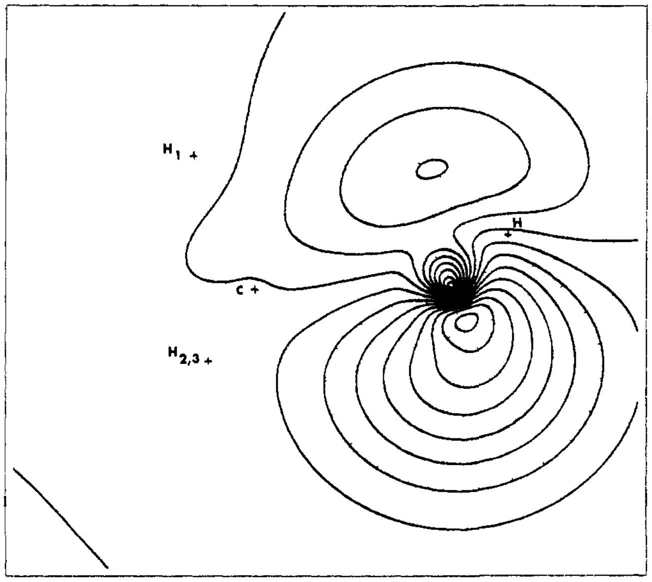

Figure 2. Plot of lone pair in staggered methylamine in symmetry plane of molecule. Zero contour is hashed, contour interval is 0.05.

on nitrogen, a bent C-N bond in the localized orbital representation, and a tilted methyl group. The assumption is that in sufficiently similar situations the same three features will also coexist. Aside from searching through the structures of other molecules, the explanation can also be tested by artificially removing one of the three features in the methylamine molecule and examining the resulting energy-optimized structure to see if the other features disappear.

In the experimental staggered conformation with a symmetric methyl group, we have tilted the amine group symmetrically toward the methyl group so that the lone pair on the nitrogen atom swings away and the C-N localized bonding orbital approaches collinearity with the C-N direction. At a C-N-H angle of 103° the center of charge of the localized C-N bond is on the C-N axis, indicating that the bond is "straight". However, the forces on the CH_3-rocking parameter decrease by only 29%. Although the change in the force is in the right direction, a causal relation between the bending of the bond and the methyl tilt should require this force to disappear completely when the bond becomes linear. We therefore conclude that the bent bond model is not satisfactory.

(c) Methylamine with Amine Planar and Methylborine with Borine Planar (Figure 1, a_3 and a_4). Four sets of calculations, the results of which are shown in Table II, were performed to compare the effect on the methyl group when a C-H bond eclipses an X-H bond, an occupied nonbonding orbital, or a similar vacant orbital. In the eclipsed conformation of methylborine, it is seen that the eclipsed methyl hydrogen atom bends back, indicating a bond-bond repulsion between the two bonds large enough to cause an asymmetry of the magnitude of the methyl group tilt. In methylamine, however, the effect is exactly opposite. The N-C-H angle is greatest when the C-H eclipses the nonbonding pair on nitrogen and least when it eclipses the N-H bond. This clearly indicates that the bond-bond repulsion, C-H···N-H, is smaller than the C-H···nonbonding electron pair repulsion in these compounds. This may be explained, at least in part, by the fact that the nonbonding pair is closer to the C-H bond, forming an angle of 90° to the C-N bond compared to 120° for the N-H bond.

(d) Nitrosomethane Eclipsed and Staggered (Figure 1, b_1 and b_2). The calculations reproduce the experimental observation[17] that the eclipsed conformation is the more stable one. The calculated methyl tilt is 2.2°, in good agreement with the

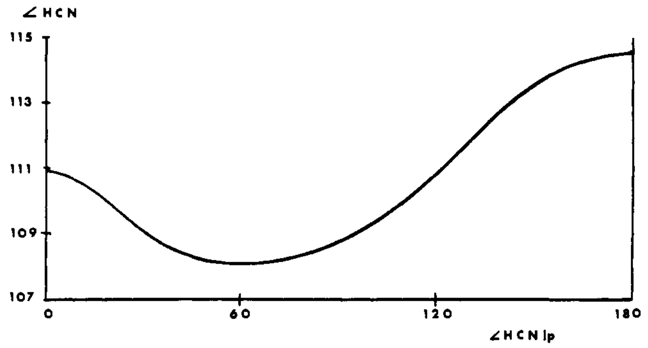

Figure 3. ∠HCN in methylamine against the dihedral angle H-C-N-lp.

experimental value of 2.5°. If one considers the double bond as two bent bonds, this structure is similar to the staggered form of methylamine. The methyl group is tilted toward the lone pair in the equilibrium conformation of both compounds, but the effect is smaller in nitrosomethane. Rotation of the substituent by 180° also nearly removes the methyl tilt in nitrosomethane.

(e) Methanol Eclipsed and Staggered (Figure 1, b_1 and b_2). The experimental equilibrium structure,[18] which is staggered with a methyl tilt of about 3.3° away from the O-H bond, is very well reproduced by the calculation. In the eclipsed conformation, the tilt is reduced, but not as much as in the compounds with only one lone pair. The difference in the C-H bond lengths in 0.006 Å, in agreement with the value found by McKean et al.,[3] also 0.006 Å.

Discussion

The series of calculations of optimal geometries presented here suggests a model of the methyl group asymmetries based on simple bond-bond repulsion arguments. The calculations on methylborine and methylamine with planar amine also indicate that in such a model the shape of the lone pair must be taken into consideration. One way of formalizing such a discussion has been suggested by Robb et al.[19] where the orbitals are localized and discussed in terms of their size. A measure of the latter is taken to be a sphere with centroid of charge given by the expectation value of the dipole length operator r_1 with respect to the localized orbital and with a radius equal to the root mean square of the distance from the electron to the centroid. In the present context this method is of limited value as the nonspherical nature of the lone pair is central to our discussion.

In all the compounds examined, the preferred conformation is the one in which the total bond-bond repulsion is minimized. Satisfaction of this condition may, however, lead to a situation in which one C-H bond is subjected to a large repulsive force and the other two to weak forces, thereby causing the asymmetry which is observed as a methyl tilt and inequality of bond lengths and angles.

The position of the lone pair, which is critical for this discussion, is not a property which is directly accessible by experimental techniques. With the use of localized orbitals, however, we may determine the direction of the lone pair, defined by the vector from the nitrogen or oxygen nucleus to the center of charge of the orbital, and the degree of p character of the lone pair, the latter being most easily studied by plotting the orbital. These two characteristics are interconnected. In a pure p orbital, as in planar methylamine, the C-N-lp angle is 90°. In nitrosomethane, the same angle is 116° and mostly sp^3. The situation is intermediate in staggered methylamine where the angle is 102°.

The repulsive effect of the lone pair is dependent on its distance from the C-H bond, which means on the C-X-lp angle

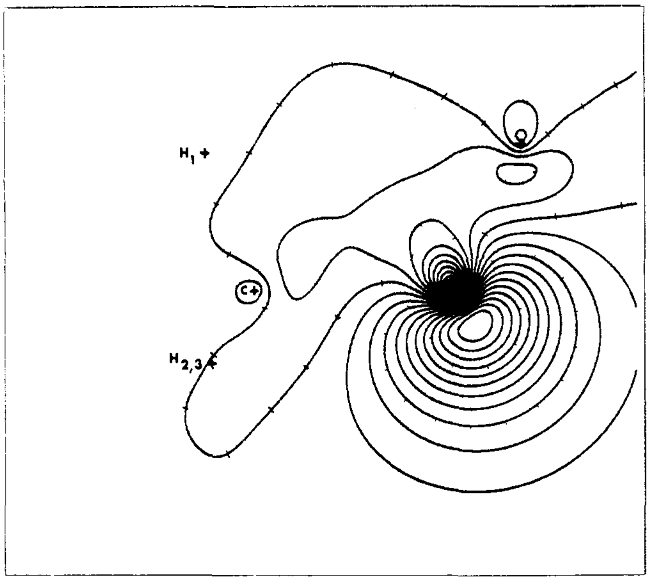

Figure 4. Plot of lone pair in eclipsed nitrosomethane, plot values as for Figure 2.

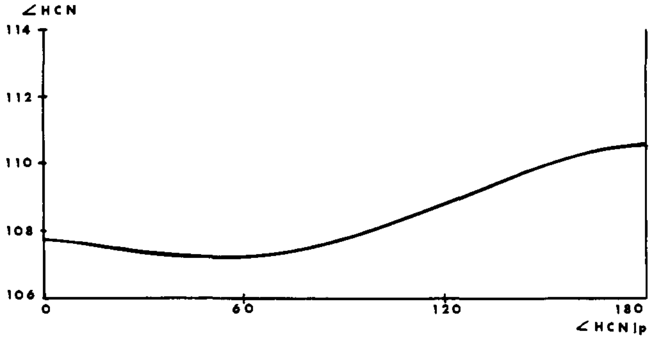

Figure 5. ∠HCN in nitrosomethane against the dihedral angle H-C-N-lp.

Figure 6. ∠HCO in methanol against dihedral angle HCOH. The scale of the latter is displaced 180° to correspond to Figures 3 and 5.

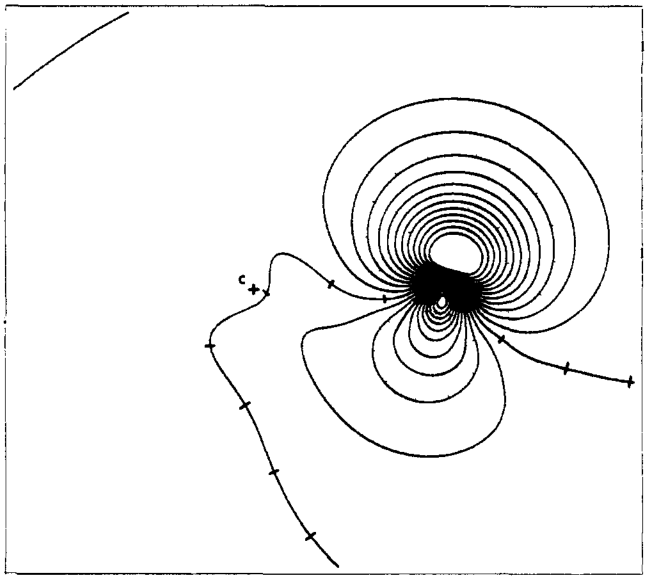

Figure 7. Plot of lone pair in staggered methanol, plotted in the plane of carbon, oxygen, and center of charge of lone pair.

as well as the C-X distance. Depending mainly on the angle, the effect may be either a weak repulsion as in CH_3NO or a strong repulsion as in planar methylamine. In the latter case, however, the nonbonding pair repels equally on both sides of the central plane. The intermediate case of staggered methylamine is particularly interesting. Here the symmetric C-H bond is repelled not only by the N-H bonds but also by the unhybridized part of the lone pair. The plot of this lone pair in Figure 2 confirms that there is a high lone pair density on the "wrong" side of the nitrogen nucleus. The importance of these "tails" of the C-H bonding orbitals for the rotational barrier of ethane has been demonstrated by the recent work of Christiansen and Palke[20] in a study using orthogonalized Hartree-product wave functions. The two repulsive forces acting on the C-H in the lone pair plane combine to cause the tilt toward the greater part of the lone pair. The same effect can be seen if the H-C-N angle is plotted against the dihedral angle H-C-N-lp starting with the C-H and N-lp eclipsed as zero (Figure 3). If the important effects in determining the H-C-N angle are the repulsion from the N-H bonds and the sp^3 part of the lone pair, the curve should show a dependence on $\cos\phi$ and $\cos 3\phi$. If there is also a contribution from the p character of the lone pair, there should also be a $\cos 2\phi$ contribution to the curve. Simple analysis shows that the curve in Figure 3 can be written as $\angle\text{H-C-N} = -1.7\cos\phi + 1.7\cos 2\phi + 0.2\cos 3\phi + 110.2°$. This approach, then, substantiates the conclusion that there is a considerable contribution from the unhybridized part of the lone pair.

In nitrosomethane, traditional chemical intuition would indicate sp^2 hybridization of the lone pair and a large C-N-lp angle. This would result in a weak lone pair repulsion of the C-H bond. This expectation is confirmed by a plot of the lone pair (Figure 4). An analysis of the H-C-H angle vs. the dihedral H-C-N-lp angle, shown in Figure 5, gives the analytical form $\angle\text{H-C-N} = -1.5\cos\phi + 0.7\cos 2\phi + 0.1\cos 3\phi + 108.4°$. A smaller contribution from the p part of the lone pair is indicated than in the case of staggered methylamine. The eclipsed form of nitrosomethane is stable because, as indicated earlier, it is the configuration with the least total bond-bond repulsions, although the single eclipsing C-H feels more repulsion than either of the two others in staggered conformations.

For methanol, analysis of the O-C-H angle variations with the dihedral angle H-C-O-H, shown in Figure 6, gives $\angle\text{O-C-H} = -3.1\cos\phi - 0.9\cos 2\phi - 0.1\cos 3\phi + 110.0°$, indicating that repulsion from the O-H bond is the most important contribution to the methyl tilt, although lone pair repulsion may participate in stabilizing the staggered conformation compared to the eclipsed. If the electronic structure around the oxygen atom is examined, it is seen that all of the electron density is drawn closer to the oxygen nucleus. This tends to reduce the bond-bond interaction and increase the significance of the nucleus-nucleus repulsion O-H···H-C as the hydrogen attached to oxygen is left with a higher positive charge. A plot of the oxygen lone pairs, shown in Figure 7, also shows that they have very much p character, which levels out the angular part of the lone pair repulsion.

The calculated differences in C–H bond lengths are in good agreement with previous calculations,[21] and with experimental values.[3] Our calculations predict equal bond distances for CH_3NO, but experimental data to test the prediction are not yet available.

Conclusions

The methyl group tilt in all of the conformations, both equilibrium and artificially constrained, of all of the compounds examined can be explained as the consequence of repulsion between the C–H bonds of the methyl group and the bonds on the adjacent atom. The repulsion between C–H and either an N–H, O–H, or N=O bond is greater than the repulsion between the C–H bond and a lone pair. The molecules adopt the configuration with the smallest total bond-bond repulsion. Since this often leads to a situation where one bond is repelled more strongly than the other two, the result is a tilt of the methyl group. The repulsion between the C–H bond and the lone pairs is of little importance because in the cases examined the lone pairs either have a high degree of p symmetry and therefore repel on both sides of the nucleus, as in methanol and methylamine, or form an angle with the C–X bond larger than does the bonded atom on X, as in nitrosomethane.

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Protonation Processes of Unusual Exothermicity

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Abstract: The protonation of guanidine and biguanide is more exothermic by 25 and 70%, respectively, than the neutralization of OH^-, the strongest base in aqueous solution. The effect is caused by the symmetrization of the mesomeric molecules during the process (resonance energy). The protonated base molecules are also more rigid, which shows up in unusually low and even negative entropy changes.

The most exothermic neutralization processes occurring in aqueous solution have reaction enthalpies not exceeding 60 kJ/mol. The protonation of OH^-, the strongest base in water, with $\Delta H = -56$ kJ/mol, is close to that limit. Although ammonia and aliphatic amines are much less basic than OH^-, their protonation enthalpies are in the same range and for some of them even slightly more negative. On the other hand, surprisingly small enthalpy changes are found in the neutralization of doubly charged anionic strong bases. The strongly exergonic character of these neutralizations (large and negative $\Delta G = -2.3RTpK = \Delta H - T\Delta S$) is, to a considerable extent, caused by the large and positive entropy change during the reaction (see Table I),

Interest in the metal complexes of biguanide made it necessary to determine the enthalpy of its protonation. Thereby we discovered that this strong base ($pK = 13.0$) is the absolute champion with respect to the exothermicity of its neutralization. This result motivated us to investigate the parent compound guanidine as well and indeed, the neutralization of this base ($pK = 13.5$) is also unusually exothermic.

Experimental Section

The data of lines 1–6 in Table I have been taken from the literature.[3] The enthalpies of the last three reactions have been determined using a flow microcalorimeter LKB 10700-1 following a described procedure.[4] The solutions of the reactants were injected by high precision burettes (Mettler DV 105).

Guanidinium chloride (Erba, Milano) was recrystallized from ethanol. A reliable pK value for guanidine is known at the ionic strength $I = 1$ M $NaClO_4$,[5] which was used to calculate the equilibrium concentrations before and after mixing a 0.05 M solution of [HGuan]Cl adjusted to $I = 1$ M with $NaClO_4$ and 1 M NaOH in various ratios.