A Theoretical Approach to Substituent Effects.[1] Structural Consequences of Methyl Hyperconjugation. Methyl Tilt Angles and C–H Bond Lengths

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Abstract: The effect of methyl hyperconjugation on the tilt angle and C–H bond lengths of methyl groups has been examined using ab initio molecular orbital theory. A perturbation molecular orbital approach is developed to explain the results in two model systems, methylborane and methylamine. The qualitative model is then used to rationalize the results observed in the set of molecules $CH_3X{=}Y$ for X = CH and N and for Y = CH_2, NH, and O. The results are interpreted in terms of two-electron interactions between the occupied π(Me) orbitals on methyl and any adjacent low-lying vacant orbitals as well as between the vacant π^*(Me) orbitals on methyl and any adjacent high-lying occupied orbitals. Although the possibility of four-electron interactions cannot be discounted, it is significant that all the results presented in this paper may be understood in terms of two-electron interactions alone. Methyl tilt angles and C–H bond lengths provide a sensitive and experimentally accessible probe for hyperconjugative interaction for a wide variety of molecules containing methyl groups.

Introduction

The phenomenon of methyl hyperconjugation has undergone extensive study during recent years. As a result the concept has passed from being one of considerable controversy[3] to one now enjoying widespread support.[1a,4-9] The methyl group is currently regarded as being capable of acting either as a hyperconjugative donor when it is adjacent to a group possessing a low-lying vacant orbital (e.g., CH_2^+, BH_2, $-CH{=}CH_2$) or as a hyperconjugative acceptor when adjacent to a group possessing a high-lying occupied orbital (e.g., O^-, CH_2^-, OH, NH_2). Probes used to study hyperconjugation have included rotational barriers[4-6] and heats of reaction,[5] and more recently there have been theoretical isotope effect studies.[7]

This paper uses ab initio molecular orbital theory to examine an additional structural consequence of hyperconjugation, namely, the tilt of a methyl group in an asymmetric environment. The tilt of methyl groups has recently been examined by Boggs et al.,[10] who interpreted their results in terms of a bond-bond repulsion model. We believe, however, that attractive forces are important in determining tilt angles and that a model based solely on repulsive forces cannot be entirely successful. Accordingly, this paper presents an alternative approach based on perturbation molecular orbital[11] (PMO) theory which takes into account both attractive and repulsive interactions and which is consistent with results for a wide range of structures.

We believe that the building of qualitative models to rationalize the quantitative results of ab initio molecular orbital calculations constitutes a key step in the continued growth of chemical understanding. To quote Hoffmann:[12] "The problem is understanding why the calculation came out the way it did." The qualitative model constructed on this basis may then be used in a predictive sense for related systems for which quantitative data are not available.

The strategy used in this paper, therefore, is to formulate, on the basis of the calculated tilt angles for constrained structures of methylborane and methylamine, a qualitative model that attempts to identify the key interactions that influence methyl tilt. The model is then tested by examination of results for a variety of systems including the set of $CH_3X{=}Y$ molecules with X = CH and N and Y = CH_2, NH, and O.

Computational Method and Results

Standard ab initio molecular orbital calculations were carried out using a modified version of the GAUSSIAN 70 series of programs[13] and the STO-3G[14] and 4-31G[15] basis sets. Subject to specified constraints all structures were fully optimized at the STO-3G level by use of either a gradient[16] or an axial iterative optimization technique.

The methylboranes and methylamines were studied with bonds to N and B atoms held coplanar in both perpendicular (**1**, **3**) and eclipsed (**2**, **4**) conformations. Such constrained geometries are particularly suitable for examining methyl tilts. Calculations were conducted in two ways: (1) the methyl group was fully optimized subject only to the constraints implied by the overall molecular symmetry (C_s), and (2) the methyl group was defined to have a C_3 axis tilted by an amount α away from the C–X axis (Figure 1), and the structures were optimized with respect to both tilt angle and the angle between the C–H bonds and the C_3 axis. All other geometric parameters were optimized in both cases.

Either set of calculations enables the tilt of the methyl group to be estimated. In the former case, the tilt may be obtained using the equation[17]

$$3\cos(\alpha_1 + 2\alpha) = 4\cos\alpha_2 - \cos\alpha_1 \qquad (1)$$

where $\alpha_1 = \angle H_1CX$ and $\alpha_2 = \angle H_2CX$ and α is the tilt angle between the hypothetical C_3 axis and the C–X bond. In the latter case, the tilt angle is obtained directly from the optimized structure. Agreement between the results of the two methods is excellent.

The sign convention that we use for tilt angles is that a positive tilt corresponds to the situation shown in Figure 1 in which the in-plane H_1 is tilted *toward* X, i.e., $\alpha_1 < \alpha_2$. For the methyl group orientation used throughout this paper, a positive value of the tilt angle corresponds to a *clockwise* tilt.

The molecules $CH_3X{=}Y$ were examined both in eclipsed conformations (e.g., **5**), in which a methyl C–H bond eclipses the X=Y double bond, and in staggered conformations (e.g., **6**), in which two methyl C–H bonds are staggered about the double bond. For these systems, single-point 4-31G energy calculations were carried out on the STO-3G optimized structures (denoted 4-31G//STO-3G).

Optimized structural parameters including calculated tilt angles (with a direction indicated by an arrow above the structures) for perpendicular and eclipsed conformations of methylborane and methylamine are displayed in Figure 2.[18] Corresponding total energies are listed in Table I. Structures and tilt angles for $CH_3X{=}Y$ molecules are shown in Figure 3 with corresponding total energies in Table II. Finally, rotational barriers for $CH_3X{=}Y$ calculated at both STO-3G//

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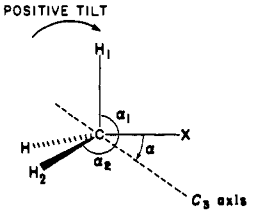

Figure 1. The tilt of the approximate C_3 axis of a methyl group with respect to the C-X bond. The tilt angle, α, is defined as the angle between the C_3 axis and the C-X bond, and is positive as illustrated.

Table I. Calculated Total Energies (STO-3G//STO-3G, hartrees) for Model Structures of Methylamine and Methylborane

	conformation	
molecule	eclipsed	perpendicular
CH_3NH_2	−94.016 16	−94.016 16
CH_3NH_2[a]	−94.016 16	−94.016 16
CH_3BH_2	−64.667 61	−64.667 64
CH_3BH_2[a]	−64.667 53	−64.667 56

[a] Local C_3 symmetry assumed for methyl group bond angles.

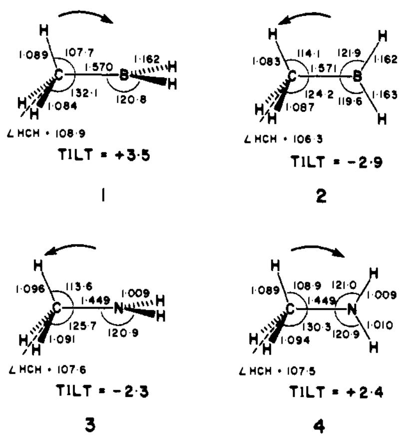

Figure 2. STO-3G optimized structures of perpendicular and eclipsed conformations of methylborane and methylamine with bonds at B and N respectively constrained to planarity. Tilt angles are given below the structures and the direction of tilt is indicated by the arrows above the structures.

STO-3G and 4-31G//STO-3G levels are presented in Table III.

Discussion

Methylborane and Methylamine. The calculated tilt angles for methylborane and methylamine in both perpendicular (**1** and **3**) and eclipsed (**2** and **4**) conformations (Figure 2) indicate that there are significant asymmetric forces acting on the methyl group. The magnitudes of the tilts are qualitatively in agreement with results obtained by Boggs et al.[10] In addition, tilt angles obtained using fully optimized structures and eq 1 are identical with those derived from the model in which the methyl group is constrained to have a C_3 axis.

The above tilts have been interpreted[10] in term of repulsive interactions, either of the bond-bond type or the lone pair-bond type. Although the tilt observed in eclipsed methylborane (**2**) can be attributed to such an interaction (specifically, between the eclipsed C-H and B-H bonds), the tilt in the perpendicular conformation (**1**), which is even larger in magnitude but in the opposite direction, is not readily explained using this model based solely on repulsive interactions.

An alternative model, using a PMO[11] approach, is based on the hyperconjugative interaction of the methyl substituent with neighboring groups. A priori, methyl may act as either a π donor or a π acceptor. This is because it possesses two degenerate, occupied π(Me) orbitals as well as two degenerate, vacant π^*(Me) orbitals.[19] The orbitals and their relative energies are represented schematically in Figure 4.

Let us now use the PMO model in order to identify the specific interactions responsible for the observed tilts in the methylboranes. In eclipsed methylborane (**2**), the relevant interaction is that between the methyl π_a(Me) orbital and the formally vacant p orbital [p(B)] on BH_2 (see Figure 5). Overlap of p(B) with π_a(Me) is clearly greater in the zone below the C-B bond than in the corresponding zone above the C-B bond owing to the contribution of orbitals on the out-of-plane methyl hydrogens to π_a(Me). There is thus a greater attractive interaction below the C-B bond than above it, and this leads immediately to a negative tilt as shown in **2**.

For the perpendicular conformation (**1**) of methylborane, the key interaction is that between the π_b(Me) orbital and the p(B) orbital of the BH_2 group, as shown in Figure 6. In this case, the p(B) orbital overlaps with orbitals of both the in-plane hydrogen above the C-B bond and the two out-of-plane hydrogens below the C-B bond. Since the overlap is greater for the closer in-plane hydrogen,[20] a positive tilt as shown in **1** occurs so as to maximize this overlap differential. The tilt of the methyl group in both conformations of methylborane may thus be attributed to attractive forces rather than the repulsive forces previously suggested.[10]

Turning now to the observed methyl tilts in perpendicular and eclipsed methylamine, we find that the direction of tilt is the opposite of that observed in the corresponding methylborane. In the eclipsed conformation (**4**), the key interactions are those between the N lone pair [p(N)] and the π_a(Me) orbital on the one hand and the π_a^*(Me) orbital on the other. The relevant interaction diagram is shown in Figure 7. The first interaction, between two occupied orbitals (interaction A) is destabilizing and repulsive. The second (interaction B), between an occupied and a vacant orbital, is stabilizing and, overall, attractive. Both interactions, however, contribute to a positive tilt. Interaction A (Figure 7) generates a positive tilt because interaction between the orbitals of the two out-of-plane hydrogens and the p(N) orbital is repulsive; this is because both orbitals are occupied. In the case of interaction B, overlap between the orbitals of the out-of-plane hydrogens and the

Table II. Calculated Total Energies (hartrees) for Conformations of $CH_3X{=}Y$ Systems

	conformation			
	HCX=Y eclipsed		HCX=Y staggered	
molecule	STO-3G//STO-3G	4-31G//STO-3G	STO-3G//STO-3G	4-31G//STO-3G
$CH_3CH{=}CH_2$	−115.660 30	−116.904 59	−115.657 85	−116.901 68
$CH_3CH{=}NH$ (CCNH anti)	−131.412 46	−132.868 33	−131.410 16	−132.865 90
$CH_3CH{=}NH$ (CCNH syn)	−131.412 93	−132.867 28	−131.411 04	−132.865 28
$CH_3CH{=}O$	−150.945 99	−152.684 99	−150.944 21	−152.683 39
$CH_3N{=}CH_2$	−131.407 56	−132.854 60	−131.405 19	−132.850 79
$CH_3N{=}NH$ (CNNH trans)	−147.144 38	−148.784 94	−147.142 23	−148.782 17
$CH_3N{=}NH$ (CNNH cis)	−147.135 96	−148.774 88	−147.133 92	−148.771 58
$CH_3N{=}O$	−166.653 73	−168.560 61	−166.652 03	−168.558 60

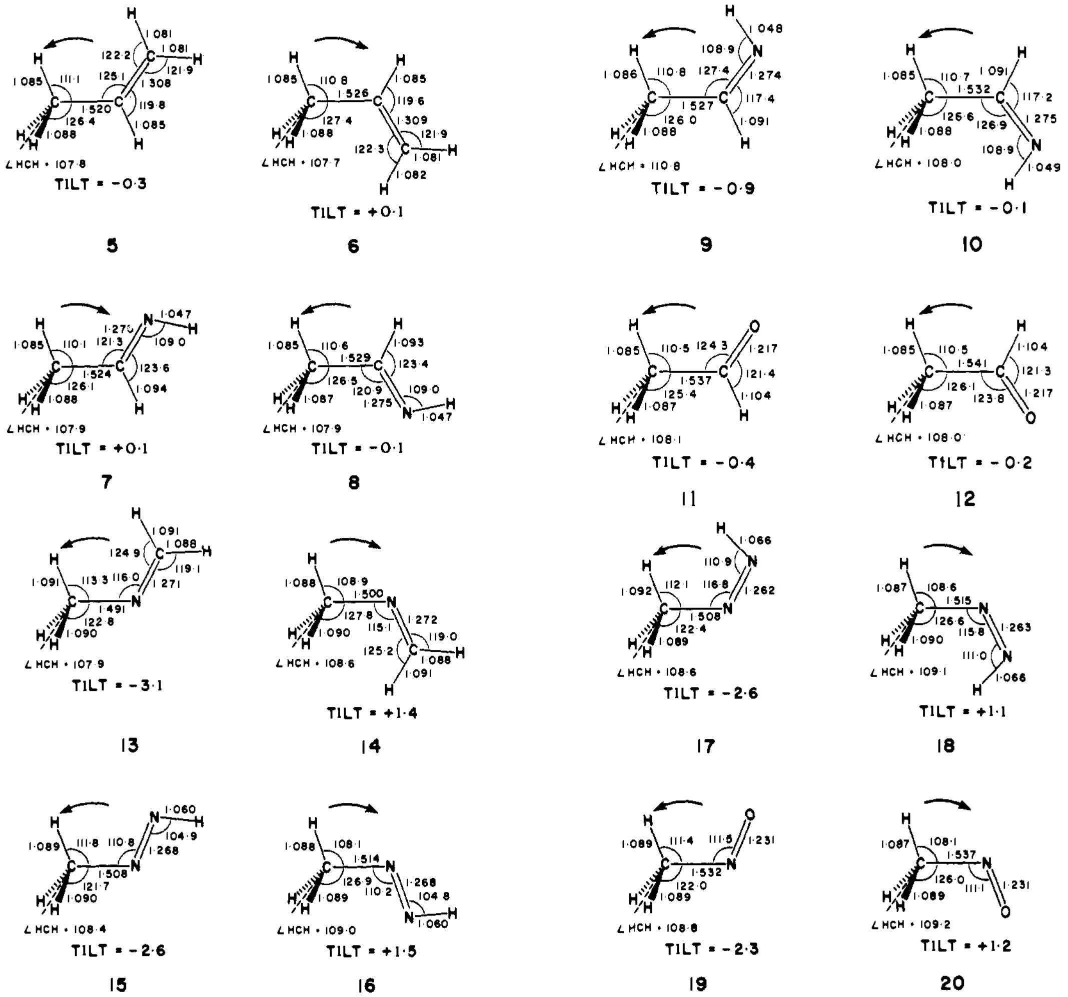

Figure 3. STO-3G optimized structures for staggered and eclipsed conformation of $CH_3X{=}Y$. Tilt angles are given below the structures and the direction of tilt is indicated by arrows above the structures.

Table III. Calculated Rotational Barriers (kcal mol^{-1}) for $CH_3X{=}Y$ Systems

molecule	STO-3G//STO-3G	4-31G//STO-3G	expt[a]
$CH_3CH{=}CH_2$	1.54	1.83	2.00
$CH_3CH{=}NH$ (CCNH anti)	1.44	1.52	1.64
$CH_3CH{=}NH$ (CCNH syn)	1.19	1.26	
CH_3CHO	1.12	1.00	1.16
$CH_3N{=}CH_2$	1.49	2.39	1.97
$CH_3N{=}NH$ (CNNH trans)	1.35	1.74	
$CH_3{=}NH$ (CNNH cis)	1.28	2.07	
$CH_3N{=}O$	1.07	1.26	1.14

[a] Taken from ref 6.

p(N) orbital is *negative*, so that, although interaction B is both stabilizing and attractive with respect to the methyl group *as a whole*, the opposite phases of the hydrogen orbitals and the p(N) orbital result in a repulsive force in the region *below* the C-N bond and a consequent positive tilt of the methyl group.

For the perpendicular conformer (**3**), a similar argument holds. Greater repulsion above the C-N bond between the p(N) lone-pair orbital and the π_b(Me) orbital due to the four-electron repulsion term (interaction A, Figure 8) and a greater *attractive* force between the p(N) lone-pair orbital and the π_b*(Me) *below* the C-N bond[21] (interaction B, Figure 8) lead to a negative tilt of the methyl group.

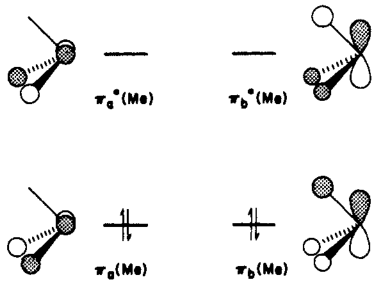

Figure 4. Group orbitals associated with the methyl substituent: two degenerate, occupied orbitals, π_a(Me) and π_b(Me), and two degenerate, vacant orbitals, π_a*(Me) and π_b*(Me).

The above discussion suggests that both two-electron and four-electron interactions contribute to the methyl tilt in methylamine. Although this in fact may be the case, we would point out that all the results in this paper are explicable solely in terms of two-electron effects. Coupled with the fact that two-electron interactions are intrinsically larger than four-electron interactions,[22] we are inclined to attribute our results to the two-electron components until more definitive proof for the importance of four-electron terms is produced.

$CH_3X{=}Y$ Systems. The previous discussion which interprets tilts in the model systems methylborane and methylamine provides basic guidelines for analyzing methyl tilts in other systems. The group of molecules we have investigated in detail

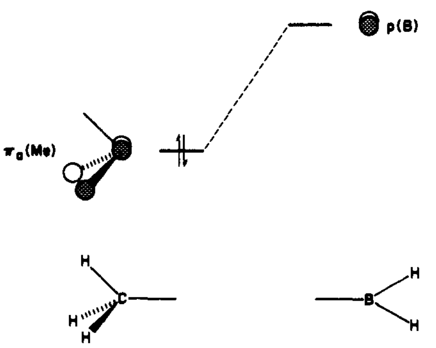

Figure 5. Energy diagram showing the interaction of a methyl π_a(Me) orbital with a vacant p orbital, p(B), on B in eclipsed CH_3BH_2.

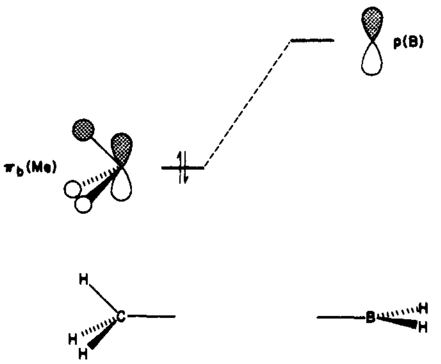

Figure 6. Energy diagram showing the interaction of a methyl π_b(Me) orbital with a vacant p orbital, p(B), on B in perpendicular CH_3BH_2.

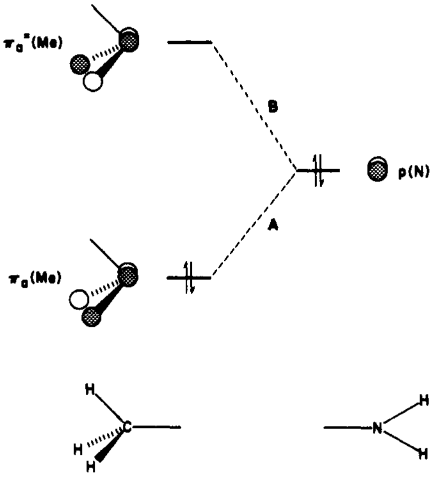

Figure 7. Energy diagram showing the interaction of π_a(Me) and π_a^*(Me) orbitals with an occupied lone-pair orbital, p(N), on N in eclipsed CH_3NH_2.

is $CH_3X{=}Y$. Recently, Hehre et al.[6] have examined methyl rotational barriers in the above system, utilizing the interaction of group orbitals in the two interacting moieties, CH_3 and $X{=}Y$, to rationalize the methyl tilt angles in this set of molecules.

The interaction of a methyl group with a double bond may be effectively described using the orbital interaction diagram shown in Figure 9. In principle, methyl may act as either a π-donating or a π-accepting group (interactions B and C, respectively). In practice, interaction B appears to be dominant: methyl is well established to act as a hyperconjugative donor when attached to a double bond. In addition, there is a destabilizing interaction, A, between the two occupied orbitals. Representation of these orbitals for eclipsed and staggered conformations of $CH_3X{=}Y$ leads to the orbital diagrams

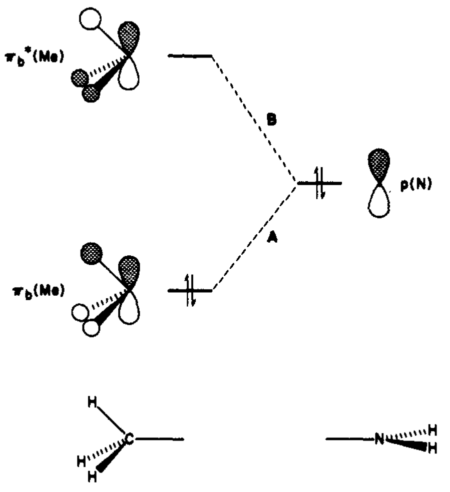

Figure 8. Energy diagram showing the interaction of π_b(Me) and π_b^*(Me) orbitals with an occupied lone-pair orbital, p(N), on N in perpendicular CH_3NH_2.

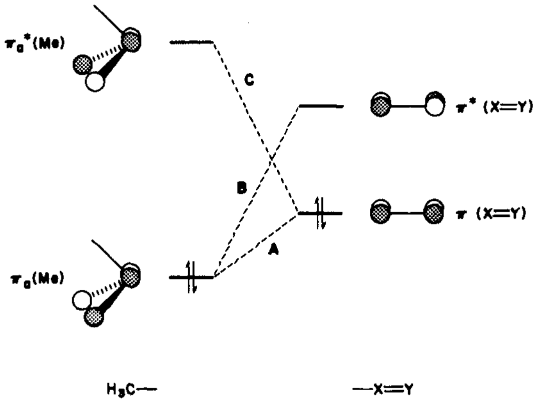

Figure 9. Energy diagram showing the interaction of the methyl group orbitals with the π and π^* orbitals of $-X{=}Y$.

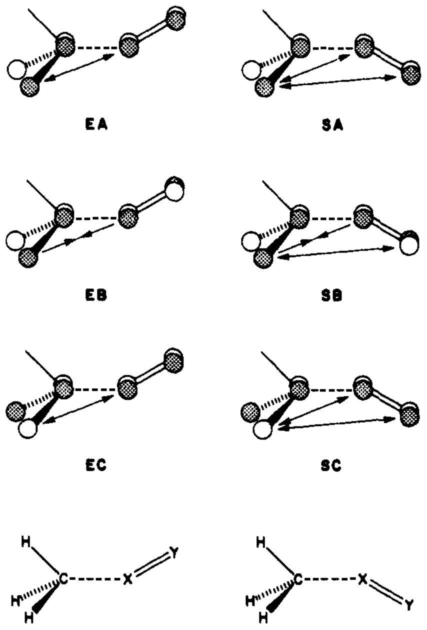

Figure 10. Attractive (→←) and repulsive (←→) forces between the methyl hydrogens and the $-X{=}Y$ group in eclipsed (E) and staggered (S) conformations of $CH_3X{=}Y$ on the basis of interacting group orbitals.

pictured in Figure 10. We emphasize here that the diagrams refer to interaction between two group orbitals and do not represent the molecular orbitals resulting from these interactions.

Effect of Methyl Conformation. The tilt of the methyl group in any *eclipsed* conformer (E) will depend on the nature of the forces between the hydrogen-atom component of the π_a(Me) and π_a^*(Me) orbitals and the orbitals on the atom to which the methyl is bonded. These are indicated in EA, EB, and EC of Figure 10. We term these particular forces 1,3 interactions. There are several components to the 1,3 interaction: (A) a weak repulsive force due to a four-electron term (shown as EA); (B) a strong attractive force resulting from the methyl hyperconjugative donation into the π^*(X=Y) orbital (shown as EB); (C) a weak repulsive force arising from two-electron interaction between π(X=Y) and π^*(Me) accompanied by negative 1,3 overlap (shown as EC); (D) if either X or Y in $CH_3X{=}Y$ is an N atom, then an additional interaction is possible in which the N lone pair interacts with the appropriate π^*(Me) orbital. Examples of such an interaction are shown in Figure 11 and are attractive.

Examination of the eclipsed $CH_3X{=}Y$ structures in Figure 3 suggests that the attractive hyperconjugative interaction between π(Me) and π^*(X=Y) (effect B) (Figure 10, EB) is generally the dominant force governing the methyl tilt. With the exception only of $CH_3CH{=}NH$, all eclipsed structures show a negative tilt. The tilt in $CH_3CH{=}NH$ appears to be reversed owing to the dominance of effect D whereby the N lone pair interacts with the π^*(Me) orbitals.

Examination of the possible interactions in the *staggered* conformations (S) of $CH_3X{=}Y$ molecules (Figure 10, SA, SB, SC) indicates that, in addition to the 1,3 interactions present in the eclipsed conformer, 1,4 interactions also need to be considered. In all cases the 1,4 interaction is repulsive. In interactions represented by diagrams SB and SC (Figure 10) the repulsion occurs because the two-electron interaction is associated with negative 1,4 overlap. As normally, the four-electron interaction is also repulsive (Figure 10, SA). We conclude therefore that all staggered conformers are likely to show more positive tilts than their eclipsed counterparts. This is true for all pairs of conformers, except those of $CH_3CH{=}NH$, which again reflect the effect of the additional interaction of the N lone pair with the π^*(Me) orbital (Figure 11, ED).

These general ideas on the factors governing the tilts of staggered conformers may be further tested by studying the effects of certain perturbations on the magnitude of the methyl tilts.

Effect of Changing X. Changing the group X in $CH_3X{=}Y$ from CH to N is found to increase the absolute magnitude of the methyl tilt angles very substantially. Thus comparison of eclipsed $CH_3CH{=}CH_2$ (**5**) and eclipsed $CH_3N{=}CH_2$ (**13**) shows a change in tilt angle from −0.3 to −3.1°. Since the tilt here is governed by the favorable two-electron 1,3-hyperconjugative term (effect B), any increase in that term will increase the tilt angle. Substitution of N for CH increases this attractive force by lowering the energy level of the π^*(X=Y) orbital. In addition, the attractive interaction between the N lone pair and the π^*(Me) orbital (illustrated in Figure 11, ED) will serve to increase the absolute magnitude of the tilt angle even further. An identical argument holds for the comparison of eclipsed $CH_3CH{=}NH$ (**9**) and eclipsed $CH_3N{=}NH$ (**17**), and an analogous argument holds for the pairs of staggered conformers **6** and **14** and **10** and **18**.

Effect of Changing Y. Comparison of eclipsed structures of $CH_3CH{=}CH_2$, $CH_3CH{=}NH$, and $CH_3CH{=}O$ indicates that there is a slight gradual increase in the absolute magnitude of the tilt angle (from 0.3 to 0.4°). This increase may be attributed to an increase in the two-electron hyperconjugative interaction of methyl with the C=Y bond (Figure 10, EB). In the eclipsed series $CH_3N{=}CH_2$, $CH_3N{=}NH$, and $CH_3N{=}O$, the reverse trend occurs and the absolute tilt angle decreases in magnitude. This may be attributed to the additional and stronger effect of the N lone pair which interacts with the π^*(Me) orbital (Figure 11, ED). The effect of the donation from nitrogen is greatest in $CH_3N{=}CH_2$ since the electronegativity of the Y moiety has a marked effect on the electron-donating ability of N. This decreases in the order $N{=}CH_2 > N{=}NH > N{=}O$. This decrease occurs as a result of a deshielding effect, which we have discussed in detail elsewhere.[23] In essence, the presence of an electronegative group on N lowers the energy of all the N orbitals, including that for the lone pair, and makes the N atom a less effective electron donor. Thus, the trend in tilt magnitudes is dominated by the negative hyperconjugative interaction of the N lone pair with the methyl group (effect D and Figure 11, ED) rather than the positive hyperconjugative donation by methyl into the N=Y double bond (effect B and Figure 10, EB). Additional evidence for the competing hyperconjugative effects may be seen by reference to the three C–H methyl bond lengths (see below).

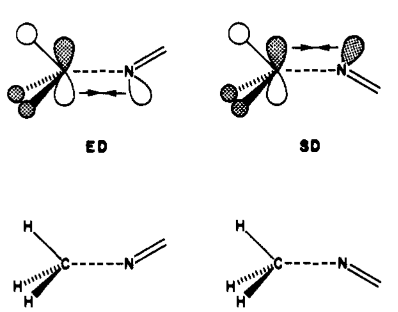

Figure 11. Attractive two-electron interactions between the lone pair on N and the π_b^*(Me) orbital on methyl in eclipsed (E) and staggered (S) conformations of $CH_3N{=}Y$.

Effect of Hyperconjugation on Methyl C–H Bond Lengths. A direct consequence of both positive and negative hyperconjugation is that the interacting C–H bonds are lengthened compared to those of a noninteracting methyl group. For positive hyperconjugation, this arises through the removal of bonding electron density from the C–H bonds of the π(Me) orbitals, whereas in negative hyperconjugation this arises through addition of electrons to the π^*(Me) orbitals which are antibonding in the C–H bonds.

These effects are readily confirmed in the present study. For instance, in perpendicular methylborane (**1**), the in-plane (or hyperconjugatively interacting) C–H bond is significantly lengthened compared to the two out-of-plane C–H bonds (1.089 Å compared to 1.084 Å). Similarly, in eclipsed methylborane (**2**), it is the out-of-plane (again hyperconjugatively interacting) C–H bonds that are lengthened compared to the in-plane C–H bond (1.087 Å compared to 1.083 Å). In the two conformations of methylamine, a similar pattern occurs, though here it is the negative hyperconjugative interaction between the p(N) lone pair and a π^*(Me) orbital that results in the specific lengthening of either the in-plane C–H bond in the perpendicular conformation (**3**) or the out-of-plane C–H bonds in the eclipsed conformation (**4**).

In the $CH_3X{=}Y$ systems, evidence for methyl hyperconjugation, as derived from the different C–H bond lengths within a particular CH_3 group, is again readily discernible. With the exception of eclipsed isomers of $CH_3N{=}CH_2$ (**13**), $CH_3N{=}NH_2$ (**17**), and $CH_3N{=}O$ (**19**), the optimized structures all indicate that the two out-of-plane C–H bonds are slightly elongated compared to the in-plane C–H bond. This is because only one [namely, π_a(Me)] of the two degenerate π(Me) orbitals is of the appropriate symmetry to interact with the π^*(X=Y) orbital. Results for the three nitrogen systems ($CH_3N{=}CH_2$, $CH_3N{=}NH$, and $CH_3N{=}O$) mentioned above provide further evidence that the competing ne-

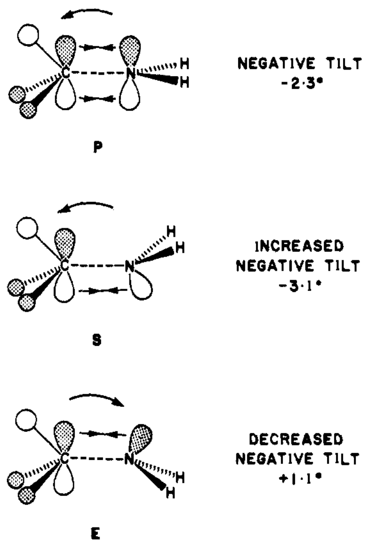

Figure 12. Attractive two-electron interactions between the lone-pair orbital on N, p(N), and the methyl π_b^*(Me) orbital and corresponding tilts for perpendicular (P), staggered (S), and eclipsed (E) conformations of methylamine.

gative hyperconjugative interaction between the lone pair on nitrogen and the π_b^*(Me) orbital is greater than the positive hyperconjugative interaction between π_a(Me) and the double bond: the in-plane C–H bond is found to be longer than (or equal to) the two out-of-plane C–H bonds for each of these systems. Of particular interest is the fact that the negative hyperconjugative interaction is most effective in the orientation where the lone pair on N is trans with respect to a methyl C–H bond (Figure 11, ED) rather than the one in which the lone pair is cis to the in-plane C–H bond (Figure 11, SD). This again reflects the fact that the overlap is more favorable in the region *below* the C–N bond than in the corresponding region above the bond.[21]

Thus the calculated C–H lengths provide strong supportive evidence for the qualitative PMO arguments we have used earlier to explain the methyl tilt angles.

Rotational Barriers in $CH_3X{=}Y$. In a recent publication, Hehre et al.[6] have investigated methyl rotational barriers in the same set of molecules, $CH_3X{=}Y$. Their calculated data were based on single-point 4-31G calculations on partially optimized STO-3G structures. Table III lists rotational barriers at STO-3G//STO-3G and 4-31G//STO-3G levels. Agreement between the 4-31G//STO-3G results and the results reported by Hehre et al.[6] is good and no significant improvement in the comparison with available experimental data occurs. The 4-31G//STO-3G results appear to be in slightly better agreement with experiment[24] than are the STO-3G//STO-3G values.

In view of the fact that the forces affecting methyl tilt angles are essentially those responsible for methyl rotational barriers, we might expect some correlation between the difference between the tilt angles in eclipsed and staggered conformations of a given $CH_3X{=}Y$ and the corresponding methyl rotational barrier. There is a general tendency for this to occur but the correspondence is not 1:1. For instance, the structures showing large rotational barriers (e.g., $CH_3N{=}CH_2$, 2.39 kcal mol^{-1}; $CH_3N{=}NH$, 2.07 kcal mol^{-1}) do show large differences of tilt angles in the eclipsed and staggered conformations (4.5 and 3.7°, respectively), whereas those structures showing low rotational barriers (e.g., CH_3CHO, 1.00 kcal mol^{-1}; *syn*-$CH_3CH{=}NH$, 1.26 kcal mol^{-1}) show small differences in the tilt angles in the two conformations (0.6 and 0.3°, respectively). The approximate correlation suggests therefore that the analysis of key interactions is a sound one but that other factors play roles in both rotational barriers and tilt angles of the methyl group.

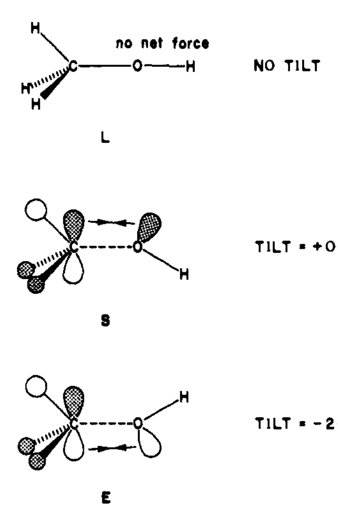

Figure 13. Dominant attractive forces between an oxygen lone-pair orbital and the methyl π_b^*(Me) orbital for linear (L, no net effect on tilt), staggered (S), and eclipsed (E) conformations of methanol.

Tilt Angles in Other Systems. Tilt angles available from the literature[25-27] for a number of other systems are listed in Table IV. The results in all cases are in keeping with the arguments presented in this paper. For instance, the ethyl cation $CH_3CH_2^+$ would be expected to behave in a similar manner to methylborane and indeed shows positive tilt in the perpendicular conformation and negative tilt in the eclipsed conformation. The absolute magnitude of the tilt is greater in the ethyl cation system than in the methylborane system owing to the fact that the vacant p orbital in ethyl cation is lower in energy than the corresponding one in methylborane. This leads to a smaller energy gap between interacting orbitals in the ethyl cation which results in larger interaction energies and correspondingly larger tilts. Likewise, the ethyl anion, which resembles methylamine, has a negative tilt in the perpendicular conformation and a positive tilt in the eclipsed conformation. Again, the magnitude of the tilt is greater in the ethyl anion system owing to the enhanced negative hyperconjugation of the high-lying lone-pair orbital with the π^*(Me) orbital of appropriate symmetry.

The tilt angles in fully optimized methylamine structures, i.e., in the absence of a planarity constraint at nitrogen, are of interest. In particular, the *change* in tilt accompanying distortions from the perpendicular structure with planar N to staggered and eclipsed conformations is noteworthy. The tilt in the perpendicular structure is −2.3°, but changes to −3.1° in the staggered conformation and to +1.1° in the eclipsed conformation. The reason for these changes may be seen in Figure 12.

We have already noted that in the perpendicular conformation (P, Figure 12) with a planar N a negative tilt occurs owing to greater overlap below the C–N bond than above it.[21] As we proceed to the staggered conformation in which the N is now pyramidal (S, Figure 12), this differential increases, which leads to an *enhanced* negative tilt. In the eclipsed conformation (E, Figure 12), however, the differential decreases to the extent that the overlap is actually greater *above* the C–N than below it and, as a consequence, a positive tilt occurs.

A similar argument explains the conformational dependence of the tilt in methanol (Figure 13). For methanol with a linear C–O–H linkage (L, Figure 13), the tilt is zero by symmetry: the attractive force between one of the p(O) lone pairs and the π_a^*(Me) orbital (similar to interaction B of Figure 7) must be exactly balanced by the attractive but opposing force between the second p(O) orbital and the methyl π_b^*(Me) orbital

Table IV. Tilt Angles from the Literature for Related Systems

molecule	conformation	tilt angle	method	ref
$CH_3CH_2^+$	"perpendicular"[a]	+5.4	4-31G	25
$CH_3CH_2^+$	eclipsed	−4.5	4-31G	25
$CH_3CH_2^-$	"perpendicular"[a]	−5.7	4-31G	27
$CH_3CH_2^-$	eclipsed	+5.1	4.31G	27
CH_3NH_2	staggered	−3.1	STO-3G	26
		−3.4	DZ	10
CH_3NH_2	eclipsed	+1.1	STO-3G	26
		0.0	DZ	10
CH_3OH	staggered	+0.4	STO-3G	26
		+3.9	DZ	10
CH_3OH	eclipsed	−2.0	STO-3G	26
		−2.2	DZ	10

[a] Because this structure does not have a planarity constraint at C, it cannot strictly be called perpendicular, but this notation is used to bring out more clearly the relationship with constrained conformations of CH_3BH_2 and CH_3NH_2.

(similar to interaction B in Figure 3). For nonlinear structures, the first of these interactions remains approximately the same but the second interaction changes, which leads to an imbalance of forces above and below the C–O bond and hence a tilt of the methyl group. In the staggered conformation (S) there is increased attraction above the C–O bond, which results in a positive tilt, while in the eclipsed conformation (E) there is increased attraction below the C–O bond, which leads to a negative tilt.

Conclusion

The tilt angles of methyl groups in a wide range of molecules can be readily explained, using a PMO approach, in terms of a limited number of key interactions that may occur between the methyl substituent and the group to which it is attached. Where the adjacent group contains a low-lying vacant orbital, the key interaction appears to be the hyperconjugative donation by the methyl π(Me) orbital of appropriate symmetry into the low-lying orbital. Where the adjacent group contains a high-lying filled orbital, the key interaction appears to be the negative hyperconjugative donation by the high-lying orbital into the vacant π^*(Me) orbital of appropriate symmetry. Although some contribution from four-electron terms undoubtedly takes place, we consider it significant that the results presented in this paper may be understood in terms of two-electron interactions alone. The PMO model is given additional support by the calculated methyl C–H bond lengths. The methyl tilt angles and C–H bond lengths constitute a sensitive and experimentally accessible probe for both positive and negative hyperconjugation.

References and Notes

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(17) We thank Dr. L. Farnell for having provided us with this relationship.

(18) Throughout this paper, bond lengths are in ångstroms and bond angles are in degrees.

(19) For an excellent account of the group orbitals of methyl, see: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(20) Proof for the statement that the overlap in perpendicular CH_3BH_2 (**1**) is greater above the C–B bond than below it may be derived by considering the case of CH_3Li. By symmetry, no tilt takes place here, which indicates that the negative tilt caused by the interaction of π_a(Me) with p(Li) (similar to that shown in Figure 5) is *exactly* balanced by a positive tilt caused by the interaction of π_b(Me) with the second p(Li) orbital (similar to that shown in Figure 6). This positive tilt must therefore be attributed to the greater additive effect of the in-plane hydrogen to the overlap term *above* the bond as compared with the contribution of the two out-of-plane hydrogens to the overlap *below* the bond.

(21) In the case of interaction between the p(N) orbital and $\pi_b{}^*$(Me) in methylamine (interaction B, Figure 8), the overlap is actually *greater below* the C–N bond (cf. footnote 20) since, owing to their opposite phases, the greater contribution of the in-plane hydrogen is now *substracted* from the 2p(C) orbital.

(22) Four-electron destabilizing terms result from the difference between two opposing perturbations, whereas the two electron term is just one of these perturbations (the stabilizing one). Hence in general one would expect two-electron terms to be intrinsically larger than four-electron terms. In fact, under a zero overlap approximation, four-electron terms are zero.

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