CH_3 and CF_3 Hyperconjugation in the Second Row

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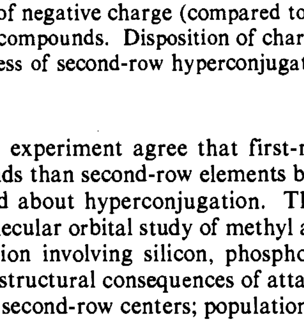
Abstract: Molecular orbital studies of methyl- and trifluoromethyl-substituted Si, P, and S compounds are used to predict the structural and energetic consequences of hyperconjugation in molecules containing second-row elements. Both occur in an experimentally observable range. The structural and energy effects in methyl compounds (tilt angles, bond-length disparities, conformational energy, and interaction energy differences) are calculated to be much smaller than in the corresponding 1st row species, on which comparison calculations were made. By contrast, the structural effects in CF_3 compounds of Si, P, and S are as large as in the C, N, and O compounds, even though the associated energy effects of the substitution are not. Although hyperconjugation is stronger in the second-row anionic species ($SiH_2CH_3^-$, $SiH_2CF_3^-$, $PHCH_3^-$, $PHCF_3^-$, SCH_3^-, and SCF_3^-) than in the neutral and cationic species, the exceptionally strong interactions found in the first-row anions ($C_2H_5^-$, $CH_2CF_3^-$, $NHCH_3^-$ etc.) are absent from the second-row compounds. Hyperconjugation is calculated to reverse the usual bond lengthening effect of negative charge (compared to the neutrals) in the C-, N-, and O-containing anions but not in the analogous Si, P, and S compounds. Disposition of charge density around second-row atoms and lone-pair orientation both contribute to the weakness of second-row hyperconjugation.

Theory and experiment agree that first-row elements form stronger π-bonds than second-row elements but the question has not been asked about hyperconjugation. This is a report of a systematic molecular orbital study of methyl and trifluoromethyl hyperconjugation involving silicon, phosphorus, and sulfur to determine the structural consequences of attaching the CH_3 and CF_3 groups to second-row centers; population analysis and relative-energy calculations are used to try to explain them.

In a study of hyperconjugation in molecules of first-row elements, Pross, Radom, and Riggs use a simple PMO argument to explain the opposite effects on CH_3 of attaching a π-acceptor and a π-donor.[1] When the attached group Y has lower than threefold symmetry about the axis of attachment to the methyl group a disparity appears in the C–H bond lengths and the axis of the CH_3 group tilts.[2] The bond-distance data and the tilt angle provide useful means of characterizing the strength of the hyperconjugative interaction and the direction of tilt indicates its sense. The tilt angle α is conveniently given by the relation $3 \cos(\alpha_1 + 2\alpha) = 4 \cos \alpha_2 - \cos \alpha_1$; the convention adopted is that a tilt of H_1 toward Y, with $\alpha_2 > \alpha_1$, is taken as *positive*.[1]



Interaction between Y and CH_3 still occurs when Y has high symmetry, as in CH_3O^-, but the tilt and bond-length disparity are absent. The magnitude of the hyperconjugative effect has to be judged then by other means. To use a structural criterion, C–H bond lengths can be compared with those in compounds in which it cannot occur, such as CH_4.

When a methyl group is bound to a π-donor group such as NH_2, the π-acceptor role is dominant. For simplicity's sake, take nitrogen to be planar with the CNH_2 plane horizontal and one of the CH bonds in the vertical plane (the so-called "horizontal" conformation[1]). Then the nitrogen $p\pi$ orbital interacts solely with the vertical carbon p orbital. This p orbital contributes to the vertical C–H bond and, as a consequence of the flow of electronic charge to the unoccupied antibonding orbital, the vertical C–H bond is lengthened and the CH_3 group as a whole tilts backward to the point where the balance between C–N bond strengthening and C–H bond weakening is optimal.

With the π-acceptor BH_2 in the perpendicular conformation, the interaction between the carbon p orbital and the empty $p\pi$ orbital of boron favors a positive tilt and a shortening of the C–H bond. It is obvious that the magnitudes of these structural changes will also depend on the orientation of the donor (acceptor) group to which CH_3 is attached, hyperconjugative interaction between N and C being reduced, for example, when the $p\pi$ orbital of a pyramidal NH_2 group is bent away from the vertical position it occupies in a planar amine.

The consequences of attaching the NH_2 or BH_2 groups in the eclipsed orientation are the opposites of what are produced in perpendicular arrangements. Tilt angles, as computed by Radom et al.,[1] for these two groups and these two orientations, are

	CH_3BH_2	CH_3NH_2
perpendicular	3.5°	−2.3°
eclipsed	−2.9°	2.4°

Radom et al. discuss their preference for the two-electron interaction just described as the major interaction but also consider the contribution of electron pair:electron pair interactions.[1]

The peculiarities of substitution by the trifluoromethyl group have received attention in a number of recent publications, and there is strong evidence that hyperconjugative interactions with this group are at least as important as the long-recognized hyperconjugative interactions of methyl.[3] Systematic calculations of CF_3-substituted compounds of second-row hydrides are necessary to permit a comparison of the strength of the interactions with those occurring in CH_3 compounds and in the corresponding first-row systems, all molecules being studied at the same level of theory.

The geometrical consequences of hyperconjugation are well reproduced by calculation at extended basis set level,[2] and it is appropriate to inspect the wave functions to find the reasons for the trends that have become apparent.

Method of Calculation and Results

Geometry optimizations, using the gradient method, were performed on compounds of second-row elements with the 4-31G basis set (P and S compounds) and the 3-21G basis set (compounds of silicon, for which the 4-31G set is not available).[4] The basis

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Table I. Optimized Bond Angle, Bond Length (pm) Data, and Bond Orders Calculated for Methyl-Substituted Silicon and Carbon Compounds, $\mathrm{CH_3{-}Y}^a$

Y	$r(\mathrm{C{-}H_1})$ $r(\mathrm{CH_{2,3}})$	$p(\mathrm{C{-}H_1})$ $p(\mathrm{C{-}H_{2,3}})$	$r(\mathrm{C{-}Y})$	$\angle(\mathrm{YCH_1})$ $\angle(\mathrm{YCH_{2,3}})$, deg	tilt angle, deg
H^b	108.3	0.742	108.3	109.5	
$\mathrm{SiH_3}$	108.7	0.786	188.2	111.0	0
$\mathrm{SiH_2^-}$	108.9	0.730	198.1	113.7	-2.5
	109.2	0.716		110.0	
H^c	108.1	0.766	108.1	109.5	
$\mathrm{CH_3}$	111.1	0.675	153.3	111.6	0
$\mathrm{CH_2^-}$	112.1	0.649	156.8	118.9	-5.6
	109.6	0.725		110.4	

[a] Optimized 3-21G level calculations with d function supplementation of the basis for the silicon compounds. [b] From a 3-21G level calculation of $\mathrm{CH_4}$, for comparison with the silicon species. [c] From a 4-31G level calculation of $\mathrm{CH_4}$, for comparison with the carbon species.

Table II. Optimized Bond Angles, Bond Lengths (pm), and Bond Orders Calculated for Methyl-Substituted Phosphorus and Nitrogen Compounds, $\mathrm{CH_3{-}Y}^a$

Y	$r(\mathrm{H{-}C_1})$ $r(\mathrm{H{-}C_{2,3}})$	$p(\mathrm{H{-}C_1})$ $p(\mathrm{H{-}C_{2,3}})$	$r(\mathrm{Y{-}C})$	$\angle(\mathrm{YCH_1})$ $\angle(\mathrm{YCH_{2,3}})$, deg	tilt angle, deg
H	108.1	0.766	108.1	109.5	
$\mathrm{PH_3^+}$	108.1	0.735	180.4	110.0	0
$\mathrm{PH_2}$	108.0	0.760	186.4	113.0	-2.4
	108.3	0.749		109.3	
$\mathrm{PH^-}$	109.8	0.721	192.0	107.6	4.6
	109.3	0.715		114.5	
$\mathrm{NH_3^+}$	107.6	0.777	152.5	108.2	0
$\mathrm{NH_2}$	108.9	0.782	145.0	114.6	-3.4
	108.1	0.792		109.5	
$\mathrm{NH^-}$	109.7	0.755	145.1	108.8	6.1
	112.1	0.636		117.8	

[a] Optimized 4-31G basis calculations; basis set supplemented by d functions for the phosphorus compounds.

Table III. Optimized Bond Angles, Bond Lengths (pm), and Bond Orders Calculated for Methyl-Substituted Sulfur and Oxygen Compounds, $\mathrm{CH_3{-}Y}^a$

Y	$r(\mathrm{C{-}H_1})$ $r(\mathrm{C{-}H_{2,3}})$	$p(\mathrm{C{-}H_1})$ $p(\mathrm{C{-}H_{2,3}})$	$r(\mathrm{Y{-}C})$	$\angle(\mathrm{YCH_1})$ $\angle(\mathrm{YCH_{2,3}})$, deg	tilt angle, deg
H	108.1	0.766	108.1	109.5	
$\mathrm{SH_2^+}$	107.6	0.745	183.6	110.5	-2.3
	107.8	0.739		107.9	
SH	108.0	0.755	182.2	106.9	3.0
	107.9	0.752		111.4	
$\mathrm{S^-}$	109.2	0.716	183.9	112.5	0
$\mathrm{OH_2^+}$	107.2	0.757	154.2	105.9	-0.9
	107.2	0.757		104.5	
OH	107.6	0.786	143.0	106.3	3.6
	108.3	0.764		109.2	
$\mathrm{O^-}$	112.2	0.641	136.1	115.7	0

[a] Optimized 4-31G basis calculations; basis set supplemented by d functions for the sulfur compounds.

Table IV. Optimized Bond Lengths (pm), Bond Angles, Bond Orders, and Tilt Angles Calculated for Silicon and Carbon $\mathrm{CF_3}$-Substituted Compounds $\mathrm{Y{-}CF_3}^a$

Y	$r(\mathrm{C{-}F_1})$ $r(\mathrm{C{-}F_{2,3}})$	$p(\mathrm{C{-}F_1})$ $p(\mathrm{C{-}F_{2,3}})$	$r(\mathrm{C{-}Y})$	$\angle(\mathrm{YCF_1})$ $\angle(\mathrm{YCF_{2,3}})$, deg	tilt angle, deg
H^b	134.5	0.439	106.6	110.6	
$\mathrm{SiH_3}$	136.1	0.330	188.5	111.7	
$\mathrm{SiH_2^-}$	137.9	0.325	194.6	118.1	-3.3
	138.3	0.320		113.1	
H^c	135.2	0.360	106.6	110.6	
$\mathrm{CH_3}$	136.1	0.362	148.6	121.0	
$\mathrm{CH_2^-}$	149.2	0.303	138.6	121.0	-3.7
	139.7	0.292		115.5	

[a] Geometry-optimized 3-21G(#) level calculations for silicon compounds, 4-31G level calculations for carbon compounds. [b] From a 3-21G level calculation of $\mathrm{CH_4}$, for comparison with the silicon species. [c] From a 4-31G level calculation of $\mathrm{CH_4}$, for comparison with the carbon species.

Table V. Optimized Bond Lengths (pm), Bond Angles, Bond Orders, and Tilt Angles Calculated for Phosphorus and Nitrogen $\mathrm{CF_3}$-Substituted Compounds, $\mathrm{Y{-}CF_3}^a$

Y	$r(\mathrm{C{-}F_1})$ $r(\mathrm{C{-}F_{2,3}})$	$p(\mathrm{C{-}F_1})$ $p(\mathrm{C{-}F_{2,3}})$	$r(\mathrm{C{-}Y})$	$\angle(\mathrm{YCF_1})$ $\angle(\mathrm{YCF_{2,3}})$, deg	tilt angle, deg
H^b	135.2	0.360	106.6	110.6	
$\mathrm{PH_2}$	136.1	0.317	187.2	114.7	-2.7
	136.3	0.306		110.6	
$\mathrm{PH^-}$	138.9	0.272	184.4	111.9	4.1
	140.4	0.258		117.9	
$\mathrm{NH_2}$	137.3	0.446	136.4	114.9	-2.6
	135.8	0.424		111.1	
$\mathrm{NH^-}$	138.3	0.304	129.9	114.4	2.8
	144.5	0.295		118.6	

[a] Geometry-optimized 4-31G(#) level calculations for phosphorus compounds, 4-31G level calculations for nitrogen-containing species. [b] From a 4-31G level calculation of $\mathrm{CH_4}$.

Table VI. Optimized Bond Lengths (pm), Bond Angles, Bond Orders, and Tilt Angles Calculated for Sulfur and Oxygen $\mathrm{CF_3}$-Substituted Compounds, $\mathrm{Y{-}CF_3}^a$

Y	$r(\mathrm{C{-}F_1})$ $r(\mathrm{C{-}F_{2,3}})$	$p(\mathrm{C{-}F_1})$ $p(\mathrm{C{-}F_{2,3}})$	$r(\mathrm{C{-}Y})$	$\angle(\mathrm{YCF_1})$ $\angle(\mathrm{YCF_{2,3}})$, deg	tilt angle, deg
H	135.2	0.360	106.6	110.6	
SH	135.5	0.320	178.4	109.0	2.8
	135.7	0.312		113.3	
$\mathrm{S^-}$	139.9	0.265	172.2	116.2	
OH	133.6	0.441	133.8	109.2	1.9
	135.7	0.422		112.2	
$\mathrm{O^-}$	141.7	0.292	123.3	116.7	

[a] Geometry-optimized 4-31G(#) level calculations for sulfur compounds, 4-31G level calculations for oxygen-containing compounds. [b] From a 4-31G level calculation of $\mathrm{CH_4}$.

sets were supplemented, for the second-row atoms only, with five d functions and are here designated the 4-31G(#) and 3-21G(#) sets to distinguish them from the standard 3-21G(*) and 4-31G(*) sets. The latter include six d functions on the larger atoms.[4] The d function exponents were 0.45, 0.55, and 0.65 for Si, P, and S, respectively, as recommended.[4] Basis sets were supplemented with diffuse functions (4-31+G and 6-31+G bases) for energy calculations on anions, as recommended by Chandrasekhar et al.,[5] but geometry optimization was always performed without the diffuse functions. Energy calculations (single determinant restricted

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[5] Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612. Exponents for the diffuse functions were obtained by optimization calculations on $\mathrm{SiH_3^-}$, $\mathrm{PH_2^-}$, and $\mathrm{SH^-}$, yielding values of 0.03, 0.04, and 0.03 respectively for Si, P, and S.

Table VII. Energy Differences (kJ mol^{-1}) and Bond Length Differences (pm) between Staggered and Eclipsed Conformations and Overlap Density Data Calculated for Methyl-Substituted Second-Row Hydrides[a]

compd	ΔE	Δr(Y–C)	Y–C bond orders p(σ)/p(π)
$SiH_3{\cdot}CH_3$	5.9	0.1	0.63/0.05
$SiH_2{\cdot}CH_3^-$	7.0	1.5	0.50/–0.02
$PH_3{\cdot}CH_3^+$	7.0	1.1	0.58/–0.01
$PH_2{\cdot}CH_3$	8.1	1.3	0.63/–0.02
$PH{\cdot}CH_3^-$	6.5	1.5	0.54/0.05
$SH_2{\cdot}CH_3^+$	7.3	1.4	0.45/–0.02
$SH{\cdot}CH_3$	5.8	0.9	0.53/–0.02
$S{\cdot}CH_3^-$			0.42/0.06

[a] The energy of the staggered conformation is lower and the bond shorter in every case. Conformational energy differences obtained from 6-31G##/4-31G(#) calculations; bond length differences and bond orders from 4-31G(#)//4-31G(#) level calculations (3-21G-(#)//3-21G(#) level for silicon compounds).

Table VIII. Energy Differences (kJ mol^{-1}) and Bond Length Differences (pm) between Staggered and Eclipsed Conformations and Overlap Density Data Calculated for Methyl-Substituted First-Row Hydrides[a]

compd	ΔE	Δr(Y–C)	Y–C bond orders p(σ)/p(π)
$CH_3{\cdot}CH_3$	11.6	1.2	0.64/0.07
$CH_2{\cdot}CH_3^-$	70.6[b]	1.3	0.67/0.06
$NH_3{\cdot}CH_3^+$	8.6	1.2	0.21/–0.09
$NH_2{\cdot}CH_3$[c]			0.49/–0.09
$NH{\cdot}CH_3^-$	30.4[b]	0.8	0.47/0.17
$OH_2{\cdot}CH_3^+$[c]			0.07/–0.09
$OH{\cdot}CH_3$	4.9	0.3	0.35/–0.03
$O{\cdot}CH_3^-$			0.33/0.28

[a] All results from 4-31G//4-31G level calculations. The energy of the staggered conformation is lower and the bond shorter in every case. [b] 6-31+G*//4-31+G* results from ref 10. [c] No local minimum for the eclipsed conformation at 4-31G level.

Table IX. pπ:pπ Overlap Integrals for Si–C, P–C, S–C, and C–C, N–C, O–C Bonds[a]

Si–C	0.195	C–C	0.192
P–C	0.170	N–C	0.163
S–C	0.154	O–C	0.135

[a] Calculated for Slater-type orbitals and at optimized bond distances found for Y·CH_3 for Y = SiH_3, PH_2, SH, CH_3, NH_2, and OH.

Hartree–Fock level) were carried out with the GAUSSIAN 80 suite of programs.[6]

Optimized geometrical data and population-analysis results are collected in Tables I–III (CH_3 compounds) and Tables IV–VI (CF_3 compounds); the tables include companion data for first-row molecules calculated with the 3-21G and 4-31G basis sets, considered to be equivalent to the supplemented bases used for the second-row species.[4] In every case, the staggered conformations are the most stable and the results refer only to these. Conformational-energy differences are given in Tables VII and VIII, and there are some overlap-integral and formal charge data in Tables IX and X.

Relative energy calculations, measuring the strength of the Si–CH_3, P–CH_3, S–CH_3 etc., interactions in energetic terms are reported in Table XI. The results were obtained from single point calculations at 6-31G# level on the 4-31G(#) level optimized geometries (3-21G(#) level optimizations in the case of compounds of silicon, for which the 4-31G basis is not available). The reliability of data of this kind has already been discussed.[7]

Table X. Charge Density Data for Methyl-Substituted First- and Second-Row Hydride[a]

	q_C	q_Y		q_C	q_Y
$SiH_3{\cdot}CH_3$	–0.96	0.75	$CH_3{\cdot}CH_3$	–0.59	–0.59
$SiH_2{\cdot}CH_3^-$	–0.84	–0.04	$CH_2{\cdot}CH_3^-$	–0.56	–0.62
$PH_2{\cdot}CH_3$	–0.63	0.08	$NH_2{\cdot}CH_3$	–0.22	–0.86
$PH{\cdot}CH_3^-$	–0.55	–0.45	$NH{\cdot}CH_3^-$	–0.16	–0.93
$SH{\cdot}CH_3$	–0.55	–0.15	$CH_3{\cdot}OH$	–0.12	–0.75
$S{\cdot}CH_3^-$	–0.46	–0.75	$O{\cdot}CH_3^-$	0.06	–0.95

[a] Mulliken gross atomic charges expressed as formal charges; basis set levels as in Tables I–VI.

Full details of calculated energies and optimized geometries are published elsewhere.[8] Where comparison is possible, results are in agreement with calculations on sulfur and phosphorus compounds by others,[9-12] but structures of CF_3 compounds are not generally available from either experimental or theoretical sources and extensive comparison is not possible.

An important, although curious, feature of the comparison between CH_3 and CF_3 compounds is that the Y–C bond is sometimes elongated in the Y–CF_3 compound relative to its length in the methyl compound (when Y is highly electronegative, according to Marsden[9]). This circumstance occurs in $SHCH_3$ and $SHCF_3$ but not in PH_2CH_3 and PH_2CF_3 (for references to the structural investigations, see ref 9), and the correct order for these compounds is obtained by the geometry optimization results reported here. (See Tables II, III, V, and VI.) Generally, optimization at the extended basis set level yielded shorter bond lengths for the Y–C bond for the CF_3 compounds than for the CH_3 compounds. This behavior was marked in the case of the anions and was true for both first- and second-row elements. In the latter, r(Y–CF_3) is less than r(Y–CH_3) by an average of ~7 pm (Si, P, and S compounds) and, in the former, by an average of ~13 pm (C, N, and O compounds).

The "long Si–C bond" predicted for SiH_3CF_3[13] was not found at the basis set level used here. Further, there are some compounds of CF_3 and second-row elements, such as $P(CF_3)_3$, for which the correct bond-length behavior is not reproduced by any but the very highest levels of calculation.[9,14] This suggests caution in the use of arguments about bonding to second-row elements based on bond-length data obtained from optimization studies at the basis set levels used here. The comparisons on which the discussion here is based do not seem likely to breach this advice.

σ-Bond orders (Tables VIII and IX) refer to calculated overlap densities involving s and p_z orbitals (taking the C–X bond distance as the z axis), and π-bond orders refer to overlap densities of p_x and p_y orbitals.

Discussion

Hyperconjugation is a π interaction and the clearest evidence for it is structural.[1,2] For model compounds of silicon, phosphorus, and sulfur the data from geometry-optimization calculations (Tables I–VI) display the same features that hyperconjugation is called on to explain in first-row compounds but the interactions are not as strong as in the compounds of the lighter elements. The

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Table XI. CH_3 and CF_3 Substituent Interaction Energies (kJ mol^{-1}) for First- and Second-Row Compounds $Y{-}CH_3$, $Y{-}CF_3$, $Y{-}F$ (Y = CH_3, CH_2^-, NH_2, NH^-, OH, O and Y = SiH_3, SiH_2, PH_2, PH^-, SH, S^-)[a]

	X =				X =		
Y	CF_3	CH_3	F	Y	CF_3	CH_3	F
SiH_3	−74.3	−51.1	189.5	CH_3	−50.3	−97.7	−110.4
SiH_2^-	43.6	−79.6	130.5	CH_2^-	158.8	−112.6	−5.6
PH_2	−96.3	−77.3	−26.4	NH_2	−45.0	−127.1	−290.4
PH^-	19.3	−93.7	−0.5	NH^-	186.4	−135.5	−99.2
SH	−113.6	−97.6	−189.9	OH	−24.4	−132.6	−403.5
S^-	20.3	−132.5	−122.8	O^-	264.8	−134.0	−172.4

[a] Interaction energies refer to the process $YX + H_2 \rightarrow YH + XH$. The values for X = CF_3 were obtained from 6-31G## level calculations on geometries optimized at 3-21G(#) level (Si compounds) and 4-31G(#) level (all other compounds). X = CH_3 and F substitution data from ref 21 (second-row species) and ref 25 (first-row species).

results of experimental search, although not entirely unequivocal, conform to this finding.[15]

Structural data for methyl- and trifluoromethyl-substituted compounds of both first- and second-row elements show hyperconjugative interactions quite strong enough to be readily observed in appropriate experimental circumstances with both first- and second-row species. Structural data for the methyl compounds indicate much weaker responses to hyperconjugation from the second-row cases than from the first-row compounds, but with CF_3 the tilt angles, C–F bond distance disparities, and FCF bond angle differences show that the second-row groups SiH_2^-, PH_2, PH^-, and SH are able to produce the same degree of structural response in CF_3 as are the first-row groups. As explained later, the energetic effects of second-row hyperconjugation are weaker, relative to first-row systems, for both CH_3 and CF_3.

Tilt Angles. The interactions of CH_3 and CF_3 with first- and second-row groups are uniform in that, without exception, AH_2-type groups induce negative tilt and AH-type groups induce positive tilt. However, this uniformity does not extend to the sense of the C–H and C–F bond-length disparities. In the second-row cases the in-plane C–H bond is generally weakened less than the out-of-plane C–H bonds when interaction with the single lone pair of the AH_2 produces negative tilt in the CH_3 or CF_3 group. The reverse generally applies to the first-row compounds, probably in consequence of the fact that bond angles around the second-row atom are much closer to 90° than in the first-row cases.[7,8]

The differences between first- and second-row centers in the direction of the response of C–H and C–F bond lengths to hyperconjugation, as well as the contrast in the strength of the interactions, must be at least partly due to the comparative sizes of the atomic cores, for the following reason. Molecular geometry is determined strongly by the way that attached atoms can be arranged around the core of the element in the middle. As elaborated elsewhere, the small size of the first-row core makes it impossible for bond angles to fall as low or the p-character of the bonding to rise as high as in compounds of the second-row elements.[16] In the case of the methyl and trifluoromethyl compounds dealt with here, the CSiH, CPH, and CSH bond angles fall within the 90–100° range while the range for the corresponding CCH, CNH, and COH bond angles is 106–160°.[7] A high level of p character in the bonds around Si, P, and S suggests a corresponding increase in the hybrid character of the lone pairs which would, therefore, be more strongly directed away from the CH_3 or CF_3 group and interact more weakly than lone pairs of CH_2^-, NH_2, NH^-, or OH.

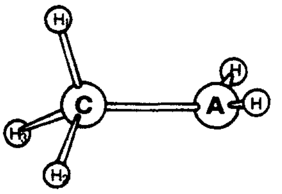
By this argument, therefore, the large core size of the heavier elements may be one reason for the relative weakness of hyperconjugation in the second row and for the structural differences referred to above. To test the idea, calculations on a sample of four molecules ($PHCH_3^-$, $PHCF_3^-$, $NHCH_3^-$, and $NHCF_3^-$) were carried out with the CPH and CNH bond angles held constant at 100.0° while the remaining geometrical parameters were subjected to optimization. The results are in accord with the hypothesis. Tilt is calculated to increase in the phosphorus-containing species as the CPH bond angle is raised to 100° and to decrease in the nitrogen compounds where the CNH bond angle is reduced to 100°.

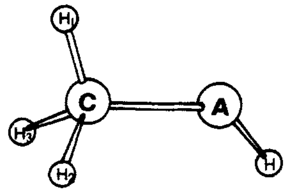
	full optimization		partial optimization	
	tilt angle	∠(CNH), ∠(CPH)	tilt angle	∠(CNH), ∠(CPH)
$NHCH_3^-$	6.1°	106.5°	5.2°	100.0°
$NHCF_3^-$	2.8°	112.0°	2.1°	100.0°
$PHCH_3^-$	4.7°	94.4°	6.3°	100.0°
$PHCF_3^-$	4.1°	90.5°	6.6°	100.0°

The geometry forced upon compounds of second-row elements by the size of the core cannot be the only reason for the weakness of the interaction. Relative to the first-row species, there must be some intrinsic weakness in the second-row hyperconjugation as well. C, N, and O compounds display CCH, CNH, and COH bond angles well in excess of those found in cases where hyperconjugation is not present, and the increases must be occurring to take advantage of an interaction which is not strong enough to support such a change in geometry in the Si, P, and S compounds.

There is one more generalization to be made about the geometrical data for the CH_3 and CF_3 compounds. In the second-row series compounds substitution of CF_3 for CH_3 results in a reduction of the bond angles at Si, P, and S, while in compounds of C, N, and O the opposite occurs. The explanation offered is that CF_3 interacts more strongly than CH_3 and to maximize the interaction the CH_2^-, NH_2, and OH_2^+ groups become flatter and CNH^- and COH angles become straighter, so as to present the lone pair in optimum orientation for π interaction with CF_3.

None of the groups discussed here are strong π-acceptors. Among the groups which bear lone pairs the AH_2-type groups (SiH_2^-, PH_2, SH_2^+, ...) display interaction between the single lone pair and the carbon pπ orbital lying in the same plane. In the diagram below this is the p orbital aligned with the CH_1 bond.





The interaction is rationalized as due to donation of lone pair density to CH_3 or CF_3 in the acceptor mode, resulting in bond weakening and a negative tilt. AH-type groups (PH^-, SH, ...) offer two lone pairs, and in the most stable conformation one of these interacts with the in-plane pπ orbital and the other with the out-of-plane pπ orbital. Lengthening of all three bonds is predicted. The p-type lone pair is expected to interact more strongly with the methyl group than the hybrid lone pair in the CAH plane. The SiH_3X and SX^- compounds possess a threefold axis of symmetry and, as a result, no tilt of the CH_3 or CF_3 axis is possible.

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However, the bond distance and bond order results provide evidence for hyperconjugative interactions of similar strength to those calculated for other CH_3 and CF_3 compounds.

Bond Length Disparities. Optimized C–H and C–F bond lengths conform closely to the trend of calculated C–H bond orders, both showing greatest response in those cases where the π interactions across the C–Y bond are strongest. The magnitudes of the calculated tilt angles are consistent with the indications of the bond length and bond order data. SiH_3, PH_3^+, and S^- compounds, which, for symmetry reasons, display no tilt and no bond length difference between different C–H and C–F bonds, all show the effects of interaction, but it has to be judged by relative C–H and C–Y bond length and bond order data.

Experimental evidence of bond weakening in methyl compounds of phosphorus and sulfur by the isolated stretching frequency technique of McKean[17] has recently been added to earlier work on first-row methyl compounds. The IR results show a readily resolvable difference between the in-plane and out-of-plane CH bonds of CH_3PH_2 (2979 and 2964 cm^{-1}, respectively). By using the McKean frequency–bond length correlation,[18] these data may be used to predict r(C–H) values of 109.3 and 109.5 pm, respectively, if due allowance is made for "offset".[2] The spectra from the deuterated derivative of CH_3SH yield a much smaller splitting (3 cm^{-1}) between the in-plane and out-of-plane CH frequencies and predict r(C–H) values of 109.3 pm for both bonds.

Splittings for compounds of the first-row elements are much larger. For CH_3NH_2 $\Delta\nu$ is 75 cm^{-1} and for CH_3OH it is 59 cm^{-1}, leading to bond length disparities of 0.8 and 0.6 pm, respectively.[2,17] These predicted values are well reproduced by the calculations reported here. (See Tables II, III, V, and VI.)

Anionic Hyperconjugation. As in the first-row compounds, the strongest interactions between Si, P, and S and CH_3 and CF_3 occur in the anions.[10,19] In $MeSiH_2^-$, $MePH^-$, and MeS^- there are C–H bond lengthenings of about 1 pm (relative to the C–H bond length in methane) but these fall well short of the lengthenings (ca. 4 pm) found for the anions of first-row elements. Conformational-energy differences and bond orders lead to the same conclusion, as do tilt angles, although the latter effects seem to be more pronounced than the very small Si–C, P–C, and S–C π-bond orders would have suggested. The indications in the structural data for the CF_3 anions are the same.

Calculated Si–C, P–C, and S–C bond distances in the methyl compounds combine to produce a different pattern from that seen in C–C, N–C, and O–C distances. In the compounds of second-row elements, the changes in Y–C distance between cation, neutral, and anion conform closely to the corresponding changes in C–H bond length in the parent hydrides, H_3S^+, H_2S, HS^-, etc. In the first-row compounds, by contrast, the changes in C–C, C–N, and C–O distances are clearly dominated by the effect of the π interactions; instead of the increase in bond length between the neutral and anionic molecules found for the hydrides (mean lengthening, 5 pm), there is a mean shortening of 3 pm.

With CF_3 as substituent, the picture is slightly different. First-row CF_3 anions again feature marked reduction of C–C, N–C, and O–C bond lengths in the anions, reversing the usual bond-lengthening effect of the negative charge. The shortening averages about 10 pm. However, with CF_3 the bond-shortening effect of hyperconjugation is apparent in the second-row molecules also; $PHCF_3^-$ and SCF_3^- display it but the silicon compound, $SiH_2CF_3^-$, does not.

d Functions. Small contributions to Si–C, P–C, and S–C overlap densities from d functions are observed. They are invariably positive. Because of this, inclusion of d functions in the basis set is important for the computation of energies and geometries[7] but it has no other chemical significance; there is no conformational dependence and no difference in the utilization of d functions between the anions and neutral compounds. The effect of adding the functions is readily explained by noting their polarizing role; the term "d orbitals" would be inappropriate.[7]

Conformational Energies. As first argued by Stamper and Taylor,[20] conformational-energy differences in $MeCH_2X$ and similar compounds may be used to distinguish between the effects of hyperconjugation and other, conformationally-independent, effects. In the compounds considered here, where there are only two heavy atoms, this is not true, since hyperconjugation affects all conformations. σ- and π-bond orders hardly differ between conformations and, except in the case of the anions, the conformational-energy differences must be ascribed mainly to nonbonded interactions.

Energy differences between eclipsed and staggered conformations in the neutral and cationic compounds of both first- and second-row elements lie in the 5–11 kJ mol^{-1} range. For the anions, the energy differences are much greater in the first-row compounds, a result in keeping with the very much greater structural effects found for these compounds. The second-row anions do show distinctly bigger effects than the other second-row compounds, but the exceptional differences found for the first-row anions are absent. As explained elsewhere, about half of the conformational energy difference is due to the relaxation of structure that accompanies rotation, maximizing the energy advantage of hyperconjugation.[8]

Relative Energy Calculations. The results obtained here may be linked with relative energy calculations on second-row elements reported in three earlier papers.[21] Interaction energies for the methyl substituent, $\Delta E(CH_3,H)$, reflect the strength of the Y–CH_3 interaction, referring to the reaction

$$Y{\cdot}CH_3 + H_2 \rightarrow YH + CH_4$$

As suggested in the original papers,[21] the relative-energy results are dominated by σ interactions and are rationalized by taking account of donor–acceptor relationships. As expected, second-row centers tend to be weaker acceptors than the analogous first-row centers, and the destabilizing interactions with σ-acceptors, NH_2, OH, and F are correspondingly much less severe. However, methyl is much milder a substituent than the other first-row groups, and the differences between interaction energies involving first- and second-row centers are small.

With the methyl compounds, one notable difference remains. In both first- and second-row systems, the more negative the charge on the central atom the more destabilizing the interactions [$\Delta E(CH_3,H)$ more negative], e.g., in the series PH_3^+, PH_2, PH^-. What distinguishes first-row centers from the heavier groups is the fact that the destabilization expected to result from removing a proton from the neutral species (as in going from $MeNH_2$ to $MeNH^-$) is offset by the extra stability gained from hyperconjugation in the anion and by an amount which reflects the strength of the interaction. Hence, the additional destabilization in the first-row compounds drops progressively: 14.9, 8.4, and 1.4 kJ mol^{-1}, for CH_2^-, NH^-, and O^-, respectively. For SiH_2^-, PH^-, and S^- the additional destabilizating contributions to the P–C interaction energy show no such decrease, the values being 28.5, 33.4, and 34.9 kJ mol^{-1}, respectively.

Relative energy calculation results (Table XI) show the most striking difference between the methyl and trifluoromethyl substituents. Substituent interaction energy trends in neutral and anionic methyl compounds are explained as due to the favorable effect of hyperconjugation in reducing, or reversing, the additional destabilization that results from interaction of CH_3 with a negatively charged species. In the $\Delta E(CF_3,H)$ results the stabilizations are much larger. It is understandable that structural alterations in the 33-electron CF_3 group may be smaller than those found in the 9-electron CH_3 group while still producing much larger effects on bond energies.

Comparison with data obtained from calculations of fluorosubstitution effects is also instructive.[21] The interaction energy

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results for the two carbon substituents X = CH_3 and CF_3 are parallel. Results for anions indicate a stabilization relative to neutrals which can be ascribed to the more effective π-acceptor character of the CF_3 substituent. However, with the σ-acceptor, π-donor substituent fluorine, the pattern changes. Anions still show stabilization relative to neutrals, but there is a very strong dependence of the ΔE(F,H) results on the σ-donor/σ-acceptor character of the substrate, with a 400 kJ mol^{-1} change in relative energy between the σ-donor SiH_3 (strongly stabilized) and the σ-acceptor SH (strongly destabilized). The effect of anionic charge on the interaction of the second-row centers with the strong σ-acceptor fluorine is probably responsible for this, rather than π-electron donation from fluorine. (See Table XI.)

Charge Distribution around First- and Second-Row Atoms. The relative weakness of hyperconjugative charge transfer to and from the methyl group in second-row anions cannot be due to overlap, which is marginally bigger for Si–C, P–C, and S–C interactions than it is for C–C, N–C, and O–C interactions, in spite of the differences in bond distances. (See Table IX.) In addition to the intrinsic weakness of π interactions involving second-row elements, part of it must be attributed to the difference in the way the charge is disposed in the molecule and the effect of this on any electron transfer between the interacting orbitals.

The lower electronegativities of second-row elements lead to a disposition of electron density which, it is suggested, inhibits the acceptor role of CH_3. For example, electron population data show a much higher net negative charge on carbon in CH_3SH than in CH_3OH, expected to make charge transfer to the methyl group after proton removal much more difficult in the second-row system. The same contrast is found in $MePH_2$ and $MeNH_2$. Atomic populations calculated for the methyl carbon and for P, S, O, and N show very clearly the contrast between the polarities in Y–C bonds in the two groups of compounds. (See Table X.) Also clear is the direction of charge transfer following removal of a proton. This reaches an extreme in CH_3O^-, reversing the expected sign of the formal charge on the carbon atom in a CH_3Y^- anion. These results are consistent with strong anionic hyperconjugation in C, N, and O compounds but with a much weaker level of interaction in the Si, P, and S compounds.

The charge data exemplify a general phenomenon of the electron-density distribution around second-row elements: the ability to tolerate large changes in charge with less drastic consequences than for first-row elements.[22] The effect of removing the proton has a much larger effect on the electron density around the second-row atoms than the first-row analogues (or around the methyl carbon in the molecules of second-row elements). Nevertheless, relative-energy calculations[21,22] show that the repulsive interactions involved are much less unfavorable in compounds of second-row elements which contain the methyl group and other substituents (e.g., the SHX series, X = BH_2, CH_3, NH_2, OH, F) than in the corresponding first-row compounds, and the greater polarizability of the heavier atoms is the major factor in this, as previously suggested.[21,23,24]

Inspection of the electron-density distribution calculated for CH_3SH and CH_3S^- with the 3-21G basis set, in which valence-shell orbitals are represented by two components, confirms the suggestion. The nonbonding sulfur 3p orbitals, with an occupation of about 1.5 e in the neutral compound, become completely filled in the anion. At the same time, the fraction of electron density accommodated in the outer component rises from 31% to 45%. In the corresponding CH_3OH to CH_3O^- process, the change in the density profile around oxygen is very small, the fraction of electronic charge in the outer component changing only from 43% to 46%. In the absence of a mechanism to delocalize charge to other parts of the molecule, the softer second-row atoms reshape the density profile to minimize the destabilizing effect of the additional charge. In a parallel study by Schleyer on the stabilization of carbanions by first- and second-row substituents, the same conclusion is reached.[24]

Conclusions

Geometry-optimized calculations of methyl- and trifluoromethyl-substituted compounds of first- and second-row species predict the structural consequences of hyperconjugation with Si, P, and S to be less pronounced than with the corresponding first-row compounds but still within a range which would allow ready identification by experimental methods. Tilt angles in the 2–4° range are calculated for the second-row species, compared with tilt angles up to 6° for carbon, nitrogen, and oxygen species. The disparities in C–H and C–F bond lengths are also smaller. Part of the reason may be the nature of the lone pair on the second-row atom, where the prevalence of high p character in bonds leaves lone pairs which, because of their hybrid character, are poorly oriented for π interaction with CH_3 or CF_3 groups.

In both first- and second-row compounds the effects of hyperconjugation are largest in the anions. The shortening of C–C, N–C, and O–C bond lengths relative to the neutrals is attributable to negative hyperconjugation. It is either not observed in the second-row cases or is very much less pronounced. Population analysis results are consistent with the idea that the high charge density expected around carbon when bound to Si, P, or S inhibits any further charge transfer to CH_3 or CF_3 in the anions.

Conformational energies provide no clear-cut measure of the strength of hyperconjugation in the compounds studied here; except in the case of the anions, where they are much larger for the first-row case than for the second row case, staggered-eclipsed conformation energy differences are of similar magnitude. Substituent interaction energies, however, show clear evidence that the effects of hyperconjugation on bond energy are much less important in Si, P, and S compounds than in the first-row analogues.

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