the paucity of variable-temperature studies on organolithium complexes may be partly responsible for the novelty of our results.

In conclusion, we have observed the first examples of lithium–proton spin–spin coupling in two transition-metal lithium complexes. Attempts to understand the results on structural and chemical bases are continuing.

Do Anomeric Effects Involving the Second-Row Substituents Cl, SH, and PH$_2$ Exist? Stabilization Energies and Structural Preferences

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Despite being separated by a saturated carbon, two geminal substituents can interact strongly. This phenomenon has become known as the anomeric effect;[3] the extensive literature has been well reviewed.[4,5] Both energetic and structural consequences are often dramatically large. As early as 1937, Brockway noticed the progressive decrease in the C–F bond lengths along the series of fluorinated methanes, CH$_3$F > CH$_2$F$_2$ > CHF$_3$ > CF$_4$.[6] Lemieux, in particular, attributed the preference of heteroatom substituents for axial rather than equatorial conformations in saturated heterocyclic ring systems (e.g., pyranose forms of sugars) to the stereoelectronic consequences of such interactions.[3] Although quantitative experimental data is sparse, Benson has recorded several dramatic instances where two first-row heteroatoms attached to the same carbon produce large stabilizations.[7] For example, even though the optimum conformations are not present,[4,8,9] 1,3-dioxane is 7.0 kcal/mol more stable than the 1,4-isomer.

-7.0 kcal/mol, expt.[7]
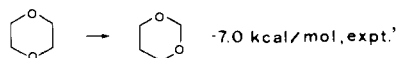
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(3) See: Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933–1944 and references quoted therein.
(4) Szarek, W. A.; Horton, D. *ACS Symp. Ser.* **1979**, *No. 87*. Wolfe, S.; Whangbo, M.-H.; Mitchel, D. J. *Carbohydr. Res.* **1979**, *69*, 1. Kirby, A. G. "The Anomeric Effect and Related Stereoelectronic Effects of Oxygen"; Springer Verlag: Berlin, 1983. Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon: Oxford, 1983. This book is an excellent source of phenomenological experimental data but largely ignores the complementary theoretical literature.
(5) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141–1150 and references cited.
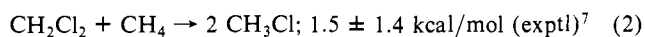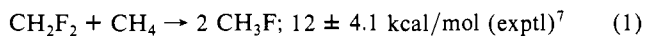(6) Brockway, L. O. *J. Phys. Chem.* **1937**, *41*, 185, 747.
(7) Benson, S. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 812–819. Also see: Rogers, A. S.; Chao, J.; Wilholt, R. L.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117–140.
(8) See, e.g.: Jeffrey, G. A.; Pople, J. A.; Binkely, J. S.; Vishveshwara, S. *J. Am. Chem. Soc.* **1978**, *100*, 373–379 and earlier papers cited. Frank, R. W. *Tetrahedron* **1983**, *39*, 3251–3252.
(9) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371–2381. Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *Ibid.* **1976**, *98*, 1663. Also see ref 4 and literature cited. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. "Ab Initio Molecular Orbital Theory"; Wiley: New York, 1985.

These structural and energetic manifestations of the anomeric effect involving first-row substituents have been studied systematically theoretically,[4,5,8,9] and the origin of the effect ("negative hyperconjugation")[5] is well established. An electronegative atom or group, X in XCH$_2$Y, lowers the energy of the orbital designated π^* CH$_2$X, because of its symmetry. π-Donation by lone pair electrons on Y into this orbital provides substantial stabilization. This also produces the bond length changes and conformational preferences observed experimentally[4,6,10] and calculationally.[4,5,8,9]

In view of the importance of the anomeric effect and the extensive studies involving first-row groups, the relative lack of information concerning the involvement of second-row substituents is surprising. Conformational effects, e.g., gauche and axial preferences of chlorine,[4,10] are among the positive evidence for the operation of such effects. In contrast, the experimental energy data on CH$_2$Cl$_2$[7] indicate the lack of any appreciable energetic effect (contrast eq 1 and 2).

$$CH_2F_2 + CH_4 \rightarrow 2\ CH_3F;\ 12 \pm 4.1\ \text{kcal/mol (exptl)}[7] \qquad (1)$$

$$CH_2Cl_2 + CH_4 \rightarrow 2\ CH_3Cl;\ 1.5 \pm 1.4\ \text{kcal/mol (exptl)}[7] \qquad (2)$$

As a consequence of the paucity of information, we have calculated the structures and energies of all possible first- and second-row disubstituted methanes, XCH$_2$Y (X, Y = F, OH, NH$_2$, Cl, SH, and PH$_2$). This extends similar earlier studies which were devoted to the interactions of first-row substituents.[8,9] All principal conformations of the XCH$_2$Y molecules were examined. The 3–21G(*)//3–21G(*) methyl stabilization energies (e.g., **3**)

1, X = N,P

2, X = N,P

3, X = O,S

4, X,X'= O,S
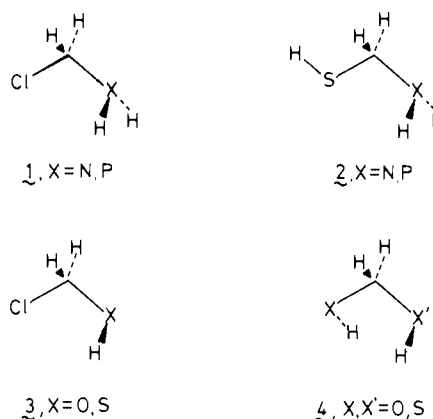
presented in Table I refer to the lowest energy geometry of each species, but a more extensive set of data is given in the supplementary material.

$$XCH_2Y + CH_4 \rightarrow CH_3X + CH_3Y \qquad (3)$$
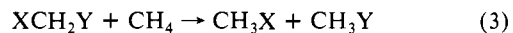
For uniformity, all of the data are calculated at the 3–21G-(*)//3–21G(*) level.[11] This represents a split-valence basis set for the first-row atoms and hydrogen but a d-orbital augmented basis for all second-row atoms. Even for normal-valent second-row molecules, d-functions generally give better geometries and relative energies.[11] In many of the more critical instances (see Table I), the results were checked against experiment or the results of higher level calculations. Errors probably do not exceed 4 kcal/mol and in most instances are expected to be considerably less. The errors in the available experimental data are equally large.

In contrast to the very large methyl stabilization energies in XCH$_2$Y systems involving any combination of the first-row groups, F, OH, and NH$_2$ (Table I, top left),[9] corresponding interactions are negligible when X and Y both involve second-row groups, Cl,

(10) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6752–6753 and references cited.
(11) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048. The GAUSSIAN82 program system (and earlier versions) was employed: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN82, Release A, Carnegie-Mellon University. Adapted for the Erlangen CDC-computer by Dr. A. Sawaryn.

Table I. Calculated Methyl Stabilization Energies, $CH_4 + XCH_2Y \rightarrow CH_3X + CH_3Y$, in kcal/mol $(3\text{-}21G(*)//3\text{-}21G(*))^a$ for XCH_2Y Species in Their Most Stable Conformations

X	NH_2	OH	F	PH_2	SH	Cl
NH_2	10.6 (12.2)	12.7 (11.5)	17.6	0.8	4.2	10.5
OH		17.4 (15.7)^b	16.2	0.5	4.7	5.8
F			13.9 (12.9)^c	0.2	1.8	1.1
PH2				0.5	0.4	−0.2
SH					0.1	−1.3
Cl						−4.3 (−3.7)^d

^{a} This basis includes d functions only on second-row atoms; the 3-21G basis is employed for the other atoms. Much of the data for reference compounds were taken from: "Carnegie-Mellon Quantum Chemistry Archive", 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University, 1983. Values in parentheses, taken from this source, are at 6-31G*//6-31G*. This basis has d functions on all non-hydrogen atoms. Also see ref 4 and 10. ^{b} Exptl: 15 ± 1.5 kcal/mol.[7] ^{c} Exptl: 12 ± 4.1 kcal/mol.[7] ^{d} The MP2/6-31G*//6-31G* value is −0.3 kcal/mol. exptl: 1.5 ± 1.4 kcal/mol.[7]

SH, and PH_2 (Table I, lower entries). This can be attributed to the combination of the inherently low π-donor ability of these groups and to the lower electronegativity of the elements of the second row relative to their first-row counterparts. Such groups are relatively poor π-donors and poor σ-acceptors. Even H_2PC-H_2Cl, which combines a second-row lone pair group (PH_2) with the most electronegative second-row atom (Cl), shows a very small effect. While the favored conformation of this molecule (**1**) has the phosphorus lone pair and the C–Cl bond in a trans-parallel orientation, the other staggered conformation is only 1.1 kcal/mol higher in energy. Second-row molecules like PH_3 and SH_2 have smaller bond angles than their first-row counterparts, e.g., NH_3 and OH_2. This bending also decreases the π-donor abilities of the lone pair orbitals on second-row groups.

The last category of XCH_2Y molecules (Table I, upper right) represents combinations of first-row substituents, X, with second-row groups, Y. Even here, some of the stabilization energies are negligibly small. This is true for all compounds involving PH_2 (XCH_2PH_2) and all compounds involving fluorine (FCH_2Y). This shows that the second-row groups are ineffective as π-donors.

However, there are significant anomeric interactions involving second-row substituents. The best combination, $ClCH_2NH_2$, has a methyl stabilization energy of 10.5 kcal/mol due to the relatively high electronegativity (σ-withdrawing ability) of chlorine and the good π-donating ability of NH_2. This also results in a preference for the trans lone pair–halogen conformation **1**. A smaller methyl stabilization energy, 4.2 kcal/mol, is found in NH_2CH_2SH which again favors a similar geometry. The SH group is best oriented as shown in **2**, but the energetic preference is not large. An appreciable stabilization energy of 5.8 kcal/mol is found in $HOCH_2Cl$ (**3**); this is a model for the many α-chlorinated ethers which have been observed experimentally to prefer gauche conformations.[4,10] The other conformations are several kcal/mol higher in energy. The final example, $HOCH_2SH$, mirrors the behavior of $CH_2(OH)_2$ which has been extensively investigated.[8,9] However, the stabilization energy of the sulfur system, 4.7 kcal/mol, is very much less than that of $HOCH_2OH$, 17.4 kcal/mol. The same gauche-(+) conformation **4** is prefered in the sulfur compound as in the oxygen case, but the magnitude of the energy differences between the various alternative conformations is considerably less.

The NH_2 π-donor, Cl σ-acceptor character of the interaction was demonstrated by model 6-31G* calculations on NH_2CH_2Cl geometries in which the NH_2 groups were held planar and C_s symmetries imposed. The methyl stabilization energy (9.7 kcal/mol vs. CH_3NH_2 with a planar NH_2 group) of the conformation like **1** was reduced to 2.5 kcal/mol by a 90° NH_2 rotation which "shut off" the N π-donor effect. This rotation decreased the C–Cl bond length by 0.07 Å. The results for FCH_2NH_2 (planar NH_2) were similar (reduction of the methyl stabilization energy from 15.8 to 8.0 kcal/mol by 90° NH_2 rotation). The residual stabilization was due to the F π-donor, NH_2 σ-acceptor interaction.

In conclusion, anomeric effects involving second-row substituents are greatly attenuated relative to their first-row counterparts. This can be attributed to the poorer π-donating and the lower elec-

tronegativity of the second-row groups. The other effects that normally control stereochemistry may thus predominate. If these results are extrapolated to groups involving elements of the lower rows in the periodic table, anomeric effects should tend to vanish. Residual interactions may be expected only in systems like NH_2CH_2Br.

The absolute energies and full description of the gemometries of all new systems calculated in this paper are available in the supplementary material. The full report, to be published subsequently, will contain additional data at higher levels of theory, but the general conclusions drawn in this paper are not expected to be altered significantly.

Supplementary Material Available: Full listings of the absolute energies and geometries of all CH_2XY species calculated in this work (5 pages). Ordering information is given on any current masthead page.

Two-Dimensional Correlation of Connected NMR Transitions

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Two-dimensional (2D) NMR correlation spectroscopy[1-5] (COSY) has been established as a powerful method for the elucidation of proton–proton scalar coupling networks. The most attractive variant so far combines multiple-quantum (MQ) filtering[6,7] with phase-sensitive data display[8] to yield a 2D spectrum

(1) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
(2) Nagayama, K.; Wüthrich, K.; Ernst, R. R. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 305.
(3) Nagayama, K.; Kumar, A.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.
(4) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.
(5) Bax, A. "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; Delft University Press: Delft, Holland, 1982.
(6) Piantini, U.; Sørensen, O. W.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6800.
(7) Shaka, A. J.; Freeman, R. *J. Magn. Reson.* **1983**, *51*, 169.
(8) Bachmann, P.; Aue, W. P.; Müller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 29. States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286. Marion, D.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967.