A systematic survey of the effects of substituents on the structures and energies of the principal organic reaction intermediates

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Abstract. Theoretical calculations at levels which approach
the accuracy of good measurements allow a much more detailed
examination of substituent effects than is possible experimentally.
A greater variety of groups and potential energy surfaces
can be studied. Important species, e.g. the parent members
of which are difficult to prepare and to measure, can be calculated
easily at an expected accuracy no different from that of
more stable entities. The substituents employed are groups
based on all the elements of the first two rows of the periodic
table, from Li through Cl. These encompass as wide a range
of electrical properties as possible, and permit results
to be assessed in terms of electronegativities. Such treatments
allow sigma (inductive) effects to be differentiated from
pi effects to a large extent. Furthermore, pi effects can
be "turned on" or "turned off" by employing BH_2, AlH_2, NH_2,
and PH_2 groups in various conformations. The application
of this method of analysis is illustrated by numerous examples,
including not only the principle reactive intermediates,
carbocations, free radicals, carbanions and carbenes, but
also basic organic groupings, e.g., ethyl, vinyl, ethinyl,
and cyclopropyl. The trends in stabilization energies, relative
to methyl, respond differently depending on the formal hybridization.
The slopes of the sigma correlation lines of ethyl and vinyl (CH_3 to F)
systems are similar, but that for ethinyl is opposite. Sigma
effects are more important than pi effects in many instances,
but not, e.g., with the ionic intermediates and singlet carbenes.
The effects of substituents on bond lengths and bond angles,
e.g., HCH angles in CH_3X, CH_2X^+, $\cdot CH_2X$, and HOX systems also
behave in regular, readily interpretable ways. Systems with
strongly electropositive substituents exhibit structural
and energetic behavior expected of carbanions, whereas strongly
electropositive substituents tend towards carbenium ions.
Relationships among the structures often reflect sigma effects,
even when pi effects of large magnitude energetically are
present.

INTRODUCTION

Organic chemistry would be dull indeed if all molecules, e.g. with
the same functional groups, behaved in just the same way. Instead,
substituents can alter reactivities substantially, and even cause
chemical reactions to take a different course. A systematic study
of substituent effects, begun by Hammett in the late 1930's (1) and
carried out extensively ever since (2), has provided much detailed
understanding of chemical behavior. However, experimental measurements,
upon which studies are traditionally based, have many inherent disadvantages.
Spectroscopic data and reactivities may be easy to determine, but
not more fundamental quantities, like heats of formation and geometries.
Many important molecules are difficult to prepare, and even harder
to study. For example, while the energies of charged species in
the gas phase may be available, geometries are not. The bond energies
of the vast majority of types of chemical bonds are unknown. This
is also true of bonds involving carbon; the energies of linkages
to most of the elements in the periodic table are not given in even
the most extensive compilation (3).

Consequently, the experimental study of substituent effects typically
deals with relatively minor variations and observables which are
easy to measure. The groups involved generally are based on the
common electronegative elements, e.g. nitrogen, oxygen, the halogens
and a few others. The possible exception of silicon, substituents
based on the metallic elements (the overwhelming majority in the
periodic table) have not been employed experimentally, because of
the difficulties involved. It is not necessary to elaborate a catalogue
of deficiencies in the extent and even the accuracy of fundamental
experimental data. Physical organic chemists have long been frustrated
by the unavailability of the geometries and energies of even simple
molecules.

COMPUTATIONS AS A SOURCE OF BASIC CHEMICAL DATA

Fortunately, the situation has changed drastically for the better
through the development of increasingly faster computers and powerful
and easy to use quantum mechanical programs, like Gaussian 82 (4).
These permit the chemist to obtain data which approach or equal
the accuracy of good measurements, but permit much more flexible
studies than are possible experimentally. John Pople and his school
havebeen the chief contributors to this development (4). Most theoretic-
ians have attempted to carry out the best possible calculations on
a given species of interest. Since the levels of approximation differed,
one result, e.g. an energy, could not be compared with the next.
Pople's approach was different, and appealed to the chemist rather
than to the quantum mechanician.Lower levels of approximation were
employed, but were used uniformly. Pople demonstrated that even
minimal basis sets (STO-3G) could give reasonably accurate results
when isodesmic reactions, in which errors tend to cancel due to
preservation of the numbers of each type of bond, were evaluated.
STO-3G has now been replaced by the more flexible 3-21G split valence
basis set, as the initial level. Higher accuracy can be achieved
with the 6-31G* basis, which includes a set of d-orbitals (which
function primarily as polarization functions) to all heavy atoms.
The geometries of the molecules reported in this study have been
optimized at 6-31G*.

A further advantage of Pople's approach has been the extensive collection
of data (5) at uniform levels which permit accuracy against the
available experimental measurements to be evaluated (6). Chapter
6 of our recent book (4) is devoted to this topic. The mean absolute
errors in calculated bond lengths between heavy atoms are 0.02 Å
with the 6-31G* basis set, and errors in bonds angles are generally
2° less at 6-31G*. This accuracy is sufficiently high for most purposes.
If more refined geometries in even closer agreement with experiment
are desired, optimizations can be carried out at electron correlated
levels.

Electron correlation corrections may be more important in some applications,
but it usually suffices to carry out single point calculations at,
e.g., the MP2 or MP4 (Møller-Plesset second or complete fourth order)
using the 6-31G* geometries. Such calculations are designated, e.g.,
MP2/6-31G*//6-31G* where the "//" means "at the geometry of".

The calculation of anions requires the use of diffuse function augmented
basis sets, such as 6-31+G* (4). The radial extension of electrons
is greater in anions than in neutral or positively charged molecules,
and diffuse functions improve the description of lone pairs on first
row atoms as well.

Wiberg's group and our own have shown recently that theoretical energies,
which are expressed in absolute units, can be converted to heats
of formation by using empirical increments similar to those suggested
by Benson for experimental data (6). The agreement of the 6-31G*
heats of formation, estimated in this manner, for a variety of neutral
molecules, free radicals, and carbocations is within 2 kcal/mol
of experiment and the errors are even lower for unstrained systems.

Such treatments of theoretical data require experimental data in
order to evaluate increments. However, Pople has shown recently
that bond dissociation energies of all of the hydrides of first

and second row elements can be calculated within 2 kcal/mol accuracy
by means of a relatively simple ab initio treatment (7). The same
approach allows the prediction of electron affinities of the same
species with similar accuracy (8). The molecules of interest in
the present study generally have uncomplicated structures and can
be expected to be well represented at the levels of theory we have
employed. While some further refinement is always possible, we believe
on the basis of considerable experience (4) that results calculated
at sufficiently high levels are meaningful and accurate and can
be discussed with the same degree of confidence as reliable experimental
measurements.

Table I illustrates how theoretical data for the methyl stabilization
energies of CH_2X^+ cations (eq. 1) have fared over the last decade.
The initial STO-3G studies (9,10) gave surprisingly good

$$CH_2X^+ + CH_4 \longrightarrow CH_3X + CH_3^+ \qquad (1)$$
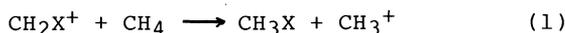
results for the first row substituents, but generally unaccepable
errors for cations with second row groups. Use of the split valence
basis sets (3-21G and 4-31G) improved many of the second row values,
but the results with lone pair substituents became worse. These
errors are not corrected until electron correlation is included.
As is often the case with isodesmic reactions, MP2 level results
(which are much less costly in computer time) are nearly the same
as MP4. We will consider the interpretation of this data below.

CHOICE OF SUBSTITUENTS. FIRST AND SECOND ROW 'SWEEPS'

Theoretical studies permit a wider selection of different types
of substituents to be employed than is feasible experimentally.
Thus, the traditional use of F, OH, NH_2, and CH_3 groups was extended,
for the first time in 1976, to BH_2, BeH, and Li, thus completing
the "sweep" of all first row elements (11). This proved to be particularly
important for the study in question, since it was found that the
electropositive elements, particularly lithium, were most effective
in reducing the planar-tetrahedral energy difference in CH_3-X derivatives.
This led, in turn, to the discovery of many unusual structures of
organolithium compounds calculationally; many of these predictions
have now been verified experimentally (12).

The extension of this approach to include all of the second row
groups, Na, MgH, AlH_2, SiH_3, PH_2, SH, and Cl, was first employed
in 1978 for the study of substituent effects on carbocations, XCH_2^+
(10). The combination of such first and second row sweeps, along
with other substituents, e.g. CN, CCH, C_2H_3, CHO, etc., has now
become a standard investigational tool in such theoretical work.
Our recent book (4) summarizes much data gathered by our groups
over many years, the effect of substituents on reactive intermediates,
carbocations (Table I), free radicals, carbanions, singlet and triplet
carbenes (Table II), as well as numerous functional groups, silicium
ions (13), cyclopropane rings (14), and many more (4). Other investigators,
notably Leroy, et al., Dill, Greenberg and Liebman, and Hopkinson
and Lien (15), among others (16) also have carried out similar studies
(15). For the most part, the reported data has been gotten at relatively
low levels of theory, e.g. 3-21G or even STO-3G. While large effects
and trends may be apparent at these levels, the accuracy is not
high enough to permit more detailed interpretation. Since this is
the goal of the present work, the data has been obtained at higher
levels, usually MP2 or MP4/6-31G*//6-31G*.

The need for good data is illustrated by the effects of substituents
on the average HCH angles of CH_3X derivatives. The first level,
STO-3G, showed a trend to smaller values for electropositive substituents.
However, nearly the same average HCH angles were found for the electronegative
substituents, contrary to experiment. Geometries of the same set
of molecules, optimized with the 4-31G basis set, showed zigzag
behavior in the corresponding electronegativity plot! Only the 6-31G*
structures show regular variation of HCH angles from nearly 111°
in CH_3F to just over 106° in CH_3Li (17). Complicated explanations
based on the influence of sigma and pi effects of substituents (18)
would have been necessary to rationalize the STO-3G and 4-31G data
(if these data had been assumed to be accurate!), but interpretation

Table I. Methyl stabilization energies of CH_2X^+ species in their most stable and in rotated geometries (kcal/mol)[a]

Species	Point Group	STO-3G[b,c]	3-21G// 3-21G[d]	3-21G(*)// 3-21G(*)[d]	/6-31G*//6-31G*[a]			Expt
					HF	MP2	MP4SDTQ	
CH_2Li^+	C_{2v}	91.3	80.9	79.6[e]	78.1	75.4	77.0	–
CH_2BeH^+	C_{2v}	26.7	18.6	20.4[e]	18.0	15.2	16.3	–
$CH_2BH_2^+$	C_{2v},perp	30.7	24.0	26.6[e]	23.0	25.8	27.4	–
	C_{2v},plan	12.0	4.2		5.0	1.8	2.7	–
$CH_2CH_3^+$	C_s,class	30.9	29.1	29.9[e]	29.5	35.0	35.5	37±3[f]
$CH_2NH_2^+$	C_{2v},plan	93.8	93.5	93.3[e]	86.5	100.0	99.6	95-97[f]
	C_{2v},perp	12.9			14.1	16.4	16.0	–
CH_2OH^+	C_s,plan	66.0	52.6	47.8[e]	53.7	66.0	66.3	60-64[f]
	C_s,perp				30.3	41.3	41.4	
CH_2F^+	C_{2v}	32.1	8.7	2.1[e]	14.9	25.3	25.9	24[h],27±3[f,g]
CH_2Na^+	C_{2v}	140.0	93.3	93	91.4	87.1	88.7	
CH_2MgH^+	C_{2v}	75.0	40.8	40	39.1	36.5	38.3	–
$CH_2AlH_2^+$	C_{2v},perp	55.5	28.6	28	26.8	25.8	27.4	–
	C_{2v},plan	50.2			22.5	20.4	21.8	–
$CH_2SiH_3^+$	C_s	34.9	16.2	16	16.1	16.8	18.6	–
$CH_2PH_2^+$	C_{2v},plan	29.6	38.4	44	41.6	63.3	62.9	–
	C_s,perp	41.7			10.2	13.1	15.4	
CH_2SH^+	C_s,plan	67.6	31.8	47	44.8	63.7	64.9	59-72[i],64[f]
	C_s,perp	22.8			2.1	8.2	10.1	
CH_2Cl^+	C_{2v}	4.8	-3.4	12	13.4	29.3	31.0	30±4[f],32.5[j]

[a]Evaluated via: $CH_2X^+ + CH_4 \rightarrow CH_3X + CH_3^+$. Some of the data is taken from the Carnegie-Mellon Quantum Chemistry Archive, R.A. Whiteside, M.J. Frisch, and J.A. Pople, Eds., Carnegie-Mellon University, 3rd. Ed., 1983; in some cases, 6-31G* and correlated values for reference compounds are based on 3-21G and 3-21G(*) geometries. Only small energy differences should result.

[b]First row elements: Y. Apeloig, P.v.R. Schleyer, and J.A. Pople, J. Am. Chem. Soc., **1977**, <u>99</u>, 1291.

[c]Second row elements: T. Clark and P.v.R. Schleyer, Tetrahedron Lett., **1979**, 4641. See this paper for STO-3G* results.

[d]"Ab Initio Molecular Orbital Theory", W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, Wiley, 1986, Table 7.1, p.348, unless otherwise indicated. Also see, J.A. Pople, Y. Apeloig, and P.v.R. Schleyer, Chem. Phys. Lett., **1982**, <u>85</u>, 489, and lit. cited.

[e]4-31G//STO-3G results from footnote b.

[f]R.W. Taft, R.H. Martin, and F.W. Lampe, J. Am. Chem. Soc., **1965**, <u>87</u>, 2490. R.H. Martin, F.W. Lampe, and R.W. Taft, ibid. **1966**, <u>88</u>, 1353. Further values (kcal/mol) are: $CH_3OCH_2^+$ (66±3), $CH_3SCH_2^+$ (74), $(CH_3)_2PCH_2^+$ (79), $CH_3NHCH_2^+$ (94), $(CH_3)_2NCH_2^+$ (106). Also see F.P. Lossing, Y.-T. Lam, and A. Maccoll, Can. J. Chem., **1981**, <u>59</u>, 2228. F.P. Lossing, J. Am. Chem. Soc., **1977**, <u>99</u>, 7526. J.L. Holmes and F.P. Lossing, Int. J. Mass. Spectrom. Ion Proc., **1984**, <u>58</u>, 113. T. Baer, J. Am. Chem. Soc., **1980**, <u>102</u>, 2482.

[g]See S.G. Lias, J.F. Liebman, and R.D. Levin, J. Phys. Chem. Ref. Data, **1984**, <u>13</u>, 695 and update material.

[h]R.J. Blint, T.B. McMahon, and J.L. Beauchamp, J. Am. Chem. Soc., **1974**, <u>96</u>, 1269.

[i]Footnote g (Data taken from M. Ray and T.B. McMahon, Org. Mass. Spectrom., **1982**, <u>17</u>, 392, which gives ΔH°_f (CH_2SH^+)=207.9±1 and PA(CH_2S)=180.9±1 kcal/mol) gives ΔH_f° (CH_2S)=21.5±2, ΔH_f°(CH_2SH^+)=201. Another value for H_f° (CH=S), 33.1±1.5 (R.E. Kutina, A.K. Edwards, G.L. Goodman, and J. Berkowitz, J. Chem. Phys., **1982**, <u>77</u>, 5508), with the reevaluated PA(CH_2S)=184.7 kcal/mol in footnote f, gives ΔH_f°(CH_2SH^+)=214 kcal/mol. At MP4/6-31G*//6-31G* + ZPE PA_0(CH_2=S)=179.7 kcal/mol. J.K. Pau, M.B. Ruggera, J.K. Kim, and M.C. Caserio, J. Am. Chem. Soc., **1978**, <u>100</u>, 4242 found (ICR) that the reaction, $CH_3OCH_2^+ + ClCH_2SCH_3 \rightarrow CH_3OCH_2Cl + CH_3SCH_2^+$, was exothermic (by ΔG=-2.4±0.5 kcal/mol, R.W. Taft and I. Koppel, footnote 19 in this paper), and concluded that "sulfur is better than oxygen at stabilizing a neighboring positive carbon". However, they failed to take the anomeric effects in the <u>neutral</u> molecules into account, which favor $ClCH_2OH$ over $ClCH_2SH$ by 6 kcal/mol (P.v.R. Schleyer, E.D. Jemmis, and G.W. Spitznagel, J. Am. Chem. Soc. **1985**, <u>107</u>, 6393). This reverses their conclusion: O is better than S in carbocation stabilization. ZPE corrections increase the values in Table I by 1.3 kcal/mol for CH_2OH^+ and 1.4 kcal/mol for CH_2SH^+, so that the final estimated theoretical difference is 1.3 kcal/mol in favor of CH_2OH^+.

[j]Via ΔH_f°(CH_2Cl^+)=228.1 kcal/mol: A. Werner, B.P. Tsai, and T. Baer, J. Chem. Phys., **1974**, <u>60</u>, 3650.

Table II. Stabilization energies of reactive intermediates (vs the parent of each species), kcal/mol. Data for the most stable forms are given in all cases.

Substituent	$XCH_2 \cdot$[a]	XCH, triplet[b]	XCH, singlet[c]	XCH_2^-[d]
H	0.0	0.0	0.0	0.0
Li	9.0	27.0	9.2	19.2
BeH	8.6	18.5	-1.6	31.8
BH_2, planar	12.2(2.3)[e]	15.6	36.8	53.3(2.1)[e]
CH_3	2.5	5.4	12.0	-3.1(4.8)[f]
NH_2	11.4	13.0	61.5	-0.5(5.0)[f]
OH	8.9	11.0	51.2	5.6(12.0)[f]
F	4.7	5.5	35.0	10.5(15.7)[f]
Na	6.3		17	16.5
MgH	7.5		–	24.5
AlH_2, planar	9.0(4.7)[e]		16	44.2(18.5)[e]
SiH_3	4.0		2	23.6(0.8)[f]
PH_2	5.2(4.4)[e]		17	21.4(0.7)[f]
SH	7.4(3.2)[e]		32	19.2(3.2)[f]
Cl	4.5		16	17.4(12.0)[f]

[a] UMP2/6-31G*//6-31G*. C. Schade, unpublished calculations.
[b] UMP4/6-31G*//3-21G, ref. 28.
[c] First row: MP4/6-31G*//3-21G[(*)], ref. 28. Second row: 3-21G[(*)]//3-21G[(*)], ref. 4.
[d] MP4/6-31+G*//6-31+G* + ZPE. G.W. Spitznagel, Dissertation, Erlangen, 1986.
[e] Perpendicular or rotated form. [f] Inversion barriers.
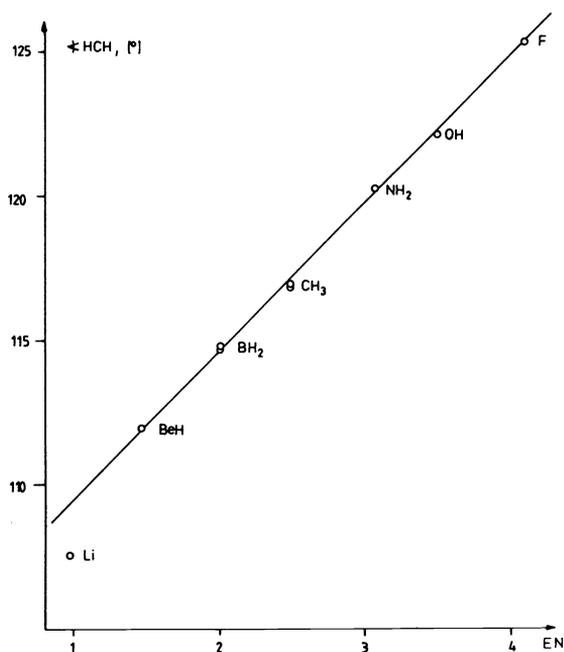
Figure 1.
Plot of the HCH angles of CH_2X^+ derivatives (6-31G* data against Allred-Rochow electronegativities of X.

of the regular 6-31G* trend is quite simple. The HCH bond angle is largely determined by the ability of the substituent to withdraw or to donate electrons along the C-X bond. There is a simple way to remember and even to predict the trends of such electronegativity effects which is very general and powerful. At the extreme, if the X group in CH_3X were to withdraw both bonding electrons fully, a planar methyl cation would result. Hence, the HCH bond angles would open. This trend is exhibited by CH_3F. The reverse is true for electropositive X substituents. These donate electrons to methyl which takes on carbanion character. Indeed, methyllithium can be considered to be a $CH_3^-Li^+$ ion pair with a pyramidal methyl carbanion moiety and a small HCH angle.

We have found that many geometrical parameters correlate linearly with electronegativity. A pertinent example is the HCH angles of CH_2X^+ cations (19) (Figure 1), which range from over 125° (X=F) to under 107° (X=Li) (19). H_2CLi^+ can be considered to be a Li^+ complex of singlet CH_2 (which has an angle of about 103°), while

the electronic structure of H_2CF^+ (sigma withdrawing fluorine) tends
towards CH_2^{2+}, which has a linear structure. The occupancy of the
p-pi MO has little effect on the HCH angle. There is a significant
pi influence on the CH bond lengths but less than expected in the
C-X distances. Thus, the C-N separation in planar $H_2C=NH_2^+$, 1.263
Å, only lengthens to 1.344 Å on 90° rotation in C_{2v} symmetry (6-31G*).
Although not linear, the electronegativity effects on C-X bond lengths
in the H_2C-X^+ cations are much larger and show parallel behavior
when plotted against the C-X length in CH_3-X (with some deviating
trends).

As pointed out some time ago, the methyl stabilization energies
of ethyl derivatives (as defined by

$$CH_3X + C_2H_6 \longrightarrow CH_4 + C_2H_5X$$
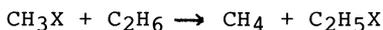
using the corresponding methyl compounds as standards) show a remarkably
linear dependence on the electronegativity of the substituent (Figure
2, bottom line). Electronegative groups, like fluorine, stabilize
ethyl relative to methyl whereas the opposite is true for electropositive
groups. The simple carbocation-carbanion analogy provides an interpretation.
The ethyl cation is considerably more stable than the methyl cation
due to hyperconjugation. In CH_3CH_2F, the effect of fluorine is to
reduce the energy of the pi*(CH_2) orbital and this enhances the
hyperconjugative stabilization provided by the attached methyl groups.
In contrast, the ethyl anion is <u>destabilized</u> relative to the methyl
anion. This is because the hyperconjugative interaction now involves
4-electron repulsion (21). Hence, electropositive X groups prefer
to be attached to methyl, rather than ethyl. A close parallel between
relative energies of a number of RLi molecules and the relative
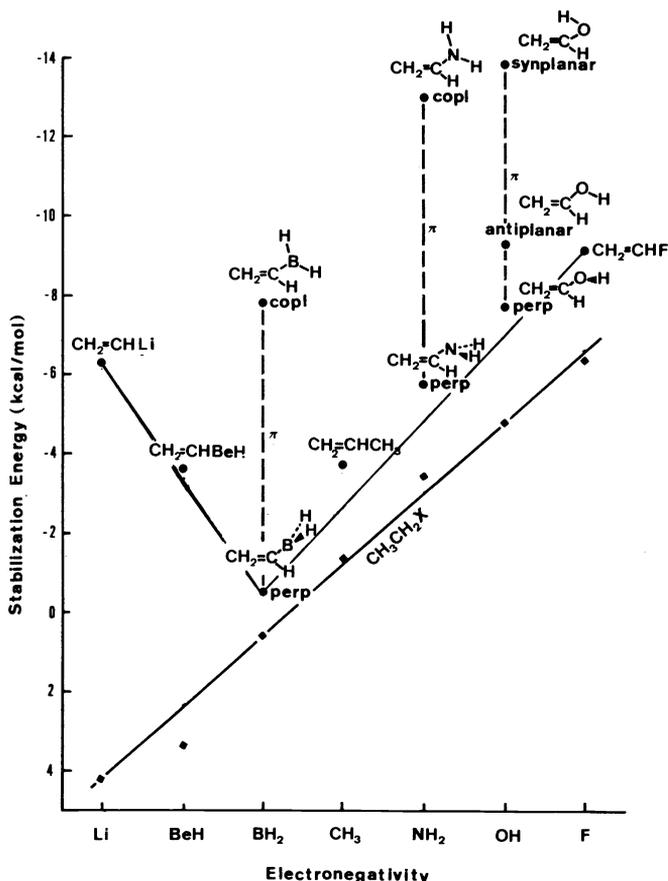
Figure 2. Electronegativity plots of the methyl stabilization ener-
gies of ethyl (bottom line) and vinyl (V-shaped line)
derivatives. For the latter, the points represent conform-
ations with minimum pi effects. Pi stabilization in the
more favorable conformations is shown by the dashed lines.

energies of the corresponding carbanions, R⁻, has been established (22). The slope of this line was quite high, about 0.75, so that energetic behavior of lithium compounds can often be equated with that expected of the corresponding carbanions. (However, many simple carbanions, e.g., ethyl, propyl, t-butyl do not exist as free entities, but only as ion pairs)(23). However, this parallel does not work very well <u>quantitatively</u> for the comparison of fluorides, RF, with the corresponding carbocations, R⁺. Obviously, C-F bonds have much more covalent character than CLi bonds.

These sigma effects are general. The slope of the $2-C_3H_7X$ vs CH_3X correlation line (14a) is higher than that of CH_3X vs C_2H_5X. Electronegative substituents favor 3°>2°>1° attachment. 1-Propyl chloride, for example, will rearrange to 2-propyl chloride. Electropositive substituents favor the opposite order, 1°>2°>3°. Boron and aluminium groups migrate from tertiary or secondary positions to primary ones on heating.

ELECTRONEGATIVITY PLOTS

As shown in the Figures, electronegativity plots are an effective means to help interpret theoretical data. Of the various electronegativity scales, we find the one by Allred and Rochow (24) to be quite satisfactory. We use values for the elements as it has been shown that XH_n group electronegativities are quite similar (25). Group electronegativities may be used for other types of substituents. For example, the sp-hybridized carbons in cyano and ethynyl substituents have a higher electronegativity than $C(sp^2)$ and higher still than $C(sp^3)$.

Many stabilization energies and geometrical parameters show linear electronegativity plots, like Figures 1 and 2. Another example is Figure 3, a plot of the MP4/6-31G* energy required to bend the angle in XOH derivatives to 180° (barrier to linearization). The corresponding
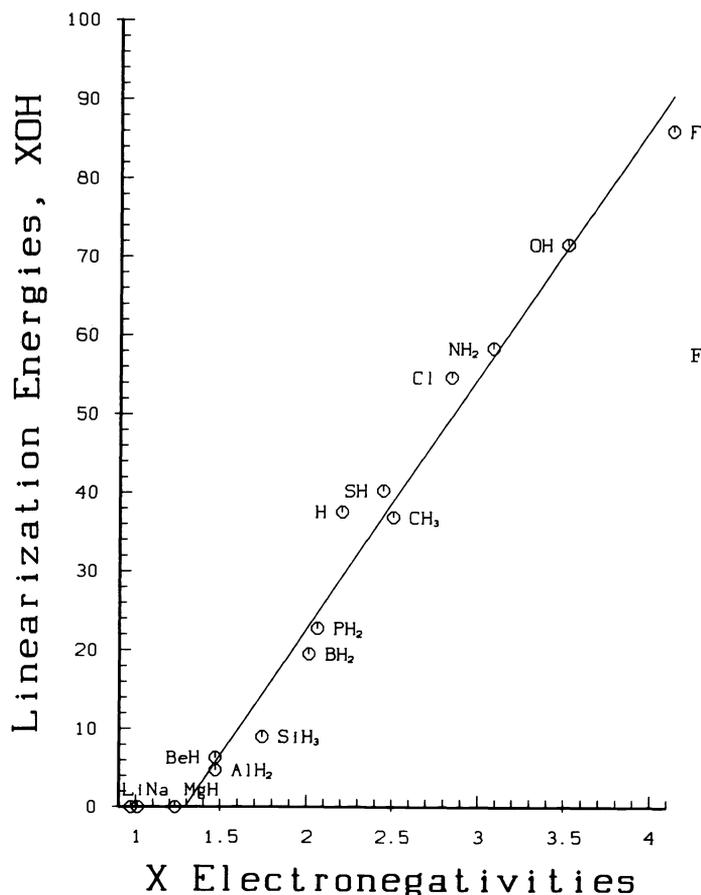
Figure 3.
   Electronegativity plot of the energy required to bend HOX angles from their equilibrium values to linear geometries. ((MP4/6-31G*//6-31G* data).
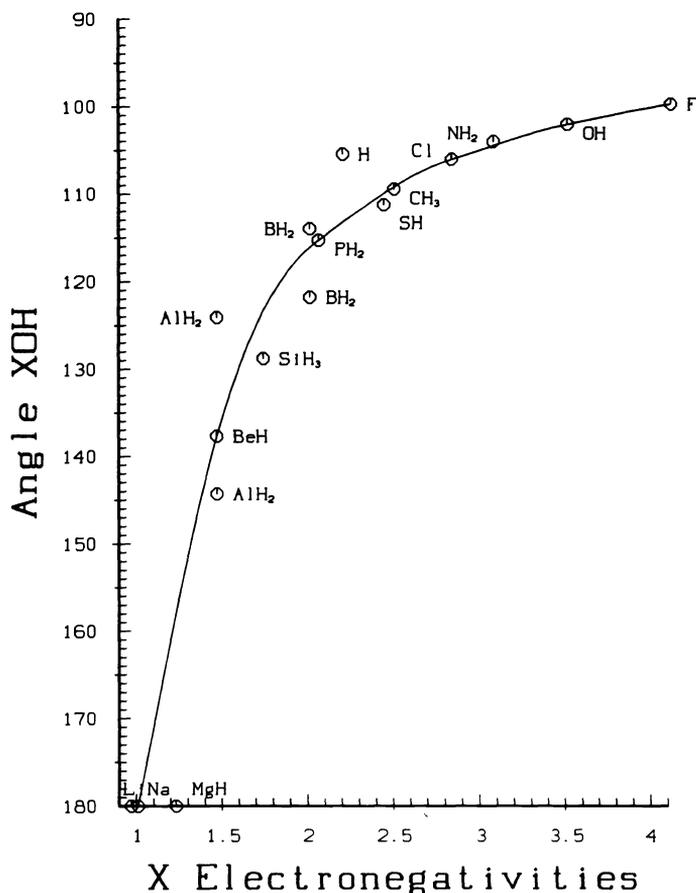
Figure 4. Electronegativity plot of the HOX equilibrium angles
(6-31G* data). For X=BH$_2$ and AlH$_2$, the upper points are
for the most stable planar geometries and the lower points
represent perpendicular conformations.

electronegativity plot, Figure 4, of the 6-31G* HOX bond angles
shows a curved behavior and no separation between first and second
row groups;   the trend to the linear structures favored by LiOH,
NaOH, and MgOH is clear.

The plots illustrate my next point. Although oxygen is a good pi-electron
donor and many of the substituents in Figures 3 and 4 are pi-acceptors
or might exhibit lone pair repulsion effects, these influences evidently
are quite small as the scatter in the data is quite modest. This
shows that the HOX bond angle and the linearization barriers are
chiefly influenced by inductive (sigma or electronegativity) effects.
Pi interactions, which are often favored in explanations of chemical
behavior, play a minor or even insignificant role. Thus, inorganic
chemists have attributed the very wide (ca. 150°) oxygen bond angle
in R$_3$SiOSiR$_3$ derivatives to "(d-p)$_{pi}$" bonding. This is unimportant
as the widening can be reproduced by basis sets without and d-functions;
the electropositive character of silicon is responsible instead.
Mislow has stressed this point in interpreting the inversion barriers
of amines, phosphines, and related systems (26).

It is important to realize that substituent effects in chemistry
often are dominated by sigma rather than by pi effects. The latter
often receive exaggerated attention in explanations of chemical
phenomena. The success of pi electron theory, e.g. in aromatic systems,
and of explanations based on frontier orbital theory (HOMO's and
LUMO's often are pi orbitals) have lead to a preoccupation with
pi effects and to the relative neglect of sigma influences. Since
sigma bonds are inherently stronger than pi bonds, sigma effects
(which are often taken for granted) can well be expected to predominate

over pi effects. While both are important, I think the time has
come to redress the balance. Pi effects are undeniably important
in many instances, but it is the sigma framework which often controls
chemical behavior.

SIGMA AND PI BOND ENERGIES IN C=X AND Si=X DOUBLE BONDS

We next compare the energies of sigma and pi bonds quantitatively
in situations where they are obviously both important: double bonds.
As mentioned in the introduction, the deficiencies in experimental
bond energy data is deplorable. Even though the energies of interaction
between chemical elements are perhaps of the most fundamental importance
to our science, research in this area is unpopular and unfunded.
Theoretical calculations can provide quite a reliable alternative
source of such data.

Systems containing double bonds to second row elements were, until
recently, quite rare. An absolute burst of activity   changed this
situation dramatically as multiple bonds involving these elements
are now known for practically all combinations (27,28) However,
the synthesis of such systems often require the use of bulky groups
to prevent further reactions; these groups preclude thermochemical
measurements. The   parent systems with hydrogen substituents are
often the most difficult to prepare, but they are the easiest to
calculate reliably.
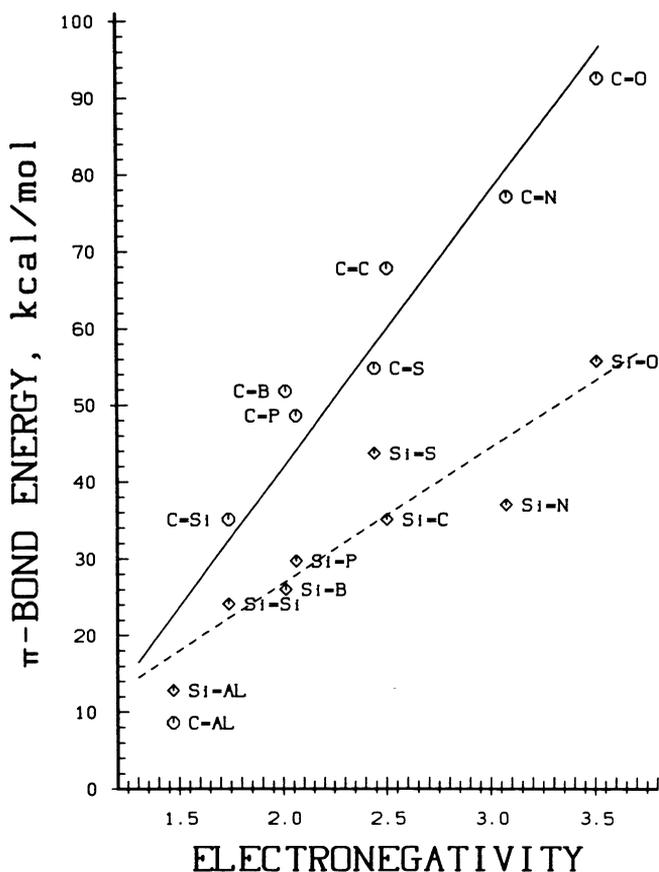
Figure 5. Plot of pi bond energies, deduced from MP4/6-31G* data (see
text), for $H_2C=XH_n$ (solid line) and $H_2Si=XH_n$ (dashed line)
vs the X electronegatives. Note that the points labelled
C=Si and Si=C refer to the same datum; if the points were
superposed (by moving the dashed curve to the left), the
apparent differences between the carbon and silicon pi bond
energies would be smaller.
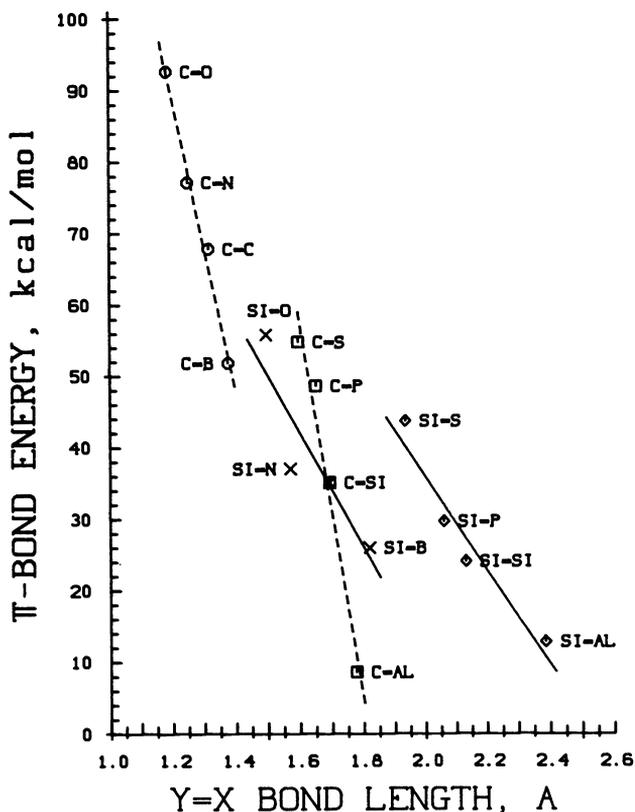
Figure 6. Plot of pi bond energies (see Figure 5 and the text) against
6-31G* bond lengths. The four families of lines depend on
the number of second row atoms, but the Si=X bond lengths
are more sensitive to energy changes than the C=X systems.

In a recent collaboration with Prof. D. Kost (27), we have estimated
the total, sigma, and pi bond energies of sets of C=X and Si=X double
bonds in the following way. The first step is to evaluate the energy
of equation 2 with MP4/6-31G*//6-31G* + ZPE data.

$$H_2Y=XH_n + YH_4 + X_{n+2} \longrightarrow 2\,YH_3-XH_{n+1} \qquad Y=C \text{ or } Si \qquad (2)$$
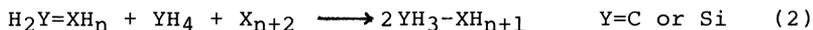
This equation measures the energy difference between the X=Y double
bond, and two X-Y single bonds. Except for C=O, which is stronger
than two C-O single bonds, double linkages are weaker (considerably
so if electropositive elements are involved) than their single bond
counterparts. We take bond dissociation energies, $\underline{D}_0^0(X-Y)$, eq 3,

$$YH_3 - XH_{n+1} \longrightarrow YH_3\cdot + \cdot XH_{n+1}, \quad D_0^0(X-Y) \qquad (3)$$
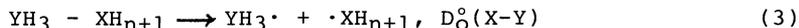
to measure the strengths of X-Y single bonds (this data has also
been estimated theoretically, but agreement with the available experimental
values is reasonably good) (27,29). Subtraction of $\underline{D}_0^0$ values from
eq 2 give the pi bond energies. These values are presented as a
electronegativity plot, Figure 5. Pi bonds are stronger when X is
more electronegative. Although Si=X pi bonds are weaker (except
for X=AlH) than their C=X counterparts, there is little differentiation
when corrected for electronegativity. Within families, X=Y bond
lengths correlate with the pi bond energies (Figure 6).

EVALUATION OF SUBSTITUENT PI EFFECTS

The BH_2, AlH_2, NH_2, and, to a lesser extent, PH_2, OH, and SH groups
are ideally suited for evaluating the extent of pi interactions.
When the vacant p or lone pair orbital of these groups are lined
up with the pi systems of species under study, pi interactions are
at a maximum. However, if the substituents are rotated by 90°, these

pi interactions are "turned off" or are at a minimum. Such variations in geometry are easily carried our calculationally, by imposing the desired local symmetry. The measurement of rotational barriers is the experimental equivalent but the usual difficulties with steric effects of bulky groups and the inability to study the parent compounds often are involved. The greater flexibility of calculations permits the NH_2 group to be held planar in order to maximize pi effects. This is a reasonable procedure, since the inversion barrier of ammonia is relatively small, but the situation is quite different with PH_2 groups where barriers are typically on the order of 35 kcal/mol. The OH and SH groups are more of a problem, since, from an energy viewpoint, there are two different kinds of lone pairs. The p-orbital lone pair is an effective pi donor, but the lone pair nominally sp^2 hybridized may not be inactive in this sense. Thus, rotating OH substituents may not "turn off" pi effects completely. Obviously, groups with spherical or conical symmetry, like Li, Na, BeH, MgH, CH_3, SiH_3, F, and Cl, cannot be "rotated"; the pi effects involving these groups must be evaluated in other ways.

There is no rigorous way of differentiating between sigma and pi energetic contributions. Even in rotational transition structures (states), e.g., for ethylene, interactions in orbitals with pi symmetry are involved. The 90° rotated transition structure can be considered to have singlet biradical character. Each of the two radical centers are stabilized by hyperconjugative interactions with the adjacent CH_2 groups in perpendicular planes. Each of these stabilizing interactions may be worth at least 3 kcal/mol, the extent to which the ethyl radical is stabilized over the methyl radical by hyperconjugation. In planar ethylene, the highest lying "sigma" orbital has antibonding pi^*_{C-C} character which should destabilize this conformation (the eclipsed vicinal CH bonds in ethylene should be at least as unfavorable as the opposed CH bonds in eclipsed ethane). Planar ethylene is destabilized and the perpendicular transition structures stabilized by such "pseudo-pi" interactions. Hence, the rotational barrier of ethylene may underestimate the pi bond energy by as much as 10 kcal/mol.

However imperfect attempted separation of sigma and pi effects may be, this differentiation is conceptually useful. The geometries, energies, total electron distributions, etc. are observable quantities in molecules which can be quite accurately reproduced or predicted by theoretical calculations. However, I doubt if chemists will ever resist the temptation to interpret observable quantities by attempting to divide them up into separate contributions, however arbitrary this may be. I do think we learn from such attempts, as illustrated by the application of our tool to vinyl derivatives (Figure 2, upper points).

This plot of the methyl stabilization energies of vinyl derivatives (16,19) is considerably more complicated than that for the ethyl derivatives (lower line, Figure 2). In the case of the vinyl groups with BH_2, NH_2, OH substituents, more than one point representing the energies of different conformations is shown. When these groups are turned 90°, pi effects are largely "shut off". These sigma-dominated points, along with those for the other substituents, give the V-shaped plot shown. The points that deviate upward from this "V" measure the energetic contribution of pi effects and are on the order of 6-10 kcal/mol. This is near the range of rotational barriers found experimentally in vinyl boranes, enamines and enols.

Why the V-shape? Our carbonium ion-carbanion analogy provides a simple rationalization. Both the vinyl carbanion and the vinyl cation are more stable than the methyl anion and methyl cation, respectively. The anion benefits from the greater s-character of the sp^2-hybridized vinyl center, and the vinyl cation from hyperconjugation of the "vacant" p-orbital with the adjacent in-plane CH_2 group. Hence, both strongly electron withdrawing and electron releasing substituents stabilize vinyl systems relative to methyl. However, relative to ethyl (note the close approach of the two lines in Figure 2), vinyl pi effects dominate (except for the electropositive substituents).

The vinyl V-shaped plot in Figure 2 is drawn arbitrarily. It implies that there are no pi effects involving fluorine, but this does not seem likely either intuitively, or by analysis of the pi electron population. Since the sp^2-hybridzed vinyl carbon is more electronegative than the sp^3-hybridized methyl or ethyl carbons, the slope of the right half of the V-shaped vinyl correlation line of Figure 2 is expected to be less than that of the ethyl line. Hence, the pi effects in vinyl systems probably are larger than implied by Figure 2.

The first thing one notices about the corresponding ethinyl substituent-electronegativity plot (Figure 7) is that the correlation line has the opposite slope as that of ethyl. The V-shaped vinyl correlation (Figure 2) thus is intermediate. The behavior of the acetylene derivatives follows from the high <u>stability</u> of the sp-hybridized ethinyl anion, HCC^-, and the extreme <u>instability</u> of the ethinyl cation, HCC^+. Indeed, the range of energies spanned in Figure 7 is one of the largest encountered. The scatter of data, evidently due to the workings of both sigma and pi effects, is rather large. How can this be best interpreted? The conical symmetry of the ethinyl group does not permit pi effects to be "shut off" by rotation. Extending the study to second row substituents may provide some help. Pi-donor effects of PH_2, SH, and Cl are believed (with good reason) to be substantially less than their first row counterparts. In addition, ethinyl groups are much more effective as sigma acceptors than as sigma donors. This means that pi-accepting groups, like BH_2 and AlH_2, can be expected to exhibit only small pi energetic effects. The correlation line drawn rather arbitrarily in Figure 7 takes these expectations into account. However, two lines of different slope for first and for second row substituents might well be a more accurate representation. On either basis, one can conclude that pi stabilizing effects of F, OH, and NH_2 substituents probably are quite important.   The well known instability of fluorine-substituted acetylenes would be even more substantial if it were not for compensating pi effects.

REACTIVE INTERMEDIATES

Substituent effects in carbonium ions (Table 1) show very large pi effects. Rotation by 90° decreases the substituent stabilization by over 70 kcal/mol for NH_2. Such differences for PH_2, SH, OH groups also are largely due to lone pair pi donation: hyperconjugation is responsible for the appreciable barriers for BH_2 and AlH_2 groups and the large stabilization of $C_2H_5^+$ vs CH_3^+. Sigma effects can be nearly as effective as pi effects in stabilizing carbenium ions, especially when electropositive metals (Na, Li, Mg, Al, Be, and Si) are involved (4,9,10,30). Transition metals are known to function similarly.

Although important, substituent effects on free radicals (4,15a) and triplet carbenes (Table II) (28) are relatively small in magnitude. Pi donor and pi acceptor, as well as sigma donor groups are effective. The vacant orbital in singlet carbenes makes this species an effective pi acceptor; large stabilization by NH_2, OH, and other good pi donor groups result. The singlet carbene lone pair also is stabilized by pi acceptors, particularly by BH_2 (28).

Carbanions show different behavior for first row (31) and for second row (32) substituents (Figure 8). Methyl groups are ineffective as pi acceptors, and the ethyl anion is destabilized relative to methyl (22,23). Electronegative first row groups exhibit a small, beneficial inductive effect, but CH_2F^- in the planar conformation would also be destabilizing (lone pair repulsion). Large pi stabilizing effects are exhibited by the BH_2 and AlH_2 groups, which can be "turned off" by rotation, and by BeH as well. While the stabilization of carbanions by BR_2 groups is well known experimentally, the activating effect of the second row substituent is more often employed synthetically (32). We have shown that d-orbital effects with Cl, SH, PH_2, and SiH_3 substituents are <u>not</u> responsible for the large stabilizing effects observed (Table I and Figure 8). Basis sets without d-functions give similar results (32). Instead, negative hyperconjugation (21) and the polarizability of the second row groups is responsible. Gas phase experimental measurements have confirmed our quantitative predictions (33).
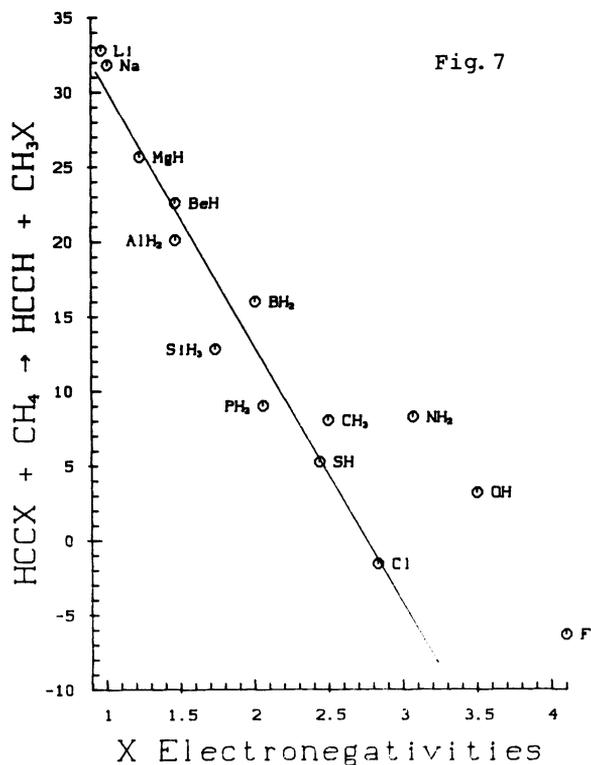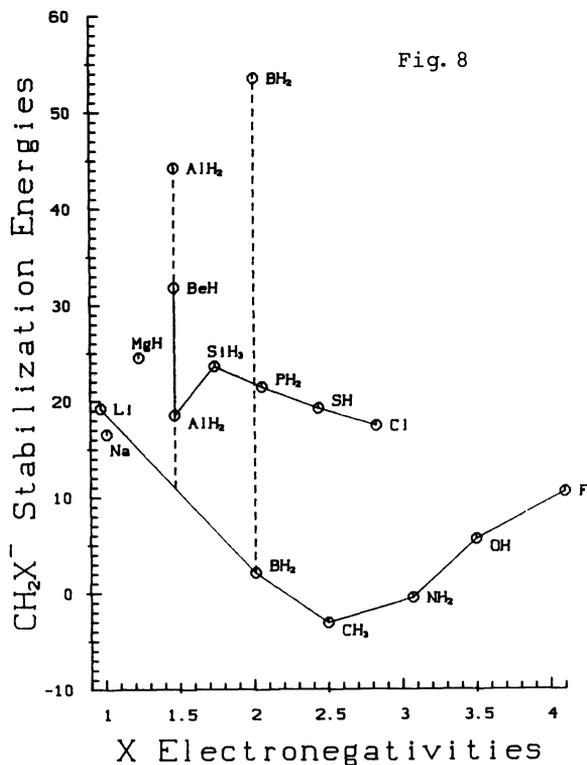
Figure 7. Electronegativity plot of the methyl stabilization energies of ethinyl drivatives (MP2/6-31G*//6-31G* data). The least squares line omitted the NH_2, OH, and F points. Compare with Figure 2.

Figure 8. Electronegativity plot of methyl stabilization energies of CH_2X^- carbanions (MP4/6-31+G*//6-31+G* data). Pi stabilizing effects are shown by dashed lines. Note the contrasting behavior of first and second row substituents.

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