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Theoretical Approach to Substituent Effects. Structures and Stabilities of Carbanions XCH_2^-

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The effect of substituents (X) on the structures and stabilities of XCH_2^- anions for X = Li, BeH, BH_2, CH_3, NH_2, OH, F, CN, NO_2, CH_3CH_2, $CH_2{=}CH$, $HC{\equiv}C$, CF_3, CHO, and C_6H_5 has been examined by using ab initio molecular orbital theory. Full optimizations have been carried out on anions XCH_2^- and corresponding neutral parents XCH_3 with the 4-31G basis set; improved energies have been obtained by use of a larger basis set (6-31G*) and by incorporation of electron correlation (MP2). A strong stabilizing effect in XCH_2^- is observed for π-accepting substituents (X = Li, BeH, BH_2, CN, NO_2, $CH_2{=}CH$, $HC{\equiv}C$, CF_3, CHO, and C_6H_5). For most of the systems in this category, the preferred anion structure is planar. For π-donor substituents (X = NH_2, OH, F), a weak stabilizing interaction takes place which may be attributed to the σ-accepting nature of these groups. Only small effects are observed for the CH_3 and CH_3CH_2 substituents. These results generally conform to the accepted views on carbanion stability derived from solution data. A comparison is presented of the stabilities of anions derived from XCH_3 by deprotonation at CH_3 on the one hand and at X on the other. The former site of deprotonation is generally favored by electropositive or unsaturated substituents while the latter is favored by electronegative substituents and by $C{\equiv}CH$.

Until recently, knowledge of the effect of substituents on the properties of carbanions was based almost exclusively on experimental observations made in solution.[2] However, in the last 15 years, gas-phase data have become available, primarily from flowing-afterglow,[3] high-pressure mass spectrometric,[4] and ion cyclotron resonance[5] experiments. It has been shown in many instances that the solution-phase results do not reflect the inherent properties of the anions so much as they reflect the effects of solvation. An alternative means of generating data appropriate to the isolated, gas-phase molecules comes from the application of ab initio molecular orbital theory. Extensive studies on cations[6] and anions[7] have shown that the theory successfully reproduces a wide range of gas-phase results, including those in which gas- and solution-phase observations are in conflict. Detailed studies of the effect of substituents (X) on carbocations (XCH_2^+) and radicals ($XCH_2\cdot$) have been reported.[8,9] In this paper the results of a systematic study, using ab initio molecular orbital theory, of the carbanions XCH_2^- (X = H, Li, BeH, BH_2, CH_3, NH_2, OH, F, CN, NO_2, CH_3CH_2, $CH_2{=}CH$, $HC{\equiv}C$, CF_3, CHO, and C_6H_5) are presented.[10] Comparison is made with experiment in those cases where the appropriate gas-phase data are available in order to assess the performance of the theory. The effect of the substituent on the structures and stabilities of these ions is examined. Finally, the possibility for deprotonation of XCH_3 at X as opposed to CH_3 is explored.

Methods and Results

Standard self-consistent-field molecular orbital calculations were carried out with a version[11a] of the Gaussian 70 series of programs[11b] modified to incorporate gradient-optimization algorithms and with the Gaussian 77/UCI program[11c] implemented on a Harris Corp. Slash 6 computer. Full geometry optimizations, subject only to specified symmetry constraints, were carried out for all molecules except toluene and benzyl anion at the level of Hartree–Fock theory with the split-valence 4-31G basis set[12] (formally denoted HF/4-31G but abbreviated here

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Table I. Calculated Total Energies (Hartrees) for 4-31G-Optimized Structures of Neutral Molecules XCH_3 and Corresponding Carbanions XCH_2^-

	XCH_3			XCH_2^-		
X	4-31G	6-31G*	MP2/6-31G*	4-31G	6-31G*	MP2/6-31G*
H	−40.139 77	−40.195 15	−40.332 33	−39.401 70	−39.466 46	−39.602 35
Li	−46.960 00	−47.015 39	−47.161 98	−46.249 73	−46.308 58	−46.473 06
BeH	−54.754 69	−54.816 00	−54.984 22	−54.080 95	−54.148 01	−54.329 00
BH_2	−65.348 44	−65.441 49	−65.646 14	−64.718 11	−64.810 63	−65.030 66
CH_3	−79.115 93	−79.228 73	−79.494 33	−78.381 26	−78.502 23	−78.769 64
NH_2	−95.071 66	−95.206 92	−95.502 27	−94.341 85	−94.483 49	−94.781 27
OH	−114.871 52	−115.034 22	−115.344 44	−114.158 53	−114.318 17	−114.631 87
F	−138.858 61	−139.033 08	−139.335 12	−138.159 68	−138.327 68	−138.630 73
CN	−131.728 27	−131.927 26	−132.334 97	−131.087 56	−131.286 23	−131.697 26
NO_2	−243.274 51	−243.659 22		−242.692 78	−243.051 43	
CH_2CH_3	−118.093 81	−118.263 62		−117.364 67	−117.542 01	
$CH{=}CH_2$	−116.905 10	−117.071 42	−117.454 48	−116.226 76	−116.393 44	−116.783 69
$C{\equiv}CH$	−115.701 33	−115.864 21	−116.239 74	−115.033 53	−115.203 83	−115.583 92
CF_3	−375.333 19	−375.816 52		−374.685 90	−375.146 84	
CHO	−152.686 53	−152.915 04	−153.345 87	−152.062 45	−152.282 70	−152.721 35
C_6H_5	−266.473 82[a]	−269.355 64[b]		−265.674 83[c]	−268.687 09[d]	

[a] STO-3G calculation using standard geometry. [b] 4-31G calculation using standard geometry. [c] STO-3G calculation with optimized CH_2^- group. [d] 4-31G calculation with geometry of footnote *c*.

simply to 4-31G) by using either a gradient-optimization procedure[13] or a modification of the Davidon–Fletcher–Powell method.[14] Calculations at this level of theory have previously been shown[15] to produce anion geometries in reasonable agreement with experiment. In order to obtain improved energy comparisons, additional calculations were performed on the 4-31G-optimized structures, first simply with the larger split-valence plus *d*-polarization 6-31G* basis set[16] (formally denoted 6-31G*//4-31G but abbreviated here to just 6-31G*) and second with electron correlation incorporated by using Møller–Plesset perturbation theory terminated at second order[17] (formally denoted MP2/6-31G*//4-31G but abbreviated here to just MP2/6-31G*). For toluene, a standard geometry[18] was used while for the benzyl anion, the geometric parameters of the CH_2^- group attached to a standard ring were optimized with the minimal STO-3G basis set.[19]

Optimized structures for anions XCH_2^- and the corresponding neutral molecules XCH_3 are presented in Figure 1.[20] Previously published data[12a,21] for a number of the uncharged species are included. Table I summarizes the corresponding total energies.

The problems associated with Hartree–Fock calculations on anions are well documented.[7,22] In particular, small basis set calculations (e.g., minimal basis set) often yield energies for anions which are actually higher than those of the corresponding free radicals formed by removal of a single electron. This would suggest that, given the freedom, these anions would prefer arrangements in which one electron was lost to the continuum. As the anions studied here are all closed-shell species and as the level of theory employed specifically restricts electrons to occupy spatial orbitals in pairs, this lower energy arrangement may generally not be achieved. Larger basis set calculations (e.g., the 6-31G* level) generally show the anions discussed in this paper to be stable with respect to electron loss.

Discussion

Comparison with Experimental Structural Data. The calculated 4-31G structural parameters are generally in good agreement with experimental values[23] (cf. Figure 1). Exceptions are the bond angles involving central heteroatoms which are overestimated. This is consistent with previous experience with the 4-31G basis set.

Comparison of Neutral (XCH_3) and Anionic (XCH_2^-) Structures. The most striking feature of the calculated geometries is the effect of the substituent on the C–X bond length of the anions compared to that of the neutral compounds. For X = Li, BeH, CN, NO_2, $CH_2{=}CH$, $HC{\equiv}C$, CHO, and CF_3, a distinct bond shortening is observed in the XCH_2^- species (between 0.10 and 0.14 Å); for X = NH_2, OH, and F, a bond lengthening is observed (between 0.07 and 0.15 Å). For X = H, CH_3, and CH_3CH_2, little variation is observed. This behavior can be understood in terms of the electronic interactions which take place between X and the adjacent anionic center.

Substituents may be classified in terms of their ability to donate or accept σ and π electrons. Thus Li, BeH, and BH_2 are σ donors, but as a result of having vacant p orbitals, they may act as π acceptors. On the other hand, NH_2, OH, and F act as σ acceptors, but in view of the lone pairs associated with these groups, they may also act as π donors. The groups CHO, $CH_2{=}CH$, $HC{\equiv}C$, NO_2, and CN are strong π acceptors since they all possess low-lying, vacant π^* orbitals. The CN and NO_2 groups are strong σ acceptors as well. The CF_3 group is a strong σ acceptor but may also act as a π acceptor due to low-lying $\pi^*_{CF_3}$ orbitals. This latter interaction is termed negative hyperconjugation[24] and may alternatively be expressed by

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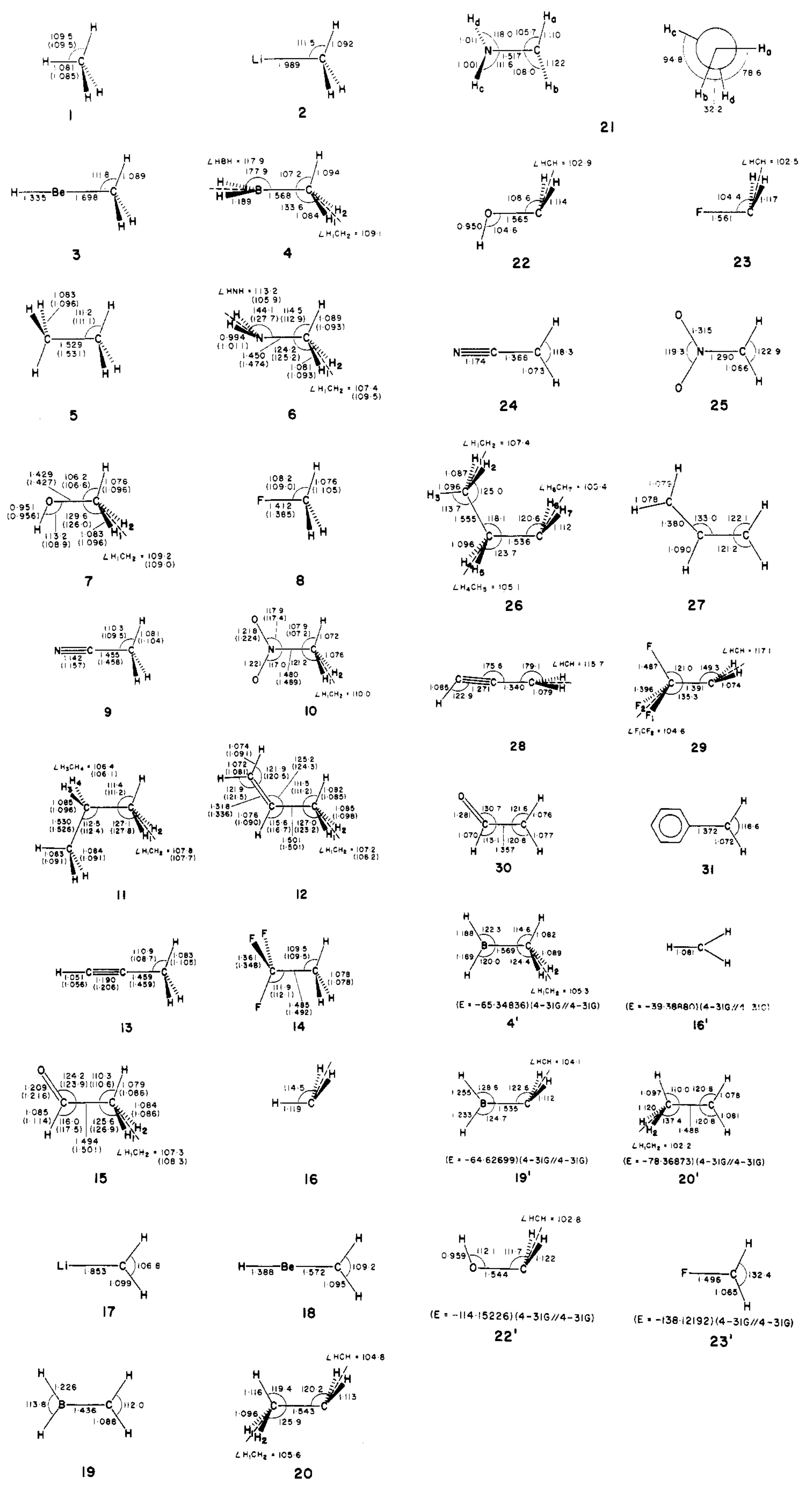


Figure 1. 4-31G-optimized structures for XCH_3 (1–15) and XCH_2^- (16–30), a partially optimized (see text) STO-3G structure for $C_6H_5CH_2^-$ (31), and 4-31G-optimized geometries for additional conformations 4′, 16′, 19′, 20′, 22′, and 23′. Available experimental values[23] are given in parentheses.

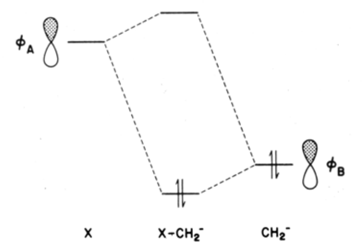
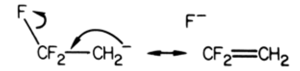


Figure 2. Two-electron stabilizing interaction between the lone-pair orbital on CH_2^- and a vacant p orbital on X in a planar XCH_2^- anion.

the resonance structures shown in eq 1. The CH_3 substituent, when adjacent to a strong π-donor group, may also act as a weak hyperconjugative π-acceptor.[21b,25]



(1)

Stabilization of XCH_2^- can take place through interaction of the CH_2^- lone-pair-type orbital with an empty π-type orbital on X. This stabilizing two-electron interaction may be expressed in perturbation molecular orbital (PMO) terms[26] by the diagram illustrated in Figure 2. Note that the geometries calculated for XCH_2^- (Figure 1) are fully consistent with such a picture. π-acceptor substituents (e.g., Li, BeH, BH_2, CHO, $CH_2{=}CH$, $HC{\equiv}C$, NO_2, CN, and CF_3) containing a low-lying vacant orbital lead to a reduction in the C–X bond length so as to facilitate the orbital overlap. Overlap of the high-lying orbital of the CH_2^- fragment with a vacant orbital at X is also facilitated by a flattening of the CH_2^- pyramid. Indeed, for X = Li, BeH, BH_2, CN, NO_2, $CH_2{=}CH$, and CHO, the XCH_2^- anions are found to be planar, with an almost planar structure being observed for X = $HC{\equiv}C$. Similar conclusions have been reached in other theoretical studies.[10a,b,f,i,j] Of the π-accepting substituents X, only for X = CF_3, CH_3CH_2, and CH_3, where the interaction is weak due to the relatively high energy of the acceptor orbitals, is a substantially pyramidal arrangement at C^- maintained.

These conclusions are supported by examination of the geometry of the $BH_2CH_2^-$ anion in its perpendicular conformation (**19′**). Here overlap between the CH_2^- lone pair and the formally vacant p orbital on B is precluded. As a result, the CH_2^- group adopts a pyramidal structure, and the C–B bond length is reduced by only 0.03 Å compared to that in neutral CH_3BH_2; in contrast, in the planar conformation (where orbital overlap is maximum), the bond length is reduced by 0.13 Å. The slight bond shortening that does occur in the perpendicular form (**19′**) may be due to favorable overlap between the CH_2^- lone pair and the $\pi^*_{BH_2}$ orbital as well as between the π_{CH_2} orbital and the vacant p orbital on B.

For the π-electron-donating, σ-electron-accepting substituents NH_2, OH, and F, there is increased pyramidalization at carbon in XCH_2^- (compared with CH_3^-) as well as an increase in C–X bond lengths (0.07–0.15 Å compared with X–CH_3). Both of these effects are consistent with a desire to minimize the four-electron destabilizing interaction between filled orbitals on X and on CH_2^-, as has been proposed by Hopkinson and Lien for XNH^-.[27] However, the fact that the offending lone pairs in the preferred conformation (**20′**) of $NH_2CH_2^-$ are almost orthogonal to one another casts doubt on the importance of the four-electron repulsion in influencing the pyramidalization and bond length effects. The increased pyramidalization can alternatively be rationalized in terms of the effect of electronegative substitution on HOMO–LUMO interactions in pyramidal forms of AH_3 molecules.[28] The increased bond lengths may be attributed to a less effective C–X σ bond in XCH_2^- compared with that in XCH_3. This latter suggestion is based on a similar effect which has been noted[29] in the series XBH_3^-, XCH_3, and XNH_3^+, both for the X–Y bond (Y = B^-, C, and N^+) and for the Y–H bond where bond lengths to Y are found to increase in the order $N^+ < C < B^-$. Thus it appears that an increased negative charge on an atom has the effect of weakening (and hence lengthening) the σ bonds associated with that atom.[30,31]

Table II. Calculated and Experimental Acidities (kcal mol^{-1}) of Carbon Acids Relative to Acetaldehyde[a]

XCH_3	4-31G	6-31G*	MP2/6-31G*	exptl[b]
$CH_3CH{=}CH_2$	−34.0	−28.6	−29.0	−24.4
$CH_3C{\equiv}CH$	−27.4	−17.6	−19.6	(−15)[c]
$CH_3C_6H_5$	−27.9[d]			−12.6
CH_3CN	−10.4	−5.5	−8.3	−5.8
CH_3CHO	0	0	0	0
CH_3NO_2	+26.6	+15.4		+7.7
mean abs dev	12.2	3.7	3.9	

[a] 4-31G-optimized structures unless otherwise noted. [b] Calculated by using $\Delta H^\circ_{\text{acid}}$ values in Table III of ref 5a unless otherwise noted. [c] Estimated value: DeFrees, D. J., unpublished experiments. [d] Calculated by using energies for structures noted in Table I.

Comparison of Theoretical and Experimental Energies. Table II presents a comparison of acidities relative to acetaldehyde, i.e., energies of reaction 2 calculated at

$$XCH_2^- + CH_3CHO \rightarrow XCH_3 + {}^-CH_2CHO \qquad (2)$$

three levels of theory. The corresponding enthalpies of reaction have previously been measured by using ion cyclotron resonance spectroscopy.[5c]

The experimental ordering of acidities (CH_3NO_2 > CH_3CHO > CH_3CN > $CH_3C{\equiv}CH$ > $CH_3CH{=}CH_2$) is reproduced by the 4-31G basis set; however, the mean error is too large to allow the theory to be used as a meaningful quantitative tool at this level. There is a substantial improvement in moving to the 6-31G* level, but significant discrepancies between theory and experiment still persist. The addition of s- and p-diffuse functions to the basis set might be expected to offer further improvement.[32] The effect of electron correlation at the MP2/6-31G* level has only been examined for three of the systems in Table II

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Table III. Calculated and Experimental Stabilization Energies (kcal mol^{-1}) for Carbanions XCH_2^- [a,b]

X	4-31G	6-31G*	MP2/6-31G*	exptl [c]
Li	17.4	13.7	25.8	
BeH	40.4	38.1	46.9	
BH_2	67.6	61.4	71.8	
CH_3	2.1	1.4	3.3	
NH_2	5.2	3.3	5.6	
OH	15.7	7.9	10.9	
F	24.6	14.6	16.1	
CN	61.1	55.0	57.9	44.4
NO_2	98.1	75.9		57.9
CH_3CH_2	5.6	4.4		
$CH_2{=}CH$	37.5	31.8	37.1	25.8
$HC{\equiv}C$	44.1	42.9	46.5	35.2 [d]
CF_3	57.0	37.0		
CHO	71.5	60.5	66.2	50.2
C_6H_5	44.4 [e]			37.6

[a] Energy changes for the reaction $XCH_2 + CH_4 \rightarrow XCH_3 + CH_3^-$. [b] 4-31G-optimized structures unless otherwise noted. [c] Calculated by using data in Table III of ref 5a together with ΔH°_{acid} (CH_4) from Table I of ref 5a. [d] Estimated value. [e] Calculated by using energies for structures noted in Table I.

and leads to somewhat worse results. This is discouraging although the small number of cases and inadequacies in the basis set preclude the drawing of any firm conclusions.

Effect of Substituents on Stabilities of Substituted Methyl Anions XCH_2^-. The effect of substituents on the stability of the methyl anion may be compared with the effect in methane by means of the isodesmic proton transfer reaction (eq 3). Energy changes for reaction 3

$$XCH_2^- + CH_4 \rightarrow XCH_3 + CH_3^- \qquad (3)$$

are listed in Table III. Positive values for these stabilization energies (SE's) indicate stabilization of the anion relative to the neutral methane.

For the sequence of substituents Li, BeH, and BH_2, stabilization energies increase in the order Li < BeH < BH_2, in line with the π-accepting ability of these groups. The two-electron stabilizing interaction for these systems is greatest for the BH_2 substituent which has the lowest lying vacant orbital. The importance of this type of interaction is readily gauged by examination of the energy of $BH_2CH_2^-$ in the perpendicular conformation where no overlap between the lone pair and the vacant p orbital may occur. The difference in stability of the perpendicular and planar forms is considerable, amounting to 57.2 kcal mol^{-1} at the 4-31G level. It is of interest to note that, despite the large reduction in the stabilizing effect of the BH_2 group in the perpendicular conformation, the overall interaction remains stabilizing compared to that for H (by 10.4 kcal mol^{-1}). This supports the suggestion that the stabilizing interaction between the $\pi^*_{BH_2}$ orbital and the CH_2^- lone-pair orbital, as well as that between the π_{CH_2} orbital and the vacant p orbital on B (which represent negative and positive hyperconjugative interactions, respectively), more than compensates for any destabilization resulting from the unfavorable σ interaction between the electropositive BH_2 group and the CH_2^- group.

The calculated stabilization energy drops sharply in moving from the strongly π-accepting BH_2 group to the weakly π-accepting CH_3 group. Our best (MP2/6-31G*) calculations yield a stabilization energy of 3.3 kcal mol^{-1}. Calculations reported recently by Kollmar,[33] using a double ζ plus polarization basis set and incorporating electron correlation through the CEPA procedure, suggest that the CH_3 substituent has a slight destabilizing effect in $CH_3CH_2^-$ of 5.0 kcal mol^{-1}.[32b] It appears likely that the small effect of the CH_3 substituent is due to two opposing components. On the one hand, CH_3 by acting as a π acceptor is stabilizing; on the other hand, it appears to be destabilizing through the σ framework.[34]

As we move through the π-donating, σ-accepting groups NH_2, OH, and F, a gradual increase in stabilization energy takes place. This increase stems from the increasing ability of these groups to stabilize the negative charge through σ withdrawal. Thus the stabilization energies increase from 5.6 kcal mol^{-1} for X = NH_2 to 16.1 kcal mol^{-1} for X = F (MP2/6-31G*). The result for X = F is consistent with experimental data available on the acid-strengthening effect of F when attached to an sp^3 center.[35]

The groups CN, NO_2, $CH_2{=}CH$, $HC{\equiv}C$, CF_3, CHO, and C_6H_5 which act as σ and π acceptors are all strongly anion stabilizing through a mixture of both σ and π interactions. The effect ranges from 32 kcal mol^{-1} for $CH_2{=}CH$ to 76 kcal mol^{-1} for the NO_2 group (6-31G*).

It appears, therefore, that the stabilization energies predominantly reflect interactions between the substituent X and the CH_2^- group. While interactions between the substituent and the neutral CH_3 moiety clearly exist, it appears as though the general trends are explicable solely in terms of interactions within the anion. The data in Table III indicate that π interactions (for X = Li, BeH, BH_2, CN, NO_2, $CH_2{=}CH$, $HC{\equiv}C$, CF_3, CHO, and C_6H_5) are far more important in stabilizing anions than σ interactions (for X = NH_2, OH, and F). Despite the fact that the electropositive groups (Li, BeH, and BH_2) are expected to destabilize the XCH_2^- species via the σ framework, the π effect more than compensates for this so that for all three groups, considerable stabilization results. Thus the difference in the stabilizing effect of BH_2 and CH_3 is a massive 68 kcal mol^{-1} as compared to the difference of only 2 kcal mol^{-1} between CH_3 and NH_2. Not unexpectedly, the CN, NO_2, and CHO substituents, which are both σ and π acceptors, bring about considerable anion stabilization. This is consistent with the well-known stability in solution of carbanions adjacent to NO_2, CN, and CHO groups.

It is of interest to compare the substituent effect in XCH_2^- with that in corresponding cations (XCH_2^+).[8] In contrast to our results which indicate that π effects are considerably more significant than σ effects in stabilizing the carbanions, σ and π effects both appear to influence XCH_2^+ stability to a similar extent. The data for substituted vinyl cations $CH_2{=}C^+X$[8b] suggest that for that system σ effects predominate over π effects.

The inversion barriers in XCH_2^- for X = H, CH_3, and F, which are calculated from the difference in energy between planar (structures **16′**, **20′**, and **23′**) and pyramidal structures, were found to be 8.1, 7.9, and 23.7 kcal mol^{-1}, respectively (4-31G//4-31G). This is consistent with both theoretical calculations[36] and experimental data[37] which indicate that substitution of electronegative elements in situations of this type leads to an increase in the inversion barrier. As noted above for bond angles, this behavior has been rationalized by Epiotis et al.[28] in terms of HOMO-LUMO interactions in the pyramidal structures.

Alternate Sites of Deprotonation. In many of the species discussed above, the substituent X possesses hy-

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[37] Data compiled in ref 28.

Table IV. Calculated Total Energies (Hartrees) for 4-31G-Optimized Structures of Anions Derived by Deprotonation at X of XCH_3

anion	4-31G	6-31G*	MP2/6-31G*
CH_3Be^-	−53.899 43	−53.962 81	−54.119 58
CH_3BH^-	−64.611 63	−64.714 60	−64.921 33
CH_3NH^-	−94.369 94	−94.515 29	−94.817 48
CH_3O^-	−114.218 40	−114.382 60	−114.700 71
CH_3CO^-	−152.010 41	−152.235 78	−152.667 98
$CH_3C{=}CH_2^-$	−116.200 30	−116.374 53	−116.760 97
$CH_3CH{=}CH^-$	−116.197 70	−116.373 27	−116.759 70
$CH_3C{\equiv}C$	−115.043 02	−115.215 51	−115.592 40

Table V. Relative Stabilities (kcal mol^{-1}) of Ions Resulting from Deprotonation at the Substituent (X) Compared to Deprotonation at CH_3^{a,b}

methyl-deprotonated ion	substituent-deprotonated ion	4-31G	6-31G*	MP2/6-31G*
$^-CH_2BeH$	CH_3Be^-	+113.9	+116.2	+131.4
$^-CH_2BH_2$	CH_3BH^-	+66.8	+60.3	+68.6
$^-CH_2NH_2$	CH_3NH^-	−17.6	−20.0	−22.7
$^-CH_2OH$	CH_3O^-	−37.6	−40.4	−43.2
$^-CH_2CHO$	CH_3CO^-	+32.7	+29.4	+33.5
$^-CH_2CH{=}CH_2$	$CH_3C{=}CH_2^-$	+16.6	+11.9	+14.3
$^-CH_2CH{=}CH_2$	$CH_3CH{=}CH^-$	+18.2	+12.7	+15.1
$^-CH_2C{\equiv}BH$	$CH_3C{\equiv}C^-$	−6.0	−7.3	−5.3

[a] A positive energy indicates preference for deprotonation at the methyl group. [b] 4-31G-optimized structures throughout.

drogens which may be abstracted under basic conditions. Additional calculations have therefore been performed on the ions resulting from deprotonation of the substituent (rather than the CH_3 group) in order to estimate the relative stabilities of the isomeric anions. The calculated 4-31G equilibrium geometries are displayed in Figure 3 while total energies at the 4-31G, 6-31G*, and MP2/6-31G* levels are presented in Table IV. The calculated isomer stabilities are tabulated in Table V, a positive value indicating a preference for deprotonation at the methyl group.

Both CH_3BeH and CH_3BH_2 are predicted to be much better carbon acids than heteroatom acids, while for CH_3NH_2 and CH_3OH deprotonation from nitrogen and oxygen is favored. The qualitative ordering can be ascribed to the differences in the electronegativities of the atom being deprotonated. The negative charge is stabilized by the more electronegative elements where the extra electron can be more tightly bound to the nucleus. Thus, deprotonation is favored at oxygen and nitrogen relative to carbon and at carbon relative to boron and beryllium. In the electropositive substituted molecules the magnitude of the preference for deprotonation at carbon is greatly enhanced by the stabilization afforded the carbanion by the empty p orbitals on boron and beryllium, while for methylamine and methanol the σ stabilization of X on the carbanion somewhat moderates the energy difference between the two isomers. The high relative energies calculated for $^-CH_2NH_2$ and $^-CH_2OH$ all but preclude the possibility for their observation, as they are predicted to be of the same order of base strength as CH_3^-, which to date is the strongest base known.[38]

Propene, propyne, and acetaldehyde possess hydrogens which are attached to unsaturated carbon atoms. It has long been recognized from solution-phase measurements

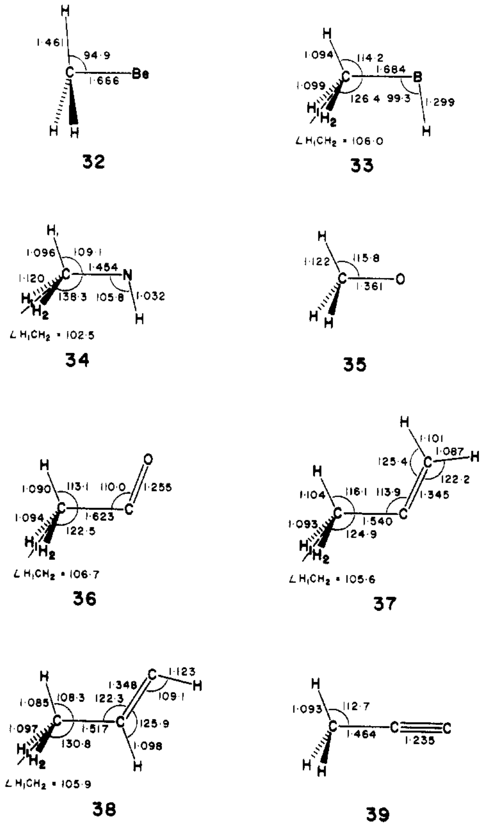
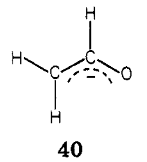


Figure 3. 4-31G-optimized structures for anions derived from deprotonation at X of XCH_3.

that, in the absence of strongly acidifying groups, carbanion stability increases with the degree of s character in the orbital holding the extra electron. In other words, carbanion stability increases with unsaturation.[2a,10h] The basis for this generalization is that on the average an s electron is closer to the nucleus than a p electron and thus is more tightly bound. It should be emphasized that this acid-strengthening effect is not due to a weakening of the carbon–hydrogen bond in the neutral compound; indeed, such homolytic bond strengths increase dramatically on going from sp^3 to sp^2 to sp carbon. Rather, the effect is concerned more with the nature of the orbital holding the negative charge in the anion; the consequent stabilization of the anion facilitates heterolytic bond breaking, i.e., increases the acidity.

With the exception of propyne, however, the calculations predict that deprotonation from the saturated methyl carbon leads to the more stable ion, in accord with conclusions reached from gas-phase deuterium-exchange reactions.[39] In each case the hybridization stabilization resulting from deprotonation at an unsaturated carbon is overwhelmed by the stabilization afforded by the delocalization of the negative charge resulting from deprotonation of the methyl group; deprotonation from the less saturated carbon would result in an ion where the charge is essentially localized in a lone-pair orbital. For example, deprotonation of the methyl group of acetaldehyde results in a resonance-stabilized enolate anion (**40**), while depro-



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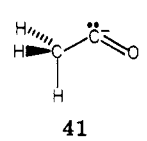

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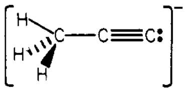
(38) CH_3 has recently been found to have a small positive electron affinity (1.8 kcal mol^{-1}): Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(39) DeFrees, D. J.; Hehre, W. J., unpublished data.

tonation of the carbonyl carbon results in a structure possessing a localized lone pair (41) orthogonal to the π system of the molecule. Likewise, for propene the allyl anion is preferred to a localized, vinyl-type anion. This is consistent with the result of a previous detailed theoretical and experimental study.[10k]

The most stable conjugate base of propyne, however, is predicted, in agreement with previous calculations,[10h] to be the propynyl anion (42) rather than the delocalized species 43. Gas-phase experiments suggest[40] that the propargyl anion (43) is less stable than 42 but that the difference in stabilities could be considerably less than the figure of 5 kcal mol^{-1} obtained theoretically. This result suggests that the gain in stabilization in going from an sp^2 to an sp lone pair is considerable and is mirrored in the empirical linear relationship between pK_a and the percentage of s character of the lone pair in the series acetylene, ethylene, cyclopropane, and ethane.[2a]



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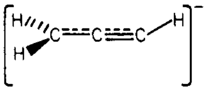

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Conclusions

Several important points emerge from this study.

(i) Relative acidities of substituted methanes XCH_3 are qualitatively well described by the 4-31G and 6-31G* basis sets. There is a substantial quantitative improvement in moving to 6-31G*, but deficiencies remaining even at this level suggest that further improvements in the basis set, e.g., addition of diffuse functions, may be required to obtain quantitatively accurate results. Electron correlation at the MP2 level with the 6-31G* basis set does not lead to improved results for the systems examined.

(ii) It appears that many of the prevalent ideas concerning the influence of substituents on carbanion stability as derived from experimental data (primarily acidities) in solution are well founded. The importance of charge dispersion through interaction with a π system is well recognized (exemplified by the acidity of protons α to a carbonyl group) and confirmed by this study. The inductive stabilization of carbanions (i.e., through the σ bond) is also confirmed, though our data suggest that, in contrast to the situation for the corresponding carbocations, π stabilization is considerably more effective than σ stabilization.

(iii) For systems XCH_3 offering competing sites of deprotonation, it is found that deprotonation at CH_3 is generally favored when X is an electropositive or unsaturated group while deprotonation at X is favored by electronegative substituents and by C≡CH.

Acknowledgment. We thank Professor P. v. R. Schleyer for helpful exchanges of information.

Registry No. CH_4, 74-82-8; $LiCH_3$, 917-54-4; $HBeCH_3$, 6917-55-1; H_2BCH_3, 12538-96-4; H_3CCH_3, 74-84-0; H_2NCH_3, 74-89-5; $HOCH_3$, 67-56-1; FCH_3, 593-53-3; $NCCH_3$, 75-05-8; O_2NCH_3, 75-52-5; $H_3CCH_2CH_3$, 74-98-6; $H_2C{=}CHCH_3$, 115-07-1; $HC{\equiv}CCH_3$, 74-99-7; F_3CCH_3, 420-46-2; $OHCCH_3$, 75-07-0; $C_6H_5CH_3$, 108-88-3; CH_3^-, 15194-58-8; $LiCH_2^-$, 55169-83-0; $HBeCH_2^-$, 74215-19-3; $H_2BCH_2^-$, 74215-20-6; $H_3CCH_2^-$, 25013-41-6; $H_2NCH_2^-$, 74215-21-7; $HOCH_2^-$, 55830-71-2; FCH_2^-, 60291-31-8; $NCCH_2^-$, 21438-99-3; $O_2NCH_2^-$, 18137-96-7; $H_3CCH_2CH_2^-$, 59513-13-2; $H_2C{=}CHCH_2^-$, 1724-46-5; $HC{\equiv}CCH_2^-$, 31139-07-8; $F_3CCH_2^-$, 27774-96-5; $OHCCH_2^-$, 64723-93-9; $C_6H_5CH_2^-$, 18860-15-6.

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Synthesis of *lin*-Benzofervenulin, *lin*-Benzotheophylline, and *lin*-Benzocaffeine

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The synthesis of 7,9-dimethylpyrimido[5,4-*g*]-1,2,4-benzotriazine-6,8(7*H*,9*H*)-dione (3) as the *lin*-benzo-separated analogue of fervenulin is reported in five steps from 7-chloro-2,4(1*H*,3*H*)-quinazolinedione. The preparation of *lin*-benzotheophylline (11) is described as arising from 1,3-dimethyl-7-hydrazino-6-nitro-2,4(1*H*,3*H*)-quinazolinedione (9) in a procedure originally designed to give 3. Methylation of 11 is shown to yield two products, one of which is *lin*-benzocaffeine (18).

The broad-spectrum antibiotic fervenulin (1) possesses the unique pyrimido[5,4-*e*]-1,2,4-triazine (i.e., 7-azapteridine) nucleus and has aroused considerable attention due to its interesting biological and chemical properties.[1] Stimulated by this, Leonard's recent successes[2] with benzo-separated purines [e.g., *lin*-benzoadenine (2)],[3] and our interest in the similarly separated pteridines,[4] *lin*-benzofervenulin[5] [7,9-dimethylpyrimido[5,4-*g*]-1,2,4-benzotri-

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[1] For leading references to fervenulin see the introductory paragraphs of: (a) Taylor, E. C.; Sowinski, F. *J. Org. Chem.* **1975**, *40*, 2321; (b) Billings, B. K.; Wagner, J. A.; Cook, P. D.; Castle, R. N. *J. Heterocycl. Chem.* **1975**, *12*, 1221; (c) Yoneda, F.; Nagamatsu, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2884; (d) Yamaguchi, H.; Kuwata, R.; Yoneda, F. *J. Heterocycl. Chem.* **1978**, *15*, 615.

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