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STABILIZATION OF METHYL ANIONS BY FIRST ROW SUBSTITUENTS

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Summary: A theoretical examination of the stabilization of simple carbanions, XCH_2^-, by substituents comprising elements of the Li-F period, reveals the particular effectiveness of the electropositive substituents, BH_2, BeH, and even Li, with vacant p-orbitals. The relative influence of pi and sigma stabilization or destabilization is assessed.

How do substituents stabilize carbanions? What is their effectiveness? Following our earlier examination of other reactive intermediates,[1] we have obtained some answers to these questions by means of *ab initio* molecular orbital calculations[2] on XCH_2^- species (X=Li, BeH, BH_2, CH_3, NH_2, OH, and F) encompassing a large range of electronic properties. Table 1 presents the results of full geometry optimization at both minimal STO-3G[3] and split-valence 4-31G[4] basis set levels; stabilization energies are given relative to CH_3^-.

Values with the 4-31G basis should be more reliable and should reflect trends reasonably well, although larger basis set calculations with inclusion of electron correlation will be required to determine more critical properties like electron affinity.[5] Quantitative experimental data on these species in the gas phase are generally not available.

Included in Table 1 are values for different substituent conformations from which estimates of the rotational barriers can be derived. While, in general, the potential energy surfaces for these carbanions are indicated to have only a single minimum each, the alternative higher energy conformations (obtained by imposing some symmetry or geometrical constraint) provide more detailed information which is useful in interpreting the results. Thus, the most stable form of $H_2C{=}BH_2^-$ is found to have a planar structure with a very short (1.44 Å at 4-31G) C-B bond and a very large stabilization energy. Such ions have been observed experimentally.[6] This species is isoelectronic with ethylene and has a similarly large rotation barrier (57.3 kcal/mol at 4-31G).

In contrast, the perpendicular conformation, calculated by imposing a symmetry plane, was indicated to have a pyramidal CH_2^- center and a longer C-B bond (1.53 Å). Although conventional pi delocalization cannot be present, this conformation is still indicated to enjoy some stabilization. The population analysis shows this to be due to sigma donation from the electropositive C^- center to boron and to pi donation from the carbanion "lone pair" to the π^*BH_2 orbital ("negative hyperconjugation").[7]

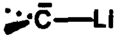
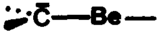
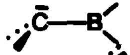
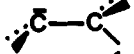
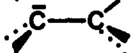
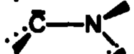
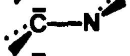
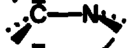
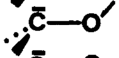
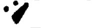
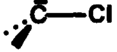
Both CH_2BeH^- and CH_2Li^- are indicated to have planar, $\underline{C}_{2v}$ structures and to be quite stabilized relative to CH_3^-. As an alkali metal with very low electronegativity, lithium is not commonly expected to be a carbanion-stabilizing substituent. One school of thought argues that carbon-lithium bonding is largely or wholely ionic;[8] on this basis, lithium-substituted carbanions would have to be formulated as $CH_2^{2-}Li^+$! Our interpretations emphasize the multicenter electron-deficient bonding capabilities of lithium involving the p-orbitals.[9] Such p-orbital involvement explains the stabilization of CH_2Li^-, its planar structure, and the short (1.85 Å) C-Li bond. To stress the point, we have calculated CH_2Na^-. Sodium is about as electropositive as lithium,[10] but the sodium p-orbitals are much higher in energy. In sharp contrast to the lithium analog, CH_2Na^- is indicated to be destabilized relative to CH_3^- to a huge extent (100 kcal mol^{-1} at STO-3G) and is calculated to be strongly pyramidal.

CH_2F^- is indicated to be strongly pyramidal, in agreement with expectation.[11] Here stabilization through sigma electron withdrawal by the very electronegative fluorine and 4-electron pi destabilization, which leads to pyramidalization, complete. The stabilization energy, largest among the electronegative substituents, indicates the importance of sigma withdrawal. Although we will present our results with second row substituents subsequently, we note here that stabilization by chlorine in CH_2Cl^- is much larger than by fluorine in CH_2F^-(-47.9 vs -24.6 kcal mol^{-1} at 4-31G, respectively), despite the lower electronegativity of chlorine.[10] The very long (2.22 Å at 4-31G) C-Cl bond in CH_2Cl^- allows the destabilizing pi interaction to be minimized relative to CH_2F^- without significantly affecting the pi-stabilization.

The OH and NH_2 substituents are better pi-donors and poorer sigma-acceptors than F. Consequently, the stabilization energies are less and preferred geometries reflect attempts to minimize the destabilizing 4-electron pi interactions. Thus, the trans-pyramidal structure of CH_2OH^- (Table 1) results from this factor and desire of the lone-pair and O-H dipoles to be opposed. $CH_2NH_2^-$ prefers a hydrazine-like geometry; the two species are isoelectronic.

Both pi- and sigma-acceptors can stabilize carbanions, although NH_2, OH and F also destabilize by pi-donation. Experimentally, good sigma acceptors, like R_3N^+ in ylids, and substituents which are both sigma- and pi-acceptors (e.g. CN, NO_2) are very effective.[12] Surprisingly, lithium can stabilize anions despite its low electronegativity. This stabilization, in accord with the axiom that lithium can stabilize almost anything,[1,9,13] is a strong argument for the involvement of p-orbitals on lithium.

Table: TOTAL ENERGIES, METHYL STABILIZATION ENERGIES[a] AND SELECTED GEOMETRICAL PARAMETERS[b] FOR CH_2X^- ANIONS

Anion		Total Energy, a.u.		ΔH_{stab}[a] (kcal mol^{-1})		Geometry[b] (4-31G)		
Geometry		STO-3G//STO-3G	4-31G//4-31G	STO-3G	4-31G	∡HCH	∡XCH	r(CX)
	C_{2v}	-45.61693	-47.24973	-54.9	-17.5	106.8	126.6	1.853
	C_{2v}	-53.36598	-54.08094	-65.8	-40.4	109.2	125.4	1.572
	C_{2v}	-63.90563	-64.71811	-81.6	-67.7	112.2	123.9	1.436
	C_s	-63.78689	-64.62676	-7.1	-10.4	104.3	109.3	1.533
	C_s	-77.42841	-78.38125	-9.0	-2.1	104.8	113.1	1.545
	C_s	-77.42284	-78.37578	-5.5	+1.3	104.9	112.6	1.555
	C_1	-93.16710	-94.34185	-16.6	-5.2	103.9	105.7,108.0	1.517
	C_s	-93.16672	-94.33556	-16.3	-1.6	101.6	101.5	1.595
	C_s	-93.15582	-94.32629	-9.8	+4.6	101.4	103.3	1.592
	C_s	-112.68988	-114.15853	-20.0	-15.8	103.0	101.5	1.565
	C_s	-112.68645	-114.15226	-18.4	-11.9	102.7	103.3	1.546
	C_s	-136.31158	-138.15968	-21.7	-24.6	102.5	99.0	1.561
	C_s	-197.88876	-	+100.3	-	96.5[c]	97.9[c]	2.042[c]
	C_s	-492.93077	-497.87870	-62.6	-47.9	103.8	92.2	2.221

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[a] The calculated energy for the reaction, $CH_3^- + CH_3X \rightarrow CH_2X^- + CH_4$. STO-3G and 4-31G total energies for CH_3X are taken from J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, J. Am. Chem. Soc., **98**, 5419 (1976); H. B. Schlegel, K. Mislow, F. Bernardi, and A. Bottoni, Theoret. Chim. Acta, **44**, 245 (1977); G. Wenke, D. Lenoir, P. Hofmann, and P. v. R. Schleyer, manuscript in preparation; J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, J. Chem. Phys., **64**, 5142 (1976); T. W. Bentley, J. Chandrasekhar, and P. v. R. Schleyer, unpublished calculations.

[b] Angles in degrees, bond lengths in Ångstrøms. [c] STO-3G optimum geometry.

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