

Stabilization of Methyl Anions by First-Row Substituents. The Superiority of Diffuse Function-Augmented Basis Sets for Anion Calculations

Günther W. Spitznagel, Timothy Clark, Jayaraman Chandrasekhar, and Paul von Ragué Schleyer

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany

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The entire set of methyl anions, XCH_2^- , substituted by first-row substituents, Li, BeH, BH_2 , CH_3 , NH_2 , OH, and F, was examined at various *ab initio* levels. Diffuse orbital-augmented basis sets, such as 4-31+G and 6-31+G*, are needed to describe the energies of these anions adequately. Estimates of proton affinities are further improved by second-order Møller-Plesset (MP2) electron correlation corrections, but relative energies are less affected. The methyl group in the ethyl anion is destabilizing, the amino substituent is borderline, but all other groups are stabilizing. Very large π effects are exhibited by BH_2 and BeH groups; inductive stabilization by the electronegative F and OH groups is less effective. Lithium also is stabilizing, but the best singlet geometry of CH_2Li^- is not planar. A planar CH_2Li^- triplet with a π^1 configuration may be lower in energy.

INTRODUCTION

Until recently, *ab initio* studies of anions presented particular problems which were not overcome by the standard basis sets and methods in common use.¹ Minimal basis sets, such as STO-3G, give anion proton affinities (PA) which are hundreds of kcal/mol higher than the experimental values. While split valence basis sets, such as 4-31G, are satisfactory for the calculation of anion geometries,² the PAs are about 30 kcal/mol too high.¹ The inclusion of *d* orbitals in the basis set (e.g., 6-31G*) and corrections for electron correlation (e.g., MP2/6-31G*) do not improve the situation.

Anions typically have weakly bound HOMOs and diffuse (flat) functions are known to be essential for their proper description.^{1,3} Consequently, we developed a triply split valence basis set, 4-31+G, which includes a set of flat *s* and *p* functions on all first-row atoms.¹ For greater efficiency, such functions were not added to hydrogen. This 4-31+G basis set was shown to reproduce the experimental proton affinities of a set of various C-, N-, O-, F-, and H-based anions very well. When corrections for electron correlation were included, the results (at the MP2/4-31+G level) were even better. It thus appears that reliable results for

anions can be achieved at rather modest theoretical levels. Hence, extensive studies are now possible. As part of a general investigation of organic anions, we have reexamined the substituted methyl anions, CH_2X^- , which have previously been calculated with basis sets more suited to neutral molecules or cations.⁴⁻⁶

Our purpose is threefold. We first wish to compare the performance of different levels of sophistication. This is done in Table I for proton affinities, in Table II for stabilization energies relative to CH_3^- , and in Table III for geometries.

Secondly, we need to establish the accuracy of the calculations. Since, for all but CH_3^- , no experimental values are available, the 4-31+G and MP2/4-31+G results were tested against those obtained at 6-31+G* and at MP2/6-31+G* levels. The pleasing consistency of values (Tables I and II) suggests that convergence has been achieved and that even more sophisticated calculations should not alter the results significantly.

Finally, we are interested in details of the geometries, energies, and electronic structures. Since these anions have already been considered several times in the literature,⁴⁻⁶ our discussion will concentrate on features not studied before, and differences revealed by the use of the diffuse basis set. For example, the CH_3 substituent in

Table I. Proton affinities of XCH_2^- (in kcal/mol).^a

X	STO-3G// STO-3G ^b	4-31G// 4-31G ^{b,c}	6-31G*// 4-31G ^c	MP2/6-31G*// 4-31G ^c	4-31+G// 4-31+G ^d	MP2/4-31+G// 4-31+G ^d	6-31+G// 4-31+G ^d	MP2/6-31+G*// 4-31+G ^d
H ^e	-559.8	-463.1	-457.2	-458.1	-433.5	-425.2	-434.6	-426.5
Li	-504.9 ^f	-445.7 ^f	-443.5 ^f	-432.3 ^f	-429.9 ^g	-429.2 ^g	-429.8 ^g	-418.4 ^g
BeH	-494.0	-422.8	-419.2	-411.1	-401.7	-391.8	-403.3	-393.6
BH ₂	-478.2	-395.5	-395.9	-386.2	-378.8	-367.1	-381.4	-369.1
CH ₃	-550.8	-461.0	-455.9	-454.7	-439.1	-430.1	-438.6	-429.5
NH ₂	-543.2	-457.9	-453.9	-452.4	-435.4	-425.8	-436.1	-425.9
OH	-539.8	-447.4	-449.3	-447.4	-425.8	-417.1	-430.9	-420.9
F	-538.1	-438.6	-442.6	-442.0	-416.9	-411.9	-425.3	-417.5

^a All values based on singlet species in their most stable geometries.^b Reference 4.^c Reference 5.^d This work.^e Experimental value at 298°C, 416.6 kcal/mol, ref. 12.^f Planar C_{2v} symmetry.^g Nonplanar C_s symmetry.

$CH_3CH_2^-$ is found to be destabilizing rather than stabilizing. Singlet CH_2Li^- is pyramidal rather than planar⁴⁻⁶; moreover, CH_2Li^- may prefer a triplet ground state. The σ and π contributions to the substituent stabilization energies are analyzed with the aid of an "electronegativity plot" (Fig. 1).

METHODS AND RESULTS

All calculations used the GAUSSIAN 76 (ref. 7) series of programs. Closed-shell species were calculated using the restricted Hartree-Fock formalism and triplet CH_2Li^- with the unrestricted Hartree-Fock method. The 4-31+G basis set (with flat function exponents: F, 0.090; O, 0.068; N, 0.053; C, 0.040; B, 0.034; Be, 0.026; and Li, 0.012) (ref. 8) was used to all geometry optimizations, which were performed by a Davidson-

Fletcher-Powell multiparameter search⁹ using analytically evaluated atomic forces.¹⁰ The optimizations were terminated when all gradients were less than 0.0025 mdyne/Å and when all geometric variables remained constant to better than 0.2% over consecutive cycles. The basis set labeled 6-31+G* was constructed by adding diffuse *s* and *p* functions with the above exponents to the standard 6-31G* basis set.¹¹ Calculations with second-order Møller-Plesset correction for electron correlation (MP2) (ref. 12) did not include the 1s orbitals for Li-F (frozen-core approximation).¹²

All geometries for the CH_3X neutrals and CH_2X^- anions were fully optimized with the 4-31+G basis (4-31+G//4-31+G; // means "at the geometry of") without symmetry constraints (to find the global minimum) and with certain imposed symmetries (in order to estimate rota-

Table II. Calculated stabilization energies (kcal/mol) for carbanions, XCH_2^- .^a

X	STO-3G// STO-3G ^a	4-31G// 4-31G ^{b,c}	6-31G*// 4-31G ^c	MP2/6-31G*// 4-31G ^c	4-31+G// 4-31+G ^d	MP2/4-31+G// 4-31+G ^d	6-31+G*// 4-31+G ^d	MP2/6-31+G*// 4-31+G ^d
Li ^e	-54.9	-17.5	-13.7	-25.8	-2.4	-6.6	-4.8	-8.1
BeH	-65.8	-40.4	-38.1	-46.9	-31.8	-33.3	-31.3	-32.9
BH ₂	-81.6	-67.7	-61.4	-71.8	-54.7	-58.0	-53.2	-57.4
CH ₃	-9.0	-2.1	-1.4	-3.3	+5.7	+4.8	+4.0	+3.0
NH ₂	-16.6	-5.2	-3.3	-5.6	+1.9	+0.6	+1.5	-0.6
OH	-20.0	-15.8	-7.9	-10.9	-7.7	-8.1	-3.7	-5.6
F	-21.7	-24.6	-14.6	-16.1	-15.6	-13.3	-9.3	-9.0

^a Equation (1), evaluated with all species in their most stable geometries.^b Reference 4.^c Reference 5.^d This work.^e Singlet.

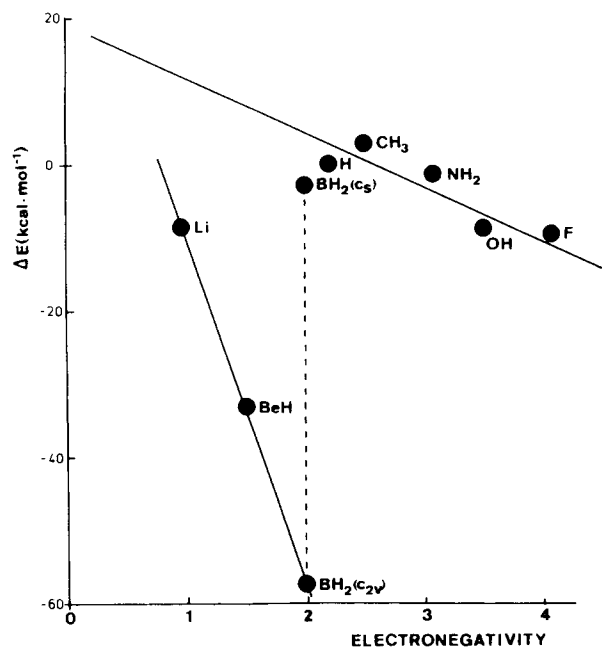


Figure 1. Stabilization energies [eq. (1), MP2/6-31+G*//4-31+G] versus substituent central atom electronegativities (Allred-Rochow values from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Wiley-Interscience, New York, 1972, p. 115) for CH_2X^- anions. The two solid lines correlate the π acceptors (Li, BeH, and BH_2) and the normal inductive substituents (the "sigma-only" line). The dotted line represents the rotation barrier (roughly the π stabilization) of CH_2BH_2^- .

tional and inversion barriers, etc.). These data, collected in Table III, are compared with the published 4-31G geometries.⁴⁻⁶

The 4-31+G geometries were then used for single point calculations at the MP2/4-31+G, 6-31+G*, and MP2/6-31+G* levels. Absolute energies are given in Table IV. It is of interest to examine the extent to which diffuse orbitals lower the absolute energies when added in the 4-31G and the 6-31G* basis sets. These lowerings, collected in Table V, are small for the neutrals with more electropositive substituents, but become more significant with CH_3NH_2 , CH_3OH , and CH_3F , where the substituents have lone pairs. As expected, the diffuse function energy lowerings in the anions are very much larger. At 4-31+G the average lowering (24 kcal/mol) is somewhat larger than that at 6-31+G* (19 kcal/mol).

The proton affinities in Table I refer to the hypothetical, motion-free state. Corrections to the zero-point energy level are needed if strict comparisons with experimental data at 0 K are to be made. (If the experimental data are at higher temperatures, further corrections are needed.) While such corrections can be determined from the

experimental or calculated frequencies, they were not made here since such experimental data are not generally available for the compounds considered.

The one exception is CH_3^- , which has an experimental PA of 416.6 ± 1.0 kcal/mol at 298 K.¹³ The zero-point energy correction which reduces the theoretical PA of CH_3^- is estimated to be 8 kcal/mol.¹⁴ Application of this correction to the MP2/4-31+G//4-31+G and MP2/6-31+G*//4-31+G values in Table I leads to PAs of 417.2 and 418.5 kcal/mol, in essentially perfect agreement with experiment. This result, and the convergence of the diffuse function PAs in Table I, suggest that the absolute errors in our calculated values may be quite small.

The calculation of relative energies by theoretical methods is an inherently easier task. The isodesmic equation (1), used to evaluate the substituent stabilization energies of the methyl anions, should tend to cancel systematic errors and differences between motion-free-state calculations and experimental results.

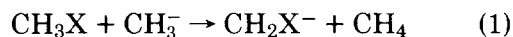


Table II affords a comparison of the STO-3G,⁴ 4-31G,^{4,6} 6-31G*,⁶ and MP2/6-31G* (ref. 6) methyl anion stabilization energies with those calculated using diffuse function-augmented methods.

PERFORMANCE OF THEORETICAL MODELS

Proton Affinities

The deficiencies of minimal basis sets for the calculation of anion proton affinities¹ are further illustrated by the results in Table I. The STO-3G proton affinities are on average well over 100 kcal/mol higher than those at the highest theoretical levels. The use of minimal basis sets cannot be recommended for calculations on anions.

The split valence 4-31G basis fares better, but the PA values are on average 30 kcal/mol higher than those obtained at MP2/4-31+G. The larger basis set, 6-31G*,¹¹ augmented with *d*-type polarization functions rather than diffuse orbitals, affords negligible improvement. The 6-31G* PAs are only about 2 kcal/mol on the average below those at 4-31G. Correction for electron correlation (MP2/6-31G*) also does not alter most of the values significantly, although the PAs for the electropositive substituents, Li, BeH, and BH_2 , are

Table III. Calculated 4-31+G (4-31G)^a geometries.^b

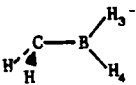
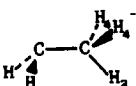
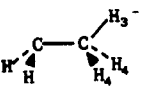
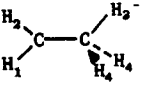
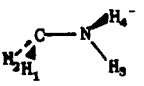
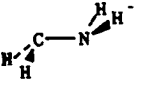
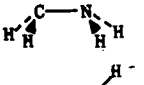
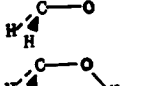
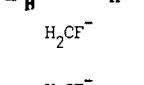
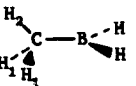
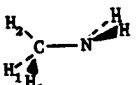
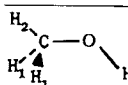
Species	Point Group	C-X	C-H	X-H	H ₁ CH ₁ (2)	XCH ₁₁ XCH ₂	Other	
CH ₃ ⁻	C _{3v}		1.085 (1.119)		114.9 (104.7)	HCH ₁₁ 141.5 (114.5)		
CH ₃ ⁻	D _{3h}		1.075 (1.081)					
H ₂ CLi ⁻ (singlet)	C _{2v}	1.910 (1.853)	1.093 (1.099)		107.9 (106.8)			
H ₂ CLi ⁻ (singlet)	C _s	1.969	1.094		107.9	LiCH ₁₁ 161.4		
H ₂ CLi ⁻ (triplet)	C _{2v}	2.008	1.099		107.4			
H ₂ CBeH ⁻	C _{2v}	1.601 (1.572)	1.089 (1.095)	1.381 (1.392)	110.3 (109.2)			
H ₂ C=BH ₂ ⁻	C _{2v}	1.458 (1.436)	1.084 (1.088)	1.220 (1.226)	112.9 (112.0)		HBH 114.9 (113.9)	
	C _s	1.535 (1.535)	1.092 (1.112)	1.243 (H ₁) (1.251) 1.224 (H ₃) (1.236)	110.0 (104.1)	BCH ₁₁ 142.2 (122.6)	CBH ₃ 125.2 (128.7) CBH ₄ 126.5 (124.6)	
	C _s	1.536 (1.543)	1.094 (1.113)	1.108 (H ₃) (1.116) 1.090 (H ₄) (1.096)	109.7 (104.8)	CCH ₁₁ 131.5 (120.2)	CCH ₃ 117.2 (119.4) CCH ₄₄ 126.0 (125.9) H ₄ CH ₄ 106.1 (105.6)	
	C _s	1.537 (1.555)	1.088 (1.108)	1.092 (H ₄) 1.097 (H ₃)	111.3 (104.9)	CCH ₁₁ 136.7 (137.7)	CCH ₃ 113.9 CCH ₄ 129.8 H ₄ CH ₄ 105.9	
	C _s	1.512 (1.488)	1.075 (H ₁) (1.081) 1.075 (H ₂) (1.078)	1.093 (H ₃) (1.097) 1.100 (H ₄) (1.120)	118.6 (118.4)	CCH ₁ 121.1 (120.8) CCH ₂ 120.3 (120.8)	CCH ₃ 109.8 (110.0) CCH ₄₄ 124.2 (137.4) H ₄ CH ₄ 105.0 (102.2)	
	C ₁	1.494 (1.517)	1.092 (H ₁) (1.122) 1.100 (H ₂) (1.110)	1.002 (H ₃) (1.011) 0.993 (H ₄) (1.001)	109.6 (103.9)	NCH ₁ 109.9 (108.0) NCH ₂ 111.8 (105.7)	ØH ₁ CNH ₄ 51.5 (94.8) ØH ₁ CNH ₃ 84.8 (32.2) CNH ₃ 119.1 (118.0) CNH ₄ 114.4 (111.6)	
	C _s	1.544 (1.595)	1.097 (1.117)	1.001 (1.010)	106.2 (101.6)	NCH ₁₁ 116.7 (108.4)	CNH ₁ 123.1 HNH 107.1	
	C _s	1.542 (1.592)	1.101	1.001	107.1 (101.4)	NCH ₁₁ 120.6	CNH ₁ 136.0 HNH 110.2	
	C _s	1.538 (1.565)	1.097 (1.114)	0.945 (0.950)	107.3 (102.9)	OCH ₁₁ 113.9 (108.6)	COH 107.4 (104.6)	
	C _s	1.535 (1.544)	1.103 (1.122)	0.954 (0.959)	108.0 (102.6)	OCH ₁₁ 117.0 (111.7)	COH 113.1 (112.1)	
H ₂ CF ⁻	C _s	1.577 (1.561)	1.099 (1.117)		106.6 (102.5)	FCH ₁₁ 105.6 (104.4)		
H ₂ CF ⁻	C _{2v}	1.482 (1.496)	1.062 (1.065)		134.1 (132.4)			
CH ₄	T _d		1.081 (1.081)		109.5 (109.5)	HCH ₁₁ 125.3 (125.3)		
CH ₃ Li	C _{3v}	1.999 (1.989)	1.092 (1.092)		107.6 (107.4)	LiCH ₁₁ 127.9 (128.2)		
CH ₃ BeH	C _{3v}	1.696 (1.698)	1.090 (1.089)	1.337 (1.335)	107.0 (107.0)	BeCH ₁₁ 128.7 (128.7)		
	C _s	1.567 (1.568)	1.084 (H ₁) (1.084) 1.095 (H ₂) (1.094)	1.189 (1.189)	109.1 (109.1)	BCH ₁₁ 133.5 (133.6) BCH ₂ 107.7 (107.2)	HBH 117.8 (117.9) CBHH 180.0 (179.9)	
CH ₃ -CH ₃	D _{3d}	1.529 (1.529)	1.084 (1.083)		107.7 (107.7)	CCH ₁₁ 127.8 (127.8)		
	C _s	1.453 (1.450)	1.081 (H ₁) (1.081) 1.089 (H ₂) (1.089)	0.993 (0.994)	107.5 (107.4)	NCH ₁₁ 124.0 (124.2) NCH ₂ 114.2 (114.5)	HNH 113.9 (113.2) CNHH 146.9 (144.1)	

Table III (continued)

Species	Point Group	C-X	C-H	X-H	H ₁ CH ₁ (2)	XCH ₁₁ XCH ₂	Other
	C _s	1.435 (1.429)	1.082 (H ₁) (1.083) 1.075 (H ₂) (1.076)	0.950 (0.951)	109.7 (109.2)	OCH ₁₁ 129.0 (129.6) OCH ₂ 105.8 (106.2)	COH 114.5 (113.2)
CH ₃ F	C _{3v}	1.427 (1.412)	1.076 (1.076)		111.5 (110.7)	FCH ₁₁ 122.1 (123.3)	

^a References 4 and 6.^b Distances in angstroms, angles in degrees. The notations, "XH₁₁" and "XHH," refer to the bisectors of the HXH angles.

improved by about 10 kcal/mol. On the average, the MP2/6-31G* values are 23 kcal/mol higher than those at the corresponding diffuse function-augmented level, MP2/6-31+G*.

The performance of the diffuse function-augmented basis sets is much better. At the Hartree-Fock level, both 4-31+G and 6-31+G* proton affinities are quite similar. The exceptions are CH₂F⁻ and CH₂OH⁻; more negative values are found with the larger basis, which describes such electron-rich species more satisfactorily. At both MP2/4-31+G and at MP2/6-31+G*, the electron correlation corrections reduce the absolute magnitudes of the proton affinities by 10 kcal/mol on the average. Since the proton affinities at these levels are quite comparable (the largest discrepancy is 5.6 kcal/mol for CH₂F⁻) and the agreement with the experimentally known value for CH₃⁻ (after correction for zero-point energies, see above) is excellent, we believe the results to be reliable for the substituted methyl anions. For most purposes, MP2/4-31+G calculations suffice.

Relative Energies

Stabilization energies, calculated relative to CH₃⁻ by means of eq. (1), are summarized in Table II. As expected, the absolute errors are very much decreased. If we use the values at MP2/6-31+G* as definitive, we can judge the accuracy of the relative energies given at the other levels. The stabilization energies are greatly overestimated at STO-3G. The results for the electropositive substituents, BH₂, BeH, and Li, are particularly poor, due to overemphasis of *p*-orbital involvement. Except for CH₂F⁻, the 4-31G//4-31G stabilization energies are better; there is further improvement at 6-31G*//4-31G. However, the situation worsens when electron correlation corrections are added (MP2/6-31G*//4-31G). The 6-31G*//4-31G stabilizations are all too large, by about 5 kcal/mol on the average (vs. MP2/6-31+G*//4-31+G). In contrast, the diffuse orbital aug-

mented basis set results (Table II, last four columns) all show relatively little variation. These variations are largest at the extremes, LiCH₂⁻ and FCH₂⁻. The MP2/4-31+G results for the most part are not improved at MP2/6-31+G*; thus, the less time-consuming calculations should suffice for most purposes.

We conclude that the methyl group in CH₃CH₂⁻ is destabilizing, rather than stabilizing.⁴⁻⁶ This result, which contrasts with the stabilizing methyl influence in CH₃O⁻ and CH₃NH⁻,^{1,13,15} is supported by our finding that the methyl group in CH₃CH₂Li is also destabilizing (relative to CH₃Li).¹⁶ All the other substituents are less stabilizing than was formerly indicated⁴⁻⁶; the effect of NH₂ is nearly zero.¹⁷ A more detailed analysis of the effects of substituents is given below.

Geometries

Tables I and II and the above discussion pertain to anions and the corresponding neutral species calculated in their most stable geometries. As can be judged from Table III by comparing 4-31G-optimized geometries with 4-31+G-optimized geometries, the addition of the diffuse functions alters most bond lengths and angles relatively little. The most notable exception is CH₂Li⁻, indicated to prefer planar, C_{2v} symmetry at 4-31G. This has been interpreted to indicate the involvement of the vacant lithium *p* orbitals. However, at the 4-31+G levels, singlet CH₂Li prefers a pyramidal arrangement (C_s symmetry). The inversion barrier through the planar form is 1.5 kcal/mol. Nevertheless, we still believe π interactions involving lithium to be important in this species; the arguments will be developed below. Also discussed separately is the finding that triplet CH₂Li⁻ is indicated to be the ground state and to prefer a planar, C_{2v} geometry.

Inversion barriers at the anionic center are overestimated at 4-31G//4-31G; e.g., (in kcal/mol): CH₃⁻, 8.1; CH₃CH₂⁻, 7.9; and CH₂F⁻, 23.7.^{5,6}

Table IV. Total energies for CH_3X and CH_2X^- species (a.u.). relative energies of isomeric forms (kcal/mol) in parentheses.

	HF/4-31+G ^a	MP2/4-31+G ^{a,b}	HF/6-31+G ^{*a}	MP2/6-31+G ^{*a,b}
CH_4 , T_d	-40.14087	-40.24229	-40.19567	-40.33379
CH_3^- , C_{3v}	-39.45004 ^c (0.0)	-39.56471 ^c (0.0)	-39.50299 (0.0)	-39.65412 (0.0)
CH_3^- , D_{3h}	-39.44925 ^c (0.5)	-39.56240 ^c (1.4)	-39.49970 (2.1)	-39.65128 (1.8)
CH_3Li , C_{3v}	-46.96337	-47.06902	-47.01750	-47.16659
CH_2Li^- , C_{2v} (singlet)	-46.27641 (1.1)	-46.40190 (3.4)	-46.32389 (1.7)	-46.49460 (3.2)
CH_2Li^- , C_s (singlet)	-46.27822 (0.0)	-46.40734 (0.0)	-46.33255 (0.0)	-46.49975 (0.0)
CH_2Li^- , C_{2v} (triplet)	-46.35203 (-46.3)	-46.43562 (-17.7)	-46.40684 (-46.6)	-46.52836 (-18.0)
CH_3BeH , C_{3v}	-54.75767	-54.87725	-54.81799	-54.98776
CH_2BeH^- , C_{2v}	-54.11749	-54.25280	-54.17522	-54.36045
CH_3BH_2 , C_s	-65.35024	-65.49702	-65.44264	-65.64908
CH_2BH_2^- , C_{2v}	-64.74661 (0.0)	-64.91193 (0.0)	-64.83475 (0.0)	-65.06082 (0.0)
CH_2BH_2^- , C_s	-64.66109 (53.7)	-64.82178 (56.6)	-64.75329 (51.1)	-64.97487 (54.6)
CH_3CH_3 , D_{3d}	-79.11752	-79.30823	-79.22948	-79.49708
CH_3CH_2^- , C_s (staggered)	-78.41769 (0.0)	-78.62297 ^c (0.0)	-78.53057 (0.0)	-78.81266 (0.0)
CH_3CH_2^- , C_s (eclipsed)	-78.41444 ^c (2.0)	-78.61975 ^c (2.0)	-78.52617 (2.8)	-78.80878 (2.4)
CH_3CH_2^- , C_s (bisected)	-78.41328 ^c (2.8)	-78.61923 ^c (2.3)		
CH_3NH_2 , C_s	-95.07855	-95.28696	-95.21111	-95.51131
CH_2NH_2^- , C_1	-94.38474 (0.0)	-94.60840 (0.0)	-94.51611 (0.0)	-94.83251 (0.0)
CH_2NH_2^- , C_s (anti)	-94.37848 (3.9)	-94.60359 (3.0)	-94.51332 (1.8)	-94.82988 (1.7)
CH_2NH_2^- , C_s (syn)	-94.36711 (11.1)	-94.59149 (10.6)	-94.50173 (9.0)	-94.81786 (9.2)
CH_3OH , C_s	-114.87977	-115.10205	-115.03977	-115.35582
CH_2OH^- , C_s (anti)	-114.70121 (0.0)	-114.43735 (0.0)	-114.35309 (0.0)	-114.68509 (0.0)
CH_2OH^- , C_s (syn)	-114.19109 (6.4)	-114.42678 (6.6)	-114.34580 (4.6)	-114.67712 (5.0)
CH_3F , C_{3v}	-138.86957	-139.09523	-139.04248	-139.35255
CH_2F^- , C_s	-138.20522 (0.0)	-138.43888 (0.0)	-138.36472 (0.0)	-138.68718 (0.0)
CH_2F^- , C_{2v}	-138.18042 (15.6)	-138.41719 (13.6)	-138.33731 (17.2)	-138.66524 (13.8)

^a All calculations used the 4-31+G optimized geometries.^b Core orbitals not included.^c Reference 1.

Much smaller values are obtained when diffuse functions are added to the basis (Table IV), e.g., at 4-31+G//4-31+G: CH_3^- , 0.5; CH_3CH_2^- , 2.7; and CH_2F^- , 15.6 kcal/mol. Hence, the pyramidalization at the carbanion site (given by the XCH_3 angles in Table III) tends to be smaller at 4-31+G than at 4-31G. The situation with singlet CH_2Li^- is exceptional in this regard.

All bond lengths to hydrogen in the anions are shortened, often significantly, in going from 4-31G//4-31G to 4-31+G//4-31+G. Similarly, the bonds between the anionic carbon and the more electronegative elements (C, N, and O; F is an exception) are shortened, but the C—B, C—Be, and C—Li bonds lengthen when diffuse functions are employed. Basis sets without flat functions do not describe the anion lone pair adequately and overestimate the involvement of antibonding or nonbonding orbitals of the substituents. The exaggerated stabilization at 4-31G by π acceptors (Li, BeH, and BH_2) results in bonds to carbon which are too short. Similarly, the excessive involvement of antibonding orbitals at 4-31G in the other cases results in lengthening of the C—H and

C—X bonds. This is shown clearly by CH_3^- . The 4-31G C—H bond lengths (1.081 Å) are normal when a planar geometry is taken and the lone pair is in a pure p orbital. In the 4-31G pyramidal structure the C—H bonds (1.119 Å) are much too long. This overestimation of the σ_{CH} contribution leads to the overlarge CH_3^- inversion barrier at 4-31G. In contrast, the 4-31+G C—H bond lengths change much less in going from planar (1.075 Å) to pyramidal (1.085 Å) geometries.

As expected from the modest energy lowerings (Table V), the geometries of the neutral molecules are influenced very little by the addition of diffuse functions. The C—F, C—O, and C—Li bonds are exceptions; all are lengthened at 4-31+G. The 4-31G values for CH_3F and CH_3OH are actually in better agreement with experiment,⁶ but it is probable that neither basis set is describing such electron-rich systems adequately.

Comparisons of the 4-31+G geometries of the anions, XCH_2^- , with those of the substituted methanes, XCH_3 (Table III), are revealing. Except when the anions are constrained to planarity, the C—H and X—H bond lengths tend to be longer

Table V. Energy lowerings due to inclusion of diffuse functions (kcal/mol).

Species	4-31+G ^b	6-31+G ^{*b}	MP2/6-31+G ^{*b}
	vs 4-31G ^c	vs 6-31G ^{*c}	vs MP2/6-31G ^{*c}
CH ₄	0.69	0.33	0.92
CH ₃ Li	2.11	1.32	2.89
CH ₃ BeH	1.87	1.25	2.22
CH ₃ BH ₂	1.13	0.72	1.84
CH ₃ CH ₃	1.00	0.47	1.72
CH ₃ NH ₂	4.32	2.63	5.67
CH ₃ OH	5.18	3.48	7.14
CH ₃ F	6.88	5.90	10.9
CH ₃ ⁻	30.3	22.9	32.5
CH ₂ Li ^{-d}	16.7	13.4	13.5
CH ₂ BeH ⁻	22.9	17.1	19.7
CH ₂ BH ₂ ⁻	17.9	15.1	18.9
CH ₂ CH ₃ ⁻	22.9	17.8	27.0
CH ₂ NH ₂ ⁻	26.9	20.5	32.2
CH ₂ OH ⁻	26.8	21.9	33.4
CH ₂ F ⁻	28.6	23.2	35.4

^a Most stable geometries unless indicated.^b 4-31+G geometries.^c 4-31G geometries.^d Planar C_{2v} singlet.

than in the neutral counterparts. The effect in going from CH₃F (CH = 1.076 Å) to CH₂F⁻ (CH = 1.099 Å) is particularly large. The pyramidal anions are stabilized by interaction of the lone pair with σ_{CH}^* orbitals; in planar CH₃⁻ and CH₂F⁻ this interaction is precluded by symmetry and the C—H bonds are actually shorter than in the neutral reference molecules, CH₄ and CH₃F.

Interactions of the anion lone pair electrons with β X—H bonds are also important. In the various HOCH₂⁻, H₂NCH₂⁻, CH₃CH₂⁻, and perpendicular H₂BCH₂⁻ structures, all X—H bonds which have an *anticoplanar* relationship with the anion lone-pair orbital are lengthened most. This effect is ascribed to negative hyperconjugation,¹⁸ which, contrary to a recent criticism,¹⁹ can be of considerable importance.

Heavy atom bond lengthenings in the anions are more dramatic, e.g., *d* (C—F) = 1.427 Å in CH₃F and 1.577 Å in CH₂F⁻, a change of 0.15 Å. The effect diminishes with OH (Δ = 0.10 Å) and NH₂ (Δ = 0.04 Å) substituents, and nearly vanishes with CH₃ (Δ = 0.01 Å). While the lone-pair repulsions contribute to this effect, involvement of the σ_{CX}^* orbitals appear to be the main factor responsible. Thus, the C—F bond length in planar H₂CF⁻ (where the π repulsive effect is at a maximum) is actually *shorter* than in the pyramidal form

(where involvement of the σ_{CF}^* orbitals is possible).

Due to conjugation, the π -acceptor groups have *shorter* CX bonds in the anions: Δ = -0.11 Å for planar BH₂, -0.096 Å for BeH, and -0.03 Å for Li [singlet (C_s)CH₂Li⁻]. Perpendicular CH₂BH₂⁻ also exhibits C—B shortening (Δ = -0.03 Å) due to negative hyperconjugation. Triplet CH₂Li⁻, with only one π electron, has a longer C—Li bond (2.008 Å) than in CH₃Li (1.999 Å) or in the singlet CH₂Li⁻ forms.

SUBSTITUENT STABILIZATION ENERGIES

Methyl stabilization energies for the CH₂X⁻ anions, derived from eq. (1), are shown in Table II. The convergence of the results for the two diffuse orbital augmented basis sets is particularly gratifying. The largest change is observed for CH₂Li⁻, for which the MP2/6-31G* stabilization energy (-25.8 kcal/mol) decreases by a factor of 3 on addition of diffuse orbitals (-8.1 kcal/mol at MP2/6-31+G*). The stabilizations due to electropositive π -acceptor substituents are generally smaller with diffuse functions than without, again reflecting the poor description of the anion HOMO by normal split-valence basis sets. The electron-rich

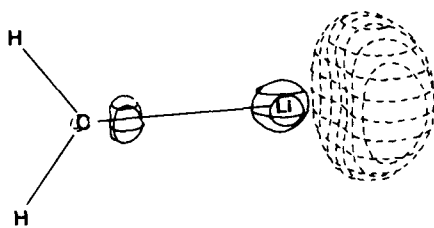


Figure 2. The higher energy of the two singly occupied molecular orbitals of triplet CH_2Li^- .

substituents show smaller, but significant, effects on addition of diffuse functions. The diffuse basis sets, for instance, are necessary in order to establish the destabilization by the methyl group in the ethyl anion, rather than the stabilization predicted by the 4-31G and 6-31G* basis set results.⁴⁻⁶ The substituents OH and F are considerably less stabilizing at 6-31+G* than at 4-31+G, even though the 6-31G* and 4-31G results were similar. For these electronegative substituents, both diffuse functions and polarization functions appear to be important.

The MP2/6-31+G* stabilization energies from Table II are plotted against the substituent central atom electronegativities²⁰ in Figure 1. Electronegativity plots of this type are useful in the interpretation of substituent effects since overall trends due to σ and π effects are brought out.²¹ The correlation lines in Figure 1 differentiate the effects of two types of substituents, the π donor/ σ acceptors, NH_2 , OH, and F, and the σ donor/ π acceptors, BH_2 , BeH, and Li. The deviation of the last three points from the σ -effect-dominated line describing the other substituents indicates the degree of extra π stabilization. This interpretation is supported by data for the strongest π acceptor, BH_2 , which can be rotated to "turn off" the π effect; points for the C_{2v} (planar) and C_s geometries are shown in Figure 1. The stabilization energy for perpendicular (C_s) CH_2BH_2^- lies a little below the "sigma-only" line, indicating some extra stabilization *via* donation to the $\pi_{\text{BH}_2}^*$ orbital (the "negative hyperconjugation" discussed earlier). Note also that the $-\text{CH}_2$ moiety in C_s CH_2BH_2^- is pyramidal whereas the most stable form, with strong π conjugation, has C_{2v} symmetry (i.e., the $-\text{CH}_2$ group is planar). Although the effect of π conjugation decreases in the order $\text{BH}_2 > \text{BeH} > \text{Li}$, there is still a relatively large (19 kcal/mol) extra stabilization in CH_2Li^- (singlet). On the basis of its electronegativity, Li should destabilize carbanions (see Fig. 1). Thus, when coupled with an extremely powerful π donor such as $-\text{CH}_2^-$, lithium can act as a π acceptor, the stabilization being

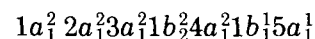
about one-third as effective as for $-\text{BH}_2$. The only destabilizing substituent (relative to H) is $-\text{CH}_3$ in which the small amount of sigma stabilization expected from Figure 1 is outweighed by repulsion between the anion lone pair and the methyl π_{CH_3} orbitals. Lone-pair repulsion effects are partly responsible for the preferred conformations of CH_2NH_2^- , in which the lone pairs are nearly orthogonal, and of CH_2OH^- . We will analyze these affects quantitatively in an additional publication which will compare first-row with second-row substituents.

CH_2Li^-

Singlet CH_2Li^- was found to be planar at 4-31G,⁴⁻⁶ but prefers a pyramidal structure by 3.2 kcal/mol (MP2/6-31+G*//4-31+G) when diffuse orbitals are included. The reason for this discrepancy is the overestimation of π stabilization due to Li by normal, split-valence, basis sets, which therefore results in a planar geometry.

Interestingly, UHF/4-31+G optimization of triplet CH_2Li^- leads to a planar structure which is 18 kcal/mol more stable than in the C_s singlet (MP2/6-31+G*//4-31+G). However, the triplet energies are still favored artificially at this level.²² Allowing for the usual UHF/RHF difference,²² singlet and triplet CH_2Li^- probably lie close in energy. Other lithium species, e.g., CH_2Li_2 ,²³ $\text{CH}_2=\text{CLi}_2$,²⁴ and CLi_3^+ ,²⁵ may also have triplet ground states.

The electronic configuration of triplet CH_2Li^- is



This means that there is only one π ($1b_1$) electron; the HOMO is a singly occupied lithium lone-pair σ orbital ($5a_1^1$, Fig. 2). The other orbitals are very similar in appearance to those for CH_2 .²⁶ The triplet can formally be regarded as an interaction between CH_2^- and an Li atom.

Even at UHF/4-31+G, no tendency for a singly occupied MO to become excessively diffuse was noted. This is an indirect suggestion that the anion is bound.²⁷ The question of electron affinities and the limitations of calculations at the levels employed here will be dealt with at length in a future publication.

CONCLUSIONS

Diffuse functions should be added to basis sets used for SCF calculations on anions. There appears

to be a good convergence of results for different diffuse augmented basis sets provided they are at least of split-valence quality.

All substituents except CH_3 (and probably NH_2) stabilize methyl anions. Li, BeH, and especially BH_2 show large π stabilizations; σ stabilization of OH and F is smaller.

"Negative hyperconjugation" (interaction of the anion lone-pair orbital with σ_{XH}^* orbitals of the substituent^{18,19}) is supported by geometry-specific bond lengthenings and the extra stabilization of perpendicular CH_2BH_2^- .

Singlet CH_2Li^- is slightly nonplanar but the C_{2v} triplet may have comparable or even greater stability.

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References

1. J. Chandrasekhar, J. G. Andrade, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5609 (1981).
2. L. Radom, in *Modern Theoretical Chemistry. Volume 4. Application of Electronic Structure Theory*, H. F. Schaefer III, Ed., Plenum, New York, 1977, Chap. 8, p. 333.
3. P. Cársky and M. Urban, *Lecture Notes in Chemistry. 16. Ab Initio Calculations. Methods and Applications in Chemistry*, Springer-Verlag, Heidelberg, 1980, p. 50.
4. T. Clark, H. Körner, and P. v. R. Schleyer, *Tetrahedron Lett.*, **21**, 743 (1980).
5. A. C. Hopkinson and M. H. Lien, *Int. J. Quantum Chem.*, **18**, 1371 (1980).
6. A. Pross, D. J. DeFrees, B. A. Levi, S. K. Pollack, L. Radom, and W. J. Hehre, *J. Org. Chem.*, **46**, 1693 (1981).
7. J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, *QCPE*, **11**, 368 (1978).
8. Diffuse orbital exponents were obtained with the 6-31G basis set by optimization of F^- , OH^- , NH_2^- , CH_3^- , BH_2^- , BeH^- , and Li^- ; J. Chandrasekhar, to be published.
9. W. C. Davidon, *Comput. J.*, **10**, 406 (1968); R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963).
10. H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, **63**, 3632 (1975).
11. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
12. J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem.*, **S9**, 229 (1976); J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, **S10**, 1 (1976); R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, **14**, 91 (1978).
13. J. E. Bartmess and R. T. McIver, Jr., in *Gas Phase Ion Chemistry*, M. T. Bowers, Ed., Academic, New York, 1979, Vol. 2, Chap. 11, p. 87.
14. H. Kollmar, *J. Am. Chem. Soc.*, **100**, 2665 (1978).
15. A. Pross and L. Radom, *J. Am. Chem. Soc.*, **100**, 6572 (1978); A. L. Hinde, A. Pross, and L. Radom, *J. Comput. Chem.*, **1**, 118 (1980).
16. P. v. R. Schleyer, J. Chandrasekhar, A. J. Kos, T. Clark, and G. W. Spitznagel, *J. Chem. Soc. Chem. Commun.*, 882 (1981).
17. Cf. T. Clark, P. v. R. Schleyer, K. N. Houk, and N. G. Rondan, *J. Chem. Soc. Chem. Commun.*, 579 (1981).
18. Y. Apeloig, *J. Chem. Soc. Chem. Commun.*, 396 (1981); J. G. Stamper and R. Taylor, *J. Chem. Res.*, S128, M1930 (1980), and references cited therein.
19. A. Streitwieser, Jr., C. M. Berke, G. W. Shriver, D. Grier, and J. B. Collins, *Tetrahedron*, **37** (Suppl. 1), 345 (1981).
20. A. L. Allred and E. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
21. A. Kos, T. Clark, J. A. Pople, and P. v. R. Schleyer, to be published.
22. See, e.g., J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1977), and ref. 12.
23. 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); W. D. Laidig and H. F. Schaefer III, *J. Am. Chem. Soc.*, **100**, 5972 (1978).
24. Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 4332 (1976); W. D. Laidig and H. F. Schaefer III, *J. Am. Chem. Soc.*, 7184 (1979).
25. J. Chandrasekhar, J. A. Pople, R. Seeger, U. Seeger, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, to appear.
26. W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic, New York, 1973, pp. 62-63. Professor Jorgensen's program was used to draw Fig. 2.
27. Cf. U. Lamanna and M. Maestro, *Theor. Chim. Acta (Berlin)*, **36**, 103 (1974).