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Stereoelectronic Properties, Stereospecificity, and Stabilization of α-Oxa and α-Thia Carbanions[1]

Jean-Marie Lehn* and Georges Wipff

Contribution from the Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France.[2]

Received February 2, 1976

Abstract: An ab initio study of the species **1–7** shows that carbanion stabilization by α-heteroatoms is subject to appreciable stereoelectronic effects. The following results are obtained: (a) stabilization of a carbanion by an adjacent sulfur atom is not due to (d–p)π bonding; (b) stabilization of $^{-}CH_2XZ$ increases in the series XZ = CH_2CH_3 < OH < OCH_3 < SH < SCH_3; (c) polarization of the electron distribution by the carbanionic charge is an important factor and stabilizes $^{-}CH_2SCH_3$ more than $^{-}CH_2CH_2CH_3$; (d) equatorial type carbanions (forms **e**) are much more stable than axial type carbanions (forms **a**) and this may explain stereochemical results in the carbanions derived from 1,3-dithiane systems; (e) these stereoelectronic effects may be interpeted in terms of a destabilizing (C^- lone pair, heteroatom lone pair) interaction in axial C^- and a stabilizing (C^- lone pair, antibonding σ* (X–Z) orbital) interaction in the equatorial C^- arrangement of a $^{-}CH_2XZ$ species; (f) the changes in bond lengths, orbital energies, and electronic distribution agree with this picture (for instance, in ^{-}CXC the length and overlap population of a X–C bond (X = O, S) respectively increase and decrease in the **e** forms (where X–C is antiperiplanar to the C^- lone pair) with respect to the **a** forms); (g) similar effects are present in the organolithium derivatives **3-Li–7-Li**.

Carbanions play an important role in chemical synthesis as well as in physical organic chemistry.[3] Control of stereochemistry in the formation of bonds to carbon and the rationalization of structural effects on carbanion properties represent two facets, synthetic on one hand and physicochemical on the other, of carbanion chemistry. A key position is occupied by carbanions $X–C^-$ formed in an α position to a heteroatom X. The present paper reports a theoretical study of the strong *stereoelectronic orientational effects* present in such carbanions, which should play a major role in the stereochemistry of carbanionic reactions.[3] Second row elements, in particular sulfur, are known to markedly increase the acidity of geminal C–H bonds[3] (see also extensive references in ref 4). To cite but two relatively recent discoveries, the Corey-Seebach synthesis of aldehydes via metalation of *m*-dithiane[5] and the so-called "contrathermodynamic" isomerization of bulky substituents from equatorial to axial position via metalation of *m*-dithiane substituted at C(2)[6] represent fascinating aspects of stabilization and stereospecificity in carbanion processes.

The fact that Me_3S^+,[8] $CH_2(2)$ in *m*-dithiane, and $HC(CH_2S)_3CH$[9] display a much higher C–H acidity than their oxygen counterparts, together with many other results, has been taken as evidence for specific (d–p)π stabilization of carbanions by the d orbitals[10] available on sulfur. Our earlier work on NH_2SiH_3 had demonstrated that the origin of the very low nitrogen inversion barrier cannot be ascribed to stronger N–Si (d–p)π conjugation in the planar vs. the pyramidal form,[12] but is due to an effect of an inductive type.[13] As in PH_3,[14] the d functions participate in bonding mainly as polarization functions,[11,15] increasing the flexibility of the basis set of atomic functions. This led us to the idea that similarly (d–p)π conjugation may well have nothing to do with stabilization of carbanions by second row elements. d functions have no effect on the conformational and bonding properties of CH_2^-–SH[16] and the irrelevance of d-orbital conjugation in both conformational properties and proton affinity of CH_2^-–SH is extnsively demonstrated in recent work by two groups.[4,18,19]

Our own interest in α-thia carbanions came, however, not only from the earlier work on NH_2–SiH_3 and its extension to $^-CH_2$–X (X = second row atom), but also from the realization that strong stereoelectronic effects could be operative in carbanions linked to heteroatoms bearing electronic lone pairs. Indeed pronounced stereospecific effects are found in species containing two or more geminal heteroatoms, like the tetrahedral intermediates occurring in ester and amide hydrolysis. On the basis of experimental kinetic results it was proposed that in a tetrahedral intermediate the bond cleaved preferentially was in antiperiplanar (app) arrangement with respect to two electronic lone pairs on geminal heteroatoms.[20,21] Our theoretical investigations of tetrahedral species CHXYZ (X, Y, Z = N, O) showed that marked stereoelectronic effects were operative and led to the conclusion that stereospecific C–X bond weakening and lengthening is strongest in the arrangement where: (1) a maximum number of lone pairs (lp's) is app to C–X; (2) the X lp is *not* app to another polar bond; (3) the species CHXYZ should take up a given overall conformation.[22-24] These two first effects may be represented by a perturbative [lp, σ^*(C–X)] interaction picture similar to that found in the so-called anomeric effect.[25-27]

Since the C–Li bond in organolithium compounds has the opposite polarity with respect to a C–X (X = O, N) bond, and since carbanions C^- may be considered as the extreme limit of "bond" polarity in the direction opposite to that in C–X, stereoelectronic effects in carbanions bearing α-heteroatoms are expected to be very pronounced, but so to say "reversed"[26] with respect to the tetrahedral species studied earlier. The wide implications with respect to both stereochemistry control and bonding theory led us to study a number of carbanions and organolithium compounds with two main goals in mind: (1) show the existence of stereoelectronic effects and clarify their role in carbanion stereochemistry and proton affinities; (2) investigate whether d-orbital participation in bonding plays a role not only in carbanion stabilization and proton affinities, but also in the stereoelectronic effects themselves.

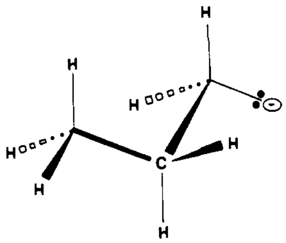
Computations were performed on a large number of systems (carbanions and their corresponding lithiated and protonated derivatives) in various conformations. Altogether 33 species have been investigated, several with different basis sets and with some limited geometry optimization.

We refrain from describing in detail all these results.[28] Rotation and inversion barriers were not our main interest here and have been thoroughly analyzed for $^-CH_2SH$ and $^-CH_2OH$ by Wolfe et al.[4] Furthermore the relevance of d-orbital conjugation has also been demonstrated.[4,18,19] For these reasons we shall limit our report to the results which we feel most interesting with respect to the points mentioned above: *stereoelectronic effects* and *stabilization effects*, with extension of the (d–p)π question to $^-CH_2SCH_3$. Our investigations can be divided into three categories of substances: (1) $^-CH_2XCH_3$ (X = CH_2, O, S; **1**, **2**, **3**, respectively), (2) $^-CH_2XH$ (**4**, **5**) and $^-CH(XH)_2$ (**6**, **7**; X = O, S), and (3) $LiCH_2SCH_3$ (3), $LiCH_2XH$ and $LiCH(XH)_2$ (X = O, S; species corresponding to **4**–**7**), which are, respectively, substrates for stereoelectronic and d-orbital effects (1), multiple substituent effects (2), and properties of organolithium compounds along the same lines (3).

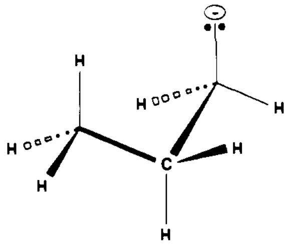
Results

Computations have been performed on the carbanions **1**–**7** as well as on the corresponding protonated (**1-H**–**7-H**) and lithiated (**3-Li**–**7-Li**) derivatives. Two types of conformations have been studied for each species, the "equatorial" type (**1e**–**7e**) and "axial" type (**1a**–**7a**), corresponding, respectively, to equatorial and axial orientation of Y = –, H, Li if the fragments **1**–**7** were included in a cyclohexane ring in the conformation shown. The conformation of species **6** and **7**, intermediate between **e** and **a** (one X–H oriented as in **e** and the other one as in **a**), was also studied; the results will not be discussed, since the properties of these conformations **6ea** and **7ea** are intermediate between **6e** and **7e** and **6a** and **7a**.[28]

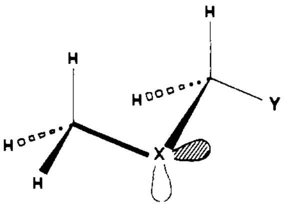
The computations have been performed either with the



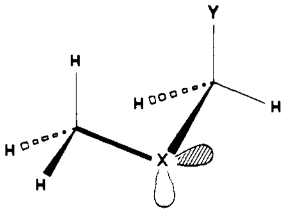
1e



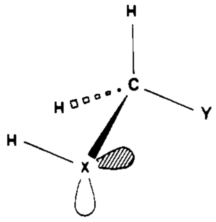
1a



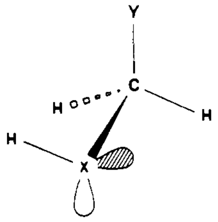
2e, X = O; Y = –
2-H, X = O; Y = H
3e, X = S; Y = –
3-H, X = S; Y = H
3e-Li, X = S; Y = Li



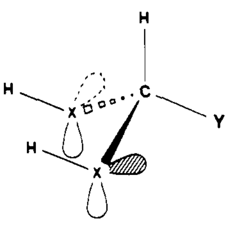
2a, X = O; Y = –
3a, X = S; Y = –
3a-Li, X = S; Y = Li



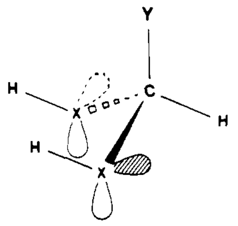
4e, X = O; Y = –
4-H, X = O; Y = H
4e-Li, X = O; Y = Li
5e, X = S; Y = –
5-H, X = S; Y = H
5e-Li, X = S; Y = Li



4a, X = O; Y = –
4a-Li, X = O; Y = Li
5a, X = S; Y = –
5a-Li, X = S; Y = Li



6e, X = O; Y = –
6-H, X = O; Y = H
6e-Li, X = O; Y = Li
7e, X = S; Y = –
7-H, X = S; Y = H
7e-Li, X = S; Y = Li



6a, X = O, Y = –
6a-Li, X = O; Y = Li
7a, X = S; Y = –
7a-Li, X = S; Y = Li

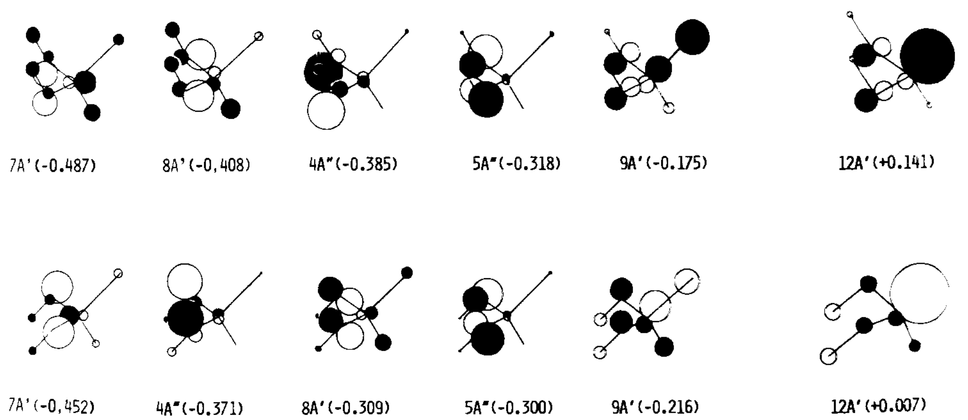


Figure 1. The five highest occupied MO's of **6a-Li** (top left), **6e-Li** (bottom left), and the HOMO of **7a** (top right) and **7e** (bottom right).

program IBMOL[29] (compounds **1** and **3**) or with the program STO-3G[30] (Ssp, compounds **1-7**). In the IBMOL computations a double basis sp set of contracted Gaussian functions was employed (Isp);[32] this set was also enlarged by adding one set of d-type functions (Ispd) on the central C atom of **1** (exponent 0.8) and on the S atom of **3** (exponent 0.6).[34] The Ispd set was used for testing the effect of d-type functions; the unbalanced description due to the inclusion of polarization functions on only one atom in **1** and **3** is not felt to be detrimental to the goal pursued. The negligible participation of these d functions in the stereoelectronic properties of **3** justifies the use of only an sp basis set for the calculations on **5** and **7**. Unless otherwise stated the following bond lengths have been used (based on previous experience with tetrahedral intermediates and partial optimization): C-C, 1.52; C-O, 1.44; C-S, 1.819; O-H, 0.97; S-H, 1.336; C-H, 1.091 in **1-4**, 1.1 in **5-7**; C-Li, 2.0 Å. All bond angles are taken as tetrahedral including the carbanion center.[36] A form of **3** with planar C^- center (which would geometrically correspond to planar C^- in the carbanion at C(2) of *m*-dithiane) was also computed. The C-S-Z (Z = H, CH_3) angles are very different from tetrahedral. Their optimized values are given in footnote *c* of Table I. The calculated values of the C-S-Z angles in CH_3SH (94.8°) and CH_3SCH_3 (97.3°) are in good agreement with the corresponding experimental values (96.5 and 98.9°, respectively).[35] The optimal values of the C-O-Z angles are found to be close to the tetrahedral value, which has therefore been used throughout. A few geometry optimizations (S-CH_3 bond lengths in **3e**, **3e-Li**, **3a**, and **3a-Li** and C-Li bond lengths in **e** and **a** forms of all lithiated species) were performed in order to confirm the conclusions drawn from analysis of the electronic structure, especially the correspondence between a decrease of bond overlap population[38] and an increase in bond length.[22,23] The effects which will be discussed are large enough that more complete geometry optimization would not alter them significantly.

The computational results which are most directly relevant to the issues discussed here are listed in Tables I-III and illustrated in Figure 1.[28]

Discussion

Electronic Lone Pairs. At the outset a few words on electronic "lone pairs" (lp's) are necessary. Depending on the issue, such lone pairs seem to display directional character or do not. "Size" and "directionality" of lone pairs may be defined quantum chemically.[40] Comparing the data available, it appears that when total energies are discussed (for instance, energies of rotamers in studies of rotation around bonds[40,41]) the lone pairs behave nondirectionally, whereas when electronic

Table I. Energetic Results

Species	Method	Total energy, au (Relative energy, kcal/mol)[a]	HOMO energy, au	Proton affinity, kcal/mol[b]
1-H	Ispd	-118.0810	-0.469	
	Isp	-118.0459	-0.469	
	Ssp	-116.8841	-0.430	
1e	Ispd	-117.3527	0.022	457
	Isp	-117.3171	0.022	458
	Ssp	-115.9969	0.172	557
1a	Ispd	(0.7)	0.021	457
	Isp	(0.3)	0.021	457
	Ssp	(0.1)	0.171	557
2-H	Ssp	-152.1322	-0.336	
2e	Ssp	-151.2698	0.152	542
2a	Ssp	(5.7)	0.177	547
3-H[c]	Ispd	-475.9866	-0.334	
	Isp	-475.8934	-0.346	
	Ssp	-471.4811	-0.244	
3e[c]	Ispd	-475.3047	-0.034	428
	Isp	-475.2120	-0.036	428
	Ssp	-470.6297	0.121	535
3a[c]	Ispd	(9.0)	0.003	437
	Isp	(8.3)	-0.002	436
	Ssp	(8.1)	0.158	543
4-H	Ssp	-113.5460	-0.353	
4e	Ssp	-112.6759	0.166	546
4a	Ssp	(5.5)	0.192	552
5-H[c]	Ssp	-432.8947	-0.259	
5e[c]	Ssp	-432.0390	0.129	537
5a[c]	Ssp	(6.3)	0.165	544
6-H	Ssp	-187.3791	-0.357	
6e	Ssp	-186.5417	0.139	526
6a	Ssp	(12.3)	0.188	538
7-H[c]	Ssp	-826.0620	-0.249	
7e[c]	Ssp	-825.2433	0.008	514
7a[c]	Ssp	(9.4)	0.142	524
3e-Li	Ssp	-478.1808	-0.201	
3a-Li[c]	Ssp	(2.6)	-0.167	
4e-Li	Ssp	-120.2395	-0.217	
4a-Li	Ssp	(1.4)	-0.190	
5e-Li[c]	Ssp	-439.5934	-0.212	
5a-Li[c]	Ssp	(1.6)	-0.170	
6e-Li	Ssp	-194.0802	-0.216	
6a-Li	Ssp	(4.7)	-0.175	
7e-Li[c]	Ssp	-832.7687	-0.203	
7a-Li[c]	Ssp	(3.4)	-0.155	

[a] Total energies of the species of the type e. The values in parentheses are the relative energies of the species of type a with respect to the corresponding, more stable species of type e. [b] Energy differences between the species listed in the first column and the corresponding protonated derivative computed by the same method. [c] Optimized C-S-Z angles (Z = H or CH_3): 97.3° (3-H); 105.6° (3e); 98.4° (3a); 94.8° (5-H); 104.8° (5e); 96.9° (5a); 94.7° (7-H); 102.7° (7e); 96.0° (7a); 97.8° (3e-Li); 99.4° (3a-Li); 97.1° (5e-Li); 96.8° (5a-Li); 96.9° (7e-Li); 96.1° (7a-Li).

Table II. Population Analysis on Carbanions and Related Protonated Species YCH_2XZ and $YCH(-XZ)_2$ (Y = – or H; X = CH_2, O, or S; Z = H or CH_3)[a, b]

Species		1e	1a	1-H	2e	2a	2-H	3e	3a	3-H	4e	4a	4-H	5e	5a	5-H	6e	6a	6-H	7e	7a	7-H
Overlap Populations (total (first line), in HOMO (second line))																						
$^-$C–X		0.359	0.355	0.364	0.251	0.238	0.262	0.263	0.244	0.259	0.256	0.244	0.266	0.262	0.244	0.262	0.253	0.237	0.265	0.261	0.239	0.259
		-0.026	-0.025	0.092	-0.047	-0.084	-0.029	-0.029	-0.087	-0.018	0.052	0.087	-0.044	-0.033	-0.088	-0.023	-0.047	-0.081	-0.024	0.030	-0.077	-0.001
	d	0.697	0.645	0.578				0.634	0.447	0.526												
	d	0.024	-0.052	0.145				0.003	-0.365	-0.089												
X–Z		0.349	0.361	0.364	0.237	0.258	0.262	0.215	0.243	0.259	0.220	0.239	0.258	0.221	0.249	0.269	0.218	0.240	0.257	0.230	0.253	0.269
		-0.006	0.003	0.092	-0.018	0.005	-0.029	-0.030	-0.002	-0.018	-0.021	0.000	0.000	-0.031	-0.003	0.000	-0.024	0.001	-0.001	-0.026	-0.002	0.000
	d	0.537	0.598	0.578				0.260	0.480	0.526												
	d	-0.034	0.005	0.145				-0.220	-0.026	-0.089												
Atomic Population (total (first line), in HOMO (second line), in YCH_2 group (third line))																						
$^-$C^c		6.434	6.436	6.173	6.350	6.364	6.067	6.473	6.487	6.265	6.352	6.367	6.061	6.470	6.482	6.255	6.185	6.218	5.881	6.443	6.453	6.269
		1.842	1.853	0.498	1.800	1.678	0.045	1.812	1.573	0.013	1.799	1.665	0.093	1.832	1.585	0.020	1.674	1.494	0.117	1.736	1.366	0.036
		8.714	8.719	9.005	8.626	8.639	8.880	8.701	8.724	9.075	8.658	8.666	8.883	8.714	8.731	8.126	7.330	7.338	7.749	7.535	7.542	8.132
	d	6.652	6.660	6.568				6.777	6.799	6.723												
	d	1.817	1.823	0.508				1.754	1.494	0.023												
	d	8.666	8.683	8.980				8.667	8.701	9.025												
X		8.148	8.170	7.988	8.307	8.326	8.240	16.051	16.067	15.849	8.386	8.404	8.302	16.121	16.135	15.890	8.383	8.407	8.307	16.088	16.110	15.887
		0.038	0.115	0.553	0.047	0.243	1.543	0.038	0.374	2.536	0.059	0.267	1.648	0.039	0.362	1.900	0.055	0.232	0.791	0.038	0.302	0.979
	d	8.183	8.201	8.040				16.110	16.140	15.947												
	d	0.053	0.124	0.523				0.075	0.428	1.774												
Z		9.138	9.111	9.005	9.067	9.034	8.880	9.247	9.209	9.075	0.955	0.929	0.816	1.165	1.133	1.044	0.950	0.924	0.819	1.144	1.118	1.046
		0.082	0.013	0.718	0.101	0.021	0.229	0.114	0.022	0.083	0.081	0.007	0.000	0.089	0.011	0.000	0.079	0.005	0.005	0.081	0.011	0.001
	d	9.149	9.115	8.980				9.222	9.159	9.025												
	d	0.108	0.027	0.737				0.149	0.048	0.114												

[a] If not specified, Ssp basis set. [b] X = CH_2 in 1, X = O in 2, 4, 6, X = S in 3, 5, 7; Z = CH_3 in 1, 2, 3; Z = H in 4, 5, 6, 7. [c] Total charge on C of the anionic site (first line); in the HOMO (second line); total charge on YCH_2 group of 1–5 or YCH group of 6, 7 (third line). [d] lspd basis set.

Table III. Populations Analysis on Lithiated Compounds[a] (Ssp basis set)

Species	3e-Li	3a-Li	4e-Li	4a-Li	5e-Li	5a-Li	6e-Li	6a-Li	7e-Li	7a-Li
Overlap Population (total (first line), in HOMO (second line))										
C–Li	0.295	0.298	0.289	0.289	0.297	0.303	0.281	0.284	0.292	0.308
	-0.001	0.110	0.231	0.187	-0.001	0.125	0.213	0.178	-0.001	0.133
C–H	0.381	0.382	0.378	0.387	0.379	0.380	0.364	0.383	0.372	0.377
	0.011	0.017	0.018	0.012	0.014	0.018	0.032	0.018	0.000	0.006
C–X	0.268	0.260	0.267	0.261	0.269	0.258	0.264	0.261	0.266	0.253
	-0.020	-0.064	-0.051	-0.070	-0.024	-0.068	-0.041	-0.046	0.001	-0.041
X–Z	0.247	0.260	0.245	0.260	0.255	0.268	0.242	0.260	0.255	0.268
	-0.016	-0.003	-0.015	0.003	0.000	0.001	-0.015	0.000	0.000	0.002
Atomic Population (total (first line), in HOMO (second line))										
Li	2.809	2.844	2.784	2.848	2.805	2.842	2.722	2.853	2.764	2.821
	0.001	0.346	0.231	0.602	0.000	0.362	0.463	0.601	0.003	0.320
(Li)CH_n^{b}	6.250	6.250	6.074	6.067	6.243	6.243	5.910	5.891	6.257	6.258
	0.018	0.446	1.000	0.751	0.025	0.532	0.890	0.612	0.040	0.555
	8.194	8.182	8.046	8.006	8.189	8.179	6.913	6.842	7.229	7.216
X	15.885	15.875	8.317	8.311	15.935	15.919	8.324	8.316	15.934	15.918
	1.820	1.124	0.585	0.591	1.875	1.054	0.176	0.375	0.978	0.555
Z	9.112	9.097	0.853	0.835	1.070	1.060	0.858	0.836	1.069	1.064
	0.077	0.039	0.102	0.004	0.000	0.006	0.081	0.002	0.001	0.006

[a] X = O or S; Z = CH_3 in 3; Z = H in 4, 5, 6, 7. [b] Total charges on C of CLi group (first line), in the HOMO (second line). Third line: total charge on CH_2 group of 3, 4, 5 or CH group of 6, 7.

structures, MO composition, and interactions are considered, lone pairs show more directional properties, inasmuch as the composition and mixing of the MO's depend on orientation (see below). One may in general recognize more or less well a σ- and a π-type lone pair MO on heteroatoms like O and S (see, for instance, ref 26, 39, and references cited therein); such is also the case in the compounds studied here even when two O or S atoms are present, but more or less strong mixing may occur.

Considering that a lone pair type MO can be analyzed in terms of either canonical or localized lone-pair orbitals, we shall treat the lp's as localized and having directional character. The perturbative interactions between orbitals are easily pictured in such a scheme.

Finally, bonding properties and reactivity, which may be rationalized inter alia in terms of the structure of the highest MO's, should show the orientational dependence found for the MO's, which in the present cases arises primarily from lp-lp and lp-bond orbital mixing.

The results obtained previously on the orientational dependence of bond length and bond strength in $CH(OH)_2NH_2$[23] justify a posteriori the description of these phenomena as orientation-dependent perturbative interactions between more or less directional lp and bond MO's. A few general comments which clearly show the orientational effects on lp MO's can be made here.

(i) In all species studied, analysis of the individual MO's shows that there are as many lp-type MO's (highly localized on the heteroatom O or S) as there are classical lp's.

(ii) Per heteroatom, one finds a π-type and σ-type lp MO; when two heteroatoms are present like in **6** and **7** there are four lp MO's: the symmetric (s) and antisymmetric (a) combinations of π type and σ type, as seen for $LiCH(OH)_2$ (**6e-Li:** 5A″, π_a; 8A′, π_s; 4A″, σ_a; 7A′, σ_s) (Figure 1) and $^-C(SH)_2$ (**7e:** 9A″, π_a; 11A′, π_s; 8A″, σ_a; 10A′,σ_s); the π-type lp MO's lie usually above those of σ type.

(iii) In the conformations of type **e**, where there is no heteroatom lp app to C^- or C-Li, the lp MO's are quite "pure", whereas strong mixing with the carbanion lp MO and the C-Li bond MO occurs in the **a** forms; in species **6a** and **7a** and **6a-Li** and **7a-Li** the mixing occurs, of course, only with the symmetric σ- and (especially) π-lp combinations, leading even to inversions in the MO sequences; thus, whereas in **6e-Li** (Figure 1) the lp sequence is π_a, π_s, σ_a, σ_s, in **6a-Li** it becomes π_a, σ_a, π_s, σ_s (from the top) with, however, mixing of the s types with the C-Li MO. **7e** and **7a** and **7e-Li** and **7a-Li** behave similarly.

Carbanion Stabilization and d-Orbital Conjugation. The much higher acidity of C-H bonds α to sulfur[3,18] as compared to C-H bonds in hydrocarbons has been usually ascribed to the possibility of (d-p)π back-bonding of the lp of the carbanions into the vacant d orbitals of sulfur. In order to test their role in carbanion stabilization by sulfur as compared to carbon, calculations have been performed on species **1** and **3** without and with inclusion of *d orbitals* on C(2) in **1** and **1-H** and on S in **3** and **3-H.** The results (Table I) show that d orbitals have no effect on the proton affinities of **1** and **3,** or conversely, on the C-H acidity of propane **1-H** and of dimethyl sulfide **3-H.** This holds for either forms **e** or **a** of **1** and **3.** The introduction of d orbitals just renders the basis set more flexible, but lowers the energies of the carbon acid and the carbanion by the same amount in both conformations of both compounds. The absence of any d-orbital effect and the very similar behavior of **1** and **3** clearly show that, contrary to the usual picture,[3] *(d-p)π bonding does not contribute to the stabilization of a carbanion (or to the acidity increase of a C-H bond) by an α-sulfur atom.* This agrees with and extends to dimethyl sulfide the results previously obtained for $^-CH_2SH$.[4,19]

As expected, the inclusion of d orbitals lowers the total energy f **3** more than that of **1,** but it affects only slightly the relative energies of the **e** and **a** forms of **1** and **3.** Similarly, the conformational properties of $^-CH_2SH$ are not appreciably affected by d orbitals on sulfur.[4] Also the electronic population of the d orbitals is the same in carbanions **1** and **3** as in the corresponding protonated species **1-H** and **3-H** (respectively, 0.30 and 0.45e).

These results also justify the use of only an sp basis set for the computations on the other sulfur-containing species **5** and **7.**

Proton Affinities. Substituent Effects. The proton affinities of species **4-7** have been calculated with the small Ssp basis set only. Table I shows that the proton affinities of **1** and **3** are calculated to be about 100 kcal/mol higher with the Ssp than with the large basis set. This is not satisfactory in absolute terms; however, it is seen that the changes in proton affinity both between **1** and **3** and between **3e** and **3a** are satisfactorily reproduced by Ssp as compared to Ispd calculations. Thus, although the absolute protonation energies listed in Table I for species **4-7** are expected to be about 100 kcal/mol too high, the *changes* and the *sequences* of protonation energies as a function of substituents calculated with the small Ssp basis set, should be meaningful.[42-44]

It is seen (Table I) that, within the same conformational family **e** or **a**, *proton affinity decreases (carbanion stabilization increases) in $^-CH_2X$ along the series of substituents X = CH_2CH_3, OH, OCH_3, SH, SCH_3.* Taking 1-propyl anion (which has a protonation energy very close to that of $^-CH_2CH_3$[19]) as a reference, one also sees that in $^-CH(XH)_2$ (X = O or S) with respect to $^-CH_2XH$ the second substituent has an effect about 1.5 times larger than the first one. The relative gas-phase carbon acidity of $CH_2(SCH_3)_2$ should thus be about 20-25 kcal/mol higher than that of CH_3SCH_3. The changes in proton affinities span about 40 kcal/mol from **1** to **7e**, i.e., about 30 p*K* units (at 25 °C).

The 12 kcal/mol difference (9 p*K* units) in proton affinities of **6e** and **7e** is in line with the fact that *m*-dioxane is not metalated in conditions where metalation of *m*-dithiane occurs easily.

Carbanion Stability. Polarization Effects. In the series of proton affinities given above, the presence of an α-heteroatom increases the C-H acidity as compared to $CH_3CH_2CH_3$. Since sulfur has about the same electronegativity as carbon and (p-d)π bonding does not contribute, how does sulfur (and by extension other second row atoms) stabilize carbanions? Qualitatively, carbanion stabilization in the gas phase may be ascribed to *polarization* of the electron distribution, i.e., to the ability of the groups attached to the anionic center to disperse the charge ove the molecule. This agrees both with the experimental results on gas-phase acidities and basicities[45] as well as with computational results.[4,19,43,44] For instance, the larger alkyl groups being more polarizable, the corresponding alcohols are more acidic, since the alkoxide is better stabilized.[44] This is contrary to the usual solution properties. Thus, in the present carbanions, polarization should also be at the origin of the relative proton affinities computed. The computed properties represent the intrinsic properties of the isolated anion; departure from this behavior in solution must be ascribed to medium effects, i.e., it provides indirectly a means of studying intermolecular effects in condensed phase.

We may now compare the carbanions **1-7** in the same **e** or **a** conformation. The substituent effects noted above follow the expected order of charge dispersion ability taking into account both polarity and polarizability of the groups.

The effect of a neighboring O atom as compared to CH_2 (about 10-15 kcal/mol stabilization, see **1** and **2**) may be ascribed to the larger electronegativity of oxygen. The much larger stabilization effect of sulfur both with respect to CH_2 (about 15-20 kcal/mol, see **1** and **3**) and to O (about 8 kcal/mol, see **4** and **5**) may be accounted for by the much larger polarizability of both the sulfur atom (3.45 Å^3)[46] and the C–S bond (1.9 Å^3)[47] with respect to the C (1.75 Å^3)[46] and O (0.73 Å^3)[46] atoms and the C–C (1.0 Å^3)[47] and C–O (0.8 Å^3)[47] bonds.

Such a polarization effect is apparent in the electron density difference diagrams of **5e**,[19] where density is shifted away from the carbanionic center into the region of the sulfur atom.

Population analyses also provide an illustration of the polarization effects[48] (Table II). In **1** the charge density alternates (C(1), C(3) > C(2)). An α-sulfur atom is itself very polarizable and enhances transmission of charge to the terminal CH_3 group in **3**, more so in **3e** than in **3a** (see below). $CH_3XCH_3 \rightarrow {}^-CH_2XCH_3$ ionization shifts more into X–CH_3 when X = S (Δ = 0.36) than when X = CH_2 (Δ = 0.29) or X = O (Δ 0.25).[48] In **6** and **7** both XH groups act as charge buffers in the course of ionization, SH being more efficient than OH. Indeed, the increase in atomic population in both X–H groups amounts to 0.29e for **7-H** → **7e**, but is only 0.20 for **6-H** → **6e** (Table II). The X–CH_3 is a better charge buffer than the less polarizable X–H groups (see Table II). The larger electron density delocalization found in forms **e** as compared to **a** is discussed below.

Stereoelectronic Effects on Carbanion Stability. The previous discussion of carbanion stabilization was complicated by the fact that protonation energies, and therefore stabilization effects, are very different in the two conformations **e** and **a** and always *larger in forms* **e** than in forms **a**. One may consider this to be conformation-dependent anisotropic polarization. However, the analysis of the electronic structure and the MO's shows that the phenomenon may in fact more be described as the result of stereoelectronic effects due to specific perturbation interactions and mixing of MO's. In all species **2**–**7** the *equatorial type conformations* **e** *are more stable than the axial carbanions* **a**. This stereospecific effect may amount to about half of the total stabilization itself. For instance, the changes in proton affinities are 8 kcal/mol for **3e** → **3a** and 20 kcal/mol for **3a** → **1a** (reference value). These results agree with the relative stability of rotamers in **4** and **5**[4,16] and with the "gauche" effect.[17,27,41] The nuclear–nuclear and electron–electron repulsions strongly disfavor the **e** forms with respect to the **a** forms (by 194 and 262 kcal/mol, respectively for the **3e,3a** pair; Ispd), the kinetic energy being unchanged. Thus, the stabilization of **e** with respect to **a** is entirely due to stronger electron–nuclear attractions. In strong contrast, **1e** and **1a** have about the same energy. It follows that in a CH_2 group, equatorial-type C–H bonds are much more acidic than axial-type C–H bonds whenever one or two O or S atoms are present in the α position. In particular, in *m*-dithiane, the equatorial C–H bond at C(2) is much more acidic than the axial one. The differences in protonation energy of **e** and **a** of 12 and 9 kcal/mol, respectively, amount to an estimated p*K* difference in the range of **9** and p*K* units for **6** and **7**, respectively. By contrast, all C–H bonds should have comparable acidity in cyclohexane itself.

These results provide an explanation for both the highly selective abstraction of the equatorial hydrogen in *m*-dithiane and the so-called "contrathermodynamic" equatorial → axial isomerization of a group as large as *tert*-butyl via protonation of the lithium derivative of 2-*tert*-butyl-*cis*-4,6-dimethyl-1,3-dithiane.[6,7] A "driving force" of at least 6 kcal/mol has been estimated for the latter process, which may be provided by the strong equatorial preference of the carbanion, even when more or less ion paired with the lithium cation. Maximum ion pairing as in **7-Li** lowers the **e**, **a** energy difference to 3.4 kcal/mol. In a condensed phase of dielectric constant higher than one, the structure of the carbanion should lie somewhere between the free anion **7** and the tight ion pair **7-Li**, so that the **e,a** energy difference in the actual lithiated species should be between about 3.5 and 9 kcal/mol.

The optimal arrangement **e** is also imposed by the bicyclic structure of the trisulfide $HC(CH_2S)_3CH$, which undergoes base-catalyzed H/D exchange 10^3 times faster than its open chain counterpart $(EtS)_3CH$.[9]

Anticipating the discussion below, one may point out that the unstable form **a** is that where the C^- lone pair or the C–Li bond is app to a heteroatom lp. Using at this point this result as a geometric, orientational indication, one may quite confidently generalize the present results and state that a *C–H bond app to an electronic lp on an α-heteroatom should be much less acidic* (*and the corresponding carbanion much less stable*) *than its gauche rotamer.* This should hold for ${}^-CH_2X$ with X = N, P as well as O, S.

Stereoelectronic Effects in Carbanions. MO Picture. The C^- lp orbital is in all carbanionic species the highest occupied MO (HOMO) followed by the MO combinations of the lp's on the heteroatoms. The stereoelectronic effects described above may be represented by a simple perturbation picture incorporating two main orbital interactions: (i) interaction of the HOMO, the carbanion lp, with the antibonding σ^* orbitals of the app O–H, S–H, O–CH_3, or S–CH_3 bonds in forms **e**; (ii) interaction of the carbanion lp with the orbital (s) built on the lp's of the heteroatom(s) in forms **a**; in terms of localized MO's this amounts to interaction of the C^- lp with the app lp (s) of the α-heteroatom(s).

Interaction i is of "anomeric" type[25,26,49] and is expected to stabilize **e** with respect to **a**; since it mixes the occupied HOMO with the antibonding σ^* orbital of the app bond, it should weaken this bond, i.e., diminish its overlap population (OP) and lengthen it[38] and strengthen the ${}^-CH_2$–X bond, similarly to the results of our previous studies of stereoelectronic interactions in tetrahedral species.[1a,22,23] Indeed the OP of the O–H, S–H, O–CH_3, and S–CH_3 are all weaker in the **e** forms (Table II). The effect is especially strong in the HOMO contribution to the total OP (Table II). Since σ^* (S–H) and σ^* (S–CH_3) are expected to lie below σ^* (O–H) and σ^* (O–CH_3), interaction of the carbanion with the former should be stronger (and more stabilizing) than with the latter, in agreement with the larger OP changes between the **a** and **e** forms in the sulfur containing species (Table II). [C^- lp, σ^* (S–H)] mixing is also nicely seen in the HOMO of **7e** (Figure 1). The largest effect by far is found in **3**: the S–CH_3 OP of **3e** is only half that in **3a**, whereas the C–CH_3 OP is comparatively little (10%) affected in **1e** with respect to **1a**; conversely the ${}^-CH_2$–S OP is much larger in **3e** than in **3a**. This leads to an appreciable lenghtening of the S–CH_3 bond in **3e**, as shown by optimization calculations: S–C = 1.836 Å in **3e** and 1.807 Å in **3a**.

Interaction ii may be said to be of the "reverse anomeric" type if one considers the C^- lp as a substituent of zero electronegativity; it mixes two occupid orbitals and is expected to disfavor **a** with respect to **e** forms.[26] The HOMO is of higher energy in **7a** than in **7e** (Table I) and mixes strongly the symmetric π lp combination with the C^- lp (Figure 1). The OP of the ${}^-CH_2$–S bond in **3a** is low compared to **3e** and is strongly negative in the HOMO (Table II). Similar results hold for the other species.[31]

Thus, in addition to the polarization effects discussed above, *the two stereoelectronic interactions* [*C^- lp, σ^** (*app X–Z bond*)] *and* [*C^- lp, app heteroatom lp*] *are expected to contribute strongly to the properties of carbanions*, stabilizing **e**-type carbanions with respect to **a**-type carbanions.[50]

In relation to the strong [C^- lp, σ^* (S–CH_3)] interaction found in **3e**, it may be noted that two and three such interactions are present, respectively, in the equatorial carbanion of *m*-dithiane and in the bridgehead carbanion of $HC(CH_2S)_3C^-$. Destabilization of carbanions by interaction with oxygen lp's has been suggested in dioxolane systems.[51]

Stereoelectronic and Stabilization Effects in the Organo-

lithium Species 3-Li-7-Li. The stabilization effects are weaker in the C-Li compounds than in the corresponding carbanions, but they follow the same sequence. The stereochemical bias in favor of **e** forms is weaker in C-Li systems (3.4 kcal/mol between **7e-Li** and **7a-Li**) than in the carbanions.[52]

Perturbative interactions between orbitals are easily discernible. Since Li is less electronegative than H, σ^*(C-Li) is expected to be higher in energy than σ^*(C-H), so that the [X lp, σ^*(C-Y)] interaction in Y-C-X (X = O or S) is larger for Y = H than for Y = Li.[26] Thus, the **e,a** orientational change affects more C-H OP's than C-Li OP's when X = O[53] (Table III). This "reverse anomeric" effect should stabilize the lp app to C-H orientation, i.e., forms **e-Li** with respect to **a-Li,** as found. The C-Li bond is usually described by the HOMO when X = O, but lies among the S lp MO's when X = S. The general observation, in line with the results on the carbanions, is that in LiCXH, C-Li strongly mixes with the σ^*(X-H) orbital of the app, X-H bond in forms **e** and with the app lp in forms **a.** The first interaction is stabilizing and the second one destabilizing. As a consequence: (a) the X-H OP is lower, the X-H bond is weaker in **e-Li** than in **a-Li;** (b) the C-Li bond is weaker in the **a-Li** forms.

These effects are illustrated on $LiCH(OH)_2$ (**6-Li**).[53] Indeed the C-Li bond lengths are, respectively, 2.023 Å in **6e-Li** and 2.127 Å in **6a-Li.** Furthermore, when Y is less electronegative than carbon the σ^*(C-Y) MO has a larger lobe on Y than on C, whereas the reverse holds for Y more electronegative than C. As a consequence, [X lp, σ^*(C-Y)] mixing increases the atomic population (AP) on Li in **6a-Li** (2.85e) as compared to **6e-Li** (2.72e) (Table III). The effect is also seen in the larger Li lobe in the HOMO of **6a-Li** with respect to **6e-Li** (Figure 1). The polarity of the C-Li bond, as described by the C and Li AP's in the HOMO, undergoes an interesting change: it is polar C(−)—Li(+) in **6e-Li** and nonpolar in **6a-Li** (Table III). The [σ(C-Li), σ^*(O-H)] interaction should stabilize and the [O lp, σ^*(C-Li)] interaction should destabilize the HOMO in **6e-Li** and **6a-Li,** respectively; indeed the HOMO of **6a-Li** is about 1 eV higher in energy than that of **6e-Li.**

Finally, the [σ(C-Li), σ^*($S-CH_3$)] interaction in **3-Li** weakens and lengthens the $S-CH_3$ bond, the bond lengths and OP's being, respectively: 1.808 Å, 0.247e in **3e-Li** and 1.799 Å, 0.260e in **3a-Li;** in the same species the C-Li bond has 2.008 Å, 0.295e and 2.019 Å, 0.298e, respectively. In **7-Li** similar phenomena are present as in **6-Li,** but because of much stronger mixing between C-Li and the four S lp orbitals, their detailed analysis is more complicated[53] and is not essential here.[28]

Geometry of the Carbanion Site. A computation (Ispd) has been performed on a form of **3** containing a planar CH_2^- site. The CH_2^- inversion barrier is calculated to be 11.3 kcal/mol with respect to **3e.** The planar form has about the same energy as **3a.** An inversion barrier of 11.0 kcal/mol has been calculated for $^-CH_2SH$.[4,36] Taking the inversion barrier in $^-CH_2OH$ to be about 15 kcal/mol above form **4e,**[4] one finds that the protonation energy of the planar site should be equal to or higher than that of propyl anion **1.** This result agrees with experimental results,[51] indicating that α-oxygen atoms facilitate the formation of an sp^3 carbanion, but hinder the formation of an sp^2 carbanion.

Conclusion

The present results show that stereoelectronic effects are of prime importance in the stabilization and stereochemistry of carbanions bearing α-heteroatoms X: $^-CH_2XZ$ (X = O, S; Z = C, H). Equatorial-type carbanions or lithium compounds (forms **e**) are appreciably more stable (and the corresponding C-H bonds are more acidic) than the axial-type forms **a,** where the ^-C lone pair or the C-Li bond is antiperiplanar to a lone pair on the heteroatom X. These effects provide a rationalization for a number of experimental results and should also have predictive power. This study completes and extends the previous theoretical picture of orientational factors in tetrahedral intermediates[22-24] and phosphate esters.[1a]

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Electron Exchange and Electron Transfer of Semiquinones in Aqueous Solutions[1a]

Dan Meisel*[1b] and Richard W. Fessenden[1c]

Contribution from the Radiation Research Laboratories and Department of Chemistry, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

Received March 1, 1976

Abstract: Rate constants for self-exchange of electrons between semiquinone radical ions and their parent quinones were measured for four benzoquinone derivatives in aqueous solutions (containing 5 M 2-propanol and 1 M acetone at pH 7). This was accomplished by measuring the effect of the concentration of the quinone on the ESR line width of the semiquinone radical ion produced by in situ photolysis. The quinones studied were benzoquinone, 2,5- and 2,6-dimethylbenzoquinone, and duroquinone. The rate constants for the electron exchange for these couples were found to be in the range of $0.5–2 \times 10^8$ M^{-1} s^{-1}. Electron transfer from one semiquinone to another quinone in this group of benzoquinone derivatives was measured using kinetic spectrophotometry and pulse radiolysis. Since one-electron reduction potentials for all of these quinone/semiquinone couples are known from pulse radiolysis determination of the equilibria, electron transfer rates can be predicted using the Marcus theory from rates of the self-exchange reactions. The calculated rates thus obtained are in good agreement with the experimentally measured rate constants. Reaction radii could be estimated and further correlations between the rates of electron transfer and the free energy changes were checked.

Electron transfer reactions have long been the subject of both experimental and theoretical studies.[2] The experimental results for these reactions are commonly discussed in terms of the Marcus[3] and Hush[4] theory, mainly because of its representation in terms of easily measurable parameters. The theory predicts the existence of a correlation between the free energy of an electron transfer reaction and the rate of this reaction as well as a correlation between the rates of the self-exchange reactions and the rates of cross electron transfer reactions. Although both these predictions have been exhaustively checked for metal ion complexes,[5] the available data for organic systems is rather scarce. A few cases have been checked for the predictions of the Marcus theory,[6-9] but these were confined mainly to organic radicals in aprotic solvents in which the radicals are very long lived. Recent studies, however, have demonstrated that electron transfer equilibria can be measured even for relatively short-lived radicals in aqueous solutions,[10-13] thus providing the missing free energy of the reaction necessary for these correlations. Indeed it was recently shown that the rate constants for the electron transfer reaction in some systems such as semiquinones, nitroaromatic radical ions, and the superoxide radical ion correlate well with the corresponding free energy of the reaction,[14] as predicted by the Marcus theory. It was estimated in that study that the rate constant for the electron exchange reaction for this type of compounds should be approximately 5×10^7 M^{-1} s^{-1} in aqueous solution. One aim of this study was to check this estimate.

Electron exchange in such aromatic systems presumably represents the simplest of electron transfer reactions, since no chemical bonds are broken or formed in the transfer and furthermore the changes in bond lengths and angles are rather small. Thus the major contribution to the energy of activation