stituents $Me_2\dot{N}$, which leads mostly to para, MeNH, which leads to both para and meta, and NH_2, which leads mostly to meta replacement. However, as has been demonstrated in related cases,[15] the methyl substituent on the nitrogen can lead to steric inhibition of conjugation, at least in the case of the Me_2N group. Furthermore, NH_2 in sodium methoxide probably exists in its basic form NH^-, a powerful donor expected to lead to meta orientation.

In the case of electron-acceptor groups, the dominant orbital interactions involve the π LUMO of the acceptor and the S benzenoid MO. This interaction always guarantees that the S level will be lower in energy than the A level. Hence, nucleophilic substitution is predicted to occur para to the substituent, as observed experimentally.[16,17]

In short, the model we have presented allows prediction of the orientation of nucleophilic substitution in polyhalobenzenes. By using the approximate indices we have suggested, one can deduce the preferred orientations with a minimum of work and no elaborate calculations.

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(13) Substituting a methyl group for the hydrogen in pentafluorobenzene results in a decrease in the energy difference between ϕ_4 and ϕ_5 since the methyl group has a vacant σ^* as well as an occupied σ MO that mixes with ϕ_5. It appears that the ϕ_5–σ^* interaction is somewhat greater than the ϕ_5–σ interaction.

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(17) The carboxylate group CO_2^- is a four-electron allylic system with the π HOMO having a node through the central atom. Hence, the carboxylate group acts as an acceptor with respect to benzene; i.e., its principal interaction with the benzene system is with its π LUMO.

A Theoretical Analysis of the Factors Determining the Conformations and Stabilities of Oxy- and Thiocarbanions

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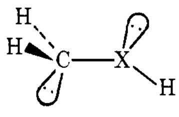
Abstract: A one-electron molecular-orbital model is proposed which rationalizes the enhanced stability of a carbanion adjacent to sulfur as compared to a carbanion adjacent to oxygen without requiring the postulate of $(p \rightarrow d)_\pi$ conjugation. It is found that the greater stability in the case of sulfur is the result of greater two-electron stabilization of the total carbanionic system, because of the enhanced electron accepting ability of SR compared to OR. The one electron factors responsible for the stabilization of an adjacent carbanionic center by XR are conformationally dependent. The model is supported by the results of detailed ab initio computations.

After some decades of fairly general acceptance,[2] the notion that expansion of the valence shell plays an important role in determining the chemical and stereochemical properties of atoms below the first row of the periodic table has begun to be questioned.[3] The questions arise because it has now become possible to evaluate in a reasonably rigorous way just what is the nature and magnitude of $(p \rightarrow d)_\pi$ conjugative effects. At the level of SCF-MO computations, such effects are negligibly small in a number of systems previously believed to constitute definitive demonstrations of valence shell expansion. For example, a recent[3a] comparative quantum chemical investigation of the static, dynamic, and chemical properties of the anions $^-CH_2OH$ (**1**) and $^-CH_2SH$ (**2**) found no evidence that d-orbital effects contribute significantly to any of the differences between the two systems, and in particular, to the enhanced acidity of protons adjacent to the second row heteroatom.

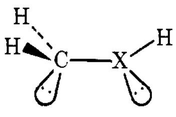
These results reveal a need for a rationalization of the different effects of oxygen and sulfur in organic molecules which does not invoke d-orbital conjugation. The purpose of the present paper is to present a model which rationalizes the behavior of the above carbanions, and to demonstrate the utility of this model via applications to some related problems of structure and reactivity. The treatment will focus particularly on the factors that influence the stabilization of a carbanionic center by adjacent SH and OH groups. The systems chosen for the discussion are the Y (**3**) and W (**4**) conformations of **1** and **2**; these conformations are energy minima on the rotation-inversion surfaces of both carbanions.[3a]

Table I. Eigenfunctions for the Group MO's of CH_2^- and XH

	Group		
MO	CH_2^-	OH	SH
ψ_1		$0.731p_x + 0.422p_y + 0.536H_s$	$0.690p_x + 0.398p_y + 0.598H_s$
ψ_2		$0.296s + 0.478p_x - 0.827p_y$	$0.416s + 0.435p_x - 0.785p_y$
ψ_3		p_z	p_z
ψ_4		$0.502s + 0.285p_x + 0.491p_y - 0.657H_s$	$0.315s + 0.388p_x + 0.674p_y - 0.489H_s$
ϕ_3	$0.483s - 0.307p_x + 0.873p_y$		



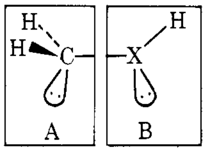
3 (Y)



4 (W)

Theory

(A) Development of the Model. The approach used here is based upon one-electron MO (OEMO) theory, in which the wave function of a total system is constructed from component fragments whose wave functions are either known or can be calculated. The "dissection" of the $^-CH_2XH$ system into component fragments, A and B, is depicted below for the W conformation.



In this procedure, an effective one-electron Hamiltonian is adopted, and overlap is included explicitly.[4]

The method will be illustrated first by reference to the oxyanion **1**. The energies and eigenfunctions of the group MO's of the $^-CH_2$ and OH fragments have been computed by the CNDO/2 method,[5] and the normalized group MO's are shown in Table I. It is seen that ϕ_3 is essentially a carbon lone pair AO, ψ_1 is a σ-bonding MO, ψ_2 is one oxygen lone pair AO, ψ_3 is the second oxygen lone pair AO, and ψ_4 is a σ antibonding MO. To be more consistent with the concepts of lone pair-lone pair, lone pair-bond pair, and bond pair-bond pair interactions, the familiar σ, n, and σ^* symbolisms will be employed to discuss interactions between delocalized MO's.

Figure 1 shows the key orbital interactions which obtain in the union of the $^-CH_2$ and OH group MO's to form the $^-CH_2OH$ system in either of the W or Y conformations. The carbon lone pair, ϕ_3, can interact with the OH group orbitals ψ_1, ψ_2, and ψ_4. Interactions 1 and 2 (ϕ_3-ψ_1, ϕ_3-ψ_2) are two-orbital four-electron *destabilizing* interactions, while interaction 3 (ϕ_3-ψ_4) is a two-orbital two-electron *stabilizing* interaction.

We now examine interactions 1, 2, and 3 as a function of conformation. The stabilization energy of the two-electron n_C-σ_{OH}^* interaction is given by the following expression:[6]

$$\Delta E^2{}_{n_C\text{-}\sigma_{OH}^*} = \frac{S^2{}_{n_C\sigma_{OH}^*}(k - \epsilon_{n_C})^2}{\epsilon_{n_C} - \epsilon_{\sigma_{OH}^*}} \qquad (1)$$

In eq 1, $S_{n_C\text{-}\sigma_{OH}^*}$ is the overlap intergral between the carbon lone pair MO, n_C, and the σ^* MO of the OH bond; ϵ_{n_C} and $\epsilon_{\sigma_{OH}^*}$ are the energies of these two orbitals, respectively; and k is an energy constant. Equation 1 has been derived from the well known perturbation expression for the two-electron stabilization upon interaction of a filled and unfilled orbital (nondegenerate case), in which the usual approximation for the interaction matrix element, $H_{ij} = kS_{ij}$, has been made.[7] Since the quantities $(k - \epsilon_{n_C})^2$ and $(\epsilon_{n_C} - \epsilon_{\sigma_{OH}^*})$ remain constant in both the Y and W conformations, it is readily appreciated that the two-electron stabilization energy, as it pertains to these two conformations, is directly dependent upon the square of the overlap. The overlap integral, $S_{n_C\sigma_{OH}^*}$, is easily evaluated from the eigenvectors given in Table I.

The individual overlap integrals between AO's were calculated using overlap matched atomic orbitals (OMAO's) in order to approximate the overlap properties of accurate SCF wave functions.[8] Table II lists $S_{n_C\sigma_{OH}^*}$ for both the Y and W conformations. The absolute value of the overlap integral is larger in the W conformation, so that the two-electron *stabilization* will be greater in the W conformation than in the Y conformation.

The next step in the analysis is to examine the four-electron destabilizing interactions 1 and 2 depicted in Figure 1. The four-electron destabilization energy is given by the equation:

$$\Delta E_{ij}{}^4 = \frac{4S_{ij}{}^2}{1 - S_{ij}{}^2}(\epsilon_0 - k) \qquad (2)$$

in which ϵ_0 is the mean of the energies of the unperturbed ϕ_i and ϕ_j MO's.[9] Equation 2 is derived by a variational solution of the two-orbital interaction problem, making the usual assumption that the interaction matrix element is proportional to overlap. The magnitude of the n_C-σ_{OH} and n_C-n_O four-electron destabilizing interactions in both the Y and W conformations is again dependent only upon the overlap, because the quantity $(\epsilon_0 - k)$ remains constant. The appropriate overlap integrals are calculated readily, and the results are shown in Table II. It can be seen that the n_C-σ_{OH} interaction will destabilize the W conformation more than the Y since $S^W{}_{n_C\sigma_{OH}} > S^Y{}_{n_C\sigma_{OH}}$, but the n_C-n_O interaction favors the W conformation since $S^Y{}_{n_Cn_O} > S^W{}_{n_Cn_O}$. Calculation of the above interaction energies utilizing the overlap data in Table II and the orbital energies in Table III for the group MO's of $^-CH_2$ and OH have been performed, and the results, which should be given qualitative significance only, are shown in Table IV.

The combination of the two-electron stabilization energy and the *total* four-electron destabilization energy favors the W conformation ($\Delta E^4_{Total}(Y) = 0.1795$ au; $\Delta E^4_{Total}(W) = 0.1695$ au). More specifically, the W conformation is favored by 0.00999 au by the total four-electron overlap repulsion energy, and by 0.0432 au by the two-electron stabilizing interaction. These results indicate that in the absence of "steric effects", the one-electron factors just discussed predict the W conformation to be lower in energy than the Y.

These procedures are now applied to the thioanion **2**. The MO overlap integrals and energies (Tables II and III) were obtained in the same manner as before and, using the same analysis, it is found that the Y conformation is favored by the n_C-σ_{SH} four-electron interaction, while the W conformation is favored by both the n_C-n_S destabilizing and the n_C-σ_{SH}^* stabilizing interactions. The data displayed in Table IV show that the total four-electron destabilization energy, $\Delta E^4{}_{n_C\sigma_{SH}} + \Delta E^4{}_{n_Cn_S}$, favors the Y conformation by 0.023 06 au, but the

Table II. Group Orbital Overlap Integrals for $^-CH_2OH$ and $^-CH_2SH$ in the Y and W Conformations

Heteroatom	$S_{n_C\sigma_{XH}}$		$S_{n_Cn_y}$		$S_{n_C\sigma_{XH}*}$	
	Y	W	Y	W	Y	W
O	0.0893	−0.1513	−0.1755	0.1235	0.0105	−0.0594
S	0.0277	−0.1346	−0.1652	0.1262	0.0676	−0.1456

Table III. MO Energies of the Interacting Group Orbitals

Group orbital	Energy, au[a]		
	n	σ	σ^*
$^-CH_2$	−0.0109		
O—H	−0.6151	−0.8059	0.2831
S—H	−0.5488	−0.6718	0.0533

[a] Energy levels taken from CNDO/2 calculations.

Table IV. The Stabilization and Destabilization Energies of $^-CH_2XH$

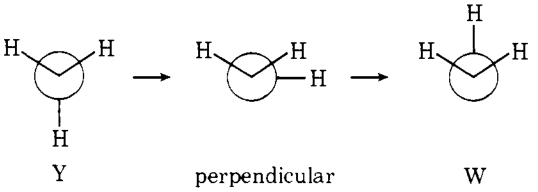
X	Interaction	Interaction energy, au[a,b]			
		Y		W	
O	n_C-σ_{XH}	0.0338	(0.0332)	0.0985	(0.0967)
O	n_C-n_X	0.1457	(0.1433)	0.0710	(0.0698)
O	n_C-$\sigma_{XH}*$	−0.0015	(−0.0015)	−0.0448	(−0.0437)
S	n_C-σ_{XH}	0.0034	(0.0033)	0.0825	(0.0811)
S	n_C-n_X	0.1323	(0.1303)	0.0763	(0.0751)
S	n_C-$\sigma_{XH}*$	−0.1332	(−0.1130)	−0.3168	(−0.3122)

[a] A minus sign signifies stabilization and a plus signifies destabilization. [b] The interaction matrix element has been approximated by $H_{ij} = kS_{ij}$ and, for the values in parentheses, by $H_{ij} = kS_{ij}(H_{ij} + H_{jj})/2$. k is set equal to 1.459 au in the first approximation and to 1.441 in the second approximation of the interaction matrix element.[7]

n_C-$\sigma_{SH}*$ two-electron stabilization energy favors the W conformation by 0.183 54 au. The difference between the two effects is 101.72 kcal/mol in favor of the W conformation. Thus, in contrast to oxyanion **1**, the four-electron overlap repulsion which favors the Y conformation is completely dominated by the two-electron stabilizing effect which favors the W conformation.

This permits the conclusion that the preferred conformation of the thioanion **2** is W, because of the large two-electron stabilization which arises from the n_C-$\sigma_{SH}*$ orbital interaction.

It is interesting to note that, in the Y → W transformation, the two-electron stabilization energy will fall to zero when the carbon lone pair and XH are orthogonal:



A "perpendicular" conformation of $^-CH_2XH$ can therefore be expected to be higher in energy than either the Y or W conformations. This is consistent with the ab initio computations,[3a] which find the perpendicular conformation to be the energy maximum of the rotation-inversion surfaces of both $^-CH_2OH$ and $^-CH_2SH$.

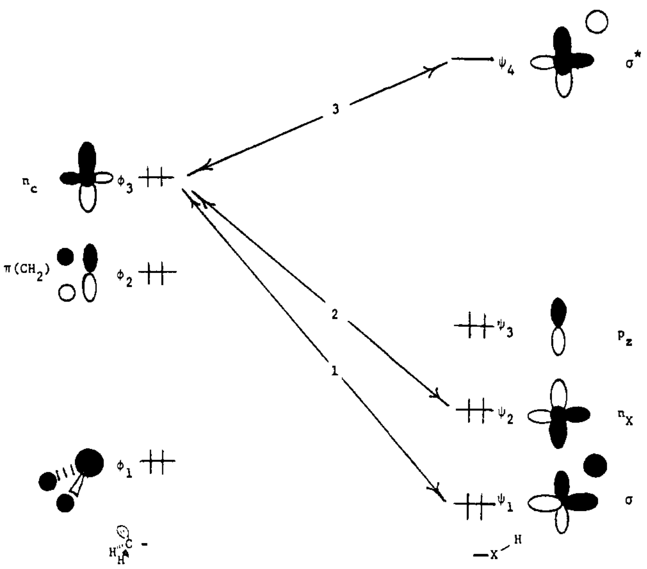


Figure 1. Interaction diagram for the union of CH_2^- and XH group orbitals. Interactions 1 and 2 are four-electron destabilizing interactions, and interaction 3 is a two-electron stabilizing interaction.

The model may now be employed to compare the different stabilizing effects of SH and OH groups upon an adjacent carbanionic center. On the basis of eq 1, the two-electron stabilization energy is directly proportional to the overlap and inversely proportional to the energy difference between the two interacting MO's, because the quantity $(k - \epsilon_{n_C})^2$ is a constant in the case of both SH and OH. The energy difference in eq 1 is smaller for sulfur than for oxygen, because of the low energy of the $\sigma_{SH}*$ MO relative to the $\sigma_{OH}*$ MO, as shown in Table III. Consequently, a prediction based solely upon the energy difference between the groups will conclude that SH should stabilize an adjacent carbon lone pair more than OH. The lower energy of the $\sigma_{SH}*$ relative to the $\sigma_{OH}*$ falls within a more general trend. Specifically, $\sigma_{RX}*$, where R = CH_3, H, etc., tends to decrease in energy as X is varied down a column of the periodic table. For example, $\sigma_{RF}* > \sigma_{RCl}* > \sigma_{RBr}* > \sigma_{RI}*$.[10] The opposite trend holds for σ_{RX}. The energy of this orbital tends to increase as X is varied down a column of the periodic table. For example, $\sigma_{RI} > \sigma_{RBr} > \sigma_{RCl} > \sigma_{RF}$.[11] The general consequences of increasing hyperconjugative ability of an R-X bond as X is varied down the column of the periodic table are discussed in a monograph.[12]

The overlap integral $S_{n_C\sigma_{SH}*}$ is also larger than $S_{n_C\sigma_{OH}*}$ in both the Y and W conformations, and this will enhance further the stabilization by SH. The reason for the larger $S_{n_C\sigma_{SH}*}$ overlap integral can be understood by consideration of the overlap integral $\langle C_{p_y}|X_{p_y} - 1s\rangle$, which approximates the n_C-$\sigma_{XH}*$ overlap integral because n_C has a major contribution from C_{p_y}, and $\sigma_{XH}*$ has a major contribution from X_{p_y} (see Table I). This approximate overlap integral is sketched below for the Y conformation, and it can be partitioned in the following way:

$$\langle n_C|\sigma_{XH}*\rangle \simeq \langle C_{p_y}|X_{p_y} - 1s\rangle$$
$$= \langle C_{p_y}|X_{p_y}\rangle - \langle C_{p_y}|1s\rangle = S_{CX} - S_{CH}{}^X$$

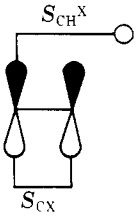
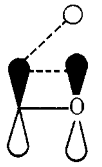


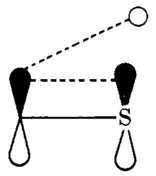
Table V. Optimized Geometries,[a] Total Energies, and Energy Components of the Y and W Conformations of $^-CH_2OH$ and $^-CH_2SH$ as Computed with a 4-31G Basis Set

	$^-CH_2OH$		$^-CH_2SH$	
	Y	W	Y	W
r(C–X)	1.5585	1.5395	2.0311	1.9569
r(X–H)	0.9508	0.9508	1.3933	1.3933
r(C–H)	1.1146	1.1146	1.0999	1.0999
∠CXH	105.81	112.07	100.02	109.32
∠HCH	103.24	103.98	107.63	107.63
α^b	69.89	65.66	72.53	63.13
Total energy, au	−114.15843	−114.15199	−436.49783	−436.49743
Electronic energy, au	−146.88768	−147.06611	−482.01513	−482.92478
Nuclear energy, au	32.72925	32.91413	45.51730	46.42735

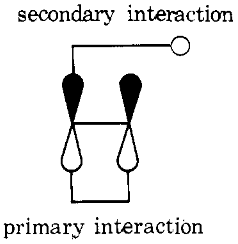
[a] Bond lengths in Å and angles in deg. [b] The angle between the C–X axis and the bisectrix of the HCH angle.

Ab initio calculations show that the π S_{CX} overlap integrals for oxygen and sulfur are comparable, i.e., $S_{CO}{}^{\pi} \approx S_{CS}{}^{\pi}$. On the other hand, the $S_{CH}{}^{X}$ overlap integral is smaller in the case of sulfur than in the case of oxygen, because the C–O bond is shorter than the C–S bond, i.e., $S_{CH}{}^{O} > S_{CH}{}^{S}$. These effects are shown schematically below:





The overlap effect can be restated in the following way: the greater n_C-σ_{XH}* overlap integral in the case of sulfur results from a *smaller* antibonding contribution by the group attached to sulfur. This can be regarded as an additional example of how secondary orbital interactions may determine chemical preferences.[13]



Examination of Table III and eq 2 reveals that the relative four-electron-*destabilization* energies for the SH and OH cases will be determined to a large degree by the overlap, since the mean of the energies of the interacting orbitals, ϵ_0, will favor OH over SH only to a small extent. As shown in Table 11, $S_{n_C\sigma_{XH}}$ is larger in the case of oxygen. Here the approximate overlap integrals have the form $\langle n_C | \sigma_{XH} \rangle \simeq S_{CX} + S_{CH}{}^{X}$. For reasons already discussed, we conclude that the n_C-σ_{XH} overlap integral will be larger for oxygen than for sulfur. It can therefore be expected that $^-CH_2OH$ will be characterized by a larger n_C-σ_{XH} four-electron destabilization energy than $^-CH_2SH$. Finally, to complete the discussion, we note that the destabilization resulting from the n_C-n_X interactions will be comparable for oxygen and sulfur, because the corresponding overlap integrals are comparable, and the energy factor does not discriminate significantly.

The above analysis may be summarized as follows: the stability of the adjacent carbanionic center is greater with SH than with OH, because the two-electron stabilization is larger and the four-electron destabilization is smaller.

(B) **Ab Initio Results.** To assess the quantitative significance of the various interactions that have been proposed to operate in the W and Y conformations, it is useful at this point to examine the ab initio wave functions computed for **1** and **2.** In the ab initio calculations on $^-CH_2SH$,[3a] a very large double ζ basis set was used, which contained two linearly independent sets of 3d functions on sulfur. It was therefore not possible to perform a full geometry optimization at all stages of the computations, and some constraints were introduced. For example, the C–S bond length was optimized for the W conformation, and was kept constant in the subsequent work.

The geometries of **1** and **2** have now been reoptimized with respect to all geometrical parameters, using the 4-31G basis sets[14] of GAUSSIAN 70.[15] The results of these calculations are presented in Table V.

For $^-CH_2OH$, the Y conformation is found to be the most stable, as computed previously,[3a] but for $^-CH_2SH$, the Y and W conformations are now found to be of comparable energy. From the standpoint of the conformational preferences, the agreement between the predictions of the OEMO model and the ab initio results is thus not very satisfactory. Clearly steric effects are underestimated by this OEMO treatment. Nevertheless, it is possible to find in the ab initio computations evidence of the stabilizing electronic interactions proposed for the W conformations. Thus, (i) the C–X bond lengths are shorter in the W conformations of both anions; (ii) the C–X overlap populations are larger in the W conformations of both anions; (iii) the electronic energy is larger in the W conformations (see Table V).

On the other hand, the OEMO prediction concerning the relative effects of SH and OH upon the stability of an adjacent carbanion does agree with the ab initio results. A measure of this relative stabilization can be obtained from the energetics of the following isodesmic process:

$$CH_3XH + CH_3^- \rightarrow {}^-CH_2XH + CH_4$$

The various additional energy values required for this comparison, computed at the 4-31G level, are: $E_{CH_3OH} = -114.870\,86$ au; $E_{CH_3SH} = -463.495\,84$ au; $E_{CH_3^-} = -39.401\,23$ au; $E_{CH_4} = -39.871\,58$ au.[16] These data reveal that the stabilization by SH is greater by ca. 16 kcal/mol.

Much of the discussion to this point has reflected an "energy approach" in which the emphasis is on the energy changes accompanying conformational interconversions. An equivalent analysis, termed the "charge transfer" approach, examines the consequences of charge transfer from an occupied to an unoccupied MO. Specifically, the n_C-σ_{XH}* interaction which results in charge transfer from n_C to σ_{XH}* will have several consequences upon the Y to W interconversion: (i) Since the n_C-σ_{XH}* interaction is greater in the W conformation in both carbanions, charge transfer into the σ_{XH}* MO is expected to lead to a decrease in the XH overlap population when Y is transformed into W. The results of the ab initio 4-31G calcu-

Table VI. Net Atomic Charges of $^{-}CH_2OH$ and $^{-}CH_2SH$ Computed at the 4-31G Level

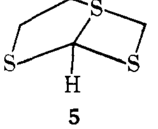
	X = S		X = O	
	W	Y	W	Y
C	−0.6191	−0.5989	−0.3058	−0.3598
X	−0.3168	−0.4126	−0.8369	−0.8549
H_C	+0.0109	+0.0156	−0.0762	−0.0526
H_X	−0.0860	−0.0196	+0.2952	+0.3201

lations confirm this expectation. (ii) The gross charges on X, C, and H should reflect the different effects of charge transfer in the Y and W conformations. That is, in the process Y → W, the gross charges on X and H should become more negative (or less positive), and the gross charge on carbon should become less negative. The gross charges on the heteroatoms in both conformations are shown in Table VI. An anomaly is noted in the case of carbon and sulfur charges in CH_2SH. Otherwise, the results agree, once again, with our predictions. It is interesting to note that the X-H hydrogen has a negative charge in the thioanion and a positive charge in the oxyanion. This is not surprising, since charge transfer is greater in the case of sulfur. The gross charge on hydrogen may therefore be viewed as an index of the "hyperconjugative effect" in the sense that it reflects the greater electron accepting ability of the S-H bond.

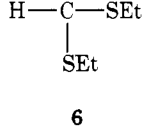
The ab initio computations are thus entirely compatible with the conclusion that the enhanced stability of a carbanion adjacent to sulfur is dominated by the two-electron n_C-σ_{SH}^* stabilizing interaction, and not by $(p \rightarrow d)_\pi$ conjugation. An interesting point is that CH_2Cl, where the n_C-σ_{XH}^* stabilizing interaction does not obtain, tends to dissociate into CH_2 and Cl fragments at the 4-31G computational level.[17]

Discussion

It follows from the treatment presented here that many of the examples of "d-orbital effects in compounds of divalent sulfur"[18] should be regarded instead as examples of large n_C-σ_{SR}^* charge transfer. This will be the case, especially, whenever a carbanion is formed adjacent to divalent sulfur. Important examples to which our model is applicable include the deprotonation of sulfides,[19] dithioacetals,[20] and trithioorthoformates.[21] In the latter case, Oae and his co-workers observed[21] that the kinetic acidity of the bridgehead proton of **5** is greater by a factor of 10^3 than that of the tertiary proton of the open chain analogue **6**. In the case of **5**, the carbanionic intermediate is constrained to the W conformational relationship with respect to the adjacent C-S bonds, and illustrates our finding that the stabilization of an adjacent carbanion by SR is conformationally dependent.[22] We believe that the d-orbital model cannot account for such results because the stabilization of the carbanion should be independent of the conformational relationship between the carbon lone pair and adjacent SR bonds.



5



$HC(SEt)_3$

6

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