

The Irrelevance of d-Orbital Conjugation. I. The α -Thiocarbanion. A Comparative Quantum Chemical Study of the Static and Dynamic Properties and Proton Affinities of Carbanions Adjacent to Oxygen and to Sulfur

Fernando Bernardi,^{1a} Imre G. Csizmadia,^{1b} Angelo Mangini,^{1c} H. Bernhard Schlegel,^{1d,2a} Myung-Hwan Whangbo,^{1d,2b} and Saul Wolfe*^{1d}

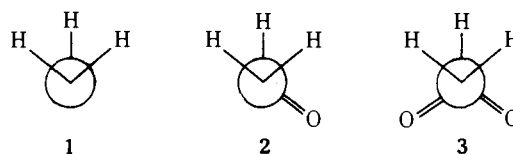
Contribution from the Laboratorio CNR dei Composti del Carbanio contenenti eteroatomi, Ozzano E., Bologna, Italy, the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, Istituto di Chimica Organica, Universita di Bologna, Bologna, Italy, and the Department of Chemistry, Queen's University, Kingston, Ontario, Canada. Received June 25, 1974

Abstract: A nonempirical molecular-orbital investigation has been made of the reactions $\text{CH}_2\text{XH} + \text{H}^+ \rightarrow \text{CH}_3\text{XH} \leftarrow \text{H}^+ + \text{CH}_2\text{X}^-$, for the systems $\text{X} = \text{O}, \text{S}$, and with optimization of all geometric parameters other than the CH, SH, and OH bond lengths. Because the computations have been performed with several basis sets containing either sp- or spd-type functions on the heteroatoms, it has been possible to assess theoretically the role of $(p \rightarrow d)_\pi$ conjugation in the case of sulfur as the source of the differences in the static and dynamic properties and proton affinities of the anions. No evidence has been obtained that any of these differences is the result of such conjugative effects. Thus, the stable structures of CH_2SH and CH_2OH correspond to W and Y conformations, respectively, because of the effect of the greater nuclear-nuclear interaction associated with the shorter C-O bond length of CH_2OH . The barrier to rotation about the C-X bond is lower in CH_2SH than in CH_2OH , and the barrier to pyramidal inversion at carbon is higher in CH_2OH than in CH_2SH because of the greater electron-withdrawing effect of oxygen upon the adjacent tricoordinate center. An examination of the higher occupied molecular orbitals and charge distributions in CH_2SH confirms the relative unimportance of $(p \rightarrow d)_\pi$ conjugation in the ground state. For example, the effect of the d-type polarization functions is more pronounced in the region of the S-H bond than in the region of the C-S bond. It is concluded that some inherent difference between sulfur and oxygen atoms is being reflected in the properties of the molecules. Two such differences are the larger size of sulfur and the presence of the low-lying d orbitals. The cumulative effect of these two differences is to make sulfur more polarizable than oxygen both in the atomic state and in the molecular state. Consequently, the gas-phase acidity of a C-H bond adjacent to sulfur is greater than that of a C-H bond adjacent to oxygen, whether d-type functions are employed on the heteroatoms or not.

The enhanced acidity of protons adjacent to sulfur in its various oxidation states has been known for nearly a century.^{3,4} For almost half this period, with some exceptions,⁵ most workers have preferred a conjugative explanation of this property. By this is meant, in current terminology, a stabilization of the transition state for proton abstraction (in the case of kinetic acidity) or a carbanion (in the case of thermodynamic acidity) by $(p \rightarrow d)_\pi$ bonding, with such bonding considered possible for a directly attached atom of the second row (phosphorus, sulfur), but not one from the first (nitrogen, oxygen).

In recent years, the validity of the d-orbital has been justified most frequently by reference to some experimental observations by Doering and Hoffmann⁶ and by Oae and his coworkers.⁷ In Doering's work, ΔG^\ddagger_{298} for deuterio-catalyzed hydrogen-deuterium exchange in Me_4N^+ , Me_4P^+ , and Me_3S^+ was found to be 36.7, 24.4, and 22.7 kcal/mol, respectively. In Oae's work, the rates of ethoxide-catalyzed tritium-hydrogen exchange of $^3\text{HCPH}(\text{SEt})_2$ and *tert*-butoxide-catalyzed tritium-hydrogen exchange of $^3\text{HCPH}(\text{OEt})_2$ were estimated to differ by a factor of 5×10^5 . To these observations may be added the finding, by Gilman and Webb,⁸ that thioanisole undergoes side-chain metalation by *n*-butyllithium, but anisole is metalated in the ring. There are a number of practical consequences of these differing properties, of which one, the Corey-Seebach reaction,⁹ merits special attention. In this reaction, *m*-dithiane is successively metalated (at C2), alkylated, and hydrolyzed to form an aldehyde. Alternatively, the alkylated dithiane may be metalated a second time and alkylated again to yield a ketone following hydrolysis. The sequence cannot be applied to *m*-dioxane, because this compound is stable to the metalation conditions.

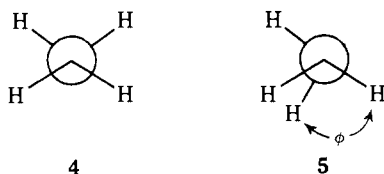
During the period 1967-1970, we performed a series of nonempirical molecular-orbital investigations of the stereochemical capabilities of some of these sulfur-stabilized carbanions.¹⁰ These led to the predictions that **1**, **2**, and **3** are the stable structures in the gas phase of the α -thio, α -sulfinyl, and α -sulfonylcarbanions, respectively. Although it was realized^{10b,11} that these results might change somewhat when it became possible to bring the quality of the computations from the minimal basis set closer to the Hartree-Fock limit, this early work did correctly anticipate the tendency of carbanions **1-3** to exist preferentially in conformations having the maximum number of gauche interactions between adjacent electron pairs and/or polar bonds; and it continues to be employed as the theoretical foundation for the discussion and interpretation of experimental observations.¹²



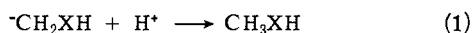
It was not at first evident why **1-3** should represent minima on conformational hypersurfaces since, intuitively, such structures ought to have been destabilized by a minimization of repulsive forces between the adjacent electron pairs and polar bonds. The postulate of $(p \rightarrow d)_\pi$ conjugation in these species offered a possible solution to the problem, provided that such conjugation could be shown to exhibit a conformational dependence.^{3e,13} However, this kind of explanation was made untenable, within the framework of the minimal basis set calculations, by the finding that the same

energy minimum resulted with and without d-type functions in the basis set; and when the d-type functions were employed, these were found not to participate in the bonding.¹⁴

Eventually, the connection was made between the structures adopted by 1–3 and those of a much larger class of molecules, characterized by the presence of two directly bonded heteroatoms.¹⁵ Thus, conformation 4, which would appear to minimize repulsive interactions between adjacent electron pairs, is an energy maximum on the rotational potential of hydrazine.¹⁶ The stable conformation is 5, with a dihedral angle, ϕ , of 94°. ¹⁷ Since an essential property of the d-orbital model is that it may *not* be applied to the treatment of molecules containing only atoms of the first row,^{4a} it is evident that the gauche effect^{15b} in hydrazine is not the result of d-orbital effects. Yet hydrazine and carbanions 1–3 have very similar structures. This fact strengthens our conclusion that d-orbital conjugation cannot be involved in a significant way in deciding the stereochemistry of sulfur-stabilized carbanions.¹⁸



It then followed logically that d-orbital conjugation might also not be an important factor in the enhanced acidity discussed above. To treat this problem quantitatively required that a comparative quantum chemical study be made of the effect of d-type functions upon the structures and/or proton affinities of carbanions adjacent to oxygen and to sulfur. The systems selected for investigation are shown in eq 1, where X is oxygen or sulfur. In the first stage of the



work, the total energy of methanol was calculated, with optimization of the C–O bond length and the COH angle;²⁰ then the total energy of CH_2OH^- , the tautomeric form of methoxide ion, was calculated²¹ with optimization of the dihedral angle, θ , associated with rotation about the C–O bond, and the pyramidal angle, ϕ , at the carbanionic center. The final geometry optimization of the C–O bond length and the COH angle has been performed in the present work, which also includes the results for CH_3OH , CH_3S^- , and CH_2SH^- , the latter at a much improved level of approximation than that employed earlier.^{10d} The principal objectives of the computations were, first, to determine whether the difference in the calculated proton affinities of CH_2OH^- and CH_2SH^- is in the proper direction; secondly, to determine whether the difference, if any, is affected by the inclusion of d-type functions in the basis set; and, thirdly, by comparison with the earlier results^{10d} and those of minimal (STO-3G) and split-valence shell (4-31G) computations using Gaussian 70²² to determine the basis set dependence of the conformational hypersurface of 1. Each of these objectives has now been reached; in addition, the large amount of data that have been generated has allowed a rather detailed comparison of systems containing C–O and C–S bonds.

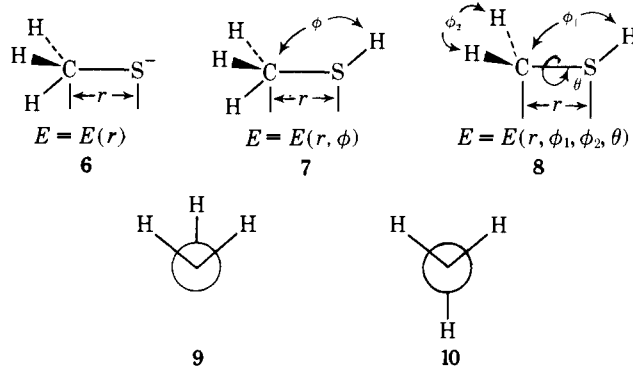
Method

Computations were performed at three levels of approximation, termed minimal basis, split-valence basis, and double ζ basis. The first two made use of the standard STO-3G and 4-31G basis sets of the Gaussian 70 programme system²² and do not include d-type functions. The double ζ calculations were performed using contracted Gaussian basis

sets, which have been optimized for C and O by Huzinaga,²³ for H by Basch et al.,²⁴ and for S by Veillard.²⁵ These basis sets were augmented, where appropriate, by one (for O)²⁶ or two (for S)²⁷ sets of d-type functions. For CH_3OH and CH_2OH^- , the full basis sets consisted of 90 and 86 primitive gtf, contracted to 34 and 32 basis functions, respectively. For CH_3SH and CH_2SH^- (or CH_3S^-), the corresponding numbers were 101 and 97, contracted to 48 and 46, respectively. The molecular orbitals were expanded in terms of these basis functions and the expansion coefficients obtained by the Roothaan procedure, using either IBMOL 4²⁸ (and IBM 360/75 or 370/165 computers) or a modified POLYATOM 2 system²⁹ (and a CDC 6600 computer). The CH, SH, and OH bond lengths were held constant throughout all of the work at 1.0910, 1.3330, and 0.9600 Å, respectively.

Results and Discussion

Geometry Optimization of CH_3S^- , CH_3SH , and CH_2SH^- . The internal parameters subjected to geometry optimization are shown in 6, 7, and 8 for CH_3S^- , CH_3SH , and CH_2SH^- , respectively. Optimization of 6 consisted of computation of the stretching potential $E = E(r)$ and, of 7, computation of two cross sections [$E = E(r)$ and $E = E(\phi)$] of the stretching–bending potential surface $E = E(r, \phi)$. The mapping of the energy hypersurface of 8, $E = E(r, \phi_1, \phi_2, \theta)$ was performed in four stages, each geometric parameter being optimized separately. Two rotational conformers were of particular interest in this study by analogy to the earlier work on CH_2OH^- :²¹ the W conformation 9 and the Y conformation 10.



Effect of Basis Set on the Computed C–S Bond Length of CH_3S^- . The results are shown in Figure 1. The energy at the optimized bond length is lower by nearly 0.5 au³⁰ when the double ζ basis set is employed, because this basis set, which contains d-type functions on sulfur, provides a more complete mathematical description of the total electron density of the molecule. It is noteworthy, however, that the same bond length (1.908 vs. 1.910 Å) is obtained with the split-valence basis set, so that this geometrical parameter is probably not sensitive to the presence or absence of d-type functions in the computations when the negative charge is placed on sulfur.

Geometry Optimization of CH_3SH . The two cross sections of the stretching–bending potential surface were obtained with the double ζ basis set. Variation of the C–S bond length, with the CSH angle set at 96.5°, afforded a minimum at 1.857 Å. Then variation of the CSH angle led to a minimum at 95.95°. In general,^{31a,b} Hartree–Fock wavefunctions overestimate bond lengths somewhat. Thus the double ζ basis set predicts a slightly longer C–S bond than is observed experimentally (1.819 Å);^{31c,d} however, the experimental CSH angle (96.5°)^{31d} is reproduced very well.

Geometry Optimization of CH_2SH^- with the Double ζ Basis Set, Including d-Type Functions. The four stages in

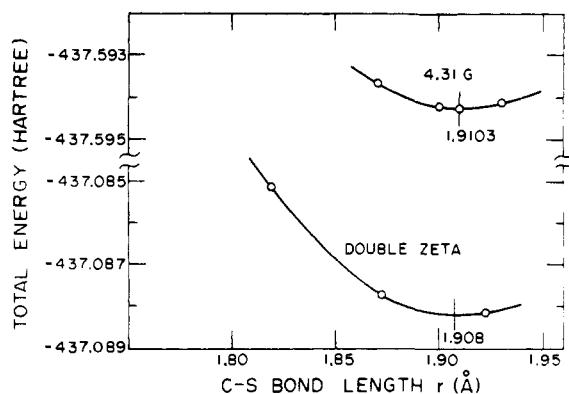


Figure 1. Optimization of the C-S bond length of CH_3S^- with the 4-31G and double ζ basis sets.

Table I. The Four Stages of the Geometry Optimization of CH_2SH^-

Cross Section	Independent variables			
	r , Å	ϕ_1 , deg	ϕ_2 , deg	θ , deg
$E = E(r)$	Variable	96.5	109.5	180
$E = E(\phi_1)$	1.8718 ^a	Variable	105	0, 180
$E = E(\phi_2)$	1.8718 ^a	107.56 ^b	Variable	0, 180
$E = E(\theta)$	1.8718 ^a	107.56 ^b	105 ^c	Variable

^a The actual r^{opt} was found to be 1.8714 Å. ^b The actual ϕ_1^{opt} at $\theta = 0^\circ$ (Y conformation) was found to be 100.17° and at $\theta = 180^\circ$ (W conformation) was found to be 107.73° . ^c The actual ϕ_2^{opt} at $\theta = 0^\circ$ was found to be 104.17° and, at $\theta = 180^\circ$, was found to be 106.48° .

Table II. Optimized Geometry of CH_2SH^- as Computed with the Double ζ Basis Set

Geometric parameter	W conformer ^a	Y conformer ^b
C-S	1.8714 Å (1.957 Å) ^c	1.8714 Å ^e
$\angle \text{CSH}$	107.73° (109.31°)	100.17°
$\angle \text{HCH}$	106.48° (106.48°)	104.17°
$\angle \text{HCS}$	106.48° (105.68°)	104.17°
θ	0° (0°)	180°
C-H ^d	1.091 Å (1.091 Å)	1.091 Å
S-H ^d	1.330 Å (1.330 Å)	1.330 Å

^a Total energy, -437.019452 hartrees. ^b Total energy, -437.016604 hartrees. ^c Data in parentheses are obtained with the 4-31G basis set. ^d Not optimized. ^e Not reoptimized for the Y conformation.

the geometry optimization are summarized in Table I. These computations revealed the W and Y conformations, as expected,²¹ to represent the energy minima of the rotation-inversion surface, with the W having the lower energy. The geometrical parameters of these two conformations are collected in Table II. It is evident that there is some relaxation in the molecule in the course of rotation about the C-S bond,³² the larger HCH and CSH angles in the W conformation being caused by a reflex effect,^{33a,b} i.e., a movement of the nuclei away from each other in the more crowded conformation.³⁴

The optimized C-S bond lengths of CH_3S^- , CH_3SH , and CH_2SH^- (W conformation) are 1.908, 1.857, and 1.871 Å, respectively. The fact that the bond is longer in CH_2SH^- than in CH_3SH suggests the absence of special, i.e., $[(p \rightarrow d)_\pi \text{ conjugative}]$ effects in this anion, because such effects are expected to be manifested by a decrease in the bond length. For example, removal of H^- from methanol to form the cation $^+\text{CH}_2\text{OH}$, which exhibits $(p-p)_\pi$ conjugation, is accompanied by a decrease of at least 0.14 Å in the C-O bond length.³⁶ It seemed desirable to check this point, and the geometry of the W conformation of CH_2SH^- was, therefore, reoptimized with the split-valence basis set.

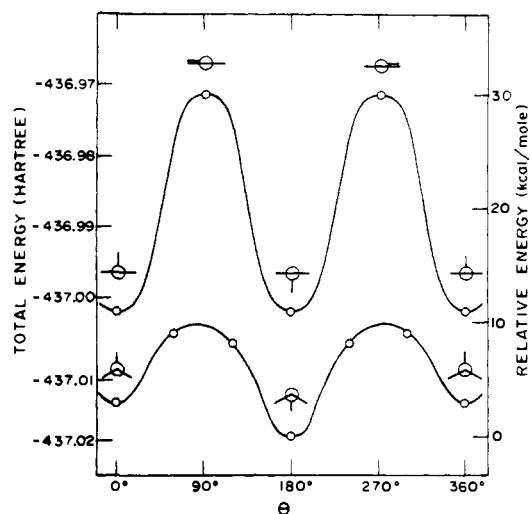


Figure 2. Cross sections of the hypersurface of CH_2SH^- corresponding to planar (upper curve, $\phi_2 = 120^\circ$) and pyramidal (lower curve, $\phi_2 = 105^\circ$) configurations at carbon.

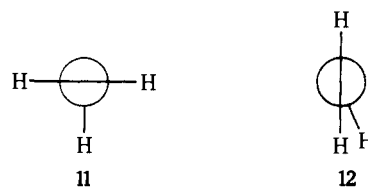
Table III. Total Energies of CH_3SH and CH_2SH^- as a Function of Rotation About the C-S Bond

Rotational angle (θ°)	Energy, hartrees		
	CH_3SH^b	CH_2SH^- ($\phi_2 = 105^\circ$) ^c	CH_2SH^- ($\phi_2 = 120^\circ$) ^c
0	-437.69073 ^d	-437.01473	-437.00196
60	-437.68919	-437.00491	
90			-436.97149
120	-437.69073	-437.00623	
180	-437.68919	-437.01928	-437.00196

^a C-S bond length 1.8718 Å. ^b CSH bond angle 96.5° . ^c CSH bond angle 107.56° . ^d Staggered conformation.

The C-S bond length was found to be 1.957 Å, i.e., longer than that of CH_3S^- or CH_3SH . The difference in the CH_2SH^- bond lengths computed by the double ζ and split-valence basis sets is a result of the great sensitivity of the geometry of this anion to changes in the quality of the basis set. The geometrical parameters obtained in the split-valence optimization are shown in parentheses in Table II.

Table III summarizes the data for rotation along the C-S bond in CH_3SH and for two cross sections of the CH_2SH^- hypersurface corresponding to rotation along the C-S bond with pyramidal (105°) and planar (120°) configurations at carbon. These latter rotational curves are shown in Figure 2, from which the greater stability of the W conformation is again evident. The minimum in the planar carbanion corresponds to the T conformation **11** and the maximum to the I conformation **12**; the computed barrier in this curve is 19.1



kcal/mol and reflects the effect of conjugative destabilization in this system.³⁷ Since the geometry was not permitted to relax during the rotation of **7** and **8**, some deviation from experimental results is anticipated in these barriers. Thus the calculated 1.01 kcal/mol barrier in CH_3SH can be expected to differ from the experimental value (1.26 kcal/mol)³⁸ because of the use of fixed CH and SH bond lengths in the calculations and the same C-S bond length and CSH angle in the eclipsed conformation as those optimized for

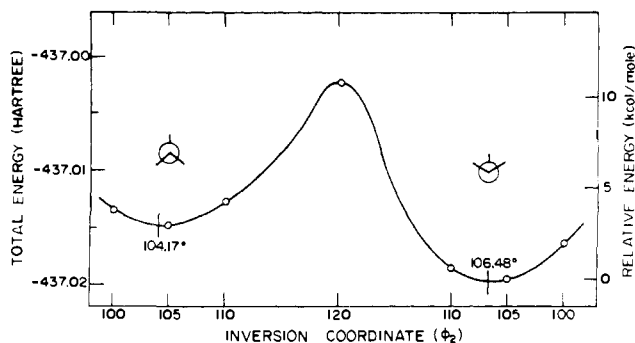


Figure 3. Interconversion of the W and Y conformations of $^-CH_2SH$ by pyramidal inversion at carbon (double ζ computations). The geometrical parameters are $r(C-S) = 1.8713 \text{ \AA}$; $\angle CSH = 107.56^\circ$.

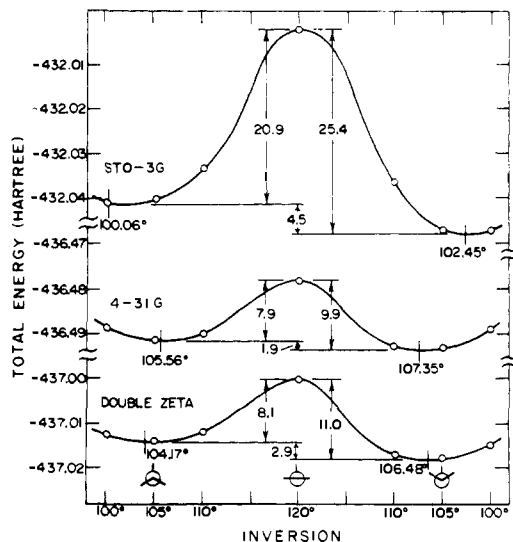


Figure 4. Pyramidal inversion at carbon in $^-CH_2SH$ as a function of basis set.

the staggered.³⁹ With this caveat in mind, the computed rotational barrier in $^-CH_2SH$ ($W \rightleftharpoons Y$) is 9.9 kcal/mol.

Figure 3 displays a cross section of the rotation-inversion surface of $^-CH_2SH$ corresponding to interconversion of the W and Y conformations by pyramidal inversion. The computed barrier is 11.0 kcal/mol. The data shown in this Figure permit the optimized carbanion valence angles to be computed.

Effect of Basis Set Upon Pyramidal Inversion at Carbon in $^-CH_2SH$. Participation of the d-type functions of sulfur in the ground state of $^-CH_2SH$, which may be associated with the existence of $(p \rightarrow d)_\pi$ conjugation, can be probed in several ways, including their effect upon the conformational hypersurface. Of particular interest was the effect of basis set upon the interconversion of the W and Y conformations by pyramidal inversion, because it is known that inversion barriers are more sensitive than rotational barriers to the quality of the basis set.⁴¹ The results of this study are summarized in Figure 4, which shows that the greater stability of the W conformation is reproduced by all basis sets.⁴² Rauk's results^{10d,44} have not been included in Figure 4, because the Y conformation was found to be a saddle point rather than a minimum on the rotation-inversion surface. The rotational cross section through the minimum of Rauk's surface is contrasted with the present double ζ rotational cross section in Figure 5.

It seems clear that improvement of the basis set from minimal to split valence to double ζ plus d-type functions leads to an improvement of the total energy of the system but to no fundamental change in the geometry of the

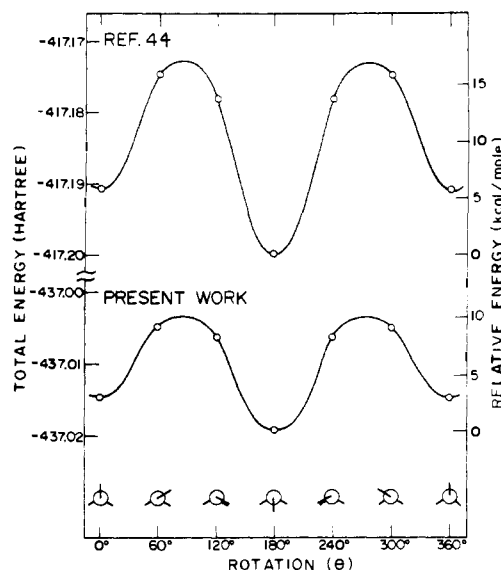
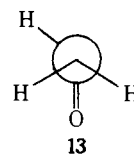


Figure 5. The total energy of $^-CH_2SH$ as a function of rotation along the C-S bond. Upper curve: minimal basis set computations. Lower curve: double ζ computations.

ground state. This is, of course, a well-known phenomenon⁴⁵ and merely serves as an additional demonstration that d-type polarization functions^{45c} have mathematical but not stereochemical significance. From the standpoint of the geometry, *there is thus no evidence for $(p \rightarrow d)_\pi$ conjugation in $^-CH_2SH$.*

However, one important difference between the double ζ computations on $^-CH_2SH$ and $^-CH_2OH$,²¹ which find both W and Y conformations to be stable, and the earlier^{10d} minimal basis set computation on $^-CH_2SH$ deserves comment. It now appears very probable that, although each of the earlier calculations¹⁰ correctly predicted stability for the conformation having the maximum number of gauche interactions between adjacent electron pairs and polar bonds (corresponding to the W conformation of $^-CH_2SH$), the relative stability of this conformation was systematically overestimated. Thus, in contrast to the present results, only one conformation (**1**, **2**, and **3**) was found to be stable. Since the energy difference between the W and Y conformations of $^-CH_2SH$ is now calculated to be 1.9 kcal/mol, as opposed to the earlier value (see Figure 5) of 6.1 kcal/mol, and since conformation **13** of the α -sulfinylcarbanion $^-CH_2SHO$ was found earlier^{10a,b} to be only 2.2 kcal/mol less stable than **2**, improvement of the earlier computation may now be expected to lead to stability for both **2** and **13**, with **13** perhaps having the lower energy. Since recent experimental investigations suggest that the kinetic acidity of an α proton anticoplanar to the SO bond of a sulfoxide is greater than that of a proton located on the bisector of the oxygen-sulfur-sulfur lone-pair angle,^{12c,d} corresponding to kinetic preference for the formation of a carbanion analogous to **13**, recomputation of $^-CH_2SHO$ with the double ζ basis set is now necessary, and such a study has been initiated.⁴⁶



The Molecular Orbitals and Charge Distribution in $^-CH_2SH$. The contribution of the d-type functions to the SCF-MO's of $^-CH_2SH$ has been assessed by consideration of the coefficient matrix and charge distribution of the

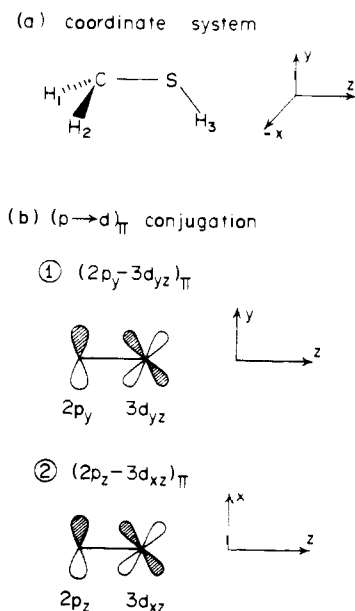


Figure 6. The nature of $(p \rightarrow d)_\pi$ conjugation in $^-CH_2SH$ (b) in terms of the coordinate system shown in (a).

anion in the *W* conformation. In the coordinate system shown in Figure 6, two $(p \rightarrow d)_\pi$ type interactions are possible, viz., $(C_{2p_y} - S_{3d_{yz}})_\pi$ and $(C_{2p_z} - S_{3d_{xz}})_\pi$. For $(p \rightarrow d)_\pi$ conjugation to be present, it is necessary that the coefficients of C_{2p_y} and $S_{3d_{yz}}$ or those of C_{2p_z} and $S_{3d_{xz}}$ be non-zero.

Figure 7 shows schematically the three highest occupied molecular orbitals (13, 12, and 11), the magnitudes of these MO being represented qualitatively by the sizes of their orbital lobes. Table IV lists the coefficients of the C_{2p} and S_{3d} functions of these three MO. The HOMO (MO 13) is essentially the carbon lone-pair orbital and, intuitively, would have been expected to exhibit the greatest $(p \rightarrow d)_\pi$ interaction. This MO belongs to the a' representation, and it contains the $(C_{2p_y} - S_{3d_{yz}})_\pi$ interaction. The $(C_{2p_y} - S_{3d_{yz}})_\pi$ interaction also appears in MO 11 (a'), which is essentially the sulfur sp^2 -type lone-pair orbital. Molecular orbital 12 (a'') is essentially the sulfur $3p$ lone-pair orbital and contains the $(C_{2p_x} - S_{3d_{xz}})_\pi$ interaction.

Comparison of the data of Table IV with those of Tables VIII and IX of ref 10b reveals that the coefficients of the sulfur $3d$ functions of the above three MO's are somewhat larger than those computed earlier for $^-CH_2SHO$.

The sulfur $3d$ -orbital coefficients are especially large in MO 11 for the $3d_{x^2}$, $3d_{y^2}$, and $3d_{z^2}$ functions. However, as we have pointed out elsewhere,^{10b} the sum of these functions should correspond mathematically to the spherically symmetrical sulfur $3s$ orbital. But because there is a non-spherical charge distribution around sulfur in $^-CH_2SH$, the coefficients of the $3d_{x^2}$, $3d_{y^2}$, and $3d_{z^2}$ functions are not the same. Nevertheless, on symmetry grounds, these orbitals cannot contribute to the $(p \rightarrow d)_\pi$ conjugative interaction.

The data of Table IV indicate that the HOMO has the greatest $(p \rightarrow d)_\pi$ interaction, as expected. However, it is clear that the $S_{3d_{yz}}$ orbital coefficients are substantially smaller than those of the C_{2p_y} orbitals in this MO so that $(p \rightarrow d)_\pi$ conjugation can hardly be considered to constitute an essential basis for the explanation of the properties of $^-CH_2SH$.

Charge distribution in $^-CH_2SH$ may be estimated from a population analysis. The net orbital populations of $S_{3d_{yz}}$ and $S_{3d_{xz}}$ are respectively 0.025 and 0.002. These weights are too small to permit chemical significance to be attached to $(p \rightarrow d)_\pi$ conjugation. Figure 8 shows the total overlap

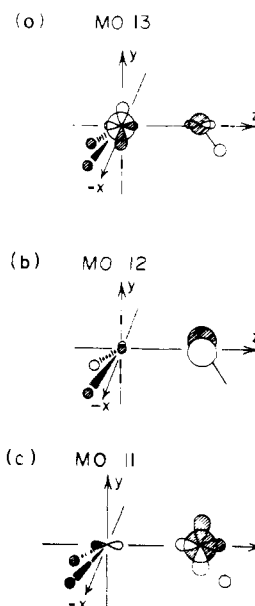


Figure 7. Schematic drawings of the three highest occupied molecular orbitals of the *W* conformation of $^-CH_2SH$.

Table IV. The Coefficients of the C_{2p} and S_{3d} Orbitals Which Are Appropriate for $(p \rightarrow d)_\pi$ Interaction^a in Molecular Orbitals 11, 12, and 13

MO No.	Symmetry	Basis type	Coefficients	
			C_{2p}	S_{3d}
13	a'	Inner	-0.2851 (y)	0.0197 (yz)
		Outer	-0.5220 (y)	0.0956 (yz)
12	a''	Inner	0.0907 (x)	-0.0039 (xz)
		Outer	0.0990 (x)	-0.0222 (xz)
11	a'	Inner	-0.0391 (y)	0.0018 (yz)
				0.0225 (x^2)
				0.0112 (y^2)
		Outer		0.0029 (z^2)
				-0.0150 (yz)
				-0.1658 (x^2)
		-0.2050 (y^2)		
		-0.2597 (z^2)		

^a Symbols in parentheses refer to the type of basis function.

populations of $^-CH_2SH$, as well as those of the three highest occupied MO for computations performed with and without d -type functions on sulfur. Molecular orbitals 12 and 13 are antibonding between carbon and sulfur, and MO 11 is bonding in the same region.

Inclusion of d -type functions increases the C-S bond overlap population of the HOMO by 0.052, which corresponds to about 18% of that obtained with an sp -basis set. In MO 12, the increase in the C-S bond overlap population upon addition of d -type functions to the basis set is 0.016, and in MO 11, it is -0.006. This latter effect is reasonable because the $(C_{2p_y} - S_{3d_{yz}})_\pi$ interaction in this MO is antibonding (see Table IV).

In the HOMO, the contribution to the C-S overlap population from the $(C_{2p_y} - S_{3d_{yz}})_\pi$ interaction is 0.086. Since the *total* overlap population of the C-S bond with an sp basis set is 0.200, one might conclude that $(p \rightarrow d)_\pi$ conjugation is important. However, it must be noted that the spd basis set gives a *total* C-S bond overlap population of 0.194, i.e., that addition of the d -type functions causes a *decrease* in the total overlap population of the C-S bond.

With d -type functions in the basis set, a rather significant change is observed in the region of the *SH* bond. The total S-H bond overlap population increases by 0.182 with inclusion of d -type functions, but the atomic population of H_3 decreases by 0.326. The same trends are seen in the

Population Analysis

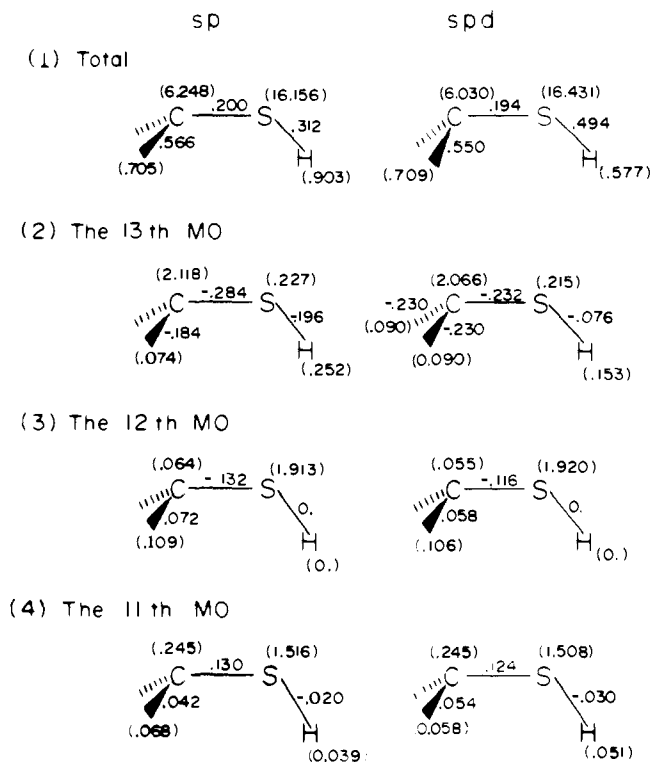
Atomic and overlap populations
with and without d functions

Figure 8. The total atomic and overlap populations of CH_2SH^- together with those of the three highest occupied molecular orbitals, as computed with sp and spd basis sets on sulfur.

HOMO: the change in the S-H bond overlap is 0.080, and in the H_3 atomic population, it is -0.099 . Thus, the effect of the d-type functions is more pronounced in the region of the S-H bond than in the region of the C-S bond. Such a result appears to be incompatible with the traditional view of the meaning of d-orbital conjugation; and it must be concluded that the presence of d-type functions on sulfur causes a redistribution of charge in the region of this atom, i.e., that they behave as polarization functions.⁴⁵ In agreement with this interpretation is the finding that the change in population in the regions of the C-H bonds is small (see Figure 8).

If the problem is now analyzed in terms of group representation theory,⁴⁸ it is noted that there is mixing of the C_{2p_y} (C_{2p_x}) and $\text{S}_{3d_{yz}}$ ($\text{S}_{3d_{xz}}$) orbitals in CH_2SH^- , because these belong to the same representation. We wish to know what chemical significance can be attached to this mathematical mixing. The question may be answered indirectly by consideration of the molecular properties calculated without the d-type functions. If these can be understood without these functions, then, from a practical standpoint, there is no need to invoke 3d-orbital participation in the chemical bonding. However, from a pedagogical standpoint, it would be desirable to offer an alternative model.

Such a model can be constructed upon recognition of the fact that there is a large electron cloud associated with the sulfur atom. Since a large electron cloud adjusts more readily to changes in the molecular environment than a small electron cloud, the generation of a charged center adjacent to the larger cloud (e.g., a carbanionic center adjacent to sulfur) will be facilitated.

It follows that it should be possible to account for differences between sulfur and oxygen in terms of some appropri-

Table V. Polarizabilities of Neutral Oxygen and Sulfur Atoms

Atom	$\langle r^2 \rangle^a$ (\AA^2)	α_{calcd}^b (\AA^3)	α^c (\AA^3)	α_{expt}^d (\AA^3)
O	0.5530	0.732	0.675	0.77 ± 0.06^d
S	1.418	3.45	2.34	

^a These values are respectively the Hartree-Fock second moments of the O_{2p} and S_{3p} orbitals of the neutral atoms. See C. Froese-Fischer, *At. Data*, 4, 301 (1972). ^b J. Thorhallson, C. Fisk, and S. Fraga, *Theor. Chim. Acta*, 10, 388 (1968). ^c Calculated from eq 2 from the second moments listed above and approximating Δ as the average of the first excitation energy and the ionization potential. For the latter quantities, see C. E. Moore, "Atomic Energy Levels", NBS Circular 467, 1949, 1952, and 1958; E. Clementi, *J. Chem. Phys.*, 38, 1001 (1963). ^d R. A. Alpher and D. R. White, *Phys. Fluids*, 2, 153 (1959); quoted by R. R. Teachout and R. T. Pack, *At. Data*, 3, 195 (1971).

ate quantity which is proportional to the size of the charge cloud. Such a quantity is the atomic polarizability.

The size of an atom, as measured by $\langle r^2 \rangle$, is related to its polarizability, α , by eq 2,⁴⁹ where Δ refers to the average energy difference between the ground state and the excited states. Table V summarizes the appropriate data for oxygen and for sulfur.

$$\alpha = 2/3 \frac{\langle r^2 \rangle}{\Delta} \quad (2)$$

Since polarizability measures the amount of distortion (change in size) suffered by the electron cloud when a unit amount of energy is supplied, this quantity clearly reveals a fundamental difference between O and S. In contrast, the d-orbital model depends explicitly upon the presence of low-lying d orbitals. Clearly, when many low-lying excited states exist, the average excitation energy Δ will become small, and the polarizability will increase. If we now consider the low-lying d orbitals to be important in some low-lying excited states, it follows that the experimental observable polarizability contains the concept of $(p \rightarrow d)_\pi$ conjugation so that in its primitive form the concept is unnecessary.⁶⁶

Completion of the Geometry Optimization of CH_2OH^- . The earlier geometry optimization of CH_2OH^- ²¹ revealed the Y conformation to represent the lower minimum, with a carbanion angle of 105° . To complete the geometry optimization, computations were performed using the double ζ basis set, with variation of the C-O bond length and COH angle. These led to values of 1.550 \AA and 114.15° and an energy of -114.312732 au.

Comparative Behavior of the Oxygen and Sulfur Anions

Basis-Set Dependence of the Proton Affinities of CH_2OH^- and CH_2SH^- . For this study, the energies of the four species CH_3XH ($\text{X} = \text{O}, \text{S}$) and CH_2SH^- ($\text{X} = \text{O}, \text{S}$) were recomputed at the geometries optimized with the double ζ basis set, i.e., sp in the case of CH_3OH and CH_2OH^- and spd in the case of CH_3SH and CH_2SH^- . The energies of CH_3OH and CH_2OH^- with an spd basis set were obtained by addition of a set of d-type functions to the double ζ basis for oxygen; those of CH_3SH and CH_2SH^- for an sp basis set were generated by deletion of integrals associated with the d-type functions from the SCF computations.

The computed energies with sp and spd basis sets on the heteroatoms are summarized in Table VI. It is evident that the proton affinity of CH_2SH^- is lower than that of CH_2OH^- with both basis sets, i.e., the gas-phase acidity of a C-H bond adjacent to sulfur is greater than that of a C-H bond adjacent to oxygen, whether d-type functions are employed on the heteroatoms or not.⁵⁰ The inclusion of the d-type functions in the basis set leads to a lowering of the energy in all cases, as expected for a more complete wave function, but the energy lowering is almost exactly the same

Table VI. The Computed Proton Affinities of $\bar{\text{C}}\text{H}_2\text{SH}$ and $\bar{\text{C}}\text{H}_2\text{OH}$ as a Function of Basis Set

Species	Basis on the heteroatom	Total energy, hartrees	Theoretical proton affinity, kcal/mol
$\bar{\text{C}}\text{H}_2\text{SH}$ (W)	sp	-436.98006	-423.3
	spd	-437.01945	-421.4
CH_3SH	sp	-437.65441	
	spd	-437.69080	
$\bar{\text{C}}\text{H}_2\text{OH}$ (Y)	sp	-114.31273	-438.3
	spd	-114.33268	-443.5
CH_3OH	sp	-115.01105	
	spd	-115.03928	

Table VII. Parameters of the Analytical Equations of the Rotation-Inversion Surfaces of $\bar{\text{C}}\text{H}_2\text{SH}$ and $\bar{\text{C}}\text{H}_2\text{OH}$

Parameter ^a	$\bar{\text{C}}\text{H}_2\text{SH}^b$	$\bar{\text{C}}\text{H}_2\text{OH}^c$
E_0	-437.01282597	-114.30253607
C_1	0.00001265	0.00001853
C_2	0.02613046	0.03809257
C_3	0.00561326	0.00639175
C_4	0.00000707	-0.00000641
C_5	0.00959275	0.00404175
C_6	0.00015319	-0.00055660
C_7	-0.00000010	0.00000047
C_8	-0.00004049	-0.00004401
C_9	0.00000009	-0.00000009

^a $\alpha = 0.0162$. ^b Rms deviation 0.00013446. ^c Rms deviation 0.00038153.

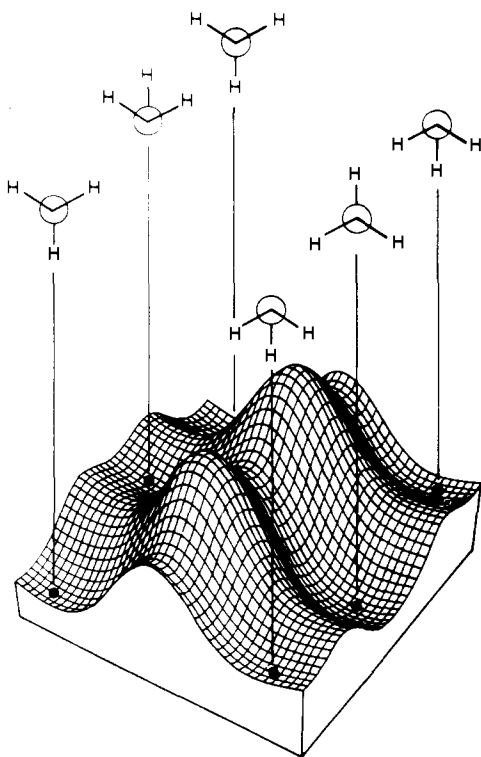


Figure 9. The rotation-inversion surface of $\bar{\text{C}}\text{H}_2\text{OH}$. The rotation and inversion barriers (Y to W) are 10.6 and 20.5 kcal/mol, respectively. The W conformation is 6.67 kcal/mol higher than the Y conformation.

in CH_3SH and in $\bar{\text{C}}\text{H}_2\text{SH}$. This equality shows that the d-type functions have the expected mathematical effect but without chemical significance in the present context. Therefore, the enhanced acidity of a proton adjacent to sulfur cannot be caused by d-orbital effects.⁵¹

Topomerization⁵² of $\bar{\text{C}}\text{H}_2\text{OH}$ and $\bar{\text{C}}\text{H}_2\text{SH}$. For both carbanions, surfaces were generated, with the double zeta basis set, for rotation about the C-X bond and inversion of the carbanion angles. Standard least-square curve fitting

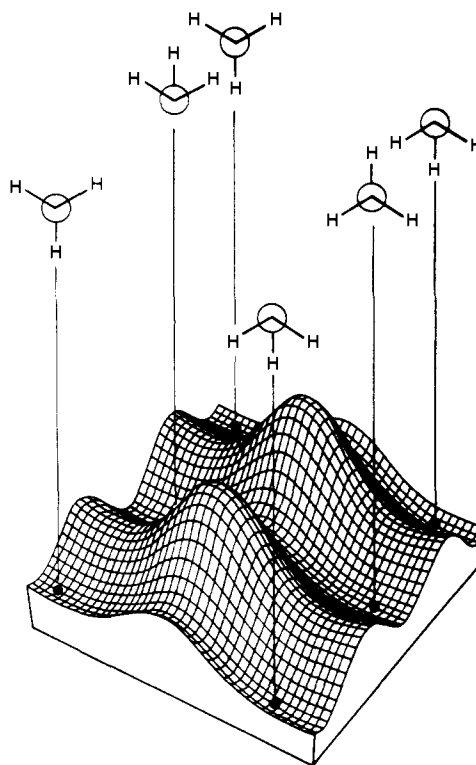


Figure 10. The rotation-inversion surface of $\bar{\text{C}}\text{H}_2\text{SH}$. The rotation and inversion barriers (W to Y) are 9.9 and 11.0 kcal/mol, respectively. The W conformation is 1.9 kcal/mol lower than the Y conformation.

methods were used to fit a suitable function of linear parameters to the set of calculated points available in each case. In order to take advantage of the symmetry of the surface, two new variables were defined: for inversion $\delta = \pm(\phi - 120^\circ)$ such that, at $\theta = 0^\circ$, plus refers to the W conformation and minus to the Y conformation, and for rotation $\epsilon = (\theta - 90^\circ)$. The function must be invariant under $(\delta, \epsilon) \rightarrow (-\delta, -\epsilon)$ and $(\delta, \epsilon) \rightarrow (\delta, \epsilon + 2n\pi)$. The following was found to be appropriate, giving a maximum of 1% deviation relative to the maximum energy difference in the surface:

$$E = E_0 + C_1\delta^2 + C_2e^{-\alpha\delta^2} + C_3 \cos 2\epsilon + C_4\delta^2 \cos 2\epsilon + C_5e^{-\alpha\delta^2} \cos 2\epsilon + C_6\delta \sin \epsilon + C_7\delta^3 \sin \epsilon + C_8\delta \sin 3\epsilon + C_9\delta^3 \sin 3\epsilon \quad (3)$$

Table VII gives the parameters of the analytic equations that were fitted to the calculated points. With the aid of these expressions, two 41×41 grids were generated, which were necessary for the plotting⁵³ of the rotation-inversion surfaces. Perspective views of these surfaces are shown in Figures 9 and 10, for $\bar{\text{C}}\text{H}_2\text{OH}$ and $\bar{\text{C}}\text{H}_2\text{SH}$, respectively.

These surfaces may now be employed to provide a theoretical description of the processes depicted in Scheme I. In this scheme, Y and W are diastereomeric, and Y and \bar{Y} and W and \bar{W} are enantiomeric. The class of compound depicted here may undergo a series of conformational changes which transform it into its own mirror image. The rate of the process, referred to as "topomerization" or "degenerate racemization," can often be studied conveniently by NMR because, when the transformation is slow on the NMR time scale, the stereochemical labels (shown here as methylene protons) are diastereotopic⁵⁴ and, usually, anisochronous; and when the process is fast, these protons are enantiotopic and isochronous. The rate constant for the process is then obtained by the usual⁵⁵ DNMR methods. One then wishes

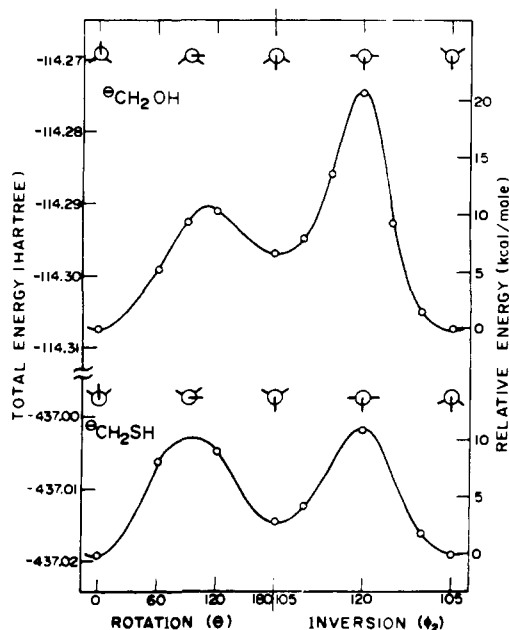
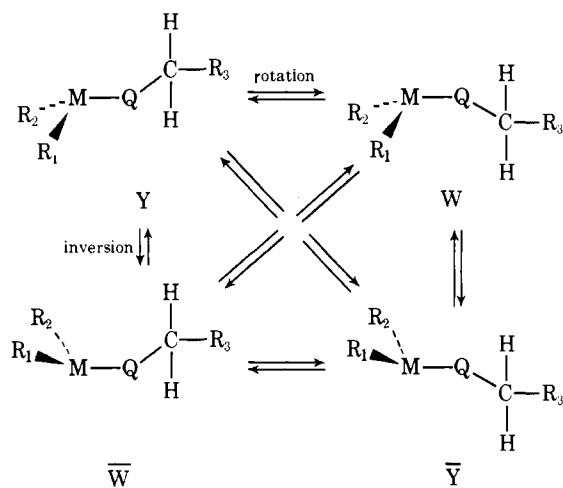


Figure 11. The reaction coordinate for topomerization of ${}^{-}\text{CH}_2\text{OH}$ (upper curve, $Y \rightleftharpoons Y$) and ${}^{-}\text{CH}_2\text{SH}$ [lower curve ($W \rightleftharpoons W$)].

Scheme I



to know what is being measured by these rate constants. The overall process must involve both rotation about the M-Q bond and pyramidal inversion at M. Linear inversion at Q can be excluded, because this process requires much higher energy than either of the other two.²⁰ Consequently, topomerization may involve rotation followed by inversion, inversion followed by rotation, or coupled rotation-inversion.⁵⁶ The first two correspond to the horizontal and vertical directions of the scheme and the third to the diagonals. As we have noted elsewhere,²¹ such molecules have twofold rotational barriers, typically in the range 10–20 kcal/mol. When M is a carbanionic center or nitrogen, the inversion barrier is also in the range 10–20 kcal/mol, especially when Q is an electron-withdrawing atom or a heteroatom bearing lone pairs.⁵⁷ Consequently, for such systems, experimental distinction between rotation-dominated and inversion-dominated topomerization is not easy. However, the studies of Raban and his coworkers⁵⁸ appear to have demonstrated that alkyl-substituted hydroxylamines (M = nitrogen; Q = oxygen) undergo inversion-dominated and sulfenamides (M = nitrogen; Q = sulfur) rotation-dominated topomerization.

The anion ${}^{-}\text{CH}_2\text{OH}$ is isotropic and isoelectronic with

hydroxylamine, and ${}^{-}\text{CH}_2\text{SH}$ is isotropic and isoelectronic with H_2NSH , the simplest sulfenamide. As discussed elsewhere,²¹ there are many similarities between the computed properties of ${}^{-}\text{CH}_2\text{OH}$ and those of H_2NOH ; we believe, therefore, that the surfaces shown in Figures 9 and 10 can be used to discuss theoretically the topomerization of hydroxylamines and sulfenamides. The process of coupled rotation-inversion proceeds via a reaction coordinate which contains one transition state between enantiomeric species; such a reaction coordinate has reflection symmetry and is termed symmetric. For both anions, the transition state associated with the symmetric reaction coordinate corresponds to the I conformation **12**. Since this is the energy maximum of both rotation-inversion surfaces, the symmetric path is disfavored energetically, and the actual path selected in each case is one which proceeds *around* this maximum. Such a reaction coordinate, characterized by the presence of a stable intermediate and two transition states, one corresponding to rotation and the other to inversion, lacks C_{2v} reflection symmetry, and is termed asymmetric.⁵⁹

Figure 11 contrasts the asymmetric reaction coordinates computed for the two carbanions. The topomerization of ${}^{-}\text{CH}_2\text{OH}$ (shown in the upper curve) is inversion dominated; the two transition states in the topomerization of ${}^{-}\text{CH}_2\text{SH}$ are nearly isoenergetic. The rotational barrier of ${}^{-}\text{CH}_2\text{SH}$ is, if anything, lower than that of ${}^{-}\text{CH}_2\text{OH}$. Since any $(p \rightarrow d)_\pi$ conjugation in ${}^{-}\text{CH}_2\text{SH}$ should surely have caused an increase in the rotational barrier,⁶⁰ it seems clear that the dynamic as well as the static properties of ${}^{-}\text{CH}_2\text{SH}$ cannot be attributed to d-orbital effects. It is unlikely, therefore, that the lower inversion barrier of ${}^{-}\text{CH}_2\text{SH}$, which is mainly responsible for the different topomerization behavior of the two carbanions, can be caused by d-orbital effects. Indeed, as was already evident from Figure 4, removal of the d-type functions from the basis set (4-31G computation) lowers the inversion barrier. It is well established^{14,57,61} that inductive effects play a major role in deciding barriers to inversion. Since oxygen (χ_{O} , 3.44)⁶² is more electronegative than either sulfur (χ_{S} , 2.58)⁶² or carbon (χ_{C} , 2.55),⁶² the higher inversion barrier of ${}^{-}\text{CH}_2\text{OH}$ can be understood in terms of inductive effects alone.⁶³

The Gauche Effect. A difference between ${}^{-}\text{CH}_2\text{OH}$ and ${}^{-}\text{CH}_2\text{SH}$ is seen in the nature of the minima of the rotation-inversion surfaces (Figures 9 and 10). For ${}^{-}\text{CH}_2\text{OH}$, the Y conformation is more stable than the W, and for ${}^{-}\text{CH}_2\text{SH}$, W is more stable than Y. Since greater stability of the W conformation is predicted by the gauche effect,¹⁵ ${}^{-}\text{CH}_2\text{OH}$ constitutes an exception. As we²¹ and others⁶⁴ have pointed out, it is useful to treat the total energy of a system in terms of the balance between nuclear repulsive and electronic attractive effects. In the present case, nuclear repulsion favors the Y conformation, and electronic attraction favors the W. In addition, nuclear repulsion changes faster than electronic attraction as the internuclear separation decreases.²¹ This means that the gauche effect will be observed whenever electronic attraction outweighs nuclear repulsion, and whether this is the case will depend upon the internuclear distances. We presently believe, therefore, that the difference in the structures of ${}^{-}\text{CH}_2\text{OH}$ and ${}^{-}\text{CH}_2\text{SH}$ results from the longer C-S bond.

Conclusions

In this work, we have examined the effect of d-type functions upon the static, dynamic, and chemical properties of carbanions adjacent to oxygen and to sulfur. We have found no evidence of d-orbital effects upon any of these properties. Obviously oxygen and sulfur influence the behavior of organic molecules in different ways, and these differences must be explained. Two reasons for the differences have

been noted above, viz., the greater polarizability of sulfur and the longer C-S bond length. Some reasonably quantitative model which incorporates these properties, and which does not invoke d-orbital conjugative effects, is now needed. Such a model has been developed recently⁶⁵ and will form the subject of future papers in this series.

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thus need not require the formal breaking of a double bond. If this argument were accepted, it would not be possible to employ the relative rotational barriers of CH_2SH and CH_2OH to rule out $(p \rightarrow d)_\pi$ conjugation in CH_2SH .

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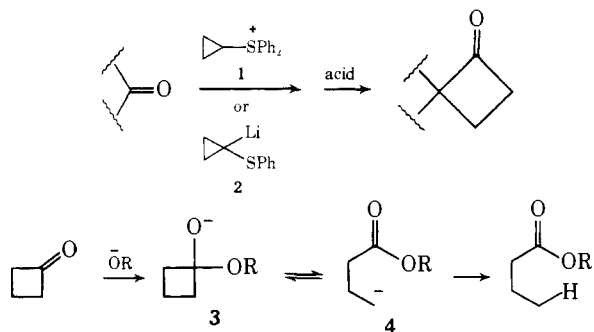
New Synthetic Reactions, Geminal and Reductive Alkylations

Barry M. Trost,¹ Mitchell J. Bogdanowicz, and (in part) Jeffrey Kern

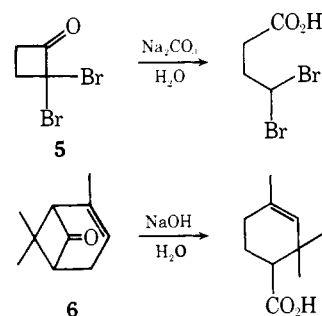
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received August 28, 1974

Abstract: Anion-stabilizing groups at the α position of a cyclobutanone facilitate ring cleavage. In conjunction with the cyclobutanone annelation utilizing sulfonium cyclopropylides and lithiated phenyl cyclopropyl sulfides, this method achieves a net replacement of the carbon-oxygen bonds of a carbonyl group by either C-H or C-R bonds (reductive alkylation) or by two C-R bonds (geminal alkylation) in a highly stereoselective fashion. A 2-aryl substituent is a sufficient anion-stabilizing group. Geminal bromine substitution at the α position of a cyclobutanone offers unusual versatility after ring cleavage since the bromines can be substituted or eliminated. In this way, one of the carbon-oxygen bonds of a C=O of an aldehyde or ketone has been replaced by a carboxyl group and the second by a methyl, ethyl, vinyl, 2-hydroxyethyl, or 2-oxoethyl substituent.

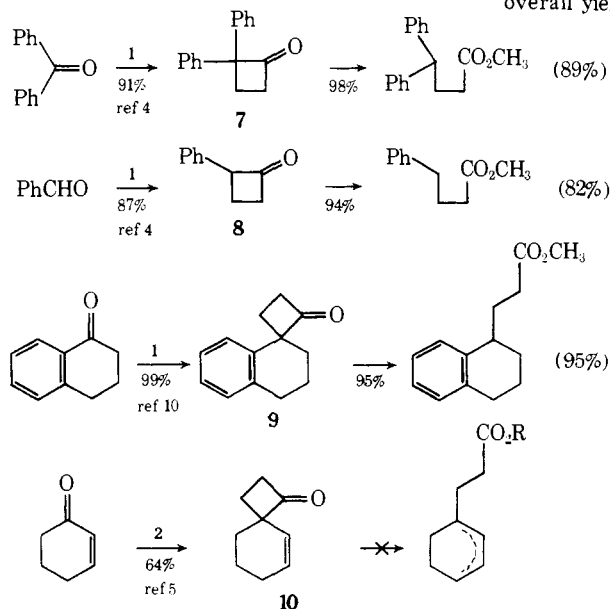
Although small strained rings have fascinated physical organic chemists for many years, their applications in synthesis remained quite limited until recently. Their strain energy provides a strong driving force for chemical reactions. The use of this potential energy to modify structure allows novel ways to develop molecular architecture. Most work focused on cyclopropanes because of their ready availability by alkylidene transfer.² The difficulty in obtaining cyclobutanes restricted their application. The recent discoveries³ for making cyclobutanones readily available especially by condensing carbonyl compounds with diphenylsulfonium cyclopropylide (**1**)⁴ or 1-lithiocyclopropyl phenyl sulfide (**2**)⁵ initiated an investigation into the scope of such intermediates in creating various carbon fragments.⁶ It might be envisioned that such cyclobutanones would undergo cleavage initiated by base. This simple scheme cannot be realized



presumably because of the high endothermicity in going from the oxygen anion **3** to the carbanion **4**. Stabilization of the developing negative charge in **4** should facilitate this process. Indeed, isolated examples exist. For example, dibromocyclobutanone **5** undergoes facile cleavage in aqueous carbonate,⁷ and chrysanthenone **6** undergoes ring cleavage with aqueous hydroxide.⁸ To investigate the applicability of such methods, we undertook an investigation of the chemistry of the cyclobutanones available by our annelation procedure as a method of elaborating a carbonyl group.^{9,10}



Initial work centered on the cyclobutanones **7-10**. Huisgen et al. reported the cleavage of 2,2-diphenyl-3-vinylcyclobutanone overall yields



cyclobutanone with hydroxylic base.¹¹ In agreement with this observation, we find that **7** undergoes smooth cleavage in