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D-ORBITAL EFFECTS AND THE STRUCTURE OF THE ALPHA-THIOCARBANION

Saul Wolfe* and Lawrence A. LaJohn
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Fernando Bernardi*
Istituto Chimico "G.Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

Angelo Mangini and Glauco Tonachini
Istituto di Chimica Organica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

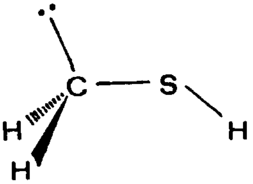
Summary: Improved computational results show that sulfur-3d orbital effects are essential for the proper description of the bonding in the alpha-thiocarbanions $^{-}CH_2SH$ and $^{-}CH_2SCH_3$. The nature of the d-orbital effects has been analyzed, and reasons for the earlier failures to find these effects have been determined.

Sulfur-containing carbanions $\bar{C}H_2$-Sabc contain a number of interrelated geometrical parameters. Because, in particular, the C-S bond lengths, C-S torsional angles and carbon valence angles of such species are strongly coupled,[1] theoretically derived geometries can be greatly in error when any one of these parameters is not optimized properly. As was found recently in a comprehensive reexamination of sulfonium and phosphonium ylides, such errors naturally bias attempts to interpret the resulting structures or to analyze the resulting wavefunctions, in ways that would not have been anticipated.[1]

The traditional difficulties associated with complete geometry optimization have been overcome through the development of methods for the efficient analytical calculation of the first derivatives (gradients) of the Hartree-Fock energy.[2] These derivatives provide the forces in the molecule; since these are zero at the equilibrium geometry, a force relaxation procedure can be used to search for this geometry.[3] Typically, fewer than N calculations are then required to optimize N variables, and the residual forces on the atoms after optimization provide a check on the accuracy of the minimization (ca ±0.001 A and ±0.05° or better, for bond lengths and bond angles, respectively). Since the analytical calculation of all gradients requires only as much computer time as the calculation of the energy alone, this approach represents an order of magnitude improvement over non-gradient optimization methods for any problem involving more than a few variables.

For the treatment of the model sulfonium ylide CH_2SH_2 the 4-31G*[4] basis set was found to be adequate.[1] In this study of the alphathiocarbanions $\bar{C}H_2SH$ and $\bar{C}H_2SCH_3$ we have used the newer 3-21G*[5] basis set, which contains d-orbitals on sulphur and gives geometries and energy differences in excellent agreement with those obtained at the 4-31G* level. All computations have been performed with the GAUSSIAN 80 series of programs[6] and the various geometries have been fully optimized with an analytical gradient procedure. In order to provide more insight into the nature of the d-orbital effect in these systems, for $\bar{C}H_2SH$ additional calculations have been performed at the 3-21G[7] level, i.e. with the same basis set without d-orbitals on sulphur, and also with basis sets of double zeta quality[8] (for C a (9s 5p) contracted to [4s 2p] with an additional set of p diffuse functions, for S a (11s 7p) contracted to [6s 4p] with and without a set of d orbitals with exponential parameter 0.52 and for H a (4s) contracted to [2s]).

Three earlier investigations on $^{-}CH_2SH$[9,10] and $^{-}CH_2SCH_3$[11] are relevant. In ref. 7, a double zeta basis set supplemented with two sets of d-type functions on sulfur was used, and a limited geometry optimization was performed. This led to C-S bond lengths of 1.857 and 1.871 A for CH_3SH and $^{-}CH_2SH$ in the W conformation 1, respectively. The work of ref 10 and 11 also made use of basis sets containing d-orbitals on sulfur, but no geometry optimization was undertaken, and all C-S bond lengths were fixed at 1.819 A, the experimental value in CH_3SH. Each of the three studies concluded that $(d\text{-}p)_\pi$ bonding does not contribute to carbanion stabilization by an adjacent sulfur atom.



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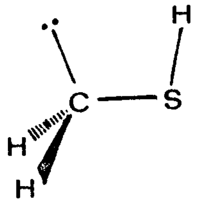

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This conclusion has now been found to be an artifact of C-S bond lengths that were too long to permit the d-orbital effects to be exerted. When the C-S bond lengths are optimized properly, the importance of $(d\text{-}p)_\pi$ bonding in an alpha-thiocarbanion becomes clear.

With the 3-21G basis set (no d-orbitals on sulfur), the calculated C-S bond length of CH_3SH is 1.895 A.[7] This is too long, compared to the experimental value of 1.819 A, or the 3-21G* value of 1.823 A.[5] When there are no d-orbitals on sulfur, the calculated C-S bond length of $^{-}CH_2SH$ is 2.118 A, and the Y conformation 2 is 1.0 kcal/mole more stable than 1 (r_{CS} = 2.069 A). Addition of d-orbitals to the basis set leads to a structure for 1 in which r_{CS} = 1.772 A, and 1 is now 4.38 kcal/mole more stable than 2 (r_{CS} = 1.875 A). Very similar results are obtained with the double zeta basis set: in the absence of d-orbitals on sulfur the C-S bond lengths of 1 and 2 are 1.962 A and 2.017 A and 1 is 0.1 kcal/mole more stable. Addition of d-orbitals to the basis set leads to C-S bond lengths of 1.793 A for 1 and 1.828 A for 2 and 1 is 2.63 kcal/mol more stable. The close agreement between these two sets of results shows very clearly that the inclusion of d-orbitals on sulfur is necessary for a correct description of the geometrical features of these species.

A decrease in the C-S bond length upon conversion of CH_3SH to $^{-}CH_2SH$ should have been, but was not previously recognized to reflect conjugative stabilization of the carbanion by the SH moiety, just as carbanion stabilization by an adjacent carbonyl group causes C-C shortening when CH_3CHO is deprotonated to $^{-}CH_2CHO$.[12,13] Indeed, in the general process $CH_3X \rightarrow {}^{-}CH_2X$, a decrease (increase) in r_{CX} can be expected to signal conjugative stabilization (destabilization) of the carbanion by X, whatever the reason for the stabilization or destabilization in any given case. However, for the specific case X = SR, the observed stabilization must be closely related to the presence of d-orbitals on sulfur, *and their availability for bonding through the use of the proper geometry.*

As seen in Figure 1, which is based on 3-21G* calculations, deprotonation of dimethyl sulfide (r_{CS} = 1.813 A) leads to a pyramidal carbanion, having the W conformation, in which the

C_1-S bond has shortened to 1.728 A and the C_2-S bond has lengthened to 1.875 A. The HOMO of this carbanion, shown in 3, is π-bonding in the C_1-S region and σ-antibonding in the C_2-S region. For the coordinate system shown, the dominant d-orbital contribution to the HOMO is made by the $3d_{xz}$ atomic orbital of sulfur, which mixes into this molecular orbital in the manner indicated. This mixing-in leads to an increase in bonding between C_1 and S, and a decrease in antibonding between C_2 and S. Both of these effects will tend to lower the energy of the HOMO and lead to stabilization of the carbanion. According to this analysis, the d-orbitals of sulfur operate as polarization functions, in just the manner discussed many years ago by Pauling.[14]

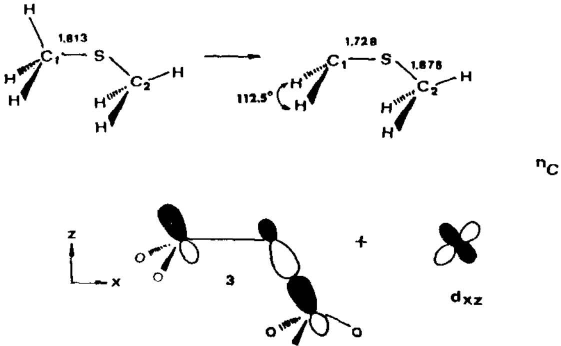


Fig.1

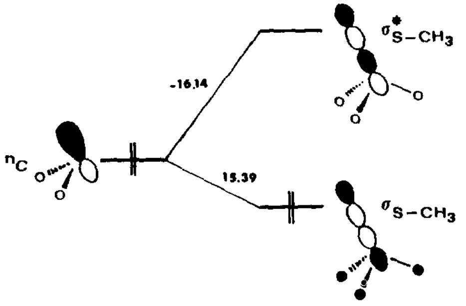
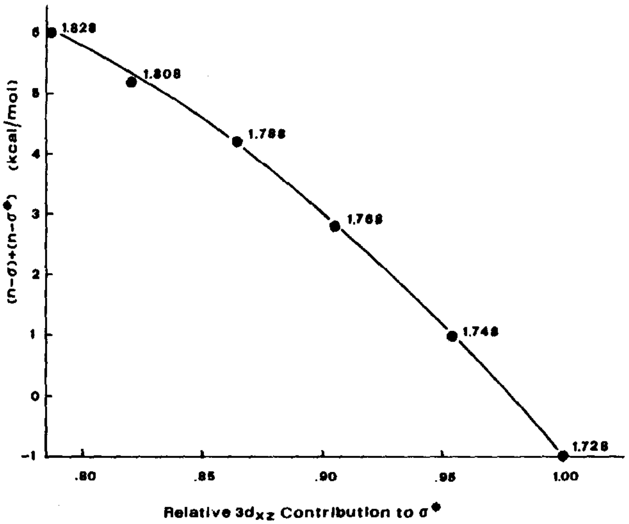


Fig.2

The changes in the C-S bond lengths resulting from the deprotonation of dimethyl sulfide, and the nodal character of the HOMO of the resulting carbanion, are reminiscent of the geometrical effects and molecular orbital behaviour found in molecules XCH_2YH which exhibit an *anomeric effect.*[15] In the case of the anomeric effect, trends associated with variation of X and/or Y have been interpreted[15] in terms of a perturbational molecular orbital (PMO) analysis which focuses upon orbital interactions associated with the p-type non-bonding orbital of Y. The counterpart of this analysis in the case of $^-CH_2$-SCH_3 is shown in Figure 2. Here the focus is on the interactions of the hybrid non-bonding orbital of C_1 with the σ and σ* C_2-S orbitals which are, respectively, destabilizing and stabilizing. The magnitudes of these interactions can be calculated by now well established procedures.[16]

Within the framework of the PMO analysis, the sulfur d-orbitals mix into σ* so as to lower its energy and increase its overlap with n_C. In the fully optimized 3-21G* structure of $^-CH_2$-SCH_3, the destabilizing and stabilizing orbital interactions are 15.39 and -16.14 kcal/mol, respectively. When the d-orbitals are removed from the sulfur, the σ* orbital energy increases, the overlap between σ* and n_C decreases by 3%, and the destabilizing and stabilizing orbital interactions are 17.77 and -12.40 kcal/mol, respectively. To avoid this net destabilization when the d-orbitals are not present, the C_1-S bond lengthens and optimization of the structure at the 3-21G level leads to a C_1-S bond length greater than 2 A.

The effect of an artificial stretch of the C_1-S bond at the 3-21G* level is particularly revealing. Figure 3 shows the changes in the $3d_{xz}$ contributions to the electron density of σ*, plotted against the sum of the stabilizing and destabilizing orbital interactions, as the C_1-S bond is stretched in 0.02 A increments from the optimized value (1.728 A) to 1.828 A, with no



reoptimization of the other parameters. As seen, an error of only 0.02 A in the C_1-S bond length would cause a 5% decrease in the d-contribution to σ*, and this is sufficient to reverse the relative magnitudes of the stabilizing and destabilizing orbital interactions. It is understandable therefore, why the previous investigations, which were based on bond lengths greater than 1.8 A, failed to find the d-orbital effects.

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