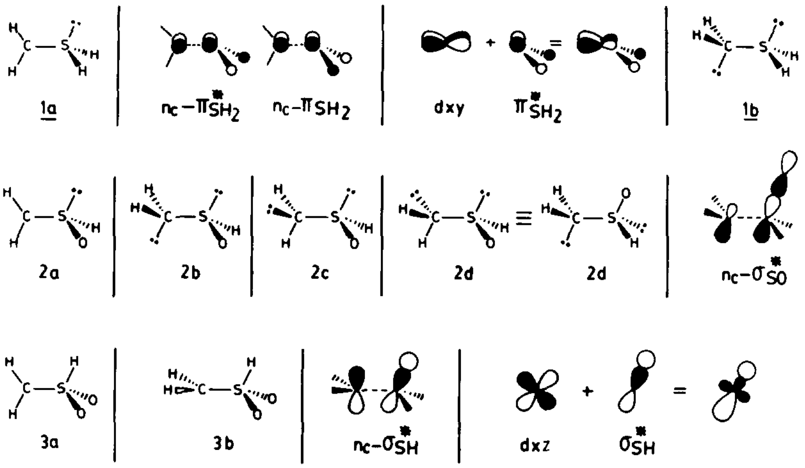
Tetrahedron Letters,Vol.24,No.38,pp 4071-4074,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

A THEORETICAL REEXAMINATION OF CARBANIONS ADJACENT TO SULFOXIDE, SULFONE AND SULFONIUM CENTRES

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

Summary: The structures and proton affinities of CH_2SR_2 *(R = H,* CH_3*),* $^-CH_2SOR$ *(R = H,* CH_3*) and* $^-CH_2SO_2R$ *(R = H,* CH_3*) have been found at the 3-21G* (d-orbitals on sulfur) and 3-21G (no d-orbitals on sulfur) levels, using gradient optimization procedures. d-Orbital effects are important in these optimized structures. The factors leading to the structures now found, and the role of the d-orbitals, have been evaluated by quantitative PMO analyses of the wavefunctions.*

This Letter is concerned with sulfur-containing carbanions of the general structure $^-CH_2Sabc$, in which the sulfur moiety is sulfonium (a = b = H, c = lone pair; 1), sulfinyl (a = O, b = H, c = lone pair; 2), sulfonyl (a = b = O, c = H; 3), methylsulfinyl (a = O, b = CH_3, c = lone pair; 4), methylsulfonyl (a = b = O, c = CH_3; 5), and dimethylsulfonium (a = b = CH_3, c = lone pair; 6). Such species may exist in a conformation of type a, in which the carbanion lone pair is approximately perpendicular to the S-c axis, or in a conformation of type b, in which the carbanion lone pair is parallel to the S-c axis. In addition, in each of a or b, the carbanionic centre may be planar or pyramidal.



The qualitative molecular orbital treatment of the model sulfonium ylide CH_2SH_2 (1) focuses on orbital interactions associated with the non-bonding orbital on carbon (n_C), which makes the dominant contribution to the HOMO of the molecule. In a structure of type 1a, in which the HCH plane bisects the HSH plane, n_C is stabilized (two orbitals, two electrons) by charge transfer to an acceptor orbital having the same symmetry, in this case $\pi^*_{SH_2}$ (see Figure 1). Because sulfur is a second row atom and, in addition, carries a net positive charge, the acceptor orbital is low-lying, and substantial charge transfer should exist. According to Walsh's Rules,[1] the resulting depopulation of n_C will cause the carbon centre to tend towards planarity, just as charge transfer from n_C to an adjacent π^*_{CO} orbital causes an enolate anion to have a planar configuration at carbon,[2] and charge transfer from n_N to $\pi^*_{PR_2}$ causes the nitrogen centre to be planar in the isoelectronic aminophosphine.[3] Rotation of the HCH moiety by 90°, as in 1b, eliminates the stabilizing orbital interaction, and replaces it with a destabilizing interaction (two orbitals, four electrons) with n_S, the non-bonding orbital on sulfur. It follows that 1a is more stable than 1b; in addition, since there is no low-lying acceptor orbital in 1b, charge transfer from n_C is unimportant in 1b, and the carbon centre will remain pyramidal.

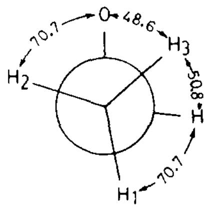
The foregoing analysis constitutes a rationalization of the results of recent detailed ab initio calculations on CH_2SH_2:[4] structure 1a is more stable than structure 1b, and the carbon centre is planar in 1a and pyramidal in 1b. However, neither the qualitative analysis nor previous calculations[5] anticipated the importance of the d-orbital effects that became apparent only when all geometries were optimized fully using gradient techniques.[6] Thus, for sulfonium ylides and related species, computations of at least 4-31G*[7] or 3-21G*[8] quality are needed to achieve agreement with known experimental information. In the case of CH_2SH_2, removal of the d-orbitals (4-31G* → 4-31G; 3-21G* → 3-21G) converts this species from a stable organic compound (r_{CS} = 1.627 Å) to a solvated carbene (r_{CS} = 2.451 Å), whose properties do not accord with reality.

The nature of the d-orbital effects, and their role, are revealed by quantitative PMO analyses[9] performed on structure 1a. In addition to the stabilizing n_C-$\pi^*_{SH_2}$ interaction considered initially, there is a destabilizing n_C-π_{SH_2} interaction with the occupied SH_2 orbital of the appropriate symmetry, which dominates when d-orbitals are unavailable on sulfur. To avoid this destabilization the carbon-sulfur bond lengthens, and optimization of the structure without the d-orbitals leads to the aforementioned unacceptably long bond. On the other hand, when the d-orbitals are employed on sulfur, d_{xy} mixes into the acceptor $\pi^*_{SH_2}$ orbital, as depicted in Figure 1, and distorts the electron density in the direction of the carbon. This leads to a large increase in the stabilizing orbital interaction, which now dominates.

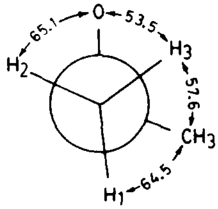
These findings indicated that the results and conclusions of earlier computations on alpha-sulfinyl[10] and alpha-sulfonylcarbanions[11] required reexamination. For the sulfinylcarbanion $^-CH_2SHO$ (2), structures 2a and 2b correspond, respectively, to 1a and 1b. Since the sulfur atom retains one lone pair, 2b should be less stable than 2a by the same qualitative reasoning as before. However, sulfur is a chiral centre in 2a, and the carbon centre of this structure can be non-planar. A non-planar carbanion in which one methylene hydrogen of 2a moves away from the sulfinyl oxygen corresponds to 2c, in which the carbon lone pair is anti-periplanar to S-H or, equivalently, lies on the bisector of the oxygen:sulfur:sulfur lone pair angle. Alternatively, a non-planar carbanion in which one methylene hydrogen of 2a moves in the direction of the oxygen atom corresponds to 2d, in which the carbon lone pair is anti-periplanar to oxygen. Structure 2c was found to be preferred in the earlier calculations, which employed the minimal basis sets and limited geometry optimization in use at that time.

For the sulfonylcarbanion $^-CH_2SHO_2$ (3), structures 3a and 3b correspond, respectively, to 1a and 1b. However, 3b differs from its congeners 1b and 2b in one important respect: the sulfur lone pairs of 1b and 2b have become a bond in 3b. The destabilizing lone pair-lone pair interaction present in 1b and 2b is, therefore, absent in 3b. Indeed, 3b may now exhibit charge transfer from n_C to σ^*_{SH}, which has the proper symmetry for such a stabilizing interaction. The meaning of this analysis is that a qualitative choice between 3a and 3b is difficult. In the earlier calculations, 3b was found to be preferred.

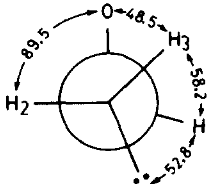
In the present work, the structures of $^-CH_2SHO$ and $^-CH_2SHO_2$ have been found using gradient optimization procedures, and both the 3-21G (no d-orbitals on sulfur) and 3-21G* (d-orbitals on sulfur) basis sets, to determine whether the geometrical effects of the 3d-orbitals parallel those seen previously with CH_2SH_2; and quantitative PMO analyses have been performed on the global minima, to determine the factors responsible for these preferred structures. The work has also been extended to include the chemically more relevant structures, proton affinities and PMO analyses of methyl sulfinyl carbanion (4), methyl sulfonylcarbanion (5) and dimethylsulfonium methylide (6). Table 1 summarizes the principal results, and A-D show the dihedral angles found, respectively, for CH_3SHO, $(CH_3)_2SO$, $^-CH_2SHO$ and $^-CH_2SOCH_3$ (3-21G* basis set).



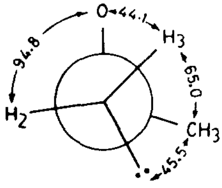
A



B



C



D

Table 1. Structures and energy relationships of sulfur containing carbanions and their protonated precursors

System	Bond Length (Å)			Relative Energy	Orbital Interactions in the HOMO[a]	
	CH_2-S	CH_3-S	S-O	(Kcal/mole)	Stabilizing[b]	Destabilizing
CH_3SHO		1.794 (1.869)[c]	1.490 (1.707)	0.0		
2	1.675 (1.940)		1.523 (1.711)	403.2	17.7	13.8
$(CH_3)_2SO$		1.791[d]	1.490[d]	0.0		
4	1.672	1.810	1.524	406.5	16.1	15.2
CH_3SHO_2		1.749 (1.828)	1.434 (1.599)	0.0		
3	1.613 (1.826)		1.459 (1.606)	386.2	36.6	34.9
$(CH_3)_2SO_2$		1.756[e]	1.438[e]	0.0		
5	1.618	1.797	1.462	390.4	30.3	24.6
$CH_3SH_2^+$		1.828 (1.944)		0.0		
1	1.627			269.0	61.3	41.9
$(CH_3)_3S^+$		1.806		0.0		
6	1.630	1.842		287.0	52.5	36.1

[a] In Kcal/mol. [b] See text and Figure 1 for the nature of these interactions. [c] Data in parentheses refer to 3-21G calculations; all other data refer to 3-21G* calculations. [d] The experimental values are 1.799 and 1.485 Å. See Ref 8,12. [e] The experimental values are 1.771 and 1.435 Å. See Ref 8,13.

The following comments pertain to the structures and energies of these species: (i) 1, 2 and 3 and their protonated precursors are reliable model systems; (ii) d-orbitals are needed on sulfur to achieve acceptable bond lengths.[4b] Their effect is most transparent when the deprotonation $CH_3Sabc \rightarrow {}^{-}CH_2Sabc$ is considered: without the d-orbitals, deprotonation leads to a longer C-S bond, for reasons discussed previously.[4] With the d-orbitals, this bond shortens (strengthens) considerably, as is observed experimentally;[14] (iii) the preferred structure of an α-sulfinylcarbanion corresponds to 2d, and is non-planar at carbon. As seen in A-D, H_1, the methyl proton that is nearly anti-periplanar to oxygen, is lost from both CH_3SHO and DMSO. Because the angles at sulfinyl sulfur are not tetrahedral, the dihedral angles in A and B are not ethane-like. Thus, in A, H_1 is 9.9° from the anti-periplanar position and, in B, it is 4.4°. The corresponding dihedral angles in the anions C and D are 20.1 and 24.4°, respectively. As will be seen, this twisting of the CH_2H_3 moiety minimizes lone pair-lone pair repulsion, and maximizes charge transfer from n_C to both S-O and S-R antibonding regions; (iv) when conformational constraint is absent, the carbanions corresponding to removal of H_2 or H_3 from A or B optimize to C and D, respectively. To obtain an estimate of the energies of these structures relative to those of C, H_1, H_2 and H_3 were removed from A, and the C-S and S-O bond lengths of the resulting anions were optimized, but C-S rotation was not permitted to occur. The relative energies and C-S bond lengths (Kcal/mole, Å) are: C (0.0, 1.675), A-H_1 (6.6, 1.718), A-H_2 (16.5, 1.737), A-H_3 (17.2, 1.754); (v) the preferred structure of an α sulfonylcarbanion corresponds to 3b, and has a planar configuration at carbon; (vi) the structure of dimethylsulfonium methylide corresponds to 1a, and it is also planar at carbon; (vii) in the gas phase, the relative acidities of protons adjacent to various sulfur-containing moieties are sulfonium >> sulfone > sulfoxide, and the 3-21G* difference in the gas phase acidities of DMSO and DMSO$_2$ is 16.1 kcal/mole, compared to the experimental difference of 8.2 kcal/mole.[15] The principal reason for the great difference between the sulfonium system and the other two is that deprotonation of a sulfoxide or sulfone creates a charged species, but deprotonation of a sulfonium cation creates a neutral species.

The HOMO's of the α-sulfonylcarbanions 3 and 5 are π-bonding in the CH$_2$-S regions and σ-antibonding in the S-R (R = H,CH$_3$) regions. These observations suggest that these HOMO's are stabilized by charge transfer from n_C to σ^*_{SR}. This stabilizing orbital interaction is shown in Figure 1, and is reminiscent of the *anomeric effect*,[16] as are the shortening of the CH$_2$-S bond and the lengthening of the S-CH$_3$ bond of 5 that result from deprotonation of dimethylsulfone. The magnitude of the (n_C-σ^*) interactions are given in Table 1, together with those of the *destabilizing* (n_C-σ) interactions associated with the occupied σ_{SR} orbitals. Most importantly, as depicted in Figure 1, *the d_{xz} orbital of sulfur mixes into* σ^*. This mixing-in (polarization effect)[17] lowers the energy of the acceptor orbital, and increases its overlap with n_C. Both effects cause an increase in the stabilization of the system, and are essential to achieve net stabilization of the HOMO.

An analogous d-orbital polarization effect (not shown) is found in the α-sulfinylcarbanions 2 and 4. Here, the acceptor orbital contains contributions from both σ^*_{SO} and σ^*_{SR}. Rotation of the carbon lone pair (n_C) towards R (see C and D) maximizes the stabilizing effect of σ^*_{SR}, and concomitantly, minimizes the (n_C-n_S) destabilizing interaction. Indeed, in the HOMO's of 2 and 4, the dominant destabilizing interaction corresponds to (n_C-σ).[18]

Acknowledgements. This work was supported by an Operating Grant from the Natural Sciences and Engineering Research Council of Canada (NSERCC). The authors thank NSERCC and Queen's University for funds to purchase the Perkin-Elmer 3251 computer, on which most of the computations were performed.

REFERENCES AND NOTES

1) A.D. Walsh, *J. Chem. Soc.*, 2260 *et seq* (1953).
2) S. Wolfe, H.B. Schlegel, I.G. Csizmadia and F. Bernardi, *Can. J. Chem.*, 53, 3365 (1975); A. Pross, D.J. DeFrees, B.A. Levi, S.K. Pollack, L. Radom and W.J. Hehre, *J. Org. Chem.*, 46, 1693 (1981).
3) A.H. Cowley, D.J. Mitchell, M.-H. Whangbo and S. Wolfe, *J. Am. Chem. Soc.*, 101, 5224 (1979).
4) (a) D.J. Mitchell, S. Wolfe and H.B. Schlegel, *Can. J. Chem.*, 59, 3280 (1981); (b) V. Král, Z. Arnold and Z. Havlas, *Coll. Czech. Chem. Commun.*, 46, 883 (1981).
5) See F. Bernardi, H.B. Schlegel, M.-H. Whangbo and S. Wolfe, *J. Am. Chem. Soc.*, 99, 5633 (1977), and also references cited in Ref. 4.
6) P. Pulay, *in* Applications of Electronic Structure Theory, *edited by* H.F. Schaefer III, Plenum Press, New York, 1977; H.B. Schlegel, Ph.D. Thesis, Queen's University, 1975; H.B. Schlegel, *J. Chem. Phys.*, 77, 3676 (1982); J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, GAUSSIAN 80, An Ab Initio Molecular Orbital Program, QCPE, 13, 406 (1981). GAUSSIAN 80 was employed in the present work.
7) P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, 28, 213 (1973). See also Ref. 4.
8) W.J. Pietro, M.M. Francl, W.J. Hehre, D.J. DeFrees, J.A. Pople and J.S. Binkley, *J. Am. Chem. Soc.*, 104, 5039 (1982), and references cited therein.
9) M.-H. Whangbo, H.B. Schlegel and S. Wolfe, *J. Am. Chem. Soc.*, 99, 1296 (1977); F. Bernardi and A. Bottoni, *in* Progress in Theoretical Organic Chemistry, Vol. 3, *edited by* I.G. Csizmadia, Elsevier, Amsterdam, 1982.
10) A. Rauk, S. Wolfe and I.G. Csizmadia, *Can. J. Chem.*, 47, 113 (1969).
11) S. Wolfe, A. Rauk and I.G. Csizmadia, *J. Am. Chem. Soc.*, 91, 1567 (1969).
12) H. Dreizler and G. Dendl, *Z. Naturforsch.*, 19A, 512 (1964); 20A, 1431 (1965).
13) H. Hargittai and I. Hargittai, *J. Mol. Struct.*, 20, 283 (1974).
14) G. Chassaing, A. Marquet, J. Corset and F. Froment, *J. Organomet. Chem.*, 232, 293 (1982).
15) J.B. Cumming and P. Kebarle, *J. Am. Chem. Soc.*, 100, 1835 (1978). For review, see A. Krief, *Tetrahedron*, 36, 2531 (1980).
16) S. Wolfe, M.-H. Whangbo and D.J. Mitchell, *Carbohydrate Res.*, 69, 1 (1979); S. Wolfe and D. Schirlin, *Tetrahedron Lett.*, 21, 827 (1980).
17) L. Pauling, *Proc. Nat. Acad. Sci. U.S.*, 44, 211 (1958).
18) In the partially optimized carbanion derived from A by removal of H$_3$ (see text), the (n_C-n_S) destabilizing interaction is 10.85 kcal/mol.

(Received in USA 15 June 1983)