

113/THE IRRELEVANCE OF d-ORBITAL CONJUGATION. II. NON-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS ON THE CH₂SH RADICAL

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Summary. — A preliminary investigation of the rotation-inversion surface of the CH₂SH radical has been performed. The non-empirical molecular orbital computations have been carried out within the framework of the Unrestricted Hartree-Fock (UHF) method, using a double zeta quality basis set which included two linearly independent *d* gaussian type functions on sulphur. The minimum of this surface was found to have trigonal planar geometry at carbon and the S—H bond in the HCH plane. Since the barrier to rotation about the C—S bond is computed to be only 0.65 kcal mole⁻¹ and the 3*d*_π gross orbital charge in the stable structure is only 0.02, it has been concluded that 3*d*-orbital conjugative effects cannot be significant in this radical.

Riassunto. — In questo lavoro vengono riportati i risultati di uno studio preliminare della superficie di energia potenziale relativa alla rotazione (intorno al legame C—S), inversione (al C) nel radicale CH₂SH. Il problema è stato studiato con un trattamento *ab-initio* MOSCF UHF ed usando un « double zeta basis set » migliorato dall'aggiunta di due funzioni gaussiane di tipo *d* linearmente indipendenti. Il minimo di questa superficie corrisponde ad una conformazione avente il carbonio planare ed il legame S—H nel piano HCH. Poiché la barriera di rotazione calcolata è di sole 0.65 kcal mole⁻¹ e la « gross orbital charge » dell'orbitale 3*d*_π nella struttura più stabile è solo 0.02, si è concluso che effetti coniugativi dovuti agli orbitali 3*d*_π non possono essere significativi in questo radicale.

The effects of α -heteroatom substitution upon the stereochemical properties and stabilities of carbonium ions, carbon radicals and carbanions have been investigated experimentally in some detail. For carbonium ion-forming reactions, the relative reactivities associated with adjacent nitrogen, oxygen and sulphur are

$N > O > S$ ⁽¹⁾ and this trend is compatible with the view that these cations are stabilized by electron-releasing conjugation (equation [1]). Theoretical support for the $p_{\pi}-p_{\pi}$ interaction depicted in equation [1] has been obtained from non-empirical molecular orbital computations on ${}^+\text{CH}_2\text{OH}$ ⁽²⁾ and ${}^+\text{CH}_2\text{SH}$ ⁽³⁾.



For radical-forming reactions, the relative reactivities associated with adjacent nitrogen, oxygen and sulphur are $N > S > O$ ⁽⁴⁾. In this case, both electron-releasing conjugation ⁽⁵⁾ (equation [2]) and electron-sharing conjugation ⁽⁶⁾ (equation [3]) have been considered to account for the observed trends. By electron-sharing conjugation is meant, in current terminology, a stabilization of the transition state (in the case of a kinetic observation) or the radical itself (in the case of a thermodynamic observation) by $(p \rightarrow d)_{\pi}$ bonding, with such bonding considered possible for an α -heteroatom from the second row (sulphur, phosphorus), but not one from the first (nitrogen, oxygen).



For carbanion-forming reactions, the relative reactivities associated with adjacent nitrogen, oxygen, sulphur and phosphorus are $P \gg N$ ⁽⁷⁾ and $S \gg O$ ⁽⁸⁾. In this case, with few exceptions ⁽⁹⁾, the d -orbital model has invariably been invoked ⁽¹⁰⁾ to account for the experimental facts.

⁽¹⁾ H. Böhme, H. Fischer, R. Frank, *Ann.*, **563**, 54 (1949).

⁽²⁾ L. M. Tel, S. Wolfe, I. G. Csizmadia, *Int. J. Quantum Chem.*, **VII**, 475 (1973).

⁽³⁾ F. Bernardi, I. G. Csizmadia, H. B. Schlegel, S. Wolfe, *Can. J. Chem.*, 1975, in press.

⁽⁴⁾ R. F. Bridger, G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

⁽⁵⁾ K. Uneyama, H. Namba, S. Oae, *Bull. Chem. Soc. Japan*, **41**, 1928 (1968); A. J. Dobbs, B. C. Gilbert, R. O. C. Norman, *J. Chem. Soc. [A]*, 124 (1971).

⁽⁶⁾ Y. Yano, S. Oae, *Mech. React. Org. Sulf. Comp.*, **4**, 167 (1969).

⁽⁷⁾ W. von E. Doering, A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

⁽⁸⁾ S. Oae, W. Tagaki, A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964).

⁽⁹⁾ H. H. Jaffé, *J. Phys. Chem.*, **53**, 185 (1954); A. Mangini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **18**, 191 (1960).

⁽¹⁰⁾ G. Cilento, *Chem. Rev.*, **60**, 146 (1960); C. C. Price, S. Oae, « Sulphur bonding », Ronald Press, New York, N. Y., 1962; K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

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As a result of cular integrals for the C—S bond and pyramidal mechanical inv appeared useful, the conformational hyp and CSH angle of to be utilized in the

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The C—H and S 1.333 Å and 107.56°.

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We have recently performed ⁽¹¹⁾ a detailed theoretical study of the static and dynamic properties and proton affinities of carbanions adjacent to oxygen and to sulphur. No evidence for *d*-orbital effects upon any of these properties was found. Consequently, it appears that the very real differences observed upon replacement of nitrogen by phosphorus, or oxygen by sulphur, must now be reinterpreted in terms of some new model which does not make use of (*p*→*d*)_π conjugation. Such a one-electron perturbation model has been developed recently ⁽¹²⁾, and is being presented elsewhere. The essence of this model is that the larger size, and therefore the greater polarisability, of sulphur as compared to oxygen causes a higher energy level for a sulphur lone pair and a lower energy level for an S—H σ* orbital.

As a result of our computations on ⁻CH₂SH, we had available a set of molecular integrals for the structures of this anion corresponding to rotation about the C—S bond and pyramidal inversion at carbon. As a first stage of a detailed quantum mechanical investigation of radicals adjacent to oxygen and to sulphur it appeared useful, therefore, to examine the rotation-inversion cross-section of the conformational hypersurface of •CH₂SH corresponding to the C—S bond length and CSH angle of the anion, because this permitted many of the same integrals to be utilized in the SCF computation.

EXPERIMENTAL

The computations were performed on a CDC 6600 computer, within the framework of the unrestricted Hartree-Fock (UHF) approximation, using a modified ^(13a) Polyatom 2 programme system ^(13b). The double zeta basis set was augmented with two linearly independent 3*d* gaussian type functions (GTF) on sulphur. Thus it consisted of a total of 97 GTF contracted to 46 basis functions. This contracted basis set has been optimized for C by Huzinaga ⁽¹⁴⁾, for H by Basch *et al.* ⁽¹⁵⁾, and for S by Veillard ⁽¹⁶⁾. The exponents of the two *d*-type functions on S were taken to be 0.25 and 2.0 as suggested by Kari ⁽¹⁷⁾.

The C—H and S—H bond lengths and the CSH angle were maintained at 1.091 Å, 1.333 Å and 107.56°, respectively, throughout all of the work.

RESULTS AND DISCUSSION

Sufficient data were available from the earlier work ⁽¹¹⁾ to permit optimisation of the C—S bond length of CH₂S• radical. These data are summarised in table 1,

⁽¹¹⁾ F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. H. Whangbo, S. Wolfe, *J. Am. Chem. Soc.*, 1975, in press.

⁽¹²⁾ F. Bernardi, N. D. Epiotis, S. Wolfe, to be published.

⁽¹³⁾ (a) J. Duke, *Chem. Phys. Lett.*, **10**, 631 (1971). (b) POLYATOM (Version 2) «Quantum Chemistry Programme Exchange», Indiana University, Bloomington, Indiana, No. 199.

⁽¹⁴⁾ S. Huzinaga, *J. Chem. Phys.*, **50**, 1371 (1969).

⁽¹⁵⁾ H. Basch, M. B. Robin, N. A. Kuebler, *J. Chem. Phys.*, **47**, 120 (1967).

⁽¹⁶⁾ A. Veillard, *Theoret. Chim. Acta*, **12**, 405 (1968).

⁽¹⁷⁾ R. E. Kari, Personal Communication.

TABLE I. — OPTIMISATION OF C—S BOND LENGTHS

Compound	Optimised bond length (r_0 in Å)	Energy (*)				
		$r = 1.7661$	$r = 1.8190$	$r = 1.8719$	$r = 1.9248$	$r = r_0$
CH ₃ SH (**)	1.8574	-437.68720	-437.69026	-437.69073	-437.68912	-437.69083
CH ₃ S•	1.8803		-437.09075	-437.09208	-437.09140	-437.09211
CH ₃ S ⁻ (**)	1.9090		-437.08511	-437.08774	-437.08814	-437.08826
•CH ₂ SH	1.8718	-437.01041		-437.01372	-437.01289	-437.01373

(*) In Hartree atomic units.

(**) Values taken from ref. (1).

and are also shown. The results obtained from the optimization of the C—S bond lengths of CH₃SH and •CH₂SH are also compared. It is evident that the trend in the bond lengths is CH₃S⁻ > CH₃S• > CH₃SH > •CH₂SH > CH₂SH. This means that the optimized C—S bond length of •CH₂SH is between 1.8574 and 1.8803 Å, the computed optimized C—S bond lengths for CH₃SH and •CH₂SH are 1.8574 and 1.8718 Å, respectively. Employing the latter bond length for the computation of the rotational energy surface of CH₂SH• is not expected to introduce a significant error into the results.

This surface energy was computed using the parameters, as defined by

The computed energy values for the surface are summarised in Table II. They were then used to find the equilibrium points. In order to define the variables were defined: δ refers to a W-type conformation (see [II]); and ϵ under $(\delta, \epsilon) \rightarrow (-\delta, \epsilon)$. It may be appropriate, giving the energy difference in the surface

$$E(\delta, \epsilon) = C_0 +$$

and are also shown in figure 1. The results obtained for the optimization of the C—S bond lengths of CH_3SH , CH_3S^- and $^-\text{CH}_2\text{SH}$ are also included for comparison. It is evident that the trend in the bond lengths is $\text{CH}_3\text{S}^- > \text{CH}_3\text{S}^\bullet > \text{CH}_3\text{SH}$. A similar trend in the bond lengths of the tautomers ($^-\text{CH}_2\text{SH} > \bullet\text{CH}_2\text{SH} > \text{CH}_3\text{SH}$) would mean that the optimised C—S bond length of $\bullet\text{CH}_2\text{SH}$ will be between 1.8574 and 1.8718 Å, the computed optimum bond lengths for CH_3SH and $^-\text{CH}_2\text{SH}$ respectively. Employment of the latter bond length for the computation of the rotation-inversion surface of $\text{CH}_2\text{SH}^\bullet$ is, therefore, not expected to introduce a significant error into the results.

This surface $E(\Theta, \Phi)$ was then computed with Θ and Φ as the independent parameters, as defined below:



The computed energy values $E(\Theta, \Phi)$ required for the generation of this surface are summarised in table 2. Standard «least square» curve fitting methods were then used to fit a function of eight linear parameters to the set of ten calculated points. In order to take advantage of the symmetry of the surface, two new variables were defined: for inversion $\delta = \pm(\Phi - 120)$, such that at $\Theta = 0$, *plus* refers to a W-type conformation (see [I]) and *minus* refers to a Y-type conformation (see [II]); and, for rotation, $\varepsilon = (\Theta - 90)$. The function must be invariant under $(\delta, \varepsilon) \rightarrow (-\delta, -\varepsilon)$ and $(\delta, \varepsilon) \rightarrow (\delta, \varepsilon + 2n\pi)$. The following was found to be appropriate, giving a maximum of 1% error relative to the maximum energy difference in the surface:

$$E(\delta, \varepsilon) = C_0 + C_1 \delta^2 + C_2 \exp(-\alpha \delta^2) + C_3 \cos 2\varepsilon + C_4 \delta^2 \cos 2\varepsilon + C_5 \delta \sin \varepsilon + C_6 \delta^3 \sin \varepsilon + C_7 \delta \sin 3\varepsilon \quad [4]$$

Fig. 1. - Optimization of the C—S bond length of CH_3S^- , $\text{CH}_3\text{S}^\bullet$ and CH_3SH .

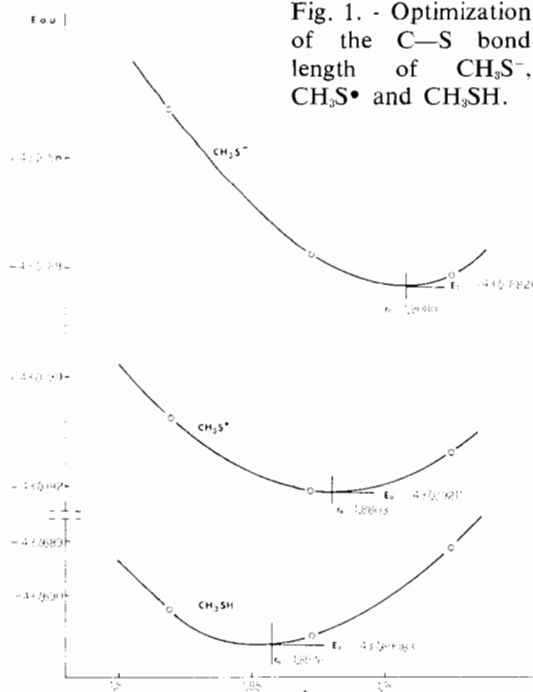


TABLE 2. — ROTATION-INVERSION SURFACE OF ${}^{\bullet}\text{CH}_2\text{SH}$

Θ°	Φ°			
	120	110	105	100
0	-437.05669 (*)	-437.04540	-437.03657	-437.02354
60			-437.04194	
90	-437.05773			
120			-437.03808	
180	-437.05669	-437.04119	-437.02976	-437.01376

(*) Total energy in Hartree atomic units.

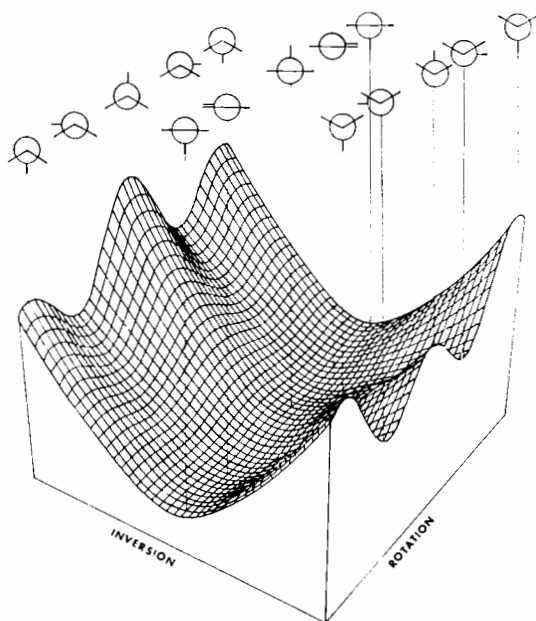


Fig. 2. - The rotation (about the C—S bond)-inversion (at C) surface.

Table 3 gives the parameters of this analytical expression, as fitted to the data of table 2. With the aid of this expression, a 41×41 grid was generated which was necessary for the plotting of the rotation-inversion surface shown in figure 2.

Selected cross-sections of this surface of the type $E(\Theta)$ and $E(\Phi)$ are presented in figures 3 and 4, respectively, to emphasize that, in terms of these computations, the CH_2SH radical has trigonal planar geometry at carbon, and that the completely

TABLE 3. — PARAMETERS ASSOCIATED WITH THE ANALYTICAL EQUATION OF THE ROTATION-INVERSION SURFACE OF ${}^{\bullet}\text{CH}_2\text{SH}$

Parameter	Fitted value
C_0	-114.05080744
C_1	0.00005953
C_2	- 0.00057573
C_3	- 0.00001904
C_4	0.00021171
C_5	0.00000011
C_6	0.00001038
C_7	- 0.00634563

planar conformation [I] interconversion of the [II] corresponds to the T co

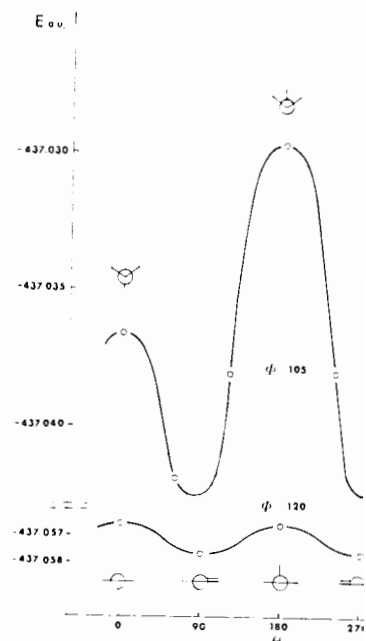
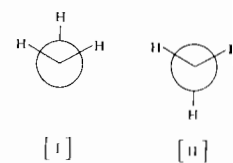


Fig. 3. - Rotational cross-section of the rotation-inversion surface.

The $(p_x - p_y)_z$ conjugation between the α -thio and α -oxycarbonium orbitals leads to a trigonal planar geometry at carbon, I-type conformation (respectively) and substantial energy difference ($\sim 19^{\text{kcal}}$ and $\sim 36^{\text{kcal}}$ m



In principle, therefore, the interconversion of the I-type conformation is not possible due to the presence of a s

planar conformation [III] is the energy minimum of the surface. The barrier to interconversion of the I-conformation [III] via rotation about the C—S bond corresponds to the T conformation [IV] and is 0.65 kcal mol⁻¹.

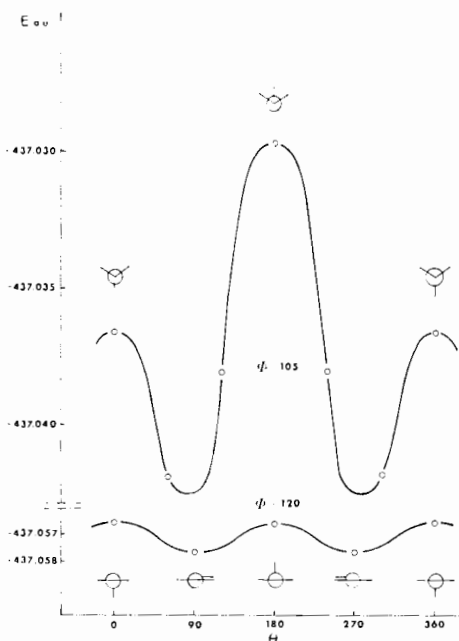


Fig. 3. - Rotational cross section of the rotation-inversion surface.

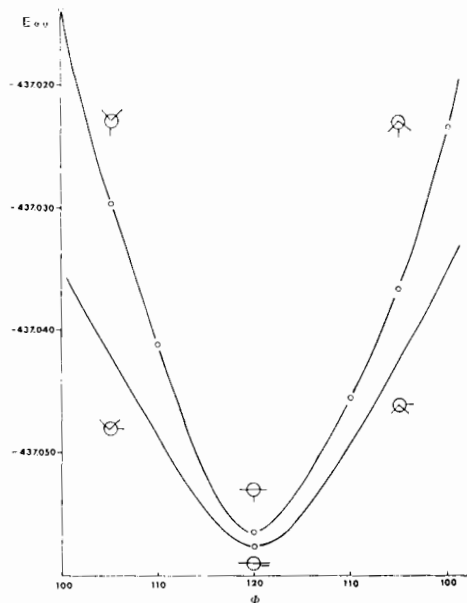
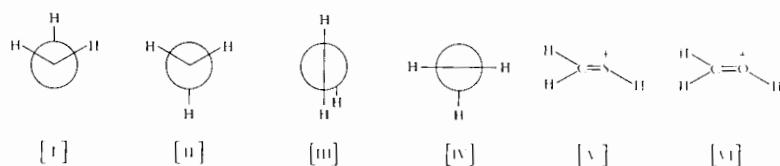


Fig. 4. - Inversion cross section of the rotation-inversion surface.

The $(p_c - p_s)_\pi$ conjugative interaction depicted in equation [1] for the α -thio and α -oxycarbonium ions is characterised in each case by trigonal planar geometry at carbon, I-type conformations in the ground state ([V] and [VI] respectively) and substantial barriers to rotation about the C—S and C—O bonds ($\sim 19^2$ and $\sim 36^3$ kcal mol⁻¹, respectively).



In principle, therefore, the presence of trigonal planar geometry at carbon and an I-type conformation in the stable structure of $\bullet\text{CH}_2\text{SH}$ might also be attributable to the presence of a stabilising conjugative interaction in this species.

And in this case the stabilizing conjugative interaction could be not only of $(p_c - p_s)_\pi$ type, but also of $(p_c - d_s)_\pi$ type. However, the computed $0.65 \text{ kcal mol}^{-1}$ barrier to rotation about the C—S bond is incompatible with this view. Since other factors such as the CSH angle and nuclear-nuclear repulsive effects will also contribute to the barrier, it is evident that conjugative interactions cannot be significant and in particular that the contribution of sulphur d_π orbital conjugative effects to this property of the radical is negligibly small.

Further evidence for this conclusion can be obtained by inspection of the coefficient matrix for the most stable conformation of the radical. This reveals that the highest occupied molecular orbital displays the greatest p_π - d_π interaction; however even in this orbital the sulphur d_π orbital participation is small, the coefficients being 0.01109 and 0.04168 for the inner and outer d_π functions respectively. This can hardly be termed significant. Lower lying molecular orbitals show less sulphur d_π orbital contribution and if we examine, in fact, the gross sulphur d_π orbital population, we find a total occupation of 0.0203 electron for the outer d_π function and 0.0005 electron for the inner d_π , with a total sulphur d_π orbital population of only 0.0208 electron and a total $(p_c - d_s)_\pi$ overlap population of 0.0163. We must conclude that p_π - d_π conjugation in $\bullet\text{CH}_2\text{SH}$ is of no importance. When the inclusion of d -type functions in the basis set leads to such small effects upon the wave function, no chemical significance can be attached to them, and their role is to act as polarisation functions for the p -orbitals ⁽¹⁵⁾.

We may conclude from this preliminary investigation of the problem that it is unlikely that $3d$ -orbital effects are responsible for the observed ⁽¹⁹⁾ chemical differences between α -thio and α -oxyradicals. A detailed comparative quantum mechanical investigation of these two systems is now in progress.

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⁽¹⁵⁾ C. A. Coulson, *Nature*, **221**, 1106 (1969).

⁽¹⁹⁾ R. O. C. Norman, *Chem. Brit.*, **6**, 66 (1970); C. Rüchardt, *Angew. Chem. Int. Ed. Engl.*, **9**, 830 (1970); I. Biddles, A. Hudson, J. T. Wiffen, *Tetrahedron*, **28**, 867 (1972).