*Journal of Organometallic Chemistry*, 214 (1981) 169—181
Elsevier Sequoia S.A., Lausanne — Printed In The Netherlands

# STRUCTURE OF GERMANONE AND GERMATHIONE THROUGH AB INITIO CALCULATIONS

GEORGES TRINQUIER, MICHEL PELISSIER,

*Laboratoire de Physique Quantique (E.R.A. 821), Université Paul Sabatier, 118, route de Narbonne 31062 Toulouse Cedex (France)*

BRUNO SAINT-ROCH and HELENE LAVAYSSIERE

*Laboratoire de Chimie des Organominéraux (E.R.A. 829), Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex (France)*

(Received December 24th, 1980)

## Summary

Ab initio quantum calculations, using pseudopotentials and including electron correlation were performed on $H_2Ge{=}O$ (1) and $H_2Ge{=}S$ (2) with double $\zeta$ (+ $d$ orbitals) basis sets. Full geometry optimization performed at the SCF level led to planar structures GeO = 1.63 Å, GeH = 1.55 Å and $\sphericalangle$HGeH = 112° for 1 and GeS = 2.02 Å, GeH = 1.55 Å and $\sphericalangle$HGeH = 110° for 2. The force constants were calculated as well as the theoretical vibrational frequencies ($\nu$(GeO) = 1038 $cm^{-1}$, $\nu$(GeS) = 586 $cm^{-1}$). As expected the Ge=X bond is strongly polarized, specially in 1. The $\sigma$ and $\pi$ $\mathrm{Ge}\overset{(+)\ (-)}{\text{——}}\mathrm{O}$ bond polarities suggest that the bonding is intermediate between $\pi$ ($H_2Ge{=}O$) and semipolar ($\mathrm{H_2Ge{:}\!\rightarrow\overline{\underline{O}}|}$) bonding. Extended CI was used to compute the Ge=X bond energies as the [$H_2GeX \rightarrow H_2Ge(^1A_1) + X(^3P)$] reaction enthalpy. They are predicted to be about 108 kcal/mol for Ge=O and 83 kcal/mol for Ge=S. 1 is found to be less stable than its germylene isomer H—Ge—OH by 18 kcal/mol.

## I. Introduction

The evidence for reaction intermediates such as $R_2Ge{=}O$ [1—4] as well as $R_2Ge{=}S$ [3,5,6], $R_2Ge{=}NR'$ [4,7—10], $R_2Ge{=}PR'$ [11] and $R_2Ge{=}CR'_2$ [12,13] raises the problem of doubly-bonded germanium compounds. To date, no structural data have been reported for these transient intermediates. This study is devoted to an investigation, through ab initio quantum chemical calculations, of the structure and energetics of two simple Ge=X frameworks, namely germanone $H_2Ge{=}O$ (1) and germathione $H_2Ge{=}S$ (2), assumed to be singlet in the ground state. Comparison is made with lighter $H_2X{=}Y$ analogs, the simplest of which, formaldehyde $H_2C=O$, is recalculated in a similar way.

After computational details (II), the following points will be considered: optimized equilibrium geometries (III), force constants and vibrational frequencies (IV), Ge=X bond energies and charge repartitions (V), and the relative stability of the H—Ge—OH germylene isomer of germanone (VI).

## II. Method and basis sets

The SCF calculations were performed using the PSHONDO program [14] which introduces non-empirical pseudopotentials in the HONDO algorithm [15]. The pseudopotentials used to represent the core electrons are those proposed by Durand and Barthelat [16]. These techniques have been applied to several molecules [17—19] and the results are comparable to those of all-electron calculations. For each atom, a valence basis set was optimized on the atomic ground state using a quadruple zeta gaussian basis set which was further contracted to the double zeta level. For germanium and sulfur, *d* gaussian functions were added as polarization functions ($\zeta_{Ge} = 0.25$, $\zeta_S = 0.54$). The details of the optimized basis sets and of the pseudopotential parameters are available upon request. Using these basis sets, the equilibrium geometries were determined by optimizing independently the geometrical parameters and the vibrational frequencies were calculated by means of the F and G matrix method [20]. A more extended basis set including *d* orbitals on carbon ($\zeta = 0.7$) and oxygen ($\zeta = 1.25$) was used to compute the charge repartition and dipole moments and the starting wavefunctions for the configuration interaction (CI). The extended CI was carried out with an improved version [22] of the CIPSI algorithm [21].

## III. Equilibrium geometries

The calculated planar ground state $C_{2v}$ geometries of **1**, **2** and formaldehyde are presented in Table 1 together with comparative values for $H_2CO$, $H_2CS$ and $H_2SiO$ [26].

Our calculated geometry of formaldehyde compares well with all-electron SCF calculations, the CO bond length being in both cases slightly larger than its experimental value. No experimental values are of course available for **1** and **2**. Our calculated Ge—O bond length in **1** (1.63 Å) is shorter than the Ge—O

TABLE 1

EQUILIBRIUM GEOMETRIES (in Å and degrees) OF $H_2X=Y$

| | This work | | | $H_2CO$ [a] | $H_2CO$, exp. [b] | $H_2CS$ [c] | $H_2SiO$ [c] |
|---|---|---|---|---|---|---|---|
| | $H_2GeO$ | $H_2GeS$ | $H_2CO$ | | | | |
| $r_{XY}$ | 1.634 | 2.020 | 1.217 | 1.217 | 1.202 | 1.594 | 1.485 |
| $r_{XH}$ | 1.547 | 1.549 | 1.092 | 1.084 | 1.100 | 1.084 | 1.472 |
| $\angle HXH$ | 111.9 | 109.8 | 116.4 | 116.8 | 116.3 | 115.2 | 109.9 |

[a] All-electron SCF calculation, ref. 23. [b] Ref. 24. [c] All-electron SCF calculation, ref. 25.

single bond length determined experimentally in $(H_3Ge)_2O$ (1.77 Å) [27], $((PhCH_2)_3Ge)_2O$ (1.73 Å) [28], (t-$Bu_2$(Me)PhO$)_2$Ge: (1.81 Å) [29] or calculated in HGeOH (1.81 Å, see Section VI). It is noteworthy that the GeO and GeS bond lengths in **1** and **2** have almost the same values as in the corresponding diatoms GeO (1.62 Å) and GeS (2.01 Å) [30]. The same trend is observed at the CI level for $H_2Si{=}O$ (1.51 Å) [25] with respect to SiO (1.51 Å) but not for formaldehyde and thioformaldehyde with respect to CO (1.13 Å) and CS (1.53 Å). The same lengthening of the double bond from $H_2C{=}O$ to $H_2C{=}S$ (+0.38 Å) is reproduced from $H_2Ge{=}O$ to $H_2Ge{=}S$ (+0.39 Å). The HGeH valence angles in **1** and **2** are (i) smaller than the HCH valence angles in formaldehyde and thioformaldehyde, (ii) comparable to ∠HSiH in $H_2SiO$ but larger than ∠HGeH in singlet germylene (93°) [19]. The GeH bond lengths are the same in **1** and **2**, and the value (1.55 Å) is smaller than in $:GeH_2$ (1.60 Å) [19] and slightly larger than in $GeH_4$ (1.53 Å) [31]. Similar variations are observed for the SiH bond length: 1.47 Å in $H_2SiO$, 1.51 Å in $SiH_2$ and 1.46 Å in $SiH_4$ [25]. The different XH bond lengths in $H_2X{=}O$ and $H_2X$: can be accounted for in terms of "$sp^2$ hybridization" versus "pure *p*-bonds" [25].

## IV. Harmonic force constants and vibrational frequencies

A set of harmonic force constants in symmetry coordinates has been calculated. The symmetry coordinates are defined as follows

| | | |
|---|---|---|
| $A_1$ | $Q_1$: | Ge=Y stretching |
| | $Q_2$: | symmetric GeH stretching |
| | $Q_3$: | symmetric HGeH bending |
| $B_2$ | $Q_4$: | antisymmetric GeH stretching |
| | $Q_5$: | HGeH rocking |
| $B_1$ | $Q_6$: | out-of-plane bending or wagging |

The calculated values $F_{ij}$ are reported in Table 2, together with corresponding calculated values from the literature for $H_2CO$, $H_2CS$ and $H_2SiO$. One must keep in mind that SCF force constants are always overestimated (compare $H_2CO$ calcd. with $H_2CO$ exp. in Table 2). However, consistent trends can be observed: (i) regular decrease, along the series $H_2CO$, $H_2SiO$, $H_2GeO$, of diagonal $F_{11}$ (X=Y stretching), $F_{22}$ and $F_{44}$ (symmetric and antisymmetric XH stretching), $F_{33}$ (symmetric HXH bending), $F_{55}$ (HXH rocking) as well as coupling $F_{13}$. (ii) halving of $F_{11}$ from $H_2CO$ to $H_2CS$ and from $H_2GeO$ to $H_2GeS$.

Except for $F_{11}$, the changes of $F_{ij}$ on going from $H_2CO$ to $H_2CS$ are not reproduced on going from $H_2GeO$ to $H_2GeS$. For instance $F_{22}$ and $F_{44}$ keep the same values in **1** and **2**. This is consistent with the same calculated GeH bond lengths in **1** and **2**, and hence is supported for equal GeH bond strengths in these two compounds, whereas the CH bonds are stronger in thioformaldehyde with respect to formaldehyde [25].

Also noteworthy in Table 2 is the positive (but weak) value of $F_{23}$ in **2**. The fairly high value of $F_{66}$ (wagging) in **1** and **2** implies a reluctance of germanium to leave planarity and is consistent with a posively charged germanium center

TABLE 2

HARMONIC FORCE CONSTANTS [a] IN SYMMETRY COORDINATES

| Force constant | | This work | | | $H_2CO$ [b] | $H_2SiO$ [c] | $H_2CS$ [c] | $H_2CO$ [d] |
|---|---|---|---|---|---|---|---|---|
| | | Description | $H_2GeO$ | $H_2GeS$ | | | | |
| $A_1$ | $F_{11}$ | GeY stretching | 8.36 | 4.54 | 14.4 | 10.57 | 7.50 | 12.90 |
| | $F_{12}$ | | 0.08 | 0.07 | 0.76 | 0.12 | 0.20 | 0.74 |
| | $F_{22}$ | sym. GeH stretching | 2.99 | 2.99 | 4.2 | 3.19 | 5.74 | 4.96 |
| | $F_{13}$ | | 0.09 | 0.10 | 0.35 | 0.15 | 0.26 | 0.41 |
| | $F_{23}$ | | −0.16 | 0.04 | −0.14 | −0.06 | −0.15 | −0.08 |
| | $F_{33}$ | sym. HGeH bending | 0.38 | 0.45 | 0.63 | 0.55 | 0.54 | 0.57 |
| $B_2$ | $F_{44}$ | antisym. GeH stret. | 2.83 | 2.85 | 4.1 | 3.15 | 5.58 | 4.85 |
| | $F_{45}$ | | 0.08 | 0.06 | 0.12 | 0.07 | 0.06 | 0.17 |
| | $F_{55}$ | HGeH rocking | 0.48 | 0.46 | 0.91 | 0.62 | 0.63 | 0.83 |
| $B_1$ | $F_{66}$ | wagging | 0.78 | 0.72 | 0.48 | 0.41 | 0.38 | 0.40 |

[a] Units are mdyn/Å, mdyn/rad, mdyn Å/rad$^2$. [b] All-electron, double ζ basis set, SCF calculation [23]. [c] All-electron, double ζ basis set, SCF calculation [25]. [d] Experiment [24].

TABLE 3

HARMONIC VIBRATION FREQUENCIES IN $cm^{-1}$

| | Symmetry | Main contribution | This work | | $H_2CO$, Exp. [a] | $H_2CS$, Exp. [b] | $H_2SiO$, Calcd. [c] |
|---|---|---|---|---|---|---|---|
| | | | $H_2GeO$ | $H_2GeS$ | | | |
| $\nu_1$ | $a_1$ | GeY stretch. | 1038 | 586 | 1746 | 1063 | 1325 |
| $\nu_2$ | $a_1$ | sym GeH stretch. | 2257 | 2254 | 2782 | 2970 | 2354 |
| $\nu_3$ | $a_1$ | GeH bending | 893 | 982 | 1500 | 1550 | 1141 |
| $\nu_4$ | $b_2$ | GeH stretch. and bending antisym. | 2207 | 2211 | 2843 | 3025 | 2348 |
| $\nu_5$ | $b_2$ | antisym. rocking | 627 | 590 | 1247 | 1438 | 786 |
| $\nu_6$ | $b_1$ | out of plane | 981 | 901 | 1167 | 993 | 771 |

[a] Ref. 24. [b] Ref. 33, 34. See discussion on assignments in ref. 25. [c] Ref. 25.

which is obtained from the wavefunctions (see Section V). Like carbonium $^+CH_3$ or siliconium $^+SiH_3$ ions, $^+GeH_3$ should strongly retain a planar geometry [32].

The calculated harmonic vibration frequencies of germanone and germathione are given in Table 3. They will be useful for the infrared characterization of these types of compound and for assignment of the observed frequencies, which is now under investigation [35]. The Ge=Y stretching frequencies are calculated at $\nu(Ge{=}O) = 1038\ cm^{-1}$ and $\nu(Ge{=}S) = 586\ cm^{-1}$. The SCF level calculations may overestimate the frequencies, but Table 3 also reveals consistent trends among the series $H_2X{=}Y$. For instance, the relative inversion of $\nu_1$ and $\nu_3$ which occurs on going from $H_2CO$ to $H_2CS$ is observed on going from $H_2GeO$ to $H_2GeS$.

## V. Charge repartition and bonding

### *a) Valence molecular orbitals*

The valence molecular orbital levels are given in Table 4. The first point to note is the similarity between all-electron and pseudopotential calculations for $H_2CO$. The levels are raised in the series $H_2CO$, $H_2SiO$ and $H_2GeO$. The $\pi$

TABLE 4

VALENCE MOLECULAR ORBITAL ENERGIES (in eV)

| | This work | | | $H_2CO$ [a] | $H_2SiO$ [b] |
|---|---|---|---|---|---|
| | $H_2CO$ | $H_2GeO$ | $H_2GeS$ | | |
| $1a_1$ | −38.04 | −33.08 | −25.23 | −38.95 | −34.52 |
| $2a_1$1— | −23.74 | −19.22 | −18.88 | −23.66 | −19.51 |
| $1b_1$ | −18.82 | −14.59 | −14.19 | −19.15 | −15.12 |
| $3a_1$ | −17.51 | −13.29 | −12.42 | −17.55 | −14.35 |
| $1b_1$ ($\pi$) | −14.31 | −11.51 | −10.00 | −14.62 | −12.45 |
| $2b_2$ ($n_{op}$) | −12.00 | −11.50 | −9.61 | −12.04 | −12.16 |

[a] All-electron double $\zeta$ basis set SCF calculation [36]. [b] All-electron extended basis set SCF calculation [25].

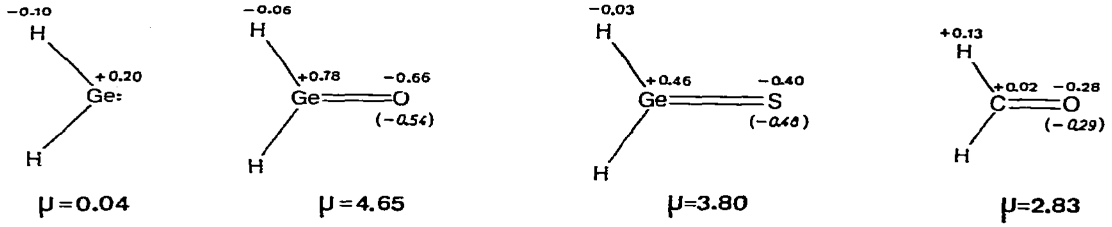


Fig. 1. Net atomic charges (π charges in parentheses) and calculated dipole moments (D).

molecular orbital ($1b_1$) becomes the HOMO in $H_2GeO$ and is accidentally nearly degenerate with the $n_{\sigma p}$ oxygen lone pair ($2b_2$). We shall see that this GeO π bond is strongly polarized, and could therefore be viewed as another (π) oxygen "lone pair". These molecular orbital levels may be related to the ionization potentials (IP's) according to Koopman's theorem (KT) and might be useful for assignments in the recently recorded PES spectra of related compounds [37]. However KT IP's do not take into account polarization and correlation effects which are very different for a lone pair or a bond [38]. Polarization effects, which strongly lower the IP's (which are positive values) are larger for lone pairs. Correlation effects strongly raise the IP of bonds, especially π bonds, while they moderately raise the IP of lone pairs. Consequently, although the Ge=O π bond possesses some "lone pair" character, the SCF calculated $\pi/n_{\sigma p}$ inversion that occurs for **1** should not be observed experimentally.

### b) *Charge repartition*

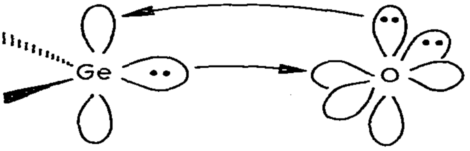
Figure 1 reproduces the charge repartition according to a Mulliken population analysis and calculated dipole moments for **1**, **2** together with $GeH_2$ and $H_2CO$. The hydrogen atoms are less negatively charged in **1** and **2** than in singlet germylene $GeH_2$. As expected, germanone and germathione are strongly polarized. Both σ and π GeX bonds are $Ge^{+}\!-\!{}^{-}X$ polarized. The strongly unsymmetrical Ge—O π bond, which is the HOMO of **1** decomposes according to

$$|\pi_{GeO}\rangle = 0.20|p_zGe\rangle + 0.20|p'_zGe\rangle - 0.08|d_{xz}Ge\rangle$$

$$+ 0.55|p_zO\rangle + 0.39|p'_zO\rangle + 0.02|d_{xz}O\rangle$$

(showing a weak participation of germanium *d* AO of appropriate symmetry).

Isodensity and differential isodensity contour maps of the π bonding MO's are drawn in Figs. 2, 3 and 4. The strong polarity of the Ge—O π bond appears clearly from its isodensity contour map and differential isodensity contour map (Fig. 3). This suggests a possible limiting form of the bonding in germanone as semipolar bond singlet germylene→oxygen ($H_2Ge\!:\rightarrow\overline{\underline{O}}|$) with a $n_\pi$-(oxygen)→$4p_z$ (germanium) back donation, forming the GeO π bond.



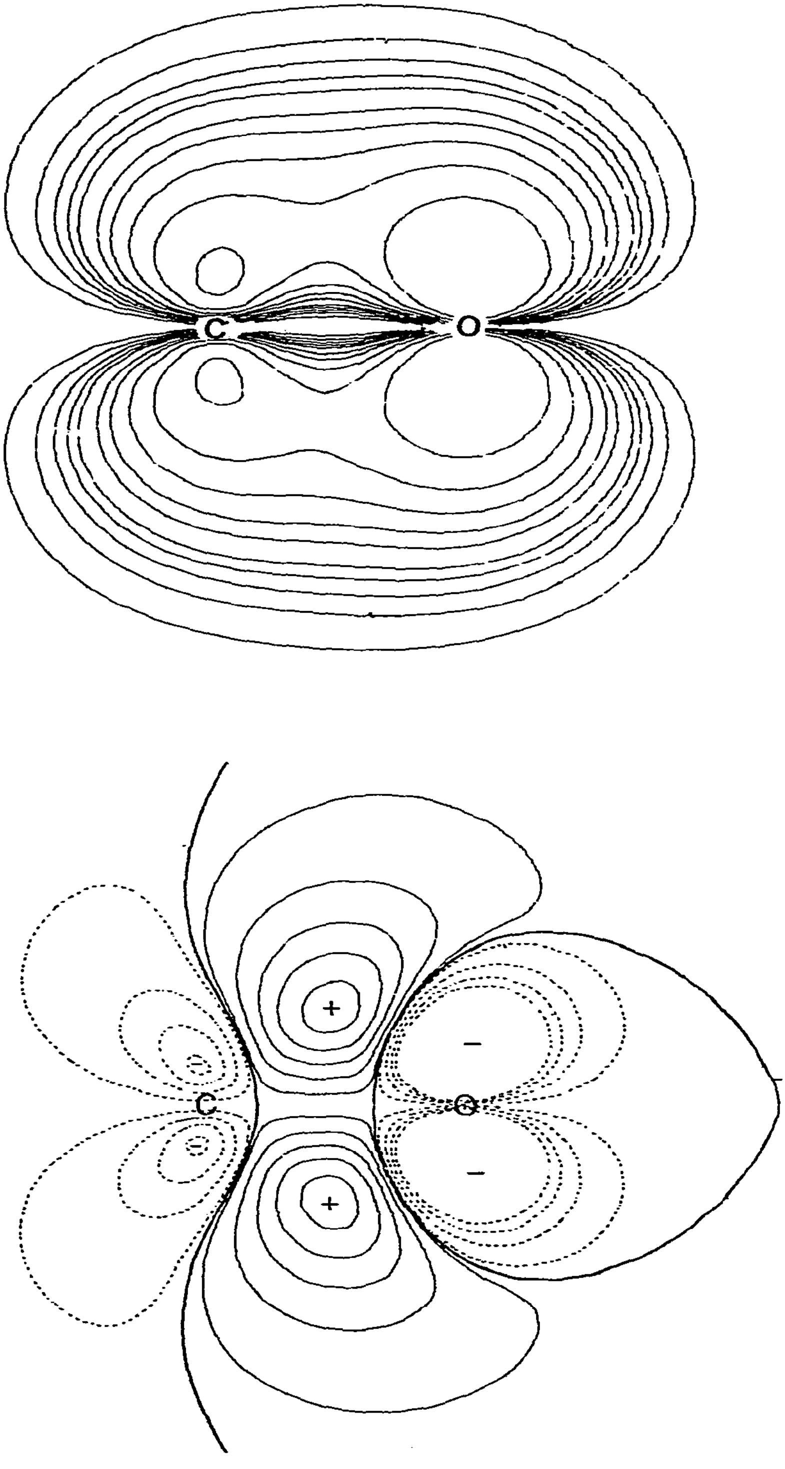


Fig. 2. Charge-density contour map (top) and density-difference contour map (bottom) for the π MO of formaldehyde. Lines plotted correspond to density $\psi^2$ = 0.002, 0.004, 0.006, 0.008, 0.01, 0.015, 0.02, 0.03, 0.05, 0.1, and differential density $\psi_\pi^2 - (\psi^2_{2p_z\mathrm{C}} + \psi^2_{2p_z\mathrm{O}})$ = −0.15, −0.01, −0.005 (dashed lines), 0 (thick lines), 0.001, 0.005, 0.01, 0.015 and 0.020 (full lines).

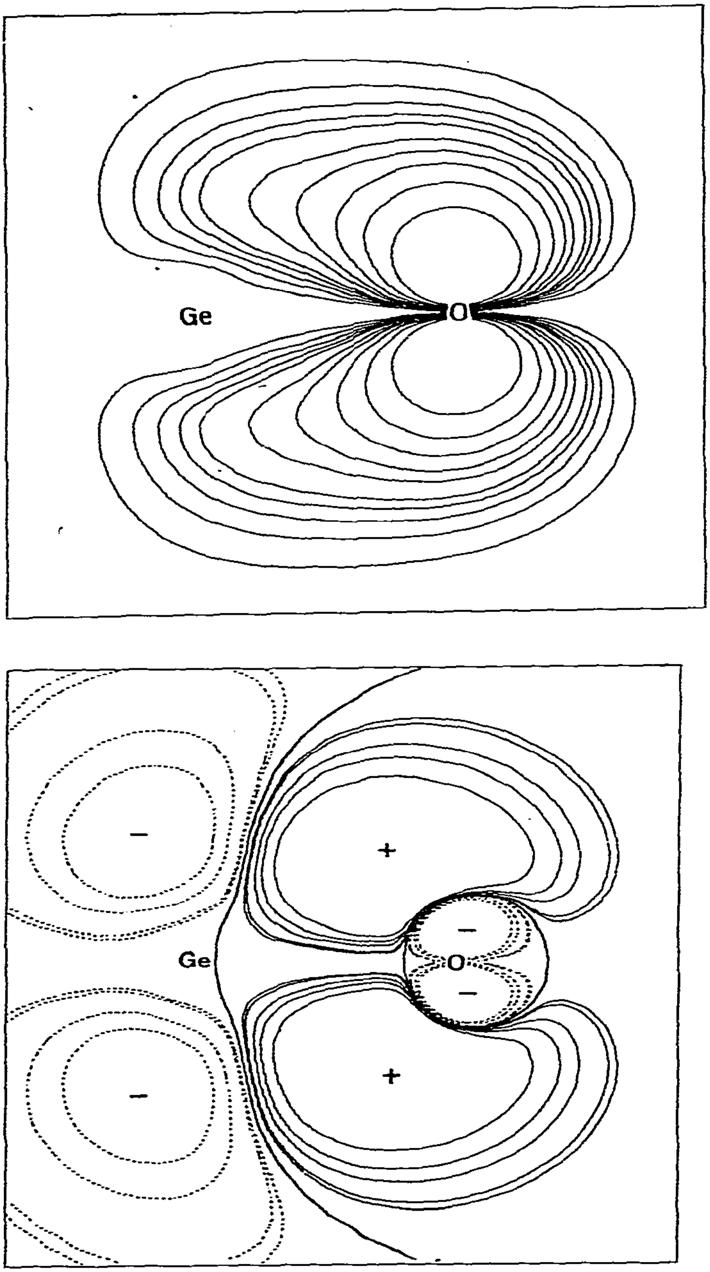


Fig. 3. Charge-density (top) and density-difference (bottom) contour maps for the $\pi$ MO of germanone. Isodensity curves correspond to the same values as in Fig. 2. Differential density curves correspond to $\psi_{\pi}^{2} - (\psi^{2}_{4p_z\mathrm{Ge}} + \psi^{2}_{2p_z\mathrm{O}}) = -0.005, -0.003, -0.001, -0.0008$ (dashed lines), 0 (thick lines), 0.0008, 0.001, 0.002, 0.003 and 0.005 (full lines).

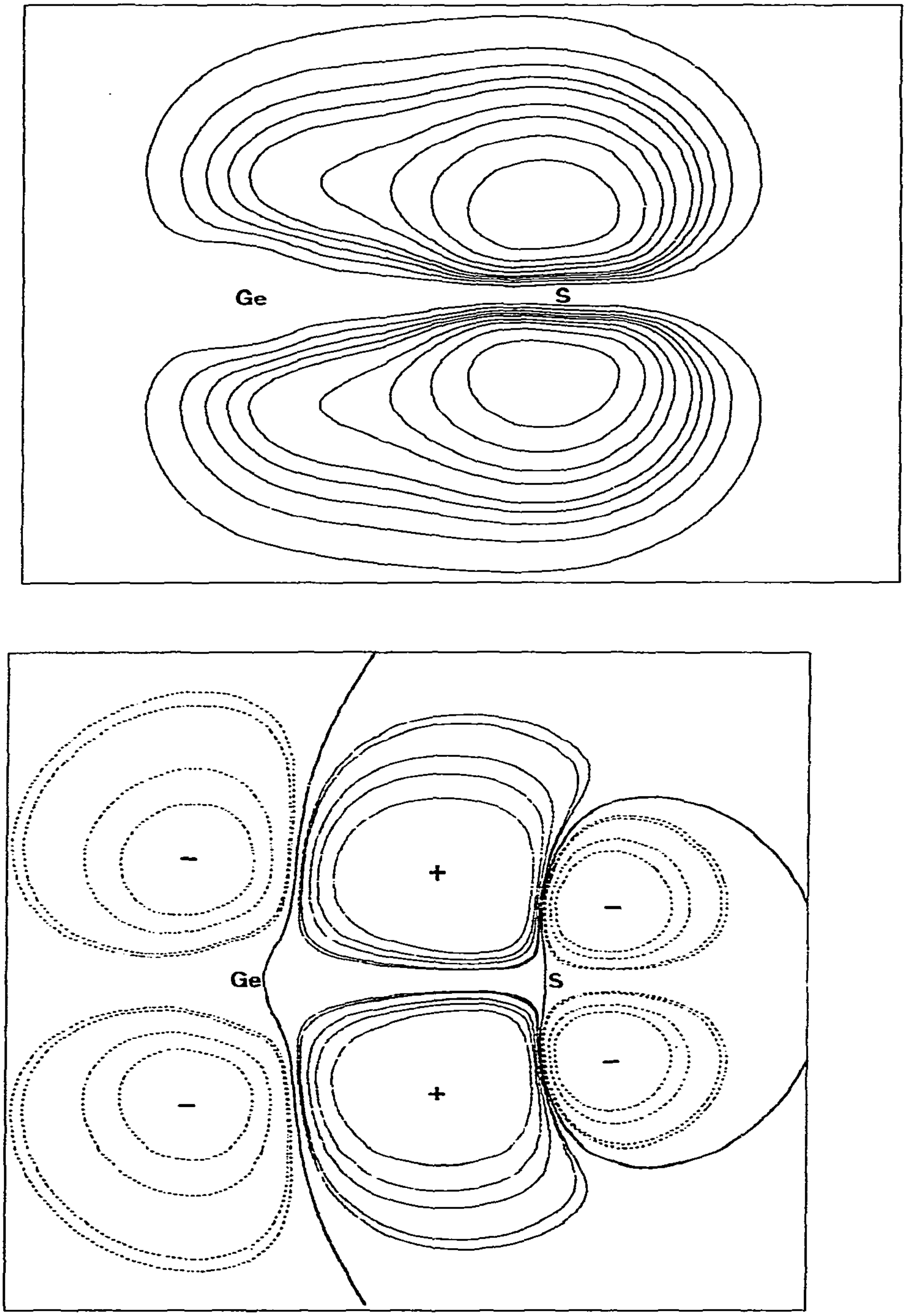


Fig. 4. Charge-density (top) and density difference (bottom) contour maps for the $\pi$ MO of germathione. Lines plotted correspond to the same values as in Fig. 3.

As a consequence of the greater size of the sulfur $3p_z$ AO, this effect is less marked in $H_2Ge{=}S$ (see Fig. 4).

There is a delocalization of the $n_{\sigma p}2b_2$ oxygen and sulfur lone pair into a *d* AO of germanium, but the total population of germanium *d* AO's remains weak in 1 and 2, although more important than in germylenes:

$GeH_2$: 0.11 $e^-$
$GeF_2$: 0.22 $e^-$
$GeMe_2$: 0.14 $e^-$
HGeOH: 0.16 $e^-$
$H_2GeO$: 0.30 $e^-$
$H_2GeS$: 0.26 $e^-$

### *c) Binding energies*

In order to get an estimate for the strength of the Ge=O and Ge=S bonds in 1 and 2, we computed the energy change in the reaction

$$H_2X{=}Y \rightarrow H_2X + Y \qquad (1)$$

all species being in their respective ground states. Of course, correlation effects contribute considerably to the energy of this reaction which is highly anisodesmic. Thus, an extented CI had to be carried out on each species involved in eq. 1: $GeH_2$ ($^1A_1$), $CH_2$ ($^3B_1$), O and S ($^3P$), $H_2CO$, $H_2GeO$ and $H_2GeS$. The CIPSI algorithm [21] in an improved version [22] was used. The variational zero-order function involves two configurations besides the SCF ground state determinant, namely the doubly excited $(\pi \rightarrow \pi^*)^2$ determinant in $H_2X{=}Y$ and the $(n_\sigma \rightarrow p)^2$ determinant in $H_2X$:. These variational wave functions have been perturbed to the second order in energy involving up to $1.8 \times 10^4$ determinants. The Möller-Plesset definition [39] was used for the description of the non-perturbed Hamiltonian. The valence correlation energies obtained under these conditions are

$H_2GeO$: 178 kcal/mol
$H_2GeS$: 128
$H_2CO$: 194
$GeH_2$ ($^1A_1$): 45
$CH_2$ ($^3B_1$): 68
O ($^3P$): 77
S ($^3P$): 67

The XY bond dissociation energies (after taking into account corrections for

TABLE 5

CALCULATED ENTHALPY (in kcal/mol) OF THE DISSOCIATION REACTION $H_2X{=}Y \rightarrow H_2X: + Y$ [a]

| | SCF | CI | Experiment |
|---|---|---|---|
| $H_2CO$ | 110 | 158 | 172 [b] |
| $H_2GeO$ | 38 | 94 | |
| $H_2GeS$ | 53 | 69 | |

[a] Each species in their respective ground state, i.e. $GeH_2$ ($^1A_1$), $CH_2$ ($^3B_1$), O and S ($^3P$). [b] Ref. 40.

TABLE 6

X=Y BOND DISSOCIATION ENERGIES (in kcal/mol) IN $H_2X{=}Y$ MOLECULES

| | $H_2C{=}Y$<br>experiment | $H_2Si{=}Y$<br>Calculated [c] | $H_2Ge{=}Y$<br>(calculated, this work) |
|---|---|---|---|
| Y = O | 172 [a] | 140 | 108 |
| Y = S | 127 [b] | | 83 |

[a] Ref. 40. [b] Refs. 40, 41. [c] Ref. 25.

zero-point vibrations) are reported in Table 5 at both SCF and CI level of theory. The importance of correlation effects is apparent. The experimental dissociation energy of formaldehyde is larger than our CI calculated value. This is not surprising since larger basis sets are required to approach the exact correlation energies. By extrapolation one can estimate the dissociation energies in **1** and **2** at 108 and 83 kcal/mol, respectively. For the GeO bond, this is much smaller than the experimental dissociation energy of the GeO molecule (156 kcal/mol [30]) but larger than an experimental value for a single GeO bond (86 kcal/mol [43]). The $\pi$ contribution to the GeO bond energy in **1** would thus be around 20 kcal/mol. Table 6 shows the consistency of our estimates with the corresponding values for lighter analogs [42].

## VI. Structure and relative stability of the hydroxygermylene isomer

Because of the relative stability of divalent compounds of germanium [44—46], it is worthwhile to evaluate the relative thermodynamic stability of hydroxygermylene H—Ge—OH with respect to its germanone isomer. To this end the hydroxygermylene molecule (assumed to be a singlet in its ground

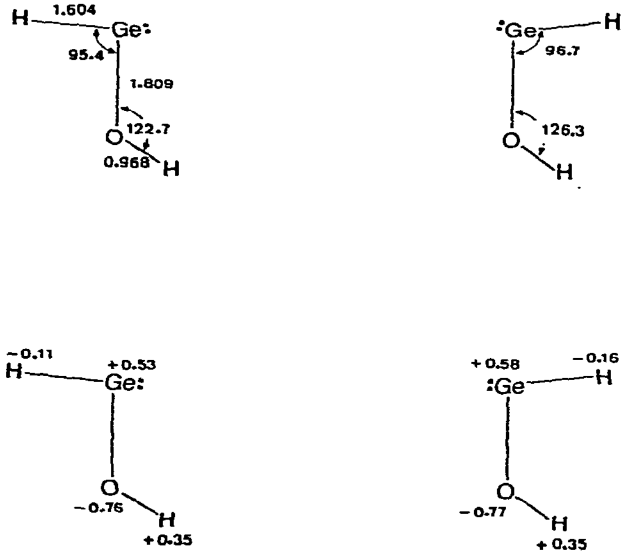


Fig. 5. Optimized geometries in Å and degrees (top) and net atomic charges in |e⁻| (bottom) of the *s-trans* and *s-cis* planar conformations of hydroxygermylene.

state [19]) was investigated through a full geometry optimization. Due to delocalization of a $n_\pi$ lone pair of oxygen into the vacant $4p_z$ AO of germanium, planar conformations are preferred. Due to the electrostatic distribution in this framework, the *s-cis* conformation is preferred to the *s-trans* by 1 kcal/mol, with a rotational barrier of 8 kcal/mol. The corresponding geometries are reported in Fig. 5, together with the net charge diagrams which show how the polarity of the GeH bond fits so as to maximize the electrostatic interaction in the *s-cis* conformation. The calculated GeO bond length is in agreement with experimental GeO bond length in $(RO)_2Ge$ (1.81 Å [29]). *s-cis* HGeOH lies 32 kcal/mol, at the SCF level, below $H_2GeO$. The CI gives a 164 kcal/mol correlation energy in *s-cis* HGeOH which is smaller than in $H_2GeO$ (178 kcal/mol). So, after CI the germanone is only 18 kcal/mol above the hydroxygermylene. This suggest that whenever an alternative exists, the $\pi$-bonded structures are not preferred in the germanium series. The same observation can be made in the silicon series [17,47,48]. The reverse situation occurs in the carbon series in which hydroxycarbene is, of course, much less stable than formaldehyde (by 52 kcal/mol at the CI level [23,49] but is low lying with respect to the $S_1$ excited state of formaldehyde, and could therefore be formed during its photolysis [50]. Its structure corresponds to a planar *s-trans* conformation, the *s-cis* conformation being 5—7 kcal/mol higher with a rotational barrier of 24—27 kcal/mol [23,49,51].

## VII. Conclusion

This study (i) provides structural and vibrational data for $H_2GeO$ and $H_2GeS$; (ii) gives an insight into the bonding in such compounds, indicating strongly polar $\pi$ bonds; (iii) gives estimated Ge—O and Ge—S bond energies of 108 and 83 kcal/mol, respectively; and (iv) shows that hydroxygermylene is more stable than its isomer germanone, the germylene-type unsaturation being preferred to the double bond-type unsaturation.

Calculations on germaethylene $H_2Ge{=}CH_2$ are in progress in extension of our study of unsaturated germanium compounds.

## Acknowledgments

The authors thank Dr. R. Pince for the vibrational calculations and Dr. J.P. Malrieu and Prof. J. Satgé for helpful discussions. This work was supported by a special grant from the U.E.R. P.C.A. Scientific Council (Université Paul Sabatier).

## References

1 H. Lavayssière, J. Barrau, G. Dousse, J. Satgé and M. Bouchaut, J. Organometal. Chem., 154 (1978) C9.
2 J. Barrau, M. Bouchaut, A. Castel, A. Cazes, G. Dousse, H. Lavayssière, P. Rivière and J. Satgé, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 273.
3 J. Barrau, M. Bouchaut, H. Lavayssière, G. Dousse and J. Satgé, Helv. Chim. Acta, 62 (1979) 152.
4 P. Rivière, J. Satgé, A. Castel and A. Cazes, J. Organometal. Chem., 177 (1979) 171.
5 H. Lavayssière, G. Dousse, J. Barrau, J. Satgé and M. Bouchaut, J. Organometal. Chem., 161 (1978) C59.

6 J. Barrau, M. Bouchaut, H. Lavayssière, G. Dousse and J. Satgé, Synth. React. Inorg. Met. Org. Chem., 10 (1980) 515.
7 M. Rivière-Baudet, G. Lacrampe and J. Satgé, C.R. Hebd. Seances Acad. Sci. Ser. C, 289 (1979) 223.
8 M. Rivière-Baudet, P. Rivière and J. Satgé, J. Organometal. Chem., 154 (1978) C23.
9 M. Rivière-Baudet, P. Rivière, J. Satgé and G. Lacrampe, Rec. Trav. Chim. Pays-Bas, 98 (1979) 42.
10 P. Rivière, A. Cazes, A. Castel, M. Rivière-Baudet and J. Satgé, J. Organometal. Chem., 155 (1978) C58.
11 C. Couret, J. Satgé, J.D. Andriamizaka and J. Escudié, J. Organometal. Chem., 157 (1978) C35.
12 T.J. Barton, E.A. Kline and P.M. Garvey, J. Amer. Chem. Soc., 95 (1973) 3078.
13 P. Rivière, A. Castel and J. Satgé, J. Amer. Chem. Soc., 102 (1980) 5413.
14 J.P. Daudey, Private communication.
15 M. Dupuis, J. Rys and H.F. King, J. Chem. Phys., 65 (1976) 111.
16 Ph. Durand and J.C. Barthelat, Theoret. Chim. Acta, 38 (1975) 283.
17 J.C. Barthelat, G. Trinquier and G. Bertrand, J. Amer. Chem. Soc., 101 (1979) 3785.
18 G. Trinquier and J.P. Malrieu, J. Amer. Chem. Soc., 101 (1979) 7169.
19 J.C. Barthelat, B. Saint-Roch, G. Trinquier and J. Satgé, J. Amer. Chem. Soc., 102 (1980) 4080.
20 E.B. Wilson, J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw-Hill Book Co. Inc., New York, 1955.
21 B. Huron, J.P. Malrieu and P. Rancurel, J. Chem. Phys., 58 (1973) 5745.
22 M. Pelissier, Thèse, Université de Toulouse, 1980.
23 J,D. Goddard and H.F. Schaefer III, J. Chem. Phys., 70 (1979) 5117.
24 J.L. Duncan, P.D. Mallinson, Chem. Phys. Lett., 23 (1973) 597; J.L. Duncan, Mol. Phys., 28 (1974) 1177.
25 R. Jaquet, W. Kutzelnigg and V. Staemmler, Theoret. Chim. Acta, 54 (1980) 205.
26 For a general discussion on the geometries of (AB)C=O and (AB)C=S, see H. Oberhammer and J.E. Boggs, J. Mol. Struct., 55 (1979) 283.
27 L.V. Vilkov and N.A. Tarasenko, Zh. Struct. Khim., 10 (1969) 1102.
28 C. Gildewell abd D.C. Liles, J. Chem. Soc. Chem. Commun., (1979) 93.
29 B. Cetinkaya, I. Gümrükcü, M.F. Lappert, J.L. Atwood, R.D. Rogers and M.J. Zaworotko, J. Amer. Chem. Soc., 102 (1970) 2088.
30 K.P. Huber and G. Herzberg, Constants of diatomic molecules, Van Nostrand Reinhold Company, New York, 1979.
31 H.W. Kattenberg, W. Gabes and A. Oskam, J. Mol. Spectrosc., 44 (1972) 425.
32 W.J. Here in Modern Theoretical Chemistry, Vol. 4, Plenum Press, New York, 1977, p 298.
33 W.C. Johns and W.B. Olson, J. Mol. Spectrosc., 39 (1971) 479.
34 M.E. Jacox and D.E. Milligan, J. Mol. Spectrosc., 58 (1975) 142.
35 H. Lavayssiere, G. Dousse, J. Satgé and B. Saint-Roch, to be published..
36 L.C. Snyder and H. Basch, Molecular wave functions and properties, John Wiley and Sons, New York, 1972.
37 G. Pfister-Guillouzo and J. Satgé, to be published.
38 D.P. Chong, F.G. Herring and D. McWilliams, J. Chem. Phys., 61 (1974) 78.
39 C. Möller and M.S. Plesset, Phys. Rev., 46 (1934) 618.
40 S.W. Benson, Chem. Rev., 78 (1978) 23.
41 A. Jones and F.P. Lossing, J. Chem. Phys., 71 (1967) 4111.
42 Other estimations of GeO and GeS bond energies are given by R.A. Howald, J. Chem. Educ., 45 (1968) 163.
43 K.F. Purcell and J.C. Kotz, "Inorg. Chemistry", W.B. Saunders Company, Toronto, 1977, p. 268.
44 J. Satgé, M. Massol and P. Rivière, J. Organometal. Chem., 63 (1973) 1.
45 G. Dousse and J. Satgé, Helv. Chim. Acta, 60 (1977) 1381.
46 Germanium dialkoxides have been recently reported: L.D. Silverman and M. Zeldin, Inorg. Chem., 19 (1980) 270, 272.
47 A.C. Hopkinson and M.H. Lien, J. Chem. Soc. Chem. Commun., (1980) 107.
48 G. Bertrand, G. Trinquier and P. Mazerolles, J. Organometal. Chem. Lib., 12 (1981) 1.
49 R.L. Lucchese and H.F. Scaefer, J. Amer. Chem. Soc., 100 (1978) 298.
50 J.R. Sodeau and E.K.C. Lee, Chem. Phys. Lett., 57 (1978) 71.
51 For dihydroxycarbene, $:C(OH)_2$, see, D. Feller, W.R. Borden and E.R. Davidson, J. Chem. Phys., 71 (1979) 4987.