

## MNDO-UHF STUDY OF THE MOLECULAR AND ELECTRONIC STRUCTURES OF CATION RADICALS DERIVED FROM TETRAMETHYLGERMANE, HEXAMETHYLDIGERMANE, AND OTHER RELATED ORGANOGERMANES

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### Summary

Calculations have been made, using the MNDO-UHF SCF method, of molecular and electronic structures of a range of neutral organogermanes and of the corresponding cation radicals. The cation radical  $(\text{GeMe}_4)^+$  is calculated to have  $D_{2d}$  symmetry as an isolated ion, while  $(\text{Ge}_2\text{Me}_6)^+$  is a  $\sigma$  radical in which the SOMO is strongly localised in the GeGe bond. The cation radicals  $(\text{Me}_3\text{Ge})_2\text{O}^+$  and  $(\text{Me}_3\text{Ge})_2\text{NH}^+$  are  $n\pi$  radicals, while  $(\text{Me}_3\text{Ge})_2\text{CH}_2^+$  dissociates to  $\text{Me}_3\text{Ge}^+$  and  $\text{Me}_3\text{GeCH}_2^+$ , which is planar at the radical centre. Both  $(\text{Me}_3\text{Ge})_2\text{O}_2^+$  and  $(\text{Me}_3\text{Ge})_2\text{S}_2^+$  have *trans*-planar skeletons.

### Introduction

The  $\gamma$ -irradiation of tetramethylgermane in dilute frozen solutions in  $\text{CFCl}_3$  yields [1] the  $(\text{GeMe}_4)^+$  cation radical, whose electron spin resonance spectrum has been interpreted in terms of a  $C_{2v}$  structure containing two distinct types of methyl group which are freely rotating about the Ge–C bonds. The use of an adamantane matrix, on the other hand, yields [2] the neutral radical  $\text{GeMe}_3^{\cdot}$  after  $\gamma$ -irradiation: this product [2] had an electron spin resonance spectrum virtually identical with that of  $\text{GeMe}_3^{\cdot}$  radicals produced [3] by reaction of  $\text{Me}_3\text{GeH}$  with  $\text{Me}_3\text{CO}^{\cdot}$ . Similar  $\gamma$ -irradiation of hexamethyldigermane in dilute frozen solutions in  $\text{CFCl}_3$  gives the  $(\text{Ge}_2\text{Me}_6)^+$  cation radical [4], which is characterised by hyperfine coupling of the unpaired electron to eighteen equivalent hydrogens, again requiring free rotation of the methyl groups about the Ge–C bonds. It was suggested [4] that  $(\text{Ge}_2\text{Me}_6)^+$  is a  $\sigma$  radical in which the unpaired electron is strongly localised in a  $\sigma$ -bonding Ge–Ge orbital.

In the present paper, we report the results of MNDO calculations, which provide information on the molecular and electronic structures, on some permethylated

germanium radicals derived from  $\text{GeMe}_4$  and  $\text{Ge}_2\text{Me}_6$ , as well as those from  $\text{Me}_3\text{GeH}$  and  $\text{Me}_3\text{GeCMe}_3$ ,  $(\text{Me}_3\text{Ge})_2\text{X}$  ( $\text{X} = \text{O}, \text{NH}$  or  $\text{CH}_2$ ), and  $(\text{Me}_3\text{Ge})_2\text{O}_2$  and  $(\text{Me}_3\text{Ge})_2\text{S}_2$ .

### Calculations

All calculations of molecular geometry and energy were made using the MNDO method [5] incorporated in the MOPAC system [6]: the atomic parameters used were those stored internally in the MOPAC system. UHF wave functions were used for all open-shell species, and all geometric variables were independently optimised unless it is stated otherwise.

### Results and discussion

#### *Radicals from $\text{GeMe}_4$ and $\text{Ge}_2\text{Me}_6$*

The neutral molecules  $\text{GeMe}_4$  and  $\text{Ge}_2\text{Me}_6$  optimised to structure having exact  $T_d$  and  $D_{3d}$  skeletal symmetry (Table 1): the molecular energies were essentially independent of detailed hydrogen conformation, indicative of free rotation of the methyl groups about their GeC bonds. The calculated GeC distance is 1.941 Å in each molecule, comparable with the value of 1.945 Å observed [7]: the calculated GeGe distance in  $\text{Ge}_2\text{Me}_6$ , 2.564 Å, is somewhat longer than the value of 2.404 Å observed [8] in the unsubstituted  $\text{Ge}_2\text{H}_6$ .

In the neutral  $\text{GeMe}_4$ , the HOMO is of  $T_2$  type, concentrated primarily in the GeC bonds. Hence vertical ionisation will yield a Jahn–Teller sensitive cation, which is expected to undergo a reduction in skeletal symmetry, along a skeletal vibration of either  $e$  or  $t_2$  type. As in previous studies of organometallic radicals [9,10], two skeletal geometries, having  $C_{3v}$  and  $C_{2v}$  symmetry, were considered. The  $C_{3v}$  isomer was calculated to have marginally the lower energy, but this symmetry does not represent a genuine minimum, nor does the resulting electronic structure possess  $C_{3v}$  symmetry. Constrained  $C_{2v}$  optimisations always converged to exact  $D_{2d}$  symmetry, corresponding to a Jahn–Teller distortion from  $T_d$  along one component of the  $e$  skeletal deformation: when the potential surface for  $(\text{GeMe}_4)^+$  was scanned along one of the angular coordinates, for values of  $\angle(\text{CGeC})$  from 110 to 180°,  $D_{2d}$  symmetry was found to be maintained throughout. The calculated  $D_{2d}$  symmetry applies to the free ion, and it was suggested in the original report of the formation of  $(\text{GeMe})_4^+$  in frozen solution [1] that the observed  $C_{2v}$  symmetry resulted from vibronic perturbations induced by the matrix.

The  $\text{GeMe}_3^{\cdot}$  radical, of  $C_{3v}$  symmetry, has a pyramidal skeleton, like its silicon [11] and tin [12,13] analogues, although unlike  $\text{CMe}_3^{\cdot}$ , which is effectively planar [14,15]. The angle between the GeC bonds and the threefold symmetry axis is calculated, for the isolated radical, to be 106.1°, slightly smaller than the value, 113°, deduced [2] for the radical in an adamantane matrix. A scan of the  $(\text{GeMe}_4)^+$  potential surface along one of the GeC bonds showed that dissociation is to  $\text{Me}_3\text{Ge}^+$  and  $\text{CH}_3^{\cdot}$ , rather than to  $\text{Me}_3\text{Ge}^{\cdot}$  and  $\text{CH}_3^+$ . Consequently formation of  $\text{Me}_3\text{Ge}^{\cdot}$  from the  $\gamma$ -irradiation of  $\text{GeMe}_4$  [2] probably requires a subsequent charge exchange reaction of the  $\text{Me}_3\text{Ge}^+$  cation, either with a further molecular of  $\text{GeMe}_4$  or with the matrix material.

The HOMO of  $\text{Ge}_2\text{Me}_6$  is of  $A_{1g}$  ( $\sigma$ -bonding) type, localised primarily in the

TABLE 1  
OPTIMISED PARAMETERS FOR PERMETHYLATED SPECIES

Molecule	Skeletal point-group	$\Delta H_f^\ominus$ (kJ mol <sup>-1</sup> )	$d(\text{GeC})$ (Å)	$d(\text{GeGe})$ (Å)	$\angle(\text{CGeC})$ (°)	$\angle(\text{CGeGe})$ (°)
$\text{Ge}_2\text{Me}_6$	$D_{3d}$	-99.9	1.941	2.564	107.7	111.2
$(\text{Ge}_2\text{Me}_6)^+$	$D_{3d}$	+682.5	1.917	3.414	117.4	99.3
$\text{GeMe}_4$	$T_d$	-132.3	1.941		109.5	
$(\text{GeMe}_4)^+$	$D_{2d}$	+888.4	1.992(×4)		125.7(×2)	
	$C_{3v}^a$	+885.9	1.911(×1)		113.6(×3)	
			2.027(×3)		105.0(×3)	
$\text{GeMe}_3$	$C_{3v}$	-15.7	1.928		112.6	
$(\text{GeMe}_3)^+$	$D_{3h}$	+680.6	1.898		120.0	

<sup>a</sup> Skeletal point group imposed, 40 geometric variables optimised: not a genuine minimum (see text).

GeGe bond, and containing contributions (from both 4s and 4p orbitals ( $|C_s| = 0.214$ ;  $|C_p| = 0.583$ ). In consequence, vertical ionisation gives a cation insensitive to Jahn-Teller distortion, and the optimised structure of the cation radical  $(\text{Ge}_2\text{Me}_6)^+$  retains the  $D_{3d}$  symmetry of its neutral parent. As with the tin analogue [10,16], conversion of  $\text{Ge}_2\text{Me}_6$  to  $(\text{Ge}_2\text{Me}_6)^+$  is accompanied by a lengthening of the central GeGe bond and a flattening of the individual  $\text{GeMe}_3$  fragments. The SOMO in  $(\text{Ge}_2\text{Me}_6)^+$  is again of  $A_{1g}$  type, strongly localised in the GeGe bond, ( $|C_s| = 0.182$ ;  $|C_p| = 0.609$ ), so that the two  $\text{GeMe}_3$  fragments are held together by only a one-electron bond.

#### Radicals from $\text{Me}_3\text{GeH}$ and $\text{Me}_3\text{GeBu}^t$

The neutral molecule  $\text{Me}_3\text{GeCMe}_3$  has  $C_{3v}$  symmetry, with a unique GeC bond distance of 2.008 Å: the HOMO is of  $A_1$  ( $\sigma$ -bonding) type, localised primarily in the central GeC bond. The resulting radical cation is of some interest, as it provides a bridge between the  $\sigma$ -radical  $(\text{Ge}_2\text{Me}_6)^+$  described above, and  $(\text{C}_2\text{Me}_6)^+$  [17,18] which is stabilised only by cage effects [9,19]. Ionisation of  $\text{Me}_3\text{GeBu}^t$  is calculated to give smooth dissociation to the two planar species  $\text{Me}_3\text{Ge}^+$  and  $\text{CMe}_3$ ; likewise  $\text{Me}_3\text{GeH}$  is calculated to give upon ionisation  $\text{Me}_3\text{Ge}^+$  and hydrogen atoms.

#### Radicals from $(\text{Me}_3\text{Ge})_2X$ ( $X = \text{O}, \text{NH}, \text{CH}_2$ )

Within the (*s*, *p*) basis set employed in the MNDO method the structure of  $(\text{Me}_3\text{Ge})_2\text{O}$  is calculated to be linear at oxygen: the experimental value of  $\angle(\text{GeOGe})$ , from electron diffraction measurements is 141° [20], although the detailed dynamics of the skeletal vibrations have not been worked out. In common with such molecules as  $(\text{Me}_3\text{Si})_2\text{O}$  and  $(\text{H}_2\text{Si})_2\text{O}$ , which MNDO calculates to be linear at oxygen,  $(\text{Me}_3\text{Ge})_2\text{O}$  may well be quasi-linear [21] with only a very small barrier at the linear configuration. Such molecules pose a very severe test of theoretical calculations, and  $(\text{H}_3\text{Si})_2\text{O}$ , for example, requires the use of *d*-functions upon oxygen before the form of the experimental [22] bending potential functions can be reproduced [23]: the use of *d*-functions on silicon alone is insufficient [23]. Both  $(\text{Me}_3\text{Ge})_2\text{NH}$  and  $(\text{Me}_3\text{Ge})_2\text{CH}_2$  have calculated structures (Table 2) which are very similar to those of the silicon analogues [24,25]. The planar nitrogen in  $(\text{Me}_3\text{Ge})_2\text{NH}$  is paralleled by planar nitrogen in both  $(\text{H}_3\text{Ge})_3\text{N}$  [26] and in  $(\text{Ph}_3\text{Si})_2\text{NH}$  [27].

TABLE 2

OPTIMISED PROPERTIES OF  $(\text{Me}_3\text{Ge})_2\text{X}$  AND  $[(\text{Me}_3\text{Ge})_2\text{X}]^+$  ( $\text{X} = \text{O}, \text{NH}, \text{CH}_2$ )

	X = O	X = NH	X = CH <sub>2</sub>
<i>Neutral molecules</i>			
$\Delta H_f^\ominus$ (kJ mol <sup>-1</sup> )	-493.7	-246.8	-217.0
$d(\text{GeX})$ (Å)	1.755 <sup>a</sup>	1.855	1.940
$\angle(\text{GeXGe})$ (°)	180.0 <sup>b</sup>	138.5 <sup>c</sup>	128.5
HOMO	O( $p\pi$ )	N( $p\pi$ )	$\sigma(\text{Ge}-\text{C}-\text{Ge})$
<i>Cation radicals</i>			
$\Delta H_f^\ominus$ (kJ mol <sup>-1</sup> )	+424.5	+545.2	<sup>d</sup>
$d(\text{GeX})$ (Å)	1.900	1.992	
$\angle(\text{GeXGe})$ (°)	180.0	139.9	

<sup>a</sup> Experimental value, 1.767 Å (ref. 20). <sup>b</sup> See text. <sup>c</sup> Bonds to N coplanar. <sup>d</sup> Dissociates to  $\text{Me}_3\text{GeCH}_2^\cdot$  and  $\text{Me}_3\text{Ge}^+$  (see text).

The forms of the HOMO in these three molecules provide the key to their subsequent behaviour upon ionisation. In  $(\text{Me}_3\text{Ge})_2\text{O}$  and  $(\text{Me}_3\text{Ge})_2\text{NH}$  the HOMO is a oxygen or nitrogen  $2p_\pi$  orbital, normal to the  $\text{GeXGe}$  fragment: consequently, ionisation to the corresponding cation radicals occurs with very little structural change. However in  $(\text{Me}_3\text{Ge})_2\text{CH}_2$ , where there is no lone pair, the HOMO of  $\sigma$  type is concentrated in the two  $\text{GeC}$  bonds, and upon ionisation the cation dissociates smoothly to  $\text{Me}_3\text{GeCH}_2^\cdot$  and  $\text{Me}_3\text{Ge}^+$ . The radical  $\text{Me}_3\text{GeCH}_2^\cdot$  is calculated to be planar at the radical centre, with the SOMO a carbon  $2p_\pi$  orbital normal to the  $\text{GeCH}_2$  plane. The unique  $\text{GeC}$  distance is 1.885 Å, the threefold  $\text{GeC}$  distance is 1.938 Å, and the threefold angle between the two type of bond is 109.4°.

#### Radicals from $(\text{Me}_3\text{Ge})_2\text{O}_2$ and $(\text{Me}_3\text{Ge})_2\text{S}_2$

Neutral  $(\text{Me}_3\text{Ge})_2\text{O}_2$  optimises to a structure whose skeletal symmetry is  $C_{2h}$ , i.e. *trans*-planar with a dihedral angle  $\sigma(\text{GeOOGe})$  of 180°. In the related peroxides  $(\text{Me}_3\text{C})_2\text{O}_2$  and  $(\text{Me}_3\text{Si})_2\text{O}_2$  the average structures, measured by electron diffraction, have apparent dihedral angles of 166 and 144° respectively [28]. In view of the dihedral angle of 180° found [29] in  $(\text{Ph}_2\text{C})_2\text{O}_2$ , it is possible that for all these permethyl peroxides, the energy minimum occurs at the *trans*-planar,  $\delta = 180^\circ$ , conformation. In  $(\text{Me}_3\text{Ge})_2\text{O}_2$ , for which the  $\text{GeC}$ ,  $\text{GeO}$ , and  $\text{OO}$  distances are calculated to be 1.937, 1.865, and 1.274 Å respectively, the HOMO is the out of phase combination of oxygen  $2p_\pi$  orbitals, of  $B_g$  symmetry. Ionisation to  $(\text{Me}_3\text{Ge})_2\text{O}_2^+$  does not follow the precepts of Koopman's theorem, and the SOMO in the radical cation is spread over the whole of the  $\text{GeOOGe}$  fragment, where it is anti-bonding for both  $\text{GeO}$  and  $\text{OO}$ . In analogous  $(\text{Me}_3\text{Ge})_2\text{S}_2^+$ , also of  $C_{2h}$  skeletal symmetry, the SOMO is of  $B_g$  type strongly localised in the  $\text{SS}$  fragment. The skeletal geometry and the SOMO calculated for  $(\text{Me}_3\text{Ge})_2\text{S}_2^+$  are both typical of those found in cation radicals of type  $\text{R}_2\text{S}_2^+$  [30–32].

#### References

- 1 B.W. Walther and F. Williams, *J. Chem. Soc., Chem. Commun.*, (1982) 270.
- 2 R.V. Lloyd and M.T. Rogers, *J. Am. Chem. Soc.*, 95 (1973) 2459.
- 3 H. Sakurai, K. Mochida, and M. Kira, *J. Am. Chem. Soc.*, 97 (1975) 929.

- 4 J.T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, (1981) 666.
- 5 M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99** (1977) 4899.
- 6 J.J.P. Stewart, *QCPE No.* 455.
- 7 J.L. Hencher and F.J. Mustoe, *Canad. J. Chem.*, **53** (1975) 3542.
- 8 B. Beagley and J.J. Monaghan, *Trans. Farad. Soc.*, **66** (1970) 2745.
- 9 C. Glidewell, *J. Chem. Res.*, (1983), (S) 22.
- 10 C. Glidewell, *J. Organomet. Chem.*, in press.
- 11 P.J. Krusic and J.K. Kochi, *J. Am. Chem. Soc.*, **91** (1969) 3938.
- 12 S.A. Fieldhouse, A.R. Lyons, H.C. Starkie, and M.C.R. Symons, *J. Chem. Soc., Dalton Trans.*, (1974) 1966.
- 13 M.J.S. Dewar, G.L. Grady, D.R. Kühn, and K.M. Merz, *J. Am. Chem. Soc.*, **106** (1984) 6773.
- 14 D. Griller, K.U. Ingold, P.J. Krusic, and H. Fischer, *J. Am. Chem. Soc.*, **100** (1978) 6750.
- 15 M.N. Paddon-Row and K.N. Houk, *J. Am. Chem. Soc.*, **103** (1981) 5046.
- 16 M.C.R. Symons, *J. Chem. Soc., Chem. Commun.*, (1981) 1251.
- 17 M.C.R. Symons and I.G. Smith, *J. Chem. Res.* (1979), (S) 382.
- 18 M.C.R. Symons, *Chem. Phys. Lett.*, **69** (1980) 198.
- 19 C. Glidewell, *J. Chem. Soc., Perkin Trans. II*, (1984) 1175.
- 20 L.V. Vilkov and N.A. Tarasenko, *Zhur, Strukt. Khim.*, **10** (1969) 1102.
- 21 W.R. Thorson and I. Nakagawa, *J. Chem. Phys.*, **33** (1960) 994.
- 22 J.R. Durig, M.J. Flanagan, and V.F. Kalasinsky, *J. Chem. Phys.*, **66** (1977) 2775.
- 23 C.A. Ernst, A.L. Allred, M.A. Ratner, M.D. Newton, G.V. Gibbs, J.W. Moscovitz, and S. Topiol, *Chem. Phys. Letts.*, **81** (1981) 424.
- 24 C. Glidewell and D.C. Liles, *J. Organomet. Chem.*, **234** (1982) 15.
- 25 A.G. Robiette, G.M. Sheldrick, W.S. Sheldrick, B. Beagley, D.W.J. Cruickshank, J.J. Monaghan, B.J. Aylett, and I.A. Ellis, *J. Chem. Soc., Chem. Commun.*, (1968) 909.
- 26 C. Glidewell, D.W.H. Rankin, and A.G. Robiette, *J. Chem. Soc. (A)* (1970) 2935.
- 27 C. Glidewell and H.D. Holden, *Acta Cryst.*, **B37** (1981) 1754.
- 28 K. Käss, H. Oberhammer, D. Brandes, and A. Blaschette, *J. Mol. Struct.*, **40** (1977) 65.
- 29 C. Glidewell, D.C. Liles, D.J. Walton, and G.M. Sheldrick, *Acta Cryst.*, **B35** (1979) 500.
- 30 T. Gillbro, *Chem. Phys.*, **4** (1974) 476.
- 31 H. Chandra, D.N. Ramakrishna Rao, and M.C.R. Symons, *J. Chem. Res.*, (1983), (S) 68.
- 32 C. Glidewell, *J. Chem. Soc., Perkin Trans. II*, (1984) 407.