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THE MOLECULAR AND ELECTRONIC STRUCTURE OF RADICAL CATIONS DERIVED FROM TETRAMETHYLTIN AND HEXAMETHYLDITIN: AN SCF-MO STUDY

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Summary

Molecular geometries and energies have been calculated, using the semi-empirical MNDO method for the closed-shell species $SnMe_4$, Sn_2Me_6, and $(SnMe_3)^+$; and using the UHF-MNDO method for the radicals $(SnMe_4)^+$, $(Sn_2Me_6)^+$ and $SnMe_3^\cdot$. The radical cation $(SnMe_4)^+$ is calculated to have C_{3v} skeletal symmetry, with a C_{2v} isomer some 15 kJ mol^{-1} higher in energy. The dinuclear radical cation $(Sn_2Me_6)^+$ is calculated to be a σ(Sn–Sn) radical, of D_{3d} skeletal symmetry: although the calculated Sn(5*s*) spin density is extremely low, the tin atoms are far from planarity. Calculated spin densities are compared with experimental hyperfine couplings.

Introduction

The electron spin resonance spectrum of matrix-isolated $(SnMe_4)^+$, formed by γ-irradiation of dilute frozen solutions of $SnMe_4$ in $CFCl_3$ shows strong hyperfine coupling to only three equivalent protons with $a(^1H)$ of ca. 13 G [1]. Since, by analogy with both $(SiMe_4)^+$ and $(GeMe_4)^+$ where free rotation about Si–C or Ge–C bonds is observed [2], free rotation is expected also about Sn–C bonds, the spectrum has been interpreted [1] in terms of a C_{3v} structure in which the three strongly coupled hydrogens are all in the same methyl group. The tin hyperfine couplings have been interpreted [1] to suggest a flattening of the Me_3Sn fragment with stretching and weakening of the unique Sn–C bond; this suggestion is supported by the formation, upon annealing of $(SnMe_4)^+$, of methyl radicals. Such a structure is quite different from that of $(CMe_4)^+$, also of C_{3v} symmetry, in which three strongly coupled hydrogens occur, one in each of three equivalent methyl groups, having their C–H vectors parallel to the three-fold rotation axis [3–5].

Similar γ-radiolysis of frozen Sn_2Me_6 solutions yields the cation $(Sn_2Me_6)^+$ whose ESR spectrum has been interpreted [6] in terms of a symmetric σ radical, again with free rotation about the Sn–C bonds, in which the two tin atoms are very

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nearly planar, as was previously suggested [7,8] for the analogous $(C_2Me_6)^+$ cation. Such planarity at tin in $(Sn_2Me_6)^+$ would require a considerable change in geometry at tin between $(Sn_2Me_6)^+$ and the strongly pyramidal radical $SnMe_3$ [9,10]. However, for the analogous pair $SiMe_3$ [11] and $(Si_2Me_6)^+$ [12,13], semi-empirical SCF-MO calculations [5] did not indicate any significant variation of geometry at silicon.

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

Calculations

All calculations of molecular geometry and energy were carried out using the MNDO method [4] as incorporated in the MOPAC system. [15] The published parameters were used for H, C and Sn [16,17]. UHF wave functions were employed for all open-shell species, and all geometric variables were optimised unless it is stated to the contrary. Optimised molecular parameters, together with observed [1,6,9] $a(^1H)$ values are given in Table 1.

Results and discussion

Closed-shell species

The optimised parameters for $SnMe_4$ (Table 1) are essentially identical with those reported previously by Dewar [17], who discusses the discrepancies between observed and MNDO calculated properties in a wide range of simple molecular compounds containing tin. Structurally, Dewar finds [17] that bond angles are generally well reproduced in test compounds, but that bond distances involving tin are usually calculated to be ca. 0.1 Å too short. Thus for $SnMe_4$, the SnC distance calculated (Table 1) is 2.064 Å, compared with the experimental [18] value of 2.134 Å. The SnC distance calculated for Sn_2Me_6 is very similar to that in $SnMe_4$. The SnSn distance calculated for Sn_2Me_6 is 2.667 Å: while there appears to be no modern experimental determination of this distance, the values observed in the analogous Sn_2Ph_6, 2.77 Å [19] and cyclo-Sn_6Ph_{12}, 2.77 Å [20] are again ca. 0.1 Å longer than the calculated SnSn distance in Sn_2Me_6. The cation $(SnMe_3)^+$ is calculated to have a planar skeleton, as expected. All these species exhibit effectively free rotation about the SnC bonds.

The radical $SnMe_3^{\cdot}$

This radical is calculated to be sharply pyramidal at the tin atom (Table 1) consistent with experimental evidence [10] and with a previous calculation [21]. In contrast the carbon analogue CMe_3 is effectively planar at the unique carbon [22–24], whereas $SiMe_3$ is also pyramidal [11]. The distinction between CMe_3 and its heavier analogues MMe_3 (M = Si, Sn) can be readily understood in terms [25] of the relative electronegativities of the central atom and the methyl ligands. In planar CMe_3 the out-of-plane skeletal bending force constant is positive because of the comparatively low electronegativity of methyl relative to the central carbon: as the central atom electronegativity is lowered, upon moving from carbon to silicon or tin, the skeletal bonding force constant becomes negative, causing a relaxation of the

TABLE 1

OPTIMISED MOLECULAR PARAMETERS

	Skeletal point group	$\Delta H_f^{\ominus}$ (kJ mol^{-1})	d(SnC) (Å)	d(SnSn) (Å)	< (CSnC) (°)	< (CSnSn) (°)	$\rho(^1H)$	$a(^1H)$ (G) [a]
Sn_2Me_6	D_{3d}	−80.6	2.067	2.667	108.0	110.9		
$(Sn_2Me_6)^+$	D_{3d}	+773.5	2.066	3.002	114.6	103.6	−0.0044	3.4 [c,d]
$SnMe_4$	T_d	−67.4	2.064		109.5			
$(SnMe_4)^+$	C_{3v} [b]	+859.9	2.349 (×1)		100.2 (×3)		+0.0199 (3H)	13–14 (3H) [e,f]
			2.071 (×3)		116.9 (×3)		−0.0030 (9H)	
	C_{2v}	+874.6	2.176 (×2)		92.1 (×1)		+0.0062 (6H)	
			2.069 (×2)		114.5 (×1)		−0.0054 (6H)	
$SnMe_3^{\cdot}$	C_{3v}	+30.5	2.053		110.0		+0.0024 (9H)	2.75 (9H) [g,h]
$(SnMe_3)^+$	D_{3h}	+782.8	2.067		120.0			

[a] G $= 10^{-4}$ T. [b] Skeletal point group imposed, 40 geometric variables optimised: for other N-atomic radicals, $3N-6$ geometric variables optimised. [c] Ref. 6. [d] $\rho[Sn(5s)]$, 0.0022; $|a_{iso}(Sn)|$, parallel −240 G, perpendicular 100 G (ref. 6). [e] Ref. 1. [f] $\rho[Sn(5s)]$, 0.0154; $|a_{iso}(Sn)|$, parallel −210 G, perpendicular 78G (ref. 1). [g] Ref. 9. [h] $\rho[Sn(5s)]$, −0.1423; $a_{iso}(^{119}Sn)$, 1550 G (ref. 10).

skeletal geometry from planar to pyramidal. In support of this mechanism [25], we note that the calculated charges for the central atom in planar MMe_3 are: M = C, $q = -0.21$; M = Si, $q = +0.64$; M = Sn, $q = +0.18$.

The SOMO in $SnMe_3$ is of A_1 type in C_{3v} skeletal symmetry, localised primarily on the tin atom and directed along the symmetry axis away from the freely-rotating methyl groups.

The radical cations $(SnMe_4)^+$ *and* $(Sn_2Me_6)^+$

Vertical ionisation of the tetrahedral $SnMe_4$, whose HOMO is of symmetry type T_2 concentrated in the SnC bonds, yields a Jahn-Teller sensitive radical cation $(SnMe)_4{}^+$: skeletal distortion along a vibration coordinate of T_2 symmetry can lead to structures of either C_{2v} or C_{3v} symmetry, depending upon the coupling of the T_2 components.

Free optimisation of the structure of $(SnMe_4)^+$ yielded the geometric parameters given in Table 1. The structure consists of an $SnMe_3$ fragment considerably flattened towards planarity (<(CSnC) 116.9°) but having an essentially unperturbed SnC bond distance, together with a unique methyl group joined to tin by a very long bond (2.349 Å): in the unique methyl group, the HCH angles are 117.4°, approaching the 120° found in the free methyl radical. Just as the unique SnC bond is lengthened upon ionisation, so also it is considerably weakened: the calculated $D(Me_3Sn^+{-}CH_3)$ value is only $+11.1$ kJ mol^{-1}, compared to a calculated value of $D(Me_3Sn{-}CH_3)$ of $+200.9$ kJ mol^{-1} for the neutral parent. Although the ESR spectrum of $(SnMe_4)^+$ is replaced by that of CH_3 upon annealing the $CFCl_3$ matrix [1] the gas-phase ion $(SnMe_4)^+$ is observed in the mass spectrum of $SnMe_4$ [26,27]: in contrast the corresponding ion $(CMe_4)^+$ is absent from the mass spectrum of CMe_4 [27], and is stabilised in the matrix only by cage effects [5,28].

The SOMO of the radical cation $(SnMe_4)^+$ is of A_1 σ type, strongly localised in the unique SnC bond; the charge distribution in the cation is such that the unique methyl group carries a positive charge of $+0.275e$, and the Me_3Sn fragment carries a charge of $+0.725e$, consistent with subsequent dissociation, after annealing of the matrix, to $(SnMe_3)^+$ and CH_3 radical. The calculated hydrogen spin densities (Table 1) are reasonably consistent with the observed [1] $a(^1H)$ values. We shall return below to the relationship between the calculated ρ values and observed a values.

When, instead of free optimisation, C_{2v} symmetry as observed [2] for $(SiMe_4)^+$ and $(GeMe)_4{}^+$ was imposed on the skeletal structure of $(SnMe_4)^+$, the resulting molecular energy is only some 15 kJ mol^{-1} higher than for the global C_{3v} minimum. Although the two independent SnC distances differ by only ca. 0.1 Å, the interbond angles (Table 1) indicate a major distortion from the tetrahedral symmetry of the neutral $SnMe_4$. Whereas in the C_{3v} isomer, the calculated $\rho(H)$ values clearly discriminate between the two types of hydrogen, rather little difference is found in the C_{2v} isomer. The SOMO in the C_{2v} isomer is concentrated in one pair of SnC bonds, where it has strongly bonding character.

In neutral Sn_2Me_6, of D_{3d} skeletal symmetry, the HOMO is of A_{1g} type, strongly localised in the SnSn bond, i.e. it is of σ(SnSn) type: hence ionisation is expected to produce radical cation, insensitive to Jahn-Teller distortion, also of D_{3d} skeletal symmetry. Free optimisation of the structure of $(Sn_2Me_6)^+$ indeed effects no change in symmetry. The resulting structure (Table 1) consists of two Me_3Sn fragments which are considerably flattened from the near-tetrahedral geometry about tin in neutral Sn_2Me_6, and which are joined by an SnSn bond longer by some 0.33 Å than that in the neutral species. The SOMO is of A_{1g} type, again strongly localised in the SnSn bond; this explains the lengthening of what is now in effect a one-electron bond. Consistent with the lengthening of this bond upon ionisation is its weakness in the radical cation: the calculated value of $D(Me_3Sn{-}SnMe_3)$ in the neutral Sn_2Me_6 is $+141.8$ kJ mol^{-1}, while that of $D(Me_3Sn^+{-}SnMe_3)$ in $(Sn_2Me_6)^+$ is only $+39.7$ kJ mol^{-1}.

The calculated angles $<$(CSnC) in $SnMe_3$ and $(Sn_2Me_6)^+$ differ by less than 5°, and the structure calculated for $(Sn_2Me_6)^+$ certainly does not support the suggestion [6] that the two tin atoms in this radical cation are very nearly planar coordinated by three methyl groups.

In view of this discrepancy, we have made a series of optimisations of the structure of $(Sn_2Me_6)^+$ in which the angles $<$(SnSnC) are fixed at a series of values between 110° (tetrahedral tin) and 90° (planar tin), under the constraint of D_{3d} skeletal symmetry: this constraint, although involving only the SnC bonds and the angles $<$(CSnSn), caused the methyl groups at the two ends of the molecule to remain wholly equivalent also. As the angle $<$(CSnSn) was decreased from 110 to 90°, the SnSn distance increased smoothly from 2.915 to 3.526 Å. However as the angle approached 90°, the calculated $\Delta H_f^{\ominus}$ rapidly exceeded the sum of the values for $(SnMe_3)^+$ and $SnMe_3$: it is only the constraint of D_{3d} skeletal symmetry which prevents the system from dissociating to two non-equivalent fragments. At all values of $<$(CSnSn) in D_{3d} symmetry, the SOMO is of σ(Sn–Sn) type, equally distributed between the two halves. When however the skeletal symmetry was relaxed from D_{3d} to C_{3v}, confining one of the independent angles $<$(CSnSn) to values approaching that for a planar tin atom it caused the other tin atom to become more pyramidal as the system smoothly dissociated to $(SnMe_3)^+$ and $SnMe_3$. Throughout this dissociation, the SOMO is concentrated on the more pyramidal of the two tin atoms.

These two series of calculations provide no evidence, at least for isolated species, that the radical cation $(Sn_2Me_6)^+$ can exist as a stable species in which the two tin atoms are both essentially planar. In contrast to the cage-stabilised [5,28] radical cation $(C_2Me_6)^+$, where the molecular energy decreases steadily as the unique carbon–carbon distance increases, in $(Sn_2Me_6)^+$ the molecular energy is at a minimum when the tin–tin distance is 3.002 Å: at longer tin–tin distances the molecular energy increases, exceeding the sum of the fragment energies for tin–tin distances greater than ca. 3.3 Å. It seems unlikely therefore that a symmetric σ(Sn–Sn) species having effectively planar tin atoms could be stabilised by cage effects. Nonetheless the 5*s* spin density at tin in $(Sn_2Me_6)^+$ is calculated to be extremely low at the optimum geometry, (Table 1), even though the two tin atoms are far from planar: the present calculations perhaps suggest that deductions of geometry from spin densities may sometimes be misleading.

Magnitude of the MNDO scale-factor.

We have previously found that the approximate values of the scale-factor appropriate for the MNDO parameterization, relating the calculated spin density at hydrogen and the observed hyperfine coupling appear to be ca. 1100 G for carbon-centred radicals [5], 850–900 G for oxygen-centred radicals [29], and ca. 1000 G for sulphur-centred radicals [30]. The limited data of Table 1 again suggest an approximate correlation between ρ and $a(^1H)$: the data suggest a value of 850 ± 200

G for tin-centred radicals, and appear to support an earlier suggestion [30] that the MNDO parameterization may yield a systematic variation of the scale factor with some property of the heteroatom. This possibility remains to be adequately tested: such tests may perhaps reveal that for a given heteroatom, somewhat different values of the scale-factor may be appropriate for cationic, neutral, and anionic radicals. If there is a linear relationship between the isotropic a(Sn), and the calculated ρ[Sn(5s)], the calculated value of ρ for $(Sn_2Me_6)^+$ implies that the isotropic a must be very small.

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