or semiempirical, is by comparisons with experiment.

The calculated ionization energies are systematically too large. The mean error in I_1 for the 24 molecules in Table II for which there are experimental data is 1.30 eV. A similar error was found in MNDO calculations for compounds of the third-period elements, in particular chlorine,[13] and was attributed to neglect of interactions between the inner electrons and valence electrons in MNDO, due to use of the core approximation. However, attempts to correct the calculated values for tin in the way used successfully for chlorine[13] failed.

As usual, dipole moments are well reproduced. The average absolute error for the eight molecules in Table II for which data are available is only 0.39 D.

Table III compares the calculated geometries with experiment. While bond angles involving tin are reproduced fairly nicely, the errors in bond lengths are greater than those for compounds of third-period elements[10-13] and much greater than for the "organic" elements, C, H, N, and O.[4] While bonds involving tin are generally too short by ca 0.1 Å, this should not be serious because the bonds are so long. Underestimation of the lengths of bonds to tin should not greatly alter the geometry of the rest of the molecule. The most serious errors are found in molecules of the type R_2SnX_2.

The calculated charge distributions usually show tin to have a formal charge of ca 1^+, regardless of the attached ligands.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 49620-83-C-0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out by using a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. Tin, 7440-31-5.

Aspects of Organotin Chemistry[1]

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Abstract: MNDO has been applied with success to four topics of current interest in organotin chemistry, leading to satisfactory interpretations of the mechanism for hydrostannylation, the structures of sandwich and half-sandwich cyclopentadienyltin compounds, the possibility of multiple bonding by tin in distannene or dimethylmethylenestannane, and the geometry of the trimethylstannyl radical.

Organotin chemistry has been increasingly studied in recent years, partly because of the growing use of organotin compounds in synthesis and partly because of the current renaissance of non-transition-metal inorganic chemistry. Since MNDO parameters for tin are now available,[1] we decided to study four topics of current interest in the organotin area, partly in the hope of resolving uncertainties and partly to check the ability of MNDO to deal with an element from the fifth period. The topics studied were (a) the mechanism of hydrostannylation; (b) sandwich and half-sandwich cyclopentadienyltin compounds; (c) the ability of tin to form multiple bonds as in distannene or dimethylmethylstannane; and (d) the structure of the trimethyltin radical.

Procedure

The calculations were carried out by using the standard MNDO method and parameters,[3] as implemented in the MOPAC[4] package of computer programs. Geometries were optimized by the derivative procedures included in MOPAC, with no assumptions other than symmetry in cases where symmetry was deliberately enforced. Radicals were calculated by the spin-unrestricted (UHF)[5a] version of MNDO (UMNDO). Transition states were located by the reaction coordinate method[5b] or by a new procedure recently developed here[6] and refined by minimizing the scalar gradient of the energy.[7] All stationary points were characterized by calculating force constants.[7] Options for all these procedures are included in MOPAC.

Applications

A. Hydrostannylation. One of the most important methods for forming tin–carbon bonds is the hydrostannylation of olefins;[8-12]

$$\underset{\mathbf{1},\ R = CH_3}{R_3SnH} + \underset{\mathbf{2},\ R' = H}{R'_2CCR'_2} \rightarrow \underset{\mathbf{3},\ R = CH_3;\ R' = H}{R_3SnCR'_2CR'_2H} \quad (1)$$

While a polar mechanism may be involved in the case of olefins carrying a strongly electron withdrawing substituent,[13] most of these reactions seem to be radical chain processes involving the following propagation steps;[8-12]

$$\underset{\mathbf{4},\ R = CH_3}{R_3Sn\cdot} + \mathbf{2} \rightleftarrows \underset{\mathbf{5},\ R = CH_3;\ R' = H}{R_3SnCR'_2CR'_2\cdot} \quad (2)$$

$$\mathbf{5} + \mathbf{1} \rightarrow \mathbf{4} + \mathbf{3} \quad (3)$$

The first step has been shown[14,15] to be reversible as indicated in

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[1] Part 69 of the series Ground States of Molecules. For Part 68 see: Dewar, M. J. S.; Grady, G. L.; Stewart, J. P. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] On sabbatical leave from St. Michael's College, Winooski, VT 05454.

[3] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

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[14] Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616.

[15] Neumann, W. P.; Albert, H. J.; Kaiser, W. *Tetrahedron. Lett* **1967**, 2041.

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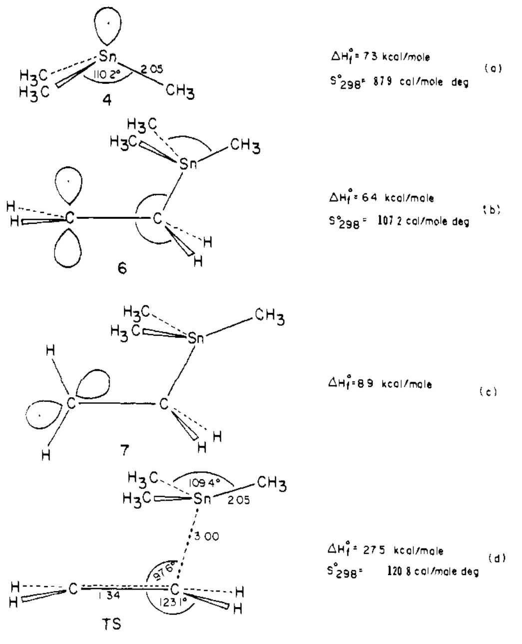
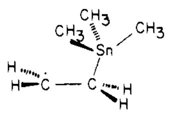


Figure 1.

eq 2, the heat of reaction being estimated to be 9[16] or between −7 and −8,[15] kcal/mol. Studies[17] of the intermediate radical **5** by ESR spectroscopy showed it to exist in two isomeric forms, which were assumed to be rotamers of **5** with the tin–carbon bond parallel (**6**) or perpendicular (**7**) to the axis of the singly occupied AO. The barrier to rotation was estimated to be ca. 2 kcal/mol. The more stable isomer was claimed to be **6**, its stability being attributed to dπ–pπ bonding.[18] The role of this has, however, been questioned.[19] Since no systematic kinetic studies or theoretical calculations have been reported for reactions of this kind, no details are known concerning their mechanisms. We have now examined the addition of trimethylstannane (**1**) to ethylene (**2**), using UMNDO.



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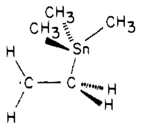

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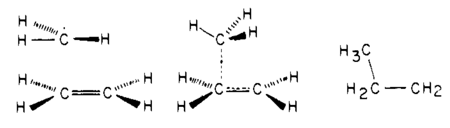

8

Calculations for **1** were reported in the previous paper[1] and for **2** in the original presentation of MNDO.[3] Figure 1 shows the geometries, heats of formation (ΔH_f, kcal/mol), and entropies (ΔS) calculated for the trimethylstannyl radical (**4**) and its adduct (**5**) with **2**. **5** is predicted to form one stable rotamer **6**, corresponding to the more stable of the two isomers observed[17] by ESR spectroscopy. UMNDO, however, predicts the other rotamer (**7**) to be a rotational transition state, higher in energy than **6** by 2.5 kcal/mol.

Conversion of **4** + **2** to **5** was predicted to be exothermic by 16.2 kcal/mol, which is about 8 kcal more negative than the experimental estimates[15,16] (7–9 kcal/mol).

Figure 1d shows the structure, heat of formation, and entropy calculated for the transition state (TS) for addition of **4** to **2** to form **5**. The barrier was very low (4.9 kcal/mol), in agreement with the experimental evidence that the addition (eq 2) is fast and reversible. The calculated enthalpies and entropies lead to a free energy of reaction of −6.5 kcal/mol at 25 °C, corresponding to a value for the equilibrium constant of 5×10^4.

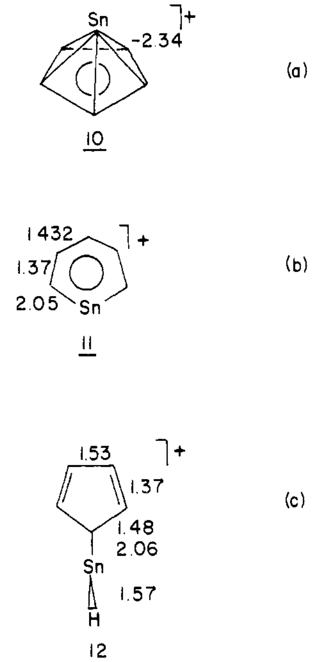

Figure 2.

The structure calculated for the TS (Figure 1d) is similar to that given[20] by MINDO/3 for the TS (**8**) for the analogous addition of methyl radical to ethylene. In each case the nascent (C–Sn or C–C bond is very long and the ethylene moiety planar, or nearly planar, while the trimethylstannyl or methyl group has a geometry close to that in the final product. The first two facts imply an early TS in each case. The third, in the case of **8** seemed to imply a "late" TS. The reason for this apparent contradiction in the case of **8** was discussed in the original paper.[20] No such problems arise in the case of the tin analogue because the trimethylstannyl radical (**4**) is predicted to be pyramidal (Figure 1), unlike methyl.

B. Tin η^5-Cyclopentadienyl Compounds. Stannocene, bis(η^5-cyclopentadienyl)tin[21] (**9**) and η^5-cyclopentadienyltin tetrafluoroborate[22] (**10**) have been prepared and studied theoretically,[21,23] the extended Huckel[23a] (EH) method being used for **9** and **10** and Xα–SW[21] method for **9**. We have now carried out detailed MNDO calculations for both of these compounds and for some of their derivatives.

While **10** was found to be the global minimum on the $C_5H_5Sn^+$ surface, the monocyclic isomer, **11**, was only a little higher in energy. The fulvene analogue (**12**) was mugh higher. Their calculated force constants indicated that all three species are genuine minima on the potential surface. Their calculated geometries are shown in Figure 2 and other calculated properties in Table I. The geometry calculated for **10** agrees reasonably well with the geometry observed in an X-ray study[23] (Figure 2a).

Figure 3 compares our MO diagram (Figure 3a) for **10** with that from the EH[23] (Figure 3b) calculations. The latter predicted

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(17) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.

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Table I. Calculated Properties of Compounds Formed from Tin(II) and Cyclopentadiene Anion

property	**10**	**11**	**12**
ΔH_f, kcal/mol	227.6	235.7	262.0
IP, eV	15.03	14.83	14.59
charge on tin	0.79	0.89	0.87
tin carbon bond order	0.40	0.78	0.75

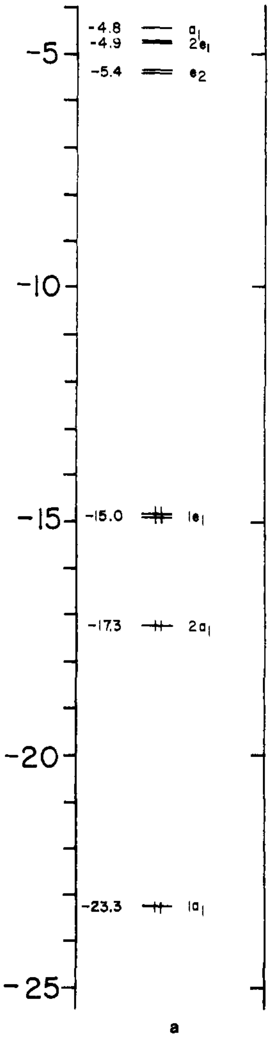


Figure 3.

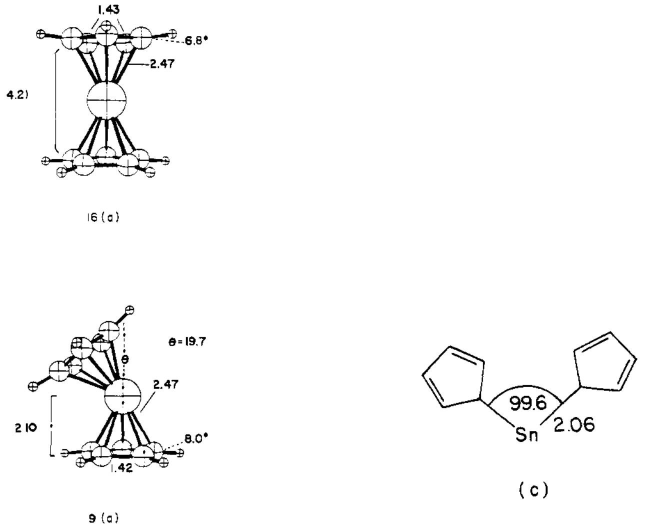
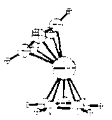


Figure 4.



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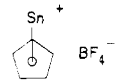

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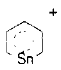

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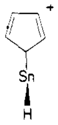

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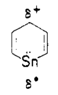

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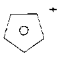
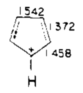


14

the HOMO to be a tin lone pair ($2a_1$) whereas MNDO predicts this orbital to be the third highest occupied MO, lying below a pair of nearly degenerate HOMOs localized on the ring. Since MNDO and Xα are two of the better procedures for calculating ionization energies, using Koopman's theorem, while EH is often very poor, the MNDO prediction is probably correct.

The cyclic isomer (**11**) is only a little higher in energy than **10**. The tin in it is clearly divalent, the lengths of the C–Sn bonds being 2.05 Å. Since these bonds are polar, the tin carries a positive formal charge. This in turn polarizes the pentadienyl π system, concentrating positive charge at the position para to tin, strenghtening the C_2C_3 and C_5C_6 bonds, and weakening the other CC bonds. The net effect is a pattern of charges and bond lengths corresponding qualitatively to the classical structure **13**.

The bonding in **12** is interesting. Note (Figure 2c) that the Sn–H bond lies on a plane orthogonal to the ring. The C–Sn bond is moreover single, judging by its bond order (0.75) and length (2.06 Å). Now the antiaromatic cyclopentadienate cation (**14**) undergoes[24] Jahn–Teller distortion, one of the resulting isomers having a geometry (**15**) similar to that calculated for **12** (Figure 2c). **12** is therefore best regarded as a derivative of **15** in which the hydrogen atoms of the cationic center have been replaced by SnH. The dispersal of charge from C_1 can be attributed to polarization of the σ bonds. The orthogonal tin geometry is also easily understood. Since the $2p_z$ AO of C_1 is empty in **12**, interaction with the empty tin p AO would lead to no change in energy. The orthogonal orientation allows the empty C_1 2p AO to hyperconjugate with the SnH bond while the empty tin p AO can likewise hyperconjugate with the C–Sn bonds.



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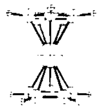

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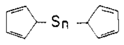

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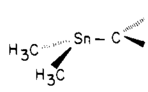

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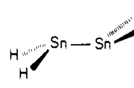

19

According to our calculations, the D_{5d} structure, **16**, is neither a minumum nor a transition state, corresponding to a stationary point with *three* negative force constants. The calculations were carried out with enforced D_{5d} symmetry, and indeed the most stable configuration was the staggered conformation (Figure 4a). When the angle at tin (θ in **9**) was allowed to relax, leading to a bent geometry, as experimentally observed,[23] a second isomer with θ 180° was obtained, which however, was also not a minimum on the potential surface. The only true minimum we could find, for the unsubstituted case, was the classical isomer **17**. Figure 4 shows the geometries calculated for **9**, **16**, and **17**, while Table II lists other calculated properties. The geometry calculated for

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[24] (a) Dewar, M. J. S.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 5836. (b) Dewar, M. J. S.; Haddon, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 255.

Table II. Calculated Properties of Compounds Formed from Tin(II) and Two Cyclopentadiene Anions

property	9	16	17
ΔH_f, kcal/mol	125.7	127.2	88.9
IP, eV	8.29	8.31	8.81
charge on tin	0.65	0.63	0.69
tin carbon bond order	0.1–0.3	0.21	0.82

Table III. Calculated Properties of Singlet and Triplet Dimethylmethylenestannane

property	18s	18t
ΔH_f, kcal/mol	42.7	41.5
IP, eV	8.44	4.19
charge on tin	0.11	0.32
Sn–C bond order	1.37	0.89

Table IV. Calculated Properties of Singlet and Triplet Distannene

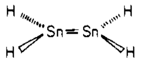
property	19s	19t
ΔH_f, kcal/mol	36.7	73.8
IP, eV	9.41	5.07
charge on tin	0.52	0.27
Sn–Sn bond order	0.30	0.61

16 is in fair agreement with experiment[23] (Figure 4b).

This structure (**16**) is similar to ones found earlier for bis(cyclopentadienyl)beryllium[25] and for some analogous boron hydrides[26] and carboranes.[27] In all of these MNDO underestimated the stabilities of nonclassical species relative to those of classical isomers. This seems to be a general failing of MNDO.[26–28]

C. Multiple Bonding by Tin. While multiple bonding by silicon has been much studied in recent years, relatively little work has been reported on the possibility of similar bonding by later group 4b elements, in particular tin.

Hehre,[29] on the basis of mass spectral and thermochemical data, estimated the π bond energy in dimethylmethylenestannane[29] (**18**) to be 45 kcal/mol, while a preliminary report[30] claims the nonplanar form (**19**) of distannene[30] to be more stable than the planar one (**20**) by >4.3 kcal/mol (18 kJ/mol). Pauling,[31] on the other hand, has argued that neither π bonding nor any kind of multiple bonding is significant for tin.

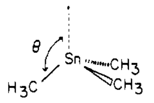

20

$H_2Sn\cdot$

21

$H_2Sn{-}SnH_2$

22



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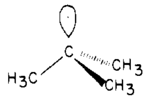
24

$CH_3\cdot$

25

$CH_3CH_2\cdot$

26

$(CH_3)_2CH\cdot$

27

MNDO calculations were carried out for the lowest singlet (18s) and triplet (18t) states of **18**, for nonplanar and planar distannene (**19**) and **20**), and for triplet distannene. Their geometries are shown in Figure 5 and other properties in Tables III and IV.

The heat of formation calculated for **18s** is greater by 12 kcal/mol than that estimated by Hehre[29] (31 kcal/mol). The possible error in the latter value is, however, uncertain. The geometries of **18s** and **18t** (Figure 5) correspond to those expected from analogy with ethylene in that the $SnMe_2$ and CH_2 residues are parallel in the singlet but orthogonal in the triplet. The parallel situation in ethylene is attributed to the formation of a CC π bond in the singlet. Here, however, the (SnC) π bond must be very weak because the tin atom in **18s** is pyramidal, the angle between the Me–Sn–Me plane and the Sn–Sn bond being 129.8°, and because **18s** and **18t** differ only very little (1.1 kcal/mol) in energy with the triplet being more stable! In ethylene, for example, the corresponding singlet–triplet energy difference is 97.1 kcal/mol.[32] Our results are thus consistent with Pauling's[31] conclusion that tin does not form π bonds. The results (Figure 5c and Table IV) for distannene (**20**) are even more interesting in this connection. Here *both* tin atoms are predicted to be pyramidal in the singlet, the angles between the HSnH planes and the Sn–Sn bond being 138.0°. The corresponding angle for a tetrahedral geometry is 125.3°. Furthermore, since π bonding is normally most efficient when it involves p AOs, the SnSn bond in **20** would be expected to become stronger the more planar the tin atoms. Not only is planar **20** predicted to be *higher* in energy than **19** by 8.5 kcal/mol but the Sn–Sn bond in it is actually *longer* (3.26 vs. 2.72 Å).

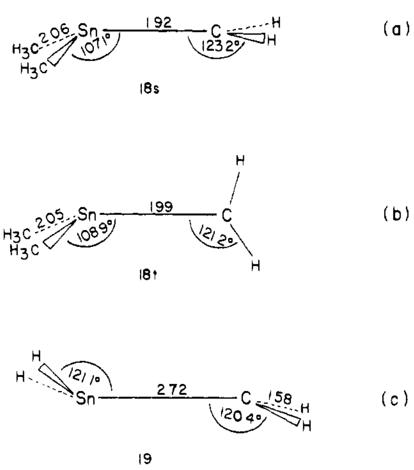

Figure 5.

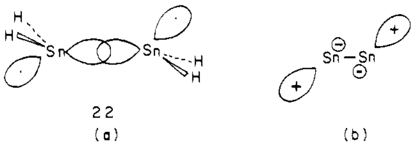

Figure 6.

If the SnSn bond in **19** were double but with a very weak π component, corresponding to a small π resonance integral between the tin atoms, the singlet–triplet separation would also be small, as it is in **18**. However, triplet **19** is in fact *higher* in energy than **19** by no less than 37.1 kcal/mol. The tin atoms in **19** cannot therefore be linked by a double bond. What then is the situation?

Consider the biradical **22** derived from two molecules of stannylene (**21**) by forming a single Sn–Sn bond. The unpaired electrons in **22** can interact conjugatively, across space, giving rise to a π or π-type bond, or σ conjugatively[33] via the intervening Sn–Sn σ bond.

The σ conjugated system in **22** is a linear four-AO system, isoconjugate with the π system in butadiene[33] (Figure 6a). The bond order between the terminal AOs is negative in both cases. The through-bond and through-space interactions therefore antagonize one another if the lone-pair AOs in **22** overlap in phase.

If the through-space interaction is the greater, the "singly occupied" AOs in **22** will then tend to be p AOs, because this will both maximize the through-space interaction and cancel[33] the through-bond one. This is the situation in the carbon analogue of **22**, i.e., ethylene ($H_2C{=}CH_2$), where the carbon atoms are consequently linked by a double ($\sigma + \pi$) bond. The remaining

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bonds are formed by sp^2 hybrid AOs of carbon, the methylene groups being consequently planar.

The strengths of π bonds rapidly decrease, however, on descending the periodic table. Since tin is in the fifth period, a tin–tin π bond is likely to be very weak and the σ conjugative interaction in **22** may well be greater than the through-space one. Since σ conjugative interactions are strongest when the interacting AOs are similar,[33] the tin atoms in **22** should then be pyramidal, corresponding to sp^3 hybridization. This is what MNDO predicts (Figure 5). Furthermore, the through-space interaction is antibonding only if the corresponding resonance integral is negative, i.e., if the corresponding overlap integral is positive. If the "singly occupied" AOs in **22** are trans to one another, the overlap integral is *negative*[33] (see Figure 6b), so the through-space interaction, such as it is, will *reinforce* the through-bond (σ conjugative) one. **22** should then have C_{2v} symmetry, as indeed the calculations again predict (Figure 5).

Since the σ conjugative interaction leads in effect to the formation of a second bond between the tin atoms, **19** should have a closed shell structure, with a singlet ground state and a large singlet–triplet separation. As noted above, this is the case. The difference in energy between the planar and C_{2v} forms of **19** should correspond to the difference between the through-space and through-bond interactions. Looked at in this way, its value does not seem unduly large.

Lappert et al[34] have reported the preparation of a derivative of **19**, R_2SnSnR_2, where R = bis[trimethylsilyl]methyl ($(Me_3Si)_2CH$), which was found to have the trans-bent structure predicted here for **19** itself. Since the repulsions between the large groups (R) must tend to make the molecule planar, the tendency to nonplanarity in **19** must be strong, as we predict. Lappert et al. postulate a weak bent double bond between the tin atoms, formed by interactions between a p AO of each Sn and a hybrid AO of the other. This, however, is in effect the standard "banana bond" description of a normal double bond and does not therefore account for the nonplanarity.

D. Trimethyltin Radical. Lloyd and Rogers[35] studied the structure of the matrix-isolated trimethyltin radical (**4**) 10 years ago, finding it to be pyramidal, the angle ($\theta = 104°$) between the threefold axis and each CSn bond differing from 90° by 14° (see ref 23). While Symons[36] has criticized the interpretations put forward by Lloyd and Rogers, their conclusions seem to have been confirmed by later workers, notably Neumann and Apoussidis,[37] who studied a number of trialkyltin radicals and found similar deviations from planarity, θ lying in the range 104–106°.

We have now carried out MNDO calculations for **4** with results in good agreement with experiment except that we find the deviation from planarity to be even greater ($\theta = 108.7°$) than the earlier estimates. Since MNDO is known to overestimate repulsions between nonbonded atoms, giving a geometry for the *tert*-butylradical (**24**) which is too planar, it seems likely that the MNDO value for θ is unlikely to be too large. There seems in any case to be little doubt that **4** is pyramidal.

While the methyl radical (**25**) is either planar or effectively[38] planar, recent experimental work[39] and theoretical calculations[39] leave no doubt that **24** is pyramidal. This is surprising, because steric repulsions and hyperconjugation should both favor planarity in **24**. Indeed, the tendency to planarity should be even greater in **24** than in **25**. Similar results follow from theoretical calculations[40] for ethyl (**26**) and isopropyl (**27**) radicals, the radical center becoming progressively more pyramidal the greater the number of methyl groups. The only satisfactory explanation so far proposed is one in terms of σ conjugation.[33] The same considerations should apply in the case of **4**.

σ conjugative interactions between AOs are greatest when the AOs have similar hybridizations. As in the case of **20**, σ conjugation should then favor a structure for **4** in which all the AOs are of the sp^3 type and the bond angles are tetrahedral. Hyperconjugation and steric repulsions in a radical $\cdot MR_3$, will tend to flatten the molecule, increasing the p character of the singly occupied AO. Since tin appears not to be able to form effective π bonds and since the steric repulsions in **4** are less than in **24**, CSn bonds being much longer than CC ones, **4** might be expected to be pyramidal with angles close to 109.5°.

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