methyl peaks collapsed into a broad singlet and the AB quartet was no longer recognizable as such. (Unfortunately, at ~130° slight decomposition began to occur and a second peak appeared on the side of the broad methyl signal.) By 142° the AB quartet had collapsed to a singlet and the methyl groups appeared as a relatively sharp single peak with the signal from the impurity still clearly visible on the side of the methyl signal. Finally, return to room temperature effected a regeneration of the AB quartet and the two methyl signals at τ 8.98 and 9.09; the presence of the impurity from the thermal decomposition was indicated by a peak between the two sharp methyl singlets.[13] These nmr studies at various temperatures indicate that there is some process operative at high temperatures that causes the equivalence of two otherwise magnetically nonequivalent methyl groups. This process is considered to be rapid ring inversion with its resultant time-averaging effect.[14]

In view of the interesting result reported, other derivatives of the α-diketone **1**, which should be less thermally labile than the dihydrazone **2**, are being prepared for purposes of kinetic measurements and possible resolution into optical isomers.

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(13) An analogous situation has been observed by Prelog and coworkers in a number of similarly substituted cyclodecane derivatives, but in each case the coalescence temperature was much lower, reflecting the lower barrier to inversion in the ten-membered ring. We are indebted to Professor Prelog for this private communication.

(14) This is not to imply that the stereochemical integrity of the hydrazone functions in the starting material is maintained at high temperatures for there may well be rapid interconversion between stereoisomers, but this phenomenon, however rapid, cannot alone cause the observed collapse of the spectrum without concurrent ring inversion.

(15) Sage Teeple Fellow, 1965–1966, and National Institutes of Health Predoctoral Fellow, 1966–1967.

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Tin-119m Mössbauer Study of Five- and Six-Coordinated Organotin(IV) Ions

Sir:

The addition of 2,2′,2′′-terpyridyl to dimethyltin dichloride in hexane precipitates an adduct which behaves as a 1:1 electrolyte in nitrobenzene.[1] The formulation of the product as $[Me_2SnCl\cdot terpy]^+[Me_2SnCl_3]^-$ (I) has been confirmed by an X-ray study.[2] The coordination about the tin in the anion is trigonal bipyramidal with the methyl groups in equatorial positions. The cation is a highly distorted octahedron with bent *trans*-methyl groups. The Sn^{119m} Mössbauer spectrum is shown in Figure 1.

A doublet spectrum is consistent with the proposals of Greenwood, *et al.*, that organotin(IV) compounds will exhibit resolvable quadrupole splittings (QS) when the symmetry about the tin atom is lower than cubic so long as at least one bond to tin is from an element possessing a lone pair of electrons.[3,4] Thus both types of tin atoms in the adduct (the five-coordinated anion and the six-coordinated cation) must be giving rise to isomer shift (IS) and QS values sufficiently similar to allow their respective resonances to fall within the envelope of the doublet produced with the narrow-line $BaSn^{119m}O_3$ source.[5]

The IS value is smaller than that for the neutral Me_2SnCl_2 precursor. We find this observation to be general in going to five- and six-coordinated species whether charged or not. The IS for tin can be expressed as

$$IS = \text{constant}\ [\rho_a - \rho_s]$$

where ρ, the total electric field at the nucleus for source and absorber, is usually replaced by $|\Psi(0)|^2$, the total electron density at the nucleus, and then by $|\psi_{ns}(0)|^2$, the total s-electron density at the tin nucleus. Populating empty tin 5d orbitals on coordination will affect the s-electron distribution by shielding so as to lower $|\psi_{ns}(0)|^2$.

Table I lists IS and QS data for various five- and six-coordinated organotin(IV) anions and cations.[6] Half-height widths are listed for each resonance line. The results for the separated ions of $[Me_2SnCl\cdot terpy]^+$-$[Me_2SnCl_3]^-$ with various gegenions confirm that Figure 1 represents the superimposition of the doublet spectrum arising from each tin atom and rule out the possibility that interionic interaction (for example, the presence of a bridging chlorine atom not specifically excluded in ref 2) might be operating to bring the two tin atoms into electrical and stereochemical equivalence in the mixed salt. The intensities of the resonances produced by the tin anion and cation, although in general not equal, are of the same order of magnitude. Thus the effective Debye temperatures and binding force constants of the two types of tin atoms are, therefore, comparable and both tin atoms must be represented in Figure 1. This pattern of results is repeated for the complex ions formed from diphenyltin dichloride, methyl- and butyltin trichlorides, as well as from tin tetrachloride itself. In each case formation of the complex moves the IS to lower values, but both types of tin atoms give rise to IS and QS values which allow their resonances to fall within a single envelope. It should be noted that methyl- and butyltin trichlorides precipitate 2:1 electrolytes with a six-coordinated $[RSnCl_5]^{2-}$ dianion. Tin tetrachloride likewise precipitates a 2:1 electrolyte,[7] but in this case the dianion possesses cubic symmetry and for the cation the Greenwood proposals predict a singlet spectrum.[3,4] We observe the apparent superimposition of the two singlet resonances.

We expected little or no decrease in IS in the formation of $[Me_3SnCl_2]^-$ from Me_3SnCl because of the likelihood that Me_3SnCl itself exists in the solid as a pentacoordinated chain polymer.[8] This is suggested by far-infrared and Raman studies which give ν(Sn–Cl) at different frequencies in the solid, melt, and solution,

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(1) J. E. Fergusson, W. R. Roper, and C. J. Wilkins, *J. Chem. Soc.*, 3716 (1965).

(2) F. W. B. Einstein and B. R. Penfold, *Chem. Commun.*, 780 (1966).

(3) T. C. Gibb and N. N. Greenwood, *J. Chem. Soc., A*, 43 (1966).

(4) N. N. Greenwood and J. N. R. Ruddick, *ibid.*, 1679 (1967).

(5) M. V. Plotnikova, K. P. Mitrofanov, and V. S. Shpinel, *Soviet Phys. JETP Letters*, 3, 209 (1966); H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, 30, 409 (1968).

(6) Various forms of evidence have been put forward recently to support the ionic nature of these species: (a) G. Tagliani, P. Zanella, and M. Fiorani, *Coord. Chem. Rev.*, 1, 249 (1966); (b) G. Tagliani and P. Zanella, *Anal. Chem. Acta*, 40, 33 (1967); (c) *J. Organometal. Chem.* (Amsterdam), 5, 299 (1966); (d) M. Wada and R. Okawara, *ibid.*, 4, 487 (1965); (e) V. G. K. Das and W. Kitching, *ibid.*, 10, 59 (1967).

(7) This species is too insoluble to allow conductivity measurements or the separation of the ions (see ref 1).

(8) H. A. Stöckler, private communication, 1968.

Table I. Sn^{119m} Mössbauer Parameters[a]

Compound	IS[b]	QS[c]	Γ_{left}	Γ_{right}	ρ = QS/IS
Me_2SnCl_2*	+1.54	3.33	0.98[e]	1.17[e]	2.16
$[Me_2SnCl \cdot terpy]^+[Me_2SnCl_3]^-$*	1.38	3.31	1.12[e]	1.20[e]	2.40
$[Me_2SnCl \cdot terpy]^+BPh_4^-$	1.46	3.58	1.56	1.38	2.45
$[Me_2SnCl \cdot terpy]^+I^-$	1.38	3.56	1.56	1.44	2.58
$[Me_2SnCl \cdot terpy]^+ClO_4^-$	1.38	3.50	1.44	1.38	2.54
$Et_4N^+[Me_2SnCl_3]^-$	1.40	3.30	1.38	1.38	2.36
Ph_2SnCl_2	1.38	2.75	1.11	1.11	1.99
$[Ph_2SnCl \cdot terpy]^+[Ph_2SnCl_3]^-$*	1.17	2.88	1.05[e]	0.92[e]	2.46
$[Ph_2SnCl \cdot terpy]^+BPh_4^-$	1.20	3.24	1.24	1.24	2.70
$[Ph_2SnCl \cdot terpy]^+ClO_4^-$	1.24	3.01	1.32	1.44	2.42
$Et_4N^+[Ph_2SnCl_3]^-$	1.25	2.62	1.38	1.26	2.10
n-$BuSnCl_3$	1.31	1.83	1.18	1.16	1.40
$[n\text{-}BuSnCl_2 \cdot terpy]^+_2[BuSnCl_5]^{2-}$*	1.07	1.94	1.05[e]	1.11[e]	1.81
$[n\text{-}BuSnCl_2 \cdot terpy]^+BPh_4^-$	1.09	1.76	1.54	1.44	1.61
$[n\text{-}BuSnCl_2 \cdot terpy]^+ClO_4^-$*	0.92	1.74	1.20	1.20	1.89
$[Et_4N]_2^+[n\text{-}BuSnCl_5]^{2-}$	1.07	1.86	1.20	1.20	1.74
Me_3SnCl	1.44	3.01	1.18	1.20	2.09
$Et_4N^+[Me_3SnCl_2]^-$	1.24	3.23	1.53	1.47	2.60
$[Me_3Sn(H_2O)_2]^+BPh_4^-$*[f]	1.42	4.10	0.72[e]	0.82[e]	2.89
$SnCl_4$	0.80[d]				
$[SnCl_3 \cdot terpy]^+_2[SnCl_6]^{2-}$	0.62			1.49	

[a] All compounds run at liquid nitrogen temperature *vs.* Sn^{119m}O$_2$ [New England Nuclear Corp; Nuclear Science and Engineering Corp.] with those indicated by an asterisk rerun *vs.* BaSn^{119m}O$_3$ [New England Nuclear Corp.]. [b] ±0.06 mm/sec. [c] ±0.12 mm/sec. [d] The average of literature values; see J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, **29**, 2191 (1967). [e] Using BaSn^{119m}O$_3$ source. [f] Prepared following the method in ref 6d.

although similar changes do not occur in $\nu(Sn\text{–}C_3)_{asym}$ and $\nu(Sn\text{–}C_3)_{sym}$.[9] The IS change shown in Table I, however, indicates that the association must be markedly weaker than that for Me_3SnF,[10] Me_3SnOH,[11] or Me_3SnCN,[12] and this is reflected in the differences in physical properties as well. We have examined the infrared spectra of the methyltin species in the solid and in nitrobenzene solutions whose concentrations approximate those used to record the nmr data. We are able to detect no change in ν(Sn–C) absorptions in the KBr region on going from the solid to solution.

The true explanation for these data must include compelling reasons for the pattern of equivalence observed for the complexes derived from each of the series of organotin halides. This pattern of equivalence is found for tin atoms of different coordination number in species of opposite charge. The sole similarity among the tin species producing superimposable spectra is the number of bonds to carbon in each case and the nature of the attached organic group. Table I shows clear differences when different organic groups (Me, n-Bu, Ph) or different numbers of organic groups are used. The IS change indicates a decrease in $|\psi_{ns}(0)|^2$ when coordination number is increased from four and it may be assumed that this represents an isotropic view of changes in s-electron density at the Sn^{119} nucleus brought about chiefly by changes in the valence electrons (5s electrons for tin). The nmr coupling constant, $J(Sn^{119}\text{–}C\text{–}H^1)$, on the other hand, based on a predominant Fermi contact interaction mechanism, presumably represents a highly anisotropic view of s-electron density—namely that directed along the axes of the tin bonding orbitals to carbon. We find $J(Sn^{119}\text{–}C\text{–}H^1)$ increases continuously in the series $Me_2SnCl_2 < [Me_2SnCl_3]^- < [Me_2SnCl \cdot terpy]^+$. In this connection we have studied analogous charged species of the fourth group: the siliconium ion $[Ph_2MeSi \cdot bipy]^+$,[13] and the diphenylmethylcarbonium ion.[14] $J(C^{13}\text{–}H^1)$ changes very little on formation of these cations from the neutral, four-coordinated species,[15] and thus we interpret the increases in $J(Sn^{119}\text{–}C\text{–}H^1)$ we observe in the tin series as arising from increasing concentration of s character in the tin–carbon bond.[16] Since $|\psi_{5s}(0)|^2$ at the tin nucleus is already low as shown by the low IS values,

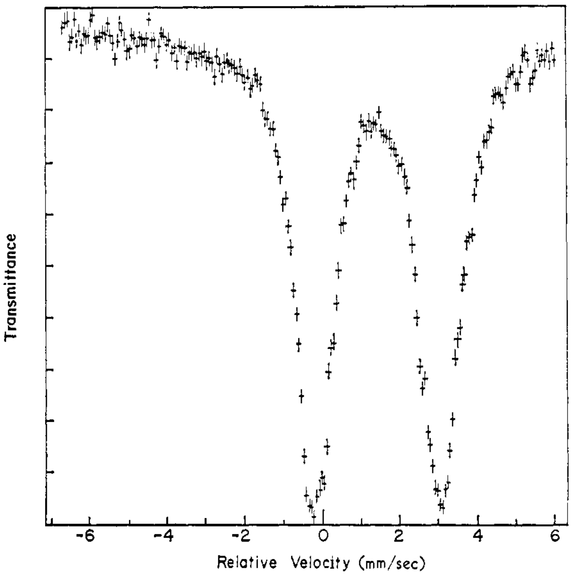

Figure 1. Sn^{119m} Mössbauer spectrum of I *vs.* a BaSn^{119m}O$_3$ source.

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(9) H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, **308**, 212 (1961).

(10) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 2332 (1964).

(11) N. Kasai, K. Yasuda and R. Okawara, *J. Organometal. Chem.* (Amsterdam), **3**, 172 (1965).

(12) E. O. Schlemper and D. Britton, *Inorg. Chem.*, **5**, 507 (1966).

(13) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963); J. Y. Corey, Ph.D. Thesis, University of Wisconsin, 1963.

(14) D. G. Farnum, private communication, 1967.

(15) Corroboration on this point for various methylcarbonium ions has come from another laboratory: G. A. Olah, private communication, 1967.

(16) The long tin–chlorine internuclear distance in $[Me_2SnCl \cdot terpy]^+$ (greater than any previously reported) may be evidence for the relative absence of s character in this bond.[2]

and since what s character exists in the tin bonds is concentrated in the bonds to carbon, then despite changes in the number of electronegative atoms (three or four) or their type (Cl or N) there is a constant value of the IS for each type of organotin species.[17]

The *trans* geometry of the hexacoordinated complex cation derived from dimethyltin dichloride is reflected in its QS value—the same as that produced by the equatorial geometry of the pentacoordinated complex anion. The values are somewhat smaller for the complex ions derived from diphenyltin dichloride, and moreover show differences outside experimental error for the separated ions which may arise from crystal-packing considerations. From these values alone (2.88–3.24 ± 0.12 mm/sec) it is difficult to establish the geometries of the ions unambiguously, but given that equivalence of QS values is produced by the dimethyltin combination of *trans*-hexacoordinated cation and equatorial pentacoordinated anion, it would seem highly unlikely that other, different combinations of diphenyltin ion geometries could lead to superimposable Mössbauer spectra as well.[18] The complex ions derived from *n*-butyltin trichloride and tin tetrachloride are all hexacoordinated. However, because of the geometry imposed by the terpyridyl ring system, it is likely that the *n*-butyl group is *trans* to a chlorine atom in both the cation as well as the anion, a situation apparently able to produce field gradient tensors of equivalent magnitude at both tin nuclei.

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[17] Similar similarities are seen for the Fe^{57} Mössbauer spectra of ferri- and ferrocyanides [J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963); N. L. Costa, J. Danon, and R. M. Xavier, *J. Phys. Chem. Solids*, 23 1783 (1962); R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).

[18] A point charge model would predict that $\Delta E_{trans} = 2\Delta E_{cis}$ for octahedral systems [R. R. Berrett and B. W. Fitzsimmons, *Chem. Commun.*, 90 (1966); *J. Chem. Soc.*, *A*, 525 (1967); B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 390 (1968)].

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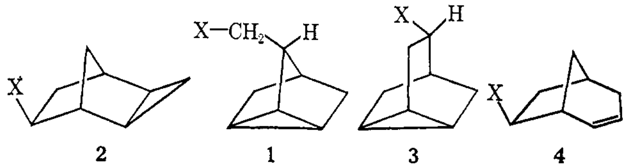
An Intermolecular "Memory Effect" in the Formation and Capture of a Potentially Symmetrical Tricyclooctyl Cation[1]

Sir:

In the ring-expansion route to bicyclooctyl[2,3] and bicyclooctenyl[4] cations, the rearrangements pass through intermediates which, although potentially symmetrical (*e.g.*, 2-bicyclo[2.2.2]octyl cation) or quasi-symmetrical at equilibrium, nevertheless show unsymmetrical behavior. Intermolecular "memory effects"[5] now are shown to occur in the cations derived from optically active tricyclooctyl substrates.[6] The results help in the formulation of the mechanism underlying the exceptionally intricate chemistry of this series.

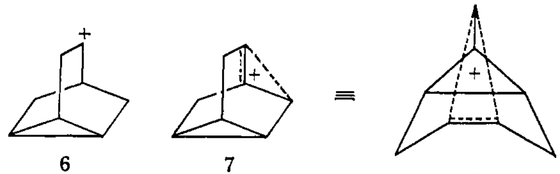
The products obtained from optically active nortricyclylcarbinyl (**1**),[7] tricyclo$[3.2.1.0^{2,4}]$octyl (**2**),[8] and tricyclo$[3.2.1.0^{2,7}]$octyl (**3**)[9] derivatives in solvolysis and nitrosative deamination are shown in Table I.

The ring expansions of nortricyclylcarbinyl substrates **1** give unrearranged (**1**) and "*exo*-cyclopropano" (**2**) products with complete retention (within experimental error) and tricyclic product **3** with partial retention of enantiomeric purity. The configurational relationships given in the structural formulas[7–9] and the data of Table I show that capture of the intermediate leading to **3c** or **3d** occurs from the same side as that occupied by the departing group in **1a** or **1b**. This memory effect cannot be a consequence of isomerization of **1a** to **3a** followed by solvolysis, since **3a** gives essentially completely racemic **3c** (Table I).[6e] There must be an unsymmetrical intermediate for **3c** in addition to the symmetrical ones (**6** and/or **7**).



2 **1** **3** **4**

a, X = OBs; **b**, X = NH_2; **c**, X = OAc; **d**, X = OH



6 **7** **7**

The same unsymmetrical species apparently occurs in the solvolyses of the "*exo*-cyclopropano" compound **2a**, which forms primary product **1c** with complete retention and tricyclic product **3c** with almost exactly the same partial retention of optical purity as that obtained from **1a**.

[1] This work was supported in part by grants from the National Science Foundation (GP6212X), the National Institute of Arthritis and Metabolic Diseases (AM-07505), and the Air Force Office of Scientific Research (M2(967)62/1006-66). We are grateful to these agencies for their support and to Mr. Kenneth Breslauer, who assisted in some of the experiments.

[2] (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); (b) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).

[3] J. A. Berson and M. S. Poonian, *ibid.*, **88**, 170 (1966).

[4] J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964).

[5] A summary of results on "memory effects" is given by J. A. Berson, *Angew. Chem.*, in press.

[6] For valuable prior studies with the racemic compounds, see (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (b) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (c) A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965); (d) K. B. Wiberg and G. Wenzinger, *ibid.*, **30**, 2278 (1965). For parallel studies with certain optically active and isotopically labeled compounds, see (e) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *J. Am. Chem. Soc.*, **90**, 3238 (1968); (f) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968).

[7] (a) Preparation of the amine from the previously described[7b] optically active *p*-bromobenzenesulfonate gives material with spectral properties identical with those of the racemate. (b) J. A. Berson and R. G. Bergman, *ibid.*, **89**, 2569 (1967). (c) Previous correlations[7b] establish configurations and maximum rotations of the **1** series.

[8] (a) The *p*-bromobenzenesulfonate is available from the acetate, prepared by the Simmons–Smith reaction[6d] on optically active *exo*-norbornenyl acetate of known[8b] configuration and maximum rotation. (b) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962).

[9] For absolute configuration and maximum rotation, see ref 6e.