

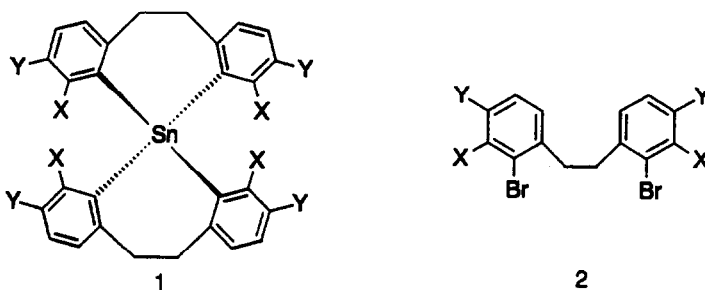
SYNTHESIS, CONFORMATIONAL ANALYSIS, AND STEREOISOMERIZATION OF 2,2':2'',2'''-BIS(ETHANO)TETRAARYLTINS

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Abstract: 2,2': 2'',2'''-Bis(ethano)tetraaryltin derivatives 1a-c were synthesized and their conformational analysis including a X-ray structure analysis of 1c and stereoisomerization have been investigated.

Conformations and stereoisomerizations of compounds of the type Ar_4Z ($Z =$ group 14 elements) have attracted considerable interest.¹ The symmetry of any conformer of this type must belong to one of the following seven point groups (D_{2d} , C_{2v} , S_4 , D_2 , C_s , C_2 , and C_1).² X-Ray analyses of Ph_4Z ($Z = C$,³ Si ,⁴ Ge ,⁵ Sn ,⁶ Pb ⁷) molecules show S_4 -symmetry in all cases. Detailed empirical force-field calculations on the stability and dynamics of tetraarylmethanes and -silanes have also been reported by Mislow and co-workers, showing D_{2d} -symmetry for tetraphenylmethane and S_4 -symmetry for tetraphenylsilane.^{1,8} Ar_4Z molecules in S_4 or D_{2d} -symmetry are obviously not chiral. Optical resolution of this type of compounds requires the fixation of conformation into one of the three (D_2 , C_2 , and C_1) symmetries. We have recently demonstrated an ethano-bridging method for the fixation of conformation and succeeded in the optical resolution of triarylboranes.⁹ The method is now applied to Ar_4Z molecules. Inspection of the molecular model indicates that ethano-bridgings of the two aryl groups in Ar_4Z lead to D_2 or S_4 -symmetry. We report synthesis, conformational analysis, and stereoisomerization of 2,2':2'',2'''-bis(ethano)tetraaryltins 1a-c.



a: $X=Y=H$, b: $X,Y= -CH=CH-CH=CH-$, c: $X=Me, Y=H$

The compounds 1a-c were synthesized via bis(2-bromoaryl)ethanes 2a-c. Di-lithiation of the dibromides 2a-c was carried out by *tert*-butyllithium (4.0 equiv) in diethyl ether at $-30^\circ C$. To this solution, tin(IV) chloride (0.5 equiv) was slowly added and the mixture was gradually warmed up to

room temperature and then refluxed for 4 h. After chromatographic separation, the ethano-bridged tetraaryltin **1** was obtained (**1a** in 14%, **1b** in 16%, **1c** in 8% yields).¹⁰ In order to clarify the conformation of **1**, an X-ray analysis of **1c** was undertaken.¹¹ Two independent molecules having very similar structures were observed in a crystal lattice. One of these structures is shown in Fig. 1. The molecule occupies a crystallographic site of C₂-axis [C₂(1) in Fig. 1] and has the two independent Sn-C bond lengths, the three C-Sn-C bond angles, and the two tilt angles of benzene rings (see caption of Fig. 1). However, the differences of these values are small and the molecule almost lies on the other two C₂-axes [C₂(2) and C₂(3) in Fig. 1] both of which are perpendicular to the C₂(1) axis. Thus, the overall structure of **1c** is very close to the D₂-structure.

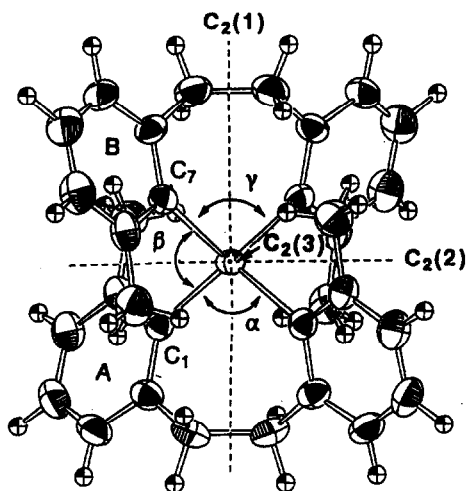


Fig. 1 ORTEP view of **1c** showing 50% thermal ellipsoids. Bond distances (Å) including Sn; C(1)-Sn 2.177(7), C(7)-Sn 2.173(7). Bond angles; $\alpha = 112.9(3)^\circ$, $\beta = 102.9(2)^\circ$, $\gamma = 111.7(4)^\circ$. The tilt angles of the aromatic rings (A, B) toward the plane defined by C(1), C(7), and Sn atoms; 72.81° for the ring A, 73.54° for the ring B.

To evaluate the stability of S₄-structure which is expected from the molecular model, molecular mechanics calculations (MM2)¹² were carried out.¹³ Fig. 2 shows the optimized geometries of the D₂- and S₄-structures of **1c** with the relative total steric energies. The S₄-structure has a higher energy than the D₂-structure by 0.8 kcal/mol, compatible with the X-ray analysis. A similar result was obtained for **1b**. However, a slightly inversed relation was obtained for **1a**.¹⁴ Assuming the D₂-structure for **1b** and **1c** in solution, the transformation to the antipode may occur by edge-flippings of the ethano-groups. If two edge-flips occur at the same time, the antipode can be directly formed. On the other hand, a single edge-flip leads to the achiral S₄-structure with a lower activation energy. Therefore the transformation can be preferably performed by sequential two edge-flips via the S₄-structure. The barrier between the D₂- and S₄-structures in Fig. 2 corresponds to the racemization energy.

Fig. 3 shows a temperature-dependent ¹H NMR spectrum (270 MHz) of the ethano-protons of **1c** (left) and the corresponding calculated spectra (right).¹⁵ A typical AA'BB'-pattern at 30 °C indicates that the transformation to the antipode is slow at that temperature. However, when the sample is warmed, the spectrum changes to a singlet at 70 °C through a coalescence temperature

of ca. 60 °C. From the rate constants obtained by simulation of the spectrum at five temperatures, the activation parameters of 1c are calculated to be $\Delta H^\ddagger = 16.7 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = 0.4 \pm 1.0$ e. u. On the contrary to 1c, the ^1H NMR spectrum of 1b showed a sharp singlet at 30 °C and split into a AA'BB'-pattern at -65 °C through a coalescence temperature of ca. -30 °C in CD_2Cl_2 . Similar treatment gives the activation parameters of $\Delta H^\ddagger = 10.8 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -2.0 \pm 1.0$ e.u. for 1b. The spectrum of 1a showed a sharp singlet in the temperature range between 30 ~ -90 °C and activation parameters could not be obtained, indicating $\Delta G^\ddagger < 8$ kcal/mol. Thus, the activation energies of the racemization of 1a-c is strongly dependent on the substituent X and increases in the order of 1a (X = H) < 1b (X = $\text{sp}^2\text{-C}$) < 1c (X = $\text{sp}^3\text{-C}$). To achieve the optical resolution of this type of compound at room temperature, an introduction either of more bulky substituents or the additional ethano-bridge(s) in X-positions would be necessary and such studies are in progress.

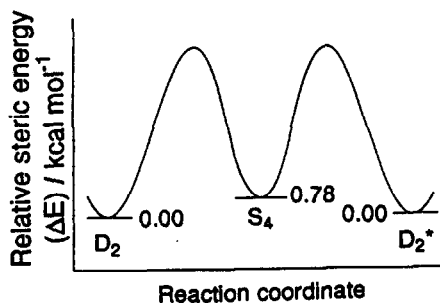
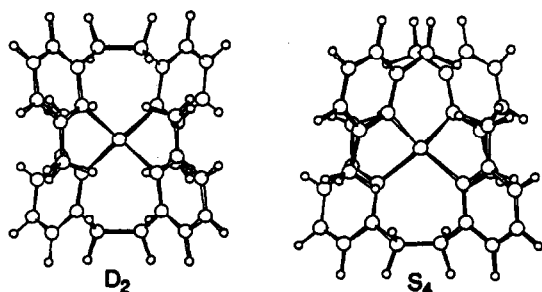


Fig. 2 Conformational analysis of 1c and the racemization path ($\text{D}_2 \rightleftharpoons \text{D}_2^*$) based on molecular mechanics calculation.

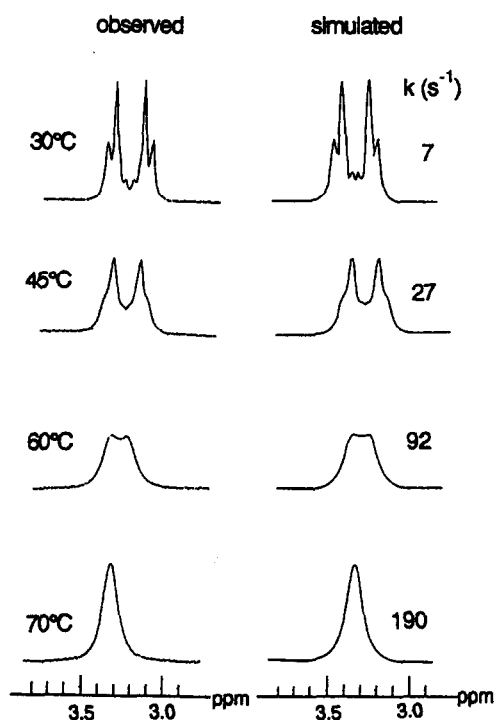


Fig. 3 Temperature-dependent 270 MHz ^1H NMR spectrum for the ethano-protons of 1c in $\text{C}_6\text{D}_5\text{Br}$ (left) and the corresponding simulated spectra (right).

References and Notes

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- 10 *Spectral and physical data* for 1a-c: 1a; colourless prisms, m.p. 169 °C, $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 3.32 (s, 8H), 7.05-7.24 (m, 12H), 7.38-7.42 (m, 4H). 1b; colourless prisms, m.p. 276 °C, $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 3.51 (s, 8H), 7.49 (d, 4H, J 8.2 Hz), 7.58 (dd, 4H, J 7.6, 6.9 Hz), 7.70 (dd, 4H, J 8.4, 6.9 Hz), 7.96 (d, 4H, J 7.6 Hz), 8.00 (d, 4H, J 8.2 Hz), 8.67 (d, 4H, J 8.4 Hz). 1c; colourless prisms, m.p. (sub.) -283 °C, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.27 (s, 12H), 3.27-3.41 (AA'BB', 8H), 6.87-6.94 (m, 4H), 7.00-7.13 (m, 8H)
- 11 *Crystal data* for 1c: $\text{C}_{32}\text{H}_{32}\text{Sn}$, monoclinic, space group $\text{C}2/c$ (No 15), $a = 17.203(2)$, $b = 17.190(2)$, $c = 17.206(2)$ Å, $\beta = 103.40(1)^\circ$, $V = 4950(1)$ Å³, $Z = 8$, $D_c = 1.437$ gcm⁻³; Rigaku AFC5R; Mo-K α radiation [$\lambda(\text{K}\alpha) = 0.71069$ Å]; $3^\circ < 2\theta < 60.1^\circ$; 7499 unique reflections, of which 3242 were treated as observed [$F_o^2 > 3\sigma(F_o^2)$]; an absorption correction was not applied; $R = 0.036$, $R_w = 0.037$. Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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- 13 Silicon (atom type: 19) parameters were modified for tin parameters as follows; van der Waals parameters (atom type, EPS, R*) 19, 0.270, 2.55; stretching parameters (bond, KS, L0) 2-19, 2.9, 2.17: 2-2, 8.067, 1.39; torsion parameters (angle, V1, V2, V3) 2-2-19-2, 0.0, 0.0, 0.4: 2-2-2-19, 0.0, 6.6, 0.0: 1-2-2-19, 0.0, 6.6, 0.0: 5-2-2-19, 0.0, 6.6, 0.0: 2-2-2-2, -0.93, 6.6, 0.0: 5-2-2-5, 0.0, 10.0, 0.0: 2-2-2-5, 0.0, 6.0, -1.06: 1-2-2-5, 0.0, 8.33, 0.0: 1-2-2-2, -0.1, 6.6, 0.0; bending parameters (angle, KS, bond angle) 2-2-19, 0.4, 120.0: 2-19-2, 0.4, 109.5: 0-2-19, 0.05. By using these parameters, X-ray structure of 1c was well reproducible [tilt angles of the aromatic rings (see Fig. 1) are in good accordance with the X-ray structure within 2°].
- 14 The D₂-structure is more stable than the S₄-structure by 1.37 kcal/mol for 1b. However, the S₄-structure is slightly more stable (0.03 kcal/mol) than the D₂-structure for 1a.
- 15 The following chemical shifts and coupling constants were used for the simulation; 1b: $\delta\text{H}_1 = \delta\text{H}_3 = 3.39$, $\delta\text{H}_2 = \delta\text{H}_4 = 3.73$, $J_{12} = J_{34} = -17$ Hz, $J_{14} = J_{23} = 3.0$ Hz, $J_{13} = 10.0$ Hz, $J_{24} = 9.0$ Hz; 1c: $\delta\text{H}_1 = \delta\text{H}_3 = 3.39$, $\delta\text{H}_2 = \delta\text{H}_4 = 3.20$, $J_{12} = J_{34} = -16.9$ Hz, $J_{14} = J_{23} = 3.0$ Hz, $J_{13} = 9.7$ Hz, $J_{24} = 9.3$ Hz.

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