

SYNTHESIS AND CRYSTAL STRUCTURE OF 7,7,14,14-TETRAMETHYLDINAPHTHO[1,8-bc:1',8'-fg][1,5]DISTANNOCIN AND ITS PHOTOCHEMICAL CONVERSION TO PERYLENE

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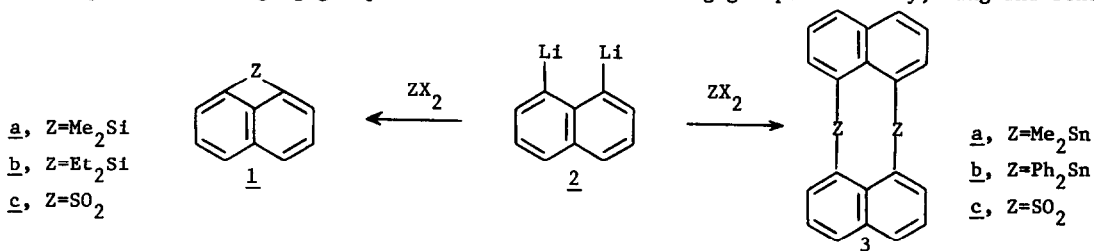
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As a possible method of synthesis of single-atom peri-bridged naphthalenes⁴ (1), we have considered the reactions of 1,8-dilithionaphthalene (2) with electrophiles of the type ZX_2 , where Z is the potential bridging group and X is a suitable leaving group. Recently, Yang and Schechter



reported that 2 reacts with dimethyl- and diethylsilicon dichloride to give 1a (Z = Me₂Si) and 1b (Z = Et₂Si), respectively.⁵ This result prompts us to disclose our observation that the reaction of 2 with dimethyltin dibromide prefers another path, leading to the "dimeric" compound 3a (Z = Me₂Sn).

Treatment of a 4.6×10^{-1} M ethereal solution of 1,8-dilithionaphthalene⁶ with 1 equiv of dimethyltin dibromide at room temperature resulted in the formation of a white precipitate, which was collected and crystallized from benzene/hexane to give 7,7,14,14-tetramethyldinaphtho[1,8-bc:1',8'-fg][1,5]distannocin (3a) as white flakes (mp 272-274°C) in 71% yield. The 300 MHz ¹H NMR spectrum of the product shows a multiplet in the aromatic region and a sharp singlet at 0.5 ppm accompanied by one pair of Sn-¹H satellite peaks (J = 54 Hz). Integration of the signals indicates an equal number of aromatic and aliphatic protons. This spectrum remains unchanged down to -100°C, below which temperature homogeneity of the solution could not be maintained. The mass spectrum of 3a shows multiplets centered on m/e 535 (rel abund. 58%), which corresponds to M⁺-15, and 505(5), 490(7), 386(53), 371(12), 275(2), 260(20), 252(100), 245(19), and 164(25). Using diphenyltin dichloride, 2 was converted to 7,7,14,14-tetraphenyldinaphtho[1,8-bc:1',8'-fg][1,5]distannocin (3b), mp 264-266°C, in 41% yield. The mass spectrum of 3b shows a molecular ion multiplet centered on m/e 798.

The conformational properties of 3a are of interest, since a structure containing tetrahedral tin atoms⁷ would be expected to have two non-equivalent pairs of methyl groups.⁸ Thus, either the tin atoms are not tetrahedral, or a rapid interconversion of conformers is responsible for the single methyl signal observed in the ¹H NMR spectrum. To distinguish between these possibilities, we have subjected a crystal of 3a to x-ray diffraction analysis.

Thin plates of 3a crystallized in the common monoclinic space group $P2_1/n$ ($P2_1/c$ -alternate setting) with a calculated density of 1.74g/cc assuming four molecules in the unit cell. Cell constants, determined from a least-squares fitting of 15 accurately measured 2θ values, were $a = 7.801(2)$, $b = 14.419(5)$, $c = 18.954(5)\text{\AA}$ and $\beta = 99.41(2)^\circ$. All unique reflections with $2\theta \leq 45^\circ$ were measured using variable rate ω -scans and MoK α radiation. After correction for Lorentz, polarization and background effects, 2605 (88%) of the 2970 reflections measured were considered observed ($F_o^2 \geq 3\sigma(F_o^2)$).

The two independent tins were easily placed from analysis of the Patterson synthesis, and the subsequent Sn-phased electron density synthesis revealed all the nonhydrogen atoms.⁹ Full-matrix least squares refinement has currently converged to an unweighted crystallographic residual of 0.095 for the observed reflections. Refinement was terminated at this point since the conformation of the molecule was established.¹⁰

A computer generated perspective drawing of 3a is shown in Figure 1. The central eight-membered ring assumes a chair-like conformation; two methyl groups occupy axial positions and two occupy equatorial positions. The peri bonds between each naphthalene ring and the tin atoms are directly above and below the plane of the naphthalene ring, a situation which commonly arises with bulky peri substituents.¹¹ The tin atoms are tetrahedral, with C(1')-Sn(1)-C(1) and C(8')-Sn(2)-C(8) angles of $127.5(6)^\circ$ and $126.6(6)^\circ$ respectively. All other C-Sn-C bond angles fell in the range $104-108^\circ$. The Sn-Sn distance is 3.56\AA . A facile chair-to-chair ring inversion process therefore accounts most simply for the observed equivalence of the methyl groups of 3a in solution.

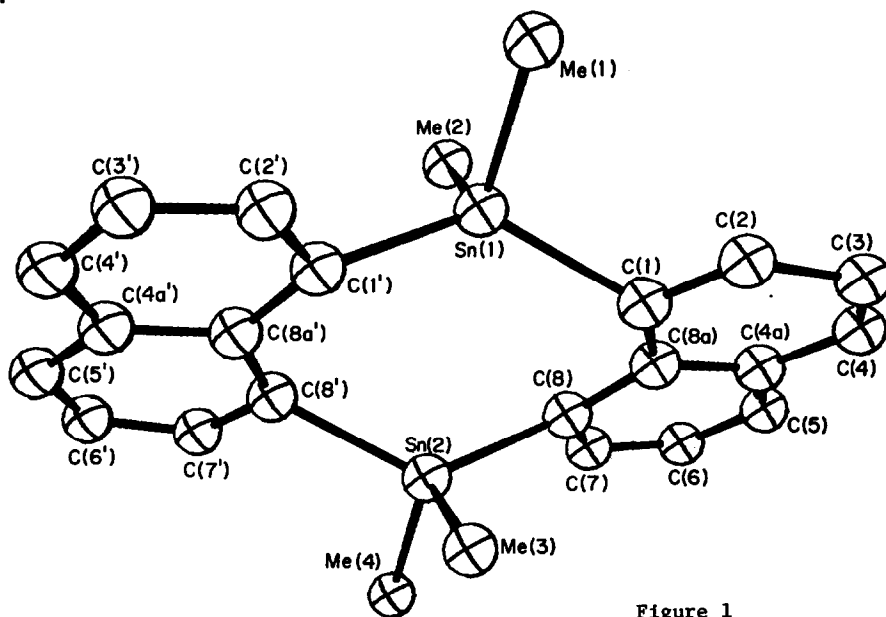
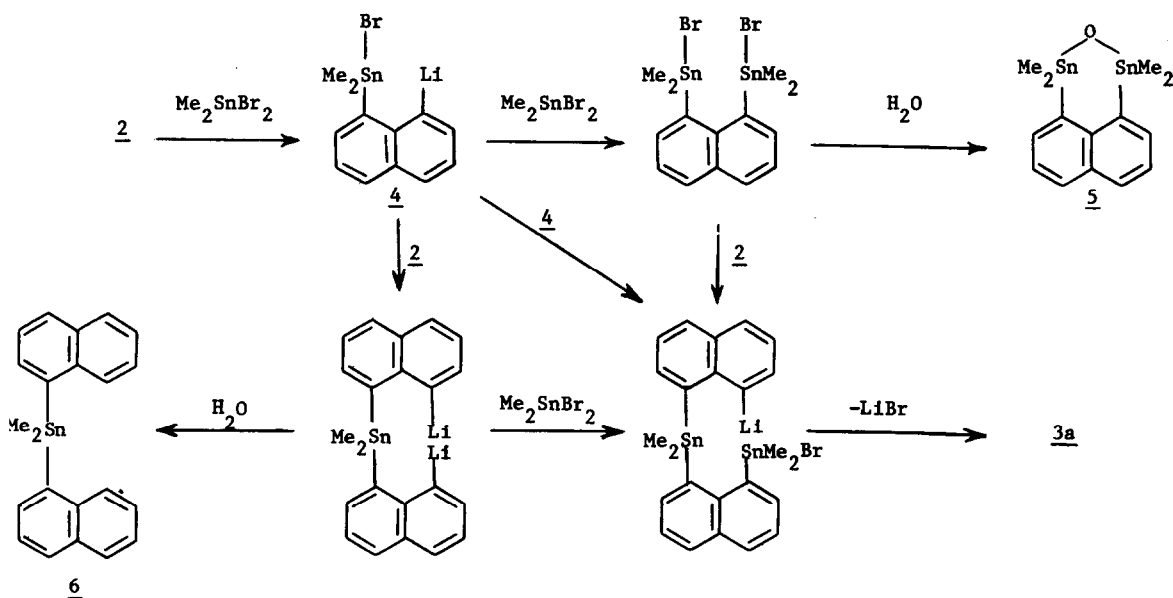
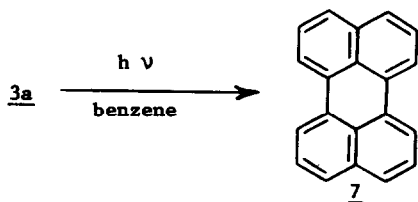


Figure 1

When the reaction of 2 with dimethyltin dibromide was carried out at higher dilution, some information about the reaction pathway could be gained. Etheral 2 ($3.0 \times 10^{-2} M$) reacted with dimethyltin dibromide at -70° to give 3a, 5, and 6¹² in a 2:10:1 ratio, along with some naphthalene, after quenching. Concentration of the reaction mixture prior to quenching gave chiefly 3a. We conclude that intermediate 4 reacted preferentially with either of the starting materials or with itself to give the observed products as outlined below, rather than undergoing cyclization to produce the desired stannete.



The photochemistry of 3a was investigated as another possible means to produce a stannete, since photolysis of dimer 3c ($Z = SO_2$) yields 1c ($Z = SO_2$).¹³ Irradiation of 3a ($\lambda_{max} = 298 \text{ nm}$) in benzene, however, caused extrusion of the dimethyltin units, giving perylene (7) in 60% yield.



REFERENCES AND NOTES

1. Taken in part from the Ph.D. Thesis of Spencer Knapp, Cornell University, 1975. The partial support of this research by the National Science Foundation (Grant No. MPS 73-04986) is acknowledged with pleasure.
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3. Camille and Henry Dreyfus Teacher-Scholar Grant Awardee 1972-1977.
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10. Tables of fractional coordinates, bond distances, bond angles and observed and calculated structure factors are available as a Supplement to Publication. To obtain a copy, contact the Photo Service, Iowa State University, Ames, Iowa 50011 requesting Supplement to Publication for this article and submitting \$.50 in the form of check, cash or money order. Give your name and complete address (including zip code) for mailing.
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12. Compound 5 forms colorless prisms, mp (dec.) 178-180°C; mass spectrum: m/e 440(M^+ , 14%), 425(100), 424(61), 395(22), 275(9), 262(28), 260(25), 246(11), 245(10), 165(16), 141(28), 135(14), 120(28); pmr (δ in $CDCl_3$): 0.60 (s, 12H, $J_{Sn-H}^{117} 57.4$ Hz, $J_{Sn-H}^{119} 60.6$ Hz), 7.35 - 7.50 (m, 4H), 7.75 - 7.95 (m, 2H). Compound 6 is a colorless oil; mass spectrum: m/e 403 (M^+ , 30%), 388(100), 254(12), 246(25), 149(56), 128(77), 127(34), 126(20), 119(50); pmr (δ in $CDCl_3$): 0.77 (s, 6H, $J_{Sn-H}^{117} 52.0$ Hz, $J_{Sn-H}^{119} 54.6$ Hz), 7.20 - 8.00 (m, 14H).
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