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Variable-Temperature ^{119m}Sn Mössbauer Study of Organotin-Substituted Styrene Monomers and Polymers

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Tin-containing organometallic polymers (OMPs) are being actively investigated as potential marine antifouling materials. The OMPs are unique in containing the organotin pesticide chemically bound to a polymer backbone, resulting in controlled release into the marine environment.[1] The binding at the tin site is crucial to the rate at which the release will take place. We report here the first application of a method based upon Mössbauer spectroscopy for distinguishing the state of binding of the tin atoms in organotin-substituted monomers and polymers.

Di-*p*-tolyldi-*p*-styryltin(IV) (I) (mp 83–84 °C) and tetra-*p*-styryltin(IV) (II) (mp 134.5–135.5 °C) are solids formed by treatment of the corresponding tin chloride with the *p*-styryl Grignard reagent. The monomers are polymerized to Ia and IIa by gentle heating to infusible solids.[2] The tin-119m Mössbauer isomer shift (IS) and quadruple splitting (QS) values for the monomers (for I, IS = 1.23 ± 0.02 and QS = 0 mm/s; for II, IS = 1.17 ± 0.02 and QS = 0 mm/s) do not change outside of experimental error on polymerization (for Ia, IS = 1.21 ± 0.02 and QS = 0 mm/s; for IIa, IS = 1.20 ± 0.02 and QS = 0 mm/s).[3] These values are typical of simple tetraorganotin compounds,[4] and the failure to detect any change in their magnitudes on polymerization has been noted before for trimethyl-[5] and triphenyl-*p*-styryltin(IV).[6]

It has been recently found that logarithmic plots of the Mössbauer resonance areas vs. temperature are linear over an accessible temperature range as expected according to the Debye model of solids in the high-temperature limit. For a thin absorber the recoil-free fraction, $f(T)$, is directly related to this area, $A(T)$, and may be used to investigate the lattice dynamics at the tin site. It is found that the more tightly bound the tin atoms, the slower will be the decrease in $f(T)$ and hence in $A(T)$, as the temperature is raised. Compounds of known structure, consisting of noninteracting monomeric molecules exhibit slopes [$a = \mathrm{d}\ln(A(T)/A(77))/\mathrm{d}T$] of ca. -1.8×10^{-2} K^{-1}. Solids in which one-, two-, or three-dimensional association is present exhibit slopes of ca. -0.9×10^{-2} K^{-1} or less.[7]

Figure 1 displays the logarithmic plot of the area under the Mössbauer resonances, normalized to 77 K for ease of comparison of data, vs. temperature in the range 77–140 K for monomers I and II and their polymers Ia and IIa.[8] The spectral intensities in the case of the monomers decay rapidly [for I, $a = -2.14$ (20) $\times 10^{-2}$ K^{-1} (regression analysis, $r = -0.990$, intercept 1.64, 4 points); for II, $a = -2.06$ (12) $\times 10^{-2}$ K^{-1} ($r = -0.998$, intercept 1.60, 3 points)], and it becomes impossible, even over extremely long counting times, to obtain usable data above ca. 100 K. By contrast, the spectral intensities for the materials after polymerization show somewhat slower decays [for Ia, $a = -1.80$ (9) $\times 10^{-2}$ K^{-1} ($r = -0.993$, intercept 1.36, 8 points); for IIa, $a = -1.95$ (3) $\times 10^{-2}$ K^{-1} ($r = -0.999$, intercept 1.51, 6 points)], and spectra can be obtained up to ca. 140 K.

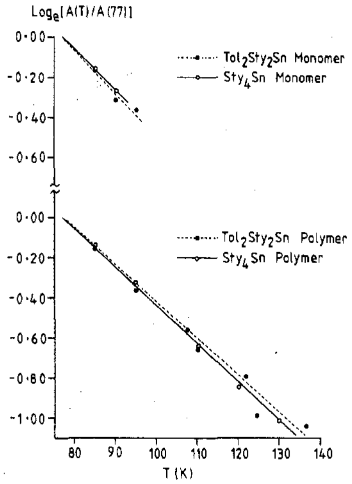

Figure 1. Logarithmic plot of the area under the Mössbauer resonances [$A(T)$] normalized to 77 K vs. temperature in the range 77–140 K for di-*p*-tolyldi-*p*-styryltin(IV) and tetra-*p*-styryltin(IV) and their polymers.

The effect of polymerization in locking the tin atom in its position must necessarily be very small, yet the effect is detectable by Mössbauer techniques in two ways. First, the temperature dependences of the recoil-free fractions are discernibly greater for the monomers than for their polymers. Second, the Debye model, by which the slopes in Figure 1 are linear, itself begins to break down, and for the monomers the resonance areas above ca. 100 K are very much smaller than expected by extrapolation of the linear plots in the range 77–100 K.

While the tin atoms are clearly more free to move in the monomers, the added constraint on polymerization is not as marked as when tin atoms are bound rigidly by bridging, directly attached electronegative substituents.[7] In the case of the tetraorganotins studied here, the tin atoms continue to be held by bonds to four carbons and, moreover, the polymerized lattice itself may be quite porous owing to the steric bulk of the atoms attached to tin.

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(8) Details of our Mössbauer spectrometer, variable-temperature controller, and data analysis procedures have been described previously.[9] The best straight line through the data points was calculated by using standard least-squares methods which were weighted on the basis of the calculated errors in the area under the Mössbauer resonance.[10]

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Registry No. I, 72611-66-6; II, 72611-67-7.

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Cyclic Boron Derivatives of Carbohydrazide[1]

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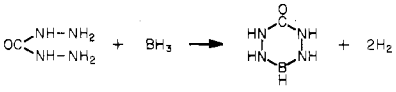
No boron derivatives of carbohydrazide, OC(NH–NH$_2$)$_2$, have been described in the literature. This lack is not really surprising since carbohydrazide is soluble only in protic media which are normally not employed in synthetic boron chemistry. For a study of reactions of carbohydrazide and similar carbonyl derivatives with boranes, some two-phase processes have recently been investigated. The present work reports the cyclization of carbohydrazide via a boryl group in such a procedure.

Results and Discussion

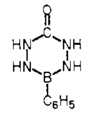
A solution of trimethylamine–borane in toluene or of tetrahydrofuran–borane in tetrahydrofuran reacts slowly with a vigorously stirred slurry of carbohydrazide in toluene or tetrahydrofuran, respectively, at elevated temperatures to yield 1,2,4,5-tetraaza-3-boracyclohexan-6-one, **1**, as is illustrated in the equation



1

A confirmation of the structure of **1** rests primarily on the data of the elemental analysis. The compound is insoluble in common organic solvents, and no NMR could be recorded. The low-quality infrared spectrum of the material (KBr pellet) exhibits a strong and broad BH absorption centered at 2395 cm^{-1}. Strong absorptions in the NH stretching region are also broad and overlapping, but a maximum at 3190 cm^{-1} is evident.

Additional support for the structure of **1** is obtained by the preparation of the B-phenylated derivative: slurry of carbohydrazide was found to react with bis(dimethylamino)phenylborane, C$_6$H$_5$B[N(CH$_3$)$_2$]$_2$, to yield **2**.



2

The mass spectrum of **2** features a parent ion peak at *m/e* 276. The compound is only very slightly soluble in anhydrous organic solvents, and a low-quality ^{1}H NMR spectrum was recorded on a saturated solution of **2** in (CD$_3$)$_2$CO; an aromatic multiplet with $\delta(^1H)$ centered at 8.4 and an NH signal (CO bonded) at $\delta(^1H)$ 9.67 were observed. The infrared spectrum of the compound (KBr pellet) exhibits a very broad absorption in the NH stretching region.

Noteworthy seems to be the formation of *B*-triphenylboroxine, $(-BC_6H_5-O-)_3$, during the preparation of **2**. Since atmospheric oxygen was carefully excluded, the boroxine is likely to have originated from a breakage of the C=O bond. On this basis one must assume that whenever a carbonyl compound such as carbohydrazide is reacted with a trigonal borane species, the formation of boroxines can be expected. This event may considerably impair the synthesis of boron derivatives of carbonyl species (or their purification).

Experimental Section

All experiments were conducted in an atmosphere free of moisture and oxygen under inert-gas cover (argon or nitrogen). Melting points (uncorrected) were determined in sealed capillaries. Infrared spectra were recored under standard operating conditions by using a Perkin-Elmer Model 621 spectrometer (frequencies are listed in cm^{-1}; abbreviations are s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder). Mass spectral data were obtained with a Hitachi Perkin-Elmer RMU-7 double-focusing instrument, and proton NMR spectra were recorded on a Varian Model T-60 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Carbohydrazide, trimethylamine–borane, and tetrahydrofuran–borane were commercial products. Bis(dimethylamino)phenylborane was prepared by the literature procedure.[2]

1,2,4,5-Tetraaza-3-boracyclohexan-6-one, 1. A mixture of 9.0 g (100 mmol) or carbohydrazide, 7.66 g (105 mmol) of trimethylamine–borane, and 200 mL of toluene is refluxed for 16 h with vigorous stirring. Solids are filtered off the hot solution and washed with hot toluene and then with hot hexane. The residue is dried under vacuum for 13 h at 80 °C to give 9.44 g of product (94.5%) which does not melt up to 400 °C. Anal. Calcd for CH$_5$ON$_4$B (mol wt 99.91): C, 12.02; H, 5.05; N, 56.09; B, 10.82. Found: C, 12.08; H, 5.33; N, 56.01; B, 10.80. Infrared spectrum (cm^{-1}): 3310/3190/3075 s (b), 2450 sh, 2395 s (b), 1660 vs (b), 1637 sh, 1525 w, 1460 sh, 1435 m, 1400 m, 1330 w (b), 1220 m, 1167 w, 1020 w (b), 925 w, 800 vw, 763 w (b), 580 mw (b). Alternately, the material is obtained by refluxing a mixture of 9.0 g of carbohydrazide and 100 mL of a 1 M solution of tetrahydrofuran–borane in tetrahydrofuran for 7 h, collecting insolubles, and washing them with hot hexane.

3-Phenyl-1,2,4,5-tetraaza-3-boracyclohexan-6-one, 2. A mixture of 9.62 g (54.6 mmol) of bis(dimethylamino)phenylborane, 4.92 g (54.6 mmol) of carbohydrazide, and 80 mL of tetrahydrofuran is refluxed with stirring for 7 h. Approximately half of the solvent is stripped off, and 9.37 g (97.5%) of colorless crystals, melting from 126 to 132 °C (with some apparent decomposition), is collected. They are recrystallized from tetrahydrofuran to yield three fractions of 2.02, 0.80, and 4.85 g, respectively. The first two fractions are significantly contaminated with *B*-triphenylboroxine (as evidenced by mass spectral data) and are discarded. The third fraction is washed with hot benzene (to remove traces of *B*-triphenylboroxine) and hot hexane (to remove adhering tetrahydrofuran) to yield (after drying under vacuum) the final product, decomposing at 132 to 135 °C. Anal. Calcd for C$_7$H$_9$ON$_4$B (mol wt 176.01): C, 47.76; H, 5.16; N, 31.84; B, 6.14. Found: C, 47.16; H, 5.58; N, 31.22; B, 6.29. Mass spectrum (70 eV; relative abundances (in parentheses) of greater than 5% only): *m/e* 176 (75.4), 175 (5.6), 130 (5.7), 104 (11.1), 103 (10.8), 91 (6.1), 78 (100), 77 (14.0), 53 (10.3), 51 (10.4), 50 (8.1). Infrared spectrum (cm^{-1}): 3415/3305/3245/3195/3075 s (vb), 1663 s (b), 1603 sh, 1440 sh, 1432 m, 1403 ms, 1332 w (b), 1260 mw, 1210 m, 1090 vw, 1067 mw, 1020 mw, 746 m, 700 m.

Registry No. 1, 72765-25-4; **2**, 72778-71-3; carbohydrazide, 497-18-7; trimethylamine–borane, 75-22-9; tetrahydrofuran–borane, 14044-65-6; bis(dimethylamino)phenylborane, 1201-45-2.

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(1) Boron–Nitrogen Compounds. 84. For part 83 of this series see D. P. Emerick, L. Komorowski, J. Lipinski, F. C. Nahm, and K. Niedenzu, *Z. Anorg. Allg. Chem.*, in press.

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