The Crystal Structure of Trimethyltin Isothiocyanate

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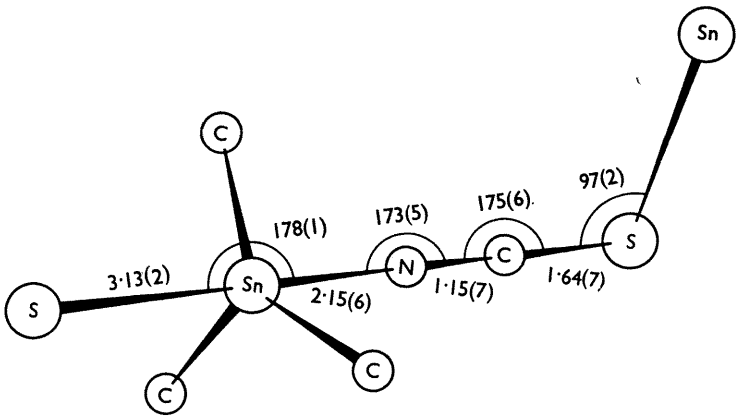
Summary The crystal structure of Me_3SnNCS consists of zig-zag –S . . . Sn–N=C=S . . . Sn– chains, bent only at sulphur, with nearly planar trimethyltin groups.

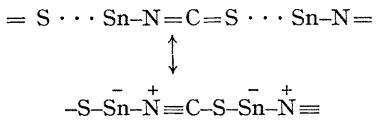
MÖSSBAUER studies[1] of trialkyltin isothiocyanates indicate that the trialkyltin groups are planar, with five-co-ordinated tin; the infra-red spectra[2] are consistent with a $R_3Sn–N=C=S$ rather than a $R_3Sn–S–C\equiv N$ structure, with a non-bonded S . . . Sn interaction and a chain structure bent at nitrogen. In view of the ambiguities in the interpretation of the spectroscopic data, and also for comparison with the structure of silyl isothiocyanate,[3] where linearity at nitrogen provides evidence of involvement of the silicon 3*d* orbitals in the bonding, we have determined the crystal structure of trimethyltin isothiocyanate by single-crystal *X*-ray diffraction.

The crystals are orthorhombic, *Pbca*; $a = 13{\cdot}20 \pm 0{\cdot}01$, $b = 10{\cdot}28 \pm 0{\cdot}01$, $c = 12{\cdot}01 \pm 0{\cdot}01$ Å, $Z = 8$, $D_c = 1{\cdot}82$. Intensities were estimated visually from equi-inclination Weissenberg photographs taken with Cu-K_α radiation. The structure was solved by the heavy atom method and has been refined by full-matrix least-squares with anisotropic temperature factors for the tin and sulphur atoms, and isotropic temperature factors for the carbon and nitrogen atoms, to a conventional '*R* index' of 0·11 for 344 unique observed reflections.



The structure consists of zig-zag chains along the *Z* axis, all the atoms except those of the methyl groups lying approximately in planes perpendicular to the *X*-axis. The S–Sn–N–C–S skeleton is linear within experimental error, the chains being bent at sulphur. The trimethyltin group is almost planar, with a mean N–Sn–C angle of $95 \pm 2°$, mean C–Sn–C angle of $119 \pm 2°$, and mean Sn–C bond length of $2{\cdot}13 \pm 0{\cdot}03$ Å. The Sn–S bond is appreciably longer than 2·47 Å found[4] for the 'single' bond in $Me_3Sn–SC(S)NMe_2$; the N–C and C–S distances are intermediate between the values in HN=C=S (1·22 and 1·56 Å)[5] and MeS–C≡N (1·16 and 1·68 Å respectively).[6]

These results are consistent with a structure intermediate between the valence-bond extremes:



The angle at sulphur is very close to the value of 99·9° found in MeSCN. The stereochemical inactivity of the nitrogen lone-pair is accounted for by the above scheme, and does not imply 'p_π–d_π bonding' between nitrogen and tin.

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