

The Low-Temperature Polymorph of Tetramethyldiphosphine-bis(monoborane): Insight into the Stabilization of Different Rotational Isomers in the Solid State

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The low-temperature (LT) polymorph of tetramethyldiphosphine-bis(monoborane), $\text{Me}_2(\text{H}_3\text{B})\text{P}(\text{BH}_3)\text{Me}_2$, was obtained by crystallization from diethyl ether at 4 °C. It crystallizes in the monoclinic space group $P2_1/c$, $a = 6.464(1)$, $b = 7.605(1)$, $c = 11.867(2)$ Å, $\beta = 119.99(1)^\circ$ (at 153 K) with 2 molecules per unit cell. This implies that the individual molecules have crystallographic inversion symmetry and a strict *anti* arrangement with respect to the central B-P-P-B skeleton. At 87.6 °C (DTA) the LT polymorph transforms to the high-temperature (HT) modification which contains the *anti* and *gauche* conformers in a 1:2 ratio ($P2_1/c$, $Z = 6$; H. L. Carrell, J. Donohue, Acta Crystallogr. **B24**, 699 (1968)). This strongly suggests that the *gauche* conformer is higher in energy and stabilized by the crystal packing of the HT modification. The P-P-B angle in the *anti* LT form ($113.91(6)^\circ$) ascertains the value of the *anti* conformer in the HT form ($114.4(6)^\circ$) which was found to be significantly different from the *gauche* conformer which centered around 110 °C.

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