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Nuclear Magnetic Resonance Analysis and Crystal Structure of 1,3,5-tris(bromomethyl)benzene

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The synthesis, characterization, and determination of the crystalline structure of the product 1,3,5-tris(bromomethyl)benzene, which will be used to form 1,3,5-tris(phenylphosphinic acid)benzene, a pro-ligand with three freely rotating phosphinic acid groups. Mesitylene was reacted *N*-bromosuccinimide using the Wohl-Ziegler reaction [1] to form 1,3,5-tribromomethylbenzene. To characterize the product, ^{1}H and ^{13}C 1D and TOCSY, HSQC and HMBC 2D nuclear magnetic resonance (NMR) experiments and infrared spectroscopy (IR) were employed. Analysis of the NMR data revealed a mixture of compounds, which were determined to be the desired product 1,3,5-tris(bromomethyl)benzene (**I**), with side products 1,3-bis(bromomethyl)-5-dibromomethylbenzene (**II**), 1,3-bis(bromomethyl)-5-methylbenzene (**III**), and 1-bromomethyl-3-dibromomethyl-5-methylbenzene (**IV**) in the molar ratio 0.40:0.19:0.16:0.25. The desired product crystallized from the mixture in chloroform by slow evaporation and its crystal structure determined by single-crystal X-ray diffraction (see Figure 1).

The crystal structure was resolved in space group $P\bar{1}$ with $Z = 2$. The structure exhibits positional crystallographic disorder in the Br3 atom, with 72% occupancy in the Br3 position and 27% in the Br3' position. Additionally, it is evident that Br1 and Br5 atoms interact with nearby hydrogen atoms in the structure, whereas Br3 and Br3' lack such interactions due to the available volume in the crystalline structure. The volume in the unit cell available for Br3 and Br3' is 17.53 Å³, significantly larger than the van der Waals volume of a bromine atom (7.79 Å³) [2].

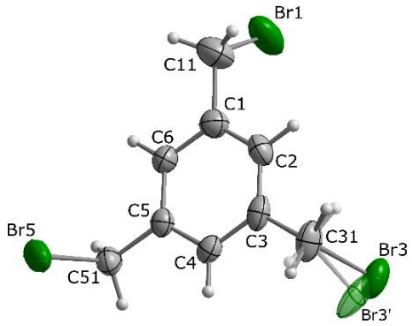

Figure 1. Thermal ellipse diagram of the crystal structure of **1**, showing the positional disorder of Br3/Br3'.

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