Secondary Interactions in Bromomethyl-substituted Benzenes: Crystal Structures of Three α,α'-Bis-bromoxylenes, 1,2,3,5-Tetrakis(bromomethyl)benzene, and 1,2,4,5-Tetrakis(bromomethyl)benzene

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X-Ray structure determinations of all three isomers of bis(bromomethyl)benzene and of two isomeric tetrakis(bromomethyl)benzenes show that the packing of the molecules is determined principally by interactions of the bromomethyl groups (C–H···Br and Br···Br), except for *ortho*-bis (bromomethyl)benzene, in which C–H···π interactions play a major role.

Key words: α,α'-Bis-bromoxylenes, X-Ray, "Weak" Hydrogen Bonds, Halogen-Halogen Contacts

Introduction

Our continued interest in the influence of bromine atoms on the packing of organic molecules in crystal structures has led us to investigate systematically a series of poly(bromomethyl)-substituted arenes. Our previous reports concerned two bromine derivatives: 1,6,7-tris(bromomethyl)naphthalene [1] and 2,2″-bis(bromomethyl)-*p*-terphenyl [2], in which "weak" hydrogen bonds C–H···Br and (for the naphthalene derivative only) short Br···Br interactions were observed.

At r. t., the bis- and tetrakis-(bromomethyl)benzene derivatives are solids that readily form crystals suitable for X-ray studies. Here we report crystal structures of all three isomeric forms of the disubstituted compound (**1** – **3**), together with two of the three possible isomers (**4**, **5**) of the tetrasubstituted compound.

Results and Discussion

The individual molecules of **1** – **5** are shown in Figs. 1 – 5. The *para* derivative **1** and the *ortho* derivative **3** crystallize with imposed inversion and twofold symmetry, respectively; compound **4** also displays inversion symmetry. The ring angles at the substituted atoms are consistently less than 120° (by *ca.* 1°) except for compound **5**; otherwise, bond lengths and angles may be considered normal, *e. g.* the narrow range of C–Br bond lengths of 1.974 – 1.982 Å over all five compounds (for individual values, the Supplemen-

Formula scheme.

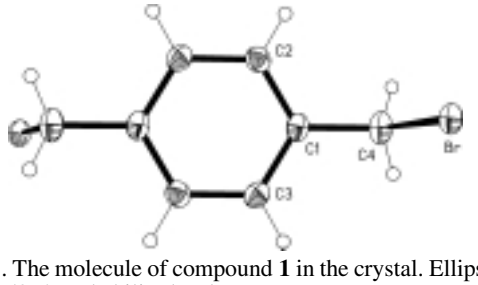

Fig. 1. The molecule of compound **1** in the crystal. Ellipsoids at the 50 % probability level.