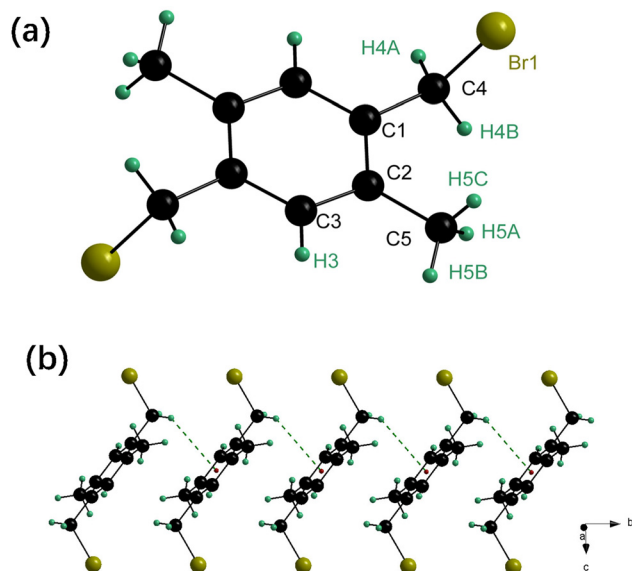


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The crystal structure of 1,4-bis(bromomethyl)-2,5-dimethylbenzene, $C_{10}H_{12}Br_2$



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Abstract

$C_{10}H_{12}Br_2$, monoclinic, $P2_1/c$ (no. 14), $a = 8.1816(14)$ Å, $b = 4.4288(7)$ Å, $c = 15.2809(19)$ Å, $\beta = 93.126(2)^\circ$, $V = 516.10(14)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0403$, $wR_{ref}(F^2) = 0.1011$, $T = 170$ K.

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Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Needle, greenish
Size:	$0.22 \times 0.12 \times 0.1$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	7.8 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	26.4° , >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	1947, 1059, 0.047
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 781
$N(\text{param})_{\text{refined}}$:	56
Programs:	CrysAlis ^{PRO} , ¹ OLEX2, ² SHELX ^{3,4}

1 Source of materials

A mixture of 48 % hydrobromic acid (100 mL), para-formaldehyde (7.7 g), and *p*-xylene (15.5 mL) in a 500 mL round-bottom flask was stirred under reflux for 48 h. The white precipitate was collected by filtration to afford approximately 35 g of the crude title compound. Recrystallisation from carbon tetrachloride yielded pure product as white needles, suitable for single-crystal X-ray diffraction analysis.

2 Experimental details

The hydrogen atoms of the methyl group were located in difference Fourier maps and then placed in idealized positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and C–H distances constrained to 0.96 Å. The remaining hydrogen atoms were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Crystal data, data collection and structure refinement details are summarized in Table 1.

3 Comment

1,4-Bis(bromomethyl)-2,5-dimethylbenzene is widely used as a key intermediate in the organic synthesis of *s*-indacenes⁵ and as a bridging building block for the preparation of novel macrocycles.⁶ Its utility stems from its straightforward and high-yielding synthesis, exemplified by the

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bromomethylation of 1,4-dimethylbenzene, which unexpectedly affords the corresponding dibromo compound in nearly quantitative yield, significantly outperforming the typically low-yielding chloromethylation reaction.⁵

The title compound, C₁₀H₁₂Br₂, features a center of inversion situated at the centroid of the benzene ring. The asymmetric unit consists of one half of the molecule positioned on an inversion center, with its labeling shown in Figure (part a). Two bromomethyl groups are located on opposite sides of the benzene ring and are nearly perpendicular to it, as indicated by the Br1–C4–C1–C3 and Br1–C4–C1–C2 torsion angles of 98.4(4)° and 82.3(5)°, respectively. The carbon atom C4 is nearly coplanar with the benzene ring, supported by the C4–C1–C2–C3 and C4–C1–C2–C5 torsion angles of 179.4(4)° and 179.3(4)°, respectively. A comparison with the crystal structures of 1,1-bis(bromomethyl)benzene,⁷ 1,4-bis(bromomethyl)benzene,⁸ and 1,2-bis(bromomethyl)benzene⁹ reveals no unusual bond lengths or angles. However, the C–Br bond length in the title compound (1.988 Å) is slightly longer than those in 1,1-bis(bromomethyl)benzene (1.967 Å), 1,4-bis(bromomethyl)benzene (1.965 Å), 1,2-bis(bromomethyl)benzene (1.975 Å), and other bromomethyl-substituted benzenes (1.974–1.985 Å).^{3–10}

The crystal packing of the title compound features only weak C–H... π interactions, with no evidence of strong or weak hydrogen bonds, significant π ... π interactions, or short Br...Br contacts. This behaviour contrasts with that of 1,4-bis(bromomethyl)benzene,⁸ which exhibits short Br...Br contacts, but resembles the packing mode observed in 1,1-bis(bromomethyl)benzene.⁷ Such a packing environment is relatively uncommon among brominated compounds.⁹ As shown in Figure, the crystal stability is primarily maintained by C4–H4... π interactions between the bromomethyl group and the centroid (C_g) of a symmetry-related benzene ring [$d(C4...C_g^i) = 2.98$ Å, $d(H4...C_g^i) = 3.562(5)$ Å, $\theta(C4-H4...C_g^i) = 119^\circ$; C_g denotes the centroid of the C1–C6 ring; symmetry code: (i) $x, 1 + y, z$]. These interactions form chains propagating along the b axis direction (Figure, part b).

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