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The twinned crystal structure of 1,3-phenylenedimethanaminium dibromide, $C_8H_{14}Br_2N_2$

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Abstract

$C_8H_{14}Br_2N_2$, monoclinic, $I2/a$ (no. 15), $a = 9.0331(9)$ Å, $b = 13.4475(14)$ Å, $c = 27.586(3)$ Å, $\beta = 94.879(9)^\circ$, $Z = 12$, $V = 3338.8(6)$ Å³, $R_{gt}(F) = 0.0582$, $wR_{ref} = 0.0885$, $T = 290$ K.

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Tables 1 and 2 contain details on the crystal structure as well as measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless needle
Size:	$0.67 \times 0.14 \times 0.04$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	7.24 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	27.0° , $>99\%$
$N(hkl)_{measured}$, $N(hkl)_{unique}$	9870, 9870
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6167
$N(param)_{refined}$:	171
Programs:	Diamond [1], CrysAlis ^{PRO} [2], SHELX [3–5]

Source of material

The title compound 1,3-phenylenedimethanaminium dibromide was synthesized by the reaction of 63% aqueous hydrobromic acid and 1,3-phenylenedimethanamine at ambient conditions. In a typical experiment 1 mmol of 1,3-phenylenedimethanamine is reacted with an excess of hydrobromic acid. The resulting light-yellow solution was stored in a desiccator equipped with a small amount of molecular sieve. Clear colourless crystals were obtained after a few days.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.34206 (7)	0.65873 (5)	0.59810 (3)	0.0450 (2)
Br2	0.38821 (8)	0.29498 (6)	0.65036 (3)	0.0508 (2)
Br3	0.81651 (7)	0.00903 (5)	0.57816 (3)	0.0446 (2)
N1	0.1378 (5)	0.4737 (4)	0.64036 (19)	0.0421 (17)
H11	0.173 (4)	0.536 (2)	0.6344 (6)	0.063*
H12	0.061 (3)	0.459 (3)	0.6176 (8)	0.063*
H13	0.213 (4)	0.428 (3)	0.6384 (5)	0.063*
N2	0.4155 (5)	0.3444 (4)	0.87023 (19)	0.0416 (17)
H21	0.320 (4)	0.317 (3)	0.8673 (2)	0.062*
H22	0.413 (4)	0.405 (2)	0.8869 (8)	0.062*
H23	0.481 (3)	0.301 (3)	0.8875 (8)	0.062*
N3	0.5516 (5)	0.1762 (4)	0.5630 (2)	0.0428 (18)
H31	0.474 (3)	0.136 (3)	0.5693 (6)	0.064*
H32	0.558 (4)	0.2278 (18)	0.5847 (8)	0.064*
H33	0.638 (4)	0.140 (3)	0.5661 (5)	0.064*
C1	0.0842 (7)	0.4706 (5)	0.6899 (2)	0.0418 (19)
H1A	0.046393	0.404593	0.695782	0.050*
H1B	0.002849	0.517270	0.691316	0.050*
C2	0.2040 (6)	0.4957 (5)	0.7292 (2)	0.0321 (16)
C3	0.2424 (7)	0.5936 (5)	0.7388 (3)	0.0418 (18)
H3	0.195975	0.644503	0.720399	0.050*
C4	0.3483 (8)	0.6149 (5)	0.7752 (3)	0.0445 (19)
H4A	0.373114	0.680905	0.781768	0.053*
C5	0.4195 (7)	0.5411 (6)	0.8024 (2)	0.0420 (18)
H5A	0.492474	0.557676	0.826850	0.050*
C6	0.3841 (7)	0.4433 (5)	0.7938 (2)	0.0336 (17)
C7	0.2749 (7)	0.4212 (5)	0.7569 (2)	0.0345 (17)
H7A	0.249017	0.355192	0.750605	0.041*
C8	0.4656 (7)	0.3617 (5)	0.8211 (2)	0.0434 (19)
H8A	0.453020	0.300785	0.802428	0.052*
H8B	0.570684	0.377590	0.824368	0.052*
C9	0.5275 (7)	0.2154 (6)	0.5133 (2)	0.048 (2)
H9A	0.526552	0.160767	0.490372	0.057*
H9B	0.608955	0.259240	0.507076	0.057*
C10	0.3830 (7)	0.2718 (6)	0.5057 (2)	0.0357 (17)
C11	0.3821 (8)	0.3735 (6)	0.5059 (3)	0.057 (2)
H11A	0.471775	0.407750	0.510117	0.069*
C12	0.250000	0.4268 (8)	0.500000	0.066 (3)
H12A	0.249998	0.495945	0.500001	0.079*
C13	0.250000	0.2213 (7)	0.500000	0.037 (2)
H13A	0.250001	0.152185	0.500000	0.044*

Experimental details

A crystal of the title compound was directly selected from the mother liquor and mounted on an Xcalibur four-circle diffractometer equipped with an EOS detector [2]. An empirical absorption correction using spherical harmonics based on multi-scans was applied [2]. The structure solution, completion and the refinement, succeeded using the SHELX program system [3–5]. All investigated crystals showed a systematic non-merohedral twinning with a systematic and perfect overlap of some groups of reflections. We finally

selected a crystal with an approximate twin ratio of 1:1. The twin operation is a twofold axis around 0.000, 0.707, 0.707 in the reciprocal lattice (0.060, 0.970 0.234 for the direct lattice). The resulting twin matrix is: –1.000, 0.000, 0.000; 0.100, 0.612, 0.387; 0.100, 1.613, –0.613. Atomic coordinates of hydrogen atoms were added using the corresponding riding model with fixed *U*_{iso} parameters. The maximum residual electron density peaks (all > 0.66 e·Å^{–3}) are right next to the bromide anions.

Comment

There is a longstanding interest of one of us (GJR) in the structural chemistry of diaminium salts and their hydrogen bonding schemes [6–9].

We have already shown that the lengths and shapes of organic cations influence or even determine the topology of the embedded polyhalogenide anions [6 and reference therein]. The final structural motif of such a system is a compromise between the accessible molecular conformations, hydrogen bonding and other weak intermolecular forces like van der Waals interactions of adjacent alkyl chains [8, 10]. In presence of aryl moieties CH– π and π – π interaction needs to be considered [11]. The 1,3-phenylenedimethanaminium cation is a typical cationic, semi-flexible tecton, which can form hydrogen-bonded and cross-linked networks. In contrast to simple aliphatic diaminium cations the conformational adjustments are restricted to rotations about the CH₂–aryl single bond (see the left part of the Figure).

There are already some 1,3-phenylenedimethanaminium salt structures listed in *The Cambridge Structural Database*. A small share of these structures contain simple counter anions like: chloride [12], perchlorate [13], sulfate [14], nitrate [15], tetraiodide [16], which form hydrogen bonded networks with the 1,3-phenylenedimethanaminium cation. Furthermore some 1,3-phenylenedimethanaminium salts with complex counter anions are in the focus of current research [17, 18] because of their physical properties.

The asymmetric unit of the title structure contains one 1,3-phenylenedimethanaminium dication in general position and another half of a 1,3-phenylenedimethanaminium dication located on a twofold axis (see the left part of the Figure). Consequently, there are three bromide counter anions in the asymmetric unit, which are all in general positions. Thus, the *Z'* parameter [19] is 1.5, a finding which is not uncommon in chemical crystallography [20–22]. The same situation has been reported for the directly structurally related 1,3-phenylenedimethanaminium dichloride [12]. Bond lengths and angles in the cation are in the range

of expectations [12–18]. The 1,3-phenylenedimethanaminium cations in the title structure use their conformational flexibility by a rotation about the C1–C2, C6–C8 and C9–C10 single bonds, respectively (left part of the Figure). A dihedral angle of $-172.4(6)^\circ$ for the atoms N1, C2, C8, N2 in this structure leads to the wellknown [16] double hook shape of the 1,3-phenylenedimethanaminium dication. The 1,3-phenylenedimethanaminium cation located on the twofold axis shows a significantly different conformation ($N3-C9-C9'-N3' = -136.9(8)^\circ$; $' = -x + 1/2, y, -z + 1$).

Cations and anions are connected via $NH\cdots Br$ hydrogen bonds (see the Figure). Each $-NH_3$ group donates at least three hydrogen bonds and each bromide anion accepts at least three of them. All $Br\cdots H$ distances are significantly below the typical van der Waals distances [23]. These hydrogen bonds construct a 2D-network in the *ab* plane. In this network three different ring types (right part of the Figure) can be assigned {graph set descriptors [24]: A: $R_4^4(16)$; B and B': $R_4^2(8)$, C: $R_3^2(6)$ }.

The title structure shows the ability of semiflexible organic cations to support the formation of an ordered crystalline material by its conformational adjustments to form a maximum of hydrogen bonds.

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