The pseudosymmetric crystal structure of bis((dimethylphosphoryl)-methanaminium oxonium tribromide, $C_6H_{25}Br_3N_2O_3P_2$

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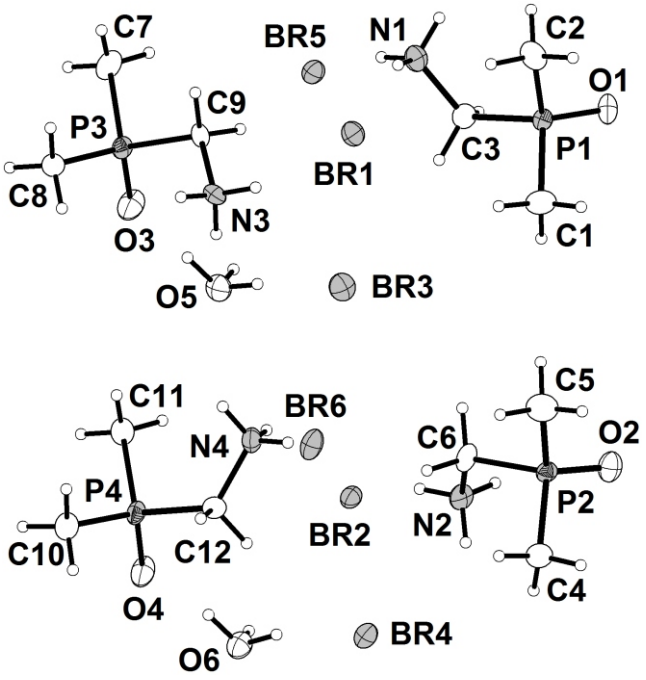

Abstract

$C_6H_{25}Br_3N_2O_3P_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.4183(3) Å, b = 11.5741(3) Å, c = 14.0587(4) Å, α = 87.417(2)°, β = 89.011(3)°, γ = 89.044(2)°, V = 1693.04(9) Å^3, Z = 4, $R_{gt}(F)$ = 0.0418, $wR_{ref}(F^2)$ = 0.0752, T = 109 K.

Table 1. Data collection and handling.

Crystal:	colourless irregular, size 0.12 0.25 0.76 mm
Wavelength:	Mo K radiation (0.71073 Å)
μ:	73.34 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	50.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18316, 6112
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5003
$N(param)_{refined}$:	320
Programs:	Crysalis PRO [12], SHELX [13], DIAMOND [14]

Source of material

(Dimethylphosphoryl)methanamine (*dpma*) is easily available by a literature known synthesis [1, 2]. In a typical reaction 0.3 g *dpma* was dissolved in 2 ml concentrated hydrobromic acid. Evaporation at room temperature yielded colourless crystals of (*dpma*H)$_2$(H$_3$O)Br$_3$.

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Experimental details

All hydrogen atoms were identified in difference Fourier synthesis. The methyl groups and the NH_3 groups were idealized and refined using rigid groups allowed to rotate about the P–C bond (AFIX 137 option of the SHELXL-2013 program [13]). The coordinates of the H-atoms at the oxonium ions were refined with the O–H distance restrained to 0.9 Å. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5U_{eq}(C) and the U_{iso} values of all other hydrogen atons were set to 1.2U_{eq}(C, N). To get usable intensities for the mass of weak superstructure reflections the exposure time had to be extended, accepting the overexposure of some very strong reflections.

Discussion

It has been shown, that the *dpma*H$^+$ cation is an excellent tecton for the construction of hydrogen bonded, one-dimensional structures [3-6]. Pseudosymmetry is a ubiquitous problem during the course of many crystal structure determinations [7]. A typical problem is the appearance of additional and weak superstructure reflections which necessiate a larger super lattice for a correct description of the true structure [8]. In more difficult cases the difference between the true symmetry and the pseudosymmetry is expressed by slightly modified intensities of reflections. In such cases additional methods should be applied (spectroscopy, optical methods, thermal analysis, *etc.*) [9]. It is obvious that some classes of compound are predestined for this effect. This contribution is part of our ongoing interest in the hydrogen bonding of phosphinic acids and its derivatives [10] and on the phenomenon of pseudosymmetry. The asymmetric unit of the title structure consists of four *dpma*H$^+$ cations, two H$_3$O$^+$ (oxonium) cations and six bromide anions. The pseudosymmetry in the title structure is caused by the fact that the bromide anions, the oxonium cations and the Me$_2$PO–CH$_2$-fragment of the *dpma*H$^+$ cations alternatively can be described, using a halved unit cell (c' = 0.5c; $P\bar{1}$). Accordingly, the average intensity of reflections with l = 2n+1 are much weaker than those with l = 2n. To analyze the differences within the roughly identical parts of the structure a comparative refinement of a structural model using the halved unit cell has been undertaken. This refinement yielded R-values similar to those of the true structure, which is not surprising, as the model refers to the stronger reflections. Extremely elongated ellipsoids of the bromide anions and the disorder of the aminium groups reflect the structural pseudosymmetry. In the true (super) structure all four crystallographic independent *dpma*H$^+$ cations show individual O–P–C–N torsion angles (O1–P1–C3–N1 = –116.9(4)°; O2–P2–C6–N2 = 47.3(4)°; O3–P3–C9–N3 = –68.6(4)°; O4–P4–C12–N4 = 123.7(3)°) to fill the needs of hydrogen bonding. For a related structure it has already been shown that the *gauche*-conformation of the *dpma*H$^+$ cation is the reason

for a pseudosymmetric arrangement [11]. Simple *dpma*H^+ salt structures may be a class of compounds which frequently feature pseudosymmetry problems. All ions are connected *via* charge supported O–H···O, O–H···Br and N–H···Br hydrogen bonds. According to the O···O distances of 2.447(5) to 2.469 Å these hydrogen bonds are all to be classified as strong. O···Br distances of 3.096(4) and 3.174(4) Å indicate medium strong hydrogen bonds, whereas the N–H···Br hydrogen bonds are significant weaker accordingly to N···Br distances of 3.215(4) to 3.408(4) Å.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(11)	2*i*	0.6337	0.0909	0.0013	0.016
H(12)	2*i*	0.6353	0.2021	0.0426	0.016
H(13)	2*i*	0.5244	0.1282	0.0559	0.016
H(1A)	2*i*	0.9951	0.1272	0.2230	0.029
H(1B)	2*i*	0.8694	0.1012	0.2825	0.029
H(1C)	2*i*	0.8774	0.2131	0.2157	0.029
H(2A)	2*i*	0.8609	0.0917	0.0326	0.022
H(2B)	2*i*	0.9886	0.1236	0.0167	0.022
H(2C)	2*i*	0.8693	0.2077	0.0203	0.022
H(3A)	2*i*	0.6305	0.0018	0.1470	0.018
H(3B)	2*i*	0.6462	0.1198	0.1896	0.018
H(21)	2*i*	0.5836	0.0509	0.6771	0.016
H(22)	2*i*	0.4895	0.0433	0.6752	0.016
H(23)	2*i*	0.5962	0.0440	0.7404	0.016
H(4A)	2*i*	0.8301	0.1199	0.7727	0.024
H(4B)	2*i*	0.8533	0.2266	0.7022	0.024
H(4C)	2*i*	0.9644	0.1363	0.7224	0.024
H(5A)	2*i*	0.9736	0.1241	0.5099	0.031
H(5B)	2*i*	0.8565	0.2110	0.5086	0.031
H(5C)	2*i*	0.8472	0.0931	0.4585	0.031
H(6A)	2*i*	0.6314	0.1702	0.6136	0.017
H(6B)	2*i*	0.6233	0.0655	0.5474	0.017
H(31)	2*i*	0.4123	0.4526	0.2504	0.016
H(32)	2*i*	0.4223	0.5479	0.1798	0.016
H(33)	2*i*	0.5125	0.4509	0.1772	0.016
H(7A)	2*i*	0.0048	0.3864	0.0663	0.026
H(7B)	2*i*	0.1182	0.2973	0.0536	0.026
H(7C)	2*i*	0.1216	0.4183	0.0011	0.026
H(8A)	2*i*	0.1989	0.6203	0.2018	0.020
H(8B)	2*i*	0.0619	0.6059	0.1599	0.020
H(8C)	2*i*	0.1811	0.6214	0.0912	0.020
H(9A)	2*i*	0.3628	0.3290	0.1322	0.012
H(9B)	2*i*	0.3616	0.4373	0.0612	0.012
H(41)	2*i*	0.3575	0.2901	0.5588	0.015
H(42)	2*i*	0.4740	0.3576	0.5534	0.015
H(43)	2*i*	0.3593	0.4003	0.5050	0.015
H(10A)	2*i*	0.0596	0.6108	0.6584	0.023
H(10B)	2*i*	0.1826	0.6235	0.5932	0.023
H(10C)	2*i*	0.1938	0.6276	0.7041	0.023
H(11A)	2*i*	0.1110	0.2986	0.5659	0.022
H(11B)	2*i*	0.1167	0.4172	0.5076	0.022
H(11C)	2*i*	0.0002	0.3906	0.5768	0.022
H(12A)	2*i*	0.3863	0.4966	0.6404	0.015
H(12B)	2*i*	0.3812	0.3777	0.6976	0.015
H(51)	2*i*	0.198(5)	0.306(3)	0.330(2)	0.017
H(52)	2*i*	0.309(1)	0.248(4)	0.367(4)	0.017
H(53)	2*i*	0.194(5)	0.186(2)	0.369(4)	0.017
H(61)	2*i*	0.190(5)	0.185(2)	0.874(4)	0.018
H(62)	2*i*	0.205(5)	0.300(3)	0.827(2)	0.018
H(63)	2*i*	0.314(2)	0.244(4)	0.857(4)	0.018

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	2*i*	0.70110(5)	0.39247(4)	0.09657(3)	0.0106(3)	0.0159(3)	0.0129(2)	0.0012(2)	0.0019(2)	0.0008(2)
Br(2)	2*i*	0.68924(5)	0.42635(4)	0.59702(3)	0.0092(3)	0.0141(2)	0.0098(2)	0.0008(2)	0.0001(2)	0.0012(2)
Br(3)	2*i*	0.52004(5)	0.24934(4)	0.35261(3)	0.0130(3)	0.0152(2)	0.0175(3)	0.0015(2)	0.0002(2)	0.0013(2)
Br(4)	2*i*	0.53276(5)	0.24237(4)	0.83808(3)	0.0121(3)	0.0132(2)	0.0139(2)	0.0001(2)	0.0029(2)	0.0005(2)
Br(5)	2*i*	0.30930(5)	0.08046(4)	0.10401(3)	0.0106(3)	0.0138(2)	0.0125(2)	0.0002(2)	0.0019(2)	0.0007(2)
Br(6)	2*i*	0.28695(5)	0.10333(4)	0.61994(3)	0.0111(3)	0.0136(2)	0.0212(3)	0.0006(2)	0.0044(2)	0.0017(2)
P(1)	2*i*	0.8429(1)	0.0562(1)	0.12808(8)	0.0089(7)	0.0114(6)	0.0105(6)	0.0010(5)	0.0011(5)	0.0006(5)
O(1)	2*i*	0.8821(3)	0.0690(3)	0.1336(2)	0.011(2)	0.012(2)	0.019(2)	0.003(1)	0.001(2)	0.002(1)
N(1)	2*i*	0.6096(4)	0.1292(3)	0.0496(3)	0.008(2)	0.018(2)	0.014(2)	0.001(2)	0.003(2)	0.001(2)
C(1)	2*i*	0.9031(6)	0.1332(4)	0.2232(3)	0.025(3)	0.020(3)	0.015(3)	0.001(2)	0.005(2)	0.004(2)
C(2)	2*i*	0.8965(5)	0.1281(4)	0.0208(3)	0.015(3)	0.012(2)	0.018(3)	0.002(2)	0.004(2)	0.002(2)
C(3)	2*i*	0.6680(5)	0.0738(4)	0.1354(3)	0.013(3)	0.019(3)	0.012(2)	0.003(2)	0.002(2)	0.002(2)
P(2)	2*i*	0.8221(1)	0.0644(1)	0.61876(8)	0.0079(7)	0.0117(6)	0.0093(6)	0.0006(5)	0.0012(5)	0.0008(5)
O(2)	2*i*	0.8568(3)	0.0608(3)	0.6320(2)	0.011(2)	0.014(2)	0.021(2)	0.001(2)	0.002(2)	0.000(1)
N(2)	2*i*	0.5721(4)	0.0249(3)	0.6828(3)	0.005(2)	0.021(2)	0.014(2)	0.001(2)	0.001(2)	0.000(2)
C(4)	2*i*	0.8734(5)	0.1463(4)	0.7152(3)	0.018(3)	0.016(3)	0.015(2)	0.001(2)	0.003(2)	0.003(2)
C(5)	2*i*	0.8817(6)	0.1307(4)	0.5117(3)	0.026(3)	0.019(3)	0.016(3)	0.000(2)	0.000(2)	0.001(2)
C(6)	2*i*	0.6498(5)	0.0881(4)	0.6096(3)	0.011(3)	0.017(3)	0.014(2)	0.003(2)	0.001(2)	0.007(2)
P(3)	2*i*	0.1758(1)	0.4360(1)	0.15377(8)	0.0058(7)	0.0122(6)	0.0111(6)	0.0007(5)	0.0003(5)	0.0003(5)
O(3)	2*i*	0.1367(3)	0.3796(3)	0.2475(2)	0.013(2)	0.023(2)	0.016(2)	0.000(2)	0.002(2)	0.007(2)
N(3)	2*i*	0.4316(4)	0.4717(3)	0.1898(3)	0.013(2)	0.017(2)	0.010(2)	0.004(2)	0.001(2)	0.004(2)
C(7)	2*i*	0.0960(5)	0.3779(4)	0.0571(4)	0.013(3)	0.019(3)	0.021(3)	0.000(2)	0.008(2)	0.002(2)
C(8)	2*i*	0.1517(5)	0.5884(4)	0.1514(3)	0.013(3)	0.015(2)	0.011(2)	0.002(2)	0.000(2)	0.000(2)
C(9)	2*i*	0.3443(5)	0.4114(4)	0.1267(3)	0.005(3)	0.012(2)	0.013(2)	0.001(2)	0.002(2)	0.002(2)
P(4)	2*i*	0.1741(1)	0.4407(1)	0.66128(8)	0.0071(7)	0.0121(6)	0.0114(6)	0.0015(5)	0.0003(5)	0.0016(5)
O(4)	2*i*	0.1341(3)	0.3885(3)	0.7563(2)	0.013(2)	0.022(2)	0.016(2)	0.004(2)	0.004(2)	0.008(2)
N(4)	2*i*	0.3886(4)	0.3613(3)	0.5564(3)	0.011(2)	0.015(2)	0.012(2)	0.004(2)	0.001(2)	0.001(2)
C(10)	2*i*	0.1497(5)	0.5932(4)	0.6533(3)	0.016(3)	0.014(2)	0.015(2)	0.002(2)	0.000(2)	0.002(2)
C(11)	2*i*	0.0910(5)	0.3798(4)	0.5671(3)	0.007(3)	0.019(3)	0.018(3)	0.000(2)	0.001(2)	0.005(2)
C(12)	2*i*	0.3473(5)	0.4210(4)	0.6426(3)	0.011(3)	0.016(2)	0.010(2)	0.000(2)	0.001(2)	0.000(2)
O(5)	2*i*	0.2243(4)	0.2577(3)	0.3782(2)	0.018(2)	0.009(2)	0.016(2)	0.000(2)	0.000(2)	0.000(1)
O(6)	2*i*	0.2316(4)	0.2525(3)	0.8757(2)	0.013(2)	0.017(2)	0.015(2)	0.000(2)	0.001(2)	0.002(2)

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