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# Structure of Hexamethylenediammonium Phthalate Trihydrate, $C_6H_{18}N_2^{2+}.C_8H_4O_4^{2-}.3H_2O$

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**Abstract.** $M_r = 336$, triclinic, $P\bar{1}$, $a = 8{\cdot}171\ (2)$, $b = 9{\cdot}168\ (1)$, $c = 12{\cdot}217\ (2)$ Å, $\alpha = 83{\cdot}04\ (1)$, $\beta = 77{\cdot}96\ (1)$, $\gamma = 89{\cdot}97\ (1)°$, $V = 888{\cdot}2\ (3)$ Å$^3$, $Z = 2$, $D_m = 1{\cdot}26\ (2)$, $D_x = 1{\cdot}26$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}06$ mm$^{-1}$, $T = 298$ K, $F(000) = 364$, $R = 0{\cdot}053$ for 3083 reflections with $I > 2\sigma(I)$. The hexamethylenediammonium ions lie on centres of symmetry and adopt a planar zigzag configuration. The two carboxyl groups of the phthalate ion are twisted by 48·8 (3)° in the same sense from the plane of the six-membered ring. The packing arrangement involves spatial segregation of polar and non-polar regions of the molecules into alternating layers perpendicular to the *c* axis.

**Introduction.** Hexamethylenediammonium phthalate (HMDAP) is an organic salt and is one of the intermediates in the manufacture of Nylon (Hirokawa, Chashi & Nitta, 1954). The determination of the crystal structure of HMDAP was undertaken as part of our interest in the structures of hexamethylenediammonium derivatives.

**Experimental.** Needle-shaped crystals at 298 K from an aqueous solution. Crystal 0·15 × 0·15 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation. 25 reflections for lattice parameters. 4004 independent reflections, 3083 with $I > 2\sigma(I)$, $\sin\theta/\lambda \leq 0{\cdot}65$ Å$^{-1}$, $h$ 0 to 10, $k$ −11 to 11, $l$ −14 to 14. Lorentz–polarization correction, no correction for absorption. 3 standard reflections, variation <2%. Space group assumed to be $P\bar{1}$ and confirmed by structure determination using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). *E* map revealed positions of all non-hydrogen atoms plus three water molecules. H atoms from three-dimensional difference Fourier maps. Full-matrix least-squares refinement. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(I)$. Anisotropic temperature factors for non-hydrogen atoms, isotropic for H atoms. Final $R = 0{\cdot}053$, $R_w = 0{\cdot}075$. In the final least-squares cycle $(\Delta/\sigma)_{\max} = 0{\cdot}2$. Excursions in final $\Delta\rho$ map $< |0{\cdot}15|$ e Å$^{-3}$. No correction for secondary extinction. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1962), for H from Stewart, Davidson & Simpson (1965).

**Discussion.** The final positional parameters are listed in Table 1,† while Table 2 lists the bond distances and bond angles for the non-hydrogen atoms.

Table 1. *Final positional parameters* (×10$^4$) *and* $B_{eq}$ *values of the non-hydrogen atoms* (*W refers to the oxygen of the water molecules*)

Estimated standard deviations are in parentheses. $B_{\text{eq}} = \frac{4}{3}\sum_i\sum_j b_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{\text{eq}}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 1303 (2) | 3682 (1) | 2506 (1) | 2·25 |
| C(2) | 1965 (2) | 2285 (1) | 2645 (1) | 2·38 |
| C(3) | 1556 (2) | 1430 (2) | 3693 (1) | 2·99 |
| C(4) | 523 (2) | 1958 (2) | 4599 (1) | 3·45 |
| C(5) | −136 (2) | 3337 (2) | 4456 (1) | 3·31 |
| C(6) | 253 (2) | 4197 (2) | 3423 (1) | 2·90 |
| C(7) | 1693 (2) | 4652 (1) | 1388 (1) | 2·47 |
| C(8) | 3213 (2) | 1670 (2) | 1733 (1) | 2·95 |
| O(1) | 1660 (2) | 4072 (1) | 518 (1) | 2·37 |
| O(2) | 2062 (2) | 5969 (1) | 1399 (1) | 4·03 |
| O(3) | 4442 (1) | 2444 (1) | 1212 (1) | 3·73 |
| O(4) | 2949 (2) | 382 (1) | 1576 (2) | 5·45 |
| N(1)*A* | 4219 (2) | 4790 (2) | 8688 (1) | 2·99 |
| C(1)*A* | 3566 (2) | 4805 (2) | 7640 (1) | 3·25 |
| C(2)*A* | 4967 (2) | 4879 (2) | 6608 (1) | 3·44 |
| C(3)*A* | 4312 (2) | 4973 (2) | 5521 (1) | 3·50 |
| N(1)*B* | 8097 (2) | −196 (2) | 1602 (1) | 3·96 |
| C(1)*B* | 7364 (2) | 611 (2) | 2566 (2) | 3·79 |
| C(2)*B* | 6294 (2) | −380 (2) | 3527 (2) | 3·83 |
| C(3)*B* | 5571 (2) | 466 (2) | 4511 (2) | 3·75 |
| *W*(1) | 4633 (2) | 1598 (1) | 9001 (1) | 3·99 |
| *W*(2) | 9528 (2) | 2102 (2) | 10036 (1) | 5·59 |
| *W*(3) | 9383 (2) | 1754 (2) | 7414 (1) | 4·51 |

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* Contribution No. 649.

† Lists of structure factors, anisotropic thermal parameters, some torsion angles, and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39434 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Bond lengths* (Å) *and bond angles* (°) *involving the non-hydrogen atoms*

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·396 (2) | C(2)–C(1)–C(6) | 119·1 (1) |
| C(1)–O(6) | 1·393 (2) | C(2)–C(1)–C(7) | 121·8 (1) |
| C(1)–C(7) | 1·511 (2) | C(6)–C(1)–C(7) | 119·1 (1) |
| C(2)–C(3) | 1·394 (2) | C(1)–C(2)–C(3) | 119·5 (1) |
| C(2)–C(8) | 1·509 (2) | C(1)–C(2)–C(8) | 123·2 (1) |
| C(3)–C(4) | 1·383 (2) | C(3)–C(2)–C(8) | 117·1 (1) |
| C(4)–C(5) | 1·379 (3) | C(2)–C(3)–C(4) | 120·8 (1) |
| C(5)–C(6) | 1·382 (2) | C(3)–C(4)–C(5) | 119·5 (1) |
| C(7)–O(1) | 1·249 (2) | C(4)–C(5)–C(6) | 120·4 (1) |
| C(7)–O(2) | 1·247 (2) | C(1)–C(6)–C(5) | 120·6 (1) |
| C(8)–O(3) | 1·242 (2) | C(1)–C(7)–O(1) | 117·8 (1) |
| C(8)–O(4) | 1·245 (2) | C(1)–C(7)–O(2) | 117·4 (1) |
| N(1)*A*–C(1)*A* | 1·484 (2) | O(1)–C(7)–O(2) | 124·8 (1) |
| C(1)*A*–C(2)*A* | 1·511 (2) | C(2)–C(8)–O(3) | 119·2 (1) |
| C(2)*A*–C(3)*A* | 1·525 (2) | C(2)–C(8)–O(4) | 116·6 (1) |
| C(3)*A*–C(3)*A*′ | 1·508 (1) | O(3)–C(8)–O(4) | 124·2 (1) |
| N(1)*B*–C(1)*B* | 1·486 (2) | N(1)*A*–C(1)*A*–C(2)*A* | 111·6 (1) |
| C(1)*B*–C(2)*B* | 1·511 (2) | C(1)*A*–C(2)*A*–C(3)*A* | 112·1 (1) |
| C(2)*B*–C(3)*B* | 1·523 (3) | C(2)*A*–C(3)*A*–C(3)*A*′ | 113·1 (1) |
| C(3)*B*–C(3)*B*′ | 1·522 (1) | N(1)*B*–C(1)*B*–C(2)*B* | 112·2 (2) |
| | | C(1)*B*–C(2)*B*–C(3)*B* | 111·3 (2) |
| | | C(2)*B*–C(3)*B*–C(3)*B*′ | 113·7 (1) |

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

| Donor | Proton | Acceptor | Angle at proton (°) | Distance (Å) |
|---|---|---|---|---|
| N(1)*A* | H(1) | O(3) | 175 (1) | 2·789 (2) |
| N(1)*A* | H(2) | O(1) | 176 (2) | 2·739 (2) |
| N(1)*A* | H(3)* | O(2) | 137 (2) | 3·100 (2) |
| N(1)*A* | H(3)* | *W*(1) | 133 (2) | 2·934 (2) |
| N(1)*B* | H(1) | *W*(1) | 168 (2) | 2·844 (2) |
| N(1)*B* | H(2) | *W*(3) | 166 (2) | 2·888 (2) |
| N(1)*B* | H(3) | *W*(2) | 166 (2) | 2·749 (3) |
| *W*(1) | H(1) | O(4) | 175 (2) | 2·724 (2) |
| *W*(1) | H(2) | O(3) | 167 (2) | 2·873 (2) |
| *W*(2) | H(1) | O(2) | 165 (3) | 2·843 (2) |
| *W*(2) | H(2) | O(1) | 173 (3) | 2·718 (2) |
| *W*(3) | H(1) | O(4) | 175 (2) | 2·725 (2) |
| *W*(3) | H(2) | O(2) | 171 (3) | 2·810 (2) |

* Bifurcated.

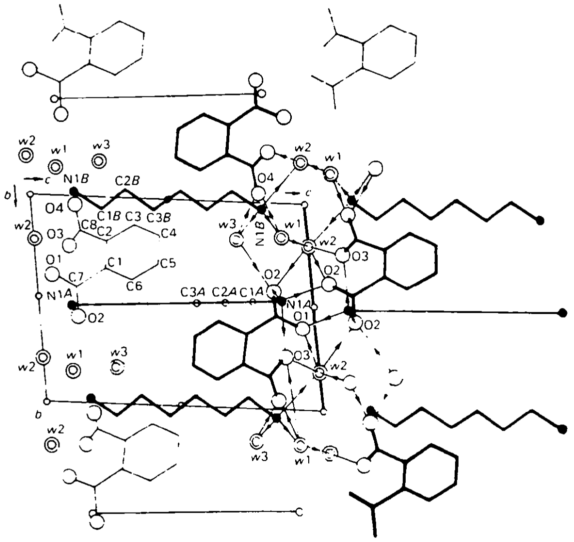

Fig. 1. Projection of the unit-cell contents down the *a** axis. In this view, one of the hexamethylenediammonium ions projects as a line.

In the crystal structure, the cation lies on a centre of symmetry. Consequently, the asymmetric unit of the crystal contains two crystallographically independent 'half' cations, denoted *A* and *B*. Both cations have essentially the same bond geometry with the exception that the bond containing the centre of symmetry is significantly shorter in *A* [1·508 (2) Å] than in *B* [1·522 (2) Å]. Both cations adopt essentially a *trans* zigzag configuration and show only slight deviations from planarity. The bond geometry compares favourably with that found in the crystal structure of hexamethylenediammonium adipate (Brown, 1966). However, a significant widening of the angle at C(3)*A* and C(3)*B* has occurred in the present structure, with values of 113·1 (1) and 113·7 (1)° as against 112·1 (2)° in the structure determined by Brown (1966). The protons on the terminal N atoms N(1)*A* and N(1)*B* are staggered with respect to the adjacent N–C bond.

The six-membered ring of the anion is quite planar but the exocyclic atom C(8) shows significant deviation [0·106 (2) Å] from the mean plane of the ring. The mean planes of the two carboxyl groups are rotated by nearly the same amount [48·9 (2), 48·7 (2)°] and in the same sense with respect to the plane of the six-membered ring. All the C–O bond lengths are equal within the accuracy of the determination.

Fig. 1 shows a view of the structure projected down the **a*** direction. In this projection cation *A* projects as a line. The structure is stabilized by a network of hydrogen bonds in which all available protons are used. The proposed scheme of hydrogen bonds is listed in Table 3. Atom N(1)*A* appears to use one of its protons in a bifurcated hydrogen bond. The 'polar' and 'non-polar' regions of the molecules are spatially segregated to form alternating layers perpendicular to the *c* axis. The non-polar layer is made up of the ring part of the anion and of the hexamethylene part of the cation, while the 'polar' layer consists largely of the ammonium and carboxyl groups and the water molecules.

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