

fonction de l'éloignement du cycle époxyde], des liaisons C—O du cycle époxyde et des liaisons S—C et S—O du groupement sulfinyle sont comparables dans les deux séries, méthyle et phényle.

Nous avons effectué le calcul du plan moyen C(1), C(2), C(3), C(6). Il montre que pour les composés (1) et (2) respectivement: (a) les atomes qui constituent le plan s'en éloignent au maximum de 0,014 et 0,008 Å; (b) le C(4) s'en écarte de 0,22 et 0,23 Å (au dessous) et le C(5) de 0,50 et 0,45 Å (au dessus), les atomes C(5) et O(2) étant situés de part et d'autre de ce plan. Ces résultats indiquent que le cyclohexyle a une conformation proche d'une demi-chaise.

Les résultats de ce travail précisent la conformation *anti* de l'isomère le moins polaire et la conformation *syn* du plus polaire et indiquent pour chacun d'eux, qu'elles sont identiques à l'état cristallisé et en solution. L'étude comparative de la stéréochimie d'époxydes diastéréoisomères dans la série bicyclo-

[4.1.0]heptane substitués par des groupements CH₃S(O) ou C₆H₅S(O) montre que pour ces deux classes d'époxydes: (a) les composés les moins polaires ont les mêmes configurations relatives et conformations et (b) les composés les polaires ont des configurations relatives identiques mais des conformations différentes.

Références

- BARILLIER, D. & VAZEUX, M. (1986). *J. Org. Chem.* **51**, 2276–2285.
 LECLAIRE, A., BARILLIER, D. & VAZEUX, M. (1987). *Acta Cryst.* **C43**, 947–949.
 LECLAIRE, A., BARILLIER, D. & VAZEUX, M. (1991). *Acta Cryst.* **C47**, 146–148.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.

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Structure of *N,N,N',N'*-Tetramethylethylenediammonium Dibromide

BY THEODORE A. ANNAN, RAJ K. CHADHA* AND DENNIS G. TUCK†

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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Abstract. C₆H₁₈N₂²⁺2Br⁻, *M_r* = 278.05, monoclinic, *P*2₁/*c*, *a* = 5.479 (2), *b* = 10.827 (5), *c* = 9.137 (4) Å, β = 95.5 (4)°, *V* = 539.5 (5) Å³, *Z* = 2, *D_m* = 1.69, *D_x* = 1.71 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 38.85 cm⁻¹, *F*(000) = 276, *T* = 298 K, *R* = 0.0265 for 753 observed reflections [*I* > 3σ(*I*)]. The HMe₂NC₂H₄NMe₂H²⁺ cation is in the *anti* conformation, due in part to strong hydrogen-bonding between the counter ion (Br⁻) and the N—H bond [*r*(H⋯Br) = 2.15 Å].

Introduction. The title compound was formed as a by-product in the crystallization of the compound Ph₃SnInBr₂.tmen in a mixture of CHCl₃/CH₃OH (50:50, *v/v*) during studies of the oxidative insertion of indium monohalides into some organotin compounds (Annan & Tuck, 1987).

Experimental. A colourless crystal, 0.13 × 0.21 × 0.34 mm, was mounted along its longest dimension

on a glass fibre with epoxy resin. Cell-parameter determination (15 reflections, 20 ≤ θ ≤ 30°, *P*2₁/*c*) and data acquisition were performed using a Syntex *P*2₁ diffractometer with Mo *K*α radiation. Intensities of three monitored reflections measured after every 60 reflections did not show any significant decay. An empirical absorption correction was applied to the data, with correction factors ranging from 1.749 to 3.168. Data reduction, including Lorentz and polarization corrections, was performed. Indices -6 ≤ *h* ≤ 6, 0 ≤ *k* ≤ 12, 0 ≤ *l* ≤ 10. Number of reflections measured 1183. 2θ_{max} = 40°.

The position of the Br atom was determined from a sharpened Patterson synthesis. A difference map based on the Br atom gave the position of all remaining non-H atoms. The structure was refined anisotropically by full-matrix least-squares methods using the program *SHELX* (Sheldrick, 1976), and the refinement covered at *R* = 0.0285. H atoms were then included in idealized positions with *r*(C—H) and *r*(N—H) = 0.95 Å, and after six more cycles of refinement, convergence was achieved at *R* = 0.0265 and *wR* = 0.0289, *w* = 1/[σ²(*F*) + 0.00017*F*²]. Max. Δ/σ = 0.03, max. height in final Δ*F* map =

* Present address: Department of Chemistry, University of California at San Diego, La Jolla, CA 92092, USA.

† To whom correspondence should be addressed.

0.62 e Å⁻³ with coordinates of -0.123, 0.577, 0.446. Scattering factors were obtained from Cromer & Mann (1968). Computation was carried out on the University of Manitoba Computer Services Department's Amdahl 580/5850 computer.

Discussion. The structure of the title compound is shown in Fig. 1. Final fractional coordinates and thermal parameters are given in Table 1, and interatomic distances and angles are presented in Table 2.*

The cation, formed by the protonation of each N atom of *N,N,N',N'*-tetramethylethylenediamine, has a centre of inversion. The geometry around each N atom is essentially tetrahedral, with an average C—N—C bond angle of 111.7 (4)°. The C—C and (average) C—N bond distances of 1.57 (1) and 1.467 (7) Å, respectively, compare favourably with those in the singly protonated tmen cation found in the compound [tmenH]₂[Sn(O₂C₆Cl₄)₃] (Annan, Chadha, Tuck & Watson, 1987), where the corresponding values are 1.503 (6) and 1.470 (6) Å. In this latter structure, the [tmenH]⁺ cation is in a folded form, suggesting an intramolecular attraction between the charged and the neutral N atoms, presumably involving an N—H...N interaction. In the case of the title compound, the opposite effect is

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53163 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

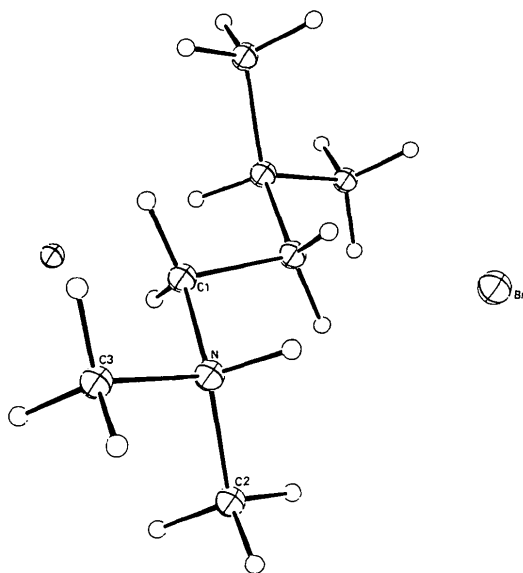


Fig. 1. ORTEP (Johnson, 1965) diagram of [C₆H₁₈N₂]Br₂. Atoms are represented by thermal ellipsoids drawn at 50% probability level. The unlabelled atoms are related to the labelled ones by a centre of inversion.

Table 1. Final fractional coordinates and thermal parameters (Å²) for non-H atoms of [C₆H₁₈N₂]Br₂

| | <i>x</i> | <i>y</i> | <i>z</i> |
|------|-------------|------------|------------|
| Br | 0.3909 (1) | 0.2239 (1) | 0.4406 (1) |
| N | 0.0436 (6) | 0.4402 (3) | 0.3080 (4) |
| C(1) | -0.0913 (7) | 0.4879 (5) | 0.4300 (4) |
| C(2) | 0.2047 (8) | 0.5315 (4) | 0.2457 (5) |
| C(3) | -0.1347 (8) | 0.3887 (4) | 0.1902 (4) |

| | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₁₂ | <i>U</i> ₁₃ | <i>U</i> ₂₃ |
|------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Br | 0.0390 (3) | 0.0304 (3) | 0.0451 (3) | 0.0091 (3) | 0.0074 (3) | 0.0060 (3) |
| N | 0.031 (2) | 0.021 (2) | 0.032 (2) | 0.001 (2) | 0.006 (2) | 0.002 (2) |
| C(1) | 0.031 (2) | 0.036 (2) | 0.031 (2) | 0.001 (3) | 0.007 (3) | -0.004 (3) |
| C(2) | 0.036 (2) | 0.037 (2) | 0.044 (2) | -0.007 (3) | 0.009 (3) | 0.005 (3) |
| C(3) | 0.038 (2) | 0.034 (2) | 0.037 (2) | 0.000 (3) | 0.006 (3) | -0.002 (3) |

Table 2. Interatomic distances (Å) and angles (°) for [C₆H₁₈N₂]Br₂

| | | | |
|------------|-----------|--------------|-----------|
| N—C(1) | 1.442 (7) | C(1)—N—C(2) | 116.8 (5) |
| N—C(2) | 1.479 (7) | C(1)—N—C(3) | 108.9 (4) |
| N—C(3) | 1.479 (7) | C(2)—N—C(3) | 109.5 (5) |
| C(1)—C(1') | 1.57 (1) | N—C(1)—C(1') | 109.9 (5) |
| H...Br | 2.15 | | |

Symmetry-equivalent position: (i) -*x*, 1-*y*, 1-*z*.

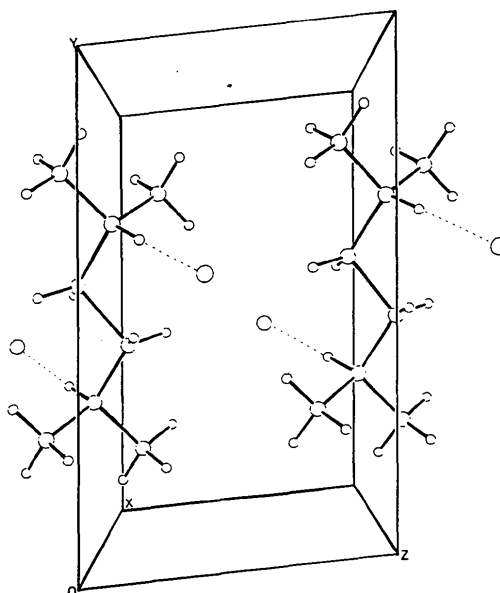


Fig. 2. Unit-cell packing diagram, showing N—H...Br interactions.

observed; the *anti* configuration places the positive nitrogen centres at their maximum distance from each other, and a further stabilization occurs through hydrogen bonding between the bromide anions and the H atoms on the nitrogen (H...Br = 2.15 Å) (Fig. 2).

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References

- ANNAN, T. A., CHADHA, R. K., TUCK, D. G. & WATSON, K. D. (1987). *Can. J. Chem.* **65**, 2670–2676.
- ANNAN, T. A. & TUCK, D. G. (1987). *J. Organomet. Chem.* **325**, 83–89.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of 2'-Deoxycytidinium Dihydrogenphosphate

BY MARIUSZ JASKÓLSKI

Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60–780 Poznań, Poland

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Abstract. $C_9H_{14}N_3O_4^+ \cdot H_2PO_4^-$, $M_r = 325.2$, orthorhombic, $P2_12_12_1$, $a = 9.742(1)$, $b = 7.0773(6)$, $c = 19.327(3) \text{ \AA}$, $V = 1332.5(3) \text{ \AA}^3$, $Z = 4$, $D_x = 1.62 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 1.99 \text{ cm}^{-1}$, $F(000) = 680$, $T = 290 \text{ K}$, $R = 0.030$ for 1193 observed reflections. The crystals are isostructural with those of cytidinium dihydrogenphosphate and also contain the characteristic infinite sugar...phosphate chains in which the dihydrogenphosphate anions are hydrogen bonded (*via* their POH donors) to O(3') and O(5') of neighboring nucleosides. In the absence of the O(2') group, the O(5')H donor forms a much stronger hydrogen bond with O(2) along the chain. Parallel to the sugar...phosphate chains there are also analogous nucleobase...phosphate hydrogen-bonded chains in which the phosphate anion accepts two hydrogen bonds [N(4)H(41)...O and N(3)H...O] from one cytosinium cation and one bond [N(4)H(42)...O] from the next cation in the chain. The 2'-deoxyribose conformation is 2E [$P = 167.5(7)^\circ$, $\tau_m = 36.4(5)^\circ$], the glycosidic torsion angle χ is *anti* [$33.7(4)^\circ$] and the side chain is *gauche*⁺ [$\gamma = 48.9(4)^\circ$].

Introduction. The first information on the synthesis and physico-chemical properties of phosphate salts of nucleosides was reported by Wiewiórowski *et al.* (1986) who described the dihydrogenphosphate salt of cytidine. The conclusions drawn by these authors were generally confirmed when the crystal structure of cytidinium dihydrogenphosphate ($CydH^+ \cdot H_2PO_4^-$) became available recently (Jaskólski, 1989), revealing that the dihydrogenphosphate anion uses both its POH donors to form ---O(3')...H—OP(O₂)O—H...O(5')--- hydrogen bonds with the ribose residues of two adjacent cytidinium units leading to infinite ribose...phosphate chains in which the

hydrogen bonds mimic the ester bonds of a real polynucleotide chain. The organization of the ions in that structure suggested a possible retention of this arrangement even on replacement of ribose by 2'-deoxyribose. However, attempts to synthesize the analogous 2'-deoxycytidinium dihydrogenphosphate salt ($dCydH^+ \cdot H_2PO_4^-$) revealed a more complicated situation. In the case of cytidine, $CydH^+ \cdot H_2PO_4^-$ seems to be the only stoichiometry with which the ions crystallize even when there is a large excess of cytidine (Bratek-Wiewiórowska, Popena, Malinowska & Wiewiórowski, 1990). In contrast, 2'-deoxycytidine reacts with orthophosphoric acid to preferentially form a hemi salt, $(dCyd)_2H^+ \cdot H_2PO_4^-$, even from solutions in which the $dCyd:H_3PO_4$ molar ratio is 1:1.5. It is possible that two $dCyd$ nucleosides share a single proton and form a homoconjugated cation with three hydrogen bonds operating within its base pair, since such cationic cytosine...H⁺...cytosine or cytosine—H⁺...cytosine base pairs have been described previously (*e.g.* Marsh, Bierstedt & Eichhorn, 1962; Tamura, Sato & Hata, 1973; Kistenmacher, Rossi, Caradonna & Marzilli, 1979; Kistenmacher, Rossi, Chiang, Caradonna & Marzilli, 1980; Westhof, Rao & Sundaralingam, 1980; Gdaniec, Brycki & Szafran, 1988) and are believed to represent a strong association similar to that present in Watson-Crick C—G base pairs. Furthermore, the crystal of neutral 2'-deoxycytidine (Young & Wilson, 1975) has two molecules in the asymmetric unit which form a C—C base pair through a doublet of N(4)H...N(3) hydrogen bonds. In contrast, neutral cytidine crystallizes without formation of base pairs (Furberg, Petersen & Rømming, 1965). The 1:1 salt, $dCydH^+ \cdot H_2PO_4^-$, crystallizes only when orthophosphoric acid is in at least 1.8-fold excess (Bratek-Wiewiórowska, Popena, Malinowska &