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### Preparation of pseudo-arsonolipids: 2-acyloxypropane-1,3-bis(arsonic acids). The crystal structure of 2-hydroxypropane-1,3-bis(arsonic acid)

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#### Abstract

Epihalohydrins react with alkaline arsenite to give in very good yields 2-hydroxypropane-1,3-bis(arsonic acid) (7), a key compound for the synthesis of pseudo-arsonolipids and more complex arsinolipids. Through a series of reduction to  $-As(SPh)_2$ , acylation, and oxidation to  $-AsO_3H_2$ , pseudo-arsonolipids, i.e. 2-acyloxypropane-1,3-bis(arsonic acids), were obtained. These pseudo-lipids are very sensitive to bases, being de-acylated. The bis(arsonic acid) (7) crystallizes in the orthorombic space group  $P2_12_12_1$  with unit cell constants a = 6.911(3), b = 17.496(8), c = 7.002(3) Å. Both arsenic atoms are essentially tetrahedral being bound to three oxygens and one carbon. All hydrogen atoms have been located. There is no intramolecular but only intermolecular hydrogen bonding involving all the As=O, As-OH, and C-OH groups. The C-OH group acts as a hydrogen donor to an acidic As-OH, and this As-OH, in turn, acts as a hydrogen donor to an As=O group. © 2002 Elsevier Science Ireland Ltd. All rights reserved.

Keywords: Epihalohydrins; The Meyer reaction; Bis(arsonic acids); X-ray diffraction

### 1. Introduction

Phospholipids, 1, are membrane building blocks (Eibl, 1984). A few lipids can also have other biochemical functions, e.g. the simplest phospholipid, phosphatidic acid (1, R' = H), acts as a second messenger (Ghosh et al., 1996), and the platelet-activating factor (Demopoulos et al., 1979) is an extremely potent chemical mediator.

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We asked whether by replacing the phosphorus atom in 1 with arsenic we will get arsenic-containing lipids with interesting properties. But such a replacement cannot be achieved because esters having an C–O–As functionality, e.g. 2, X = O, are hydrolytically very unstable (Long and Ray, 1973). However, compounds having an C–As bond are hydrolytically stable and we prepared the arsonolipids 2,  $X = CH_2$  (Serves et al., 1995), 3 (Tsivgoulis et al., 1991; Serves et al., 1993) and the arsinolipids 4 (Kordalis and Ioannou, 2000) and 5 (Ioannou, 2002). The arsonolipids 3, so far studied in more detail, have interesting biophysi-

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cal (Serves et al., 1993; Gortzi et al., 2001; Fatouros et al., 2001) and biochemical (Rogers et al., 1996; Supuran et al., 1996) properties. Liposomes made of 3/PC/cholesterol showed a promising selective in vitro toxicity towards certain cancer cell lines (Gortzi et al., 2002).



ally distilled (b.p. 140-2 °C/1.8 mmHg). The impure and the distilled acid had the same mobility on TLC (CHCl<sub>3</sub>/MeOH 10:1,  $R_f$  0.46). Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were from Aldrich.

AsO<sub>3</sub>H<sub>2</sub>

AsO<sub>3</sub>H<sub>2</sub>



If the biological activity of the lipids **3** is due to their As(V), then a molecule having more As(V) groups might be more potent provided that it can be incorporated into liposomes. With this thought in mind we prepared molecules of the type **6** having the very lipophilic docosanoyl group, and the quite hydrophilic 2-[2-(2-methoxyethoxy) ethoxy]acetyl group. In this report we describe the preparation of these two pseudo-arsonolipids, Scheme 1, and the crystal structure of their parent bis(arsonic acid), 2-hydroxypropyl-1,3-bis(arsonic acid), **7**, because its analytical and IR data were puzzling.

### 2. Experimental

### 2.1. Materials

Epibromohydrin (Ferak) and epichlorohydrin (Aldrich) were redistilled. Docosanoic acid (Aldrich) was used without further purification. 2-[2-(2-methoxyethoxy) ethoxy]acetic acid (Aldrich) technical grade ( $\sim 50\%$  purity) was fraction-

Dichloromethane for acylations was dried over A4 molecular sieves. De-aerated methanol and petroleum ether were prepared by boiling, stoppering, and cooling to room temperature, r.t. Silica gel 60 H (Merck) was used for TLC.

### 2.2. Methods

TLCs were run on microslides. Visualization was done with I<sub>2</sub> [for 7 and 'AsO<sub>3</sub><sup>3-'</sup> (Serves et al., 1993; Tsivgoulis et al., 1998)] and by spraying with 35% sulfuric acid and charring. PhS-containing compounds gave a characteristic pink and then purple colour before charring. IR spectra of solid samples were taken in KBr discs and of oily samples in NaCl plates on a Perking Elmer, model 16PC, FT-IR spectrometer, while <sup>1</sup>H NMR (at 400 MHz) and <sup>13</sup>C NMR (at 100 MHz) spectra were obtained on a Bruker, model DPX Avance, spectrometer. Melting points were taken on an Electrothermal, model IA9100, apparatus. Elemental analyses were done by C.N.R.S., Vernaison, France.

# 2.3. Synthesis of 2-hydroxypropane-1,3-bis (arsonic acid) (7)

To a solution of arsenic trioxide (9.90 g, 50 mmol As<sub>2</sub>O<sub>3</sub>) in 23.1 ml 13 M NaOH (300 mmol), epibromohydrin (6.85 g, 50 mmol) was added. The mixture was stirred at r.t. for 3 days, and then at 80 °C for 8 h. The cooled (ice/water) slightly vellowish viscous solution was slowly acidified by hydrochloric acid (calculated 41.6 ml 6 M HCl for 250 mmol HO<sup>-</sup>), transferred to a centrifuge tube and left at +4 °C overnight to crystallize. The solid was recrystallized twice from 30 ml boiling water. Centrifugation and drying in vacuo over phosphorus pentoxide gave the product 7 (8.88 g, 58%) as a white crystalline solid, pure by TLC (MeOH/conc. NH<sub>3</sub> 4:1,  $R_f$  0.55). It is soluble in ethylene glycol, boiling water, moderately soluble in water at r.t. and in boiling methanol, sparingly soluble in methanol at r.t. ( $\sim 10$  mg per 1 ml MeOH), and insoluble in boiling acetone or ether. It foams at ~176 °C and decomposes at 183– 185 °C. Calculated for  $C_3H_{10}O_7As_2$  (*M*<sub>r</sub> 307.95) C 11.70, H 3.27%; found C 10.62, H 3.06%. IR (KBr): 3354 sharp, s, 3150 broad, w, 2988 sharp, mw, 2932 mw, 2592 broad, w, 2322 broad, m, 1648 broad, m, 1442 m, 1390 m, 1190 broad, ms, 1084 ms, 950 ms, 886 vs, 830 shoulder, ms, 790 vs, 777 vs, 724 shoulder, ms, 622 ms. <sup>1</sup>H NMR (D<sub>2</sub>O),  $\delta$ : 2.88 (d, *J* 6.6 Hz, 4H, CH<sub>2</sub>As), 4.64 (m, 1H, CHOH). <sup>13</sup>C NMR (D<sub>2</sub>O),  $\delta$ : 44.28 (CH<sub>2</sub>As), 63.35 (CHOH).

### 2.4. Synthesis of 2-docosanoyloxypropane-1,3-bis (arsonic acid) (6), $R = C_{21}H_{43}$

To the bis(arsonic acid) 7 (924 mg, 3 mmol) suspended in de-aerated methanol (15 ml), thiophenol (2.56 ml, 25.2 mmol) was added under nitrogen and stirred at r.t. for 3 h. Removal of methanol and drying in vacuo gave a white solid which was freed from excess thiophenol and most diphenyl disulfide by extracting under nitrogen with de-aerated petroleum ether (2 × 20 ml) by gently swirling the flask. Drying in vacuo gave the product **8** (1.972 g, expected 1.932 g) as an oil contaminated with diphenyl disulfide. TLC (CHCl<sub>3</sub>: product  $R_f$  0.62; PhSSPh  $R_f \sim 1$ ). Solubilities, IR and <sup>1</sup>H NMR data of a purer sample have been published (Ioannou, 2002). The product **8** was not stable (TLC analysis) and therefore it was used without delay.

To the impure product 8 [1.792 g, assuming to contain 3 mmol of the bis(dithioarsonite), 8], docosanoic acid (1.330 g, 3.9 mmol), DMAP (37 mg, 0.3 mmol), and dry dichloromethane (30 ml) were added, de-aerated, and flushed with nitrogen. A solution of DCC (772 mg, 3.75 mmol) in dry dichloromethane (10 ml) was added dropwise, during 90 min, at r.t., and the system stirred at r.t. overnight. After 3 h reaction TLC (CHCl<sub>3</sub>) showed the presence of product at  $R_{\rm f} \sim 1$ , the excess of docosanoic acid at  $R_{\rm f}$  0.3, traces of dicyclohexylurea at  $R_{\rm f}$  0.15, traces of an unknown impurity at  $R_{\rm f}$  0.06, and no starting compound 8 at  $R_{\rm f}$  0.60. The soft solid, obtained after evaporation and drying in vacuo, was suspended in ether (30 ml) and filtered through celite, washing with ether  $(3 \times 4 \text{ ml})$ . The filtrate had no dicyclohexylurea and became opalescent [probably by air oxidation in the presence of moisture of the  $-As(SPh)_2$  group in 9 to  $-AsO_3H_2$  (Kamai and Chadaeva, 1957; Cullen et al., 1984)]. It was

transferred to a centrifuge tube, water (3 ml) and 30% hydrogen peroxide (1.50 ml, 13.6 mmol H<sub>2</sub>O<sub>2</sub>) were added and stirred vigorously at r.t. for 2 h. The product precipitated as a white solid absorbing the added water. Centrifugation and washing the precipitate with boiling ether  $(1 \times 20 \text{ ml})$ gave the product (1.796 g, expected 1.893 g) contaminated by traces of docosanoic acid and diphenyl disulfide. The pure product 6, R = $C_{21}H_{43}$ , (1.446 g, 76%) was obtained by triturating the solid with boiling ether (5  $\times$  20 ml). From the ether extracts more product (74 mg) was isolated. The product gave trailing spots in acidic solvents: CHCl<sub>3</sub>/MeOH/AcOH 4:2:1 and 6:2:1 with  $R_f 0.32$ and 0.40, respectively. It is soluble in DMSO, CHCl<sub>3</sub>/MeOH 1:1 and warm methanol, and insoluble in chloroform and methanol. M.p.: 178-180 °C dec. Calculated for  $C_{25}H_{52}O_8As_2$  ( $M_r$ 630.51) C 47.62, H 8.31%; found C 47.69, H 8.42%. IR (KBr): 2914 vs, 2850 vs, 1742 m, 1472 mw, 1152 m, 1014 mw, 908 m, 884 m, 819 m, 786 m, 777 m. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 0.85 (t, J 6.8 Hz, 3H, CH<sub>3</sub>), 1.23 (s, 36H, (CH<sub>2</sub>)<sub>18</sub>), 1.51 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 2.27 (t, J 7.2 Hz, 2H, CH<sub>2</sub>COO), 2.77 (d, J 6.0 Hz, 4H, CH<sub>2</sub>As), 5.41 (quintet, J 6.2 Hz, 1H, CH). A very strong peak at 3.43-3.44ppm attributable to water in DMSO (Williams and Fleming, 1995, p. 162) was seen in various runs.

# 2.5. Attempted synthesis of the tetralithium salt of 2-docosanoyloxypropane-1,3-bis(arsonic acid)

To a solution of the acid (0.1 mmol) in methanol, a saturated solution of lithium hydroxide (0.4 mmol) in methanol was added. The solid, which was obtained had no ester (at 1742 cm<sup>-1</sup>) but an acid (RCOOH) group at 1722 cm<sup>-1</sup> and the  $-AsO_3^{2-}$  group at 844 cm<sup>-1</sup>. Its <sup>1</sup>H NMR spectrum in D<sub>2</sub>O showed no RCOOC*H* proton at 5.41 ppm but a quintet at 4.37 ppm due to HO–C*H*. The RCOOH was not detected because it was insoluble in D<sub>2</sub>O.

2.6. Synthesis of 2-[2-(2 methoxyethoxy)ethoxy] acetyloxypropane-1,3-bis(arsonic acid) (6),  $R = C_6 H_{13} O_3$ 

The reduction of 7 (3 mmol scale), acylation of 8 and oxidation of 9 were done as described in

Section 2.4. Since the product was water soluble, the ether was syringed off, the oil washed with ether  $(1 \times 20 \text{ ml})$  and freeze-dried to give the impure (by the polyether acid) product. This was triturated with boiling ether  $(5 \times 20 \text{ ml})$  to give the product 6,  $R = C_6 H_{13} O_6$  (1.13 g, expected 1.40 g) as a white very hygroscopic powder which by NMR contained ~8% of polyether acid. It is soluble in water, methanol, and DMSO and insoluble in ether, acetone, acetonitrile and ethyl acetate. M.p.: at 92–93 °C froaths and at 162–164 °C the froath melts. Calculated for  $C_{10}H_{22}O_{11}As_2$  $(M_{\rm r})$ 468.12) containing 8% polyether acid (C<sub>7</sub>H<sub>14</sub>O<sub>5</sub>, M<sub>r</sub> 178.18): C 27.37, H 4.99%. Found C 27.48, H 4.87%. IR (KBr): 3422 m, 2930 s, 1758 s, 1650 ms, 1568 w, 1468 w, 1198 s, 1122 vs, 1098 vs, 902 vs, 867 sh, 770 vs. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), δ: 2.79 (d, J 5.6 Hz, 4H, CH<sub>2</sub>As), 3.24 (s, 3H, CH<sub>3</sub>O), 3.43 (t, J 4.0 Hz, 2H, CH<sub>3</sub>OCH<sub>2</sub>), 3.52 (m, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>2</sub>), 3.60 (t, J 4.0 Hz,  $CH_2OCH_2COO$ ), 3.73 (broad,  $H_2O$  in DMSO), 4.01 (s, acid  $CH_2COOH$  impurity), 4.10 (s, 2H, CH<sub>2</sub>COO), 5.49 (quintet, J 6.0 Hz, 1H, CH).

Attempts at removing the polyether acid by dissolving the impure product in methanol and precipitating by ether were unsuccessful for the product was now contaminated with  $\sim 5\%$  acid and  $\sim 2\%$  methanol.

Attempts at the preparation of the tetralithium salt of **6** ( $\mathbf{R} = C_6 H_{13} O_3$ ) in methanol using lithium hydroxide in methanol as in Section 2.5 also resulted in *hydrolysis*.

### 2.7. X-ray crystallographic study of 7

Colorless, prismatic crystals of 7 suitable for X-ray analysis were grown from a dilute aqueous solution. Details of the crystal data and a summary of collection and refinement parameters for 7 are given in Table 3. The crystal used for data collection was mounted in capillary. Diffraction measurements were performed at r.t. on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the  $11 < 2\theta < 23^{\circ}$  range. Intensity data were recorded using a  $\theta - 2\theta$  scan with scan

speed 4.0° min<sup>-1</sup> and scan range  $2.25^{\circ} + \alpha_1 \alpha_2$  separation. Three standard reflections showed less than 3% variation and no decay. Lorenz polarization and  $\psi$ -scan absorption corrections were applied using Crystal Logic software.

The structure was solved by direct methods using SHELXS-86 (Sheldrick, 1986) and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-93 (Sheldrick, 1993). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by difference maps and refined isotropically. The largest shift/esd in the final cycle was 0.054.

### 2.8. Supplementary material

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC 179737. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

#### 3. Results and discussion

### 3.1. Preparations

For the preparation of 7 from epihalohydrins, the reaction requires 5NaOH Scheme 1 and not 6NaOH (per one molecule of  $As_2O_3$  to give 2'Na<sub>3</sub>AsO<sub>3</sub>') because one molecule of NaOH is produced during the ring opening reaction. However, we used 6NaOH because the excess NaOH helps in increasing the concentration of the reactive nucleophile,  $AsO_3^{3-}$  (Serves et al., 1994a) in the Meyer reaction (Meyer, 1883):

$$\mathbf{RX} + \mathbf{Na_3}\mathbf{AsO_3} \rightarrow \mathbf{RAsO_3}\mathbf{Na_2} + \mathbf{NaX}$$
(1)

A larger excess of sodium hydroxide or conducting the reaction at 70 °C lowered the yield of 7 because more glycerol and/or 2,3-dihydroxypropylarsonic acid were produced (TLC estimation). Epibromohydrin gave more product than epichlorohydrin because it is less volatile and because bromide is a better leaving group than chloride. The reaction is best conducted first at RT till all the oily epihalohydrins disappear, probably due to faster attack of the nucleophile at the epoxide carbon (Serves et al., 1994a,b) and then at 80 °C to complete the displacement of the halide. The bis(arsonic acid) 7 crystallized from water as anhydrous, as did the propane-1,3-bis(arsonic acid) (Ellerman et al., 1986), and it is worth noting that both acids have the same melting points (183–185 °C). The %C in 7 was lower than expected and could not be explained by the presence of impurities. This was one reason for determining its structure by X-ray analysis.

The reduction  $7 \rightarrow 8$  was done in order to convert the acid to a dichloromethane soluble compound to facilitate the acylation which follows. We used this technique for the preparation of 3(Serves et al., 1993), 4 (Kordalis and Ioannou, 2000) and 5 (Ioannou, 2002). The complete removal of diphenyl disulfide from the product 8, in this case, was not imperative because the disulfide does not interfere with the acylation which follows. If desired, the most efficient removal of diphenyl disulfide was found to be by petroleum ether extractions (Ioannou, 2002). The bis(dithioarsonites) 8 and 9, like some other aliphatic dithioarsonites (Kamai and Chadaeva, 1957; Cullen et al., 1984), are unstable in the presence of dioxygen and moisture. Therefore, 8 was used immediatelly. For the acylation of 8 we used an excess of fatty acid over both 8 and DCC. The reasons are: (a) the fatty anhydride can react to a certain extent with the dithioarsonite (Kamai and Chadaeva, 1957):

$$R'As(SPh)_2 + 2(RCO)_2O$$
  

$$\rightarrow R'As(OCOR)_2 + 2RCOSPh$$
(2)

and (b) if excess DCC over fatty acid is used, it cannot be easily removed from the product 6, while all dicyclohexylurea can be filtered off especially from etheral suspensions.

The docosanoyl **6** could easily be purified by extracting the docosanoic acid with ether. However, this method did not work well with the polyether **6**. When both **6** in methanol were treated with methanolic lithium hydroxide (1:4)



Fig. 1. Molecular structure of 7. Hydrogen atoms attached to C(1) and C(3) have been omitted. Open bonds indicate hydrogen bonds; oxygen atoms from neighboring molecules are also shown to emphasize the hydrogen bond scheme.

mol/mol) the tetralithium salt of 7 and free fatty or polyether acids were obtained, instead of the tetralithium salts of 6, indicating intramolecular assistance to hydrolysis (see also Ramirez et al., 1976).

### 3.2. Spectra

The IR spectrum of 7 in KBr in the C–OH region shows a strong, sharp peak at  $3354 \text{ cm}^{-1}$  indicative of an intramolecular single bridge hydrogen bonding (Williams and Fleming, 1995, p. 41). Since 7, Fig. 1, has only intermolecular hydrogen bonds, this peak is due to hydrogen bonding C–OH…OH–As (Section 3.3). In 7 and in the related propane-1,3-bis(arsonic acid) (Ellerman et al., 1986) the AsO–H and As=O groups are involved in strong hydrogen bonding as indicated by the position of their vibrations in the region

2900–2300 and at 900 cm<sup>-1</sup>, respectively. The splitting (790 and 777 cm<sup>-1</sup>) observed for 7, in KBr or in Nujol, can be attributed to asymmetrical and symmetrical stretching vibrations of the As–OH bond because there is only one As–OH bond length (1.69–1.71 Å), Table 1.

The v(As=O) of the C<sub>15</sub>, C<sub>17</sub>-C<sub>20</sub> alkylarsonic acids is found at 905 cm<sup>-1</sup> (McBreatry et al., 1968) while in the shorter ones (C<sub>4</sub>-C<sub>14</sub>, C<sub>16</sub>) is at 940 cm<sup>-1</sup> (McBreatry et al., 1968; Dietze, 1971). The v(As=O) of the lipids **6** is at ~ 900 cm<sup>-1</sup> indicating strong hydrogen bonding, as strong as the long chain alkylarsonic acids.

In the <sup>1</sup>H NMR spectra, the  $CH_2As$  in 2,3-dihydroxypropylarsonic (Tsivgoulis et al., 1991), propane-1,3-bis(arsonic acid) (Ellerman et al., 1986), and 7 in D<sub>2</sub>O resonate at 2.60, 2.70 and 3.00 ppm, respectively, indicating that 7 is least ionized.

Table 1 Bond lengths (Å) and angles (°) for compound 7  $\mathbf{7}$ 

As(1)–O(3)	1.654(5)
As(1)–O(2)	1.694(4)
As(1)–O(1)	1.695(5)
As(1)-C(1)	1.911(8)
As(2)–O(6)	1.650(5)
As(2)–O(4)	1.703(5)
As(2)–O(5)	1.708(5)
As(2)–C(3)	1.905(7)
O(7)–C(2)	1.416(8)
C(1)–C(2)	1.513(9)
C(2)–C(3)	1.533(9)
O(3)-As(1)-O(2)	111.0(3)
O(3)–As(1)–O(1)	112.0(3)
O(2)–As(1)–O(1)	98.8(3)
O(3)–As(1)–C(1)	111.2(3)
O(2)-As(1)-C(1)	114.7(3)
O(1)-As(1)-C(1)	108.7(3)
O(6)-As(2)-O(4)	111.4(3)
O(6)-As(2)-O(5)	112.6(3)
O(4)-As(2)-O(5)	101.7(3)
O(6)–As(2)–C(3)	115.0(3)
O(4)-As(2)-C(3)	108.5(3)
O(5)-As(2)-C(3)	106.6(3)
C(2)–C(1)–As(1)	112.2(5)
O(7)–C(2)–C(1)	112.0(6)
O(7)-C(2)-C(3)	110.9(5)
C(1)-C(2)-C(3)	109.4(6)
C(2)-C(3)-As(2)	110.9(5)

Hydrogen bonds (	(Å and	°) for	compound	7
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Table 2

D–H…A	d(D–H)	d(HA)	d(DA)	<(DHA)
O(1)-HO1O(3) <sup>a</sup>	0.89(10)	1.65(10)	2.523(7)	166(9)
O(2)-HO2O(6) <sup>b</sup>	1.00(8)	1.66(8)	2.615(7)	157(7)
O(4)-HO4O(3) <sup>c</sup>	0.832(5)	1.754(5)	2.582(7)	173.7(4)
O(5)-HO5O(6) <sup>d</sup>	0.61(9)	2.09(9)	2.656(8)	155(10)
O(7)-HO7O(1) <sup>b</sup>	0.82(11)	1.99(11)	2.797(7)	167(9)

Symmetry transformations used to generate equivalent atoms.

<sup>a</sup> x + 1/2, -y + 1/2, -z + 2.

<sup>b</sup> x - 1/2, -y + 1/2, -z + 1.

 $x^{c} - x, y + 1/2, -z + 3/2.$ 

 $^{d} - x + 1/2, -y + 1, z - 1/2.$ 

This, coupled with a large downfield resonance of the CH–OH proton (4.75 vs 4.10 ppm in 2,3-dihydroxypropylarsonic acid) probably indicates either protonation, CH–OH<sub>2</sub><sup>+</sup>, or very strong hydrogen bonding by the flanking  $-AsO_3H_2$  groups.

### 3.3. Crystal structure of 2-hydroxypropane-1,3-bis(arsonic acid) (7)

The molecular structure of **7** is shown in Fig. 1. Crystal data, data collection, and structure refinement details are shown in Table 3, bond distances and angles are collected in Table 1, while hydrogen bonding distances and angles are depicted in Table 2.

Overall, the As–C, As–OH, and As=O bond lengths in 7 and in other arsonic and arsinic acids, either aliphatic or aromatic, which have been studied, do not show great variations, falling in the regions of 1.88-1.92, 1.70-1.74, and 1.61-1.67 Å, respectively (aromatic arsonic: Doak and Freedman, 1970; Marx et al., 1996; aliphatic arsonic: Smith et al., 1971; Falvello et al., 1977; Kamiya et al., 1983; aliphatic arsinic: Trotter and Zobel, 1965; Smith et al., 1969; Goedken et al., 1993). In general, the bond lengths are As–OH > As=O, with the exception of the dimeric dimethylarsinic acid where As–OH  $\cong$  As=O = 1.62 Å (Trotter and Zobel, 1965).

The torsion angles: As(1)-C(1)-C(2)-C(3)176.5°, As(1)-C(1)-C(3)-As(2) 2.5°, and As(2)–C(3)–C(2)–C(1)  $-174.8^{\circ}$ , indicate a nearly planar molecular AsC<sub>3</sub>As backbone in 7.

The coordination around each arsenic atom in 7 is essentially tetrahedral as indicated by the interatomic angles given in Table 1. However, the HO(2)-As(1)-O(1)H angle is only 98.8°, probably because it has to accommodate the H(7) which hydrogen-bonds to O(1), i.e. the As(1)O<sub>3</sub> group has five while the As(2)O<sub>3</sub> group has four hydrogen bonds.

In the solid bis(arsonic acid) 7 the hydrogen bonding, Fig. 1 and Table 2, results in a complex three dimensional association. All hydrogen bonds deviate from linearity by 6-25°. In propane-1,3-diphosphonic acid each P=O participates in two hydrogen bonds (Gebert et al., 1977) and in propane-1,3-bis(arsonic acid) it is proposed that each As=O is involved in two hydrogen bonds (Ellerman et al., 1986). In our 7 each As=O oxygen also participates in two hydrogen bonds with two different As-OH groups from neighboring molecules. These hydrogen bonds are quite short, lying in the range of 2.52-2.66 Å, and therefore are strong. No intramolecular hydrogen bonding of the As=O with the C-OH group, which would give a six-membered ring, was observed. The C-OH group is then hydrogenbonded to the oxygen of an As-OH group of another molecule which acts as an acceptor. This hydrogen bond is significantly longer (2.80 Å) than the other bonds and, therefore, weaker and is responsible for the sharp peak observed at 3356  $cm^{-1}$  in the IR spectrum of 7.

Table 3

Crystal data, data collection and structure refinement details for compound 7

Formula $C_3H_{10}As_2O_7$ M       307.95         Crystal habit       Prism         Crystal colour       Colourless         Crystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal system       Orthorombic         Space group $P2_{12}_{12}_{1}$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ 4 $V$ (Å <sup>3</sup> )       846.6(6) $D_{calc}$ (g cm <sup>-3</sup> )       2.416 $\mu$ (Mo $K_{\alpha}$ ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ 600 $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8$ , $0 \le k \le 20$ , $0 \le l \le 8$ Reflections collected       1667         Independent reflections       1496 ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )] $A15$ Maximum and minimum $1.00$ and $0.28$ transmission $Wa2^b = 0.1090$ Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443$ , $wR2^b = 0.1102$ $wR2^b = 0.1102$ Weighing scheme, $w^c$	Parameter	
$M$ $307.95$ Crystal habitPrismCrystal colourColourlessCrystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal systemOrthorombicSpace group $P2_12_12_1$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo $K_{\alpha}$ ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum $1.00$ and $0.28$ transmission $rameters$ refinedParameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices (all data) $R1^a = 0.0454, \ wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Formula	$C_3H_{10}As_2O_7$
Crystal habitPrismCrystal colourColourlessCrystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal systemOrthorombicSpace group $P_{2_12_12_1}$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo K $_{\alpha}$ ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum $1.00$ and $0.28$ transmission $rameters$ refinedParameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices ( $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, \ wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Μ	307.95
Crystal colourColourlessCrystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal systemOrthorombicSpace group $P2_12_12_1$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo K $_{\alpha}$ ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum $1.00$ and $0.28$ transmission $ransmission$ Parameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices ( $I \ge 2\sigma$ ( $I$ )] $R1^a = 0.0443$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Crystal habit	Prism
Crystal size (mm) $0.10 \times 0.30 \times 0.50$ Crystal system       Orthorombic         Space group $P2_12_12_1$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo K <sub><math>\alpha</math></sub> ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, 0 \le k \le 20, 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum $1.00$ and $0.28$ transmission $Parameters refined$ Parameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices (all data) $R1^a = 0.0454, wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Crystal colour	Colourless
Crystal system       Orthorombic         Space group $P_{2_12_12_1}$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo K <sub><math>\alpha</math></sub> ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, 0 \le k \le 20, 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum $1.00$ and $0.28$ transmission $Parameters refined$ Parameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices ( $II$ data) $R1^a = 0.0443, wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual ( $e$ Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Crystal size (mm)	$0.10 \times 0.30 \times 0.50$
Space group $P2_12_12_1$ $a$ (Å) $6.911(3)$ $b$ (Å) $17.496(8)$ $c$ (Å) $7.002(3)$ $Z$ $4$ $V$ (Å <sup>3</sup> ) $846.6(6)$ $D_{calc}$ (g cm <sup>-3</sup> ) $2.416$ $\mu$ (Mo K <sub><math>\alpha</math></sub> ) (mm <sup>-1</sup> ) $7.894$ $F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, 0 \le k \le 20, 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496$ ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )] $1455$ Maximum and minimum transmission $100$ and $0.28$ Parameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2$ ( $F_o^2$ ) + ( $0.0894P$ ) <sup>2</sup> + $0.2641P$ ]         Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Crystal system	Orthorombic
a (Å)       6.911(3)         b (Å)       17.496(8)         c (Å)       7.002(3)         Z       4         V (Å <sup>3</sup> )       846.6(6) $D_{calc}$ (g cm <sup>-3</sup> )       2.416 $\mu$ (Mo K <sub><math>\alpha</math></sub> ) (mm <sup>-1</sup> )       7.894 $F(000)$ 600 $\theta$ range for data collection (°)       2.33–25.00         Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected       1667         Independent reflections       1496 ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )]       1455         Maximum and minimum transmission       1.00 and 0.28         transmission       1.073         Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, WR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, WR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Space group	$P2_{1}2_{1}2_{1}$
	a (Å)	6.911(3)
c (Å)       7.002(3)         Z       4         V (Å <sup>3</sup> )       846.6(6) $D_{calc}$ (g cm <sup>-3</sup> )       2.416 $\mu$ (Mo K <sub>a</sub> ) (mm <sup>-1</sup> )       7.894 $F(000)$ 600 $\theta$ range for data collection (°)       2.33–25.00         Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected       1667         Independent reflections       1496 ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )]       1455         Maximum and minimum transmission       1.00 and 0.28         transmission       1.073         Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, WR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, WR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	b (Å)	17.496(8)
Z       4         V (Å <sup>3</sup> )       846.6(6) $D_{calc}$ (g cm <sup>-3</sup> )       2.416 $\mu$ (Mo K <sub>a</sub> ) (mm <sup>-1</sup> )       7.894 $F(000)$ 600 $\theta$ range for data collection (°)       2.33–25.00         Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected       1667         Independent reflections       1496 ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )]       1455         Maximum and minimum transmission       1.00 and 0.28         transmission       1.073         Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, WR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, WR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	<i>c</i> (Å)	7.002(3)
$V$ (Å <sup>3</sup> )       846.6(6) $D_{calc}$ (g cm <sup>-3</sup> )       2.416 $\mu$ (Mo K <sub>a</sub> ) (mm <sup>-1</sup> )       7.894 $F(000)$ 600 $\theta$ range for data collection (°)       2.33–25.00         Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected       1667         Independent reflections       1496 ( $R_{int} = 0.0536$ )         Observed reflections [ $I > 2\sigma$ ( $I$ )]       1455         Maximum and minimum transmission       1.00 and 0.28         transmission       1.073         Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, WR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, WR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Z	4
$\begin{array}{llllllllllllllllllllllllllllllllllll$	V (Å <sup>3</sup> )	846.6(6)
$ \begin{array}{ll} \mu \ ({\rm Mo} \ {\rm K}_{\alpha}) \ ({\rm mm}^{-1}) & 7.894 \\ F(000) & 600 \\ \theta \ {\rm range for data \ collection \ (^{\circ})} & 2.33-25.00 \\ {\rm Index \ ranges} & -8 \leqslant h \leqslant 8, \ 0 \leqslant k \leqslant 20, \\ 0 \leqslant l \leqslant 8 \\ {\rm Reflections \ collected} & 1667 \\ {\rm Independent \ reflections} & 1496 \ (R_{\rm int} = 0.0536) \\ {\rm Observed \ reflections \ } I > 2\sigma \ (I)] & 1455 \\ {\rm Maximum \ and \ minimum}} & 1.00 \ {\rm and} \ 0.28 \\ {\rm transmission} \\ {\rm Parameters \ refined}} & 145 \\ {\rm GoF \ on \ } F^2 & 1.073 \\ {\rm Final \ } R \ {\rm indices \ } [I > 2\sigma \ (I)] & R1^a = 0.0443, \\ wR2^b = 0.1090 \\ {\rm Final \ } R \ {\rm indices \ (all \ data)} & R1^a = 0.0454, \\ wR2^b = 0.1102 \\ {\rm Weighing \ scheme, \ w^c} & 1/[\sigma^2 \ (F_o^2) + (0.0894P)^2 \\ + 0.2641P] \\ {\rm Residual \ (e \ \AA^{-3})} & 0.978, -0.752 \\ {\rm Absolute \ structure \ parameter} & 0.31(3) \\ \end{array} $	$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.416
$F(000)$ $600$ $\theta$ range for data collection (°) $2.33-25.00$ Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected $1667$ Independent reflections $1496 \ (R_{int} = 0.0536)$ Observed reflections $[I > 2\sigma (I)]$ $1455$ Maximum and minimum $1.00 \ \text{and} \ 0.28$ transmission $1.073$ Parameters refined $145$ GoF on $F^2$ $1.073$ Final $R$ indices $[I > 2\sigma (I)]$ $R1^a = 0.0443, \ wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, \ wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 \ (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å^{-3}) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	$\mu$ (Mo K <sub><math>\alpha</math></sub> ) (mm <sup>-1</sup> )	7.894
$\begin{array}{lll} \theta \mbox{ range for data collection (°)} & 2.33-25.00 \\ \mbox{Index ranges} & -8 \leqslant h \leqslant 8, \ 0 \leqslant k \leqslant 20, \\ & 0 \leqslant l \leqslant 8 \\ \mbox{Reflections collected} & 1667 \\ \mbox{Independent reflections} & 1496 \ (R_{\rm int} = 0.0536) \\ \mbox{Observed reflections} & I > 2\sigma \ (I) \end{bmatrix} & 1455 \\ \mbox{Maximum and minimum} & 1.00 \ \mbox{and } 0.28 \\ \mbox{transmission} \\ \mbox{Parameters refined} & 145 \\ \mbox{GoF on } F^2 & 1.073 \\ \mbox{Final } R \ \mbox{indices} \ [I > 2\sigma \ (I)] & R1^a = 0.0443, \\ & wR2^b = 0.1090 \\ \mbox{Final } R \ \mbox{indices} \ (all \ \mbox{data}) & R1^a = 0.0454, \\ & wR2^b = 0.1102 \\ \mbox{Weighing scheme, } w^c & 1/[\sigma^2 \ (F_o^2) + (0.0894P)^2 \\ & + 0.2641P] \\ \mbox{Residual (e $ Å^{-3}$)} & 0.978, -0.752 \\ \mbox{Absolute structure parameter} & 0.31(3) \\ \end{array}$	F(000)	600
Index ranges $-8 \le h \le 8, \ 0 \le k \le 20, \ 0 \le l \le 8$ Reflections collected1667Independent reflections1496 ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )]1455Maximum and minimum transmission1.00 and 0.28Parameters refined145GoF on $F^2$ 1.073Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443, \ wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454, \ wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å^{-3})0.978, -0.752Absolute structure parameter0.31(3)	$\theta$ range for data collection (°)	2.33-25.00
$0 \leqslant l \leqslant 8$ Reflections collected 1667 Independent reflections 1496 ( $R_{int} = 0.0536$ ) Observed reflections [ $I > 2\sigma$ ( $I$ )] 1455 Maximum and minimum 1.00 and 0.28 transmission Parameters refined 145 GoF on $F^2$ 1.073 Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) 0.978, -0.752 Absolute structure parameter 0.31(3)	Index ranges	$-8 \!\leqslant\! h \!\leqslant\! 8, \ 0 \!\leqslant\! k \!\leqslant\! 20,$
Reflections collected1667Independent reflections1496 ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )]1455Maximum and minimum1.00 and 0.28transmission145Parameters refined145GoF on $F^2$ 1.073Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )0.978, -0.752Absolute structure parameter0.31(3)		$0 \leq l \leq 8$
Independent reflections1496 ( $R_{int} = 0.0536$ )Observed reflections [ $I > 2\sigma$ ( $I$ )]1455Maximum and minimum transmission1.00 and 0.28Parameters refined145GoF on $F^2$ 1.073Final $R$ indices [ $I > 2\sigma$ ( $I$ )] $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final $R$ indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )0.978, -0.752Absolute structure parameter0.31(3)	Reflections collected	1667
Observed reflections $[I > 2\sigma(I)]$ 1455Maximum and minimum transmission1.00 and 0.28Parameters refined145GoF on $F^2$ 1.073Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )0.978, -0.752Absolute structure parameter0.31(3)	Independent reflections	1496 ( $R_{\rm int} = 0.0536$ )
Maximum and minimum transmission1.00 and 0.28Parameters refined145GoF on $F^2$ 1.073Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )0.978, -0.752Absolute structure parameter0.31(3)	Observed reflections $[I > 2\sigma (I)]$	1455
transmission         Parameters refined       145         GoF on $F^2$ 1.073         Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Maximum and minimum	1.00 and 0.28
Parameters refined       145         GoF on $F^2$ 1.073         Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	transmission	
GoF on $F^2$ 1.073         Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Parameters refined	145
Final R indices $[I > 2\sigma(I)]$ $R1^a = 0.0443$ , $wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	GoF on $F^2$	1.073
$wR2^b = 0.1090$ Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> ) $0.978, -0.752$ Absolute structure parameter $0.31(3)$	Final R indices $[I > 2\sigma (I)]$	$R1^{a} = 0.0443,$
Final R indices (all data) $R1^a = 0.0454$ , $wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)		$wR2^{\rm b} = 0.1090$
$wR2^b = 0.1102$ Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Final <i>R</i> indices (all data)	$R1^{\rm a} = 0.0454,$
Weighing scheme, $w^c$ $1/[\sigma^2 (F_o^2) + (0.0894P)^2 + 0.2641P]$ Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)		$wR2^{\rm b} = 0.1102$
+ 0.2641P]         Residual (e Å <sup>-3</sup> )       0.978, -0.752         Absolute structure parameter       0.31(3)	Weighing scheme, $w^{c}$	$1/[\sigma^2 (F_o^2) + (0.0894P)^2$
Residual (e $A^{-3}$ )0.978, -0.752Absolute structure parameter0.31(3)	° 7	+ 0.2641P]
Absolute structure parameter $0.31(3)$	Residual (e $A^{-3}$ )	0.978, -0.752
	Absolute structure parameter	0.31(3)

<sup>a</sup>  $R1 = \Sigma(|F_{\rm o}| - |F_{\rm c}|)/\Sigma|F_{\rm o}|.$ 

<sup>b</sup> wR2 = { $[\Sigma w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]$ }<sup>±</sup>.

 $^{\circ}P = (\max(F_{o}^{2}, 0) + 2F_{c}^{2})/3.$ 

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