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THE CRYSTAL STRUCTURE OF n-PROPYLARSONIC ACID

MILTON R. SMITH, RALPH A. ZINGARO AND EDWARD A. MEYERS
Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)

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SUMMARY

The crystal structure of n-propylarsonic acid has been determined by single crystal X-ray diffractometer methods. The crystal is orthorhombic, *Pccn*, $a = 14.561(4)$, $b = 11.024(4)$, $c = 7.692(3)$ at 22°, 8 molecules/unit cell. The coordination around As is roughly tetrahedral, with As–O(1) = 1.708(5), As–O(2) = 1.719(5), As–O(3) = 1.652(4) and As–C(1) = 1.917(7) Å, and the molecules are linked into chains of dimers along the *c*-axis by hydrogen bonds O(1)···O(2) = 2.581(6) and O(3)···O(2) = 2.573(6) Å. The other bond distances are C(1)–C(2) = 1.51 (2) and C(2)–C(3) = 1.28(2) Å, where the pronounced apparent shortening of the latter bond seems to be associated with very large thermal motions of C(2) and C(3). These large thermal movements probably occur since the chains along the *c* axis are held together by van der Waals' forces.

The hydrogen atoms could not be located with certainty, and the final *R* for As, O and C atoms only was 0.036.

INTRODUCTION

Recently, extensive series of both di-n-alkylarsinic acids[1], $R_2As(O)(OH)$, and n-alkylarsonic acids[2], $RAs(O)(OH)_2$, where $R = CH_3$ to $R = n\text{-}C_{20}H_{41}$, have been prepared and some of their physical properties measured[1-4]. In the case of the arsinic acids, single crystal studies[5,6] have proved helpful in the interpretation of the low temperature powder X-ray data and may prove to be useful in the detailed interpretation of the crystalline phase transition that occurs in certain of these compounds[7].

The chemical and physical behavior of the arsonic acids[4] appears to be more complex than that of their arsinic acid analogues, since upon heating the former there are indications of several endothermic processes prior to melting, decomposition occurs at higher temperatures, and the long crystal spacing found from the powder X-ray data is a rather irregular function of chain length. Thus, it seemed desirable to obtain single crystal X-ray data for some of these compounds in order to assist the interpretation of their other physical properties.

In earlier X-ray work, the structures of phenylarsonic acid[8], *p*[9]- and *m*[10]-aminophenylarsonic acid have been determined, but no similar studies of n-alkylarsonic acids have been reported. The single crystal X-ray structure determination of n-propylarsonic acid is reported in this study.

EXPERIMENTAL

Single crystals of n-propylarsonic acid were grown from an aqueous solution that had been saturated at an elevated temperature and then cooled. Several crystals were examined with a Syntex Autodiffractometer by means of Mo-$K\alpha$ radiation monochromatized by reflection from the (002) plane of an oriented graphite crystal at the angle $2\ \theta mn = 12°15'$ for $\lambda = 0.7107$ Å. These measurements were supplemented by photographic examination with a Buerger precession camera equipped with a Polaroid cassette. The crystals were orthorhombic, space group *Pccn*. Unit cell dimensions were obtained by the least-squares refinement of $2\ \theta$ ($\lesssim 35°$) values from 38 reflections of general indices which were manually measured on the diffractometer at 22°. There was no significant α_1, α_2 splitting, and $\lambda = 0.7107$ Å. $a = 14.561(4)$, $b = 11.024(4)$, $c = 7.692(3)$, d(X-ray)$= 1.807(2)$ g/cc for $Z = 8$. The density determined by flotation in a mixture of CCl_4 and n-C_7H_{16} was 1.83(2) g/cc.

Preliminary data which were collected for two crystals, A and B, showed a rapid decline of intensity with increasing $2\ \theta$. The data used for the structure determination were obtained from two other crystals, C and D, which were larger than A. The intensities of 877 independent observed reflections ($I > 3\ \sigma$) were measured by scanning in $2\ \theta$ over a range of 2.5° at a rate that varied linearly from 0.5°/min for reflections with peak intensities of 50 cps, to 4°/min for reflections with peak intensities greater than or equal to 1000 cps for crystal C or 750 cps for crystal D. For peak intensities less than 50 cps, a scan rate of 8°/min was used. For crystal D, the intensities of reflections (hkl) were measured for $l = 0, 1, 2$ and the remaining data were collected from crystal C in two parts, with the crystal alignment checked and improved approximately midway through the run. For both C and D, throughout each run, groups of 24 intensities were measured, followed by the measurement of two check reflections, (0, 6, 0) and (10, 0, 0), and one other reflection which coincided with the ϕ-axis of the instrument (006 for crystal C and $\overline{1}\overline{1}4$ for crystal D). No correction for drift in the standards was made. The *maximum* fluctuation from the mean in the standards varied from < 1.5% to 3% in a run. [The three groups of data, two from crystal C and one from D, were refined anisotropically, with six H atoms included, unit weights and three scale factors at first. The reflections were put on a common scale by means of these scale factors. The ratios of scale factors as calculated from a comparison of the standard reflections (0, 6, 0) and (10, 0, 0) from the three runs varied from the least square values by only 0.5% to 0.7%.] The maximum $2\ \theta$ value was 65°. The dimensions of C were $0.47 \times 0.23 \times 0.17\ mm^3$ and of D, $0.50 \times 0.23 \times 0.19\ mm^3$ ($\mu = 57.0\ cm^{-1}$). Lorentz and polarization corrections, and an experimental (ϕ scan)[11] absorption correction were applied to the data. The polarization correction was taken as the average of the expressions

$$P_1 = \frac{\cos^2 2\,\theta + |\cos 2\,\theta mn|}{1 + |\cos 2\,\theta mn|} \quad \text{and} \quad P_2 = \frac{\cos^2 2\,\theta + \cos^2 2\,\theta mn}{1 + \cos^2 2\,\theta mn}$$

A three dimensional Patterson function was calculated from a limited set of data (394 reflections) obtained from crystal A, and trial coordinates for the As atom found. A Fourier synthesis was then calculated with these coordinates for As and the positions of O and C atoms were obtained. With the full set of data from crystals C and

D, least-squares refinement was carried out and a difference synthesis calculated. A number of small peaks were observed on the difference map, but clearcut positions for the hydrogen atoms were not obtained.

At this stage, with anisotropic temperature factors for As, C, and O atoms, weights estimated from counting statistics, scattering factors for O and C taken from the International Tables[12], and the scattering factor for As (corrected for anomalous dispersion) taken from Cromer's[13,14] tables, R_1, the value of the discrepancy index, was $R_1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.038$.

In an attempt to accentuate the contributions of the H atoms to the difference map, a weighted difference synthesis was calculated*,

$$\Delta\rho = \frac{1}{V}\sum_h \sum_k \sum_l \omega(F_o - F_c)\cos 2\pi(hx+ky+lz)$$

in which $\omega = f_H$ = scattering factor for hydrogen[11]. Also, the positions expected for the six H atoms attached to O(1), O(3), C(1) and C(2) were calculated. The two sets of positions obtained for the three H atoms connected to O(1) and C(1) agreed well, but the hydrogen attached to O(3) was poorly defined, and there were marked discrepancies between the calculated positions of the two H atoms connected to C(2) and those obtained in the weighted difference map. In addition, the map showed a very broad but low magnitude positive peak in the vicinity of C(3). Large numbers of cycles of least-squares refinement were carried out with both calculated and observed positions for six isotropic H atoms, with unit weights. Both models appeared to approach the same final result with $R_1 = 0.030$ and $R_2 = [\Sigma\omega(F_o - F_c)^2/\Sigma\omega F_o^2]^{\frac{1}{2}} = 0.025$. Despite these low values for R_1 and R_2, the results were considered unsatisfactory for several reasons. First, the C(2)–C(3) distance was extremely short, 1.22 Å, and the angle C(1)–C(2)–C(3) was very large, 130°. Qualitatively this appeared reasonable, since a large-amplitude rotational motion of the terminal methyl group around the C(1)–C(2) axis should produce both these effects[15]. Quantitatively, this model seemed less satisfactory, since the projection of C(2)–C(3) on the axis C(1)–C(2) was 0.79 Å, compared to a value of 0.51 Å predicted for a normal C–C bond of length 1.54 Å with a C–C–C angle of 109.5°. Second, the distances and angles associated with the H atoms connected to C(2) were abnormal, their isotropic temperature factors became negative, and the H atom connected to O(3) also did not refine satisfactorily.

An empirical weighting scheme was obtained from a plot of $|\Delta F|$ *vs.* $|F_o|$: for $|F_o| < 35$, $\sigma = 2.28 - 0.0337\,|F_o|$; for $|F_o| > 35$, $\sigma = 0.64 + 0.0131\,|F_o|$. Refinement of the structure with hydrogens excluded gave $R_1 = 0.036$, $R_2 = 0.042$ and $\Sigma = [\Sigma\omega(F_o - F_c)^2/(N - V)]^{\frac{1}{2}} = 1.25$ where $N = 877$ (number of observations) and $V = 64$ (number of parameters varied). The final results for this model are given in Table 1. Similar calculations were performed (a) with six hydrogens included, namely those attached to O(1), O(3), C(1) and C(2), $R_1 = 0.029$, $R_2 = 0.033$, $\Sigma = 0.99$ for $N = 877$, $V = 88$, and (b) with three hydrogens included, namely those attached to O(1) and C(1), $R_1 = 0.033$, $R_2 = 0.038$ and $\Sigma = 1.13$ for $N = 877$, $V = 76$. Difficulties similar to those described above (when unit weights were used) were encountered with the

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* A discussion of the theoretical basis for this function will be published elsewhere.

TABLE 1

ATOMIC COORDINATES OF n-$C_3H_7As(O)(OH)_2$ OBTAINED IN ANISOTROPIC REFINEMENT WITH EMPIRICAL WEIGHTS

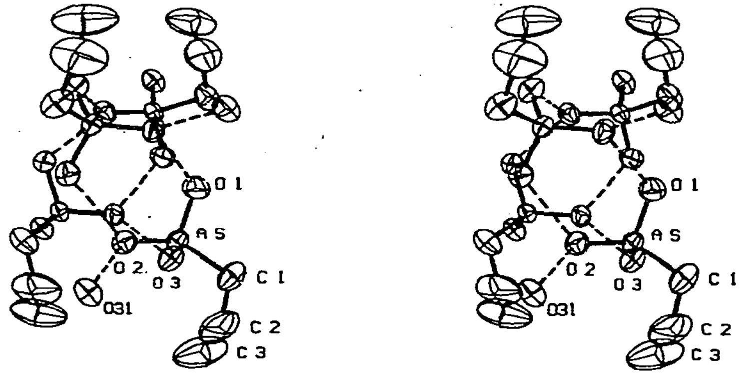
Standard deviations are in parentheses and apply to the last digit of a number; values of β_{ij} have been multiplied by 10^2.

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	0.15847(3)	0.09195(5)	0.09195 (5)	0.328(2)	0.645(3)	1.249(6)	−0.087(7)	−0.060(10)	0.022(14)
O(1)	0.1236(2)	0.2355(4)	0.0461(6)	0.46(2)	0.71(3)	2.65(9)	0.04(5)	−0.32(7)	0.16(10)
O(2)	0.2682(2)	0.0944(4)	0.1518(4)	0.35(4)	0.84(3)	1.81(3)	−0.09(4)	−0.16(5)	0.25(10)
O(3)	0.1401(2)	0.0097(3)	−0.0893(5)	0.55(2)	0.86(3)	1.47(6)	−0.22(4)	0.12(7)	−0.14(9)
C(1)	0.0752(4)	0.0273(6)	0.2667(8)	0.53(3)	1.07(7)	1.37(11)	−0.18(8)	0.23 (10)	−0.12 (14)
C(2)	0.0981(8)	−0.0999(10)	0.3258(16)	1.61(10)	1.70(13)	5.42(32)	−0.07(17)	1.92(31)	1.04(36)
C(3)	0.1165(11)	−0.1899(8)	0.2340(14)	3.12(17)	1.10(10)	2.18(24)	−0.21(20)	1.53(36)	0.06(25)

H atoms attached to O(3) and C(2). The estimates of uncertainties are based upon block-diagonal squares refinements, and a comparison of them with a limited number of earlier full-matrix refinements indicates that the block-diagonal estimates are approximately 0.9 of the full-matrix estimates. Tables of structure factors are available*.

DISCUSSION

A stereographic projection of the structure of n-propylarsonic acid with H atoms excluded is shown in Fig. 1. The atomic parameters are given in Table 1 and some pertinent bond distances and angles in Table 2.



n-$C_3H_7As(O)(OH)_2$ n-$C_3H_7As(O)(OH)_2$

Fig. 1. Stereographic views of n-propylarsonic acid along the *c*-axis. (The atom labelled O31 is an oxygen atom of type O3 located in the unit cell above that which contains O3).

The arsenic atom is bonded to one carbon and three oxygen atoms which form a slightly distorted tetrahedron. The As–C(1) bond distance, 1.917(7) Å, is not significantly different from the As–C bond distances, 1.95(2) Å in $(C_4H_9)_2As(O)(OH)$[6], 1.91(4) Å In $(CH_3)_2As(O)OH$[5], and 1.96(2) Å in $[(CH_3)_2AsS]_2$[16]. The As–O bonds, As–O(1) = 1.708(5) and As–O(3) = 1.719(5) are in reasonable agreement with each other and agree fairly well with the distance As–O(2) = 1.74(1) Å in di-n-butylarsinic acid. These bond distances are apparently longer than the mean value 1.62(3) Å reported for dimethylarsinic acid. The third As–O bond distance in this structure, As–O(2) = 1.652(4) Å, is significantly shorter than the other two present in it. This would be expected from the formula of the molecule, Fig. 2.

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* A listing of the values of the observed and calculated structure factors has been deposited as NAPS document no. 01282 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2 for microfiche or $5 for a photocopy. Advance payment is required. Make checks payable to: ASIS-NAPS.

TABLE 2

DISTANCES AND ANGLES FROM THE CRYSTAL STRUCTURE OF n-PROPYLARSONIC ACID

Standard deviations are in parentheses and apply to the last digit of a number.

Distances (Å)		Angles (°)	
As–O(1)	1.708(5)	O(1)–As–O(2)	109.3(2)
As–O(2)	1.652(4)	O(1)–As–O(3)	104.5(2)
As–O(3)	1.719(5)	O(2)–As–O(3)	111.8(2)
As–C(1)	1.917(7)	C(1)–As–O(1)	108.2(3)
C(1)–C(2)	1.511(16)	C(1)–As–O(2)	116.5(3)
C(2)–C(3)	1.247(19)	C(1)–As–O(3)	105.8(3)
O(1)–O(2)′	2.581(6)	As–C(1)–C(2)	114.2(6)
O(2)–O(3)′	2.573(6)	C(1)–C(2)–C(3)	127.9(13)
		O(1)′–O(2)–As	121.5(2)

Dihedral angle between the planes defined by three atoms: O(1)–As–O(2)···O(1)–O(2)–O(1)′ 20.0 (2)°

Maximum and minimum values of the interatomic distance[17]

	Maximum	Minimum
C(1)–C(2)	1.767 Å	1.537 Å
C(2)–C(3)	1.821	1.251

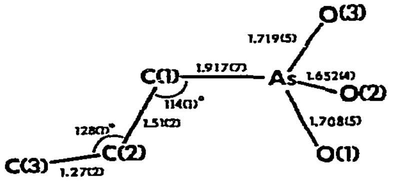

Fig. 2. Schematic drawing of n-propylarsonic acid with hydrogen atoms excluded.

where O(2) is double bonded to the arsenic atom. The analogous As–O(1) bond distance, 1.67(1) Å, in $(C_4H_9)_2As(O)OH$ is not significantly different from the As–O(2) bond distance in $C_3H_7As(O)(OH)_2$.

The two hydrogen bonds, O(1)–H···O(2) = 2.581(6) and O(3)–H···O(2) = 2.573(6) Å are not significantly different from each other, although the former is associated with dimers that are approximately parallel to the *ab* plane, while the latter binds these dimers together into infinite chains along the *c* axis. The crystal structure of phenylarsonic acid[8] also exhibits dimers which are bonded to form infinite chains. Those hydrogen bonds, however, are of considerably different length, 2.49 and 2.64 Å.

The bond distance C(1)–C(2) = 1.511(16) Å appears to be slightly shorter than normal and the angle As–C(1)–C(2) = 114.2(6)° slightly larger than normal as might be expected from the large temperature factors for C(2). The bond distance C(2)–C(3) = 1.247(19) and bond angle C(1)–C(2)–C(3) = 127.9(13)° differ a great deal from the expected values of approximately 1.54 Å and 109.5°, again probably because of the large thermal amplitudes of C(2) and C(3). In the crystal, columns of hydrogen bonded dimers extend along the *c* axis, as depicted in Fig. 1. The forces between these one-dimensional polymers along *c* are of the van der Waals' type, and this weak bonding is probably the reason for the large thermal amplitudes of C(2) and C(3).

The maximum and minimum distances[17] for C–C distances are given in Table 2. The closest intermolecular contacts for C(2) and C(3) are C(2)···O(1)=3.83, C(3)···O(1)=3.97, C(2)···O(2)=3.83, C(3)···O(2)=3.79 and C(2)···C(3)=3.91 Å, with all other greater than 4 Å.

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