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THE CRYSTAL STRUCTURE OF DI-n-BUTYLARSINIC ACID

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SUMMARY

The crystal structure of di-n-butylarsinic acid has been determined from 1257 independent photographically recorded intensities. For convenience, a non-conventional triclinic cell, $B\bar{1}$ was chosen, $a=8.38(2)$, $b=13.12(3)$, $c=10.39(2)$ Å, $\alpha=91.5(5)$, $\beta=89.8(5)$, $\gamma=98.5(5)^\circ$, $z=4$/cell, d(calcd.) = 1.31, d(measured) = 1.32 g/cc, $R=0.096$ with unit weights, anisotropic temperature factors and no contribution of H-atoms included. The acid molecules are present as non-planar, H-bonded dimers across the centers of symmetry in the cell. The configuration around As is nearly tetrahedral, the average distance As–C = 1.95(2) Å, As–O(1) = 1.67(1), As–O(2) = 1.74(1) Å, O(1)–O′(2) = 2.47(2) Å, and the dihedral angle between O(1)–As–O(2) and O(1)–O(2)–O′(1)–O′(2) is 140.0(7)° with a chair configuration for the dimer ring. The average distance C–C = 1.55(5) Å, angle C–C–C = 110(2)°. The intra-dimer C–C contracts are $\geqq 4.5$ Å, while there are a number of inter-dimer distances close to 4 Å.

INTRODUCTION

The crystal structure of di-n-butylarsinic acid has been determined as part of the study of the physical properties of a series of di-n-alkylarsinic acids with alkyl groups that range from CH_3- to $C_{20}H_{41}$-. The structure of dimethylarsinic acid has been determined[1], but studies of the structures of other members of the series have not been reported. Since a phase transition occurs for members of this series whenever the chain length is greater than n-pentyl[2], it seemed desirable to determine the structure of di-n-butylarsinic acid for future comparison of its configuration in the crystal with those of longer chain analogues.

EXPERIMENTAL

Di-n-butylarsinic acid was synthesized and purified according to previously published methods[3]. Single crystals were grown as colorless prisms elongated along the c-axis by evaporation of an aqueous solution. A crystal approximately 0.3 × 0.4 × 2 mm^3 was mounted in a thin-walled glass capillary, and aligned on a Buerger precession camera. The crystal was triclinic and was indexed, for convenience, on the basis of a non-conventional B-centered cell, with $a=8.38(2)$, $b=13.12(3)$, $c=10.39(2)$ Å, $\alpha=91.5(5)$, $\beta=89.8(5)$, $\gamma=98.5(5)^\circ$, Z = 4/cell, d(X-ray) = 1.31, d(flotation) = 1.32 g/cc, space group $B\bar{1}$. Intensity data for the $(0kl)$, $(h0l)$, (hhl) and $(h\bar{h}l)$ zones were collected

TABLE 1

ATOMIC COORDINATES OF $(n\text{-}C_4H_9)_2As(O)OH$ OBTAINED IN ANISOTROPIC REFINEMENT WITH UNIT WEIGHTS

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

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	0.5051(1)	0.0119(1)	0.2982(1)	0.0132(1)	0.0071(1)	0.0076(1)	0.0014(1)	0.0004(1)	0.0013(1)
O(1)	0.6716(4)	0.0358(4)	0.3881(4)	0.0087(6)	0.0097(4)	0.0062(5)	0.0015(4)	0.0011(5)	0.0023(4)
O(2)	0.3422(5)	0.0358(4)	0.3936(5)	0.0091(6)	0.0102(4)	0.0093(6)	0.0032(4)	0.0030(5)	0.0006(4)
C(1)	0.4699(8)	−0.1315(6)	0.2339(8)	0.0146(11)	0.0074(5)	0.0109(10)	−0.0004(5)	0.0018(9)	0.0045(7)
		0.1067(6)	0.1558(8)	0.0177(12)	0.0058(5)	0.0095(9)	0.0005(6)	0.0007(10)	0.0012(6)
C(3)	0.4500(10)	−0.2034(7)	0.3489(8)	0.0226(15)	0.0082(6)	0.0101(10)	0.0012(8)	0.0049(11)	0.0019(7)
C(4)	0.5529(10)	0.2191(6)	0.2075(8)	0.0240(16)	0.0063(5)	0.0109(11)	0.0017(8)	0.0030(11)	0.0017(7)
C(5)	0.4166(11)	−0.3191(6)	0.2947(11)	0.0240(17)	0.0055(5)	0.0250(19)	0.0009(8)	0.0030(15)	0.0037(8)
C(6)	0.5701(14)	0.2900(8)	0.0997(11)	0.0379(26)	0.0078(7)	0.0185(16)	0.0018(11)	0.0027(17)	0.0033(9)
C(7)	0.4048(17)	−0.3921(9)	0.4109(15)	0.0461(33)	0.0088(9)	0.0363(28)	0.0032(15)	0.0124(25)	0.0089(13)
C(8)	0.5959(17)	0.4086(8)	0.1488(15)	0.0495(35)	0.0061(7)	0.0400(29)	0.0042(13)	0.0037(26)	−0.0009(12)

with the Buerger precession camera, Zr filtered Mo-K_α radiation (λ=0.7107 Å). Equiinclination Weissenberg data were collected for the zones ($hk0$) to ($hk5$) with Ni filtered Cu-K_α radiation (λ=1.5418 Å) and multiple film packs.

Optical densities of the reflections were visually estimated by comparison with a Welch Densichron standard film strip and converted to relative intensities by an internal calibration procedure. Lorentz, polarization and absorption corrections were applied to the intensities. The crystal was treated, for absorption corrections, as a cylinder of radius 0.018 cm; μR(Mo-K_α)=0.55; μR(Cu-K_α)=0.74. A total of 1257 independent reflections were observed.

Patterson functions were calculated* from the data of the three major zones, and trial coordinates obtained for the As atom. It was assumed that the space group was centrosymmetric and the straightforward applicaton of Fourier methods** to the data of the three major zones permitted the coordinates of the O and C atoms to be obtained. Least squares refinement*** of all data with scattering factors taken from the International Tables, individual atom isotropic temperature factors, individual zone scale factors and unit weights were carried out. All reflections were placed on a common scale and duplicate reflections were averaged; R=0.131; with the As atom changed to anisotropic, R=0.110; and with all atoms anisotropic R= 0.096; (previous experience with other structures determined from photographic data similarly collected has convinced us that no significant differences in final parameters are obtained with the use of alternative weighting schemes). The final atomic parameters are given in Table 1, and bond distances and angles[5] in Table 2. A final three dimensional electron density difference map was calculated and examined. Background fluctuations (±122) were less than one fourth the peak heights observed for the carbon atoms ($\geq$580). Neither abnormal features, nor a clearcut collection of H-atoms were observed.

DISCUSSION

Di-n-butylarsinic acid is present as centrosymmetric H-bonded dimers in the crystal (Fig. 1). The atoms bonded at As form a slightly distorted tetrahedron. The angles C(1)–As–C(2), 110.7(7)° and O(1)–As–O(2), 107.9(5)° agree well with corresponding angles in dimethylarsinic acid, 110(2) and 109(2)° [1]. The As–C bond distances are equal within the estimated errors, and have a mean value of 1.95(2) Å, compared to 1.96(2) Å in $[(CH_3)_2AsS]_2$[6] and 1.91(4) Å in $(CH_3)_2As(O)OH$[1]. The As–O bond distances are As–O(1)=1.67(1) and As–O(2)=1.74(1) Å. The first distance is not significantly different from the mean value, 1.62(3) Å reported for $(CH_3)_2As(O)OH$[1], but the second value does appear to be significantly longer. The As–O(1) and As–O(2) bonds within the structure also appear to be significantly different, but if the least squares estimate of the error were too small by a factor of two, these distances would not be considered significantly different.

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* Computed with the Program FOUR, written by Dr. Charles Fritchie, Tulane University, New Orleans, La.

** See footnote p. 4.

*** Some computations were performed with BDL 4, supplied us by Dr. Ray Davis, University of Texas, Austin, Texas. Others were performed with the program written by W. R. Busing *et al.*, see ref. 4.

TABLE 2

BOND DISTANCES AND ANGLES FOR $(n\text{-}C_4H_9)_2As(O)OH$

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

Distances (Å)		Angles (°)	
As–O(1)	1.67(1)	O(1)–As–O(2)	107.9(5)
As–O(2)	1.74(1)	C(1)–As–C(2)	110.7(7)
As–C(1)	1.96(2)	C(1)–As–O(2)	109.8(7)
As–C(2)	1.95(2)	C(1)–As–O(1)	111.0(7)
C(1)–C(3)	1.53(2)	C(2)–As–O(2)	108.6(7)
C(3)–C(5)	1.59(2)	C(2)–As–O(1)	108.6(7)
C(5)–C(7)	1.55(3)	C(3)–C(1)–As	109(1)
C(2)–C(4)	1.54(2)	C(4)–C(2)–As	110(1)
C(4)–C(6)	1.47(3)	C(6)–C(4)–C(2)	109(2)
C(6)–C(8)	1.61(3)	C(5)–C(3)–C(1)	108(1)
O(1)–O′(2)	2.47(2)	C(8)–C(6)–C(4)	112(2)
C(7)–C″(7)	3.95(5)	C(7)–C(5)–C(3)	108(2)
C(1)–C″(6)	3.98(3)	As–O(1)–O′(2)	117.1(6)
C(2)–C″(1)	4.07(2)	As–O(2)–O′(1)	116.4(6)
C(5)–C″(6)	4.12(3)	*Dihedral angle between planes*	
C(2)–C″(2)	4.20(4)	As–O(1)–O(2)	
C(8)–C″(7)	4.20(4)	O(1)–O′(2)–O′(1)	140.0(7)

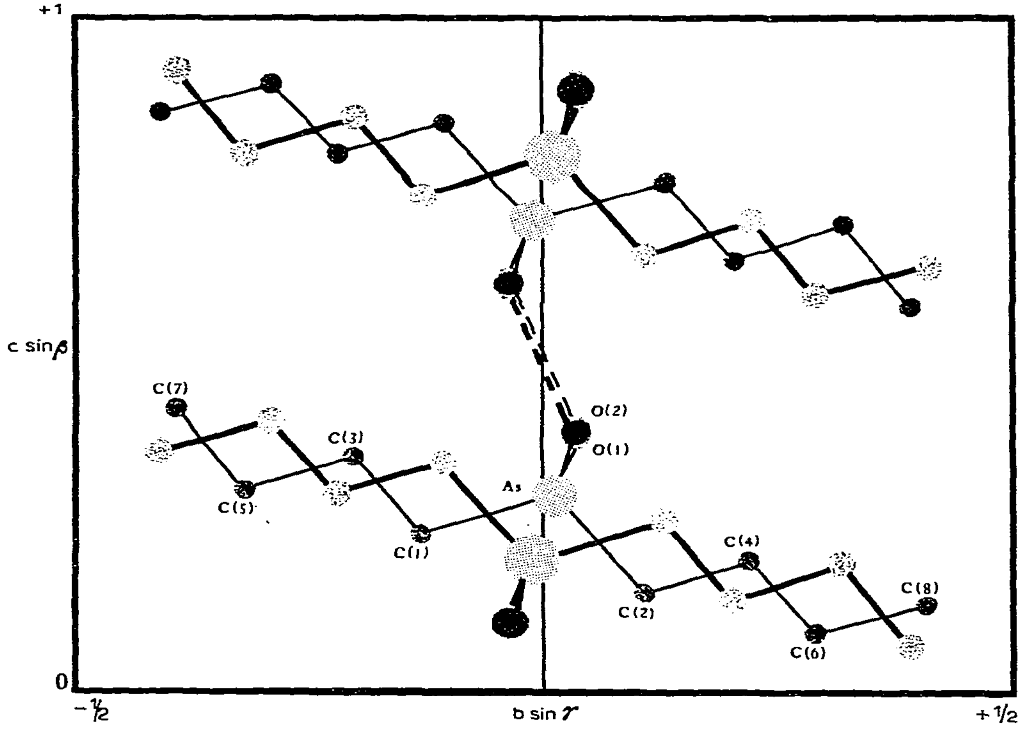

Fig. 1.

The distance between H-bonded oxygens in di-n-butylarsinic acid is short, 2.47(2) Å, compared to 2.57(6) Å for $(CH_3)_2As(O)OH$[1] but the H-bond is probably not symmetrical. The ring formed by the two As and four O atoms in the H-bonded dimer resembles the "chair" configuration in cyclohexane, with the dihedral angle between the planes O(1)–As–O(2) and O(1)–O(2)–O′(2)–O′(1) = 140.0(7)°.

In the alkyl chains, the average C–C bond distance is 1.55(5) Å, the average C–C–C bond angle is 110(2)°. None of the deviations from these averages is considered significant, although the deviations of the distances C(4)–C(6) and C(6)–C(8) are large.

It is of interest to compare the non-bonded C–C contacts within a dimer (intra-dimer contacts) with those between different dimers (inter-dimer contacts). The intra-dimer contacts are long, C(7)–C′(4) = 4.50(4), C(7)–C′(8) = 4.58(5), C(4)–C′(3) = 4.62(2) Å. The inter-dimer contacts are in reasonable agreement with the Van der Waals' contact distance of 4.0 Å[7], C(7)–C″(7) = 3.95(5), C(1)–C″(6) = 3.98(3), C(1)–C″(2) = 4.07(3), C(5)–C″(6) = 4.12(4) Å, C(2)–C″(2) = 4.20(4), C(8)–C″(7) = 4.20(4) with other contacts greater than 4.2 Å.

Although it was not obvious to us at first, the structure of di-n-butylarsinic acid (unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$) is very similar to that of dimethylarsinic acid[1] (unit cell vectors $\vec{a}'$, $\vec{b}'$, $\vec{c}'$), since the $[As(O)OH]_2$ units can be made to nearly superpose in the two structures with $\vec{a}' = \frac{1}{2}(\vec{a} - \vec{c})$, $\vec{c}' = -\frac{1}{2}(\vec{a} + \vec{c})$. The primative unit cell of di-n-butylarsinic acid calculated in this manner is, $a' = 6.66$, $b' = 13.12$, $c' = 6.69$ Å, $\alpha' = 83.6$, $\beta' = 77.5$, $\gamma' = 94.2°$.

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