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CORRELATION OF CRYSTAL STRUCTURE AND PHASE TRANSITION IN DI-*n*-ALKYLARSINIC ACIDS

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ABSTRACT

Single crystals of a series of di-*n*-alkylarsinic acids, $R_2As(O)OH$, $R = CH_3$ to n-C_8H_{17} have been prepared and examined with X-rays. The room temperature forms of these acids are triclinic and unit cell dimensions have been determined. The crystal phase transition which occurs for the *n*-hexyl-, *n*-heptyl-, and *n*-octyl-compounds was observed and unit cell dimensions obtained for the high temperature monoclinic form of the *n*-hexyl- and *n*-octyl acids. Various functions of the cell dimensions were calculated. The *b*-dimension increases regularly with chain length in the low temperature form. The unit cell volume of the low temperature form, as a function of chain length, shows a break at $R = n$-C_5H_{11}. The cell volumes of the high temperature form of n-C_6H_{13} and n-C_8H_{17} lie close to the line drawn through the cell volumes of the low temperature form for $R = CH_3$ to $R = n$-C_4H_9.

INTRODUCTION

Many long-chain compounds exhibit polymorphism in the solid state[1]. A large amount of experimental work and speculation has been devoted to the origin of this property and to other unusual characteristics that are exhibited by these materials[2–8]. Perhaps the most useful of all of the techniques that have been employed for their investigation is X-ray diffraction. Pioneering work has been done with powder X-ray data[9–12], but single crystal studies have become more prominent in recent years since they normally yield much more information regarding the molecular structures which are the basis of the physical properties[13].

Recently, a series of di-*n*-alkylarsinic acids, $R_2As(O)OH$, was prepared in which R varied from CH_3 to n-$C_{20}H_{41}$ inclusive[14,15]. A crystalline phase transition was observed for all members of the series in which the chain was six carbons or longer ($N_c \geq 6$). Enthalpies of transition and melting and X-ray powder data were obtained for the complete series[15]. The structure of $(n\text{-}C_4H_9)_2As(O)OH$ was determined in a single crystal X-ray study[16].

Considerable difficulty was encountered in attempts to grow single crystals of many of these compounds, but this problem has now been overcome to the extent that single crystals have been obtained for the compounds in which N_c = 1–8 inclusive.

This work includes a report of the space groups and unit cell dimensions of these compounds. An attempt is made to relate the crystal parameters to the occurrence of the phase transition, and some X-ray data for the high temperature form of the acids with $N_c = 6$ and $N_c = 8$ is presented.

EXPERIMENTAL

Single crystals of dimethyl- and diethyl-arsinic acids were grown from a saturated water solution by slow evaporation. Di-*n*-propylarsinic acid crystals were grown in an apparatus in which a temperature gradient could be maintained between different regions of a single solution. The apparatus consisted of two aluminum blocks, separated by an air gap. The blocks could be heated separately and were equipped with thermometers. The blocks had been cut so that a shallow, covered, circular glass container could be placed in good thermal contact with both halves at the same time and a temperature gradient maintained across the container. The aqueous solution, saturated at room temperature was introduced into the container and a small amount of solid acid was placed carefully in the solution on the hot (~35°C) side. Single crystals of good quality were removed from the cool (~26°C) region after approximately 12 h. Single crystals of di-*n*-butylarsinic acid were grown by slow evaporation of an aqueous solution. The method used for the di-*n*-pentyl, di-*n*-hexyl, and di-*n*-heptyl acids was the same as that used for the di-*n*-propyl acid, except that the solvent was a mixture of 95% ethanol and glacial acetic acid. Crystals of the di-*n*-octyl acid were grown by slow evaporation of a solution of the acid in 95% ethanol and glacial acetic acid.

Single crystals were mounted on a Buerger precession camera equipped with a Polaroid cassette and examined with Mo Kα radiation ($\lambda = 0.7107$ Å). The density of the crystals (except $N_c = 1$) was determined by flotation in mixtures of known density of CCl_4 and n-C_7H_{16}. Single crystals of the *n*-hexyl, *n*-heptyl, and *n*-octyl acids were heated by a hot air or N_2 stream while mounted on the X-ray apparatus and series of precession photographs were taken below and above the temperature of the phase transition. The unit cell, probable space group and calculated (X-ray) and observed (flotation) density of the compounds are given in Table I. There remains some doubt as to the space group of the high temperature form. The crystals obtained above the phase transition for $N_c = 6$ and $N_c = 8$, although they appear to be single, show heavy background scattering and a steep decline of intensity with increasing θ. The *n*-heptyl single crystals became powders upon passage through the transition.

RESULTS AND DISCUSSION

A crystalline phase transition has been observed for the di-*n*-hexyl-, di-*n*-heptyl-, and di-*n*-octyl-arsinic acids.[7,8]. In Fig. 1, the cell edges *a,b,c* are plotted *vs.* N_c, the number of carbon atoms in the chain, and in Fig. 2, the cell angles α, β, γ *vs.* N_c. The outstanding feature of Fig. 1 is the very regular change of *b* with N_c, corresponding to the equation $b = 2.537N_c + 2.925$.

TABLE I

UNIT CELL DIMENSIONS[a], PROBABLE SPACE GROUP, AND DENSITY OF DI-n-ALKYL ARSINIC ACIDS, $R_2As(O)OH$

R	*a*(Å)	*b*(Å)	*c*(Å)	α(°)	β(°)	γ(°)	d_0(g/ml)[b]	d_c(g/ml)[c]	*Space group*
CH_3[d]	8.34	6.82	10.16	59.5	89.3	106.0	—	1.95	$B\bar{1}$
C_2H_5	8.30	7.98	10.26	83.2	89.3	100.3	1.68	1.66	$B\bar{1}$
n-C_3H_7	8.40	10.57	10.35	87.6	89.6	98.5	1.40	1.42	$B\bar{1}$
n-C_4H_9[d]	8.38	13.12	10.39	91.5	89.9	98.6	1.32	1.31	$B\bar{1}$
n-C_5H_{11}	8.30	15.53	10.14	94.1	90.5	97.4	1.28	1.29	$B\bar{1}$
n-C_6H_{13}	8.41	18.15	10.14	96.4	90.6	97.9	1.24	1.21	$B\bar{1}$
n-C_6H_{13}[e]	8.79	17.51	10.42	90.0	90.0	93.7	—	1.15	monoclinic
n-C_7H_{15}	8.30	20.65	10.06	97.4	90.0	97.9	1.19	1.20	$B\bar{1}$
n-C_8H_{17}	8.26	23.26	9.83	97.1	88.8	95.6	1.12	1.19	$B\bar{1}$
n-C_8H_{17}[e]	8.52	23.04	10.30	90.0	90.0	95.5	—	1.10	monoclinic

[a] Uncertainties in unit cell lengths (a, b, c,) obtained in this work are estimated to be approximately ±0.25%; in cell angles, ±0.5°. All data are for room temperature, approximately 25°C, except for n-C_6H_{13}[e], and n-C_8H_{17}[e]. [b] d_0 Is the density measured by flotation. [c] d_c Is the density calculated from the unit cell volume, 4 molecules of $R_2As(O)OH$ per unit cell. [d] The cell dimensions for CH_3[17] and n-C_4H_9[16] are taken from the single crystal structure determinations, and were only verified in this work. The unit cell dimensions for $(CH_3)_2As(O)OH$ given here were calculated from those used in the single crystal study[17]. [e] These cell dimensions were obtained at a temperature of approximately 120°.

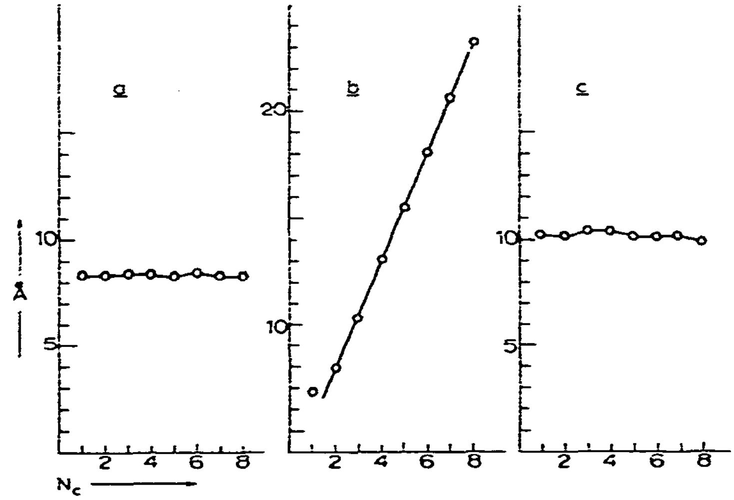

Fig. 1. Unit cell dimensions (*a*, *b*, *c*) *vs*. number of carbons atoms per chain (N_c).

The $N_c = 1$ acid does not fit this line well and there is very little indication of alternation. The triclinic cell dimensions *a* and *c* are practically unchanged from $N_c = 1$ to $N_c = 8$. The angles of Fig. 2 show more irregular behavior, but there does not appear to be any obvious correlation of these individual triclinic unit cell parameters with the occurrence of the phase transition.

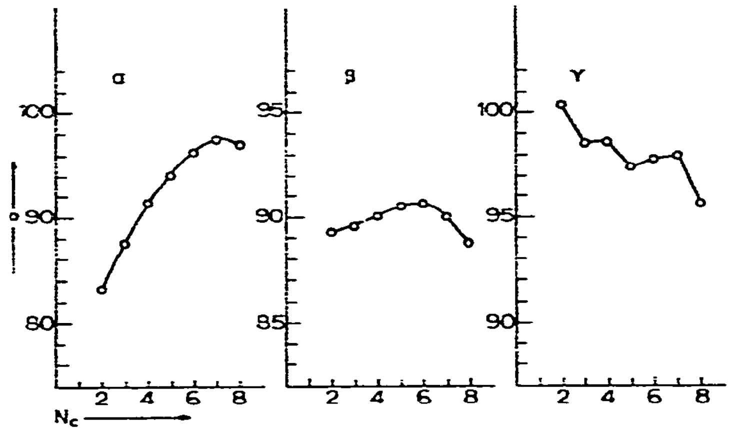

Fig. 2. Unit cell angles (α, β, γ) *vs.* number of carbon atoms per chain (N_c).

Graphs of the (X-ray) density and of the unit cell volume *vs.* N_c, presented in Figs. 3 and 4, seem to be more enlightening. In the graph of the density, a rather pronounced break occurs at $N_c = 5$, and in the triclinic cell volume plot, $N_c = 1$ to 4 seem to fall on one line, $N_c = 6$ to 8 on a second line, with $N_c = 5$ between the two lines. Both of these functions of N_c show an irregularity in the vicinity of $N_c = 6$ where the phase transition is first observed, and the unit cell volume appears to divide the arsinic acids into groups in the same way that the occurrence of the phase transition does. Moreover, the volumes of the unit cells of the high temperature monoclinic forms lie reasonably close to the line extrapolated from the points $N_c = 1$–4. Mea-

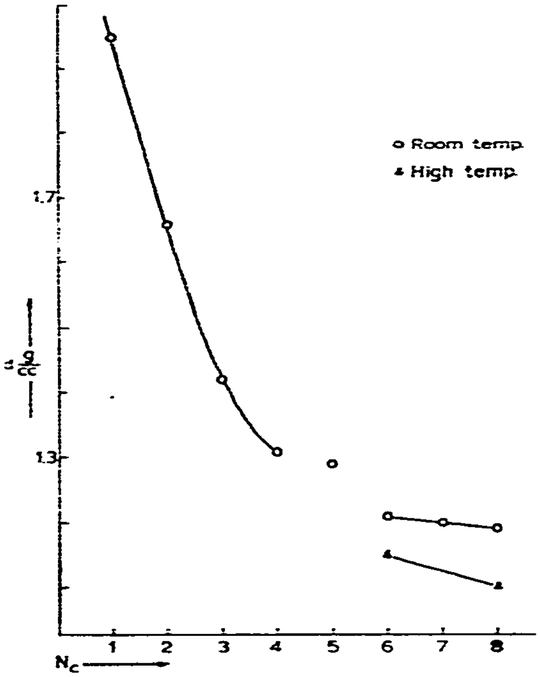

Fig. 3. X-ray densities (*d*) *vs.* number of carbon atoms per chain (N_c). Circles are for room temperature forms and triangles for high temperature forms.

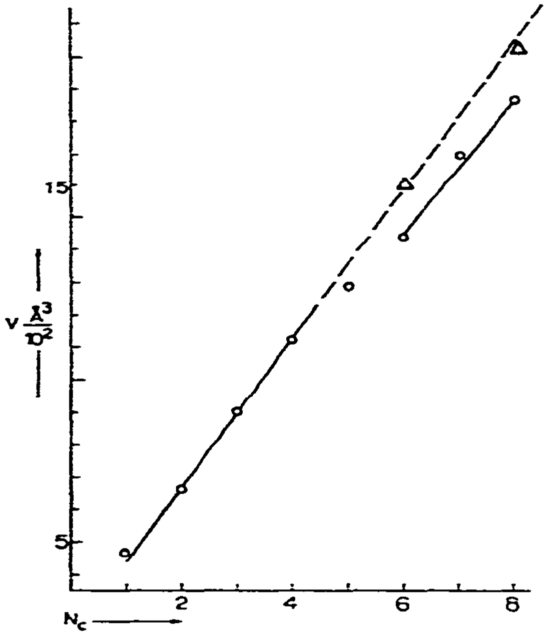

Fig. 4. Unit cell volumes (V) *vs.* number of carbon atoms per chain (N_c). Circles are for room temperature forms and triangles for high temperature forms.

surements of the cell dimensions of the low temperature forms of the acid $N_c = 8$ just below the transition show only a slight expansion from the room temperature value given in Table I. Thus it appears that the phase transition that occurs may be accompanied by a lattice expansion which places all of the cell volumes on one straight line, with the possible exception of $N_c = 5$.

In an attempt to isolate the origin of this behavior of the unit cell volumes, the areas of the three faces of each of the unit cells were calculated and the graphs of these areas *vs.* N_c are shown in Fig. 5. In the triclinic form, the areas of the two faces

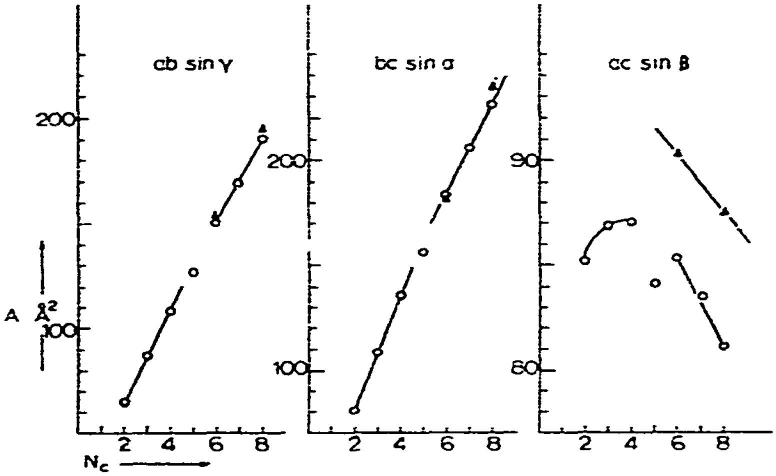

Fig. 5. Areas of unit cell faces (A) *vs.* number of carbon atoms per chain (N_c). Circles are for room temperature forms and triangles for high temperature forms.

which involve the long spacing *b*, show straight line behavior for $N_c = 2$–4 and $N_c = 6$–8, while $N_c = 5$ appears to belong to neither group. However, these deviations are small. The area ac sin β of the triclinic cell has a sharp break at $N_c = 5$. A view of the structure of $(n\text{-}C_4H_9)_2As(O)OH^{16}$ is shown in Fig. 6. There is a close contact between terminal methyl groups in dimers at (x, y, z) and $(x, y+1, z)$. Most of the close van der Waals' contacts, however, occur between atoms in chains of adjacent dimers located at (x, y, z), $(x, y, z+1)$ and (x, y, z), $(x+1/2, y, z+1/2)$. It seems likely that the sharp fall in area, ac sin β, at $N_c = 5$ is associated with a reorientation of the alkyl chains and a consequent change in the collection of close van der Waals' contacts between dimers.

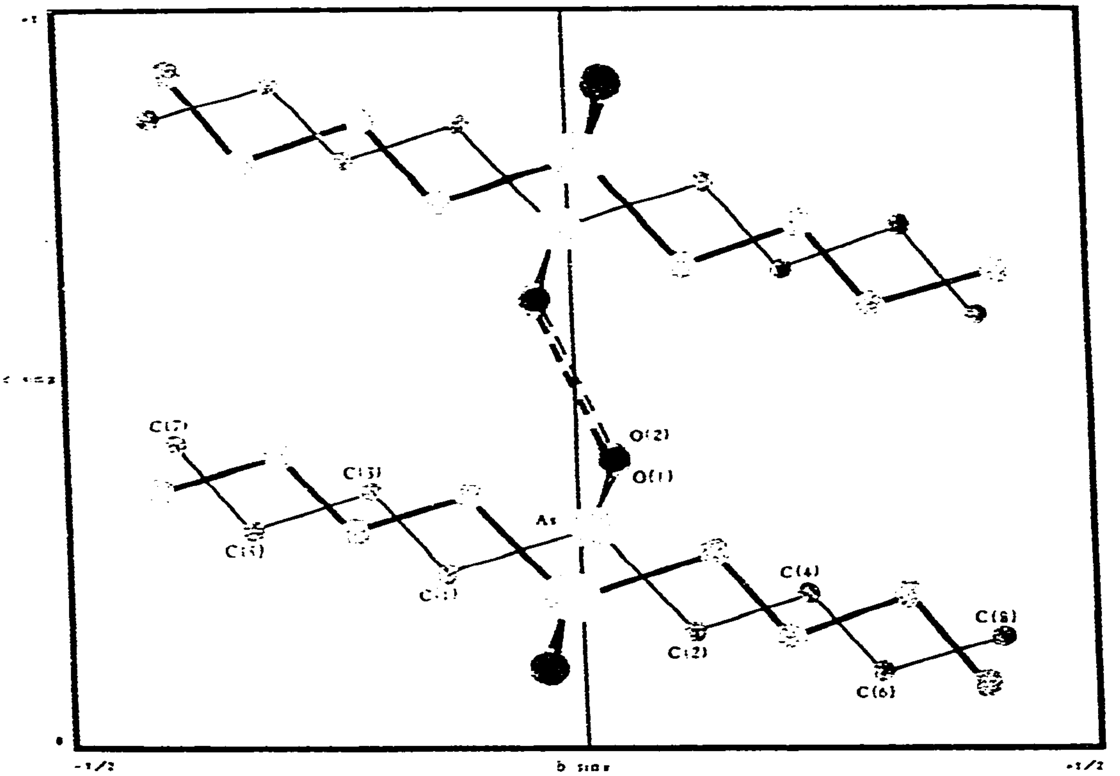

Fig. 6. Structure of $(n\text{-}C_4H_9)_2$ As(O)OH projected along *a*.

The areas of the faces of the monoclinic cells for $N_c = 6$ and $N_c = 8$ are also shown in Fig. 5. The areas ab sin γ and bc show a small increase in the high temperature form (~3%). The greatest change for the C_6 and C_8 cell areas are in the face ac. These increase ~7% and ~8% for the C_6 and C_8 acids respectively. This is further support for the reorientation of the chains and changes in the van der Waals' contacts.

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