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THE ENTHALPIES OF FUSION AND TRANSITION AND X-RAY POWDER PATTERNS OF 20 DI-*n*-ALKYLARSINIC ACIDS

MILTON R. SMITH, KURT J. IRGOLIC, EDWARD A. MEYERS, AND RALPH A. ZINGARO
Department of Chemistry, Texas A&M University, College Station, Texas 77840 (U.S.A.)

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ABSTRACT

The enthalpies and temperatures of fusion and of transition for twenty arsinic acids, $R_2As(O)OH$, have been measured by DTA, where R = *n*-alkyl, CH_3 through *n*-$C_{20}H_{41}$ inclusive. A crystalline transition occurs for acids *n*-C_6H_{13} through *n*-$C_{20}H_{41}$, but not for CH_3 through *n*-C_5H_{11}. The enthalpies of transition vary from 3.9 kcal/mole (C_6) to 12.2 kcal/mole (C_{17}), and show an alternation with change from an even acid to an odd acid. The enthalpies of melting show a reverse alternation, so that the total enthalpy of fusion plus transition does not show a regular pattern of alternation. The X-ray powder patterns for the twenty acids have also been obtained, as well as single crystal data for the C_4 and C_8 acids. These data indicate that all of the compounds crystallize in the triclinic system and that the [010] spacing of the cell chosen increases regularly with chain length.

INTRODUCTION

The synthesis of sixteen *n*-alkylarsinic acids ($R_2As(O)OH$) was reported recently[1]. As a result, a complete series of these compounds has become available in which the *n*-alkyl group varies from C_1 to C_{20}. It was observed[1] that there was an alternation in the melting points of the acids with increasing chain length and that an endothermic process occurred just prior to melting for some of the compounds. With the exception of dimethylarsinic acid, little was known about the physical properties and structures of these compounds, so a systematic investigation of some of their properties seemed desirable.

In this study, the enthalpies of transition and melting for the available arsinic acids have been measured by DTA, and X-ray powder patterns have been obtained and correlated with the single crystal data available[2,3].

EXPERIMENTAL

Materials

Commercially available, Fisher Purified Grade, dimethylarsinic acid was crystallized from hot ethanol. Diethylarsinic acid was prepared in a manner similar to that described previously[1] with the exception that HgO was substituted for H_2O_2 as the oxidizing agent in the preparation. (The yield with HgO was 67% whereas no product was obtained from H_2O_2 oxidation.) Dipropyl- and dibutyl-arsinic acids were prepared by the method described by Quick and Adams[4], and the acids C_5–C_{20} were available[1].

In order to obtain finely divided samples that did not require grinding for DTA and X-ray powder studies, portions of the acids were recrystallized by rapid cooling of hot saturated carbon tetrachloride solutions. Single crystals of dibutylarsinic acid were grown as colorless prisms from slowly cooled aqueous solutions. Only twinned crystals of dioctylarsinic acid could at first be obtained in crystallizations attempted from a number of solvents and under a variety of experimental conditions. However, crystals of suitable quality at last were grown by the slow evaporation of an ethanol–acetic acid solution.

Indium metal, purity 99.999%, was purchased from K & K Laboratories, Inc.

DTA methods

A Robert L. Stone Co. Model KA-2H differential thermal analysis apparatus with J-2 furnace platform, F-1D furnace and SH-11BR4-InZ (dual) sample holder was used. The reference thermocouple was Pt–Pt 10% Rh and the differential thermocouples were Platinel II. This instrument was equipped with dual amplifiers and recorders which made it possible to run two samples simultaneously. In order to lower the heating rate to 1.70 ±0.4 °C/min with the program rate set at its lowest value, a 39,000-Ω resistor was installed in series with the 5000-Ω variable potentiometer in the T. C. selectro switch circuit. Chart speeds where 24.4 and 24.9 in./min for the X_1 and X_2 recorders, respectively, and the range for both recorders was 96 μV full scale. Samples and reference material were contained in small aluminum pans, 0.25 in. in diameter and 0.125 in. in depth, stamped from aluminum kitchen foil with a small die and cutter.

In order to calibrate the DTA apparatus, six samples of indium of approximately 2 mg (m.p. 157°, heat of fusion 0.781 kcal/mole)[5] were weighed in the aluminum sample pans on a microbalance to ±0.003 mg. Thermograms of three pairs of indium samples were run *vs.* 4.0 mg of aluminum as reference from 25 to 200 °C. Endothermic peaks were observed at 157 °C. Areas encompassed by these fusion peaks for the six indium samples were each measured three times with a planimeter. From these areas and the known heat of fusion of indium the responses of the X_1 and X_2 systems were calculated in cal/area. Three values each for the X_1 and X_2 systems were averaged and these mean values used in subsequent calculations. Standard deviation for the calibrated responses (cal/area) of the X_1 and X_2 systems was 2.3%.

For each of the twenty arsinic acids, two samples of approximately 3 mg each were weighed in aluminum sample pans on a microbalance to ±0.003 mg and subsequently run simultaneously against 4.0 mg aluminum from 25 to 200 °C. The curves which resulted displayed well defined peaks and very little drift in the base lines. Each area below the base line was measured three times with a planimeter and the average area used for the calculation of uncorrected ΔH in Table I. The standard deviation for all values of ΔH was 3.5%. Due to the difficulty of resolving the two overlapping endotherms of the C_{17} acid, the deviation might be larger in this case.

TABLE I

ENTHALPIES OF FUSION AND OF THE CRYSTAL TRANSITION FOR DIALKYLARSINIC ACIDS

R	*Temp.* (°*K*) (*transition*) *fusion*	ΔH *uncorrected* (*kcal/mole*) (*transition*) *fusion*	ΔH *correted* (*kcal/mole*) (*transition*) *fusion*
CH_3	473	5.17	4.96
C_2H_5	411	4.64	4.75
C_3H_7	408	5.11	5.27
C_4H_9	412	6.90	7.04
C_5H_{11}	405	8.34	8.60
C_6H_{13}	(393)	(3.75)	(3.93)
	405	5.65	5.82
C_7H_{15}	(389)	(4.63)	(4.86)
	399	6.94	7.20
C_8H_{17}	(379)	(4.62)	(4.95)
	402	8.26	8.55
C_9H_{19}	(383)	(5.48)	(5.81)
	399	8.78	9.11
$C_{10}H_{21}$	(380)	(5.51)	(5.85)
	400	9.76	10.12
$C_{11}H_{23}$	(384)	(6.77)	(7.18)
	396	10.33	10.78
$C_{12}H_{25}$	(385)	(7.09)	(7.50)
	398	11.38	11.81
$C_{13}H_{27}$	(388)	(8.26)	(8.72)
	396	12.08	12.60)
$C_{14}H_{29}$	(390)	(8.93)	(9.38)
	397	13.38	13.91
$C_{15}H_{31}$	(390)	(10.55)	(11.09)
	396	14.56	15.19
$C_{16}H_{33}$	(389)	(10.77)	(11.33)
	395	15.31	15.97
$C_{17}H_{35}$	(390)	(11.57)	(12.17)
	393	15.63	16.39
$C_{18}H_{37}$	394	29.45	30.80
$C_{19}H_{39}$	393	32.80	34.41
$C_{20}H_{41}$	(383)	(9.02)	(9.55)
	393	17.51	18.37

Since the output voltage of the differential thermocouples is a function of temperature, and since this output voltage directly affects the area of any DTA peak observed, it was necessary to introduce a correction factor into the calculation of ΔH at temperatures different from 157°C. For example, from tables published by Olsen and Freeze[6], the output voltage of the differential thermocouples at 157°C was calculated to be 0.0386 mV per degree difference between sample and reference temperatures. At 200°C, the calculated output voltage was 0.0402 mV/degree difference. Thus, the uncorrected ΔH of fusion of dimethylarsinic acid (m.p. 200°C) is too large by a factor of 0.0402/0.0386. The inverse of this ratio is 0.960 and is the T. C. correction factor which has been applied to give the value of the corrected ΔH which is also listed in Table I. The ΔH of fusion and transition for the other acids are similarly corrected.

X-ray methods

A small colorless prism of dibutylarsinic acid was selected from crystals grown from a slowly cooled aqueous solution and placed in a thin-walled (0.01 mm) glass capillary. From precession photographs (MoKα radiation, λ = 0.7107 Å, Zr filter) the unit cell was identified as triclinic. For convenience, the reflections were indexed on the basis of a *B*-centered cell, a = 8.38(2), b = 13.12(3), c = 10.39(2) Å, α = 91.5(5), β = 89.8(5), γ = 98.5(5)°, Z = 4/cell, d(X-ray) = 1.31, d(flotation) = 1.32 g/cm^3.

A number of crystals of dioctylarsinic acid, grown under a variety of conditions, were examined with a Buerger precession camera (Zr filter, MoKα radiation) and in all cases some twinning or other irregularity was observed. From the best crystals, grown from ethanol–acetic acid, it was found that the crystals were triclinic, with a = 8.3, b = 23.0, c = 10.0 Å, α = 98, β = 89, γ = 95°, Z = 4/cell, d(X-ray) = 1.15, d(flotation) = 1.12 g/cm^3.

A finely divided sample of each of the twenty arsinic acids was packed and smoothed into a 1 × 1 × 0.2 cm^3 cavity in a flat plastic plate for examination at room temperature with a GE XRD-5 X-ray diffraction unit equipped with SPG spectrogoniometer, No. 2SPG detector and No. 2SPG Speedomax recorder. Ni filtered Cu radiation (λ = 1.5418 Å) at 35 kvp and 21-mA settings were used with 1° beam slit. The counting range was varied, as required, from 1000 to 5000 counts/sec, the scan rate was 1°/min and 2θ ranged from 2 to 40° (approximately).

RESULTS

Differential thermal analysis (DTA)

The numerical results obtained from the DTA measurements of the twenty arsinic acids studied are given in Table I. Three DTA curves, typical of those obtained, are shown in Fig. 1. A well resolved, endothermic peak was observed prior to melting for the C_6 through C_{17} acids and for the C_{20} acid. No such peak was observed for the C_1 through C_5 acids and only a shoulder on the low temperature side of the peak that corresponds to melting was observed for the C_{18} and C_{19} compounds. The largest temperature difference between the melting point and the transition endotherm was 23° for the C_8 acid and the smallest measured difference was 3° for the C_{17} compound. Thermogravimetric analyses of the C_1, C_4, C_7, C_8, C_{14}, C_{15}, C_{18}, and C_{20} acids showed that no weight losses took place in the samples up to 250°C. Therefore, the endothermic peaks cannot be attributed to either decomposition or anhydride formation, but are likely to be due to a crystalline transition.

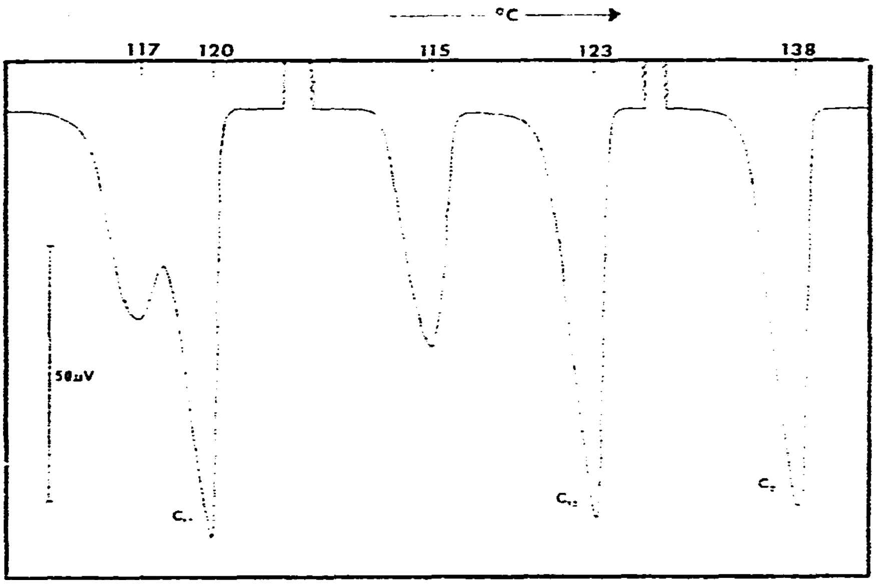

Fig. 1. Some representative DTA thermograms for the dialkylarsinic acids.

In Fig. 2, the enthalpies of transition, the enthalpies of fusion and the sums of these two quantities are plotted against the number of carbon atoms per alkyl chain. The phenomenon of alternation is most apparent in the values measured for the enthalpies of transition, ΔH_{tr}. Proceeding from an acid with an odd number of carbon atoms in each chain to the next higher even member of the series, the increase in ΔH_{tr} is always small and in many cases is practically zero. Proceeding from an even acid to the next higher odd member of the series, a marked increase in ΔH_{tr} is observed.

The values of ΔH_f show a trend toward a reverse alternation, *i.e.*, the increase in ΔH_f in going from an odd to the next higher even member of the series is, in many cases, greater than that observed in going from even to odd. The combination of these trends causes ΔH_T, the sum of the heats of fusion and transition, to display no regular pattern of alternation. The value for the C_{20} compound is somewhat displaced from the trend established by the lower members of the series.

In Fig. 3 the values of the entropies of transition, ΔS_{tr}, the entropies of fusion, ΔS_f, and the sum of the two entropies, ΔS_T, have been plotted against the number of carbon atoms in each alkyl chain. The entropies show essentially the same behavior as that observed for the enthalpies, *e.g.*, the plot of ΔS_{tr} shows the pattern of alternation while that for ΔS_T does not. The value for the C_{20} compound is again significantly removed from the established trend of the other members.

X-ray data

The results of single crystal X-ray data obtained from examination of dibutylarsinic acid[3] as well as cell dimensions obtained for dioctylarsinic acid were used to assist in the interpretation of the powder data, since they supply values of the cell dimensions for two members of the series, and so permit the reflections observed to be indexed. The crystal spacings as obtained from the powdered acids are shown in Table II. Except for the C_1 acid, the [100] and [001] spacings remain essentially constant while the [010] spacings increase regularly. The increase in the [010] spacings also exhibits a slight, but probably real, alternation. The incremental increase in d_{010} is greater in going from an even to an odd member (2.64 Å from C_4 to C_5) than in going from the odd to the next higher even member (2.41 Å from C_5 to C_6). This alternation is relatively consistent although some exceptions are noted, *e.g.*, from C_{14} to C_{15}. In Fig. 4, the number of atoms in the alkyl chain have been plotted against the [010] crystal spacings. Although a straight line may be drawn through the first nineteen points, the C_{20} derivative is once again far removed from the plot.

TABLE II

CRYSTAL SPACINGS IN THE DIALKYLARSINIC ACIDS DETERMINED BY X-RAY POWDER STUDIES

R	d_{100} (Å)	d_{010} (Å)	d_{001} (Å)
CH_3	7.90	5.60	8.46
C_2H_5	8.38	7.91	10.36
C_3H_7	8.34	10.58	10.30
C_4H_9	8.38	12.99	10.38
C_5H_{11}	8.38	15.63	10.42
C_6H_{13}	8.38	18.04	10.30
C_7H_{15}	8.22	20.56	10.30
C_8H_{17}	8.30	22.97	10.18
C_9H_{19}	8.30	25.65	10.15
$C_{10}H_{21}$	8.38	27.99	10.02
$C_{11}H_{23}$	8.38	30.68	10.12
$C_{12}H_{25}$	8.34	32.90	9.90
$C_{13}H_{27}$	8.34	35.51	10.06
$C_{14}H_{29}$	8.38	37.99	9.90
$C_{15}H_{31}$	8.24	40.18	10.42
$C_{16}H_{33}$	8.34	43.09	10.40
$C_{17}H_{35}$	8.34	45.92	10.06
$C_{18}H_{37}$	8.30	48.14	9.96
$C_{19}H_{39}$	8.30	50.52	10.02
$C_{20}H_{41}$	8.34	60.07	10.12

DISCUSSION

The theory of quantitative differential thermal analysis has been discussed by Smothers and Chiang[7]. David[8] has shown that DTA apparatus which has been calibrated with a single, easily handled material may be used under nearly equilibrium conditions for the measurement of reliable enthalpies of fusion of organic and inorganic compounds. In the present study care has been taken to hold constant as many variables as possible in order to obtain reliable values of the enthalpies of fusion and transition.

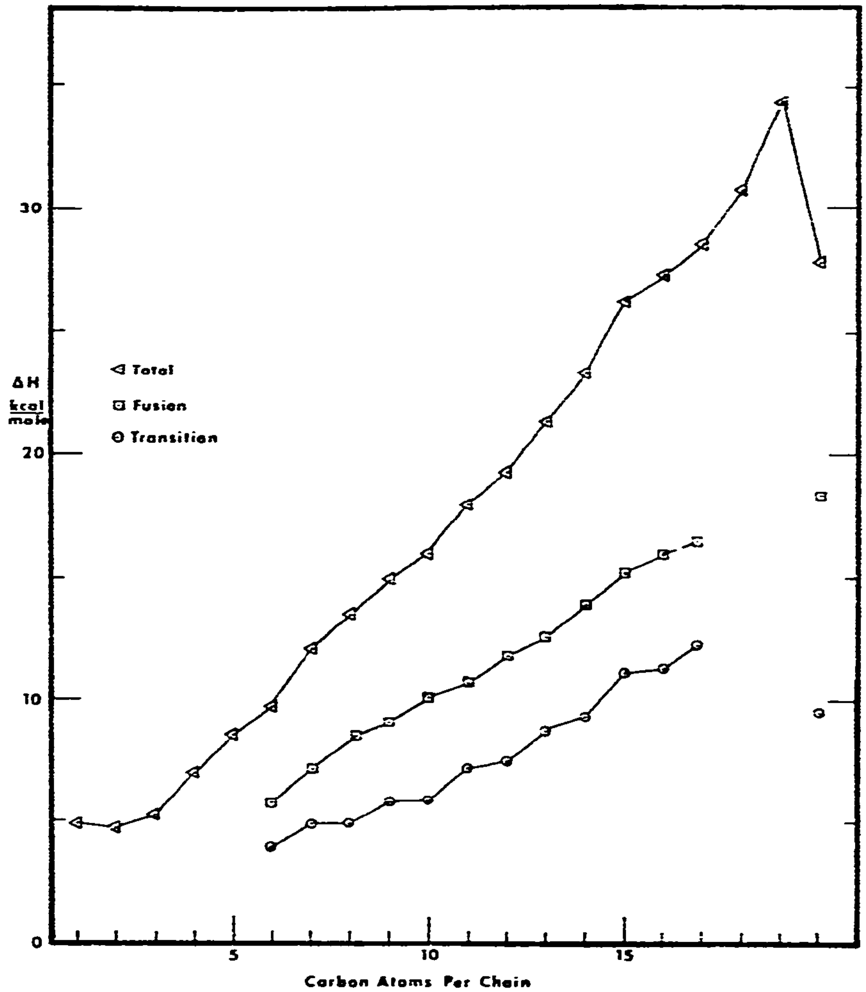

Fig. 2. Plot of ΔH of transition, fusion, and total *vs.* the number of carbon atoms per chain.

The graph of $\Delta S_T = \Delta S_{tr} + \Delta S_f$ *vs.* the number of carbon atoms per chain for the twenty arsinic acids (Fig. 3) consists of a practically linear portion for the higher members of the series but shows a marked deviation from linearity for the lower members. Since no evidence for a phase transition was observed for the C_1 through C_5 acids, ($\Delta S_{tr} = 0$), it is necessary to consider whether the observed deviation from linearity is likely to be due to marked differences in structure of the room temperature modifications of the crystals of the lower and higher members.

Values of ΔS_T are available for *n*-alkylbenzenes and *n*-alkylcyclohexanes[9] and for the odd and even series of saturated carboxylic acids[10]. Graphs like those in Fig. 3 were examined for these series and found to exhibit the same general behavior as shown by the arsinic acids. It is known in the cases cited[9,10] that the crystal structures of the compounds in each series are similar, so that the explanation of the deviation of ΔS_T for lower members from the extrapolated behavior of ΔS_T from the higher members has been sought in other causes, such as hindered rotation of long chains

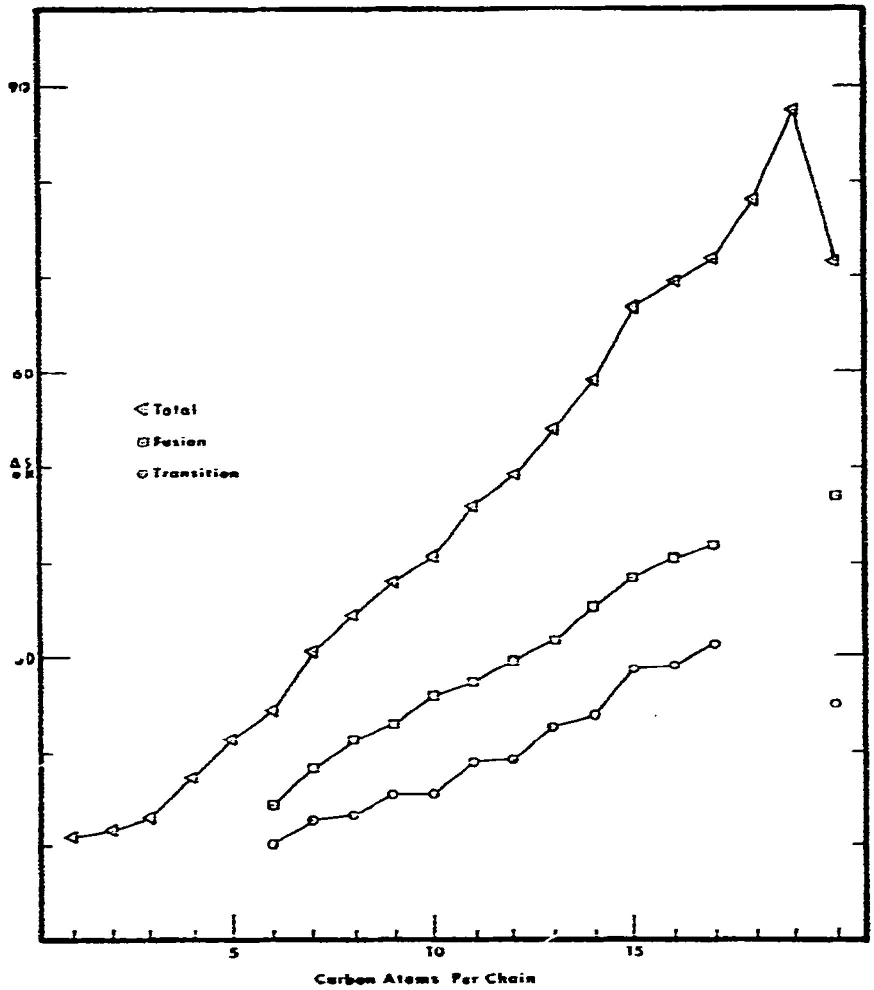

Fig. 3. Plot of ΔS of transition, fusion, and total *vs.* the number of carbon atoms per chain.

in the melt[9]. Thus the behavior shown in Fig. 3 does not contradict the hypothesis that the crystal structure of the room temperature modification of all the arsinic acids is similar, with the possible exception of the C_{20} compound.

Enthalpies of crystal transitions prior to melting have been studied for a number of long chain compounds. Garner and co-workers[11,12] have measured the enthalpies of the $\alpha \rightarrow \beta$ transition for several odd saturated carboxylic acids. These enthalpies are rather small, 1–2 kcal/mole, for acids with as many as 25 carbon atoms in the alkyl chain. The ethyl esters of these acids[13,14], display much larger enthalpies for the $\alpha \rightarrow \beta$ transition. These range from 3.96 for the C_{17} derivative to 8.05 kcal/mole for C_{30}. The enthalpies of transition of the arsinic acids are similar to the enthalpies of transition of ethyl esters which have the same number of carbon atoms. For example, ΔH_{tr} for the C_{10} arsinic acid (20 carbon atoms) is 5.85 kcal/mole, while for the ethyl ester of eicosanoic acid it is 5.46 kcal/mole.

Further similarities between the arsinic acids, and the carboxylic acids and

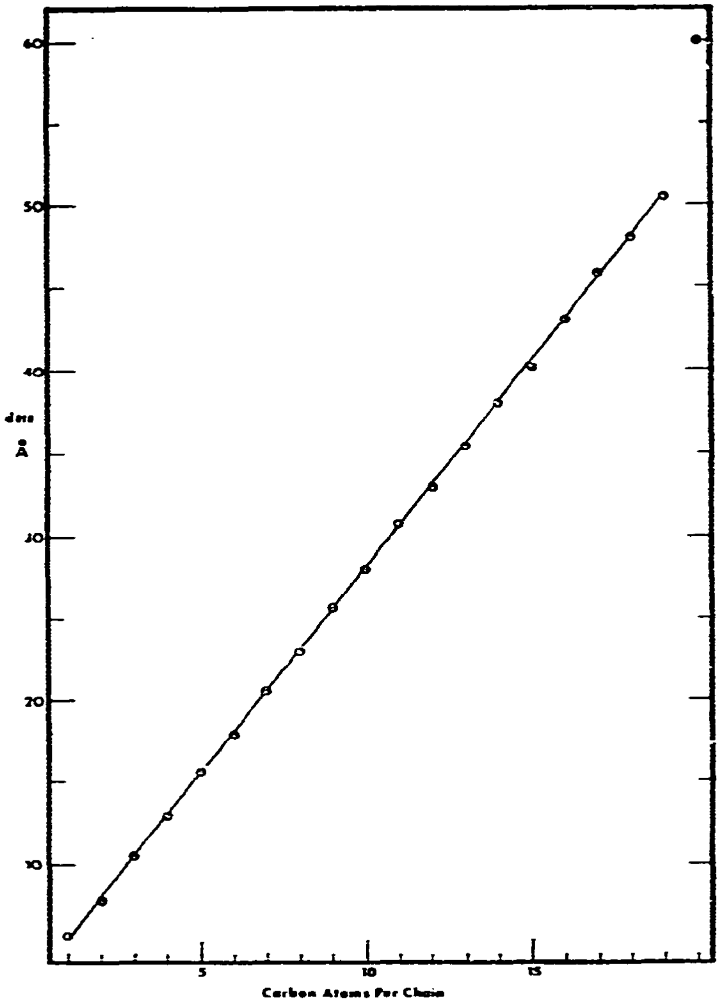

Fig. 4. Plot of the [010] crystal spacings *vs*. the number of carbon atoms per chain.

their ethyl esters are shown by the X-ray powder patterns. For the arsinic acids, the [100] and [001] spacings remain nearly constant, while the [010] spacing increases with increasing chain length. The results obtained by Mueller and Shearer[15,16] are similar. Long crystal spacings of a number of ethyl esters of saturated carboxylic acids were investigated by Francis *et al.*[17,18]. These compounds show polymorphism and even-odd alternation in the long crystal spacings. In the arsinic acid series, there appears to be a slight alternation in the long spacing, d_{010} for the members through C_{13}. This variation is not apparent from C_{14} through C_{20}, but it becomes progressively more difficult to measure [010] with the required degree of accuracy.

It would be possible to speculate at length regarding the origin of the alternation in properties, and about the structures of the arsinic acids above and below the transition temperature. However, these speculations will remain such until further studies are made of the crystal structures of these materials. Attempts are presently being made, to determine the crystal and molecular structure of the high-temperature form of these compounds. From the present work, it appears likely that the low temperature forms of the arsinic acids have similar crystal structures, and that the transition observed in the higher members of the series has some resemblance to that of the ethyl esters of saturated carboxylic acids. A detailed analysis, based on the contacts between the units in the crystals, awaits further work.

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