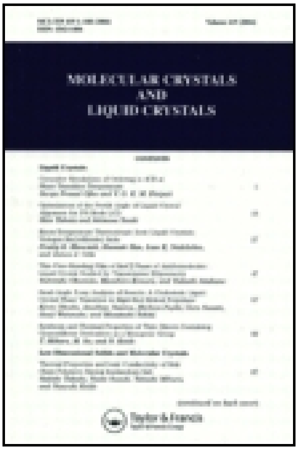

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X-ray Diffraction Studies on Some Even-Chain-Length Lead(II) Carboxylates

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X-ray Diffraction Studies on Some Even-Chain-Length Lead(II) Carboxylates

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X-ray diffraction is used to study structural changes associated with thermotropic phase transitions in a homologous series of even-chain-length lead(II) carboxylates from hexanoate to octadecanoate. For homologues above lead(II) dodecanoate, a lamellar structure with a monolayer molecular organization is indicated at all temperatures up to the melting point. For shorter-chain compounds, the lamellar structure appears to be a bilayer one. In these compounds, the layer spacing decreases markedly with temperature at the crystal-to-mesophase transition point and thereafter remains constant in the temperature range of the mesophase. It is suggested that the layer planes tilt with respect to an axis defined by the hydrocarbon chains on forming a smectic mesophase.

INTRODUCTION

It has been established, recently, that at least one smectic phase is present in the thermotropic phase sequence for certain even-chain-length lead(II) carboxylates[1,2] with 12 carbon atoms or less per chain. Whilst Burrows *et al.*[2] have suggested that this phase is one of the S_A type, at least in the case of lead(II) decanoate, our studies,[1] based on x-ray diffractometry and optical microscopy, indicate a possible S_c structure for this mesophase. Nevertheless, both studies agreed on a bilayer structure for this phase. A mesophase was not observed in the phase sequence for lead(II) tetradecanoate and higher homologues, probably indicative of a different packing arrangement of molecules within lamellar planes. Indeed, such modifications in chain packing, with increasing chain length, were reported in copper(II) carboxylates[3] and suggested for mercury(II) hexadecanoate and octadecanoate.[4]

In this work, the structural changes accompanying thermotropic phase changes in even-chain-length lead(II) hexanoate to octadecanoate, inclusive, are investigated by x-ray diffraction.

EXPERIMENTAL

Materials

The compounds studied were of general formula: $(CH_3(CH_2)_nCOO)_2Pb$ ($n = 4 \ldots 16$). They were prepared as described by Adeosun and Sime[5] and purified by repeated crystallisations from toluene until the melting points were constant. The I.R. spectra showed the compounds to be free of water and excess of fatty acids. The purity of the compounds were checked by carbon (C) and hydrogen (H) elemental analyses. The C and H data were in good agreement with expected values.

X-ray Diffractometry

The compounds were studied by x-ray diffraction of powder samples sealed in glass capillaries of 0.7 mm diameter. The sample of interest was introduced into the capillary by a vacuum melt technique after which the capillary was sealed to minimize any effects of humidity. Each sample was irradiated for 1 hr with Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å). Diffraction patterns were recorded on flat film at a sample-to-film distance of 80.03 mm. The temperature of the sample was controlled by a heated copper block which acted, also, as a collimator for the x-ray beam.

RESULTS AND DISCUSSION

Though the elementary cell parameters could not be derived from the diffraction patterns, they did indicate, from the many reflections observed at ambient temperature, a lamellar structure. This is consistent with the structures reported for these compounds.[1,2,6] A representative x-ray photograph of lead(II) hexadecanoate at 297.5K is shown in Figure 1. A diffuse band was always observed at a Bragg spacing of ca. 9.9Å, probably indicative of some disordered arrangement of molecules within the layers. It is not clear whether this disordering is significant in view of the relatively weak diffraction of x-rays by alkyl chains compared to that of lead ions. For homologues above PbC_{12}, the diffraction patterns in the temperature range, 337–387K, were almost identical to those obtained at ambient temperatures.

The Bragg spacing, d, for each room-temperature crystal structure was calculated from the diameter of the inner diffraction ring by: $d = n\lambda/(2 \sin \theta)$ where n is the order of diffraction, λ is the wavelength of radiation used and θ is the diffraction angle. These values are compared in Table I with molecular lengths (l) calculated from models

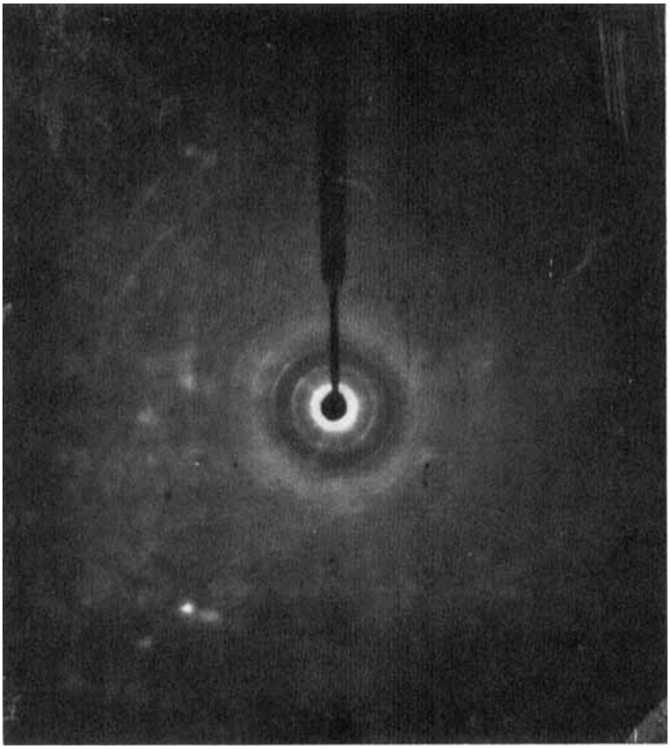

FIGURE 1 X-ray Pattern of PbC_{16} at 297.5K.

TABLE I

Data for Bragg spacings at room temperature and calculated molecular lengths

N_c	d/Å	*l*/Å
6	20.5	11.3
8	26.3	13.8
10	30.9	16.3
12	34.8	18.9
14	19.0	21.4
16	22.9	23.9
18	24.5	26.5

N_c = number of carbon atoms in the chain. Errors in *d* values are within ± 1Å whilst those in *l* are within ± 2Å.

for each compound using the published data of Grant and Dunnell[7] for C—C bond lengths and angles and 2.4Å as the ionic diameter of Pb^{2+}. The data suggest a bilayer structure for the compounds up to PbC_{12} and a monolayer structure for those from PbC_{14} on, both consistent with an orthogonal arrangement of carboxylate chains to the planes containing Pb^{2+} ions. Additionally, these results, in conjunction with the published phase diagram[1] for this series of compounds, suggest that only in those compounds with a room-temperature bilayer structure was a smectic mesophase present in the phase sequence. For homologues higher than PbC_{12} a monolayer crystal structure is apparent and, in these, crystalline polymorphism was observed only.

Whilst *d* remained constant with increasing temperature, up to melting, for homologues above PbC_{12}, for PbC_{12} and below, *d* varied appreciably with temperature over a narrow range (Figure 2). The transition temperature to mesophase, as determined by calorimetric and optical microscopy techniques,[1] falls roughly within this range (338–380K). On forming the mesophase, the *d* value, thereafter, remained virtually constant with increasing temperature. However, at a given temperature (379.5K), *d* varied linearly with N_c in the crystalline phase for PbC_{14} and higher homologues and in the smectic phase for the lower homologues. These results point to a similarity of structures within each of these two groups of homologues.

For the homologues PbC_6 to PbC_{12}, inclusive, the x-ray pattern from the mesophase consisted of a relatively sharp inner ring and a diffuse liquid-like outer ring characteristic of diffraction from a structure with S_A or S_c organization. The *d* spacing did not vary within the temperature range of this phase. Burrows *et al.*,[2] Ellis[1] and Adeosun and Sime[5] have shown, from spectroscopic and calorimetric data,

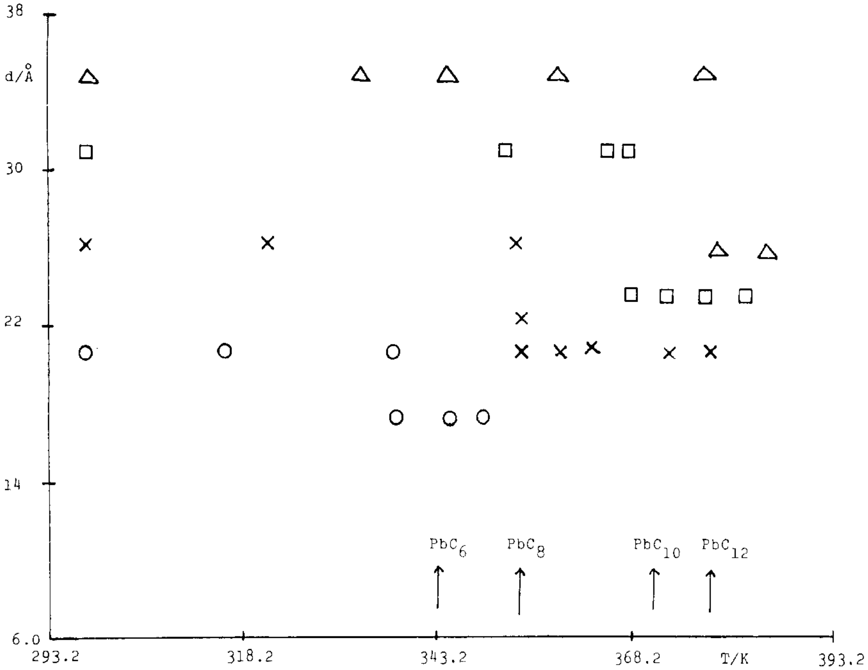

FIGURE 2. Layer spacing as a function of chain length and temperature. O, PbC_6; X, PbC_8; □, PbC_{10}; Δ, PbC_{12}; ↑ represents transition to smectic phase.

that the major process occurring on heating these compounds was the stepwise disordering of hydrocarbon chains in the lattice on forming the various phases. For example, in the case of PbC_{10}, d is reduced from ca. 30.9Å for the unheated crystal structure to ca. 23Å for a mesophase. For a mesophase of the S_A type, such a marked reduction in d is large, but not impossible. The first 10 percent reduction could be as a result of the onset of orientational disorder of the direction of the long axis of the molecule.[8,9] There can be an additional, possibly quite large, reduction because of the transition from all-trans to disordered chains.[2,10-12] Another possibility is the formation of a disordered tilted structure as the molecular organization in the mesophase.[9,10,13,14] However, the mesophases were not found to be optically uniaxial and thus probably are not S_A. The layer planes might tilt with respect to an axis defined by the hydrocarbon chains, and the phase could be S_c.

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