Acta Cryst. (1953). **6**, 797

Density and Unit Cell of *n*-Hexatriacontane

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(*Received* 28 *April* 1953)

n-Hexatriacontane, $C_{36}H_{74}$, is orthorhombic with the unit cell $a = 7{\cdot}440 \pm 0{\cdot}02$, $b = 4{\cdot}955 \pm 0{\cdot}01$, $c = 47{\cdot}61 \pm 0{\cdot}10$ Å. Density calculated from X-ray data is 0·9593±0·004 g.cm.$^{-3}$ at 20° C., observed 0·9609±0·0002 g.cm.$^{-3}$. Thermal expansion and densities of the hexagonal form and of the liquid are given, and chain cross-sections are discussed. They are 17·64 at −183° C., 18·43 at 20° C., 20·30 for the hexagonal form at 75° C. and 22·65 Å^2 for the liquid at 76° C. In the liquid, the chains are packed in a square lattice. The interchain distance does not alter much on the melting of the hexagonal form.

Introduction and results

There are numerous density data for liquid paraffins, but measurements for the solid state are scarce. Seyer, Patterson & Keays (1944) give density–temperature curves for *n*-paraffins from $C_{18}H_{38}$ to $C_{34}H_{70}$. Since their measurements were obtained dilatometrically, they are probably not accurate on an absolute scale.

In order to provide more accurate absolute values, the density of pure *n*-hexatriacontane, $C_{36}H_{74}$, was measured in the range 20–76° C. using the flotation apparatus described in the paper by Vand (1953). The flotation mixture was ethanol–water.

In addition, the unit cell was determined by the X-ray powder method. At 20° C. the sample of *n*-hexatriacontane studied, m.w. = 507·00, is orthorhombic, or nearly orthorhombic, the unit cell being

$$a = 7{\cdot}440 \pm 0{\cdot}02,\ b = 4{\cdot}955 \pm 0{\cdot}01,\ c = 47{\cdot}61 \pm 0{\cdot}10\ \text{Å}\,.$$

The volume of the unit cell V is 1755±7 Å^3 and it contains two molecules. The density calculated from X-ray data is $D_X = 0{\cdot}9593 \pm 0{\cdot}004$ g.cm.$^{-3}$ at 20° C.

In the orthorhombic form, the chains are perpendicular to (001). Monoclinic forms with tilted chains also exist. The orthorhombic form transforms into a hexagonal form with rotating chains at 73·5° C. The hexagonal form melts at 75·5° C. On transition and on melting, a large decrease in density is observed.

The measurements of density at different temperatures are given in Fig. 1. The thermal expansion between 20° C. and 60° C. is linear within experimental error. In this range, the density can be represented by

$$D(t) = 0{\cdot}9687 - 0{\cdot}00039t\,,$$

where the temperature t is in deg. Centigrade. The observed density at 20° C. is 0·9609±0·0002 g.cm.$^{-3}$, in excellent agreement with the density determined from X-ray data.

At 75° C. the density of the hexagonal form is 0·8706 g.cm.$^{-3}$ and at 76° C. the density of liquid hexatriacontane is 0·7802 g.cm.$^{-3}$, in good agreement with 0·7819 g.cm.$^{-3}$, given in *Beilstein* for this paraffin at its melting point. The accuracy of our density figures at higher temperatures is lower than at room temperature.

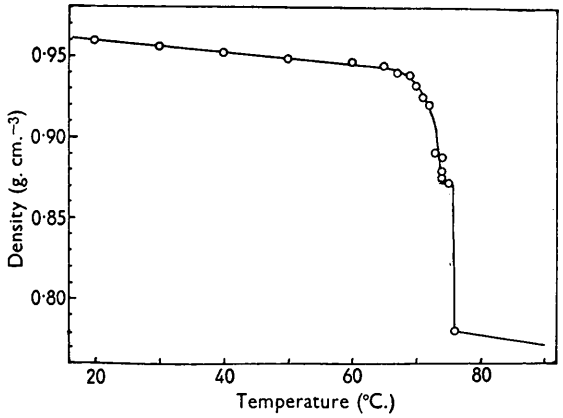

Fig. 1. *n*-Hexatriacontane. Density as a function of temperature.

The measurements above 76° C. were discontinued because of the volatility of ethanol (b.p. 78·3° C.). *iso*-Propyl alcohol–water mixtures were tried, but the paraffin was found to be slightly soluble in the mixture at higher temperatures.

Discussion of the results

As the long spacing d of *n*-paraffins in their orthorhombic form is practically independent of temperature, its room-temperature value can be used to calculate the variation of the cross-section S of the hydrocarbon chain with temperature, using the rela-

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tion $S = kM/Dd$, where $k = 1{\cdot}6604$ and M is the molecular weight. Substituting for n-hexatriacontane, $S = 17{\cdot}68/D$ which gives $S = 18{\cdot}43 \pm 0{\cdot}04$ Å^2 at 20° C. At other temperatures in the 20–60° C. range,

$$S = 18{\cdot}287 + 0{\cdot}0073t\,.$$

Vand & de Boer (1947) pointed out that at room temperature the cross-section of paraffin chains varies with the number N of carbon atoms in the chain. They give an empirical formula

$$S = 18{\cdot}08(1+0{\cdot}54/N) \text{ in kX.}^2\,,$$

which, for $N = 36$, gives $S = 18{\cdot}35$ kX.^{2} = $18{\cdot}39$ Å^2, in good agreement with the observed value. At liquid-air temperature (−183° C.), all paraffins have practically the same cell dimensions $a = 7{\cdot}195$, $b = 4{\cdot}90$ Å and the same $S = 17{\cdot}64$ Å^2, as can be judged from X-ray data of Müller (1930). Extrapolation from our room-temperature formula to −183° C. gives $S = 16{\cdot}951$ Å^2, which is considerably lower than the observed value. One can thus conclude that over wider ranges of temperature, thermal expansion of n-paraffins is markedly non-linear and is probably negligible at very low temperatures.

The long spacing of the hexagonal form is practically the same as that of the orthorhombic form. Assuming constancy of the effective 'long spacing', i.e. effective length of the molecule, to persist up to the liquid state, in spite of some folding of the chains, the cross-sections can be calculated. One obtains for the hexagonal form 20·30 Å^2 at 75° C. and for the liquid form 22·65 Å^2 at 76° C., i.e. expansions from the liquid-air cross-section of 17·64 Å^2 by 2·66 and 5·01 Å^2 respectively, whereas at room temperature, the expansion is by 0·79 Å^2, which is about 30% of the expansion reached in the hexagonal form. In the hexagonal form, $a = \sqrt{3}.b$ and $S = (1/2\sqrt{3})a^2$, so that from S we obtain $a = 8{\cdot}40$, $b = 4{\cdot}85$ Å. Assuming that the chains in liquid paraffin pack in a square array, as observed by electron diffraction, $a = \sqrt{S} = 4{\cdot}86$ Å.

This interchain distance is remarkably close to that of the hexagonal form, which seems to confirm our assumption that, in the liquid state, the chains form in fact a roughly square array and that no great error is made by taking the long spacing to represent the length of the molecule. In the orthorhombic form at room temperature, the interchain distance is $\frac{1}{2}\sqrt{(a^2+b^2)} = 4{\cdot}47$ Å. These values give us some insight into the mechanism of the transition and melting of n-paraffins.

According to measurements of dielectric constant and magnetic dipolar broadening of nuclear resonance absorption lines in solid long-chain compounds (Andrew, 1950), a certain number of the chains rotate at room temperature. If we assume that the area taken by a rotating chain is 20·30 Å^2, and that at liquid-air temperature there is no rotation, then the thermal expansion to 18·43 Å^2 at 20° C. could be accounted for by 30% of the chains rotating at that temperature. The proportion of rotating chains is probably less, because chain vibrations also contribute to the thermal expansion. The number of rotating chains would rapidly increase with increasing temperature, until the hexagonal form is reached.

Owing to effects similar to meshing of gears, if any chain rotates, its neighbours tend to rotate in the opposite direction and a formation of even-membered loops of meshing chains is favoured. In the hexagonal form, a hexagonal mesh of six-membered loops of chains rotating in alternate directions probably develops, each loop enclosing a chain rotating more or less at random at its centre. At the melting point, this structure breaks down and all chains rotate forming a square mesh, the interchain distances remaining practically unaltered.

The structure expands on melting on account of larger volume required by the square packing. This packing is no longer resistant to shear, hence this form is liquid. In addition, long spacings disappear but the chains still seem to stay roughly parallel to each other over short distances.

I wish to thank Mr C. W. Bunn for the specimen of n-hexatriacontane, D. A. Paterson for help in measuring the densities and Prof. J. M. Robertson for his great interest.

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