

# Why is the melting point of propane the lowest among *n*-alkanes?

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Ethane, propane and *n*-butane form layer structures in the solid state. By describing their molecular geometries as a rectangle, an irregular pentagon and an irregular hexagon, respectively, it is shown here that propane cannot close-pack like its congeners. The melting point of propane is therefore lower than expected in the series.

A continuing challenge in understanding the physico-chemical properties of *n*-alkanes and their derivatives has been to establish the structure-property relationships among the lower members ( $C_n \leq 5$ ). A well-known, but less understood, phenomenon in these series of compounds is the melting point alternation; that is, members with an even number of carbon atoms melt at a relatively higher temperature than the odd ones. Other solid state physical properties also show a similar trend. We have carried out crystal structural investigations of *n*-alkanes,<sup>1</sup>  $\alpha,\omega$ -alkanediols,  $\alpha,\omega$ -alkanediamines,<sup>2</sup>  $\alpha,\omega$ -alkanedithiols<sup>3</sup> and  $\alpha,\omega$ -alkanedicarboxylic acids<sup>4</sup> to establish the connections between the alternating physical properties and solid state structures. In the course of our investigations on the series of *n*-alkanes we noted that the melting point of propane ( $-187.7^\circ\text{C}$ ) is the lowest among *n*-alkanes (Fig. 1); it is not only lower than those of ethane ( $-183.3^\circ\text{C}$ ) and *n*-butane ( $-138.3^\circ\text{C}$ ) but also than that of methane ( $-182.5^\circ\text{C}$ ). This unusually low melting point of propane has attracted our attention and here we present a plausible explanation for it.

In the heavier analogues ( $C_n \geq 5$ ) of the above mentioned series we showed that the odd members cannot pack as closely as the even ones, or they are forced to take up torsional strain because of their molecular geometry, and therefore have relatively lower melting points. We have developed a simple geometrical model to illustrate the even-odd effects in these heavier analogues. The model is based on molecular symmetry and shape, and depicts even and odd members as parallelograms and trapezoids, respectively. The model requires that: (a) molecules are arranged into layers, (b)

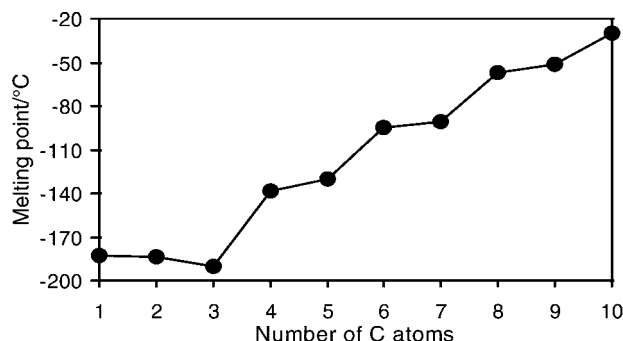


Fig. 1 The melting point alternation in *n*-alkanes.

methylene groups of successive molecules are intergrooved to form columnar stacks and (c) end groups interact with end groups only. In the lower members there is significant interference between the patterns of end groups and methylene groups, and the model is therefore not applicable. Such an interference results in entirely different structures for the lower members, which precludes a one-to-one comparison among these members. Here we shall focus our emphasis on the crystal packing of propane and its very low melting point and contrast it to those of *n*-butane and ethane.

The crystal structure of propane ( $P2_1/n$ ,  $Z = 4$ ) was determined at 30 K.<sup>1</sup> It is constituted of layers of molecules in successive (101) planes, as shown in Fig. 2(a). Adjacent layers are at a typical close-packing separation of 3.60 Å. The inter-layer distance is calculated here and also in the following cases as the distance between successive lattice planes in which molecules are located. The layers in the structure of propane are not perfectly flat but slightly corrugated, because the molecular plane is slightly inclined ( $10^\circ$ ) with respect to the layer plane. The crystal structures of the stable forms of ethane and

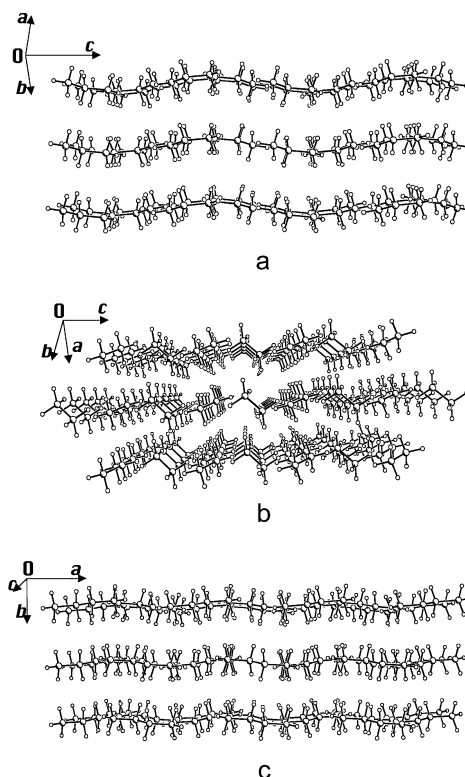
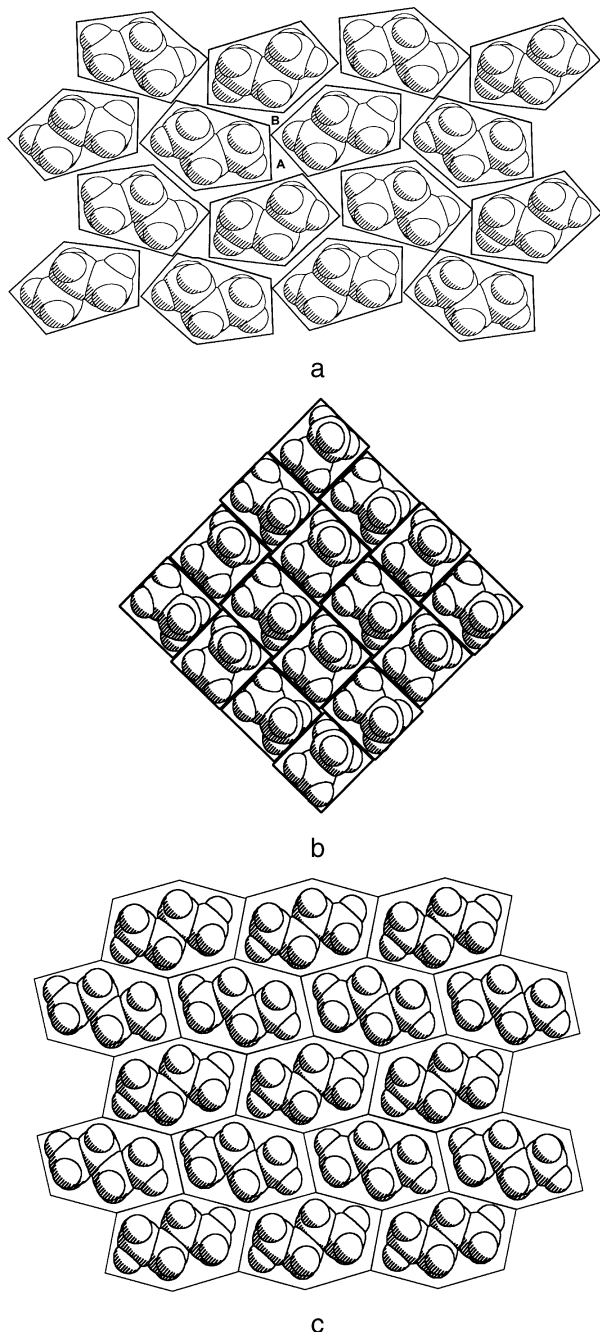


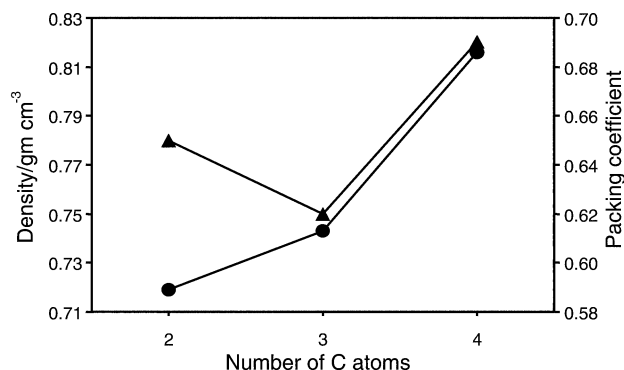
Fig. 2 Crystal structures of (a) propane, (b) ethane and (c) *n*-butane showing three consecutive layers. Note that molecules are inclined with respect to the layer in ethane.



**Fig. 3** (a) View down  $[101]$  showing the layer structure in propane. Molecules are represented as irregular pentagons. Note that there are two types of gaps (A and B) in the pattern. (b) Layer structure in ethane. Molecules are represented as rectangles. Note that the pattern has almost no gaps. (c) Layer structure in *n*-butane. Molecules are represented as irregular hexagons. Note that there are no gaps in the pattern. Compare (b) and (c) and contrast these with (a).

*n*-butane (determined at 90 K)<sup>5,6</sup> can also be dissected into layers [Figs. 2](b) and (c). As in propane, the layers in *n*-butane are at a close packing separation of 3.64 Å. The layer separation in ethane (3.38 Å) is smaller than in propane and *n*-butane, indicating some interlayer contacts. This is also reflected by the fact that while the molecular plane coincides with the layer plane in propane and *n*-butane, it deviates significantly in the case of ethane. It follows that while intra- and interlayer arrangements contribute significantly to the packing of ethane, intralayer arrangements assume greater importance in the case of propane and *n*-butane.

Fig. 3(a) shows the molecular arrangement within a layer in the structure of propane. Figs. 3(b) and (c) display the corresponding arrangements for ethane and *n*-butane. A molecule of propane can be described in the plane of its carbon skele-



**Fig. 4** Trends of density (●) and packing coefficients (▲) with increasing number of C atoms. Note that the density of propane lies below the line joining the densities of ethane and *n*-butane.

ton as an irregular pentagon. Similarly, ethane and *n*-butane can be depicted as a rectangle and an irregular hexagon, respectively. These polygons are developed on the basis of van der Waals surfaces. From Figs. 3(b) and (c) it may be seen that the packing of rectangles and hexagons is such that it leaves either very little space (in ethane),<sup>7</sup> or no space (in *n*-butane) between adjacent polygons. These packing patterns are driven by the juxtaposition of complementary portions (crests and troughs) on ethane or *n*-butane molecules. We shall now examine the layer structure of propane. Without the consideration of pentagons, the packing within the layer would appear quite normal with various methylene-methyl close-packing motifs. However, this does not explain the relatively lower packing density and coefficients<sup>8</sup> of propane compared to those of ethane and *n*-butane (Fig. 4). The gaps in the pattern become evident when the packing of pentagons is considered. There are two types of gaps [A and B in Fig. 3(a)] and each molecule is surrounded by a total of six gaps (three A and three B). While there are several ways in which pentagons can be arranged into a two-dimensional lattice,<sup>9</sup> the pattern shown in Fig. 3(a) certainly results in a maximum number of complementary close-packing contacts and therefore is observed. The gaps in the patterns of pentagons are inevitable because fivefold symmetry is forbidden for periodic close packing. On the other hand, the geometries of ethane and *n*-butane represent symmetries that are not forbidden for periodic close-packing. The gaps in the packing pattern of propane lower its packing efficiency. It is for this reason that the melting point of propane is much lower than expected in the homologous series.

Finally, it may be said that the application of two-dimensional geometrical models is only possible because *n*-alkanes form layer structures in the solid state. Though the description of three-dimensional molecules as two-dimensional geometrical objects seems to be rather simplistic, we find that it helps in the understanding of physical phenomena that are otherwise difficult to perceive.

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