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Calculation of Lattice Sums and Heats of Sublimation of Long-Chain Even *n*-Alkanes

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Crystal energies at 0 K and 25°C of three polymorphic forms of the normal alkanes $C_{28}H_{58}$ and $C_{36}H_{74}$ have been calculated from crystal structure data with a Lennard-Jones 6–12 potential. Taking into account the side packing and end packing energies, a general expression for the heat of sublimation at 25°C has been derived, *viz* $\Delta H^0_{\rm sub} = 8{\cdot}24 n_{\rm C} + 4{\cdot}10$ kJ mol^{-1}, where $n_{\rm C}$ is the number of C atoms in the molecule. The agreement with the two known experimental values (for $C_{18}H_{38}$ and $C_{32}H_{66}$) is within 1%.

Introduction

In the search for an explanation of the observed growth kinetics of paraffin crystals growing from solution (Grassi, 1973; Simon, Grassi & Boistelle, 1974; Doussoulin, 1975; Boistelle & Doussoulin, 1976; Madsen, 1976*a*) we needed information about the energies of interaction of one molecule at some given position in the crystal with other molecules belonging either to the crystal or to the solution. For a molecule at the repeatable step the total energy (half-crystal energy) is closely related to the heat of sublimation which is, however, unknown for octacosane and hexatriacontane, the paraffins we have studied. Knowing the crystal structure and the potential energy of two molecules as a function of their separation we are able to calculate the half-crystal energy as well as other important interaction energies. Conversely, an independent knowledge of the heat of sublimation of some long-chain alkane of similar structure would provide us with a test of adequacy of the potential function used. Finally, we are interested in equilibrium shapes of crystals; these are deducible from surface energies which, in turn, may be calculated from appropriate lattice sums.

Structural features

Octacosane, $C_{28}H_{58}$, and hexatriacontane, $C_{36}H_{74}$, which are of particular interest to us, crystallize in several different crystal phases. The structures of monoclinic and orthorhombic phases of $C_{36}H_{74}$ have been determined by Shearer & Vand (1956) and by Teare (1959), respectively. The orthorhombic polytypic structure of $C_{28}H_{58}$ has been determined by Boistelle, Simon & Pepe (1976). From these three

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structures, all other homologues may be deduced by extrapolation (Nyburg & Potworowski, 1973). Each structure consists of stacked layers and, for the problem we are concerned with, we shall distinguish the molecular side packing energy (within a layer) from the end group packing energy (between two adjacent layers).

From thermodynamic data Mnyukh (1963) has calculated lattice energies of *n*-alkanes up to $C_{16}H_{34}$ and established a relation of the form

$$U^0 = -(An_C + B). \tag{1}$$

For the triclinic (n_C even) structures $A = 7{\cdot}39$ and $B = 12{\cdot}45$ kJ mol^{-1}. These values correspond to the side packing and end group packing energies. In addition, Mnyukh showed that the crystal energy of the last member of the triclinic series is nearly equal to that of the monoclinic phase with the same number of C atoms. From earlier experimental data reviewed by Broadhurst (1962) and Turner (1971) it was expected that this last member had $n_C = 26$, whereas more recently Nyburg & Potworowski (1973) predicted triclinic structures up to $C_{36}H_{74}$. Our own observations seem to confirm the latter prediction, since we obtained triclinic octacosane crystals from light petroleum ether solution between 0 and 10 °C, whereas at room temperature we obtained only the monoclinic or orthorhombic (polytypic modification) phase. The cell parameters of the triclinic phase, with predicted values (Nyburg & Potworowski, 1973) in parentheses, are: $a = 4{\cdot}267$ (4·28), $b = 4{\cdot}805$ (4·82), $c = 37{\cdot}657$ Å (37·58), $\alpha = 86{\cdot}77$ (87), $\beta = 69{\cdot}30$ (69·11), $\gamma = 72{\cdot}90°$ (72·70), space group $P\bar{1}$.

Method of calculation

The Lennard–Jones 6–12 potential

$$U(r) = \varepsilon \left(\frac{r^{*12}}{r^{12}} - 2\frac{r^{*6}}{r^{6}} \right) \tag{2}$$

is known to be a good representation of the potential of London (or van der Waals) forces, *i.e.* forces between non-polar molecules. Its direct applicability is limited to atoms or small molecules, but a multicentre model may be used for larger molecules. We choose a model with n_C centres, with each centre at a C nucleus and all centres equivalent despite the fact that end groups are CH_3 instead of CH_2. The total interaction between two molecules is thus the sum of n_C^2 interactions of the form (2). The potential energy per molecule of a crystal is equal to the energy of interaction of one molecule situated at the repeatable step with all other molecules in the crystal; we thus have

$$U_p^0 = \varepsilon \sum_k \sum_{ij} \left(\frac{r^{*12}}{r_{ijk}^{12}} - 2\frac{r^{*6}}{r_{ijk}^{6}} \right) \tag{3}$$

where $1 \le i,j \le n_C$, and $\sum_k$ is the sum over all molecules in the crystal.

It is assumed that the intermolecular spacing in the crystal corresponds to the minimum value of U_p^0. Hence we may calculate r^* from $\partial U_p^0/\partial r^* = 0$. We find

$$r^* = \left(\sum_k \sum_{ij} r_{ijk}^{-6} / \sum_k \sum_{ij} r_{ijk}^{-12} \right)^{1/6}. \tag{4}$$

The total energy of a crystal is equal to the sum of the potential and kinetic energy of lattice modes. For polyatomic non-linear molecules we have three translational and three rotational degrees of freedom per molecule. We shall assume the validity of the Debye theory for the former. If ν_D is the vibration frequency of a single molecule in its potential well with all the other molecules held fixed, we have for the Debye temperature

$$\theta_D = \sqrt{5/3}\, h\nu_D/k. \tag{5}$$

Strictly, in view of the anisotropy of our crystals, we ought to consider three different frequencies, but we believe that the root-mean-square value will do. Denoting by $U_p(\mathbf{r})$ the potential energy of a molecule as a function of its displacement $\mathbf{r}$ from its equilibrium position we find for the force constant in the $\mathbf{x}$ direction

$$\begin{aligned} f_x &= \partial^2 U_p/\partial x^2|_{x=0} \\ &= \sum_k \sum_{ij} \left[U''(r_{ijk}) \frac{x_{ijk}^2}{r_{ijk}^2} + U'(r_{ijk}) \left(\frac{1}{r_{ijk}} - \frac{x_{ijk}^2}{r_{ijk}^3} \right) \right] \end{aligned} \tag{6}$$

and similarly for f_y and f_z, where $x_{ijk}^2 + y_{ijk}^2 + z_{ijk}^2 = r_{ijk}^2$, and U' and U'' are the first and second derivative of $U(r)$ as given by (2). The mean force constant is then

$$\begin{aligned} \bar{f} &= \tfrac{1}{3}(f_x + f_y + f_z) \\ &= \tfrac{1}{3} \sum_k \sum_{ij} \left[U''(r_{ijk}) + \frac{2}{r_{ijk}} U'(r_{ijk}) \right]. \end{aligned} \tag{7}$$

Using (2) and multiplying by two because we perform the sums over only half of the crystal we obtain

$$\bar{f} = \varepsilon \sum_k \sum_{ij} \left(88 \frac{r^{*12}}{r_{ijk}^{14}} - 40 \frac{r^{*6}}{r_{ijk}^{8}} \right) \tag{8}$$

and ν_D is found from

$$\nu_D = \sqrt{\bar{f}/m}/2\pi. \tag{9}$$

The thermal energy of a crystal at temperature T is, according to the Debye theory,

$$U_D = 3RTD(\theta_D/T) \tag{10}$$

where

$$D(\theta_D/T) = \frac{3T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3 \mathrm{d}x}{e^x - 1}. \tag{11}$$

The rotational lattice modes show up as distinct bands in low-frequency Raman spectra (Olf & Fanconi, 1973; Vergoten, Fleury, Tasumi & Shimanouchi, 1973). This suggests that the Einstein theory is better for these vibrations than the Debye theory. We thus have

$$\theta_{Ei} = h\nu_i/k = hc\tilde{\nu}_i/k \tag{12}$$

where $\tilde{\nu}_i$ is the wavenumber. Vergoten *et al.* (1973) found six frequencies for hexatriacontane, so the energy per mol equals half the sum of the six Einstein functions, *viz*

$$U_E = \tfrac{1}{2} \sum_{i=1}^{6} R\theta_{Ei}[\exp(\theta_{Ei}/T) - 1]^{-1}. \tag{13}$$

At 0 K we have

$$U_D^0 = \tfrac{9}{8} R\theta_D \tag{14}$$

$$U_E^0 = \frac{R}{4} \sum_{i=1}^{6} \theta_{Ei}\ . \tag{15}$$

Finally, we wish to calculate ΔH for the transformation crystal → ideal gas at 25°C. We assume that the energy of intramolecular vibrations is the same in the two states. Then we have first a contribution of $4RT$ ($\tfrac{3}{2}RT$ for translation $+\tfrac{3}{2}RT$ for rotation $+pV$), and next an energy of configuration from the C–C bonds which are not in the *trans* conformation. Departing from the rotational isomeric state approximation (Volkenstein, 1963) and using the matrix method for establishing the configurational partition function (Flory, 1969) we may show (Madsen, 1976*b*) that the configurational energy may be written

$$\begin{aligned} U_{\text{conf}} = \frac{\lambda_1 - 1}{\lambda_1(\lambda_1 - \lambda_2)} \Big\{ & [(1-\lambda_2)E_\sigma + \sigma\psi(E_\sigma + E_\psi) \\ & + \sigma\omega(E_\sigma + E_\omega)] \left(n_C - 3 - \frac{\lambda_2}{\lambda_1 - \lambda_2}\right) \\ & + \left[(\lambda_1 - 1)E_\sigma - \sigma\psi(E_\sigma + E_\psi) - \sigma\omega(E_\sigma - E_\omega)\right] \frac{\lambda_1}{\lambda_1 - \lambda_2} \Big\} \end{aligned} \tag{16}$$

where E_σ is the energy of an isolated *gauche* conformation (2·22 kJ mol^{-1}), E_ψ is the energy of interaction between two neighbouring *gauche* conformations of the same sign (0·50 kJ mol^{-1}), E_ω is the energy of interaction between two neighbouring *gauche* conformations of opposite sign (9·0 kJ mol^{-1}), and

$$\sigma = \exp(-E_\sigma/RT)$$

$$\psi = \exp(-E_\psi/RT)$$

$$\omega = \exp(-E_\omega/RT)$$

$$\lambda_1 = \tfrac{1}{2}\{1 + \sigma(\psi+\omega) + \sqrt{[1 - \sigma(\psi+\omega)]^2 + 8\sigma}\}$$

$$\lambda_2 = \tfrac{1}{2}\{1 + \sigma(\psi+\omega) - \sqrt{[1 - \sigma(\psi+\omega)]^2 + 8\sigma}\}\ .$$

Results

The LJ potential falls off rapidly with distance. For instance, the contribution to the lattice sum of a molecule for which the centre of gravity is at a distance of 23 Å from the origin is only 7×10^{-5} of the total. We have cut off the sums at this level, thus taking into account 99 molecules altogether. Table 1 gives the results for the different phases of $C_{28}H_{58}$ and $C_{36}H_{74}$.

The difference between results for the different structures may be more or less spurious, because both U_p^0 and r^* are very sensitive to small differences in nearest-neighbour distances. The small uncertainty in the atomic positions easily admits the discrepancies found here. As the standard deviation on r^* is of the same magnitude as that of the atomic positions, we regard the adequacy of our treatment as fully verified. Furthermore, as pointed out by Mnyukh (1963), the lattice energy at 0 K of paraffins having the same n_C is lower for the monoclinic phase than for the orthorhombic one. From this point of view, the values of U_p^0/ε are in the proper order.

So, if Mnyukh's values are valid up to $n_C = 36$, and after correction for the zero-point energy which enters into B (see later), we find

$$U_p^0 = -281{\cdot}24 \text{ kJ mol}^{-1} \text{ for } C_{36}H_{74}.$$

Using the calculated lattice sums for the monoclinic phase we obtain $\varepsilon/k = 55{\cdot}26$ K, from which

$$U_p^0 = -219{\cdot}56 \text{ kJ mol}^{-1} \text{ for } C_{28}H_{58}.$$

Table 1. *Lattice sums and r^* for three phases of octacosane and hexatriacontane*

		Phase			
Alkane		Monoclinic	Polytypic	Orthorhombic	Mean
$C_{28}H_{58}$	U_p^0/ε	−477·85	−486·07	−487·68	
	r^* (Å)	4·682	4·673	4·669	4·675 ± 0·007
$C_{36}H_{74}$	U_p^0/ε	−612·10	−620·19	−626·00	
	r^* (Å)	4·670	4·665	4·670	4·668 ± 0·003
					4·672 ± 0·006 Å

Table 2. *Debye theory parameters*

Alkane	f/ε, Å^{-2}	$\nu \times 10^{-12}$, s^{-1}	θ_D, K	U_D^0 kJ mol^{-1}	U_D kJ mol^{-1}
$C_{28}H_{58}$	1461	2·0227	125·36	1·173	6·329
$C_{36}H_{74}$	1877	2·0254	125·53		

Results for lattice mode calculations are summarized in Tables 2 and 3. We find very nearly the same Debye temperature for the two alkanes. This is to be expected, since the mass as well as the force constant are very nearly proportional to n_C. For similar reasons we expect the same rotational vibrational frequencies; they have not been measured for octacosane.

Table 3. *Einstein theory parameters*

$\tilde{\nu}_i$, cm^{-1}	θ_{Ei}, K	U^0_{Ei} kJ mol^{-1}	U_{Ei} at 25 °C kJ mol^{-1}
5	7·2	0·030	2·449
8	11·5	0·048	2·432
81	116·5	0·484	2·026
113	162·5	0·676	1·865
139	200	0·831	1·740
182	262	1·089	1·547
Total U_E, kJ mol^{-1}		1·579	6·027

Table 4. *Calculated energies for octacosane and hexatriacontane, in* kJ mol^{-1}

Alkane	$C_{28}H_{58}$	$C_{36}H_{74}$	A	B
U^0_p	−219·56	−281·24	−7·46	−11·46
U at 0 K	−216·79	−278·49	−7·46	−8·71
U at 25 °C	−204·63	−266·13	−7·46	3·65
H at 25 °C	−204·59	−266·09	−7·46	3·65
U_{conf} at 25 °C	19·72	25·97	0·78	−2·16
ΔH^0_{sub} at 25 °C	234·23	301·98	8·24	4·11

The calculated energies and enthalpies are summarized in Table 4.

Discussion

In order to be able to determine the parameter ε in the Lennard–Jones expression (2), we have had to make use of some independently known crystal energy; we have chosen the formula of Mnyukh, (1), which we have used for hexatriacontane. The self-consistency of our calculations is obvious. The question of whether our value of ε/k agrees with data for short-chain hydrocarbons from viscosity or second virial coefficient is difficult, because in the latter case molecules are treated as nearly spherical, and consequently a value of r somewhat greater than ours is found. It is interesting to note, however, that our value of ε/k is close to $\frac{1}{4}$ of the value for butane and $\frac{1}{5}$ of the value for pentane; these molecules are the shortest ones which 'look like' long-chain alkanes, yet are small enough to keep the single-centre treatment valid.

Our calculations were performed in such a way that side packing and end group packing contributions may be extracted separately. With the representation $U=An_C+B$ we find for U^0_p/ε

$$A=-16{\cdot}106;\; B=-26{\cdot}89\;(C_{28}H_{58})$$
$$A=-16{\cdot}363;\; B=-23{\cdot}00\;(C_{36}H_{74})$$
$$A=-16{\cdot}23;\; B=-24{\cdot}94\;(\text{mean})\,.$$

This yields the values in the two last columns in Table 4. Only B is affected by lattice mode contributions, since they are independent of chain length. The difference between U and H at 25 °C is too small to show up in A and B.

In order to agree with the predicted transition from triclinic to monoclinic structure at $n_C=36$, our value of A should be numerically larger than that of Mnyukh, whereas B should be smaller, and such is, in fact, the case. Finally, calculated values of ΔH^0_{sub} at 25 °C should agree with experimental ones. ΔH^0_f for a gaseous paraffin may be calculated from increments per CH_3 and CH_2 (*Landolt-Börnstein*, 1961), and ΔH^0_f is known for two solid paraffins, $C_{18}H_{38}$ and $C_{32}H_{66}$, from calorimetry (Parks, West, Naylor, Fujii & McClaine, 1946). Subtraction yields $\Delta H^0_{\text{sub}}=154{\cdot}1\pm 2{\cdot}4$ kJ mol^{-1} for $C_{18}H_{38}$ and $266{\cdot}6\pm3{\cdot}2$ kJ mol^{-1} for $C_{32}H_{66}$. Our calculated values are 152·43 kJ mol^{-1} for $C_{18}H_{38}$ and 267·79 kJ mol^{-1} for $C_{32}H_{66}$. This agreement justifies our treatment, and we may feel confident with calculations of other quantities by this method.

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