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Interatomic Potential Functions for Hydrocarbons from Crystal Data: Transferability of the Empirical Parameters

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The transferability of (6-exp) interatomic non-bonded potential functions for hydrocarbons previously derived from low-temperature structures extrapolated to 0 K, sublimation heats and elasticity data of model molecular crystals, was tested by calculation of properties of other crystals not involved in the earlier optimization process. Equilibrium structures and sublimation heats were calculated, in agreement with experiment, for methane CH_4, adamantane $(CH_2)_6(CH)_4$, 2,2-paracyclophane $(CH_2)_4(C_6H_4)_2$ and 3,3-paracyclophane $(CH_2)_6(C_6H_4)_2$ crystals. The solid–solid phase-transition characteristics of adamantane were described consistently with the same potential force field. For the cubic phase of adamantane the orientationally disordered molecular arrangement, suggested by X-ray experiment, was predicted theoretically. The calculation of the structures and heats of sublimation of the same crystals were repeated with a set of potential functions derived recently [Williams, *Acta Cryst.* (1974). A**30**, 71–77] on the basis of experimental data not extrapolated to 0 K. The difference between the two approaches is discussed and illustrated by comparing the calculated results.

Introduction

The theoretical calculation of the structure and properties of any organic compound by the atom–atom potential method (Kitaigorodsky, 1973) usually requires knowledge of the potential interaction energy of non-bonded C and H atoms. The 'hydrocarbon' part of the energy expression for complicated molecules can be expressed in terms of the known $C\cdots C$, $C\cdots H$ and $H\cdots H$ potential curves, derived independently from the properties of pure hydrocarbons, if the assumption of transferability of interatomic potentials is valid. Many successful applications of the method show that this assumption works in general (Kitaigorodsky & Mirskaya, 1972). This does not mean, however, that any empirical set of non-bonded potential parameters is transferable from one molecular system to another irrespective of the way it has been developed, especially if these parameters have been obtained as part of the total potential force field.

At present one can find various sets of nonbonded potential parameters for hydrocarbons derived from experimental data. Some have been obtained as part of the total force field from structure and properties of free molecules [Warshel & Karplus, 1972; Engler, Andose & Schleyer, 1973; see also reviews by Altona & Faber (1974) and Golebiewski & Parczewski (1974)] or from the simultaneous consideration of a molecule and its crystal [see for example, consistent force-field calculations made by Lifson & Warshel (1968) and Warshel & Lifson (1970)]. For others only crystal data were used and no intramolecular interactions were considered (Kitaigorodsky & Mirskaya, 1962, 1964; Williams, 1966, 1967, 1974; Momany, Vanderkooi & Scheraga, 1968; Ferro & Hermans, 1970; Mirskaya, Kozlova & Bereznitskaya, 1974; Hagler, Huler & Lifson, 1974; Hagler & Lifson, 1974; Momany, Carruthers, McGuire & Scheraga, 1974). Comparison of the various $C\cdots C$, $C\cdots H$ and $H\cdots H$ potential curves shows a diversity of absolute values ascribed to the same non-bonded parameters. On the one hand this discrepancy comes from the dependence of the empirical parameters on the type and accuracy of the experimental data involved. On the other, not only the absolute values but even the meaning of the same parameters may be different according to the set of initial assumptions of the theory (number of terms in the energy expression, number and values of fixed parameters, and so on).

Depending upon the values of the parameters the results of their use may also differ. This dependence is not straightforward (some properties are sensitive to the choice of the potentials whereas others are not) and has to be determined by direct calculation.

Calculations of this kind are performed in the present work to illustrate several aspects of the problem of transferability of van der Waals interatomic parameters.

Numerical examples are given confirming that it is possible to develop a set of potentials for hydrocarbons which is transferable, with reasonable accuracy, from one molecular system to another. A set of interatomic potential functions, fitted to the properties of model molecular crystals [namely, our recent potentials for hydrocarbons (Mirskaya, Kozlova & Bereznitskaya, 1974, henceforth referred to as MKB)], is applied to the calculation of properties of other crystals not involved in the earlier optimization process. The agreement with

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experimental data is as good as that obtained for the model compounds.

A second series of calculations is performed in order to show how the theoretical results for structure and energy of molecular crystals depend on the choice of the interatomic potential curves, even if they do not differ very much. The above calculations are repeated with another set of C···C, C···H and H···H potential curves here referred to as the W74 set. These curves are the van der Waals part of the recent hydrocarbon potential force field derived by Williams (1974) (the total intermolecular energy was represented by two terms: the van der Waals energy and the Coulombic energy). This force field was obtained as a result of calculations based on structure data of 18 hydrocarbon crystals, half of them aromatic and half saturated hydrocarbons. For the interatomic potential functions the same (6-exp) Buckingham form was used as in our work, while in the other works mentioned above the Lennard-Jones (6–12) or (6–9) potentials were used. The absolute values of the W74 van der Waals parameters are the closest to ours although they were not the only empirical parameters of the theory. There are also some differences shown in the next section where the two MKB and W74 sets are compared.

Potential parameters

The values of the parameters of the (6-exp) potential curves used in this work are given in Table 1. These parameters are A, B and α if the potentials are written in the form $\varphi = -Ar^{-6} + B \exp(-\alpha r)$, or, alternatively, ε, r_0 and λ if the modified Buckingham form $\varphi = [\varepsilon\lambda/(\lambda-6)]\,[-(r_0/r)^6 + (6/\lambda) \exp \lambda(1 - r/r_0)]$ is used (r is the interatomic distance).

The MKB set of parameters is the refined version of the one used previously (Kitaigorodsky & Mirskaya, 1964; Kitaigorodsky, 1973). These potential functions were fitted to structure and heat-of-sublimation data and to the latest available elasticity data for the model hydrocarbon crystals (mainly for naphthalene, anthracene and benzene). Only those experimental data were used in the optimization process which could be extrapolated to absolute zero. At this temperature the effects of molecular and lattice vibrations are minimized and crystal properties are mainly determined by the lattice potential energy. The zero-point vibrational corrections to the energy were introduced when necessary (they are usually small for crystals with polyatomic molecules and without strong intermolecular interactions, such as hydrogen bonds [Kitaigorodsky, 1973]). Provided experimental data for high temperatures were taken for comparison, the free energy of a crystal should be calculated and minimized (Warshel & Lifson, 1970). In our approach the effect of the electrostatic part of the lattice energy on the equilibrium structure and physical properties of model compounds was estimated to be insignificant (Kitaigorodsky & Mirskaya, 1965), so as a first approximation the van der Waals parameters were the only empirical parameters of the theory.

The W74 set of C···C, C···H and H···H potential curves was also derived from the experimental structures of pure hydrocarbon crystals (including those we used as models) but without low-temperature constraints, and from the sublimation heats of two of them (benzene and n-hexane) reduced to 0 K. So far as structure data available for various temperatures were used, and only potential energy was calculated, the averaged thermal effects were incorporated into the derived potential parameters. Apart from the van der Waals parameters, one more empirical parameter was involved in the fitting procedure, the charge separation in the C–H bond. That caused some changes in Williams's previous hydrocarbon potential curves (Williams, 1970) derived similarly but without charges. The changes were not large. More than others the values of ε, the well-depths of the potentials, shifted.

Comparison of the two sets of parameters (Table 1) shows that the λ's, the steepnesses of the corresponding potential curves, are almost the same, while the coordinates of the minima, the ε's and the r_0's, differ somewhat.

For better understanding of the sources of the differences in the values of the parameters and, as a consequence, in the results of their applications, the main dissimilarities of the two approached are outlined in Table 2.

Among the items in Table 2, those of taking observables at different temperatures and of introducing different kinds of adjustable parameters seem to be the most important. The possible consequences of using different combining rules for C···H interactions have

Table 1. *Values of the van der Waals potential parameters for hydrocarbons*

Set of parameters	Atom pairs	$A\left(\frac{\text{kcal}}{\text{mole}}\,\text{Å}^6\right)$	$B\left(\frac{\text{kcal}}{\text{mole}}\right)$	α (Å^{-1})	$\varepsilon\left(\frac{\text{kcal}}{\text{mole}}\right)$	r_0 (Å)	λ
MKB*	C···C	421	$7{\cdot}16\times10^4$	3·68	0·080	3·80	14
	C···H	118	$1{\cdot}86\times10^4$	3·94	0·049	3·30	13
	H···H	29	$4{\cdot}90\times10^3$	4·29	0·030	2·80	12
W74†	C···C	449·7	$7{\cdot}15\times10^4$	3·60	0·071	3·93	14·1
	C···H	134·4	$1{\cdot}43\times10^4$	3·67	0·036	3·56	13·1
	H···H	40·2	$2{\cdot}87\times10^3$	3·74	0·019	3·18	11·9

* Mirskaya, Kozlova & Bereznitskaya (1974).
† Williams (1974).

been discussed elsewhere (Mirskaya, 1973). The existence of a correlation between the ultimate values of the parameters to be adjusted and the assumed values of the remaining parameters of the total empirical force field is evident.

Calculation procedure

Both the MKB and W74 parameter sets were applied to the calculation of lattice potential energies and equilibrium structures of four completely or partly saturated hydrocarbon crystals (Fig. 1). The compounds were chosen because of the availability of thermal expansion and heat of sublimation data for comparison. Preference was given to molecules containing saturated C atoms in order to check whether the MKB parameters fitted mainly to the properties of unsaturated hydrocarbons are transferable to saturated ones. The MKB set was also used for the calculation of the phase transition characteristics of, and for investigation of molecular motion in, the adamantane crystal. This could give additional information about the consistency of the force field developed.

A detailed description of the way we used the atom–atom potential model can be found elsewhere (Kitaigorodsky & Mirskaya, 1962, 1964, 1972; Kitaigorodsky, 1973). The following are a few amplifying remarks.

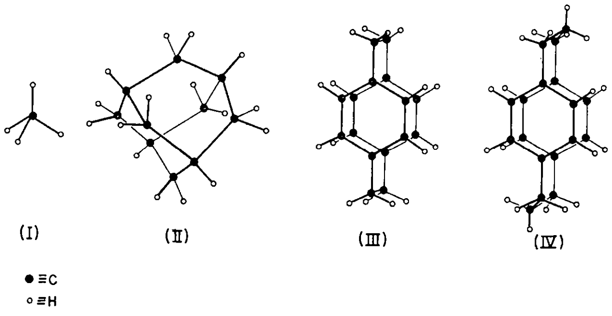

Fig. 1. The structure of the methane, CH_4 (I), adamantane, $(CH_2)_6(CH)_4$ (II), 2,2-paracyclophane, $(C_6H_4)_2(CH_2)_4$ (III), and 3,3-paracyclophane, $(C_6H_4)_2(CH_2)_6$ (IV), molecules.

The lattice binding energy was calculated as a sum of pairwise interaction energies of all atoms of the reference molecule with all atoms of the surrounding molecules in the crystal. The space group of the crystal was taken from the X-ray experiment, and lattice energy was considered as a multidimensional function of all the structural crystal variables compatible with the given space group. These variables were the unit cell axes and angles, $a,b,c,\alpha,\beta,\gamma$, and the rotational angles describing the orientation of the reference molecule in crystal space. The molecules themselves were kept 'rigid', that is, it was assumed that for small variations of the crystal parameters the arrangement of the atoms in the molecules was stable.

Starting with the experimental crystal structure the structural parameters were varied to give the minimum of the potential energy surface, corresponding to a theoretical equilibrium structure. Actually, in this way one calculates the crystal structure at absolute zero, with an accuracy governed by the zero-point vibrational effects. (If the energy is minimized with respect to molecular rotations and translations in the fixed unit cell at a particular temperature, one gets the equilibrium crystal structure at this temperature).

Almost all the calculations could be performed with the *PCK*6 computer program (Williams, 1972). The convergence-acceleration facilities of the program were used and the rate of convergence was investigated as a function of the summation limit, R, and of the convergence constant K_6. Fig. 2 shows the equilibrium values of the lattice energy, U, and of the cubic lattice parameter, a, as functions of R for methane. $K_6=0$ means that the convergence-acceleration procedure was omitted. $K_6=0{\cdot}175$ is the optimal K_6 value for methane (see below). One can see that for $K_6=0{\cdot}175$ the cut-off distance $R=7$ Å is already sufficient to ensure convergence (similar results were obtained also for 3,3-paracyclophane). In practice, one gets the same lattice sums as above with separate R's for C···C,

Table 2. *Sources of information and some assumptions about the values of the potential parameters*

Set of parameters	MKB	W74
Observables	Sublimation heats, crystal structures and elasticity data extrapolated to 0 K	Sublimation heats and crystal structures, not necessary at low temperatures
Adjustable non-bonded parameters	Six van der Waals parameters (A_{CC}, B_{CC}, α_{CC}, A_{HH}, B_{HH}, α_{HH})	Four van der Waals parameters (A_{CC}, B_{CC}, A_{HH}, B_{HH}) and charge separation in the C–H bond
α_{CC}, α_{HH}	Fitted to the elasticity data of hydrocarbon crystals at 0 K	Assumed (α_{CC} is taken from graphite, α_{HH} from quantum-mechanical calculations for H_2 molecules)
Assumed C–H bond length	1·08 Å	1·027 Å for aromatic and 1·040 Å for aliphatic carbon
Combining rules for C···H interactions	Geometric mean rule for the total potentials (Mirskaya, 1973), leading to $\varepsilon^{CH}=(\varepsilon^{CC}\varepsilon^{HH})^{1/2}$, $r_0^{CH}=(r_0^{CC}+r_0^{HH})/2$, and $\lambda^{CH}\simeq(\lambda^{CC}+\lambda^{HH})/2$	Geometric mean rule for the attractive and repulsive terms, separately, that is, $A^{CH}=(A^{CC}A^{HH})^{1/2}$, $B^{CH}=(B^{CC}B^{HH})^{1/2}$ and $\alpha^{CH}=(\alpha^{CC}+\alpha^{HH})/2$

C···H and H···H interactions equal to 8, 7 and 6 Å, respectively. These cut-off distances are approximately twice as large as the equilibrium r_0 values for the corresponding potential curves (Table 1). Fig. 3 shows that the lattice energy values are not independent of the value of the convergence constant K_6. $K_6=0{\cdot}15$ was found to be optimal for adamantane and for the two paracyclophanes, and $K_6=0{\cdot}175$ for methane.

Results and discussion

Lattice energy and equilibrium crystal structure

The results of the lattice-energy minimization process for both the MKB and W74 sets of potential parameters are summarized in Tables 3 and 4, where they are also compared with the available experimental data. The heat of sublimation of the low-temperature tetragonal phase of adamantane has not been measured; corresponding data for the cubic phase are available only for elevated temperatures and will be discussed below. The experimental unit-cell sizes in Table 4 are given at the lowest measured temperatures. Also in Table 4 the θ's, the angles of rotation of the molecules in the crystals from their experimental positions to the calculated equilibrium positions, are given (derived from the resulting rotation matrices).

Table 3. *Comparison of lattice energies, $U_{\min}$, and sublimation heats at 0 K, ΔH_s^0*

Compound	$-U_{\min}$(kcal/mole) MKB	 W74	ΔH_0^s, kcal/mole
Methane	2·35	1·85	2·49(1)
Adamantane (tetragonal)	19·5	15·9	–
2,2-Paracyclophane	24·4	20·3	24·2(2)*
3,3-Paracyclophane	25·9	21·7	25·9(3)*

(1) Breitling, Jones & Boyd (1971) (the energy value includes zero-point vibrational corrections).
(2) Boyd (1966).
(3) Chyi-feng Shieh, McNally & Boyd (1969).
* ΔH_0^s values obtained from the relation $\Delta H_s^0=\Delta H_s^{298}+2RT$ (Rae & Mason, 1968).

Let us firstly consider the results for the MKB set and then compare them with those for the W74 set. Table 3 demonstrates the good agreement of the lattice energies in the minima of the potential energy surfaces with the heats of sublimation at 0 K. From Table 4 one can see that the equilibrium orientations of the molecules in the crystals are very close to the experimental ones (θ values are small). Comparison of the positions of the minima of the potential-energy surfaces with the experimental unit-cell sizes (Table 4) shows that the MKB set gives the expected thermal volume contraction for all crystals. At present it is difficult to estimate the absolute values of the deviations of the theoretical unit-cell sizes from the experimental ones in every case, because of the lack of precise thermal expansion data, but on average these deviations are small and of the same order of magnitude as for the model compounds and other hydrocarbon crystals (Kitaigorodsky & Mirskaya, 1972). This confirms that the MKB set is transferable from one molecular system to another. It also means that these potential curves work equally well for aromatic and aliphatic hydrocarbons, and there is still no direct evidence that on this level of approximation special separation of potential parameters is needed for the same atoms in various valence states.

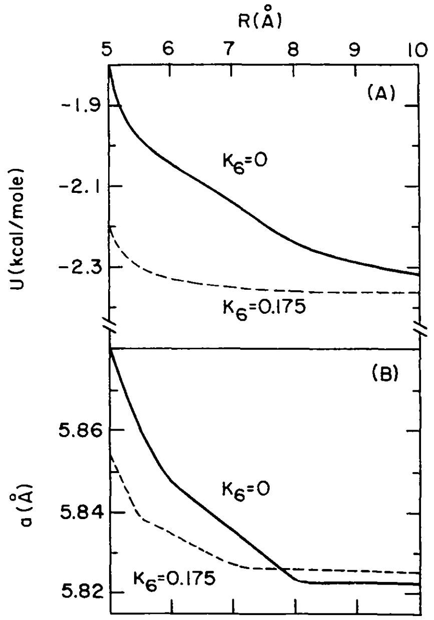

Fig. 2. Convergence of the results of the energy minimization: equilibrium values (*A*) of the lattice energy, *U*, and (*B*) of the cubic lattice parameter, *a*, of methane as functions of the cut-off distance, *R*, and the convergence constant, K_6.

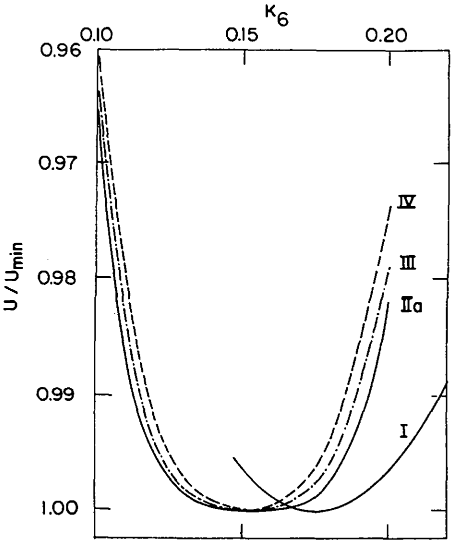

Fig. 3. Dependence of the lattice energy values, *U*, on the value of the convergence constant, K_6. I methane, II*a* tetragonal adamantane, III 2,2-paracyclophane, IV 3,3-paracyclophane.

For the W74 set all the calculated lattice energy values are significantly smaller (Table 3) and all the unit-cell parameters are significantly larger (Table 4) than those for the MKB one. The changes in the molecular orientations are about the same, namely, θ values are small. One would expect such a result from a comparison of the positions of the minima of the interatomic potential curves (Table 1): for the W74 set the three ε values are smaller and the three r_0 values are larger than those for the MKB, although at first sight the differences do not seem to be large. Thus one can see a relation between potential curves and the results of their application.

It is not justifiable to compare directly the results for the W74 set with experimental data because it represents only part of the total potential force field, albeit the most significant one. The absence of the Coulombic term can explain the fact that all the lattice energy values are smaller than experimental ones (Table 3). For example, the Coulombic term for tetragonal adamantane was estimated by Williams (1974) to be 1·46 kcal/mole.

As to the calculated unit-cell parameters for the W74 set, one would expect them to be close to the experimental ones at the elevated temperatures for which the energy parameters were fitted. This is the case for some of the unit-cell parameters, but not for others, which are significantly larger than their experimental values (Table 4). This cannot be related only to the omission of the electrostatic interactions [electrostatic energy is a much slower function of structure parameters than the van der Waals energy; with the total force field Williams has got similar results for benzene and n-hexane (Williams, 1974; Hall & Williams, 1975)]. Rather, it indicates an inherent limitation of energy sets based on experimental data at elevated temperatures, which is due to the fact that the effect of temperature on the unit-cell parameters is not uniform. First, it is different in different crystals. Second, it is different for different parameters of the same crystal, since molecular crystals are in general highly anisotropic in the thermal expansion coefficients (Kitaigorodsky, 1973).

A suggestion which is made by Tables 3 and 4 is that even small differences in the interatomic potential parameters may lead to significant changes in the results of the calculations of structure and properties of molecular compounds. That is why it is always desirable, when choosing empirical sets of van der Waals potential parameters for particular purposes, to consider carefully the basic assumptions underlying the methods of their derivation.

Molecular motion and phase transition in solid adamantane.

As a further application of the MKB atom–atom potential force field and a further test of its consistency, additional calculations of the properties of the adamantane crystal were performed. Of special interest are the phase-transition characteristics and the question of possible molecular rotation in this crystal.

A solid–solid phase transition is observed in adamantane at 208·6 K (Chang & Westrum, 1960). Below this point the crystal is tetragonal, space group $P\bar{4}2_1c$, $Z=2$. Its structure at 163 K was solved by Nordman & Schmitkons (1965) and refined by Donohue & Goodman (1967). This tetragonal phase is ordered, although a n.m.r. line-narrowing which takes place at 140–160 K (McCall & Douglass, 1960; Waugh & Fedin, 1962; Resing, 1969) indicates a space reorientation of the molecules. This motion can only be reorientation among the indistinguishable positions, corresponding to the proper symmetry of the molecules which is $\bar{4}3m$ (the allowed jumps are 120 and 180°),

Table 4. *Summary of theoretical and experimental structure data*

Compound	Space group	Variable unit-cell parameters	Unit-cell dimensions (Å, °) Theory (equilibrium) MKB	W74	Experiment	T(K)	θ, deg.(a) MKB	W74
Methane	$F\bar{4}3m$	a	5·83	6·18	5·82	14·3(1)	0	0
Adamantane (tetragonal)	$P\bar{4}2_1c$	a	6·45	6·68	6·60	163(2) (3)	0·36	1·17
		c	8·63	9·00	8·81			
2,2-Paracyclophane	$P4_2/mnm$	a	7·48	7·75	7·69	93(4)*	1·93	2·08
		c	9·19	9·41	9·23			
3,3-Paracyclophane	$P2_1/n$	a	9·81	9·98	9·72	298(5)	2·72	2·33
		b	7·79	8·03	8·14			
		c	8·09	8·48	8·52			
		β	90·2	90·4	90·7			

(1) Schallamach (1939).
(2) Nordman & Schmitkons (1965).
(3) Donohue & Goodman (1967).
(4) Lonsdale, Milledge & Krishna Rao (1960).
(5) Gantzel & Trueblood (1965).
(a) θ is the angle of rotation of molecule in crystal about its initial position as a result of the lattice-energy minimization procedure.
* As a starting point for the minimization process the room-temperature structure of 2,2-paracyclophane was used with $a=7{\cdot}781$ and $c=9{\cdot}29$ Å (Hope, Bernstein & Trueblood, 1972).

and is likely to continue also above the transition point (Brot, 1969).

At high temperatures adamantane crystallizes in a face-centred cubic lattice. In the early work by Nowacki (1945) it was considered to be of $F\bar{4}3m$ symmetry ($Z=4$) but the later least-squares refinement of the structure by Nordman & Schmitkons (1965) showed slight preference for the disordered centrosymmetric space group $Fm3m$ [the same observation was cited by Stockmeyer (1969)]. The latter space group is so-called orientationally disordered (Darmon & Brot, 1967) and corresponds to a random distribution of the molecules among two distinct equilibrium orientations which differ by 90° about a line joining two opposite methylene groups.

There is also a third opinion about possible ordering in cubic adamantane based on the estimate of the lattice heat capacity C_v. According to the data of Breitling, Jones & Boyd (1971) adamantane appears to conform to the temperature-independent total C_v of $(9/2)R$ expected for free rotation (however, the authors note that this could well be an experimental artefact).

We have made an attempt to find out which of the proposed molecular arrangements is the most probable from the point of view of its potential energy. The lattice energy of the uniformly ordered cubic crystal (space group $F\bar{4}3m$) was calculated as a function of the cubic unit cell parameter, a, and compared with those of orientationally disordered (space group $Fm3m$) and statistically disordered (free rotation of molecules) models.

The ways of representing the adamantane molecule in the three cases were as follows. In the ordered crystal (or.) the molecule had its ideal symmetry $\bar{4}3m$ and corresponding atomic positional parameters were taken from Kitaigorodsky (1961). In the orientationally disordered crystal (o.d.) the two distinct equilibrium orientations of the molecules, mentioned above, were assumed to be equally probable. The new centrosymmetric molecule was then built on the site of the old molecule which contained double amounts of all the H atoms and of the C atoms of methine groups (the total number of atoms in each molecule is then 46 instead of 26). The coordinates of the 'new' atoms were obtained from the 'old' ones by the operation of a centre of symmetry. Accordingly, the probabilities of occupying these 'doubled' positions were considered as $\frac{1}{2}$ instead of 1, and the energy expression for the interaction of the 'whole' atom with the 'half' one, and of two 'half' atoms contained the factors $\frac{1}{2}$ and $\frac{1}{4}$ respectively.

In the statistically disordered crystal (s.d.) all orientations of molecules in the face-centred cubic lattice were assumed to be equally probable. Every molecule could be treated as a sphere having four concentric layers in accordance with the molecular geometry: two layers of C atoms, located at 1·776 and 1·540 Å from the centre, containing respectively six atoms of methylene and four atoms of methine C atoms; and two layers of H atoms, belonging to the same groups, having radii 2·556 and 2·620 Å and containing 12 and four atoms respectively. Atoms belonging to a given layer were taken as having the same probability of being at any point on the layer. In this case the lattice energy is given by

$$U=(\tfrac{1}{2})\,[-A_{\rm CC}\sum\overline{r_{\rm CC}^{-6}}-2A_{\rm CH}\sum\overline{r_{\rm CH}^{-6}}-A_{\rm HH}\sum\overline{r_{\rm HH}^{-6}}$$
$$+B_{\rm CC}\sum\overline{\exp(-\alpha_{\rm CC}r_{\rm CC})}+2B_{\rm CH}\sum\overline{\exp(-\alpha_{\rm CH}r_{\rm CH})}$$
$$+B_{\rm HH}\sum\overline{\exp(-\alpha_{\rm HH}r_{\rm HH})}]\,.$$

Corresponding formulae for the averaged lattice sums have been derived (Kitaigorodsky & Mirskaya, 1962). Those for interacting layers having radii R_i and R_j in a face-centred cubic lattice with the unit-cell parameter, a, are

$$\sum\overline{r_{ij}^{-6}}=\frac{2\xi_i}{R_i^5R_j}\left\{\frac{1+6(\xi_i+\xi_j)^2}{[1-2(\xi_i+\xi_j)^2]^3}-\frac{1+6(\xi_i-\xi_j)^2}{[1-2(\xi_i-\xi_j)^2]^3}\right\}$$
$$+(\xi_i^6/R_i^6)\,[17{\cdot}807+62{\cdot}640(\xi_i^2+\xi_j^2)]\,,$$

where

$$\xi_i=R_i/a\,,$$

$$\overline{\exp(-\alpha r_{ij})}=(\tfrac{1}{4}dR_iR_j\alpha^3)\,[(\alpha p_1+2)\exp(-\alpha p_1)$$
$$-(\alpha p_2+2)\exp(-\alpha p_2)+(\alpha p_3+2)\exp(-\alpha p_3)$$
$$-(\alpha p_4+2)\exp(-\alpha p_4)]\,,$$

where d is the distance between centres of spheres, and

$$p_1=d+R_i+R_j\,,\quad p_3=d-R_i-R_j$$
$$p_2=d-R_i+R_j\,,\quad p_4=d+R_i-R_j\,.$$

The $\sum\overline{\exp(-\alpha r_{ij})}$ has been restricted to the first coordination sphere (12 neighbours at $d=a/\sqrt{2}$ from

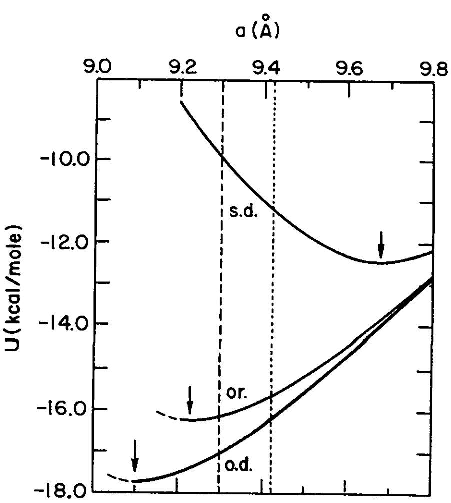

Fig. 4. Comparison of the lattice energies, U, as functions of the lattice parameter, a, of three models of cubic adamantane: or. – uniformly ordered structure; o.d. – orientationally disordered; s.d. – statistically disordered. Arrows indicate the minima of the $U(a)$ curves. Dashed and dotted lines correspond to the a values at the point of phase transition and at room temperature respectively.

the reference molecule), while $\sum r_{ij}^{-6}$ has been taken out to $d \simeq 2{\cdot}345\ a$ (12 coordination spheres).

The dependence of the lattice energy of each of the three models on the unit-cell parameter, *a*, is shown in Fig. 4. The range of *a* values on the plot includes that at room temperature (9·426 Å) and at the phase transition (9·30 Å), and continues up to the maximum possible near the melting point (the latter two were estimated from the volume thermal expansion coefficient at room temperature $\alpha_v = (4{\cdot}4\text{–}4{\cdot}7)\,.\,10^{-4}\ \text{deg}^{-1}$ (Mirskaya, 1963; Breitling *et al.*, 1971).

Comparing the three *U*(*a*) curves one can see that the o.d. structure is the most favourable energetically, while the s.d. crystal has the highest potential energy for all the range of *a* values. Moreover, the equilibrium *a* value for the s.d. crystal (9·68 Å) is larger than that at room temperature, which does not agree with the positive expansion coefficient of the crystal. The difference between the energies of o.d. and or. crystals is not significant at the large *a*'s but it increases rapidly when *a* decreases and reaches 0·8 kcal/mole at the transition point. If the cubic phase of adamantane were to exist beyond the transition point the o.d. molecular arrangement would lead, at equilibrium, to a 1.5 kcal/mole lower energy than the or. one, and to the lowest unit-cell volume, that is, to the closest molecular packing. One can compare the coefficients of molecular packing $k = V_0/V_{\text{mol}}$ corresponding to the minimum points of the *U*(*a*) curves [V_0 is the volume of the molecule in the gas phase, which is 144 Å^3 for adamantane (Kitaigorodsky, 1961), and V_{mol} is the volume per molecule in the crystal]. These are 0·77, 0·73 and 0·63 for o.d., or. and s.d. crystals respectively.

It is interesting to compare the absolute values of the lattice energies for the three models with the experimental heat of sublimation. As was mentioned above, the heat of sublimation of cubic adamantane is available only at 333·2 K (Bratton, Szilard & Cupas, 1967) and is 14·0 ± 0·2 kcal/mole. From general thermodynamic considerations it follows that the difference between the absolute values of the lattice energy *U* and the sublimation heat ΔH_s at some temperature *T* may be compared to the difference in the vibrational energies of solid (U^s_{vib}) and gas phases (U^g_{vib}) at this temperature minus *RT*, the work of expansion of the gas. At high temperatures, when all librational and translational crystal modes are excited, $U^s_{\text{vib}} \simeq 6RT$, $U^g_{\text{vib}} \simeq 3RT$, and then $U - \Delta H_s \simeq 2RT$, which equals 1·3 kcal/mole for 333·2 K. So the value to be compared with the lattice energy at 333·2 K is 14·0 + 1·3 = 15·3 kcal/mole. According to the thermal-expansion data, the unit-cell size at this temperature is about 9·48 Å. For this *a* value lattice energies of s.d., or. and o.d. crystals are 11·6, 15·3 and 15·7 kcal/mole, respectively (Fig. 4). The agreement with experiment is satisfactory for the last two models; however, on the basis of these data it is not justified to choose between these two models because of the experimental errors in ΔH_s and the very rough estimates of the vibrational corrections to the potential energy.

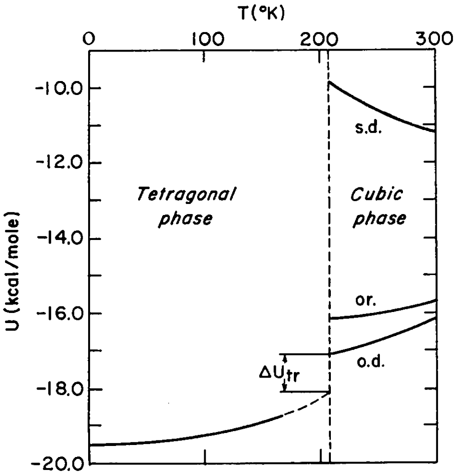

Fig. 5. Lattice energy of the adamantane crystal plotted against absolute temperature. Notation is the same as in Fig. 4.

In Fig. 5 the same potential energy values for the cubic phase are plotted against the absolute temperature in the range between room temperature and the point of phase transition. To transfer from *a* values to the temperature scale the thermal expansion coefficient at room temperature, α_v, was used. It was assumed that in this temperature interval α_v is constant. The resulting *U*(*T*) curves show how the potential lattice energy changes during the real thermal transformations occurring in cubic adamantane. Also in Fig. 5 the *U*(*T*) curve for the tetragonal phase is shown. Because of the lack of data on the thermal-expansion tensor for the low-temperature phase the last curve was obtained in the following way. The energy value at 0 K (−19·5 kcal/mole) is the well depth of the potential-energy surface, the same as given in Table 3; that at 163 K (−18·7 kcal/mole) corresponds to the unit-cell dimensions given by Nordman & Schmitkons (1965). The derivative of the curve is zero at 0 K (minimum of the potential energy). The extrapolation of this curve to 208·6 K gives an expected value of the energy of the tetragonal crystal at the transition point.

Now one can estimate the energy of the phase transition, ΔU_{tr}. As follows from Fig. 5, its value is about 1 kcal/mole, if the transformation goes from tetragonal to o.d. structure, and larger for transitions to or. and s.d. phases. The value of 1 kcal/mole agrees well with the experimental heat of transition (0·807 kcal/mole) derived by Westrum (1961) from the heat capacity data (the author emphasizes that this is a minimal value for the transition enthalpy which would almost certainly be larger if the proper extrapolation of the $C_p(T)$ curves of both the high- and low-temperature forms to the transition point could be done).

Fig. 6 provides the theoretical value of the volume change at the transition point, ΔV_{tr}, which can also be compared with the experimental data. The two $V_{\text{mol}}(T)$ curves shown on the plot contain both experimental and theoretical parts which supplement each other surprisingly well. The completely experimental part of the curve 1, in the range 200–300 K, is smoothly continued to the absolute zero to the same equilibrium o.d. crystal as in Fig. 4. For two other models V_{mol} at 0 K is larger. Curve 2 (tetragonal phase) has one experimental (163 K) point and one theoretical (0 K) point. Its derivative (volume thermal expansion coefficient) is zero at 0 K by definition. If this curve is extrapolated to the transition point, one gets for ΔV_{tr} a value of about 5–6 Å^3/mol which agrees well with the experimental one of 5·7 Å^3/mol (Pistorius & Resing, 1965). Comparison of the curves 1 and 2 shows that even the best of the cubic structures (o.d.) would not be so close packed at absolute zero as the tetragonal crystal: k, close-packing coefficients for the corresponding minimum points of the potential energy surfaces, are equal to 0·77 and 0·80 respectively. This may be one of the reasons (besides dynamical effects) why the phase transition in the adamantane crystal occurs.

Summarizing the theoretical picture obtained for the adamantane crystal one can conclude that at high temperatures when the crystal is cubic and a values are large, there is no large difference in the potential energies of the three molecular arrangements, including the extreme cases of ideal order and complete disorder in the molecular orientations. At lower temperatures, and especially near that of the phase transition, the details of molecular geometry become more and more significant and then the o.d. structure appears to be the most favourable energetically. That this is indeed the true structure is indicated further by the values of the volume and energy changes at the phase transition (ΔV_{tr} and ΔU_{tr}) which agree with the corresponding observables only for this model. Finally, this same model follows from the X-ray data for cubic adamantane.

The values of the lattice energy predicted here for the cubic phase near the transition point and for the tetragonal phase have yet to be checked experimentally. The same is true of the predicted crystal structure of the tetragonal form at absolute zero. But it is already clear that the MKB van der Waals potential force field describes the properties of solid adamantane reasonably and gives results in a good agreement with the available experimental data. The same conclusion is suggested by the results obtained for other hydrocarbon crystals.

All this encourages one to hope that this force field for hydrocarbon atoms can be successfully used for various applications of the atom–atom approximation and also as a starting point in the development of new potential force fields for more complicated systems containing molecules with large electrical moments, free charges, hydrogen bonds and so forth.

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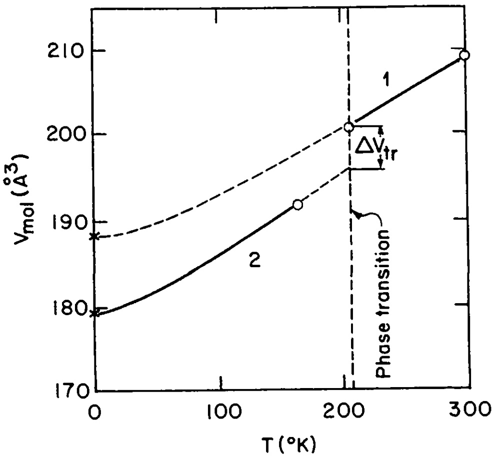

Fig. 6. Volume per molecule in the adamantane crystal as a function of temperature. ○ – experimental values, × – theoretical values, corresponding to the minima of the lattice-energy surfaces. 1 – cubic crystal (o.d. structure), 2 – tetragonal crystal.

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The Interpretation of Quasi-kinematical Single-Crystal Electron Diffraction Intensity Data from Paraffins

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Single-crystal *hk*0 electron diffraction patterns from thin (≤240 Å) rhomboid n-hexatriacontane (n-$C_{36}H_{74}$) crystals contain intensity data which are well fit by the commonly observed $O_{\perp}$ methylene subcell phasing model but not by a true unit cell model which contains two mutually displaced monolayers. The apparent diffraction from a monolayer in these lamellar crystals is thought to be due to bend distortions of the crystal plate. Intensity data conform to a kinematical interpretation as a first approximation, thus allowing *a priori* structural elucidation, but eventually will require an *n*-beam dynamical correction.

Introduction

The elucidation of molecular conformation in the solid state for many biologically interesting long-chain lipids has often been frustrated by the reluctance of such compounds to give crystals of suitable size and quality for conventional crystallographic structural determinations. The veracity of this statement is underscored by the fact that the first three-dimensional X-ray crystal structure analysis of a phospholipid, for example, was completed only recently using three-dimensional X-ray diffraction data of poor quality (Hitchcock, Mason, Thomas & Shipley, 1974).

With the encouragement of pioneering Russian structural work on organic materials, it is believed that the crystal size criterion may be overcome by the use of electron diffraction intensity data from readily available thin microcrystals for the crystallographic analysis of unknown lipid structures. The very small crystal thickness (a hundred ångströms or less) for which one can obtain high-resolution single-crystal diffraction patterns is an expression of the very large scattering cross section of matter for electrons (Vainshtein, 1964, p. 4). This large scattering cross section in itself demands a proof that a given diffraction data set adequately conforms to the kinematical diffraction assumption used in X-ray crystallography and thus allows an *a priori* determination of an unknown crystal structure. Much of the Russian literature on electron diffraction determination of organic crystal structures described the