The temperature variation of T_{11} and L_{11} between 381 and 423 K is consistent within the error limits with harmonic potentials.

It is obvious from our results that different models – at least the cubic harmonic and the Gaussian approximation – give comparable results as far as R values are concerned. The only way out of this difficulty is an increase of the signal-to-noise ratio in the measurements of Bragg data. The background cannot be reduced below the level given by the diffuse scattering due to the sample. So the only other way out which apparently has not been tried so far is high-resolution X-ray and neutron scattering.

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Examination of Semiempirical Atom–Atom Potential Functions for Cl···Cl Non-Bonded Interactions

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Abstract

Three semiempirical atom–atom potential functions suggested by different authors to describe non-bonded Cl···Cl interactions are examined *via* calculation of some thermodynamic properties of hexachlorobenzene, C_6Cl_6, and p-dichlorobenzene, $C_6H_4Cl_2$, crystals. All thermodynamic quantities are evaluated with the cell model as a statistical mechanical basis. The calculation results provide some evidence to support the existence of positional disorder in the high-temperature phases of p-dichlorobenzene.

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Introduction

In the present paper we test three potential functions suggested by different authors to describe non-bonded Cl···Cl interactions in the crystals of chlorinated benzenes. The test involves calculation of some thermodynamic quantities of hexachlorobenzene (HCB) and p-dichlorobenzene (DCB) crystals and subsequent comparison of the calculation results with experiment. As a statistical mechanical basis for the thermodynamic calculations we use a classical self-consistent-field approximation which is frequently called the cell model (Barker, 1963). The applicability of the cell model itself to molecular organic crystals has been previously demonstrated by us by calculating the thermodynamic properties of a number of organic crystals including the crystals of benzene (Pertsin, Nauchitel & Kitaigorodsky, 1975), naphthalene, anthracene (Pertsin & Kitaigorodsky, 1976*a*), pyrene (Ivanov, Antipin, Pertsin & Struchkov, 1981), adamantane (Pertsin & Kitaigorodsky, 1976*b*), phenanthrene (Pertsin, Ivanov & Kitaigorodsky, 1981), acenaphthene, toluene, hexamethylbenzene, hexamethylenetetramine, tolan, hexafluorobenzene (Pertsin & Ivanov, 1981). In all the cases the agreement between calculated and observed quantities proved to be very good, especially at temperatures above 100 K. For entropy, for instance, the cell model reproduced observed values with an accuracy of the order of 0·5 J mol^{-1} K^{-1}, which is much better than the accuracy ensured by the usual quasiharmonic approach (Filippini, Gramaccioli, Simonetta & Sufritti, 1975).

The three potential functions we have chosen to examine are those of Mirsky & Cohen (1978) (hereafter referred to as MC), Reynolds, Kjems & White (1974) (RKW), and Bates & Busing (1974) (BB). The potential of MC is of the Buckingham (6-exp) type

$$\varphi_{\rm MC} = -2980r^{-6} + 4580\exp(-2\cdot26r)$$

and was fitted to the crystal structure and heat of sublimation of HCB, extrapolated to zero temperature. The RKW potential, which is also of the (6-exp) type,

$$\varphi_{\rm RKW} = -2300r^{-6} + 426\,000\exp(-3\cdot65r),$$

was derived by fitting to the room-temperature structures of tetrachlorobenzene, DCB (α phase), and HCB; the lattice frequencies of the last two compounds were also fitted.

Bates & Busing have derived two different potential functions, *viz* of the (6-exp) and (6-exp-1) type, by fitting them to the crystal structure and heat of sublimation of HCB. The two potential functions proved to be almost equally successful in predicting the lattice energy and optically active lattice frequencies of HCB, though the crystal structure of HCB was reproduced appreciably better with the (6-exp-1) potential.

The latter result was interpreted by BB as indicating the importance of electrostatic interactions in the HCB crystal. There is, however, an obvious objection to such an interpretation. Indeed, inasmuch as crystal properties are governed by the intermolecular potential as a whole but not by its individual constituents, and since the atom–atom representation is not a rigorous representation of the true intermolecular potential, the atom–atom potential parameters, when inferred from the crystal properties, absorb ultimately all constituents of the true intermolecular potential, whatever the analytical form adopted for the atom–atom potential functions. There is therefore no justification to treat the sum of r^{-1} terms as an electrostatic energy, of r^{-6} terms as a dispersion energy, and of exponential terms as an exchange energy. This point has been noted, for instance, in a paper of Derissen & Smit (1978). For further reference one can use the paper of Wasiutynski, van der Avoird & Berns (1978) where the sum of empirical atom–atom Coulombic terms has been found, for ethylene, to have nothing in common with the *ab initio* electrostatic energy.

The better results obtained by BB with the (6-exp-1) potential are, in our opinion, a mere consequence of introduction of one more adjustable parameter into their potential model. There is no doubt that the use of, say, a (6-exp-2) potential function would also improve the results, even though the terms proportional to r^{-2} bear no relation to the electrostatic energy.

Thus, from the physical point of view, both the (6-exp) and (6-exp-1) potentials of BB are equally justified. Here we prefer to use the BB potential of the (6-exp) form

$$\varphi_{\rm BB} = -1495r^{-6} + 185710\exp(-3\cdot52r),$$

which is much more convenient for the time-consuming thermodynamic calculations because it allows us to avoid cumbersome summation of the Coulombic terms in reciprocal space.

It is to be noted that for compounds containing, aside from chlorine, hydrogen and carbon atoms the RKW and BB functions are to be used in combination with the H$\cdots$H and C$\cdots$C potentials of Williams (1967), while the MC function should be combined with those of Mirsky (1976).

Method of calculation

In the application of the cell model to a molecular organic crystal one treats the crystal as a classical system of N rigid molecules with three translational and three rotational degrees of freedom. Unlike the quasiharmonic approximation, the cell model involves no assumption of harmonicity of the potential energy. Instead of this, it neglects correlations in motion of individual molecules. As explained by Barker (1963), both these features inherent to the cell model make it a very good high-temperature model of the crystal state. By assuming the molecular motions to be uncorrelated the cell model reduces the configurational integral of the system to the form

$$Q = \exp(-U_0/kT)\, v_f^N, \tag{1}$$

where U_0 is the lattice energy of the crystal. The quantity v_f in (1) is the so-called 'free volume' defined by

$$v_f = \int_\Delta \exp\left\{-\frac{u(q)-u(0)}{kT}\right\} {\rm d}q, \tag{2}$$

where $q = \{q_1, q_2, \ldots, q_6\}$ is a six-dimensional vector describing the position and orientation of a molecule, $u(q)$ is the potential energy of interaction of the molecule at q with its neighbors fixed at their equilibrium sites ($q = 0$), Δ is the volume of configurational phase space per molecule. Note that $Nu(0) = 2U_0$.

The non-ideal part of the free energy is easily evaluated from (1) as $-kT \ln Q$, while the ideal part is calculated by the standard formula for the free energy of the ideal gas of polyatomic molecules, with the molecular mass and moments of inertia. The internal energy is given by

$$E = N\langle u\rangle - U_0 + 3NkT, \tag{3}$$

where the angular brackets denote the statistical averaging over the states of the initial molecule

$$\langle u\rangle = v_f^{-1} \int\limits_{\Delta} u(q) \exp\left\{-\frac{u(q) - u(0)}{kT}\right\} \mathrm{d}q. \tag{4}$$

Sufficiently accurate estimates of the integrals in (2), (4) can be obtained with the importance-sampling (Monte Carlo) method. Let us denote the integrand in (2) or (4) as $p(q)$ and let $g(q)$ be a positive valued function such that

$$\int\limits_{\Delta} g(q)\, \mathrm{d}q = 1. \tag{5}$$

If $q^{(1)}, q^{(2)}, \ldots, q^{(n)}$ are independent random points distributed within Δ with the probability density function $g(q)$, then the quantity

$$\theta_n = (1/n) \sum_{l=1}^{n} p[q^{(l)}]/g[q^{(l)}] \tag{6}$$

yields the desired estimate of the integral at sufficiently large n. The best convergence of (6) is observed when $g(q) \simeq p(q)$. Considering that the behavior of $p(q)$ in Δ is mainly determined by the exponential term and that the potential surface $[u(q) - u(0)]/kT$ can, to a first approximation, be described by a diagonal quadratic form $\sum_{s=1}^{6} q_s^2/2\sigma_s^2$, it is reasonable to take

$$g(q) = C \exp\left(-\sum_{s=1}^{6} q_s^2/2\sigma_s^2\right), \tag{7}$$

where C is a normalizing factor defined by (5). The best parameters of the distribution (7), σ_s, can be found by the least-squares fitting of the above quadratic form to $[u(q) - u(0)]/kT$. Note that the distribution (7) is usually very sharp so that

$$C \simeq \prod_{s=1}^{6} (2\pi\sigma_s^2)^{-1/2}. \tag{8}$$

Since (7) contains no cross terms, all six coordinates of the initial molecule can be generated independently of each other, with the normal distribution

$$g_s(q_s) = (\sqrt{2\pi}\sigma_s)^{-1} \exp(-q_s^2/2\sigma_s^2). \tag{9}$$

Because of the extreme sharpness of the distributions (7),(9) the choice of Δ is immaterial. In the existing program the molecular translations are restricted by the Wigner–Seitz cell and the molecular rotations by the symmetrically independent part of the orientational phase space. In fact, the generation of the molecular states according to (7) results only in small translations (0·1–0·2 Å) and librations (2–4°) of the initial molecule about its equilibrium position.

Two important remarks should be made in conclusion of this section of the paper. Firstly, inasmuch as the cell model treats the molecules as rigid, it yields only intermolecular (or 'crystalline') contributions to the thermodynamic quantities. The corresponding experimental quantities to be compared with the calculation results can be readily inferred from calorimetric data by subtracting intramolecular contributions calculated from internal mode vibration frequencies. Throughout this paper we shall present all observed thermodynamic quantities without their intramolecular parts.

Secondly, the cell model may in principle be used to derive the equilibrium unit-cell parameters of a crystal at non-zero temperature. Calculations of such a type have been performed by minimizing the free energy of the system with respect to the unit-cell parameters. It turned out, however, that the calculations gave somewhat underestimated unit-cell dimensions and thermodynamic quantities really observed at higher pressures (Pertsin, 1976). Because of this we prefer here to use observed unit-cell parameters so that the test of the intermolecular potential will be more reliable. For the HCB crystal we have specially measured the unit-cell dimensions at seven temperatures between 124 and 293 K. The X-ray data listed in Table 1 were taken on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. For low-temperature work a Syntex LT-1 attachment was employed to maintain the desired temperature to ±1 K. The room-temperature data of Table 1, when transformed to a $P2_1/n$ setting, show a good agreement with those reported by Brown & Strydom (1974).

Table 1. *Unit-cell parameters of the HCB crystal at seven temperatures between* 124 *and* 293 K

$P2_1/c$, $Z = 2$.

T (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
124	7·980 (2)	3·767 (1)	16·421 (4)	116·60 (2)	441·5 (2)
143	7·986 (3)	3·772 (1)	16·434 (5)	116·62 (2)	442·6 (3)
190	8·003 (1)	3·788 (1)	16·479 (3)	116·68 (1)	446·4 (1)
216	8·013 (1)	3·799 (1)	16·505 (3)	116·72 (1)	448·8 (1)
263	8·028 (1)	3·815 (1)	16·548 (4)	116·78 (2)	452·4 (2)
270	8·034 (4)	3·821 (2)	16·564 (8)	116·80 (3)	453·9 (3)
293	8·050 (3)	3·835 (1)	16·600 (6)	116·86 (3)	457·2 (3)

Results and discussion

1. *Hexachlorobenzene*

The importance-sampling estimates of the thermodynamic functions were obtained by sampling 1000 random points in Δ. This ensured an accuracy of about 0·06 kJ mol^{-1} for the free and internal energies and of 1·3 J mol^{-1} K^{-1} for entropy. The experimental crystalline contributions to the thermodynamic functions were inferred from the calorimetric data of Hildenbrand, Kramer & Stull (1958) and internal-mode fundamental frequencies reported by Bates, Thomas, Bandy & Lippincott (1971). The room-temperature enthalpy of sublimation was taken as quoted by Bates & Busing (1974).

Since the cell model is essentially a high-temperature model of the crystal state, it was reasonable to test the intermolecular potentials at as high a temperature as possible. Table 2 presents the enthalpy of sublimation and the entropy of HCB at 293 K, calculated with the three potential sets under examination. In deriving ΔH^0_{293} the gaseous phase was assumed ideal ($H_{\text{gas}} = 4RT$ + internal-mode contribution). Also presented in Table 2 are the corresponding observed quantities.

Inspection of Table 2 shows that the MC potential results in an appreciably overestimated entropy. Considering that the entropy is mainly sensitive to the steepness of the potential field, the observed discrepancy does not seem very surprising because the MC potential function is too soft. The RKW potential yields a somewhat better entropy value but a very large enthalpy of sublimation. The best total agreement with experiment is observed with the BB potential. The calculated and observed entropies are, as seen, practically coincident. As to the enthalpy of sublimation, the discrepancy is not very meaningful because it is of the same order of magnitude as usually observed for organic solids among various determinations.

Further examination of the reliability of the BB potential was performed by calculating the temperature dependence of the basic thermodynamic functions of the HCB crystal at temperatures between 124 and 293 K (the unit-cell dimensions were taken from Table 1). The results of these calculations are listed in Table 3. We present only the free energy and entropy since the internal energy can be readily deduced from them. The heat capacities C_v, though calculated by us, are not given in Table 3 in view of the lack of the corresponding experimental data. The comparison between the calculated and observed free energies is given in Table 3 with reference to their values at 293 K. This has been done because the value calculated at the highest temperature should, in principle, be most accurate and hence most preferable as a reference point.

Table 2. *The enthalpy of sublimation and entropy of the HCB crystal at* 293 K

	Calculated			Observed
	MC	RKW	BB	
ΔH^0_{293} (kJ mol^{-1})	93·4	121·8	87·9	97·1
S^0_{293} (J mol^{-1} K^{-1})	136·1	111·8	120·6	120·2

As seen from Table 3, the calculation results agree very closely with experiment. The difference between the calculated and observed entropies lies within the limits of statistical error (1·3 J mol^{-1} K^{-1}) throughout the whole temperature range examined. For the free energy, the deviations do not exceed 4%, which may be regarded as a sufficiently good result.

2. *p-Dichlorobenzene*

The cell-model calculations of the thermodynamic properties of the DCB crystal were carried out with the unit-cell dimensions from Wheeler & Colson (1976). The importance-sampling estimates of the thermodynamic functions were obtained with nearly the same standard deviations as for HCB. In deriving the experimental values of the crystalline contributions to the thermodynamic functions use was made of the calorimetric data of Dworkin, Figuière, Ghelfenstein & Szwarc (1976) and internal-mode vibration frequencies reported by Scherer & Evans (1963). The room-temperature enthalpy of sublimation was taken from Walsh & Smith (1961).

Table 4 compares the calculated and observed values of the enthalpy of sublimation and the entropy of the α phase of DCB at 300 K. As seen from the table, the three potential sets are nearly equivalent in predicting the enthalpy of sublimation. As with HCB, the MC and BB potentials somewhat underestimate ΔH, while the RKW potential yields an overestimated value. As to the entropy, only the soft MC potential function provides a sufficiently correct estimate. Both the RKW and BB potentials result in perceptibly underestimated values, as great as 8·8–9·6 J mol^{-1} K^{-1} lower than the observed one.

Table 3. *The free energy and entropy of the HCB crystal in the temperature range between* 124 *and* 293K

	$-F^0_T$ (kJ mol^{-1})	$F^0_T - F^0_{293}$ (kJ mol^{-1})		S^0_T (J mol^{-1} K^{-1})	
T (K)	calc	calc	obs	calc	obs
293	112·7	–	–	120·6	120·2
270	109·8	5·94	5·74	115·6	115·1
263	108·9	7·75	7·41	113·9	113·9
216	103·5	18·38	17·71	102·6	103·0
190	100·6	23·53	22·69	95·5	95·9
143	96·1	31·44	30·23	80·0	81·2
124	94·6	33·95	32·70	72·9	74·1

Table 4. *The enthalpy of sublimation and the entropy of the DCB crystal at* 300 K

	Calculated			Observed
	MC	RKW	BB	
ΔH^0_{300} (kJ mol^{-1})	57·4	72·4	55·3	64·9
S^0_{300} (J mol^{-1} K^{-1})	121·4	111·8	111·0	120·6

The failure of the BB potential in calculation of the entropy of DCB is unexpected in view of the excellent agreement observed with HCB where the Cl···Cl non-bonded interactions account for a much greater portion of the total intermolecular energy. It is not unlikely that the discrepancy between the calculated and observed entropy results from positional disorder which seems to occur in the high-temperature phases of DCB (Wheeler & Colson, 1976). If the Cl atoms of the DCB molecule in the α and β phases are displaced above and below the carbon plane, as is the case in the γ phase, the observed average planarity of the α- and β-phase molecules implies that the molecules are distributed with equal probabilities among two possible positions related by the mirror plane coincident with the plane of the carbon ring. With such a model for positional disorder one should add to the calculated entropies in Table 4 a value of $R\ \ln 2 = 5{\cdot}9$ J mol^{-1} K^{-1}, which considerably improves the results obtained with the RKW and BB potentials.

The final test of the MC, RKW and BB potentials was performed by calculating the thermodynamic functions of the three phases of DCB at 100 K. The aim was to see if the calculations put the free energies and entropies of the three phases in the correct sequence:

$$F^0_{100}(\gamma) < F^0_{100}(\alpha) < F^0_{100}(\beta);$$

$$S^0_{100}(\gamma) < S^0_{100}(\alpha) < S^0_{100}(\beta).$$

The calculation results are listed in Table 5. Given in parentheses are the values corrected for the possible disorder in the α and β phases ($F^0_{100} + RT\ln 2$, $S^0_{100} + R\ln 2$). As seen from Table 5, the MC potential arranges the free energies of the three DCB phases in a wrong sequence and the correction for possible disorder leaves the situation unchanged. The RKW and BB potentials yield the proper sequence for the free energy but not for entropy. The addition of contributions due to disorder corrects the sequence for entropy but rearranges the RKW values for the α- and γ-phase free energies. The correct sequence for both free energy and entropy is only observed when we use the BB potential function and treat the α and β phases as being disordered. Note that the differences between the calculated α- and γ-phase entropies and between the β- and α-phase entropies are very close to the corresponding entropy changes observed in experiment [4·61 and 0·71 J mol^{-1} K^{-1}, as reported by Dworkin *et al.* (1976)].

Table 5. *The free energy and the entropy of the DCB crystal at* 100 K

Potential	Phase	F^0_{100} (kJ mol^{-1})	S^0_{100} (J mol^{-1} K^{-1})
MC	β	−64·56 (−65·15)	58·6 (64·48)
	α	−64·14 (−64·73)	58·2 (64·06)
	γ	−64·06	58·2
RKW	β	−77·08 (−77·69)	51·9 (57·8)
	α	−80·01 (−80·60)	50·2 (56·1)
	γ	−80·51	51·5
BB	β	−59·87 (−60·33)	50·2 (56·1)
	α	−60·67 (−61·25)	49·0 (54·8)
	γ	−62·55	50·7
	γ*	−62·30	50·2

The values presented in the lowest row of Table 5 and marked by an asterisk were calculated assuming the γ-phase molecules to be planar. A comparison of the values with those obtained with the real non-planar molecule shows that the observed distortions from planarity make the γ-phase crystal structure 0·25 kJ mol^{-1} more stable. The latter value is quite sufficient for a 0·05 Å out-of-plane displacement of the Cl atoms (Wheeler & Colson, 1976; Radcliff & Steele, 1969).

Conclusions

Examination of three Cl···Cl potential functions *via* cell-model calculation of the thermodynamic properties of the HCB crystal reveals a distinct advantage of the BB potential over the other two. The applicability of the BB potential to DCB is not so obvious and depends in great measure on the existence of positional disorder in the α and β phases of DCB. Although some evidence in favor of this disorder has been available (Wheeler & Colson, 1976), its details and origin still remain to be elucidated.

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Cell Reduction and Lattice Symmetry Determination

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Abstract

Simple inspection of the reduced form of a unit cell can fail to detect the correct lattice symmetry, because of the effects of measurement errors, computer rounding errors and uncertainties in interpretation of almost equal numbers. A procedure which is insensitive to these effects consists of the generation of a list of lattice vectors sorted on length, together with angles between pairs of them. The list includes the edges, face diagonals and body diagonals of the reduced cell, and the sums and differences of any of these which are similar in length. The correct unit cell is easily recognized in the vector list.

Introduction

The determination of the unit cell is an essential first step in a crystal structure determination, once a suitable single crystal has been obtained. With the development of computer-controlled diffractometers, this process has become progressively automated. On many machines it is now possible to mount and centre a crystal, and then leave the control software to locate reflexions and determine a unit cell without any human intervention. That such a use of automatic procedures can lead to the selection of unsuitable unit cells has been recently demonstrated (Marsh & Schomaker, 1979; Ilsley, Albright, Anderson, Glick & Oliver, 1980). Problems arise particularly when the cell is centred or has a very long axis.

Mighell & Rodgers (1980) have proposed that unit cells should be checked routinely by reduction procedures, and the correct Bravais lattice type deduced from the form of the reduced cell. The use of automatic procedures for the recognition and interpretation of the reduced form is, however, dangerous because of the effects of errors in the unit-cell parameters, rounding errors in calculations and the question of equality or inequality of computed non-integral numbers (Ilsley *et al.*, 1980). Small changes in cell dimensions can lead to completely different results for the reduced cell in special cases (Andrews, Bernstein & Pelletier, 1980), making interpretation of the reduced form difficult.

For this reason, we have devised a procedure for checking a unit cell by performing a reduction to a standard form and then generating a list of selected lattice vectors together with the angles between pairs of them. This method is insensitive to the problems of