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Intermolecular Potential-Function Models for Crystalline Perchlorohydrocarbons

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Abstract

Nonbonded potential parameters were derived from the crystal structures of five perchlorohydrocarbons. Intermolecular interactions were represented by interatomic (exp–6–1) nonbonded potential functions. Optimized values for the nonbonded potential parameters were obtained by four different methods. These methods are: direct fit to structural parameters; Taylor's series approximation for direct fit; force minimization with diagonal-weight matrix; and force minimization with full-weight matrix. The direct fit to structural parameters method gave the best results but was expensive of computer time. The Taylor's series approximation for direct fit method was satisfactory. The force minimization with diagonal weights method gave poor results. Force minimization with full weights was the best of the approximation methods, and was almost as good as the direct-fit method. The transferability of the nonbonded potential parameters among the five compounds was established within threshold error limits. Anisotropic potential functions for chlorine, which have been suggested by other workers for the polymorphic 1,4-dichlorobenzene crystal structures, were not found necessary to achieve threshold fits to these perchlorohydrocarbon structures.

Introduction

Nonbonded interatomic potential functions which can be used to reproduce successfully the crystal structures of aromatic and aliphatic hydrocarbons have been available for several years (Williams, 1972; Williams & Starr, 1977). Recently, attempts have been made to extend this approach to molecular crystals of chlorinated hydrocarbons.

Bonadeo & D'Alessio (1973) fitted nonbonded potential functions of the (exp–6) type to the crystal structures and lattice frequencies of 1,4-dichlorobenzene (α and β phases), 1,3,5-trichlorobenzene, and hexachlorobenzene. Reynolds, Kjems & White (1974) performed a similar calculation by fitting (exp–6) nonbonded potential functions to the crystal structures of 1,4-dichlorobenzene (α phase), tetrachlorobenzene, and hexachlorobenzene; the lattice frequencies of the first and last compound were also fitted. Neither of these papers considered the possibility of the presence of net atomic charges in the molecules.

Bates & Busing (1974, hereafter referred to as BB) fitted (exp–6–1) potential functions to the crystal structure of hexachlorobenzene. They found a net charge of −0·1058 e on the Cl atoms, with opposite charges on the C atoms. They showed that the net-atomic-charge model was superior to the earlier no-charge models. They also calculated the lattice frequencies in hexachlorobenzene and found better agreement with the net-charge model.

Wheeler & Colson (1976) considered nonbonded interactions in a qualitative manner for the crystal structures of the α, β, and γ phases of 1,4-dichlorobenzene. They noted especially that the β crystal form has a remarkably short Cl···Cl distance of 3·38 Å between atoms in different molecules. The shortest Cl···Cl distances in the α and γ forms are 3·73 and 3·79 Å, respectively. These authors conclude that inclusion of anisotropy in the Cl···Cl nonbonded potential function is essential to understand the molecular packing in these structures.

Munowitz, Wheeler & Colson (1977) quantitatively tested several isotropic (exp–6–1) Cl···Cl functions by using them to predict the crystal structures of the three phases of 1,4-dichlorobenzene. However, no numerical values for the nonbonded potential parameters tested are divulged in their paper, making it difficult to evaluate the work independently. These authors conclude that isotropic functions are not satisfactory for Cl···Cl interactions in the 1,4-dichlorobenzene crystal structures.

There can be no doubt that, for ultimate accuracy, an anisotropic nonbonded potential is required for every atom type. This anisotropy complicates the model. And since the anisotropy may vary from molecule to molecule, transferability may be more difficult to achieve with anisotropic potentials. Thus, there is a compromise between accuracy *versus* simplicity and transferability in deriving nonbonded potential parameters.

A threshold of accuracy is needed, above which anisotropic treatment is justified. This threshold cannot be completely rigorous, and will vary according to the purpose at hand. For our purpose we established

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thresholds of 1% accuracy in the lattice constants, 1° in the cell angles, 2° in the molecular rotation, and 0·1 Å in the molecular translation. This judgement of accuracy requires that most, but not necessarily all, of the structural parameters be fitted within the threshold accuracy. Otherwise, a shift to anisotropic or other type of more complicated functions is justified.

Munowitz, Wheeler & Colson did not achieve this threshold of accuracy, using isotropic functions, for the three phases of 1,4-dichlorobenzene. However, they did not examine the full range of isotropic functions. Also, it may be noted that thermal effects may be important in this type of structure, where polymorphic phase transitions occur at certain temperatures. It is possible that a systematic examination of isotropic functions, including consideration of the effects of thermal motion, could result in a model satisfying the threshold accuracy requirement.

In view of the success of the BB isotropic model for hexachlorobenzene, a determination was needed of the transferability and extendability of this model to other Cl-containing crystals. We have selected five well determined crystal structures of perchlorohydrocarbons to make this test. The absence of H atoms reduces the number of potential parameters to consider. We found, as is detailed below, that care needs to be taken in the selection of the method of derivation of the nonbonded potential parameters from the data.

Basis structures and nonbonded potential functions

Fig. 1 shows the molecules whose crystal structures were utilized for the derivation of the nonbonded potential parameters. Table 2 gives the references to the experimentally determined crystal structures; it also shows the observed structural parameters which are to be fitted by the nonbonded potential parameters. For one rigid molecule in the asymmetric unit, the maximum number of observables are six lattice constants, three molecular rotations, and three molecular translations. In the table the three independent molecular rotations, if allowed, have been combined into a single rotation for the threshold comparison. Similarly, the three independent translations have been combined into a single translation. The actual number of observed quantities to be fitted is reduced by symmetry to a total of 38 observables for the five structures. The observed heat of sublimation of hexachlorobenzene at 0 K, with correction for zero-point energy as shown by BB, was used to scale the potential functions.

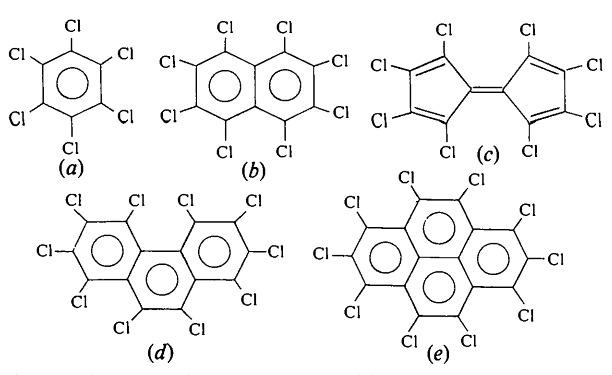

Fig. 1. The molecular structures of (*a*) hexachlorobenzene, (*b*) octachloronaphthalene, (*c*) octachloropentafulvalene, (*d*) decachlorophenanthrene and (*e*) decachloropyrene.

The assumed form of the nonbonded potential functions was the isotropic (exp–6–1) type:

$$E(r_{jk}) = B\exp(-Cr_{jk}) - Ar_{jk}^{-6} + q_j q_k r_{jk}^{-1},$$

where r_{jk} is a nonbonded distance between atoms j and k in different molecules, and A, B, C, and the net atomic charges q were the nonbonded parameters. We further assume the geometric mean combining law, so that we may write

$$E(r) = b_m b_n \exp[-(c_m + c_n) r/2] - a_m a_n r^{-6} + q_j q_k r^{-1}.$$

The molecule is considered to be rigid and stationary in the unit cell, *i.e.* no thermal motion is explicitly contained in the model.

In the last equation the subscripts m and n are used to indicate classification of the coefficients into atomic types. For transferability reasons we assign the same values for all C atoms, using the values of Williams & Starr (1977). All Cl atoms are similarly assumed to have the same nonbonded parameters, to be determined. C atoms not bonded to Cl are assumed to have zero net charge.

There is a strong correlation between b and c such that it is difficult to vary both simultaneously. We have selected the value of $c = 3{\cdot}51$ Å^{-1} for Cl (previously used by BB) and have optimized only b. The only other parameters to be optimized are a and q for Cl. The ratio of observables to parameters is quite good, at 38 to 3.

Optimization methods

(1) *Direct minimization*

The optimum generalized nonbonded potential parameters, q_j, are those which reproduce most closely the observed generalized structural parameters, p_i. Since the structural parameters are not all on the same scale, we define a weighted r.m.s. difference function, R_p, to minimize

$$R_p(q_j) = \left[N^{-1} \sum_i w_i (\Delta p_i)^2\right]^{1/2},$$

where Δp_i is the difference between the observed and calculated ith structure parameters, and N is the total number of structure parameters. The weights, w, are the inverse squares of the allowed error thresholds for the parameter type, as given above.

The predicted values for the structure parameters are obtained exactly by minimization of the lattice energy for a particular choice of nonbonded potentials. Starting from the observed structure, usually many cycles of Newton–Raphson refinement are necessary in order to find the location of the lattice-energy minimum with good accuracy. Although the evaluation of the lattice sums may be speeded up considerably by using the accelerated-convergence method (Williams, 1971), considerable computer time is still required. The lattice-energy minimization must be repeated for each trial choice of the nonbonded potential parameters. Thus this method, although the most accurate, is expensive of computer time.

(2) *Structural parameter shift estimation*

To overcome the computational time required to locate the minimum of R_p, Hagler & Lifson (1974) suggested using a Taylor's series expansion of the gradient vector (whose elements are negatives of the forces, F_i) of the lattice energy:

$$\mathbf{F}(p_i, q_j^0) = \mathbf{F}(p_i^0, q_j^0) + \mathbf{H}\,\Delta\mathbf{p} + \ldots,$$

where **H** is the Hessian, or second-derivative matrix, of the energy surface with respect to the structural parameters. Since at the lattice-energy minimum $\mathbf{F}(p_i, q_j^0) = \mathbf{0}$, therefore $\Delta\mathbf{p} = -\mathbf{H}^{-1}\ \mathbf{F}(p_i^0, q_j^0)$. This is an analytical expression for the predicted structural parameter shifts. Substitution into R_p yields also an analytical expression whose minimum can be found with respect to the q_j. Actually the equivalent simpler expression $\sum_i w_i(\Delta p_i)^2$ may be minimized. This procedure requires only a single evaluation of the lattice energy and its derivatives, at the observed structure. The advantage of the method is great speed as compared to the direct minimization method described above. The disadvantage of the method is loss of accuracy because of the neglect of higher-order terms in the Taylor's series expansion of the forces. Also, the derivatives of Δp_i with respect to q_j are very complex analytical expressions involving the inverse of **H**. These derivatives are usually evaluated by numerical approximation.

(3) *Force minimization with diagonal-weight matrix*

This method seeks to minimize the magnitude of the gradient vector of the lattice energy. The components of the gradient vector are the forces, F_i, which should vanish at the observed structure when the correct nonbonded potentials are used. Because of the different scaling of the structural parameters, the components of the gradient vector are weighted to yield the residual function $R_{\rm FD}$:

$$R_{\rm FD} = \sum_i w_{ii}[F_i(p_i, q_j)]^2.$$

The weights, w_{ii}, are discussed below in connection with the full-weight matrix method.

The derivatives of $R_{\rm FD}$ with respect to q_j are easy to obtain in simple analytical form. We define **B** as a (nonsquare) matrix of derivatives, where $B_{ij} = \partial F_i/\partial q_j$. The forces are again expanded in a first-order Taylor's series, this time as a function of the nonbonded potential parameters rather than the structural parameters:

$$F_i(p_i^0, q_j) = F_i(p_i^0, q_j^0) + \sum_j [\partial F_i(p_i^0, q_j^0)/\partial q_j]\,\Delta q_j + \ldots.$$

Substitution yields the matrix equation

$$\mathbf{B}^t\,\mathbf{w}\mathbf{B}\,\Delta\mathbf{q} = -\mathbf{B}^t\,\mathbf{w}\mathbf{F}(p_i^0, q_j^0),$$

which may be used iteratively to find shifts Δq_j towards the optimum values of q_j.

(4) *Force minimization with full-weight matrix*

Instead of minimizing only the magnitude of the force gradient, cross terms can be included with appropriate weights to define the function R_F:

$$R_F(q_j) = \sum_i \sum_k w_{ik} F_i(p_i^0, q_j)\,F_k(p_k^0, q_j).$$

The solution for the optimum values of q_j which minimize R_F is the same as before, except now the off-diagonal weights may be nonzero. It can be shown (Busing, 1970) that near convergence the weight matrix is

$$\mathbf{w} = [\mathbf{H}^t\,\mathbf{V}\mathbf{H}]^{-1},$$

where **V** is a diagonal matrix with $V_{ii} = \sigma^2(p_i)$, the variance or error threshold assigned to the observed structural parameters.

As we shall see, rather different results can be obtained with the diagonal- and full-weight methods, even though they superficially appear quite similar. The full-weight method does require the extra matrix inversion indicated, but little additional time or programming effort is needed for this.

The diagonal weights for method (3) are obtained in the same manner as the full weights, except that only the diagonal elements of the Hessian are used. The matrix inversion is now trivial, so that $w_{ii} = V_{ii}^{-1} H_{ii}^{-2}$.

Obviously, the calculated forces vanish as the nonbonded parameters go to zero, so that it was necessary to scale the nonbonded energy in some way. This was accomplished by requiring that the calculated lattice energy of hexachlorobenzene be equal to the observed heat of sublimation at absolute zero temperature. The side condition was incorporated by adding the penalty function

$$w'(E_{\rm lattice} - \Delta H_s^0)^2$$

for hexachlorobenzene; w' is adjusted sufficiently large to obtain the desired fit between the observed and calculated lattice energies.

The lattice sum was treated by a convergence-acceleration technique (Williams, 1971). It is necessary to use convergence acceleration to achieve accuracy in the lattice sums, particularly the Coulombic sums. We estimate that our lattice sums are converged within 1%. Both the first and second derivatives of the lattice energy were evaluated analytically rather than numerically. This procedure saves time and increases accuracy.

Results and discussion

The optimized potential parameters obtained by each method from the set of five perchlorohydrocarbon structures are shown in Table 1. The potential parameters of BB are also shown for comparison. Each of the five sets of nonbonded potential parameters was tested by finding the corresponding minimum-energy structures (Williams, 1979) for the five perchlorohydrocarbon crystal structures. The differences between the calculated and observed structural parameters are shown in Table 2.

The BB nonbonded parameters are surprisingly good, even though they were derived from only one structure. Because of the larger number of structures fitted, the present parameters should be more accurate than those of BB, using the full-weight force method in each case. The BB parameters predict the lattice energy of hexachlorobenzene too small (see below).

The parameters from the force minimization with diagonal weights are surprisingly bad (method 3). The difficulty with method (3) arose mainly in fitting the molecular angular orientation in hexachlorobenzene. Method (3) has previously been used, apparently successfully, for hydrocarbons and a variety of other types of crystals. We have also encountered some problems using the diagonal-weight method for the crystal structures of the halogens (Hsu & Williams, 1980). In that case also the use of full weights remedied the problems, making it the method of choice.

BB used the full-weight force method in their work, although the exact values of their weights were not specified. The present work shows that the full-weight force method may be extended to the set of five perchlorohydrocarbon structures. The structural parameter shift estimation method is not quite as good as the full-weight force method. This method was also found to be slightly less good than the force method for hydrocarbon structures (Williams & Starr, 1977). Very

Table 1. *The nonbonded potential parameters*

The first set was derived from hexachlorobenzene by Bates & Busing (1974). The other sets were derived in this work from all five perchlorophydrocarbon crystal structures. Our assumed values for carbon are $a = 49·13$, $b = 606·0$, $c = 3·60$, and $q(\mathrm{C}) = -q(\mathrm{Cl})$ (Williams & Starr, 1977). The units are Å and kJ mol^{-1}.

Parameter	BB	Method (1)	Method (2)	Method (3)	Method (4)
a	85·42	87·98	91·36	86·64	89·10
b	942·8	961·6	1018·7	931·2	974·9
q	0·1058	0·1090	0·1022	0·0842	0·1019

Table 2. *Structural parameter shifts obtained by minimization of the lattice energy using the nonbonded potential parameter sets of Table* 1

References are given to the experimental crystal structure determinations. The number of independent observed structural parameters is given following the name of the compound.

Structural parameter and observed value	BB	Method (1)	Method (2)	Method (3)	Method (4)
Hexachlorobenzene; Brown & Strydom (1974); 4 lattice constants + 3 rotations					
a (8·0476 Å)	−0·05	−0·06	−0·01	0·17	−0·04
b (3·8363 Å)	−0·02	−0·02	−0·04	0·00	−0·05
c (14·8208 Å)	0·17	0·14	0·22	−0·54	0·18
β (92·13°)	−0·5	−0·3	−0·9	−8·1	−1·1
θ (0·0°)	1·5	1·4	2·2	24·5	2·9
Octachloronaphthalene; Gafner & Herbstein (1963); 4 lattice constants + 3 rotations + 3 translations					
a (19·48)	0·15	0·14	0·19	0·07	0·13
b (7·30)	−0·13	−0·14	−0·12	−0·16	−0·13
c (9·76)	0·05	0·04	0·07	0·01	0·04
β (111·55)	−0·8	−0·8	−0·5	−0·4	−0·6
θ (0·0)	0·4	0·4	0·2	0·1	0·3
t (0·0 Å)	0·16	0·17	0·12	0·06	0·12
Octachloropentafulvalene; Ammon, Wheeler & Agranat (1973); 4 lattice constants + 1 rotation + 1 translation					
a (14·998)	0·04	0·03	0·09	−0·01	0·03
b (7·911)	−0·06	−0·07	−0·04	−0·08	−0·05
c (11·8068)	0·03	0·03	0·05	−0·01	0·02
β (103·38)	1·6	1·6	1·6	1·6	1·6
θ (0·0)	1·8	1·8	1·8	1·8	1·8
t (0·0)	0·00	0·00	0·00	0·01	0·00
Decachlorophenanthrene; Herbstein, Kapon & Merksamer (1976); 3 lattice constants + 1 rotation + 1 translation					
a (5·065)	−0·03	−0·02	−0·02	−0·08	−0·03
b (17·946)	−0·01	−0·03	0·04	−0·07	−0·02
c (18·554)	0·25	0·19	0·33	0·34	0·25
θ (0·0)	0·0	0·2	0·1	0·5	0·0
t (0·0)	0·09	0·08	0·11	0·10	0·06
Decachloropyrene; Hazell & Jagner (1976); 4 lattice constants + 3 rotations + 3 translations					
a (21·462)	0·16	0·15	0·19	0·11	0·15
b (7·494)	−0·02	−0·03	−0·00	−0·04	−0·01
c (10·803)	0·05	0·05	0·08	−0·01	0·04
β (92·8)	0·0	0·1	−0·0	0·4	0·2
θ (0·0)	0·6	0·6	0·6	0·9	0·7
t (0·0)	0·12	0·12	0·13	0·13	0·12
Calculated lattice energy of hexachlorobenzene (observed value was taken as −98·74 kJ mol^{-1})					
E_{lattice}	−91·7	−96·0	−100·0	−98·6	−98·6
Discrepancy index for all structures					
R_p	0·827	0·815	0·908	2·998	0·869

likely the difficulties with the structural parameter shift estimation method are caused by non-negligible contributions of higher-order terms in the Taylor's series expansion. Hagler & Lifson (1974) have commented on this point.

Because of the significant differences obtained by the different methods of derivation, we directly minimized R_p by external variation of the q_j on a grid. As expected (method 1), this gave the lowest possible value of R_p. Method (4) is sufficiently close to method (1) that it is doubtful if the extra computer time required for method (1) is justified. Method (2) appears to be fairly satisfactory, but seems to offer no particular advantage over method (4).

Our test of the BB parameters gave a heat of sublimation for hexachlorobenzene of 91·66 kJ mol^{-1}, as compared to the observed value of 98·74 kJ mol^{-1}. Thus, although these parameters give an excellent fit to the structure, the fit to the heat of sublimation is not so good. This apparent relaxation of the scaling condition to the lattice energy may be the reason why the BB R_p value is slightly less than our result using the force method with full weights. In our calculations we obtained a better fit to the heat of sublimation of hexachlorobenzene, as is shown in Table 2.

Except for the results of method (3), the R_p value was always found to be less than the threshold value of 1·0. This fit is considered to be sufficiently good as to make the introduction of explicit anisotropy into the potential functions unnecessary.

The net atomic charges of 0·1 e do not lead to a large Coulombic contribution to the lattice energy, compared to hydrocarbons. Thus, hexachlorobenzene has the largest Coulombic contribution of the five perchlorohydrocarbons considered: 6·6%. For comparison, our calculations show that benzene, with net atomic charges of 0·15 e, has a Coulombic contribution of 21%.

Since the ratio of Coulombic contributions is smaller than predicted from the square of the ratio of the net atomic charges, the packing in hexachlorobenzene must not favor Coulombic interaction as much. The dispersion attraction between Cl atoms is much larger than the dispersion attraction between H atoms, so that it is more likely that Cl atoms will be close together. The proximal chlorines will reduce the Coulombic packing energy, because of their Coulombic repulsion.

Several theoretical estimates of the net charge on the Cl atoms in hexachlorobenzene are available. Clark, Chambers, Kilcast & Musgrave (1972) obtained a value of −0·093 e using CNDO/2 molecular-orbital methods. Wulfsberg & West (1972) estimated this charge as −0·18 e based on an interpretation of nuclear quadrupole resonance data. Pedersen & Carlson (1975) obtained a charge of −0·061 e from an *ab initio* SCF–MO calculation using a STO-3G basis set. It is known that STO-3G basis sets usually yield smaller net atomic charges than larger and more accurate basis sets, such as 6-31G (Steiner, 1976). However, no larger basis-set calculations for hexachlorobenzene are available at this time.

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