The observed entropy change at 255 K of $2\cdot20(2)$ J mol^{-1} K^{-1} was previously fitted by a model in which 17 possible molecular configurations above the transition were assumed to be reduced to two configurations in the low-temperature phase (Abrahams *et al.*, 1981). The configurational entropy change associated with the transition is then $\frac{1}{8}R \ln(17/2) = 2\cdot22$ J mol^{-1} K^{-1}, in excellent agreement with experiment. The present structure determination shows that molecule (I) is fully ordered below the phase-transition temperature and hence has but a single configuration. At 298 K, however, the disorder associated with each pair of molecules (II) gives rise only to three of the four configurations possible, since one configuration would result in the unacceptably short O$\cdots$O distance of $2\cdot5$ Å. The total number of configurations at 298 K is hence 3^2, for a corresponding predicted entropy change of $\frac{1}{8}R \ln 9 = 2\cdot28$ J mol^{-1} K^{-1}.

The dependence of the phase-transition temperature on applied hydrostatic pressure may be estimated from the Clapeyron equation, using the known changes in entropy and unit-cell volume, as about $0\cdot25$ K MPa^{-1}.

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Fluorine Nonbonded Potential Parameters Derived from Crystalline Perfluorocarbons

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Abstract

Fluorine-fluorine nonbonded potential-energy functions of the $(\exp-6-1)$ type were derived by least squares from the crystal structures of seven perfluorocarbons. Potential-derived site-charge models for the molecules were obtained using *ab initio* wavefunctions calculated with a 6-31G basis set. The best fit to the calculated molecular electric potential was obtained with a C–F bond-charge model. In addition, extended-charge, net-atomic-charge and no-charge models were considered. The best fits to the crystal structures were also obtained using nonbonded parameters derived using the bond-charge model. A plot of the resulting F$\cdots$F nonbonded potential showed that fluorine in perfluorocarbons is as space filling as oxygen in oxohydrocarbons.

Introduction

Nonbonded interatomic potential functions of the $(\exp-6-1)$ type have previously been derived by this research group from the crystal structures of hydrocarbons (Williams & Starr, 1977), azahydrocarbons (Williams & Cox, 1984), oxohydrocarbons (Cox, Hsu & Williams, 1981), perchlorocarbons (Hsu & Williams, 1980), and the noble gases (Williams, 1972a). References and comparisons with the work of other research groups are given in the cited papers.

General descriptions of the method were given by Williams (1972b, 1981). It was apparent that in the sequence of elements carbon, nitrogen, oxygen and neon that fluorine also needed consideration. Our work on fluorine indicated, as described in this paper, that fluorine does not appear to fit into a smooth progression from carbon to neon.

In the present work nonbonded interatomic potential functions for F$\cdots$F interaction were derived from experimental crystal structure data of perfluorocarbons. The necessary C$\cdots$C potential was transferred from the previous work on hydrocarbons quoted above, and the C$\cdots$F potential was obtained with the geometric mean combining law. Electrostatic interactions were obtained using site-charge models which were calculated from *ab initio* molecular wavefunctions.

The resulting F$\cdots$F nonbonded potential parameterizations were tested by relaxing the lattice constants and molecular positions to find the minimum-energy configurations for seven perfluorocarbon crystal structures. In this process the observed space group and number of molecules per cell were retained. The shifted structures were compared with the crystal structures observed by X-ray or neutron diffraction.

The atom-atom nonbonded potential-energy model for molecular crystals has proven to be a practical approximation. The nonbonded energy is modelled as a sum of repulsive and dispersive energy components, plus Coulombic interaction between charge sites.

When atoms approach each other at short distance, their electron clouds begin to overlap. Since the available low-energy electronic orbitals are already filled, the Pauli exclusion principle prohibits this overlap. The electron clouds of the interacting atoms may distort to avoid interpenetration, which gives rise to a strong repulsion. Since the radial dependence of the electron density is exponential, the amount of overlap and therefore the repulsion is also approximately exponential (Starr, 1976).

At long distances instantaneous dipole-dipole polarization gives rise to dispersion attractive forces between the atoms. By use of perturbation theory it has been shown that the dispersion energy can be represented by a series of terms of which the first is $-Ar^{-6}$. It is a reasonable approximation to use only the leading term, since the higher-order terms are smaller and may be partially included by the least-squares adjustment process.

Because of electronegativity differences, the electric potential around molecules is not zero; spatial regions near electronegative atoms will tend to have a negative potential. Part of the intermolecular energy originates from this nonzero electric potential. This energy of interaction can be evaluated from a site-charge model. Site-charge models can be obtained

which approximate the molecular electric potential. These charge sites in different molecules interact *via* Coulomb's law to yield an electrostatic or Coulombic intermolecular energy. The mathematical form of Coulomb's law indicates that heterosite interactions follow a geometric mean combining rule.

There is also a theoretical basis for the use of a geometric mean combining rule for the dispersion energy. The geometric mean combining rule for repulsion has only an empirical basis. A test of this rule was made with the present data (see below).

To a good approximation it appears that an energy increment for repulsion or dispersion is characteristic of the two species of atoms independently of what type of molecules they are contained in. That is, the repulsion and dispersion parts of the nonbonded potential are characteristic of the element. This is referred to as the transferability property. Making use of this property, we assume that carbon-carbon potential-energy functions derived from hydrocarbons can be transferred to perfluorocarbons. Transferability is not expected in general for the site charges, since they may vary considerably for the same element in different molecular bonding situations.

The lattice energy may be approximated by a pairwise sum over nonbonded atoms in different molecules using an (exp $-6-1$)-type potential function. This function can be used to evaluate lattice energies and through minimization determine a minimum-energy crystal structure. In contrast to the strongly bonded molecular structure, the packing structure is determined entirely by the weak nonbonded interactions. For the (exp -6) part transferable potentials are desired, depending only on the species of the atom. For the Coulombic part atomic subtypes with characteristic site charges are desired. The suitability of the nonbonded potential model may be checked by relaxing the lattice constants and molecular position to find the minimum-lattice-energy structure, with retention of the observed space group and number of molecules per cell.

The basis crystal structure data

A search of the literature revealed seven perfluorocarbons whose crystal structures had been experimentally well determined by either X-ray or neutron diffraction methods. These crystal structures were: hexafluorobenzene, C_6F_6 (Boden, Davis, Stam & Wesselink, 1973; Baharie & Pawley, 1977); octafluorocyclooctatetraene, C_8F_8 (Laird & Davis, 1982); decafluorobiphenyl, $C_{12}F_{10}$ (Gleason & Britton, 1976); dodecafluoro-1,2;3,4;5,6-triethanobenzene, $C_{12}F_{12}$ (Cobbledick & Einstein, 1976); decafluorodiphenylacetylene, $C_{14}F_{10}$ (Goodhand & Hamor, 1979); decafluorofluoranthene, $C_{16}F_{10}$ (Goodhand &

Table 1. *Crystal data for seven perfluorocarbon molecules*

Substance		Space group	Molecules per cell	a (Å)	b (Å)	c (Å)	β (°)	Reference
(I)	C_6F_6	$P2_1/n$	6	16·772	8·997	5·900	93·95	(a)
(II)	C_8F_8	$P2_1/c$	4	9·96	7·04	12·66	111·6	(b)
(III)	$C_{12}F_{10}$	$Fdd2$	8	13·49	26·54	6·31	—	(c)
(IV)	$C_{12}F_{12}$	$P6_3/m$	2	8·977	8·977	8·757	—	(d)
(V)	$C_{14}F_{10}$	$Pbca$	8	9·59	9·59	27·34	—	(e)
(VI)	$C_{16}F_{10}$	$C2/c$	8	18·92	4·84	29·01	105·34	(f)
(VII)	$C_{20}F_{24}$	$C2/c$	4	15·368	15·326	10·066	105·75	(g)

References: (a) Baharie & Pawley (1977); (b) Laird & Davis (1982); (c) Gleason & Britton (1976); (d) Cobbledick & Einstein (1976); (e) Goodhand & Hamor (1979); (f) Goodhand & Hamor (1981); (g) Cobbledick & Einstein (1977).

Hamor, 1981); and tetracosafluorotetrapropano-cyclooctatetraene, $C_{20}F_{24}$ (Cobbledick & Einstein, 1977).

Table 1 summarizes the crystal data and Fig. 1 illustrates the molecular structures. Five of the molecules in the data base have only CF groups and the remaining two molecules have only CF_2 groups,

Fig. 1. Molecular structures of the perfluorocarbon crystal data base.

besides carbon atoms. The molecular packing shows considerable variety. Structures (II), (V) and (VI) exhibit the simple case where one molecule is in a general position in the cell and the surrounding molecules are related by the space-group symmetry operations. In this situation the structural variables are six molecular rotations and translations, in addition to the lattice constants.

In structure (III) the biphenyl molecules are required to have twofold symmetry in the c lattice direction; the space group also is polar in the c direction. The molecular degrees of freedom are thus reduced to only a rotation about the z axis. In (IV) the triethanobenzene molecules have unusually high $\bar{6}$ symmetry; only a rotation of the molecule about the z axis is symmetry allowed. In (VII) the substituted cyclooctatetraene molecule has twofold symmetry in the b direction; thus rotation about and translation along the y axis is symmetry allowed.

The most complex molecular packing is shown by the simplest molecule, hexafluorobenzene. We found this structure difficult to model because of its relative complexity. There are six molecules crystallizing per unit cell in a space group of order four; thus there are one and one-half molecules in the crystallographic asymmetric unit. One molecule is in a general position and another molecule is placed on an inversion center. The two crystallographically independent molecules have the same molecular structure within experimental error. In addition to the lattice constants, the structural variables are six rotations and translations of one molecule, and three rotations of the second molecule. With inclusion of the four lattice constants this structure has thirteen degrees of freedom.

A *powder neutron diffraction study of hexa-fluorobenzene* at 83 K was made by Baharie & Pawley (1977). A single-crystal X-ray structure determination at 120 K was made by Boden, Davis, Stam & Wesselink (1973). Space group and unit-cell dimensions at 256 K were reported by Bertolucci & Marsh (1974). Table 2 summarizes the results of these investigations. The a and b lattice constants show expected thermal expansion. The c lattice constant and the cell angle show more erratic behavior. The two crystal-structure determinations yielded different bond lengths.
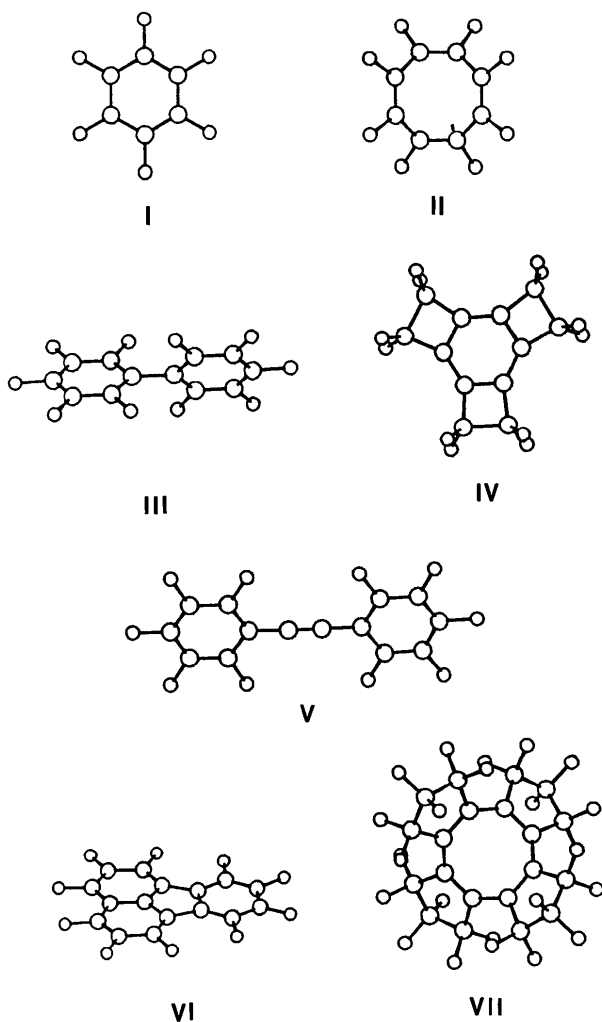
Table 2. *Comparison of crystal and molecular data for hexafluorobenzene*

Unit cell				Bond lengths (Å)		
a (Å)	b (Å)	c (Å)	β (°)	C–C	C–F	Reference
16·772 (2)	8·997 (1)	5·900 (1)	93·95 (1)	1·383 (4)	1·288 (7)	(a)
16·82*	9·17*	5·76*	95·8*	1·36 (2)	1·320 (17)	(b)
17·02 (5)	9·51 (1)	5·84 (4)	91·8 (3)	—	—	(c)
—	—	—	—	1·408 (6)	1·324 (6)	(d)
—	—	—	—	1·397†	1·321*	(e)

References: (a) Powder neutron diffraction at 83 K (Baharie & Pawley, 1977). (b) Single-crystal X-ray diffraction at 120 K (Boden, Davis, Stam & Wesselink, 1973). (c) Single-crystal X-ray diffraction at 256 K (Bertolucci & Marsh, 1974). (d) Gas electron diffraction (Bauer, Katada & Kimura, 1968). (e) Raman spectroscopy (Schlupf & Weber, 1973).

* Error not stated.
† Assumed value.

The two gas-phase molecular structure determinations shown in Table 2 are in good agreement for the C–F bond length. In the Raman spectroscopic determination the C–C bond length was assumed, while the experimental value obtained by electron diffraction appears a little large compared to the value of 1·397 Å in unsubstituted benzene. In this study we adopted the experimental electron diffraction values for the molecular structure and the experimental neutron diffraction values for the crystal structure.

It is desirable that at least one of the observed crystal lattice energies (heat of sublimation) be known in order to scale properly the nonbonded potential. Of the crystals considered, apparently only the thermodynamic properties of hexafluorobenzene have been determined (Counsell, Green, Hales & Martin, 1981) from which we obtained an energy of $-56·6\ kJ\ mol^{-1}$. As further discussed below, this crystal lattice energy of structure (I) was used as a side condition during the derivation of the nonbonded potential parameters.

Potential-derived site-charge models

The (exp−6−1) nonbonded potential function model, which is mathematically defined in the next section, includes Coulombic interaction between site charges. If no charge sites are included in the model, it is referred to as no charge (NC). The electric potential around the molecule may be modelled by placing site charges at the nuclear positions; this is the net-atomic-charge model (AC). Lone-pair or bonding-pair electrons may alternatively be positioned at non-nuclear sites. The two types of sites considered here are an extended charge site located on the extension of the C–F bond axis (EC) and a bond-charge site (BC) located at the center of the C–F bond.

In principle, site charges may be derived from crystal structure data by optimizing their values so as to best fit the data. This approach has been used for hydrocarbons (Williams & Starr, 1977) and for perchlorocarbons containing only CCl groups (Hsu & Williams, 1980). In both of these cases the model was simplified so that only a charge scale factor needed

to be derived from the structures. For the methyne, methylene and methyl groups of the hydrocarbons identical charge separation was assumed for the C–H bonds; for the perchlorocarbons only a single type of chlorine was present. In both cases isolated carbon atoms were assigned zero charge.

If it is necessary to assign many different types of charge sites, the dependence of the structure parameters on the site charges is too small and the number of site charges that must be determined becomes too large to allow derivation of these charges from crystal structure data. An alternative method for obtaining site charges in molecules is to calculate them from the quantum-mechanical molecular wavefunction.

Simple electronegativity considerations are not adequate for obtaining net atomic charges. With the availability of fast computers, it is now possible to calculate good *ab initio* molecular wavefunctions. From these wavefunctions the electric potential can be calculated at points in space around the molecule. The electric potential is an exactly defined physical property in quantum mechanics (Scrocco & Tomasi, 1978). The accuracy of this calculation is good, since the electric potential is the expectation value of a one-electron operator which is correct to one order higher than the wavefunction used.

Site charges in the molecule can be found by requiring them to reproduce the surrounding electric potential. Best least-squares-fit values for these site charges can be obtained. The technique is called the potential-derived (PD) charge method. Net atomic charges have been obtained by the PD method for a number of representative small molecules (Cox & Williams, 1981). The PD method is clearly superior to traditional population analysis, and is not limited to any particular type of wavefunction as is population analysis.

The PD method is also not limited to only the definition of nuclear site charges. In the case of aromatic nitrogen heterocyclic molecules it has been shown important to include additional lone-pair electron sites on the nitrogen atoms in order to fit either the molecular electric potentials (Williams & Weller, 1983) or the crystal structures (Williams & Cox, 1984). Also, non-nuclear charge sites have been shown

important in the water molecule and water dimer (Williams & Craycroft, 1985).

A third method for obtaining site charges which is applicable to simple molecules is to require them to reproduce experimentally known multipole moments. The quadrupole moment of hexafluorobenzene is known (Battaglia, Buckingham & Williams, 1981) so that site charges can be assigned so as to reproduce this moment. Both the second and third methods assume that isolated-molecule site charges are not significantly changed or polarized in the crystal environment. In the study on water dimer referenced above the maximum charge polarization in water dimer, as compared to the monomer, was found to be less than about 10% except when a strong hydrogen-bonding interaction was occurring. The quadrupole moment of hexafluorobenzene is discussed further below.

To find PD charges a grid of points was set up in a van der Waals shell around the molecule. In this work we used a grid with spacing 1 Å and a shell thickness of 1·2 Å beginning at a minimum distance of 2·9 Å from carbon and 2·55 Å from fluorine.

Ab initio wavefunctions for perfluorocarbon molecules were calculated with the *GAUSSIAN*80 computer program (Singh & Kollman, 1982). The investigations of Cox & Williams (1981) indicated that a split-valence atomic Gaussian function basis set as large as 6-31G (Hehre, Ditchfield & Pople, 1972) was needed to obtain sufficiently accurate site charges. However, because of computer limitations the only molecule in the crystal structure data which

Fig. 2. Molecular structures used for site-charge calculations.

could be handled with this basis set was hexafluorobenzene. The site-charge model for hexafluorobenzene was used to estimate site charges in structures (II), (III), (V), and (VI), which contain only CF groups or isolated carbons.

Structures (IV) and (VII) contain CF_2 groups, for which site charges also were needed. Molecules (VIII) and (IX) (Fig. 2), which looked like fragments of (IV) and (VII), were used as models. The qualitative difference between the two structure types was that (IX) [and (VII)] contained an extra CF_2 group bonded between adjacent CF_2 groups. Molecules (VIII) and (IX) were small enough to permit the calculation of their *ab initio* wavefunctions with the available computational facilities.

The values for the site charges were obtained by least-squares fitting of the molecular electric potentials at the grid points. Although the AC model was initially preferred because of its relative simplicity, we were prepared to use the EC or BC models if there were significant improvements in fitting the calculated electric potential. The criterion of fit was minimization of the function R, where n is the number of atoms and m is the number of grid points:

$$R = \sum_i^m w_i \left[V_i^o - \sum_j^{n-1} q_j r_{ij}^{-1} + \left(\sum_j^{n-1} q_j - Z \right) r_{in}^{-1} \right]^2.$$

V^o is the calculated quantum-mechanical electric potential at point i, w_i is a weighting factor, q_j is the site charge at site j, r_{ij} is the distance between site j and the ith grid point, and Z is the net charge on the molecule, which is zero for our case. The number of independent site charges is $(n-1)$ since there is a dependency condition that the sum of the site charges be equal to zero. Also, the symmetry of the molecule establishes further dependency conditions. The minimum value of R was found by taking the first partial derivatives of R with respect to the independent charges and solving the resulting set of linear equations by the usual least-squares method. The weight for each point was taken as unity which had previously been found satisfactory (Cox & Williams, 1981).

In order to make quantitative comparisons between the fits to the electric potentials we define the r.m.s. fit parameter, S (in kJ mol^{-1}), where

$$S = \left[m^{-1} \sum_i (V_i^o - V_i^c)^2 \right]^{1/2}$$

and a relative r.m.s. fit, s, where

$$s = S \Big/ \left[m^{-1} \sum_i (V_i^o)^2 \right]^{1/2}.$$

We tested the AC, EC and BC site-charge models with molecules (I), (VIII) and (IX). For (VIII) and (IX) we used molecular geometry as derived from the experimental crystal structure; for (I) we used
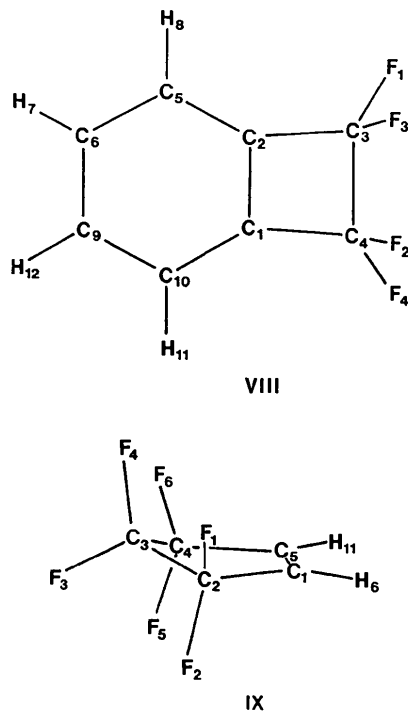
molecular geometry as found by electron diffraction. The choice for the experimental molecular geometry of (I) was discussed above.

Table 3 shows fits obtained with the three site-charge models for the three molecules. For (I), the AC model gave a relative fit of 11·0%. When an extended site was added at 0·25 Å (model EC), the relative fit improved to 4·3%. When a bond-center site was added (model BC) the relative fit further improved to 2·1%. Thus, the BC model best fitted the surrounding electric potential of (I). For (VIII) and (IX), similar comparative results were obtained for the three site-charge models. Although the BC model was still clearly best, the AC models for (VIII) and (IX) were relatively better than for (I). We concluded that overall the BC model was significantly superior to either the AC or the EC models in fitting the electric potential.

Table 4 shows values for the site charges. For molecule (I) the charges of the CF groups always sum to zero by symmetry. In the cases of (VIII) and (IX) the sums of the CF_2 group charges, while small, were not exactly zero. Further, in (IX) there were differences between the charges of the central CF_2 group compared to the adjacent CF_2 groups. In analyzing this situation, we concluded that it was reasonable to make small adjustments in the charges so that the CF_2 groups had zero charge and so that all CF_2 groups in (IX) had similar charges. We did not require that all CF_2 groups in both molecules have similar charges. Table 4 shows that somewhat different values were obtained for (VIII) and (IX). The most notable similarity between them is the charge on fluorine in model BC. This uniformity of the fluorine charge may be consistent with the superior modelling capability of BC. The AC and EC models show more charge fluctuations between (VIII) and (IX).

Experience with various atomic basis sets (Cox & Williams, 1981) indicated that the 6-31G basis set normally overestimates site charges. The amount of overestimation was determined by comparison of the observed dipole moments of molecules with operator dipole moments calculated directly from the *ab initio* wavefunctions. Since dipole moments obtained from PD charge distributions agree closely with the operator-calculated dipole moments, it is reasonable to scale the PD site charges so that they reproduce observed dipole moments.

These same considerations can be extended to the quadrupole moment of (I). The 6-31G wavefunction gave an operator quadrupole moment $Q_{zz} = 48·85 \times 10^{-40}$ C m² *vs* an observed $Q_{zz} = 31·7 \times 10^{-40}$ C m² (Battaglia, Buckingham & Williams, 1981). The ratio of Q_{zz} (observed) to Q_{zz} (calculated) is equal to 0·65. We therefore scaled the PD charges by this factor in all subsequent work with the crystal structures. The practical effect was essentially

Table 3. *Fitting the electric potential with site-charge models* (kJ mol⁻¹, %)

	AC		EC		BC	
Structure	S	s	S	s	S	s
(I)	2·4	11·0	1·0	4·3	0·5	2·1
(VIII)	1·7	5·3	1·2	3·6	0·9	2·8
(IX)	1·5	4·5	1·1	3·4	0·9	2·9

Table 4. *Average PD values for neutral group* $C-F_n$ *site-charge models* $(e \times 10^3)$

Model site	AC		EC			BC		
Structure	C	F	C	F	E	C	B	F
(I)	174	−174	95	243	−338	−86	466	−380
(VIII)	734	−367	308	175	−329	24	405	−417
(IX)	682	−341	436	3	−221	364	204	−386

to make the scaled PD charges for hexafluorobenzene reproduce the observed quadrupole moment of this molecule. The dipole and/or quadrupole moments of the other molecules were not available for comparison, but the same charge scaling factor was used for them.

The scaled PD charge models attempt to represent the details of the electric potential surrounding the molecule as closely as possible. Even given a set of site charges that well reproduce the molecular electric potential, there remains the task of determining a set of nonbonded potential parameters that can be used with the charges to model correctly the observed crystal structures of perfluorocarbons.

Derivation of nonbonded potential parameters

The (exp$-6-1$) function represents a model where each atom is assigned interaction parameters a_j, b_j, c_j and q_j such that the pairwise nonbonded potential energy is given by

$$E_{jk} = b_j b_k \exp\left[-(c_j + c_k) r_{jk}\right] - a_j a_k r_{jk}^{-6} + q_j q_k r_{jk}^{-1},$$

where r_{jk} is a nonbonded interatomic distance between atom j and atom k in different molecules. Alternatively, this function can be written

$$E_{jk} = B_{jk} \exp\left(-C_{jk} r_{jk}\right) - A_{jk} r_{jk}^{-6} + q_j q_k r_{jk}^{-1};$$

where $B_{jk} = b_j b_k$, $C_{jk} = c_j + c_k$ and $A_{jk} = a_j a_k$. The physical significance of the terms is that $B \exp(-C r_{jk})$ is the short-range strong repulsive term; $-A r_{jk}^{-6}$ is the weak longer-range attractive dispersion energy term; and $q_j q_k r^{-1}$ is the very-long-range Coulombic energy which can be either repulsive or attractive between site electrical charges.

The atom-atom potentials must be summed over the entire crystal lattice. In practice a summation limit of perhaps 10 Å is used. This summation limit is more than adequate for obtaining an accurate energy for the exponential repulsion. However, the dispersion sum is not fully converged at 10 Å. The convergence

behavior of the Coulombic sum is much worse and very erratic results can be obtained by truncation of the sum at 10 Å. Convergence of the Coulombic sum improves if care is taken to sum over electrically neutral domains; however, a significant truncation error is still present. Truncation errors of the dispersion and Coulombic lattice sums can readily be reduced to insignificance by using the accelerated convergence technique (Williams, 1971). We used this technique throughout this work with the goal of obtaining all lattice sums to an accuracy of 1% or better.

The possible structural variables for a lattice containing rigid molecules are the unit-cell edge lengths a, b and c; the unit-cell angles α, β and γ; the molecular rotations θ_1, θ_2 and θ_3; and the molecular translations t_1, t_2 and t_3. If there is more than one molecule in the crystallographic asymmetric unit there are additional molecular rotations and translations. The condition for equilibrium is that the first-derivative vector (gradient) of the lattice energy be zero and that the second-derivative matrix (Hessian) be positive definite. These are conditions of zero force, which includes compression, shear and torque; and the requirement of a relative minimum rather than a maximum or saddle point of the energy surface. Very often some of the structural variables are not independent but are set by the space-group symmetry.

Therefore at the observed structure (equilibrium), all calculated forces should be zero; if they are not the form of the nonbonded potential energy is not optimum. The best empirical values for A, B, C and q are sought. The method of optimization of potential parameters is essentially to find by a least-squares fitting procedure the optimum values of the adjustable parameters such that the forces at the observed structure vanish. These parameters must also yield a positive-definite Hessian. Let q_j be a generalized potential parameter and p_i be a generalized structural parameter.

To find the optimum values for q_j, a diagonal force function, R, is set up and minimized:

$$R(A, B, C, q) = \sum_{k=1}^{N} \sum_{i=1}^{M} w_i F_i^2$$
$$+ \sum_{k=1}^{N} w_k'(E_{\text{cryst}} - E_{\text{cryst}}^o)^2,$$

where $w_i = [1/\sigma(p_i)]^2$ is the diagonal weight and $F_i = -(\partial E_k/\partial p_i)$ designates a generalized force due to a change of the energy of the kth crystal structure with respect to the ith structural parameter. There are N structures with M variables per structure. The energy terms in the equation normalize the calculated lattice energy to the observed lattice energy, E_{cryst}^o.

Instead of minimizing only the magnitude of the force gradient, cross terms can be included with appropriate weights to define the more general full-

matrix force method, where

$$R = \sum_{k=1}^{N} \sum_{i=1}^{M} \sum_{j=1}^{N} w_{ij} F_{ik}(p_i^o, q_j) F_{jk}(p_k^o, q_j)$$
$$+ \sum_{k=1}^{N} w_k'(E_k - E_k^o)^2.$$

The energy weights w_k' are set sufficiently large so as to get the desired agreement between the observed and calculated energies. The solution for the optimum values of q_j that minimize R is the same as before, except now the off-diagonal weights may be nonzero. The weight matrix near convergence (Busing, 1970) is now $w_{ij} = [H_k^t V_k H_k)^{-1}]_{ij}$, where V_k is a diagonal matrix with elements $V_{ii} = \sigma^2(p_i)$. The Hessian, where $H_{ij} = \partial^2 E/\partial p_i \partial p_j$ is the second-derivative matrix of the energy surface with respect to the structural parameters. It represents the curvature of the energy and must be a positive-definite matrix at the minimum. If the Hessian is a diagonal matrix then the diagonal force method and the full-matrix force methods become identical. In practice the off-diagonal elements of the Hessian are large.

In order to find the optimum or best q_j (generalized potential parameter) the minimum of R is found:

$$\partial R/\partial q_j = 0, \qquad j = 1, 2, 3, \ldots.$$

This is not a force since q is a potential parameter. The standard technique of a Taylor's series expansion about a trial model is used for the potential parameters, where

$$R(q_j) = R(q_j^o) + \sum_j \Delta q_j \, \partial R/\partial q_j + \ldots.$$

$R(q_j^o)$ is the trial model and the second term is the shifts in q_j leading to a smaller R. Once q_j is obtained $R(q_j)$ is then substituted in for $R(q_j^o)$ for the next cycle. The lower the R value the better the predicted structural fit.

Nonbonded parameters for carbon were taken as derived from hydrocarbon and azahydrocarbon crystal structures (Williams & Cox, 1984). The transferability of the carbon potentials was shown with these data, as well as for oxohydrocarbons (Cox, Hsu & Williams, 1981) and perchlorocarbons (Hsu & Williams, 1980). A transferability test for the hydrocarbon carbon potential to perfluorocarbons is reported below.

There is a strong correlation between the nonbonded potential parameters B and C such that it is difficult to vary both simultaneously. Usually it is best to make a reasonable estimate of C and vary B. Theoretical estimates have been made for values of C by Starr (1976). The exponent used here for fluorine ($C = 4.16$) was obtained by interpolation between carbon ($C = 3.60$) and neon ($C = 4.36$). Small errors in the choice of C can be accommodated by a compensating shift in the value of B. Heteroatomic non-

bonded potential parameters were taken as the geometric mean. Assumption of the geometric mean combining law greatly reduces the number of independent nonbonded parameters. Coulomb's law requires the use of the geometric mean for site-charge interactions. The number of independent parameters to be optimized has now been reduced to two; A and B for fluorine. Since there are 54 observations of zero forces in the crystal structures, and one energy side condition, the ratio of observables to variables is quite good.

Optimum full-matrix least-squares values of A and B for fluorine were found using the computer program $NBP85$ (Williams, 1985a). Table 5 gives values derived using the NC, AC, EC and BC site-charge models. The parameter sets were subsequently tested by finding the crystal structure of minimum energy with computer program $PCK85$ (Williams, 1985b).

Testing of the nonbonded potentials

The $NBP85$ computer program found optimum values for nonbonded potential parameters given a set of observed crystal-structure parameters, with a crystal energy side condition. The success of the molecular-packing analysis was measured against how well observed crystal structures can be modelled. The computer program $PCK85$ found optimum values for crystal-structure parameters given a set of nonbonded potential parameters.

The atom–atom model contains known approximations, which are discussed in the references given in the *Introduction*. Because of these approximations exact fits to crystal structures are not expected. The concept of threshold accuracy is that, on average, the total effect of all approximations in the model will cause a threshold error of modelling, or greater. If the approximate atom–atom model succeeded in modelling crystal structures to threshold accuracy, no further improvement was expected without upgrading the model. A fit of better than threshold with the approximate model was believed fortuitous. We defined threshold accuracy values of 1% in the lattice constants, 1° in the cell angles, 2° in the molecular rotation, and 0·1 Å in the molecular translation. The threshold factor was the average ratio of the structure parameter shifts obtained with the model to the threshold expectations.

Table 6 shows the shifts in the crystal structures of the seven perfluorocarbons using four models. It was immediately apparent that hexafluorobenzene was a difficult structure to model. Since there are thirteen structural degrees of freedom in this structure, we also carried out a parallel calculation with four degrees of freedom where only the lattice constants were varied. In the latter case the shifts were more comparable to the other structures.

Table 5. *Crystal-structure derived values for fluorine nonbonded potential parameters* (kJ mol^{-1}, Å)

Parameter	NC	AC	EC	BC
A	982·8	908·7	848·0	844·0
B	384259·0	403832·0	365246·0	363725·0

Table 6. *Fitting the crystal structure data with the site-charge models*

Structure parameter	Site-charge model			
	NC	AC	EC	BC
(I) a (%)	−2·1	−2·6	−2·8	−2·6
a^* (%)	2·9	3·4	3·0	3·0
b (%)	10·0	9·6	8·4	7·9
b^* (%)	0·3	0·6	0·4	0·4
c (%)	−3·7	−2·1	−1·3	−0·9
c^* (%)	2·4	2·7	2·6	2·5
β (°)	2·4	1·7	2·2	2·2
β^* (°)	0·7	0·4	0·4	0·4
$\theta(1)$ (°)	12·6	10·5	10·3	9·7
$\theta(2)$ (°)	7·7	8·2	7·8	7·4
$t(2)$ (Å)	0·35	0·35	0·39	0·37
(II) a (%)	−2·0	−0·5	−0·9	−0·9
b (%)	2·2	2·0	1·9	1·7
c (%)	−0·4	0·4	−0·2	0·0
β (°)	−1·8	−0·6	−1·0	−0·8
θ (°)	5·8	3·2	3·5	3·3
t (Å)	0·13	0·06	0·08	0·08
(III) a (%)	−1·9	−1·4	−2·2	−2·4
b (%)	1·2	0·8	1·2	1·8
c (%)	−0·8	0·1	−0·1	−0·5
θ (°)	0·9	0·6	1·0	1·1
(IV) a (%)	−0·4	−0·1	−0·1	−0·1
c (%)	−1·6	−2·6	−2·0	−2·1
θ (°)	0·0	0·7	0·4	0·4
(V) a (%)	−2·8	−1·3	−0·7	−0·2
b (%)	3·6	2·5	1·3	0·6
c (%)	−0·3	0·1	0·1	0·1
θ (°)	2·6	1·7	1·1	0·7
t (Å)	0·10	0·09	0·07	0·06
(VI) a (%)	−0·5	−3·0	−2·0	−1·5
b (%)	−1·6	5·0	2·9	2·1
c (%)	2·2	−2·0	−1·0	−0·8
β (°)	0·3	−2·7	−1·8	−1·4
θ (°)	2·6	3·4	2·4	2·0
t (Å)	0·15	0·15	0·12	0·10
(VII) a (%)	−0·8	0·1	−0·3	−0·3
b (%)	−1·1	−0·6	−1·0	−0·9
c (%)	−1·9	−1·8	−2·0	−2·0
β (°)	0·5	1·3	1·3	1·3
θ (°)	0·3	0·8	0·8	0·8
t (Å)	0·08	0·08	0·08	0·09
Threshold factor	2·04	1·98	1·74	1·63

* Molecular rotations and translation held constant.

The bottom line of Table 6 shows the average threshold factor for the seven structures. It was apparent that the improvement in fit obtained with any of the various site-charge models was not very great. The conclusion that site charges are unimportant for fluorocarbons in general may be premature, however. Consider a fluorocarbon molecule that has hydrogen atoms. The C–H bonds would have opposite polarity to the C–F bonds. The Coulombic interaction between hydrogen and fluorine would be very important in determining the molecular packing. The Coulombic effect would be less important in perfluorocarbons because no such bonds of reverse polarity were present.

The relatively small improvements in fit obtained with the various site-charge models confirmed the assertion made above that it was difficult to derive values for site charges from crystal data. It was also found difficult just to derive an overall charge scaling factor from the data, a procedure that was successful in hydrocarbons and perchlorocarbons. Fortunately the PD method allowed an independent estimate of the site charges.

The improvement in fit to the model crystal structures was fully consistent with the improvement in fit obtained with the various PD charge models. Since the perfluorocarbon crystal structures are not extremely sensitive to the choice of site-charge models, the improvement in fitting the crystal structures was not as great as the improvement in fitting the electric potential.

Because threshold accuracy of modelling was not yet achieved, two further modifications of the model were considered. The geometric-mean combining law for the C···F potential was relaxed so that an independent value of B_{CH} was allowed. It was found that B_{CH} did not shift much from the geometric mean and that there was no significant improvement in the model. In another attempt to improve the model, the C–F bond lengths in all the molecules were shortened by 4%. Naturally, this caused shifts in the potential parameters. However, the modelling of the crystal structures was not very sensitive to this change and was not significantly improved.

Table 7 shows the crystal energy and its repulsion, dispersion and Coulombic components. The total observed crystal energy of (I) was fitted as a side condition. If desired, the fluorine potential could be scaled to a different value for the energy of (I), or to other crystal energies as they become available. The energy values for crystals (II)-(VII) are predictions only, based on the present parameterization. For most of the structures the Coulombic energy contributed around 10%, which was not a greater proportion than the Coulombic energy of hydrocarbons generally. Thus, in spite of fluorine's large electronegativity the fluorocarbons studied were not found to be more polar than hydrocarbons. Structure (VI) has an unusually low Coulombic energy, but the same phenomenon also occurs in certain hydrocarbon crystal structures (Williams & Cox, 1984).

It was of interest to test the transferability property of the carbon nonbonded potential obtained from hydrocarbons. If A and B for carbon were varied, in addition to A and B for fluorine, the number of adjustable potential parameters doubles to four. Because of this increase in adjustable parameters a better fit was expected. In fact, we found that when the carbon potential was allowed to vary, using the BC model, the threshold factor remained essentially unchanged at 1·67. However, there were large shifts in all four adjustable parameters.

Table 7. *Crystal energy and components of per-fluorocarbons* (kJ mol^{-1})

Structure	Total	Repulsion	Dispersion	Coulombic
(I)	−56·6	54·1	−104·2	−6·5
(II)	−72·1	48·6	−113·7	−7·0
(III)	−101·1	51·7	−145·7	−7·1
(IV)	−106·9	54·9	−151·5	−10·3
(V)	−116·7	70·4	−177·5	−9·6
(VI)	−125·3	82·1	−207·1	−0·3
(VII)	−132·5	48·3	−169·1	−11·7

Fig. 3 gives a comparison of the parameter sets with and without allowing the carbon A and B values to vary. There was a redistribution of the dispersion energy from fluorine to carbon. The carbon A value increased by 40%, and the fluorine A value decreased by 37%. The shifts in B were smaller. The carbon B value increased by 15%, and the fluorine B value decreased by 15%. The net effect of these changes was to make the curves nearly superimpose at short repulsive distances. At larger distances nonbonded energy was distributed more toward the carbon potential and away from the fluorine potential.

These results remind us that it is necessary to use potential-energy parameter sets that are internally consistent. Thus, although the matched sets for carbon and fluorine, with and without varying the carbon potential, each gave acceptable models for perfluorocarbon crystal structures, a mixed set obviously would not give acceptable results.

Table 8 gives a set of nonbonded (exp − 6) potentials for hydrogen, carbon, nitrogen, oxygen and fluorine which is designed to be internally consistent and transferable. Fig. 4 shows plots of these functions with neon added for comparison. Pauling (1960) gives the van der Waals radii of these atoms as 1·2, 1·7, 1·5, 1·40 and 1·35 Å respectively, omitting neon. If a repulsive force of 10^{-10} N is selected to characterize the nonbonded potentials in the figure the corresponding radii where that force is reached are 1·15, 1·65, 1·53, 1·44 and 1·44 Å. These figures agree fairly well with Pauling's van der Waals radii, with hydrogen and carbon being somewhat smaller, and nitrogen
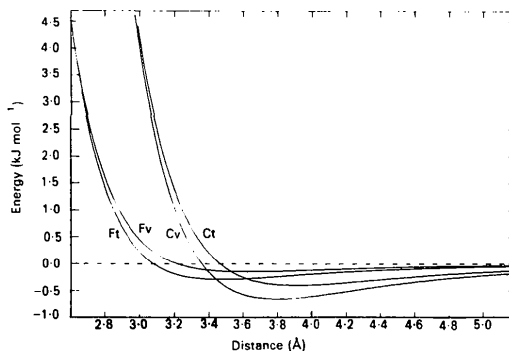

Fig. 3. Comparison of carbon and fluorine nonbonded potentials with and without transfer of the carbon potential from hydrocarbons.

Table 8. *A set of nonbonded (exp − 6 − 1) potential parameters designed to be internally consistent and transferable*

Atom	A	B	C	Reference
H	136·4	11971	3·74	Williams & Cox (1984)
C	2439·8	369743	3·60	Williams & Cox (1984)
N	1378·4	254529	3·78	Williams & Cox (1984)
O	1123·6	230064	3·96	Cox, Hsu & Williams (1981)
F	844·0	363725	4·16	This work

and oxygen being somewhat larger than Pauling's values.

Perhaps the most notable feature of the 10^{-10} N radii is that fluorine appears to be about the same size as oxygen, in disagreement with an expected Periodic-Table trend from carbon to neon. The size of the fluorine atom can also be seen in the nonbonded potential curves shown in Fig. 4. The fluorine size is probably not an artifact produced by transferring the carbon potential from hydrocarbons since allowing the carbon potential to vary does not affect the fluorine size very much. It is also probably not an artifact of the neglect of thermal motion, since all structures and potentials are treated on the same basis. This apparent nonperiodicity of the fluorine size will no doubt serve to stimulate further interpretation and research.
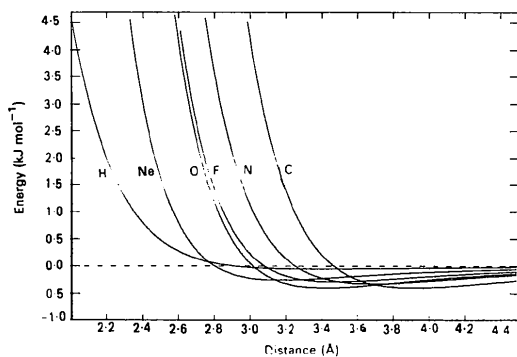
Fig. 4. Plots of carbon, nitrogen, and hydrogen (Williams & Cox, 1984), oxygen (Cox, Hsu & Williams, 1981), fluorine (this work, BC model) and neon (Williams, 1972a) nonbonded potentials.

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