

Nonbonded Potential Function Models for Crystalline Oxohydrocarbons

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Abstract

Nonbonded O...O potential parameters of the (exp – 6) type were derived from five selected oxohydrocarbon crystal structures, which do not have hydrogen bonds: β -oxygen, carbon dioxide (CO₂), trioxane (C₃H₆O₃), tetroxocane (C₄H₈O₄) and succinic anhydride (C₄H₄O₃). Previously established hydrocarbon H and C nonbonded parameters were transferred. Net atomic charges were calculated separately by obtaining a least-squares fit to the molecular electric field calculated by the *ab initio* self-consistent-field molecular-orbital method. The resulting O...O nonbonded potential was found to transfer well to the structures of pentoxecane (C₅H₁₀O₅), 1,4-cyclohexanedione (C₆H₈O₂) and diglycolic anhydride (C₄H₄O₄). The potential did not transfer well to the structures of *p*-benzoquinone (C₆H₄O₂) and furan (C₄H₄O). The addition of an approximate weak hydrogen-bonding potential for a C–H...O hydrogen bond improved the fit to the latter two structures.

Introduction

The importance of O–H...O hydrogen bonding in chemical and biological systems has led to extensive research into the nature of this interaction by investigation of empirical potential function models. Nonbonded potential parameters for hydrogen and carbon have been derived from crystals. These potentials successfully predict the heats of sublimation and observed equilibrium crystal structures of hydrocarbons (Williams & Starr, 1977). However, we believe that presently available oxygen nonbonded potential parameters for intermolecular interaction of oxohydrocarbon molecules in crystals can be improved in accuracy.

It should be noted that nonbonded potential parameters for intramolecular interaction in oxohydrocarbons are available for use in molecular mechanics calculations (see, for instance, Allinger, 1976). The intramolecular force field is complicated by interactions with rotations about bonds, bond bending and bond stretching. An advantage of using crystal struc-

tures for the determination of nonbonded potential parameters is that these complications are not present.

At the present time, there seems to be no compelling reason to doubt that intramolecular nonbonded interactions have the same potential energy as intermolecular interactions, provided that the interactions with bond rotation, bond bending and bond stretching are properly separated. The intramolecular interactions between distant parts of a protein molecule, for instance, are believed to be identical to intermolecular interactions.

Therefore, ultimately molecular-mechanics nonbonded potential parameters need to be reconciled with those derived from purely intermolecular sources. The reconciliation of molecular-mechanics nonbonded parameters with intermolecular nonbonded parameters is beyond the scope of this paper.

Usually, nonbonded potential parameters for oxygen and empirical potential functions for the O–H...O hydrogen bond are derived from crystal or dimer data simultaneously. This is done because such compounds as carboxylic acids are hydrogen bonded in the dimer or crystalline forms. The potentials derived by McGuire, Momany & Scheraga (1972) are based on semi-empirical CNDO/2 interaction energy calculations, however, which have led to overestimated interaction energies and to equilibrium structures which have too short H...O separations and wrong angles. In their subsequent paper (Momany, Carruthers, McGuire & Scheraga, 1974), the potential parameters were improved but there still remained large discrepancies between calculated and observed structural data (see their Table VII). In further work, Momany (1976) calculated the lattice energies of formic acid and acetic acid. However, the absolute values and the relative magnitudes of the lattice energies are not in agreement with experimental results. Also, the potential (1–4–6–12) determined by Minicozzi & Stroot (1970) for formic acid contains too many empirical parameters which were derived from too few experimental data.

The main problem for describing the crystals of carboxylic acids using the atom–atom potential scheme is the presence of hydrogen bonds. Recently, there have been efforts to derive intermolecular potential functions

for carboxylic acids from experimental data (Derissen & Smit, 1978) and from *ab initio* calculation (Smit, Derissen & van Duijneveldt, 1979). These potential function models have been tested and the results which they have published were found not to be reproducible (see below). They described the hydrogen bonds using Lippincott-Schroeder or exponential potential functions, and the remaining intermolecular interactions with $(\exp - 6 - 1)$ atom-centered potentials. The parameters in their potentials do not fit the experimental observed structures and heats of sublimation of formic acid dimer and acetic acid dimer satisfactorily. The nonbonded potential parameters for H, C and O interactions and the empirical potential functions for the O—H...O hydrogen bond were derived simultaneously. Therefore, it is unknown whether the poor fit is due to the inaccurate nonbonded potential parameters or to the use of wrong potential functions for the hydrogen bond.

For the purpose of simplifying the situation, the goal of this work was to derive the nonbonded potential parameters for oxygen only from well-determined crystal structures of oxohydrocarbons which do not include O—H...O hydrogen bonds. Established nonbonded potential parameters for H and C, which have been derived from 18 crystal structures of hydrocarbons are used (Williams & Starr, 1977). These parameters have already been shown to be transferable to perchlorohydrocarbons (Hsu & Williams, 1980). Thus, only the oxygen nonbonded potential parameters need to be determined from the oxohydrocarbon crystal structures. The nonbonded potentials for interactions between different kinds of atoms are obtained from the geometric-mean combining law.

The importance of the electrostatic energy term for hydrocarbons and perchlorohydrocarbons has been established. The net charge of an atom clearly depends on its bonding environment, and will be different for the same atom type in different types of molecules. It is difficult to derive net atomic charges directly from crystal data because of the existence of so many different bonding situations in molecules, which leads to too many adjustable parameters in the fitting process.

Accordingly, several authors have proposed various elaborations of the atom-atom potential for dealing explicitly with the electrostatic energy term (Fyfe & Harold-Smith, 1976; Mulder & Huiszoon, 1977; Smit, Derissen & van Duijneveldt, 1977; Carozzo, Corongiu, Petrongolo & Clementi, 1978). Recently, Hirshfeld & Mirsky (1979) have examined what algebraic form is appropriate for approximating the intermolecular electrostatic energy. They compared three variously idealized representations; atomic moment, atomic point charge and molecular moment. They found that the use of molecular moments led to serious errors at short intermolecular distances such as found in crystals. The

atomic-moment model was found to be most accurate, but this model is cumbersome and contains a large number of adjustable parameters. Their conclusion is that the atomic point charge model is an adequate approximation model.

A number of methods for obtaining atomic point charges can be found in the literature. The traditionally utilized Mulliken charges obtained from *ab initio* quantum mechanical molecular orbital calculations are demonstrably unreliable (Steiner, 1976). Therefore, a better method, in which the atomic point charges are derived by fitting the calculated electrostatic potential surrounding the molecule, was selected for the present study (Momany, 1978). This method is further described below.

Description of calculations

We selected five well determined oxohydrocarbon crystal structures from which to derive the oxygen nonbonded parameters: carbon dioxide, β -oxygen, trioxane, 1,3,5,7-tetroxocane and succinic anhydride. The absence of hydrogen bonds simplified the situation and reduced the number of potential parameters to be considered. The observed crystal structure parameters (Table 1) and atomic coordinates were taken from the literature. Table 1 also shows the five additional observed crystal structures which were used to test the transferability of the nonbonded potential parameters. The observed heats of sublimation of carbon dioxide and β -oxygen at zero degrees absolute temperature with correction for zero-point energy were taken as 29.37 kJ mol⁻¹ (Donkersloot & Walmsley, 1971) and 9.94 kJ mol⁻¹ (English & Venables, 1974), respectively. These values were used to scale the potential functions.

The intermolecular potential for oxohydrocarbons which do not include a hydrogen bond may be obtained in the atom-atom model from the interatomic potentials of H—H, H—C, H—O, C—C, C—O and O—O interactions. The interatomic potential was expressed as the semi-empirical Buckingham $(\exp - 6 - 1)$ form:

$$V_{jk} = b_j b_k \exp [-(c_j + c_k)r_{jk}/2] - a_j a_k r_{jk}^{-6} + q_j q_k r_{jk}^{-1}.$$

This function* is applied to atoms j and k in different molecules separated by nonbonded interatomic distance r_{jk} . For the purpose of transferability the parameters a , b and c for all hydrogen and all carbon are assigned to be the same values as those of Williams & Starr (1977). All oxygens are similarly assumed to have the same nonbonded parameters, to be determined. In principle, the net atomic charges q can be derived from known crystal structures. However, too

* A referee has suggested that an effective dielectric constant should be included in the Coulombic part of this potential.

Table 1. *Crystal data for observed oxohydrocarbon crystal structures*

The first five structures were used to define the oxygen nonbonded potential. The units are Å and °.

Compound	Space group	<i>a</i>	<i>b</i>	<i>c</i>	β	References
Carbon dioxide	<i>Pa3</i>	5.54	5.54	5.54	90.00	(a, b)
β -Oxygen	<i>R3m</i>	3.307	3.307	11.256	120.00	(c)
Trioxane	<i>R3c</i>	9.320	9.320	8.196	120.00	(d)
Tetroxocane	<i>C2/c</i>	11.455	4.160	12.232	108.40	(e)
Succinic anhydride	<i>P2₁2₁2₁</i>	6.963	11.710	5.402	90.00	(f)
Pentoxecane	<i>Pbcn</i>	8.154	10.673	7.666	90.00	(g)
1,4-Cyclohexanedione	<i>P2₁</i>	6.65	6.21	6.87	99.81	(h)
Diglycolic anhydride	<i>P2₁/c</i>	17.080	5.143	11.716	111.33	(i)
<i>p</i> -Benzoquinone	<i>P2₁/a</i>	7.055	6.795	5.767	101.467	(j)
Furan	<i>P4₁2₁2</i>	5.69	5.69	11.92	90.00	(k)

References: (a) Keesom & Kohler (1934a); (b) Keesom & Kohler (1934b); (c) Hörl (1962); (d) Busetti, Del Pra & Mammi (1969); (e) Chatani, Yamauchi & Miyake (1974); (f) Ehrenberg (1965); (g) Chatani & Kitahama (1973); (h) Mossel & Romers (1964); (i) Brisse & Sygusch (1975); (j) Trotter (1960); (k) Fourme (1972).

many adjustable parameters are needed for oxo-hydrocarbons if all net atomic charges are varied. Therefore, in the present work the atomic charges were estimated by fitting the calculated molecular electric field.

The parameters *b* and *c* are highly correlated such that it is difficult to vary both simultaneously. This suggests that the hardness parameter *c* be estimated rather than derived. Starr (1976) has determined the repulsive exponent for a series of elements by fitting the overlap of the electron densities. From his results the parameter *c* for oxygen was estimated and the value 3.96 was used. Therefore, the only parameters to be optimized are *a* and *b* for oxygen. The ratio of observed structural parameters to the adjustable potential parameters is quite good, at 23 to 2.

The method for optimizing the potential parameters in the present study is the force minimization method with full-matrix weights (Hsu & Williams, 1980). This method has been found to be successful for hydrocarbons, halogens and perchlorohydrocarbons. The idea of this force minimization method is to find by a least-squares fitting procedure the optimum values of the adjustable potential parameters such that the forces at the observed structure vanish. The residual function, R_F , was set up and minimized:

$$R_F(a_o, b_o) = \sum_{IJ} w_{IJ} F_I F_J + w' [V_{\text{CO}_2} - E_{\text{obs}(\text{CO}_2)}]^2 + w'' [V_{\text{O}_2} - E_{\text{obs}(\text{O}_2)}]^2.$$

A Taylor's series expansion about a trial model for the potential parameters is used. The last two terms are penalty functions which normalize the calculated lattice energies to the observed lattice energies for carbon dioxide and β -oxygen. The weights w' and w'' are taken sufficiently large to get the desired agreement. The w_{IJ} were obtained as described by Hsu & Williams (1980).

The lattice sum was treated by a convergence

acceleration technique (Williams, 1971). It was estimated that the lattice sums were converged within 1%. For the purpose of saving computer time and ensuring accuracy, both the first and second derivatives of the lattice energy were evaluated analytically, rather than numerically.

Atomic point charge model

The most widely used method for calculating the charges associated with atoms in molecules is the 'population analysis' procedure proposed by Mulliken (1955). His definition of atomic charge has been applied extensively and has provided much useful information. Kern & Karplus (1964), however, showed that atomic basis sets which give equally good self-consistent-field molecular energies can give very different Mulliken charges. There have been several critical discussions and comparative studies of various methods of calculating net atomic charges (see, for instance, Politzer & Harris, 1970; Steiner, 1976).

The Mulliken net atomic charge is not a defined physical property in quantum mechanics (see, for instance, Steiner, 1976). The molecular electrostatic potential field, however, is a defined physical property in quantum mechanics. Scrocco & Tomasi (1978) have recently reviewed the calculation and interpretation of electrostatic molecular potentials.

The molecular electrostatic potential field cannot be accurately fitted with a net atomic charge empirical model, particularly within the molecular volume inside the van der Waals radii of the atoms in the molecule. In this region, which is significantly inside the electron cloud of the molecule, the electrostatic potential is always strongly positive because of exposure to the nuclear charge.

However, if one considers only the region of space outside the van der Waals spheres of the atoms, a fit to

the molecular electrostatic field by an empirical net atomic charge model sufficiently good for the present purposes can be obtained. In other words, a net atomic charge model for intermolecular interaction of adequate accuracy can be derived from the calculated molecular electrostatic potential field.

The details of the process of fitting the net atomic charge model to the molecular electrostatic field are discussed by Cox & Williams (1981). It is pertinent to mention here that little additional calculational effort is required beyond that needed to obtain Mulliken charges. By far the largest amount of computer time is needed to obtain the SCF-MO wavefunction. The evaluation of the molecular electrostatic field from the wavefunction and the fitting of the empirical net atomic charges require relatively little additional time.

The *ab initio* self-consistent-field molecular-orbital calculations for the electrostatic potential surrounding the molecule also depend on the choice of the basis set of atomic orbitals. The requirement of the present work for choosing the basis set is that the basis set should be large enough to calculate the molecular electrostatic potential with acceptable accuracy but not so large as to prohibit calculation for medium size molecules. In order to allow extension of the method to larger molecules, the basis set should be kept as small as is practical. Hehre & Pople (1970) have examined the minimal Gaussian basis set STO-3G by calculating electric dipole moments and comparing them with experimental values for a series of simple organic compounds. They found the agreement with experimental data was moderate. For oxygen compounds, the agreement was even better than that of the other compounds. To extend this examination, the larger basis sets 6-31G (Hehre, Ditchfield & Pople, 1972) and double- ζ (Snyder & Basch, 1972) were tested to calculate the electric dipole moments of water, ammonia, formaldehyde and hydrogen fluoride in this study. Table 2 shows the calculated dipole moments based on the STO-3G, 6-31G and double- ζ basis sets and the experimental data for the four compounds which are mentioned above. The table shows that the minimal STO-3G basis set is better for the calculation of the dipole moment than either the 6-31G or the double- ζ basis sets. This better agreement for the

smaller basis set is probably the result of fortuitous cancellation of errors. Nevertheless, it suggested to us that perhaps the STO-3G basis set might give a reasonably accurate representation of the molecular electrostatic field, from which we could derive net atomic charges.

We have examined both the Mulliken charges and the field-derived net atomic charges for a variety of small molecules, for several choices of basis sets (Cox & Williams, 1981). The results of the examinations showed that the Mulliken charges were rather sensitive to the choice of basis set, as expected. The field-derived net atomic charges were found to be much less dependent on the choice of basis set. We concluded that even the minimal STO-3G basis set gave fairly reasonable net atomic charges, with large savings in computer time as compared to the larger basis sets. The recently announced 3-21G basis set (Pople, 1980) may be even better for this purpose.

The *ab initio* SCF molecular orbitals were calculated with computer program *GAUSSIAN-74* (Jeffrey & Yates, 1978), which is an updated version of *GAUSSIAN-70* (Hehre, Lathan, Ditchfield, Newton & Pople, 1972). These MO's were used as input to the one-electron properties package of the computer program *POLYATOM* (Neumann, Basch, Kornegay, Snyder, Moskowitz, Hornback & Leibmann, 1974) which was used to calculate the electric field of the molecules. A net atomic charge model was then fitted

Table 2. *Calculated and observed dipole moments*

Molecule	STO-3G	6-31G	DZ	Obs.	References
Water	1.78	2.63	2.68	1.846	(a)
Ammonia	1.66	2.32	2.33	1.468	(b)
Formaldehyde	1.53	3.01	3.11	2.339	(c)
Hydrogen fluoride	1.41	2.30	2.37	1.82	(d)

References: (a) Birnbaum & Chatterjee (1952); (b) Coles, Good, Bragg & Sharbaugh (1951); (c) Shoolery & Sharbaugh (1951); (d) Weiss (1963).

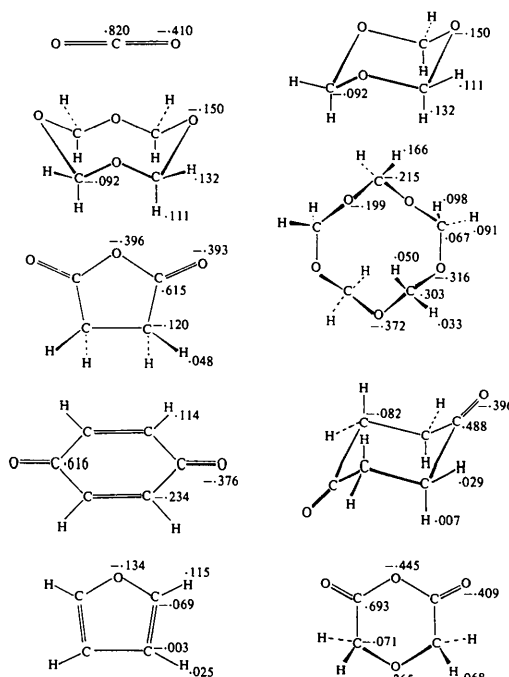


Fig. 1. The net atomic charges obtained by a least-squares fit to the *ab initio* SCF calculated electric field of the molecules (units are the electronic charge).

to this calculated electric field. The calculated atomic point charges were obtained by using a least-squares fitting procedure to reproduce the calculated molecular electric fields (Cox & Williams, 1981). These field-derived charges are shown in Fig. 1. The field-derived net atomic charges are significantly different from the traditional Mulliken charges.

Results and discussion

The aim of the present study was to derive a set of nonbonded potential parameters, capable of describing the equilibrium structures and lattice energies for crystals of oxohydrocarbons. The O...O parameters were derived from the five oxohydrocarbon crystal structures and two lattice energies as described above. To satisfy the transferability requirement, the already established nonbonded parameters for C and H interactions were used.

Since there is a principal difficulty for deriving the net atomic point charge from crystal data, which has been discussed above, the charges were calculated separately by least-squares fitting to the molecular electric field. Therefore, the only adjustable potential parameters, which were derived subsequently from the five well-determined crystal structures of oxohydrocarbons, are a_o and b_o . The optimized values for a_o and b_o are 33.52 and 479.65, respectively, in units of kJ mol^{-1} and \AA . Fig. 2 shows a plot of the $(\exp - 6)$ parts of the present nonbonded potentials.

The potential parameters for oxohydrocarbons were tested in two ways. The first of these was to investigate how well the parameters reproduce the crystal data from which they were derived. Secondly, the transferability of the parameters with respect to the crystal structures and lattice energies which were not used in the derivation was studied.

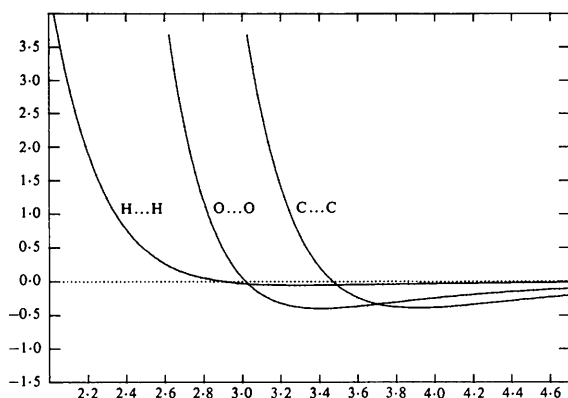


Fig. 2. The $(\exp - 6)$ parts of the present nonbonded potentials for H...H, O...O and C...C interactions. The abscissa gives the nonbonded distance in \AA ; the ordinate gives the nonbonded energy in kJ mol^{-1} .

The accuracy of the potential parameters is reflected by how well they predicted the five oxohydrocarbon crystal structures which were used to derive them. The predicted structure deviations, which were found with the computer program *PCK6* (Williams, 1979), appear in Table 3. These values and lattice energies for these five compounds are quite satisfactory. Even the worst fits, which are the lattice constants a and b of trioxane, deviate less than 3% from the observed values.

To test further the transferability and accuracy of the present potential parameters, another set of five well-determined crystal structures of oxohydrocarbons was selected. Based on the present parameters and field-derived atomic point charges, the corresponding minimum-energy structures for these five oxohydrocarbons were found. The predicted structural parameter deviations are also shown in Table 3.

The present potential parameters can predict the crystal structures of 1,4-cyclohexanedione, 1,3,5,7,9-pentoxecane and diglycolic anhydride satisfactorily. However, they do not accurately predict the structures of *p*-benzoquinone and furan. It was considered that these two compounds may have weak intermolecular C—H...O hydrogen bonds in their crystals. These two compounds have hydrogens attached to sp^2 carbon, while the hydrogens in all the other compounds were attached to sp^3 carbon. Sutor (1963) has made a search for short ($< 3.1 \text{ \AA}$) C...O contacts in crystals and concluded that such short contacts may involve weak hydrogen bonds of the C—H...O=C type, where the first C atom forms part of a conjugated system. Allerhand & Schleyer (1963) also concluded that hydrogen attached to sp^2 carbon is more active toward hydrogen bonding than hydrogen attached to sp^3 carbon. There is available a recent review of hydrogen bonding by C—H groups (Green, 1974).

Table 4 shows the intermolecular H...O distances less than 2.8 \AA for all of the presently considered crystal structures. The short intermolecular H...O distances in crystalline 1,4-cyclohexanedione, furan and *p*-benzoquinone suggest the possible existence of C—H...O hydrogen bonds. The sum of the van der Waals radii of H and O is 2.6 \AA . 1,4-Cyclohexanedione has four H...O distances less than 2.6 \AA ; furan has one; and *p*-benzoquinone has two such short distances. In addition 1,4-cyclohexanedione does not have hydrogens attached to sp^2 carbon, as do the other two compounds.

In order to investigate the possible existence of hydrogen bonds in the crystals of furan and *p*-benzoquinone, the attractive exponential function, $-De^{-Fr}$, which was used to represent the hydrogen-bond function, was applied to the H...O intermolecular distances which were shorter than 2.6 \AA . Based on the present nonbonded potential parameters and the arbitrary hydrogen-bond function, where D equals $34093.9 \text{ kJ mol}^{-1}$ and F equals 3.85 \AA^{-1} , the

Table 3. *Predicted structure parameter deviations for ten oxohydrocarbon crystal structures at the calculated energy minimum*

The first four columns give the calculated changes in the lattice constants. The last four columns indicate the calculated changes in the molecular rotation and translation (diglycolic anhydride has two molecules in the asymmetric unit). The units are Å and °.

Crystal	Δa	Δb	Δc	$\Delta\beta$	$\Delta\theta_1$	Δr_1	$\Delta\theta_2$	Δr_2
β -Oxygen	-0.05	-0.05	0.02	—	—	—	—	—
Carbon dioxide	0.12	0.12	0.12	—	—	—	—	—
Trioxane	0.26	0.26	0.05	—	0.3	—	—	—
Tetroxocane	-0.10	-0.09	-0.08	-3.2	2.2	0.18	—	—
Succinic anhydride	-0.01	0.03	-0.07	—	7.3	0.14	—	—
Pentoxecane	-0.34	0.42	0.11	—	2.9	0.36	—	—
Cyclohexanedione	0.07	0.07	0.34	-2.8	1.7	0.11	—	—
Diglycolic anhydride	0.27	-0.04	-0.40	-0.9	3.8	0.13	4.6	0.12
Benzoquinone	0.39	-0.27	0.12	2.0	19.3	—	—	—
Benzoquinone*	0.14	-0.25	-0.41	1.8	7.6	—	—	—
Furan	-0.22	-0.22	1.60	—	8.3	0.04	—	—
Furan*	-0.06	-0.06	0.29	—	10.5	0.12	—	—

* Calculation includes an approximate hydrogen-bond function.

calculated structure deviations for these two compounds are shown in Table 3. The results show that the additional hydrogen-bond function improves the accuracy of prediction of the *p*-benzoquinone and furan crystal structures. Before the addition of hydrogen-bond functions the calculated molecular rotation for *p*-benzoquinone was off by 19.3°. After this addition it was only off by 7.6°. For furan, the additional exponential function showed a marked improvement of fit to the *c* lattice constant; before the addition of the hydrogen-bond function this constant was 1.60 Å too large. After the addition the disagreement is reduced to 0.29 Å. A more accurate hydrogen-bond function would be expected to improve further the agreement for *p*-benzoquinone and furan.

Comparison with previously published potentials

For comparison of various sets of previously published O...O potential parameters, several recent parameter sets for nonbonded intermolecular interaction of

oxygen atoms were selected to predict the crystal structure of β -oxygen.

Table 5 gives the deviations of the calculated lattice constants of β -oxygen, based on the selected sets of potential parameters and the present parameters. The nonbonded potentials of Momany, Carruthers, McGuire & Scheraga (1974) and of Hagler, Huler & Lifson (1974) are of the (6-12) potential type while those of Kitaigorodsky, Mirskaya & Nauchitel (1970) and of Derissen & Smit (1978) are the (exp - 6) type. It should be noted that the nonbonded potentials of Lifson, Hagler & Dauber (1979) for carboxylic acid crystals are identical to those of Hagler, Huler & Lifson (1974) as far as this application is concerned. It is apparent that the present oxygen parameters give the best fit to the β -oxygen crystal structure, while retaining good accuracy for the oxohydrocarbon structures. Fig. 3 shows a graphical comparison of the non-Coulombic parts of various O...O potentials. The figure shows

Table 4. *Intermolecular H...O distances less than 2.8 Å*

Compound	Distance
Trioxane	2.560, 2.599, 2.793
Tetroxocane	2.678, 2.796
Succinic anhydride	2.587, 2.656, 2.746, 2.783
Pentoxecane	2.553, 2.607, 2.686, 2.772
1,4-Cyclohexanedione	2.435, 2.544, 2.547, 2.577, 2.610, 2.664, 2.749
Diglycolic anhydride	2.502, 2.505, 2.643, 2.660, 2.718, 2.726, 2.730, 2.791, 2.794
<i>p</i> -Benzoquinone	2.354, 2.450
Furan	2.505

Table 5. *Deviation of calculated values for the lattice constants of β -oxygen for various sets of potential parameters*

References	$\Delta a (= \Delta b)$	Δc
(a) (for carbonyl oxygen)	-0.32	-0.51
(a) (for hydroxyl oxygen)	-0.21	-0.27
(b)	-0.24	-0.32
(c)	-0.20	-0.26
(d) (set II)	0.28	0.81
(d) (set III)	0.16	0.53
(d) (set IV)	0.11	0.43
(e) (set B)	-0.64	-1.22
This work	-0.05	0.02

References: (a) Momany, Carruthers, McGuire & Scheraga (1974); (b) Hagler, Huler & Lifson (1974); (c) Kitaigorodsky, Mirskaya & Nauchitel (1970); (d) Derissen & Smit (1978); (e) Smit, Derissen & van Duijneveldt (1979).

that there is considerable disagreement between the curves; the present curve seems to be about in the center of the curve distribution.

It is difficult to do further comparisons of the various sets of published potential parameters by calculating the lattice constants of the oxohydrocarbons because the different sets of published parameters use different methods to estimate the net atomic charges. Momany *et al.* (1974) and Derissen & Smit (1978) used CNDO/2 Mulliken charges which we believe not as good as our field-derived charges. Hagler *et al.* (1974) did not give a general method for the calculation of net atomic charges for molecules other than amides or carboxylic acids. Allinger & Chung (1976) use a bond-dipole model for the electrostatic part of the nonbonded potential in their molecular mechanics calculations. They also use additional force centers for lone-pair electrons. Kitaigorodsky *et al.* (1970) make an initial subtraction of estimated quadrupole-quadrupole energy from the lattice energy of carbon dioxide. This procedure cannot be extended at present to the oxohydrocarbons whose multipole moments are not known experimentally.

In the paper of Smit, Derissen & van Duijneveldt (1979) (henceforth referred to as SDD), the net atomic charges were derived by fitting the calculated molecular electric field, which is consistent with present work. Therefore, a more elaborate comparison of the present parameters with their parameters can be made. Table 6 shows the results of using SDD nonbonded potential parameters to calculate the crystal structures of the present oxohydrocarbon set, excluding *p*-benzoquinone and furan. The calculations for the latter two structures were discontinued after very large shifts were

obtained with no apparent convergence to reasonable structures.

A survey of the table shows that the present nonbonded parameter set gives a much better fit to the lattice constants of oxohydrocarbons than the SDD parameter set. The poor fit to the crystal structures of the present molecules indicates that the SDD nonbonded potential parameters are not transferable from the carboxylic acid system to the oxohydrocarbon system.

The present nonbonded potential parameters cannot be tested by predicting the crystal structures of the SDD molecular set. This is because all of the carboxylic acid molecules considered have strong O—H...O hydrogen bonds in the crystal form, and we have not yet derived an accurate potential function for such bonds. It would be inconsistent to use the SDD hydrogen-bond function with the present nonbonded potential parameters.

In the present study the SDD published results have also been checked by recalculation, using a modified version of the *PCK6* molecular packing analysis program, based on their potentials. SDD used exponential functions to represent the intermolecular O—H...O hydrogen bonds and used $(\exp - 6 - 1)$ atom-centered potentials to describe the nonbonded interactions. We obtained the exact input structural data and potential parameter data used by SDD (Derissen, 1980) and recalculated the SDD structures to find the minimum lattice energy. In all cases (formic acid and acetic acid dimers, and the crystal structures of formic acid, acetic acid and two forms of oxalic acid) we obtained lower energy minima than obtained by SDD.

Table 7 illustrates our results with the formic acid crystal structure. The steepest descent calculation of SDD gave their best results, with a minimum lattice energy of $-56.5 \text{ kJ mol}^{-1}$. With the same potential parameters and structural data, we obtained a lower minimum lattice energy of $-59.7 \text{ kJ mol}^{-1}$. The Hessian matrix (of the second derivatives of the lattice energy) was not positive definite at the observed structure; it did become so at our calculated minimum. Our calculated structure was shifted farther from the observed structure than SDD's result. For example, the total molecular angular shift in the formic acid crystal was particularly large, at 0.57 rad .

Further study is needed to understand exactly why researchers can arrive at different values for the calculated energy minima, using the same starting structures and potential energy functions. One of us (Williams, 1981) has recently noted that Mirsky & Cohen (1978) also obtained nonoptimized energy minima in the process of testing potential functions for chlorine-chlorine interactions in chlorinated benzene and molecular chlorine crystals.

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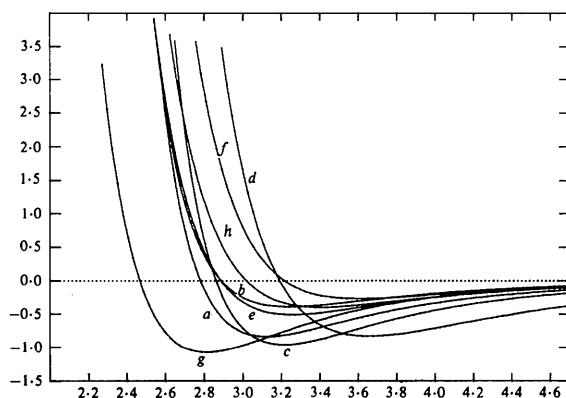


Fig. 3. The non-Coulombic parts of various O...O nonbonded potentials. The scale is the same as Fig. 2. Curve (a) carbonyl, Momany, Carruthers, McGuire & Scheraga (1974); (b) hydroxyl, Momany *et al.* (1974); (c) 12-6, Hagler, Huler & Lifson (1974); (d) 9-6, Hagler *et al.* (1974); (e) Kitaigorodsky, Mirskaya & Nauchitel (1970); (f) set III, Derissen & Smit (1978); (g) set B, Smit, Derissen & van Duijneveldt (1979); (h) this work.

Table 6. Predicted structure parameter deviations for eight oxohydrocarbon crystal structures at the calculated energy minimum, using the nonbonded potential parameters of SDD

Crystal	Δa	Δb	Δc	$\Delta\beta$	$\Delta\theta_1$	Δr_1	$\Delta\theta_2$	Δr_2
β -Oxygen	-0.64	-0.64	-1.22	—	—	—	—	—
Carbon dioxide	0.04	0.04	0.04	—	—	—	—	—
Trioxane	0.12	0.12	-0.49	—	2.1	—	—	—
Tetroxocane	-0.07	-0.32	0.12	2.2	2.3	0.20	—	—
Succinic anhydride	0.14	-0.17	-0.16	—	4.7	0.15	—	—
Pentoxecane	-0.61	0.36	-0.18	—	0.8	0.59	—	—
Cyclohexanedione	-0.03	0.39	0.05	-4.5	7.7	0.05	—	—
Diglycolic anhydride	0.24	-0.15	-0.40	-0.0	3.1	0.12	1.8	0.15

Table 7. Recalculation of the results of Smit, Derissen & van Duijneveldt (SDD) for the formic acid crystal based on their parameters, using least-squares or Newton-Raphson (LS) and steepest descents (SD) methods

The calculated lattice energy values include SDD's estimate of 7.53 kJ mol⁻¹ for the molecular deformation energy in going from the gas to the crystal.

Structure parameter	Obs.	LS	SDD SD	This work LS
θ (rad)	0	-0.02	-0.04	0.57
φ (rad)	0	-0.30	-0.09	
χ (rad)	0	-0.01	-0.02	
X	0	-0.40	0.06	
Y	0	0.03	-0.22	-0.31
a	10.241	10.62	10.18	9.84
b	3.544	3.30	3.39	3.22
c	5.356	5.22	5.07	5.11
E (exp)	-61.9	-47.3	-47.3	-47.4
E (min)		-52.3	-56.5	-59.7

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The Superstructure of the Intermediate Pyrrhotite. II. One-Dimensional Out-of-Step Vector of Fe Vacancies in the Incommensurate Structure with Compositional Range from Fe_9S_{10} to $\text{Fe}_{11}\text{S}_{12}$

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Abstract

Satellite reflections appear parallel to c^* : only even and odd orders around main reflections with h and k both even and both odd, respectively, which are explained by assuming that two kinds of out-of-step vectors, such as $(\mathbf{a} + \mathbf{b})/4$ and $(\mathbf{a} - \mathbf{b})/4$, occur alternately at intervals of $c/4$ along the orthorhombic c axis. The main origin of the superstructure is the ordering of the Fe vacancies, the distribution of which in four different Fe rows parallel to the c axis is studied in terms of Fourier expansion.

Introduction

The intermediate pyrrhotite with the compositional range from Fe_9S_{10} (5C type) to $\text{Fe}_{11}\text{S}_{12}$ (6C type) has a superstructure of the NiAs type with various incommensurate c periods from 5 to 6 times as long as a sub-period (Morimoto, Gyobu, Tsukuma & Koto, 1975). Their lattices are orthorhombic C -centered with $\mathbf{a} = 2\mathbf{A}_1$, $\mathbf{b} = 2\mathbf{A}_1 + 4\mathbf{A}_2$ and $\mathbf{c} = N\mathbf{C}$ where \mathbf{A}_1 , \mathbf{A}_2 and \mathbf{C} represent the hexagonal subcell vectors of the NiAs type and N is generally incommensurate ($5 \leq N \leq 6$). $|\mathbf{A}_1|$ and $|\mathbf{A}_2| \sim 3.5$, and $|\mathbf{C}| \sim 5.7$ Å.

The 5C and 6C types are respectively commensurate with just 5 and 6 times the length of a sub-period. These are the limiting cases of the incommensurate types. In part I (Koto, Morimoto & Gyobu, 1975), the structure of the 6C type has been studied. The main origin of the superstructure is the ordering of Fe vacancies as in the 4C type, Fe_7S_8 (Bertaut, 1953). The structure of the 6C type is statistical and a filled layer of Fe atoms alternates with two consecutive partially defective layers along the c axis. The distribution of the Fe vacancies in the two structures of the 4C and 6C types is explained by a one-dimensional out-of-step vector at intervals of $c/4$ along the c axis, as shown in Fig. 1 (Koto, Morimoto &

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