Table 4. *Comparison of experimental B values of* KBr *at* 4·2 *and* 295 K *with the theoretical values of Reid & Smith* (1970)

	Present experiments				Theory (Reid & Smith 1970)	
	B_K (Å^2)		B_{Br} (Å^2)			
Temperature	Uncorrected	TDS corrected	Uncorrected	TDS corrected	B_K (Å^2)	B_{Br} (Å)
295 K	2·45 ± 0·07	2·55 ± 0·07	2·12 ± 0·04	2·20 ± 0·04	2·26	2·46
4·2 K	0·431 ± 0·05		0·35 ± 0·02		0·350	0·272

the same for the NaCl structure (Groenewegen & Huiszoon, 1972; Huiszoon & Groenewegen, 1972). It is interesting to note that the calculated values of Reid & Smith, using the shell model in the quasiharmonic approximation near 125 K, also show this behaviour. Above this temperature the calculations suggest that the lighter ion has the smaller thermal motion. However, the measured values at 295 K (Table 4) disagree slightly in that the bromide anion has a somewhat smaller B value than the cation. This has also been reported by other authors (see Table 1). The explanation could be that additional anharmonic effects, perhaps including a Q^4 term in the analysis, should be incorporated in the calculation.

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Intermolecular Interactions in Crystals of Carboxylic Acids. IV. Empirical Interatomic Potential Functions

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An intermolecular force field for carboxylic acids has been derived by a least-squares fit of the parameters of non-bonded atom–atom potentials and a hydrogen-bond potential to experimental data. The latter include heats of dimerization and dimer structures of formic, acetic and propionic acid, and heats of sublimation and crystal structures of acetic, α and β-oxalic, α and β-fumaric and isophthalic acid. It was found that (exp − 6 − 1) atom–atom potentials and the Lippincott–Schroeder potential for the hydrogen bonds reproduce fairly well the experimental energies as well as the structures. The transferability of the potentials was studied with respect to the crystal structure of allene dicarboxylic acid and to the crystal structure and the lattice energy of formic acid, and was found to be good. A comparison is made with the results of other authors.

Introduction

The most widely used method of calculating lattice energies of molecular crystals is the atom–atom potential method (Kitaigorodsky, 1973; Williams, 1966, 1974). In this method the lattice energy is calculated as the sum of pairwise interactions between the molecules in the crystal, the interaction energy between a pair of molecules being represented by interactions between the atoms of the molecules.

These atom–atom interactions are described by central forces; usually one distinguishes repulsion, attraction and electrostatic contributions which are often in the form of extended Buckingham type (exp $-$ 6 $-$ 1) or Lennard–Jones type (12 $-$ 6 $-$ 1) potentials, both of which include Coulomb terms. The parameters occurring in the energy expressions are derived by requiring that good agreement is obtained between calculated and observed equilibrium structures, heats of sublimation and sometimes force constants of a number of compounds.

This method has been applied successfully, especially to crystals of hydrocarbons. For this class of compounds it appeared that sets of potential parameters, carefully derived from a limited number of representative compounds, are transferable to similar compounds, resulting in good predictions for energies and structures (Mirsky, 1976) and thermodynamic properties (Filippini, Gramaccioli, Simonetta & Suffritti, 1975).

For carboxylic acids the situation is unsatisfactory. The potentials of McGuire, Momany & Scheraga (1972) are based on semi-empirical CNDO/2 interaction-energy calculations. Nowadays it is well known that these calculations lead to overestimated interaction energies and to equilibrium structures that involve too short separations (Schuster, 1976). In a subsequent paper (Momany, Carruthers, McGuire & Scheraga, 1974) the potentials of McGuire, Momany & Scheraga (1972) were improved, but large discrepancies between observed and calculated structural data (their Table VII) remain. In further work, Momany (1976) calculated the lattice energies U of formic and acetic acid. However, both the absolute and the relative magnitudes of the lattice energies [U(formic acid) $>$ U(acetic acid)] are not in agreement with recent experimental results (de Kruif & van Ginkel, 1977). The potentials of Minicozzi & Stroot (1970) for formic acid have not been tested with respect to their transferability, and it seems to us that this ($-$ 1 $-$ 4 $-$ 6 $-$ 12) potential contains too many empirical parameters derived from too few experimental data. The recent model of Skorczyk (1976) and the EPEN model of Shipman, Burgess & Scheraga (1975) have been published since we started our work; the applicability of these models to carboxylic acids has not yet been investigated.

The main problem in the description of crystals of carboxylic acids within the atom–atom potential scheme is the presence of hydrogen bonds. Hagler, Huler & Lifson (1974) succeeded in fitting (12 $-$ 6 $-$ 1) atom–atom potentials to amide crystals, which contain weaker hydrogen bonds than carboxylic acid crystals. In the latter crystals the non-bonded O—H$\cdots$O interactions are usually described by special terms, such as the GHB potential of Momany *et al.* (1974) or the Stockmayer potential (Giglio, 1969). The best known potential for linear hydrogen bonds is the Lippincott & Schroeder (1955) potential, which has been adapted and modified for crystals by many authors (*e.g.* Chidambaram, Balasubramanian & Ramachandran, 1970, and references cited therein). The Lippincott–Schroeder potential describes the hydrogen-bond energy, the equilibrium structure and the dynamic proton behaviour reasonably well. However, the parameter values given by Lippincott & Schroeder can probably be improved for crystals, since these values were derived for equilibrium properties of isolated O—H$\cdots$O fragments, neglecting the remaining intermolecular interactions.

In this paper it is our aim to derive a set of atom–atom potentials that is capable of describing as accurately as possible the equilibrium structures and energies in dimers and crystals of carboxylic acids. We describe the hydrogen bonds with the Lippincott–Schroeder potential, and the remaining intermolecular interactions with (exp $-$ 6 $-$ 1) atom-centred potentials. The parameters in the potentials are fitted to experimentally observed structures and enthalpies of dimers and crystals, following Williams (1974) and Kitaigorodsky (1973).

In the other papers of this series (Smit, Derissen & van Duijneveldt, 1977, 1978*a*, 1978*b*) we attempted to describe intermolecular interactions in carboxylic acids, using *ab initio* quantum-mechanical methods in order to obtain non-empirical results.

Details of the method

A correct expression for the intermolecular interactions must lead to a minimum in the free energy at the experimental (equilibrium) structure. The approximations made by Williams (1966) and others, which we shall also adopt, imply that at the temperature of the observed structure the lattice energy shows a minimum. In addition, molecules are treated as rigid bodies, and many-body effects are neglected. The degrees of freedom with respect to which the lattice energy should be minimum are the cell constants, the three orientations θ, φ, χ and the three translations X, Y, Z of the independent molecules in the crystallographic unit cell. The lattice energy at the minimum has to be in agreement with the experimental heat of sublimation, ΔH_{sub}.

In dimers, only rotational and translational degrees of freedom have to be considered, and the minimum dimerization energy must be in agreement with the observed enthalpy of dimerization, ΔH_{dim}.

We calculate the lattice energy according to the expression

$$\Delta U^{\text{lat}} = \tfrac{1}{2} \sum_i \sum_j{}' V_{ij}^{xy} + V_{\text{HB}} + V_{\text{def}} \tag{1}$$

and the dimerization energy, defined as $U_{\text{dimer}} - 2U_{\text{monomer}}$, as

$$\Delta U^{\text{dim}} = \sum_i \sum_j{}' V_{ij}^{xy} + V_{\text{HB}} + V_{\text{def}}. \tag{2}$$

In these expressions V_{ij}^{xy} represents the energy contribution of the atoms i and j involving the chemical elements x and y, V_{HB} is a hydrogen-bond energy and V_{def} a deformation energy. The summation over i is over all atoms of a reference molecule; the summation over j covers all atoms of all other molecules in the crystal, or the atoms of the other molecule in the dimer.

The atom–atom potential V_{ij}^{xy} is given by

$$V_{ij}^{xy} = B^{xy} \exp(-C^{xy} r_{ij}) - A^{xy} r_{ij}^{-6} + q_i q_j r_{ij}^{-1}. \tag{3}$$

A^{xy}, B^{xy}, C^{xy} are the atom–atom potential parameters, q_i are atomic point charges and r_{ij} is the distance between the atoms i and j. For the r^{-1} and r^{-6} sums we used a convergence-acceleration method (Williams, 1971). For the sum of the exponentials we required convergence within 0·1%, allowing truncation at about 6 Å. The prime in the summation indicates that O···H and O···O repulsion and attraction terms in the hydrogen bonds have to be excluded (the Coulomb terms are retained). Instead, the O—H···O interactions are described by the hydrogen-bond potential:

$$\begin{aligned} V_{\text{HB}} = D\Bigg\{ 1 - \exp\left[\frac{-n(r_{\text{OH}} - r_{\text{OH}}^0)^2}{2r_{\text{OH}}}\right] \\ - \frac{1}{g} \exp\left[\frac{-ng(r_{\text{H}\cdots\text{O}} - r_{\text{H}\cdots\text{O}}^0)^2}{2r_{\text{H}\cdots\text{O}}}\right]\Bigg\} \\ + A\exp(-br_{\text{O}\cdots\text{O}}) - Br_{\text{O}\cdots\text{O}}^{-m}. \end{aligned} \tag{4}$$

In this equation D, n, r_{OH}^0, g, $r_{\text{H}\cdots\text{O}}^0$, A, b, B and m are empirical parameters introduced by Lippincott & Schroeder (1955). In equations (1) and (2) V_{def} is an energy term introduced to account for molecular deformations other than the O—H stretch ones (these are already included in V_{HB}) which occur in the transition of hydrogen-bonded molecules from the crystal to free molecules in the gas phase (Derissen, 1977). Energy contributions due to non-linearity of the hydrogen bonds and conformational changes may also be included in V_{def}. For V_{def} in the crystals we calculated 1·0 kcal mol^{-1}, excluding the O—H deformation energy of 0·8 kcal mol^{-1} (Derissen, 1977). This value was used unless otherwise specified.

In order to reduce the number of empirical parameters, and in order to be able to use the convergence acceleration for the r^{-6} sums, a number of constraints were introduced:

$$A^{xy} = (A^{xx}A^{yy})^{1/2}, \; B^{xy} = (B^{xx}B^{yy})^{1/2}, \\ C^{xy} = (C^{xx} + C^{yy})/2. \tag{5}$$

We used Lippincott & Schroeder's (1955) values for r_{OH}^0, $r_{\text{H}\cdots\text{O}}^0$, g and m. In view of the size of the molecules involved, we obtained the atomic point charges q_i from CNDO/2 Mulliken populations (Dobosh, 1973). As an illustration, the values of the carboxylic group point charges, averaged over all molecules considered in this paper, are given in Table 1.

Table 1. *Average point charges, with the standard deviations, of the carboxylic groups used, calculated from gross Mulliken populations from CNDO/2 wave functions*

Charges are in electron units (1 e = 1·6022 × 10^{-19} C).

Atom	Average charge	Standard deviation
C	0·390	0·020
$\text{O}_{\text{carbonyl}}$	−0·315	0·030
$\text{O}_{\text{hydroxyl}}$	−0·250	0·020
H	0·175	0·030

Numerical values for the energy parameters defined above were obtained by a least-squares optimization. We minimized the expression

$$R = \sum w \left(\frac{\partial \Delta U}{\partial p}\right)^2 + \sum w'(\Delta U - \Delta U_{\text{obs}})^2. \tag{6}$$

Here ΔU and ΔU_{obs} are calculated and observed energies respectively. The first sum is over all independent structural degrees of freedom p of all compounds, the second sum is over the lattice and dimerization energies. The weighting factors w and w' will be described in the section on the derivation of the parameters.

Starting values for atom–atom parameters involving C and H were taken from Williams (1974) and involving O from Kitaigorodsky, Mirskaya & Nauchitel (1970). For the parameters in V_{HB} we started from Schroeder & Lippincott's (1957) values for O—H···O bonds, but in the case of A and B we obtained starting values by requiring the calculated dimerization energy of formic acid to be about −16 kcal mol^{-1} (this was done because in contrast to Schroeder & Lippincott we do not obtain A and B implicitly from expressions involving an equilibrium distance R_{OO}^0, but we treat these coefficients as adjustable constants, as is done with all the other para-

Table 2. *Empirical atom–atom and hydrogen-bond parameters for carboxylic acids, with standard deviations in parentheses*

Units correspond to energies in kcal mol^{-1} and distances in Å (1 kcal = 4184 J, 1 Å = 10^{-10} m). For all sets $r^0_{\rm OH}$ = 0·97 Å, $R^0_{\rm H\cdots O}$ = 0·97 Å, g = 1·45 and m = 1 [see equations (3) and (4)].

Parameter	Set I	Set II	Set III	Set IV
$A_{\rm OO}$	259·4	317·8 (35)	239·4 (43)	247·9 (45)
$B_{\rm OO}$	77000	115340 (17500)	102496 (27600)	99422 (31250)
$C_{\rm OO}$	4·18	3·936 (0·05)	4·064 (0·09)	4·070 (0·11)
$A_{\rm CC}$	449·0	747·6 (62)	677·1 (86)	613·5 (82)
$B_{\rm CC}$	71400	49362 (14700)	68119 (31250)	68644 (32250)
$C_{\rm CC}$	3·60	3·587 (0·10)	3·665 (0·14)	3·609 (0·15)
$A_{\rm HH}$	40·1	29·3 (7·4)	36·7 (11·0)	30·8 (10·0)
$B_{\rm HH}$	2870	1383 (540)	1765 (1200)	824 (860)
$C_{\rm HH}$	3·74	3·693 (0·15)	3·845 (0·23)	3·965 (0·35)
D	118·0	116·7 (7·0)	114·9 (8·4)	113·4 (8·9)
n	9·18	9·339 (0·24)	9·139 (0·29)	9·192 (0·32)
A	43·00 × 10^5	43·87 (2·43) × 10^5	44·12 (3·03) × 10^5	44·08 (3·15) × 10^5
b	4·815	4·811 (0·02)	4·807 (0·03)	4·806 (0·03)
B	18·2	20·0 (1·5)	18·8 (1·9)	19·0 (1·8)

meters). Our resulting set of starting values is listed as set I in Table 2.

A total number of 14 potential parameters was varied to fit 8 observed energies and 62 structural data, which will be specified in the next section.

Experimental data

In view of the approximations in the method, the set of experimental data should include accurate heats of sublimation and dimerization and crystal and dimer structures for carboxylic acids with rigid molecular structures, and should all be measured at about the same temperature. Structures with carboxylic group disorder (Leiserowitz, 1976*a*), internal rotations in the crystalline or gas phase or other deformations only deserve consideration when the energy effects can be taken into account. The positions of all atoms, including hydrogens, must be accurately known. This means that for hydrogen atoms neutron diffraction data or reliable calculated positions must be used. Heats of sublimation should be converted to lattice energies and temperature effects should be taken into account.

The relation between enthalpy of sublimation and lattice energy for molecular crystals may be given as (Warshel & Lifson, 1970)

$$\Delta H_{\rm sub} \equiv H^g - H^{cr} = 4RT + (\varepsilon_0^g - \varepsilon_0^{cr}) + (U^g_{\rm vibr} - U^{cr}_{\rm vibr}) - \Delta U^{\rm lat}_{\rm obs} \tag{7}$$

where ε_0 and $U_{\rm vibr}$ are the zero-point vibration energy and the energy of vibration at temperature T, $\Delta H_{\rm sub} > 0$ and $\Delta U^{\rm lat}_{\rm obs} < 0$. Expression (7) is approximated by (Mirsky, 1976)

$$\Delta H_{\rm sub} \simeq -\Delta U^{\rm lat}_{\rm obs} - 2RT. \tag{8}$$

If the heat of sublimation is known at a temperature different from that of the structure determination it must be corrected with a term $(c_p^g - c_p^{cr})\Delta T$. The Δc_p is of the order of -10 cal mol^{-1} deg^{-1} for carboxylic acids near room temperature.

For dimerization the expression relating ΔH and ΔU is

$$\Delta H_{\rm dim} \equiv 2H^m - H^d = 4RT + (2\varepsilon_0^m - \varepsilon_0^d) + (2U^m_{\rm vibr} - U^d_{\rm vibr}) - \Delta U^{\rm dim}_{\rm obs}. \tag{9}$$

Here $\Delta H_{\rm dim} > 0$ and $\Delta U^{\rm dim}_{\rm obs} < 0$. The terms ε_0 and $U_{\rm vibr}$ can be evaluated by the methods of statistical thermodynamics assuming harmonic vibrations, using frequencies obtained by normal coordinate analysis.

We used a data set consisting of the dimer structures of formic, acetic and propionic acid, the crystal structures of α- and β-oxalic, α- and β-fumaric and isophthalic acid, and the corresponding heats of dimerization and sublimation. We shall now specify these data (see also Table 3).

Formic acid dimer

The molecular structures of monomer and dimer used were those determined by Almenningen, Bastiansen & Motzfeldt (1969) with corrected hydrogen positions (Smit, Derissen & van Duijneveldt, 1977). The dimerization energy $\Delta U^{\rm dim}_{\rm obs}$ was calculated to be $-16{\cdot}0$ kcal mol^{-1}, using $\Delta H_{\rm dim}$ = 14·1 ± 1·5 kcal mol^{-1} (Mathews & Sheets, 1969). The vibrational energy differences were calculated using the calculated frequencies of Cyvin, Alfheim & Hagen (1970) for the monomer and those of Alfheim, Hagen & Cyvin (1971) for the dimer. The deformation energy $V_{\rm def}$ caused by changes in molecular geometry on dimerization (excluding the O—H stretch deformation) was calculated as 0·9 kcal mol^{-1}, using the molecular mechanics method following Derissen (1977).

Table 3. *Structural data and energies, as observed experimentally and calculated with the four parameter sets* I–IV

Cell constants and rigid-molecule translations X, Y, Z in Å, rigid-molecule rotation angles θ, φ, χ in rad, energies in kcal mol^{-1}. In parentheses after the name of each compound the origin and rotation axes are defined. LS and SD refer to least-squares and steepest-descent methods respectively. ΔU(exp) is a lattice or dimerization energy calculated for the experimental structure (given in the text as $\Delta U^{\mathrm{lat}}_{\mathrm{exp}}$ or $\Delta U^{\mathrm{dim}}_{\mathrm{exp}}$), and ΔU(min) is the analogous quantity for the optimum structure. R_{OO} is the O$\cdots$O hydrogen-bond distance in the optimized structure, and V(HB) is the hydrogen-bond energy contribution to ΔU(exp).

Structural	Observed	Set I	Set II	Set III		Set IV
parameter	value	SD	SD	LS	SD	SD
Formic acid dimer (C; **x** ∥ C—H, **y** in COO plane)						
χ	0	0·08	0·04	0·03	0·05	0·03
X	0	0·08	0·05	0·05	0·05	0·04
Y	0	−0·05	−0·02	−0·07	−0·03	−0·02
R_{OO}	2·701	2·590	2·613	2·622	2·622	2·626
ΔU(exp)	−16·0	−14·90	−15·46		−15·14	−15·14
ΔU(min)		−16·94	−16·34	−15·96	−15·96	−15·72
V(HB)		−13·24	−12·94		−12·38	−12·46
Acetic acid dimer ($\mathrm{C_{carboxyl}}$; **x** ∥ C—C, **y** in COO plane)						
χ	0	0·08	0·04	0·03	0·05	0·03
X	0	0·06	0·04	0·04	0·04	0·03
Y	0	−0·05	−0·02	−0·06	−0·03	−0·02
R_{OO}	2·683	2·598	2·622	2·630	2·630	2·635
ΔU(exp)	−15·0	−15·20	−15·82		−15·44	−15·46
ΔU(min)		−16·80	−16·40	−15·96	−15·96	−15·76
V(HB)		−13·60	−13·22		−12·62	−12·28
Propionic acid dimer ($\mathrm{C_{carboxyl}}$; **x** ∥ $\mathrm{C_{carboxyl}}$—Cα, **y** in COO plane)						
χ	0	0·07	0·03	0·01	0·03	0·01
X	0	0·08	0·05	0·05	0·05	0·05
Y	0	−0·04	−0·01	−0·06	−0·02	−0·01
R_{OO}	2·719	2·597	2·622	2·630	2·629	2·635
ΔU(exp)	−15·30	−15·14	−15·76		−15·38	−15·32
ΔU(min)		−16·94	−16·58	−16·12	−16·12	−15·90
V(HB)		−13·12	−12·94		−12·38	−12·10
α-Oxalic acid (centre midpoint C—C; **x** ∥ **a**, **y** ∥ **b**, **z** ∥ **c**)						
a	6·548	6·62	6·74	6·91	6·67	6·68
b	7·844	7·79	7·85	7·76	7·80	7·78
c	6·086	6·18	6·35	6·30	6·27	6·28
θ	0	−0·06	−0·04	−0·02	−0·05	−0·05
φ	0	−0·06	−0·07	0·02	−0·06	−0·07
χ	0	0·13	0·13	0·10	0·10	0·07
R_{OO}	2·702	2·638	2·661	2·678	2·675	2·687
ΔU(exp)	−23·4	−24·10	−23·16		−23·50	−23·48
ΔU(min)		−25·48	−25·79	−24·96	−24·85	−24·52
V(HB)		−13·47	−13·26		−12·58	−12·28
β-Oxalic acid (centre midpoint C—C; **x** ∥ **a**, **y** ∥ **b**, **z** = **a** × **b**)						
a	5·330	5·25	5·30	5·30	5·30	5·31
b	6·015	6·06	6·25	6·26	6·15	6·15
c	5·436	5·40	5·53	5·42	5·47	5·46
cos β	−0·436	−0·452	−0·414	−0·454	−0·444	−0·461
θ	0	0·11	0·11	0·06	0·10	0·09
φ	0	0·07	0·04	0·04	0·04	0·04
χ	0	0·07	0·04	0·06	0·05	0·05
R_{OO}	2·674	2·633	2·665	2·672	2·671	2·677
ΔU(min)	−23·1	−22·96	−23·08		−23·02	−22·97
ΔU(min)		−25·13	−24·97	−24·36	−24·33	−24·05
V(HB)		−13·59	−13·24		−12·54	−12·20
Acetic acid ($\mathrm{O_{hydroxyl}}$; **x** ∥ **a**, **y** ∥ **b**, **z** ∥ **c**)						
a	13·310	13·34	13·33	13·41	13·29	13·21
b	4·090	3·92	3·85	3·60	3·73	3·62
c	5·769	5·64	5·61	5·88	5·50	5·37
θ	0	−0·08	−0·06	−0·11	−0·06	−0·07
φ	0	−0·06	−0·05	−0·10	−0·07	−0·08
χ	0	−0·16	−0·12	−0·04	−0·12	−0·07

Table 3 (*cont.*)

Structural parameter	Observed value	Set I	Set II	Set III		Set IV
		SD	SD	LS	SD	SD
Acetic acid (*cont.*)						
X	0	−0·03	−0·06	−0·07	−0·10	−0·17
Y	0	−0·06	−0·00	0·13	−0·03	−0·02
R_{OO}	2·627	2·630	2·645	2·654	2·647	2·652
ΔU(exp)	−16·3	−14·27	−16·11		−16·01	−15·99
ΔU(min)		−15·07	−17·06	−17·08	−17·50	−18·16
V(HB)		−6·80	−6·47		−6·08	−5·86
α-Fumaric acid (0,0,0; $\mathbf{x} \parallel \mathbf{a}$, $\mathbf{y} \parallel \mathbf{b}$, $\mathbf{z} = \mathbf{a} \times \mathbf{b}$)						
a	7·619	7·58	7·61	7·60	7·62	7·62
b	15·014	15·10	15·08	15·18	15·08	15·01
c	6·686	6·64	6·66	6·14	6·62	6·58
cos β	−0·375	−0·444	−0·428	−0·331	−0·462	−0·459
θ	0	0·01	0·03	0·01	0·01	−0·05
φ	0	−0·03	−0·01	−0·02	−0·01	−0·02
χ	0	−0·06	−0·04	−0·04	−0·04	−0·03
θ'	0	0·02	0·02	0·01	0·01	0·00
φ'	0	0·02	0·01	0·03	0·01	0·02
χ'	0	−0·04	−0·02	−0·02	−0·03	−0·03
X'	0	−0·01	−0·01	−0·44	−0·03	−0·04
Y'	0	−0·14	−0·07	−0·00	−0·11	−0·11
Z'	0	0·00	0·00	−0·09	0·00	0·01
R_{OO}	2·682	2·633	2·663	2·665	2·668	2·675
	2·685	2·634	2·665	2·667	2·670	2·677
	2·685	2·632	2·659	2·654	2·665	2·674
ΔU(exp)	−31·5	−27·38	−30·98		−30·40	−30·44
ΔU(min)		−29·45	−32·02	−31·58	−31·72	−31·32
V(HB)		−13·56	−13·24		−12·56	−12·24
β-Fumaric acid (centre midpoint C=C; $\mathbf{x} \parallel \mathbf{a}$, $\mathbf{z} \parallel \mathbf{a} \times \mathbf{b}$, $\mathbf{y} = \mathbf{z} \times \mathbf{x}$)						
a	5·264	5·24	5·25	5·06	5·25	5·25
b	7·618	7·59	7·62	7·62	7·62	7·63
c	4·487	4·46	4·48	4·32	4·46	4·44
cos α	−0·290	−0·279	−0·266	−0·258	−0·285	−0·315
cos β	0·064	0·104	0·102	0·099	0·115	0·112
cos γ	−0·706	−0·724	−0·725	−0·705	−0·737	−0·734
θ	0	0·03	0·02	0·04	0·01	−0·01
φ	0	0·04	0·03	0·00	0·04	0·04
χ	0	−0·05	−0·04	−0·02	−0·06	−0·05
R_{OO}	2·671	2·631	2·657	2·664	2·662	2·671
ΔU(exp)	−31·5	−27·56	−30·99		−30·32	−30·32
ΔU(min)		−29·55	−32·31	−31·75	−31·62	−30·98
V(HB)		−13·60	−13·26		−12·52	−12·16
Isophthalic acid [C(1); $\mathbf{x} \parallel \mathbf{a}$, $\mathbf{y} \parallel$, $\mathbf{z} = \mathbf{a} \times \mathbf{b}$]						
a	3·758	3·75	3·47	3·43	3·46	3·48
b	16·364	16·06	16·24	16·10	16·23	16·26
c	11·703	11·69	11·62	12·20	11·60	11·56
cos β	−0·005	0·043	0·048	0·096	0·041	−0·033
θ	0	−0·04	−0·03	−0·02	−0·03	−0·03
φ	0	−0·03	0·00	0·03	0·01	0·09
χ	0	−0·03	−0·03	−0·01	−0·03	−0·02
X	0	−0·01	0·01	−0·01	0·02	0·04
Y	0	−0·14	−0·14	0·06	−0·11	−0·11
Z	0	0·13	0·10	0·06	0·12	0·16
R_{OO}	2·681	2·661	2·676	2·696	2·685	2·674
	2·581	2·633	2·650	2·644	2·655	2·657
ΔU(exp)		−31·66	−41·97		−39·94	−38·21
ΔU(min)		−33·79	−46·00	−42·65	−43·85	−41·67
V(HB)		−13·37	−12·89		−11·92	−11·49
Goodness of fit						
$\frac{1}{n}\sum[\Delta U(\mathrm{obs}) - \Delta U(\mathrm{exp})]^2$		39·28	1·65		3·76	3·69
$\frac{1}{n}\sum[\Delta U(\mathrm{exp}) - \Delta U(\mathrm{min})]$		1·78	1·57	1·25	1·42	1·19

Acetic acid dimer

The molecular structures of monomer and dimer were taken from Derissen (1971*a*) except for C—H which was shortened to 1·09 Å. $\Delta U_{\text{obs}}^{\text{dim}}$ was calculated as −15·0 kcal mol^{-1} using ΔH_{dim} = 14·2 ± 0·7 kcal mol^{-1} (Mathews & Sheets, 1969) and the calculated vibration frequencies for monomer and dimer (Fukushima & Zwolinski, 1969). The relatively large difference in $\Delta U_{\text{obs}}^{\text{dim}}$ with formic acid is mainly caused by the zero-point energy difference $2\varepsilon_0^m - \varepsilon_0^d$, which is −2·54 kcal mol^{-1} for formic acid and −0·60 kcal mol^{-1} for acetic acid. V_{def} was calculated to be 1·0 kcal mol^{-1}.

Propionic acid dimer

The molecular structures of monomer and dimer were taken from Derissen (1971*b*) with C—H = 1·09 Å. $\Delta U_{\text{obs}}^{\text{dim}}$ was estimated as −15·3 kcal mol^{-1}, being the value for acetic acid minus 0·3 kcal mol^{-1}. This value was chosen, because Clague & Bernstein (1969) found a difference of 0·3 kcal mol^{-1} with acetic acid in the enthalpy, and the frequencies for propionic acid monomer and dimer are not known with sufficient accuracy.

α- and β-oxalic acid

The crystal structure at room temperature (Derissen & Smit, 1974) was used. Hydrogen atoms were placed at O—H = 1·01 Å with an angle C—O—H = 110·5° in the COO plane. The heat of sublimation of α and β-oxalic acid was determined by Bradley & Cotson (1953) (α: 23·45, β: 22·28 kcal mol^{-1}). In our opinion the difference between these values is too large. We therefore measured the heat of transition of α- to β-oxalic acid on a Perkin Elmer DSC-1B differential scanning calorimeter and found 0·31 ± 0·03 kcal mol^{-1} at 120 to 123 °C. De Kruif (1976) redetermined the vapour pressure of α-oxalic acid, from which $\Delta H_{\text{sub}}^{273}$ = 22·4 ± 0·2 kcal mol^{-1} was calculated. The heat of sublimation for β-oxalic acid is then found to be $\Delta H_{\text{sub}}^{273}$ = 22·1 ± 0·2 kcal mol^{-1}. In our calculations we used $\Delta U_{\text{obs}}^{\text{lat}}$ = −23·4 and $\Delta U_{\text{obs}}^{\text{lat}}$ = −23·1 kcal mol^{-1} at T = 293 K, and V_{def} = 0·6 and 1·6 kcal mol^{-1}, for α- and β-oxalic acid respectively.

Acetic acid

The crystal structure at 278 K (Nahringbauer, 1970) was used, with the hydroxylic hydrogen atom located as for oxalic acid and the methyl hydrogens forming a tetrahedron with C—H = 1·08 Å, with one hydrogen atom eclipsed with C=O (in agreement with the neutron diffraction determination at 133 K by Jönsson, 1971). The heat of sublimation was measured and found to be $\Delta H_{\text{sub}}^{224}$ = 16·7 ± 0·6 kcal mol^{-1} (de Kruif, 1976). It appeared that at 224 K the vapour consists almost completely of dimers. Using ΔH_{dim} = 14·2 ± 0·7 kcal mol^{-1} (Mathews & Sheets, 1969) we obtained for the transition of crystal to monomer at T = 278 K: $\Delta U_{\text{obs}}^{\text{lat}}$ = −16·3 kcal mol^{-1} [calculated as $\frac{1}{2}(-\Delta H_{\text{sub}}^{278} - \Delta H_{\text{dim}}) - 2RT$].

α- and β-fumaric acid

In the crystal structures at room temperature of α- and β-fumaric acid (Brown, 1966; Bednowitz & Post, 1966), the hydroxylic hydrogen atoms were positioned as for oxalic acid. The aliphatic hydrogen atom was located at C—H = 1·08 Å on the bisector of the C=C—C angle. The heat of sublimation $\Delta H_{\text{sub}}^{378}$ = 29·5 ± 0·4 kcal mol^{-1} (de Kruif & van Ginkel, 1977) was used for both α- and β-fumaric acid, as it is not known for which modification it was measured. We used $\Delta U_{\text{obs}}^{\text{lat}}$ = −31·5 kcal mol^{-1} at T = 293 K for both α- and β-fumaric acid.

Isophthalic acid

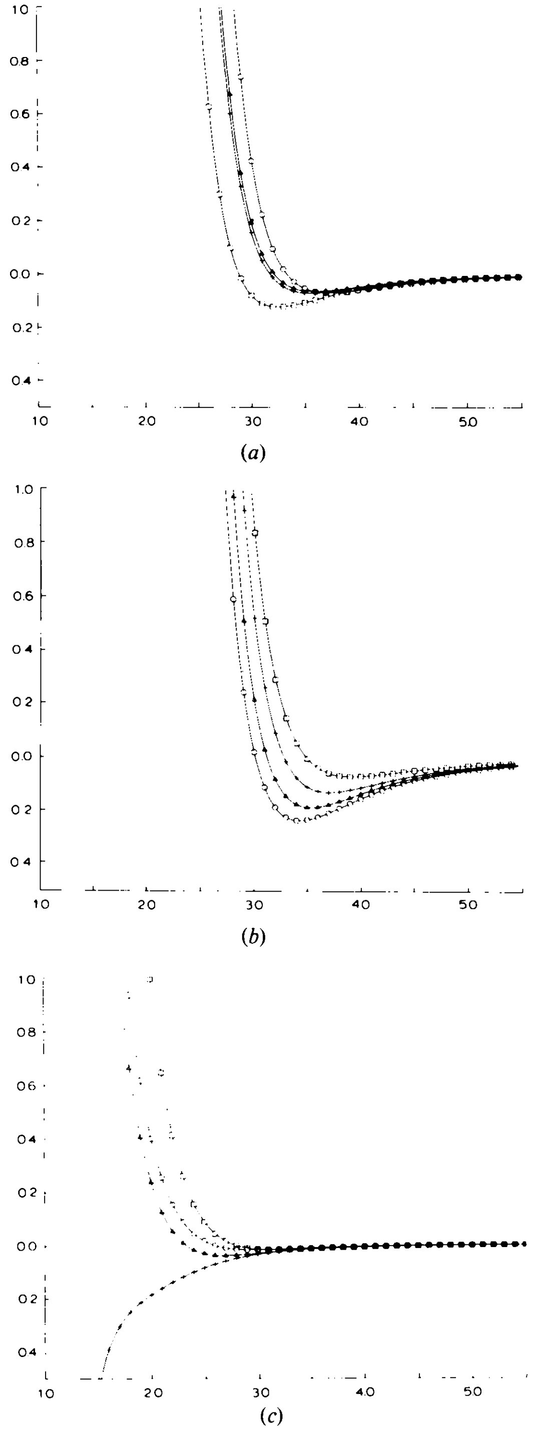
The crystal structure at room temperature (Derissen, 1974) was used, with the hydrogen atoms placed on calculated positions (as described for fumaric acid). The heat of sublimation, $\Delta H_{\text{sub}}^{523}$ = 25·5 kcal mol^{-1} of Kraus, Beranek, Kochloefl & Bazant (1962) (yielding $\Delta U_{\text{obs}}^{293} \simeq -29$ kcal mol^{-1}) is rather small compared with the same quantity for the related compound terephthalic acid $\Delta H_{\text{sub}}^{573}$ = 31·1 (same authors) or $\Delta H_{\text{sub}}^{625}$ = 33·3 kcal mol^{-1} (Lucchesi & Lewis, 1968). Our calculated values of $|\Delta U_{\text{obs}}^{\text{lat}}|$ are about 8 kcal mol^{-1} higher. We omitted this energy in our calculations.

The crystal structures of formic acid (Holtzberg, Post & Fankuchen, 1953), propionic acid (Strieter, Templeton, Scheuerman & Sass, 1962), benzoic acid (Sim, Robertson & Goodwin, 1955), and terephthalic acid I (Bailey & Brown, 1967) do not fulfil our requirements.

Derivation of the parameters

From the starting values already described (set I, Table 2), the parameters of the atom–atom potentials and of V_{HB} were refined by means of Marquardt's (1963) method of least-squares minimization of expression (6). We used a modified version of Busing's (1970) program *WMIN* to achieve this.

A selection of the results is presented in Table 2. Sets II, III and IV were obtained by the introduction of several different weight schemes w. For set II we chose a weighting scheme in the context of Busing's (1970) description. The variance V_{ii} to be assigned to structural parameter p_i, however, is problematical. One might base this variance on experimental errors, but in our case such refinements diverged. We therefore assigned an *a priori* tolerance to all structure parameters p_i (1% tolerance for cell dimensions, 0·02 rad for rotations, 0·05 Å for translations), and we took V_{ii} equal to the reciprocal of the square of the absolute tolerance. Set III is based on Hagler & Lifson's (1974) work. We took their expression (9), but we interpreted the matrix $(\mathbf{F}^{-1})^{\dagger}\,\mathbf{F}^{-1}$ as a weighting matrix. This means that the matrix of derivatives $\partial(\mathbf{F}^{-1}\nabla\mathbf{V})/\partial\mathbf{p}$ is approximated by $\mathbf{F}^{-1}\partial\nabla\mathbf{V}/\partial\mathbf{p}$; this was done in order to avoid the tedious calculation of the derivatives of $\mathbf{F}^{-1}$. Set IV was obtained by application of a diagonal weighting matrix **w**, following Williams (1966, 1974). The weights of all $\partial U/\partial p$ were taken as unity.



(*a*)

(*b*)

(*c*)

Fig. 1. Curves for the (exp − 6) part of the potentials, □ set I, ○ set II, △ set III, + set IV, for (*a*) the O—O, (*b*) the C—C and (*c*) H—H interactions (kcal mol^{-1} *vs* Å units, 1 kcal = 4184 J, 1 Å = 10^{-10} m).

In all weighting schemes the relative magnitudes of the weights w of derivatives of energy to structure parameters and the weights w' of energies have to be chosen. We chose w' in such a way as to guarantee a sufficient but not too large a contribution of the energy terms in (6), *viz* $w' = 2500$, corresponding to $\sigma_U =$ 0·02 kcal mol^{-1}.

From Table 2 it is not possible to prefer any of the parameter sets derived. The largest difference with the starting set is seen in $B_{\rm HH}$, which may be due to Williams' (1974) shortened C—H interaction bond lengths. We also listed the standard deviations obtained from the least-squares calculations. It is clear that the repulsion parameters $B_{\rm HH}$, $B_{\rm CC}$ and $B_{\rm OO}$ are not well determined by the information contained in our set of data. In Fig. 1 the potential curves $V^{xy}(r)$ for sets I–IV are drawn. It is seen that $V^{\rm HH}$ for set IV has no repulsive part and therefore may be considered to be in conflict with the physical background of our atom–atom potential model.

Application of the potentials

Since it is our aim to reproduce and to predict structures and energies of dimers and crystals of carboxylic acids accurately, we tested our potentials in two ways. First, we investigated how well they reproduce the data from which they were derived. Second, we studied the transferability of the parameters with respect to two crystal structures and a lattice energy which were not used in the derivation.

Our starting set I has been successfully applied in the determination of the crystal structure of 1,4-naphthalene dicarboxylic acid by packing-energy considerations (Derissen, Schoone & Timmermans, 1978), and it was also used in our study on acetic acid crystal structures (Derissen & Smit, 1977).

We optimized the nine individual structures for each set of parameters starting at the observed structures. Severe problems were encountered during the optimizations. The least-squares method and a step-optimized steepest-descent method led to very different solutions for a number of compounds. This is illustrated in Table 3 for set III under the headings LS and SD respectively, and is probably caused by the occurrence

Table 4. *Structural data and lattice energies observed and calculated for formic and allene dicarboxylic acid crystals*

See also legend to Table 3. The results are for SD refinements.

Structural parameter	Observed value	Set I	Set II	Set III	Set IV
Formic acid crystal (H_{alkyl}; $\mathbf{x} \parallel H_C—H_O$, $\mathbf{z} \parallel H_C—H_O \times H_O—C$, $\mathbf{y} = \mathbf{z} \times \mathbf{x}$)					
a	10·241	10·303	10·292	10·288	10·241
b	3·544	3·573	3·611	3·563	3·526
c	5·356	5·314	5·412	5·368	5·342
θ	0	0·00	−0·02	−0·02	−0·04
φ	0	−0·04	−0·03	−0·02	−0·04
χ	0	−0·06	−0·04	−0·04	−0·01
X	0	0·07	0·02	−0·05	0·00
Y	0	−0·19	−0·11	−0·15	−0·10
R_{OO}	2·625	2·637	2·652	2·669	2·678
ΔU(exp)	−14·8	−12·18	−12·69	−12·76	−12·92
ΔU(min)		−12·90	−13·21	−13·22	−13·32
V(HB)		−6·79	−6·45	−6·06	−5·83
Allene dicarboxylic acid [C(3); $\mathbf{x} \parallel \mathbf{a}$, $\mathbf{y} \parallel \mathbf{b}$, $\mathbf{z} \parallel \mathbf{c}$]					
a	15·108	15·15	15·20	15·17	15·19
b	8·214	8·16	8·19	8·15	8·09
c	4·527	4·38	4·44	4·36	4·28
θ	0	0·08	0·04	0·05	0·05
φ	0	0·05	0·03	0·03	0·02
χ	0	−0·02	0·00	−0·01	−0·01
X	0	0·00	0·00	0·00	0·03
Y	0	−0·02	−0·03	0·00	0·00
R_{OO}	2·572	2·611	2·622	2·635	2·634
	2·663	2·644	2·687	2·686	2·701
ΔU(exp)		−28·38	−30·99	−29·98	−29·52
ΔU(min)		−29·51	−31·49	−30·81	−30·63
V(HB)		−13·32	−12·93	−12·22	−11·83

of local minima of nearly equal depth in the neighbourhood of the experimental structure. The two methods of optimization may then lead to different solutions, since their depth in hyperspace is different (Kowalik & Osborne, 1968). The steepest-descent refinements for the crystals converged slowly after rapid initial improvements. In view of the large computing times involved, we terminated the optimizations after 30 cycles, which yielded energies that were unstable in the second or third decimal place. It should be realized that in this way in some cases the minimum may not yet be reached. We shall nevertheless discuss the structures obtained by means of the steepest-descent method, since the energies are usually equal to or lower than those obtained with the least-squares method. It should be noted that the minima thus found do not necessarily coincide with the minimum closest to experiment.

From Table 3 it is inferred that all three sets of parameters, and even the starting set, reproduce the structures fairly well. Unit-cell axes parallel to the hydrogen bonds are usually very well reproduced (*e.g.* a of α-fumaric acid and b of β-fumaric acid), while in the other directions cell constants may deviate up to a few tenths of an ångstrom. The hydrogen-bond lengths R_{OO} show slightly less variation in the optimized crystal structures than in the individual experimental structures. In the dimers the R_{OO} values obtained are 0·05–0·08 Å too short. In the optimized structures, molecules are found to be displaced by up to 0·1 rad from their observed orientations and by up to 0·17 Å from their observed positions. It is difficult to appreciate these deviations, since they are correlated with the cell dimensions, and their magnitudes depend very much on the steepness of the potential with respect to the coordinate involved [see also Hagler & Lifson (1974) for a discussion of the latter effect]. We conclude from these optimized structures that none of the potential sets II–IV may be favoured.

Table 3 lists the observed energies ΔU_{obs} and the lattice or dimerization energies ΔU_{exp}, calculated for the experimental structure. The sets II–IV reproduce the energies fairly well. The criterion of minimum $\sum (\Delta U_{obs} - \Delta U_{exp})^2$ slightly favours set II. When the sum of the differences in energy calculated for the experimental structure and for the optimized structure, $\sum (\Delta U_{exp} - \Delta U_{min})$, is taken as a criterion, set IV is slightly better. We also listed the hydrogen-bond contribution V_{HB} to ΔU_{exp}. It is seen that V_{HB} is a rather constant contribution per hydrogen bond, ranging from about 6.7 kcal mol^{-1} for set I to 6·0 kcal mol^{-1} for set IV.

For testing the transferability of our potentials, a useful set of data became available in the course of our study. These data are the crystal structure of formic acid at 81 K (Nahringbauer, 1975), its lattice energy as derived from vapour pressure measurements (de Kruif, 1976) and calculated following Minicozzi & Stroot (1970), and the crystal structure of allene dicarboxylic acid (Leiserowitz & Nader, 1973; Leiserowitz, 1976*b*). We located the hydrogen atoms at calculated positions for formic acid, as described by Smit *et al.* (1977) and for allene dicarboxylic acid as for fumaric acid. In Table 4 the equilibrium properties calculated for these crystals are compared with the experimental data (the structures were again optimized by means of the steepest-descent method). For formic acid all sets yield a good description of the structure. The lattice energy obtained with set IV appears to be closest to experiment, and is smaller in absolute value than that of acetic acid, in agreement with experiment (de Kruif, 1976). For allene dicarboxylic acid the structure obtained with set II is slightly better than that obtained with the other sets. The experimental lattice energy is not known, but we expect it to be about equal to that of fumaric acid, *viz* $-31{\cdot}5$ kcal mol^{-1}.

Summarizing our results, we can say that our potentials describe fairly well both the energies and the structures of the carboxylic acids considered. We have a (slight) preference for the parameters of set III above those of set II because the weight scheme used in set III is free from arbitrariness whereas set II parameters depend on the tolerances assigned to the structure parameters. Set IV is rejected because its H—H potential has no repulsive behaviour at short distances.

Comparison with other authors

A survey of the results for the formic acid dimer and crystal, the acetic acid dimer and crystal and α-oxalic acid obtained by other authors and by us (set III) is given in Table 5. In the work of Minicozzi & Bradley (1969) and that of Minicozzi & Stroot (1970) the number of varied parameters exceeded the number of observations in the fitting procedure. We therefore shall not compare our results with theirs.

For the formic acid and acetic acid dimer our values of $\Delta U^{\rm dim}_{\rm exp}$, which denotes the dimerization energy calculated for the experimental structure, agree fairly well with Momany's (1976) results, but his $R_{\rm OO}$ values for the optimized structures are 0·03–0·05 Å closer to experiment than our values. For the three crystals our calculated values on the whole are in better agreement with experiment than the values of Momany (1976) and Momany *et al.* (1974), except in the case of the *b* and *c* axes of acetic acid which we calculated about 0·25 Å too short. In our opinion the values of $-23{\cdot}6$ and $-9{\cdot}96$ kcal mol^{-1} which Momany *et al.* (1974) quote for the observed lattice energies of formic and acetic acid, respectively, are erroneous, probably because they misinterpreted the observed heats of sublimation. We

Table 5. *Comparison of the results of several authors*

Abbreviations: ABM: Almenningen, Bastiansen & Motzfeldt (1969); D: Derissen (1971*a*); DS: Derissen & Smit (1974); HPF: Holtzberg, Post & Fankuchen (1953); N70: Nahringbauer (1970); N75: Nahringbauer (1975); M: Momany (1976); MB: Minicozzi & Bradley (1969); MS: Minicozzi & Stroot (1970); MCGS: Momany, Carruthers, McGuire & Scheraga (1974). For other symbols and units see legend to Table 3.

Compound		Reference	a	b	c	$R_{\rm OO}$	$\Delta U_{\rm obs}$	$\Delta U^{\rm dim/lat}_{\rm exp}$	$\Delta U^{\rm dim/lat}_{\rm min}$
Formic acid crystal	81 K	N75	10·241	3·544	5·356	2·625			
	223 K	HPF	10·23	3·64	5·34	2·58			
	0 K	MS					−14·6		
	calc.	MCGS	10·96	3·47	5·14	2·59	−14·4		−13·4
	calc.	M	11·07	3·17	4·72	2·57	−23·6	−22·3	−25·8
	calc.	This work	10·288	3·563	5·368	2·669	−14·8	−12·8	−13·2
Acetic acid crystal	83 K	N70	13·214	3·924	5·766	2·625			
	268 K	N70	13·310	4·090	5·769	2·626			
	calc.	MCGS	13·39	3·91	5·70	2·66	−10·0		−14·3
	calc.	M	13·22	3·92	5·74	2·657	−18·5	−19·4	−19·4
	calc.	This work	13·29	3·73	5·50	2·647	−16·3	−16·0	−18·2
α-Oxalic acid	293 K	DS	6·548	7·844	6·086	2·702			
	calc.	MCGS	6·31	7·06	6·91	2·80	−23·5		−25·9
	calc.	This work	6·67	7·80	6·27	2·675	−23·4	−23·5	−24·9
Formic acid dimer	exp.	MB					−16·2		
	exp.	ABM				2·701			
	calc.	M				2·677	−15·8	−16·1	
		This work				2·622	−16·0	−15·1	−16·0
Acetic acid dimer	exp.	D				2·683			
	calc.	MB							−18·6
	calc.	M				2·668	−16·1	−16·4	
	calc.	This work				2·630	−15·0	−15·5	−16·0

note in passing that in our work the rigid-molecule degrees of freedom were simultaneously varied with the cell constants; this was not done in the two papers just mentioned.

An objection can be raised against Momany's (1976) interpretation of the potentials in physical terms such as electrostatic, polarization and dispersion energy. In our opinion this decomposition has no significance in his approach since atom–atom potentials are fitted as an entity and not as individual components. The parameters are therefore correlated, and the individual terms can hardly be related to physical properties. This point can be illustrated as follows.

The point-charge model used in the present study is based upon CNDO/2 calculations and in the case of formic acid makes a contribution to the lattice energy that is three to four times smaller than the contribution from point-charge models based upon *ab initio* calculations (Smit *et al.*, 1977, Table V). The introduction of the latter point-charge models would thus substantially affect the remaining energy contributions to the lattice energy, and therefore the other atom–atom potential parameters.

Concluding remarks

The empirical potential parameters derived in the present paper can be applied for carboxylic acids to the calculation of lattice energies with an accuracy of 5 to 10% and to the prediction of equilibrium structures, with an accuracy that depends very much on the steepness of the potential near equilibrium.

The approximations used in this and other work on atom–atom potentials, *viz* optimization of the energy instead of the free energy, rigid-body and quasi-harmonic approximations and atom and pair approximations, may cause (small) systematic errors which are not considered in the scope of this paper. They must be kept in mind when experimental data are compared with calculated quantities using our potentials. Points to be considered in future research also include alternative representations of the electrostatic charges and expressions with a smaller number of parameters than the Lippincott–Schroeder potential for the hydrogen bonds. The methods of structure optimization have to be improved in connection with convergence problems concerning the location of the minimum closest to the experimental structure, and computing time.

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Aspects of Symmetry in Electron Diffraction Patterns and Optical Transforms of Very Small Homo-atomic Aggregates using Computer Simulation

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This study investigates the reasons why it may happen that the first simulation of an electron diffraction pattern is not always centrosymmetrical whereas the second one is bound to be so. The formal link between the two simulations is established. A number of examples are given.

Introduction

Performance in selected-area electron diffraction is improving constantly. Twenty years ago resolution was about 2000 Å on a single grain; but quite recently an improved value of about 22 Å has been achieved by Geiss (1975) thanks to the latest progress in electron microscopes and the use of solid-state detectors.

Geiss's achievement, added to current interest in the problem of the structure of atom aggregates, and linked in particular with the study of nucleation, would seem to confirm the interest in the computer simulation of the diffraction patterns of such aggregates. This is, in fact, the subject of previous articles by the present authors (Larroque, Brieu & Lafourcade, 1976; Brieu, Larroque & Lafourcade, 1977) and here we would like to refer back to some aspects of these calculated patterns and in particular to the symmetries which are elicited.

Simulated electron diffraction pattern

If we assume u and v to be any two atoms of the aggregate, $\mathbf{r}_{uv}$ the interatomic vector of the pair uv and $\mathbf{S}$ the