

values are clearly more reliable it is doubtful if their accuracy is in general as good as is implied by their tabulation to two decimal places without further indication of their reliability, particularly for values close to absorption edges.

Dispersion corrections for other characteristic X-radiations have been calculated by Cromer & Liberman (1970) and these have also been tabulated in *International Tables for X-ray Crystallography* (1974). Although, as stated therein, it is difficult to assess the accuracy of these corrections, values have been given to three decimal places which must certainly imply a quite unrealistic accuracy. No variation with θ is given since it is stated that in general this variation is probably less than the uncertainty in the calculated values. However, reference to previously tabulated values (e.g. *International Tables for X-ray Crystallography*, 1962; Cooper, 1963) and to recent results given by Hazell (1975) shows that in general the values of Af' and Af'' vary by at least 5 to 10% over the possible range of $\sin \theta/\lambda$ and in many cases by several times this factor. Since X-ray atomic scattering factors decrease so rapidly with $\sin \theta/\lambda$ this change in the dispersion corrections may become quite important.

The tabulation of dispersion corrections to two or three

decimal places, without indication of either their reliability or their variation with $\sin \theta/\lambda$, is therefore misleading for two reasons. It implies that the tabulated values have an unrealistic accuracy and that their dependence on $\sin \theta/\lambda$ is negligible. However, it is suggested that, although the values may be unreliable, their variation with $\sin \theta/\lambda$ is nevertheless a systematic effect which is in many cases sufficiently significant to merit being taken into account.

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Could acetic acid crystallize as dimers? By J. L. DERISSEN and P. H. SMIT, *Department of Chemistry, Structural Chemistry Group, State University of Utrecht, Padualaan 8, Utrecht, The Netherlands*

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It is shown that hypothetical acetic acid crystal structures can be constructed which are built from dimers and which have a lattice energy equivalent to that of the experimental chain structure. The lattice energy was calculated by the atom–atom potential method with a modified Lippincott–Schroeder potential for the hydrogen bonds.

As far as is known, monocarboxylic acids in the gaseous state occur as monomers or as hydrogen-bonded cyclic dimers, the degree of association depending on the temperature and vapour pressure. These dimers have also been observed for most monocarboxylic acids in the crystalline state. But there are a few exceptions: formic and acetic acid form hydrogen-bonded chains (Nahringbauer, 1970), and in one of its modifications chloroacetic acid is found to be tetrameric (Kanters & Roelofs, 1976). These exceptions require an explanation, and we wondered whether a molecular-packing analysis might shed some light on this problem.

In principle therefore, we have to study the free energy as a function of the crystal structure. The structure corresponding to the minimal free energy at a given temperature is the stable one. But, as Kitaigorodsky (1970) argued, one may confine oneself to the calculation of minima in the lattice energy. In that case all the structures belonging to the lowest minima with comparable depths have to be considered. The stable structure will be governed by the delicate balance of lattice-energy and entropy terms yielding the minimal free energy.

But even such a lattice-energy analysis may be a hopeless task, as one has to look at all possible space groups and cell dimensions for each structure proposed.

Yet, acetic acid seemed to be suited for tractable calculations. Its crystal structure has been accurately determined (Nahringbauer, 1970), and an expected space group and a set of cell parameters for a hypothetical crystal of dimers could be derived by assuming a structural analogy with fluoro-

acetic acid (Kanters & Kroon, 1972) and with propionic acid (Strieter, Templeton, Scheurman & Sass, 1962), which have the usual dimer structures (Table 1). The molecular structure of the centrosymmetric crystalline acetic acid dimer was assumed from analogies between the crystal structures of β -oxalic acid (Derissen & Smit, 1974) and acetic acid, and is given in Table 2.

We then performed a lattice-energy analysis for hypothetical acetic acid dimer crystal structures with two centrosymmetric dimers per cell in $P2_1/c$ and with the cell dimensions of Table 1. For this purpose 2275 independent structures were generated by rotation of the dimer in steps of 15° around three perpendicular axes through the centre of

Table 1. *Space group and cell constants of acetic acid dimer crystal from analogy with fluoroacetic acid and with propionic acid*

	Propionic acid	Fluoro-acetic acid	Acetic acid dimer	Acetic acid chains
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Z	4	4	4	4
d (g cm^{-3})	1.22	1.60	1.27	1.266
a (Å)	4.04	4.30	4.1	13.32
b (Å)	9.06	7.55	7.7	4.08
c (Å)	11.00	9.98	10.0	5.77
β ($^\circ$)	91	85.2	90	

Table 2. Structural data for the cyclic dimer of point group C_{2h} used in the calculations

The methyl group was placed in the staggered position with respect to the hydroxyl H atom. The centre of symmetry was located 1.92 Å from C on the x axis along the C-C bonds.

C-H	1.09 Å	C-C-H	109.47°
C-C	1.50	H-C-H	109.47
C=O	1.22	C-C=O	124
C-O	1.32	C-C-O	113
O-H	1.01	C-O-H	110
O...O	2.65		

symmetry. The lattice energy U was calculated for each structure by the atom-atom potential method (Kitaigorodsky, 1970), the convergence acceleration technique (Williams, 1971) and the programme *WMIN* (Busing, 1970). We used the following expression for U :

$$U = \frac{1}{2} \sum_{ij} \sum' V_{ij}^{xy} + V_{HB}$$

Here V_{ij}^{xy} is the energy contribution of the atoms i and j , of the chemical elements x and y , calculated as

$$V_{ij}^{xy} = B^{xy} \exp[-C^{xy}r_{ij}] - A^{xy}r_{ij}^{-6} + q_i q_j r_{ij}^{-1}$$

The prime in the summation indicates that the $H \cdots O$ and $O \cdots O$ interactions involved in the hydrogen bond were excluded. They were replaced by a linear Lippincott-Schroeder hydrogen-bond potential:

$$V_{HB} = D \left\{ 1 - \exp \left[\frac{-n(r_{OH} - r_{OH}^0)^2}{2r_{OH}} \right] - \frac{1}{g} \exp \left[\frac{-ng(r_{H \cdots O} - r_{H \cdots O}^0)^2}{2r_{H \cdots O}} \right] \right\} + B \exp[-Cr_{O \cdots O}] - Ar_{O \cdots O}^{-m} + V_{def}$$

The values of the coefficients used in these expressions are listed in Table 3. They were taken from Williams (1974), Kitaigorodsky, Mirskaya & Nauchitel (1970), Lippincott & Schroeder (1955) (slightly modified) and from CNDO/2 Mulliken populations (Dobosh, 1973). [These are good starting values for an improved set of parameters which at the moment we are deriving for carboxylic acids. For comparison: Momany, Carruthers, McGuire & Scheraga (1974) calculated $-59.8 \text{ kJ mol}^{-1}$ for the lattice energy of acetic acid, the same as our result. The potential correctly describes the energy of both linear and cyclic dimer hydrogen bonds.]

Table 3. Coefficients used in the energy expressions for carboxylic acids

For mixed interactions the relations $A^{xy} = (A^{xx}A^{yy})^{1/2}$, $B^{xy} = (B^{xx}B^{yy})^{1/2}$ and $C^{xy} = (C^{xx} + C^{yy})/2$ were used.

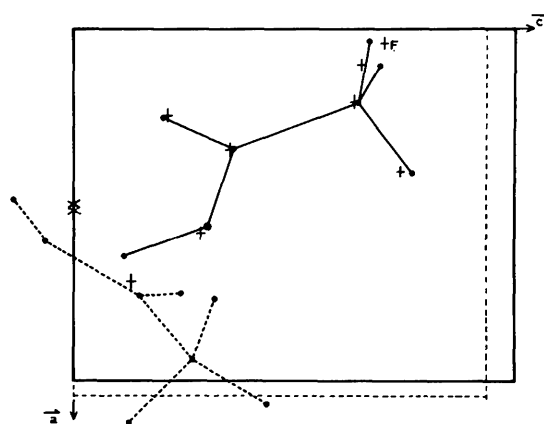
V_{def} is the energy of deformation for the process dimer \rightarrow monomer, calculated by the molecular-mechanics method. All coefficients are in units of kcal mol^{-1} and Å.

$A_{O \cdots O}$	259.4	$B_{O \cdots O}$	77 700	$C_{O \cdots O}$	4.18		
$A_{C \cdots C}$	449.0	$B_{C \cdots C}$	71 400	$C_{C \cdots C}$	3.60		
$A_{H \cdots H}$	40.1	$B_{H \cdots H}$	2 870	$C_{H \cdots H}$	3.74		
D	118.0	B	4 300 000	Charges from CNDO/2 (in electrons)			
n	9.18	C	4.815	O_H	-0.264	H_O	+0.159
r_{OH}^0	0.97	A	18.2	$O=$	-0.329	H_1	+0.035
$r_{H \cdots O}^0$	0.97	m	1	C	+0.412	H_2	+0.045
g	1.45	V_{def}	1.0	C_x	-0.100	H_3	+0.042

We found two minima with $U < -55 \text{ kJ mol}^{-1}$ in the lattice energy: after least-squares refinement of the rotation angles and the cell constants structure *A* yielded -58.9 and structure *B* $-58.6 \text{ kJ mol}^{-1}$, while for the experimental chain crystal structure the lattice energy was calculated as $-59.7 \text{ kJ mol}^{-1}$. The structures *A* and *B* are shown in Fig. 1 and Table 4. It is seen that *A* closely resembles the structure of fluoroacetic acid, while *B* is quite different.

Table 4. Cell constants and atomic fractional coordinates for the acetic acid dimer crystal structures *A* and *B*

	Dimer structure <i>A</i>			Dimer structure <i>B</i>		
a	4.07 (5) Å			4.23 (2) Å		
b	7.73 (5)			7.97 (4)		
c	10.03 (9)			9.44 (6)		
β	87.2 (1.3)°			88.6 (3)°		
	x	y	z	x	y	z
-O	0.560	-0.129	0.153	0.575	-0.226	-0.035
=O	0.246	0.096	0.101	0.719	-0.043	-0.131
C	0.337	-0.009	0.183	0.725	-0.184	0.081
C_x	0.209	-0.016	0.326	0.900	-0.328	0.145
H_0	0.638	-0.119	0.056	0.461	-0.125	-0.073
H_1	0.412	0.003	0.391	1.076	-0.375	0.068
H_2	0.096	-0.141	0.346	0.734	-0.428	0.173
H_3	0.027	0.086	0.344	1.018	-0.286	0.240

Fig. 1. An ac projection of the acetic acid dimer crystal structures *A* (drawn) and *B* (dashed) and of fluoroacetic acid (+).

We may infer from our calculations that the hypothetical dimer crystal structures *A* and *B* and the experimental chain structure of acetic acid are equivalent with respect to their lattice energies. In view of the accuracy of the method, the differences calculated for the lattice energies are insignificant. We compared these results with the SCF perturbation method of Crowe & Santry (1973) which yielded -49.3 , -48.8 and -48.4 kJ mol⁻¹ for the dimer structures *A* and *B* and the chain structure respectively, thereby also attributing practically equal lattice energies to the three crystal structures. We may conclude that as long as the entropy is not taken into account, nothing can be said of the actual appearance of an acetic acid dimer crystal structure, but we have shown that structures with a packing energy as large as that of the experimental structure can indeed be constructed theoretically.

Clearly it would be interesting to determine the crystal structure of the high-pressure modification of acetic acid, which was shown to exist by Bridgman (1916).

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Commission on Crystallographic Apparatus and Commission on Charge, Spin and Momentum Densities

A Critique of Zachariasen's Theory of Extinction*

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A description and assessment of the theory and application of Zachariasen's theory of extinction [Zachariasen (1973). *Acta Cryst.* **23**, 558–564] is given.

Introduction

Extinction was first described by Darwin (1914) and can be described in terms of his mosaic block model. If the blocks are large and if a significant amount of energy is removed from the main beam by the planes close to the surface of each block, the remaining volume will receive less incident intensity, giving a diffracted intensity less than the kinematic value. This is primary extinction and is concerned with coherent scattering.

If the main beam intersects a significant number of blocks sufficiently well aligned to diffract a parallel beam of X-rays simultaneously, each block will take some energy out of

the main beam, reducing the incident beam and, therefore, the scattered intensity. This is secondary extinction and is concerned with incoherent scattering.

The kinematic theory depends on there being the same incident intensity at all points in the crystal and, therefore, when extinction is present, the relationship between the integrated intensities and the structure factor is unknown and the data cannot be processed. In a paper entitled *A General Theory of X-ray Diffraction in Crystals*, Zachariasen (1967) attempted to relate measured intensities to the true kinematic structure factor when extinction was present. This theory greatly renewed interest in extinction and, for a theory which has had such widespread use, an assessment of the approximations used in its development and of its applications is obviously important.

Description and assessment of the theory

The theory is based on two differential equations pertaining to diffraction within a small, perfect crystal.

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