

Incorporation of Inter- and Intramolecular Forces in the Calculation of Crystal Packing and Lattice Vibrations

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A general method for the simultaneous calculation of the effect of inter- and intramolecular forces on crystal packing and lattice dynamics is described. The crystal energy is analytically represented as a function of the $3n$ Cartesian coordinates of the n atoms in the asymmetric unit and the 6 unit-cell parameters. The equilibrium geometry and the lattice vibrations are consistently derived from the same crystal potential. The applicability of the method for both rigid and flexible molecules is demonstrated by calculations of benzene, biphenyl and β -ionylideneacetic acid. The computer programs developed in this work are available.

Introduction

The calculation of lattice energies using semi-empirical potential functions has recently become a powerful tool for the determination of crystal packing. Several methods of calculation have been proposed (Williams, 1972; Coiro, Giglio & Quagliata, 1972), and several crystal structures have been solved with the aid of such calculations (Ahmed & Kitaigorodsky, 1972; Coiro, Giglio, Lucano & Puliti, 1973). A limitation of the above-mentioned approaches is that the energy is considered to be dependent only on a limited number of degrees of freedom such as rotations and translations of the asymmetric unit or rotations of parts of the molecule around certain bonds. Such a set of coordinates is too restrictive for the treatment of non-rigid molecules and is not adequate for the study of the coupling of inter- and intramolecular effects (*e.g.* the complete treatment of the lattice dynamics). This limitation was partially overcome by the treatment of Warshel & Lifson (1970), in which the energy was given as a function of the Cartesian coordinate of all the atoms in the unit cell and of the unit-cell parameters. However, this method did not take advantage of the crystal symmetry and was therefore computationally restricted to lattices with one medium-sized molecule per unit cell. In the present paper we develop an extension of the Warshel & Lifson method which removes the above-mentioned serious limitation. This extension makes it possible to treat crystals with several symmetry-related molecules in the unit cell. Calculations can be carried out in the complete $(3n+6)$ -dimensional space, composed of the $3n$ Cartesian coordinates of the n atoms in the asymmetric unit and the 6 unit-cell parameters, or in the restricted subspace of rotations, translations and subrotations around single bonds. The Cartesian treatment permits

consistent calculations of crystals of flexible molecules, where it is quite possible that small changes of bond angles from their 'standard values' are more efficient in the relaxation of steric repulsion than rotation or torsions. Furthermore, the Cartesian approach enables one to treat the lattice dynamics in a straightforward manner. Thus it is quite easy to calculate simultaneously the complete set of inter- and intramolecular normal modes and to evaluate the atomic thermal ellipsoid. The proposed scheme allows for the study of the effects of intermolecular forces on molecular conformation (Warshel, Huler, Rabinovich & Shakked, 1974) and on the intramolecular normal modes (see below).

In the next section of this paper we describe the method in detail. In the last section applications to rigid and flexible molecules are presented.

Method of calculation

Energy minimization

The energy per molecule, V , is expressed as the sum of the intermolecular interactions (which are represented by an atom-atom potential) and the intramolecular energy. That is

$$V = \frac{1}{2} \sum_{i', s'} \sum_{i, l} V_{\text{inter}}(r_{s' i', i l}^l) + V_{\text{intra}}$$

where

$$r_{s' i', i l}^l = |\mathbf{r}(i') + \mathbf{R}^l - \mathbf{r}(i)| = |\mathbf{r}(i') - \mathbf{r}(i)|.$$

Here \mathbf{R}^l is the translation vector which relates the l unit cell to a central unit cell and can be expressed as $\mathbf{R}_l = \mathbf{L}\mathbf{T}_l$ where

$$\mathbf{L} = \begin{bmatrix} L_{11} & L_{12} & L_{31} \\ 0 & L_{22} & L_{32} \\ 0 & 0 & L_{33} \end{bmatrix} \quad \mathbf{T}^l = \begin{bmatrix} l_1 \\ l_2 \\ l_3 \end{bmatrix}.$$

The L_{ij} are related to the unit-cell parameters $a, b, c, \alpha, \beta, \gamma$, and the l_i are integers. \mathbf{r}_i^t is the position vector (in the Cartesian coordinate space) of the atom t of the molecule s in the central unit cell. \mathbf{r}_i^t can be expressed as a function of the coordinates of the atom t in the reference molecule ($s=1$) by

$$\mathbf{r}_i^t = \mathbf{L}\theta^s\mathbf{L}^{-1}\mathbf{r}_i^1 + \mathbf{L}\mathbf{U}^s = \sigma^s\mathbf{r}_i^1 + \mathbf{L}\mathbf{U}^s.$$

The 3×3 matrix θ^s and the three-dimensional vector \mathbf{U}^s are respectively the rotational and translational part of the symmetry operation by which the molecule s is generated from the molecule 1.

In its general form the crystal potential V is a function of the $3n$ coordinates \mathbf{r}_i^t and the 6 components of \mathbf{L} . These $3n+6$ elements define a vector \mathbf{q} . The equilibrium geometry \mathbf{q}_{eq} is evaluated by the minimization of V with respect to the components of \mathbf{q} . Since \mathbf{q} has in general many components, it is imperative to utilize minimization techniques which employ the first and second derivatives of V . For every intramolecular or intermolecular interaction the first and second derivatives with respect to the corresponding components of \mathbf{q} are computed analytically. In the case of intramolecular interactions (which of course do not depend on the unit-cell parameters) the computation of the derivatives is similar to that of Warshel & Lifson (1970). For an intermolecular interaction $V' = V(r_{st}^t, r_t)$ which is a function of the distance between the atom at \mathbf{r}_i^t and the atom at $\mathbf{r}_j^{t'}$ ($\mathbf{r}_j^{t'} = \sigma^s\mathbf{r}_j^1 + \mathbf{L}[\mathbf{U}^s + \mathbf{T}^j]$) the first derivatives with respect to the coordinates of the corresponding atoms in the asymmetric unit are given by

$$\frac{\partial V'}{\partial r_i^t} = - \sum_k \sigma_{ki}^s \frac{\partial V'}{\partial r_k^t}$$

and the second derivatives, by

$$\frac{\partial^2 V'}{\partial r_i^t \partial r_j^{t'}} = \sum_{k,m} \sigma_{ki}^s \sigma_{mj}^{s'} \frac{\partial^2 V'}{\partial r_k^t \partial r_m^{t'}}.$$

The same intermolecular interaction depends on the unit-cell parameters, and the corresponding derivatives are

$$\frac{\partial V'}{\partial L_{ij}} = -(U_j^s + T_j^t) \frac{\partial V'}{\partial r_i^t}$$

and

$$\frac{\partial^2 V'}{\partial L_{ij} \partial L_{km}} = (U_j^s + T_j^t) (U_m^s + T_m^t) \frac{\partial^2 V'}{\partial r_i^t \partial r_k^t}.$$

Mixed second derivatives are expressed as

$$\frac{\partial^2 V'}{\partial r_k^t \partial L_{ij}} = (U_j^s + T_j^t) \sum_m \sigma_{mk}^s \frac{\partial^2 V'}{\partial r_i^t \partial r_m^t}.$$

The above analytical first and second derivatives are used for the minimization of the energy in the $3n+6$ multi-dimensional space of the vector \mathbf{q} . At the be-

ginning of the minimization procedure we employ the steepest-descent method, in which the steps toward the minimum are determined iteratively by

$$\Delta \mathbf{q} = -K \nabla_{\mathbf{q}} V$$

where K is a scaling factor. Close to the minimum first derivative methods are not convergent. Therefore at that point we use the modified Newton-Raphson procedure in which the quadratic estimate of the step toward the minimum is given by

$$\Delta \mathbf{q} = -\mathbf{F}^+ \nabla_{\mathbf{q}} V$$

where \mathbf{F}^+ is the generalized inverse of the second-derivatives matrix.

When the intramolecular force field is not known or the molecule is sufficiently rigid, a standard geometry can be assumed and the energy can be minimized with respect to the three translations and the three rotations of the molecule. The derivatives with respect to translations and rotations are obtained by a simple transformation of the previously computed derivatives in the \mathbf{q} space. For a rigid molecule, \mathbf{r}_i^t can be expressed as

$$\mathbf{r}_i^t = \mathbf{R}(\varphi_1, \varphi_2, \varphi_3) [\mathbf{r}^0(i) - \mathbf{r}_{CM}^0] + \mathbf{r}_{CM}$$

where $\mathbf{r}^0(i)$ and \mathbf{r}_{CM}^0 are respectively the initial position vectors of the atom t and of the centre of mass of the molecule. $\mathbf{R}(\varphi_1, \varphi_2, \varphi_3)$ is the Euler matrix defined in the standard way (Goldstein, 1959).

The derivatives with respect to the three translational degrees of freedom (T_i) and the three rotational degrees of freedom (φ_i) are given by

$$\frac{\partial V}{\partial T_i} = \sum_t \frac{\partial V}{\partial r_i^t}$$

and

$$\frac{\partial V}{\partial \varphi_i} = \sum_k \sum_t \frac{\partial V}{\partial r_k^t} \frac{\partial r_k^t}{\partial \varphi_i}$$

where the $\partial V / \partial r_i^t$ are the previously obtained derivatives and $\partial r_k^t / \partial \varphi_i$ is obtained by differentiating the Euler matrix in the above expression for \mathbf{r}_i^t .

Second derivatives are expressed as

$$\frac{\partial^2 V}{\partial T_i \partial T_j} = \sum_{t,t'} \frac{\partial^2 V}{\partial r_i^t \partial r_j^{t'}}$$

$$\begin{aligned} \frac{\partial^2 V}{\partial \varphi_i \partial \varphi_j} &= \sum_{t,t'} \sum_{k,m} \frac{\partial^2 V}{\partial r_k^t \partial r_m^{t'}} \frac{\partial r_k^t}{\partial \varphi_i} \frac{\partial r_m^{t'}}{\partial \varphi_j} \\ &+ \sum_t \sum_k \frac{\partial V}{\partial r_k^t} \frac{\partial^2 r_k^t}{\partial \varphi_i \partial \varphi_j} \end{aligned}$$

and

$$\frac{\partial^2 V}{\partial \varphi_i \partial T_j} = \sum_{t,t'} \sum_k \frac{\partial^2 V}{\partial r_j^t \partial r_k^t} \frac{\partial r_k^t}{\partial \varphi_i}.$$

Minimization can also be carried out with respect to torsion of the molecule around given bonds. For a

torsion θ_i around the bond formed by atoms i and $i+1$ the corresponding derivative is given by

$$\frac{\partial V}{\partial \theta_i} = \sum_k \sum_{t=i+2} \frac{\partial V}{\partial r_{k(i)}} \frac{\partial r_{k(i)}}{\partial \theta_i}$$

where

$$\frac{\partial r_{k(i)}}{\partial \theta_i} = [\mathbf{n} \wedge \mathbf{r}'(i)]_k$$

\mathbf{n} is a unit vector in the direction of the bond between atom i and atom $i+1$. $\mathbf{r}'(i)$ is the vector from atom i to atom t . Of course, only the atoms on one side of the $i, i+1$ bond are displaced when the minimization is carried out in the space of the subrotations. Second derivatives with respect to subrotations are calculated numerically from the first derivatives.

Vibrational modes

One of the advantages of the Cartesian treatment is the possibility of calculating the crystal normal modes using the same second derivative matrix employed in the minimization procedure (Warshel & Lifson, 1970). The vibrational frequencies of the crystal are obtained for a given wave vector \mathbf{k} from the secular equation

$$[\mathbf{F}(\mathbf{k}) - 4\pi^2\omega^2\mathbf{M}] = 0$$

where

$$[\mathbf{F}(\mathbf{k})]_{st,s't'} = \sum_{i'} \frac{\partial^2 V}{\partial \mathbf{r}(i') \partial \mathbf{r}'(i')} \exp(i\mathbf{k} \cdot \mathbf{R}_{i'}),$$

\mathbf{M} is the diagonal matrix of the atomic masses and ω is the frequency. Since all the dynamical degrees of freedom are included in the calculation the dimension of the matrix \mathbf{F} is $3n\sigma$ where σ is the number of molecules in the unit cell. However, in our calculations we form the dynamical matrix \mathbf{F} from a set of σ square submatrices of dimension $3n$. Each of these submatrices is calculated by considering the interaction of one arbitrarily chosen molecule in the central unit cell with each one of the σ different types of molecules in the crystal. This method of calculating the \mathbf{F} matrix saves computer time and assures correct symmetry for the dynamical matrix at any point in the Brillouin zone. The dynamical equation can be solved for appropriate values of \mathbf{k} and the resulting eigenvectors can be used to calculate the atomic thermal ellipsoids. A more detailed study of this type of calculation will be given elsewhere.

Examples

Some test cases are presented in this section in order to demonstrate various features of our computational scheme. The calculations were made using the potential surfaces of the quantum-mechanical extension of the 'consistent force field' to conjugated molecules (Warshel & Karplus, 1972). These potential surfaces (referred to as *QCFF/PI*) were obtained from a set of empirical energy functions and semiempirical integrals which were consistently fitted to a large set of equilib-

rium geometries, vibrational frequencies, atomization energies, excitation energies and crystal properties of conjugated and non-conjugated hydrocarbons.

Benzene

The benzene molecule has been treated both as a rigid and a non-rigid molecule. In the framework of the rigid-body approximation the crystal of benzene (*Pbca*) possesses only three molecular degrees of freedom (three rotations). The first and second derivatives with respect to the translational degrees of freedom are zero, owing to crystal symmetry. Several initial positions of the molecule were chosen in order to examine the convergence of the minimization procedure. Two of these initial positions are presented in Table 1 and Fig. 1 together with the final position which is the same in all cases regardless of the initial position. It can be seen from the table that the calculated minimum is close to the experimental results. In the case of a molecule for which diffraction data are known, the calculated minimum should be an adequate starting point for a structure-factor refinement.

Table 1. *Initial and equilibrium Cartesian coordinates in the rigid-body minimization of benzene (Å)*

\mathbf{r}_A and \mathbf{r}_B are two arbitrarily chosen initial set of coordinates which converge to the same final equilibrium position \mathbf{r}_{eq} . Δr_A and Δr_B are the distances between initial and final positions of the corresponding atoms.

		\mathbf{r}_A	Δr_A	\mathbf{r}_B	Δr_B	\mathbf{r}_{eq}	\mathbf{r}_{exp}^*
C(1)	x	-0.115		1.164		-0.257	-0.446
	y	-0.694		0.688		1.362	1.312
	z	-1.195	2.36	0.308	1.61	-0.046	-0.047
C(2)	x	-0.564		-0.056		-0.948	-1.017
	y	-1.276		1.356		0.561	0.421
	z	-0.014	2.07	0.324	1.30	0.858	0.858
C(3)	x	-0.444		-1.229		-0.692	-0.569
	y	-0.578		0.664		-0.812	-0.902
	z	1.195	0.44	0.008	1.80	0.902	0.902
H(1)	x	-0.217		2.091		-0.429	-0.773
	y	-1.217		1.208		2.443	2.356
	z	-2.152	4.20	0.571	2.88	-0.083	-0.083
H(2)	x	-0.999		-0.111		-1.694	-1.816
	y	-2.274		2.415		0.986	0.735
	z	-0.011	3.67	0.568	2.33	1.525	1.526
H(3)	x	-0.797		-2.168		-1.229	-1.013
	y	-1.036		1.189		-1.423	-1.583
	z	2.099	0.75	0.026	3.19	1.607	1.607

* From Bacon, Curry & Wilson (1964).

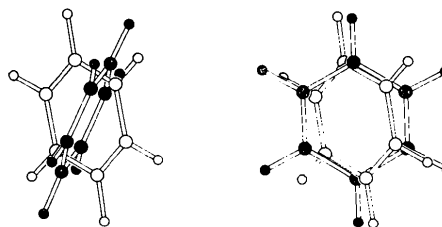


Fig. 1. Initial (shaded atoms) and equilibrium (open atoms) molecular orientations for two different test cases of rigid-body minimization of the benzene crystal (see also Table 1).

Since benzene is a relatively rigid molecule the main interest in performing the calculation without assuming rigidity is to analyse the crystal effect on the intramolecular normal modes (site effect and factor group splitting). In order to derive the set of normal modes we applied the procedure which was described above at $\mathbf{k}=0$. Table 2 presents the calculated and observed splitting between the highest and lowest components of the multiplets of the infrared-active normal modes of benzene, which have been thoroughly studied by Taddei, Bonadeo, Marzocchi & Califano (1973). It can be seen that the order of magnitude of the predicted splitting agrees well with the experimental results.

Table 2. Calculated and observed splitting (in cm^{-1}) between the highest and lowest components of the multiplets of the infrared-active modes of benzene

Normal mode	Δv_{obs}^*	$\Delta v_{\text{ca. c}}$
ν_{11}	26.3	11.9
ν_{12}	1.5	2.4
ν_{13}	—	2.2
ν_{14}	3.5	0.5
ν_{15}	7.8	5.3
ν_{16}	14.5	14.9
ν_{17}	12.8	24.0
ν_{18}	7.0	6.2
ν_{19}	5.4	2.9
ν_{20}	—	4.1

* Taken from Taddei, Bonadeo, Marzocchi & Califano (1973).

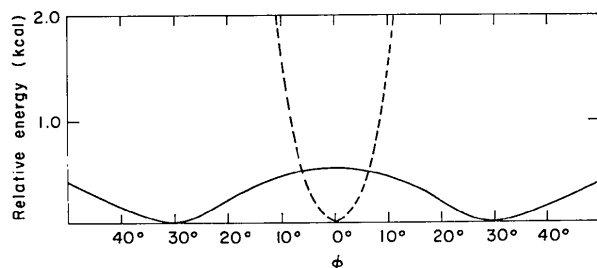


Fig. 2. Adiabatic potential surface for gaseous (—) and crystalline (---) biphenyl

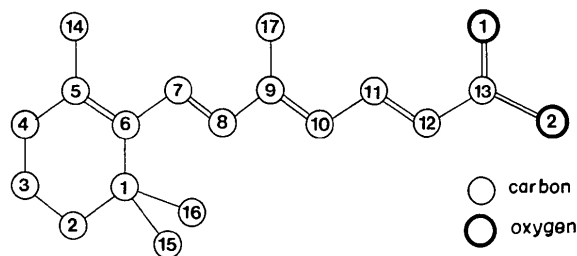


Fig. 3. Numbering of the atoms of *trans*- β -ionylidene- γ -crotonic acid.

Biphenyl

Biphenyl is an example of a flexible molecule which exhibits different conformations in the crystal (Trotter, 1961; Hargreaves & Rizvi, 1962) and in the gas phase (Bastiansen, 1949). In order to study the crystal effect we performed adiabatic minimizations both for the isolated (gas phase) molecule and for the molecule in the crystal. That is, the torsional angle around the bond connecting the two phenyl rings was constrained to a given value while minimizing the energy with respect to all Cartesian degrees of freedom. Our calculated

Table 3. Observed and calculated structure of 9,10-*trans*- β -ionylidene- γ -crotonic acid

Numbering of the atoms and experimental data from Koch (1972). Lengths in Å, angles in deg.

Bonds	Obs.	Calc.
C(1)—C(2)	1.559	1.546
C(2)—C(3)	1.457	1.522
C(3)—C(4)	1.517	1.525
C(4)—C(5)	1.509	1.497
C(5)—C(6)	1.359	1.370
C(6)—C(7)	1.449	1.497
C(7)—C(8)	1.343	1.354
C(8)—C(9)	1.435	1.479
C(9)—C(10)	1.364	1.366
C(10)—C(11)	1.423	1.459
C(11)—C(12)	1.341	1.363
C(12)—C(13)	1.463	1.439
C(13)—O(1)	1.224	1.246
C(13)—O(2)	1.306	1.318
C(1)—C(16)	1.532	1.538
C(1)—C(15)	1.548	1.538
C(5)—C(14)	1.521	1.504
C(9)—C(17)	1.496	1.496

Bond angles

C(1)—C(2)—C(3)	114.0	113.0
C(2)—C(3)—C(4)	110.0	109.5
C(3)—C(4)—C(5)	113.5	111.7
C(4)—C(5)—C(6)	124.5	124.5
C(5)—C(6)—C(1)	120.9	121.9
C(5)—C(6)—C(7)	118.3	117.0
C(6)—C(7)—C(8)	131.9	127.6
C(7)—C(8)—C(9)	125.8	123.7
C(8)—C(9)—C(10)	118.6	119.9
C(9)—C(10)—C(11)	126.6	125.2
C(10)—C(11)—C(12)	124.4	121.2
C(11)—C(12)—C(13)	121.7	124.2
C(12)—C(13)—O(1)	122.6	124.8
C(12)—C(13)—O(2)	115.2	116.9

Torsional angles

C(6)—C(1)—C(2)—C(3)	-46.1	-45.3
C(1)—C(2)—C(3)—C(4)	61.0	61.4
C(2)—C(3)—C(4)—C(5)	-42.6	-46.8
C(3)—C(4)—C(5)—C(6)	12.2	21.3
C(4)—C(5)—C(6)—C(1)	2.5	6.3
C(5)—C(6)—C(7)—C(8)	169.0	158.0

Unit-cell parameters

<i>a</i>	10.391	10.251
<i>b</i>	13.481	13.269
<i>c</i>	7.546	7.357
α	108.12	109.02
β	127.81	128.35
γ	68.01	67.05

adiabatic potential surfaces for the crystal and the gas phase are presented in Fig. 2, where each surface is given relatively to its own minimum. The energy of the crystal (corrected for the zero-point energy of the lattice modes) is 18.7 kcal lower than that of the gas. This is in good agreement with the measured sublimation energy of biphenyl (18.1 kcal; Aihara, 1959). It can be seen from Fig. 2 that while the minimum in the crystal is at the planar conformation, the gas-phase minimum is at $\sim 30^\circ$. We believe that no significance should be attributed to the difference between this value and the value of $\sim 40^\circ$ obtained from electron-diffraction measurement (Bastiansen, 1949), as the gas potential surface is very shallow (see Fig. 2). The correct thermal population has to be taken into account before comparing the location of the minimum with the average value observed in the electron-diffraction experiment. In crystalline biphenyl, on the other hand, the torsional potential is much steeper and the molecular conformation is well determined by the intermolecular forces.

9,10-*trans*- β -Ionylidene- γ -crotonic acid

This molecule belongs to the class of flexible conjugated molecules in which the interplay between steric repulsion and conjugation energy determines the equilibrium geometry. Unlike biphenyl the molecule does not possess intramolecular symmetry elements. The potential surface of this molecule cannot be described by one adiabatic coordinate since there are several coupled torsional coordinates. In this case the conjugation energy must be calculated consistently since one cannot assume the same torsional potential for torsions around single bonds with different bond orders. Our *QCFF/PI* gives the conjugation energy consistently and provides the analytical derivatives of the quantum-mechanical π energy. This permits fast minimization of the crystal energy with respect to the complete set of independent variables. In Table 3 the calculated equilibrium geometry is compared with the corresponding observed structure (see Fig. 3 for the numbering of the atoms). It can be seen that the cal-

culated results reproduce quite well the observed deviations of the C-C-C bond angles from the standard value of 120° . Of course, this type of relaxation cannot be reproduced by methods which consider only torsional degrees of freedom.

The MCA computer program

The method which is described in this paper provides a tool for the evaluation of equilibrium geometries and vibrational normal modes in molecular crystals. A program (named *Molecular Crystals Analysis, MCA*) based on this method was written in Fortran IV. The program is written in such a way that it uses directly the intramolecular potential surfaces which are provided by the *QCFF/PI* program. The program packages which include the *MCA* and the *QCFF/PI* programs are available upon request from the authors.

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