Acta Cryst. (1986). **B42**, 610-613

A Lattice-Dynamical Calculation of Crystallographic Thermal Parameters for *N*,*N*-Dimethyl-2-nitrovinylamine

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(*Received* 1 *October* 1985; *accepted* 11 *June* 1986)

Abstract

Crystallographic thermal parameters for the title compound are found with a lattice-dynamical calculation within the harmonic approximation and the external Born-von Kármán formalism using an atom-atom potential function in the form: $V(r) = -A/r^6 + B\exp(-Cr)$, where the constants A, B and C have been taken from the literature. The agreement with experimental results is acceptable, $R = 0{\cdot}18$.

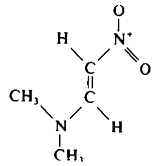
Introduction

In recent years atom-atom potential functions have become a very well established basis for predicting equilibrium conformations, packing energies and conformational properties in molecular crystals. Lattice-dynamical properties have been investigated by this method as well, and the calculation of crystallographic vibrational parameters has proved to be fruitful, providing a source of information for these parameters independent of crystal structure analysis.

Calculations on hydrocarbons have been extensive and successful (Filippini, Gramaccioli, Simonetta & Suffritti, 1973) because existing potential parameters for carbon and hydrogen atoms are known to be adequate and have been thoroughly tested. Less attention has been devoted to other chemical elements, and most of the available parameter sets have been fitted to reproduce static properties, which are less sensitive to the chosen potential than dynamical ones. Therefore a correct description of the lattice dynamics and vibrational parameters is not guaranteed.

In an effort to study the suitability of these potential functions for the calculation of crystallographic thermal parameters for compounds with elements different from C and H we undertook, as a first step, the study of phenothiazine (Criado, Conde & Márquez, 1984) which was successful, though with carbon and hydrogen atoms present in a very large molecular proportion.

The next step is the treatment of a compound with a large proportion of non-C and H atoms, where the influence of their potential parameters is expected to be more prominent. For this purpose, we have selected *N*,*N*-dimethyl-2-nitrovinylamine ($C_4H_8N_2O_2$)



whose crystal structure, monoclinic $P2_1/n$, $Z = 4$, has been solved (final $R = 0{\cdot}070$ over 1202 independent reflections) in our department (Diánez, López-Castro & Márquez, 1985), because its molecular motion fits rigid-body behaviour very well and because there are no hydrogen bonds governing the crystal packing.

Method of calculation

Lattice-dynamical vibrational modes may be obtained in a straightforward way, within the harmonic approximation, for rigid-body molecular movements adopting the external Born-von Kármán formalism, where each molecule is considered to have six degrees of freedom (Born & Huang, 1954).

From these modes, the rigid-body crystallographic tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) can be obtained as a sum over all the allowed modes $\mathbf{q}_j$ inside the Brillouin zone (Willis & Pryor, 1975). Further details of the method can be found in an earlier paper (Criado, Conde & Márquez, 1984).

Potential-energy parameters

The crystal potential energy is calculated as a sum of pairwise contributions between atoms belonging to different molecules. Each contribution is in a Buckingham form: $V(r) = -A/r^6 + B\exp(-Cr)$, where A, B and C are empirical constants depending on the atomic pair involved. Mixed interactions between different atomic chemical kinds are obtained from pure contributions using the usual combination rules for parameters in the following way: geometric law for A, arithmetic law for C and B adjusted to obtain the arithmetic mean for the position of minimum energy. Williams (1967) parameters have

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[*] Part of a Doctorial thesis.

0108-7681/86/060610-04$01.50

Table 1. *Potential parameters*

$V(r) = -A/r^6 + B\exp(-Cr)$.

	A (kJ mol^{-1} Å^6)	B (kJ mol^{-1})	C (Å^{-1})	r_0 (Å)*
C-C	2377·65	350 075·18	3·60	3·88
C-H	521·16	36 694·48	3·67	3·30
H-H	114·28	11 109·64	3·74	3·37
N-N	1084·17	175 812·00	3·78	3·59
C-N	1605·33	248 981·19	3·69	3·73
H-N	352·04	2 760·10	3·76	3·19
O-O	1085·84	325 252·20	4·18	3·25
O-C	1606·59	353 377·93	3·89	3·56
O-H	352·46	36 419·45	3·96	3·02
O-N	1085·01	243 759·99	3·98	3·42

* r_0 is the minimum-energy distance.

been adopted for C and H atoms and Mirskaya & Nauchitel (1971, 1972) parameters for N, the same as used on phenothiazine. For O, Kitaigorodskii (1969) parameters have been selected, and all are shown in Table 1.

Results

The C-H experimental bond lengths were normalized to a value of 1·09 Å, yet maintaining experimental bond angles.

A previous Newton-Raphson energy minimization process was necessary in order to achieve the equilibrium configuration, which agrees quite well with the experimental one, a translation of the centre of mass of 0·05 Å and a rotation of 2·8°, the former below the usual threshold values (Hsu & Williams, 1980), and the latter slightly above, confirming the suitability of the chosen parameters.

A cut-off distance was used as usual and a value of 6 Å was enough to ensure stability in conformational and dynamical results, with a calculated packing energy of 44·9 kJ mol^{-1}. An Ewald-Bertaut-Williams convergence method (Williams, 1971) for minimization of the packing energy, with a cut-off distance of 6 Å in direct space, 0·6 Å^{-1} in reciprocal space and a convergence constant of 0·25, gave similar shifts for the equilibrium configuration and a packing energy value of 56·3 kJ mol^{-1}; therefore, a cut-off distance of 6 Å in direct space represents 80% of the whole packing energy for this parameter set. From this starting point we calculated the optical frequencies at $\mathbf{q} = 0$ and the full dispersion curves (Fig. 1). Calculated values for optical frequencies ν are: A_g, 2·96, 2·22, 1·65, 1·58, 1·08, 0·74 THz; A_u, 2·75, 2·43, 2·05, 1·14, 0·97 THz; B_g, 3·15, 2·51, 1·72, 1·45, 1·03, 0·86 THz; and B_u, 3·12, 2·41, 1·96, 1·10 THz.

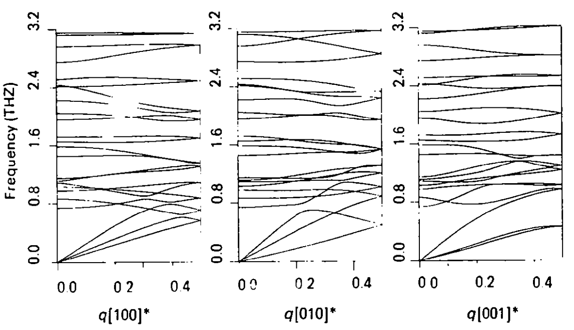

Fig. 1. Calculated dispersion curves. q is given in units of 2π of the reciprocal unit vectors.

Table 2. *Rigid-body movement tensors expressed in the principal inertia axes of the molecule*

Lattice dynamics — Schomaker-Trueblood fit

$$\mathbf{T} = \begin{pmatrix} 388 & 14 & -78 \\ 14 & 470 & 94 \\ -78 & 94 & 767 \end{pmatrix} \qquad \begin{pmatrix} 440 & -13 & -21 \\ -13 & 560 & 31 \\ -21 & 31 & 566 \end{pmatrix} \times 10^{-4}\ \text{Å}^2$$

$$\mathbf{L} = \begin{pmatrix} 52 & -2 & 8 \\ -2 & 46 & -5 \\ 8 & -5 & 141 \end{pmatrix} \qquad \begin{pmatrix} 37 & -10 & -3 \\ -10 & 27 & -15 \\ -3 & -15 & 224 \end{pmatrix} \times 10^{-4}\ \text{rad}^2$$

$$\mathbf{S} = \begin{pmatrix} 5 & -9 & -33 \\ 34 & -2 & -14 \\ -7 & 11 & -10 \end{pmatrix} \qquad \begin{pmatrix} (12) & -24 & -12 \\ 27 & (-8) & -19 \\ 1 & 2 & (-4) \end{pmatrix} \times 10^{-4}\ \text{rad Å}$$

Rigid-body vibration tensors were calculated at 300 K, also from this configuration, performing a sampling over the allowed modes in a uniform mesh inside the Brillouin zone with 13 divisions along each reciprocal-lattice basic vector. The contribution of the modes with $\mathbf{q} = 0$, where a divergence appears, was calculated following the method of Kroon & Vos (1978). Computing time was saved by using the information for two molecules related by the screw symmetry axis and reducing the sampling region to the Brillouin zone asymmetric unit ($\frac{1}{4}$BZ). Information from the remaining two molecules is redundant with time-reversal symmetry and therefore was not used.

Table 2 shows the resulting **T**, **L** and **S** tensors, together with those obtained from a least-squares Schomaker-Trueblood fit of the individual experimental thermal parameters.

From the lattice-dynamical **T**, **L** and **S** tensors we have calculated the corresponding individual thermal parameters U_{ij} (Willis & Pryor, 1975), which can be directly compared with the experimental ones. Table 3 shows both, together with those obtained from the Schomaker-Trueblood-fitted **T**, **L** and **S**. An agreement factor has been considered in the form:

$$R = \sum_i \sum_{j\geq i} |U_{ij}\,(\text{expt}) - U_{ij}\,(\text{cal})| / \sum_i \sum_{j\geq i} |U_{ij}\,(\text{expt})|$$

yielding a value of 0·18 for the lattice-dynamical U_{ij} and 0·07 for Schomaker-Trueblood-fitted ones. This last value indicates an excellent adjustment of the molecular motion to a rigid-body behaviour considering the relatively large standard deviations for experimental U_{ij} and the systematic errors introduced by the thermal diffuse scattering contribution. The lattice-dynamical R value is similar to some encountered in hydrocarbons (Filippini, Gramaccioli, Simonetta

Table 3. *Thermal crystallographic parameters* ($\text{Å}^2\times10^4$)

$$T(\mathbf{H})=\exp\left[-2\pi^2\sum_i\sum_i U_{ij}\mathbf{a}_i^*.\mathbf{a}_j^*H_iH_j\right],\ \mathbf{H}=(h,k,l).$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1) (*a*)	674 (13)	652 (13)	548 (11)	173 (11)	190 (10)	90 (10)
(*b*)	680	650	730	130	100	30
(*c*)	677	695	591	91	21	77
N(2)	590 (11)	519 (10)	487 (10)	27 (9)	136 (8)	9 (8)
	510	560	660	40	30	−70
	557	483	547	69	9	−15
C(1)	592 (13)	566 (13)	526 (12)	53 (11)	125 (10)	17 (10)
	480	480	720	80	50	−50
	591	526	578	34	−8	13
C(2)	560 (12)	493 (12)	527 (12)	93 (10)	133 (10)	−23 (10)
	430	500	650	50	10	−80
	544	492	541	48	−27	−23
C(21)	666 (16)	703 (17)	591 (14)	−34 (14)	89 (12)	−33 (14)
	660	710	680	0	−60	−110
	729	720	552	30	−70	−29
C(22)	717 (18)	748 (19)	685 (17)	−94 (15)	185 (14)	93 (14)
	740	880	810	−100	130	40
	734	773	674	−113	16	84
O(11)	735 (12)	1036 (16)	611 (11)	−21 (12)	41 (9)	−6 (11)
	820	940	670	80	−20	0
	823	1021	551	19	−56	50
O(22)	922 (15)	939 (16)	805 (14)	−2 (12)	310 (11)	242 (12)
	940	850	940	110	270	180
	866	943	742	−23	−23	88

(*a*) Experimental thermal parameters and their standard deviations. (*b*) Lattice-dynamical thermal parameters. (*c*) Thermal parameters obtained by rigid-body least-squares adjustment of the experimental ones.

& Suffritti, 1973), but we should like to obtain a lower value similar to that in phenothiazine (0·116).

In order to determine the dependence on the chosen potential parameters we have repeated the above calculations with a second set. Williams parameters for C and H have proved to be the best and have been widely used to obtain crystallographic thermal parameters (Filippini, Gramaccioli, Simonetta & Suffritti, 1973), anharmonic effects (Jindal & Kalus, 1983), thermodynamical properties (Filippini, Gramaccioli, Simonetta & Suffritti, 1975) and in molecular-dynamics simulations (Della Valle & Pawley, 1984); therefore no attempt has been made to change them. We have selected recently obtained parameter sets for nitrogen (Williams & Cox, 1984) and oxygen (Cox, Hsu & Williams, 1981) which have been adjusted over a large number of compounds. The agreement factor R was 0·236 for this set, similar to though worse than the former. It is difficult to make a comparison for two parameter sets from a single compound calculation; it is necessary to test a wide range of them. Therefore, we can just conclude that, as far as this particular compound is concerned, the first parameter set produces a better agreement with experimental results, but it does not mean that it is better in an absolute way.

Discussion

A better agreement could be obtained, of course, with a parameter least-squares adjustment in order to reproduce properties for this particular compound. But it has been repeatedly shown that parameters so obtained are not, in general, transferable to other compounds, and it represents a violation of the universatility hypothesis (Kitaigorodskii, 1973) which is the basis of the atom-atom device method. On the other hand, parameters obtained from a wide range of compounds properly selected have worked surprisingly well in most cases and seem to have better physical foundations than fitted parameters.

The main shortcoming of the atom-atom method resides in the possible existence of other contributions to the packing energy which are not included in the potential function adopted. For this reason, for a particular compound an adjustment to the potential parameters absorbs these other effects, giving artificial values for them which work well only for this compound and are not transferable. Similarly, special peculiarities in the packing arrangement may make these other contributions more prominent, for instance, in our previous work on phenothiazine the adopted parameter set reproduced fairly well the crystal structure and crystallographic thermal parameters of the monoclinic modality, whereas for orthorhombic phenothiazine, space group *Pnma*, where the molecules lie on special mirror positions, the same set produced a small energy maximum in the position of the mirror plane, rendering lattice-dynamical results meaningless (Criado, Conde & Márquez, unpublished).

For these reasons, and taking into account the fact that our compound contains N and O, we have not tried any further adjustment. For hydrocarbons the Coulomb-energy term is small but not negligible (Williams, 1974), but for organic molecules containing N or O atoms the Coulomb-energy contribution is quite important, and it can be as much as 50% (Williams & Cox, 1984). In contrast, the force effect of the Coulomb-energy contribution is relatively smaller than the energy effect because its functional form causes the energy to vary less with distance than other energy types. Therefore, the Coulomb term could improve the results as a small correction.

Changes in our computer programs will be made to allow for the Coulomb-energy contribution and, simultaneously, accurate net-atomic-charge quantum-mechanical calculations will be carried out in order to establish the influence of Coulomb interactions upon calculated lattice-dynamical crystallographic thermal parameters.

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Acta Cryst. (1986). B**42**, 613-621

Hydrogen Bonding and Thermal Vibrations in Crystalline Phosphate Salts of Histidine and Imidazole

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(*Received* 19 *February* 1986; *accepted* 30 *June* 1986)

Abstract

Salts of composition Im.H_3PO_4 and L-His.2H_3PO_4 were prepared and analyzed by X-ray crystallography. The Im salt forms a rather complicated crystal structure with two chemical formula units in the crystal chemical unit and the crystals of the His salt contain unionized molecular H_3PO_4. There are networks of short strong hydrogen bonds in both crystals, and the hydrogen bonding noticeably affects the O-atom thermal vibrations. The hydrogen-bonding geometries indicate that N–H···O–P and P–O–H···O–P bonds are generally the strongest N–H···O and O–H···O bonds that can form in biochemical systems, and the strong hydrogen bonding significantly affects the P–O bond strengths. Crystal data: L-histidinium dihydrogen orthophosphate orthophosoric acid, $C_6H_{10}N_3O_2^+.H_2PO_4^-.H_3PO_4$, $M_r = 351{\cdot}15$, monoclinic, $P2_1$, $a = 9{\cdot}16(1)$, $b = 8{\cdot}90(1)$, $c = 8{\cdot}81(1)$ Å, $\beta = 111{\cdot}38(5)°$, $V = 669(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}75$, $D_x = 1{\cdot}74$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}371$ mm^{-1}, $F(000) = 364$, $T = 293(2)$ K, $R = 0{\cdot}030$ for 2945 data with $I \geq 2{\cdot}5\sigma(I)$; imidazolinium dihydrogen orthophosphate, $(C_3H_5N_2^+.H_2PO_4^-)_2$, $M_r = 332{\cdot}15$, monoclinic, $P2_1/c$, $a = 8{\cdot}53(1)$, $b = 12{\cdot}72(1)$, $c = 15{\cdot}93(1)$ Å, $\beta = 126{\cdot}13(5)°$, $V = 1396(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}59$, $D_x = 1{\cdot}58$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}344$ mm^{-1}, $F(000) = 688$, $T = 293(2)$ K, $R = 0{\cdot}046$ for 3382 data with $I \geq 2{\cdot}5\sigma(I)$.

Introduction

Crystalline salts were prepared by reaction of orthophosphoric acid with the bases L-histidine and imidazole, and the products were studied by X-ray crystallography in order to look at the structure of N–H···O–P hydrogen bonds that could be expected to form in the salt crystals. Such hydrogen bonds are of interest because of their widespread biological occurrence. For example, hydrogen bonds between phosphate groups and histidyl imidazolyl groups are involved in the active-site substrate-binding mechanism of ribonuclease (Richards, Wyckoff, Carlson, Allewell, Lee & Mitsui, 1972), and in the regulation of the oxygen affinity of deoxyhemoglobin by 2,3-diphosphoglycerate (Perutz & Ten Eyck, 1972).

The salt crystals prepared in this study have interesting and surprising crystal structures. The imidazolium phosphate salt, which has 1:1 stoichiometry, Im.H_3PO_4, crystallized with two chemical formula units in the crystal chemical unit, $(ImH^+.H_2PO_4^-)_2$. The histidinium phosphate salt, which has 1:2 stoichiometry, His.2H_3PO_4, was found to be the 1:1 salt co-crystallized with the unionized molecular acid in the crystal chemical unit, $HisH^+.H_2PO_4^-.H_3PO_4$. In both crystal structures the N–H···O and O–H···O hydrogen bonds are very strong, and they form intricate three-dimensional networks. Thermal-vibration analyses indicate that for the phosphate group a rigid-body libration model

0108-7681/86/060613-09$01.50