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Translational and Librational Lattice Frequencies in 6-*N*,*N*-Diacetylaminochrysene and 2,4-Dinitrobenzoic Acid Crystals

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The root-mean-square libration amplitude derived from non-rigid-body thermal motion analysis of 6-*N*,*N*-diacetylaminochrysene and 2,4-dinitrobenzoic acid predicts torsional frequencies in satisfactory agreement with the Raman spectra. Translational and librational lattice frequencies of the whole molecules derived from the *L* and *T* components are generally consistent with the spectroscopic results.

INTRODUCTION

Cruickshank's pioneering work[1] led to the recognition of the importance of atomic vibration parameters in the study of molecular motion in crystals. Schomaker and Trueblood[2] used the anisotropic temperature factors of atoms to derive the thermal rigid-body vibration parameters of molecules in molecular crystals.

To extend the applicability of the rigid-body model, several approaches, considering the restricted motion of internally rigid segments attached to a rigid core, have been proposed. These sub-groups participating in core motion simultaneously produce their own torsional oscillations relative to the core about specified torsional oscillation axes which are usually bonds joining them to the core. A simple model of Dunitz and White[3] incorporates these non-rigid librations.

The first calculations of lattice frequencies derived from X-ray data, were carried out by Cruickshank with the crystals of anthracene[4], naphthalene[5], and benzene[6] as object of examination. After that studies were carried out by Pawley[7] for naphthalene and anthracene. Recently, Brock and Dunitz[8] used rigid-body translational and librational tensors to determine lattice frequencies for naphthalene molecule. Bellows *et al.*[9] calculated translational and librational frequencies for 1,4-dihalonaphthalenes, while Prince *et al.*[10] used hydrogen amplitudes to predict methyl torsional frequency in durene.

For molecules with perceptible torsional motions of rigid atomic groups attached to the core, 6-*N*,*N*-diacetylaminochrysene (DAAC) and 2,4-dinitrobenzoic acid (DNBA) were chosen in order to make comparison between the

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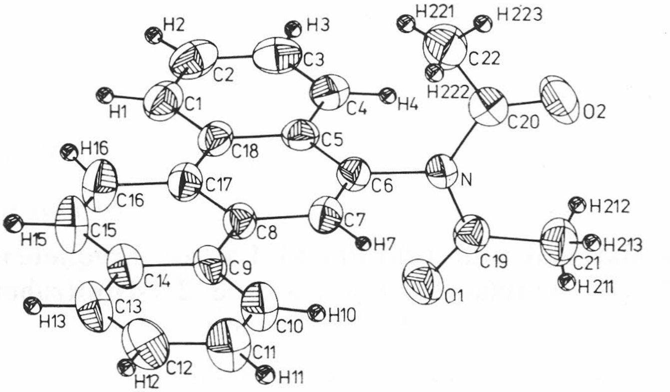

Figure 1. Molecular structure of 6-*N*,*N*-diacetylaminochrysene. The thermal ellipsoids (at 50 per cent probability) were calculated by the ORTEP program (Johnson[17]) from X-ray diffraction data.

translational and librational lattice frequencies derived from the X-ray crystal structure refinement with those obtained from the Raman spectra.

Crystals of DAAC are orthorhombic, of space group *Pbca,* with 8 molecules in the unit cell[11]. As seen in Figure 1, the molecules are comprised of the rigid chrysene nucleus and -*N*,*N*-diacetylamino-group attached almost perpendicularly to that core.

DNBA crystallizes in monoclinic space group $P2_1/c$, with 4 molecules in a cell[12]. The molecules are paired by hydrogen bonding between the carboxy-groups (O—H . . . O 2.656(3) Å), the two halves of the dimer being related by the center of symmetry. The anisotropic thermal ellipsoids of the DNBA molecule are shown in Figure 2.

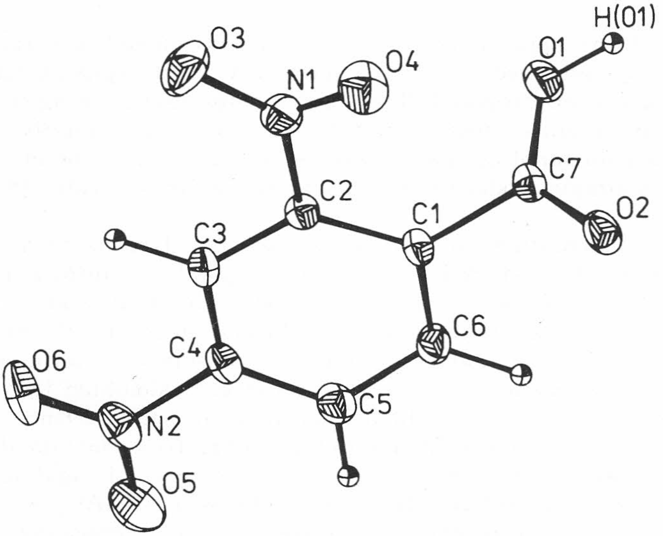

Figure 2. Molecular structure of 2,4-dinitrobenzoic acid. The thermal ellipsoids (at 50 per cent probability) were calculated by the ORTEP program (Johnson[17]) from X-ray diffraction data.

EXPERIMENTAL

Finely ground samples were introduced into the powder sample holder. Raman spectra were taken at room temperature with Cary 82 spectrophotometer by Varian, supplied with an argon ion laser of Spectra Physics, type 164 — 03. The green line 514.5 nm was used for excitation. Light power in samples was 100 mwatt; spectral band slitwidth 1—2 cm^{-1}, scan rate 0.5 cm^{-1} sec^{-1}, and time constant 2 sec for DAAC and 5 sec for DNBA.

Figures 3 and 4 show the Raman spectra of polycrystalline 6-*N*,*N*-diacetylaminochrysene and 2,4-dinitrobenzoic acid, respectively.

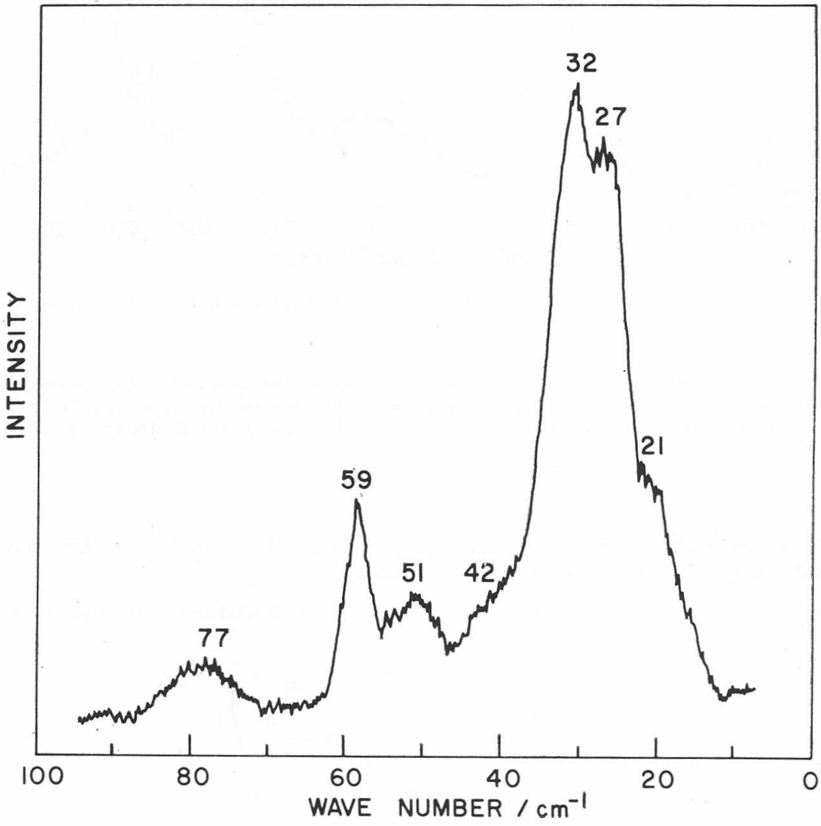

Figure 3. Raman spectrum of polycrystalline 6-*N*,*N*-diacetylaminochrysene from 5 to 100 cm^{-1}.

LATTICE FREQUENCIES

The relation between the mean-square amplitude $\langle u^2(i) \rangle$ and the vibrational frequency ν_i of the *i*-th normal oscillator can be expressed after Cyvin[13]:

$$\langle u^2(i) \rangle = kT/4\pi^2 \nu_i m \qquad (1)$$

where k is Boltzmann's constant, T — the absolute temperature and m — the mass of the molecule. The normal frequencies are given by:

$$\nu_i = kTm/4\pi^2 \check{\Sigma}(i) \qquad (2)$$

where $\check{\Sigma}(i)$ is the mean-square amplitude matrix.

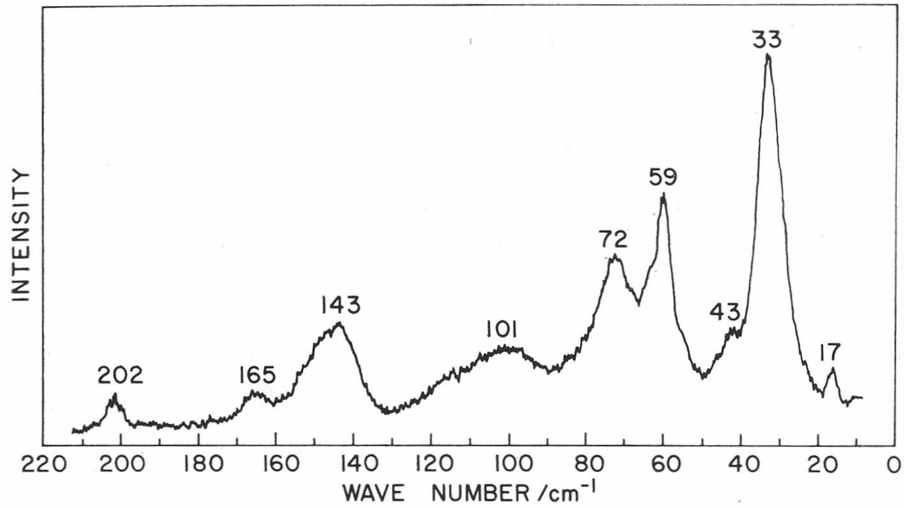

Figure 4. Raman spectrum of polycrystalline 2,4-dinitrobenzoic acid from 5 to 220 cm^{-1}.

As the coordinates, which are actually used to describe the modes of the oscillator, are not usually normal coordinates, the set of eqs. (1) can be expressed in the reference system. This is accomplished by the normal coordinate transformation:

$$\breve{\Sigma}\,(i) = kT\breve{F}^{-1} \tag{3}$$

where $\breve{F}$ is the force constant matrix, of which the elements F_{ij} are referred to as force constants for the set of coupled oscillators.

Since $\breve{\Sigma}\,(i)$ is a symmetric 6×6 matrix, it is partitioned it into four 3×3 matrices:

$$\breve{\Sigma}\,(i) = \left(\begin{array}{c|c} \breve{T}\,(i) & \breve{S}^{T}\,(i) \\ \hline \breve{S}\,(i) & \breve{L}\,(i) \end{array}\right) \tag{4}$$

where:

$$\breve{T}\,(i) = \langle\, \breve{u}\,(i)\, \breve{u}^{\mathrm{T}}\,(i)\,\rangle \tag{5a}$$

$$\breve{L}\,(i) = \langle\, \breve{\Theta}\,(i)\, \breve{\Theta}^{\mathrm{T}}\,(i)\,\rangle \tag{5b}$$

$$\breve{S}\,(i) = \langle\, \breve{u}\,(i)\, \breve{\Theta}^{\mathrm{T}}\,(i)\,\rangle \tag{5c}$$

where $\breve{u}\,(i)$ is an instantaneous translational displacement of the rigid molecule i from its equilibrium position:

$$\breve{u}\,(i) = \begin{pmatrix} u_1\,(i) \\ u_2\,(i) \\ u_3\,(i) \end{pmatrix}, \quad \breve{u}^{\mathrm{T}}\,(i) = [u_1\,(i)\, u_2\,(i)\, u_3\,(i)],$$

and $\breve{\Theta}\,(i)$ is an instantaneous librational displacement from its equilibrium of a rigid molecule i.

The quantum theoretical formulation of (1) is known after Cruickshank[14], as:

$$L^{ii} = \frac{h}{8\pi^2 I_i \nu_i} \coth \frac{h\nu}{2kT} \tag{6}$$

where L^{ii} is the diagonal component of $\tilde{L}$, h-Planck's constant and I_i — moment of inertia of the system of particles about one of the three coordinate axes.

The corresponding quantum formula to eq. 3 was found by making use of the series expansion of (6):

$$\tilde{\Sigma}(i) = kT\,[\tilde{F}^{-1} + \frac{1}{48}\left(\frac{h}{\pi kT}\right)^2 \tilde{A} - \frac{1}{11520}\left(\frac{h}{\pi kT}\right)^4 \tilde{A}\tilde{F}\tilde{A} + \ldots] \tag{7}$$

where $\tilde{A}$ is the matrix of the kinetic energy, Cyvin[13].

Following Cruickshank[14], effective frequencies ν_{M}^{eff} from each translational tensor were calculated using the equations:

$$\frac{1}{3}\,Tr\,(\tilde{T}) = \frac{3h^2\,T}{4\pi^2\,mk\Theta_M^{\,2}}\,[\phi\,(x) + \frac{x}{4}] \tag{8}$$

$$\nu_{M}^{eff} = k\Theta_M/hc \tag{9}$$

where Θ_M is Debye temperature,

$$X = \Theta_M/T \quad \text{and} \quad \phi\,(x) = \frac{1}{x}\int_0^x \frac{\xi d\xi}{e^{\xi} - 1}$$

Then the possible molecular motions of three different groups of atoms in DAAC and four groups in DNBA were analyzed in terms of three rigid-body tensors of the second rank: $\tilde{T}$ describing translational motion, $\tilde{L}$, describing librational motion, and $\tilde{S}$ describing the interaction of translation and libration[2]. The $\tilde{T}$, $\tilde{L}$ and $\tilde{S}$ tensors represent the mean values over the optical lattice spectra of a crystal. With X-ray intensity data, the elements of these tensors may be derived from a least-squares fit of the anisotropic temperature factors, U^{ij}, of individual atoms.

Although from IR and Raman spectra we can only determine the maximum frequencies of the optical branches at the limit of the wave vector $k \to 0$, the mean values over the external lattice spectra are not far from the fundamental modes of the optical branches.

Thus, the frequencies which are calculated from the thermal rigid-body parameters can be compared with the external optical fundamentals, which are determined from Raman spectra.

RESULTS AND DISCUSSION

The results of a rigid-body motion analysis were obtained by the method of Schomaker and Trueblood[1], for the model regarding particular fragments of the molecule as vibrating independently. All analyses of the U^{ij} values were performed according to Trueblood's THMB program[15]. The r.m.s. discrepancy between the observed and calculated U^{ij} serves as a measure of applicability of this analysis and, thus, of the rigidity of a particular grouping.

Analysis of the atomic vibrational tensors in terms of a rigid-body motion yielded the results shown in Tables I and II. The agreement between the

TABLE I

Summary of Rigid-Body Thermal-Motion Analysis for DAAC

translational tensor $\tilde{T}$ $(\text{Å}^2 \times 10^5)$

$$\begin{pmatrix} 3301\ (182) & -125\ (29) & -152\ (11) \\ & 3053\ (171) & -480\ (117) \\ & & 4581\ (127) \end{pmatrix}$$

librational tensor $\tilde{L}$ $(\text{rad}^2 \times 10^5)$

$$\begin{pmatrix} 162\ (22) & -20\ (9) & 23\ (15) \\ & 179\ (13) & -40\ (12) \\ & & 181\ (47) \end{pmatrix}$$

cross tensor $\tilde{S}$ $(\text{Å} \times \text{rad} \times 10^5)$

$$\begin{pmatrix} 92\ (29) & 59\ (41) & -133\ (38) \\ 61\ (32) & -118\ (29) & -39\ (12) \\ -132\ (74) & -40\ (28) & 31\ (16) \end{pmatrix}$$

	Eigenvalues	Eigenvectors		
T_1	4730 $(\text{Å}^2 \times 10^{-5})$	-0.07827	-0.26918	0.95991
T_2	3349	0.93818	-0.34556	-0.02040
T_3	2862	-0.33719	-0.89896	-0.27958
L_1	231 $(\text{rad}^2 \times 10^{-5})$	0.36905	-0.65719	0.65719
L_2	149	0.92941	0.26096	-0.26096
L_3	140	0.24533	0.70711	0.70711

The tensors are referred to a Cartesian coordinate system defined by $X \parallel \mathbf{a}$, $Y \parallel \mathbf{b}$, $Z \parallel \mathbf{c}$; the origin is at the center of mass.

Tensor of Inertia $\tilde{I}$

	Eigenvalues	Eigenvectors		
I_1	1301.3 $(10^{-40}\ \text{g} \cdot \text{cm}^2)$	-0.38588	-0.14178	-0.91159
I_2	2756.1	-0.69872	-0.60030	0.38914
I_3	3576.2	-0.60240	0.78711	0.13258

These eigenvectors are relative to a Cartesian crystal system. The third line is the normal to the best plane. Center of mass referred to the crystal axes: $X = 0.06264$, $Y = 0.22355$, $Z = 0.14892$.

observed and calculated U^{ij} values is about as good as can be expected from experimental uncertainties.

Translational motion is reasonably isotropic in both molecules, while libration is nearly anisotropic in DAAC and quite anisotropic in DNBA, with the only appreciable motion corresponding to a r.m.s. amplitude of 4.6° about an axis L_1 in DNBA. It can be seen that the largest libration in these two compounds is about the axis of the smallest inertia.

DAAC and DNBA have site symmetry 1, so that the cross tensor $\tilde{S}$ does not vanish and the normal modes represent linear combinations of translation and libration modes. Because of this, normal frequencies can be observed both in the Raman and IR spectra.

TABLE II

Summary of Rigid-Body Thermal-Motion Analysis for DNBA

translational tensor $\tilde{T}$
($Å^2 \times 10^5$)

$$\begin{pmatrix} 3502\ (175) & -59\ (44) & 175\ (85) \\ & 2501\ (159) & -362\ (151) \\ & & 3073\ (242) \end{pmatrix}$$

librational tensor $\tilde{L}$
($rad^2 \times 10^5$)

$$\begin{pmatrix} 80\ (51) & 69\ (30) & 121\ (35) \\ & 604\ (70) & -110\ (32) \\ & & 369\ (36) \end{pmatrix}$$

cross tensor $\tilde{S}$
($Å \times rad \times 10^5$)

$$\begin{pmatrix} -17\ (14) & 104\ (69) & 89\ (43) \\ -67\ (29) & 204\ (60) & 64\ (40) \\ 298\ (38) & -53\ (19) & -187\ (49) \end{pmatrix}$$

	Eigenvalues	Eigenvectors		
T_1	3599 ($Å^2 \times 10^{-5}$)	0.88540	-0.18794	0.42515
T_2	3153	0.46438	0.39818	-0.79108
T_3	2325	-0.02061	0.89785	0.43982
L_1	648 ($rad^2 \times 10^{-5}$)	-0.03927	-0.93543	0.35132
L_2	387	-0.40869	-0.30580	-0.85992
L_3	17	0.91183	-0.17735	-0.37028

Tensor of Inertia $\tilde{I}$

	Eigenvalues	Eigenvectors		
I_1	435.2 (10^{-40} g · cm^2)	-0.62322	-0.68722	0.37327
I_2	1207.3	0.59699	-0.72637	-0.34057
I_3	1563.9	0.50518	0.01059	0.86295

The third line is the normal to the best plane. Center of mass referred to the crystal axes: $X = 0.73584$, $Y = 0.21207$, $Z = 0.07557$. The tensors are referred to the orthogonal system (X, Y, Z) related to the monoclinic axes (x, y, z) by having $\mathbf{Z} \parallel \mathbf{z}$ and $\mathbf{Y} \perp \mathbf{zx}$. Then for any column vector $\mathbf{r}$

$$R = \begin{pmatrix} a \sin\beta & 0 & 0 \\ 0 & b & 0 \\ a \cos\beta & 0 & c \end{pmatrix} \cdot \mathbf{r}$$

Translational frequencies have been assigned at 291 K for the three optical lattice modes involving translational displacements of the DAAC and DNBA molecules. The results are given in Table III, along with those from thermal parameters.

The agreement of »X-ray frequencies« and spectroscopic data seems to be satisfactory.

Θ_M is higher for DNBA than for DAAC. This is entirely in accord with expectations because of the presence of hydrogen bonding linking molecules

TABLE III

»X-Ray Translational Frequencies« and Raman Data as well as Characteristic Temperature for DAAC and DNBA

root-mean-square amplitude of translational vibration (Å)	»X-ray translational frequency« (cm^{-1})	Raman frequency (cm^{-1})	Characteristic temperature (K)
	DAAC		59.64
0.209	18.2	21	
0.189	24.8	27	
0.173	30.0	32	
	DNBA		81.33
0.190	20.8	17	
0.178	30.3	33	
0.152	45.9	43	

of DNBA in the crystal lattice; in DAAC, on the other hand, there are only weak Van der Waals interactions between molecules.

Librational frequencies calculated from thermal parameters for DAAC and DNBA are given in Table IV, along with those observed in Raman spectra. It can be seen that the librations around the three molecular axes in DAAC have frequencies in inverse proportion to the moments of inertia. It is consistent with the spectroscopic results of Dumas and Michel[16] for hexamethylbenzene. Similarly, in contrast to DAAC, the frequency of vibration around the OZ axis is significantly higher than that around OY axis, though the component of the moment of inertia around OZ is three times that around OY. This suggests that the force constants for angular oscillations around the OZ axis are significantly lower than those around the OY axis.

Although Table IV indicates quantitative agreement between the diffraction and spectroscopic frequencies, there are some differences between them. The lack of high agreement may be due to the fact that from the IR and Raman spectra we can only determine the maximum frequencies of the optical branches at the limit of the wave vector equal to zero.

The mean-square amplitudes derived for the torsional motion of the substituents from the analysis of non-rigid-body librations in DAAC and DNBA are listed in Table IV along with the moments of inertia (I). They were used to calculate the frequencies of torsional vibrations of —$N(COCH_3)_2$-group in DAAC and carboxy-, ortho-NO_2- and para-NO_2-groups in DNBA from eq. 6. A comparison of the resulting frequencies with the observed Raman values is shown in the table IV. Actually, only the torsional frequencies of the $N(COCH_3)_2$-group in DAAC and *p*-nitro-group in DNBA agree closely with spectroscopic data. The lack of quantitative agreement between the Raman and diffraction frequencies may be due to the neglect of possible anharmonicity in torsional oscillations and the steric interaction between *o*-nitro- and carboxy-group.

TABLE IV

Comparison of Librational and Torsional Frequencies of DAAC and DNBA, Derived from Non-Rigid Body Thermal Motion Analysis with Observed Raman Frequencies; OX, OY and OZ Refer to the Principal Axes of Inertia

Axis of libration	Moment of inertia I (10^{-40} g·cm^2)	Mean-square amplitude of angular vibration (°)	»X-ray torsional frequency« (cm^{-1})	Raman frequency (cm^{-1})
DAAC				
OX	3576.2	2.1	47.7	42
OY	2756.1	2.2	53.1	51
OZ	1301.3	2.8	61.5	77
$N(COCH_3)_2$-tor.	454.3	5.2	55.4	59
DNBA				
OX	1207.3	3.6	49.4	59
OY	435.2	4.6	63.6	72
OZ	1563.9	0.8	211.7	202
carboxy-tor.	68.3	4.9	81.1	101
ortho-NO_2-tor.	61.1	8.2	96.3	143
para-NO_2-tor.	61.3	9.7	154.6	165

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SAŽETAK

Translacijske i libracijske frekvencije rešetke u kristalima 6-*N*,*N*-diacetilaminokrizena i 2,4-dinitrobenzojeve kiseline

Tadeusz Więckowski

Srednje kvadratno odstupanje libracijske amplitude, izvedeno iz analize termičkog gibanja nekrutoga tijela, predviđa za 6-*N*,*N*-diacetilaminokrizen i 2,4-dinitrobenzojevu kiselinu torzijske frekvencije koje se zadovoljavajuće slažu s Ramanovim spektrima. Translacijske i libracijske frekvencije rešetke za cijele molekule, izvedene iz komponenata L i T, općenito su u skladu sa spektroskopskim rezultatima.