Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 6 December 1999
Accepted 12 April 2000

Dynamics of molecules in crystals from multi-temperature anisotropic displacement parameters. II. Application to benzene (C_6D_6) and urea [$OC(NH)_2$]

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The temperature evolution of atomic anisotropic displacement parameters (ADP's) of perdeuterobenzene and of urea in the temperature range between 12 and 123 K is investigated in terms of the model presented in paper I. For the benzene molecule, the temperature-dependent contributions to the ADP's are well described by three molecular librations and three molecular translations. For the urea molecule, the analysis revealed a low-frequency high-amplitude normal mode (~64 cm^{-1}), which combines out-of-plane deformations of the NH_2 groups with molecular libration. The pyramidalization motion allows the hydrogen-bonding pattern to be retained quite well, whereas this pattern is heavily distorted in the higher-frequency molecular librations. The results presented for urea go a step beyond those obtainable in a conventional rigid-body or segmented-rigid-body analysis because they show how correlations of atomic displacements in molecular crystals can be determined from the temperature evolution of ADP's. For both molecules, the analysis reveals temperature-independent contributions to the ADP's accounting for the high-frequency internal vibrations. It is the first time that such contributions have been extracted directly from single-crystal diffraction data for light atoms like hydrogen and deuterium *as well as* for heavier atoms like carbon, nitrogen and oxygen. These contributions agree well with those calculated from independent spectroscopic information.

1. Introduction

Anisotropic displacement parameters (ADP's), derived routinely from diffraction experiments, are the sum of many different contributions: the mean square atomic displacements from all possible motions (libration, translation, internal vibrations), those coming from disorder (static or dynamic) and those reflecting systematic error either in the diffraction data or in the refinement model. In a standard structure analysis, usually performed at a single temperature, it is very difficult, if not impossible, to evaluate the relative importance of the various contributions and to assess the physical significance of the ADP's. This situation is unsatisfactory for an experimental method that claims to provide the most accurate information on structure in the solid state, but also because the ADP's represent about two thirds of the numerical information obtained from a single-crystal structure determination. In spite of such difficulties, methods to derive information on motion from ADP's have been developed (Schomaker & Trueblood, 1968; Johnson, 1970; Dunitz & White, 1973; Trueblood, 1978; Trueblood & Dunitz, 1983; Schomaker & Trueblood, 1998; He & Craven, 1985, 1993; Bürgi, 1989). They are all based on Cruickshank's approach, developed for molecular crystals, in which it can be assumed that the major contributions to the observed ADP's come from rigid-body libration and translation (Cruickshank, 1956*a*,*b*). The generalized rigid-body model has been formulated by Schomaker & Trueblood (1968) and is by now widely used to extract mean square amplitudes of translational and librational oscillations from experimentally determined ADP's.

In his assessment of the limitations of the rigid-body model, Cruickshank said: 'It is not possible to extend this kind of analysis to determine the internal vibrations of a non-rigid molecule as the effects of the internal and rigid-body vibrations cannot be separated'. He was probably a bit too pessimistic! From the temperature dependence of mean square amplitudes, it is not only possible to separate contributions due to a rigid body from those due to internal motions but also to estimate the contributions from disorder and systematic errors. A theoretical basis for such analyses has been described in paper I (Bürgi & Capelli, 2000) and it is here illustrated by analysing ADP's of two molecules, benzene and urea, determined at several temperatures to show how to obtain in practice an interpretation of the ADP's that is consistent over several temperatures. For both examples, the simultaneous analysis of all experimental data leads to results that cannot be obtained with previous thermal-motion analyses at a single temperature. For benzene, the terms accounting for internal motion of the H atoms can be obtained directly from the ADP's, as can those of the C atoms; as a consequence, the description of translational and librational motion is significantly improved, especially at low temperature. In the case of urea, it is possible to refine the frequency and displacement vectors of a low-frequency motion that combines molecular libration with molecular deformation, specifically NH_2 out-of-plane bending. The example illustrates an effect that is largely neglected in molecular crystals, namely the coupling between internal and external motions, but that in this case leads to a physically more meaningful interpretation of the ADP's than was available previously.

2. Benzene

Benzene is a prototypical molecule in organic chemistry that has been extensively studied with many different techniques. The crystal structure of benzene has been investigated both by X-ray (Cox, 1928, 1932; Cox *et al.*, 1955, 1958; Cox & Smith, 1954) and neutron diffraction (Bacon *et al.*, 1964; Jeffrey *et al.*, 1987). Thermal-motion analyses of the anisotropic displacement parameters of the C atoms have also been reported (Cox *et al.*, 1955, 1958; Cox & Smith, 1954; Jeffrey *et al.*, 1987).

Johnson (1970), in his crystal structure studies by neutron diffraction, recognized that ADP's for light atoms like hydrogen and deuterium include significant contributions from internal molecular vibrations. As a consequence, they need to be corrected before they can be included in a rigid-body translation and libration analysis. Corrections for internal molecular vibrations can be estimated from spectroscopic data, under the assumption that internal and lattice modes are uncorrelated. An early example of this kind of analysis was given by Johnson (1970) who showed for the H atoms in phenyl rings that the mean square amplitudes that cannot be attributed to external vibrations are quite similar to those calculated for benzene by spectroscopic normal-mode analysis of the internal vibrations. Jeffrey applied this correction procedure to the ADP's of the deuterium atoms in perdeuterobenzene determined in his neutron diffraction experiments at 15 and 123 K (Jeffrey *et al.*, 1987). A rigid-body model fitted the corrected ADP's quite well.

In the simultaneous analysis of the neutron data at 15 and 123 K presented here, it is no longer necessary to correct *a priori* the experimental ADP's with extraneous spectroscopic information. Instead, the correction terms for internal motion are considered as refinable parameters, determined in the analysis, and compared *a posteriori* with the spectroscopic information. The smaller internal motion amplitudes of the heavier atoms, which have been neglected in previous thermal-motion analysis, are treated in the same way.

2.1. Experimental

Benzene crystallizes in space group *Pbca* with site symmetry $\bar{1}$. Although this symmetry is lower than the D_{6h} symmetry of the molecule in the gas phase, the deviations of bond lengths and angles from D_{6h} are small in the crystal, a fact that will simplify the model needed to analyse the ADP's. The working coordinate system for this analysis was chosen to be the same as in Jeffrey *et al.* (1987); the x axis is in the C1—D1 direction, the y axis is perpendicular to the x axis and in the molecular plane; the z axis is perpendicular to the molecular plane and completes a right-handed Cartesian system with the origin at the molecular centre of mass (Fig. 1).

The anisotropic displacement parameters obtained by neutron diffraction experiments on perdeuterobenzene at 15 and 123 K (Jeffrey *et al.*, 1987) have been analysed with a model composed of six temperature-dependent normal modes built from the following degrees of freedom: three independent molecular librations (l_x, l_y and l_z) and three independent molecular translations (t_x, t_y and t_z). For each normal mode, a frequency is refined. Because of the centre of inversion in the molecule, the corresponding displacement vectors (eigenvectors) belong to different irreducible representations [A_g and A_u, respectively (Cotton, 1990)] and contain only three components, either librations or translations but not both (Schomaker & Trueblood, 1968). The lowest internal frequency in the solid state is 352.2 cm^{-1} and the intermolecular interactions are weak; it can thus be assumed that the mixing between internal and external modes is small and that, at the temperatures of the neutron diffraction experiments, all internal-mode amplitudes follow in good approximation the zero-point motion regime and are thus temperature independent (Taddei *et al.*, 1973). To account for the temperature-independent internal vibrations, two $\boldsymbol{\varepsilon}$ tensors were included in the model, one for the C atoms and one for the D atoms. The principal axes of these tensors were chosen to be along the C—D bonds (ε_{11}), perpendicular to the C—D bonds in the molecular plane (ε_{22}), and perpendicular to the molecular plane (ε_{33}). This implies that the internal contributions show almost D_{6h} symmetry.

The number of independent observations is 72 (six observations for six crystallographically independent atoms at two temperatures; Fig. 2 left) and the number of parameters is 24 (six frequencies, six independent vector components and twelve $\boldsymbol{\varepsilon}$ tensor components). The final agreement factor is

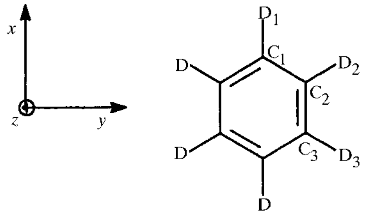

Figure 1
Molecular structure of perdeuterobenzene at 15 K, showing the atomic labels and the orientation of the working coordinate system.

$$wR2 = \left[\sum w(U_{\rm obs} - U_{\rm calc})^2 / \sum wU_{\rm obs}^2\right]^{1/2} = 0.019$$

and the goodness of fit is

$$\mathrm{GoF} = \left[\sum w(U_{\rm obs} - U_{\rm calc})^2/(n_{\rm obs} - n_{\rm par})\right]^{1/2} = 1.0.$$

The average difference between observed and calculated U^{ij}'s is ~0.0007 Å^2, *i.e.* about one to three times as large as the uncertainties of the experimental ADP's reported by Jeffrey *et al.* (1987). This clearly indicates that the model can explain the observations satisfactorily. In Fig. 2, root-mean-square-amplitude surfaces for observed U^{ij}'s and the difference tensor $(U^{ij}_{\rm obs} - U^{ij}_{\rm calc})^{1/2}$ are compared. To be visible, the difference tensors had to be magnified by a factor of four.

2.2. Results and discussion

The results of the ADP analysis, namely molecular translation and libration frequencies, corresponding eigenvectors and temperature-independent contributions from the intramolecular vibrations are summarized in Tables 1 and 3. Derived quantities, like the **L** and **T** tensor elements, can be calculated from the frequencies and eigenvectors, and are given in Table 4. The various results will be compared with the corresponding information obtained from non-diffraction techniques and from previous thermal-motion analysis. Our model represents the best fit to the experimental ADP's of the benzene molecule at both 15 and 123 K.

Table 1 lists the normal modes with their characteristic frequencies and eigenvectors. The second column refers to an effective normal mode with a frequency of 70 (1) cm^{-1}; it is a libration about an axis that is almost in the molecular *xy* plane ($l_z \sim 0$), passes through the origin and is rotated by ~−19° with respect to the *x* axis. The third column describes a libration with a frequency of 84 (1) cm^{-1}. The corresponding axis is almost in the molecular plane, passes through the origin and is rotated by ~−19° with respect to the *y* axis, *i.e.* orthogonal to the previous one. The fourth column corresponds to an in-plane libration of the benzene ring about an axis that is almost orthogonal to the molecular plane (~83°).

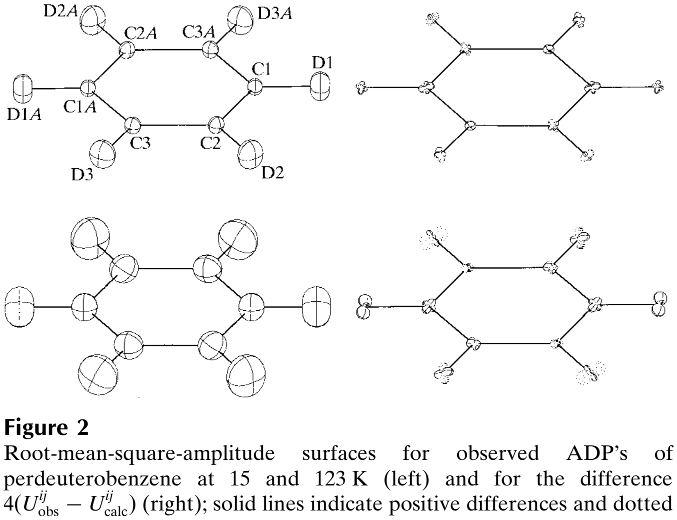

Figure 2
Root-mean-square-amplitude surfaces for observed ADP's of perdeuterobenzene at 15 and 123 K (left) and for the difference $4(U^{ij}_{\rm obs} - U^{ij}_{\rm calc})$ (right); solid lines indicate positive differences and dotted lines negative ones (Hummel *et al.*, 1990).

The next three columns correspond to translational normal modes: two of them are nearly degenerate with frequencies of 43.1 (2) and 44.9 (2) cm^{-1}; they correspond to in-plane translations orthogonal to each other and rotated by ~45° with respect to the *x* and *y* axes of the working coordinate system. The last normal mode represents a translation in a direction almost orthogonal to the molecular plane (~80°). All librational motions have higher frequencies than the translational ones. This can be understood in terms of the relation between a specific type of motion and the chemical environment in the benzene crystals. The D atoms are displaced from their equilibrium position by the same distance as the C atoms in a translational motion but about twice as far in a librational motion. The displacement from equilibrium increases the weak intermolecular energies, *e.g.* those arising from the interatomic D—π interactions; the effect is bigger for the librational than for the translational normal modes (see Fig. 3).

The model just described considers a single molecule in the average potential of its crystal environment (see paper I). This corresponds to approximating an entire phonon branch with a single effective frequency (Table 1). The validity of this approximation may be tested by comparing the frequency values obtained from our analysis with the frequency distribution functions for intermolecular modes of benzene from lattice dynamic calculations or inelastic neutron scattering measurements of the dispersion curves. The phonon spectrum of crystalline benzene C_6H_6 has been measured by inelastic incoherent neutron scattering at 80 K by Bokhenkov *et al.* (1978) and density-of-state curves have been calculated on the basis of the experimental data for two sets of parameters. In both cases, the density-of-states function extends between 0 and 140 cm^{-1} with maxima at ~45, 80 and 120 cm^{-1}. The first part of the curve increases smoothly from zero and reaches a peak at 40–45 cm^{-1}, while the second consists of a broad maximum extending from 60 to 100 cm^{-1}. The third feature is

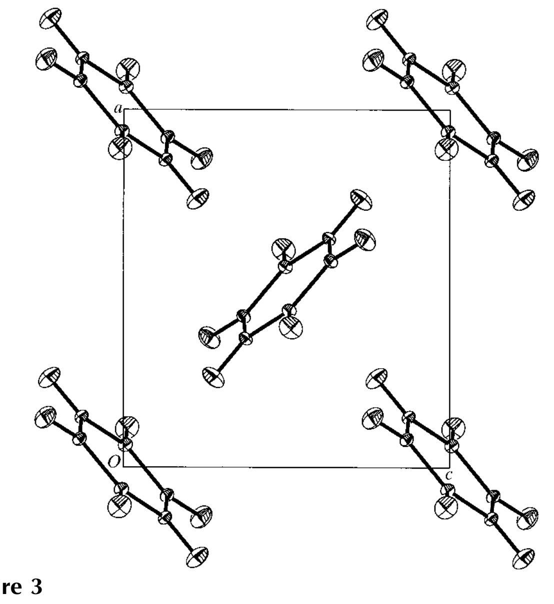

Figure 3
Parallel projection of the packing of C_6D_6 in the crystallographic *ac* plane at 15 K. The ellipsoids are shown at 50% probability.

Table 1
Normal frequencies $\tilde{\gamma}$ and eigenvectors **V** for C_6D_6 derived from ADP's pertaining to 15 and 123 K.

$\tilde{\nu}_i$ (cm^{-1})	70.3 (7)	84.1 (11)	60.2 (5)	43.1 (2)	44.9 (2)	51.2 (6)
l_x	0.943 (9)	0.314 (25)	−0.111 (29)	0.000	0.000	0.000
l_y	−0.319 (26)	0.947 (9)	−0.031 (18)	0.000	0.000	0.000
l_z	0.095 (30)	0.065 (16)	0.993 (3)	0.000	0.000	0.000
$t_x - t_y$	0.000	0.000	0.000	0.727 (38)	0.683 (40)	0.075 (25)
$t_y + t_x$	0.000	0.000	0.000	−0.666 (40)	0.727 (38)	−0.170 (26)
t_z	0.000	0.000	0.000	−0.171 (23)	0.074 (29)	0.983 (4)

Table 2
Comparison between frequencies obtained from ADP analysis and from a calculation of lattice modes at the origin of the Brillouin zone (LD; Filippini & Gramaccioli, 1989); units are cm^{-1}.

	ADP analysis	Lattice dynamic (LD) calculation at 15 K		Average of LD values at 15 K
Libration	70.3, 84.1, 60.2	87, 73, 37	(*A*)	84
(**g** modes)	(71.5)	130, 82, 64	(B_1)	
		96, 86, 78	(B_2)	
		132, 93, 47	(B_3)	
Translation	43.1, 44.9, 51.2	104, 70, 59	(*A*)	60
(**u** modes)	(46.4)	98, 59, 0	(B_1)	
		110, 57, 0	(B_2)	
		90, 76, 0	(B_3)	

a relatively narrow maximum at ~120 cm^{-1}. The frequencies obtained by ADP analysis fall within the first two maxima of this density-of-states curve. Frequencies calculated from a lattice dynamical model are available for perdeuterobenzene at 15 K but only at the origin of the Brillouin zone (Filippini & Gramaccioli, 1989). Again, the values obtained by ADP analysis fall in the range of the calculated phonon frequencies (Table 2).

The temperature-independent contributions to ADP's are listed in Table 3 together with corresponding values calculated from a harmonic force field that reproduces experimental IR and Raman data. The latter were calculated with the program *ASYM* (Hedberg & Mills, 1993), using the geometry of the molecule at 15 K and the empirical symmetry force field based on estimated harmonic frequencies in the gas phase from Goodman *et al.* (1991). The values used by Jeffrey to correct the ADP's of the D atoms before doing a rigid-body analysis are shown at the bottom of Table 3; for the out-of-plane vibrations, they were taken from Johnson (1970) and for the C—D radial stretch from Cyvin (1968).

The temperature-independent $\boldsymbol{\varepsilon}$'s are tensorial quantities. For both D and C atoms, the first diagonal element of the tensor (ε_{11}) refers to displacements along the C—D bond direction, the second element (ε_{22}) to the in-plane and the third element (ε_{33}) to the out-of-plane displacements. Overall, the ε_{ii} obtained directly from ADP's agree very well with those calculated from the force field. By far the largest discrepancies are found for the out-of-plane displacements of the D atoms. However, the more recent values based on the force field of Goodman *et al.* (1991) are closer to our experimental ones than the earlier values used by Jeffrey. At present, the reason for the remaining difference, 0.0023 Å^2 in ε_{33}, is unclear. For a molecule with overall D_{6h} symmetry, the site symmetries at carbon and deuterium are C_{2v}; this requires the off-diagonal elements ε_{ij} to be zero. The fact that this is also found in our analysis indicates that the influence of the crystal environment on the high-frequency vibrations is small.

The frequencies and the eigenvectors obtained in the ADP analysis (Table 1) can be used to calculate the mean square amplitudes of rigid-body translation and libration. The following equation illustrates the relation between the molecular **L**, **T** and **S** tensors, the six rigid-body degrees of freedom (l_x, l_y, l_z, t_x, t_y, t_z), and the corresponding normal-mode quantities:

$$\begin{bmatrix} \mathbf{L}(\tau) & \mathbf{S}(\tau) \\ \mathbf{S}^T(\tau) & \mathbf{T}(\tau) \end{bmatrix} = \begin{bmatrix} \langle l_x l_x \rangle & \langle l_x l_y \rangle & \langle l_x l_z \rangle & \langle l_x t_x \rangle & \langle l_x t_y \rangle & \langle l_x t_z \rangle \\ \langle l_y l_x \rangle & \langle l_y l_y \rangle & \langle l_y l_z \rangle & \langle l_y t_x \rangle & \langle l_y t_y \rangle & \langle l_y t_z \rangle \\ \langle l_z l_x \rangle & \langle l_z l_y \rangle & \langle l_z l_z \rangle & \langle l_z t_x \rangle & \langle l_z t_y \rangle & \langle l_z t_z \rangle \\ \langle t_x l_x \rangle & \langle t_x l_y \rangle & \langle t_x l_z \rangle & \langle t_x t_x \rangle & \langle t_x t_y \rangle & \langle t_x t_z \rangle \\ \langle t_y l_x \rangle & \langle t_y l_y \rangle & \langle t_y l_z \rangle & \langle t_y t_x \rangle & \langle t_y t_y \rangle & \langle t_y t_z \rangle \\ \langle t_z l_x \rangle & \langle t_z l_y \rangle & \langle t_z l_z \rangle & \langle t_z t_x \rangle & \langle t_z t_y \rangle & \langle t_z t_z \rangle \end{bmatrix} = \mathbf{g}\mathbf{V}\boldsymbol{\delta}(\tau)\mathbf{V}^T\mathbf{g}^T. \quad (1)$$

The matrix **g** allows for the mass adjustment of the normal coordinates and depends only on atomic masses and coordinates; **V** is the eigenvector matrix; $\boldsymbol{\delta}(\tau)$ is the diagonal matrix of the temperature-dependent normal-mode displacements and τ indicates the temperature (for a complete description of the equation see paper I).

Values calculated with the results from Table 1 are reported in Table 4. They are compared with those obtained by Jeffrey *et al.* (1987) from a rigid-body analysis of the experimental ADP's (Schomaker & Trueblood, 1968) after applying the corrections reported in Table 3 to the U^{ij}'s of the D atoms. The second column in Table 4 gives the values for the **L** and **T** tensors calculated at 15 K from a lattice dynamic model (Filippini & Gramaccioli, 1989).

The values for **L** and **T** obtained by ADP analysis are quite close to the lattice dynamical values at 15 K, while both differ clearly from those calculated by Jeffrey *et al.* (1987). At 15 K, the elements of Jeffrey's libration tensor are about an order of magnitude smaller than the ones calculated from ADP analysis. At 123 K, the differences are less dramatic but Jeffrey's libration tensor is still smaller than the one calculated in this work. On the other hand, Jeffrey's translation tensors

Table 3
Top three rows: temperature-independent contribution to ADP's ($\boldsymbol{\varepsilon}$ tensors) derived from the temperature evolution of ADP's; middle three rows: $\boldsymbol{\varepsilon}$ tensors calculated with a force field that reproduces vibrational frequencies of C_6D_6 in the gas phase; bottom three rows: values given by Jeffrey *et al.* (1987) to correct his experimental ADP's for internal motions.

	$\boldsymbol{\varepsilon}$(D) (Å^2)			$\boldsymbol{\varepsilon}$(C) (Å^2)		
ADP analysis	0.0052 (1)	0.0000 (1)	0.0000 (1)	0.0014 (1)	0.0000 (1)	0.0000 (1)
		0.0083 (1)	0.0000 (1)		0.0007 (1)	0.0000 (1)
			0.0110 (2)			0.0015 (1)
Force-field calculation	0.0044	0.0000	0.0000	0.0013	0.0000	0.0000
		0.0089	0.0000		0.0008	0.0000
			0.0133			0.0016
Thermal-motion analysis	0.0043	0.0000	0.0000	–	–	–
(Jeffrey *et al.*, 1987)		0.0102	0.0000		–	–
			0.0169			–

Table 4
Rigid-body libration (**L**) and translation (**T**) tensors calculated from the frequencies and eigenvectors given in Table 1, from a lattice dynamical model and determined from a conventional **TLS** analysis.

T		ADP analysis as a function of T			Lattice dynamic calculations (Filippini & Gramaccioli, 1989)			Thermal-motion analysis (Jeffrey *et al.*, 1987)		
15 K	**L** (rad^2)	0.0022 (1)	0.0001 (1)	0.0000 (1)	0.0022	0.0002	0.0000	0.0002 (1)	0.0001 (1)	0.0000 (1)
			0.0019 (1)	−0.0000 (1)		0.0018	0.0000		0.0005 (1)	−0.0000 (1)
				0.0013 (1)			0.0012			0.0008 (1)
	T (Å^2)	0.0047 (1)	0.0001 (1)	−0.0001 (1)	0.0051	−0.0002	−0.0003	0.0059 (1)	0.0001 (1)	−0.0002 (1)
			0.0047 (1)	−0.0001 (1)		0.0053	0.0000		0.0061 (1)	0.0001 (1)
				0.0040 (1)			0.0043			0.0089 (2)
123 K	**L** (rad^2)	0.0056 (1)	0.0005 (1)	0.0001 (1)				0.0025 (1)	0.0005 (1)	0.0001 (1)
			0.0043 (1)	−0.0002 (1)					0.0039 (1)	−0.0002 (1)
				0.0039 (1)						0.0034 (1)
	T (Å^2)	0.0181 (1)	0.0006 (1)	−0.0008 (1)				0.0193 (1)	0.0006 (1)	−0.0008 (1)
			0.0179 (1)	−0.0005 (1)					0.0194 (1)	−0.0005 (1)
				0.0136 (3)						0.0185 (2)

are larger than those derived from ADP analysis at both temperatures.

These differences are due to two major problems in Jeffrey's treatment of the ADP's. Firstly, the values used for correcting the out-of-plane ADP's of the D atoms are too large by ~0.004–0.006 Å^2 (Table 3). Secondly, the correction for internal motion was performed for the D atoms only; but corresponding contributions to the ADP's of the C atoms cannot be neglected because they are about 3–5 times as big as the estimated uncertainties of the observed ADP's.[1]

In the ADP analysis presented here, the number of refinable parameters is between 18 and 24, depending on whether or not the off-diagonal elements of the temperature-independent $\boldsymbol{\varepsilon}$ tensors are refined, and it is independent of the number of temperatures at which the structure has been measured. In a traditional thermal-motion analysis, the number of parameters is 12 at each single temperature (if the diagonal correction terms for internal vibrations are considered as adjustable parameters, the number increases to 15 or 18).

From our analysis, we can conclude that a model of motion designed to fully explain observed ADP's over a range of temperatures requires temperature-independent contributions accounting for internal motions not only for the light atoms such as H or D but also for the other atoms in the molecule, as in this case for the C atoms. Note that our analysis does not do an *a priori* correction of the ADP's with information derived from non-diffraction techniques but it determines the temperature-independent correction terms directly from the diffraction data. For C_6D_6, these values are more reliable than those obtained from old force-field calculations and in good agreement with those obtained by modern *ab initio* methods. The model of motion used in the ADP analysis is therefore not only suitable to describe the temperature evolution of mean-square-amplitude quantities, such as **U**, **L** and **T**, but it is also physically meaningful.

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[1] The ADP's calculated with a lattice dynamical model and given by Filippini & Gramaccioli (1989) were analysed in the same way as the experimental ADP's of Jeffrey *et al.* (1987). However, the results revealed problems and inconsistencies in the calculated numbers. In Table 2 of Filippini & Gramaccioli (1989), the contributions to U^{ij}'s from internal vibrations are reported. After applying the required transformations to account for the different coordinate systems, their numbers should correspond to the elements of the $\boldsymbol{\varepsilon}$ tensors reported in our Table 2. Inconsistencies were found between the in-plane components of the $\boldsymbol{\varepsilon}$ tensors: for D1, the C—D stretch component was about 0.0103 Å^2, while for D2 and D3 it was more reasonable, about 0.0060 Å^2. In addition, the in-plane components were always bigger than the out-of-plane components, probably due to the dated force field used in the calculation. When we tried to analyse the U^{ij}'s calculated from lattice dynamics at two temperatures and corrected for the contributions from internal vibrations (both given in Table 2 of Filippini & Gramaccioli, 1989) with a traditional Schomaker & Trueblood (1968) rigid-body model, the values of the components of the **L** and **T** tensors given by Filippini & Gramaccioli (see third column in our Table 3) could be reproduced only within a 10% margin. From these observations, we suggest the presence of errors or misprints in Table 2 of Filippini & Gramaccioli (1989).

3. Urea

The urea molecule is prototypical because of its two peptidic bonds. In the crystal lattice, the planar C_{2v}-symmetric molecules are interconnected by an extensive network of hydrogen bonds. The carbonyl O atom shows a particularly unusual hydrogen-bond pattern: it accepts four N—H hydrogen bonds (Fig. 5*a*). Swaminathan *et al.* (1984) measured the ADP's of urea by neutron diffraction at 12, 60 and 123 K and performed thermal-motion analyses on their data. If they corrected the ADP's with the help of spectroscopic information to account for internal motion of the H atoms, a rigid-body model was found to be adequate to explain motion in the molecular plane but inadequate to account for out-of-plane motion. Additional degrees of freedom have been introduced in the model, namely torsion around the C—N bonds to simulate deformation of the NH_2 groups, but no coupling terms between rigid-body motions and NH_2 torsions have been allowed because some of the corresponding parameters may be indeterminate (Bürgi, 1989; Schomaker & Trueblood, 1998). The analysis resulted in a physically meaningless negative value for the mean square amplitude of the torsional motion of the H atoms at 123 K.

Here we present an alternative analysis of the same data, which accounts for the ADP's at 12, 60 and 123 K in terms of a single model. Two features in the model are new and important:

(i) several different molecular deformation coordinates are tested and differentiated with respect to their potential in accounting correctly for the temperature dependence of the observed mean square amplitudes;

(ii) coupling terms between molecular coordinates with the same irreducible representation are determined.

The final model does not give unphysical negative mean square displacements and reveals a chemically meaningful interpretation of the observed ADP's.

3.1. Experimental

The analysis has been performed in a working Cartesian coordinate system with its x axis parallel to the molecular twofold axis (the C—O bond direction) and the z axis perpendicular to the molecular plane. The origin is at the centre of mass of the molecule. All models include two $\boldsymbol{\varepsilon}$ tensors to account for temperature-independent contributions to the ADP's, one for the H atoms and one for all other atoms in the molecule. The principal axes of the $\boldsymbol{\varepsilon}$ tensor for the H atoms were chosen to be along the N—H bond (ε_{11}), perpendicular to the N—H bond in the molecular plane (ε_{22}) and perpendicular to the molecular plane (ε_{33}); the principal axes of the $\boldsymbol{\varepsilon}$ tensor of the other atoms were chosen to be parallel to the working coordinate system.

In the reference model, the temperature-dependent part of the ADP's is represented with three rigid-body translations and three rigid-body librations. They belong to the four different irreducible representations of the molecular point group C_{2v} (Cotton, 1990): the translation in the direction of the x axis (t_x) transforms as the irreducible representation A_1, the libration about the x axis (l_x) as A_2, the translation along the z axis (t_z) and the libration about the y axis (l_y) as B_1, the translation along the y axis (t_y) and the libration about the z axis (l_z) belong to B_2. Therefore, t_x and l_x cannot form modes of motion together with any other libration or translation coordinates but correspond to normal modes. Conversely, t_z can combine with l_y and t_y with l_z.

The results obtained with the reference model are comparable with those of models (ii) and (iii) of Swaminathan *et al.* (1984), in which the experimental U^{ij}'s were corrected for internal-mode contributions. The overall agreement factor is 0.079 and the goodness of fit 2.5. Only the 30 independent in-plane components of the ADP's are described satisfactorily while the 15 out-of-plane components are poorly accounted for. This can be seen from the difference tensors ($U_{\rm obs} - U_{\rm calc}$) shown in Fig. 4(*a*).

For an improved description of the out-of-plane components of the ADP's, it is necessary to add flexibility to the rigid-body model. This is achieved by defining additional internal coordinates to account for 'soft' molecular deformations. An indication about the nature of such low-energy degrees of freedom comes from the spectroscopic observation that the wagging motions of the NH_2 groups in the gas phase have low frequencies (King, 1972; Li *et al.*, 1987). In addition, a number of *ab initio* calculations in the gas phase show that the equilibrium structure of urea is slightly non-planar at the N atoms (Kontoyianni & Bowen, 1992; Meier & Coussens, 1992; Ha & Puebla, 1994). We interpret these observations as indications of soft out-of-plane motion of the H atoms in the

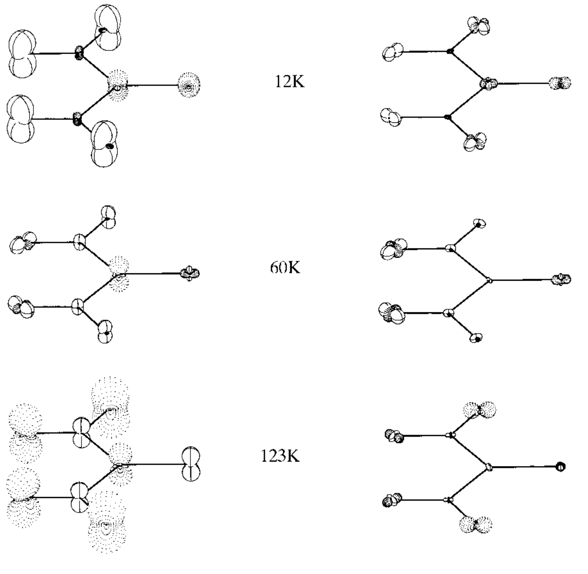

Figure 4
Difference tensor $4(U^{ij}_{\rm obs} - U^{ij}_{\rm calc})^{1/2}$ at 12, 60 and 123 K for the urea molecule obtained (*a*) with a rigid-body model and (*b*) with model w1 which includes an additional molecular coordinate to account for the out-of-plane motion of the H atoms. The representations are given as root-mean-square surfaces, solid lines indicating positive differences and dotted lines negative ones (Hummel *et al.*, 1990).

crystal. This softness was introduced into the model of motion in two alternative ways: either through atomic or through group coordinates.

In the first case, out-of-plane motion is defined for each H atom separately. The coordinates of two symmetry-equivalent H atoms are combined into a symmetric and an antisymmetric combination with respect to the mirror plane perpendicular to the molecular plane (irreducible representations B_1 and A_2, respectively). Group coordinates affect both H atoms belonging to an NH_2 group. A torsion about the C—N bond displaces the geminal H atoms by the same amount in the opposite direction to the molecular plane, while a wagging motion of the H atoms displaces the two H atoms in the same direction and by the same amount out of the molecular plane. With two NH_2 groups, there are again two possible combinations for both the wagging and the torsional coordinates: the symmetric modes, which retain the mirror plane perpendicular to the molecular plane and have irreducible representation B_1, and the antisymmetric ones, which retain the molecular twofold axis and have irreducible representation A_2. Eight models have been investigated, each one including three librations, three translations and one of the eight out-of-plane deformation coordinates described above. The two $\boldsymbol{\varepsilon}$ tensors to account for the temperature-independent contributions to the ADP's are retained. In all models, six normal-mode frequencies have been refined whose eigenvectors may contain any symmetry-allowed combination of the seven molecular coordinates.

The description of the experimental ADP's is improved significantly for four of the eight models: the agreement factor dropped to 0.026–0.033 and the goodness of fit to 0.84–1.1 (Fig. 4*b*). The results for the in-plane motion are the same for all four models and are summarized in Table 5(*a*), while those for the out-of-plane motion are given for the best four models in Table 5(*b*). The symbol *u* in Table 5(*b*) represents the out-of-plane molecular coordinate. In model h1, this coordinate is the antisymmetric out-of-plane displacement of the H1 atoms (irreducible representation A_2) and in model h2 it is the symmetric out-of-plane displacement of the H2 atoms (B_1). In model w1, the symbol *u* represents the antisymmetric wagging of the two NH_2 groups (A_2), while in model w2 it represents the symmetric wagging (B_1).

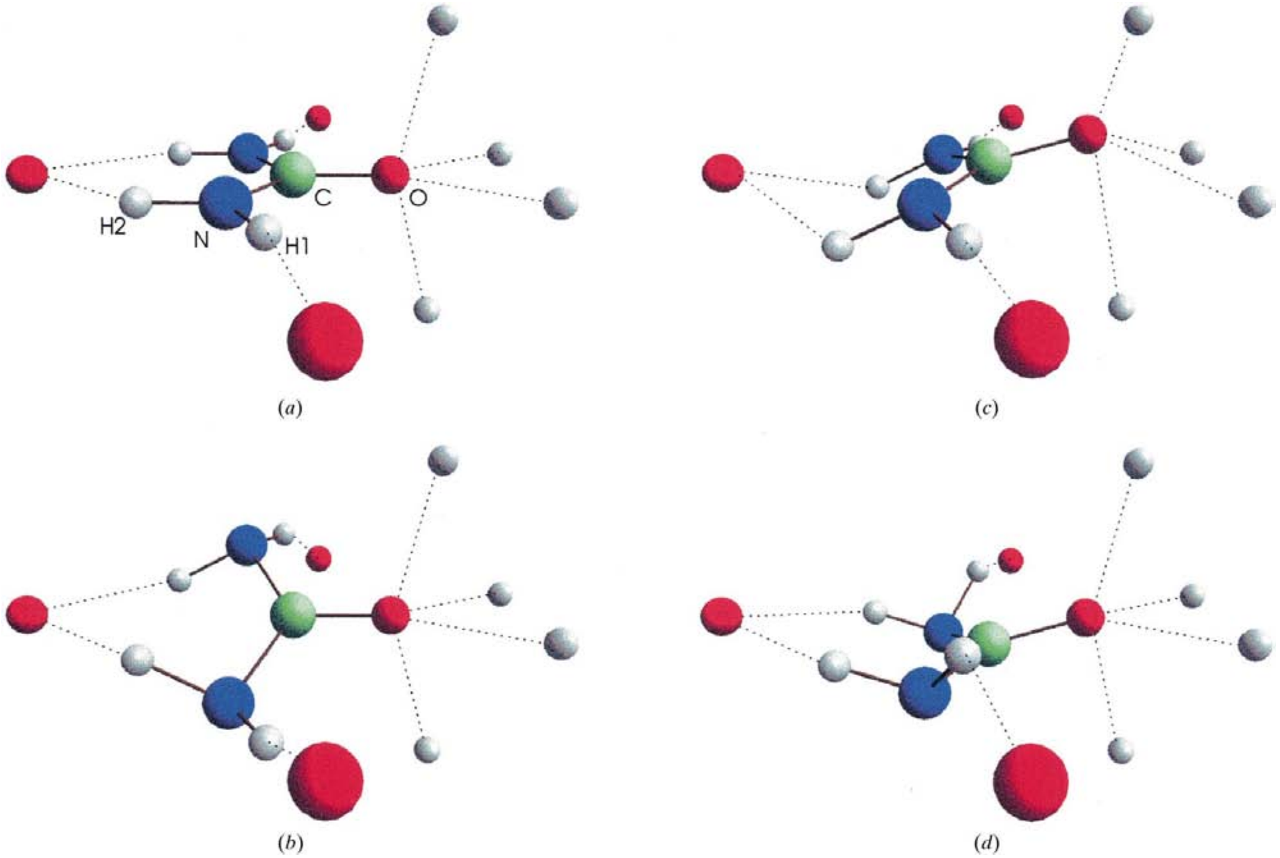

Figure 5
Cartesian displacements for the normal modes associated with the lowest out-of-plane frequencies obtained with models w1 (*b*) and w2 (*c* and *d*). The normal mode with a frequency of 64 cm^{-1} in model w1 corresponds to a libration about an axis coinciding with the C—O bond direction and is combined with an antisymmetric pyramidalization of the NH_2 groups (*b*). The normal mode with frequency 101 cm^{-1} in model w2 corresponds to a libration about an axis almost passing through the N—N direction and a small admixture of NH_2 pyramidalization, which increases the hydrogen displacements (*c*), while the normal mode with frequency 55 cm^{-1} corresponds to a libration about an axis in the molecular plane and passing through the O atom combined with a symmetric pyramidalization of the NH_2 groups (*d*). The molecule at equilibrium position and with atomic labels is shown in (*a*). The surrounding hydrogen bonding of the molecule is given to show the distortion of the hydrogen bonds due to the molecular motions.

Table 5
Normal frequencies $\tilde{\nu}_i$ (cm^{-1}), eigenvectors $\mathbf{V}$ and $\boldsymbol{\varepsilon}$ tensors (Å^2).

(a) For in-plane motions of urea

$\tilde{\gamma}$†		Eigenvectors	$\boldsymbol{\varepsilon}_{\rm ip}$(H)		$\bar{\boldsymbol{\varepsilon}}_{\rm ip}$(C, N, O)	
136 (5)	B_2	0.99 (1) l_z − 0.13 (3) t_y	66 (2)	7 (2)	15 (1)	−1 (1)
103 (3)	A_1	t_x		120 (3)		13 (1)
61.2 (7)	B_2	0.99 (1) t_y + 0.13 (3) l_z				

(b) For four models of out-of-plane motion of urea (for a complete description of the models, see text)

Model	R‡	GoF§	$\tilde{\gamma}_i$†		Eigenvectors	ε_{33}(H)	$\bar{\varepsilon}_{33}$(C, N, O)
h1	3.34	1.09	54.5 (6)	A_2	0.99 (1) l_x + 0.17 (1) u	259 (4)	35 (2)
			n.d.¶	B_1	0.99 (1) l_y + 0.14 (2) t_z		
			70 (2)	B_1	−0.14 (2) l_y + 0.99 (1) t_z		
w1	2.71	0.88	63.6 (6)	A_2	0.97 (1) l_x + 0.23 (1) u	263 (6)	16 (2)
			150 (6)	B_1	0.99 (1) l_y − 0.13 (1) t_z		
			60.1 (9)	B_1	0.13 (1) l_y + 0.99 (1) t_z		
h2	2.56	0.84	99 (2)	A_2	l_x	223 (7)	21 (2)
			109 (3)	B_1	0.77 (2) l_y − 0.61 (2) t_z − 0.18 (3) u		
			51.7 (4)	B_1	0.64 (2) l_y + 0.74 (2) t_z + 0.22 (2) u		
w2	2.56	0.84	90 (11)	A_2	l_x	214 (16)	19 (3)
			101 (2)	B_1	0.82 (3) l_y − 0.49 (3) t_z − 0.30 (9) u		
			54 (2)	B_1	0.57 (4) l_y + 0.72 (6) t_z + 0.40 (4) u		

† Frequencies are given with the corresponding irreducible representations. ‡ $wR2 = [\sum w(U_{\rm obs} - U_{\rm calc})^2/\sum wU^2_{\rm obs}]^{1/2} \times 100\%$. § GoF = $[\sum w(U_{\rm obs} - U_{\rm calc})^2/(n_{\rm obs} - n_{\rm par})]^{1/2}$. ¶ Not determined (the value of the frequency is too high to be determined: >1000 cm^{-1}).

3.2. Results and discussion

The rigid-body model is sufficient to explain the in-plane components of the ADP's of urea, but is inadequate to explain the components perpendicular to the molecular plane, even though it includes a temperature-dependent and a temperature-independent contribution to the ADP's. As shown in Fig. 5(a), the out-of-plane components of the ADP's for the H atoms calculated with the reference rigid-body model are too small at 12 K while at 123 K they are too big. For the corresponding components of the N and O atoms, the reverse trend is found. In their analysis, Swaminathan *et al.* (1984) arrived at similar conclusions.

The four models that include deformations of the NH$_2$ groups have been found to give a significantly improved description of the experimental ADP's, although, at first sight, they look different (Table 5b). The symmetry of the molecular deformations in models h1 and w1 (A_2) differs from that in h2 and w2 (B_1). Even for the same symmetry of deformation, numerical results are quite different. Yet there are significant similarities, some of them obvious, others more hidden. This will be illustrated for the statistical descriptors, the highest out-of-plane frequencies and the atomic displacement patterns encoded in the eigenvectors.

From a statistical point of view, all four models are nearly equally good: the goodness of fit is about 1.0 and the standard uncertainties of most model parameters are quite small. Although models h2 and w2 have an additional parameter in the eigenvector matrix compared with h1 and w1, the concomitant lowering of the agreement factor, especially relative to model w1, is not significant in terms of a χ^2 test (Hamilton, 1964). Note that including two out-of-plane coordinates in the models, torsion or wagging, does not improve the description of the ADP's and that the two models with torsional deformation are not given in Table 5 because corresponding R values are of the same order of magnitude as that obtained with the rigid-body model (~7%).

The frequency associated with the second normal mode (B_1, mostly a libration l_y about the y axis) refines to the highest value in all four models. In model h1, it is too high to be determined reliably.

The third similarity is less obvious; it concerns the way the out-of-plane deformation combines with molecular libration and translation. Deformation of the NH$_2$ groups can either increase or reduce the librational and translational displacements of the H atoms, depending on the sign of the u coordinate in the corresponding eigenvectors. In the A_2 modes of models h1 and w1 and in the lower-frequency B_1 mode of models h2 and w2, the respective out-of-plane coordinates always reduce the displacements of the H atoms. In the higher-frequency B_1 mode of models h2 and w2, pyramidalization of the NH$_2$ group increases the displacement slightly.

The resultant Cartesian displacements for the A_2 mode of model w1 and for the two B_1 modes of model w2 are shown in detail in Fig. 5. Each molecule is represented with its molecular hydrogen-bonding environment to show the distortion of the hydrogen bonds in the different molecular motions. In mode A_2 of model w1, a libration about the x axis and an antisymmetric wagging of the NH$_2$ groups combine so as to maintain optimal hydrogen bonding (Fig. 5b). In the lower-

Table 6
Frequencies of lattice vibrations for t_x and l_x (in cm^{-1}) at the origin and at other special points of the Brillouin zone as observed by inelastic neutron scattering (Lefebvre *et al.*, 1975) and as calculated with a generic force field (Parlinski & Chapuis, 1999).

	Inelastic neutron scattering (Lefebvre *et al.*, 1975)					Force-field calculation (Parlinski & Chapuis, 1999)					
	$\Gamma(000)$	$Z(00\frac{1}{2})$	$M(\frac{1}{2}\frac{1}{2}0)$	$\tilde{\gamma}$†	$\tilde{\gamma}_b$‡	$\Gamma(000)$	$Z(00\frac{1}{2})$	$M(\frac{1}{2}\frac{1}{2}0)$	$A(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	$\tilde{\gamma}$†	$\tilde{\gamma}_b$‡
t_x	0, 98	151, 173	68, 68	93	115	0, 91	154, 177	64, 64	164, 164	110	131
l_x	51,§ 88§	51,§ 88§	72,§ 72§	70	71	20, 105	41, 89	67, 67	64, 64	65	65

† Average frequency including all special points listed ‡ Average frequency excluding the origin of the Brillouin zone. § Calculated value.

Table 7
Comparison of vibration tensors for internal modes in urea calculated from spectroscopic data at 100 K by Ishii & Scheringer (1979) (first three rows) and from an *ab initio* calculation using the crystal field method by Rousseau *et al.* (1998) (second three rows).

	ε(H1)			ε(H2)			ε(C)			ε(O)			ε(N)			$\bar{\varepsilon}$(C, N, O)		
Spectroscopic data	54	−1	0	53	−3	0	8	0	0	8	0	0	7	−1	0	8	−1	0
(Ishii & Scheringer, 1979)		134	0		135	0		9	0		8	0		9	0		9	0
			245			240			16			2			5			8
Ab-*initio* calculation	54	1	0	53	1	0	9	0	0	8	0	0	7	−1	0	8	−1	0
(Rousseau *et al.*, 1998)		142	0		140	0		9	0		8	0		9	0		9	0
			265			260			16			2			6			7

frequency *B*1 mode of model w2, NH_2 pyramidalization similarly helps to preserve hydrogen bonding (Fig. 5*d*), whereas in the higher-frequency one the combination of displacements clearly deforms the hydrogen bonds at both the O and H2 atoms (Fig. 5*c*). In summary, all four models minimize hydrogen out-of-plane displacements by appropriate combination of libration, translation and NH_2 deformation in their low-frequency normal modes. This result was unexpected and significant. It implies that it is energetically more favourable to pyramidalize the NH_2 groups, leaving the hydrogen bonds undisturbed, than to rotate a planar rigid urea molecule in its crystalline hydrogen-bonded environment. Hence, it follows that the ease of NH_2 pyramidalization of urea in the gas phase found by microwave spectroscopy (King, 1972) is retained to some extent in the hydrogen-bonded solid state.

Given the statistical indistinguishability of the four models in Table 5(*b*), their physical details can only be judged by comparison against external information obtained with different experimental techniques. Table 6 shows frequencies of lattice vibrations for normal modes with irreducible representations A_1 and A_2 (t_x and l_x, respectively) measured by inelastic neutron scattering at the origin and at two special points (*Z* and *M*) of the Brillouin zone (Lefebvre *et al.*, 1975) as well as corresponding calculated values obtained from an *ab initio* generic force field [Parlinski & Chapuis (1999); the special point $A(\frac{111}{222})$ at the boundary of the Brillouin zone was also calculated]. The agreement between measured and calculated frequencies is quite good. The frequency from ADP analysis for t_x is 103 (3) cm^{-1}, *i.e.* in the general range of the lattice dynamical averages. In the case of l_x, the various average quantities in Table 6 are the same. They favour model w1 for which a value of 64 cm^{-1} has been obtained by ADP analysis. Analogous comparison for the other normal modes with irreducible representations B_1 and B_2 are much more complicated because of the coupling occurring between molecular coordinates with the same irreducible representation (respectively l_y, t_z and l_z, t_y).

Table 7 shows the values of the temperature-independent contributions to the ADP's calculated from spectroscopic data (Ishii & Scheringer, 1979) and from an *ab initio* calculation in the crystal phase (Rousseau *et al.*, 1998). The calculated values have been transformed into the local coordinate system of the $\boldsymbol{\varepsilon}$ tensors used in the present analysis and refer to 100 K. The agreement between spectroscopically derived values and *ab intio* calculated ones is quite impressive, with the possible exception of ε_{33} for the H atoms. The discrepancy can be partially explained by invoking errors in the assignment of the out-of-plane vibrations that can cause deviations of up to 30% in the vibrational tensors (Ishii & Scheringer, 1979).

The in-plane components of the $\boldsymbol{\varepsilon}$ tensor of the H atoms from ADP's (Table 5), spectroscopy and *ab initio* calculations (Table 7) show small but systematic differences: ε_{11} from diffraction is larger than ε_{11} from spectroscopy, while the reverse holds for ε_{22} (as in the case of benzene). The diffraction value of ε_{33} obtained for model w1 agrees best with the spectroscopic and *ab initio* calculated values. The same observation applies to ε_{33}(C, N, O), in spite of the fact that the values of $\bar{\varepsilon}_{33}$(C, N, O) given in Tables 5(*a*) and 5(*b*) are about twice the values of $\bar{\varepsilon}_{33}$(C, N, O) in Table 7. From this comparison, it appears again that model w1 is most consistent with non-diffraction information.

A further differentiation of the models with the help of diffraction experiments would require additional data at temperatures higher than 123 K, so that the classical region of the temperature dependence of the mean square amplitudes could be explored more fully.

Table 8

Rigid-body libration (**L**), translation (**T**) and screw-coupling (**S**) tensors for the in-plane (i.p.) and out-of-plane motions (o.o.p.) calculated from the frequencies and eigenvectors refined with model w1 as compared with those determined by Swaminathan *et al.* (1984).

The coordinate system is defined with the x axis along the C═O bond and with the z axis orthogonal to the molecular plane. The Cartesian coordinates used by Swaminathan *et al.* (1984) in their thermal-motion analysis and originally proposed by Ishii & Scheringer (1979) have been transformed to the coordinates used in this work using the transformation matrix [1 0 0; 0 0 −1; 0 1 0]. This transformation applies also to U^{ij}'s.

		ADP analysis from model w1			Thermal-motion analysis (Swaminathan *et al.*, 1984)		
		12 K	60 K	123 K	12 K	60 K	123 K
i.p.	L_{33} (rad^2)	0.0014 (1)	0.0015 (1)	0.0021 (1)	0.0013	0.0015	0.0019
	T_{11} (Å^2)	0.0027 (1)	0.0032 (1)	0.0050 (2)	0.0040	0.0047	0.0067
	T_{22} (Å^2)	0.0046 (1)	0.0073 (1)	0.0132 (3)	0.0061	0.0085	0.0148
	S_{32} (rad Å)	0.0003 (1)	0.0005 (1)	0.0011 (1)	0.0004	0.0005	0.0011
o.o.p.	L_{11} (rad^2)	0.0053 (1)	0.0082 (1)	0.0149 (3)	0.0055	0.0087	0.0150
	L_{22} (rad^2)	0.0026 (1)	0.0028 (1)	0.0038 (3)	0.0033	0.0048	0.0080
	T_{33} (Å^2)	0.0046 (1)	0.0075 (2)	0.0136 (4)	0.0062	0.0091	0.0150
	S_{23} (rad Å)	0.0004 (2)	0.0008 (1)	0.0016 (2)	0.0013	0.0020	0.0042

The limitation in the data presently available can be estimated with the help of the modified Einstein approximation described in paper I. At the Einstein temperature (Einstein, 1907)

$$\Theta_E(K) = (hc/k_B)\tilde{\nu} = 1.44\tilde{\nu}(\mathrm{cm}^{-1}), \qquad (2)$$

a harmonic oscillator with frequency $\tilde{\nu}$ closely follows the classical model; specifically, ~95% of the total mean square amplitude is of classical origin (see Fig. 3 in paper I). This implies that, for the higher frequencies to be determined reliably, ADP's must be available at sufficiently high temperatures. In the present case, the highest temperature is only 123 K, indicating that frequencies larger than ~85 cm^{-1} are not well determined.

After having identified model w1 as being the most consistent with all available non-diffraction information, it remains to compare the **L**, **T** and **S** tensors derived from this model with the corresponding values obtained by Swaminathan *et al.* (1984) for their segmented rigid-body model (iv) and to analyse the origin of the unphysical negative mean-square-amplitude quantity reported by these authors. Table 8 shows that only L_{33} and S_{32} are the same in both analyses, while all other elements are larger in Swaminathan's work. The in-plane translation elements T_{11} and T_{22} are larger, at all temperatures, by ~0.0015 Å on average. The difference is practically equal to the in-plane components of the $\boldsymbol{\varepsilon}$ tensors of the heavier atoms given in Table 5(*a*) and shows that what is taken into account by the $\boldsymbol{\varepsilon}$ tensors in our model has to be compensated in a conventional rigid-body analysis by increasing the components of the **T** tensor. An analogous observation has been reported for benzene in a preceding section.

In Swaminathan's work, differences of the observed atomic displacement parameters of H and N atoms along the internuclear vectors $\Delta u_{\mathrm{NH}} = \langle u_{\mathrm{H}}^2\rangle - \langle u_{\mathrm{N}}^2\rangle$ were assumed to represent the mean square amplitude of the N—H bond stretching and have been used as a constant contribution to the model atomic displacement parameters. The differences vary between 0.0046 and 0.0057 Å^2, and are thus comparable to the difference of the ε_{11} components for hydrogen and nitrogen calculated with model w1 [$\Delta\varepsilon = \varepsilon_{11}(\mathrm{H}) - \bar{\varepsilon}_{11}(\mathrm{N, C, O}) = 0.0051$ Å^2). Swaminathan *et al.* (1984) account for in-plane angle bending of the H atoms in terms of a rotation about an axis perpendicular to the molecular plane and passing through the N atom. Its mean square amplitude Ω_2 varies in the range 0.0116 to 0.0101 rad^2, in good agreement with the in-plane ε_{22} component for the H atoms given in Table 7; if the latter is transformed from Å to rad units, it is 0.0119 rad^2.

The comparison of out-of-plane components is more complicated because of the different models of motion used in describing these degrees of freedom. The agreement between the values of L_{11} determined by us and by Swaminathan *et al.* (1984) is good; larger discrepancies, which increase with temperature, are found for L_{22} (Table 8; the latter may imply a slight overcorrection of bond lengths at 60 and 123 K in the earlier analysis).

The important differences between the two models are found in the contributions to U^{33}(H1) and U^{33}(H2), which are given in Table 9 at 12, 60 and 123 K. In model (iv) of Swaminathan *et al.* (1984), the out-of-plane components of the ADP's are parameterized with four overall rigid-body amplitudes (L_{11}, L_{22}, T_{33} and S_{23}) plus an additional torsion about the C—N bond with mean square amplitude Ω_1. Couplings between the internal and external motions were not considered. Because of its definition as a torsional mode, the contribution of Ω_1 is the same for H1 and H2 and it is directly comparable with $\langle uu\rangle$ (Table 9). In our model, there is the additional contribution from the coupling element $\langle ul_x\rangle$ and the temperature-independent term ε_{33}. The former has a negative sign and is far from being negligible: its absolute value is always bigger than the contribution from $\langle uu\rangle$. This is relevant especially in the case of H1 at 123 K where the contribution coming from the coupling element dominates the internal contributions to U^{33} (see line 'sum INT' in Table 9). The large negative values deriving from $\langle ul_x\rangle$ are another expression of the fact that pyramidalization preferentially combines with molecular libration and translation in a way that keeps hydrogen displacements small. We conclude that the physically impossible negative value of the contribution coming from Ω_1 at 123 K in Swaminathan *et al.* (1984) is a

Table 9

Contributions to U^{33}(H1) and to U^{33}(H2) from translations, librations and internal motions calculated according or in analogy to Table 1 of Schomaker & Trueblood (1968).

		ADP analysis from model w1 (Å^2)			Thermal-motion analysis (Swaminathan *et al.*, 1984) (Å^2)		
		12 K	60 K	123 K	12 K	60 K	123 K
H1	y^2L_{11}	0.0216	0.0336	0.0608	0.0226	0.0356	0.0612
	x^2L_{22}	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002
	T_{33}	0.0046	0.0075	0.0136	0.0062	0.0091	0.0150
	$-2xS_{23}$	0.0001	0.0002	0.0005	0.0004	0.0006	0.0013
	sum **LTS**†	*0.0264*	*0.0414*	*0.0750*	*0.0293*	*0.0454*	*0.0777*
	ε_{33}	0.0263	0.0263	0.0263	–	–	–
	$2xq\langle ul_x\rangle$‡	−0.0144	−0.0226	−0.0408	–	–	–
	$q^2\langle uu\rangle$‡	0.0024	0.0038	0.0068	0.0125§	0.0042§	−0.0112§
	sum INT¶	*0.0142*	*0.0075*	*−0.0077*	*0.0125*	*0.0042*	*−0.0112*
	$U_{\rm calc}$	0.0407	0.0489	0.0673	0.0418	0.0496	0.0663
	$U_{\rm obs}$	0.0420	0.0495	0.0662	0.0420	0.0495	0.0662
H2	y^2L_{11}	0.0068	0.0105	0.0190	0.0071	0.0112	0.0192
	x^2L_{22}	0.0070	0.0075	0.0103	0.0089	0.0131	0.0217
	T_{33}	0.0046	0.0075	0.0136	0.0062	0.0091	0.0150
	$-2xS_{23}$	0.0014	0.0027	0.0054	0.0043	0.0066	0.0138
	sum **LTS**†	*0.0198*	*0.0282*	*0.0483*	*0.0265*	*0.0400*	*0.0697*
	ε_{33}	0.0263	0.0263	0.0263	–	–	–
	$2xq\langle ul_x\rangle$‡	−0.0092	−0.0142	−0.0257	–	–	–
	$q^2\langle uu\rangle$‡	0.0031	0.0048	0.0087	0.0125§	0.0042§	−0.0112§
	sum INT¶	*0.0202*	*0.0169*	*0.0093*	*0.0125*	*0.0042*	*−0.0112*
	$U_{\rm calc}$	0.0400	0.0451	0.0576	0.0390	0.0442	0.0583
	$U_{\rm obs}$	0.0388	0.0439	0.0588	0.0388	0.0439	0.0588

† Partial sum of the contributions coming from rigid-body motion. ‡ q indicates the distance of the H atom from the C—N axis, used to define the out-of-plane coordinate u. § Contribution from the torsional motion Ω_1. ¶ Partial sum of the contributions coming from the internal coordinate u and the temperature-independent $\boldsymbol{\varepsilon}$ tensor.

result of neglecting the coupling elements between external and internal modes.

In conclusion, the analysis of the ADP's of the urea molecule at 12, 60 and 123 K revealed at least one unexpected result: external degrees of freedom combine with a significant proportion of a pyramidalization of the NH_2 group to give rise to low-frequency normal modes. Such couplings between external and internal vibrations are usually not taken into account in calculations in the crystal phase. They are assumed to be small because of the large frequency gap found in the IR and Raman spectra at the origin of the Brillouin zone [a possible exception is Derreumaux *et al.* (1990): their Table IV indicates a coupling of libration and NH_2 pyramidalization but the text does not give any details]. This work shows that this assumption may be wrong in the presence of reasonably strong intermolecular interactions.[2]

4. Conclusions

The temperature evolution of the anisotropic displacement parameters of benzene and urea from neutron diffraction experiments has been analysed in terms of a model that takes into account the temperature dependence of mean square amplitudes and can separate the temperature-dependent low-frequency high-amplitude contributions to ADP's from the temperature-independent high-frequency low-amplitude ones. For both molecules, the numerical results obtained by ADP analysis are in good agreement with corresponding spectroscopic data or with results from *ab initio* calculations.

In the case of benzene, a temperature-dependent rigid-body model has been successfully fitted to the observed data. Temperature-independent contributions to ADP's from high-frequency internal motions have been extracted directly and for the first time from the diffraction data, for both D and C atoms.

For urea, the experimental data could be explained only by combining molecular libration and translation with a pyramidalization of the NH_2 groups into a low-frequency normal mode. Pyramidal deformations could be distinguished from torsional ones. The analysis has also shown that, contrary to segmented rigid-body analysis at a single temperature (Bürgi, 1989; Schomaker & Trueblood, 1998), the coupling elements between internal and external motions are accessible through the temperature evolution of ADP's. In other words, ADP's are a sensitive probe for correlations between atomic displacements, which may not be accessible from spectroscopic data alone. Measuring such correlations from the temperature evolution of ADP's allows one to investigate experimentally how molecular structure in the condensed phase responds to a change in environment and how molecular environment adapts to changes in molecular structure. These phenomena are intimately connected with structural changes occurring during chemical reactions.

We hope to have shown that ADP analysis reproduces dynamical features observed with other techniques, thus indicating the usefulness of ADP's for studying the dynamics

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[2] Supplementary data containing relevant parts of the output file of the ADP analysis performed on neutron diffraction data from urea are available from the IUCr electronic archives (Reference: BK0074). Services for accessing these data are described at the back of the journal.

of molecular crystals even when results from other techniques are not easily available. Effects due to anharmonicity, disorder and the use of approximate spherical atomic form factors, which complicate the analysis of ADP's, will be discussed in later papers.

The authors are grateful to Professors K. Parlinski, G. Chapuis and C. Van Alsenoy and Mr B. Rousseau for providing numerical data used in Tables 6 and 7, respectively.

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