

# The Crystal Structure and Molecular Thermal Motion of Urea at 12, 60 and 123 K from Neutron Diffraction

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## Abstract

Lattice parameters for urea have been measured at seven temperatures in the range 12 to 173 K and the crystal structure has been determined at 12, 60 and 123 K from neutron diffraction data. With 342 reflections ( $\sin \theta/\lambda < 0.77 \text{ \AA}^{-1}$ ) measured for an octant of reciprocal space, full-matrix least-squares refinement gave  $R_w(F^2) = 0.030, 0.029$  and  $0.029$  at 12, 60 and 123 K. The atomic anisotropic thermal parameters are consistent with overall rigid-body motion together with intramolecular librations of the  $\text{NH}_2$  groups. With increasing temperature, the H-atom motion out of the molecular plane becomes dampened with respect to the overall rigid-body motion. The effect appears to be due to the H-bonding which couples the molecules in the crystal. After correction for thermal motion, including anharmonic N–H stretching, there is good agreement in the bond lengths at 12, 60 and 123 K. [Crystal data:  $P4_21m$ ; 12 K:  $a = 5.565$  (1),  $c = 4.684$  (1)  $\text{\AA}$ ; 30 K:  $a = 5.565$  (1),  $c = 4.685$  (1)  $\text{\AA}$ ; 60 K:  $a = 5.570$  (1),  $c = 4.688$  (1)  $\text{\AA}$ ; 90 K:  $a = 5.576$  (1),  $c = 4.689$   $\text{\AA}$ ; 123 K:  $a = 5.584$  (1),  $c = 4.689$  (1)  $\text{\AA}$ ; 150 K:  $a = 5.590$  (1),  $c = 4.692$  (1)  $\text{\AA}$ ; 173 K:  $a = 5.598$  (1),  $c = 4.694$  (1)  $\text{\AA}$ .]

## Introduction

The crystal structure of urea ( $\text{CH}_4\text{N}_2\text{O}$ ) has been studied repeatedly because of its simplicity.\* Thus the number of atomic parameters to be determined is a minimum since the molecule lies in a special position of the space group  $P4_21m$  where the molecular point symmetry ( $mm2$ ) is fully utilized. A feature of chemical interest in the urea structure is that it appears to provide the only instance of a carbonyl O atom which accepts four  $\text{N-H}\cdots\text{O}$  hydrogen bonds (Fig. 1).

\* See Caron & Donohue (1964, 1969) for references to earlier work.

The crystal structure of urea has been determined from neutron diffraction data at room temperature by Pryor & Sanger (1970) and at 60, 123 and 293 K by Guth, Heger, Klein, Treutmann & Scheringer (1980). The present neutron diffraction studies were undertaken when large discrepancies were found between the anisotropic thermal parameters at 123 K reported by Guth *et al.* (1980) and the corresponding values obtained from an X-ray analysis at the same temperature (Swaminathan, Craven, Spackman & Stewart, 1984). It seemed desirable to investigate these discrepancies as part of a detailed extensive study of the molecular structure and thermal motion of urea over a range of temperature. Accordingly, our neutron diffraction data were collected at 12, 60 and 123 K.

## Experimental

Urea crystals grown from aqueous urea solution with a trace amount of ammonium bromide. Crystal used for neutron diffraction study had forms  $\{110\}$  and  $\{001\}$ ; crystal  $0.8 \times 0.8 \times 1.8$  mm, measured with a microscope, volume  $1.15 \text{ mm}^3$  in agreement with volume ( $1.17 \text{ mm}^3$ ) calculated from crystal weight ( $1.55 \text{ mg}$ ) and density ( $1.330 \text{ g cm}^{-3}$ ) measured by flotation in benzene/bromoform. Neutron data collected at Brookhaven High Flux Beam Reactor,

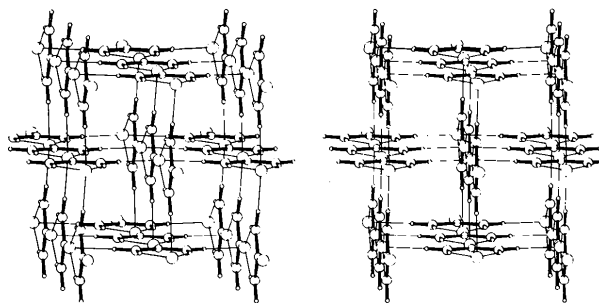


Fig. 1. The crystal structure of urea viewed approximately along the  $c$  axis.

Table 1. Lattice parameters (Å) for urea

The e.s.d. in all values is 0.001 Å.

	12 K	30 K	60 K*	90 K	123 K*†	150 K	173 K
<i>a</i>	5.565	5.565	5.570	5.576	5.584	5.590	5.598
<i>c</i>	4.684	4.685	4.688	4.689	4.689	4.692	4.694

\* There is agreement within experimental error with the neutron values of Guth *et al.* (1980): *a* = 5.572 (8), *c* = 4.686 (8) Å at 60 K; *a* = 5.578 (5), *c* = 4.695 (5) Å at 123 K.

† X-ray values (Mo K $\alpha$ ) at 123 K (Swaminathan, Craven, Spackman & Stewart, 1984) are *a* = 5.578 (1), *c* = 4.686 (1) Å. These agree with the X-ray values of Mullen & Hellner (1978), *a* = 5.576 (3), *c* = 4.686 (3) Å.

monochromated beam from (220) planes of Ge single crystal, transmission geometry;  $\lambda = 1.0791$  (2) Å, determined using standard KBr crystal (*a*<sub>0</sub> = 6.6000 Å at 295 K). Urea crystal mounted with <001> direction approximately 12° from  $\varphi$  axis of four-circle diffractometer, following experimental procedures previously described (Weber, Craven & McMullan, 1983). Crystal temperature maintained with a closed-cycle helium refrigerator\* within  $\pm 0.5^\circ$  of preset values.† Lattice parameters (Table 1) determined by least-squares fit to  $\sin^2 \theta$  values of 32 reflections with  $50 < 2\theta < 55^\circ$  measured at seven temperatures from 12 to 173 K.

Intensity data for reflections in one octant of reciprocal space comprising two equivalent sectors collected at 12, 60 and 123 K by  $\omega/2\theta$  step scan, scan width  $3.36^\circ$  in  $\Delta 2\theta$  up to  $\sin \theta/\lambda = 0.39 \text{ \AA}^{-1}$ . Beyond this and up to the max.  $\sin \theta/\lambda = 0.77 \text{ \AA}^{-1}$ , scan width computed according to  $\Delta 2\theta^\circ = (0.2 + 7.82 \tan \theta)$ . Intensities of two reflections monitored every 50 reflections, constant within 2%. Integrated intensities evaluated assuming background consists of first and last tenths of the total number of steps; data corrected for absorption by an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973);  $\mu = 0.23 \text{ mm}^{-1}$  calculated assuming mass absorption coefficient for hydrogen to be  $25.3 \text{ m}^2 \text{ kg}^{-1}$  (McMullan & Koetzle, 1979). Intensities of symmetry-related reflections agreed within 2%.

Refinements carried out with modified version of full-matrix least-squares program of Busing, Martin & Levy (1962);  $\sum w(F_o^2 - F_c^2)^2$  minimized,  $w = \sigma^{-2}(F^2)$ ,  $\sigma^2(F^2) = \sigma^2 + (0.01 F^2)^2$ , the sum being over reflections in an octant of reciprocal space. Neutron coherent scattering lengths from Koester (1977). In the initial stages of refinement, isotropic extinction parameter used as a variable in addition to scale factor and nuclear positional and thermal parameters; goodness of fit improved greatly (from 1.45 to 1.14

\* Air Products & Chemicals, Inc., Displex Model CS-202.

† The reported temperatures (Table 1) include a correction of  $+2.5^\circ$  based on a prior calibration with reference to the magnetic phase transition in FeF<sub>2</sub> at 78.4 K (Hutchings, Schulhof & Guggenheim, 1972).

Table 2. Structure refinements

	12 K	60 K	123 K
No. of reflections	342	341	342
$R_w(F^2)^*$	0.030	0.029	0.029
$R(F^2)$	0.025	0.025	0.028
Goodness of fit, <i>s</i>	1.38	1.29	1.14
$g_{11} (\times 10^4 \text{ rad}^{-1})^\dagger$	5.7 (6)	5.4 (5)	5.3 (5)
$g_{33}$	34 (3)	34 (3)	35 (3)

\*  $R_w(F^2) = \{\sum w \Delta^2 / \sum w F_o^4\}^{1/2}$ ,  $R(F^2) = \sum \Delta^2 / \sum F_o^2$ ;  $s = \{\sum w \Delta^2 / (\sum n_{\text{obs}} - \sum n_{\text{param}})\}^{1/2}$ , where  $\Delta = |F_o|^2 - |F_c|^2$ , and the summation is over reflections in two equivalent sectors in reciprocal space.

† Extinction parameters are for a model of type I with Lorentzian mosaicity, having  $g_{11} = g_{22}$ ;  $g_{12} = g_{13} = g_{23} = 0$ .

Table 3. Nuclear positional parameters ( $\times 10^4$ )

The atoms are in the special position of space group  $P\bar{4}2_1m$  at  $x, \frac{1}{2} + x, z$ ;  $-x, \frac{1}{2} - x, z$ ;  $\frac{1}{2} + x, -x, -z$ ;  $\frac{1}{2} - x, x, -z$ . The values are at: (I) 123 K, (II) 60 K, (III) 12 K.

		<i>x</i>	<i>y</i>	<i>z</i>
C	I	0	5000	3280 (2)
	II	0	5000	3265 (2)
	III	0	5000	3260 (2)
O	I	0	5000	5962 (2)
	II	0	5000	5954 (2)
	III	0	5000	5953 (2)
N	I	1447 (1)	6447	1785 (1)
	II	1455 (1)	6455	1771 (1)
	III	1459 (1)	6459	1766 (1)
H(1)	I	2557 (4)	7557	2841 (4)
	II	2569 (4)	7569	2832 (3)
	III	2575 (3)	7575	2827 (3)
H(2)	I	1431 (4)	6431	-348 (3)
	II	1438 (4)	6438	-371 (3)
	III	1441 (4)	6441	-380 (3)

for the 123 K data) when anisotropic extinction parameters  $g_{11}$  and  $g_{33}$  (Becker & Coppens, 1974) introduced, giving 29 variables for each refinement; details of refinements at the three temperatures are given in Table 2. The final positional and anisotropic thermal parameters are given in Tables 3 and 4.\*

## Discussion

At each temperature and for each atom in the molecule, the mean-square (m.s.) amplitude of nuclear thermal motion is considerably less along the tetragonal *c*-axis direction than in directions normal to *c* (Table 4). Also, the *a* and *c* lengths are almost proportional to the temperature in the range 30 to 173 K (Fig. 2) but the expansion is smaller for *c* than *a* ( $0.4$  vs  $2.31 \times 10^4 \text{ K}^{-1}$ ). These observations can be explained qualitatively in terms of the molecular arrangement and the three-dimensional H-bonding network in the crystal structure (Fig. 1). As seen in the projection down *c*, the structure is quite open with

\* Lists of observed and calculated structure factors and experimental and calculated thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39212 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Nuclear anisotropic thermal parameters ( $\times 10^4 \text{ \AA}^2$ )

The temperature-factor expression is

$T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$ , with  $U_{ij}$  values referred to the crystal axial system. The values are at: (I) 123 K, (II) 60 K, (III) 12 K.

		$U_{11} = U_{22}$	$U_{33}$	$U_{12}$	$U_{13} = U_{23}$
C	I	147 (5)	65 (3)	1 (4)	0
	II	88 (4)	47 (3)	-1 (3)	0
	III	63 (4)	35 (3)	2 (3)	0
O	I	197 (6)	63 (4)	17 (5)	0
	II	121 (5)	39 (4)	1 (4)	0
	III	87 (5)	32 (4)	2 (4)	0
N	I	286 (4)	95 (2)	-147 (2)	2 (3)
	II	167 (3)	69 (2)	-84 (2)	3 (3)
	III	113 (3)	59 (2)	-52 (2)	4 (2)
H(1)	I	440 (11)	216 (7)	-222 (8)	-31 (9)
	II	325 (9)	196 (8)	-170 (7)	-25 (8)
	III	277 (9)	185 (7)	-143 (6)	-29 (8)
H(2)	I	430 (10)	140 (6)	-158 (8)	19 (8)
	II	331 (9)	122 (6)	-108 (8)	21 (8)
	III	294 (8)	116 (6)	-94 (7)	15 (7)

X-ray diffraction values at 123 K for  $U_{11}$ ,  $U_{33}$ ,  $U_{12}$  are 138 (6), 59 (4), -31 (7) for C; 200 (7), 66 (4), 10 (11) for O; 276 (5), 100 (3), -155 (5) and -15 (3) ( $U_{13}$ ) for N (Swaminathan, Craven, Spackman & Stewart, 1984). According to the  $\chi^2$  test, these values and the above neutron diffraction values can be accepted as having a common probability distribution at the 93% level of confidence. There are highly significant differences from the neutron diffraction values reported by Guth *et al.* (1980), such as  $U_{33} = 0.0119 (5) \text{ \AA}^2$  for the O atom at 123 K. In a similar  $\chi^2$  test involving the two sets of neutron diffraction values, the confidence level is less than 1%.

the molecules and the H-bonds confined to planes parallel to (110), ( $1\bar{1}0$ ) which intersect and leave tunnels having a square cross section  $3.94 \times 3.94 \text{ \AA}$ . The largest amplitudes of atomic vibration are normal to  $c$  because of the relatively greater freedom for motion of the  $\text{NH}_2$  groups into the tunnels. Motion parallel to  $c$  is hindered because it occurs within the walls of the tunnels where the atoms are closely packed.

A detailed analysis of thermal parameters for the individual nuclei requires that assumptions be made concerning the nature of the molecular vibrations. Corrections to the urea bond lengths of Guth *et al.* (1980), which were proposed by Scheringer (1980), involve the rigid-body motion of urea together with important intramolecular motion of the H atoms. The latter was determined from the infrared and Raman spectra of crystalline urea, assuming that the molecules vibrate independently (Yamaguchi, Miyazawa, Shimanouchi & Mizushima, 1957; Saito, Machida & Uno, 1971; Ishii & Scheringer, 1979). However, the results of the present structure determinations of urea at 12, 60 and 123 K indicate that the H-atom motion is significantly influenced by the intermolecular H-bonding interactions in the crystal structure.

Four models describing the thermal motion of urea in the crystal have been tested by comparison of the calculated anisotropic thermal parameters at 12, 60 and 123 K with those obtained from the neutron diffraction data.\* The thermal-motion analyses were carried out in the molecular axial system defined by

Ishii & Scheringer (1979) because the thermal parameters are then easily related to the molecular geometry. In this Cartesian system, the  $x$  axis is along the molecular twofold axis and the  $y$  axis is normal to the molecular plane. The transformed anisotropic thermal parameters consist of eighteen independent  $U_{11}$ ,  $U_{22}$ ,  $U_{33}$  and  $U_{13}$  observations. For least-squares fitting, using programs by Craven & He (1982), the residual  $\sum w\Delta^2$  was minimized, where  $\Delta = |(U_{ij})_o| - |(U_{ij})_c|$  and  $w = \sigma^{-2}(U_{eq})$ , and the agreement indices were taken to be  $R_w = \{\sum w\Delta^2 / \sum w(U_{ij})_o^2\}^{1/2}$  and  $s = \{\sum w\Delta^2 / (m-n)\}^{1/2}$ , where  $(m-n)$  is the number of degrees of freedom. Owing to the  $2mm$  symmetry of urea, the rigid-body model for the thermal vibrations (Schomaker & Trueblood, 1968) requires eight molecular parameters;  $T_{11}$ ,  $T_{22}$ ,  $T_{33}$ ,  $L_{11}$ ,  $L_{22}$ ,  $L_{33}$ ,  $S_{23}$  and  $S_{32}$ . Although there are ten degrees of freedom, the four parameters  $T_{22}$ ,  $L_{11}$ ,  $L_{33}$  and  $S_{32}$ , which describe m.s. displacements normal to the molecular plane, are determined with only one degree of freedom. They depend exclusively on the five  $(U_{22})_o$  values. The remaining four parameters which describe m.s. displacements within the molecular plane are thus determined with nine degrees of freedom. Because of this partitioning,  $R_w$  values are given for the out-of-plane ( $U_{22}$ ) and in-plane ( $U_{11}$ ,  $U_{33}$ ,  $U_{13}$ ) components as well as for the overall fit of the models (Table 5).

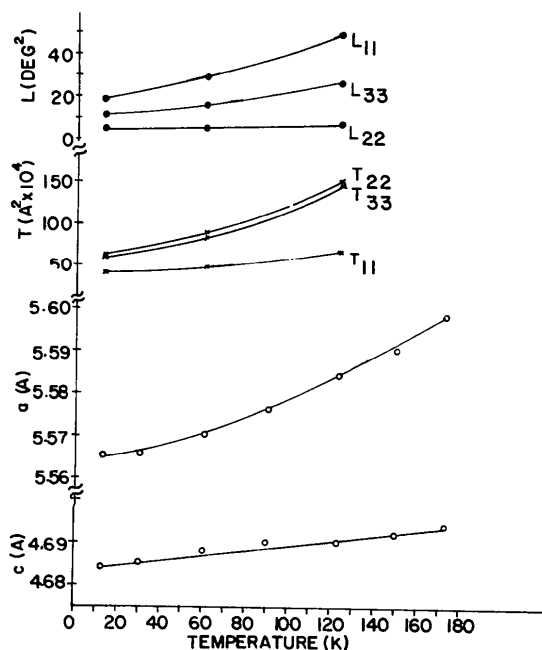


Fig. 2. M.s. amplitudes of overall rigid-body librational ( $L_{ii}$ ) and translational ( $T_{ii}$ ) motion and the crystal lattice translations ( $a$ ,  $c$ ) as a function of temperature. The temperature dependence is greatest for  $L_{11}$ ,  $L_{33}$ ,  $T_{22}$ ,  $T_{33}$  and  $a$ . Thus, there is a correlation between the directions of preferred atomic thermal motion and greatest thermal expansion in the crystal structure, these being normal to  $c$ .

\* See deposition footnote.

Table 5. Agreement factors in the thermal-motion analysis

Weighted  $R$  factors,  $R_w = \{\sum w\Delta^2/\sum wU_o^2\}^{1/2}$ , are given where  $U_o$  values are experimentally determined  $(U_{ij})_o$  values transformed to the molecular axial system of Ishii & Scheringer (1979) and  $\Delta = |U_o| - |U_c|$ . Models for the thermal motion are: (i) simple rigid body; (ii) rigid body with internal modes taken as the  $U_o$  values at 12 K; (iii) rigid body with internal modes estimated from IR spectra (Scheringer, 1980); (iv) rigid body with two internal librational parameters. For each model and temperature, the agreement is given for all  $\Delta$  values (overall), for  $U_{22}$  values only (out-of-plane), and for  $U_{11}$ ,  $U_{33}$  and  $U_{13}$  values (in-plane).

	Model	12 K	60 K	123 K
(i)	Overall	0.20	0.13	0.09
	Out-of-plane	0.15	0.04	0.06
	In-plane	0.30	0.24	0.16
(ii)	Overall	—	0.07	0.12
	Out-of-plane	—	0.08	0.13
	In-plane	—	0.04	0.04
(iii)	Overall	0.13	0.17	0.18
	Out-of-plane	0.15	0.19	0.20
	In-plane	0.07	0.06	0.05
(iv)	Overall	0.03	0.02	0.02
	Out-of-plane	0	0	0
	In-plane	0.05	0.04	0.03

(i) In the first model, it was assumed that the entire urea molecule vibrates as a simple rigid body. The fit was poor (Table 5), with overall values of  $s = 7.5$ ,  $5.1$  and  $4.9$  at 12, 60 and 123 K, respectively. When the H atoms are excluded, the remaining four atoms of the molecule lie on two intersecting straight lines so that the complete rigid-body model cannot be fitted by least squares (Johnson, 1970). If the  $S$ -tensor components are arbitrarily set to zero (following Scheringer, 1980), the fit for the  $\text{OCN}_2$  group gives  $R_w = 0.04$ , but such a model has ambiguous physical interpretations.

(ii) In this model, it is assumed that at 12 K the  $(U_{ij})_o$  values give an estimate of the zero-point motion of the atoms. As the temperature is raised to about 300 K, the internal modes are supposed to remain close to their ground state (Ishii & Scheringer, 1979) and to be unaffected by intermolecular coupling. Thus, the  $(U_{ij})_o$  values for 12 K can be subtracted from the values at the higher temperatures to give differences which should conform to simple rigid-body motion. Although the overall fit for this model (Table 5) was no better than for (i), the fit is satisfactory for the thermal motion within the molecular plane.

(iii) In this model, our neutron data are used to test the proposal (Scheringer, 1980) that the m.s. amplitudes for non-rigid vibrational modes can be estimated from spectroscopic studies of urea (see Table 2 in Ishii & Scheringer, 1979).<sup>\*</sup> It follows as in model (ii) that the  $(U_{ij})_o$  values, after subtraction of the estimated contributions from intramolecular

modes, should conform to simple rigid-body motion. The results obtained were similar to those for model (ii), with satisfactory agreement only for the in-plane thermal motion (Table 5).

(iv) In this model, the urea molecule is assumed to vibrate as a rigid body but with the inclusion of two selected librations to simulate non-rigid motion of the  $\text{NH}_2$  groups (Dunitz & White, 1973). The non-rigidity of the  $\text{NH}_2$  groups is strongly indicated by the observed differences  $\Delta_{AB} = \langle u_A^2 \rangle - \langle u_B^2 \rangle$ , where  $\langle u_A^2 \rangle$  and  $\langle u_B^2 \rangle$  are mean-square displacements for intramolecular pairs of atoms  $A$  and  $B$ , calculated along the internuclear line  $A \cdots B$  using the  $(U_{ij})_o$  values. Whereas at 12 K the values  $\Delta_{\text{CO}} = 0.0003$  (5),  $\Delta_{\text{CN}} = 0.0001$  (4) and  $\Delta_{\text{ON}} = 0.0008$  (5)  $\text{\AA}^2$  are consistent with an effectively rigid  $\text{OCN}_2$  group,<sup>\*</sup> there are highly significant  $\Delta$  values involving H atoms. Thus  $\Delta_{\text{NH}(1)} = 0.0046$  (8),  $\Delta_{\text{NH}(2)} = 0.0057$  (7),  $\Delta_{\text{CH}(1)} = \Delta_{\text{CH}(2)} = 0.0078$  (9),  $\Delta_{\text{OH}(1)} = 0.0121$  (9) and  $\Delta_{\text{OH}(2)} = 0.0112$  (9)  $\text{\AA}^2$ . The value  $\Delta_{\text{HH}} = 0.0021$  (10)  $\text{\AA}^2$  is only marginally significant. In this model, the  $\Delta_{\text{NH}}$  values are assumed to represent the m.s. amplitudes for N–H bond stretching and they are included as fixed contributions to the  $(U_{ij})_c$  values. Within each of the equivalent  $\text{NH}_2$  groups, librational axes are introduced so that the two H atoms librate with m.s. amplitude  $\Omega_1$  about the C–N bond, and with m.s. amplitude  $\Omega_2$  about an axis through the N atom and normal to the plane of the molecule. Since the thermal parameters represent time averages for each atom with no indication of how the H-atom motions are correlated, the parameter  $\Omega_1$  does not distinguish between symmetric displacements of H atoms from the molecular plane, or their torsional motion or some combination of out-of-plane motions. Similarly, the parameter  $\Omega_2$  represents either a scissor motion or an in-plane bending motion or a combination of such in-plane motions.

With the inclusion of  $\Omega_1$  and  $\Omega_2$  as parameters, the out-of-plane thermal motion is determined with no degrees of freedom. Thus the observed and calculated  $U_{22}$  values agree exactly and  $T_{22}$ ,  $L_{11}$ ,  $L_{33}$ ,  $S_{32}$ ,  $\Omega_1$  are completely specified in terms of the assumed model. The fit for the in-plane thermal motion is an improvement over the other models (Table 5), giving  $s = 1.34$ ,  $1.04$ ,  $1.16$  at 12, 60 and 123 K. The resulting molecular thermal parameters are in Table 6.

The direction of least molecular translational motion ( $T_{11}$ ) is along the direction of the symmetry axis, and is almost independent of temperature (12–123 K). The least librational motion ( $L_{22}$ ) is about the axis normal to the molecular plane and this is also

<sup>\*</sup> So far as we know, spectroscopic data have not been reported for crystalline urea at reduced temperature.

<sup>\*</sup> A value  $\Delta = 0$  is a necessary but not sufficient condition for a bond to be rigid. However, for the  $\text{OCN}_2$  framework, the effects of non-rigidity are likely to be very small for 12 to 123 K (Ishii & Scheringer, 1979). At 123 K,  $\Delta_{\text{CO}} = 0.0002$  (5),  $\Delta_{\text{CN}} = 0.0001$  (3),  $\Delta_{\text{ON}} = 0.0003$  (5)  $\text{\AA}^2$ .

almost temperature independent (Fig. 2). The  $S_{32}$  component, which correlates the rigid-body libration about the molecular  $z$  axis with the translation normal to the molecular plane, has considerable magnitude even at 12 K.

It is of interest that among the parameters  $\Omega_1$ ,  $\Omega_2$  and  $\Delta_{\text{NH}}$  which describe the non-rigidity of the molecule, the two which are concerned with in-plane motion ( $\Omega_2$  and  $\Delta_{\text{NH}}$ ) are found to be independent of temperature within the experimental error. The average m.s. amplitudes for the three temperatures are  $0.0051(5) \text{ \AA}^2$  for N-H bond stretching and  $0.0111(6) \text{ \AA}^2$  for H...H in-plane motion. These are in reasonable agreement with spectroscopic and electron diffraction values  $0.0053$ ,  $0.0061 \text{ \AA}^2$  (N-H) and  $0.0081$ – $0.0144 \text{ \AA}^2$  (H...H) for gaseous  $\text{NH}_3$  (Cyvin, 1968), and with the corresponding spectroscopic values  $0.0053 \text{ \AA}^2$  and  $0.0135 \text{ \AA}^2$  for urea estimated by Ishii & Scheringer (1979) and included in model (iii).<sup>\*</sup> In contrast, the parameter  $\Omega_1$ , which describes out-of-plane motion of the H atoms, decreases notably with increasing temperature, having a negative value at 123 K.<sup>†</sup> The effect described by the  $\Omega_1$  libration can be seen qualitatively in the experimental data in terms of the relative elongation of the probability ellipsoids normal to the molecular plane as the temperature increases (Fig. 3). The elongation for the C, N and O atoms is noticeably greater than for the H atoms.

The principal advantage of model (iv) over models (ii) and (iii) comes from the greater flexibility in describing the out-of-plane vibrations of the H atoms. In model (iii) the m.s. amplitude for internal out-of-plane motion of the H atoms has a constant value of  $0.0244 \text{ \AA}^2$  (Ishii & Scheringer, 1979), considerably greater than the values derived from  $\Omega_1$  in Table 6, which are  $0.0164$ ,  $0.0055$  and  $-0.0146 \text{ \AA}^2$  at 12, 60 and 123 K.

A reasonable explanation for the temperature dependence of  $\Omega_1$  comes from the cross-linking of urea molecules by H bonding. As the temperature

Table 6. *Molecular thermal motion in urea*

Results are presented for model (iv), in which the molecule has overall rigid-body motion, with additional libration of rigid  $\text{NH}_2$  groups about the C-N bond ( $\Omega_1$ ) and an axis normal to the molecular plane through the N atom ( $\Omega_2$ ). Values of  $\Delta_{\text{NH}} = \langle u_{\text{H}}^2 \rangle - \langle u_{\text{N}}^2 \rangle$  for motion along the N-H bonds are used as fixed contributions to  $\langle U_{ij} \rangle_c$  values to account for N-H bond-stretching vibrations. The analysis is carried out in the Cartesian molecular axial system of Ishii & Scheringer (1979), with  $x$  along the molecular twofold axis and  $y$  normal to the molecular plane. The five parameters  $T_{22}$ ,  $L_{11}$ ,  $L_{33}$ ,  $S_{32}$ ,  $\Omega_1$  are given without e.s.d.'s because they are determined with no degrees of freedom.

		12 K	60 K	123 K
Translational tensor ( $\text{\AA}^2 \times 10^4$ )	$T_{11}$	40(2)	47(2)	67(3)
	$T_{22}$	62	91	150
	$T_{33}$	61(2)	85(2)	148(2)
Librational tensor [ $^\circ$ ] <sup>2</sup>	$L_{11}$	18.1	28.5	49.1
	$L_{22}$	4.3(5)	4.9(4)	6.4(5)
	$L_{33}$	10.7	15.6	26.4
Cross tensor ( $^\circ \text{\AA} \times 10^3$ )	$S_{23}$	-21(5)	-29(5)	-64(6)
	$S_{32}$	-74	-116	-238
Internal librations [ $^\circ$ ] <sup>2</sup>	$\Omega_1$	54	18	-48
	$\Omega_2$	38(2)	36(2)	33(3)
N-H stretching motion ( $\text{\AA}^2 \times 10^4$ )	$\Delta_{\text{NH}(1)}$	46(8)	51(8)	49(9)
	$\Delta_{\text{NH}(2)}$	57(7)	54(8)	46(8)

increases and the massive  $\text{OCN}_2$  fragment undergoes almost rigid vibration with increasing m.s. amplitude, the restraint imposed by H-bonding on the lighter H atoms is expected to cause a damping of their m.s. displacements relative to a system of uncoupled molecules. However, model (iv), like the others considered here, is limited by the assumption that the molecules in the crystal are vibrating independently. If the molecules are coupled by H-bonding, as inferred from model (iv), the proper physical interpretation of the thermal motion must await more advanced experimental and theoretical treatments in which the lattice vibrations are taken into account explicitly.

The bond lengths and angles for urea are given in Table 7, together with the corrections for thermal motion based on model (iv). Estimates of the correction for anharmonic thermal motion are also included

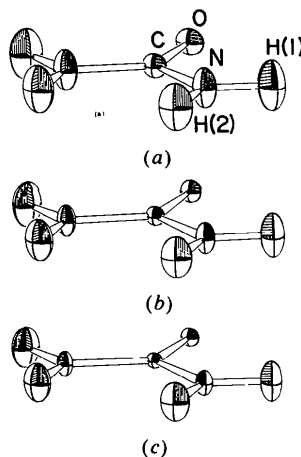


Fig. 3. Thermal ellipsoids for urea shown at the 50% probability level (Johnson, 1976), (a) 123 K, (b) 60 K, (c) 12 K.

<sup>\*</sup> We have also analyzed the  $U_{ij}$  values determined by neutron diffraction for urea in the 1:1 complex with hydrogen peroxide at 81 K (Fritchie & McMullan, 1981). The m.s. amplitudes for N-H stretching are  $0.0050$ ,  $0.0055(5) \text{ \AA}^2$ . With model (iv), which gives  $R_w = 0.013$  and  $s = 2.07$ , the values  $\Omega_1 = 9(4)$  and  $\Omega_2 = 39(2)$ <sup>02</sup> are very similar to those obtained for the crystal structure of urea.

<sup>†</sup> For each H atom, the m.s. displacements due to the rigid-body motion and the internal librations are additive [equation (1) in Dunitz & White (1973)]. If a non-rigid mode makes a negative contribution, as in the  $\Omega_1$  libration, this may be considered as a damping or counteractive effect on the rigid-body contribution. Of course, the resultant m.s. displacement of all atoms in all directions must be positive in order for the model to have physical significance. For urea at 123 K, the rigid-body contributions to the out-of-plane m.s. displacement are  $0.0808 \text{ \AA}^2$  for H(1) and  $0.0734 \text{ \AA}^2$  for H(2), while the contribution from the  $\Omega_1$  libration is  $-0.0146 \text{ \AA}^2$ . The resultant m.s. displacements ( $0.0662$ ,  $0.0588 \text{ \AA}^2$ ) are larger than any others in the structure.

Table 7. *Interatomic distances (Å) and angles (°) for urea*

		C-O	C-N	N-H(1)	N-H(2)		
(i) Intramolecular bond lengths							
Uncorrected values*		12 K 1.262 (1)	1.345 (1)	1.009 (2)	1.005 (2)		
		60 K 1.261 (1)	1.343 (1)	1.009 (2)	1.004 (2)		
		123 K 1.258 (1)	1.341 (1)	1.007 (2)	1.000 (2)		
Values corrected for harmonic thermal motion		12 K 1.265 (1)	1.349 (1)	1.022 (3)	1.018 (3)		
		60 K 1.265 (1)	1.349 (1)	1.021 (3)	1.015 (3)		
		123 K 1.264 (1)	1.351 (1)	1.015 (3)	1.005 (3)		
		average†	1.265 (1)	1.019 (4)	1.013 (7)		
Values corrected for harmonic motion and anharmonic bond stretching		12 K (as above)	(as above)	1.008 (4)	1.001 (4)		
		60 K (as above)	(as above)	1.006 (4)	0.999 (4)		
		123 K (as above)	(as above)	1.000 (4)	0.991 (4)		
		average	(as above)	1.005 (4)	0.997 (5)		
Urea, 295 K (Pryor & Sanger, 1970)‡		1.260 (3)	1.352 (2)	0.998 (5)	1.003 (4)		
Urea in the complex with hydrogen peroxide, 81 K (Fritchie & McMullan, 1981)§		1.266 (1)	1.346 (1)	1.005 (2)	1.002 (2)		
Deuterated urea in the complex with parabanic acid, 116 K (Weber, Ruble, Craven & McMullan, 1980)§		1.258 (1)	1.347 (1)	0.997 (3)	1.007 (3)		
			1.349 (1)	0.992 (3)	0.996 (3)		
(ii) Bond angles							
Uncorrected values		12 K 121.4 (1)	117.2 (1)	119.1 (1)	120.6 (1)	120.3 (2)	
		60 K 121.4 (1)	117.2 (1)	119.1 (1)	120.7 (1)	120.3 (2)	
		123 K 121.5 (1)	117.0 (1)	119.0 (1)	120.8 (1)	120.2 (2)	
Values corrected for harmonic thermal motion		12 K 121.4 (1)	117.2 (1)	119.1 (1)	120.5 (1)	120.4 (2)	
		60 K 121.4 (1)	117.3 (1)	119.2 (1)	120.6 (1)	120.2 (2)	
		123 K 121.4 (1)	117.2 (1)	119.2 (1)	120.7 (1)	120.1 (2)	
Values from Pryor & Sanger (1970)‡		121.7 (1)	—	119.0 (3)	120.2 (3)	—	
(iii) H-bond distances and angles							
		N...O	N-H(1)...O	N-H...O	N...O	N-H(2)...O	N-H...O
12 K		2.985 (1)	1.992 (2)	1.67.2 (2)	2.955 (1)	2.058 (2)	1.47.4 (2)
60 K		2.989 (1)	1.998 (2)	1.67.0 (2)	2.958 (1)	2.062 (2)	1.47.4 (2)
123 K		2.998 (1)	2.009 (2)	1.66.8 (2)	2.960 (1)	2.067 (2)	1.47.6 (2)

\* The C-O, C-N bond lengths agree with the values of Guth *et al.* (1980) for 60 and 123 K. Their N-H(2) bond lengths are significantly longer [1.022 (5), 1.015 (3) Å at 60 and 123 K respectively].

† For average values, e.s.d.'s are from the sample variance.

‡ These are room-temperature neutron diffraction values including corrections for harmonic thermal motion.

§ These are determined from neutron diffraction with harmonic-motion corrections and N-H bond-stretching corrections obtained by thermal-motion analysis assuming model (iv).

for the N-H bonds (Kuchitsu & Bartell, 1961; Weber, Craven & McMullan, 1983). These are given by  $\delta = 3a\Delta/2$ , where  $a = 2.0(1) \text{ \AA}^{-1}$  expresses the asymmetry of the Morse potential function for N-H stretching and  $\Delta = \langle u_N^2 \rangle - \langle u_H^2 \rangle$  is the value for harmonic motion along the N-H bond calculated from neutron diffraction data. For the N-H bonds, the harmonic and anharmonic corrections are almost equal in magnitude and are opposite in sign.

The corrected bond lengths and angles for the OCN<sub>2</sub> group obtained at the three temperatures are in good agreement (Table 7). The N-H bond lengths fall within a larger range when thermal corrections are applied. However, this is insignificant because of the increased e.s.d.'s. Average N-H(1) and N-H(2) bond lengths are insignificantly different for both corrected (1.3  $\sigma$ ) and uncorrected (1.6  $\sigma$ ) values. As shown in Table 7, corrected bond lengths and angles also agree within experimental error with corresponding room-temperature values of Pryor & Sanger (1970), and with urea in the 1:1 crystal complexes with hydrogen peroxide (Fritchie & McMullan, 1981) and parabanic acid (Weber, Ruble, Craven & McMullan, 1980).

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## The Geometry of Small Rings. VII.\* Geometric Variations in Bicyclo[1.1.0]butane: Comparison with Higher Bicyclo[*n*.1.0]alkanes (*n* = 2–4)

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### Abstract

The molecular geometry obtained by X-ray methods for 22 derivatives of bicyclo[1.1.0]butane (I) has been analysed in conjunction with relevant microwave results. Substructure (I) exists in a variety of environments, classified here in terms of the number of atoms (*t*) which bridge the 2,4-methylenes and the number (*r*) which bridge the 1,3-methines (*i.e.* [*r*.1.1]propellanes). Parent (I) has *t* = *r* = 0 and the lengths of the 1–3 bridge and 1–2 side bonds are identical [ $d_{13} = 1.497$  (3),  $d_{12} = 1.498$  (4) Å; Cox, Harmony, Nelson & Wiberg (1969). *J. Chem. Phys.* **50**, 1976–1980]; the dihedral angle between cyclopropyl rings ( $\varphi$ ) is 121.7 (5)° and the bridgehead-substituent valence angle ( $\rho$ ) is 128.4 (3)°. In 2,4-bridged derivatives  $\varphi$  is constrained to decrease as *t* decreases from 3 to 1. For non-propellanes (*r* = 0) this produces synchronized geometric distortions:  $d_{13}$  decreases [to 1.408 (3) Å at  $\varphi = 94.1$  (2)°] while  $d_{12}$  and  $\rho$  both increase. This inter-dependence is examined here by simple- and multiple-regression techniques: the positive linear correlation of  $d_{13}$  with  $\varphi$  has >99.5% significance, the negative  $d_{13}$ – $\rho$  correlation is >98% significant. These systematic geometric variations are augmented by non-systematic effects induced by 1,3- or 2,4- $\pi$ -acceptor substituents, indicative of the

appreciable  $\pi$  character in the 1–3 bond. The [*r*.1.1]propellanes have highly inverted C(1,3) tetrahedra and bonding effects do not follow the trends for *r* = 0 structures. A comparison of (I) with higher bicyclo[*n*.1.0]alkanes (*n* = 2–4) shows clear correlations of geometry with strain energies and NMR coupling constants.

### Introduction

Bicyclo[*n*.1.0]alkanes (Table 1, I–IV for *n* = 1–4) are strained systems characterized by cyclopropane fusion to a carbocycle of size *n* + 2. The total strain energy ( $E_s$ , Table 1) in these bicyclic systems increases rapidly with decreasing *n*, and for (II)–(IV)  $E_s$  approximates  $\sum E_s$  for the two component rings [VIII + (V–VII)]. For bicyclobutane (I)  $E_s$  exceeds  $\sum E_s$  for two cyclopropane rings by ~42 kJ mol<sup>-1</sup> (superstrain), and the molecule exhibits a range of unusual properties in comparison to the more normal (III) and (IV) (Wiberg, 1968*a*; Greenberg & Liebman, 1978). The characteristics of bicyclopentane (II) lie between these two extremes, a fact which is not readily deduced from total  $E_s$  values.

The NMR coupling constants  $^1J_{CH}$  in Table 1 show that the bridgehead methine proton in (III) and (IV) is cyclopropane-like (*i.e.* ethylenic, see VIII, IX).  $^1J_{CH}$  then increases through (II) to an acetylenic (acidic) value of 202 Hz in (I), close to the 220 Hz for the

\* Part VI: Allen (1984).