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Thermal Effects in Urea: The Crystal Structure at −140 °C. and at Room Temperature*

By Natalie Sklar, Michael E. Senko† and Ben Post
Polytechnic Institute of Brooklyn, Brooklyn 1, *N.Y.*, *U.S.A.*

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The crystal structure of urea has been analyzed on the basis of ($h0l$) and ($hk0$) data obtained at room temperature and at −140 °C. Fourier and least-squares methods were used. Results generally agree well with those previously reported by Vaughan & Donohue (1952), but several of the atomic temperature factors differ significantly from those reported by Worsham, Levy & Peterson (1957) on the basis of neutron diffraction measurements.

Coefficients of thermal expansion have been measured, and changes in atomic coordinates, bond lengths and angles with temperature have been computed. The only major dimensional change with temperature involves the intermolecular hydrogen bond lengths which decrease considerably with decreasing temperature, resulting in a corresponding decrease in unit cell dimensions.

Introduction

Because of its chemical importance and the relative simplicity of its crystal structure, urea was one of the first organic compounds to be investigated by X-ray diffraction methods. Several analyses of its crystal structure have been reported, culminating in a comprehensive study by Vaughan & Donohue (1952). In that work all reflections accessible to Cu radiation were measured with great care, and the analysis, by Fourier and least squares methods, was far more detailed than was the general practice at that time. This was one of the first instances in which anisotropic atomic temperature factors were used in a structure refinement. Unfortunately, the effects of symmetry on the temperature factors were not properly taken into account, leading to some errors in the determination of those factors.

More recently, Worsham, Levy & Peterson (1957) reported the results of a neutron diffraction study of the crystal structure of urea based on the analysis of ($h0l$) data. The atomic position parameters which they found differed only slightly from those reported by Vaughan & Donohue, but the temperature factors reported in the studies differed markedly.

The present work was undertaken in part to determine whether the apparent differences between the two sets of temperature factors were real. It was also felt that the analysis of a simple structure, like that of urea, at more than one temperature, would yield some useful insights into the effects of temperature on crystal structures.

Experimental

Urea crystallizes in the tetragonal system; the space group is $P\bar{4}2_1m$; there are two molecules in the unit cell. Cell dimensions at room temperature are:

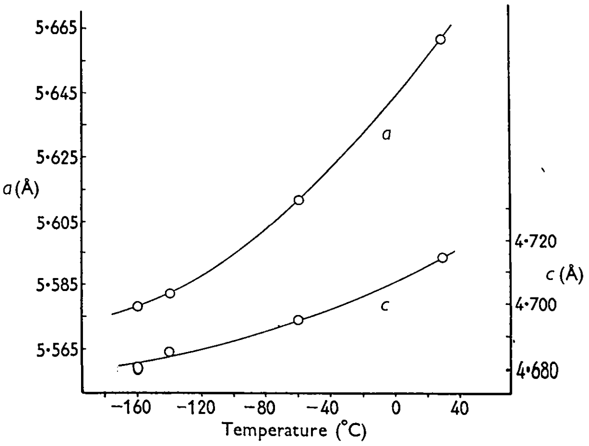
$$a=5\cdot662,\ c=4\cdot716\pm0\cdot002\ \text{Å}\ .$$

At −140 °C.,

$$a=5\cdot582,\ c=4\cdot686\pm0\cdot002\ \text{Å}\ .$$

Atomic positions are:

2 C in (c): $0, \frac{1}{2}, z;\ \frac{1}{2}, 0, \bar{z}$.
2 O in (c): $0, \frac{1}{2}, z';\ \frac{1}{2}, 0, \bar{z}'$.
4 N in (e): $x, \frac{1}{2}+x, z;\ \bar{x}, \frac{1}{2}-x, z;\ \frac{1}{2}+x, \bar{x}, \bar{z};$
$\frac{1}{2}-x, x, \bar{z}$.



	Room temperature	a (Å)	c (Å)
Vaughan & Donohue	—	5·661	4·712
This work	28 °C.	5·662	4·716
	−60	5·612	4·696
	−140	5·582	4·686
	−160	5·578	4·680
Lonsdale *et al.*	−180	5·576	4·690

Fig. 1. Lattice constants *versus* temperature.

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† IBM Research Laboratories, Poughkeepsie, N.Y.

The eight hydrogen atoms are in 2 additional sets of fourfold (*e*) positions.

There are thus eight positional parameters to be determined. In addition there are two independent temperature factors for carbon and for oxygen, and four each for one nitrogen and two hydrogen atoms. Vaughan & Donohue found that the molecules are planar as had previously been reported on the basis of an infra-red investigation (Waldron & Badger, 1950). The molecules are held together in the crystal by a network of intermolecular N–H · · · O bonds.

In the present work (*hk*0) and (*h*0*l*) reflections were measured at −140 °C. and at room temperature, using filtered Mo *K*α radiation. Each of the four sets

Table 1. *Urea*

Structure factors: *h*0*l*

Room temperature			−140 °C.		
hkl	$\lvert F_o \rvert$	$\lvert F_c \rvert$	*hkl*	$\lvert F_o \rvert$	$\lvert F_c \rvert$
101	11·3	11·3	101	12·0	12·3
102	10·1	10·2	102	11·6	12·2
103	7·6	7·9	103	8·8	9·1
104	1·2	1·2	104	1·2	1·4
105	2·7	2·7	105	3·9	4·4
106		0·04	106	0·5	0·5
107	3·2	3·1	107	5·2	5·7
108	1·2	1·2	108	1·9	2·0
301	7·3	7·0	109		0·2
302	2·8	2·5	1,0,10		0·4
303	2·1	2·2	1,0,11	0·8	0·8
304	6·0	6·4	1,0,12	0·8	0·8
305		0·2	301	9·3	8·2
306	1·8	1·8	302	4·0	3·6
307		0·4	303	3·3	3·1
308	1·4	1·2	304	9·2	9·6
501		0·2	305		0·4
502		0·06	306	3·0	3·1
503	1·3	1·3	307		0·5
504	1·9	2·0	308	3·1	3·1
505	0·7	0·7	309	1·5	1·7
506		0·6	3,0,10	1·6	1·7
507	0·9	0·9	501		0·1
701	0·9	1·0	502		0·2
702		0·4	503	2·6	2·6
703	0·7	0·8	504	3·8	3·7
704		0·4	505	1·4	1·2
705		0·6	506	1·1	1·2
706		0·01	507	2·2	2·1
707	0·8	0·7	508	2·0	1·9
001	4·3	3·7	701	2·5	2·5
002	10·2	10·8	702	2·2	1·8
003	2·7	2·7	703	2·4	2·2
004	4·0	4·3	704		0·4
005	5·1	5·3	705	1·9	1·9
006	1·9	2·1	706		0·1
007		0·4	707	2·7	2·7
008	1·5	1·7	708	0·9	0·9
200	11·8	10·2	901		
201	11·4	10·8	902		0·2
202	2·2	2·2	903	0·8	0·9
203	5·2	5·5	904	1·6	1·6
204	3·6	3·6	11,0,1		0·1
205	0·6	0·6	11,0,2		0·2
206		0·4	11,0,3		0·5
207		0·07	11,0,4	0·9	0·9
208		0·03	001	3·8	3·9
400	2·1	2·0	002	11·2	11·7
401	6·9	5·9	003	3·9	3·8
402	1·8	1·9	004	5·3	6·1
403	5·2	5·1	005	6·5	6·4
404	1·9	1·8	006	3·6	3·7
405	1·1	0·9	007		0·3
406	0·9	0·8	008	3·4	3·5
600	3·4	3·4	009	1·6	1·6
601	1·3	1·2	0,0,10	1·5	1·5
602	0·7	0·7	0,0,11		0·1
603	0·6	0·6	0,0,12	1·4	1·2
604	1·1	1·0	200	11·5	12·0
808	1·3	1·2	201	13·6	13·2
			202	2·9	2·7
			203	6·5	7·0
			204	4·3	4·2
			205	0·5	0·5
			206	1·1	1·0
			207		0·5
			208		0·1
			209		0·4
			2,0,10		0·8
			2,0,11	1·5	1·5
			2,0,12	0·7	0·6
			400	2·4	2·0
			401	9·1	7·9
			402	2·8	2·8
			403	7·8	7·6
			404	2·4	2·2
			405	2·1	1·5
			406	2·5	2·3
			407		0·5
			408		0·9
			409	0·9	1·0
			4,0,10		0·5
			4,0,11	2·0	1·7
			600	7·1	6·7
			601	1·9	1·9
			602	1·7	1·7
			603	0·5	0·5
			604	2·3	2·2
			605	1·8	1·9
			606	1·2	1·1
			607		0·1
			608	1·2	1·2
			800	4·0	3·5
			801	1·4	1·4
			802		0·7
			803	0·7	0·8
			804	1·4	1·4
			805	0·8	0·8
			10,0,1	1·1	1·2
			10,0,2		0·2
			10,0,3	1·2	1·4
			10,0,4		0·6
			12,0,0	0·9	0·8

Table 1 (*cont.*)

Structure factors: *hk*0

	Room temperature		−140 °C.	
hkl	F_o	F_c	F_o	F_c
200	12·1	12·6	12·8	12·9
400	2·1	2·5	2·2	1·2
600	3·2	3·0	6·8	6·9
800	1·3	1·1	4·2	4·3
110	27·0	−32·0	30·3	−33·1
210	12·5	12·7	14·6	14·4
310	4·6	−5·3	5·0	−5·1
410	1·0	−1·1	2·3	−2·4
510	3·8	−3·6	6·0	−5·0
610	0·9	−0·7	2·3	−2·7
710	2·3	−1·8	5·7	−5·3
220	11·2	13·8	13·6	15·3
320	3·4	−3·2	4·0	−4·6
420	6·3	6·1	7·9	8·5
520	2·1	1·7	4·6	4·8
620	2·3	2·1	4·1	3·9
820			1·8	2·2
330	8·5	−9·4	14·3	−14·6
430			1·6	−1·1
530	3·6	−3·3	6·3	−6·3
730			0·8	−0·6
830			0·8	0·7
930			2·0	−2·4
440	4·2	4·6	9·2	9·6
540	0·4	−0·3	1·2	−1·4
640			1·3	1·6
10,4,0			1·7	1·8
550			3·4	−3·3
650			1·5	2·0
750			1·7	−1·5
950			1·8	−1·4
660			2·4	2·7
860			2·4	1·8
770			2·7	−2·8

of data was recorded with film and with a scintillation counter. In general, agreement between the two sets of data was good; the average discrepancy between the two sets of F_o's (i.e., film *vs.* counter) was less than 4%. The F_o's listed in Table 1 are based on the scintillation counter measurements except for the few cases (very high angle reflections at −140 °C.) where individual reflections could not, for experimental reasons, be measured with the counter; for these, film data were used.

We may note that while at room temperature almost no useful data were obtained at Bragg angles greater than 30° (Mo $K\alpha$ radiation), at −140 °C. moderately strong reflections were recorded at the highest angles accessible to the Weissenberg camera; presumably the use of Ag radiation would have yielded additional useful data. Also, while measurements at anyone temperature are susceptible to the many systematic errors that plague crystallographers (absorption, extinction, etc.) the *differences* between intensities measured at different temperatures with the same crystal are almost entirely free from these errors.

Measurements were also made of the thermal expansion of urea in order to obtain lattice constants applicable to −140 °C. These were made on powdered samples, using Cu $K\alpha$ radiation, with a diffractometer adapted for low temperature measurements. Results are shown in Fig. 1.

Analysis of data

All four sets of data were first analyzed by conventional Fourier methods. Refinements were based on analyses of difference maps which were recomputed until no further improvements were detected. In these calculations two temperature factors were assigned to each atom. Calculations were made on an IBM 650 computer.

In addition, a detailed least squares analysis of the two sets of (*h0l*) data was made using the Busing & Levy least squares program adapted for the IBM 704 computer. All atoms are resolved in the (*h0l*) projection; overlap of atoms in the (*hk*0) projection interferes seriously with analysis of that set of data. It is clear that complete analysis of the temperature motion cannot be made from the (*h0l*) data alone, since B_{12} cannot be determined from these measurements. In all cases, refinements were started using position parameters determined by Vaughan & Donohue. In the electron density calculations, hydrogen positions were determined from difference maps. In the least squares analysis no effort was made to refine hydrogen temperature factors; they were kept fixed at the values reported by Worsham, Levy & Peterson.

Results

Values of F_o and F_c are listed in Table 1. F_c (*h0l*) are based on least squares results; F_c (*hk*0) were computed in the course of refinement of electron density difference maps. At the completion of the Fourier refinements, R_{h0l} was $8\frac{1}{2}\%$ for the room temperature data and 5·2% for the low temperature data. R_{hk0} was 7% for both sets of data. Missing reflections were not included in the above. The least squares refinement yielded values of 5·8% and 5·9% respectively for the room and the low temperature (*h0l*) data. Inclusion of absent reflections raised these R values to 5·9% and 6·3%. Atomic position coordinates determined by Worsham, Levy & Peterson, and Vaughan & Donohue, and in the present work, are listed in Table 2. Agreement among the X-ray results is better than agree-

Table 2. *Urea*

Atomic position coordinates

				Sklar, Senko & Post			
				Room temperature		−140 °C.	
		Worsham, Levy & Peterson	Vaughan & Donohue	Fourier	Least-squares	Fourier	Least-squares
C)	*z*	0·3330 ± 0·0010	0·3308 ± 0·0032	0·3303	0·3300 ± 0·0011	0·3278	0·3272 ± 0·0004
O)	*z*	0·5968 ± 0·0011	0·5987 ± 0·0019	0·5996	0·5980 ± 0·0008	0·5966	0·5966 ± 0·0004
N)	*x*	0·1439 ± 0·0009	0·1429 ± 0·0021	0·1432	0·1433 ± 0·0009	0·1459	0·1455 ± 0·0004
	z	0·1832 ± 0·0005	0·1848 ± 0·0017	0·1834	0·1847 ± 0·0007	0·1806	0·1800 ± 0·00035
H_1	*x*	0·2522 ± 0·0026		0·270	0·243 ± 0·023	0·254	0·269 ± 0·026
	z	0·2839 ± 0·0021		0·286	0·281 ± 0·011	0·284	0·279 ± 0·011
H_2	*x*	0·1365 ± 0·0019		0·134	0·142 ± 0·016	0·143	0·142 ± 0·020
	z	0·9724 ± 0·0014		0·018	0·028 ± 0·019	0·002	0·972 ± 0·020

Table 3. *Urea*

Bond lengths (Å) and angles

			Sklar, Senko & Post			
			Room temperature		−140 °C.	
	Worsham, Levy & Peterson	Vaughan & Donohue	Fourier	Least-squares	Fourier	Least-squares
C–O	1·243 ± 0·006	1·262 ± 0·016	1·269	1·264 ± 0·006	1·259	1·262 ± 0·003
C–N	1·351 ± 0·007	1·335 ± 0·013	1·339	1·336 ± 0·007	1·343	1·341 ± 0·003
N–H · · · O	2·994 ± 0·006	2·989	2·980	2·998 ± 0·005	2·968	2·968 ± 0·003
N–H · · · O′	3·034 ± 0·005	3·035	3·034	3·036 ± 0·007	2·985	2·963 ± 0·004
N–C–N	117·0 ± 0·3°	118·0 ± 1·3°	117·8	118·2 ± 0·3°	118·2	118·2 ± 0·15°
N–C–O	121·5 ± 0·25°	121·0 ± 0·65°	121·1	120·9 ± 0·3°	120·9	120·9 ± 0·15°

ment of any of these with the neutron diffraction results, although in no case do the reported atomic parameters show statistically significant differences. Agreement between Fourier and least squares results obtained in the present investigation is particularly good.

In Table 3 we have listed bond lengths and angles reported in the various investigations. Small, but apparently real, changes in atomic coordinates occur when the temperature is lowered to −140 °C., but intra-molecular dimensions show no significant changes in this temperature interval. The only large dimensional changes observed involved the inter-molecular hydrogen bond lengths; and these are reflected in the reduction of unit cell size at the lowered temperature. Each room temperature N–H · · · O bond differs from the corresponding one at low temperature by about 5 standard deviations.

A substantial improvement in precision accompanies the use of low temperature data. The standard deviations of atomic coordinates and of bond lengths fell by a factor of two when the temperature was lowered to −140 °C. The improvement would undoubtedly be even greater in the case of softer organic crystals, having larger temperature factors than urea.

Temperature factors are listed in Table 4. In the column headed 'Grenville-Wells', we have listed corrected values of temperature factors computed by Grenville-Wells (1956) using Vaughan & Donohue's (*h*0*l*) and (*hk*0) data. We find it difficult to accept these values in spite of their rather good agreement with the neutron diffraction results. They indicate extremely highly anisotropic temperature motion for oxygen ($B_{11} = 3{\cdot}5$, $B_{33} = 0{\cdot}6$); there is little evidence of such extreme anisotropy in the electron density maps published by Vaughan & Donohue. The ratios of

Table 4. *Urea*

Temperature factors

		Room temperature				−140 °C.	
		Worsham, Levy & Peterson	Vaughan & Donohue	Grenville-Wells	Sklar, Senko & Post (Least-squares)	Sklar, Senko & Post Fourier	Least-squares
N)	B_{11}	4·86 ± 0·20	6·8	5·2	5·20 ± 0·16	2·5	2·57 ± 0·07
	B_{33}	1·39 ± 0·09	1·9	1·5	1·80 ± 0·09	0·9	0·98 ± 0·03
	B_{13}	0·14 ± 0·24			0·08 ± 0·09		0·05 ± 0·04
C)	B_{11}	2·35 ± 0·24	3·9	3·3	2·75 ± 0·14	1·6	1·34 ± 0·07
	B_{33}	0·85 ± 0·14	1·9	1·5	1·56 ± 0·16	0·8	0·88 ± 0·04
O)	B_{11}	3·74 ± 0·34	3·9	3·5	3·65 ± 0·16	1·7	1·63 ± 0·06
	B_{33}	0·80 ± 0·12	1·9	0·6	1·68 ± 0·08	0·9	0·78 ± 0·03

B_{11} to B_{33} computed by Grenville-Wells are $3\frac{1}{2}$ for nitrogen and almost 6 for oxygen. If anything, the electron density sections indicate, to us at least, that the anisotropy of the nitrogen atom is greater than that of the oxygen. Our analysis of our own (*h0l*) data indicates $B_{11}=3{\cdot}65$ and $B_{33}=1{\cdot}68$ for oxygen (at room temperature).

Our room temperature (least squares) results for B_{11} differ little from those of Worsham, Levy & Peterson. The B_{33} results, however, differ significantly. The Worsham, Levy & Peterson results are consistently lower than ours by as much as 50%.

Our low temperature measurements are useful in this connection. The temperature factors of all the atoms show a fairly uniform decrease of about 50% between room temperature and −140 °C. In this temperature range, the temperature factors are approximately proportional to the absolute temperatures. It is difficult to reconcile these findings with those reported by Worsham, Levy & Peterson. The *decrease* in our B_{33} terms between room temperature and −140 °C. was almost as large as the *total* room temperature values reported by Worsham, Levy & Peterson for the nitrogen and carbon atoms, and larger than the value reported for the oxygen atom. The B_{13} cross term for the nitrogen atom is very small and may be ignored.

The causes of these differences between the X-ray and the neutron diffraction results are not clear. It is well known that computed 'temperature factors' are particularly sensitive to the types of form factors assumed for the atom at rest. It may be that the differences reflect errors in the neutron, or the X-ray, atomic form factors. Possibly the three dimensional neutron diffraction analysis of urea reported under way at the Oak Ridge National Laboratories will clear up this point.

Table 5. *Urea*

Peak heights and central curvatures

	Peak heights (e.Å^{-2})		Central curvatures (e.Å^{-4})	
	Room temp.	−140 °C.	Room temp.	−140 °C.
C	9·9	14·4	A_{hh} 130 A_{ll} 180	320 420
O	12·3	18·6	A_{hh} 130 A_{ll} 170	370 430
N (*h0l*)	9·6	13·6	A_{hh} 60 A_{ll} 120	140 250
N (*hk0*)	8·0	12·3	A_{hk} 40 $A_{h\bar{k}}$ 70	130 185

Peak heights and curvatures of the 'heavy atom' peaks have been listed in Table 5. These were computed from the room temperature and the low temperature electron density maps. We have also included data for nitrogen obtained from (*hk*0) maps. These are of considerably lower reliability than the others because of overlap effects in this projection.

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The Magnetic Anisotropy and Electron Distribution in Succinimide

By R. Mason

Department of Crystallography, University College, London, W.C. 1, *England**

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A three-dimensional least-squares analysis of the crystal and molecular structure of succinimide is reported. The final discrepancy factor $R=0{\cdot}091$ corresponds to average e.s.d.'s of 0·011 Å and 0·6° for the bond lengths and angles respectively. The principal molecular diamagnetic susceptibilities (−55·1, −45·1 and $-41{\cdot}6.10^{-6}$ c.g.s.e.m.u.), together with the inter- and intra-molecular bond lengths, are discussed in relation to the electron distribution in the molecule.

The refinement

A least-squares analysis of 30 (*hk*0), (0*kl*), (*h*0*l*) and (*hkl*) spacings gave the *Pbca* unit cell dimensions as,

$$a=7{\cdot}537\pm0{\cdot}008,\ b=9{\cdot}651\pm0{\cdot}011,\ c=12{\cdot}938\pm0{\cdot}015\ \text{Å}\ .$$

The three-dimensional least-squares refinement, based on the two-dimensional analysis (Mason, 1956) and an isotropic temperature factor $B=2{\cdot}6$ Å^2, reduced the residual factor

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* Now at Department of Chemistry, Imperial College, London, S.W. 7.