

Collection and Interpretation of Neutron Diffraction Measurements on Urea

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Problems in the collection and analysis of accurate diffraction data have been explored in a careful study of urea. Initial neutron measurements on non-spherical crystals show that little confidence can be placed in the values of extinction parameters derived for a non-spherical crystal of a hydrogenous material used in a neutron-diffraction experiment. It is also shown that multiple Bragg scattering is an important source of error. Uncertainties in the absorption and extinction corrections can be overcome by using a spherical crystal with $\mu R \approx 0.5$. Corrections for the effects of multiple Bragg scattering were made by correlating complete sets of data measured at three different wavelengths. A number of models based on rigid-molecule vibrations and anharmonic interactions between atoms were used to treat the effects of thermal vibration. The best results were obtained from a refinement of the spherical-crystal data using general thermal parameters plus corrections for curvilinear motion, but a rigid-molecule treatment, with fewer vibrational parameters, was not much worse. Anharmonic effects did not seem to be appreciable. To look for possible 'bonding features' in urea, difference syntheses computed from X-ray data and calculated X-ray structure factors based on the neutron results were plotted. It was not possible to remove the deep negative differences at the atomic positions by adjusting a scale factor and a thermal diffuse scattering correction, and it is probable that a real discrepancy exists between the observed and calculated structure factors.

1. Introduction

To explore some of the problems involved in the collection and analysis of accurate diffraction data, a careful study has been made of a simple organic material, urea, $\text{CO}(\text{NH}_2)_2$, which has high symmetry, is not a ring compound, and has very anisotropic thermal vibrations.

The more recent investigations of urea by X-ray and neutron diffraction are those of Vaughan & Donohue (1952), Lobachev & Vainshtein (1961), Grenville-Wells (1956), Worsham, Levy & Peterson (1957), Sklar, Senko & Post (1961) and Caron & Donohue (1964). However, only the data of Vaughan & Donohue (1952) represent a full three-dimensional set of measurements (X-ray data) and Caron & Donohue (1964) have analysed these results for the effects of thermal vibrations using the conventional anisotropic model and a rigid-body analysis.

The space group of urea is $P\bar{4}2_1m$ (No. 113 in *International Tables for X-ray Crystallography*, 1969) having two molecules per unit cell. C and O atoms occupy special positions (*c*), and N, H(1) and H(2) occupy special positions (*e*). A diagram of one molecule is shown in Fig. 1. There are eight structural parameters.

2. Data collection

Neutron-diffraction measurements were carried out on crystals of hydrogen urea, grown from an aqueous urea solution doped with ammonium bromide, using the computer-controlled neutron diffractometer described by Pryor, Ellis & Dullow (1968). An ω - 2θ scan was used with a full width of 2° and a counter aperture of 1.6 cm at 30 cm radius. Background was

measured at 3° of ω and 6° of 2θ on either side of the peak. For strong reflexions, the measurement time was limited to that necessary to obtain 20,000 counts and for weak reflexions, to 40 minutes per reflexion. The orientation of each crystal was general (usually a $\langle 110 \rangle$ axis was within 10° of the φ axis) and was determined, together with the lattice parameters, by centring several high-angle reflexions, as described by Busing & Levy (1967). The lattice parameters of Sklar, Senko & Post (1961) ($a = 5.662$, $c = 4.716$ Å) were confirmed within the accuracy of the present measurements (± 0.003 Å).

To avoid decomposition of the crystal due to absorption of moisture, it was protected by an air-tight quartz glass cover. Crystals would otherwise decompose over 3 or 4 days, as shown by decrease in the intensity of a standard reflexion with time.

Several sets of data were collected at various wavelengths on crystals of different size. Usually several symmetry-related equivalents of each reflexion were measured. The first measurements, called the H-urea (i) data, were collected on two approximately regular shaped crystals weighing 110 mg (dimensions $6.9 \times 4.2 \times 3.2$ mm) and 17 mg (dimensions $3.2 \times 2.4 \times 1.7$ mm). A second set, the H-urea (ii) data, were collected on an approximately spherical crystal; it was actually ovoid with major axes $4.5 \times 3.2 \times 3.0$ mm and weighed 45 mg. The H-urea (i) data consisted of:

110 mg crystal:

209 reflexions ($\times 4$ variants) at $\lambda = 1.17$ Å	
18	$\lambda = 1.54$
10	$\lambda = 0.84$

17 mg crystal:

34	$\lambda = 1.17$
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The H-urea (ii) data consisted of:

45 mg spherical crystal:

190 reflexions at $\lambda = 1.05 \text{ \AA}$
191 $\lambda = 1.17$
97 $\lambda = 1.54$

3. Absorption and extinction corrections

3.1. Initial strategy

From the whole assembly of H-urea (i) data – on crystals of different size, at different wavelengths, and with equivalent reflexions of different path lengths – an attempt was made to deduce the extinction parameters introduced by Zachariasen (1967), quite separate from the final structure refinement. First it was necessary to apply absorption corrections and subsequently analyse the data for extinction effects.

3.2. Absorption corrections

Absorption in hydrogenous materials arises mainly from the neutron incoherent scattering of the hydrogen atoms which have a cross section of 80 barns if the atoms are free, or 20 barns if the atoms are bound. For a real crystal the degree of freedom of the hydrogen atoms is undetermined and the value of the absorption coefficient μ is uncertain. Also the value of μ is not easily measured because it is a single-crystal property and, in any case, can be sensitive to the exact amount of small-angle scattering included in the total cross section measurement. It is even possible that μ may vary with the direction of neutron propagation in the crystal.

For a given value of μ the transmission factor $A(\mu) = \frac{1}{v} \int \exp(-\mu T) dv$, and the mean path length $\bar{T} = \frac{\int T \exp(-\mu T) dv}{\int \exp(-\mu T) dv}$, where T is the path length, were calculated using a Fortran program written by Dr G. W. Cox and Dr M. M. Elcombe of this Establishment.

3.3. Extinction corrections

Zachariasen (1967) describes the effects of extinction in terms of two parameters r and g and the application of his theory to a neutron diffraction experiment leads to the following expression for the extinction factor y

$$y = \left\{ 1 + \frac{Qr}{\lambda} \left[\frac{3r + (2\bar{T} - 3r)}{\sqrt{1 + (r/\lambda g)^2}} \right] \right\}^{-1/2}, \quad (1)$$

where

$$Q = \frac{\lambda^3 N_c^2 F^2}{\sin 2\theta}.$$

When primary extinction can be neglected, equation (1) becomes

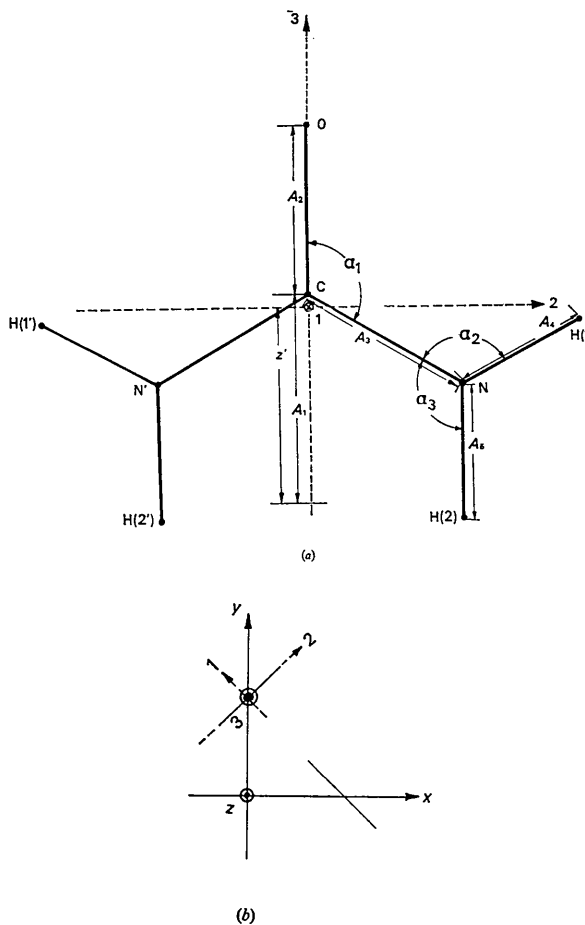


Fig. 1. The internal coordinates ($A_1, A_2, A_3, A_4, A_5, \alpha_1, \alpha_2, \alpha_3$) and inertial axes (1, 2, 3) for one molecule of urea; (a) in the plane of the molecule, $Z' = \sum_i m_i z_i / \sum_i m_i$; (b) looking down the c axes.

Table 1. Dependence of the extinction parameters r and g , and the values of R_w for the absorption-extinction-corrected data, and for absorption-corrected data, on the value chosen for the absorption coefficient for H-urea (i).

Absorption coefficient μ (cm^{-1})	Extinction parameters (determined by trial and error)		R_w from a C-refinement (absolute weights used)	
	r (cm)	g	Absorption-extinction-corrected data (00l reflexions removed)	Absorption-corrected data (10 reflexions removed)
2.0	25×10^{-5}	3×10^5	6.72%	9.74%
2.4	8×10^{-5}	2×10^5	4.44%	9.75%
2.8	3×10^{-5}	2×10^5	5.75%	9.97%
3.22	1×10^{-5}	2×10^5	8.36%	10.47%

$$y = \left[1 + \frac{2Q\bar{T}r^*}{\lambda} \right]^{-1/2}, \quad (2)$$

with

$$r^* = r \left[1 + \left(\frac{r}{\lambda g} \right)^2 \right]^{-1/2}. \quad (3)$$

There are two important types of real crystals defined by the different values of $r/\lambda g$:

Type I:

$$r/\lambda g \gg 1, y = [1 + 2gQ\bar{T}]^{-1/2} \quad (4)$$

Type II:

$$\left(\frac{r}{\lambda g} \right) \ll 1, y = \left[1 + \frac{2Q\bar{T}r}{\lambda} \right]^{-1/2} \quad (5)$$

with equation (1) covering the intermediate type. It is important to note that equation (5) is quite general for a type II crystal since it also applies in the case where primary extinction cannot be neglected.

3.4. Analysis of H-urea (i) data

The assemblage of H-urea (i) data was analysed to give values for the extinction parameters r and g . A least-squares procedure led to a very broad minimum of the mean square deviation, and a trial-and-error procedure had to be adopted to determine optimum values. Once r and g were determined, the various measurements were corrected for extinction effects, collated, and analysed using the different refinement procedures described in § 4.

Now extinction and absorption effects both cause the apparent intensity to vary with path length in the crystal, but for extinction the variation is intensity dependent while for absorption it is not. Thus the derived extinction parameters will obviously depend on the value chosen for μ , and if this is chosen incorrectly the data may be under- or overcorrected for the effects of extinction. This effect shows up in the value of the weighted R index R_W for the least-squares refinement of the corrected data or, more sensitively, in plots of the mean value of $\Delta = |F_{\text{obs}} - F_{\text{calc}}|$ in various ranges of $|F_{\text{obs}}|$ after least-squares refinement of the data.

The above points are illustrated in Table 1 which shows that the value of r , in particular, and the value of R_W obtained from the least-squares refinement of the experimental structure factors, are very dependent on the value chosen for μ .

The absorption coefficient was determined experimentally by measuring the total cross section of five of the larger crystals by counting through a 0.4 mm iris in the monochromatic beam. This was done at three wavelengths (1.17, 0.84, 1.54 Å) and gave a consistent result, $\mu = 3.22 (\pm 0.20) \text{ cm}^{-1}$. There was no indication that the cross section varied with wavelength. Assuming that the apparent absorption cross section for the single crystal arises solely from incoherent hydrogen scattering, 3.22 cm^{-1} corresponds to 61 barns and 2.4 cm^{-1} to 45 barns.

Table 1 shows that the lowest value of R_W for the absorption-extinction-corrected H-urea (i) data corresponded to $\mu = 2.4 \text{ cm}^{-1}$ and not to the measured value of $\mu = 3.22 \text{ cm}^{-1}$. In these refinements the 001 series of reflexions gave large negative values for ΔF . This was taken to be evidence of anisotropic extinction and these reflexions were omitted from the refinement. The ten strongest reflexions were omitted from the refinement of the absorption-corrected data. It is interesting to note (see column (6) of Table 5) that the much-used procedure of taking the absorption-corrected data, and analysing it without an extinction correction, after merely omitting a few of the strongest lines, gives poor results.

In Table 5, and the associated discussion of the results, the H-urea (i) data is absorption-extinction corrected, with $\mu = 2.4 \text{ cm}^{-1}$ and the extinction parameters of Table 1. The values of r and g that apply in this case show the crystal to be type II.

In a further attempt to determine μ , additional accurate intensity measurements on the large and small H-urea crystals were taken of a number of reflexions that were so weak that they would not be affected by extinction effects. The value of μ was then chosen to make the absorption-corrected intensities lie in the same ratio as the masses of the two crystals. The results are shown in Table 2.

Table 2. Intensity ratio of weak reflexions from the 110 and 17 mg H-urea crystals

Reflexion <i>h k l</i>	Intensity ratio (statistical accuracy about 2%)	Derived absorption coefficient, $\mu (\text{cm}^{-1})$
5 1 4	4.65	5.5
6 1 3	5.45	4.5
6 0 2	10.56	< 0.0
4 2 4	8.83	0.3

Clearly this apparently straight forward method of determining μ was unsuccessful; the intensities of the outer reflexions seem to be subject to random errors. It is likely that these errors are caused by multiple Bragg scattering. Experiments and calculations similar to those recently reported by Coppens (1968) confirmed that multiple Bragg scattering could indeed be a frequent source of error in the determination of intensities of the weaker reflexions.

Thus, in the analysis of the H-urea (i) data, there was the difficulty that the absorption coefficient could not be experimentally determined and its uncertainty cast doubt on the extinction corrections. Also it seemed certain that multiple Bragg scattering was an important source of error in the weaker intensities. To overcome these problems, the second series of experiments on the spherical crystal, H-urea (ii) were carried out.

3.5. Analysis of H-urea (ii) data

To detect the large errors caused by multiple Bragg scattering, complete sets of data were taken at three

wavelengths using the spherical crystal and the measurements were inter-compared. The data were then refined with a single extinction parameter included in the structural refinement.

For this spherical crystal, with $\mu R \approx 0.48$, the transmission factor and mean path length are independent of crystal orientation and vary only slowly with the angle θ . Thus, any uncertainty in the absorption coefficient, and hence in the value of μR , mainly affects the scale factor and hardly alters the relative scale of the low and high angle data. The absorption correction and mean path length for a given reflexion from a spherical crystal must be calculated by numerical integration, except for $\theta=0$ and 90° where an analytical expression may be used. The required formulae for $A(\mu)$ and \bar{T} are derived in Appendix 1.

To correct for the effects of extinction, neglecting the effects of primary extinction, a correction factor $(y')^{-1/2}$ defined by

$$(y')^{-1/2} = \left[1 + \frac{2r^*F_o^2\bar{T}\lambda^2}{V_c^2} \right]^{1/4}, \quad (6)$$

was applied to the calculated structure factor in the least-squares-refinement procedure, as a reasonable approximation to equation (2). In equation (6), r^* is defined by equation (3) and F_o is the observed structure factor on an absolute scale.

The sets of data measured at three different wavelengths were refined for a scale factor, and extinction parameter r^* , plus various models of the positional and thermal parameters. The values of R_w and r^* obtained from these refinements are shown in Table 3.

The values of r^* given in Table 3 are reasonably independent of wavelength, even though the correlation between r^* and the scale factor was in all cases about 94%. Thus the spherical crystal was also type II (so that $r=r^*$) and a final value of $r^*=2600$ (or $r=2600 \text{ \AA}$) was taken to be correct. The $C+R$ refinements were repeated using this value of r^* as a fixed parameter and at the end of each refinement the values of the observed structure factors, corrected for absorption and extinction effects and reduced to an absolute scale, were printed out.

The three sets of F_{obs} were listed side by side and compared. If the various values of F_{obs} for a particular reflexion were in reasonable agreement, the average value was taken. If they disagreed it was assumed, particularly if the reflexion was weak, that the high

value was caused by multiple Bragg scattering and it was rejected. Twenty-two reflexions were rejected from one or another of the data sets in this way, but none of the reflexions were entirely rejected from all sets of data.

This set of averaged data, referred to as the H-urea (ii) data, and taken to be the best, is listed in Table 4. On the most elaborate $C+R$ refinement it gave $R_w=2.86\%$ (see Table 5). Most of the discussion is based on the various refinements of this data. The extinction corrections were quite large for the strong reflexions e.g. $y=0.48$ for the 110 with $F=3.31$, and $y=0.90$ for the 511 with $F=1.61$.

3.6. The importance of using a spherical crystal

We conclude from the H-urea (i) experiments that, for neutron experiments on hydrogenous crystals, the interaction between absorption and extinction is so great, and the correct value of the absorption coefficient is so uncertain, that little confidence can be placed in any attempt to derive extinction parameters unless the crystal is spherical. This conclusion is very pertinent to recent attempts to use a non-isotropic, tensor formulation of extinction effects (Coppens & Hamilton, 1969) and to the recent attempts by Michell, Smith & Sabine (1969) to relate the extinction parameters derived from a diffraction experiment via Zachariasen's theory, with the defect structure observed directly in the crystal.

4. Refinement of the atomic parameters

4.1. Methods of refinement

Hypotheses were tested by conventional, full-matrix, least-squares refinements using specially written computer programs. The formulation of the various hypotheses, and the results obtained in testing them, are discussed in later parts of this section.

Three different approaches were used to treat the problem of assigning weights to the observed structure factors.

(i) Absolute weighting scheme

For the H-urea (i) data an estimated standard deviation (e.s.d.) $\sigma(F_{\text{obs}})$ was calculated for each structure factor by making use of the measured intensities of the variants of each reflexion. Absolute weights $W=[\sigma(F_{\text{obs}})]^{-2}$ were then averaged over ranges of the magnitude of F_{obs} .

Table 3. Values of R_w and r^* for different refinements of the three sets of data collected from the spherical crystal of H-urea

Wavelength	$\lambda=1.05 \text{ \AA}$		$\lambda=1.17 \text{ \AA}$		$\lambda=1.54 \text{ \AA}$	
	$R_w(\%)$	r^*	$R_w(\%)$	r^*	$R_w(\%)$	r^*
Conventional	3.84	2100 (400)	5.29	3400 (700)	5.31	2600 (900)
Conventional + curvilinear effect	3.77	1900 (400)	5.31	3100 (700)	5.21	2500 (800)

(ii) *Empirical weighting scheme*

In the absence of a number of measurements of the intensity of each reflexion, as for the H-urea (ii) data, an empirical weighting scheme must be used. One frequently used weighting scheme is obtained by calculating an e.s.d. for each reflexion using the relations $\sigma(F_{\text{obs}}) = \sigma_I \sin 2\theta/2 F_{\text{obs}} K$, with $\sigma_I = \sigma_{\text{stats}} + \beta I$, where $(\sigma_{\text{stats}})^2$ is the variance due to counting statistics for the reflexion with intensity I and β is commonly set at 0.03. This scheme gave weights which were similar to those obtained for the absolute weighting scheme.

(iii) *Self-consistent weighting scheme*

If a consistent set of weights has been used to analyse the experimental data, then the average value of $W\Delta^2$ should not vary with the magnitude of F_{obs} . Therefore, at the end of refinement, average values of $W\Delta^2$ can be calculated in ranges of $|F_{\text{obs}}|$ and a self-consistent set of relative weights chosen to make the values of $W\Delta^2$ of approximately constant magnitude. This weighting scheme was used to analyse each set of data and gave a final set of weights similar to that from the other schemes for $F_{\text{obs}} < 1.2$ and for the few higher F_{obs} , but for $1.2 < F_{\text{obs}} < 2.6$ they were two to three times larger.

In principle it is possible, when an absolute weighting scheme is used, to confirm that the data are free from error and that the model is adequate by evaluating $\chi^2 = \sum W\Delta^2/(n-p)$, where n is the number of observations and p is the number of variable parameters in the refinement, which should be near unity. For the H-urea

(i) data and an absolute weighting scheme, $\chi^2=5$; a similar result applied to the H-urea (ii) data and an empirical weighting scheme. The final analyses of the H-urea (ii) data were carried out with a self-consistent weighting scheme in which $W=7, 10, 15, 15, 20, 20, 15, 10, 5$ for $|F_{\text{obs}}|$ in the ranges 0.0 to 0.4, 0.4 to 0.8, etc. Different weighting schemes (or even the use of unit weights) in the various refinements caused no significant changes in any of the parameters.

4.2. *Refinement of structural parameters*

The urea structure can be described by eight conventional fractional coordinates. An option in the least-squares program allowed for the refinement of the structure in terms of eight internal coordinates: 5 distances and 3 angles as shown in Fig. 1. This type of refinement was carried out by adding eight equations to the program to convert the parameters, and also adding the terms of an (8×8) Jacobian matrix to convert the derivatives to the internal coordinate form. The purpose of this option was to obtain direct estimates of the errors in the bond lengths and angles, and of the correlations between them, and between these and other parameters.

The correlations between the internal coordinate parameters were in some cases as high as 80%. To see if these correlations affected the values of the bond lengths and angles obtained from this type of refinement, the data were also refined using conventional fractional coordinates. The correlation between these parameters was never greater than 20%, but the bond

Table 4. *Absorption-extinction-corrected structure factors on an absolute scale for the H-urea (ii) data*

The observed structure factors are compared with those calculated on the basis of a $C+R$ refinement using the parameters given in column (2) of Table 3. Fourteen reflexions (001, 215, 226, 306, 333, 401, 502, 521, 533, 542, 553, 631, 643, 750) are missing from the list. These were random and inadvertent omissions from the experimental schedule.

hkl	F_{cal}	F_{obs}	hkl	F_{cal}	F_{obs}	hkl	F_{cal}	F_{obs}	hkl	F_{cal}	F_{obs}	hkl	F_{cal}	F_{obs}	hkl	F_{cal}	F_{obs}
002	2.76	2.75	220	0.80	0.81	405	0.38	0.38	512	0.70	0.67	615	0.57	0.56	731	0.52	0.55
003	3.16	3.19	221	2.99	2.98	406	0.38	0.40	513	0.95	0.97	620	0.89	0.92	732	0.33	0.35
004	2.69	2.67	222	2.20	2.18	410	0.33	0.30	514	0.70	0.75	621	0.65	0.64	733	0.93	0.92
005	2.16	2.16	223	1.21	1.22	411	0.54	0.56	515	0.13	0.16	622	0.58	0.61	740	0.34	0.32
006	1.39	1.39	224	1.80	1.85	412	1.10	1.11	516	0.32	0.27	623	0.34	0.28	741	0.23	0.22
007	0.57	0.65	225	0.48	0.48	413	0.72	0.74	520	0.84	0.85	624	0.67	0.69	742	0.59	0.61
101	2.73	2.84	301	1.75	1.72	414	1.55	1.57	522	1.12	1.07	630	0.01	0.14	751	0.36	0.31
102	1.77	1.80	302	2.00	1.95	415	0.48	0.47	523	1.34	1.32	632	0.35	0.27	800	0.62	0.58
103	1.19	1.22	303	0.52	0.64	416	0.66	0.66	524	0.53	0.56	633	0.24	0.23	801	0.30	0.30
104	0.31	0.35	304	2.55	2.52	420	2.55	2.53	525	0.76	0.79	634	0.71	0.72	802	0.23	0.17
105	1.15	1.10	305	0.36	0.37	421	1.46	1.51	530	1.26	1.22	640	0.52	0.45	810	0.06	0.16
106	0.53	0.57	310	0.84	0.75	422	1.27	1.35	531	0.64	0.65	641	0.66	0.63	811	0.29	0.29
107	2.12	2.08	311	2.27	2.24	423	0.71	0.67	532	0.80	0.80	642	0.50	0.50	812	0.14	0.16
110	3.24	3.32	312	1.41	1.41	424	0.79	0.78	534	0.88	0.87	644	0.44	0.46	820	0.43	0.39
111	1.67	1.63	313	2.77	2.78	425	0.20	0.18	535	0.40	0.42	650	0.45	0.47	821	0.40	0.44
112	2.66	2.66	314	0.62	0.59	426	0.40	0.41	540	0.22	0.20	651	0.24	0.26	830	0.26	0.22
113	0.50	0.49	315	0.36	0.35	430	0.66	0.58	541	0.30	0.22	652	0.71	0.71			
114	2.20	2.17	316	0.39	0.33	431	1.78	1.80	543	0.30	0.17	653	0.55	0.50			
115	0.89	0.88	320	0.61	0.52	433	1.09	1.07	544	0.66	0.67	660	0.19	0.20			
116	1.20	1.15	321	0.57	0.58	434	0.20	0.16	545	0.34	0.35	661	0.41	0.36			
117	0.90	0.92	322	0.90	0.89	435	0.84	0.88	550	0.58	0.55	701	0.69	0.75			
200	3.11	3.05	323	1.19	1.25	436	0.42	0.42	551	0.74	0.74	702	0.29	0.17			
201	1.73	1.72	324	1.07	1.09	440	1.40	1.35	552	0.64	0.65	703	0.23	0.21			
202	0.62	0.55	325	0.80	0.84	441	0.56	0.52	554	0.55	0.53	704	0.18	0.16			
203	2.54	2.54	326	0.42	0.50	442	0.86	0.82	600	1.71	1.71	710	0.94	1.00			
204	0.53	0.61	330	2.89	2.86	443	0.40	0.35	601	0.62	0.60	711	0.41	0.44			
205	0.33	0.35	331	1.25	1.28	444	0.98	1.03	602	0.87	0.79	712	0.41	0.35			
206	0.04	0.14	332	1.78	1.76	445	0.58	0.60	603	0.20	0.25	713	0.17	0.16			
210	1.42	1.32	334	1.03	1.09	501	0.20	0.18	604	0.57	0.50	714	0.46	0.52			
211	0.06	0.16	335	0.54	0.44	503	0.60	0.61	605	0.19	0.10	720	0.06	0.17			
212	2.30	2.30	336	0.61	0.60	504	1.03	1.02	610	0.29	0.37	721	0.25	0.21			
213	2.63	2.61	400	1.00	0.96	505	0.47	0.44	611	0.80	0.77	722	0.26	0.25			
214	1.89	1.91	402	1.88	1.93	506	0.36	0.33	612	0.48	0.44	723	0.25	0.27			
216	0.93	0.96	403	2.63	2.67	510	1.56	1.56	613	0.77	0.82	724	0.56	0.53			
217	0.81	0.78	404	0.53	0.58	511	1.54	1.61	614	0.40	0.40	730	0.44	0.39			

lengths and angles (and the e.s.d.'s) calculated from the conventional parameters were identical with those obtained from the internal coordinate refinement.

The best set of structural parameters corresponds to those listed in column (5) of Table 5 for the C+R refinement of the H-urea (ii) data. The equivalent set of fractional coordinates is:

$$z_C = 0.3315 (0.0004), z_O = 0.5988 (0.0005), \\ x_N = 0.1438 (0.0002),$$

$$z_N = 0.1811 (0.0003), x_{H(1)} = 0.2524 (0.0006), \\ z_{H(1)} = 0.2846 (0.0010), \\ x_{H(2)} = 0.1406 (0.0007), z_{H(2)} = -0.0315 (0.0007).$$

(The e.s.d.'s are shown in brackets.)

Interatomic distances and angles based on these parameters are given in Table 6 where they are compared with the results of previous authors. An important correction that must be applied to the bond lengths of molecules whose thermal vibrations are described

Table 5. Various refinements of the neutron data

Data set	(1)				(2)				(3)				(4)			
	H-urea (ii) Averaged data				H-urea (ii) Averaged data				H-urea (ii) Averaged data				H-urea (ii) Averaged data			
Refinement	C				C+R				R(1st order)				R(2nd order)			
Carbon position	1.563 (2)				1.564 (2)				1.565 (3)				1.565 (3)			
C-O	1.253 (3)				1.260 (3)				1.248 (5)				1.256 (5)			
C-N	1.332 (2)				1.352 (2)				1.330 (3)				1.350 (3)			
N-H(1)	0.991 (6)				0.998 (5)				0.995 (10)				1.006 (9)			
N-H(2)	0.998 (4)				1.003 (4)				1.004 (5)				1.010 (5)			
O-C-N	121.7 (0.1)				121.7 (0.1)				121.8 (0.2)				121.8 (0.2)			
C-N-H(1)	119.1 (0.3)				119.0 (0.3)				119.0 (0.5)				119.0 (0.5)			
C-N-H(2)	120.8 (0.3)				120.2 (0.3)				121.4 (0.5)				120.9 (0.5)			
C — $\beta_{11}\beta_{12}\beta_{33}$	197	3	153		199	0	152			$R_{11} = 68$	(6)			$R_{11} = 67$	(6)	
	(5)	(6)	(7)		(5)	(6)	(7)			$R_{22} = 70$	(20)			$R_{22} = 72$	(19)	
O — $\beta_{11}\beta_{12}\beta_{33}$	292	15	130		291	18	129			$R_{33} = 383$	(19)			$R_{33} = 386$	(18)	
	(9)	(13)	(8)		(8)	(12)	(8)									
N — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	407	-218	214	2	402	-216	210	2		$T_{11} = 382$	(20)			$T_{11} = 381$	(18)	
	(5)	(6)	(5)	(3)	(5)	(5)	(5)	(3)		$T_{22} = 305$	(10)			$T_{22} = 300$	(9)	
H(1) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	520	-309	469	-7	533	-330	457	-11		$T_{33} = 165$	(7)			$T_{33} = 163$	(7)	
	(17)	(18)	(22)	(13)	(16)	(17)	(20)	(12)								
H(2) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	464	-156	277	37	468	-153	280	37								
	(14)	(20)	(14)	(10)	(13)	(18)	(13)	(10)								
b_C	0.695 (8)				0.699 (7)				0.695 (10)				0.698 (10)			
b_N	0.953 (7)				0.953 (6)				0.933 (8)				0.939 (8)			
b_H	-0.386 (7)				-0.391 (6)				-0.379 (7)				-0.384 (7)			
$R_w\%$	3.08				2.86				5.23				4.94			
$R_u\%$	4.15				3.85				6.50				6.12			
	(5)				(6)				(7)				(8)			
Data set	H-urea (i) $\mu = 2.4 \text{ cm}^{-1}$ (00l reflexions removed)				H-urea (i)* $\mu = 2.4 \text{ cm}^{-1}$				D-urea $\mu = 0.6 \text{ cm}^{-1}$				D-urea $\mu = 0.6 \text{ cm}^{-1}$			
Refinement	C				C				C+R				R (2nd order)			
Carbon position	1.568 (2)				1.573 (4)				1.564 (2)				1.564 (3)			
C-O	1.250 (3)				1.239 (6)				1.257 (3)				1.260 (6)			
C-N	1.338 (2)				1.335 (4)				1.350 (2)				1.348 (3)			
N-H(1)	0.993 (6)				0.986 (13)				1.001 (5)				1.008 (8)			
N-H(2)	1.012 (5)				1.034 (11)				1.014 (5)				1.019 (5)			
O-C-N	122.0 (0.1)				122.3 (0.2)				121.8 (0.1)				121.8 (0.1)			
C-N-H(1)	119.5 (0.3)				119.5 (0.7)				119.3 (0.3)				119.6 (0.3)			
C-N-H(2)	120.4 (0.3)				121.4 (0.7)				120.3 (0.3)				119.7 (0.3)			
C — $\beta_{11}\beta_{12}\beta_{33}$	187	7	99		133	11	55		212	2	147			$R_{11} = 39$	(4)	
	(5)	(5)	(6)		(10)	(10)	(14)		(5)	(6)	(7)			$R_{22} = 98$	(18)	
O — $\beta_{11}\beta_{12}\beta_{33}$	265	3	87		241	-15	67		271	6	129			$R_{33} = 404$	(19)	
	(7)	(10)	(8)		(15)	(20)	(17)		(8)	(10)	(8)					
N — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	371	-204	179	3	295	-189	135	4	422	-227	194	0		$T_{11} = 350$	(18)	
	(5)	(5)	(5)	(3)	(10)	(10)	(11)	(6)	(6)	(6)	(4)	(3)		$T_{22} = 336$	(8)	
H(1) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	488	-295	359	-21	419	-285	218	14	534	-300	348	-39		$T_{33} = 167$	(7)	
	(20)	(21)	(20)	(11)	(43)	(48)	(38)	(22)	(15)	(18)	(15)	(8)				
H(2) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	408	-139	211	34	283	-106	159	33	469	-148	214	36				
	(15)	(17)	(15)	(8)	(27)	(32)	(34)	(18)	(12)	(15)	(9)	(6)				
b_C	0.696 (10)				0.686 (19)				0.688 (11)				0.676 (14)			
b_N	0.936 (9)				0.955 (15)				0.955 (10)				0.916 (14)			
b_H	-0.356 (8)				-0.372 (13)				0.481 (7)				0.456 (10)			
$R_w\%$	4.44				9.75				4.71				8.06			
$R_u\%$	4.97				10.61				5.03				8.27			

Table 5 (cont.)

Data set	(9)				(10)				(11)	
	Vaughan & Donohue (1952)				X-ray as listed by Caron & Donohue (1964)					
Refinement	C + R				C				R (2nd order)	
Carbon position	1.566 (4)				1.567 (4)				1.569 (4)	
C-O	1.261 (5)				1.251 (5)				1.257 (5)	
C-N	1.357 (5)				1.336 (4)				1.358 (4)	
N-H(1)	0.967 (48)				0.948 (49)				1.055 (68)	
N-H(2)	0.838 (62)				0.823 (60)				0.779 (60)	
O-C-N	121.4 (0.2)				121.6 (0.2)				121.6 (0.2)	
C-N-H(1)	120.2 (1.8)				119.5 (1.9)				122.7 (2.5)	
C-N-H(2)	114.9 (2.0)				116.4 (3.0)				115.8 (4.2)	
C — $\beta_{11}\beta_{12}\beta_{33}$	252	8	161		237	8	171		$R_{11} = 38$ (10)	
	(10)	(16)	(15)		(9)	(15)	(15)		$R_{22} = 75$ (23)	
O — $\beta_{11}\beta_{12}\beta_{33}$	316	55	161		330	41	162		$R_{33} = 447$ (24)	
	(9)	(15)	(11)		(9)	(15)	(11)			
N — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	438	-216	206	4	448	-220	207	2		
	(10)	(13)	(11)	(13)	(10)	(13)	(12)	(8)	$T_{11} = 395$ (27)	
H(1) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	380	-322	295	293	439	-314	52	188	$T_{22} = 409$ (15)	
	(138)	(188)	(128)	(137)	(147)	(204)	(208)	(140)	$T_{33} = 182$ (11)	
H(2) — $\beta_{11}\beta_{12}\beta_{33}\beta_{13}$	443	-512	467	360	457	-386	279	241		
	(150)	(175)	(224)	(112)	(163)	(231)	(173)	(152)		
b_C	Scale				Scale				Scale	
b_N	= 1.006 (0.011)				= 1.010 (0.011)				= 1.007 (0.012)	
b_H										
$R_w\%$	4.25				4.30				5.24	
$R_u\%$	3.93				3.86				4.83	

Notes:

- (i) The various refinement methods are:
 C conventional thermal parameters
 C + R as for C + curvilinear effect calculated with $R_{11} = 0.006$, $R_{22} = 0.007$, $R_{33} = 0.039$
 R (1st order) thermal parameters are the three rotations and three translations with a linear approximation
 R (2nd order) the curvilinear effect is included
- (ii) Units are:
 Distances and angles are in Å and degrees respectively
 β 's [see equation (24)] are $\times 10^4$
 R_{11} etc. in $\text{rad}^2 (\times 10^4)$
 T_{11} etc. in $\text{Å}^2 (\times 10^4)$
 b 's in $10^{-12} \text{ cm. atom}^{-1}$

* Absorption corrected only, 10 strong reflexions removed from refinement.

in terms of a rigid-body model is the finite-arc correction and this is discussed in § 4.4 below.

4.3. Refinement of conventional thermal parameters

It is a well known result from the theory of lattice dynamics in the harmonic approximation (Maradudin, Montroll & Weiss, 1963) that the probability distribution of a thermally excited atom in a solid, $t(\mathbf{u})$, is given by $\exp(-\text{quadratic form in the displacement } \mathbf{u})$. Writing the quadratic form in the usual vector-matrix notation and normalizing gives:

$$t(\mathbf{u}) = (2\pi)^{-3/2} [\det \mathbf{B}]^{-1/2} \exp(-\frac{1}{2} \mathbf{u}^T \mathbf{B}^{-1} \mathbf{u}). \quad (7)$$

The matrix \mathbf{B} describes the thermal vibration ellipsoid of the atom. The eigenvectors of \mathbf{B} are the direction cosines of the major axes of the vibration ellipsoid, the corresponding amplitudes of vibration being the eigenvalues of \mathbf{B} . Thus the mean displacement in the direction defined by a unit vector \mathbf{z} is $\mathbf{z}^T \mathbf{B} \mathbf{z}$.

The traditional Debye-Waller factor is obtained from the Fourier transform of $t(\mathbf{u})$:

$T(\mathbf{Q}) = F\{t(\mathbf{u}); \mathbf{Q}\} = \exp(-\frac{1}{2} \mathbf{Q}^T \mathbf{B} \mathbf{Q})$, where \mathbf{Q} is the scattering vector of amplitude $4\pi \sin \theta / \lambda$.

In the usual notation this equation is often written: $T(\mathbf{Q}) = \exp(-\mathbf{h}^T \boldsymbol{\beta} \mathbf{h})$, where \mathbf{h} are the Miller indices of a reflexion.

The number of independent β_{ij} 's for the atoms in urea is reduced because the atoms occupy special symmetry positions. There are 18 independent β_{ij} 's: for the carbon and oxygen atoms β_{11} , β_{12} , β_{33} ; for the N, H(1) and H(2) atoms, β_{11} , β_{12} , β_{33} , β_{13} . Refinements carried out using these conventional anisotropic temperature factors are referred to as C refinements.

Values of the β_{ij} 's obtained for the various sets of data are shown in columns (1), (2), (5), (6) and (7) of Table 5. The significance of the comparison between columns (1) and (2) is discussed in the following section.

Of immediate interest is the difference between the β 's for H-urea (i) [column (5)] and H-urea (ii) [column (1)]. For β_{11} and β_{12} the agreement is just within statistical limits and it may be supposed that these

β 's are known to an accuracy of 2 or 3%. However, the values of β_{33} for H-urea (i) are about 30% smaller than those for H-urea (ii).

It was apparent from the studies of extinction corrections that improper corrections will reflect in the apparent value of the thermal parameters, and this can be seen by comparing the results for the absorption-extinction-corrected H-urea (i) data [column (5)] with those obtained for the absorption-corrected H-urea (i) data [column (6)]. It seems likely that the H-urea (i) crystal suffered from anisotropic extinction effects which caused an apparently low value of β_{33} . Indeed, with H-urea (i) even after the best extinction corrections were applied, the strong 00*l* series of reflexions were consistently too low in intensity and were omitted from the refinement. Thus even after taking care to correct for the effects of extinction, it is nevertheless possible to make errors of around 30% in the determination of temperature factors. The standard deviations obtained in the refinement are no guide to the actual reliability of the results.

In the above calculations it was assumed that the thermal diffuse scattering included in the Bragg reflexion can be described as being proportional to Q^2 so that, using the approximation that $1 + aQ^2 = \exp(aQ^2)$, it has the effect of a small, though unknown, addition to the diagonal terms of the **B** matrix (Willis, 1969).

4.4. Rigid molecule hypothesis

In the traditional Born-von Karman theory of lattice dynamics, upon which equation (7) is based, the lattice is described in terms of the displacements of the atoms. For a compact molecule a description in terms of the rotations and translations of the supposedly rigid molecules is more economical and leads to the following expression for the Debye-Waller factor (see Cruickshank, 1956 and Pawley, 1968),

$$T(\mathbf{Q}) = \exp \left\{ -\frac{1}{2} [\mathbf{Q}^T \mathbf{T} \mathbf{Q} + \mathbf{V}^T \mathbf{R} \mathbf{V}] \right\}, \quad (8)$$

where **V** is a matrix form derived from **a**, the radius vector to the atom from the centre of libration of the molecule; **T** is the matrix describing the displacements (translations) of the (rigid) molecule and **R** the matrix

describing the librations (angular displacements) (*i.e.* if a unit vector \hat{z} defines a direction, then just as $\hat{z}^T \mathbf{T} \hat{z}$ is the mean-square displacement in that direction, so $\hat{z}^T \mathbf{R} \hat{z}$ is the mean-square libration about that axis).

Equation (8) assumes that translational and librational motions convolute, without any correlation between them. Schomaker & Trueblood (1968) have formulated a theory that allows for correlation between the **T** and **R** matrices and they introduce an asymmetric matrix **S** which has zero (or, more strictly, indeterminate) diagonal elements.

The matrices **T**, **R** and **S** were expressed in the inertial axes of the molecule, shown in Fig. 1. In this coordinate system **T** and **R** are diagonal and there are, therefore, only six thermal parameters rather than the 18 conventional β_{ij} . This is referred to as a 'Rigid 1st order' - R(1st order) - refinement. The result of such a refinement of the H-urea (ii) data is shown in column (3) of Table 5. It should be compared with the *C* refinement of column (1). The R (1st order) refinement gives a fairly good description of the thermal motion, though the more elaborate conventional description gives a lower value of R_w .

A separate program was used to determine rigid body parameters for the urea molecule from the β 's obtained from a *C* refinement of the H-urea (ii) data. The observed β 's were weighted on the basis of their e.s.d.'s so that the values of χ^2 have their usual statistical significance. The results of these calculations are shown in Table 7.

The following comments can be made:

- (i) The rotations are markedly anisotropic.
- (ii) The major cause of the deviations from the rigid body hypothesis is the motion of the hydrogen atoms. H(1) vibrates about 30% less in the *xy* plane than the rigid-molecule would require, while both of them vibrate more in the *z* direction.
- (iii) Even the O-C-NN group is not described by the rigid-molecule theory with high accuracy; the deviations, though in all cases small, are statistically significant.

(iv) Least-squares refinement of the H-urea (ii) data using a rigid-body model gives much lower e.s.d.'s for

Table 6. *Interatomic distances for urea*

	VD ^(a) (c)	LV ^(e) (c)	SSP ^(a) (c)	CD ^(a) (d)	WLP ^(b) (c)	Present ^(b) (d)
C-O	1.262 (0.016) Å	1.28 Å	1.264 (0.006) Å	1.276 (0.008) Å	1.243 (0.006) Å	1.260 (0.003) Å
C-N	1.335 (0.013)	1.35	1.336 (0.007)	1.356 (0.007)	1.351 (0.007)	1.352 (0.002)
N-H...O	2.989	2.97	2.998 (0.005)	2.985 (0.007)	2.994 (0.006)	2.978 (0.008)
N-H...O'	3.035	3.02	3.036 (0.007)	3.009 (0.008)	3.034 (0.005)	3.035 (0.005)
O-C-N	121.0 (0.65)°	120.9°	120.9 (0.3)°	120.5 (0.3)°	121.5 (0.25)°	121.7 (0.1)°
N-H(1)					0.988 (0.020) Å	0.998 (0.005) Å
N-H(2)					0.995 (0.007)	1.003 (0.004)
C-N-H(1)					119.8 (0.8)°	119.0 (0.3)°
C-N-H(2)					118.1 (0.9)°	120.2 (0.3)°

(a) X-ray data.

(b) Neutron data.

(c) Uncorrected for libration effects.

(d) Corrected for libration effects.

(e) Electron diffraction data.

VD Vaughan & Donohue (1952).

LV Lobachev & Vainshtein (1961).

SSP Sklar, Senko & Post (1961).

CD Caron & Donohue (1964).

WLP Worsham, Levy & Peterson (1957).

the appropriate parameters than those obtained by using the two-stage approach of first refining for conventional β 's and then deriving the rigid-body parameters from them.

For the urea molecule there are only two independent terms in the correlation matrix S : S_{21} and S_{12} . When these are introduced as free parameters into the refinement, following the formulation of Pawley (1968), the improvement in R_w is on the verge of significance (from $R_w=4.94\%$ to $R_w=4.77\%$) and the parameters are $S_{21}=0.0040$ (0.0012) and $S_{12}=-0.0005$ (0.0005). Thus it is not necessary to include the S matrix in the case of the urea molecule.

4.5. The curvilinear correction

An important consequence of the molecular libration is a correction that arises when the arc motion of an atom is approximated by a linear motion. There is said to be an error in the radial direction of $\frac{1}{2}r\varphi^2$, where φ^2 is the mean-square libration of an atom at radius r (see Cruickshank, 1956, 1961). In recent years such corrections to the atomic positions have frequently been applied. However, the procedure of applying a finite-arc correction to positions determined from a refinement phrased in terms of linear motion is not entirely adequate. It is preferable to describe the motion, $t(\mathbf{u})$, in real space as a genuine finite arc motion and to take the Fourier transform of this 'smearing function'. When this is done, a formula is obtained which consists of equation (8) plus corrections. If this new expression for $T(Q)$ is used in the refinement of the data, finite arc corrections to the atomic positions at the end of refinement are no longer pertinent. The two procedures are by no means entirely equivalent. The derivation of the formulae that are required for what is referred to as the 'Rigid 2nd order' - R(2nd order) - refinement are given in Appendix 2.

An additional option that allows for the use of the 18 conventional β_{ij} as free parameters plus the curvilinear effect for fixed values of R_{11} , R_{22} , R_{33} has also been incorporated into the least-squares program and is referred to as a $C+R$ refinement.

Examine now the four refinements of the H-urea (ii) data: C , $C+R$, R(1st order) and R(2nd order) in columns (1) to (4) of Table 5. The following comments can be made:

(i) The reduction in R_w in going from C to $C+R$ and in going from R(1st order) to R(2nd order) is slight but, since there are no extra parameters, significant.

(ii) There is no change in the apparent vibration amplitudes.

(iii) The major effect is to increase the apparent bond lengths. The effects of the curvilinear correction are shown in Table 8 and to within the accuracy of the present data it makes no difference to the bond lengths whether the data are refined conventionally, and the bond lengths corrected by $\frac{1}{2}r\varphi^2$ (referred to as the Cruickshank correction) or refined using the curvilinear formulation of Appendix 2.

(iv) This does not mean that the effect of the curvilinear correction is negligible for the individual structure factors. As an example of this, the values of the calculated structure factors, F_{calc} , for the refinements of columns (1) and (2) of Table 5 are given in Table 9 for a number of individual reflexions showing appreciable discrepancies. It is apparent that variations like this may influence a Fourier difference map.

As a final demonstration of the magnitude of the curvilinear corrections a set of structure factors was calculated using the parameters of column (4) of Table 5 and then analysed using a C refinement. This procedure gave, within one e.s.d., the parameters of column (1) of Table 5 with $R_w=2.20\%$.

4.6. Anharmonic effects

Dawson, Hurley & Maslen (1967), Cooper, Rouse & Willis (1968) and Rouse, Willis & Pryor (1968) have pointed out that anharmonic interactions can have a detectable effect on diffraction intensities. They treat this case by modifying equation (7) to be:

$$t(\mathbf{u}) = N \exp \left\{ -\frac{1}{2} \mathbf{u}^T \mathbf{B} \mathbf{u} \right\} [1 + \text{cubic form in } u_1, u_2, u_3] \quad (9)$$

where N is a normalizing constant, and both the

Table 7. Rigid body parameters for the urea molecule.

These are determined (a) from least-squares refinement of the H-urea (ii) data [see column (2), Table 3]; (b) from a least-squares fit to β 's that correspond to a C refinement of the H-urea (ii) data; and (c) from a least-squares fit to the conventional β 's of the O-C-NN group that correspond to a C refinement of the H-urea (ii) data.

Rigid body parameters*	Least-squares refinement of H-urea (ii) data	Least-squares fit to conventional β 's of whole urea molecule	Least-squares fit to conventional β 's of O-C-NN group
R_{11}	0.0067 (0.0006) rad ² -4.7°	0.0058(0.0022) rad ² -4.4°	0.0041 (0.0018) rad ² -3.7°
R_{22}	0.0072 (0.0019) -4.9	0.0089(0.0070) -5.4	0.0104 (0.0070) -5.8
R_{33}	0.0386 (0.0018) -11.3	0.0317(0.0053) 10.2	0.0502 (0.0051) -12.8
T_{11}	0.0381 (0.0018) Å ²	0.0447(0.0083) Å ²	0.0318 (0.0058) Å ²
T_{22}	0.0300 (0.0009)	0.0304(0.0051)	0.0311 (0.0033)
T_{33}	0.0163 (0.0007)	0.0174(0.0032)	0.0180 (0.0022)
R_w	—	15.6%	6.2%
χ^2	—	55.0	19.0

* The values of $R^{1/2}$ in degrees are also shown.

quadratic form $\mathbf{u}^T \mathbf{B}^{-1} \mathbf{u}$ and the cubic form are limited by symmetry. This approach has been justified by a series of experiments on various fluorite compounds. For UO_2 at room temperature (Willis, 1963; Rouse, Willis & Pryor, 1968) such influences are below 1%, but for BaF_2 at 300°C (Cooper, Rouse & Willis, 1968) they approach 10% in F .

One of the aims of the present experiments was to see if such effects could be detected in an organic crystal. A major difficulty was to formulate a theory. If general cubic forms, subject only to symmetry arguments, are introduced for the atoms of urea, 26 anharmonic parameters [almost identical to the 'third order cumulants' recently discussed by Johnson (1969)] would be required. In order to limit the number of parameters to be varied in the refinement, a physical model was adopted based on the following hypotheses:

(i) that anharmonic influences operate only between atoms which are bonded neighbours, and are directed along the bond;

(ii) that the anharmonic effect should be formulated not as a structure factor theory, but as a pair-correlation theory, expressing the fact that the anharmonic interactions influence not the probability distribution of one atom, but pair-probability distribution of two atoms.

This theory is presented in Appendix 3 and could be incorporated into the refinement with the introduction of three anharmonic coefficients: one for each of the O-C bonds, the C-N bonds and the N-H bonds.

When these anharmonic parameters were introduced into the refinement of the H-urea (ii) data the decrease in R_w was not significant and the e.s.d.'s of the anharmonic parameters were larger than the actual parameter values. This showed that anharmonic effects, at least in the way they have been formulated here, are not significant at the 2% to 3% level of F .

4.7. Scattering lengths

In all cases the improvement gained by refining the three scattering lengths b_C , b_N and b_H (assuming $b_O = 0.577 \times 10^{-62}$ cm) rather than a single scale factor, was barely significant. Averaging the values from the best refinements of H-urea (i) and (ii), and D-urea, we have:

$$b_C = 0.694 \text{ (6)}, b_N = 0.950 \text{ (6)}, b_H = -0.382 \text{ (15)}$$

Of these b_C is significantly greater than the value quoted by the *Neutron Diffraction Commission* (1969). We are unable to account for this discrepancy, but it should be noted that neither the refinement model (see columns 1, 2, 3, 4 of Table 5) nor severe extinction (see columns 5 and 6) have a really significant effect on the apparent scattering lengths.

4.8. Collection and refinement of data on D-urea

A series of experiments similar to, though less complete than, those on H-urea (i) were also performed on deuterated urea (D-urea). The treatment of this data, and the conclusions about the interaction of absorption

Table 8. Comparison of bond lengths

(a) from a C refinement of the H-urea (ii) data [column (1) of Table 3], (b) from a C refinement of the H-urea (ii) data followed by the Cruickshank correction, (c) from a $C+R$ refinement of the H-urea (ii) data [column (2) of Table 3].

Bond	Bond lengths		
	C refinement	C refinement plus Cruickshank correction	$C+R$ refinement
C-O	1.253 (0.003) Å	1.262 (0.003) Å	1.260 (0.003) Å
C-N	1.332 (0.003)	1.355 (0.003)	1.352 (0.002)
N-H(1)	0.991 (0.006)	1.008 (0.006)	0.998 (0.005)
N-H(2)	0.998 (0.004)	1.005 (0.004)	1.003 (0.004)

Table 9. A selection of structure factors

h	k	l	F_{cal} (expressed as a magnitude and phase angle)			
			C refinement		$C+R$ refinement	
			Magnitude	Phase angle	Magnitude	Phase angle
3	2	0	0.61	0°	0.56	0°
4	1	0	0.33	0	0.25	0
5	1	2	0.70	-61.0	0.66	-63.3
6	1	0	0.29	0	0.42	0
5	0	3	0.60	-90.0	0.51	-90.0
6	1	2	0.48	-23.7	0.57	-15.7
4	3	4	0.20	-32.3	0.20	-23.6
7	0	1	0.69	-90.0	0.78	-90.0
7	1	1	0.41	4.6	0.42	-0.5
6	2	3	0.34	14.3	0.33	6.8
5	4	3	0.30	-55.7	0.33	-51.9
7	1	2	0.41	-15.1	0.44	-19.4
6	3	3	0.24	82.0	0.22	77.5
6	1	4	0.40	-62.9	0.41	-69.8
7	0	3	0.23	-90.0	0.32	-90.0
5	0	1	0.21	-90.0	0.05	-90.0

and extinction, follow the same lines as those of H-urea (i). The degree of deuteration appeared (from the refinement of the hydrogen scattering length) to be only about 83%. Two refinements, *C+R* and *R*(2nd order), of these data are given in columns (7) and (8) of Table 5. Neither the positional parameters of the molecule, nor the thermal parameters, nor the unit cell parameters were significantly affected by deuteration.

5. X-ray data

In view of recent interest in the problem of detecting bonding effects from X-ray observations, it had been our intention to collect a set of three dimensional X-ray data on urea. However, urea does not seem to be a good subject for an accurate X-ray study. It has already been mentioned that the large crystals used in the neutron studies showed evidence of decomposition after a few days exposure to air, and this effect was greater for the small X-ray crystals. Several small crystals were

cut, mounted, and examined photographically on a Weissenberg camera. When these were mounted on a diffractometer the angle settings to maximize the Bragg peaks appeared to shift slowly with time by a few degrees.

However, a set of three-dimensional X-ray data of apparently good accuracy is already available (Vaughan & Donohue, 1952; reanalysed by Caron & Donohue, 1964) and, as a preliminary exploration of some of the difficulties involved in these studies, we have reanalysed these data.

The atomic scattering factors for oxygen, carbon and nitrogen were calculated using the $O(^3P)$, $C(^3P)$, $N(^4S)$ Hartree-Fock wave functions of Clementi (1965) while the atomic scattering factor for hydrogen was taken from *International Tables for X-ray Crystallography* (1959). The X-ray data as listed by Caron & Donohue (1964) were then refined using various models and the results are shown in columns (9), (10) and (11) of Table 5. These refinements were found to be slightly sensitive

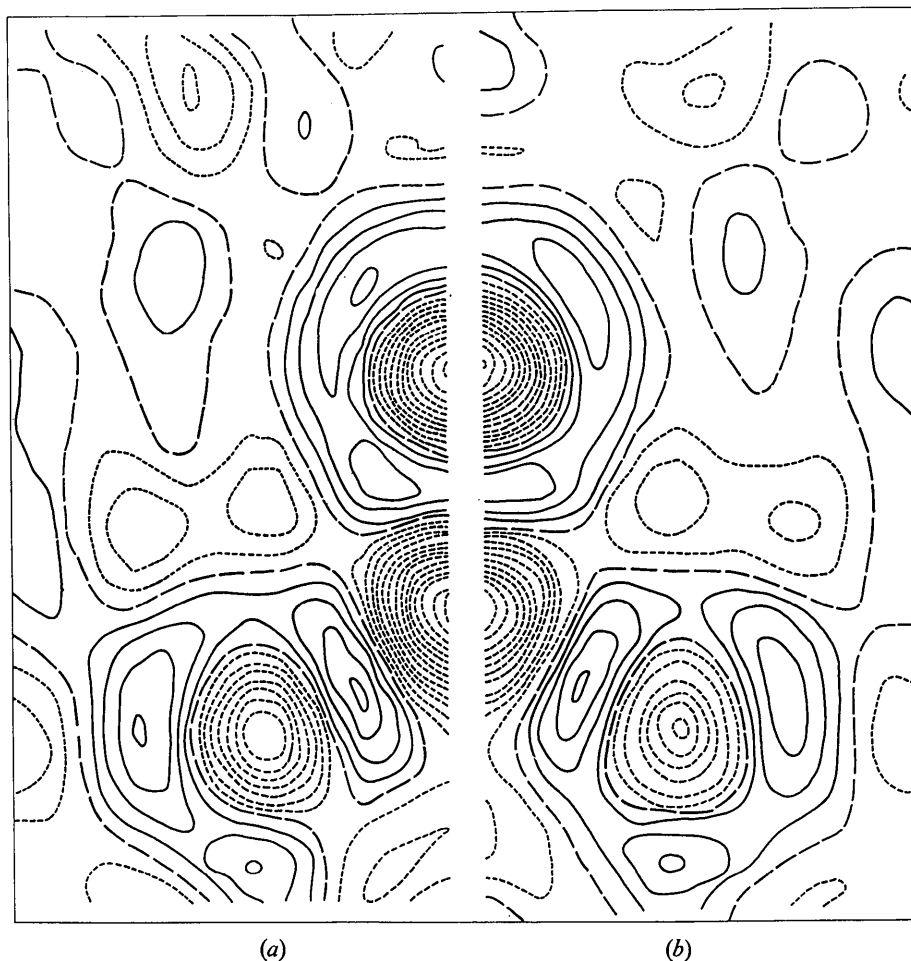


Fig. 2. Difference Fourier map in the plane of the urea molecule (a) with and (b) without the curvilinear motion correction discussed in § 4.5. Each straight line contour represents $0.1 \text{ e.}\text{\AA}^{-3}$, while the finely dashed contours represent $-0.1 \text{ e.}\text{\AA}^{-3}$. The zero level contours are shown by the coarsely dashed lines.

to the choice of weights and, as for the neutron case, a self-consistent weighting scheme was used in the final analysis.

Examination of these results shows that there is hardly any difference between the $C+R$ and C refinements and that the rigid-molecule hypothesis also gives good agreement factors. The structural parameters agree very well with those of the corresponding neutron refinement, and the thermal parameters for the carbon, oxygen and nitrogen atoms seem consistently higher than the corresponding neutron parameters. Obviously not very much reliability can be placed on the X-ray thermal parameters for hydrogen. The rigid-molecule thermal parameters are very similar to the neutron diffraction values, except for T_{22} which is significantly larger in the X-ray case.

To look for possible bonding features in urea a series of X-ray structure factors were calculated using the neutron positional and thermal parameters, and the Fourier difference map between these and the observed X-ray data examined. This procedure is affected by the difficulty in matching the scale factors. Another difficulty is that the thermal diffuse scattering contribution to the Bragg peaks may not have been the same in the X-ray and neutron experiments, with the result that there may be an apparent difference in the Debye-Waller factors (Willis, 1969) which would cause distortion in the difference Fourier map. Thus, a least-squares refinement based on the relation:

$$|F_{xo}| = K(1 + aQ^2) |F_{nc}| \quad (10)$$

was first of all carried out, where F_{nc} is the X-ray structure factor calculated from the neutron positional and thermal parameters, K is a scaling factor, and $(1 + aQ^2)$ a thermal diffuse scattering correction. Using the observed structure factors F_{xo} listed by Caron & Donohue (1964) gave the results $K=1.04$ (0.01) and $a = -0.115$ (0.012) with $R_u = 5.1\%$.

Difference maps were next prepared using the phases corresponding to the refinements in columns (9) and (10) of Table 5 for F_{xo} . The whole procedure was done twice: with and without the curvilinear motion correction discussed above in § 4.5. In Fig. 2, the two maps are shown as the left and right hand halves of the symmetric molecule.

Note first that the curvilinear motion correction does not make any appreciable difference to the Fourier difference map. Otherwise, the most striking feature of the maps is the deep troughs, with surrounding ridges, which occur at the atomic positions. There seems to be little evidence of electron differences in the bonds.

It is, however, not advisable to try to deduce too much from these calculations; the X-ray data are not accurate enough, and there are many ways in which the experimental and computational procedures could distort the result. But it does seem to suggest that the electron distributions of the atoms in urea extend more

widely in space than those calculated from the Hartree-Fock wave functions of Clementi (1965).

6. Summary of conclusions

6.1. Experimental procedure

Initial neutron diffraction measurements on H-urea (i) and D-urea showed that there was a large interaction between the corrections for absorption and extinction. Multiple Bragg scattering was also found to be an important source of error in the weaker intensities and there was no straightforward experimental procedure to determine the absorption coefficient. The interaction between absorption and extinction and the uncertainty in the value of μ showed that little confidence could be placed in the values of extinction parameters derived for a non-spherical crystal of a hydrogenous material used in a neutron diffraction experiment.

Subsequent experiments on H-urea (ii) showed that the uncertainties in the absorption and extinction corrections could be overcome by using a sphere of radius R such that $\mu R \leq 0.5$. The H-urea (ii) data were also corrected for the effects of multiple Bragg scattering by correlating complete sets of data measured at three different wavelengths.

Each of the crystals used in these studies was found to be of type II.

6.2. Refinement of neutron data

Of the various models that were used to account for the effects of thermal vibrations in urea, the best results were obtained from the $C+R$ refinement of the H-urea (ii) data ($R_w = 2.86\%$, see column (2) of Table 5), although the rigid-molecule hypothesis was not far from being correct ($R_w = 4.94\%$, column (4) of Table 5). The more rigorous treatment of the effects of thermal motion in finite arcs (Appendix 2) made very little difference. There was no difference between the thermal parameters obtained from the R(1st order) or R(2nd order) refinement of the H-urea (ii) data, and it made no difference to the bond lengths whether the data were refined conventionally, and the bond lengths corrected using the Cruickshank correction, or refined using the curvilinear formulation. However, as discussed in § 4.5, the effect of the curvilinear correction was not negligible for the individual structure factors. The effects of correlation between translational and librational motions, as described by the asymmetric matrix S of Schomaker & Trueblood (1968), were found to be negligible.

Analysis of the H-urea (ii) data also showed that anharmonic effects, at least in the way they have been formulated here, were not significant at the 2 to 3% level of F .

6.3. X-ray difference Fourier syntheses

In plotting difference Fourier syntheses between observed X-ray data, and calculated X-ray structure

factors based on the neutron results, the curvilinear corrections did not seem important. It was not possible to remove the deep negative differences at the atomic positions by adjusting a scale factor and a thermal diffuse scattering correction and it is probable that a real discrepancy exists between the observed and calculated structure factors.

During this work, one of us (PLS) was employed at the School of Physics, University of N.S.W. under a research contract from the Australian Atomic Energy Commission. We are grateful for the interest and encouragement of Professor J. F. McConnell, School of Physics, University of New South Wales in this

project. We are also much indebted to our colleague J. C. Taylor for showing us how to grow the urea crystals, and to T. M. Sabine for helpful criticism.

APPENDIX 1

Calculation of A and \bar{T} for a sphere

We wish to calculate the transmission factor

$$A = \frac{1}{v} \int e^{-\mu T} dv, \tag{A1.1}$$

and the mean path length

$$\begin{aligned} \bar{T} &= \frac{1}{A} \frac{dA}{d\mu} \\ &= \frac{1}{Av} \int T e^{-\mu T} dv, \end{aligned} \tag{A1.2}$$

for each reflexion passing through a spherical crystal of radius R cm and absorption coefficient μ cm⁻¹; v being the crystal volume and T the path length through the crystal in centimetres.

Consider a thin slice of the sphere with radius r cm as shown in Fig. 3. Also consider a beam coming through the slice at an angle θ to the y axis and being reflected after travelling a distance T cm through the crystal as shown in Fig. 4. The path length T can be shown to be

$$\begin{aligned} T &= \sqrt{R^2 - z^2 - (x \cos \theta - y \sin \theta)^2} \\ &+ \sqrt{R^2 - z^2 - (x \cos \theta + y \sin \theta)^2} - 2x \sin \theta. \end{aligned} \tag{A1.3}$$

To calculate A and \bar{T} for a sphere, the integrals (A1.1) and (A1.2) must be evaluated using the path length T defined by equation (A1.3). This can only be done analytically for the two special cases $\theta=0^\circ$ and $\theta=90^\circ$ giving the results;

$$\begin{aligned} \text{for } \theta=0^\circ, \quad A &= \frac{3}{2(\mu R)^3} \left\{ \frac{1}{2} - e^{-2\mu R} \left[\frac{1}{2} + \mu R + (\mu R)^2 \right] \right\} \\ \bar{T} &= \frac{3}{\mu} \left[1 - \frac{e^{-2\mu R}}{A} \right] \end{aligned} \tag{A1.4}$$

for $\theta=90^\circ$,

$$\begin{aligned} A &= \frac{3}{4\mu R} \left\{ \frac{1}{2} - \frac{1}{16(\mu R)^2} [1 - (1 + 4\mu R)e^{-4\mu R}] \right\} \\ \bar{T} &= \frac{3}{\mu} \left[1 - \frac{(1 - e^{-4\mu R})}{(4\mu R)A} \right]. \end{aligned} \tag{A1.5}$$

For all other values of θ , equations (A1.1) and (A1.2) must be calculated using numerical integration techniques. If a Gaussian type integration formula is used (Abramowitz & Stegun, 1965) the following equations are obtained:

$$A = \frac{3}{4\pi} \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n (1 - u_i^2) \sqrt{1 - u_j^2} w_i w_j w_k g(x_j, y_k, z_i), \tag{A1.6}$$

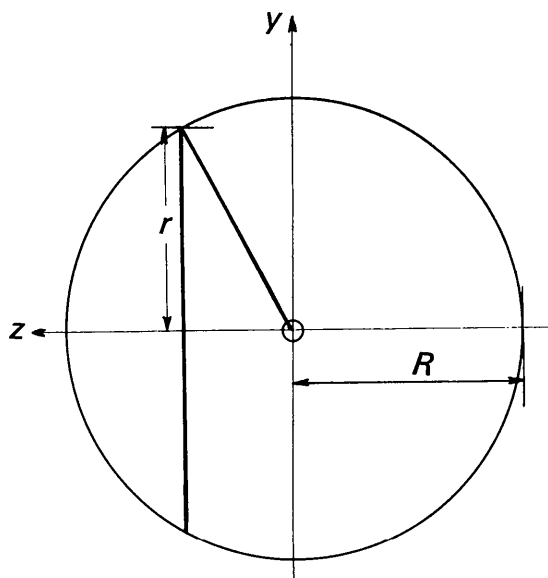


Fig. 3. Spherical crystal of radius R cm.

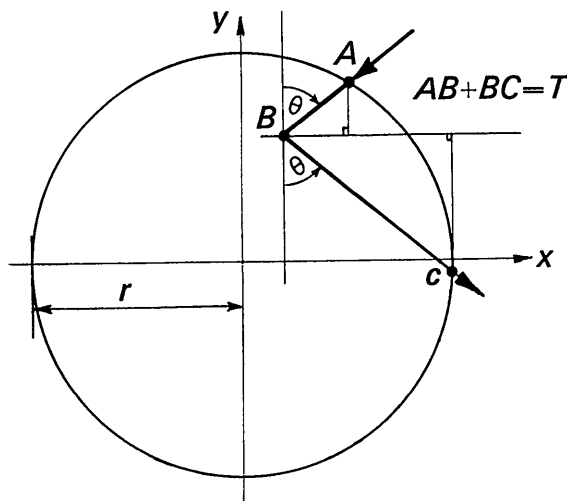


Fig. 4. Slice of radius r cm from a spherical crystal of radius R cm.

$$\bar{T} = \frac{3}{4\pi A} \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n (1-u_i^2) \sqrt{1-u_i^2} w_i w_j w_k f(x_j, y_k, z_i), \quad (A1.7)$$

where

$$\begin{aligned} z_i &= u_i R \\ x_j &= u_j R \sqrt{1-u_i^2} \\ y_k &= u_k R \sqrt{(1-u_i^2)(1-u_j^2)}, \end{aligned} \quad (A1.8)$$

and the u_i are the i th zeros of the n th order Legendre polynomial $P_n(u)$, the associated weights w_i being

given by $\frac{2}{(1-u_i^2)^2} [P'_n(u_i)]^2$. The functions $g(x_j, y_k, z_i)$

and $f(x_j, y_k, z_i)$ are defined by the relations,

$$g(x_j, y_k, z_i) = e^{-\mu T(x_j, y_k, z_i)} \quad (A1.9)$$

$$f(x_j, y_k, z_i) = T(x_j, y_k, z_i) \exp[-\mu T(x_j, y_k, z_i)], \quad (A1.10)$$

where

$$\begin{aligned} T(x_j, y_k, z_i) &= \{[R^2 - z_i^2 - (x_j \cos \theta - y_k \sin \theta)^2]^{1/2} \\ &\quad + [R^2 - z_i^2 - (x_j \cos \theta + y_k \sin \theta)^2]^{1/2} \\ &\quad - 2x_j \sin \theta\}. \end{aligned} \quad (A1.11)$$

A and \bar{T}/R are functions of μR only and tables of A and \bar{T}/R versus μR have been calculated using the numerical integration formulae described above. The values of A versus μR agree very well with the values given in *International Tables for X-ray Crystallography* (1959) (Note: A value of $n=16$ was used in these calculations), and the table of \bar{T}/R versus μR is included here (Table 10).

APPENDIX 2

Fourier transform of an atom vibrating in a finite arc

This problem has been previously considered by Kay & Behrendt (1963), Dawson (1969) and Maslen (1968). The required formula is derived here in a simpler form and is in proper agreement with the formulae quoted by these authors.

Consider an atom at a distance a from the centre of libration, displaced a distance \mathbf{u} from its rest position. Describing \mathbf{u} in a Cartesian system in which the 3 axis is along a , and the 1 and 2 axes are in the directions of the major axes of libration, gives:

$$\mathbf{u} = a \left\{ \sin \theta_2, a \sin \theta_1, -2a \left[\sin^2 \left(\frac{\theta_1}{2} \right) + \sin^2 \left(\frac{\theta_2}{2} \right) \right] \right\} \quad (A2.1)$$

where θ_1 and θ_2 are the angles of libration about axes 1 and 2. If these angles are large, many formidable difficulties arise. Indeed, the whole rigid molecule formulation would be invalidated by the failure of finite rotations to commute. So, assuming the librations are small, and replacing $\sin(\theta/2)$ by $(\theta/2)$,

$$\mathbf{u} = \left\{ a\theta_2, a\theta_1, -\frac{a}{2}(\theta_1^2 + \theta_2^2) \right\}. \quad (A2.2)$$

The angular displacement probability distribution, $t(\mathbf{u})$, in this set of coordinates may be expressed in the form,

$$t(\mathbf{u}) = N \exp \left[-\frac{1}{2} \left(\frac{\theta_1^2}{\omega_1^2} + \frac{\theta_2^2}{\omega_2^2} \right) \right], \quad (A2.3)$$

where N is a normalizing factor such that

Table 10. Values of \bar{T}/R for a sphere as a function of θ for various values of μR

μR	\bar{T}/R									
	$\theta=0^\circ$	5°	10°	15°	20°	25°	30°	35°	40°	45°
0.5	1.4183	1.4159	1.4087	1.3966	1.3801	1.3596	1.3357	1.3093	1.2811	1.2521
1	1.3253	1.3196	1.3027	1.2757	1.2403	1.1991	1.1541	1.1076	1.0611	1.0160
2	1.1135	1.0983	1.0571	0.9981	0.9310	0.8644	0.8017	0.7456	0.6959	0.6526
3	0.9019	0.8754	0.8115	0.7342	0.6602	0.5981	0.5463	0.5046	0.4698	0.4412
4	0.7233	0.6860	0.6094	0.5342	0.4718	0.4261	0.3901	0.3627	0.3403	0.3220
5	0.5897	0.5431	0.4635	0.4003	0.3524	0.3209	0.2959	0.2776	0.2624	0.2502
6	0.4942	0.4394	0.3621	0.3128	0.2762	0.2539	0.2358	0.2228	0.2121	0.2033
7	0.4253	0.3637	0.2907	0.2535	0.2249	0.2086	0.1948	0.1853	0.1773	0.1706
8	0.3751	0.3076	0.2389	0.2114	0.1884	0.1763	0.1655	0.1580	0.1520	0.1467
9	0.3376	0.2656	0.2004	0.1802	0.1613	0.1521	0.1435	0.1375	0.1328	0.1285
10	0.3092	0.2337	0.1710	0.1563	0.1405	0.1333	0.1265	0.1215	0.1179	0.1142
μR	$\theta=50^\circ$	55°	60°	65°	70°	75°	80°	85°	90°	
0.5	1.2230	1.1947	1.1680	1.1436	1.1221	1.1044	1.0912	1.0829	1.0801	
1	0.9734	0.9337	0.8977	0.8658	0.8385	0.8161	0.7994	0.7890	0.7854	
2	0.6149	0.5822	0.5539	0.5296	0.5091	0.4922	0.4793	0.4710	0.4681	
3	0.4170	0.3966	0.3791	0.3640	0.3512	0.3404	0.3318	0.3260	0.3239	
4	0.3068	0.2938	0.2828	0.2731	0.2649	0.2578	0.2520	0.2478	0.2462	
5	0.2400	0.2311	0.2238	0.2172	0.2116	0.2066	0.2025	0.1994	0.1982	
6	0.1961	0.1897	0.1845	0.1797	0.1758	0.1721	0.1691	0.1668	0.1657	
7	0.1654	0.1605	0.1567	0.1531	0.1501	0.1474	0.1451	0.1433	0.1424	
8	0.1428	0.1389	0.1361	0.1332	0.1309	0.1288	0.1270	0.1256	0.1249	
9	0.1255	0.1223	0.1201	0.1178	0.1161	0.1144	0.1129	0.1118	0.1112	
10	0.1119	0.1093	0.1075	0.1056	0.1042	0.1028	0.1016	0.1008	0.1003	

$$\int t(\mathbf{u})d\mathbf{u}=1, \quad (A2.4)$$

and ω_1^2 and ω_2^2 are the mean-square angles of libration about axes 1 and 2.

To obtain the required temperature factor the Fourier transform of (A2.3) must be taken, *i. e.*

$$T(\mathbf{Q}) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} t(\mathbf{u}) \exp(i\mathbf{Q} \cdot \mathbf{u}) d\theta_1 d\theta_2 \\ = NT_1 T_2, \quad (A2.5)$$

where, for small ω_1 and ω_2 , it has been possible to take the integral limits $+\infty$ to $-\infty$ and

$$T_1 = \int_{-\infty}^{+\infty} \exp\left[-\frac{\theta_1^2}{2} \left(\frac{1}{\omega_1^2} + iQ_3 a\right)\right] \exp[iQ_2 a \theta_1] d\theta_1, \quad (A2.6)$$

and T_2 is a similar expression in Q_1 and ω_2 .

Using standard Fourier transform theory Erdélyi (1954), gives

$$T_1 = \frac{(2\pi)^{1/2}}{\left(\frac{1}{\omega_1^2} + iQ_3 a\right)^{1/2}} \exp\left[-\frac{1}{2} \left\{ \frac{(Q_2 a)^2}{\left(\frac{1}{\omega_1^2} + iQ_3 a\right)} \right\}\right]. \quad (A2.7)$$

Setting $p_1 = aQ_3\omega_1^2$ and $p_2 = aQ_3\omega_2^2$

$$T(\mathbf{Q}) = (1 + ip_1)^{-1/2} (1 + ip_2)^{-1/2} \\ \exp\left\{-\frac{a^2}{2} \left[\frac{(Q_1\omega_2)^2}{(1 + ip_2)} + \frac{(Q_2\omega_1)^2}{(1 + ip_1)} \right]\right\}. \quad (A2.8)$$

This is the formula on which the R(2nd order) refinements are based.

At a further level of approximation, (A2.8) becomes

$$T(\mathbf{Q}) = \exp\left\{-\frac{a^2}{2} [(Q_1\omega_2)^2 + (Q_2\omega_1)^2]\right\} \\ \exp\left\{\left[\frac{i(p_1 + p_2)}{2}\right] (a^2[(Q_1\omega_2)^2 + (Q_2\omega_1)^2] - 1)\right\} \quad (A2.9)$$

and letting $p = p_1 + p_2 = aQ_3(\omega_1^2 + \omega_2^2)$, the Debye-Waller factor, W , is given by $W = a^2[(Q_1\omega_2)^2 + (Q_2\omega_1)^2]$ and (A2.9) can be reduced to the form.

$$T(\mathbf{Q}) = \exp\left(-\frac{W}{2}\right) \exp\left[\frac{ip}{2}(W-1)\right].$$

If $W \ll 1$ and p is small, this reduces to

$$T(\mathbf{Q}) = \exp\left(-\frac{W}{2}\right) \exp[-i\mathbf{Q} \cdot \delta a], \quad (A2.10)$$

where

$$\delta a = -\frac{a}{2}(\omega_1^2 + \omega_2^2).$$

Equation (A2.10) shows that $T(\mathbf{Q})$ is equivalent to the rectilinear (harmonic) Debye-Waller factor combined with a radial shift, δa , which is the finite-arc correction frequently applied at the end of harmonic refinement. However, W is by no means negligible (indeed it is frequently greater than 1) and this cannot be considered to be an acceptable procedure. The derivatives with respect to the libration amplitudes were calculated by a finite difference process in the present refinement programs.

APPENDIX 3

Anharmonic interactions between atoms

The structure factor for a crystal with n atoms in the unit cell is given by the expression (for the harmonic case)

$$F = \sum_k b_k \exp(i\mathbf{Q} \cdot \mathbf{r}_k) T_k(\mathbf{Q}). \quad (A3.1)$$

Similarly,

$$F^* = \sum_j b_j \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) T_j(\mathbf{Q}),$$

Therefore,

$$FF^* = \sum_k \sum_j b_k b_j^* \exp[i\mathbf{Q} \cdot (\mathbf{r}_k - \mathbf{r}_j)] T_k(\mathbf{Q}) T_j(\mathbf{Q}) \\ = \sum_{\substack{k \\ j \neq k}} b_k^2 T_k^2(\mathbf{Q}) + \sum_{\substack{k \\ j \neq k}} b_k b_j \exp[i\mathbf{Q} \cdot (\mathbf{r}_k - \mathbf{r}_j)] \\ \times T_k(\mathbf{Q}) T_j(\mathbf{Q}), \quad (A3.2)$$

where each pair term is of the form,

$$b_1 b_2 [\exp(i\mathbf{Q} \cdot \mathbf{r}) + \exp(-i\mathbf{Q} \cdot \mathbf{r})] T_1(\mathbf{Q}) T_2(\mathbf{Q}) \quad (A3.3)$$

with

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1. \quad (A3.4)$$

This term arises from a pair distribution function of the two atoms at \mathbf{r}_1 and \mathbf{r}_2 , which may be expressed as

$$g_p(\mathbf{r}) = b_1 b_2 \{\delta(\mathbf{r}) + \delta(-\mathbf{r})\} \exp[-\frac{1}{2}(\mathbf{r}^T \mathbf{B}_{12}^{-1} \mathbf{r})] \quad (A3.5)$$

where

$$\mathbf{B}_{12} = \mathbf{B}_1 + \mathbf{B}_2.$$

Introduction of a modification into equation (A3.5) to express the fact that the two atoms, in those cases where they are close neighbours, tend to keep apart from one another, leads to the expression

$$g_p(\mathbf{r}) = b_1 b_2 \{\delta(\mathbf{r}) + \delta(-\mathbf{r})\} \exp[-\frac{1}{2} \mathbf{r}^T \mathbf{B}_{12}^{-1} \mathbf{r}] \{1 + f(r_1)\}, \quad (A3.6)$$

where r_1 is the component of \mathbf{r} directed along the bond and $f(r)$ is required to be a simple expression such that $f(-r) = -f(r)$. The simplest expression would thus be $f(r) = \epsilon r$, but this is undesirable on physical

grounds since $\frac{\delta g}{\delta r} \neq 0$ at the actual equilibrium separation.

The form $f(r) = \epsilon r^3$ was thus chosen.

Now consider the anharmonic part of equation (A3·6),

$$g_{pa}(\mathbf{r}) = b_1 b_2 \{ \delta(\mathbf{r}) + \delta(-\mathbf{r}) \} * \exp \left[-\frac{1}{2} \mathbf{r}^T \mathbf{B}_{12}^{-1} \mathbf{r} \right] \varepsilon r_1^3. \quad (A3\cdot7)$$

The Fourier transform of equation (A3·7), G_{pa} , is thus the anharmonic correction to the intensity. The transform is easily evaluated, by separating the three space coordinates, if the matrix \mathbf{B}_{12} has a major axis along \mathbf{r} ; otherwise it is rather untidy. However, if this complexity in what is, after all, a small correction, is ignored, then \mathbf{B}_{12} can be taken as an isotropic form and the transform of

$$g_{pa}(\mathbf{r}) = b_1 b_2 \{ \delta(\mathbf{r}) + \delta(-\mathbf{r}) \} * \exp \left[-\frac{r^2}{2\gamma^2} \right] \varepsilon r_1^3 \quad (A3\cdot8)$$

is required. The transform of equation (A3·8) can be shown to be

$$G_{pa}(\mathbf{Q}) = -2b_1 b_2 \exp \left(-\frac{W_{12}}{2} \right) \varepsilon Q_1 \gamma^4 \sin(\mathbf{Q} \cdot \mathbf{r}) \times (3 - \gamma^2 Q_1^2), \quad (A3\cdot9)$$

where W_{12} is the conventional Debye–Waller exponent, $\mathbf{Q}^T(\mathbf{B}_1 + \mathbf{B}_2)\mathbf{Q}$ and Q_1 is $\mathbf{Q} \cdot \mathbf{f}$ the component of \mathbf{Q} along the bond. Note, in particular, the terms in Q_1 and Q_1^3 ; the term in Q_1 will vanish for atoms in symmetrical sites when the G_{pa} for the various bonds are added. The anharmonic analyses referred to in this paper are based on the above formula for G_{pa} summed over all pairs of atoms. The value of γ^2 , the projection of the \mathbf{B}_{12} matrix in the bond direction was set at the value of 0·03, a mean value of the mean-square vibration amplitude for each atom, and the variable parameters are the three ε 's for C–N, C–O and N–H bonds.

One could, of course, more simply formulate an anharmonic hypothesis in terms of atoms rather than atom pairs, *i.e.* write,

$$t(r) = t_{\text{harmonic}}(1 + \varepsilon r^3), \quad (A3\cdot10)$$

and take the transform to obtain $T(\mathbf{Q})$'s for each atom, which would then be introduced in the usual way when calculating the structure factor. Such a formulation was tested in refining the data, but the results were not quoted here. A disadvantage of this formulation is the very high correlation between the ε 's and the bond lengths.

Using a Lennard-Jones model to give the third derivative of interatomic potentials it may be deduced that ε should be positive and of the order of 1000 \AA^{-3} .

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