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The Positions of Hydrogen Atoms in Urea by Neutron Diffraction*

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Neutron diffraction measurements of the $h0l$ reflections from urea confirm that the hydrogen atoms are coplanar with the rest of the molecule. Unusually large amplitudes of thermal displacement were found. The apparent N–H distance, uncorrected for thermal effects, is 0·99 Å, and the C–N–H angles are close to 120°.

Introduction

The crystal structure of urea is well known; studies by Mark & Weissenberg (1923), Hendricks (1928), Wyckoff (1930) and Wyckoff & Corey (1934) established the space g[illegible] unit cell and approximate parameters. Vaughan & Donohue (1952), in a highly accurate study, determined precise oxygen, nitrogen and carbon parameters and obtained good indications of the hydrogen atoms in positions coplanar with the rest of the molecule. This indication of planarity corroborated similar findings from infra-red work (Keller, 1948; Waldron & Badger, 1950) and is supported by more recent proton magnetic resonance studies (Andrew & Hyndman, 1953). In addition, values have recently been reported for N–H bond lengths and for H–N–H and C–N–H bond angles (Andrew & Hyndman, 1955; Kromhout & Moulton, 1955), deduced also from results of proton resonance experiments.

The present work was started prior to the appearance of the proton resonance results, with the intention of obtaining precise proton positions to corroborate further the planarity of the amide grouping and to obtain accurate values for the distances and angles which involve hydrogen atoms in the amide group. The present results allow instructive comparisons to be made of neutron diffraction findings with those of X-ray and proton resonance work.

Unit cell and space group

The space group of urea has been shown to be D^3_{2d}-$P\bar{4}2_1m$; the unit cell contains two molecules; atoms have been assigned to the following positions:

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

and

8 H in two additional sets of (e) positions

(*International Tables for X-ray Crystallography*, 1952). The lattice constants adopted are those reported by Vaughan & Donohue (1952):

$$a = 5{\cdot}661, \quad c = 4{\cdot}712 \text{ Å}.$$

Each molecule lies in a mirror plane and contains a twofold rotation axis; the asymmetric unit is one-half molecule.

Experimental

Urea crystals, approximately 1 cm. in each dimension, were grown by evaporation at 43° C. from a solution of urea, ammonium bromide, and water (Bunn, 1933). A cylinder 3·2 mm. in diameter weighing 41·6 mg. was cut from a large crystal and shaped with the b crystal axis coinciding with the cylinder axis. The cylindrical specimen was dipped several times in liquid nitrogen to reduce extinction. The crystal was then accurately oriented for collection of $h0l$ data, and complete neutron diffraction data in this zone were measured out to $\sin \theta/\lambda = 0{\cdot}77$; the wave length was 1·062 Å. Data collection was carried out as previously described (Peterson & Levy, 1952). Automatic reorientation of the crystal for the various reflections was accomplished by means of a crystal rotator and associated timing circuits.

Preliminary measurements on a crystal oriented to give $hk0$ reflections were made in order to confirm the tetragonal symmetry of urea. Space-group absences of D^3_{2d} were checked and confirmed. Some exploration was made for superlattice reflections but none was observed.

Preliminary treatment of data

Observed structure factors were computed in the usual way and put on an absolute scale by calibration with the 400 reflection of NaCl. Signs were attached to these structure factors on the basis of Vaughan & Donohue's

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* Based on work peformed under the auspices of the United States Atomic Energy Commission.

(1952) parameters. For this purpose the origin was shifted to $(\frac{1}{4}, 0)$ to coincide with a center of symmetry present in the $h0l$ projection. Structure factors in Table 1 are reported on this basis. The atomic parameters were refined by the Fourier method with back shift to correct for series-termination errors. Because of the large temperature motions and resulting partial overlap in projection it was found advisable to determine new back-shift corrections at each stage of refinement. The large magnitudes and asymmetries of the temperature motions are strikingly evident in the Fourier projection shown in Fig. 1. The Fourier method was applied until no significant parameter changes were suggested. Then additional refinement of the C, N, O and H temperature parameters was attempted by trial variation. The measure of agreement between calculated and observed structure factors obtained was $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 7{\cdot}4\%$ when unobserved reflections were included at one-half the minimum observed value.

Table 1. *Structure factors for urea at room temperature*

$h0l$	F_c*	F_o†	$h0l$	F_c*	F_o†
001	−1·24	1·26	400	−0·17	0·17
2	−2·74	2·80	1	−1·06	1·09
3	−3·34	3·33	2	1·99	2·00
4	−2·99	2·96	3	2·74	2·77
5	2·49	2·49	4	−0·64	0·54
6	1·67	1·67	5	−0·42	0·35
7	−0·83	0·84	6	−0·39	0·44
101	2·66	2·60	501	0·16	0·16
2	1·79	1·88	2	−0·40	0·49
3	−1·26	1·34	3	−0·49	0·60
4	0·29	0·29	4	1·09	1·12
5	−1·28	1·31	5	−0·57	0·50
6	0·72	0·81	6	−0·38	0·16
7	2·68	2·69	600	−1·87	1·96
200	−2·92	2·78	1	0·55	0·56
1	1·84	1·78	2	0·86	0·89
2	0·60	0·65	3	−0·25	0·34
3	−2·63	2·73	4	0·58	0·65
4	0·60	0·62	5	−0·30	0·20
5	0·46	0·43	701	−0·84	0·83
6	0·22	0·31	2	−0·25	0·29
301	1·91	1·90	3	0·34	0·31
2	2·10	2·10	4	−0·16	0·20
3	0·46	0·51	800	0·67	0·56
4	−2·84	2·77	1	−0·30	0·29
5	0·40	0·40	2	−0·25	0·20
6	1·45	1·37			

* Nuclear scattering amplitudes were C, 0·661; O, 0·58; N, 0·94; H, −0·378; all in cm. × 10^{-12}.

† Experimental structure factors have been increased by 2·2% from the original absolute scale, in accordance with the least-squares scale factor.

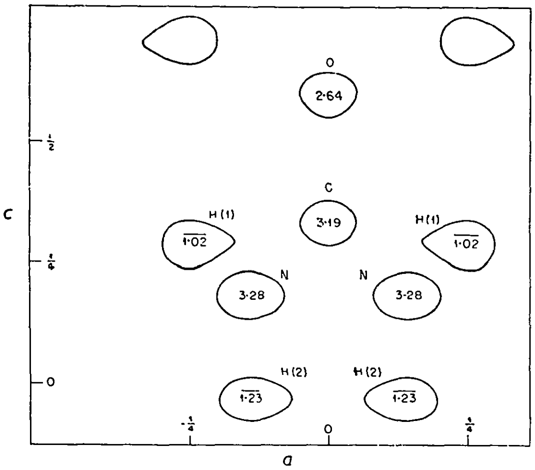

Fig. 1. Fourier projection of the urea structure along the b axis. Half-height contours are shown. Extreme values of scattering density (Fermi units per Å^2) are numerically indicated.

Least-squares refinement

Further parameter refinement was subsequently carried out by means of a complete weighted least-squares treatment, varying all independent position and temperature parameters and the scale factor (22 parameters in all). The analysis was carried out on a high-speed computer, the Oracle, in a manner previously applied (Busing & Levy, 1957; Peterson & Levy, 1957). General asymmetric temperature factors of the form

$$\exp-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh] \quad (1)$$

were assumed. For the atom positions occupied in urea the coefficients β are constrained by symmetry (Levy, 1956; Trueblood, 1956) giving three independent coefficients for C and O and four for N and H. These relationships are listed in Table 2. It is apparent that only two coefficients for C and O and only three coefficients for N and H are determinable from $h0l$ data alone. Thus a complete description of the temperature motion in urea is not available from the present data.

Table 2. *Symmetry relations between thermal parameters of positions* (*c*) *and* (*e*) *of space group* D^3_{2d}–$P\bar{4}2_1m$

Positions	h^2	k^2	l^2	hk	kl	lh
(*c*) $0, \frac{1}{2}, z$	β_{11}	β_{11}	β_{33}	β_{12}	0	0
$\frac{1}{2}, 0, \bar{z}$	β_{11}	β_{11}	β_{33}	$-\beta_{12}$	0	0
(*e*) $x, \frac{1}{2}+x, z$	β_{11}	β_{11}	β_{33}	β_{12}	β_{23}	$\beta_{31} = \beta_{23}$
$\bar{x}, \frac{1}{2}-x, z$	β_{11}	β_{11}	β_{33}	β_{12}	$-\beta_{23}$	$-\beta_{23}$
$\frac{1}{2}+x, \bar{x}, \bar{z}$	β_{11}	β_{11}	β_{33}	$-\beta_{12}$	β_{23}	$-\beta_{23}$
$\frac{1}{2}-x, x, \bar{z}$	β_{11}	β_{11}	β_{33}	$-\beta_{12}$	$-\beta_{23}$	β_{23}

The reflections were assigned weights equal to the reciprocal of the variance of F estimated according to the formula

$$W^{-1} = \frac{1}{4n}\,\frac{F^2}{E^2}\,[(E+2B)+(0{\cdot}02E)^2]\,,$$

where W is the weight, F is the structure-factor magnitude, E the integrated intensity, B the background intensity, and n the number of times the reflection was observed. The term $(0{\cdot}02E)^2$ is intended

Table 3. *Parameters of the urea structure with their standard errors*

			Neutron diffraction	
Atom	Parameters	X-ray result (V. & D.)	Preliminary refinement	Least squares
	Scale factor	—	1·000	1·022 ±0·011
C	z	0·3308±0·0032	0·334	0·3330±0·0010
	$4\beta_{11}/b_1^2$	3·9	3·0	2·35 ±0·24
	$4\beta_{33}/b_3^2$	1·9	1·0	0·85 ±0·14
O	z	0·5987±0·0019	0·595	0·5968±0·0011
	$4\beta_{11}/b_1^2$	3·9	3·2	3·74 ±0·34
	$4\beta_{33}/b_3^2$	1·9	1·2	0·80 ±0·12
N	x	0·1429±0·0021	0·144	0·1439±0·0009
	z	0·1848±0·0017	0·183	0·1832±0·0005
	$4\beta_{11}/b_1^2$	6·75	5·5	4·86 ±0·20
	$4\beta_{33}/b_3^2$	1·9	1·3	1·39 ±0·09
	$4\beta_{31}/b_3b_1$	0	0	−0·14 ±0·24
H(1)	x	—	0·259	0·2522±0·0026
	z	—	0·284	0·2839±0·0021
	$4\beta_{11}/b_1^2$	—	6·0	6·33 ±0·64
	$4\beta_{33}/b_3^2$	—	3·5	3·54 ±0·43
	$4\beta_{31}/b_3b_1$	—	0	−0·68 ±0·92
H(2)	x	—	0·141	0·1365±0·0019
	z	—	0·975	0·9724±0·0014
	$4\beta_{11}/b_1^2$	—	6·5	6·72 ±0·53
	$4\beta_{33}/b_3^2$	—	2·0	1·82 ±0·18
	$4\beta_{31}/b_3b_1$	—	0	−0·45 ±0·69

Table 4. *Apparent interatomic distances and angles and their standard errors*

	Distances	
	V. & D.	This work
C–O	1·262±0·016 Å	1·243±0·006 Å
C–N	1·335±0·013	1·351±0·007
N–O	2·989	2·994±0·006
N–O′	3·035	3·034±0·005
N–H(1)	—	0·988±0·020
N–H(2)	—	0·995±0·007
H(1)–O′	—	2·062±0·021
H(2)–O	—	2·080±0·011

	Angles	
	V. & D.	This work
N–C–O	121·0°±27′	121° 30′±15′
N–C–N	118·0°±54′	117° 0′ ±21′
H(1)–N–C	—	119° 49′±50′
H(2)–N–C	—	118° 5′ ±55′
H–N–H	—	122° 8′
N–H(1) · · · O′	—	167° 27′
N–H(2) · · · O	—	151° 43′
C–O · · · H(1)	—	105° 50′
C–O · · · H(2)	—	148° 25′
H(1) · · · O · · · H(1)′	—	148° 20′
H(2) · · · O · · · H(2)′	—	63° 10′
H(1) · · · O · · · H(2)′	—	76° 44′

to allow for non-statistical errors, like inconstancy of the primary beam and absorption errors.

The least-squares refinement was carried through three stages to convergence, utilizing 53 observations and 22 variable parameters. Following the final cycle, the matrix of the normal equations was inverted for the purpose of error estimation. Changes in position parameters as a result of the refinement were small except for hydrogen, for which the shifts were large enough to cause the two distinct N–H distances to change from 1·04 and 0·98 Å to 0·988 and 0·995 Å respectively. Thus two distances which appeared to be different were shown to be essentially equal. This error in the Fourier result must be attributed to overlap errors in projection which were not completely corrected by the backshift.

The structure-factor agreement improved considerably as a result of the least-squares refinement, the R factor being reduced to 4·34% including unobserved reflections at half minimum value, or to 3·94% omitting unobserved reflections. Table 1 demonstrates the excellence of this agreement. In Table 3, input and output least-squares parameters are listed and compared with the X-ray values of Vaughan & Donohue. The temperature-factor coefficients are listed in the form $4\beta_{ij}/b_ib_j$, where β_{ij} is a coefficient in expression (1) and b_i is the corresponding reciprocal-axis length. In this form they bear a close analogy to the conventional Debye–Waller B. It can be seen that the X-ray and neutron values for the position parameters are in agreement within the combined standard errors of the two experiments and that the thermal parameters* are in, at least, rough agreement.

Discussion

The urea molecule

Hydrogen atoms were found to occupy two sets of (*e*) positions of the space group, which places them in a mirror plane along with C, O, and N. Thus the neutron diffraction results confirm the earlier findings that the urea molecule, as well as the amide group it contains, is planar.

Interatomic distances and bond angles resulting from the least-squares analysis are listed in Table 4 along with their standard-error estimates. The agreement with the comparable values determined by Vaughan & Donohue is again excellent. The two crystallographically distinct types of hydrogen are identified in the urea molecule sketched in Fig. 2 as H(1) and H(2), where H(2) is the one *trans* to the carbonyl oxygen. The two N–H distances are seen to be equal, within the precision of the measurement, with an apparent value of 0·99 Å. This is compared in Table 5 with proton resonance estimates of this bond length. These apparent interatomic distances are the distances between the centroids of the distributions of the atomic nuclei which are represented by the temperature factors. When one or both of these distributions are extended in the plane normal to the internuclear distance, as in urea, the true mean internuclear distance may be significantly greater, as has been recognized in other recent studies (Cox, Cruickshank & Smith, 1955; Busing & Levy, 1957; Peterson & Levy, 1957). A rigorous estimate of the actual distance requires knowledge of the *joint* distribution of the nuclei. In the corrections applied in the studies cited, either the motion of one atom has been neglected, or the relative displacement of the two has been reasonably assumed to be distributed independently of the position of either individually. These simplifying circumstances do not hold in the present structure, where the various temperature factors suggest that the molecule undergoes librational motion in which the displacements of the atoms are strongly correlated. In addition, of course, complete descriptions of the individual distributions have not been obtained. All interatomic distances reported must therefore be regarded as lower limits.

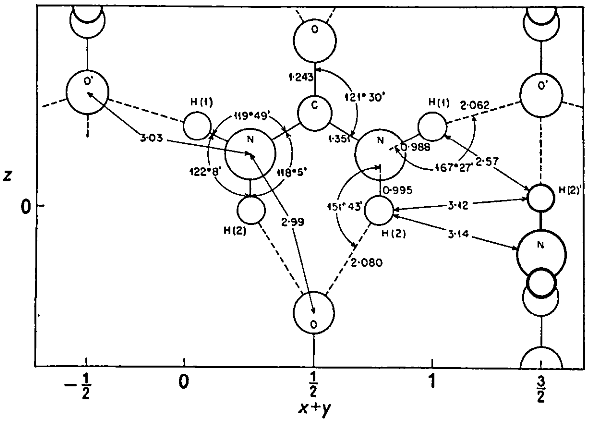

Fig. 2. Structural relationships in urea.

Table 5. *Comparison of distances and angles with proton resonance values*

Distance	This work	Andrew & Hyndman	Kromhout & Moulton
N–H	0·99±0·02 Å	1·046±0·01 Å	1·036±0·009 Å
Angle			
H–N–H	122° 8′	119·1°±2°	—
C–N–H	118° 5′±55′ 119° 49′±50′	120·5°±2°	—

The bond angles of approximately 120° found for H(1)–N–C, H(2)–N–C and H(1)–N–H(2) are in fair agreement with the proton resonance results, as can be seen in Table 5. These angles and the planar structure of urea are consistent with the assignment of sp^2 hybridization to the bonds about C and N. This amide group configuration seems to be of rather general occurrence, as is indicated by such diverse studies as electric dipole moments of unsubstituted and *N*-monosubstituted amides (Bates & Hobbs, 1952; Worsham & Hobbs, 1954), the proton resonance and infra-red work already referred to and many X-ray studies (Donohue, 1952).

The hydrogen bonds

H(1) lies more nearly on a straight line between N and O of adjacent molecules than does H(2) and might thus be expected to participate to a greater extent in hydrogen bonding. The near equality of the H(1)–O and H(2)–O distances as well as the N–H(1) and N–H(2) distances does not seem to bear out this expectation, however. It is noteworthy that the N–H(1)–O′ angle (see Fig. 2) is observed to be 167°27′, rather than 180°, which would minimize the electrostatic energy of the N–H$^+$–O$^-$ grouping. Reference to the figure shows that this angle could be enlarged to 180° without affecting the symmetry of the structure by a simple translation of the array of molecules lying in the (110) plane with respect to those in the $(1\bar{1}0)$ plane. The H_1–O′ distance could be held constant by a slight compression of the structure and there does not appear to be any close contact to oppose either adjustment strongly. The closest contact, that between H(1) and H(2)′, a distance of 2·57 Å, is actually

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* Vaughan & Donohue's temperature-factor expression assumes cylindrical symmetry about the z direction for C and O, and that principal axes for N are parallel and perpendicular to c.

slightly greater than the expected van der Waals separation. A clue to this problem may be furnished by the coordination angles about oxygen. If the urea structure were altered as described above, the C–O–H(1) angle would be about 118°; actually it is 105° 50′. This smaller C–O–H(1) angle is suggestive of a directive influence of the oxygen atom, which in turn may imply an exchange contribution to the hydrogen bond. The C–O–H(1) angle, which lies in the plane normal to that of the recipient molecule, would then result as a compromise between 118° favored by a simple electrostatic interaction, and a smaller value, in the extreme 90°, favored by maximum overlap with the π electrons of oxygen. Resonance with structures having a double C–N bond, as discussed, for example, by Vaughan & Donohue (1952), would contribute further to the stability of the interaction.

The C–O–H(2) angle lies in the plane of the urea molecule and is observed to be 148°. Here, it is clear that the structure cannot accommodate a value to optimize overlap with the unshared pairs of oxygen. Neither, of course, is an angle of 180° permitted by the arrangement.

Thermal motion

The large anisotropy of the temperature motion in urea is of considerable interest and should be explored further. A correlation between the quantities $4\beta_{ij}/b_i^2$ and the distance of the atom from the center of gravity of the urea molecule can be noticed upon reference to Table 3. This indication of librational motion about one or more axes in urea agrees generally speaking with the X-ray findings (Vaughan & Donohue, 1952).

In a recent paper, Grenville-Wells (1956) has given positional and thermal parameters resulting from a partial least-squares refinement of Vaughan & Donohue's X-ray data with form factors given by McWeeny (1951), rather than the older ones of James & Brindley used by Vaughan & Donohue. The resulting thermal parameters are in rather satisfactory agreement with those of the present study.

Precision of the determination

The standard deviation of an observation of unit weight as estimated from the residuals,

$$\left(\sum_i W_i \frac{(F_o-F_c)^2}{m-n}\right)^{\frac{1}{2}},$$

for this investigation turned out to be 2·2. For appropriately weighted data and normally distributed errors the expected value of this function is unity, but experience has shown (Peterson & Levy, 1957; Busing & Levy, 1957) that such a value is seldom attained. The deviation from unity is most likely due to under-estimation of observational errors, but might well be due partly or wholly to failure of the conventional temperature factor to describe the temperature motion in this case where displacements are so unusually large.

We have benefitted from stimulating discussions of this structure with Professors C. A. Coulson and V. Schomaker.

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