Table 6 (cont.)

5. Plane through origin, O(1), O(2):

$$+0\cdot815X-0\cdot576Y-0\cdot057Z+0=0 .$$

Distances from this plane of:

$$C(8)+0\cdot038 \text{ Å}$$
$$C(4)+0\cdot117 \text{ Å}$$

6. Angles between plane normals:

1. and 2.	$2\cdot8°$
1. and 3.	$47\cdot5°$
1. and 4.	$38\cdot9°$

are both considerably less than in nitromesitylene (Trotter, 1959) where the angle is $66\cdot4°$ – also for a nitro group adjacent to a methyl group.

Also, in 4-chloro-2,6-dinitrophenol (Richards, 1960), the nitro group which is not hydrogen bonded is rotated out of the ring plane by $34\cdot3°$. In the present structure, there is evidence of overcrowding and accompanying strain in the neighbourhood of the nitro groups; all six short intermolecular contacts listed in Table 5 involve atoms in this part of the structure, and the bonds C(6)–N(1) and C(2)–N(2) have apparently been urged away from the methyl group as evidenced by the angles, $3\cdot1°$ and $5\cdot0°$ respectively, that these bonds make with their geometrically ideal directions defined by appropriate pairs of opposite atoms across the ring (see last part of Table 4).

The various bonds and angles within the molecule (Table 4) all appear reasonable and do not call for comment. The only chemically equivalent bonds that differ significantly from one another are C(1)–C(6) and C(1)–C(2).

The authors wish to thank Drs P. Tollin and D. Young, of Dundee University for much advice and the use of their $I(\theta,\varphi)$ and Patterson section programs; and also Dr G. A. Mair, Oxford University, for the least-squares and Fourier programs written for the St. Andrews I.B.M. 1620 Computer.

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The Crystal Structure of Uronium Nitrate (Urea Nitrate) by Neutron Diffraction*

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Uronium nitrate, $(NH_2)_2COH^+NO_3^-$, crystallizes with symmetry $P2_1/c$ and lattice parameters $a = 9\cdot5434(6)$, $b = 8\cdot2010(5)$, $c = 7\cdot4982(4)$ Å, and $\beta = 124\cdot246(6)°$. The crystal structure, determined from 1744 independent experimental neutron diffraction intensities, shows a layer arrangement with all atoms approximately at $z = \frac{1}{4}$ or $\frac{3}{4}$. The acidic proton is on the carbonyl oxygen atom with an O–H distance of $1\cdot006(3)$ Å and forms a hydrogen bond to a nitrate oxygen atom with an $O–H\cdots O$ distance of $2\cdot596(2)$ Å. Four other hydrogen bonds of the type $N–H\cdots O$ join the uronium and nitrate ions into a two-dimensional network. The only contacts between the layers are of the van der Waals type. The C–O distance, $1\cdot298(2)$ Å, and C–N distances, $1\cdot312(1)$ and $1\cdot315(1)$ Å, are longer and shorter, respectively, than the corresponding distances in urea.

Introduction

The discovery that the acidic proton in acetamide hemihydrochloride (Takei & Hughes, 1959; Peterson

& Worsham, 1959) is centered in a hydrogen bond between the carbonyl oxygen atoms of two adjacent acetamide molecules led to the consideration of similar compounds as further examples of the basic nature of the amide carbonyl oxygen. The prevalence of salts of urea made these compounds obvious choices for consideration and, of these, so-called urea nitrate was

chosen for a neutron diffraction investigation of its structure, partly because of the ease with which crystals of a suitable size can be grown.

The results reported below show that in this substance the acid proton is located on the carbonyl oxygen atom, making this material an even more striking example of the basic character of this oxygen atom in amides. Because the compound $(NH_2)_2COH^+NO_3^-$ is ionic, its correct name is uronium nitrate (*Nomenclature of Inorganic Chemistry*, 1960).

Experimental

The compound was prepared by crystallization at $0\,^\circ C$ from an aqueous solution containing equimolar amounts of reagent grade urea and nitric acid. Clear crystals were obtained by recrystallization from methanol solution.

Uronium nitrate crystallizes in the monoclinic system; its space group was shown by systematic absences on X-ray precession photographs to be $P2_1/c$. The (00*l*) plane is a pronounced cleavage plane, the ease of this cleavage being very similar to that of mica.

The lattice constants were determined by least-squares refinement based on X-ray diffractometer measurements of the Bragg angles for 12 high-angle reflections. The wavelength of the Cu $K\alpha_1$ radiation was taken to be $1\cdot54051$ Å, and the results are $a= 9\cdot5434$ (6) Å, $b=8\cdot2010$ (5) Å, $c=7\cdot4982$ (4) Å, $\beta= 124\cdot246$ (6)$^\circ$. Here, as in the remainder of this paper, the figure in parenthesis is the least-squares standard error of the least-significant digit.

A clear crystal approximately 2–3 mm in each dimension which weighed $16\cdot1$ mg was mounted on the Oak Ridge automatic neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) and studied at room temperature (approximately $22\,^\circ C$). About 2000 measurements were made of reflections with $2\theta < 109^\circ$ using neutrons with wavelength $1\cdot077$ Å. After omission of duplicate measurements made for checking the reliability of the equipment, independent measurements of 1744 reflections remained. Observed structure factors were calculated and put on an absolute scale by calibration with the 400 reflection of a weighed NaCl reference crystal. Absorption correction factors ranging from $0\cdot62$ to $0\cdot75$ were calculated (Busing & Levy, 1957) with a theoretical absorption coefficient $\mu= 0\cdot204$ mm^{-1}. Later a value of $\mu=0\cdot186$ mm^{-1} was obtained by direct measurement, but the corrections were not recalculated as the net effect of this error is only to make all the observed structure factors about 2 per cent too large. The procedures, programs, and data-processing systems for these calculations have been described elsewhere (Brown & Levy, 1964). The results are listed in Table 1. Neutron diffraction examination of expected space-group absences confirmed that the space group is $P2_1/c$.

Structure determination

The pronounced cleavage parallel to the (00*l*) face and the known planar structures of the urea molecule (Worsham, Levy & Peterson, 1957) and the nitrate ion strongly indicated that the molecules and ions lie entirely in planes parallel to (001). Furthermore, the normal decline of the 00*l* structure factors for $l=2n$ indicated that these planes of molecules are at either $z=0, \frac{1}{2}$ or $z=\frac{1}{4}, \frac{3}{4}$. The distance of $3\cdot10$ Å between such planes as calculated from the lattice parameters is consistent with this planar structure.

The assumption that the relationship of the uronium and nitrate moieties would be similar to that reported for *N*-methyluronium nitrate (Bryden, 1957) reduced the number of unknown parameters to four: ϱ, an orientation angle of the group in the x, y plane; the x and y translations of this group; and the z coordinates which could be either 0 or $\frac{1}{4}$. A computer program was written which stepped each of these parameters through its entire range of possible values. For each trial arrangement, structure factors were computed for selected reflections and compared with the corresponding observations. The structures yielding the best agreement were saved and printed at the end of the search.

An initial search based on 15 observations yielded three 'best' structures, but none of these could be refined satisfactorily by the method of least squares. The results did indicate, however, that the z coordinates are approximately $\frac{1}{4}$ rather than 0. It was later noted that this conclusion could have been deduced from the near absence of the 0*kl* reflections with k odd.

We then made another search using a somewhat finer grid ($\Delta\varrho=6^\circ$, $\Delta x=\Delta y=0\cdot3$ Å) and computing the agreement with the observed structure factors of 30 low-angle reflections carefully chosen to avoid possible extinction effects. The model which showed the best agreement appeared to be chemically reasonable and subsequent least-squares refinement showed it to be the correct structure.

The discrepancy index $R=\Sigma||F_o|-s|F_c||/\Sigma|F_o|$ for 1311 non-zero reflections was $0\cdot48$ for the trial structure. Full-matrix least-squares refinement based on F^2 using individual isotropic temperature factors reduced R to $0\cdot23$, and refinement with anisotropic temperature factors yielded a final R of $0\cdot055$. The agreement measure $\sigma=[\Sigma w(F_o^2-s^2F_c^2)^2/(m-n)]^{1/2}$ (where w is the weight of an observation, s is the scale factor, and $(m-n)$ is the number of degrees of freedom) was reduced from $9\cdot56$ to $5\cdot49$ and finally to $1\cdot02$ by this refinement. The thirty-five reflections of highest intensity were omitted from the final cycles of refinement because they appeared to show some extinction effects. These reflections are marked with an E in Table 1, which lists the calculated and observed structure-factor squares with the standard errors of the latter. These errors are based on counting statistics combined with a constant-fractional error, $0\cdot03$ F^2. The neutron scattering amplitudes for C, N, and H (but not O) atoms

Table 1. *Calculated and observed structure-factor squares for uronium nitrate*

The columns headed H, CALC, OBS, and SIG contain, respectively, the index h, the calculated and observed F^2, and the standard error of F_o^2 in units of 10^{-25} cm^2 for reflections with indices k and l listed in the subheadings. The signs are those of the calculated structure factors. Reflections marked with an E were omitted from the least-squares refinement because they were assumed to be affected by extinction.

	H	CALC	OBS	SIG
	** H 0 0 *******			
	1	8	8	1 -
E	2	629	456	14 -
	3	11	12	1 +
E	4	536	459	14 -
	5	147	154	5 -
	6	271	267	9 +
	7	67	65	3 -
	8	217	222	8 -
	9	27	26	3 +
	10	45	42	3 +
	11	0	-1	2 -
	** H 1 0 *******			
	1	0	0	1 +
E	2	183	176	6 -
	3	0	-1	1 -
	4	1	3	1 -
	5	85	87	3 -
	6	1	3	2 -
	7	27	32	3 +
	8	81	83	4 +
	9	22	24	2 +
	10	4	1	2 -
	11	2	2	2 -
	** H 2 0 *******			
E	0	301	253	8 +
	1	0	-1	1 -
	2	140	136	4 -
	3	21	23	2 -
	4	11	11	2 +
	5	186	181	6 +
	6	133	130	5 +
	7	27	27	3 +
	8	18	18	2 -
	9	25	22	3 -
	10	3	5	2 +
	11	11	15	2 -
	** H 3 0 *******			
	1	0	1	1 -
E	2	401	379	12 +
	3	3	5	2 +
	4	12	12	2 +
	5	11	11	2 +
	6	406	381	12 -
	7	0	-3	2 +
	8	67	63	3 +
	9	29	32	3 -
	10	2	3	2 +
	11	2	3	2 +
	** H 4 0 *******			
	0	15	17	2 -
	1	90	92	3 +
	2	95	99	4 +
	3	113	113	4 -
	4	0	1	2 -
	5	21	23	2 +
	6	148	150	6 -
	7	4	6	2 +
	8	101	106	5 +
	9	7	4	2 -
	10	0	3	2 +
	11	4	1	2 +
	** H 5 0 *******			
E	1	598	526	16 +
	2	82	86	3 -
	3	21	17	2 -
	4	25	29	2 +
	5	146	145	5 -
	6	1	0	2 +
	7	112	119	5 +
	8	9	11	2 -
	9	1	2	2 +
	10	7	6	2 +
	** H 6 0 *******			
E	0	864	709	22 -
	1	49	52	3 -
	2	279	270	9 +
	3	3	2	2 +
	4	5	6	2 -
	5	0	1	2 -
	6	203	208	7 -
	7	2	3	2 -
	8	54	56	3 +
	9	13	11	2 -
	10	10	11	2 -
	** H 7 0 *******			
	1	21	23	2 +
	2	155	155	6 +
	3	40	39	3 -
	4	109	111	4 -
	5	14	16	2 -
	6	2	3	2 +
	7	51	55	3 +
	8	1	-2	2 -
	9	0	1	2 +
	** H 8 0 *******			
	0	90	92	4 -
	1	86	88	4 -
	2	41	41	3 +
	3	194	156	7 +
	4	1	2	2 +
	5	0	-2	2 +
	6	7	5	2 +
	7	1	-1	2 -
	8	3	-1	2 +
	9	6	4	2 +
	** H 9 0 *******			
	1	35	38	3 -
	2	210	212	7 +
	3	24	23	3 +
	4	52	52	3 -
	5	10	11	2 +
	6	23	24	3 +
	7	24	26	2 -
	8	21	23	2 -
	** H 10 0 *******			
	0	103	103	4 +
	1	1	0	2 +
	2	5	3	2 -
	3	15	16	2 +
	4	0	4	2 -
	5	21	21	2 -
	6	14	12	2 -
	7	15	12	2 -
	** H 11 0 *******			
	1	227	213	7 -
	2	0	-3	2 -
	3	63	60	3 -
	4	26	26	3 -
	5	72	70	4 +
	** H 12 0 *******			
	0	31	29	3 -
	1	10	10	2 -
	2	31	31	3 -
	** H 1 1 *******			
	-12	27	26	3 -
	-11	22	18	2 +
	-10	1	1	2 -
	-9	63	71	4 -
	-8	78	83	4 +
	-7	21	21	2 -
	-6	22	26	2 +
	-5	74	72	3 +
	-4	5	6	1 -
	-3	0	-1	1 -
E	-2	480	407	12 -
	-1	11	12	1 +
	0	0	0	1 -
	1	7	7	1 -
E	2	397	362	11 +
	3	1	0	1 +
	4	0	1	2 -
	5	53	56	3 -
	6	2	0	2 -
	7	7	6	2 +
	8	32	32	3 -
	9	21	22	2 +
	10	0	1	2 -
	11	4	2	2 -
	** H 2 1 *******			
	-12	0	-2	2 -
	-11	1	4	2 -
	-10	39	41	3 +
	-9	173	169	6 +
	-8	233	233	8 -
	-7	196	195	7 -
	-6	128	127	5 +
	-5	213	222	7 -
	-4	24	26	2 -
	-3	23	20	2 +
E	-2	775	650	20 -
	-1	0	1	1 +
E	0	1213	796	24 +
	1	6	6	1 -
E	2	611	548	17 -
	3	25	25	2 +
	4	20	18	2 -
	5	97	96	4 -
	6	70	67	4 +
	7	103	105	4 -
	8	88	87	4 -
	9	74	66	4 +
	10	16	18	2 +
	** H 3 1 *******			
	-12	4	6	2 +
	-11	9	8	3 +
	-10	4	7	2 +
	-9	59	64	3 -
	-8	5	6	2 -
	-7	14	13	2 -
	-6	6	7	2 -
	-5	41	45	2 -
	-4	15	17	2 +
	-3	301	281	9 +
	-2	0	2	1 +
	-1	217	200	6 +
	0	2	3	1 -
	1	199	190	6 -
	2	0	1	1 +
	3	215	213	7 -
	4	7	8	2 -
	5	27	27	2 +
	6	2	0	2 +
	7	7	6	2 +
	8	5	6	2 +
	9	15	13	2 +
	10	2	3	2 -
	** H 4 1 *******			
	-11	1	-1	2 +
	-10	36	37	3 +
	-9	1	-1	2 +
	-8	285	285	10 -
	-7	6	1	2 -
	-6	307	298	10 +
	-5	69	69	3 +
E	-4	632	557	17 +
	-3	72	73	3 +
	-2	163	156	5 -
	-1	6	7	2 -
	0	43	43	2 -
	1	12	14	2 -
	2	131	128	5 -
	3	80	83	3 +
	4	404	370	12 +
	5	36	36	3 +
	6	137	147	5 +
	7	8	9	2 -
	8	122	126	5 -
	9	1	2	2 +
	10	13	12	2 +
	** H 5 1 *******			
	-11	13	10	3 -
	-10	7	11	2 -
	-9	17	18	2 +
	-8	2	2	2 +
	-7	41	39	3 +
	-6	402	382	12 +
	-5	61	65	3 -
	-4	209	200	7 -
	-3	9	10	2 -
	-2	263	261	8 -
	-1	20	21	2 +
	0	0	3	2 -
	1	9	11	2 -
	2	207	208	7 +
	3	5	7	2 +
	4	159	166	6 +
	5	24	26	3 +
	6	233	232	8 -
	7	16	19	2 -
	8	0	1	2 -
	9	6	2	2 -
	10	4	5	2 +
	** H 6 1 *******			
	-11	58	57	3 +
	-10	13	13	2 +
	-9	7	9	2 +
	-8	1	1	2 +
	-7	19	20	2 -
	-6	27	32	3 -
	-5	107	113	4 -
	-4	0	2	2 -
	-3	101	102	4 -
	-2	29	28	2 +
	-1	220	214	7 +
	0	54	55	3 -
	1	198	198	7 +
	2	8	12	2 +
	3	65	68	3 -
	4	0	3	2 +
	5	70	68	3 -
	6	19	17	2 -
	7	4	3	2 -
	8	1	2	2 +
	9	3	0	2 +
	** H 7 1 *******			
	-10	6	4	2 -
	-9	1	2	2 +
	-8	0	0	2 +
	-7	193	185	7 -
	-6	0	2	2 +
	-5	70	70	3 +
	-4	229	226	8 -
	-3	43	46	3 +
E	-2	697	601	19 +
	-1	10	8	2 -
	0	0	2	2 +
	1	4	4	2 +
E	2	601	569	18 -
	3	21	21	2 -
	4	155	156	6 +
	5	38	40	3 -
	6	0	4	2 -
	7	83	83	4 +
	8	0	-2	2 -
	9	0	3	2 -
	** H 8 1 *******			
	-9	9	7	3 -
	-8	13	13	2 +
	-7	2	0	2 +
	-6	6	5	2 -
	-5	3	3	2 +
	-4	111	110	4 +
	-3	111	105	4 -
	-2	8	8	2 +
	-1	18	19	2 +
E	0	653	610	19 -
	1	18	19	2 +
	2	7	8	2 +
	3	70	73	4 -
	4	69	74	4 +
	5	2	-1	2 +
	6	4	3	2 -
	7	1	2	2 +
	8	10	11	2 +
	** H 9 1 *******			
	-8	30	25	3 +
	-7	7	10	2 -
	-6	5	3	2 -
	-5	15	15	2 -
	-4	0	2	2 -
	-3	12	12	2 +
	-2	1	1	2 -
	-1	14	16	2 -
	0	0	0	2 +
	1	11	10	2 +
	2	0	-2	2 -
	3	6	11	2 -
	4	0	0	2 +
	5	7	8	2 +
	6	5	10	2 +
	7	2	4	2 +
	** H 10 1 *******			
	-7	12	10	2 -
	-6	35	32	3 +
	-5	15	14	2 -
	-4	3	2	2 -
	-3	19	22	2 +
	-2	3	3	2 +
	-1	5	5	2 +
	0	3	3	2 -
	1	7	8	2 +
	2	6	3	2 +
	3	12	11	2 +
	4	4	4	2 -
	5	6	8	2 -
	6	13	16	2 +
	** H 11 1 *******			
	-6	140	134	5 -
	-5	1	1	2 -
	-4	158	152	6 +
	-3	7	5	2 -
	-2	23	25	2 -
	-1	22	22	3 -
	0	0	0	2 +
	1	26	28	3 +
	2	22	20	2 +
	3	1	1	2 +
	4	114	116	5 -
	** H 12 1 *******			
	-3	38	41	3 -
	-2	1	-1	2 +
	-1	43	43	3 +
	0	1	3	2 -
	1	38	34	3 +
	** H 0 2 *******			
	-13	5	4	2 +
	-12	7	7	2 -
	-11	0	1	2 -
	-10	92	91	4 -
	-9	24	27	2 -
	-8	479	477	15 +
	-7	84	83	4 +
E	-6	416	360	11 -
	-5	221	199	7 +
E	-4	611	387	12 +
	-3	6	6	1 -
E	-2	589	539	16 +
	-1	0	1	1 +
E	0	1967	1069	32 -
	1	18	16	1 +
E	2	388	349	11 +
	3	16	17	2 -
	4	271	260	9 +
	5	59	59	3 +
	6	109	110	5 -
	7	28	31	3 +
	8	62	57	3 +
	9	15	14	2 -
	10	15	14	2 -
	** H 1 2 *******			
	-13	25	24	2 -
	-12	16	14	3 -
	-11	7	4	2 -
	-10	12	15	2 -
	-9	70	71	3 +
	-8	124	127	5 +
	-7	42	41	3 +
	-6	0	1	2 +
	-5	156	154	5 -
	-4	1	2	1 -
	-3	0	-2	1 +
	-2	180	172	5 -
	-1	0	0	1 +
	0	0	1	1 +
	1	1	3	1 +
	2	110	109	4 +
	3	1	1	2 +
	4	0	-1	2 +
	5	22	18	2 +
	6	3	3	2 +
	7	11	9	2 -
	8	32	30	3 -
	9	4	1	2 -
	10	0	3	2 +
	** H 2 2 *******			
	-12	5	1	2 +
	-11	20	22	2 +
	-10	9	11	2 -
	-9	63	64	3 +
	-8	32	36	3 +
	-7	64	66	3 -
	-6	235	236	8 -
	-5	233	229	7 -
	-4	11	12	2 -
	-3	31	31	2 +
	-2	146	145	5 +
	-1	1	-1	1 -
	0	223	214	7 -
	1	4	3	1 +
	2	82	80	3 +
	3	5	6	2 +
	4	7	6	2 -
	5	77	76	4 -
	6	46	45	3 -
	7	6	11	2 -
	8	8	5	2 +
	9	5	6	2 +
	10	1	1	2 -
	** H 3 2 *******			
	-12	25	26	3 -
	-11	8	6	2 +
	-10	0	2	2 +
	-9	77	79	4 -
	-8	149	156	6 +
	-7	0	-1	2 +
E	-6	549	500	16 -
	-5	20	22	2 +
	-4	3	2	2 +
	-3	9	11	2 +
E	-2	369	349	11 +
	-1	2	3	1 -
	0	0	2	1 +
	1	0	-1	1 -
	2	200	201	7 -
	3	2	0	2 -
	4	29	31	2 -
	5	2	2	2 -
	6	194	199	7 +
	7	0	0	2 -
	8	19	23	2 -
	9	5	4	2 +
	** H 4 2 *******			
	-12	2	4	3 +
	-11	13	10	2 -
	-10	0	-2	2 -
	-9	11	13	2 +
	-8	200	193	7 -
	-7	2	-1	3 -
	-6	217	214	7 +
	-5	53	53	3 -
	-4	3	4	2 +
	-3	130	126	4 +
	-2	136	135	5 -
	-1	44	45	2 -
	0	16	16	2 +
	1	91	95	4 -
	2	45	46	3 -
	3	58	58	3 +
	4	0	2	2 -
	5	3	8	2 -
	6	66	68	4 +
	7	4	1	2 -
	8	33	33	3 -
	9	3	4	2 +
	** H 5 2 *******			
	-12	1	-2	2 -
	-11	40	36	3 -
	-10	11	11	2 +
	-9	1	4	2 +
	-8	17	20	2 -
	-7	229	232	8 +
	-6	3	7	2 +
	-5	208	203	7 -
	-4	36	39	3 +
	-3	35	36	2 -
	-2	64	61	3 -
E	-1	533	494	15 +
	0	5	7	2 -
	1	348	345	11 -
	2	62	61	3 +
	3	5	7	2 +
	4	15	17	3 -
	5	60	60	3 +
	6	0	5	2 +
	7	32	32	3 -
	8	2	4	2 +
	9	1	7	2 -
	** H 6 2 *******			
	-11	5	4	2 -
	-10	19	17	2 +
	-9	23	22	3 +
	-8	77	79	4 -
	-7	10	12	2 +
	-6	307	308	10 +
	-5	0	5	2 +
	-4	3	6	2 +
	-3	8	10	2 -
	-2	252	246	8 -
	-1	50	51	3 +
E	0	673	601	19 +
	1	21	22	2 +
	2	198	201	7 -
	3	0	1	2 -
	4	4	0	2 +
	5	0	3	2 +
	6	80	78	4 +
	7	0	-2	2 +
	8	25	23	2 -
	** H 7 2 *******			
	-11	8	8	2 -
	-10	5	2	2 +
	-9	0	1	2 -
	-8	0	1	2 +
	-7	95	99	4 +
	-6	0	1	2 +
	-5	21	16	2 -
	-4	136	137	5 -
	-3	42	47	3 -
	-2	169	168	6 +
	-1	21	19	3 +
	0	0	-2	2 -
	1	11	11	3 -
	2	75	79	4 -
	3	20	24	3 +
	4	52	55	3 +
	5	5	7	2 +
	6	5	3	2 -
	7	15	15	2 -
	8	1	1	2 +
	** H 8 2 *******			
	-10	23	23	2 +
	-9	23	22	3 -
	-8	7	7	2 -
	-7	0	-1	2 +
	-6	7	1	2 -
	-5	0	1	2 +
	-4	3	2	2 -
	-3	209	200	7 -
	-2	28	29	3 -
	-1	82	79	4 +
	0	69	74	4 +
	1	52	52	3 +
	2	30	27	3 -
	3	96	96	4 -
	4	0	1	2 -
	5	1	4	2 -
	6	3	3	2 -
	7	1	2	2 +
	** H 9 2 *******			
	-9	0	-1	2 +
	-8	44	41	3 -
	-7	31	31	3 -
	-6	41	40	3 +
	-5	7	10	2 +
	-4	58	57	3 -
	-3	35	36	3 +
	-2	188	183	7 +
	-1	36	38	3 -
	0	0	1	2 +
	1	20	22	3 +
	2	157	154	6 -
	3	8	11	3 -
	4	35	39	3 +
	5	8	11	2 -
	6	9	11	2 -
	** H 10 2 *******			
	-8	4	5	2 +
	-7	27	29	3 +
	-6	27	27	3 +
	-5	34	33	3 +
	-4	0	0	2 -
	-3	21	25	3 -
	-2	6	5	2 +
	-1	2	2	2 -
	0	88	89	4 -
	1	0	1	2 -
	2	4	3	2 +
	3	4	9	2 -
	4	0	3	2 +
	5	7	6	2 +
	** H 11 2 *******			
	-6	25	20	3 +
	-5	89	90	4 +
	-4	36	38	3 -
	-3	58	60	3 -
	-2	0	1	2 -
	-1	197	189	7 -
	0	1	-4	2 +
	1	149	152	6 +
	2	0	-1	2 -
	3	40	38	3 +
	** H 12 2 *******			
	-3	0	-2	2 +
	-2	25	27	3 +
	-1	11	12	2 +
	0	19	20	2 +
	** H 1 3 *******			
	-13	4	8	2 -
	-12	42	43	3 +
	-11	51	49	3 -
	-10	9	9	2 +
	-9	94	94	4 +
	-8	122	126	5 -
	-7	34	38	2 +
	-6	38	40	2 -
	-5	58	59	3 -
	-4	4	4	2 +
	-3	1	2	1 -
E	-2	374	348	11 +
	-1	4	2	1 -
	0	0	2	1 -
	1	1	1	2 +
	2	206	195	7 -
	3	0	0	2 -
	4	6	8	2 +
	5	18	19	2 +
	6	1	6	2 -
	7	1	0	2 -
	8	9	8	2 +
	9	4	5	2 -
	** H 2 3 *******			
	-13	21	21	2 +
	-12	0	0	2 -
	-11	2	3	2 +
	-10	68	68	4 -
	-9	246	245	8 -
	-8	388	357	12 +
	-7	207	205	7 +
	-6	149	151	5 -
	-5	282	281	9 +
	-4	13	11	2 +
	-3	19	19	2 -
E	-2	579	534	16 +
	-1	9	11	2 -
E	0	753	636	20 -
	1	17	13	2 +
	2	283	273	9 +
	3	19	19	2 -
	4	9	7	2 +
	5	24	23	2 +
	6	26	25	3 -
	7	32	31	3 +
	8	23	17	2 +
	9	19	10	2 -
	** H 3 3 *******			
	-13	60	59	3 -
	-12	5	9	2 -
	-11	22	20	3 -
	-10	6	7	2 -
	-9	124	129	5 +
	-8	3	5	2 +
	-7	17	20	2 +
	-6	12	17	2 +
	-5	35	36	2 +
	-4	25	28	2 -
	-3	241	238	8 -
	-2	0	1	1 -
	-1	132	134	5 -
	0	9	7	2 +
	1	100	106	4 +
	2	1	2	2 -
	3	90	90	4 +
	4	2	5	2 +
	5	11	14	2 -
	6	0	0	2 -
	7	2	8	2 -
	8	2	1	2 -
	** H 4 3 *******			
	-12	8	8	2 +
	-11	6	5	2 -
	-10	59	61	3 -
	-9	0	1	2 +
	-8	411	403	13 +
	-7	1	1	2 +
	-6	400	382	12 -
	-5	62	63	3 -
E	-4	549	504	16 -
	-3	42	44	2 -
	-2	132	130	5 +
	-1	3	3	2 +
	0	20	21	2 +
	1	16	18	2 +
	2	69	72	3 +
	3	51	50	3 -
	4	143	142	5 -
	5	9	11	2 -
	6	39	43	3 -
	7	4	4	2 +
	8	35	34	3 +
	** H 5 3 *******			
	-12	1	0	2 -
	-11	28	25	3 +
	-10	8	12	2 +
	-9	30	28	3 -
	-8	3	6	2 -
	-7	64	70	4 -
	-6	432	406	13 -
	-5	81	86	4 +
	-4	193	192	7 +
	-3	12	14	2 +
	-2	158	161	6 +
	-1	20	20	2 -
	0	0	2	2 +
	1	2	0	2 +
	2	78	76	4 -
	3	2	3	2 -
	4	83	87	4 -
	5	4	2	2 -
	6	86	86	4 +
	7	3	3	2 +
	8	0	0	2 -
	** H 6 3 *******			
	-12	8	7	2 +
	-11	153	152	6 -
	-10	15	18	2 -
	-9	9	8	2 -
	-8	1	3	2 -
	-7	32	33	3 +
	-6	29	33	3 +
	-5	103	109	4 +
	-4	2	4	2 +
	-3	81	78	4 +
	-2	53	52	3 -
	-1	134	139	5 -
	0	38	39	3 +
	1	102	107	4 -
	2	1	3	2 -
	3	22	24	3 +
	4	1	1	2 -
	5	28	28	3 +
	6	8	6	2 +
	7	0	4	2 +
	** H 7 3 *******			
	-11	11	17	2 -
	-10	8	9	2 +
	-9	1	2	2 -
	-8	0	3	2 -
	-7	264	264	9 +
	-6	1	3	2 -
	-5	72	69	3 -
	-4	233	231	8 +
	-3	50	52	3 -
	-2	499	493	16 -
	-1	9	11	2 +
	0	1	1	2 -
	1	0	2	2 -
	2	315	323	11 +
	3	5	5	2 +
	4	72	77	4 -
	5	13	11	2 +
	6	1	1	2 +
	7	22	22	2 -
	** H 8 3 *******			
	-10	113	109	5 +
	-9	11	8	2 +
	-8	14	12	2 -
	-7	2	5	2 -
	-6	6	4	2 +
	-5	3	4	2 -
	-4	98	105	4 -
	-3	87	90	4 +
	-2	12	13	2 -
	-1	8	12	2 -
	0	412	406	13 +
	1	9	11	2 -
	2	7	6	3 -
	3	23	24	3 +
	4	24	29	2 -
	5	1	0	2 -
	6	2	-1	2 +
	** H 9 3 *******			
	-9	110	105	4 -
	-8	30	30	3 -
	-7	12	11	2 +
	-6	2	6	2 +
	-5	16	16	2 +
	-4	0	-2	2 +
	-3	10	8	2 -
	-2	2	-1	2 +
	-1	11	10	2 +
	0	1	2	2 -
	1	5	9	2 -
	2	1	0	2 +
	3	1	-1	2 +
	4	0	1	2 -
	5	1	2	2 -
	** H 10 3 *******			
	-8	20	18	2 -
	-7	14	19	2 +
	-6	42	43	3 -
	-5	18	22	2 +
	-4	1	0	2 +
	-3	14	14	2 -
	-2	1	5	2 -
	-1	2	-1	2 -
	0	3	4	2 +
	1	5	6	2 -
	2	7	4	3 -
	3	3	3	2 -
	4	3	5	2 +
	** H 11 3 *******			
	-6	175	173	6 +
	-5	0	2	2 +
	-4	138	134	5 -
	-3	12	16	2 +
	-2	18	19	2 +
	-1	7	7	2 +
	0	1	1	2 -
	1	13	15	2 -
	2	15	17	2 -
	** H 0 4 *******			
	-13	9	6	2 -
	-12	19	18	3 +
	-11	1	-1	2 +
	-10	129	126	5 +
	-9	10	10	2 +
E	-8	613	490	15 -
	-7	48	50	3 -
	-6	376	356	11 +
	-5	206	201	7 -
E	-4	387	375	12 -
	-3	4	4	1 +
	-2	333	312	10 -
	-1	3	4	2 +
E	0	974	811	25 +
	1	16	15	2 -
	2	141	141	5 -
	3	10	8	3 +
	4	80	88	4 -
	5	13	9	2 -
	6	29	27	3 +
	7	7	10	2 -
	8	13	10	2 -
	** H 1 4 *******			
	-13	58	56	3 +
	-12	12	16	2 +
	-11	12	13	2 +
	-10	19	23	2 +
	-9	118	115	5 -
	-8	119	122	5 -
	-7	38	41	3 -
	-6	0	1	2 -
	-5	136	134	5 +
	-4	0	-1	2 +
	-3	0	3	1 -
	-2	106	107	4 +
	-1	0	3	2 +
	0	0	1	2 -
	1	4	5	2 -
	2	39	39	3 -
	3	1	2	2 -
	4	0	-1	2 +
	5	3	6	2 -
	6	3	1	2 -
	7	3	1	2 +
	8	8	6	2 +

Table 1 (cont.)

The page consists of a dense multi-column crystallographic structure-factor listing. Each column group is headed by:

H   CALC   OBS   SIG

with reflection blocks separated by lines of the form `** H k l *******` (e.g. `** H 2 4`, `** H 3 4`, `** H 4 4`, `** H 5 4`, `** H 6 4`, `** H 6 5`, `** H 6 6`, `** H 2 5`, `** H 7 5`, `** H 1 6`, `** H 7 6`, `** H 3 7`, `** H 0 8`, `** H 6 8`, `** H 6 9`, etc.).

were adjusted, together with the other parameters, in the last two cycles of refinement, and this reduced R from 0·0552 to 0·0545 (significant at a confidence level greater than 0·995, Hamilton, 1965a), but made no significant change in the coordinates. The final parameters, including these scattering factors, are listed in Table 2.

Fig. 1 shows the layer $z \simeq \frac{1}{4}$ in schematic form. The atoms are represented as 50% probability ellipsoids describing the thermal motion. Also shown in the Figure are interatomic distances and angles with their standard errors.

Discussion

The present results show clearly that the acidic proton is attached to the carbonyl oxygen atom of urea and forms a strong hydrogen bond to an oxygen atom of the nitrate ion. (See Fig. 1.) The uncorrected O–H distance is 1·006 (3) Å, almost identical to the O–D distances, 1·000 (9) and 1·007 (5), found in solid D_2O (Peterson & Levy, 1957). The mean O–H distance averaged over thermal motion is 1·014 (3) if the hydrogen atom is assumed to 'ride' on the oxygen atom (Busing & Levy, 1964). The O–H$\cdots$O distance and angle are 2·596 (2) Å and 178·2 (3)°, respectively.

The location of the proton on the carbonyl oxygen atom confirms the conclusion of Redpath & Smith (1962) based on their nuclear magnetic resonance study and contradicts the interpretation by Davies & Hopkins (1957) of the infrared spectrum. This structure as well as that of acetamide hemihydrochloride (Peterson & Worsham, 1959) indicates that the basicity of amides is due to the proton affinity of the carbonyl oxygen atom rather than that of the amine group.

The uronium ion, like the urea molecule (Worsham, Levy & Peterson, 1957), is nearly planar with the H(1)

atom showing the largest displacement, 0·033 (4) Å, from the plane defined by N(2), N(3) and O(4). This planarity may be ascribed to partial double-bond character of the C–N and C–O bonds. The C–O–H angle 113·6 (2)°, is intermediate between the tetrahedral angle of 109·5° expected for sp^3 hybridization of the oxygen atom and the 120° value expected for sp^2 hybridization.

Table 3 lists C–O and C–N distances in urea, uronium nitrate, and some related compounds. A comparison of these values clearly shows that the addition of a proton to the oxygen atom of urea increases the C–O distance and reduces the C–N distances significantly.

The principal resonance structures for urea are of the types A and B:
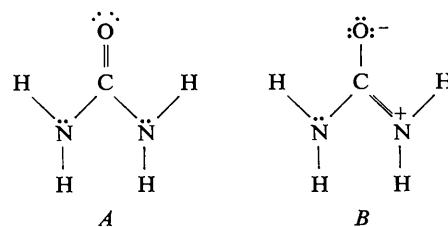
Addition of a proton to the oxygen atom has the effect of stabilizing the structures of type B, and this accounts for the observed differences in bond lengths. A similar effect would be expected for acetamide, and the tabulated distances seem to confirm this prediction.

The marked cleavage mentioned earlier is readily explained by the two-dimensional hydrogen-bonding scheme shown in Fig. 1. The uronium and nitrate ions are joined in an alternating sequence in the y direction by the O–H$\cdots$O bond (2·596 Å) at one end of the

Table 2. Final parameters for uronium nitrate

The coordinates x, y, and z and the temperature factor coefficients β_{ij} have been multiplied by 10^4. The latter are defined by the expression for the temperature factor:

$$\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	1976 (1)	4111 (1)	2548 (2)	93 (2)	53 (1)	210 (3)	4 (1)	92 (2)	7 (1)
N(1)	3113 (1)	9167 (1)	2541 (2)	100 (1)	51 (1)	240 (2)	1 (1)	106 (1)	3 (1)
N(2)	3345 (1)	3767 (1)	2612 (2)	116 (1)	70 (1)	306 (3)	4 (1)	139 (2)	0 (1)
N(3)	1013 (1)	2960 (1)	2542 (2)	117 (1)	62 (1)	322 (3)	−3 (1)	137 (2)	14 (1)
O(1)	3525 (2)	7727 (1)	2500 (4)	160 (2)	55 (2)	439 (6)	7 (2)	203 (4)	7 (2)
O(2)	1883 (2)	9460 (2)	2608 (4)	156 (2)	76 (2)	552 (8)	−2 (2)	232 (4)	−4 (3)
O(3)	3964 (2)	10292 (2)	2513 (3)	129 (2)	62 (1)	366 (5)	−4 (1)	162 (3)	2 (2)
O(4)	1501 (2)	5605 (1)	2489 (3)	127 (2)	53 (1)	343 (5)	9 (1)	144 (3)	9 (2)
H(1)	4077 (4)	4624 (4)	2565 (6)	162 (4)	128 (4)	401 (10)	−22 (3)	186 (6)	0 (5)
H(2)	3668 (4)	2584 (3)	2654 (6)	186 (5)	104 (3)	438 (11)	30 (3)	206 (7)	1 (5)
H(3)	1299 (4)	1766 (3)	2563 (5)	187 (5)	69 (3)	406 (10)	−6 (3)	182 (6)	12 (4)
H(4)	−24 (4)	3276 (3)	2483 (7)	156 (4)	128 (4)	468 (10)	−3 (3)	198 (5)	13 (5)
H(5)	2286 (3)	6439 (3)	2515 (5)	168 (4)	68 (2)	363 (8)	0 (3)	162 (5)	6 (4)

	C	N	O	H
Scattering amplitudes, cm × 10^{-15}	666 (5)	921 (4)	577	−363 (3)
	[661]	[940]	[577]	[−378]

[Amplitudes of atoms of the same chemical element were constrained to be equal. That of oxygen was not varied. The figures in brackets are the values tabulated by Bacon (1963).]

uronium ion and by two N–H···O bonds (2·981, 2·920 Å) at the other. Parallel chains are then linked in the x direction by two more N–H···O bonds (2·904, 2·969 Å). These hydrogen bonds are the only close contacts between the ions of a given layer. The layers are separated by 3·099 Å, and there are no hydrogen bonds between them. Taking the van der Waals radii of Kitaigorodski (1961), $R_C = 1·80$, $R_N = 1·57$, and $R_O = 1·36$, we find that the limiting interlayer contact appears to be a C···O(3) distance of 3·122 (2) (Å).

This hydrogen-bonding scheme is very similar to that found in N-methyluronium nitrate (Bryden, 1957). The phosphoric acid salt of urea (Sundra-Rao, Turley

Table 3. C–O and C–N bond lengths in some related compounds

Compound	C–O	C–N
Urea [a]	1·243 (6)	1·351 (7)
Uronium nitrate	1·298 (2)	1·312 (1), 1·315 (1)
N-Methyl uronium nitrate [b]	1·28	1·29, 1·30
Uronium phosphate [c]	1·29	1·32, 1·34
Acetamide (gas) [d]	1·21 (2)	1·36 (2)
Acetamide (orthorhombic) [e]	1·25 (2), 1·27 (2)	1·35 (2), 1·32 (2)
NaBr.2CH₃CONH₂ [f]	1·21 (2), 1·24 (2)	1·30 (2), 1·32 (2)
Acetamide hemihydrochloride [g]	1·269 (7)	1·309 (7)

(a) Worsham, Levy & Peterson, 1957.
(b) Bryden, 1957.
(c) Sundra-Rao, Turley & Pepinsky, 1957.
(d) Kimura & Aoki, 1953.
(e) Hamilton, 1965b.
(f) Piret, Rodrique, Gobillon & van Meerssche, 1966.
(g) Peterson & Worsham, 1959.

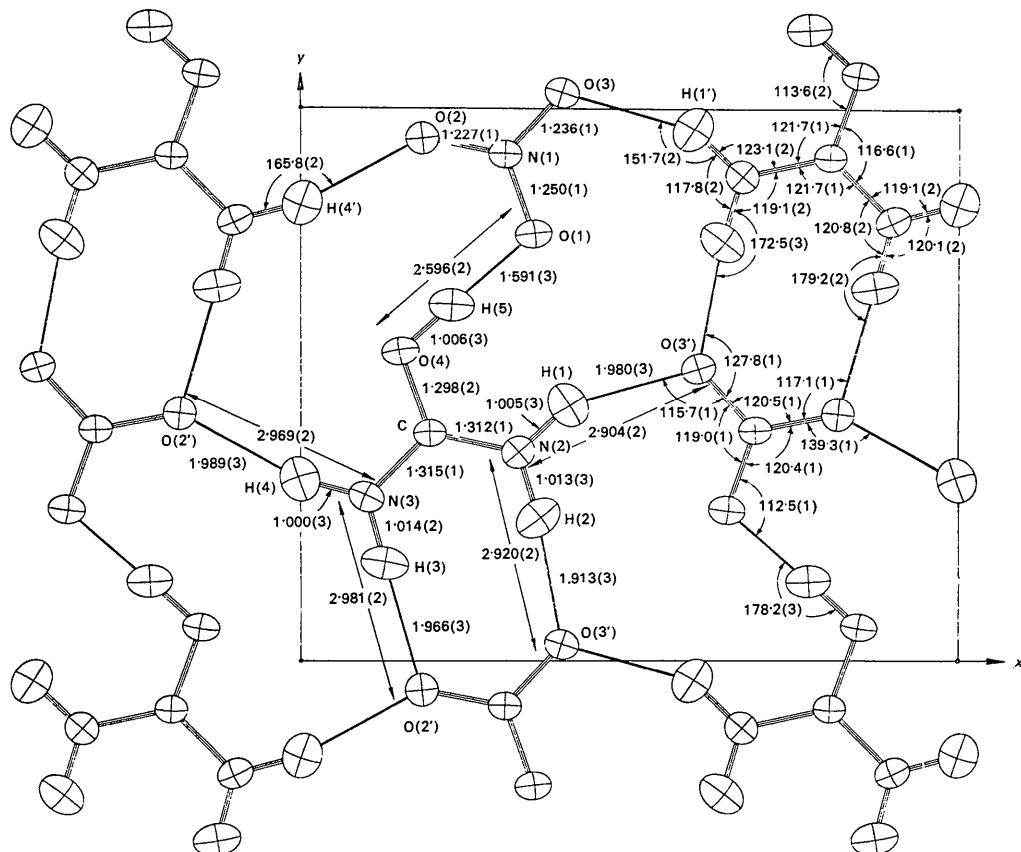Fig. 1. A single layer of the uronium nitrate crystal at $z \simeq \frac{1}{4}$, showing interatomic distances and bond angles, and their standard errors. Atoms are drawn as 50% probability ellipsoids to illustrate their thermal motion. The distances given have not been corrected for this motion.

& Pepinsky, 1957) has quite a different arrangement, however, and it is difficult to see how that structure could contain a planar uronium ion.

The temperature motion in the plane at $z \simeq \frac{1}{4}$ can be seen from the 50% probability ellipsoids of atom positions in Fig. 1. For every atom, the largest principal thermal displacement is perpendicular to the layer and is therefore not seen in the Figure. Of the principal axes in the plane of the Figure, the larger one for each atom is approximately normal to a radius from the center of the uronium or nitrate ion, suggesting librational motion in this plane. Analysis of this thermal motion by Johnson (1967) using the method suggested by Schomaker & Trueblood (1968) shows that the two ions, uronium and nitrate, can be considered individually to be rigid bodies with principal axes of translation and libration almost parallel to **a**, **b** and **c***. This analysis shows that the largest root mean square principal translations for the nitrate and uronium ions are 0·21 Å and 0·20 Å, respectively, perpendicular to the layer, *i.e.* along **c***. The larger root mean square principal librations are 11° about the *b* axis for the nitrate ion, and 7° about the *a* axis and 6° about the *b* axis for the uronium ion.

Computer programs used in this work, with their accession numbers in the *World List of Crystallographic Computer Programs* (1966), are as follows:

Least-squares refinement	*XFLS*	389
Distances and angles	*ORFFE*	363
Structure drawing	*ORTEP*	387
Structure-factor table	*EDIT*	393

Note added in proof: – Since the acceptance of this paper we have learned that the same crystal structure has been solved by two other proups using X-ray diffraction data. The work of S. Harkema & D. Feil will appear in *Acta Crystallographica*,* and that of J. C. B. White & S. A. Mason has been submitted for publication in the *Australian Journal of Chemistry*.

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* In this Part, p. 589.

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