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The crystal structure of urea oxalic acid (2:1). By S. HARKEMA, J. W. BATS, A. M. WEYENBERG* and D. FEIL, *Chemical Physics Laboratory, Twente University of Technology, Enschede, The Netherlands*.

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The crystal structure of urea oxalic acid, $2[\text{CO}(\text{NH}_2)_2] \cdot (\text{COOH})_2$ has been determined using three-dimensional X-ray data, collected on an automatic diffractometer. The space group is $P2_1/c$. The lattice constants are: $a=5.058$ (3), $b=12.400$ (3), $c=6.964$ (2) Å, $\beta=98.13$ (7)°. The number of molecules in the unit cell is two. The structure consists of layers of urea and oxalic acid molecules held together by hydrogen bonds. The positions of all hydrogen atoms have been found. The compound is not a uronium salt.

Introduction

The structures of protonated urea and thiourea cations have been investigated in recent years by a number of methods. These techniques include infrared spectroscopy (Janssen, 1961; Kutzelnigg & Mecke, 1961), nuclear magnetic resonance (Stewart & Siddall, 1970), X-ray and neutron diffraction. The work done on uronium nitrate by the last two methods (Harkema & Feil, 1969; Worsham & Busing, 1969) shows that the extra proton is attached to the oxygen atom of urea and that measurable changes in geometry occur when urea is protonated. The same applies to the structure of *N*-methyluronium nitrate (Bryden, 1957; Selman & Harkema, 1971). As part of our investigations on bonding in urea compounds we decided to determine accurately the structure of urea oxalic acid. A preliminary report on the determination of this structure has been given by Schuch, Merritt & Sturdvant (1950).

Experimental

Crystals of urea oxalic acid (2:1) were prepared by evaporation of an aqueous solution of urea and oxalic acid in the stoichiometric ratio. The crystals formed in this way have a pronounced cleavage plane which indicates a two-dimensional hydrogen-bonding network.

Data were collected on a Nonius automatic diffractometer at room temperature. A crystal of size $0.3 \times 0.2 \times 0.2$ mm was mounted with the b axis parallel to the goniometer axis. Reflexions with $\theta < 35^\circ$ were measured with Zr-filtered Mo $K\alpha$ radiation ($\lambda=0.70926$ Å) using the $\theta-2\theta$ scanning technique. In this way 1058 independent reflexions were measured, each having an intensity greater than twice the corresponding standard deviation from counting statistics. The space group of the crystal is $P2_1/c$, in accordance with previous work (Lonsdale, 1941).

The cell dimensions found are: $a=5.058$ (3), $b=12.400$ (3), $c=6.964$ (2), $\beta=98.13$ (7)° (here as in the rest of the paper the values given in brackets represent the standard deviation in the last decimal place of the number given). The number of molecules in the unit cell is 2, consisting of 2 molecules of oxalic acid and 4 molecules of urea (Lonsdale, 1941). From the very strong $10\bar{2}$ reflexion it is clear that all molecules must be approximately parallel to the $(10\bar{2})$ plane. No correction for absorption was applied ($\mu=1.3$ cm $^{-1}$).

Structure determination

As the general position in the space group $P2_1/c$ is fourfold, the oxalic acid molecules must lie on centres of symmetry.

With the help of the known molecular geometries, a model of the structure was constructed and rotated in the plane containing the molecules until an acceptable hydrogen bonding scheme was found. Coordinates for the heavy atoms obtained in this way were used as input for the least-squares program. The identity of the atoms in the urea molecule was established from the isotropic temperature factors resulting from refinement with one atomic form factor (that of nitrogen) for all atoms.

The weighting scheme used in the refinement was the same as that reported for uronium nitrate (Harkema & Feil, 1969). Four cycles of refinement with anisotropic temperature factors gave an R factor of 7.1%.

A difference Fourier synthesis made at this stage clearly revealed the hydrogen atoms. Inclusion of the hydrogen atoms and refinement of their positions and isotropic temperature factors, together with the positions and anisotropic temperature factors of the other atoms, gave a final R value of 4.0%. In the last stages of refinement a secondary-extinction correction was applied (Zachariasen, 1963; Larson, 1970). Observed and calculated structure factors are collected in Table 1.

Final positional parameters are given in Table 2. Table 3 shows the vibration parameters obtained from the least-squares analysis. The labelling of the atoms is given in Fig. 1, which shows a projection of the structure on the $(10\bar{2})$

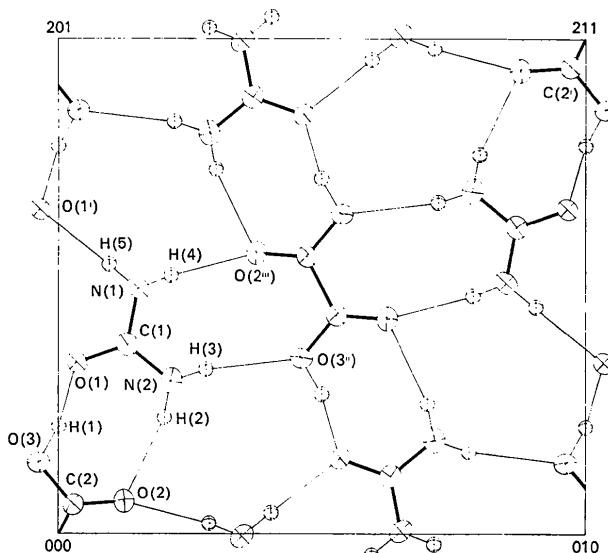


Fig. 1. Projection of the crystal structure of urea oxalic acid on $(10\bar{2})$. The vibration ellipsoids of the heavy atoms are scaled to include 50% probability. The hydrogen atoms have arbitrary, small isotropic vibration parameters.

* Present address: AKZO research, Arnhem, The Netherlands.

Table 1. Observed and calculated structure factors ($\times 10$) for urea oxalic acid

H	K	L	P0	PC	H	K	L	P0	PC	H	K	L	P0	PC	H	K	L	P0	PC	H	K	L	P0	PC												
1	0	0	227	211	-4	1	2	29	36	-5	2	1	60	59	7	3	0	10	6	1	6	2	69	66												
1	0	0	230	214	-4	1	2	22	62	-5	2	1	23	28	3	4	0	10	6	1	6	2	69	66												
1	0	0	219	309	-4	1	2	22	30	-5	0	1	22	28	3	4	0	10	6	1	6	2	69	66												
-2	0	0	311	309	-5	1	2	56	58	-1	2	2	310	298	1	3	1	45	9	-2	0	105	104	3	4	10	12	10								
3	0	0	135	132	-6	1	2	21	22	-1	2	2	24	242	2	3	1	74	8	-3	0	105	104	3	4	10	12	10								
1	0	0	17	17	-7	1	2	11	12	-2	2	2	82	59	-3	1	1	113	139	4	0	50	52	1	5	0	296	298								
-4	0	0	37	26	-8	1	2	10	8	-3	2	2	37	38	3	3	1	100	102	5	0	50	52	1	5	0	186	188								
5	0	0	36	46	-9	1	2	10	8	-3	2	2	100	102	5	0	50	52	1	5	0	296	298	3	5	8	17	13								
-5	0	0	26	46	-1	1	3	122	120	4	2	2	201	205	4	3	1	82	92	-5	0	108	113	-3	5	0	85	86								
6	0	0	25	31	-1	1	3	128	127	4	2	2	15	205	5	3	1	28	29	6	0	85	86	-2	5	9	11	11								
-7	0	0	62	60	-2	1	3	184	185	6	2	2	6	67	6	3	1	27	26	6	0	16	17	4	0	86	87	2	5	9	10	6				
8	0	0	21	20	-3	1	1	41	41	6	2	2	70	70	7	3	0	10	6	-7	0	104	104	5	0	105	104	3	4	10	12	10				
0	0	0	24	24	-3	1	1	113	112	6	2	2	28	27	0	3	1	120	119	1	1	1	100	102	5	0	43	45	-1	6	0	117	117			
1	0	0	210	175	-4	1	1	77	81	-1	2	1	167	158	-1	2	1	111	122	-1	1	1	100	102	5	0	43	45	-1	6	0	117	117			
2	0	0	245	250	-4	1	1	53	52	-1	2	1	119	118	1	3	1	222	223	2	1	1	69	72	2	4	26	26	2	3	1	69	72			
2	0	0	29	29	-5	1	1	16	16	-2	2	1	150	157	3	3	1	291	131	1	1	1	62	59	0	1	56	56	1	5	0	24	24			
3	0	0	254	254	-6	1	1	41	40	-2	2	1	70	72	2	3	1	150	157	3	3	1	52	52	-1	5	36	35	1	5	0	24	24			
4	0	0	179	185	-1	2	1	113	111	0	3	2	115	113	0	4	2	255	152	-2	5	91	90	-8	0	60	64	-2	5	90	101	9	1	11	11	
5	0	0	35	35	-1	1	14	152	152	0	3	2	14	12	4	5	2	116	109	1	2	187	149	2	5	90	90	6	0	61	62	2	5	90	122	31
6	0	0	94	94	-2	1	145	139	-5	3	2	50	50	5	3	2	24	24	2	2	217	168	2	5	60	65	-2	5	22	23	3	2	2	94	192	
7	0	0	36	34	-2	1	25	23	6	2	2	32	31	6	3	2	53	50	-2	2	133	135	1	2	21	20	1	2	1	44	44					
8	0	0	37	37	-2	1	16	16	6	2	2	32	31	6	3	2	27	26	2	2	60	68	0	1	38	38	1	2	1	22	23					
9	0	0	241	235	-4	1	1	33	32	0	3	1	100	149	-1	3	1	174	180	4	2	114	121	5	1	65	72	2	5	7	1	11	11			
10	0	0	64	64	-1	1	1	70	72	1	2	1	65	67	1	3	1	78	76	1	2	73	71	-6	1	52	54	-2	5	153	154					
11	0	0	416	413	-5	1	1	10	2	-2	2	1	129	115	2	3	1	108	125	-5	2	81	82	0	1	219	196	-1	2	1	21	22				
12	0	0	114	117	-1	1	1	38	38	-2	2	1	180	187	3	3	1	40	43	6	2	102	10	1	1	52	55	2	5	10	20	15				
13	0	0	129	129	-1	1	1	92	91	-4	2	1	79	74	-4	3	1	33	32	2	2	21	21	-2	5	1	19	19	1	2	1	65	65			
14	0	0	24	23	-2	1	1	62	61	4	2	1	14	16	4	3	1	14	12	-7	2	16	13	2	5	56	53	-6	1	21	21	2	5	93	90	
15	0	0	104	104	-1	1	1	21	21	10	2	1	55	55	5	3	1	31	31	-8	2	117	117	1	2	1	17	17	1	2	1	17	17			
16	0	0	52	64	-3	1	1	87	91	-2	2	1	33	31	7	3	1	12	11	1	4	58	54	-2	5	68	67	1	2	32	32	3	2	116	116	
17	0	0	25	25	-2	1	1	26	25	-2	2	1	26	25	2	3	1	129	129	-1	3	87	88	0	1	51	57	-1	2	165	162	4	2	156	156	
18	0	0	136	132	-5	1	1	16	16	-2	2	1	27	27	1	4	3	222	227	3	1	12	9	5	2	72	78	-2	5	87	93	5	1	64	64	
19	0	0	27	27	-5	1	1	43	41	-1	2	1	55	54	5	5	2	37	36	3	3	20	59	5	1	6	6	1	2	15	14	7	1	3	45	45
20	0	0	44	41	-1	1	17	18	-1	2	1	56	55	3	3	4	9	10	-3	3	66	69	7	2	42	41	4	6	2	12	12	2	5	2	93	97
21	0	0	130	148	-1	1	1	31	34	0	2	1	25	22	3	3	8	87	82	5	3	11	16	-1	2	21	22	2	5	1	19	19	1	2	102	103
22	0	0	64	64	-1	1	1	59	60	2	1	2	27	27	0	3	1	20	20	1	2	117	117	1	2	1	21	21	0	1	2	21	21	1		
23	0	0	14	16	-2	1	1	28	26	-6	2	1	25	27	5	3	4	68	68	0	3	89	82	2	5	63	68	-2	5	2	117	117	1	2	117	117
24	0	0	25	26	-1	1	1	68	68	6	2	1	14	15	-6	3	1	17	16	-1	4	90	87	-1	3	61	61	7	2	126	127	6	2	117	117	
25	0	0	15	15	-2	1	1	16	16	2	2	1	20	19	-1	3	1	107	105	3	3	117	115	1	2	117	117	1	2	117	117	1	2	117	117	
26	0	0	57	55	-1	1	1	16	16	2	2	1	16	17	-1	3	1	22	22	2	3	77	77	3	3	26	26	1	2	124	125	5	2	117	117	
27	0	0	14	15	-4	1	1	25	39	-1	3	1	25	24	-2	4	3	31	32	4	5	63	64	-1	3	63	64	8	2	24	24	2	5	11	11	
28	0	0	24	24	-2	1	1	16	16	-2	2	1	26	25	2	3	7	7	9	3	1	16	17	2	3	77	77	1	2	117	117	1	2	117	117	
29	0	0	61	61	-2	1	1	17	17	2	2	1	27	27	2	3	7	7	9	8	3	11	12	-2	5	64	65	1	2	29	29	2	5	11	11	
30	0	0	6	29	-2	1	1	27	27	2	2	1	27	27	2	3	7	7	9	8	3	11	12	-2	5	64	65	2	2	29	29	2	5	11	11	
31	0	0	8	15	-1	1	1	26	26	6	2	1	27	27	6	3	7	7	9	8	3	11	12	-2	5	64	65	2	2	29	29	2	5	11	11	
32	0	0	5	12	-1	2	1	62	65	-5	2	1	27	29	4	3	5	23	26	7	3	45	25	2	5	6	5	2	2	117	117	1	2	117	117	
33	0	0	1	2	22	22	-1	2	1	26	25	2	3	1	21	21	-1	2	6	25	22	1	3	5	6	5	2	2	117	117	1	2	117	117		
34	0	0	1	1	2	24	24	-2	2	1	27	27	2	3	1	11	12	-1	2	6	25	24	2	3	5	6	5	2	2	117	117	1	2	117	117	
35	0	0	1	1	2	25	25	-1	2	1	27	27	2	3	1	11	12	-1	2	6	25	24	2	3	5	6	5	2	2	117	117	1	2	117	117	
36	0	0	1	1	2	26	26	-2	2	1	27	27	2	3	1	11	12	-1	2	6	25	24	2	3												

Table 3. *Vibration parameters*

The temperature factor for the heavy atoms was: $\exp[-2\pi^2(h^2 a^{*2} U_{11} + 2hk a^* b^* U_{12} + \dots)]$.

The temperature factor for the hydrogen atoms was: $\exp[-(B \sin^2 \theta/\lambda^2)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0.0396 (6)	0.0312 (8)	0.0578 (10)	-0.0069 (6)	-0.0136 (5)	-0.0043 (9)
N(2)	0.0480 (8)	0.0281 (8)	0.0635 (10)	0.0025 (6)	-0.0127 (7)	-0.0017 (9)
O(1)	0.0331 (5)	0.0257 (8)	0.0537 (7)	-0.0022 (3)	-0.0129 (3)	-0.0030 (4)
O(2)	0.0377 (5)	0.0234 (8)	0.0602 (7)	-0.0016 (3)	-0.0093 (5)	0.0013 (4)
O(3)	0.0289 (5)	0.0288 (8)	0.0498 (7)	-0.0006 (3)	-0.0096 (3)	0.0035 (4)
C(1)	0.0317 (6)	0.0281 (8)	0.0347 (7)	-0.0022 (6)	0.0007 (5)	-0.0022 (4)
C(2)	0.0266 (5)	0.0257 (16)	0.0344 (7)	0.0025 (6)	0.0009 (5)	-0.0004 (4)
H(1)	7.3 (6)					
H(2)	4.8 (4)					
H(3)	4.9 (5)					
H(4)	6.1 (6)					
H(5)	4.9 (5)					

Table 4. *Bond distances (Å)*

Urea-oxalic acid	Oxalic acid dihydrate	Urea
(a), (d), (g)	(b), (e), (g)	(c), (e), (f)
C(2)-C(2')	1.521 (5)	1.536 (3)
C(2)-O(2)	1.209 (3)	1.212 (4)
C(2)-O(3)	1.289 (5)	1.291 (5)
O(3)-H(1)	0.96 (4)	1.026 (7)
C(1)-N(1)	1.318 (6)	
C(1)-N(2)	1.321 (4)	
C(1)-O(1)	1.260 (3)	
N(2)-H(3)	0.86 (2)	
N(1)-H(4)	0.84 (2)	
N(2)-H(2)	0.86 (4)	
N(1)-H(5)	0.88 (3)	
O(1)···O(3)	2.472 (5)	
O(2)···N(2)	2.999 (5)	
O(3'')···N(2)	3.123 (3)	
O(2'')···N(1)	2.911 (3)	
O(1')···N(1)	2.941 (4)	

(a) Present work.

(b) Sabine, Cox & Craven (1969).

(c) Pryor & Sanger (1970).

(d) X-ray.

(e) Neutron.

(f) Bond lengths corrected for thermal motion.

(g) Bond lengths not corrected for thermal motion.

Table 5. *Bond angles (°)*

Urea-oxalic acid	Oxalic acid dihydrate	Urea
(a), (d), (g)	(b), (e), (g)	(c), (e), (f)
C(2')-C(2)-O(2)	121.8 (2)	121.0 (3)
C(2')-C(2)-O(3)	112.3 (3)	112.4 (3)
O(2)-C(2)-O(3)	125.9 (2)	126.6 (3)
C(2)-O(3)-H(1)	110 (3)	114.4 (6)
O(1)-C(1)-N(1)	119.8 (3)	
O(1)-C(1)-N(2)	122.2 (2)	
N(1)-C(1)-N(2)	118.1 (3)	
C(1)-N(1)-H(5)	118 (3)	
C(1)-N(2)-H(2)	118 (2)	
C(1)-N(1)-H(4)	122 (3)	
C(1)-N(2)-H(3)	123 (2)	
H(4)-N(1)-H(5)	120 (3)	
H(2)-N(2)-H(3)	118 (4)	

(a) Present work.

(b) Sabine, Cox & Craven (1969).

(c) Pryor & Sanger (1970).

(d) X-ray.

(e) Neutron.

(f) Bond lengths corrected for thermal motion.

(g) Bond lengths not corrected for thermal motion.

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Structural studies of metal dithiocarbamates. V. The crystal and molecular structure of bis-(*N,N*-diethyldithiocarbamato)tellurium(II) By C. FABIANI, R. SPAGNA, A. VACIAGO and L. ZAMBONELLI, *Laboratorio di Strutturistica Chimica 'Giordano Giacomello', CNR, Città Universitaria, 00100 Roma, Italy*

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A correction to a reference in *Acta Cryst.* (1971) **B27**, 1499 is given.

L. P. (1969). *Nature, Lond.* **221**, 550 should read LAWTON, S. L. & KOKOTAILO, G. T. (1969). *Nature, Lond.* **221**, 550.

Reference

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