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*.

The crystal structure of urea oxalic acid, $2[CO(NH_2)_2].(COOH)_2$ 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 & Sturdivant (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 $\theta < 35°$ 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.

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

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 $(10\bar{2})$
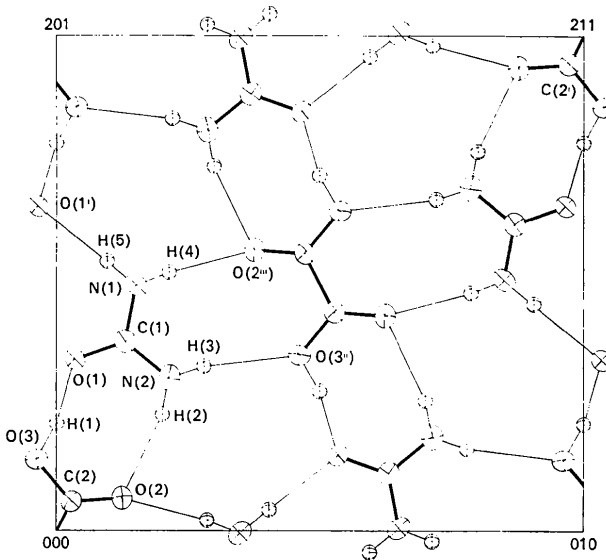

Fig. 1. Projection of the crystal structure of urea oxalic acid on $(10\bar{2})$. The vibration ellipsoids of the heavy atoms are scaled to include 50% probability. The hydrogen atoms have arbitrary, small isotropic vibration parameters.

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

plane. This figure was prepared with the *ORTEP*-program (Johnson, 1965).

Table 2. *Final atomic parameters*

	x/a	y/b	z/c
N(1)	0·9970 (3)	0·1507 (2)	0·4857 (2)
N(2)	0·6215 (3)	0·2136 (1)	0·3047 (2)
O(1)	0·7033 (2)	0·0348 (1)	0·3319 (2)
O(2)	0·1552 (2)	0·1245 (2)	0·0388 (2)
O(3)	0·2864 (2)	−0·0380 (1)	0·1502 (2)
C(1)	0·7709 (3)	0·1307 (1)	0·3729 (2)
C(2)	0·1237 (2)	0·0284 (1)	0·0517 (2)
H(1)	0·446 (4)	0·002 (2)	0·211 (3)
H(2)	0·475 (4)	0·201 (2)	0·227 (3)
H(3)	0·680 (4)	0·278 (2)	0·319 (3)
H(4)	0·049 (4)	0·213 (2)	0·513 (3)
H(5)	0·090 (4)	0·095 (2)	0·537 (3)

Discussion of the results

The structure of urea oxalic acid consists of nearly planar urea and oxalic acid molecules held together by a two-dimensional hydrogen-bonding network. The acidic proton is attached to the oxalic acid molecule. The compound, unlike uronium nitrate, is not a uronium salt. This difference may be related to the difference in acid strength between oxalic acid and nitric acid.

The bond distances and angles found in the title compound are given in Tables 4 and 5 respectively. These geometric data are compared with the results of recent structure determinations on related compounds. In accordance with the fact that the compound studied is an addition compound, differences in bond lengths and angles are very small when one compares the urea and oxalic acid molecules in this compound with urea and oxalic acid dihydrate. As usual, bond lengths involving hydrogen atoms determined by X-ray diffraction are shorter than the ones determined by neutron diffraction. This effect is due to the assumption commonly made in X-ray analysis that the electron density of bonded atoms is spherically symmetric. A theoretical study of the geometry of the uronium ion and the urea molecule is in progress.

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Table 3. *Vibration parameters*

The temperature factor for the heavy atoms was: $\exp[-2\pi^2(h^2\,a^{*2}\,U_{11}+2h\,k\,a^*\,b^*\,U_{12}+\cdots)]$.
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 (a), (d), (g)	Oxalic acid dihydrate (b), (e), (g)	Urea (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)		} 1·352 (2)
C(1)–N(2)	1·321 (4)		
C(1)–O(1)	1·260 (3)		1.260 (3)
N(2)–H(3)	0·86 (2)		
N(1)–H(4)	0·84 (2)		} 1·003 (4)
N(2)–H(2)	0·86 (4)		
N(1)–H(5)	0·88 (3)		} 0·998 (5)
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.

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Table 5. *Bond angles* (°)

	Urea–oxalic acid (a), (d), (g)	Oxalic acid dihydrate (b), (e), (g)	Urea (c), (e), (f)
C(2')–C(2)–O(2)	121·8 (2)	121·0 (3)	121·7 (1)
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)		} 121·7 (1)
O(1)–C(1)–N(2)	122·2 (2)		
N(1)–C(1)–N(2)	118·1 (3)		116·6 (1)
C(1)–N(1)–H(5)	118 (3)		} 119·0 (3)
C(1)–N(2)–H(2)	118 (2)		
C(1)–N(1)–H(4)	122 (3)		} 120·2 (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*

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

In a paper of the above title (Fabiani, Spagna, Vaciago & Zambonelli, 1971) the reference to the structure of lead(II) bis-(O,O-diisopropylphosphorodithioate) is incorrect. On page 1504, column 1, line 20 (Guzy, Raynor & Stodulski, 1969) should read (Lawton & Kokotailo, 1969) and in the list of references Guzy, C. M., Raynor, J. B. & Stodulski, 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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