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The Crystal Structure and Thermal Expansion of Two Modifications of N-Methylurea–Oxalic Acid (2:1)

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Abstract

The crystal structures of the orthorhombic and monoclinic modifications of N-methylurea–oxalic acid, $2[H_2N.CO.NHCH_3].(COOH)_2$, $2C_2H_6N_2O.C_2H_2O_4$, have been determined from X-ray data collected on an automatic diffractometer. The structures consist of layers of N-methylurea and oxalic acid molecules. The molecules are held together by hydrogen bonds. The compounds are addition compounds. Orthorhombic modification: space group *Pnma*, $a = 10.4220$ (2), $b = 6.4274$ (1), $c = 16.1253$ (5) Å at 295 (1) K, $D_c = 1.46$ Mg m^{-3}, $Z = 4$, Cu *K*α radiation ($\lambda = 1.5418$ Å), $R_w = 0.059$. The elements of the thermal-expansion tensor at 295 (1) K are $\alpha_a = 14$ (5), $\alpha_b = 274$ (14), $\alpha_c = 29$ (6) $\times$ 10^{-6} K^{-1}. Monoclinic modification: space group *P*2$_1$/*c*, $a = 5.1429$ (3), $b = 10.5498$ (5), $c = 10.3102$ (5) Å, $\beta = 101.910$ (5)° at 295 (1) K, $D_c = 1.44$ Mg m^{-3}, $Z = 2$, Mo *K*α radiation ($\lambda = 0.7107$ Å), $R_w = 0.069$. The elements of the thermal-expansion tensor at 295 (1) K are $\alpha_1 = 23$ (5), $\alpha_2 = 24$ (5), $\alpha_3 = 188$ (9) $\times$ 10^{-6} K^{-1}. At 182 K an exothermic and irreversible phase transition takes place, the monoclinic changing into the orthorhombic modification.

Introduction

We have previously reported that urea can form two kinds of compounds with an acid: uronium salts or addition compounds (Harkema & ter Brake, 1979). This also applies to N-methylurea. It can form salts (*e.g.* N-methyluronium nitrate) or addition compounds (*e.g.* N-methylurea–oxalic acid). The addition compound N-methylurea–oxalic acid (2:1) can be prepared in two modifications: monoclinic and orthorhombic.

Orthorhombic modification

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

Data were collected on a Philips PW 1100 automatic diffractometer at room temperature [295 (1) K]. Reflexions with $4 < \theta < 68°$ were measured with graphite-monochromated Cu *K*α radiation ($\lambda = 1.5418$ Å) and the ω–2θ scanning technique. 1078 independent reflexions were measured, of which 1049 had a net

intensity greater than the corresponding standard deviation from counting statistics. No correction for absorption was applied ($\mu = 1 \cdot 14$ mm^{-1}).

The systematic extinctions were: $0kl$: $k + l = 2n + 1$; $hk0$: $h = 2n + 1$. The corresponding space group is *Pnma* or *Pna2$_1$* (*International Tables for X-ray Crystallography*, 1952). We assumed that the space group was *Pnma*, which was justified later.

The cell dimensions are listed in Table 1. The unit cell contains eight molecules of *N*-methylurea and four of oxalic acid, corresponding to four molecules of the addition compound: *N*-methylurea–oxalic acid (2:1).

From the very strong 040 reflexion it is clear that all molecules must be approximately parallel to the (010) plane. As the general position in the space group *Pnma* is eightfold, the molecules must lie on special positions. Because the structure consists of layers, there are two possibilities:

(*a*) The molecules are approximately in the planes $y = 0$ and $\frac{1}{2}$. Then the oxalic acid molecules must lie on the inversion centres. The layers are related by the mirror planes $y = \frac{1}{4}$ and $\frac{3}{4}$.

(*b*) The molecules are in the mirror planes $y = \frac{1}{4}$ and $\frac{3}{4}$. The layers are related by the inversion centres in $y = 0$ and $\frac{1}{2}$. A consequence of the first alternative is that reflexions hkl with $k = 2n + 1$ are very weak. This was not the case, so the *N*-methylurea and oxalic acid molecules are in the planes $y = \frac{1}{4}$ and $\frac{3}{4}$.

With *MULTAN* (Germain, Main & Woolfson, 1971) an E map for the plane $y = \frac{1}{4}$ was obtained. The positions of the heavy atoms were found. The coordinates were used as input for the least-squares program.

The weighting scheme used is that normally used in our laboratory (de With, Harkema & van Hummel, 1976). We used only the significant reflexions (*i.e.* with a net intensity greater than the corresponding standard deviation from counting statistics). In the last cycles of refinement a correction for isotropic secondary extinction was applied (Zachariasen, 1963; Larson, 1970).*

* Lists of structure factors and anisotropic thermal parameters for both forms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34436 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Final positional parameters are given in Table 2. The labelling of the atoms is given in Fig. 1, which shows the layer $y = \frac{1}{4}$. Fig. 2 gives a stereoview of two parallel layers. Both figures were prepared with *ORTEP* (Johnson, 1965). The bond distances and angles are given in Tables 3 and 4 respectively.

In order to determine the thermal-expansion tensor, approximately 70 reflexions, distributed throughout reciprocal space and in the θ range 5–48°, were

Table 2. *Final fractional atomic parameters of the orthorhombic modification of N-methylurea–oxalic acid* (2:1)

|	x	y	z
C(1)	0·3151 (2)	0·2500 (0)	0·0761 (2)
C(2)	0·2490 (2)	0·2500 (0)	0·2213 (1)
C(3)	0·0002 (2)	0·2500 (0)	0·5976 (1)
C(4)	0·0765 (2)	0·2500 (0)	0·7396 (1)
C(5)	0·3677 (2)	0·2500 (0)	0·4493 (1)
C(6)	0·4440 (2)	0·2500 (0)	0·5313 (1)
N(1)	0·2201 (2)	0·2500 (0)	0·1416 (1)
N(2)	0·1554 (2)	0·2500 (0)	0·2779 (1)
N(3)	0·1015 (2)	0·2500 (0)	0·6590 (1)
N(4)	0·1741 (2)	0·2500 (0)	0·7938 (1)
O(1)	0·3658 (1)	0·2500 (0)	0·2436 (1)
O(2)	−0·0384 (1)	0·2500 (0)	0·7639 (1)
O(3)	0·4412 (1)	0·2500 (0)	0·3854 (1)
O(4)	0·2520 (1)	0·2500 (0)	0·4490 (1)
O(5)	0·5597 (1)	0·2500 (0)	0·5315 (1)
O(6)	0·3714 (1)	0·2500 (0)	0·5958 (1)
H(1)	0·300 (2)	0·374 (4)	0·039 (2)
H(2)	0·399 (4)	0·2500 (0)	0·096 (3)
H(3)	0·135 (3)	0·2500 (0)	0·129 (2)
H(4)	0·077 (3)	0·2500 (0)	0·267 (2)
H(5)	0·180 (3)	0·2500 (0)	0·332 (2)
H(6)	−0·053 (2)	0·115 (3)	0·607 (1)
H(7)	0·044 (4)	0·2500 (0)	0·545 (2)
H(8)	0·176 (3)	0·2500 (0)	0·645 (2)
H(9)	0·252 (3)	0·2500 (0)	0·782 (2)
H(10)	0·155 (3)	0·2500 (0)	0·847 (2)
H(11)	0·394 (4)	0·2500 (0)	0·328 (3)
H(12)	0·425 (4)	0·2500 (0)	0·647 (2)
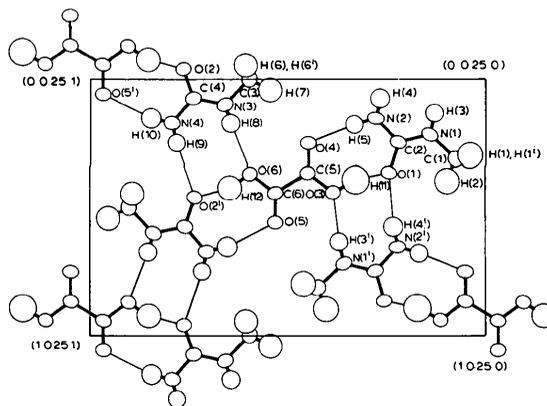
Fig. 1. The layer $y = \frac{1}{4}$ of the orthorhombic modification of *N*-methylurea–oxalic acid (2:1). The vibration ellipsoids of the atoms are scaled to include 50% probability.

Table 1. *Lattice constants of the orthorhombic modification of N-methylurea–oxalic acid* (2:1) *at different temperatures*

T (K)	a (Å)	b (Å)	c (Å)	V (Å^3)
295 (1)	10·4220 (2)	6·4274 (1)	16·1253 (5)	1080·18 (4)
264·2 (6)	10·4172 (4)	6·3745 (3)	16·112 (1)	1069·91 (9)
245·7 (5)	10·4149 (4)	6·3469 (3)	16·104 (1)	1064·51 (9)
222·2 (4)	10·4117 (8)	6·3088 (5)	16·096 (2)	1057·3 (2)
199·0 (6)	10·4086 (9)	6·2746 (5)	16·088 (2)	1050·7 (2)
198·1 (5)	10·4080 (9)	6·2732 (5)	16·085 (3)	1050·2 (2)
174·5 (5)	10·405 (1)	6·2397 (6)	16·077 (3)	1043·8 (2)
152·7 (6)	10·403 (2)	6·210 (1)	16·073 (5)	1038·4 (4)
119·7 (8)	10·3985 (4)	6·1749 (3)	16·068 (1)	1031·72 (9)

accurately centred. This procedure was followed for nine temperatures with the same crystal. At the set points the temperatures were stable within 1 K. Cell constants were optimized by least squares on the Bragg angles of the measured reflexions. Results are collected in Table 1. The measured data have been fitted to a three-term polynomial in T by least squares. Results are collected in Table 5. From the polynomials the elements of the expansion tensor and their e.s.d.'s at 295 (1) K are: $\alpha_a = 14$ (5), $\alpha_b = 274$ (14), $\alpha_c = 29$ (6) × 10^{-6} K^{-1} (Nye, 1969).

Monoclinic modification

Crystals of N-methylurea–oxalic acid (2:1) were prepared by slow evaporation of an aqueous solution of
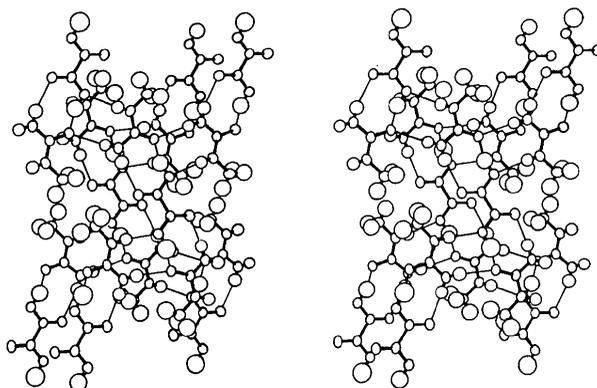

Fig. 2. Stereoview of two parallel layers of the orthorhombic modification of N-methylurea–oxalic acid (2:1). The vibration ellipsoids of the atoms are scaled to include 50% probability.

Table 3. *Bond distances (Å) of the orthorhombic modification and comparable bond distances of the monoclinic modification of N-methylurea–oxalic acid* (2 : 1), *N-methylurea and oxalic acid dihydrate*

	N-Methylurea–oxalic acid (2:1) Pnma, (a), (d), (f)	N-Methylurea (c), (d), (f)	Oxalic acid dihydrate (b), (e), (f)	N-Methylurea–oxalic acid (2:1) P2₁/c, (a), (d), (f)	
C(1)–N(1)	1·446 (3)	⎧1·439 (2)		⎧1·448 (4)	C(1)–N(1)
C(3)–N(3)	1·448 (3)	⎩1·439 (2)		⎩1·448 (4)	C(1)–N(1)
C(1)–H(1)	1·00 (3)				
C(1)–H(2)	0·93 (4)				
C(3)–H(6)	1·04 (2)				
C(3)–H(7)	0·97 (4)				
				1·00 (4)	C(1)–H(1)
				0·96 (5)	C(1)–H(2)
				0·86 (5)	C(1)–H(3)
C(2)–N(1)	1·320 (3)	⎧1·336 (2)		⎧1·320 (3)	C(2)–N(1)
C(4)–N(3)	1·325 (3)	⎩1·336 (2)		⎩1·320 (3)	C(2)–N(1)
C(2)–N(2)	1·336 (3)	⎧1·340 (2)		⎧1·331 (3)	C(2)–N(2)
C(4)–N(4)	1·342 (3)	⎩1·340 (2)		⎩1·331 (3)	C(2)–N(2)
C(2)–O(1)	1·269 (2)	⎧1·248 (1)		⎧1·266 (3)	C(2)–O(1)
C(4)–O(2)	1·260 (2)	⎩1·248 (1)		⎩1·266 (3)	C(2)–O(1)
N(1)–H(3)	0·91 (3)	⎧0·82 (2)		⎧0·84 (3)	N(1)–H(4)
N(3)–H(8)	0·81 (3)	⎩0·82 (2)		⎩0·84 (3)	N(1)–H(4)
N(2)–H(4)	0·84 (3)	⎧0·85 (2)		⎧0·83 (3)	N(2)–H(5)
N(4)–H(9)	0·83 (3)	⎩0·85 (2)		⎩0·83 (3)	N(2)–H(5)
N(2)–H(5)	0·91 (3)	⎧0·90 (2)		⎧0·91 (3)	N(2)–H(6)
N(4)–H(10)	0·88 (3)	⎩0·90 (2)		⎩0·91 (3)	N(2)–H(6)
C(5)–C(6)	1·543 (3)		1·536 (3)	1·521 (3)	C(3)–C(3ⁱ)
C(5)–O(3)	1·284 (3)		⎧1·291 (5)	⎧1·297 (3)	C(3)–O(2)
C(6)–O(6)	1·287 (3)		⎩1·291 (5)	⎩1·297 (3)	C(3)–O(2)
C(5)–O(4)	1·205 (3)		⎧1·212 (4)	⎧1·215 (3)	C(3)–O(3)
C(6)–O(5)	1·205 (2)		⎩1·212 (4)	⎩1·215 (3)	C(3)–O(3)
O(3)–H(11)	1·05 (4)		⎧1·026 (7)	⎧1·03 (3)	O(2)–H(7)
O(6)–H(12)	0·99 (4)		⎩1·026 (7)	⎩1·03 (3)	O(2)–H(7)
N(1ⁱ)–O(3)	2·939 (2)			⎧2·982 (3)	N(1ⁱ)–O(2)
N(3)–O(6)	2·992 (2)			⎩2·982 (3)	N(1ⁱ)–O(2)
N(2)–O(4)	2·938 (3)			⎧3·006 (3)	N(2)–O(3)
N(4)–O(5ⁱ)	3·059 (3)			⎩3·006 (3)	N(2)–O(3)
N(2ⁱ)–O(1)	3·038 (2)			⎧3·157 (3)	N(2ⁱ)–O(1)
N(4)–O(2ⁱ)	3·138 (2)			⎩3·157 (3)	N(2ⁱ)–O(1)
O(1)–O(3)	2·419 (2)			⎧2·450 (3)	O(1)–O(2)
O(2ⁱ)–O(6)	2·449 (2)			⎩2·450 (3)	O(1)–O(2)

Notes: (a) Present work. (b) Sabine, Cox & Craven (1969). (c) Huiszoon & Tiemessen (1976). (d) X-ray. (e) Neutron. (f) Not corrected for thermal motion.

Table 4. *Bond angles of the orthorhombic modification and comparable bond angles of the monoclinic modification of N-methylurea–oxalic acid* (2:1), *N-methylurea and oxalic acid dihydrate*

	N-Methylurea–oxalic acid (2:1) *Pnma*, (a), (d), (f)	*N*-Methylurea (c), (d), (f)	Oxalic acid dihydrate (b), (e), (f)	*N*-Methylurea–oxalic acid (2:1) *P*2₁/*c*, (a), (d), (f)	
C(1)–N(1)–C(2)	123·6 (3)	{122·5 (2)		{123·2 (3)	C(1)–N(1)–C(2)
C(3)–N(3)–C(4)	121·8 (2)	{122·5 (2)		{123·2 (3)	C(1)–N(1)–C(2)
C(1)–N(1)–H(3)	121 (3)	{122 (2)		{117 (3)	C(1)–N(1)–H(4)
C(3)–N(3)–H(8)	120 (3)	{122 (2)		{117 (3)	C(1)–N(1)–H(4)
C(2)–N(1)–H(3)	116 (2)	{115 (2)		{120 (3)	C(2)–N(1)–H(4)
C(4)–N(3)–H(8)	118 (3)	{115 (2)		{120 (3)	C(2)–N(1)–H(4)
C(2)–N(2)–H(4)	125 (3)	{119 (2)		{120 (3)	C(2)–N(2)–H(5)
C(4)–N(4)–H(9)	126 (4)	{119 (2)		{120 (3)	C(2)–N(2)–H(5)
C(2)–N(2)–H(5)	117 (3)	{117 (2)		{119 (3)	C(2)–N(2)–H(6)
C(4)–N(4)–H(10)	118 (3)	{117 (2)		{119 (3)	C(2)–N(2)–H(6)
N(1)–C(1)–H(1)	109 (2)				
N(1)–C(1)–H(2)	113 (3)				
N(3)–C(3)–H(6)	107 (1)				
N(3)–C(3)–H(7)	105 (3)				
				111 (3)	N(1)–C(1)–H(1)
				120 (4)	N(1)–C(1)–H(2)
				110 (4)	N(1)–C(1)–H(3)
N(1)–C(2)–N(2)	119·9 (2)	{116·6 (2)		{119·7 (3)	N(1)–C(2)–N(2)
N(3)–C(4)–N(4)	119·3 (2)	{116·6 (2)		{119·7 (3)	N(1)–C(2)–N(2)
N(1)–C(2)–O(1)	119·6 (2)	{122·0 (1)		{119·8 (3)	N(1)–C(2)–O(1)
N(3)–C(4)–O(2)	119·5 (2)	{122·0 (1)		{119·8 (3)	N(1)–C(2)–O(1)
N(2)–C(2)–O(1)	120·5 (2)	{121·4 (2)		{120·5 (2)	N(2)–C(2)–O(1)
N(4)–C(4)–O(2)	121·2 (2)	{121·4 (2)		{120·5 (2)	N(2)–C(2)–O(1)
H(1)–C(1)–H(1ⁱ)	105 (2)				
H(1)–C(1)–H(2)	111 (3)				
H(6)–C(3)–H(6ⁱ)	113 (2)				
H(6)–C(3)–H(7)	112 (3)				
				81 (4)	H(1)–C(1)–H(2)
				125 (7)	H(1)–C(1)–H(3)
				108 (5)	H(2)–C(1)–H(3)
H(4)–N(2)–H(5)	119 (4)	{117 (2)		{121 (4)	H(5)–N(2)–H(6)
H(9)–N(4)–H(10)	116 (4)	{117 (2)		{121 (4)	H(5)–N(2)–H(6)
C(5)–C(6)–O(5)	121·3 (2)		{121·0 (3)	{121·5 (2)	C(3ⁱ)–C(3)–O(3)
C(6)–C(5)–O(4)	121·2 (2)		{121·0 (3)	{121·5 (2)	C(3ⁱ)–C(3)–O(3)
C(5)–C(6)–O(6)	112·9 (2)		{112·4 (3)	{113·6 (2)	C(3ⁱ)–C(3)–O(2)
C(6)–C(5)–O(3)	112·3 (2)		{112·4 (3)	{113·6 (2)	C(3ⁱ)–C(3)–O(2)
C(5)–O(3)–H(11)	115 (3)		{114·4 (6)	{116 (2)	C(3)–O(2)–H(7)
C(6)–O(6)–H(12)	110 (2)		{114·4 (6)	{116 (2)	C(3)–O(2)–H(7)
O(3)–C(5)–O(4)	126·5 (2)		{126·6 (3)	{124·9 (2)	O(2)–C(3)–O(3)
O(5)–C(6)–O(6)	125·8 (2)		{126·6 (3)	{124·9 (2)	O(2)–C(3)–O(3)

Notes: (a) Present work. (b) Sabine, Cox & Craven (1969). (c) Huiszoon & Tiemessen (1976). (d) X-ray. (e) Neutron. (f) Not corrected for thermal motion.

N-methylurea and oxalic acid in the stoichiometric ratio. The crystals have a pronounced cleavage plane, which indicates a two-dimensional hydrogen-bonding network.

Data were collected on a Philips PW 1100 automatic diffractometer at room temperature [295 (1) K]. Reflexions with $4 < \theta < 35°$ were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and the ω–2θ scanning technique. 2363 independent reflexions were measured, of which 1482 had a net intensity greater than the corresponding standard deviation from counting statistics. No correction for absorption was applied ($\mu = 0.14$ mm^{-1}).

The systematic extinctions were: $h0l$: $l = 2n + 1$; $0k0$: $k = 2n + 1$. The corresponding space group is $P2_1/c$ (*International Tables for X-ray Crystallography*, 1952).

The cell dimensions are listed in Table 6. The unit cell contains four molecules of *N*-methylurea and two of oxalic acid, corresponding to two molecules of the addition compound: *N*-methylurea–oxalic acid (2:1).

From the very strong 102 reflexion it is clear that all molecules must be approximately parallel to the (102) plane. As the general position in the space group $P2_1/c$ is fourfold, the oxalic acid molecules must lie on centres of inversion. With the help of the known molecular

geometries, different models of the structure were constructed, 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.

Refinement of their positions and isotropic temperature factors with only the significant reflexions gave a weighted R of 26·4%. Conversion to anisotropic temperature factors, with only the significant reflexions, gave a weighted R of 11·7%. A difference synthesis at this stage clearly revealed the H atoms, except those belonging to the methyl group. Therefore we included only four H atoms. Refinement of their positions and isotropic temperature factors, together with the positions and anisotropic temperature factors of the other atoms, with only the significant reflexions, gave a weighted R of 9·1%. A difference synthesis of the remaining electron density in the plane containing the H atoms of the methyl group with $SPFT$ (van de Waal, 1975) showed six peaks:

(a) We assumed two possible orientations for the methyl group. Inclusion of six H atoms with multiplicity 0·5, and refinement of the positions and isotropic temperature factors of the H atoms, together with the positions and anisotropic temperature factors of the other atoms, with only the significant reflexions, gave a weighted R of 6·5%. In the last cycles a correction for isotropic secondary extinction was applied (Zachariasen, 1963; Larson, 1970). One of the H atoms belonging to the methyl group showed a large temperature factor and a distance to the C atom of 1·3 Å.

(b) We assumed one possible orientation for the methyl group. Inclusion of three H atoms with multiplicity 1·0 and refinement of the positions and isotropic temperature factors of the H atoms, together

with the positions and anisotropic temperature factors of the other atoms, with only the significant reflexions, gave a weighted R of 6·9%. In the last cycles of refinement a correction for isotropic secondary extinction was applied (Zachariasen, 1963; Larson, 1970). The C—H distances are in reasonable agreement with expectations (1 Å), but one of the H—C—H angles is too small.

We conclude that there is disorder in the positions of the H atoms of the methyl group. The parameters of the H atoms belonging to the methyl group cannot be determined accurately from our data set. We continued using the results for one possible orientation of the methyl group.

Final positional parameters are given in Table 7.* The labelling of the atoms is given in Fig. 3, which shows a projection of the structure of one layer on the (102) plane. Fig. 4 shows a stereoview of two parallel layers. The bond distances and angles are given in Tables 3 and 4 respectively.

In order to determine the thermal-expansion tensor, approximately 80 reflexions, distributed throughout reciprocal space and in the θ range 8–47°, were accurately centred with Cu $K\alpha$ radiation. This procedure was followed for four temperatures with the same crystal. Results are collected in Table 6. The

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* See previous footnote.

Table 7. *Final fractional atomic parameters of the monoclinic modification of N-methylurea–oxalic acid* (2:1)

	x	y	z
C(1)	0·8364 (7)	0·4078 (3)	0·0844 (3)
C(2)	0·5591 (5)	0·3376 (2)	0·2357 (2)
C(3)	0·0939 (4)	0·4640 (2)	0·4652 (2)
N(1)	0·7029 (5)	0·3116 (2)	0·1467 (2)
N(2)	0·4409 (5)	0·2438 (2)	0·2879 (2)
O(1)	0·5378 (3)	0·4510 (1)	0·2721 (2)
O(2)	0·2178 (4)	0·5360 (1)	0·3958 (2)
O(3)	0·1192 (4)	0·3497 (1)	0·4752 (2)
H(1)	0·986 (8)	0·370 (3)	0·048 (4)
H(2)	0·98 (1)	0·454 (5)	0·137 (5)
H(3)	0·724 (9)	0·462 (5)	0·044 (5)
H(4)	0·728 (5)	0·236 (3)	0·127 (3)
H(5)	0·452 (5)	0·170 (3)	0·261 (3)
H(6)	0·331 (5)	0·263 (3)	0·344 (3)
H(7)	0·349 (5)	0·491 (3)	0·348 (3)

Table 5. *Fit to the measured data of the orthorhombic modification of N-methylurea–oxalic acid* (2:1)

$x = K_0 + K_1 T + K_2 T^2$, where x denotes a, b or c.

x	K_0	$K_1 \times 10^3$	$K_2 \times 10^6$	P^*
a	10·3859 (7)	0·09 (1)	0·10 (2)	0·9994
b	6·065 (5)	0·70 (5)	1·8 (1)	0·9999
c	16·058 (3)	−0·02 (3)	0·84 (8)	0·9976

* P is the correlation coefficient between measured and calculated unit-cell dimensions.

Table 6. *Lattice constants of the monoclinic modification of N-methylurea–oxalic acid* (2:1) *at different temperatures*

T (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
295 (1)	5·1429 (3)	10·5498 (5)	10·3102 (5)	101·910 (5)	547·35 (5)
262·1 (4)	5·1288 (3)	10·5425 (5)	10·2792 (5)	102·206 (5)	543·24 (5)
231·4 (7)	5·1148 (3)	10·5371 (6)	10·2495 (6)	102·462 (7)	539·38 (6)
204·9 (7)	5·1039 (4)	10·5344 (6)	10·2240 (7)	102·677 (7)	536·31 (7)

Table 8. *Fit to the measured data of the monoclinic modification of N-methylurea–oxalic acid* (2 : 1)

$x = K_0 + K_1 T + K_2 T^2$, where x denotes a, b, c or β.

x	K_0	$K_1 \times 10^3$	$K_2 \times 10^6$	P^*
a	5·02 (2)	0·4 (1)	0·1 (3)	0·9999
b	10·557 (8)	−0·30 (6)	1·0 (1)	0·9998
c	10·015 (7)	1·06 (6)	−0·2 (1)	1·0000
β	103·94 (8)	−4·5 (7)	−8 (1)	1·0000

* P is the correlation coefficient between measured and calculated unit-cell dimensions.
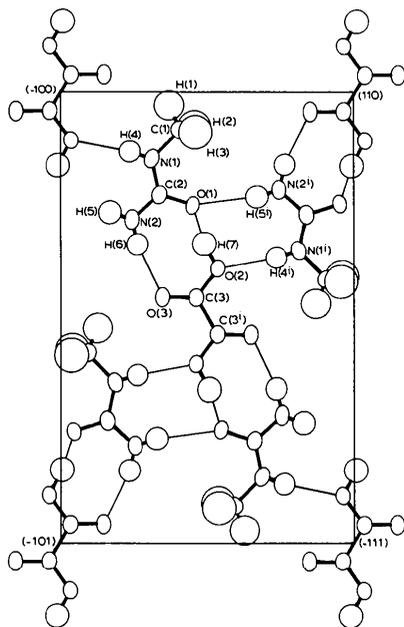
Fig. 3. Projection of the structure of one layer of the monoclinic modification of *N*-methylurea–oxalic acid (2:1). The vibration ellipsoids of the atoms are scaled to include 50% probability.
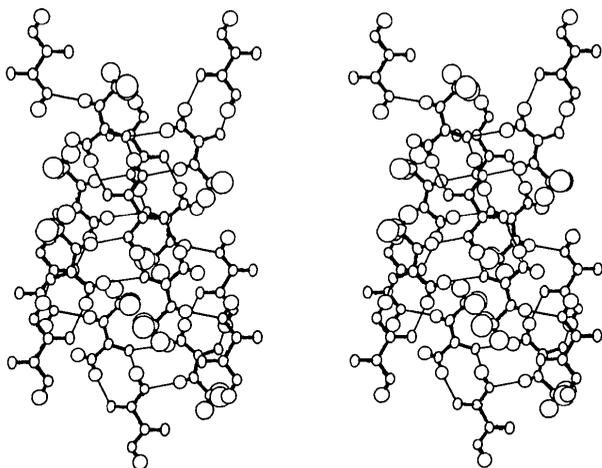

Fig. 4. Stereoview of two parallel layers of the monoclinic modification of *N*-methylurea–oxalic acid (2:1). The vibration ellipsoids of the atoms are scaled to include 50% probability.

measured data have been fitted to a three-term polynomial in T by least squares. Results are collected in Table 8. From the polynomials the elements of the expansion tensor and their e.s.d.'s at 295 (1) K are: $\alpha_1 = 23$ (5), $\alpha_2 = 24$ (5), $\alpha_3 = 188$ (9) $\times 10^{-6}$ K^{-1} (Nye, 1969). The direction cosines of the expansion tensor relative to the crystal axes are given in Table 9.

Discussion

The crystal structure of the title compound consists of urea and oxalic acid molecules, as in urea–oxalic acid (2:1). The compound therefore is an addition compound and not an *N*-methyluronium salt. *N*-Methylurea and oxalic acid molecules are held together by a two-dimensional hydrogen-bonding network in the (010) and (102) planes for the orthorhombic and monoclinic modifications respectively. Hydrogen bonds are assumed whenever the distance between an O and a H atom is <2·4 Å (Olovsson, 1978). Dimensions of the hydrogen bonds are given in Table 3. The layers of molecules are held together by van der Waals interactions. This difference in interactions explains why the (010) and (102) planes are (mica-like) cleavage planes, for the orthorhombic and monoclinic modifications respectively. The very strong anisotropy of the bonding forces between the molecules in the crystal also explains the large differences in the lengths of the principal axes of the thermal-expansion tensors. From Table 9 it is clear that the direction of the longest axis of the expansion tensor coincides with the normal to the cleavage plane, for both modifications.

Since the compound is an addition compound, one expects bond lengths and angles not to differ significantly when one compares the corresponding bond lengths in the orthorhombic and monoclinic modifications of the title compound with those in oxalic acid dihydrate and *N*-methylurea. Data on these compounds are given in Tables 3 and 4. It can be seen that there is a fair agreement of bond lengths and angles in the different compounds. Some of the differences, however, are significant from a crystallographic point of

Table 9. *Direction cosines of the principal components of the expansion tensor (in columns) relative to the crystal axes of the monoclinic modification of N-methylurea–oxalic acid* (2 : 1) *at* 295 (1) K

The last column gives the direction cosines of the normal on the (102) plane.

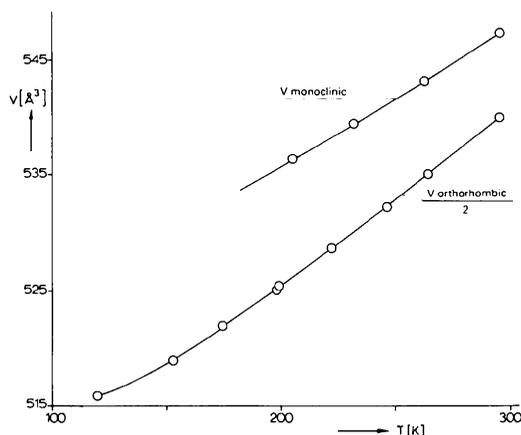| $\alpha_1 = 23$ (5) $\times 10^{-6}$ K^{-1}	$\alpha_2 = 24$ (5) $\times 10^{-6}$ K^{-1}	$\alpha_3 = 188$ (9) $\times 10^{-6}$ K^{-1}	
0·79	0·00	0·62	0·63
0·00	1·00	0·00	0·00
−0·77	0·00	0·64	0·63

Fig. 5. Plot of the unit-cell volume of the monoclinic modification and half the unit-cell volume of the orthorhombic modification of N-methylurea–oxalic acid (2:1) against temperature.

view, and may be due to differences in hydrogen bonding in the different compounds.

From Figs. 1 and 3 we see that the crystal structures of the orthorhombic and monoclinic modifications in the planes are very much alike. The monoclinic modification has a crystallographic inversion centre at the C—C bond in oxalic acid. This does not apply to the orthorhombic modification, although the atomic positions are almost in agreement with an inversion centre at the same place. Other differences between the crystal structures are: the orientation of the methyl group, the distance between two parallel layers (3·21 and 3·24 Å for the orthorhombic and monoclinic modifications respectively), and the positions of two parallel layers with respect to each other.

During the measurement of lattice constants of the monoclinic modification at different temperatures, we discovered a phase change at ca 180 K. The monoclinic changes into the orthorhombic modification. A

differential thermal analysis showed the temperature where the phase transition takes place to be 182 K. The phase transition is exothermic and irreversible. Fig. 5 is a plot of the unit-cell volume of the monoclinic modification and half the unit-cell volume of the orthorhombic modification against temperature. The unit-cell volume of the monoclinic modification is 1·3% greater than half the unit-cell volume of the orthorhombic modification. This difference is due to the difference in distance between two parallel planes (0·9%) and to the small differences in atomic positions in the planes (0·4%).

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The Crystal and Molecular Structures of Disiloxane (at 108 K) and Hexamethyldisiloxane (at 148 K)

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Abstract

At 108 K crystals of disiloxane, SiH_3OSiH_3, are orthorhombic, space group $P2_12_12_1$, with $a = 4.66$, $b = 7.79$, $c = 12.97$ Å (e.s.d.'s 0·3% assumed) and $Z = 4$.

Crystals of hexamethyldisiloxane (at 148 K) are monoclinic, space group $P2_1/c$, with $a = 12.53$, $b = 8.34$, $c = 12.16$ Å, $\beta = 120.9°$ (e.s.d.'s 0·3% assumed) and $Z = 4$. Crystals were grown *in situ* on a Weissenberg goniometer fitted with low-temperature