

A new refinement of the orthorhombic polymorph of acetamide

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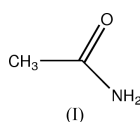
Key indicators

Single-crystal X-ray study
 $T = 146\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.058
 wR factor = 0.116
Data-to-parameter ratio = 19.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of orthorhombic acetamide, $\text{C}_2\text{H}_5\text{NO}$, were obtained from a mixture of ethyl acetate and dilute ammonia. The previously reported structure [Hamilton (1965). *Acta Cryst.* **18**, 866–870] was confirmed, with two molecules in the asymmetric unit. The molecules are hydrogen bonded to form columns. Neighboring columns are connected by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions.

Comment

The common crystalline modification of acetamide is rhombohedral, with space group $R3c$. Its structure was initially determined by Senti & Harker (1940) and was subsequently redetermined several times (Denne & Small, 1971; Ottersen, 1975; Jeffrey *et al.*, 1980; Zobel *et al.*, 1992). The existence of an orthorhombic modification of acetamide was reported by Senti & Harker (1940). Hamilton (1965) reported growing crystals of the orthorhombic polymorph from the melt and determined its structure. The preparation of crystals of orthorhombic acetamide from the melt has also been reported by Watanabe *et al.* (1986). We have found that crystals of orthorhombic acetamide, (I), can easily be obtained from a mixture of ethyl acetate and dilute ammonia (see *Experimental* section). We present here the results of a structure analysis from data collected at 146 K.



The present result confirms the structure reported by Hamilton (1965). The asymmetric unit contains two independent molecules (Figs. 1 and 2). Corresponding bond distances in the two molecules differ by less than 1 standard uncertainty, while corresponding bond angles agree within 2 standard uncertainties. The bond distances and angles in orthorhombic acetamide also agree perfectly with values reported for rhombohedral acetamide at 108 K (Ottersen, 1975). The methyl groups of both independent molecules adopt a conformation with one $\text{C}-\text{H}$ bond almost in the plane of the non-H atoms and eclipsed by the $\text{C}-\text{N}$ bond. A different conformation, with one $\text{C}-\text{H}$ bond perpendicular to the non-H plane, was found for rhombohedral acetamide, while a conformation with one $\text{C}-\text{H}$ bond eclipsed by the carbonyl group was predicted for gaseous acetamide from *ab initio* molecular orbital calculations (Jeffrey *et al.*, 1980). Thus the orientation of the methyl group is mainly determined by

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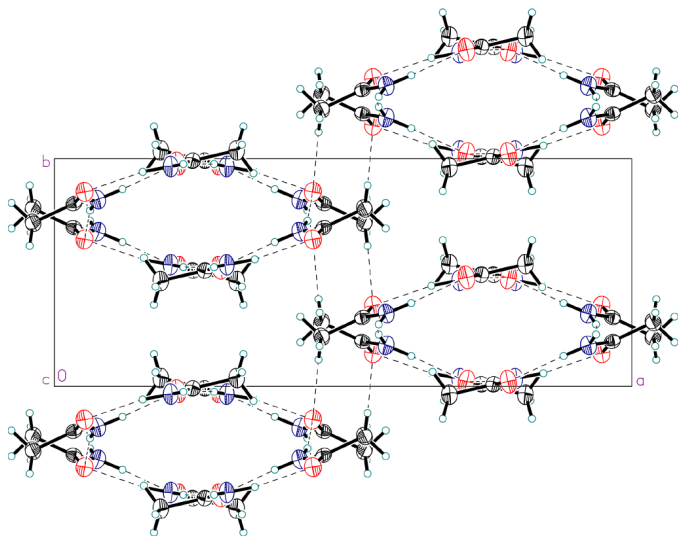


Figure 1
Projection of the structure of (I), viewed down *c*, with hydrogen bonds shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radius.

crystal packing forces. This observation is consistent with the low barrier of rotation about the C—C bond (Jeffrey *et al.*, 1980).

The molecules are linked by hydrogen bonds (Table 1) to form four-stringed columns parallel to the *c* axis (Figs. 1 and 2). Each molecule is connected by hydrogen bonds to three neighboring molecules. Two symmetry-independent molecules are connected by two hydrogen bonds to form a dimer. In addition, each molecule is connected to two symmetry-related molecules of its own kind, forming chains parallel to *c*. A weak intermolecular C—H...O interaction with an H...O distance of 2.62 Å also contributes to the chain structure. Neighboring columns are connected by intermolecular C—H...O interactions with an H...O distance of 2.49 Å, as shown in Fig. 1. A three-dimensional network of hydrogen bonds occurs in the rhombohedral modification. The melting point of orthorhombic acetamide has been reported as 344 K (Müller, 1914) and thus is 10 K lower than the melting point of 354 K reported for rhombohedral acetamide (The Merck Index, 1996). This observation is in agreement with the stronger three-dimensional bonding in the latter modification.

Experimental

The formation of acetamide from a mixture of ethyl acetate and ammonia was first reported by Phelps & Phelps (1908). Equal amounts of ethyl acetate and a 25% ammonia solution were mixed. Some ethanol and chloroform were added. The mixture was stored in an uncovered beaker. After one to two weeks the liquid phase had evaporated and the bottom of the beaker was covered with thin rods of orthorhombic acetamide, (I). Crystals of (I) are deliquescent and were only obtained during periods of low humidity. During days of high humidity the crystals redissolved by absorbing moisture from the air.

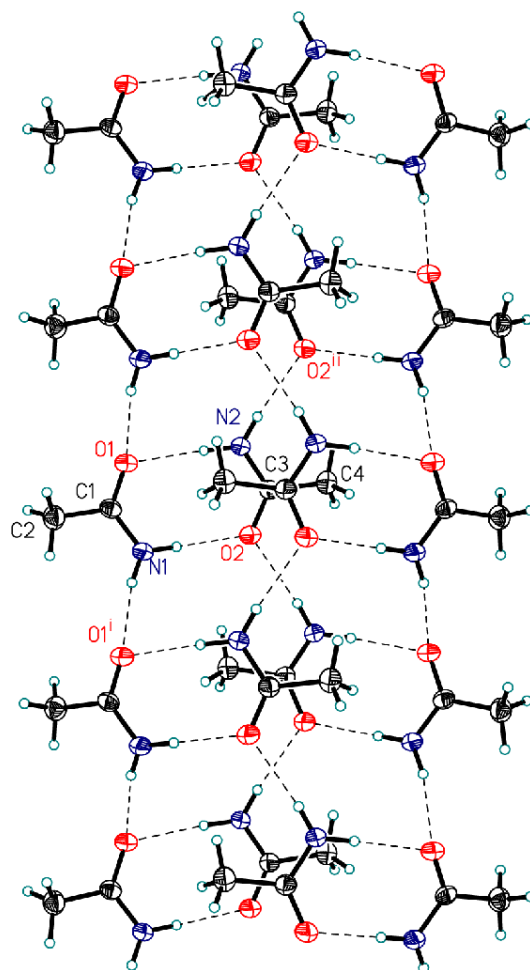


Figure 2
Hydrogen-bonded four-stringed column of (I), viewed down *b*, showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. Hydrogen bonds are indicated by dashed lines.

Crystal data

C₂H₅NO
M_r = 59.07
 Orthorhombic, *Pccn*
a = 19.021 (4) Å
b = 7.5084 (14) Å
c = 9.4038 (16) Å
V = 1343.0 (4) Å³
Z = 16
D_x = 1.169 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 213 reflections
 θ = 3–26°
 μ = 0.09 mm⁻¹
T = 146 (2) K
 Rod, colorless
 0.50 × 0.16 × 0.08 mm

Data collection

Siemens SMART 1K CCD diffractometer
 ω scans
 12 606 measured reflections
 1767 independent reflections
 1134 reflections with $I > 2\sigma(I)$

R_{int} = 0.074
 θ_{max} = 29.0°
 h = -26 → 23
 k = -10 → 9
 l = -12 → 12

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.058
 $wR(F^2)$ = 0.116
 S = 1.11
 1767 reflections
 91 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.19 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.25 e Å⁻³

Table 1
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H01···O2	0.90 (2)	2.03 (2)	2.925 (2)	177.6 (15)
N1—H02···O1 ⁱ	0.87 (2)	2.01 (2)	2.868 (2)	168.1 (15)
N2—H03···O1	0.95 (2)	2.05 (2)	2.991 (2)	171.6 (14)
N2—H04···O2 ⁱⁱ	0.86 (2)	2.09 (2)	2.949 (2)	172.7 (14)
C2—H2A···O1 ⁱⁱⁱ	0.98	2.49	3.471 (2)	178
C4—H4B···O2 ⁱⁱ	0.98	2.62	3.451 (2)	143

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The H atoms were located in a difference Fourier synthesis. Those at N were refined with individual isotropic displacement parameters. The methyl groups were constrained to tetrahedral geometry, with a fixed distance H—C = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.6U_{\text{eq}}(\text{C})$. The torsion angles about the C—C bonds of the methyl groups were refined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

XP in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

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