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Trimethylurea

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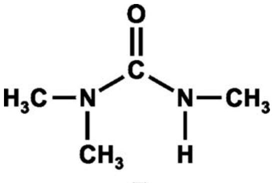
The title compound, $C_4H_{10}N_2O$, crystallizes with two independent molecules in the space group $Cmc2_1$. The first molecule lies in a crystallographic mirror plane with $x = 0$, whereas the second molecule lies on a general position with $x \simeq \frac{1}{3}$. Each molecule forms classical N—H···O=C hydrogen bonds, thereby leading to chains of molecules parallel or antiparallel, respectively, to the polar *c* axis.

Comment

In the course of our studies of adducts of di(organosulfonyl)amines with various *N*-methyl-substituted ureas [methylurea (Henschel *et al.*, 2002; Wölper *et al.*, 2010), 1,1-dimethylurea (Henschel *et al.*, 2002; Wölper *et al.*, 2010), 1,3-dimethylurea (Wijaya *et al.*, 1997; Hamann, Henschel *et al.*, 2002), tetramethylurea (Hamann, Wijaya *et al.*, 2002; Zerbe *et al.*, 2008) and trimethylurea (Wölper *et al.*, 2011; Döring *et al.*, 2012)], we recently noted to our surprise that the structure of trimethylurea itself has never been published. The structures of the other *N*-methylureas have been determined as follows: methylurea, space group $P2_12_12_1$, Huiszoon & Tiemessen (1976); 1,1-dimethylurea, $P2_1/n$, Pathirana *et al.* (1994), and as a footnote/supplementary material also by Fairlie *et al.* (1994); 1,3-dimethylurea, space group corrected from *Cc* to *Fdd*2 by Marsh (2004), Pérez-Folch *et al.* (1997); tetramethylurea, a liquid at room temperature, *C*2/*c*, Frampton & Parkes (1996). The latter two structures both display imposed twofold symmetry.



(I)

We report here the hitherto 'missing' structure of trimethylurea, (I). The compound as purchased proved to contain single crystals and one of these was used to determine the structure. The suppliers Alfa Aesar were unfortunately unable to provide details of crystallization conditions; our recrystallization experiments have so far failed to provide evidence of any other crystalline forms. The same crystal form was obtained from, for example, tetrahydrofuran/*n*-heptane by liquid diffusion.

The title compound crystallizes in the space group $Cmc2_1$ with $Z = 12$ ($Z' = \frac{3}{2}$). The first independent molecule (unprimed atoms) lies in the mirror plane at $x = 0$, whereas the second molecule (primed atoms) occupies a general position in the plane at $x \simeq \frac{1}{3}$ (Fig. 1). Molecule 2 has an r.m.s. deviation from planarity of only 0.03 Å; a least-squares fit of both molecules also gives an r.m.s. deviation of 0.03 Å. In both molecules, the NH hydrogen is *trans* to the C=O group, as is observed for all the methylated ureas for which this configuration is possible; one may speculate that this facilitates the formation of hydrogen-bonded chains of molecules.

Molecular dimensions, such as the C=O bond lengths of 1.2438 (19) and 1.243 (3) Å and the N—C—N angles of 117.25 (15) and 117.4 (2)°, may be considered normal.

The packing involves classical N—H···O=C hydrogen-bond systems (Table 1), linking adjacent molecules *via* the *c*-glide operator and thus leading to chains of molecules with the simple and common graph-set *C*(4), parallel to the polar *c* axis (Fig. 2). The chains involve exclusively either molecule 1 or molecule 2, and, as defined by the general direction of the H···O vector, are, respectively, parallel or antiparallel to the *c* axis. The chain pattern as seen along the *b* axis (Fig. 3) is thus *AABAAB* at intervals of *ca a*/6; in other words, there are twice as many chains antiparallel to the *c* axis as parallel to the *c* axis, which is an unusual packing feature. The pattern of chains then extends itself by *b*-axis translation to form the layers perpendicular to the *a* axis as noted above for the individual molecules.

For 1,3-dimethylurea, which also forms hydrogen-bonded chains in a polar space group but has only one independent molecule, all chains are necessarily parallel to the polar *c* axis (Pérez-Folch *et al.*, 1997). We have recently reinvestigated the 1,3-dimethylurea system and have established the presence of a new polymorph, upon which we shall report.

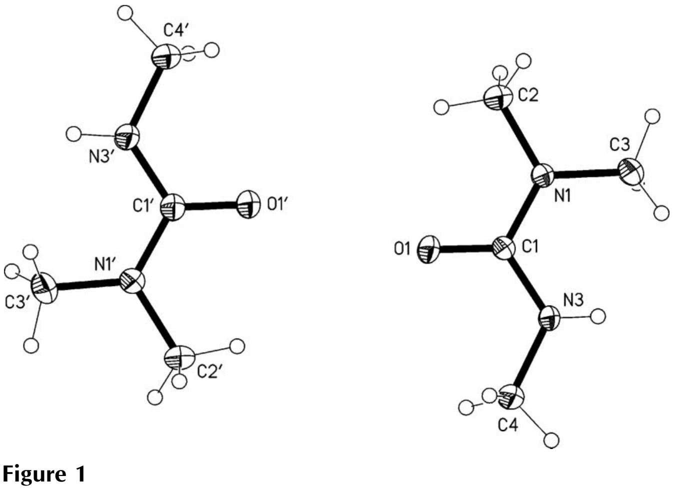


Figure 1
Both molecules of the title compound, projected parallel to the *a* axis. Only one position of each disordered methyl group (at C3 and C3′) is shown. Ellipsoids represent 50% probability levels.

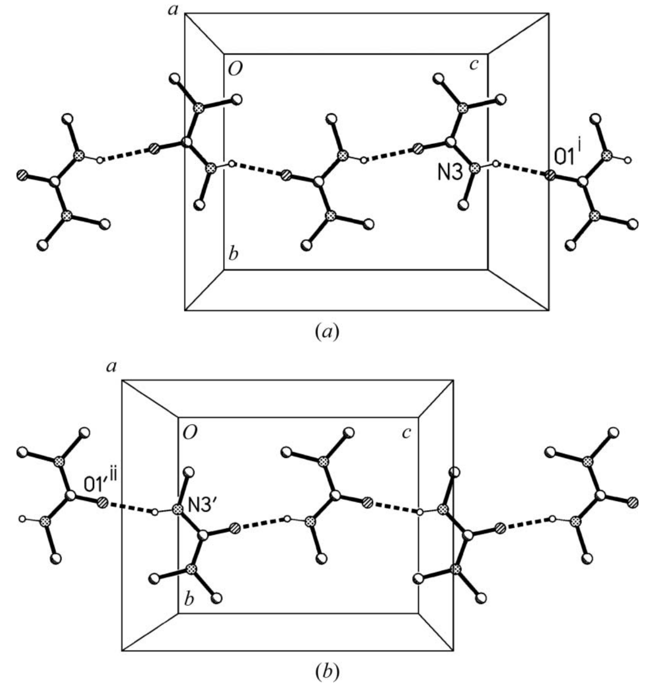


Figure 2
(*a*) The hydrogen-bonded chain of molecule 1 in the region $x \simeq 0$ and (*b*) the hydrogen-bonded chain of molecule 2 in the region $x \simeq \frac{1}{3}$. In both cases, hydrogen bonds are indicated by dashed lines and H atoms not involved in hydrogen bonding have been omitted.

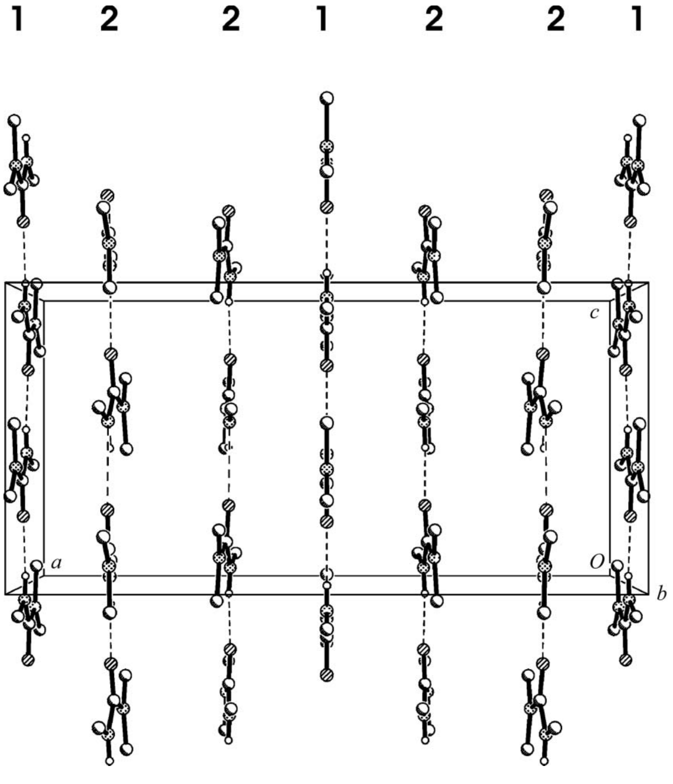


Figure 3
Packing diagram of the title compound viewed parallel to the *b* axis, showing mutually antiparallel chains of molecules 1 and 2 (correspondingly labelled).

Experimental

Crystals of (I) were obtained from Alfa Aesar and were used as supplied (see *Comment*).

Crystal data

$C_4H_{10}N_2O$
$M_r = 102.14$
Orthorhombic, $Cmc2_1$
$a = 20.5281\ (15)$ Å
$b = 8.1474\ (3)$ Å
$c = 9.9637\ (4)$ Å
$V = 1666.43\ (15)$ Å^3
$Z = 12$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 100$ K
0.4 × 0.3 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
36795 measured reflections
1214 independent reflections
1172 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.087$
$S = 1.08$
1214 reflections
117 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H01$\cdots$O1^{i}	0.81 (4)	2.10 (4)	2.859 (3)	155 (4)
N3′—H01′$\cdots$O1′^{ii}	0.88 (3)	2.00 (3)	2.8431 (19)	162 (3)

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

In the treatment of the H atoms for molecule 1 (in the mirror plane), the NH hydrogen was refined freely. Methyl H atoms were identified in difference syntheses; the geometry was idealized (C—H = 0.98 Å and H—C—H = 109.5°) and the methyl groups refined as rigid groups allowed to rotate but not tip. For all methyl H atoms, $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(C). For atoms C2 and C4, one H atom lay to a good approximation in the mirror plane; this H atom was retained, together with one of the other methyl H atoms, with half and full occupation, respectively, and the group was refined using a riding model. For atom C3, the H atoms were not in the mirror plane and a disordered model with three half-occupied H atoms was thus used.

In the treatment of the H atoms for molecule 2 (in the general position), the NH hydrogen was refined freely. The methyl H atoms were identified and incorporated into rigid groups as above. For atoms C2′ and C4′, the H-atom positions were acceptable, but the methyl group at C3′ showed indistinct maxima and refined slowly. For this reason, a model of six half H atoms was used, corresponding to two equally spaced and half-occupied positions of the methyl H atoms. Even this model converged slowly, and the true disorder may be more serious. In both molecules, there is a short intramolecular contact from the NH hydrogen to one of the disordered H atoms at C3 (1.96 Å for molecule 1 and 1.84 Å for molecule 2; the latter leads to an 'Alert B' message from *checkCIF*).

In the absence of significant anomalous dispersion, Friedel opposite reflections were merged and the Flack (1983) parameter is thus meaningless.

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Data collection: *CrysAlis PRO* (Oxford Diffraction, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3085). Services for accessing these data are described at the back of the journal.

References

Döring, C., Taouss, C., Freytag, M., Jones, P. G. & Blaschette, A. (2012). *Z. Naturforsch. Teil B*. In preparation.

Fairlie, D. P., Woon, T. C., Wickramasinghe, W. A. & Willis, A. C. (1994). *Inorg. Chem.* **33**, 6425–6428.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Frampton, C. S. & Parkes, K. E. B. (1996). *Acta Cryst.* C**52**, 3246–3248.

Hamann, T., Henschel, D., Lange, I., Moers, O., Blaschette, A. & Jones, P. G. (2002). *Z. Naturforsch. Teil B*, **57**, 1051–1065.

Hamann, T., Wijaya, K., Moers, O., Blaschette, A. & Jones, P. G. (2002). *Z. Naturforsch. Teil B*, **57**, 1152–1164.

Henschel, D., Hamann, T., Moers, O., Blaschette, A. & Jones, P. G. (2002). *Z. Naturforsch. Teil B*, **57**, 113–121.

Huiszoon, C. & Tiemessen, G. W. M. (1976). *Acta Cryst.* B**32**, 1604–1606.

Marsh, R. E. (2004). *Acta Cryst.* B**60**, 252–253.

Oxford Diffraction (2011). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Pathirana, H. M. K. K., Weiss, T. J., Reibenspies, J. H., Zingaro, R. A. & Meyers, E. A. (1994). *Z. Kristallogr.* **209**, 696.

Pérez-Folch, J., Subirana, J. A. & Aymami, J. (1997). *J. Chem. Crystallogr.* **27**, 367–369.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Siemens (1994). *XP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wijaya, K., Henschel, D., Moers, O., Blaschette, A. & Jones, P. G. (1997). *Z. Naturforsch. Teil B*, **52**, 1219–1228.

Wölper, C., Rodríguez-Gimeno, A., Chulvi Iborra, K., Dix, I., Freytag, M., Jones, P. G. & Blaschette, A. (2011). *Z. Naturforsch. Teil B*, **66**, 1161–1174.

Wölper, C., Rodríguez-Gimeno, A., Chulvi Iborra, K., Jones, P. G. & Blaschette, A. (2010). *Z. Naturforsch. Teil B*, **65**, 1363–1371.

Zerbe, E.-M., Roca Piñol, S., Hamann, T., Freytag, M., Jones, P. G. & Blaschette, A. (2008). *Z. Naturforsch. Teil B*, **63**, 1276–1290.

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