

- KAPECKI, J. A., BALDWIN, J. E. & PAUL, I. C. (1968). *J. Amer. Chem. Soc.* **90**, 5800–5805.
- KOREN, B., STANOVNIK, B. & TIŠLER, M. (1975). *Org. Prep. Proced. Int.* **7**, 55–59.
- LYNCH, T. R., MELLOR, I. P. & NYBURG, S. C. (1971). *Acta Cryst.* **B27**, 1948–1954.
- MELLOR, I. P. & NYBURG, S. C. (1971a). *Acta Cryst.* **B27**, 1954–1958.
- MELLOR, I. P. & NYBURG, S. C. (1971b). *Acta Cryst.* **B27**, 1959–1963.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY System, Version of June 1972. Technical Report TR-192 of the Computer Science Center, Univ. of Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

*Acta Cryst.* (1976). **B32**, 1604

## Monomethylurea: a Redetermination

BY C. HUISZON AND G. W. M. TIEMESSEN

*Chemical Physics Laboratory, Twente University of Technology, P.O. Box 217, Enschede, The Netherlands*

(Received 22 January 1976; accepted 26 January 1976)

**Abstract.** C<sub>2</sub>H<sub>6</sub>N<sub>2</sub>O, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 8.4767 (6), *b* = 6.9809 (5), *c* = 6.9227 (6) Å at 20°C. *D*<sub>m</sub> = 1.204 g cm<sup>-3</sup> [Corey & Wyckoff, *Z. Kristallogr.* (1933), **85**, 132–142], *D*<sub>c</sub> = 1.2007 g cm<sup>-3</sup> with *Z* = 4; Mo *K*α radiation (*λ* = 0.7107 Å); *R*<sub>w</sub> = 0.035.

**Introduction.** An early investigation of the crystal structure of monomethylurea was carried out by Corey & Wyckoff (1933). As was concluded by these authors the structure they proposed might not be correct. This conclusion has been confirmed by the present work.

The crystal used was taken from commercially available monomethylurea (Fluka A. G., Switzerland). The linear dimensions of the crystal were about 0.4 mm. Data were collected at room temperature, 20°C, with a computer-controlled single-crystal diffractometer (Philips, PW 1100) using graphite-monochromated Mo *K*α radiation, *λ* = 0.7107 Å. The built-in program for the accurate determination of lattice constants (Hornstra & Vossers, 1973) was used. Each of the four sets of equivalent reflexions *hkl*, *h̄kl*, *hk̄l*, *hkl̄* was recorded in the *θ* range of 3 to 35° using the *θ*–2*θ* scan mode, scan width 1.4°. Background counting was done during one half of the total scanning time at each side of the reflexion. In the refinement the weighted mean, *I*<sub>*hkl*</sub>, of each set of four equivalent

reflexions was chosen for the intensity of the reflexion *hkl*:

$$I_{hkl} = \left( \sum_i I_i / \sigma_i^2 \right) / \left( \sum_i 1 / \sigma_i^2 \right),$$

where the summations extend over the four equivalent reflexions and *σ*<sub>*i*</sub> are the individual errors due to counting statistics. The standard deviation in *I*<sub>*hkl*</sub>, *σ*, was calculated from the expression

$$1/\sigma = \left( \sum_i 1/\sigma_i^2 \right)^{1/2}.$$

The structure was solved with the program *MULTAN* of Germain, Main & Woolfson (1971). The refinement was carried out with the program *ORFLS* of Busing, Martin & Levy (1962). First positional and anisotropic thermal parameters of the non-hydrogen atoms were refined. After the location of the hydrogen atoms in a difference Fourier map a complete refinement including atomic positions, anisotropic thermal parameters of the heavy atoms, isotropic thermal parameters of the hydrogen atoms, a scale factor and an isotropic extinction factor (Larson, 1969) was carried through. The function minimized was  $\sum w(|F_o| - k|F_c|)^2$ , where the summation extends over all reflexions having an intensity larger than twice their standard deviation due to counting statistics, *k* is the scale factor, *|F<sub>o</sub>|* and *|F<sub>c</sub>|* are the observed and calculated structure factors, respectively. The weight, *w*, for each reflexion

Table 1. Atomic parameters for monomethylurea

The anisotropic temperature factor is of the form:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$  and the isotropic temperature factor:  $\exp(-8\pi^2U \sin^2 \theta/\lambda^2)$ . The positional parameters are  $\times 10^4$  (for the H atoms  $\times 10^3$ ). The thermal parameters for non-hydrogen atoms are given in  $10^{-3} \text{ \AA}^2$ , the values of *U* are in  $\text{ \AA}^2$ . Standard deviations are shown in parentheses and refer to the last digits.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(1)	3305 (1)	8051 (2)	4727 (2)	37.8 (6)	39.7 (6)	43.6 (6)	-3.5 (5)	4.7 (5)	4.7 (5)
O(1)	2000 (1)	8784 (1)	4337 (1)	40.0 (4)	56.4 (5)	54.4 (5)	5.2 (4)	-1.4 (4)	2.0 (4)
N(1)	3982 (2)	8296 (2)	6459 (2)	48.7 (7)	74 (1)	49.1 (7)	12.8 (7)	-3.5 (6)	-10.0 (7)
N(2)	4087 (2)	6964 (2)	3460 (2)	50.3 (7)	61.6 (7)	51.3 (7)	11.6 (7)	-1.3 (6)	-7.7 (6)
C(2)	3476 (3)	6535 (3)	1571 (3)	101 (2)	75 (1)	56 (1)	23 (1)	-10 (1)	-19 (1)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(1)	353 (2)	914 (3)	727 (2)	0.066 (5)
H(2)	489 (2)	782 (3)	666 (2)	0.067 (5)
H(3)	419 (3)	592 (4)	79 (4)	0.107 (8)
H(4)	269 (5)	547 (7)	170 (6)	0.21 (2)
H(5)	298 (3)	753 (4)	92 (3)	0.10 (1)
H(6)	494 (2)	656 (3)	384 (3)	0.064 (5)

was  $w = \sigma^{-2}$ , where  $\sigma$  is the estimated standard deviation of the structure factor.  $\sigma$  was estimated as  $\sigma = 2s + 0.01|F_o|$ , where  $s$  denotes the standard deviation in  $|F_o|$  due to counting statistics. Atomic scattering factors for C, O and N as calculated (Harkema, 1971) from accurate atomic wave functions (Clementi, 1965) were used. The scattering factor for H was taken from Stewart, Davidson & Simpson (1965). The *R* index obtained was 0.038 (weighted *R*: 0.035). The number of significant reflexions used for the refinement was 692.\*

**Discussion.** Atomic positions and thermal parameters are given in Table 1. The numbering of the atoms is shown in Fig. 1, which has been drawn with the aid of the program ORTEP (Johnson, 1965). Bond lengths and bond angles have been collected in Table 2. The

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31651 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



Fig. 1. Stereoscopic pair showing the monomethylurea molecule. Ellipsoids of the non-hydrogen atoms are at the 40% probability level.

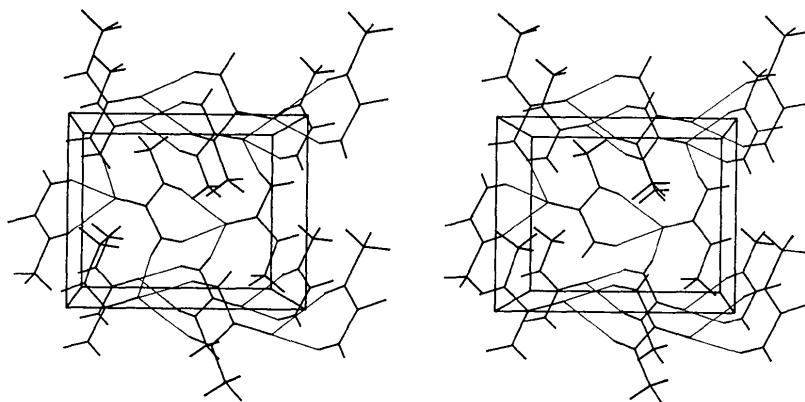


Fig. 2. Stereoscopic pair showing the molecular packing of monomethylurea. The thin lines indicate the hydrogen bonds. The *a* axis points to the right, the *b* axis away from the reader, and the *c* axis points up.

molecule, without allowance for the hydrogen atoms of the methyl group, is planar. The equation of the best plane through the heavy atoms and the atomic deviations from this plane are listed in Table 3. It is noted that the present molecular structure differs considerably from the structure which can be calculated from the atomic coordinates given by Corey & Wyckoff (1933).

Table 2. Bond distances and angles

Standard deviations in the last digits are shown in parentheses.

C(1)–O(1)	1.248 (1) Å	N(1)–H(2)	0.85 (2) Å
C(1)–N(1)	1.340 (2)	N(2)–H(6)	0.82 (2)
C(1)–N(2)	1.336 (2)	C(2)–H(3)	0.92 (3)
C(2)–N(2)	1.439 (2)	C(2)–H(4)	1.00 (5)
N(1)–H(1)	0.90 (2)	C(2)–H(5)	0.93 (2)
N(1)–C(1)–O(1)	121.4 (2)°	N(2)–C(2)–H(3)	113 (2)°
N(2)–C(1)–O(1)	122.0 (1)	N(2)–C(2)–H(4)	108 (3)
N(1)–C(1)–N(2)	116.6 (2)	N(2)–C(2)–H(5)	116 (2)
C(1)–N(2)–C(2)	122.5 (2)	H(3)–C(2)–H(4)	98 (3)
H(2)–N(1)–H(1)	123 (3)	H(3)–C(2)–H(5)	111 (3)
H(2)–N(1)–C(1)	119 (2)	H(4)–C(2)–H(5)	107 (3)
C(1)–N(2)–H(6)	115 (2)	H(1)–N(1)–C(1)	117 (2)
H(6)–N(2)–C(2)	122 (2)		

Table 3. Atomic deviations from the best plane through the non-hydrogen atoms

Equation of plane:  $0.4672x + 0.8104y - 0.3534z = 4.6999$  Å.

Atom	Deviation	Atom	Deviation
C(1)	0.007 (1) Å	H(1)	0.09 (2) Å
O(1)	0.001 (1)	H(2)	0.03 (2)
N(1)	–0.010 (1)	H(6)	0.03 (2)
N(2)	0.012 (1)		
C(2)	–0.010 (2)		

Table 4. Hydrogen-bond parameters

Standard deviations in the last digits are shown in parentheses.

Bond*	N–H	N–H···O	H···O	∠N–H···O
1	0.85 (2) Å	2.993 (2) Å	2.22 (2) Å	151 (1)°
2	0.82 (2)	2.949 (2)	2.17 (2)	159 (2)
3	0.90 (2)	2.970 (2)	2.08 (2)	167 (2)

\* Bonds 1 and 2 are between the oxygen atom, O(1), of the molecule at  $x, y, z$  and the atoms N(1), H(2) and N(2), H(6) of the molecule at  $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$ . Bond 3 is the bond between the oxygen atom, O(1), of the molecule at  $x, y, z$  and the atoms N(1) and H(1) of the molecule at  $\frac{1}{2} - x, 2 - y, -\frac{1}{2} + z$ .

A packing diagram of the crystal structure, drawn with the aid of the program *STER* (van de Waal, 1973), is given in Fig. 2. The molecules are linked by hydrogen bridges. Each oxygen atom is involved in three hydrogen bonds of the type  $O \cdots H-N$ . The geometries of these bonds are given in Table 4. The separations between the oxygen atom and the hydrogen atoms are much less than the sum of the van der Waals radii of these atoms, which is  $2.53 \text{ \AA}$  (Kitaigorodsky, 1961). As stated by Hamilton & Ibers (1968), this is an unmistakable criterion for hydrogen bonding.

Mr G. J. van Hummel is thanked for his technical assistance.

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CLEMENTI, E. (1965). *IBM Res. Rev.* **9**, 2-19.
- COREY, B. R. & WYCKOFF, R. W. G. (1933). *Z. Kristallogr.* **85**, 132-142.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368-376.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 16. New York, Amsterdam: W. A. Benjamin.
- HARKEMA, S. (1971). Thesis, Twente Univ. of Technology, Enschede, The Netherlands.
- HORNSTRA, J. & VOSSERS, H. (1973). *Philips Tech. Rev.* **33**, 61-73.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KITAIGORODSKY, A. I. (1961). *Organic Chemical Crystallography*, p. 7. New York: Consultants Bureau.
- LARSON, A. C. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291-294. Copenhagen: Munksgaard.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- WAAL, B. W. VAN DE (1973). *STER. A Fortran Program for Drawing Crystal Structures*, Progress Report 12, Chemical Physics Laboratory, Twente Univ. of Technology, Enschede, The Netherlands.

*Acta Cryst.* (1976). **B32**, 1606

### 4b,9a,13b-Triazadibenzo[*a,e*]acephenanthrylene-9,14-dione

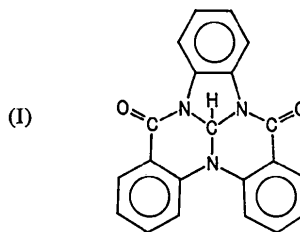
BY R. L. HARLOW AND S. H. SIMONSEN

*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.*

(Received 15 October 1975; accepted 2 February 1976)

**Abstract.**  $C_{21}H_{13}N_3O_2$ ,  $M = 339.35$ , orthorhombic,  $Pca2_1$  (No. 29),  $Z = 4$ . At  $-40^\circ\text{C}$ ,  $a = 18.458$  (4),  $b = 10.924$  (2),  $c = 7.673$  (2)  $\text{\AA}$ ,  $V = 1547 \text{ \AA}^3$ ,  $D_c = 1.457 \text{ g cm}^{-3}$ . At  $25^\circ\text{C}$ ,  $D_m = 1.44 \text{ g cm}^{-3}$ . Mo  $K\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 1.04 \text{ cm}^{-1}$ .  $R = 0.065$ , 1118 reflections measured on a Syntex diffractometer. The structure of a novel, fused-ring heterocyclic compound is confirmed. As a result of an  $H \cdots H$  intramolecular interaction, the conformations of the two chemically-equivalent halves of the molecule are found to be quite different.

**Introduction.** The synthesis and preliminary structural information for the title compound (1) have been previously communicated (Cass, Katritzky, Harlow & Simonsen, 1976). Thin, plate-like crystals were grown by sublimation; the yellow crystal selected for this investigation had dimensions of  $0.09 \times 0.27 \times 0.44 \text{ mm}$  perpendicular to (100), (010) and (001). The possible space groups,  $Pcam$  and  $Pca2_1$  (systematic absences:  $0kl$ ,  $k$  odd and  $h0l$ ,  $h$  odd), and a set of approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs. Space group  $Pcam$ , with  $Z = 4$ , requires that the molecule be situated on a twofold axis, across a mirror plane, or about a center of symmetry; because the molecule can possess none of these symmetries (assuming an ordered structure),  $Pca2_1$  was selected as the correct space group. This choice was later confirmed by the 'E' statistics and, of course, by the successful refinement of the structure.



The crystal was mounted on a Syntex  $P2_1$  diffractometer equipped with a low-temperature apparatus which kept the crystal cooled to  $-40^\circ\text{C}$ . Mo  $K\alpha$  radiation, monochromated with a graphite crystal, was used throughout this study. The unit-cell parameters were refined using the Bragg angles (as determined by the Syntex centering routine) of 52 reflections.

Intensity data for 1322 unique reflections ( $4^\circ < 2\theta < 48^\circ$ ) were collected using the  $\omega$ -scan technique. Scans of  $1.0^\circ$  were employed with scan rates which ranged from  $0.5$  to  $5.0^\circ \text{ min}^{-1}$ , depending on the number of counts accumulated in a rapid preliminary scan. Background measurements were taken at both ends of the scan with  $\omega$  displaced by  $\pm 1.0^\circ$  from the  $K\alpha$  peak; the time of each measurement was one-half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption.