Acta Cryst. (1978). B**34**, 3102–3104

3a,6a-Dimethylglycouril
{3a,6a-Dihydro-3a,6a-dimethylimidazo[4,5-*d*]imidazole-2,5(1*H*,6*H*)-dione}*

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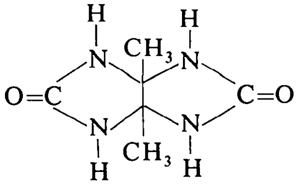
(*Received* 23 *January* 1978; *accepted* 17 *May* 1978)

Abstract. $C_6H_{10}N_4O_2$, $M_r = 170{\cdot}17$, orthorhombic, *Cmcm*, $a = 7{\cdot}357\,(2)$, $b = 10{\cdot}836\,(5)$, $c = 10{\cdot}180\,(6)$ Å; $Z = 4$, $D_c = 1{\cdot}389$, $D_m = 1{\cdot}39$ g cm^{-3} (flotation); final $R = 0{\cdot}040$ (463 reflections with $I > 3\sigma I$). Crystallographic symmetry requires the molecule to have point symmetry 2*mm*. In the molecule are two planar five-membered rings with a 65·0° angle between the plane normals of the rings. Each molecule is hydrogen bonded to four neighboring molecules by eight N—H···O hydrogen bonds [$d_{\mathrm{N}\cdots\mathrm{O}} = 2{\cdot}869\,(2)$ Å].

Introduction. The title compound (I) was prepared by the dropwise addition, at room temperature, of concentrated hydrochloric acid (or 85% phosphoric acid) to a magnetically stirred aqueous solution of urea and 2,3-butanedione. The crystalline condensation product was separated after 30 min; the yield was over 96%; no formation of other products was observed. Independently of the acid used, the reaction product showed similar physical properties (Table 1) and was presumed to have a glycouril structure (I) (Biltz, 1908; Franchimont & Klobbie, 1888; Kouno & Ueda, 1971; Veniamin & Vakirtzi-Lemonias, 1970). Other structures for (I) have been reported in the literature (see, for example, Lugosi, Thibert, Holland & Lam, 1972).



(I)

Table 1. *Chemical, crystal, and refinement data for* $C_6H_{10}N_4O_2$

Elemental analysis	%C:H:N = 42·44:5·89:32·85
Melting point	>340°C (decomp.)
a, *b*, *c**	7·357 (2), 10·836 (5), 10·180 (6) Å
V	811·55 Å^3
μ(Mo $K\alpha$)	1·16 cm^{-1}
Criterion for $\sigma(I)$	$\sigma(I)^2 = I + 0{\cdot}00066\,I^2$
Criterion for $\sigma(F_o)$	$\sigma(F_o) = [F_o^2 + \sigma(I)/\mathrm{Lp}]^{1/2} - F_o$
Weighting function	$w = [\sigma(F_o)]^{-2}$
Function minimized	$\sum w(F_o - \lvert F_c\rvert)^2$
$R = \sum\lvert \lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum F_o$	0·040 (463 reflections, $I > 3\sigma I$)
$R_w = [\sum w(F_o - \lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$	0·044
Maximum and average shift/error	0·04, 0·01

* The lattice constants were determined by a least-squares refinement using 15 reflections with 2θ values ranging between 20–34°.

The reaction product is a protochromogen or color precursor due to the intense orange color produced when heated in the presence of 4*M* phosphoric acid. This color reaction has been proven to be very suitable for the determination of urea in biological fluids (Henry, Cannon & Winkelman, 1974) *via* the carbamidodiacetyl colorimetric assay, which has long been the method of choice in many clinical laboratories (Fearon, 1939; Whealty, 1948). However, little appears to be known concerning both the structure of the orange pigment and the mechanism of reaction between urea and diacetyl (or diacetyl monoxime) in the presence of mineral acids. The present X-ray study was undertaken to establish the conformation of the protochromogen. Transparent, colorless crystals were obtained by slow crystallization from a dilute aqueous solution. Preliminary precession photographs established the space group as *Cmc*2$_1$, *C*2*cm*, or *Cmcm*. A crystal plate (0·29 × 0·15 × 0·035 mm) was mounted on a four-circle diffractometer for data collection. The radiation used was graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å). 1428 reflections were collected to $2\theta = 60°$. Equivalent reflections were averaged to a unique

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* The X-ray structure determination described in this paper was supported by the Food and Drug Administration, FDA-NBS Interagency Agreement 224758253.

† Summer employee, Office of Science, Food and Drug Administration.

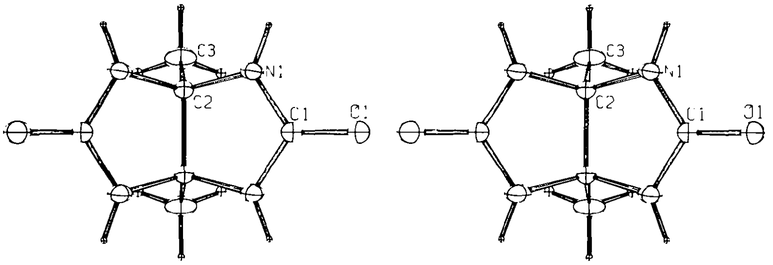

Fig. 1. A projection of the molecule onto the xz plane. The atoms are represented by thermal ellipsoids at the 25% level of probability.

set of 674 reflections of which 463 had an intensity $>3\sigma I$. The weighted R value between symmetry-equivalent reflections was 0·04. Five standard reflections were measured after every 100 reflections with no significant change in intensities during the course of the experiment. The data were corrected for Lorentz and polarization factors but not for absorption. Additional experimental data are given in Table 1. Statistics of normalized structure factors (E) supported the assignment of the centrosymmetric space group *Cmcm*. A satisfactory refinement confirmed this choice.

The structure was solved by using the program *MULTAN* written by Germain, Main & Woolfson (1971) and was refined by a full-matrix least-squares method. The scattering factors used were those of Cromer & Mann (1968) for the heavy atoms, and those of Stewart, Davidson & Simpson (1965) for H. Calculations were performed using the XRAY system (Stewart, 1976). After the first isotropic refinements, a difference Fourier synthesis showed the location of the H atoms. The final cycle of refinement was calculated using anisotropic thermal parameters for all atoms except H which were refined isotropically. The weighting scheme used and the final R values are given in Table 1.* The resulting difference synthesis revealed no peak higher than 0·3 e Å^{-3}. The final positional parameters and their estimated standard deviations are given in Table 2.

Discussion. A stereoview (Johnson, 1965) and the numbering scheme are shown in Fig. 1, bond distances and angles in Fig. 2. Each N has one shorter [1·338 (2) Å] and one longer [1·440 (2) Å] bond to C; similar bonding has also been found in other compounds such as dixanthenylurea (Hubbard, Mighell & Fatiadi, 1978). There are two mirrors present in the molecule, one passing through the atoms C(1)—O(1) and the other through the atoms C(2)—C(3). The five-membered rings are essentially planar with a maximum deviation from the plane of 0·014 Å for C(1). The angle between the normals to the planes of the two rings is 65·0°.

In this structure there are two unconnected sheets of hydrogen-bonded molecules parallel to the xz plane. A portion of one of these sheets is shown in Fig. 3. Each molecule in the sheet is bonded to four others. The N atom is the donor in one hydrogen bond whereas the O atom is the acceptor of two hydrogen bonds with $N\cdots O$ = 2·869 (2) Å and $\angle N—H\cdots O$ = 174°. A similar type of hydrogen bond was observed in both dixanthenylurea with $N\cdots O$ = 2·957, 2·928 Å and $\angle N—H\cdots O$ = 151, 153° respectively, and the 1:1 compound ammonium *P,P*-dithiophosphacyanurate: urea (Andersson & Stålhandske, 1976) with $N\cdots O$ = 2·853 (3) Å and $\angle N—H\cdots O$ = 167°.

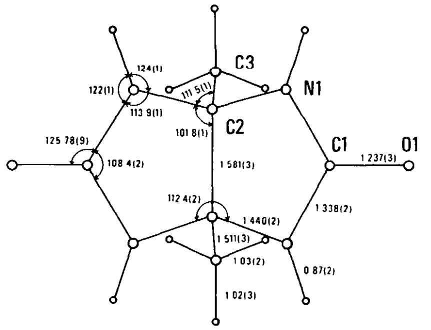

Fig. 2. Bond lengths (Å) and angles (°) of the unique atoms in the molecule. The standard deviations are given in parentheses.

Table 2. *Final positional atomic parameters with standard deviations given in parentheses*

	x	y	z
O(1)	0	0·7699 (2)	0·5326 (1)
N(1)	0·1476 (2)	0·6666 (1)	0·3675 (1)
C(1)	0	0·7072 (2)	0·4311 (2)
C(2)	0·1074 (2)	0·5979 (2)	0·25
C(3)	0·2014 (4)	0·4739 (2)	0·25
H(N1)	0·2572 (29)	0·6810 (15)	0·3958 (15)
H1(C3)	0·3371 (46)	0·4911 (26)	0·25
H2(C3)	0·1651 (34)	0·4299 (22)	0·3353 (20)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33635 (8pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

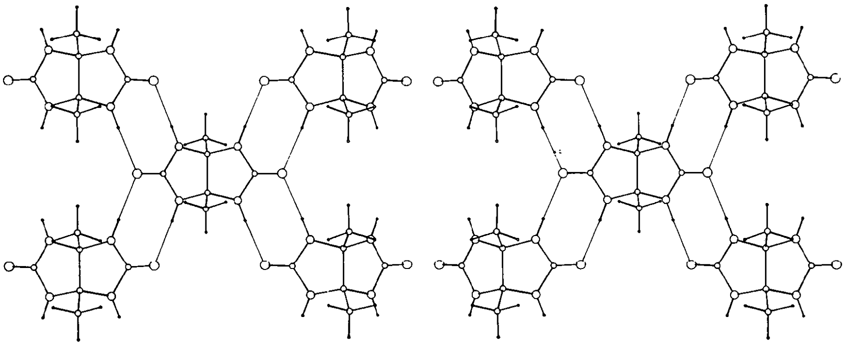

Fig. 3. A stereoview of a portion of an infinite sheet of hydrogen-bonded molecules. The two mirrors of *Cmcm* (⊥ to the plane of the figure) intersect at the midpoint of the central molecule; screw axes relate the central to the other four molecules.

The authors wish to thank Dr A. Perloff for determining the cell parameters and space group from precession photographs.

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Acta Cryst. (1978). B**34**, 3104–3107

Methyl α-D-Xylopyranoside*

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(*Received* 13 *February* 1978; *accepted* 22 *May* 1978)

Abstract. $C_6H_{12}O_5$, $M_r = 164\cdot16$, monoclinic, $P2_1$, $Z = 4$, $a = 11\cdot197$ (1), $b = 6\cdot722$ (1), $c = 11\cdot123$ (1) Å, $\beta = 111\cdot79$ (1)°, [λ(Cu $K\alpha_1$) = 1·54051 Å], $V = 777\cdot37$ Å^3, $d_m = 1\cdot406$, $d_c = 1\cdot402$ g cm^{-3}. The structure was solved by *MULTAN* and refined to $R_F = 0\cdot033$ for 1777 unique reflections measured with Cu $K\alpha$ radiation. The two independent molecules in the asymmetric unit have slightly distorted $^4C_1$ chair conformations; one distortion is in the direction of a twist and the other towards the boat conformation. The acetal C—O bond lengths and valence angles are in good agreement with those observed in other methyl α-pyranosides and predicted by *ab initio* quantum-mechanical calculations. All the hydroxyl groups are

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* Research supported by NIH Grant No. GM-21794 and performed under the auspices of the US Energy Research and Development Administration.