# The Crystal and Molecular Structure of Hexahydro-1,2-dimethyl-3,6-pyridazinedione at −165 °C

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The crystal and molecular structure of the title compound, $C_6H_{10}N_2O_2$, has been determined using 3284 reflections above background level collected at $-165$ °C. The crystals are monoclinic, space group $C2/c$ with cell dimensions $a = 19.107(5)$ Å, $b = 6.099(2)$ Å, $c = 12.893(3)$ Å, $\beta = 113.59°(2)$. The structure model was refined to an $R$ of 0.056. In order to reduce the influence of valence electron asphericity on the structural parameters low-angle data were excluded from the final refinements. The heavy atom parameters converged to their final values for a minimum $\sin \theta/\lambda$ cutoff of 0.65 Å$^{-1}$, leaving 1840 reflections used in the refinement, the $R$-factor obtained is 0.037. The molecule has a "twisted boat" conformation with close to $C_2$ symmerty. Compared with hexahydro-3,6-pyridazinedione the loss of hydrogen bonding leads to a lengthening of the $C-N$ bonds by about 0.020 Å and a shortening of the $C=O$ bonds by about 0.019 Å.

The structure determination of hexahydro-1,2-dimethyl-3,6-pyridazinedione (HDMP) is part of a series of structure investigations of 3,6-pyridazinediones and related compounds, of which part of the purpose is to study the effect of hydrogen bonding on the peptide linkage, the $N-C=O$ fragment. The experimental results have been complemented by a series of theoretical studies using hydrogen-bonded complexes of formamide as model systems (for a review see Ref. 1).

In the crystal structure of hexahydro-3,6-pyridazinedione [2] the molecules are bound together by $N-H\cdots O$ hydrogen bonds such that each $N-C=O$ fragment participates in two intermolecular hydrogen bonds around a center of symmetry forming hydrogen-bonded dimers of the type found for formamide.[3] The structure of hexahydro-3,6-pyridazinedione has recently been reinvestigated using a more extensive data set in order to study the deformation electron densities.[4] In order to get further quantitative results on the effect of hydrogen bonding on the peptide linkage, i.e. the changes in molecular parameters induced by the formation of hydrogen bonds, it was of interest to study a hexahydro-3,6-pyridazinedione which was not involved in hydrogen bonding. In the unreduced 3,6-pyridazinediones the possibility of hydrogen bonding has been deliberately eliminated by successive methyl substitution of the hydrogen atoms bonded to the nitrogen and oxygen atoms, and a similar approach could be used for hexahydro-3,6-pyridazine-dione. The results from a series of structure determinations of some simple amides in the gaseous state,[5-8] imply that introduction of a methyl group at the nitrogen atom has little or no effect on the $C-N$ bond length, whereas a small lengthening ($\sim 0.005$ Å) of the $C=O$ bond is indicated. A structure determination of HDMP was, therefore, carried out.

## EXPERIMENTAL

1,2-Dimethyl-3,6-pyridazinedione was synthesized by the method of Eichenberger et al.[9] and reduced [10] to give HDMP. The product was recrystallized in ethanol. The crystals grew as platy needles.

Oscillation and Weissenberg photographs indicated monoclinic symmetry and the system-

atic absences were those characteristic of the space group $C2/c$. The density indicated eight molecules in the unit cell.

A computer-controlled Syntex $P\bar{1}$ four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation and equipped with a modified Enraf-Nonius liquid nitrogen cooling device was utilized in the determination of unit cell parameters and the collection of intensity data. Cell constants were determined by a least-squares treatment of the angular coordinates of fifteen reflections with $2\theta$-values between 40 and 45°. The temperature at crystal site was $-165$ °C.

Three-dimensional intensity data were recorded using the $\omega - 2\theta$ scanning mode with scan speed variable from 2 to 6° min⁻¹, depending on the peak intensity of the reflection. Background counting time was equal to 0.7 × scan time. All reflections with $2\theta$-values less than 55° were recorded using a crystal of dimensions $0.2 \times 0.2 \times 0.5$ mm. Due to icing this crystal was lost and a crystal of dimensions $0.2 \times 0.2 \times 0.4$ mm was used in the recording of reflections with $2\theta$-values larger than 55°. Of these only those which had integrated counts larger than 5 cps determined in a 2 s scan over the reflection were recorded. The intensities of three standard reflections which were remeasured after every sixty reflections were essentially constant throughout each recording run. The intensities of these reflections were used in scaling the two data sets to a common scale.

The estimated standard deviations were taken as the square root of the total counts with a 2 % addition for experimental uncertainties. Of the 3632 reflections measured ($2\theta_{max} = 80°$), 3284 had intensities larger than twice their standard deviations. These were regarded as observed, whereas the remaining were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 which is described in Ref. 11.

The atomic scattering factors used were those of Doyle and Turner[12] for oxygen, nitrogen, and carbon, and of Stewart et al.[13] for hydrogen.

## CRYSTAL DATA

Hexahydro-1,2-dimethyl-3,6-pyridazinedione, $C_6H_{10}N_2O_2$, $M = 142.15$ amu. Space group $C2/c$, cell dimensions at $-165$ °C: $a = 19.107(5)$ Å, $b = 6.099(2)$ Å, $c = 12.893(3)$ Å, $\beta = 113.59°(2)$, $V = 1376.9(6)$ Å³. $D_{obs}$ (flotation, 19 °C) $= 1.36$ g cm⁻³, $Z = 8$, $D_{calc} = 1.371$ g cm⁻³. $F(000) = 608$.

## STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by the MULTAN[14] program assembly. The heavy atom structure model was refined with anisotropic temperature factors to a conventional $R$ of 0.08. The hydrogen atoms were found as the ten largest peaks in a difference Fourier synthesis calculated using this structure model. These were included in the refinement with isotropic temperature factors. Full-matrix least-squares refinement of all positional and thermal parameters converged to an $R$ of 0.056 and a weighted $R_w$ of 0.068. The "goodness of fit" ($G$) ($\{[\sum(F_0 - |F_c|)^2]/(m-s)\}^{\frac{1}{2}}$) is 3.48.

In order to remove the influence of the valence electron asphericity on the structural parameters the low-angle data were excluded from the final refinements. Full-matrix least-squares refinements of all parameters involving the heavy atoms were performed with minimum $\sin \theta / \lambda$-cutoffs of 0.50, 0.65 and 0.75 Å⁻¹. The

*Table 1.* Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by: $\exp\{-2\pi^2[U_{11}(a^*h)^2 + \cdots + 2U_{23}(b^*c^*kl)]\}$.

| ATOM | X | Y | Z | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|---|---|---|
| O1 | .69976(4) | .53782(11) | .42852(5) | .0234(2) | .0225(2) | .0198(2) | .0009(2) | .0097(2) | -.0046(2) |
| O2 | .56946(4) | 1.11657(10) | .66612(5) | .0264(2) | .0196(2) | .0219(2) | .0024(2) | .0109(2) | -.0034(2) |
| N1 | .61500(4) | .77558(10) | .68336(5) | .0224(2) | .0173(2) | .0158(2) | .0025(2) | .0094(2) | .0020(1) |
| N2 | .65535(3) | .63186(10) | .56249(4) | .0202(2) | .0170(2) | .0143(2) | .0029(1) | .0066(1) | .0015(1) |
| C3 | .65233(4) | .65365(10) | .45561(5) | .0179(2) | .0173(2) | .0143(2) | -.0013(2) | .0059(1) | -.0015(1) |
| C4 | .68284(4) | .84814(12) | .38969(5) | .0206(2) | .0235(3) | .0137(2) | .0025(2) | .0062(2) | .0024(2) |
| C5 | .62292(4) | 1.03876(11) | .46877(6) | .0224(2) | .0175(2) | .0199(2) | .0006(2) | .0097(2) | .0031(2) |
| C6 | .60113(4) | .98677(10) | .56686(5) | .0188(2) | .0164(2) | .0158(2) | .0002(2) | .0057(1) | -.0205(1) |
| C7 | .57615(6) | .67629(14) | .66826(7) | .0329(3) | .0247(3) | .0222(2) | .0220(2) | .0172(2) | .0046(2) |
| C8 | .71581(5) | .58551(12) | .64873(6) | .0251(2) | .0197(2) | .0188(2) | .0340(2) | .0061(2) | .0032(2) |

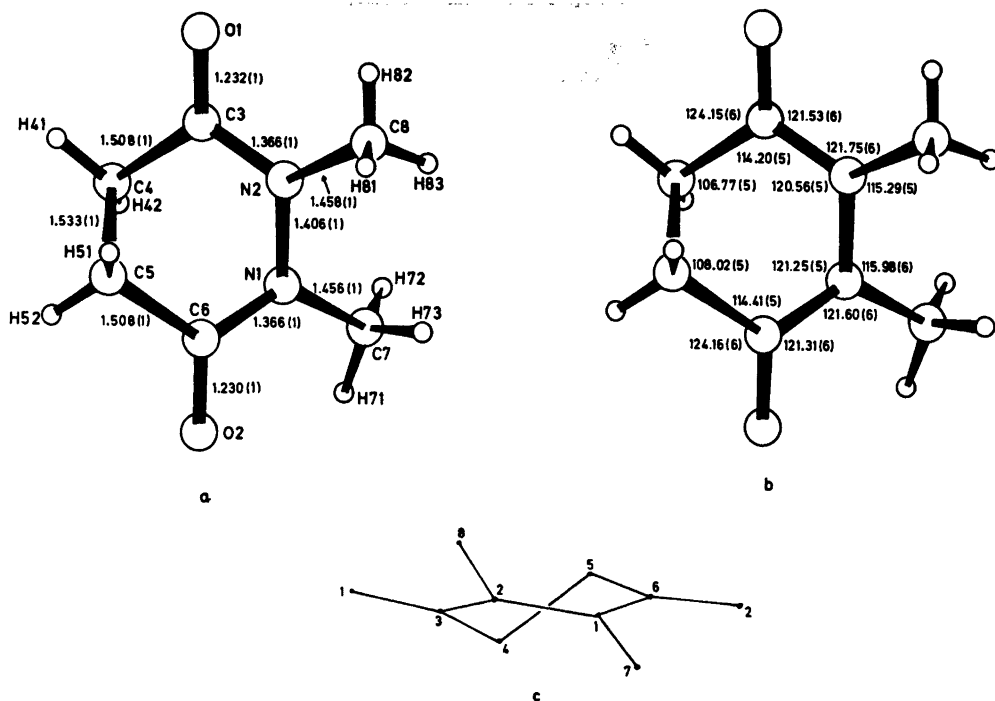| ATOM | X | Y | Z | B | ATOM | X | Y | Z | B |
|---|---|---|---|---|---|---|---|---|---|
| H41 | .6149(8) | .8689(25) | .3255(13) | 2.0(3) | H42 | .5496(8) | .8887(24) | .3685(12) | 1.7(3) |
| H51 | .6760(8) | 1.0635(24) | .4960(12) | 1.6(3) | H52 | .5973(9) | 1.1672(26) | .4327(13) | 2.2(3) |
| H71 | .5485(9) | .7800(27) | .0707(13) | 2.5(3) | H72 | .5523(10) | .5465(32) | .6343(15) | 3.6(4) |
| H73 | .6122(10) | .6351(30) | .7436(16) | 3.7(4) | H81 | .7598(10) | .6051(29) | .6973(14) | 3.8(3) |
| H82 | .7348(10) | .4825(29) | .6142(15) | 3.0(3) | H83 | .6952(10) | .4385(32) | .6926(16) | 3.8(4) |

*Fig. 1.* (a) Bond lengths (Å) corrected for thermal libration effects. (b) Bond angles (°). (c) A view of the molecule as seen in the least-squares plane calculated using all nonhydrogen atoms.

number of reflections in the refinement, final $R$, $R_w$ and $G$ factors are as follows: cutoff 0.50 Å$^{-1}$: 2598, 0.050, 0.054, 2.22; cutoff 0.65 Å$^{-1}$: 1840, 0.037, 0.036, 1.18; cutoff 0.75 Å$^{-1}$: 1172, 0.039, 0.038, 1.07. The heavy atom parameters converged to their final values for the 0.65 Å$^{-1}$ cutoff in agreement with the refinement of hexamethylenetetramine,[15] although this cutoff is lower than that of 0.75 Å$^{-1}$ found for similar compounds (hexahydro-3,6-pyridazinedione,[4] diformylhydrazine [16] and carbohydrazide [17]). Atomic parameters for nonhydrogen atoms obtained in the refinement with a minimum $\sin \theta/\lambda$ cutoff of 0.65 Å$^{-1}$ are listed in Table 1, together with the parameters found for hydrogen atoms in the refinement using all data. A list of observed and calculated structure factors is available from the authors upon request.

The r.m.s. difference between the observed $U_{ij}$'s and those calculated from the "rigid-body" model [18] is 0.0007 Å$^2$, which indicates that the molecule may be regarded as a rigid body. The atomic positions were accordingly corrected for the vibrational motion. The eigenvalues of $T$ are 0.14, 0.12 and 0.11 Å$^2$, and the r.m.s. librational amplitudes are 3.1, 2.1 and 1.7°.

## DISCUSSION

Bond lengths and bond angles are listed in Fig. 1 where also the numbering of the atoms is indicated. The lengths of corresponding bonds are equal, the maximum deviations being 0.002 Å between N1 – C7 and N2 – C8, and between C3 – O1 and C6 – O2. On the other hand, there are significant differences in corresponding bond angles. The C4 – C5 – C6 and N2 – N1 – C6 angles are opened by about 1.3° compared with, respectively, the C5 – C4 – C3 and N1 – N2 – C6 angles. These angular differences are probably coupled to the differences in the torsional angles around the N2 – C3 and N1 – C6 bonds and the C3 – C4 and C5 – C6 bonds. (Torsional angles are listed in Table 2). The

*Table 2.* Selected torsional angles (°), the angles are positive in a right-hand screw.

| Angle | (°) | Angle | (°) |
|---|---|---|---|
| C6 – N1 – N2 – C3 | – 29.73(9) | C3 – C4 – C5 – C6 | – 64.07(7) |
| N1 – N2 – C3 – C4 | – 0.49(9) | C5 – C6 – N1 – N2 | 7.80(8) |
| C8 – N2 – C3 – C4 | – 162.07(6) | C5 – C6 – N1 – C7 | – 159.36(7) |
| N2 – C3 – C4 – C5 | 45.71(7) | C4 – C5 – C6 – N1 | 38.31(7) |
| O1 – C3 – C4 – C5 | – 130.35(7) | C4 – C5 – C6 – O2 | – 137.71(7) |
| C7 – N1 – N2 – C3 | 138.12(7) | C6 – N1 – N2 – C8 | 132.98(6) |
| N1 – N2 – C3 – O1 | 175.68(6) | O2 – C6 – N1 – N2 | – 176.06(7) |

corresponding torsional angles N1 – N2 – C3 – C4 and C5 – C6 – N1 – N2, and the angles N2 – C3 – C4 – C5 and C4 – C5 – C6 – N1 differ by about 7.3°. The molecule has a "twisted boat" conformation with roughly $C_2$ symmetry, the twofold axis passing through the midpoints of the N1 – N2, and C4 – C5 bonds, in agreement with the conformation found for hexahydro-3,6-pyridazinedione[2],[4] (a view of HDMP as seen along the twofold axis is given in Fig. 1c).

A comparison of the lengths found for the C – O and C – N bonds in HDMP and hexahydro-3,6-pyridazinedione clearly shows the effect of hydrogen bonding on the conjugation over the N – C=O fragment. The formation of the one N – H···O hydrogen bond found in hexahydro-3,6-pyridazinedione[4] leads to a shortened C – N bond [1.346(1) Å] and a lengthened C – O bond [1.245(1) Å]. Taking into consideration the lengthening of about 0.005 Å of the C – O bond induced by introducing a methyl group at the nitrogen atom (see Ref. 1 for a discussion of this), the formation of one N – H···O bond leads to a lengthening of the C – O bond by about 0.019 Å and a shortening of the C – N bond by about 0.020 Å. These values are in good agreement with those found for the unreduced 3,6-pyridazinediones,[1] (0.015 Å and 0.025 Å, respectively). However, both for these unreduced compounds and for the simple amides,[1] which have two N – H···O bonds, the results obtained imply that the shortening of the C – N bond is significantly larger than the corresponding lengthening of the C – O bond. Theoretical calculations (see Ref. 1 for a review) have shown that the increased conjugation over the N – C=O fragment induced by hydrogen bonding is caused by a transfer of $\sigma$-electronic charge from the oxygen to the nitrogen atom

*via* the hydrogen bond which is counteracted by a greater participation of the nitrogen lone pair in the conjugated system. This greater participation of the nitrogen lone pair affects the whole ring system in the semiaromatic 3,6-pyridazinediones whereas in the hexahydro-3,6-pyridazinediones the effect is mainly found in the N – C = O fragments. This difference in the two systems may be a reason for the difference in the effect on the N – C and C – O bonds, although more data is clearly necessary on the reduced system.

The loss of hydrogen bonding in HDMP compared with hexahydro-3,6-pyridazinedione,[4] *i.e.* the reduced conjugation over the N – C = O fragments, leads to some changes in the molecule. The N – N bond is lengthened from 1.398(1) to 1.406(1) Å, and the torsional angle C3 – N2 – N1 – C6 has increased from 25.6(2)° in hexahydro-3,6-pyridazinedione to 29.73(9)° in HDMP. An increase is also found in the C6 – C5 – C4 – C3 angle from 56.3(2) to 64.07(7)°. The configurations around C3, C6 and around the nitrogen atoms are also affected by the decrease in conjugation, the C3 and C6 atoms

*Table 3.* Deviations from least-squares planes (Å × 10³). The deviations for those atoms used to define a plane are given in italicized numbers.

| Atom | Plane A | Atom | Plane B |
|---|---|---|---|
| O1 | *6* | O2 | *6* |
| N2 | *6* | N1 | *6* |
| C3 | *– 21* | C6 | *– 21* |
| C4 | *6* | C5 | *6* |
| C5 | 1 093 | C4 | 951 |
| N1 | 65 | N2 | 108 |
| C7 | – 782 | C8 | 1 051 |

are found 0.027 Å out of the plane through, respectively, O1, N2 and C4, and O2, N1 and C5 (see Table 3), whereas this value is only 0.005 Å in hexahydro-3,6-pyridazinedione. The results also show much less planarity around the nitrogen atoms in HDMP than in hexahydro-3,6-pyridazinedione implying a larger degree of $sp^3$-hybridization of the nitrogens.

All *intra*-ring bond angles in HDMP have decreased compared with those found for hexahydro-3,6-pyridazinedione, the changes vary from 0.25° (N1−C6−C5) to 3.1° (C3−C4−C5). The largest angular differences are found in the *exo*-cyclic angles around the nitrogen atoms, in hexahydro-3,6-pyridazinedione the N−N−H1 angle is 125(4)° and the C−N−H1 angle is 113(4)°, whereas in HDMP the angles N1−N2−C8 and N2−N1−C7 are 115.98(6) and 115.29(5)°, respectively and the C3−N2−C8 and C6−N1−C7 are 121.75(6) and 121.60(6)°. These differences may be caused by the involvement of H1 in the hydrogen bond.

The shortest intermolecular contacts are of normal van der Waals lengths.

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