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The Crystal and Molecular Structure of 1-Methyl-3,6-pyridazinedione

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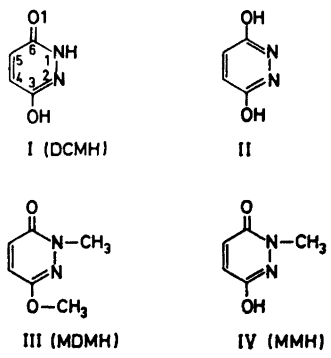
The crystal and molecular structure of 1-methyl-3,6-pyridazinedione has been determined by X-ray methods using 2473 reflections above background level collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions: $a = 3.89_7$ Å; $b = 13.95_5$ Å; $c = 10.61_7$ Å; $\beta = 99.5_4°$. Estimated standard deviations in bond lengths are about 0.001 Å, and in angles 0.1°. The molecule is found to exist as the monolactim and is planar. The bond lengths indicate a resonance stabilization of the heterocycle, although less than what was found in 4,5-dichloro-3,6-pyridazinedione.

The structure determination of 1-methyl-3,6-pyridazinedione was carried out as part of a series of structure investigations of 3,6-pyridazinediones and related compounds.[1-4]

Significant differences were found in the pyridazine moieties of 4,5-dichloro-3,6-pyridazinedione [1] (I), DCMH, and 1-methyl-3-methoxy-6-pyridazone [3,4] (III), MDMH. The bond lengths indicated a larger resonance stabilization of DCMH than of MDMH. The hydrogen bonds in DCMH, which involve N1 and both oxygens, may imply a structure intermediate between the monolactim (I) and the dilactim (II). 1-Methyl-3,6-pyridazinedione, MMH, was, on the basis of the structure found for DCMH, assumed to exist as the monolactim (IV) with an oxygen-oxygen hydrogen bond in the solid state. It was of interest to determine if the pyridazine moiety of MMH corresponds to that of DCMH or that of MDMH. Structural parameters available for formamide [5,6] indicate that N−H···O hydrogen bonds have a large effect on the resonance stabilization of the peptide moiety (O=C−N<). Significant differences were also found in the O1−C6 and C6−N1 bond lengths of DCMH [1] and MDMH.[3,4] The introduction of a methyl-group at the 1-position of the pyridazine moiety in the 3,6-pyridazinedione should therefore be expected to have a significant effect on the resonance stabilization of the heterocycle.



EXPERIMENTAL

MMH was synthesized from 3,6-pyridazinedione by the method of Eichenberger *et al.*[7] The product was recrystallized by slow evaporation of a water solution. Rectangular, colorless crystals were formed. A crystal of dimensions 0.6 × 0.3 × 0.3 mm. was selected for the crystallographic work.

Oscillation, Weissenberg and precession photographs indictated monoclinic symmetry; all reflections ($h0l$) for l odd, and ($0k0$) for k odd, were systematically absent. This uniquely defines the space group as $P2_1/c$. Unit cell parameters were determined on a Syntex-P$\bar{1}$ diffractometer using Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation. The angular coordinates of fifteen symmetry-independent reflections were utilized

in the least-squares refinement of cell dimensions. The computer program used is part of the diffractometer program library.

Three-dimensional intensity data were recorded using a computer-controlled Syntex-P$\bar{1}$ four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation. The temperature was kept constant within 1 °C at 20 °C. The $\omega - 2\theta$ scan was utilized with scan speed variable from 1 to 12° min^{-1}, depending on the peak intensity of the reflections. Background was counted for half the scanning time at each end of the scan range. Reflections for which the counts exceeded 10^5 cps were remeasured with reduced primary beam intensity. The intensities of three standard reflections were measured after every 100 reflections, the variations in the check reflection intensity were less than 2 %. No corrections for these variations were applied to the intensity data.

The estimated standard deviations were taken as the square root of the total count with a 2 % addition for experimental uncertainties. Of the 4977 unique reflections measured ($2\theta_{max} = 92°$), 2473 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections, and the remaining reflections were excluded from further calculations. The intensities were corrected [8] for Lorentz and polarization effects.

The atomic scattering factors used were those of Doyle and Turner [9] for oxygen, nitrogen, and carbon, and of Stewart *et al.*[10] for hydrogen.

CRYSTAL DATA

1-Methyl-3,6-pyridazinedione, $C_5H_6N_2O_2$, monoclinic.

$a = 3.897$ (0.0005) Å; $b = 13.955$ (0.002) Å; $c = 10.617$ (0.002) Å; $\beta = 99.54°$ (0.01°).

Figures in parentheses are estimated standard deviations.

$V = 569.3$ Å^3; $M = 126.1$ amu; $Z = 4$; $D_{calc} = 1.471$ g/cm^3; $F(000) = 264$.

Absent reflections: ($h0l$) for l odd; ($0k0$) for k odd; space group $P2_1/c$.

STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by a computer procedure [11] based on direct methods, utilizing Sayre's equation.[12]

All programs used in subsequent calculations are part of a local assembly of computer programs for CYBER-74 and are described in Ref. 13.

The structure model was refined to a conventional R of 0.20. Introduction of anisotropic thermal parameters for all non-hydrogen atoms and least-squares refinement yielded an R of 0.082. All six hydrogens were located in a difference fourier synthesis. These were included in the least-squares refinement with isotropic thermal parameters. Results from the full-matrix least-squares refinements using various parts of the data set are summarized in Table 1.

It is worth noting that only marginal shifts are found for the N1 – N2 bond length, and also for the nitrogen positions. A significant shortening is usually found for the nitrogen-nitrogen bond

Table 1. Results from the least-squares refinements. R, R_w and R_t are the conventional, the weighted and the conventional for the total data-set correlation factors, respectively (for a more detailed explanation see Ref. 4). G is the "goodness-of-fit". The estimated standard deviation of the scale factor is given in parentheses. The bond lengths are corrected for librational motion (see Fig. 1 for the numbering of the atoms).

No.	sin θ/λ limit on the data (Å^{-1})	Number of reflections used in the refinement	R	R_w	R_t	G	Scale	Mean e.s.d in bond ($\times 10^4$)	Bond lengths (Å) N1 – N2	C4 – C5
I[a]	<0.65	1140	.043	.051	.071	2.30	.077(5)	16	1.373	1.345
II[a]	–	2473	.067	.063	–	2.54	.082(3)	12	1.372	1.352
III[b]	>0.50	1906	.067	.058	.077	2.35	.085(5)	13	1.371	1.356
IV[a]	>0.60	1533	.077	.063	.075	2.43	.084(8)	17	1.371	1.356
V[b]	>0.65	1333	.083	.066	.077	2.52	.085(10)	21	1.370	1.356
VI[b]	>0.70	1103	.090	.072	.088	2.59	.087(14)	29	1.373	1.359

[a] All positional and thermal parameters refined. [b] All positional and thermal parameters refined for non-hydrogen atoms.

when the low-angle data (sin $\theta/\lambda < 0.6$) are excluded from the refinement.[1,3,4] The lengthening of the carbon-carbon double bond is as expected.[4] The other bond lengths show no dependence on the lower sin θ/λ-cut of the data, this has been noted earlier.[1,4]

Only marginal differences are found in the thermal parameters from refinements III, IV, and V, while those from refinements I and II are generally larger and those from refinement VI are generally smaller than these. This is probably coupled with the changes in the scale factor. The total discrepancy between the atomic vibration tensor components and those calculated from the rigid-body parameters found by analysis of the librational, translational and screw motion of the molecule is 0.0013 Å^2 for refinement I, 0.0011 Å^2 for II, III, and IV, 0.0012 Å^2 for V, and 0.0015 Å^2 for VI. This indicates that the molecular model in all cases may be regarded as a rigid body. The atomic coordinates were accordingly corrected for the librational motion.

The results indicate that the valence electrons in this case have no significant effect on the structure model when all data with sin $\theta/\lambda < 0.50$ is excluded from the refinement. Results from refinement III will therefore be used in the discussion. A listing of structure amplitudes is available from the author upon request. The final parameters for non-hydrogen atoms are listed in Table 2. Atomic parameters for hydrogen atoms, from refinement II, are given in Table 3. The eigenvalues of **T** are 0.18, 0.16, and 0.14 Å^2. The r.m.s. librational amplitudes are 5.2, 4.6, and 2.0° with the major axis nearly parallel to a line through C4–C6 (see Fig. 1 for the numbering of the atoms).

Standard deviations in molecular dimensions were calculated from the correlation matrix ignoring standard deviations in cell parameters.

DISCUSSION

Bond lengths and bond angles are listed in Fig. 1 where the numbering of the atoms is indicated.

The heterocycle is planar, the atoms being displaced from a least-squares plane through the six ring atoms by less than 0.009 Å (see Table 4). O2 deviates significantly from the plane, similar displacements have been found both in DCMH [1] and MDMH.[3,4]

Both the N1–N2 and the C4–C5 bond lengths are similar to those found in MDMH.[4] The other bond lengths, however, indicate a slightly larger resonance stabilization of MMH than of MDMH. The C3–C4 and the C5–C6

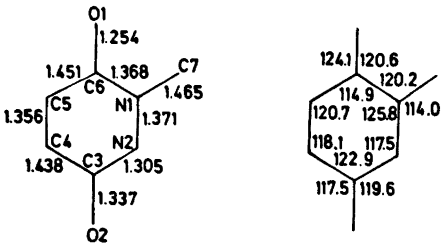


Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects) and bond angles (°). Estimated standard deviations in bond lengths are 0.001 Å and in angles 0.1°. Structure model obtained from the refinement using high-angle data (III).

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations (× 10^5) for non-hydrogen atoms. The temperature factor is given by exp $-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$.

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{33}
O1	96119(41)	12057(7)	60217(11)	7951(93)	316(3)	665(7)	587(30)	−1678(42)	41(8)
O2	32460(44)	41070(7)	32861(10)	9453(109)	267(3)	615(7)	576(28)	−1581(45)	0(7)
N1	61950(29)	18016(6)	42547(8)	4746(58)	243(3)	442(5)	14(21)	−344(26)	−6(6)
N2	44993(32)	25170(7)	35236(9)	5334(64)	257(3)	442(5)	80(22)	−517(28)	−5(6)
C3	48873(37)	33874(7)	39621(10)	5467(74)	257(3)	460(6)	187(25)	−411(33)	−22(7)
C4	69703(42)	36173(8)	51660(11)	6584(94)	273(4)	547(7)	163(28)	−872(41)	−108(8)
C5	85674(40)	28914(8)	58770(11)	5802(81)	308(4)	501(7)	197(29)	−886(37)	−100(8)
C6	82042(33)	19139(7)	54235(9)	4588(65)	285(4)	457(6)	120(25)	−448(29)	5(7)
C7	56059(49)	8467(8)	36957(14)	7653(109)	248(3)	669(9)	32(31)	−912(49)	−76(9)

Table 3. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms. The e.s.d. is given in parentheses and are in the last digit of the corresponding parameter. H11, H12, and H13 are the three hydrogens in the methyl group.

Atom	x	y	z	B
H8	199(7)	391(2)	258(3)	4.7(5)
H9	715(7)	429(2)	543(2)	4.1(4)
H10	995(6)	297(2)	671(2)	3.5(4)
H11	728(8)	50(2)	397(3)	5.0(5)
H12	556(9)	86(3)	284(3)	6.3(7)
H13	379(11)	55(3)	403(4)	7.1(8)

Table 4. Deviations from a least-squares plane through the six ring atoms. Plane equation: $(-0.2085x - 0.0084y + 0.0426z)R - 0.221 = 0$.

Atom	Deviation (Å $\times 10^3$)	Atom	Deviation (Å $\times 10^3$)
N1	−9	C6	6
N2	5	C7	3
C3	2	O1	7
C4	−6	O2	31
C5	3		

bonds are in MMH 1.438 Å and 1.451 Å, respectively, while they in MDMH were found to be 1.430 Å and 1.460 Å. Also, the N2−C6 bond length is slightly shorter in MMH (1.368 Å) than in MDMH (1.374 Å), and a lengthening of the C6−O1 bond is found (1.254 Å in MMH, 1.245 Å in MDMH). This bond is similar to that in DCMH (1.257 Å), but significantly longer than the carbon-oxygen bond lengths of 1.236 Å and 1.241 Å found in 1,2-dimethyl-3,6-pyridazindione,[2] while the N1−C6 bond is of the same length as the nitrogen-carbon bonds in that molecule. The differences found in the pyridazine moieties of MDMH and MMH may be due to the oxygen-oxygen hydrogen bond which the latter is found to have (see Fig. 2).

However, significant differences are found between the MMH and the DCMH [1] molecules, indicating a much larger resonance stabilization of the latter. The N1−C6 bond is in DCMH only 1.345 Å, much shorter than in both MMH and MDMH. The C3−C4 and C4−C5 bonds

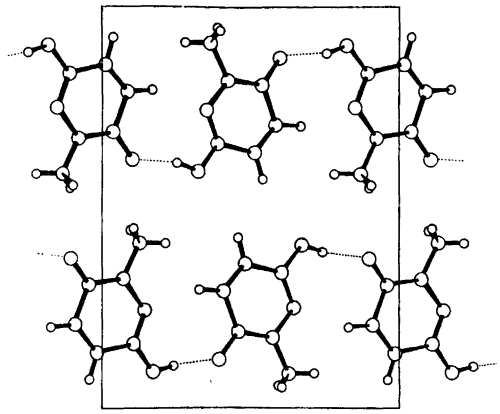


Fig. 2. The crystal structure as seen along the a-axis. Hydrogen bonds are indicated by dotted lines.

in DCMH are equal in length (1.451 Å), and the N1−N2 bond is significantly shorter than in MMH (1.353 Å in DCMH, 1.371 Å in MMH), while the C4−C5 bond is longer (1.362 Å in DCMH, 1.356 Å in both MMH and MDMH). These differences in the pyridazine moieties of the three molecules (DCMH, MMH and MDMH) imply that the N1−O1 hydrogen bond, which is found in DCMH, have a large effect on the resonance stabilization of these systems. This is also indicated by the large differences in molecular dimensions found for formamide [5,6] and acetamide [14–16] in the crystalline and gas state. The differences found between DCMH, MMH, and MDMH indicate that the O1−O2 hydrogen bond has only a small effect on the resonance stabilization of the pyridazine moiety.

The molecular arrangement in the crystal is visualized in Fig. 2, and may be described as layers perpendicular to (102). Within these layers the molecules are hydrogen bonded. The hydrogen bond length from O2 to O1, in position $(-1.0+x, 0.5-y, -0.5+z)$ is 2.616 Å.

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