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The Crystal and Molecular Structure of 1-Methyl-3-methoxy-6-pyridazone

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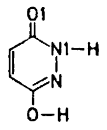
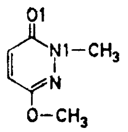
The crystal and molecular structure of 1-methyl-3-methoxy-6-pyridazone (monolactim dimethyl maleic hydrazide) has been determined by X-ray methods using 1125 reflections above background level collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 4.07_4$ Å; $b = 11.54_1$ Å; $c = 14.97_1$ Å; $\beta = 97.3_3$°. The carbon-oxygen and the nitrogen-nitrogen bond lengths are found to be shorter when all reflections with $\sin \theta/\lambda < 0.40$ are excluded from the refinement. Estimated standard deviations in bond lengths are about 0.006 – 0.007 Å, and in angles 0.4 – 0.5°. The heterocycle is planar, and the bond lengths indicate some resonance stabilization. The pyridazinedione moiety is significantly different from that in 4,5-dichloro-3,6-pyridazinedione.

The structure determination of 1-methyl-3-methoxy-6-pyridazone (monolactim dimethyl maleic hydrazide) (MDMH) was carried out as part of a series of structure investigations of 3,6-pyridazinediones.

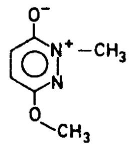
In the X-ray structure determination of 4,5-dichloro-3,6-pyridazinedione[1] (DCMH) the molecule is found to be in the monolactim form (I). It is planar and the bond lengths indicate considerable resonance stabilization of the heterocycle. A similar resonance stabilization may occur in MDMH (II, III).



I



II



III

In the crystal structure of DCMH, N1 and both oxygen atoms were engaged in hydrogen bonds. The present structural work was carried out to determine the effect of the replacement of the two hydrogens by methyl groups. An electron diffraction study indicated a shortening of the C–O1 bond length.[2]

EXPERIMENTAL

MDMH was synthesized from 3,6-pyridazinedione by the method of Eichenberger *et al.*[3] The product was recrystallized by sublimation. Rectangular, colorless plate-shaped crystals were formed. The crystals are extremely fragile and have a high vapour pressure.

Oscillation, Weissenberg and precession photographs indicated 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$\bar{1}$ automatic diffractometer using Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation. Fifteen reflections were measured. The computer program used in the refinement of cell parameters is part of the diffractometer program library.

Three-dimensional intensity data were recorded using an automatic Syntex-P$\bar{1}$ four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation. The take-off angle was 4°, and the temperature was kept constant within 1° at 19°C.

A crystal of dimensions 0.9 x 0.2 x 0.1 mm mounted in a lithium glass capillary tube, was used for the data collection. The $\omega - 2\theta$ scanning mode was utilized with scan speed variable from $1 - 12°$ min^{-1} depending on the peak intensity of the reflection. Background counting time was equal to the scan time. 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 50 reflections, and the data were adjusted according to the variations in the test reflection intensity. The estimated standard deviations were taken as the square root of the total count with a 2 % addition for experimental uncertainty.

Of the 4519 unique reflections measured ($2\theta_{\text{max}} = 80°$), 1125 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 for Lorentz and polarization effects.

The atomic scattering factors used were those of Doyle and Turner[4] for carbon, nitrogen, and oxygen.

CRYSTAL DATA

1-Methyl-3-methoxy-6-pyridazone, $C_6H_8N_2O_2$, melting point: 68°C; monoclinic. $a = 4.074$ (0.002) Å; $b = 11.541$ (0.006) Å; $c = 14.971$ (0.007) Å; $\beta = 94.33°$ (0.04°). Figures in parentheses are estimated standard deviations. $V = 698.1$ Å^3; $M = 140.1$; $Z = 4$; $D_{\text{calc}} = 1.333$ g/cm^3; $F(000) = 296$. Absent reflections: ($h0l$) for l odd; ($0k0$) for k odd; space group $P2_1/c$.

STRUCTURE DETERMINATION

The phase problem was solved by a computer procedure[5] based on direct methods, utilizing Sayre's equation.[6]

The structure model was refined[7] to an R of 0.165, using all 849 observed structure factors with $\sin\theta/\lambda < 0.70$. Introduction of anisotropic thermal parameters for all non-hydrogen atoms and full-matrix least-squares[8] refinement yielded a conventional R of 0.079, and a weighted R_w of 0.085.

Attempts to locate the hydrogen atoms were not successful. A difference Fourier map[7] indicated that the methyl hydrogen atoms were disordered.

Some of the results from this refinement (A) are given in Fig. 1 and Table 3. The overdetermination ratio was 9.4.

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[9] of the molecule, is 0.0024 Å^2.

Table 1. Observed and calculated structure factors. The columns are l, $10|F_o|$, $10\ F_c$.

H=	0, K=	0
2	345	-335
4	300	-195
6	116	115
8	83	82
10	316	292
12	56	-55
14	54	65
16	45	45
H=	0, K=	1
1	312	-322
2	504	514
3	82	-72
4	236	157
5	56	-24
6	73	63
7	26	1
8	213	-208
9	70	-61
10	154	137
11	48	-35
12	25	28
13	64	-60
14	27	23
15	36	37
17	40	-47
18	38	40
20	27	24
H=	0, K=	2
0	604	-552
1	670	-694
2	54	-90
3	416	174
5	136	-134
6	114	-97
7	144	-152
8	401	-168
9	95	81
11	45	-41
12	78	78
14	143	-150
15	41	-48
17	47	-53
18	37	33
H=	0, K=	3
1	18	57
2	81	-8
3	550	541
4	300	270
5	233	187
6	244	-193
8	34	25
9	81	78
10	54	-53
11	36	-38
12	40	-40
13	157	156
14	120	120
15	37	37
16	71	-80
19	25	-17
H=	0, K=	4
0	35	-45
1	33	4
2	123	-87
3	62	28
4	312	-284
5	110	98
6	192	165
7	32	40
8	63	62
9	106	107
10	62	-55
11	35	-34
12	96	-94
13	58	-59
15	92	91
16	23	17
17	42	43
H=	0, K=	5
1	294	-241
2	142	168
3	91	68
4	318	-295
5	232	-208
6	38	-22
7	74	80
9	50	-65
10	24	23
11	130	-134
12	92	98
13	80	77
14	127	-125
15	38	-42
H=	0, K=	6
1	97	-101
2	311	262
3	291	-244
4	159	135
5	194	178
6	48	-28
7	59	55
9	47	-35
11	56	-55
12	136	132
H=	0, K=	7
1	18	-22
2	47	70
3	49	-37
4	26	-4
6	97	105
7	30	-25
8	31	18
9	54	57
10	101	-104
11	41	35
12	100	98
13	93	-94
14	23	30
17	27	-18
18	29	15
19	32	34
H=	0, K=	8
0	232	214
1	28	24
2	219	-218
3	74	-65
4	46	-44
5	62	-72
6	49	-45
8	38	-38
10	30	30
11	42	34
12	73	-78
13	84	-88
14	35	-33
H=	0, K=	9
1	148	145
2	235	244
4	44	-53
6	42	-35
7	34	30
8	77	-80
10	32	35
11	58	65
H=	0, K=	10
0	153	-154
1	163	-165
3	107	103
4	64	67
5	46	44
6	69	75
7	29	-33
9	29	32
10	38	-43
13	29	32
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3	80	-78
5	22	20
7	65	-70
10	51	-53
H=	0, K=	12
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2	64	68
5	24	27
6	27	20
7	29	-30
13	29	-38
14	34	33
15	29	25
H=	0, K=	13
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3	23	5
5	80	-27
6	24	-11
7	38	38
8	37	51
14	28	-27
15	34	-35
16	33	27
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0	46	-48
3	33	-23
6	43	-42
H=	0, K=	15
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6	31	35
7	31	6
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3	33	21
9	34	-18
11	34	28
12	32	-17
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5	28	5
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0	29	-21
3	29	22
H=	0, K=	19
5	30	23
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-6	90	82
-4	163	145
-2	305	-178
0	473	-388
2	1974	1738
4	116	-118
6	94	-93
8	33	40
12	130	132
16	35	35
18	29	18
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-14	29	-25
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-12	49	-45
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-10	77	-67
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0	321	-445
1	158	-141
2	24	-22
3	315	-274
4	310	295
5	66	-68
6	48	60
8	37	47
9	34	15
10	103	-108
12	60	56
13	29	-25
15	36	-38
17	27	-20
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-8	50	37
-7	103	-78
-6	258	-198
-5	443	205
-4	200	-128
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-2	38	15
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0	104	-73
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2	419	-395
3	381	-367
5	67	78
6	19	-17
7	92	-93
8	33	-41
9	49	-63
10	96	-88
11	51	53
14	60	61
15	23	14
16	78	-75
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1	61	80
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4	22	-14
5	316	298
6	176	165
7	127	123
8	98	-95
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11	36	36
12	32	-35
13	31	-28
15	75	77
16	63	63
17	25	25
18	41	-40
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-14	40	32
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0	166	-125
1	46	-14
2	22	-24
4	103	-102
7	49	57
8	81	86
11	50	48
12	21	-18
14	41	-47
15	46	-45
17	38	39
20	27	-8
H=	1, K=	5
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3	168	-155
4	136	125
5	41	43
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7	127	-114
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13	68	-68
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5	192	-184
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4	174	-170
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13	37	34
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11	24	22
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7	105	107
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6	99	95
7	94	-96
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6	110	114
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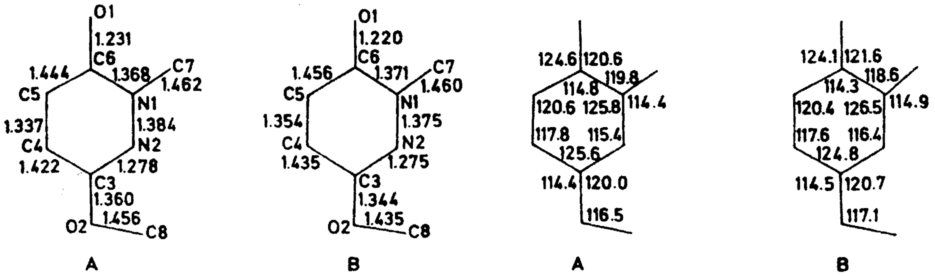

Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects), and bond angles (°). A: Results from low-angle data. B: Results from high-angle data.

This indicates that the molecule may be regarded as a rigid body. The atomic positions were accordingly corrected for the librational motion. The r.m.s. librational amplitudes are 5.8°, 2.9°, and 2.7°.

In both DCMH and 1,2-dimethyl-3,6-pyridazinedione [10] it was found that the nitrogen and oxygen atomic positions were influenced by the valence electrons. In order to reduce this influence it was decided to exclude all structure factors with sin $\theta/\lambda < 0.40$, and to include observed structure factors with sin $\theta/\lambda > 0.70$ (to give 802 F_o's). Least-squares refinement (B) of all positional and anisotropic thermal parameters resulted in a conventional R of 0.090,

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$) for nonhydrogen atoms (high angle data refinement). 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_{23}
O1	3387	17369	49069	9690	866	431	−1072	2514	−57
	144	43	29	382	34	17	173	138	39
O2	61467	11386	19606	9770	703	441	367	2497	81
	138	39	29	384	32	18	151	139	35
N1	25798	24505	37160	6021	514	371	−60	1415	−37
	121	34	29	296	27	17	143	112	34
N2	40703	23505	29474	5299	628	299	110	1153	145
	110	38	25	293	28	15	131	106	32
C3	47362	13253	27106	6059	570	340	−101	1386	60
	145	44	33	339	30	18	170	130	39
C4	40536	2936	31874	7125	464	425	−67	1343	70
	155	42	35	427	29	21	161	153	41
C5	25671	4155	39391	6580	571	380	−455	1298	126
	156	45	34	392	33	20	168	147	41
C6	17383	15609	42475	5693	683	298	−687	1032	40
	150	45	32	342	36	17	171	125	39
C7	18197	36347	39618	9097	603	595	80	2360	−36
	193	53	47	519	35	31	222	213	53
C8	67879	21320	14387	8416	812	434	110	2247	230
	185	53	39	448	40	22	215	176	50

and a weighted R_w of 0.090. This structure model (B) yielded a conventional R of 0.116 for the total data set. The final parameters are listed in Table 2. The overdetermination ratio is 8.9. A comparison between observed and calculated structure factors is given in Table 1.

The total discrepancy between the atomic vibrational tensor components and those calculated from the rigid-body parameters found by analysis of the librational, translational, and screw motion [9] of the molecule, is 0.0022 Å^2. This indicates again that the molecule may be regarded as a rigid body, and the atomic positions were accordingly corrected for the librational motion. The eigenvalues of **T** are 0.22, 0.19, and 0.16 Å^2. The r.m.s. librational amplitudes are 5.4°, 2.8, and 1.7°. The major axis of libration is nearly parallel to the N2 – C5 line.

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

Differences between the results from the two refinements are significant. The thermal parameters are generally smaller in refinement B, in agreement with previous results.[11] The three carbon-oxygen bonds are found to be shorter in refinement B (Fig. 1, Table 3), as is expected.[12] However, this shortening

Table 3. Bond lengths (Å) and bond angles (°). Estimated standard deviations are in parentheses. Results from the low angle data are given on the second line for each bond or angle.

	Bond length	e.s.d. ($\times 10^4$)	Corrected bond length		Bond angle	e.s.d.
O1 – C6	1.218	(70)	1.220	O1 – C6 – C5	124.1	(.59)
	1.229	(55)	1.231		124.6	(.40)
O2 – C3	1.343	(70)	1.344	O1 – C6 – N1	121.6	(.48)
	1.357	(54)	1.360		120.6	(.40)
N1 – N2	1.373	(60)	1.375	O2 – C3 – N2	120.7	(.49)
	1.382	(49)	1.384		120.0	(.41)
N2 – C3	1.274	(67)	1.275	O2 – C3 – C4	114.5	(.47)
	1.276	(58)	1.278		114.4	(.38)
C3 – C4	1.434	(72)	1.435	N1 – N2 – C3	116.4	(.45)
	1.419	(64)	1.422		115.4	(.37)
C4 – C5	1.352	(77)	1.354	N2 – C3 – C4	124.8	(.46)
	1.335	(64)	1.337		125.6	(.40)
C5 – C6	1.454	(74)	1.456	C3 – C4 – C5	117.7	(.47)
	1.442	(64)	1.444		117.8	(.45)
N1 – C6	1.369	(66)	1.371	C4 – C5 – C6	120.4	(.56)
	1.366	(55)	1.368		120.6	(.46)
N1 – C7	1.459	(74)	1.460	C5 – C6 – N1	114.3	(.52)
	1.460	(63)	1.462		114.8	(.36)
O2 – C8	1.430	(75)	1.435	C6 – N1 – N2	126.5	(.41)
	1.454	(62)	1.456		125.8	(.36)
				C6 – N1 – C7	118.6	(.50)
					119.8	(.40)
				N2 – N1 – C7	114.9	(.45)
					114.4	(.36)
				C3 – O2 – C8	117.1	(.52)
					116.5	(.37)

of the carbon-oxygen bonds was not found in DCMH,[1] where the oxygen atoms participated in hydrogen bonds. The shortening of nitrogen-nitrogen bonds which is observed here has been noted previously in similar structures.[1,10]

In the discussion, only results from the refinement based on high-angle data are considered.

DISCUSSION

Bond lengths and bond angles are listed in Table 3 and also in Fig. 1, where the numbering of the atoms is indicated.

Table 4. Deviations from a least-squares plane through the six ring atoms.

Atom	Deviations (Å)	Atom	Deviations (Å)
N1	0.002	C6	−0.001
N2	−0.001	O1	−0.034
C3	−0.002	O2	−0.025
C4	0.004	C7	−0.012
C5	−0.002	C8	−0.077

The heterocycle is planar, the atoms being displaced from a least-squares plane through the six ring-atoms by less than 0.004 Å (see Table 4). The oxygen atoms deviate significantly from the plane; the same displacement was found in DCMH.[1]

The N1 − C6 bond length of 1.371 Å is shorter than the nitrogen-carbon bonds reported for phenylhydrazine [13] and phenylhydrazine hydrochloride.[14] Also C7 is close to the plane of the heterocycle, and the nitrogen-nitrogen bond length of 1.375 Å is significantly shorter than the corresponding bond length of 1.406 Å found in 1,2-dimethyl-3,6-pyridazinedione.[10] On this basis it may be concluded that N1 is sp^2-hybridized.

The bond lengths, the planarity of the molecule and the sp^2-hybridized N1-atom indicate that the heterocycle is resonance stabilized. However, the short C6 − O1 bond length of 1.220 Å and the long C6 − N1 bond length of 1.371 Å (which is significantly longer than the carbon-nitrogen bond length of 1.325 Å found in diformylhydrazine [15]) indicate only a small contribution from resonance structure III.

The differences between MDMH and DCMH are significant. The double bonds are more localized in MDMH. The N1 − C6 single bond (1.371 Å) is longer in MDMH than it is in DCMH (1.345 Å), and the N2 − C3 double bond is shorter (1.275 Å in MDMH, 1.305 Å in DCMH). Also the nitrogen-nitrogen bond (1.375 Å) is longer (1.353 Å in DCMH), while the C4 − C5 bond (1.354 Å) is shorter (1.362 Å in DCMH). The differences may indicate that the hydrogen bonds in DCMH, which involve N1 and both oxygen atoms, establish an electronic structure between the monolactim and the dilactim. This would give a large contribution from a resonance structure similar to III in the solid state.

The O2 – C8 bond length of 1.435 Å is as expected for bonds between oxygen and an sp^3-hybridized carbon atom. The deviation of C8 from the molecular plane is probably caused by packing effects.

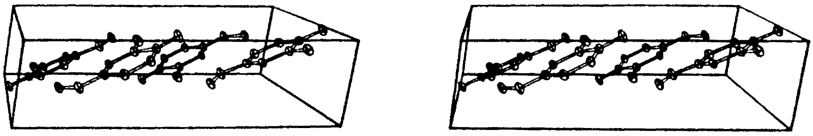

Fig. 2. Stereoview of the packing of 1-methyl-3-methoxy-6-pyridazone molecules in the unit cell, showing ellipsoids of 20 % probability. C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

The molecular arrangement in the crystal is visualized in Fig. 2, and may be described as layers perpendicular to (102). Many short intermolecular van der Waals contacts (3.15 – 3.55 Å) are observed, the interplanar spacing is approximately 3.25 Å.

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