# The Structure of 1-Methyl-3-methoxy-6-pyridazon at —165 °C

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The crystal structure of 1-methyl-3-methoxy-6-pyridazon has been determined by X-ray methods using 2402 reflections above background level collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 4.01_9$ Å; $b = 11.46_8$ Å; $c = 14.85_2$ Å; $\beta = 98.6_3°$ at −165 °C. Estimated standard deviations in bond lengths are about 0.002 Å and in angles 0.1°. Significant differences were found between the pyridazine moieties of the title compound and of 4,5-dichloro-3,6-pyridazindione. The dependence of the bond lengths on the lower sin θ/λ cutoff has been studied.

X-Ray crystallographic structure determinations of 1-methyl-3-methoxy-6-pyridazon,[1] MDMH, (I) and 4,5-dichloro-3,6-pyridazinedione,[2] DCMH, (II) indicated considerable differences in the ring systems of the two molecules. DCMH was found to have a large contribution from the aromatic resonance structure

I
MDMH

II
DCMH

III
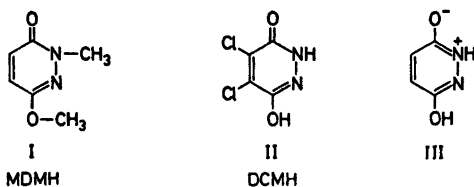
III. This was probably furthered by the formation of intermolecular hydrogen bonds from the nitrogen and the hydroxyl-oxygen to the carbonyl-oxygen. On the other hand the bond lengths of MDMH imply only a small contribution from a resonance structure similar to III.

The estimated standard deviations in the molecular dimensions found in the earlier determination of MDMH were rather large (about 0.007 Å in bond lengths), and in order to obtain sufficient observations for refinement with high-angle data, the lower sin θ/λ limit was set at 0.4 Å⁻¹. It was therefore decided to repeat the

structure determination to obtain a more accurate structure. It was further hoped that a new dataset would give the opportunity to study the dependence of the observed nitrogen-nitrogen bond length on the lower sin θ/λ cutoff for the data used in least squares refinement.

EXPERIMENTAL

A Syntex-P$\bar{1}$ computer controlled diffractometer with graphite-monochromatized MoKα radiation ($K\alpha_1$, $\lambda = 0.70926$ Å; $K\alpha_2$, $\lambda = 0.71354$ Å) and a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The diffractometer was equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). Cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of fifteen independent reflections with 2θ-values from 11 to 25°. The temperature at crystal site was −165 °C. The work was carried out using a crystal of dimensions 0.4 × 0.25 × 0.25 mm.

Three-dimensional intensity data were recorded utilizing the $\omega - 2\theta$ scanning mode with scan speed varying from 2 to 24° min⁻¹. The scan range was from 1.0° below the $K\alpha_1$-peak to 1.0° above the $K\alpha_2$-peak. Background was measured for half the scan-time at each end of the scan-range. Reflections with 2θ-values higher than 45°, which had integrated counts of less than 7, determined in a $2s$ scan over the peak, were not measured. The variations in the intensities of three standard reflections, which were remeasured after every 50 reflections, were random and less than three times their estimated standard deviations. Accordingly no correction for these variations was applied to the intensity data.

Standard deviations were assigned to the reflections according to the formula,

$$\sigma(I) = [s^2(CT + B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$$

where s is the scan speed, CT is the integrated count, B_1 and B_2 are the background counts, and the intensity is $I = s(CT - B_1 - B_2)$. A value

of 0.02 was assigned to the empirical parameter p to account for experimental uncertainties. Out of the 3358 unique reflections measured ($2\theta_{max} = 90°$), 2402 had intensities larger than twice their standard deviations, the remainder being excluded from further calculations.

The intensities were corrected for Lorentz and polarization effects. This program together with those employed for all the subsequent calculations, is part of an assembly of programs for CYBER-74 computer, which is described in Ref. 3.

Atomic form factors used were those of Doyle and Turner [4] for oxygen, nitrogen, and carbon, and of Stewart et al.[5] for hydrogen. Core and valence electron scattering factors utilized for carbon, nitrogen, and oxygen are those given by Stewart (Tables I and III in Ref. 6).

CRYSTAL DATA

1-Methyl-3-methoxy-6-pyridazon, $C_6H_8N_2O_2$, monoclinic, space group $P2_1/c$. $a = 4.019$ (0.001) Å [4.074 (0.002)], $b = 11.468$ (0.004) Å [11.541 (0.006)], $c = 14.852$ (0.005) Å [14.971 (0.007)], $\beta = 98.63°$ (0.03°) [97.33 (0.04)].* Results from the earlier investigation [1] are given in brackets. Figures in parentheses are estimated standard deviations. $V = 676.8$ Å³; $M = 140.1$ amu; $Z = 4$; $D_{calc} = 1.375$ g/cm³; $F(000) = 296$.

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* This value was erroneously given in Ref. 1.

REFINEMENT PROCEDURE

The structure model [1] was refined with anisotropic thermal parameters for all nonhydrogen atoms to a conventional R factor of 0.08 and a weighted R_w of 0.11, using the 1382 structure factors with $\sin \theta/\lambda < 0.7$. Attempts to locate the hydrogen atoms in a difference Fourier synthesis were not successful. Their positions were therefore calculated, one hydrogen in each methyl group was assumed to be *anti* to C3 and C6, respectively (see Fig. 1 for the numbering of the atoms). These atoms 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 (I – VIII). Standard deviations in molecular dimensions were calculated from the correlation matrix ignoring standard deviations in cell dimensions.

Errors in parameters connected with the asphericity of the electron density have been discussed.[3,7-11] The contribution from valence-electrons to the atomic form factors at $\sin \theta/\lambda$-values > 0.6 Å⁻¹ is very small,[12] and it may be assumed that the core-electrons do not participate in the bonding.[11] For most of the bond lengths in the present structure differences in the results obtained with low- and high-angle

Table 1. Results from the least-squares refinements. $R_w = |\sum w(F_o| - |F_c|)^2/\sum wF_o^2|^{\frac{1}{2}}$, $R = (\sum|F_o - |F_c||)/\sum F_o$, R_1 is for the observations used in the refinement, R_t is for the total number of observations. G is the "goodness-of-fit": $(|\sum w(F_o - |F_c|)^2|/(m-s))^{\frac{1}{2}}$, where m is the number of observations and s is the number of parameters refined. The e.s.d. given is the average estimated standard deviation in nonhydrogen bond lengths. Only those reflections which had $\sin \theta/\lambda$-values less than or larger than (as indicated) the figure given in the first column were used in the refinement. The e.s.d. of the scale factor is in the last digit and is given in parentheses.

No.	$\sin \theta/\lambda$ (Å⁻¹)	Number of observations	R_w	R_1	R_t	G	Scale	Bond lengths (Å) N1–N2	C4–C5	E.s.d. (Å × 10⁴)
I[a]	<0.7	1382	.044	.042	.062	1.92	.170(2)	1.374	1.341	18
II[b]	All data	2402	.051	.055	–	1.73	.172(2)	1.372	1.343	15
III[b]	>0.4	2071	.049	.057	.059	1.40	.180(3)	1.370	1.350	15
IV[b]	>0.5	1793	.053	.062	.060	1.28	.182(4)	1.370	1.353	16
V[b]	>0.55	1613	.054	.064	.057	1.21	.178(5)	1.368	1.355	17
VI[b]	>0.6	1427	.055	.065	.056	1.17	.173(7)	1.365	1.354	19
VII[b]	>0.7	1020	.063	.073	.059	1.17	.169(13)	1.363	1.353	30
VIII[b]	>0.75	802	.071	.079	.068	1.20	.183(20)	1.362	1.350	43

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

Table 2. Fractional atomic coordinates and thermal parameters ($\times 10^5$) for nonhydrogen atoms. The estimated standard deviations are in parentheses and are in the last digit given for the corresponding parameter. Results from refinement VI are given on the first line, while the second line is results from refinement II. 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_{33}	B_{12}	B_{23}
O1	2121(49)	17377(13)	48981(10)	4340(93)	310(7)	172(4)	−409(43)	929(32)	−22(9)
	2056(25)	17354(8)	48944(6)	4341(69)	324(6)	174(4)	−374(35)	909(25)	−38(8)
O2	61179(50)	11461(11)	19417(10)	4455(96)	239(7)	186(4)	127(35)	991(34)	30(8)
	61058(24)	11448(8)	19407(6)	4519(72)	245(6)	182(4)	124(31)	1009(26)	51(7)
N1	24982(42)	24605(11)	37045(9)	2832(72)	189(6)	153(4)	−1(32)	570(27)	8(8)
	24855(26)	24599(8)	37050(7)	2938(66)	203(6)	153(4)	−29(32)	549(25)	−5(8)
N2	39875(40)	23670(12)	29397(9)	2650(77)	216(6)	144(4)	13(33)	475(28)	17(7)
	39882(26)	23699(9)	29369(6)	2753(67)	248(6)	140(4)	−35(32)	483(25)	15(8)
C3	46836(48)	13192(13)	26940(11)	2999(84)	207(7)	146(4)	44(38)	546(31)	28(9)
	46734(32)	13202(11)	26973(8)	2761(73)	253(7)	140(4)	−38(39)	434(28)	32(9)
C4	40327(50)	2857(13)	31750(11)	3176(96)	215(7)	176(5)	−37(39)	522(34)	40(9)
	40231(33)	2884(10)	31784(8)	3242(86)	195(7)	177(5)	10(38)	444(31)	27(10)
C5	25463(48)	3971(13)	39304(10)	3074(91)	224(7)	155(5)	−123(39)	440(33)	35(9)
	25494(33)	4009(11)	39273(8)	3238(84)	225(7)	160(5)	−229(38)	418(32)	43(9)
C6	16544(49)	15522(12)	42276(10)	2827(86)	232(7)	136(4)	−163(37)	430(29)	16(9)
	16499(33)	15501(10)	42266(8)	2709(76)	250(7)	137(4)	−244(37)	292(28)	27(9)
C7	16707(57)	36445(14)	39490(13)	3923(107)	224(7)	229(6)	−21(44)	830(41)	−19(10)
	16633(36)	36477(11)	39475(9)	4295(94)	215(7)	238(5)	−25(44)	913(37)	−16(10)
C8	67345(54)	21548(15)	14163(12)	3410(93)	325(8)	167(5)	5(45)	615(32)	105(10)
	67278(36)	21586(11)	14159(8)	3809(85)	310(8)	174(5)	14(44)	715(31)	119(10)

Table 3. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms. The estimated standard deviations are in the last digit of the corresponding parameter and are given in parentheses.

Atom	x	y	z	B
H4	468(4)	−42(2)	294(1)	1.6(3)
H5	192(5)	−23(2)	426(1)	2.5(4)
H71	253(5)	417(2)	355(1)	3.8(5)
H72	256(6)	382(2)	457(2)	4.9(5)
H73	−81(6)	373(2)	393(1)	4.7(5)
H81	783(4)	184(2)	93(1)	1.7(3)
H82	833(4)	270(1)	178(1)	1.9(4)
H83	463(4)	256(1)	118(1)	1.6(3)

data refinements are small, and of the same order as the standard deviations. However, the N1−N2 and the C4−C5 bonds are significantly altered (see Table 1). This has been noted earlier.[1,2] The C4−C5 double bond is not changed significantly when structure factors with sin θ/λ-values down to 0.5 Å^{-1} are included in the refinement, while the nitrogen-nitrogen bond seems to be affected up to a sin θ/λ-value of 0.7 Å^{-1}. The standard deviations rise sharply

between refinement VI (structure factors > 0.6 Å^{-1}) and refinement VII (structure factors > 0.7 Å^{-1}), it is doubtful that the differences in molecular dimensions in these two refinements have any physical meaning. Parameters obtained from refinement VI will therefore be used in the discussion. A listing of structure amplitudes is available from the author upon request. Final parameters obtained in refinement VI and II are listed in Table 2, parameters for hydrogen atoms (from refinement I) are in Table 3.

Only small changes are found in thermal parameters obtained from the different high-angle data refinements (III − VIII), while those from refinement I and II are larger. The total discrepancy, Δ, 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 molecules is 0.0017 Å^2 for the low-angle data refinement (I), 0.0011 Å^2 for refinement II, and 0.0009 Å^2 for the high-angle data refinements (III − VI), while refinement VII and VIII yielded 0.0010 Å^2. The difference between the results obtained in refinement I and VI may indicate a tendency of the thermal parameters

to reflect some of the asphericity of the valence electrons.

The thermal motion analysis based on the parameters from refinement VI showed rather large discrepancies for C8 and yielded one slightly negative libration axis. It was therefore decided to exclude C8 from the analyses. The total discrepancy, Δ, is 0.0006 Å², and the atomic positions were corrected for the librational motion. The eigenvalues of T are 0.14, 0.12, and 0.11 Å². The r.m.s. librational amplitudes are 3.1, 2.3, and 1.5° with the direction of the major axis nearly parallel to the C6−N1 bond.

In order to study the valence electron distribution in the MDMH and DCMH [2] molecules, L-shell [6] and extended L-shell refinements [13] were carried out. Differences found between corresponding atoms in the two symmetry-independent DCMH molecules were large and of the same order as the differences between the MDMH and DCMH molecules.

DISCUSSION

Bond lengths and bond angles are listed in Fig. 1, where the numbering of the atoms is indicated. Only the C3−N2 and C6−O1 bond lengths deviate significantly from those found earlier.[1] This may be due to errors in the data collected at room temperature.

The heterocycle is planar, the atoms being displaced from a least-squares plane through the six ring atoms by less than 0.01 Å (see Table 4), and the bond lengths indicate a resonance stabilization of the molecule. The

Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects) and bond angles (°). The estimated standard deviations in bond lengths are 0.002 Å and in angles 0.1°. Structure model obtained from the refinement using high-angle data (VI).

Table 4. Deviations (Å) from a least-squares plane through the six ring atoms. Plane eqn.: $(0.2263\ X + 0.0000\ Y + 0.0383\ Z)\cdot R\ -3.391 = 0$.

Atom	Deviation	Atom	Deviation
N1	.006	O1	−.043
N2	.002	O2	−.028
C3	−.008	C7	−.018
C4	.004	C8	−.082
C5	.004	H4	.009
C6	−.010	H5	−.038

N1−N2 bond of 1.367 Å is considerably shorter and the C4−C5 double bond of 1.356 Å considerably longer than the corresponding bond lengths (1.406 Å and 1.337 Å, respectively) found in 1,2-dimethyl-3,6-pyridazindione.[14] Also, the C3−N2 double bond of 1.300 Å is significantly longer than the pure C−N double bond length of 1.278 Å.[15]

However, difference in molecular dimensions found for DCMH [2] and the present structure are significant. The N1−C6 bond of 1.374 Å, which is equal to the N−C bond found in the microwave investigation of formamide,[16] was 1.345 Å in DCMH. The bond lengths C5−C6, C6−N1, N1−C1, and C6−O1 are of the same order as those found in 1,2-dimethyl-3,6-pyridazindione,[14] which is a nonplanar molecule. The C3−C4 bond, on the other hand, is short in comparison with that in DCMH (1.430 Å in the present structure and 1.450 Å in DCMH). Other bond lengths also imply a larger resonance stabilization of DCMH than of MDMH. This may indicate that hydrogen bonds, which in DCMH involve N1 and both oxygen atoms, are important in the resonance stabilization of these and similar compounds. The hydrogen bonds in DCMH may imply a structure intermediate between the monolactim and the dilactim. Large difference are also found in the bond lengths of formamide in the non-hydrogen-bonded [16] and hydrogenbonded [17] case. However, corresponding C−N and C−O bond lengths of 1.374 Å and 1.235 Å, respectively, were found in 1,2,3-benzotriazin-4(3H)-one,[18] which has an N−H···O hydrogen bond. These bond lengths are similar to those found in 1,2-dimethyl-3,6-pyridazindione,[14] and may imply that the hydrogen bond has little, if any, effect on the resonance stabilization.
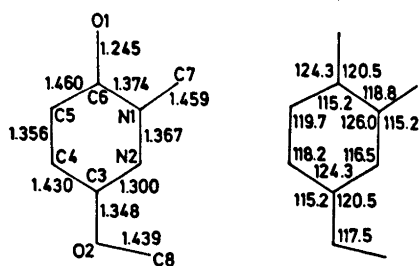
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