

The Crystal and Molecular Structure of 1,2-Dimethyl-3,6-pyridazinedione

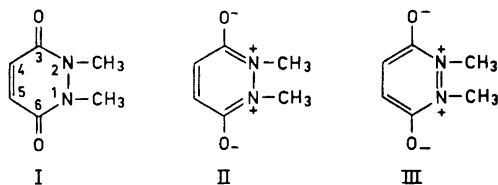
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The crystal and molecular structure of 1,2-dimethyl-3,6-pyridazinedione (*N,N*-dimethylmaleic hydrazide) has been determined by X-ray methods using 2113 reflections above background level collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a=8.82$, Å; $b=5.72$, Å; $c=13.25$, Å; $\beta=100.5^\circ$. Estimated standard deviations in bond lengths are about 0.0016 Å, and in angles 0.1°. The molecule is found to be non-planar with a C4–C5-bond length of 1.33, Å. The dihedral angle around the N–N-bond is 29.8° , but the bond lengths indicate a resonance stabilization of the O–C–N-system.

The structure determination of 1,2-dimethyl-3,6-pyridazinedione was carried out as part of a series of structure investigations of 3,6-pyridazinediones.

N,N-Dimethylmaleic hydrazide may be resonance stabilized by structures II and III. These resonance structures would give a nearly planar molecule, but resonance structures involving charge separation are not usually favoured.



The molecule is easily hydrogenated to give 1,2-dimethylhexahydro-3,6-pyridazinedione, and also undergoes bromine addition.¹ On this basis Eichenberger *et al.*¹ conclude that *N,N*-dimethylmaleic hydrazide is not aromatic.

The structure of 4,5-dichloro-3,6-pyridazinedione has been published.² The present structural work was carried out to determine the effect of *N,N*-disubstitution on the heterocyclic system.

EXPERIMENTAL

1,2-Dimethyl-3,6-pyridazinedione was synthesized from 3,6-pyridazinedione by the method of Eichenberger *et al.*¹

The product was recrystallized by slow evaporation of a chloroform/ethyl ether solution. Large rectangular, slightly yellow crystals were formed.

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 Picker manual diffractometer using $\text{CuK}\beta$ ($\lambda = 1.3922 \text{ \AA}$) and $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. 24 reflections and their Friedel equivalents were measured. The computer program used in the least square calculations of cell parameters, and programs employed in all subsequent calculations are part of an assembly of programs for CDC-3300 computer.³

Three-dimensional intensity data were recorded on an automatic Picker four-circle diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation. The take off angle was 4° , and the temperature during the data collection was $18 \pm 1^\circ\text{C}$.

A crystal of dimensions $0.4 \times 0.35 \times 0.25 \text{ mm}$ was used for the data collection. The $w - 2\theta$ scanning mode with a 2θ scan speed of 1° min^{-1} was utilized. Background counts were taken for 30 sec at each of the scan range limits. Intensities of three standard reflections were measured for every 100 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.

Out of the 2841 unique reflections measured ($2\theta_{\text{max}} = 70^\circ$), 2113 had intensities larger than twice the standard deviation. These were regarded as "observed" reflections whereas the remaining reflections were excluded from further calculations.

The intensity data were corrected for Lorentz and polarization effects.

Atomic form factors used were those of Doyle and Turner⁴ for oxygen, nitrogen, and carbon, and of Stewart *et al.*⁵ for hydrogen.

CRYSTAL DATA

1,2-(N,N')-Dimethyl-3,6-pyridazinedione, $\text{C}_6\text{H}_8\text{N}_2\text{O}_2$, monoclinic. $a = 8.827(0.001) \text{ \AA}$; $b = 5.722(0.001) \text{ \AA}$; $c = 13.254(0.002) \text{ \AA}$; $\beta = 100.58^\circ(0.01^\circ)$. Figures in parentheses are estimated standard deviations.

$V = 658.0 \text{ \AA}^3$, $M = 140.1$; D_{obs} (floatation) = 1.41 g/cm^3 ; $Z = 4$; $D_{\text{calc}} = 1.413 \text{ g/cm}^3$; $F(000) = 296$.

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 based on direct methods, using symbolic addition⁶ and tangent refinement.⁷

The structure model was refined to an R of 0.17. Introduction of anisotropic thermal parameters and least squares refinement resulted in an R of 0.093.

Attempts to locate the hydrogen atoms were not successful, and they were placed in calculated positions (Table 3). A difference Fourier map indicated that the methyl hydrogen atoms were disordered and six hydrogen atoms with half weight were therefore placed around each methyl carbon atom.

In order to reduce valence electron influence it was decided to use only structure factors with $\sin \theta/\lambda$ greater than 0.46 in the refinement.

Table 1. Continued.

0	8	8	14	5	2	8	0	38	-	40	3	8	5	41	-	45	5	8	1	10	-	9	-1	9	1	14	-	12
1	8	8	14	-	15	2	8	1	23	-	25	3	8	2	40	-	40	5	8	0	19	17	-2	9	1	11	-	0
1	8	7	21	-	21	2	8	4	36	-	40	4	8	9	22	22	5	8	1	13	15	-2	9	0	13	-	0	
1	8	6	23	-	23	2	8	5	13	-	14	4	8	1	10	10	1	9	0	10	10	1	2	6	99	-	83	
1	8	5	45	-	46	2	8	8	18	-	20	4	8	4	35	-	39	1	9	2	12	18	-3	2	8	-	73	
1	8	4	13	-	15	3	8	8	17	-	16	4	8	6	23	-	25	0	9	2	18	-	21	2	3	0	-	174
1	8	3	11	-	10	3	8	7	35	-	35	5	8	4	17	19	0	9	1	24	-	25	2	3	1	100	-	87
1	8	1	17	-	14	3	8	6	42	-	42	5	8	2	13	10												

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$) 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	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O1	42603	17762	36483	2081	2688	681	1927	1178	117
	18	22	10	20	32	7	40	20	23
O2	9878	71535	57226	1459	3663	562	1348	505	-824
	14	25	9	14	41	6	35	14	23
N1	19929	64726	42923	977	1881	444	644	210	-120
	11	18	7	11	25	5	25	11	16
N2	28472	50364	37516	1034	1904	408	429	400	70
	11	17	7	11	25	5	26	11	17
C3	35509	30490	41568	1119	1816	490	578	530	64
	14	19	9	12	29	6	29	13	20
C4	34786	35756	52303	1224	2262	483	727	425	399
	15	24	9	14	32	6	32	15	22
C5	27482	40274	57627	1208	2733	406	499	343	118
	15	25	9	14	36	5	34	14	22
C6	18504	59992	52817	985	2372	425	355	215	-469
	13	22	9	12	31	6	29	13	21
C7	9190	81033	36837	1286	2676	665	1393	153	371
	17	27	13	16	39	8	40	18	28
C8	32060	59518	27923	1669	2941	414	497	533	388
	19	27	10	19	40	6	43	17	24

Table 3. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters for hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Weight	<i>B</i>
H41	3988	1152	5566	1.0	3.0
H51	2798	3742	6513	1.0	3.0
H71	1033	9830	3614	0.5	3.0
H711	-61	7906	3951	0.5	3.0
H712	791	7493	2967	0.5	3.0
H72	-102	7580	3295	0.5	3.0
H721	699	9336	4171	0.5	3.0
H722	1482	8798	3167	0.5	3.0
H81	2772	5669	2053	0.5	3.0
H811	3089	7676	2868	0.5	3.0
H812	4321	5544	2846	0.5	3.0
H82	4104	7043	2861	0.5	3.0
H821	3432	4587	2373	0.5	3.0
H822	2278	6805	2431	0.5	3.0

Least squares refinement of positional and anisotropic thermal parameters for non-hydrogen atoms yielded a conventional R of 0.057 and a weighted R of 0.052. The overdetermination ratio was 17.3, 91 parameters being refined on the basis of 1577 reflections with $\sin \theta/\lambda$ between 0.46 and 0.81. This structure model yielded a conventional R of 0.075 for the whole data-set. A total difference Fourier map showed no electron density above $0.3 \text{ e}/\text{\AA}^3$.

A comparison of observed and calculated structure factors is given in Table 1, and the final parameters for non-hydrogen atoms are listed in Table 2.

Table 4. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (\AA) and B -values (\AA^2) along the principal axes of vibration given by the components of a unit vector \mathbf{e} in fractional coordinates ($\times 10^3$).

Atom	$(u^2)^{\frac{1}{2}}$	B	e_x	e_y	e_z
O1	.313	7.71	99	66	38
	.225	3.99	8	101	-60
	.162	2.07	-58	126	28
O2	.283	6.33	55	138	-22
	.237	4.42	87	-26	59
	.163	2.11	-51	104	44
N1	.211	3.50	79	97	-25
	.194	2.97	57	19	72
	.158	1.98	-61	144	8
N2	.209	3.45	98	68	39
	.180	2.56	16	87	-62
	.168	2.22	-59	135	21
C3	.224	3.97	92	49	52
	.190	2.84	42	83	-55
	.161	2.04	-55	145	14
C4	.235	4.34	87	92	40
	.197	3.05	-61	23	56
	.175	2.41	45	-147	34
C5	.228	4.12	84	119	17
	.199	3.11	79	-128	12
	.184	2.67	10	8	-74
C6	.222	3.89	37	128	-41
	.192	2.91	105	-13	43
	.166	2.18	-29	118	49
C7	.254	5.10	87	107	-6
	.245	4.75	6	50	73
	.167	2.20	75	-129	23
C8	.259	5.28	105	65	26
	.219	3.78	-47	152	15
	.176	2.45	5	56	-71

Magnitudes and directions of the principal axes of the ellipsoids of vibration are given in Table 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 of the molecule, is 0.0017 \AA^2 . This indicates that the molecule may be regarded as a rigid body.

The atomic positions were accordingly corrected for the librational motion. The eigenvalues of T are 0.19, 0.18, and 0.16 Å. The r.m.s. librational amplitudes are 4.7, 4.2, and 3.4°.

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

DISCUSSION

Bond lengths and bond angles are listed in Table 5 and also in Fig. 1, where the numbering of the atoms is indicated. Dihedral angles around the N1–N2, N1–C6, and N2–C3 bonds are listed in Table 7.

The non-aromatic nature of the molecule is revealed not only by the non-planarity of the molecule (see Table 6), but also by the bond lengths. The C4–

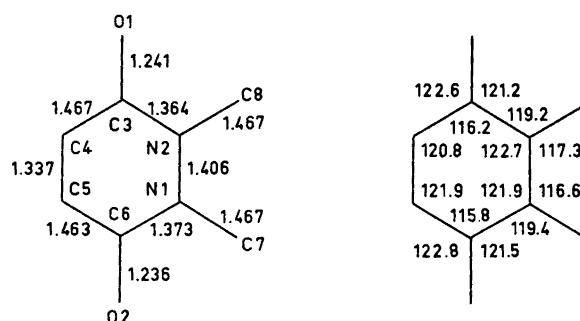


Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects) and bond angles (°) in *N,N*-dimethylmaleic hydrazide.

Table 5. Bond lengths (Å) and bond angles (°). Estimated standard deviations in parentheses.

	Bond length	E.s.d. ($\times 10^4$)	Corrected bond length		Bond angle	E.s.d.
C3–O1	1.238	(16)	1.241	O1–C3–N2	121.2	(.11)
C6–O2	1.233	(16)	1.236	O1–C3–C4	122.6	(.12)
N1–N2	1.399	(13)	1.406	O2–C6–N1	121.5	(.12)
N1–C6	1.367	(16)	1.373	O2–C6–C5	122.8	(.12)
N2–C3	1.358	(14)	1.364	C3–N2–N1	122.7	(.09)
C3–C4	1.461	(16)	1.467	C4–C3–N2	116.2	(.10)
C4–C5	1.331	(19)	1.337	C5–C4–C3	120.8	(.11)
C5–C6	1.457	(17)	1.463	C6–C5–C4	121.9	(.11)
N1–C7	1.463	(15)	1.467	N1–C6–C5	115.8	(.10)
N2–C8	1.463	(15)	1.467	N2–N1–C6	121.9	(.09)
				C8–N2–C3	119.2	(.10)
				C8–N2–N1	117.3	(.10)
				C7–N1–N2	116.6	(.10)
				C7–N1–C6	119.4	(.10)

Table 6. Deviations from a least squares plane through: O1, O2, C3, C4, C5, and C6.
(Eqn.: $(0.0908X + 0.1062Y + 0.0188Z)R - 3.967 = 0.$)

Atom	Deviation (Å)	Atom	Deviation (Å)
O1	-0.015	C6	0.065
O2	-0.049	N1	0.192
C3	0.023	N2	0.189
C4	-0.045	C7	-0.040
C5	0.044	C8	0.617

Table 7. Dihedral angles (°) with estimated standard deviations in parentheses.

Planes	Angle	E.s.d.
C6-N1-N2-C3	2.0	(0.17)
C7-N1-N2-C8	29.6	(0.17)
C5-C6-N1-N2	5.0	(0.17)
O2-C6-N1-C7	10.6	(0.19)
N1-N2-C3-C4	4.9	(0.17)
C8-N2-C3-O1	13.4	(0.17)

C5 bond length of 1.337 Å indicates a pure double bond,⁹ and is significantly shorter than the corresponding bond lengths, 1.395 Å and 1.362 Å, reported for pyridazine⁸ and 4,5-dichloro-3,6-pyridazinedione.²

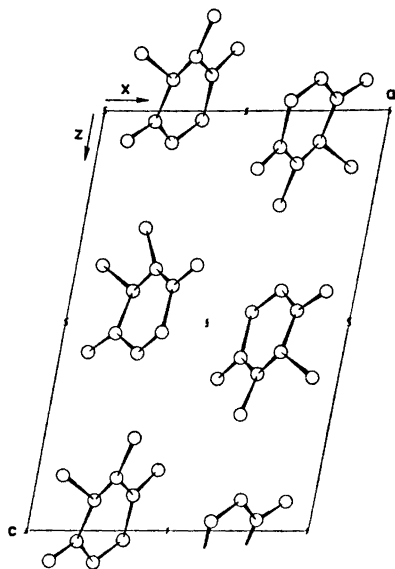


Fig. 2. The crystal structure as seen along the *b* axis.

The C–O bonds (mean length 1.238 Å) are slightly longer than those found for C–O double bonds in similar structures.^{10–12} This may indicate a resonance stabilization of the O–C–N system. Further the C–N bonds (mean length 1.369 Å) are considerably shorter than those reported for phenylhydrazine¹³ and phenylhydrazine hydrochloride.¹⁴

The N1–N2 bond length of 1.406 Å is significantly longer than the nitrogen-nitrogen bond lengths of 1.330 Å and 1.353 Å reported for pyridazine⁸ and 4,5-dichloro-3,6-pyridazinedione,² suggesting only a small contribution from resonance structures II and III. This is also indicated by the dihedral angle C7–N1–N2–C8 of 29.6°.

The molecular arrangement in the crystal is visualized in Fig. 2 and may be described as layers parallel to (100).

REFERENCES

1. Eichenberger, K., Staehelin, A. and Druey, J. *Helv. Chim. Acta* **37** (1954) 837.
2. Ottersen, T. *To be published*.
3. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
4. Doyle, P. A. and Turner, P. S. *Acta Cryst. A* **24** (1968) 390.
5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
6. Zachariassen, W. H. *Acta Cryst.* **5** (1952) 68.
7. Hughes, E. W. *Acta Cryst.* **6** (1953) 871.
8. Werner, W., Dreizler, D. and Rudolph, H. D. *Z. Naturforsch.* **22a** (1967) 531.
9. Bastiansen, O. and Trætteberg, M. *Tetrahedron* **18** (1962) 147.
10. Shintani, R. *Acta Cryst.* **13** (1960) 609.
11. Tomiie, Y., Koo, C. H. and Nitta, I. *Acta Cryst.* **11** (1958) 774.
12. Sabelli, C. and Zanazzi, P. F. *Acta Cryst. B* **28** (1972) 1173.
13. Srinivasan, S. and Swaminathan, S. *Z. Krist.* **127** (1968) 442.
14. Koo, H. C. *Bull. Chem. Soc. Japan* **38** (1965) 286.

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