

Table 2). The phenyl rings are planar, the mean and maximum atom-to-plane distances being 0.008 and 0.022 Å ($\sigma = 0.008$ Å), respectively. The P atom does not lie in the plane of any ring; the distances being 0.021 (2), 0.080 (3) and 0.042 (2) Å, respectively. As usual, coordination makes the C—P—C angles (mean 104.2°) greater than those involving uncoordinated phosphine (mean 102.6°) (Daly, 1964; Jones, 1980; Fenske, Basoglu, Hachgenei & Rogel, 1984; Albinati, Anklin, Ganazzoli, Ruegg & Pregosin, 1987). The Re—P—C angles are unequal, indicating that coordination does not take place exactly along the direction of the lone pair. The largest angle involves phenyl ring 2, for which a short intramolecular H...Br contact has been pointed out earlier. Such a distortion, which decreased steric hindrance, is not energy costly and is common in triarylphosphine complexes.

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A New Polymorph of Maleic Hydrazide

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Abstract. 1,2-Dihydropyridazine-3,6-dione, $C_4H_4N_2O_2$, $M_r = 112.09$, monoclinic, $P2_1/c$, $a = 6.891$ (2), $b = 9.674$ (2), $c = 6.946$ (1) Å, $\beta = 100.07$ (2)°, $V = 455.9$ (2) Å³, $Z = 4$, $D_x = 1.63$ (1) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 10.31$ cm⁻¹, $F(000) = 232$, m.p. above 306–308 K (temperature of decomposition), $T = 292$ K, final $R = 0.043$ for 715 observed reflections. In the crystalline state the molecules of maleic hydrazide are present in the monolactim form (*i.e.* 3-hydroxy-6-pyridazinone). They are connected head-to-tail into planar chains along *a* by hydrogen bonds in which the O(3)···O(6') distance is 2.605 (1) Å. The

chains are linked into pairs by hydrogen bonds N(1)···O(6) of 2.925 (1) Å. The geometry of the hydrogen bonds and the pattern formed by the molecules within such pairs of chains are very similar in the title structure and the previously reported triclinic polymorph of maleic hydrazide; however, the arrangements of these pairs of chains in the crystal lattices are markedly different.

Introduction. Maleic hydrazide (*i.e.* 1,2-dihydropyridazine-3,6-dione, hereinafter referred to as MH), is applied as a growth inhibitor in agriculture (Cradwick, 1975); the molecules of MH can act either as a

purine analogue forming base pairs with uracil and thymine (nucleoside formation through O atom), or as a pyrimidine analogue forming base pairs with adenine (nucleoside formation through N). Crystals of MH were investigated by X-rays by Cradwick (1976); the crystals were reported to be triclinic, space group $P\bar{1}$, $a = 5.83$ (2), $b = 5.78$ (2), $c = 7.31$ (2) Å, $\alpha = 79.0$ (3), $\beta = 99.5$ (3), $\gamma = 107.2$ (3)°, $V = 229.4$ (13) Å³, $Z = 2$, $D_x = 1.62$ g cm⁻³ (this polymorph will be referred to as MH1). In the crystalline state the molecules of MH are present in the monolactim form (*i.e.* 3-hydroxy-6-pyridazinone). In this paper a new monoclinic polymorph of MH, referred to as MH2, is reported. The main aim of the study of its structure was to compare the molecular configuration (position of the hydroxyl H atom), the intermolecular hydrogen bonds formed by the MH molecules, and the molecular arrangement in the two polymorphs. It was also intended to analyse the possibility of transformations of bistable —OH---O= hydrogen bonds between the molecules of MH. Such transformations involve a transition of the proton between the donor and acceptor sites in the hydrogen bond simultaneous with a transformation of the molecules in which the sequence of the single and double bonds of the conjugated π -electron bond system is changed. Our previous studies were concentrated on the crystals of simple cyclic β -diketoalkanes, in which transformations of the hydrogen bonds were induced by varying temperature or pressure (Katrusiak, 1990*a,b*, 1991*a,b*, 1992). In those crystals the intermolecular forces were dominated by strong —OH---O= bistable hydrogen bonds, shorter than 2.6 Å, linking the molecules into chains. There are no other strong intermolecular interactions, while in the crystals of MH the hydrogen bonds and the molecular structure are additionally stabilized by >NH---O= hydrogen bonds.

Experimental. Polymorph MH2 was crystallized by slow evaporation of a solution of maleic hydrazide in acetic acid. The crystals obtained were elongated colourless prisms with well developed faces. All the crystals had the same habit characteristic for polymorph MH2. The sample used for measurements was a fragment (0.3 × 0.3 × 0.3 mm) cut from a larger crystal. The unit-cell dimensions and the intensity data were measured on a KUMA-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The orientation matrix was obtained by the least-squares fit to 25 reflections ($11 < 2\theta < 37^\circ$). 2θ - θ scans with variable scan speed depending on reflection intensity (1.5–30.0° min⁻¹) were applied in intensity measurements. After every 250 reflection measurements two control reflections were monitored and showed no systematic variation in their intensity throughout the data collection. 930 reflec-

tions were measured to $2\theta_{\max} = 125^\circ$ ($h = 8/8, k = 0/11, l = 0/8$), 715 of which were independent and had $I \geq 1.96\sigma(I)$ and were included in the refinement. The background and intensity for each reflection were obtained by the integration of the peak-scan counts. Only Lp corrections were applied.

The structure was solved by direct methods (Sheldrick, 1986). After anisotropic refinement of the non-H atoms, all the H atoms were located from a ΔF map. The H atoms were refined with isotropic temperature factors. The full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$, converged to final $R = 0.043$, $wR = 0.052$, $S = 1.1$ for 89 refined parameters. The maximum parameter change in the last cycle of refinement was 0.01 Δ/σ . The final coordinates and thermal parameters are listed in Table 1.* The highest and the lowest densities in the final ΔF map were 0.25 and -0.25 e Å⁻³, respectively. Most of crystallographic calculations were performed with *SHELX76* (Sheldrick, 1976) on an IBM-XT computer. Drawings of molecular packing were prepared with the program *PLUTO* (Motherwell, 1976).

Discussion. The geometry of the MH molecules in polymorphs MH1 and MH2 is identical within experimental e.s.d.'s, in terms of both the bond lengths and valency angles (Table 2) and the configuration. No statistically significant deviations from planarity are observed for the molecules. Also, only slight differences can be noted in the ring geometry between MH and the molecule of 4,5-dichloro-3-hydroxy-6-pyridazinone (hereinafter 2ClMH) (Otterson, 1973). In the three structures the hydroxyl H atom assumes the same position, hereinafter referred to as the *syn* configuration [with respect to N(2)], though there is no steric hindrance which would restrict the other configuration of the OH group: the H(4)⋯H(1) distance for the *anti* configuration would be about 2.4 Å, longer than the sum of the van der Waals radii of the H atoms. Fig. 1 shows the charge distribution in the MH1 molecule calculated by the MNDO method (Dewar & Thiel, 1977). This drawing also shows the direction of the dipole moment of the molecule [$\mu = 3.14$ D (1D = 3.336×10^{-30} C m)]. It can be seen that the *syn* configuration of H(1) is stabilized by its electrostatic interactions with N(2), while the *anti* configuration would lead to repulsive forces with a small positive net charge of H(4). The *anti* configuration would also result in a considerable increase of the dipole moment of the

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55419 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0409]

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2) for polymorph MH2

Isotropic temperature factors are given for the H atoms. For non-H atoms $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	U_{iso}/U_{eq}
N(1)	0.7376 (2)	0.1104 (1)	0.1054 (2)	0.045
N(2)	0.9292 (2)	0.1485 (1)	0.1129 (2)	0.043
C(3)	0.9621 (2)	0.2804 (1)	0.1295 (2)	0.037
O(3)	1.1468 (2)	0.3258 (1)	0.1384 (2)	0.053
C(4)	0.8131 (2)	0.3795 (1)	0.1390 (3)	0.046
C(5)	0.6261 (2)	0.3364 (1)	0.1309 (2)	0.042
C(6)	0.5824 (2)	0.1915 (1)	0.1121 (2)	0.037
O(6)	0.4129 (2)	0.1406 (1)	0.1039 (2)	0.054
H(1)	0.717 (4)	0.028 (4)	0.083 (4)	0.07 (1)
H(3)	1.236 (5)	0.244 (5)	0.132 (5)	0.13 (2)
H(4)	0.844 (4)	0.472 (3)	0.149 (4)	0.07 (1)
H(5)	0.520 (3)	0.398 (3)	0.135 (3)	0.06 (1)

Table 2. Bond lengths (\AA) and valency angles ($^\circ$) in polymorph MH2 (this work) compared with those in the triclinic polymorph MH1 (Cradwick, 1976)

	MH2	MH1
N(1)—N(2)	1.363 (1)	1.364 (5)
N(1)—C(6)	1.334 (1)	1.329 (5)
N(2)—C(3)	1.298 (1)	1.304 (5)
C(3)—O(3)	1.338 (2)	1.337 (5)
C(3)—C(4)	1.415 (2)	1.422 (6)
C(4)—C(5)	1.346 (2)	1.336 (6)
C(5)—C(6)	1.435 (2)	1.437 (6)
C(6)—O(6)	1.260 (2)	1.257 (5)
N(1)—H(1)	0.82 (4)	0.90 (5)
O(3)—H(3)	1.00 (4)	0.89 (7)
N(2)—N(1)—C(6)	128.1 (1)	127.9 (4)
N(1)—N(2)—C(3)	115.0 (1)	115.0 (3)
N(2)—C(3)—O(3)	118.5 (1)	118.9 (4)
N(2)—C(3)—C(4)	123.6 (1)	124.0 (4)
O(3)—C(3)—C(4)	117.9 (1)	117.1 (4)
C(3)—C(4)—C(5)	119.0 (1)	117.7 (4)
C(4)—C(5)—C(6)	119.4 (1)	120.9 (4)
N(1)—C(6)—C(5)	114.9 (1)	114.5 (4)
N(1)—C(6)—O(6)	120.8 (1)	120.4 (4)
C(5)—C(6)—O(6)	124.3 (1)	125.1 (4)
N(2)—N(1)—H(1)	114 (2)	121 (3)
C(3)—O(3)—H(3)	109 (2)	116 (5)

Table 3. Dimensions of the hydrogen bonds (\AA , $^\circ$) in polymorphs MH1 (Cradwick, 1976) and MH2 (this work)

	MH1	MH2
O(3)---O(6 ⁱ)	2.600 (11)	2.605 (1)
H(3)---O(6 ⁱ)	1.73 (6)	1.62 (4)
O(3)—H(3)---O(6 ⁱ)	165 (7)	166 (4)
N(1)---O(6 ⁱⁱ)	2.874 (10)	2.925 (1)
H(1)---O(6 ⁱⁱ)	1.97 (6)	2.18 (3)
N(1)—H(1)---O(6 ⁱⁱ)	177 (6)	152 (3)

Symmetry code for MH1: (i) $x - 1, y - 1, z$; (ii) $2 - x, 2 - y, 1 - z$.
Symmetry code for MH2: (i) $x + 1, y, z$; (ii) $1 - x, -y, -z$.

molecule to $\mu_{anti} = 4.13$ D. Thus, the configuration of the OH group in MH is fixed, unlike in the molecules of simple cyclic β -diketoalkanes where neither of the hydroxyl group configurations, *syn* or *anti*, is favoured (Katrusiak, 1992).

A striking feature of polymorphs MH1 and MH2 is that the hydrogen bonds in these structures are very similar, their geometry is presented in Table 3. The hydrogen-bonded molecules form the same motif (see Fig. 2): the molecules are linked head-to-tail by short —OH---O= hydrogen bonds forming, in this way, planar chains with identical orientation of the molecules within one chain. Lengths of the

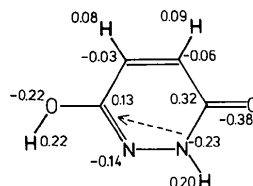


Fig. 1. Net atomic charges in the molecule of MH. Direction of the dipole moment of the molecule is indicated by the arrow. The calculations were performed with the MNDO method (Dewar & Thiel, 1977) and were based on the molecular geometry determined for MH2 in this study.

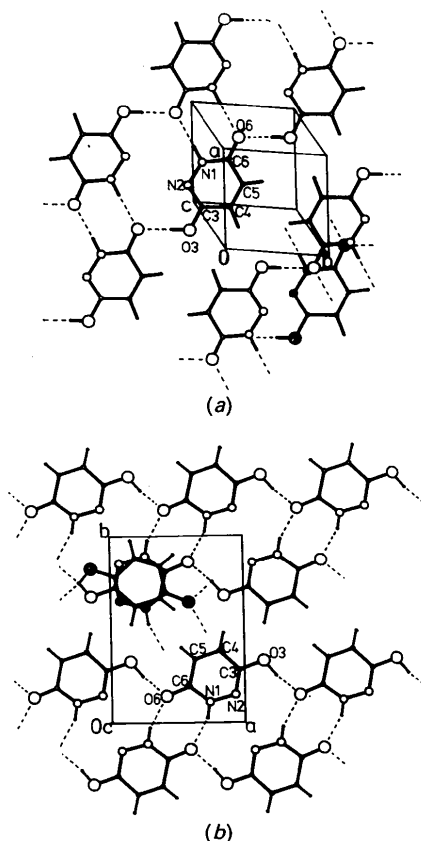


Fig. 2. Pairs of chains of hydrogen-bonded molecules of maleic hydrazide: (a) in polymorph MH1 viewed perpendicular to the molecular rings, and (b) in polymorph MH2 viewed along *c*. Each drawing contains one molecule from the overlapping chain (shaded atoms). The hydrogen bonds are indicated by the dashed lines.

—OH---O= hydrogen bonds in MH1 and MH2 are the same within e.s.d.'s (Table 3). The chains, in turn, are linked into pairs by N(1)H---O(3) hydrogen bonds. Two such symmetry-related hydrogen bonds link each molecule of one chain with one molecule of the neighbouring chain (Fig. 2). The $\text{N}(\text{H})\cdots\text{O}=\text{O}$ hydrogen bond in MH2 is significantly longer than that in MH1 (Table 3). This elongation can be caused by the strong inclination of this hydrogen bond to the planes of the molecules in MH2 (Fig. 3); ideally the hydrogen bond should be coplanar with the electron pair of the O(sp^2)-acceptor centre. In both MH1 and MH2 the symmetry operations relating the molecules within one chain are translations (Table 3), and the chains within each pair are related by centres of symmetry. Consequently, the hydrogen-bonded chains are parallel, but not coplanar (see Fig. 3). The deviation from coplanarity of the hydrogen-bonded chains can be conveniently described by the distance between the planes fitted to the molecules of the two chains; this distance is 0.38 Å for polymorph MH1 and 1.30 Å for polymorph MH2. Also the arrangement of the pairs of chains in polymorphs MH1 and MH2 is markedly different, as shown in Fig. 2 and 3. In polymorph MH1 the pairs of chains are approximately parallel and arranged into sheets along the crystallographic plane (112); the molecules of close neighbouring pairs only slightly overlap and the direction of the overlapping chains is antiparallel. In polymorph MH2, the pairs of chains form a herring-bone pat-

tern and the close chains are markedly non-parallel: the rings of the molecules of close neighbouring chains overlap and the overlapped chains have the same polarization along the chain direction. According to the MNDO calculation (Fig. 1) the dipole moment of the molecules lies at an angle of about 45° to the direction of the chains. The y components of the dipole moments of the overlapping molecules are antiparallel and their x components are parallel. In polymorph MH1 the dipole moments of the close molecules are antiparallel as they are related by centres of symmetry. Thus, it appears that the main difference in the intermolecular forces between the two polymorphs are the electrostatic interactions between the near, but not hydrogen-bonded, molecules. The arrangement of the molecules within the pairs of chains observed in MH1 and MH2 is also characteristic for 2CIMH. The length of the hydrogen bond in that crystal (two symmetry independent molecules are present in the orthorhombic structure of 2CIMH) are 2.598 and 2.589 Å between O(3)⋯O(6') and 2.953 and 2.963 Å between N(1)⋯O(6). The arrangement of the pairs of chains in 2CIMH is not similar to that in MH1 or MH2. The —OH---O= hydrogen bonds are slightly shorter and the $\text{N}(\text{H})\cdots\text{O}=\text{O}$ hydrogen bonds are significantly longer than those in MH1 and MH2. The similar pattern of the hydrogen-bonded molecules in the two polymorphs of MH and in 2CIMH shows the important role of the geometrical features of hydrogen bonds for the structure and properties of the aggregates which they form.

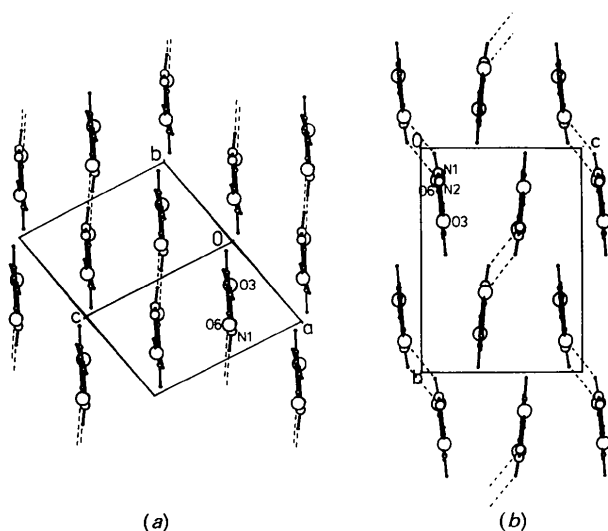


Fig. 3. Molecular packing of the pairs of chains in polymorphs (a) MH1 and (b) MH2. The hydrogen bonds are indicated by the dashed lines (only $\text{N}(\text{H})\cdots\text{O}=\text{O}$ hydrogen bonds are visible in these projections).

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