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# Polymorphism of maleic hydrazide. I

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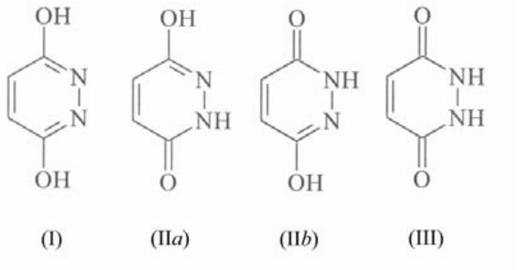
The third polymorph (denoted MH3) of maleic hydrazide (3,6-dihydroxypyridazine in the monolactim form, 6-hydroxy-3-pyridazinone, $C_4H_4N_2O_2$) has been studied by X-ray diffraction and shown to be monoclinic, space group $P2_1/n$. Polymorph MH3 was found as the prevailing form along with the rare triclinic polymorph MH1, space group $P\bar{1}$, but they were obtained separately from monoclinic MH2, space group $P2_1/c$. The structure of MH1, previously studied by photographic methods, has been redetermined. Polymorph MH3 exhibits the same scheme of molecular association into hydrogen-bonded ribbons as in MH1 and MH2, but the arrangements of the aggregates and details of their supramolecular conformations are different. The accommodation of the supramolecular conformations to the requirements of close packing of the aggregates in crystal lattices, as well as the symmetries of the polymorphs, are analyzed.

## 1. Introduction

The growing interest in maleic hydrazide, denoted MH, originates from its biological properties. MH molecules can act either as purine or pyrimidine analogs, forming base pairs with uracil and thymine (by nucleoside formation through O), or with adenine (by nucleoside formation through N), respectively. From this arose the applications of MH as a growth inhibitor in agriculture (Cradwick, 1975). Pyridazine is also used as a carrier of active groups in medicines (see *e.g.* Katrusiak *et al.*, 2001; Maes *et al.*, 2001, and references cited therein). Of the three tautomers, dilactim (I), lacton–lactim (II*a*), interconvertible to lactim–lacton (II*b*), and dilacton (III),



only the lacton–lactim form has been found in the solid state of MH and its derivatives (Cradwick, 1976; Katrusiak, 1993*a*; Ottersen, 1973; Becker *et al.*, 1998; Paradies, 1992). Theoretical *ab initio* calculations showed that form (II) is more stable than (III) and form (III) is more stable than (I) in the gas phase, but in solution the difference between (II) and (III)

**Table 1**
Crystal data and unit-cell dimensions at normal conditions (298 K) of three polymorphs of maleic hydrazide.

| | MH1 | MH2 | MH3 |
|---|---|---|---|
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| Unit cell: | | | |
| $a$ (Å) | 5.797 (3) | 6.892 (2) | 6.604 (1) |
| $b$ (Å) | 5.817 (3) | 9.673 (2) | 9.904 (1) |
| $c$ (Å) | 7.307 (3) | 6.960 (1) | 10.534 (4) |
| $\alpha$ (°) | 78.82 (3) | 90 | 90 |
| $\beta$ (°) | 99.38 (3) | 100.05 (2) | 104.04 (4) |
| $\gamma$ (°) | 107.12 (3) | 90 | 90 |
| $V$ (Å$^3$) | 229.5 (1) | 456.9 | 465.94 (9) |
| $Z$ | 2 | 4 | 4 |
| $D_x$ (g cm$^{-3}$) | 1.622 | 1.630 | 1.599 |

practically disappears (Fabian, 1990, 1991; Hofmann *et al.*, 1991). So far two polymorphs of MH have been reported: the triclinic form MH1 (Cradwick, 1975) and the monoclinic form MH2 (Katrusiak, 1993*a*). Both these structures have an identical pattern of OH···O and NH···O hydrogen bonds linking the monolactim molecules into double chains. They differ primarily in the arrangement of the parallel ribbons and by distortions of their geometry. Here we report a third polymorph of MH, denoted MH3. The unit-cell dimensions and symmetry of all three polymorphs are listed in Table 1. Primarily we wanted to obtain the triclinic polymorph MH1 in order to investigate its thermodynamic behavior and to redetermine its structure which had been previously determined from photographic data (Cradwick, 1975). Over several years our attempts to crystallize the triclinic form resulted mainly in form MH3. Form MH1 was finally found by observing the speed of dissolution of crystals in acetic acid: we noticed that certain crystals were hardly affected and remained with sharply defined edges and faces, while others were rounded and looked like small flattened ellipsoids. It occurred that polymorph MH3 dissolved slower than MH1. The ribbons of hydrogen-bonded lacton–lactim molecules characteristic to MH1 and MH2 have also been observed in MH3. The structures, symmetries and molecular arrangements in the three polymorphs have been analysed and related to the distortions of the hydrogen-bonded motifs. It is our intention to use the parameters and the structural relations introduced in this paper to describe the thermal stability of maleic hydrazide (Katrusiak, 2001*b*).

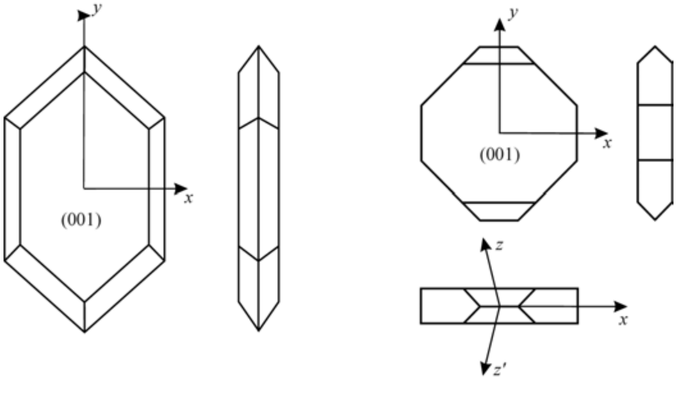


**Figure 1**
Two crystal habits of twinned crystals of the maleic hydrazide polymorph MH3.

## 2. Experimental

Crystals of MH3 were obtained by slowly cooling a solution of MH in acetic acid solution. Two crystal habits, both mimicking orthorhombic symmetry, were found (Fig. 1), although most of the crystallites did not have well developed faces. The subsequent X-ray diffraction study showed that the crystals were twinned about (001) planes, as indicated in Fig. 1. Thus, the intensities of reflections have been measured for a twinned sample using a four-circle KM-4 diffractometer equipped with a scintilation point detector and a copper-anode X-ray tube, for a better separation of reflections. Samples of polymorph MH1 were isolated by slowly dissolving the mixture of MH1 and MH3, as described above; hence, the oval shape of the MH1 sample used for the X-ray analysis. Unit-cell dimensions of polymorphs MH3 and MH1 were both investigated independently using data acquired on two Kuma KM4 diffractometers, one equipped with a point detector and the other with a CCD camera, and at different temperatures, in order to avoid bias in the unit-cell dimensions (Herbstein, 2000). Their crystal data are summarized in Table 2.[1] The crystal structure of MH3 was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and the H atoms were located from a $\Delta F$ map and refined with isotropic temperature factors. Although the MH1 structure originally determined by Cradwick (1975) was used as the starting model, the atoms have been labelled in conformity with IUPAC nomenclature. All H atoms were located from a $\Delta F$ map and refined. The original choice of unit cell (Cradwick, 1975) has been retained, which transforms to the reduced cell (denoted by subscript $r$: $a_r = b$, $b_r = a$, $c_r = c$, $\alpha_r = 180^\circ - \beta$, $\beta_r = \alpha$, $\gamma_r = 180^\circ - \gamma$) according to the matrix:

$$M_{3\rightarrow r} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

*SHELXL*97 (Sheldrick, 1997) was used to refine both structures. The final atomic coordinates have been deposited.[1]

## 3. Discussion

### 3.1. Molecular aggregation

In all three polymorphs the molecules are present in the monolactim form and their molecular dimensions, listed in Table 3, are equal within error. The crystal structures of polymorphs MH1, MH2 and MH3 are shown in Fig. 2. The structures contain the same O—H···O motif linking molecules into chains, and the chains are linked by N—H---O interactions into double-chain ribbons (see Table 4). They

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0045). Services for accessing these data are described at the back of the journal.

**Table 2**
Experimental details.

| | MH3 | MH3 |
|---|---|---|
| Crystal data | | |
| Chemical formula | $C_4H_4N_2O_2$ | $C_4H_4N_2O_2$ |
| Chemical formula weight | 112.09 | 112.09 |
| $a$ (Å) | 5.8181 (10) | 6.6070 (15) |
| $b$ (Å) | 5.8000 (10) | 6.9070 (7) |
| $c$ (Å) | 7.3090 (10) | 10.539 (3) |
| $V$ (Å$^3$) | 466.68 (17) | 229.74 (6) |
| $Z$ | 4 | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.595 | 1.620 |
| Radiation type | Cu $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.128 | 0.133 |
| Temperature (K) | 293 (2) | 300 (1) |
| Crystal colour | Colourless | Colourless |
| Crystal size (mm) | 0.4 × 0.4 × 0.2 | 0.5 × 0.3 × 0.15 |
| Data collection | | |
| Diffractometer | Kuma KM-4 | Kuma KM-4 CCD |
| No. of measured, independent and observed reflections | 737, 671, 580 | 2196, 1153, 808 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{\rm int}$ | 0.0273 | 0.0454 |
| $\theta_{\rm max}$ (°) | 61.97 | 29.71 |
| Range of $h, k, l$ | $0 \rightarrow h \rightarrow 6$<br>$0 \rightarrow k \rightarrow 7$<br>$-12 \rightarrow l \rightarrow 11$ | $-7 \rightarrow h \rightarrow 7$<br>$-7 \rightarrow k \rightarrow 8$<br>$-9 \rightarrow l \rightarrow 9$ |
| Refinement | | |
| Refinement on | $F^2$ | $F^2$ |
| $R[F^2>2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.0475, 0.1036, 1.093 | 0.0535, 0.0882, 1.01 |
| No. of reflections and parameters used in refinement | 671, 89 | 1153, 90 |
| H-atom treatment | Mixed | Mixed |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0983P)^2 + 0.0404P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0100P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{\rm max}$ | 0.000 | 0.000 |
| $\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å$^{-3}$) | 0.26, −0.196 | 0.302, −0.224 |
| Extinction method | None | *SHELXL*97 |
| Extinction coefficient | – | 0.035 (13) |

Computer programs used: *SHELXS*86 (Sheldrick, 1985), *SHELXL*97 (Sheldrick, 1997).

have the common features of O—H---O links between molecules related by translation – along [110] in MH1, [100] in MH2 and [010] in MH3 – and of molecules linked by pairwise N—H---O hydrogen bonds about centres of symmetry. Thus, in all three polymorphs the planes of the molecules within one ribbon are restricted by symmetry to be parallel (Fig. 3). Although the hydrogen-bonding scheme is identical for polymorphs MH1, MH2 and MH3, significant differences in the mutual positions of molecules within the ribbons can be noted. The chains are not planar, but the molecules are inclined in the manner resembling scales, as shown in Figs. 3 and 4. The molecules are inclined to the mean planes of the ribbons: to plane ($\bar{1}12$) in MH1, (001) in MH2 and (100) in MH3; consequently, the molecules are not coplanar within the ribbons and the distances between the planes fitted to the O—H---O and N—H---O bonded molecules are different. The parameters describing the mutual positions of the molecules within the ribbons are listed in Table 5. The dimensions of the OH---O bonds are very similar, and their length is not affected by the departures from coplanarity of the hydrogen-bonded molecules ($\Delta_{\rm O\cdots O}$ in Table 5). However, the length of the NH---O bonds is clearly correlated with the non-planarity of the ribbons: the larger $\Delta_{\rm N\cdots O}$ distance between the planes of NH---O bonded molecules (Table 5), the longer the N···O distance (Table 4). The minimum N···O distance corresponding to the coplanar MH molecules can be assessed from this dependence as 2.844 Å.

Hydrogen transfers in the NH---O═ bonds would lead to the lactim–lactim form, which is energetically unfavoured (see §1). Hydrogen transfers in the asymmetric —OH---O═ bonds (Katrusiak, 1992) would lead to an unrealistic structure of the MH molecule. Also impossible are simultaneous hydrogen transfers in the —OH---O═ and NH---O═ bonds. Thus, the network of hydrogen bonds in the ribbons is unlikely to transform, even though the Donohue angles C—O···O′ and O···O′═C′ favour the hydrogen transfers (Katrusiak, 1993*b*, 1998). The unfavourable Donohue angles introduce strains in the hydrogen bonds, which could be released by rearrangements involving distortions of the molecules from coplanarity within the ribbons. The clear differences in the structure of the ribbons reflect different stabilizing effects of the crystallographic environments in polymorphs MH1, MH2 and MH3.

### 3.2. Supramolecular arrangement

The ribbons of hydrogen-bonded MH molecules can be regarded as supramolecular entities forming crystal structures MH1, MH2 and MH3. They are stable chemically (hydrogen transfers are unlikely) and their conformations are restricted by their symmetry and the network of hydrogen bonds. The most apparent feature differentiating the polymorphs is the mutual position of the ribbons.

It can be seen from Fig. 4 that the ribbons are arranged in layers in the crystal plane ($\bar{1}12$) in MH1, (001) in MH2 and (100) in MH3. In MH3 the ribbons are nearly coplanar within the sheets, in MH1 the ribbons are inclined by a few degrees and in MH2 significant inclination of the ribbons allows us to consider alternative sheets parallel to $(01\bar{2})$ or (012). However, such an alternative sheet would consist alternately of ribbons and of single chains belonging to the ribbons of the sheets parallel to (012) and intersecting with the $(01\bar{2})$ sheet along [100].

The structures of the polymorphs clearly differ due to the positions of the ribbons relative to their neighbours, but also in the symmetry relations between the neighbouring ribbons: centre-of-symmetry and simple translations along **a** or **c** in MH1; a glide plane perpendicular to the sheets and a $2_1$ screw axis along the sheets and perpendicular to the ribbons in MH2; and a glide plane perpendicular to the ribbons and a screw axis parallel to the ribbons in MH3 (Fig. 5). A consequent difference between the polymorphs is the orientation of the neighbouring ribbons, as schematically shown in Fig. 5. Each chain in one ribbon can be assigned a polarity in the direction indicated by the molecular dipole moment [from N(2) to O(6)] projected on the chain direction. As can be seen from Fig. 5 the neighbouring ribbons are parallel in MH1, but antiparallel in MH2 and MH3.

A number of other differences can be noted. The translations of the centres of symmetry between the pairs of NH---O bonds linking molecules, regarded as the central point of one ribbon, to the centres of the closest neighbouring ribbon are differently expressed by the lattice vectors. For example, these centres are translated: by $(c\cos\beta)/2$ along the ribbons and by $b/2$ perpendicular to the ribbons within the sheets in MH2; and by $b/2$ parallel to the ribbons and by $(c \pm a\cos\beta)/2$ perpendicular to the ribbons within the sheets in MH3.

The molecules of neighbouring ribbons partly overlap and the degree of this overlapping characterizes the interactions between the molecules. The relative translations of the centres of partly overlapping molecules (defined by the centres of the rings) of the neighbouring sheets, denoted $\delta_r$ for the translation of the neighbouring ribbons along their direction and $\delta_p$ perpendicular to the ribbons within the sheets, are listed in Table 6. The dipole moment of the molecule is directed approximately from N(1) to O(6) (Katrusiak, 1993*a*), so the value of $\delta_l$ close to zero in MH1, and that of $\delta_l$ close to $l/2$ in MH3

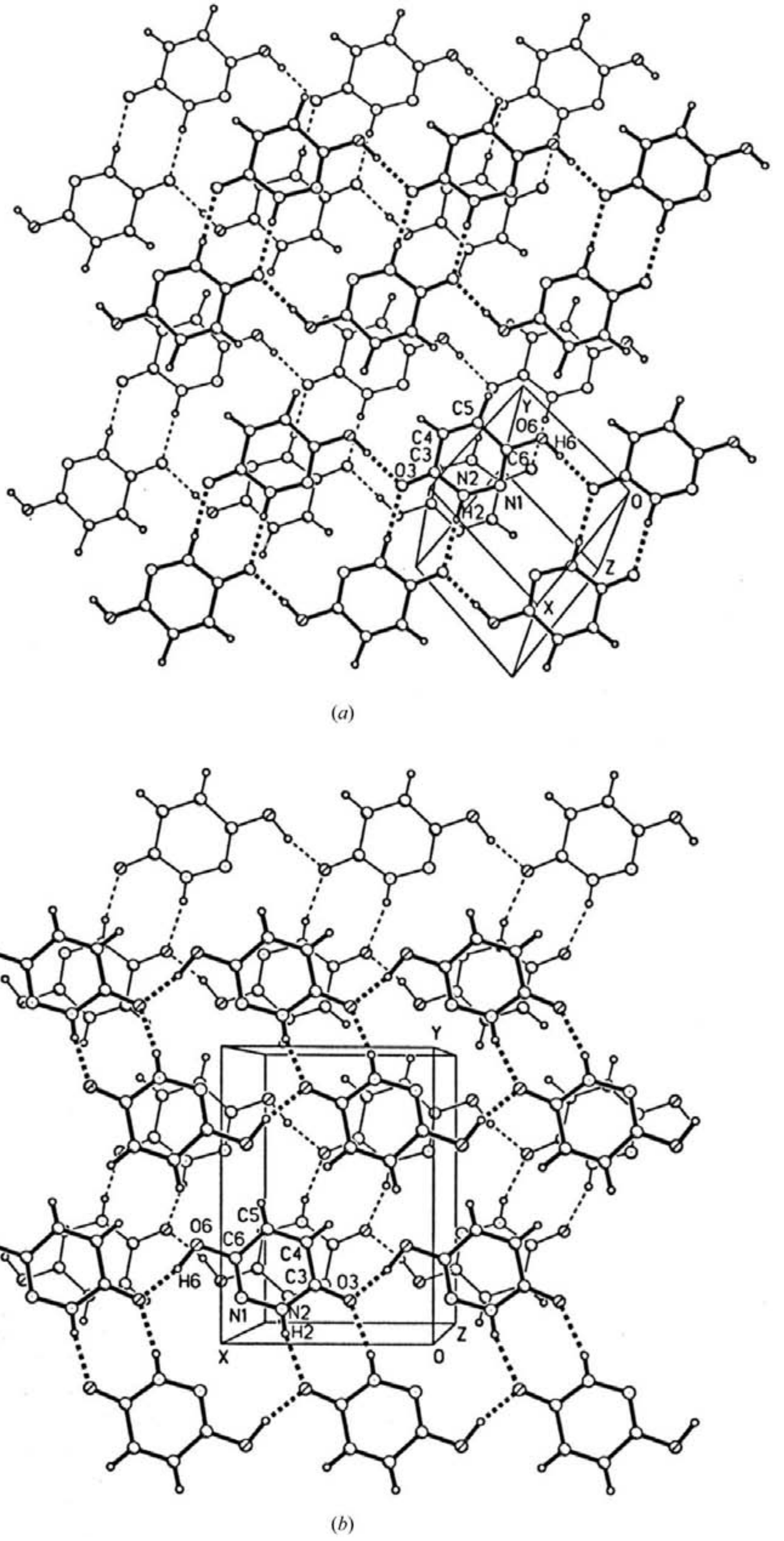

**Figure 2**
Crystallographic autostereograms (Katrusiak, 2001*a*) of polymorphs (*a*) MH1, (*b*) MH2 and (*c*) MH3 viewed perpendicular to the hydrogen-bonded ribbons. The hydrogen bonds are indicated by dashed lines. The bonds of the closest and furthest molecules have been drawn using thick and thin lines, respectively.

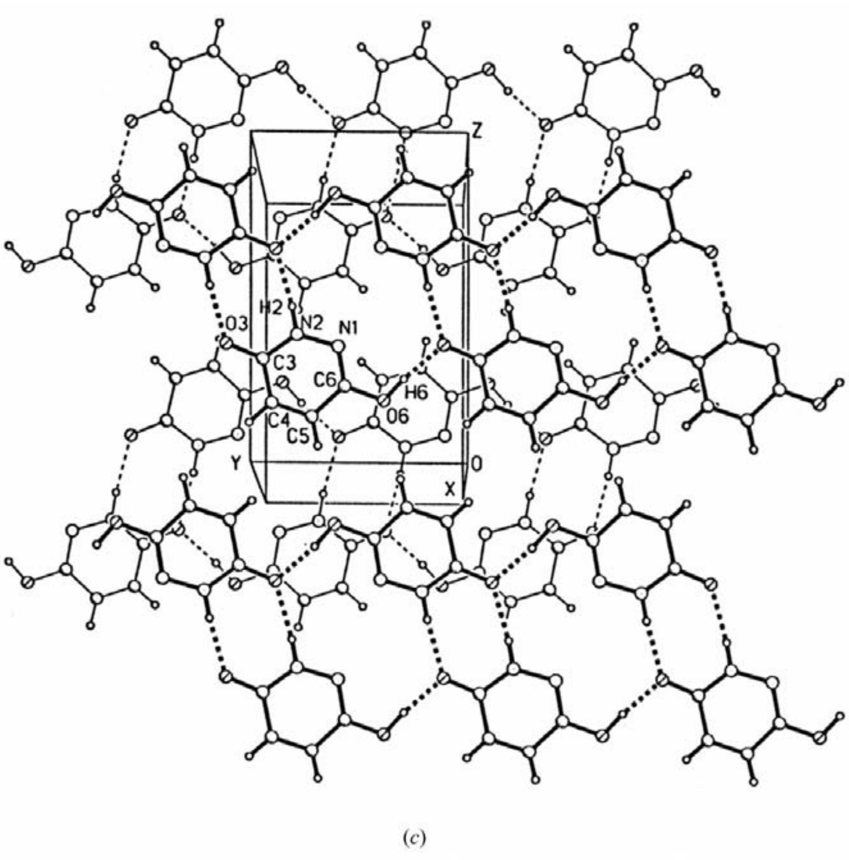

**Figure 2 (continued)**

are favoured electrostatically, as the molecules are antiparallel in MH1 and parallel in MH3. The small value for $\delta_l$ in MH2, where the molecular dipole moments projected on the chain direction are parallel, is electrostatically unfavoured. This may contribute to the increased intersheet distance in MH2 compared with MH1 and MH3 (Table 6), and with the thermal instability of polymorph MH2 (Katrusiak, 2001*b*).

### 3.3. Close packing of molecules

Despite considerable differences in the arrangements of the ribbons, as explained above, most intermolecular contacts of the corresponding atoms in the polymorphs are consistent within a few hundredths of an ångstöm. The closest contacts are almost identical: the greatest difference noted for the atom C(6) is shorter by a mere 0.16 Å in MH3 compared with MH1 or MH2, and for none of the other closest contacts does the difference exceed 0.1 Å. The largest difference among second-closest contacts is that for N(1), slightly exceeding 0.2 Å between MH1 and MH3, and only five other differences are greater than 0.1 Å. This shows that the molecules are similarly densely packed in MH1, MH2 and MH3, and that the close-packing rule (Kitaygorodski, 1976) is one of the crucial conditions in the formation of these polymorphic structures. It can be further inferred that these varied molecular arrangements and symmetries interplay with the distortions of the ribbon energies of formation of the polymorphs. This would indicate that the most strained ribbons (*i.e.* strained hydrogen bonds), as measured by the $\Delta_{O\cdots O}$ and $\Delta_{N\cdots O}$ parameters listed in Table 4, are those in the most dense MH2 (see Table 1), while the least strained ribbons are those in the least dense MH3.

### 3.4. Space groups and isostructurality

The same or equivalent space group symbols, as found for MH2 and MH3, are not uncommon among polymorphs. Indeed, one may assume that their occurrences are more frequent than would be expected from the random statistical distribution. Numerous examples exist of the same space group occurring for polymorphs or of closely related phenomena of phase transitions between two phases of the same symmetry (often described as isostructural or isosymmetric phase transitions): two of the polymorphs of dibenzoylmethane crystallize in space group *Pbca* (Etter *et al.*, 1987; Hollander *et al.*, 1973; Jones, 1976; Williams, 1966); both polymorphs $\alpha$ and $\beta$ of resorcinol crystallize in space group $Pna2_1$ (Robertson & Ubbelohde, 1938); three polymorphs of naphthazarin, *A*, *B* and *C*, have the space group $P2_1/c$ (Pascard-Billy, 1962; Cradwick & Hall, 1971; Shiau *et al.*, 1980; Herbstein *et al.*, 1985); the white and yellow polymorphs of dimethyl 3,6-dichloro-2,5-dihydroxytelphthalate are both $P\bar{1}$ (Byrn *et al.*, 1972); two polymorphs of 4,5-dichloro-3(2*H*)-pyridazinone occur in space group $P2_1/c$ (Lynch *et al.*, 1985); two polymorphs of oxalic acid dihydrate crystallize in the equivalent space groups $P2_1/c$ and $P2_1/a$ (Coppens & Sabine, 1969). 1,3-Cyclohexanedione undergoes an isosymmetric transition within space group $P2_1/c$ (Katrusiak, 1990, 1991); similarly, $P2_1/c$ to $P2_1/c$ transitions occur in tin(II) chloride dihydrate (Kitahama & Kiriyama, 1977), dimethylaminobenzonitrile (Jameson *et al.*, 1994) and in 6-hydroxy-4,4,5,7,8-pentamethyldihydrocoumarin (Budzianowski & Katrusiak, 2001), 1,2,4,5-tetrabromobenzene $\beta$ and $\gamma$ transform within $P2_1/a$ symmetry (Gafner & Herbstein, 1960; Gafner, 1964); a $P2_12_12_1$ to $P2_12_12_1$ transition occurs in oxitropium bromide (Zamir *et al.*, 1993); $KTiOPO_4$ (KTP) undergoes a $Pna2_1$ to $Pna2_1$ phase transition (Allan *et al.*, 1992). Numerous other examples of polymorphs and transformations within the same space group can be given (Katrusiak, 2001*b*; Tomaszewski, 1992). Despite considerable attention (Christy, 1995) the isostructural phase transitions are not unequivocally defined. The same space group symbol is hardly a necessary condition for the isostructurality and translational symmetry is equally relevant (Kálmán *et al.*, 1993; Fábián & Kálmán, 1999). In this respect MH2 and MH3 are no more mutually isostructural than either

**Table 3**
Selected bond lengths (Å) and angles (°) for MH1 and MH3.

| | MH1 | MH3 |
|---|---|---|
| N(1)−C(6) | 1.306 (2) | 1.293 (3) |
| N(1)−N(2) | 1.370 (2) | 1.368 (2) |
| N(2)−C(3) | 1.339 (3) | 1.341 (3) |
| N(2)−H(2) | 1.04 (3) | 0.91 (3) |
| C(3)−O(3) | 1.262 (2) | 1.254 (2) |
| C(3)−C(4) | 1.440 (3) | 1.436 (3) |
| C(4)−C(5) | 1.342 (3) | 1.339 (3) |
| C(4)−H(4) | 1.05 (3) | 0.88 (3) |
| C(5)−C(6) | 1.418 (3) | 1.426 (3) |
| C(5)−H(5) | 1.04 (2) | 0.97 (3) |
| C(6)−O(6) | 1.335 (2) | 1.337 (2) |
| O(6)−H(6) | 1.03 (3) | 0.95 (3) |
| C(6)−N(1)−N(2) | 115.52 (18) | 115.27 (19) |
| C(3)−N(2)−N(1) | 127.02 (17) | 127.52 (17) |
| C(3)−N(2)−H(2) | 117.0 (14) | 115.8 (15) |
| N(1)−N(2)−H(2) | 116.0 (14) | 116.5 (15) |
| O(3)−C(3)−N(2) | 120.65 (19) | 120.58 (18) |
| O(3)−C(3)−C(4) | 124.1 (2) | 124.6 (2) |
| N(2)−C(3)−C(4) | 115.21 (18) | 114.8 (2) |
| C(5)−C(4)−C(3) | 120.0 (2) | 120.2 (2) |
| C(5)−C(4)−H(4) | 124.9 (13) | 123.8 (16) |
| C(3)−C(4)−H(4) | 115.1 (13) | 116.0 (16) |
| C(4)−C(5)−C(6) | 118.6 (2) | 118.37 (19) |
| C(4)−C(5)−H(5) | 124.0 (12) | 122.8 (16) |
| C(6)−C(5)−H(5) | 117.4 (12) | 118.8 (16) |
| N(1)−C(6)−O(6) | 118.56 (19) | 119.02 (18) |
| N(1)−C(6)−C(5) | 123.60 (19) | 123.8 (2) |
| O(6)−C(6)−C(5) | 117.84 (18) | 117.12 (18) |
| C(6)−O(6)−H(6) | 114.9 (14) | 112.1 (16) |

**Table 4**
Dimensions of hydrogen bonds in MH1, MH2 and MH3.

| Polymorph | MH1 | MH2 | MH3 |
|---|---|---|---|
| O(3)···O(6$^{i}$) (Å) | 2.598 (2) | 2.605 (1) | 2.609 (2) |
| O(3)---H(6$^{i}$) (Å) | 1.57 (3) | 1.62 (4) | 1.66 (3) |
| O−H---O (°) | 174 (2) | 166 (4) | 173 (3) |
| Symmetry code (i) | $x + 1, y + 1, z$ | $x - 1, y, z$ | $x, y + 1, z$ |
| N(2)···O(3$^{ii}$) (Å) | 2.871 (2) | 2.925 (1) | 2.855 (2) |
| H(2)---O(3$^{ii}$) (Å) | 1.85 (3) | 2.18 (3) | 1.95 (3) |
| N−H---O (°) | 166 (2) | 152 (3) | 175 (2) |
| Symmetry code (ii) | $2 - x, 2 - y, 1 - z$ | $1 - x, 1 - y, 1 - z$ | $-x, 2 - y, 1 - z$ |

**Table 5**
Parameters describing the arrangement of molecules in the ribbon aggregates in polymorphs MH1, MH2 and MH3 .

$\Delta_{O\cdots O}$ and $\Delta_{N\cdots O}$ denote the distances between the planes fitted to the OH---O and NH---O bonded molecules, respectively, $\zeta$ is the inclination angle of the plane fitted to the molecule and the crystal plane parallel to the sheet, and $l$ is the length of one OH---O bonded segment of the ribbon.

| | MH1 | MH2 | MH3 |
|---|---|---|---|
| $\Delta_{O\cdots O}$ (Å) | 0.344 (1) | 0.104 (1) | 0.210 (1) |
| $\Delta_{N\cdots O}$ (Å) | 0.434 (1) | 1.182 (1) | 0.225 (1) |
| $\zeta$ (mol per sheet) (°) | 7.96 (7) | 5.02 (3) | 3.92 (10) |
| Segment length $l$ (Å) | 6.900 (3) | 6.891 (2) | 6.9071 (7) |

of them with MH1. The symmetry of polymorphs is naturally strongly weighted by the uneven distribution of space groups (Nowacki, 1942, 1943, 1967) and detailed statistical analysis should be carried out before drawing definite conclusions. The chemical molecule is the main origin of molecular association and formation of crystal structures, and thus the polymorphic forms and their transformations can be ultimately connected and clearly rationalized. At the same time no general rules governing the symmetry changes at the first-order phase transition are known. Although clearly various types of isosymmetric polymorphs and phase transitions can be distinguished, it is plausible that the occurrences of the same and equivalent space groups of polymorphs, such as $P2_1/c$ and $P2_1/n$ in MH2 and MH3, can be treated as a manifestation of the space group frequencies in nature (Katrusiak, 2001*b*). It is also possible that the isostructural phase transitions, where a

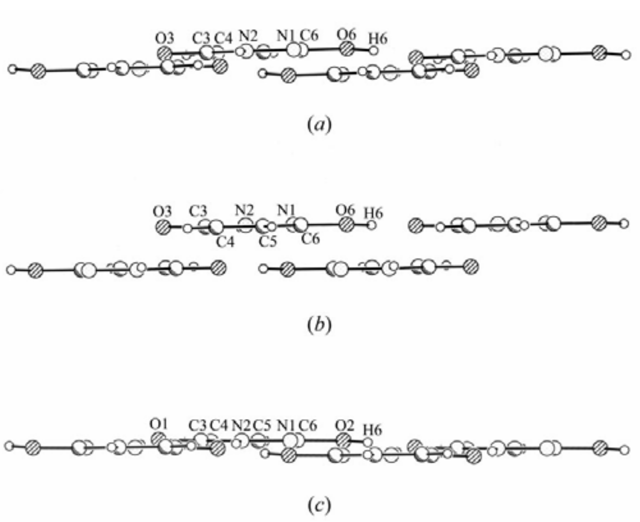

**Figure 3**
Two segments of the hydrogen-bonded molecules in the ribbon aggregates viewed parallel to the molecular plane and perpendicular to the chain direction in (*a*) MH1, (*b*) MH2 and (*c*) MH3.

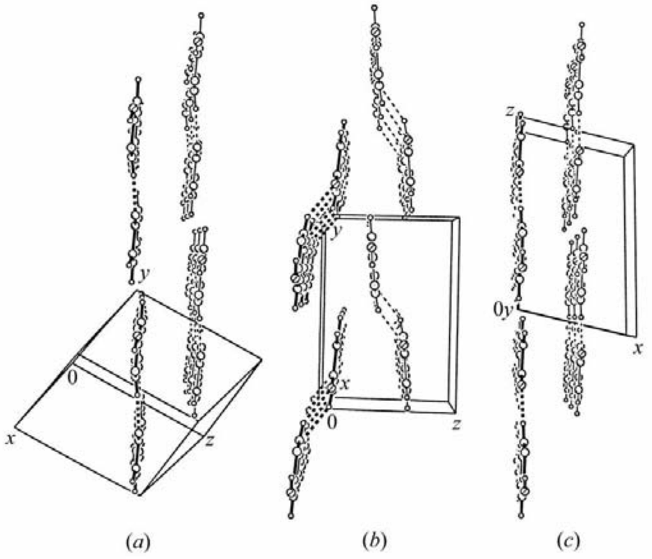

**Figure 4**
Perspective drawings of the maleic hydrazide polymorph structures viewed down the hydrogen-bonded ribbons along directions (*a*) [110] in MH1, (*b*) [100] in MH2 and (*c*) [010] in MH3.

**Table 6**
Translations of centres of molecules relative to the molecules of the close neighbouring ribbon along the ribbon, $\delta_l$, and perpendicular to the ribbon within the sheet, $\delta_p$.

The asterisks denote the antiparallel orientation of the overlapping molecules; the positive signs have been assigned to the displacements toward the N atoms ($\delta_p$) and carbonyl ($\delta_l$) atoms. The interribbon distance ($d$) is approximated by the distance between crystal planes parallel to the sheets of the ribbons (see the text).

| | MH1 | MH2 | MH3 |
|---|---|---|---|
| $\delta_l$ (Å) | +0.142* | 0.559 | 3.450 |
| $\delta_p$ (Å) | +1.134* | −0.230* | +0.400* |
| Interribbon distance $d$ (Å) | 3.168 (2) | 3.419 (1) | 3.205 (1) |

portion of the structure collapses at high pressure or freezes at low temperature while the space group and translational symmetry remain unchanged [*e.g.* as in 1,3-cyclohexanedione, KTP, or tin(II) chloride dihydrate], may systematically increase the number of first-order phase transitions between identical space groups.

## 4. Conclusions

Three forms of MH provide a unique example of polymorphic structures built of similar hydrogen-bonded aggregates. The same hydrogen-bonded supramolecular aggregates organize into different lattices of different symmetries, which induces strains in the hydrogen bonds to satisfy the close-packing condition. The varied interactions and crystal habits are likely reasons for the different thermal stability and reactivity of the polymorphs (Katrusiak, 2001*b*).

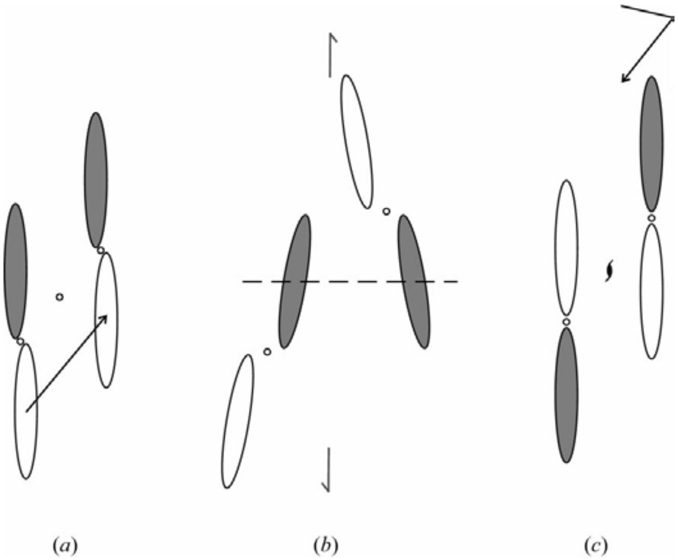

**Figure 5**
Schematic drawing of polymorphic structures (*a*) MH1, (*b*) MH2 and (*c*) MH3 viewed as in Fig. 4. The symbols representing chains of OH---O bonded molecules with the hydroxyl groups directed upwards off the page are shaded and the chains with the hydroxyl groups downward by open ones. Symmetry elements relating the chains within the ribbons (centres of symmetry) and with the neighbouring ribbons have been indicated.

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addenda and errata

# Polymorphism of maleic hydrazide. I. Erratum

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In the recently published article by Katrusiak (2001) the crystal data of two polymorphs of maleic hydrazide have been printed with errors or omissions in Tables 1 and 2. It was the author's intention that the measurements of the unit-cell dimensions were possibly accurate, as the comparison of densities and unit-cell volumes of polymorphs are of particular importance. Therefore, these measurements were carried out at varied temperatures to eliminate possible differences owing to the thermal expansion of the crystals, and two different diffractometers, one with a point detector and another one with a CCD, were used to eliminate systematic errors. From these data the unit-cell dimensions at normal conditions were estimated and listed in Table 1, while the crystal data of the diffractometric experiments were duly related in Table 2. It was hoped that this procedure would provide the reader with reliable crystal data. Overestimated precision of routinely reported unit-cell dimensions has been extensively discussed by other authors (*e.g.* see Herbstein, 2000). The ambiguity resulting from different equipment, data collecting techniques, wavelengths *etc.* is further aggravated by the vague definition of the so-called room temperature. This temperature is assumed as 293 K and indeed this is the default value if not specified otherwise in programs writing CIF files, even though diffractometers are usually enclosed in safety boxes, where slowly circulating air is heated up by step motors, electronics, cables *etc.* or even by the X-ray tube if its heat is not totally balanced by the cooling system. Therefore, the temperature in the safety box is higher than outside: when the temperature in our laboratory is air-conditioned to 293 K, the difference in temperatures outside and inside the safety box is 3.5°. Additionally, the temperature of the measurement, even when measured with high relative precision, may considerably differ from the absolute scale. Meanwhile, the crystal data in Tables 1 and 2 were treated as redundant and after acceptance of the manuscript the crystal data were removed from Table 2 in the proof. The author's request to include these missing data resulted in the multiple errors (Katrusiak, 2001). The correct tables, as originally submitted, are reproduced below.

**Table 1**
Crystal data and unit-cell dimensions at normal conditions (298 K) of the three polymorphs of maleic hydrazide.

| | MH1 | MH2 | MH3 |
|---|---|---|---|
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| $a$ (Å) | 5.797 (3) | 6.892 (2) | 6.604 (1) |
| $b$ | 5.817 (3) | 9.673 (2) | 6.904 (1) |
| $c$ | 7.307 (3) | 6.960 (1) | 10.534 (4) |
| $\alpha$ (°) | 78.82 (3) | 90 | 90 |
| $\beta$ | 99.38 (3) | 100.05 (2) | 104.04 (4) |
| $\gamma$ | 107.12 (3) | 90 | 90 |
| $V$ (Å$^3$) | 229.5 (1) | 456.9 | 465.94 (9) |
| $Z$ | 2 | 4 | 4 |
| $D_x$ (g cm$^{-3}$) | 1.622 | 1.630 | 1.599 |

**Table 2**
Selected crystal data and structure refinements for MH1 and MH3.

| | MH1 | MH3 |
|---|---|---|
| Empirical formula | $C_4H_4N_2O_2$ | $C_4H_4N_2O_2$ |
| Formula weight | 112.09 | 112.9 |
| Temperature (K) | 300 (1) | 300 (2) |
| Wavelength (Å) | 0.71073 | 1.54178 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/n$ |
| $a$ (Å) | 5.8181 (10) | 6.6070 (15) |
| $b$ (Å) | 5.8000 (10) | 6.9070 (7) |
| $c$ (Å) | 7.3090 (10) | 10.539 (3) |
| $\alpha$ (°) | 78.80 (3) | 90 |
| $\beta$ (°) | 99.36 (3) | 104.00 (4) |
| $\gamma$ (°) | 107.13 (3) | 90 |
| Volume (Å$^3$) | 229.74 (6) | 466.68 (17) |
| $Z$, calculated density (g cm$^{-3}$) | 2, 1.620 | 4, 1.595 |
| Absorption coefficient (mm$^{-1}$) | 0.133 | 1.128 |
| $F$(000) | 116 | 232 |
| Crystal size (mm) | 0.5 × 0.3 × 0.15 | 0.4 × 0.4 × 0.2 |
| $\theta$ range for data collection (°) | 3.69–29.71 | 7.21–61.97 |
| Limiting indices $h, k, l$ | −7/7, −7/8, −9/9 | 0/6, 0/7, −12/11 |
| Reflections collected/unique | 2196/1153 | 737/671 |
| $R_{\rm int}$ | 0.0454 | 0.0273 |
| Completeness to $\theta$ (°) | 88.8% to 29.71 | 91.9% to 61.97 |
| Data/restraints/parameters | 1153/0/90 | 671/0/89 |
| Goodness-of-fit on $F^2$ | 1.010 | 1.093 |
| Final $R1/wR2$ indices ($I > 2\sigma_I$) | 0.0535/0.0823 | 0.0475/0.0969 |
| $R1/wR2$ indices (all data) | 0.0869/0.0882 | 0.0550/0.1036 |
| Extinction coefficient | 0.035 (13) | 0 |
| Largest difference peak/hole (e Å$^{-3}$) | 0.30/−0.22 | 0.26/−0.20 |

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