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2-Phenyl-4-hydroxyphthalazin-1-one: A Benzoannelated Derivative of Maleic Hydrazide

DAN BECKER,† MARK BOTOSHANSKY, NOGA GASPER, FRANK H. HERBSTEIN* AND MIRIAM KARNI
Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel.
E-mail: chr03fh@tx.technion.ac.il

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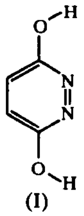
Abstract

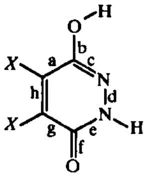
The monoclinic crystals (space group $P2_1/a$, $Z = 8$) of 2-phenyl-4-hydroxyphthalazin-1-one, $C_{14}H_{10}N_2O_2$, have two independent molecules (A and B) in the asymmetric unit. Both occur as the lactim–lactam (hydroxy–one) structure, which is also found in the parent molecule maleic hydrazide (both triclinic and monoclinic polymorphs), dichloromaleic hydrazide and luminol (3-aminophthalhydrazide). The molecular arrangement is based on strings of alternating A and B molecules linked by hydroxyl···carbonyl hydrogen bonds, with only van der Waals interactions between adjacent strings. Comparison is made of the measured bond lengths for (monoclinic) maleic hydrazide and values from high-level *ab initio* calculations, and reasonably good agreement is obtained, with indications of improvements when allowance is made for electron correlation and hydrogen bonding.

1. Introduction

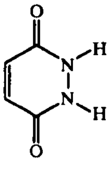
Maleic hydrazide,‡ a starting material for the synthesis of drugs and a powerful plant growth inhibitor, could exist in any of the tautomeric forms (I), (II) or (III). Occurrence of the lactim–lactam tautomer (II) in both the solid state and in solution is favoured by all the evidence: the crystal structures of triclinic (Cradwick, 1976) and monoclinic (Katrusiak, 1993) maleic hydrazide, and dichloromaleic hydrazide (Ottersen, 1973); IR spectroscopy of maleic hydrazide in the vapour phase (Rodionova & Levin, 1967) and in the crystal (Mashima, 1962; polymorph not specified); ^{1}H broad-line NMR, IR and Raman spectroscopies (all in the solid state, but the polymorph not specified; Lippert *et al.*, 1975); NMR studies of maleic hydrazide and derivatives in dimethyl sulfoxide solution (Katritzky & Waring, 1964; Ohashi *et al.*, 1964); UV spectroscopy of aqueous solutions (Barlin, 1974); other physico-chemical evidence is summarized by Katritzky & Lagowski (1963; see pp. 366–368). Semi-empirical quantum mechanical methods (AM1, PM3, MNDO; Fabian, 1990) give somewhat equivocal results for the relative stabilities of the tautomers (Fabian, 1991), but *ab initio* methods [3-21G (also Fabian, 1990) and 6-31G* basis sets (Hofmann *et al.*, 1991)] show that (II) is more stable than (III) and (I) in the vapour phase by 8.4 and 37.2 kJ mol^{-1}, respectively, while (II) and (III) become of comparable importance in solution.



(I)



(II)



(III)

(II*a*): maleic hydrazide, X = H;
(IIc): dichloromaleic hydrazide, X = Cl.

Analogous structures (tautomers when R = H) can be written for the annelated benzene derivative§ [(IV), (V*a*,*b*), (VI*a*,*b*); throughout this paper the suffix '*a*' represents R = H and '*b*' represents R = phenyl]. For R = H it was concluded (Rowe & Peters, 1933) that (IV) exists in acid or neutral solution and (V*a*) in alkali hydroxide solution, while there was no evidence to support the phthalaz-1,4-dione tautomer (VI*a*) first advanced by Curtius & Foersterling (1895). The relatively sparse evidence supporting tautomer (V*a*) is summarized by Katritzky & Lagowski (1963, see p. 368). The relative energies from semi-empirical calculations depend on which method is used (Fabian, 1991), while *ab initio* calculations have not yet been reported. Thus, when crystals of 2,3-dihydro-2-phenyl-1,4-phthalazinedione serendipitously became available to us (see *Experimental*) we decided to determine which tautomer appears in the solid state and to carry out parallel *ab initio* computations (briefly reported here and more extensively elsewhere).

A search of the Cambridge Data File (Allen *et al.*, 1991; Version 5.10, October, 1995) produced only one additional crystal structure of a molecule analogous to those discussed here: that of 3-aminophthalhydrazide [luminol; (V*c*); Paradies, 1992; structure analysis at

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† Deceased.

‡ Indexed in *Chem. Abstr.* under 3,6-pyridazinedione, 1,2-dihydro-; system number 123-33-1.

§ Indexed in *Chem. Abstr.* under 1,4-phthalazinedione, 2,3-dihydro-2-phenyl; system number 5439-98-5.

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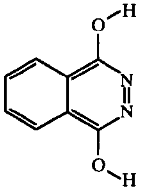
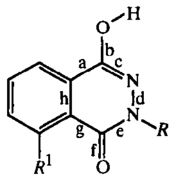
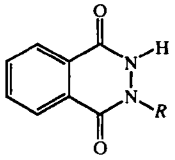
173 K]. This is triclinic ($P\bar{1}$, $Z = 6$; pseudo-trigonal) with the three molecules in the asymmetric unit forming a hydrogen-bonded triangle. The molecule is found as the lactim–lactam tautomer.



(IV)



(V)



(VI)

(V*a*): $R = R^1 = \text{H}$;
(V*b*): $R = \text{phenyl}$; $R^1 = \text{H}$;
(V*c*): (luminol): $R = \text{H}$; $R^1 = \text{NH}_2$.

2. Experimental

Our intention had been to prepare *N*-anilinophthalimide [(VII), *R* = phenyl; reported as bright yellow compact crystals, m.p. 457 K] by condensation of phthalic anhydride and phenylhydrazine in dioxane, followed by elimination of water at 373 K (reaction *A*; Chattaway & Wünsch, 1911). Our early experiments yielded only the isomeric 2-phenyl-4-hydroxyphthalazin-1-one [(V*b*), *R* = phenyl; off-white needles, m.p. 487 K; recrystallized from ethanol], according to reaction *B*, and (VII) was only obtained later after the addition of a small amount of toluenesulfonic acid to the reaction mixture. Although the details of the mechanisms of reactions *A* and *B* have not been elucidated, the following points can be noted. Compounds (V*b*) and (VII) are both stable when heated to 513 K for 6 h, but (VII) can be converted into (V*b*) by heating it with an alcoholic solution of sodium ethoxide or with glycerol, to 513 K (50% transformation after 6 h; Chattaway & Tesh, 1920). Ohta (1942) reported that condensation of

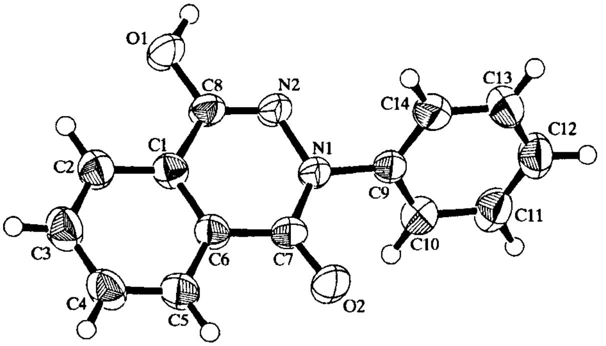


Fig. 1. Displacement ellipsoid plot (Johnson, 1976) of the title compound (for molecule *A*), showing atom numbering with ellipsoids drawn at the 50% probability level. The diagram for molecule *B* is very similar. *A* and *B* molecules are distinguished using the appropriate suffixes.

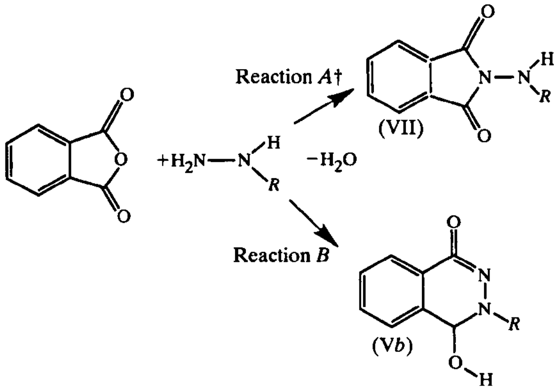
Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{14}H_{10}N_2O_2$
Chemical formula weight	238.24
Cell setting	Monoclinic
Space group	$P2_1/a$
a (Å)	12.083 (4)
b (Å)	18.854 (6)
c (Å)	10.760 (3)
β (°)	107.29 (3)
V (Å^3)	2340.4 (13)
Z	8
D_x (Mg m^{-3})	1.352
D_m (Mg m^{-3})	1.350
Density measured by	Flotation
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	25
θ range (°)	4.2–12.1
μ (mm^{-1})	0.093
Temperature (K)	293 (2)
Crystal form	Block
Crystal size (mm)	0.8 × 0.5 × 0.4
Crystal colour	Light yellow
Data collection	
Diffractometer	Philips PW 1100/20
Data collection method	$\omega/2\theta$ scans
Absorption correction	None
No. of measured reflections	4356
No. of independent reflections	4126
No. of observed reflections	2793
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0197
$\theta_{\max}$ (°)	25
Range of h, k, l	$-14 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 22$ $0 \rightarrow l \rightarrow 12$
No. of standard reflections	3
Intensity decay (%)	0.6
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0500
$wR(F^2)$	0.1131
S	1.072
No. of reflections used in refinement	4126
No. of parameters used	405
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.3521P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	−0.009
$\Delta\rho_{\max}$ (e Å^{-3})	0.13
$\Delta\rho_{\min}$ (e Å^{-3})	−0.21
Extinction method	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection	Philips Eindhoven (1973)
Cell refinement	Philips Eindhoven (1973)
Data reduction	*PROCN*, extensively modified version (Goldberg, 1990) of *PROC* (Hornstra & Stubbe, 1973)

Table 1 (*cont.*)

Structure solution	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)
Molecualr graphics	*ORTEP*II (Johnson, 1976); *TEXSAN* (Molecular Structure Corporation, 1992)

phthalic anhydride and phenylhydrazine gave a mixture of (VII) (appeared first) and (VI*b*) (obtained by concentrating mother liquors). Boiling (VII) with phenylhydrazine gave (V*b*).



† Only in the presence of toluenesulfonic acid.

3. Results

3.1. *Crystal structure*

The occurrence of the lactim–lactam structure (V*b*) is shown unequivocally (Fig. 1). Full experimental details are given in Table 1. Bond lengths and angles in the two independent molecules (*A* and *B*) are not significantly different. The torsion angle τ(N2—N1—C9—C14) is 60.5 (3)° for molecule *A* and −48.0 (3)° for molecule *B* (coordinates are given in Table 2 and bond lengths and angles in Table 3). The phthalazine ring of molecule *A* is planar to within 0.009 Å, with O2 deviating by 0.040 Å; however, the phthalazine ring of molecule *B* is slightly folded so that the planes defined by C1–C6 and by N1, N2, C1, C6–C8, O1, O2 are inclined by 1.74 (15)° to one another.†

3.2. *Hydrogen-bonding schemes*

Among the four crystals considered here, the simplest hydrogen-bonding pattern is found in 2-phenyl-4-hydroxyphthalazin-1-one. The molecular arrangement is based on strings of alternating *A* (conformer with $\tau = \pm 61°$) and *B* (conformer with $\tau = \pm 50°$) molecules

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1*A*	0.05163 (14)	0.64539 (9)	0.4066 (2)	0.0445 (5)
N2*A*	0.14819 (15)	0.60655 (9)	0.4766 (2)	0.0460 (5)
N1*B*	0.57233 (15)	0.56942 (9)	0.8745 (2)	0.0432 (4)
N2*B*	0.64527 (15)	0.60613 (9)	0.9793 (2)	0.0455 (5)
O1*A*	0.23650 (15)	0.49966 (9)	0.5216 (2)	0.0612 (5)
O2*A*	−0.12259 (15)	0.65880 (9)	0.2566 (2)	0.0742 (6)
O1*B*	0.6770 (2)	0.70302 (9)	1.1088 (2)	0.0640 (5)
O2*B*	0.41012 (14)	0.55690 (9)	0.7047 (2)	0.0652 (5)
C1*A*	0.0522 (2)	0.50176 (11)	0.3643 (2)	0.0438 (5)
C2*A*	0.0537 (2)	0.42852 (13)	0.3429 (3)	0.0545 (6)
C3*A*	−0.0394 (2)	0.39683 (14)	0.2542 (3)	0.0598 (7)
C4*A*	−0.1340 (2)	0.43710 (14)	0.1852 (3)	0.0607 (7)
C5*A*	−0.1368 (2)	0.50901 (14)	0.2043 (2)	0.0558 (6)
C6*A*	−0.0429 (2)	0.54207 (11)	0.2946 (2)	0.0459 (5)
C7*A*	−0.0430 (2)	0.61851 (12)	0.3160 (2)	0.0488 (6)
C8*A*	0.1465 (2)	0.53912 (12)	0.4556 (2)	0.0453 (5)
C9*A*	0.0615 (2)	0.72010 (11)	0.4352 (2)	0.0442 (5)
C10*A*	−0.0186 (2)	0.75298 (13)	0.4849 (2)	0.0525 (6)
C11*A*	−0.0088 (2)	0.82502 (13)	0.5117 (3)	0.0603 (7)
C12*A*	0.0806 (3)	0.86329 (14)	0.4885 (3)	0.0643 (7)
C13*A*	0.1596 (2)	0.83028 (14)	0.4386 (3)	0.0642 (7)
C14*A*	0.1509 (2)	0.75839 (13)	0.4116 (2)	0.0531 (6)
C1*B*	0.5015 (2)	0.69978 (12)	0.9368 (2)	0.0456 (5)
C2*B*	0.4651 (2)	0.76493 (13)	0.9728 (3)	0.0560 (6)
C3*B*	0.3599 (2)	0.79220 (15)	0.9013 (3)	0.0671 (8)
C4*B*	0.2909 (2)	0.7563 (2)	0.7921 (3)	0.0675 (8)
C5*B*	0.3254 (2)	0.69203 (14)	0.7577 (3)	0.0585 (7)
C6*B*	0.4311 (2)	0.66270 (12)	0.8306 (2)	0.0454 (5)
C7*B*	0.4676 (2)	0.59328 (12)	0.7968 (2)	0.0471 (5)
C8*B*	0.6098 (2)	0.66673 (11)	1.0073 (2)	0.0454 (5)
C9*B*	0.6198 (2)	0.50204 (11)	0.8533 (2)	0.0435 (5)
C10*B*	0.5545 (2)	0.44071 (13)	0.8403 (3)	0.0569 (6)
C11*B*	0.6037 (3)	0.37653 (14)	0.8252 (3)	0.0693 (8)
C12*B*	0.7171 (3)	0.3730 (2)	0.8246 (3)	0.0721 (8)
C13*B*	0.7816 (3)	0.4336 (2)	0.8368 (3)	0.0740 (8)
C14*B*	0.7329 (2)	0.49883 (14)	0.8505 (3)	0.0607 (7)
HO1*A*	0.295 (3)	0.5240 (17)	0.586 (4)	0.105 (11)
HO1*B*	0.748 (3)	0.6781 (18)	1.152 (4)	0.115 (12)

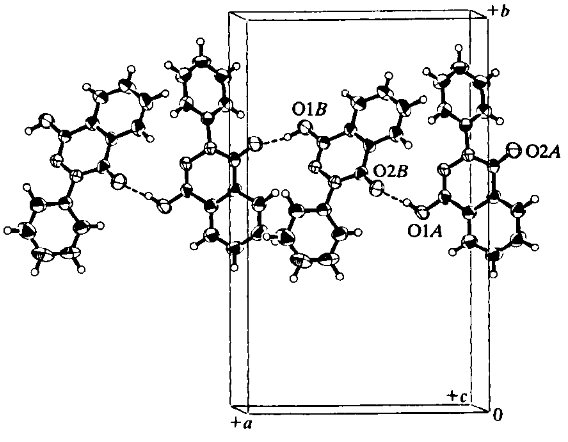


Fig. 2. View of the alternating *A* and *B* molecules linked by hydroxyl···carbonyl hydrogen bonds in the crystallographically independent strings [*d*(O1*A*···2*B*) = 2.602 (3), *d*(O1*B*···O2*A*) = 2.644 (3) Å].

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1320). Services for accessing these data are described at the back of the journal.

Table 3. *Selected geometric parameters (Å, °)*

N1*A*—C7*A*	1.361 (3)	N1*B*—C7*B*	1.369 (3)
N1*A*—N2*A*	1.394 (2)	N1*B*—N2*B*	1.391 (2)
N1*A*—C9*A*	1.439 (3)	N1*B*—C9*B*	1.440 (3)
N2*A*—C8*A*	1.290 (3)	N2*B*—C8*B*	1.287 (3)
O1*A*—C8*A*	1.335 (2)	O1*B*—C8*B*	1.339 (3)
O2*A*—C7*A*	1.243 (3)	O2*B*—C7*B*	1.236 (3)
C1*A*—C6*A*	1.396 (3)	C1*B*—C6*B*	1.393 (3)
C1*A*—C2*A*	1.401 (3)	C1*B*—C2*B*	1.398 (3)
C1*A*—C8*A*	1.447 (3)	C1*B*—C8*B*	1.444 (3)
C2*A*—C3*A*	1.377 (3)	C2*B*—C3*B*	1.374 (4)
C3*A*—C4*A*	1.390 (4)	C3*B*—C4*B*	1.397 (4)
C4*A*—C5*A*	1.373 (4)	C4*B*—C5*B*	1.368 (4)
C5*A*—C6*A*	1.401 (3)	C5*B*—C6*B*	1.399 (3)
C6*A*—C7*A*	1.459 (3)	C6*B*—C7*B*	1.461 (3)
N1*A*—C7*A*—C6*A*	116.2 (2)	N1*B*—C7*B*—C6*B*	115.8 (2)
N2*A*—C8*A*—C1*A*	124.5 (2)	N2*B*—C8*B*—C1*B*	124.9 (2)
C7*A*—N1*A*—C9*A*—C10*A*	61.9 (3)	C7*B*—N1*B*—C9*B*—C10*B*	−51.3 (3)
N2*A*—N1*A*—C9*A*—C14*A*	60.5 (3)	N2*B*—N1*B*—C9*B*—C14*B*	−48.0 (3)

linked by hydroxyl· · ·carbonyl hydrogen bonds, with only van der Waals interactions between adjacent strings (Fig. 2, Table 4); the two independent conformers within the same string are approximately enantiomeric. Phenyl substitution precludes the amine nitrogen from acting as a hydrogen-bond donor and shields the imine nitrogen from acting as an acceptor. However, these restrictions disappear in all the other crystals considered here. Similar strings of —OH· · ·O= hydrogen-bonded molecules [(I) to (II), (I) to (II); *d*(O· · ·O) = 2.598 (4), 2.611 (4); 2.589 (4), 2.590 (4) Å] are found in dichloromaleic hydrazide [space group *Iba*2, two molecules (I) and (II) in the asymmetric unit (Ottersen, 1973)]. However, there is also N—H· · ·O=C bonding between molecules (I) and (II) [*d*(N—H· · ·O) = 2.953 (4), 2.954 (4); 2.963 (4), 2.957 (4) Å]. Triclinic maleic hydrazide (Cradwick, 1976) has a (planar) layer structure involving —OH· · ·O= hydrogen bonding [*d*(O· · ·O) = 2.599 (11) Å] and N—H· · ·O=C [*d*(N—H· · ·O) = 2.873 (10) Å], and similar hydrogen bonding [*d*(O· · ·O) = 2.605 (1) Å] and N—H· · ·O=C [*d*(N—H· · ·O) = 2.925 (1) Å], but with non-planar layers, is found in the monoclinic polymorph (Katrusiak, 1993); the two polymorphs also differ in the mutual arrangements of adjacent layers. The hydrogen-bonding scheme proposed by Lippert *et al.* (1975) for maleic hydrazide, before crystallographic results became available, was incorrect in that it included N—H· · ·O=C, but not O—H· · ·O=C hydrogen bonding. In luminol pairs of molecules are linked by —OH· · ·O= and >N—H· · ·N hydrogen bonding to form triangular units, and there is also one intramolecular >N—H· · ·O=C hydrogen bond per molecule.

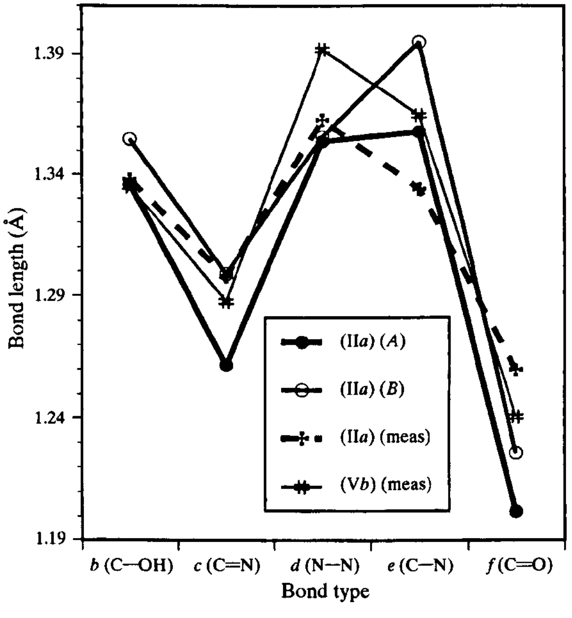


Fig. 3. Comparison plot of selected bond lengths (see schemes for nomenclature). Two sets of computed values are given for maleic hydrazide (II*a*) (see Table 4) and compared with the measured values in the monoclinic polymorph. The less accurate measured values for (V*b*) are also shown.

3.3. *Comparison of MO calculations and experimental results*

Our first set of *ab initio* computations for (IV) (C_{2v}, planar), (V*a*) (C_1) and (VI*a*) (C_2) was carried out using the *Gaussian*92 package of programs (Frisch *et al.*, 1992). Geometries were optimized at the HF/6-31G* level (Hariharan & Pople, 1973) using the symmetry restraints noted above. Single-point energy calculations at the optimized structures were performed at the MP3/6-31G* level (Møller & Plesset, 1934). The relative energies, including the contributions from zero-point vibra-

Table 4. *Hydrogen bonding geometry (Å, °)*

O—H···O═C	O—H	O···O	H···O	O—H···O	O···O═C
O1*A*^{i}—H···O2*B*^{i}	0.95 (4)	2.644 (3)	1.70 (4)	172 (3)	163.1 (2)
O1*B*^{i}—H···O2*A*^{ii}	0.96 (4)	2.608 (3)	1.68 (4)	161 (2)	161.0 (1)

Symmetry codes: (i) *x*, *y*, *z*; (ii) 1 + *x*, *y*, 1 + *z*.

Table 5. *Comparison of calculated bond lengths (Å) for maleic hydrazide (IIa) and 2-hydro-4-hydroxyphthalazin-1-one (Va) at different levels of computation, calc A and calc B, and with measured (meas) values (standard uncertainties, s.u.'s, from least-squares analyses in parentheses) for maleic hydrazide (monoclinic polymorph) and 2-phenyl-4-hydroxyphthalazin-1-one (Vb)*

Bond	(II*a*) (calc *A*)	(V*a*) (calc *A*)	(II*a*) (calc *B*)	(V*a*) (calc *B*)	(II*a*) (meas)	(V*b*) (meas)
a	1.450	1.459	1.436	1.450	1.415 (2)	1.446 (3)
b (C—OH)	1.336	1.337	1.355	1.357	1.338 (2)	1.337 (4)
c (C═N)	1.262	1.259	1.299	1.292	1.298 (2)	1.288 (3)
d (N—N)	1.354	1.362	1.356	1.368	1.363 (1)	1.392 (3)
e (C—N)	1.358	1.354	1.395	1.383	1.334 (1)	1.365 (8)
f (C═O)	1.202	1.203	1.226	1.228	1.260 (2)	1.239 (7)
g	1.472	1.480	1.464	1.477	1.435 (2)	1.460 (2)
h	1.330	1.391	1.355	1.411	1.346 (2)	1.394 (3)

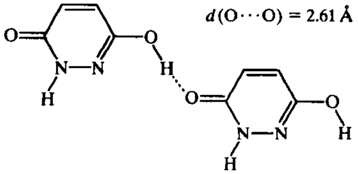
Note: (*a*) The calculated values are for the two *ab initio* methods described in the text: *A* is HP/6-31G* and *B* is B3LYP/6-31G*. (*b*) The (II*a*) (meas) values are for the monoclinic polymorph. The s.u.'s are the experimental values given by Katrusiak (1993) and are between 1/5 and 1/3 of those given for the triclinic polymorph (Cradwick, 1976). More realistic s.u.'s would be obtained by multiplying the bracketed values by ~1.5. Comparison of unit-cell volumes suggests that the monoclinic polymorph is the more stable at 300 K. (*c*) The (V*b*) (meas) values are the means for the *A* and *B* molecules; the bracketed values are the differences between the separate *A* and *B* values. (*d*) The C—C bond lengths in the annelated benzene ring of (V*b*) are, reading clockwise from *h* and described as in §3, 1.394 (3) (*h*), 1.400 (2), 1.370 (5), 1.393 (7), 1.375 (3) and 1.399 (2).

tional energies, are (V*a*) 0.0, (VI*a*) 14.10 and (IV) 38.24 kJ mol^{-1}. These values are similar to analogous values for maleic hydrazide (0.0, 8.3 and 34.2 kJ mol^{-1}; Hofmann *et al.*, 1991). The (V*a*) structure was found to be planar, but the N atoms in (VI*a*) were pyramidal with τ(H—N—N—H) = 61.25° [in maleic hydrazide as (III): 62°]. We have also carried out *ab initio* molecular orbital calculations for maleic hydrazide [only as (II*a*)] and 2-hydro-4-hydroxyphthalazin-1-one [only as (V*a*)] at the B3LYP/6-31G*//B3LYP/6-31G* level (Parr & Yang, 1989), thus including the effect of electron correlation in the geometry optimization.

We first compare bond lengths (values in Table 5; bonds designated in the schemes) for maleic hydrazide (II*a*) and 2-hydro-4-hydroxyphthalazin-1-one (V*a*) calculated at the HF/6-31G* level (calc *A* in Table 5) and find very good agreement (root mean-square discrepancy for bonds *b*–*f* is 0.004 Å); an analogous comparison at the B3LYP/6-31G* level (calc *B*) gives a root mean-square discrepancy of 0.008 Å. These results are interpreted as showing that the additional annealated benzene ring has little influence on the (gas phase) geometry of the substituted hetero ring. On comparing the results of the two methods for (II*a*) we find (as is well known) that the bond lengths calculated at the B3LYP/6-31G*level are mostly longer than those calculated at the HF/6-31G* level (only C—C bonds *a* and *g* with differences of 0.014 and 0.008 Å show the opposite trend).

When we compare measured and calculated bond lengths we find that only the measured bond lengths for the monoclinic polymorph of maleic hydrazide are sufficiently precise to warrant comparison with theory; the root mean-square discrepancies between computation and measurement at the two levels are 0.033 (HF/6-31G* level) and 0.032 Å (B3LYP/6-31G* level). Similar trends for the various methods of calculation and for measured values are shown in Fig. 3, where differences in detail are also apparent.

We focus on bond *f* (C═O). Consideration of measured values shows that this bond length increases when the carbonyl bond is involved in hydrogen bonding. Perhaps the first suggestion of this kind – that the lengthening is due to effects of hydrogen bonding in the solid state which are not taken into account in computations for the isolated molecules – was that of Ottersen (1975) for acetamide; the considerable amount of later work has been critically reviewed by Jeffrey (1992). For example, the computed MO (HF/3-21G) C═O bond length in (gas phase) acetamide is 1.216 Å (Jeffrey *et al.*, 1980), while the measured value in (hydrogen-bonded) acetamide at 15 K (neutron diffraction) is 1.250 Å (corrected for thermal motion; Jeffrey *et al.*, 1980). We find similar differences between computed and measured values for maleic hydrazide: 0.058 Å at the HF/6-31G* level and 0.034 Å at the B3LYP/6-31G* level. Thus, allowance for electron correlation increases the computed C═O bond length, improving agreement with experiment. [However, a contrary effect is found for bond *e* (C—N); here, the difference between computed and measured values is 0.024 Å at the HF/6-31G* level, but 0.061 Å at the B3LYP/6-31G* level.]



We have also investigated the effect of using a hydrogen-bonded (—OH···O=C) dimer model of maleic hydrazide for the computation of d(C=O) at the HF/6-31G* and B3LYP/6-31G* (bracketed values) levels. For the carbonyl not involved in hydrogen bonding, d(C=O) = 1.204 (1.229) Å while, for that involved, d(C=O) = 1.212 (1.240) Å. Thus, we find that inclusion of electron-correlation and hydrogen-bonding effects improves the agreement between gas-phase (computed) and solid-phase (measured) bond lengths for the carbonyl bond of maleic hydrazide. It is still not possible to carry out calculations on models large enough to allow realistic comparisons between theory and experiment.

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