

Polymorphism in hydrazonium salt of 3,5-pyrazoledicarboxylic acid

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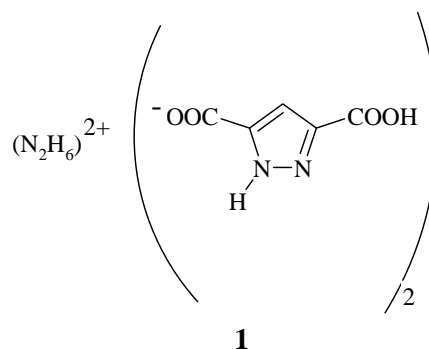
Two polymorphic structures of hydrazonium monobasic salts of 3,5-pyrazoledicarboxylic acid are described. In both instances, one-dimensional infinite chains formed by acid molecules through O–H...O hydrogen bonding (1.68 Å, 177.1°; 1.71 Å 169°) are inter-linked by hydrazonium dications to form two-dimensional sheets. The subtle structural difference between the two forms arises in the packing of hydrazonium dications. In form **A**, the hydrazonium dications are relatively close packed compared to those in form **B**. The closest N...N distance between two hydrazonium dications of inversion related layers in form **A** is 2.03 Å whereas the closest N...N distance between two similar hydrazonium dications (disordered) is 4.89 Å for form **B**. This account for the higher packing fraction (78% vs 76.2%) of form **A** compared to form **B**.

Keywords: Hydrazonium salt, 3,5-pyrazoledicarboxylic acid, polymorphism, crystal structure, hydrogen bonding

IPC: Int.Cl.⁸ C07D

A molecule is said to be polymorphic if the same chemical substance adopts more than one distinct crystalline packing arrangement in the solid state^{1,2}. The occurrence of polymorphs implies that the free energy differences between the various crystalline forms are small^{3,4}. Reproducibly getting the correct polymorph of a given compound is of utmost importance for the proper formulation of pharmaceuticals, dyes, explosives and pigments^{5,6}. A proper understanding of polymorphism is important in implementing crystal engineering strategies⁷. Carboxylic acid group is the most commonly studied functional group in crystal engineering⁷. This research group has been studying the different type and structures of salts formed by hydrazine with dibasic acids⁸⁻¹¹. Dibasic acids are known to form N₂H₅HA, (N₂H₅)₂A and N₂H₆A type of salts (H₂A = dibasic acid) with hydrazine. Though crystal structures of a number of hydrazinium salts of the dibasic acids have been reported¹²⁻¹⁴, there appears to be one report¹⁵ available upto now in the Cambridge Structural Database (CSD)¹⁶ on the hydrazonium salt of the third type and there is no crystal structure reported on the salt of type N₂H₆(HA)₂. These hydrazinium salts are of interest due to their wide use as additives in propellants, drugs to treat cancer and Hodgkin's

disease, and explosives¹⁷. Herein are reported two polymorphic modifications (forms **A** and **B**) of N₂H₆(HA)₂ type salt **1** formed by hydrazine with 3,5-pyrazoledicarboxylic acid.



Results and Discussion

The crystals of form **A** were obtained from the crystallization of 1:2 mixture of hydrazine hydrate and 3,5-pyrazoledicarboxylic acid in water. The compound adopts centrosymmetric triclinic modification (**Table I**). The asymmetric unit contains two carboxylate ions and a hydrazonium dication (**Figure 1**). In crystal structure, both the independent acid molecule form infinite 1-D chains through O–H...O hydrogen bonding (1.68 Å, 177.1°; 1.71 Å,

Table I — Crystallographic data for forms **A** and **B**

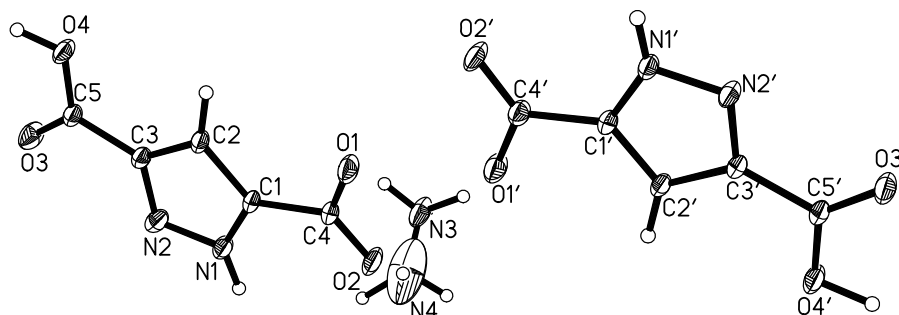
	Form A	Form B
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	7.7560(1)	5.8747(1)
$b/\text{\AA}$	9.1242(1)	7.2106(1)
$c/\text{\AA}$	9.3857(2)	9.1393(2)
α°	83.145(1)	68.983(1)
β°	80.839(1)	80.137(1)
γ°	78.022(1)	68.082(1)
$V/\text{\AA}^3$	638.885(17)	334.953(10)
Z	2	1
D	1.790	1.707
μ	0.157	0.149
T/K	133(2)	110(2)
Reflections	14438	8017
Unique reflections	3123	1785
Reflections with $I > 2\sigma(I)$	2045	1410
$R_1 [I > 2\sigma(I)]^a$	0.0633	0.0476
wR_2	0.1748	0.1333
$C_k^*[\%]^b$	78	76.2

^a Crystallographic reliability index. ^b Packing fraction (calculated in *PLATON*)¹⁹.

169.0°). The hydrogens of the carboxylic acid group and the oxygens of the carboxylate group are involved in the chain formation. A recent study of published structures in the Cambridge Crystallographic Database on the competition of different acceptors for carboxyl donor also shows that recognition of -CO₂H functional group with carboxylate groups is more common and the acid-carboxylate group O-H...O hydrogen bond is found in case of 96% of crystal structures that have the constituent moieties¹⁸. The 1-D chains thus formed by independent acid molecules of form **A** are connected by hydrazonium dications through N-H...O and N-H...N hydrogen bonds to form a 2-D tape as shown in **Figure 2**. The hydrazonium

dications act as bridges between the tapes of neighboring layer. The layers are inter-connected by hydrazonium dications in such a way that each layer is connected to one inversion related layer and a translation related layer to form a square grid-like network as shown in **Figure 3**.

The crystals of form **B** were obtained along with some precipitated material from the crystallization of 1:1 hydrazine hydrate and 3,5-pyrazoledicarboxylic acid. The expected product of this experiment was to obtain the salt of the type N₂H₅HA. But the X-ray diffraction of the crystals revealed that it is a polymorph of form **A** in triclinic space group, $P\bar{1}$. The asymmetric unit contains one monocarboxylate anion and a disordered hydrazonium dication (**Figure 4**). The hydrazonium dication is centered around the inversion center. The carboxylate groups assemble to form infinite 1-D chain *via* O-H...O hydrogen bond (1.68 Å, 174.1°) as seen in the case of form **A**. Such inversion related chains are connected by the hydrazonium dications to form 2-D tape and the tapes in turn are inter-connected to form a square-grid network. The packing pattern of the acid molecules remains the same in both the structures. The main difference between these two forms arises in the packing of the hydrazonium dications. In form **A**, the hydrazonium dications are relatively close packed compared to those in form **B**. The closest N.....N distance between two hydrazonium dications of inversion related layers in form **A** is 2.03 Å whereas the closest N.....N distance between two similar hydrazonium dications (disordered) is 4.89 Å for form **B** (**Figure 5**). A CSD search showed the typical intermolecular N.....N distances to be in the order of 2.7 Å in case of monocations of N₂H₅. The very short N.....N distance in case of **A** is due to unresolved disorder in the hydrazonium moiety as indicated by large anisotropic thermal parameters for N4. The true N.....N distance is probably longer than 2.03 Å but definitely shorter than that of form **B**. The

**Figure 1** — Molecular structure of Form **A** with 50% thermal ellipsoids

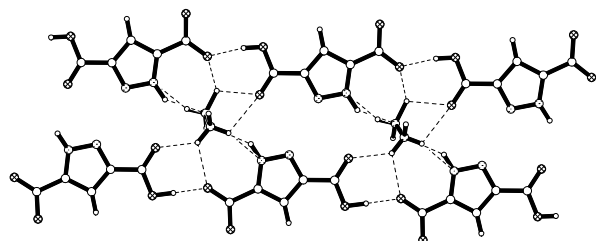


Figure 2 — The two-dimensional hydrogen-bonding pattern observed in form A

form **B**. This account for the higher density (1.79 vs 1.71) of form **A** compared to form **B**.

Experimental Section

Synthesis

Form A

Stoichiometric quantities of 10% hydrazine hydrate (2.5 mL, 5 mmole) and the acid (1.741 g, 10 mmole), in 1:2 ratio, were mixed in 50 mL of water and heated over a water-bath. The resulting solution ($pH = 2.5$) was allowed to crystallize at RT. Colorless crystals of

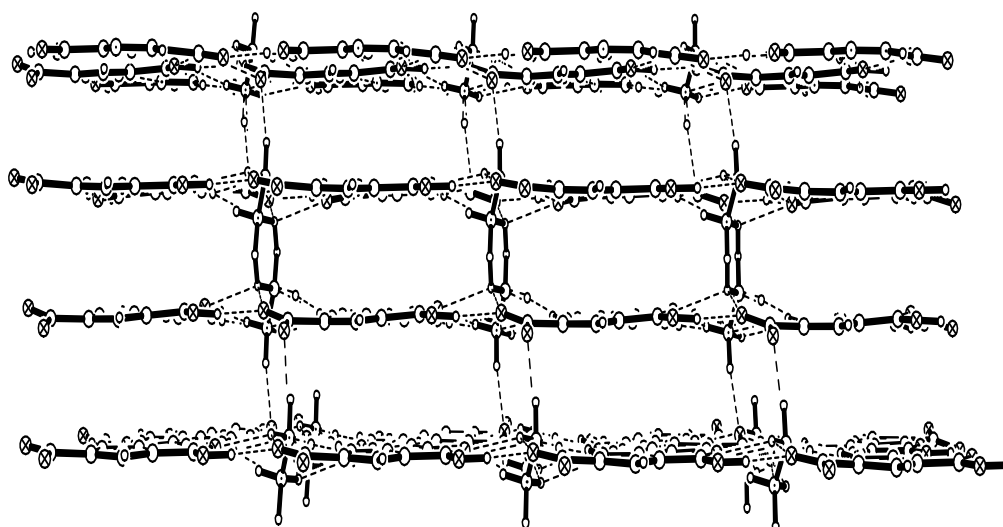


Figure 3 — The square grid pattern observed in form A

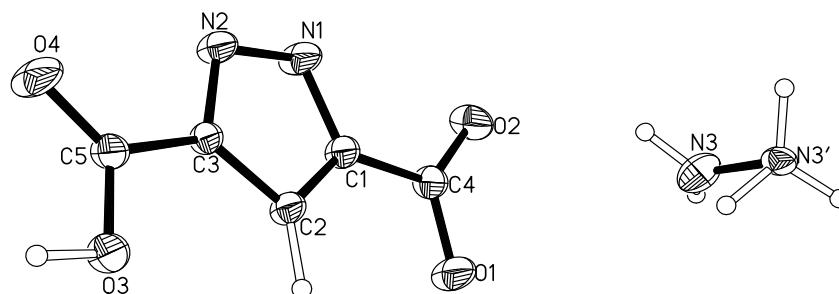


Figure 4 — Molecular structure of Form **B** with 50% thermal ellipsoids

various bond distances and bond angles of form **A** and **B** are given in **Table II**. Several attempts to obtain better structure with different crystals were unsuccessful even though several data sets were collected. As powder diffraction patterns are independent of cell indexing, X-ray powder diffraction patterns (**Figure 6**) were calculated from the single crystal coordinates which clearly indicate that the two compounds are different polymorphs. The packing fraction¹⁹ for form **A** is 78% while it is 76.2% for

suitable size for X-ray diffraction were obtained after a week. The crystals were filtered off and washed with absolute alcohol and dried in vacuum.

Form B

The hydrazonium salt of form **B** was prepared by mixing 10% hydrazine hydrate (2.5 mL, 5 mmole) and the acid (0.8705 g, 5 mmole) in 1:1 molar ratio in 50 mL of water. The resulting solution was heated over a steam-bath for about 20 min to get clear

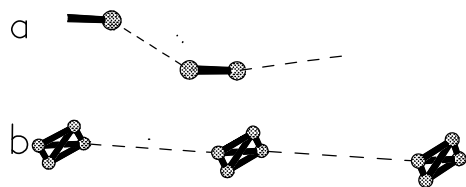


Figure 5 — The arrangements of hydrazonium dications in (a) form **A** and (b) form **B**

solution ($pH = 3.5$). Colorless rectangular shaped shiny crystals were obtained alongwith some precipitated material from the above solution at RT after a week. The crystals of the salt were washed with ice-cold absolute alcohol and air-dried. The precipitated material was found to be hydrazinium (monocation) hydrogen-3,5-pyrazoledicarboxylate (N_2H_5HA), as expected.

Table II — Bond angles and distances for form **A** and form **B**

Form A		Form B	
O(1)-C(4)	1.267(3)	O(1)-C(4)	1.2800(18)
O(2)-C(4)	1.248(3)	O(2)-C(4)	1.2316(18)
O(3)-C(5)	1.216(3)	O(3)-C(5)	1.3188(17)
O(4)-C(5)	1.324(3)	O(4)-C(5)	1.2088(18)
O(4)-H(4)	0.9210	N(1)-N(2)	1.3375(16)
O(1')-C(4')	1.294(3)	N(1)-C(1)	1.3500(18)
O(2')-C(4')	1.232(3)	N(2)-C(3)	1.3445(17)
O(3')-C(5')	1.221(3)	C(1)-C(2)	1.3878(18)
O(4')-C(5')	1.315(3)	C(1)-C(4)	1.4828(18)
O(4')-H(4')	0.9988	C(2)-C(3)	1.3914(17)
N(1)-N(2)	1.343(3)	C(3)-C(5)	1.4720(17)
N(1)-C(1)	1.349(3)	N(3)-N(3')#1	0.668(3)
N(1)-H(1)	0.9625	N(3)-N(3')	1.278(4)
N(2)-C(3)	1.346(3)	N(3)-N(3')#1	1.411(8)
N(3)-N(4)	1.214(7)	N(3')-N(3)#1	0.668(3)
N(3)-H(3A)	0.9612	N(3')-N(3')#1	1.473(6)
N(3)-H(3B)	1.0526		
N(3)-H(3C)	0.9001	N(2)-N(1)-C(1)	108.36(12)
N(4)-H(4A)	1.1580	N(1)-N(2)-C(3)	108.53(11)
N(4)-H(4B)	1.1989	N(1)-C(1)-C(2)	109.52(11)
N(4)-H(4C)	0.9000	N(1)-C(1)-C(4)	121.16(13)
N(1')-N(2')	1.340(3)	C(2)-C(1)-C(4)	129.30(13)
N(1')-C(1')	1.349(3)	C(1)-C(2)-C(3)	104.01(12)
N(1')-H(1'N)	0.9250	N(2)-C(3)-C(2)	109.58(11)
N(2')-C(3')	1.349(3)	N(2)-C(3)-C(5)	119.87(12)
C(1)-C(2)	1.397(4)	C(2)-C(3)-C(5)	130.55(13)
C(1)-C(4)	1.488(3)	O(2)-C(4)-O(1)	125.39(12)
C(2)-C(3)	1.398(3)	O(2)-C(4)-C(1)	120.45(13)
C(2)-H(2)	1.02(3)	O(1)-C(4)-C(1)	114.16(12)
C(3)-C(5)	1.474(3)	O(4)-C(5)-O(3)	124.45(13)
C(1')-C(2')	1.385(3)	O(4)-C(5)-C(3)	122.53(14)
C(1')-C(4')	1.479(3)	O(3)-C(5)-C(3)	113.01(11)
C(2')-C(3')	1.393(3)	N(3')#1-N(3)-N(3')	93.0(6)
C(2')-H(2'C)	0.9976	N(3')#1-N(3)-N(3')#1	64.8(5)
C(3')-C(5')	1.482(3)	N(3')-N(3)-N(3')#1	28.22(18)
		N(3')#1-N(3')-N(3)	87.0(6)
C(5)-O(4)-H(4)	108.7	N(3')#1-N(3')-N(3')#1	60.1(5)
C(5')-O(4')-H(4')	104.8	N(3)-N(3')-N(3')#1	26.9(2)
N(2)-N(1)-C(1)	109.0(2)		
N(2)-N(1)-H(1)	112.5		
C(1)-N(1)-H(1)	138.1		
N(1)-N(2)-C(3)	107.9(2)		
N(4)-N(3)-H(3A)	108.6		
N(4)-N(3)-H(3B)	111.9		
H(3A)-N(3)-H(3B)	109.9		

—Contd

Table II — Bond angles and distances for form **A** and form **B**—*Contd*

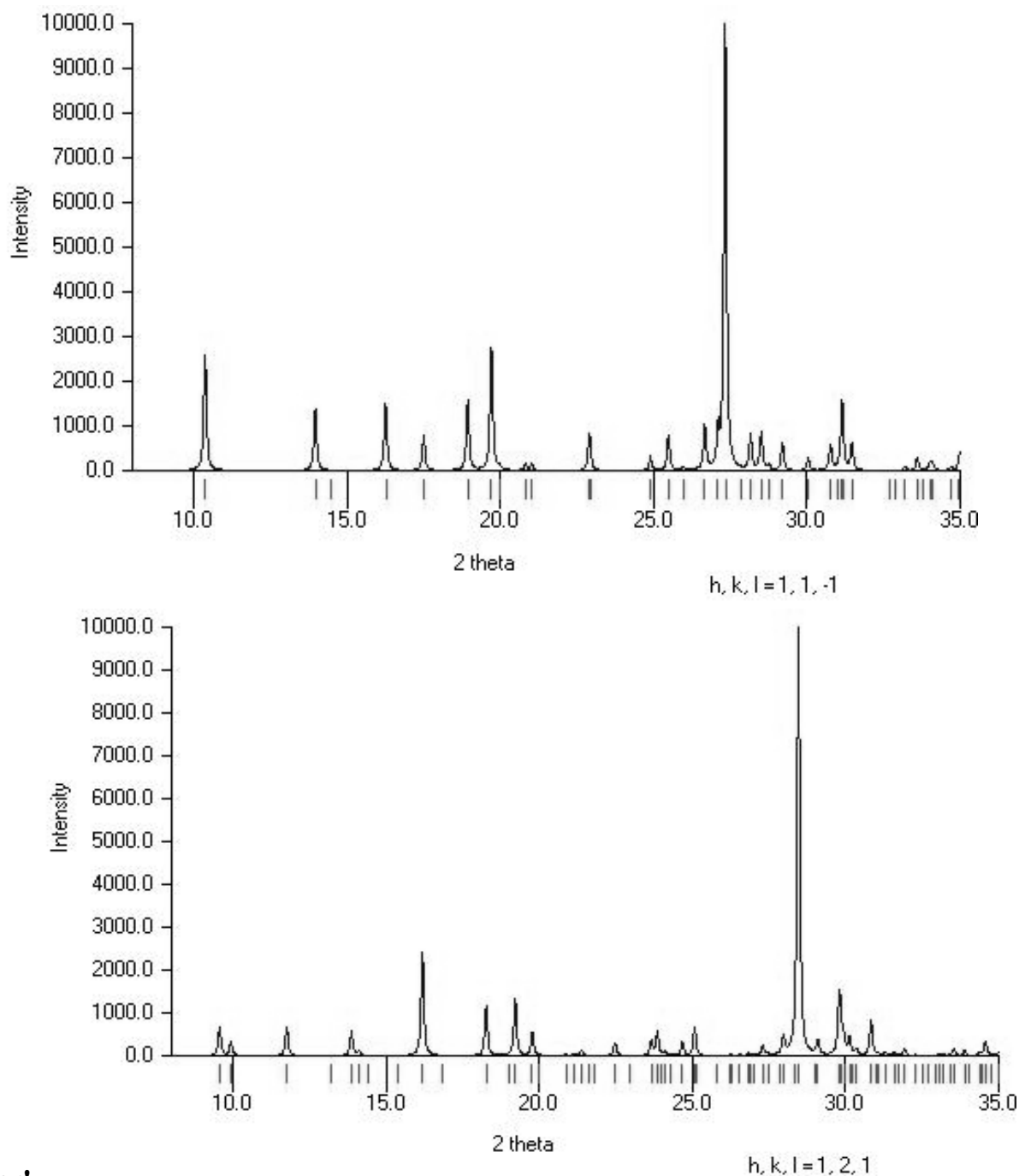
Form A	Form B
N(4)-N(3)-H(3C)	108.2
H(3A)-N(3)-H(3C)	109.1
H(3B)-N(3)-H(3C)	109.1
N(3)-N(4)-H(4A)	109.3
N(3)-N(4)-H(4B)	112.7
H(4A)-N(4)-H(4B)	120.5
N(3)-N(4)-H(4C)	103.6
H(4A)-N(4)-H(4C)	104.4
H(4B)-N(4)-H(4C)	104.4
N(2')-N(1')-C(1')	108.5(2)
N(2')-N(1')-H(1'N)	111.4
C(1')-N(1')-H(1'N)	139.9
N(1')-N(2')-C(3')	108.0(2)
N(1)-C(1)-C(2)	109.4(2)
N(1)-C(1)-C(4)	122.6(2)
C(2)-C(1)-C(4)	127.9(2)
C(1)-C(2)-C(3)	103.5(2)
C(1)-C(2)-H(2)	128.8(18)
C(3)-C(2)-H(2)	127.4(18)
N(2)-C(3)-C(2)	110.1(2)
N(2)-C(3)-C(5)	119.4(2)
C(2)-C(3)-C(5)	130.4(2)
O(2)-C(4)-O(1)	125.6(2)
O(2)-C(4)-C(1)	119.1(2)
O(1)-C(4)-C(1)	115.3(2)
O(3)-C(5)-O(4)	124.9(2)
O(3)-C(5)-C(3)	122.6(2)
O(4)-C(5)-C(3)	112.5(2)
N(1')-C(1')-C(2')	109.9(2)
N(1')-C(1')-C(4')	121.8(2)
C(2')-C(1')-C(4')	128.2(2)
C(1')-C(2')-C(3')	103.7(2)
C(1')-C(2')-H(2'C)	129.4
C(3')-C(2')-H(2'C)	126.2
N(2')-C(3')-C(2')	109.9(2)
N(2')-C(3')-C(5')	119.9(2)
C(2')-C(3')-C(5')	130.2(2)
O(2')-C(4')-O(1')	125.5(2)
O(2')-C(4')-C(1')	121.7(2)
O(1')-C(4')-C(1')	112.8(2)
O(3')-C(5')-O(4')	125.4(2)
O(3')-C(5')-C(3')	122.0(2)
O(4')-C(5')-C(3')	112.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z

Crystal data

Preliminary examinations and data collections were performed using a Bruker SMART CCD 1K area detector system single crystal X-ray diffractometer. The SMART/SAINT software packages were used for

data collections and data reduction, respectively and the SHELXTL-PLUS software package was used for structure solution and refinement^{20,21}. Hydrogen atoms were calculated in their idealized geometries and treated isotropically using appropriate riding models.



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Figure 6 — Calculated powder patterns for forms **A** and **B**

Comparable cell parameters were obtained by cell determinations on several crystals of both the samples at low temperature and RT. Also, cell searches were carried out with reflections from the data sets on Form **A** using cell_now²² to make sure that other cell parameters or volumes comparable to Form **B** were not available. Powder diffraction patterns were calculated using Mercury program²³.

Conclusions

Two polymorphs of the hydrazone salt of a dibasic acid have been structurally characterized by low temperature X-ray diffraction. Although, the arrangement of the acid molecules remains the same in both the structures, the variations in the arrangement of the hydrazone dication are evident in the two polymorphs. This study also highlights the

fact that subtle variations in packing pattern can lead to polymorphism.

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