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Anion directed supramolecular architecture of pyrazole based ionic salts†

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The reaction of 3,5-diphenylpyrazole ($Pz^{Ph2}H$) with different inorganic acids affords salts *viz.*, $Pz^{Ph2}H_2^+ \cdot H_2PO_4^-$ (1), $Pz^{Ph2}H_2^+ \cdot NO_3^- \cdot H_2O$ (2), $Pz^{Ph2}H_2^+ \cdot Cl^-$ (3), $8Pz^{Ph2}H_2^+ \cdot 4HSO_4^- \cdot 2SO_4^{-2} \cdot 3H_2O$ (4) and $Pz^{Ph2}H_2^+ \cdot ClO_4^- \cdot H_2O \cdot CH_3OH$ (5) with different structures. The present study demonstrates that the formation of hydrogen bond between protonated pyrazoles and anions provides a sufficient driving force for the directed assembly of an extensive supramolecular frame work. Theoretical studies reveal that with the increase in the strength of the inorganic acid, the hydrogen bond interaction energy increases. Using Gaussview to analyse the optimized geometries obtained at DFT(B3LYP)/6-31G(d,p) level of theory further revealed that the orientation of molecules remained the same both in the solid and gaseous phases.

Introduction

The development of the receptor for anions has become a challenging area of research because of its importance for molecular recognition in biological systems as well as in supramolecular chemistry.¹⁻⁶ A series of neutral amine, amide, urea, pyrrole, indole and imidazolium receptors have been reported in the literature.⁷⁻¹³ The ditopic pyrazole ligand with various substituents at the 3 or 5 position is an excellent candidate for molecular engineering as various substituents can increase or decrease the electron density on pyrazole ring. Being a positional isomer of imidazole, pyrazole is ubiquitous in biochemical structure and its function.^{14,15} Pyrazoles also play significant role in various fields such as in catalysis, pharmacological, antimicrobial, fungicidal, herbicidal, coordination and supramolecular chemistry.16-20 Although the various metal complexes of pyrazole have been widely used for both anion as well as cation receptors,²¹⁻²⁹ its use as an anionic sensor has not been explored significantly expect in a few recent work.30-33

In earlier studies the anion binding was studied both in solution and the solid state (crystallographic data).^{31,32,34,35} Presently the computational power and algorithm has reached to such a level that reasonably accurate details of binding energy for isolated species in the gas phase can be obtained using Gaussian 03 and methods implemented. Rao and Sastry³⁶ have reported the proton affinity of pyrazole systems based on the calculation performed by density functional theory (DFT). The present paper reports the synthesis, crystal structure and DFT calculation for the pyrazole based ionic salts and demonstrates the significant role played by anions in deciding the hydrogen bond interaction energy and supramolecular structure.

Results and discussion

Salts 1–5 were prepared by the reaction of $Pz^{Ph2}H$ with corresponding acid, *i.e.*, H_3PO_4 , HNO_3 , HCl, H_2SO_4 and $HClO_4$ in methanol–water solution (Chart 1). The colourless crystals suitable for X-ray data collection were obtained by slow evaporation of resultant reaction mixture. The different formulations were confirmed by elemental analysis, IR, NMR and crystallographic structure analyses of these salts. 3,5-diphenylpyrazole



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similar to other hetero-aromatics containing N-H group and shows N-H stretching vibration in the region of 3600-3300 cm⁻¹. In this region the position of the vibrations largely depend on the extent of hydrogen bonding. These vibrations are shifted to lower frequency (longer wavelengths) side with band widening in all the five salts as compared to the free 3,5-diphenylpyrazole. The hydrogen bonding characteristic of salts 1-5 in the solution was studied by ¹H-NMR spectroscopy. The prominent downfield chemical shift in the NMR spectra observed in each case with respect to the free ligand $[((CD_3)_2CO, 270 \text{ MHz}) 7.12 (s, 1 \text{ H}, \text{pz})]$ 7.30-7.50 (m, 6 H, Ph), 7.85-7.95 (m, 4 H, Ph), 12.52 (s, br, 1 H, NH)] suggested the existence of hydrogen bonding in the solution. The crystallographic data and structure refinement parameters are given in Table 1. The selected hydrogen bonding data are summarized in Table 2. Optimized Cartesian coordinates and Mulliken charges for each atom are provided in Table S1 (ESI).†

$$Pz^{Ph2}H_2^+ \cdot H_2PO_4^-$$
(1)

Salt 1 crystallizes in orthorhombic with the space group $P2_12_12$. The unit cell contains one protonated $Pz^{Ph2}H_2^+$ and one dihydrogen phosphate anion (Fig. 1) bonded together through a variety of hydrogen bonds (Fig. S1).† In the unit cell, deprotonated phosphoric acid and protonated pyrazole form a cationic anionic pair where both NH groups of pyrazole are involved in the hydrogen bonding with the anion. The geometry around the phosphorus in dihydrogen phosphate is almost regular tetrahedron with an average bond angle of 109.25° (O1–P1–O2, 106.4; O2–P1–O4, 105.1; O4–P1–O3, 115.5; O3–P1–O1, 110.0). The four $Pz^{Ph2}H_2^+$ interacted with each other through the C–H… π interaction (C12–H12… π , 3.17; C14–H14… π , 3.61 Å) between the π electron density of phenyl ring present on pyrazole and adjacent phenylic CH, resulting in the formation of

Table 1 Crystal data and structure refinement parameters of salts $1-5^a$

a cavity as shown in Fig. 2. This cavity is occupied by two dihydrogen phosphate ion through various non-covalent interactions (Table 2). The trapped dihydrogen phosphate anions self-dimerized in $R_2^2(8)$ motif through O-H···O interaction (O1-H1...O3, 1.80 Å, i.e. OH group of one dihydrogen phosphate with the oxygen of the other dihydrogen phosphate and vice-versa) as reported in other cases (Fig. S1).^{+3,37-40} The C-H···· π interaction (3.21–3.37 Å) among these pyrazoles also formed small cavity which was empty (Fig. 3). It is important to mention here that these two different type of cavities are present in salt 1. The larger one is occupied by the dimer of the dihydrogen phosphate, whereas the smaller one is vacant and can be used for trapping other suitable ions. To the best of our knowledge, the existence of two different type of cavities in the same salt using pyrazole and phosphoric acid is not available in the literature even today. The presence of different non-covalent interactions resulted in cationic and anionic host-guest structure where the pyrazole acts as host and dihydrogen phosphate anion as a guest molecule (Fig. 3).

$$Pz^{Ph2}H_2^+ \cdot NO_3^- \cdot H_2O \tag{2}$$

The unit cell of salt **2** (Fig. 4) consists of protonated $Pz^{Ph2}H_2^+$, nitrate anion and one mole of crystalline water. The geometry around the nitrogen in nitrate ion is trigonal planar with an average bond angle of 119.9° (O1–N3–O2, 118.9; O2–N3–O3, 121.4; O3–N3–O1, 119.5). Similar to the salt **1**, the cavity formation also occurs in salt **2** through C–H··· π interactions (C6–H6··· π , 3.01; C8–H8··· π , 3.87 Å) (Fig. 5) of four Pz^{Ph2}H₂⁺. In the cavity, the nitrate anion and water are linked with Pz^{Ph2}H₂⁺ through N–H···O interaction involving four NH of two diagonal pyrazoles and oxygen atoms of nitrate/water (N1–H1···O1W, 1.79; N2–H2A···O1, 1.91 Å). The water molecule present in the lattice also forms O–H···O interaction (O(1W)–H(1W1)···O(1),

	1	2	3	4	5
Empirical formula	C15H15N2O4P	C15H15N3O4	C15H13ClN2	C120H114N16O27S6	C16H19ClN2O6
Formula weight	318.26	301.30	256.72	2404.63	370.78
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P_{21212}	$P2_1/n$	$P2_1/n$	$P2_1$	Pbca
aĺÅ	16.115(3)	6.2530(2)	8.1846(2)	14.7258(7)	18.4041(17)
b/Å	18.888(4)	14.4187(5)	17.0013(4)	20.1708(8)	8.4011(7)
c/Å	4.9329(12)	15.9581(6)	9.4108(2)	20.1033(7)	22.587(2)
6/°	90.00	93.3700(10)	99.5070(10)	104.689(10)	90.00
V/Å ³	1501.5(6)	1436.30(9)	1291.52(5)	5776.1(4)	3492.3(5)
Ζ	4	4	4	2	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.408	1.393	1.320	1.383	1.410
μ/mm^{-3}	0.203	0.103	0.278	0.202	0.254
Crystal size/mm	0.28 imes 0.27 imes 0.25	0.27 imes 0.25 imes 0.24	$0.32 \times 0.29 \times 0.26$	$0.23 \times 0.21 \times 0.18$	$0.19 \times 0.15 \times 0.16$
θ range/°	1.66-28.25	1.90-28.33	2.40-28.33	1.05-28.33	1.80-26.68
Reflections collected	3721	3530	3177	27489	3687
Independent reflections	3229	2868	2570	17694	2640
Parameters	196	205	163	1545	244
Flack parameter	-0.06(9)			0.28(4)	_
$\operatorname{GOF}(F^2)$	1.037	1.034	1.032	1.022	1.056
R_1 ; w $R_2 [I > 2\sigma(I)]$	0.0356; 0.0802	0.0372; 0.0939	0.0363; 0.0907	0.0588; 0.1144	0.0727; 0.1002
R_1 ; w R_2 (all data)	0.0455; 0.0854	0.0498; 0.1026	0.0480; 0.0986	0.1041; 0.1235	0.2103; 0.2369
$a R_1 = \sum F_0 - F_c / \sum F_c $	$WR_2 = \{\sum [W(F_0^2 - F_c)]$	$(F_{o}^{2})^{2}]/\sum w(F_{o}^{2})^{2}\}^{1/2}.$			

Table 2	Selected hydrogen	bond p	parameters	(Å,	°) for	salts 1-5

D–H…A	d(D-H)	<i>d</i> (H···A)	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
1				
$O(1)-H(1)\cdots O(3) \#1$	0.84	1.80	2.622(19)	167
O(2)–H(2)···O(4) #2	0.84	1.89	2.673(2)	155
$N(1)-H(1A)\cdots O(3)$	0.88	1.84	2.659(19)	154
$N(2)-H(2B)\cdots O(4) \#2$	0.88	1.81	2.659(19)	161
$C(12)-H(12A)\cdots\pi$ #3	0.95	3.17	4.042(8)	153
$C(14)-H(14A)\cdots \pi \#4$	0.95	3.61	4.529(9)	161
2	invalent atoms: $\#1 - x + 2, -3$	y + 1, z + 2x, y, z - 1 + 3 - 5/2	$-x, l_2 + y, -z + 4x - 1/2, l_2$	y + y, 1 - z
O(1W)–H(1W1)····O(1) #1	0.83	2.01	2.847(13)	176
O(1W)–H(1W2)···O(2) #2	0.80	2.24	2.975(14)	150
$O(1W) - H(1W2) \cdots O(3) #2$	0.80	2.35	3.094(13)	152
$N(1)-H(1)\cdots O(1W)$	0.88	1.79	2.648(14)	163
$N(2)-H(2A)\cdots O(1)$	0.88	1.91	2.704(13)	148
$C_2 = H_2 \cdots O_2 \#_3$	0.95	2.55	3.449(2) 3.364(2)	102
C11_H11O1W	0.95	2.50	3.304(2)	155
C12–H12····O2 #1	0.95	2.66	3.286(2)	124
C14–H14…O1 #4	0.95	2.60	3.506(1)	163
С6–Н6…π #5	0.95	3.01	3.901(1)	159
$C8-H8\cdots\pi$ #6	0.95	3.87	4.487(3)	129
Symmetry transformations used to generate equ y - 1/2, $3/2 - z #5 x - 1/2$, $y - 1/2$, $3/2 - z #6$	ivalent atoms: $\#1 - x + 1, -y + 5x - 3/2, 3/2 - y, \frac{1}{2} + z$	+1, -z + 1 # 2 - x, -y + 1, -z	$+1 #3 \frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$	#4 3/2 - x,
3				
$N(1)-H(1A)\cdots Cl(1)$	0.88	2.17	3.039(10)	168
$N(2)-H(2B)\cdots Cl(1) \#1$	0.88	2.17	3.033(12)	165
$C(11) - H(11A) \cdots CI(1)$ $C(15) H(15A) \cdots CI(1) \#2$	0.95	2.80	3.688(15)	155
Symmetry transformations used to generate equ	1.95 ivalent atoms: #1 $-x + 1$, -1	z_{100} v + 1, -z #2 x + 1/2, -v + 1/2	2. z + 1/2	140
4	, , ,			
$O(1C)-H(1C)\cdots O(3B)$	0.84	1.63	2.450(3)	164
$O(1D) - H(1D) \cdots O(2A) \# 1$	0.84	1.66	2.499(3)	1/6
$O(1E) - H(1E) \cdots O(4C) \# 2$ $O(1E) - H(1E) \cdots O(3A)$	0.84	1.70	2.555(4)	170
$O(1F) - H(1F) \cdots O(4A)$	0.84	2 64	3 153(4)	121
$O(1W) - H(1W1) \cdots O(2D)$	0.82	1.94	2.753(4)	169
$O(1W)-H(1W2)\cdots O(4F)$	0.82	1.92	2.743(4)	172
$O(2W)-H(2W1)\cdots O(2B)$	0.82	2.01	2.828(3)	171
$O(2W)-H(2W2)\cdots O(4E)$	0.80	1.96	2.769(4)	177
$O(3W)-H(3W1)\cdots O(1B)$	0.82	1.99	2.803(3)	168
$O(3W) - H(3W2) \cdots O(4E)$ N(1A) H(1AA) $O(2E)$	0.80	1.97	2.761(4)	169
$N(1A) = \Pi(1AA) \cdots O(2F)$ $N(2A) = H(2AB) \cdots O(4A)$	0.88	1.70	2.038(3)	105
$N(2A) = H(2AB) \cdots O(1A)$ N(1B) = H(1BA) \cdots O(1B) #3	0.88	1.80	2.715(5)	157
$N(2B)-H(2BB)\cdots O(2W) #3$	0.88	1.84	2.691(4)	163
N(1C)–H(1CA)····O(2C) #3	0.88	1.87	2.716(3)	162
N(1C)-H(1CA)····O(3C) #3	0.88	2.63	3.064(4)	111
N(2C)-H(2CB)····O(4B) #3	0.88	1.88	2.722(3)	160
$N(1D)-H(1DA)\cdots O(4D)$ #2	0.88	1.85	2.706(3)	163
$N(2D)-H(2DA)\cdots O(1A)$	0.88	1.91	2.777(4)	170
$N(1E) - H(1EA) \cdots O(3W)$ $N(2E) - H(2EP) \cdots O(2P)$	0.88	1.84	2.689(4)	160
N(2E) - H(2EB) - O(2B) N(1F) - H(1FA) - O(1W)	0.88	1.85	2.650(3)	158
$N(2F)-H(2FB)\cdots O(3F)$	0.88	1.76	2.631(4)	170
$N(1H)-H(1HA)\cdots O(3C)$	0.88	1.82	2.648(4)	156
$N(2H)-H(2HB)\cdots O(3E)$ #1	0.88	1.78	2.644(4)	167
N(1G)-H(1GA)···O(3D) #2	0.88	1.82	2.666(4)	161
$N(2G)-H(2GB)\cdots O(1A)$	0.88	1.86	2.662(4)	151
$N(2G)-H(2GB)\cdots O(4A)$	0.88	2.47	3.192(4)	139
C(2C)-H(2CA)···O(1D) C(2P)-H(2CA)···O(4E)	0.95	2.66	3.601(4)	170
V(2E) - H(2EE) O(2E)	0.95	2.32	3.244(4) 2.632(4)	103
$C(5F) = H(5FA) \cdots O(3F)$	0.95	2.35	3 264(5)	158
$C(2D)-H(2DB)\cdots O(1E)$	0.94	2.49	3.436(4)	171
$C(2F)-H(2FA)\cdots O(1C)$	0.95	2.38	3.309(4)	164
C(9F)–H(9FA)····O(1C)	0.95	2.66	3.569(5)	172
$C(5H)-(5AA)\cdots O(4A)$	0.95	2.46	3.380(4)	162
$N(2A)-H(2AB)\cdots O(4A)$	0.88	1.84	2.713(4)	170
$C(12H) - H(12H) \cdots O(2B)$	0.95	2.52	3.413(5)	155
$C(2E) - H(2EA) \cdots O(3A)$	0.94	2.57	3.313(4) 3.424(4)	1/0
$(JD) - \Pi(JDA) \cdots O(IA)$	0.73	2.32	5.424(4)	1.59

Table 2 (Contd.)

D–H···A	d(D-H)	$d(\mathbf{H}\cdots\mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
$C(2B)-H(2BA)\cdots\pi$	0.95	3.59	3.413(4)	71
$C(15E)-H(15F)\cdots\pi$	0.94	3.88	3.580(4)	64
π…π	_	3.55		_
Symmetry transformations used to ger	nerate equivalent atoms: #1 x	+1, y, z # 2 x - 1, y, z # 3 x,	y, z - 1	
5	*			
O(1S)-H(1S)····O(1B) #1	0.84	1.90	2.743(8)	177
$O(1S) - H(1S) \cdots O(1A) \#1$	0.84	2.20	3.045(7)	178
O(1W)–H(1W1)····O(1A) #2	0.81	2.03	2.837(6)	177
$O(1W) - H(1W1) \cdots O(1B) #2$	0.81	2.27	3.078(8)	171
$O(1W) - H(1W1) \cdots O(3B) #2$	0.81	2.50	3.040(8)	125
$O(1W) - H(1W2) \cdots O(2A)$	0.82	2.02	2.776(5)	153
$O(1W) - H(1W2) \cdots O(3B)$	0.82	2.14	2.950(8)	170
$N(1)-H(1A)\cdots O(1S)$	0.88	1.81	2.670(4)	165
$N(2)-H(2B)\cdots O(1W)$	0.88	1.83	2.689(4)	164
$C(6)-H(6)\cdots\pi$	0.94	3.31	3.719(3)	107
$C(7)-H(7)\cdots\pi$	0.95	3.58	4.282(4)	132
Symmetry transformations used to ger	nerate equivalent atoms: #1 x	y + 1, z # 2 - x + 1, -y, -z + 1	+ 1	

2.01; O(1W)–H(1W2)···O(2), 2.24; O(1W)–H(1W2)···O(3), 2.35 Å) with the oxygen of nitrate ion (Fig. S2).† Interestingly, the formation of a small size cavity is not observed in salt **2** during the packing as the C–H··· π distance between the phenyl group of those pyrazoles lie in the range of 9.505–10.550 Å (which are too large to form such a cavity) (Fig. 6).

$$Pz^{Ph2}H_2^+ \cdot Cl^-$$
(3)

The hydrochloride salt of $Pz^{Ph2}H$ (salt 3), crystallizes in the monoclinic crystal system with $P2_1/c$ space group and its ORTEP view is shown in Fig. 7. The unit cell consists of one $Pz^{Ph2}H_2^+$ and one chloride ion. The proton gets transferred from the HCl to $Pz^{Ph2}H$ and forms protonated pyrazole. Both the pyrazol-1yl NH and the protonated NH are available for hydrogen bonding and involved in the principle N–H…Cl interaction (N1–H1A…Cl1, 2.17; N2–H2B…Cl1, 2.17 Å) (Fig. S3).† The chloride ion shows the primary N–H…Cl as well as secondary C–H…Cl interactions as reported earlier.^{41–45} The cationic host pyrazole assembly in



Fig. 1 ORTEP drawing with 50% probability of salt 1.

salt 3 forms different three dimensional packing as compared to salts 1 and 2 because of different orientation of the pyrazoles and the chloride ions. Unlike the salts 1 and 2 the molecular components of salt 3 form pseudo cavity for trapping chloride ion (Fig. 8). The C-H… π distance in salt 3 is found to be in the range of 12.53 Å, which seems to be too large for the formation of a true cavity.

$$8Pz^{Ph2}H_{2}^{+} \cdot 4HSO_{4}^{-} \cdot 2SO_{4}^{2-} \cdot 3H_{2}O$$
(4)



Fig. 2 Formation of cavity through $C-H\cdots\pi$ interaction between cationic pyrazoles trapping two anionic dimers with various $N-H\cdotsO$ and $C-H\cdotsO$ interaction in salt 1. Colour code: C = grey; P = cyan; O = red; N = blue.



Fig. 3 Three dimensional packing of salt 1, entrapping anionic dihydrogen phosphate dimers in the pyrazole cage. Colour code: C = grey; P = cyan; O = red; N = blue.

The salt 4 has been found to contain seventeen moieties viz... eight Pz^{Ph2}H₂⁺, four bisulphate, two sulphate and three water molecules in a unit cell (Fig. 9). The possible source of bisulphate is the deprotonation of sulphuric acid which may further undergo deprotonation resulting in the formation of sulphate anion. The tetrahedral geometry were observed around the sulphur atom in both bisulphate as well as in sulphate ion with an average bond angle of 108.9 and 109.85 (for bisulphate, O1C-S1C-O2C, 108.8; O2C-S1C-O3C, 110.4; O3C-S1C-O4C, 112.3; O4C-S1C-O1C, 104.1; for sulphate, O1A-S1A-O2A, 109.2; O3A-S1A-O1A, 109.3; O2A-S1A-O4A, 109.6; O4A-S1A-O3A, 111.3°). Out of eight $Pz^{Ph2}H_2^+$, the six $Pz^{Ph2}H_2^+$ form two sets of three each (blue and red) and the rest two lies as such in the lattice (green). During packing the three partial overlapped $Pz^{Ph2}H_2^+$ (blue and red) form the continuous chain via C-H··· π and $\pi \cdots \pi$ interaction (C(2B)-H(2BA) $\cdots \pi$, 3.59; C(15E)-H $(15F)\cdots\pi$, 3.88; $\pi\cdots\pi$, 3.55 Å). These blue and red chains are connected to the green through other interactions. Out of eight,



Fig. 4 ORTEP drawing with 50% probability of salt 2.

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only six $Pz^{Ph2}H_2^+$ show different N–H···O and C–H···O interactions (N(2A)–H(2AB)···O(4A), 1.84; N(1B)–H(1BA)···O(1B), 1.80; N(2C)–H(2CB)···O(4B),1.88; N(2D)–H(2DA)···O(1A), 1.91; N(2E)–H(2EB)···O(2B),1.85; N(2G)–H(2GB)···O(1A),1.86; C(5H)–(5AA)···O(4A), 2.46; N(2A)–H(2AB)···O(4A), 1.84; C(12H)–H(12H)···O(2B), 2.52; C(2E)–H(2EA)···O



Fig. 5 Cationic pyrazole cage in salt 2 trapping nitrate anions through N–H···O and C–H···O interactions. Colour code: C = grey; O = red; N = blue; H₂O = green.



Fig. 6 Three dimensional packing of salt 2. Guest nitrate anions are entrapped in the cage formed by the host cationic pyrazole assembly. Colour code: C = grey; O = red; N = blue; $H_2O = green$.

(3A), 2.37; C(5D)-H(5DA)···O(1A), 2.52 Å) with the sulphate anions (Fig. S5).† The bisulphate anion also shows the N-H···O and C-H...O interactions with different atoms of nearby Pz^{Ph2}H₂⁺ (Table 2, Fig. S6).[†] The water molecules are involved in O-H···O interactions through its hydrogen atom with the oxygen of sulphate as well as bisulphate anions in the range 1.92-1.97 Å. The cluster of sulphate, bisulphate and water molecules are interlinked together through O-H…O interaction and the two groups of these cluster within a chain are linked through $Pz^{Ph2}H_2^+$ (green) (Fig. S7).⁺ The different primary (N-H···O, O-H···O) and secondary (C-H···O) non-covalent interactions link the sulphate, bisulphate and water molecule on either side of the chain formed by the protonated $Pz^{Ph2}H_2^+$ (Fig. 10). The larger distance between the $Pz^{Ph2}H_2^+$ of two parallel chains (5.721 Å) is found to be responsible for the non formation of cavity in salt 4. The structure of this salt is unique in the sense that both sulphate as well as the bisulphate anions are simultaneously linked with different $Pz^{Ph2}H_2^+$ in one unit cell.



Fig. 7 ORTEP drawing with 50% probability of salt 3.



Fig. 8 Space-fill view of chloride anions encapsulated by protonated pyrazoles forming pseudo cavity. Colour code: C = grey; N = blue; Cl = cyan.

$$Pz^{Ph2}H_2^+ \cdot ClO_4^- \cdot H_2O \cdot CH_3OH$$
(5)

The salt **5** crystallizes in the orthorhombic with *Pbca* space group. Its unit cell contains one protonated $Pz^{Ph2}H_2^+$, water, methanol and perchlorate anion (Fig. 11). The tetrahedral geometry was observed around chlorine atom in perchlorate ion with an average bond angle of 109.47° (O1A–Cl1–O2A, 109.3; O2A–Cl1–O3A, 109.8; O3A–Cl1–O4A, 109.6; O4A–Cl1–O1A, 109.2). During packing the

 $Pz^{Ph2}H_2^+$ are arranged in one dimensional chain where the two adjacent $Pz^{Ph2}H_2^+$ are linked through $C-H\cdots\pi$ interaction between phenylic CH and π electrons of phenyl group on neighbouring pyrazoles in head to tail fashion (C6–H6 $\cdots\pi$, 3.31; C7–H7 $\cdots\pi$, 3.58 Å). The parallel chains are linked by each other with perchlorate, methanol and water molecules present in the lattice through C– H \cdots O and N–H \cdots O interactions (Table 2). Both the pyrazol-1-yl NH as well as the protonated NH are involved in the principle N– H \cdots O interaction with the oxygen of water and methanol (N(1)–H



Fig. 9 ORTEP drawing with 50% probability of salt 4.



Fig. 10 Alternate channels of host framework formed by the self-assembly of the cationic protonated pyrazoles with guest sulphate anions, pink; bisulphate, yellow; water, cyan on both side in salt 4.



Fig. 11 ORTEP drawing with 50% probability of salt 5.

 $(1A)\cdots O(1S)$, 1.81; N(2)–H(2B) $\cdots O(1W)$, 1.83 Å). The perchlorate, methanol and water molecules are interlinked through O–H $\cdots O$ interaction among each other (O(1S)–H(1S) $\cdots O(1B)$, 1.90; O(1S)–H (1S) $\cdots O(1A)$, 2.20; O(1W)–H(1W1) $\cdots O(1A)$, 2.03; O(1W)–H (1W1) $\cdots O(1B)$, 2.27; O(1W)–H(1W1) $\cdots O(3B)$, 2.50; O(1W)–H (1W2) $\cdots O(2A)$, 2.02; O(1W)–H(1W2) $\cdots O(3B)$, 2.14 Å) as shown in Fig. S9.† Unlike the structure of **4**, the salt **5** consists of continuous discrete chain of perchlorate, methanol and water that runs parallel on either side of the chain formed by the pyrazoles. The presence of perchlorate, methanol and water molecules may be responsible for the larger separation between two parallel chain of pyrazoles (7.95– 8.52 Å) and resulting in the absence of a cavity (Fig. 12).

It is important to point out that the orientation as well as short range C-H… π distances in salts 1 and 2 play important role in the formation of cavity for trapping dihydrogen phosphate and nitrate anions, respectively. On the other hand in the case of salts 3-5, the long C-H… π distances and orientation of Pz^{Ph2}H₂⁺ do not permit the formation of cavity and these salts show entirely different type of three dimensional structures.

Anion selectivity

Since $Pz^{Ph}2H$ forms salt with different anions, an attempt has been made to test the selectivity of this ligand by performing a particular experiment under the same reaction condition in which salts 1–5 were prepared. Thus, an aqueous methanolic solution containing one equivalent of the $Pz^{Ph}2H$ was added to a solution containing one equivalent (1.0 mmol) of each H₃PO₄, HNO₃, HCl, H₂SO₄ and HClO₄ at room temperature (25 °C, pH = 1.63). Suitable colourless crystals were obtained by slow evaporation and subjected to characterization by single-crystal X-ray method. The single-crystal X-ray data clearly indicated (*a* = 14.345(5); *b* = 20.187(7); *c* = 20.111(5) Å; α = 90.00; β = 106.01(6); γ = 90.00°; *V* = 5779.2(3) Å³) that in the mixture of the acids, the ligand was superiorly selective for sulphate and bisulphate anions simultaneously because of the extensive electrostatic as well as non-covalent interactions.^{1,2}

DFT calculations

In Gauss view the position of the anion and protonated pyrazoles were fixed in such a way so that the distance between the two will be in the approximate range as were in the solid phase (obtained from the crystallographic data) before submitting to the Gauss 03 suite of programs and then allowed them for optimization of minimum potential energy. The internal degree of freedom were allowed to relax during the calculation. The optimized structural parameters of all individual acid, pyrazole and their salts were calculated at B3LYP/6-31G(d,p) basis sets and tabulated in

Table 3 Hydrogen bond interaction energy

S. No	Salt	Hydrogen bond interaction energy (Kcal mol ⁻¹)
1	$Pz^{Ph2}H_2^+ \cdot H_2PO_4^-$	9.28
2	$Pz^{Ph2}H_2^+ \cdot NO_3^-$	13.69
3	$Pz^{Ph2}H_2^+ \cdot Cl^-$	18.23
4	$Pz^{Ph2}H_2^+ \cdot HSO_4^-$	19.39
5	$Pz^{Ph2}H_2^+ \cdot ClO_4^-$	24.52



Fig. 12 Ball and stick view of stacked cationic pyrazoles forming host assembly trapping perchlorate, methanol and water molecule in between the channels in salt 5. Colour code: C = grey; N = blue; $Clo_4^- = green$; $CH_3OH = blue$; $H_2O = cyan$.



Fig. 13 Optimized geometry of salts (a) 1 (b) 2 (c) 3 (d) 4 (e) 5.

Table S2.† Each optimized geometry showed positive vibrational frequencies showing that the optimized structure was the global minimum on the potential energy surface. Single point energy calculations were performed and zero point corrected total energies for various species were recorded. In addition to the characterization of these salts, the gas phase geometries, harmonic vibrational frequencies and binding energies of a series of pyrazole salts were computed. The hydrogen bond interaction energies were determined using the following equation,

$$\Delta E = E_{\text{Salt}} - (E_{\text{Pyrazole}} + E_{\text{Acid}})$$

Where E_{Salt} , E_{Pyrazole} and E_{Acid} are the zero point corrected total energies of salt, pyrazole and acid. We have removed the solvent and water molecules to check the relative stability.

The DFT calculation shows that with the change of the acid, the hydrogen bond interaction energy changes for each salt (Table 3). Greater is the strength of the acid, larger would be the hydrogen bond interaction energy which is in accordance with the value of first protonation constant for different acids as given below.⁴⁶

$$\begin{aligned} & Pz^{Ph2}H_{2}^{+} \cdot ClO_{4}^{-} > Pz^{Ph2}H_{2}^{+} \cdot HSO_{4}^{-} > Pz^{Ph2}H_{2}^{+} \cdot Cl^{-} \\ & > Pz^{Ph2}H_{2}^{+} \cdot NO_{3}^{-} > Pz^{Ph2}H_{2}^{+} \cdot H_{2}PO_{4}^{-} \end{aligned}$$

The comparison of bond lengths and angles of the salts (obtained from theoretical calculation and crystallographic data) are given in Table S2.[†] The negligible difference in the energy between the optimized structure and crystal structure of these salts suggest that the orientation and interaction remain almost the same both in gaseous and the solid phase (Fig. 13, Table S3).[†]

Conclusion

In the present work we have reported the anion directed supramolecular frame work which involves a change in the number and type of interaction and the orientation of the molecules in the three dimensional space. In salts 1-2, the dihydrogen phosphate and nitrate anions reside in the cavity, whereas in salt 3. $Pz^{Ph2}H_{2}^{+}$ forms only a pseudo cavity for chloride ion. In case of salts 4-5, the cavity disappears and chain of pyrazoles and anions run in a parallel fashion. To the best of our knowledge this is the first example of the Pz^{Ph2}H used as receptor for both sulphate as well as bisulphate simultaneously. The presence of phenyl groups on 3 and 5 position of pyrazole ring as two wings play important role in trapping the anions of different size. Also, both phenyl groups arrange themselves in such a way to form a cavity through C-H $\cdots\pi$ interaction. In conclusion, we have demonstrated that the variation of anion plays a significant role in controlling the structure of salts. The theoretical calculation reveals that increase in the strength of the acid increases the hydrogen bond interaction energy as the perchloric acid has maximum hydrogen bond interaction energy. The results show that both in solid and gaseous phase, the structure of salts remain the same.

Experimental

General

All manipulations were performed in air using commercial grade solvents, pre-dried by the literature method.⁴⁷ Pz^{Ph2}H was prepared by the procedure reported earlier.⁴⁸ Hydrochloric acid (HCl, 35%), nitric acid (HNO₃, 65%) and sulphuric acid (H₂SO₄, 98%) were purchased from Rankem (Laboratory reagent grade)

whereas the orthophosphoric acid (H₃PO₄, 85%) and perchloric acid (HClO₄, 70%) were from S. D. Fine-Chem Limited. Crystallized salts were carefully dried under vacuum for several hours prior to elemental analysis on Elementar Vario EL III analyzer. IR spectra were obtained on a Thermo Nikolet Nexus FTIR spectrometer in KBr. ¹H-NMR spectra were recorded on Bruker-D-Avance 500 spectrometer with Fourier transform technique using TMS (tetramethylsilane) as internal standard.

Synthesis of $[Pz^{Ph2}H_2^+ \cdot H_2PO_4^-]$. To the 10 mL methanolwater solution of $Pz^{Ph2}H$ (0.22 g, 1.0 mmol), 0.5 mL of H_3PO_4 (v/v%, 10:0.5 mL) was added and the resulting solution was stirred for 6 h. The colourless crystals of salt 1 in 56% (0.18 g, 0.56 mmol) yield, suitable for X-ray data collection were obtained by slow evaporation of solvent at room temperature. ¹H-NMR ((CD₃)₂CO, 500 MHz, ppm): 7.18 (s, 1 H, pz), 7.33– 7.52 (m, 6 H, Ph), 7.87–7.99 (m, 4 H, Ph), 12.55 (s, br, 2 H, NH). Anal. calcd for C₁₅H₁₅N₂O₄P (318.28): C 56.61, H 4.75, N 8.80%. Found: C 56.42, H 4.60, N 8.63%. IR (KBr/cm⁻¹): 3560w, 3420m, 2386b, 1634s, 1478s, 906m, 764m, 678m.

Synthesis of [Pz^{Ph2}H_2^+ \cdot NO_3^- \cdot H_2O]. Salt **2** was prepared by same procedure as outlined above for **1** using HNO₃. Yield: 70% (0.21 g, 0.69 mmol). ¹H-NMR ((CD₃)₂CO, 500 MHz, ppm): 7.18 (s, 1 H, pz), 7.35–7.54 (m, 6 H, Ph), 7.87–7.99 (m, 4 H, Ph), 12.57 (s, br, 2 H, NH). Anal. calcd for $C_{15}H_{15}N_3O_4$ (301.30): C 59.79, H 5.02, N 13.95%. Found: C 60.10, H 5.12, N 13.57%. IR (KBr/ cm⁻¹): 3764w, 3691w, 2725b, 1625s, 1317m, 1104w, 1040m, 830m.

Synthesis of [Pz^{Ph2}H_2^+ \cdot Cl^-]. Salt **3** was prepared by same procedure as outlined above for **1** using HCl. Yield: 74% (0.19 g, 0.74 mmol). ¹H-NMR ((CD₃)₂CO, 500 MHz, ppm): 7.21 (s, 1 H, pz), 7.36–7.55 (m, 6 H, Ph), 7.89–7.99 (m, 4 H, Ph), 12.59 (s, br, 2 H, NH). Anal. calcd for C₁₅H₁₃ClN₂ (256.72): C 70.18, H 5.10, N 10.91%. Found: C 70.42, H 5.15, N 10.77%. IR (KBr/cm⁻¹): 3515w, 3120m, 2309w, 1622s, 1427s, 1390m, 854s, 770s, 682m.

Synthesis of [8Pz^{Ph2}H_2^+ \cdot 4HSO_4^- \cdot 2SO_4^{2-} \cdot 3H_2O].Salt 4 was prepared by same procedure as outlined above for 1 using H₂SO₄. Yield: 36% (0.86 g, 0.35 mmol). ¹H-NMR ((CD₃)₂CO, 500 MHz, ppm): 7.29 (s, 1 H, pz), 7.41–7.59 (m, 6 H, Ph), 7.93–8.00 (m, 4 H, Ph), 12.65 (s, br, 2 H, NH). Anal. calcd for C₁₂₀H₁₁₄S₆N₁₆O₂₇ (2404.63): C 59.94, H 4.78, N 9.32, S 8.00%. Found: C 59.71, H 4.92, N 9.50, S 8.07%. IR (KBr/cm⁻¹): 3671w, 3129b, 2378m, 1467s, 1328s, 786m, 804s, 650m.

Synthesis of [Pz^{Ph2}H_2^+ \cdot ClO_4^- \cdot H_2O \cdot CH_3OH].Salt**5**was prepared by same procedure as outlined above for**1**using HClO₄. Yield: 59% (0.22 g, 0.59 mmol). ¹H-NMR ((CD₃)₂CO, 500 MHz, ppm): 7.31 (s, 1 H, pz), 7.43–7.61 (m, 6 H, Ph), 7.93–8.11 (m, 4 H, Ph), 12.69 (s, br, 2 H, NH). Anal. calcd for C₁₆H₁₉ClN₂O₆ (370.78): C 51.83, H 5.16, N 7.56%. Found: C 51.66, H 5.02, N 7.37%. IR (KBr/cm⁻¹): 3601w, 3409m, 2723b, 1624s, 1475s, 1267m, 1140m, 1077s, 767s, 685m.

X-Ray crystal structure determination

The X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71070$ Å) at 100 K. In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied.⁴⁹ Crystal structures were solved by Direct methods. Structure solution, refinement and data output were carried out with the SHELXTL program.^{50,51} Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images and hydrogen bonding interactions were created in the crystal lattice with DIAMOND and MERCURY software.^{52,53}

Computational study

Geometry optimization of different species involved during the course of present investigation were done using density functional method (B3LYP) with 6-31G(d,p) basis set as implemented in the Gaussian 03 suite of program.^{54,55} The input for the simulation was the z-matrix generated by Gauss view⁵⁶ that was also used for visualizing the optimized structures of molecules. ChemCraft, version 1.5 software was used for comparing the optimized structure with the crystallographic one.

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