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PAPER

Reduced Schiff-base assisted novel dihydrogenphosphate–water polymer†

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Reduced Schiff bases with a common *p*-nitro-*o*-phenylenediamine moiety have been synthesised and their structures have been characterized by single-crystal structural analysis. Schiff bases having self-complementary H-bond donors and H-bond acceptors can form a ''scissors'' like structure through intermolecular H-bonding interaction. Reduced Schiff bases interact with biologically important dihydrogenphosphate ion and form stable complexes. Furthermore, dihydrogenphosphate and water form an unprecedented self-assembled dihydrogenphosphate–water $[H_2PO_4{\cdot}H_2O]_n^{n-}$ 1D supramolecular polymer upon complexation with reduced Schiff bases.

Introduction

Design and syntheses of molecular receptors for recognition and sensing of phosphate ions are of considerable current research interest due to their biological and environmental importance.[1] In this respect, development of molecular receptors for recognition of phosphate ions using amine, amide,[2] urea,[3] thiourea,[4] pyrrole,[5] imidazole,[6] pyridine moieties and metal assisted organic frameworks[7] bearing multiple binding sites have received tremendous attention. Recently, several groups reported tripodal receptors for encapsulation of dihydrogenphosphate ion.[8–10] Among these, Kim and co-workers have reported redox-active ferrocene appended aryl triazole, which can recognize dihydrogenphosphate ion electrochemically[11] and Hossain *et al.* reported a cyclic octamer of dihydrogenphosphate.[12] In all these cases, single-crystal X-ray diffraction shows that dihydrogenphosphate ion or its dimer are surrounded/encapsulated by the ligand and exhibit beautiful supramolecular structures. However, the water–dihydrogenphosphate H-bonded ligand is almost unexplored, although a water–phosphate chain is involved in physiological processes.[13]

Very recently, we have reported the *p*-nitro-*o*-phenylenediamine group and imidazo[1,2-*a*]pyridine group containing reduced Schiff base for selective recognition of dihydrogenphosphate ion *via* an ''unlock–lock'' mechanism.[14] This finding encouraged us to further investigate whether the pyridyl group is essential for binding the dihydrogenphosphate ion or not. To explore this possibility, we have designed and synthesized two new compounds **2** and **3** (Scheme 1). These two compounds and their dihydrogenphosphate complexes were structurally characterized by X-ray single-crystal diffraction analysis.

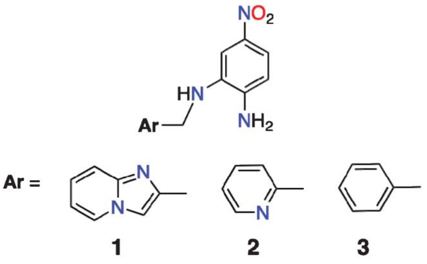
Interestingly, X-ray crystal analysis shows that compound **1** and dihydrogenphosphate ion lead to the $[H_2PO_4{\cdot}H_2O]_2^{2-}$ cluster while compounds **2** and **3** form complexes with dihydrogenphosphate and exhibit interesting 1D dihydrogenphosphate–water $[H_2PO_4{\cdot}H_2O]_n^{n-}$ polymer structure, which is structurally unique compared with the reported dihydrogenphosphate ion containing polymer.

Our designed reduced Schiff bases contain both H-bond donor (primary amine, $-NH_2$ and secondary amine, –NH–) and H-bond acceptor sites (pyridine moiety and NO_2 group containing ''O'' atom, Scheme 2). We expect that they would be ideal receptors for anions or neutral molecules owing to both H-bond accepting and H-bond donating capability. Therefore, we have chosen dihydrogenphosphate as a guest molecule, which has both H-bond acceptor ''O'' and ''O^-'' atoms and H-bond donor –OH groups (Scheme 2).

Experimental

Materials and methods

All reagents and solvents were used as received from commercial sources without further purification. Tetrabutylammonium



Scheme 1 Compounds used in these studies.

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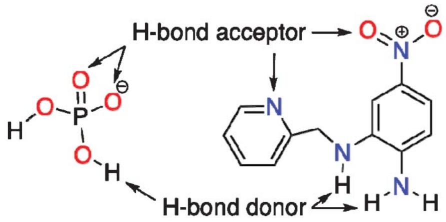
† CCDC reference numbers CCDC 867103 (**2**), 867102 (**3**), 867417 ($\mathbf{2}{\cdot}H_2PO_4^-$) and 867101 ($\mathbf{3}{\cdot}H_2PO_4^-$). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25502b



Scheme 2 H-Bond donors and acceptors in dihydrogenphosphate and receptor **2**.

dihydrogenphosphate ($Bu_4N^+H_2PO_4^-$) was purchased from Sigma-Aldrich Chemical Company.

IR spectra (KBr pellet, 4000–400 cm^{-1}) were recorded on a Parkin Elmer model 883 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker, Avance 300 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as internal standard.

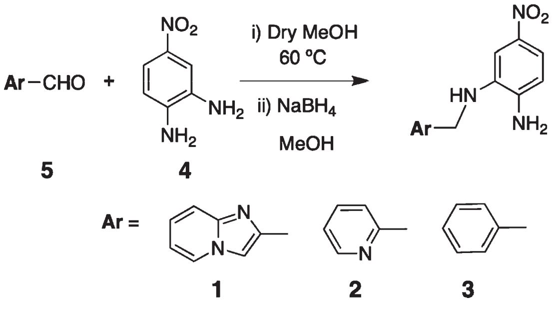
Suitable single crystals of compounds **2**, **3**, **2**·H_2PO_4 and **3**·H_2PO_4 were mounted at 293(2) K on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The crystal was positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structure was solved using the Patterson method by using SHELXS97. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program.[15] All calculations were carried out using SHELXS97, SHELXL97, PLATON99, ORTEP-32 and WinGX system Ver-1.64.[16]

Syntheses

Compounds **2** and **3** were prepared by following the synthetic procedure[14] of compound **1** and are presented in the following synthetic scheme 3.

Compound **2**. Yield: 85%, ^{1}H NMR in CD_3CN, 300 MHz, δ (ppm): 4.50 (s,–CH_2–), 4.85 (s,–NH_2), 6.70 (d, J = 8.7 Hz, 1H), 7.23–7.76 (m, 5H), 8.57 (d, J = 4.8 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_3CN, 20 °C) δ (ppm) 48.52, 105.68, 112.01, 115.69, 116.92, 121.31, 121.96, 134.57, 136.42, 142.89, 148.74; IR (KBr): 3419, 3350, 3170, 1667, 1636, 1598, 1580, 1523, 1492, 1465, 1433, 1386, 1341, 1301, 1252, 1210, 1097, 1000, 841, 766, 744, 641 cm^{-1}. ESI-MS (m/z) calc. for M$^+$ ($C_{12}H_{12}N_4O_2$) 244.09, found 245.04 (M + H)$^+$.

Compound **3**. Yield: 80%, ^{1}H NMR in CD_3CN, 300 MHz, δ (ppm): 4.42 (s,–CH_2–), 4.84 (s,–NH_2), 6.68 (d, J = 8.4 Hz, 1H), 7.29–7.46 (m, 7H), 7.57 (d, J = 8.7 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_3CN, 20 °C) δ (ppm) 47.00, 105.60, 111.85, 115.60, 116.89, 126.78, 127.13, 128.14, 134.46, 138.73, 142.80; IR (KBr): 3473, 3380, 1638, 1600, 1576, 1522, 1475, 1454, 1429, 1358, 1274, 1149, 1105, 859, 733, 696 cm^{-1}. ESI-MS (m/z) calc. for M$^+$ ($C_{13}H_{13}N_3O_2$) 243.10, found 244.00 (M + H)$^+$.



Scheme 3 Synthetic scheme of compounds.

Results and discussion

Compounds **2** and **3** were synthesized according to our published procedure as that of compound **1**.[14] The purity and characterization of the compounds were verified by ^{1}H and ^{13}C NMR, IR and mass spectrometric analysis. Interestingly, single crystals suitable for X-ray diffraction for all three compounds were obtained from methanol–water mixtures. Crystal data and refinement details for compounds **2**, **3**, **2**·$H_2PO_4^-$ and **3**·$H_2PO_4^-$ are given in Table 1.

Compound **2** was crystallized in space group *C*2/*c*. Crystal analysis shows that the N atom of the pyridine molecule and N atoms of the *o*-phenylenediamino moiety are at a relative twist angle of 62.54° (Fig. 1). The crystal lattice shows that compound **2** forms a "scissors" like dimer and is connected by four intermolecular H-bonding interactions. In such cases one molecular unit containing primary amine (N1H1B) and secondary amine (N2H2A) act as H-bond donors and the other molecular unit containing the pyridine N4 atom acts as a H-bond acceptor and *vice versa* (distances 3.206 and 3.217 Å respectively, Fig. 1, Table 2). Due to these intermolecular H-bonding interactions, two molecular units come close together, and two pyridine rings are further connected by π–π interaction (3.790 Å). Furthermore, the N1H1A atom of the primary amine is connected with another molecular unit containing O1 and O2 atoms of the –NO_2 group through H-bonds (distances 3.364 and 3.265 Å, respectively) and forms a 1D supramolecular polymer (Fig. 2).

Interestingly, a similar type of "scissors" like structure has been reported in case of compound **1** (Fig. 1).[14] However, in such cases the twist angle between *o*-phenylenediamine and imidazo[1,2-*a*]pyridine moieties is about ~76.38°, which is slightly higher than in case of compound **2** (~62.54°). As a result an increase in intermolecular donor–acceptor distances were observed and hence, a solvent (water) molecule is required as an intermediate H-bond donor–acceptor during the crystallization of compound **1**. The water molecule O1w acts as H-bond acceptor and forms an H-bond with H-bond donor N2H2, N3H3C of *o*-phenylenediamine. On the other hand, the N5 atom of the imidazo[1,2-*a*]pyridine moiety acts as H-bond acceptor and O1wH1 (water) acts as H-bond donor. Because of these intermolecular H-bonding interactions two imidazole[1,2-*a*]pyridine moieties come close together and are connected by strong π–π interaction. Interestingly, these π–π interactions facilitate to form a further π–π interaction between two nitrobenzene moieties (in compound **1**, Fig. 3). However, such type of π–π interaction is absent in the case of compound **2** (Fig. 1).

Table 1 Crystal data and refinement details for compounds **2**, **3**, **2**·$H_2PO_4^-$ and **3**·$H_2PO_4^-$

Parameters	**2**	**3**	**2**·$H_2PO_4^-$	**3**·$H_2PO_4^-$
Formula	$C_{12}H_{12}N_4O_2$	$C_{13}H_{13}N_3O_2$	$C_{28}H_{52}N_5O_7P$	$C_{29}H_{53}N_4O_7P$
M_r	244.26	243.27	601.72	600.72
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*2$P2_1/c$	*P*-1	$P2_1/n$
a/Å	15.007(13)	13.1110(4)	9.602(5)	9.7398(15)
b/Å	10.891(9)	5.9151(2)	13.194(5)	14.884(2)
c/Å	16.137(14)	16.3090(5)	15.104(5)	23.545(4)
α/°	90	90	113.014(5)	90
β/°	114.279(10)	110.012(1)	94.332(5)	98.880(2)
γ/°	90	90	105.702(5)	90
V/Å^3	2404(4)	1188.44(7)	1659.6(12)	3372.4(9)
Z	8	4	2	4
D_c/g cm^{-3}	1.350	1.365	1.204	1.181
R_{int}	0.1012	0.0457	0.0678	0.1177
No. unique data	2289	2431	6579	6400
No. data with $I > 2\sigma(I)$	1235	1958	5090	3731
*R*1, *wR*2	0.0469, 0.1347	0.0358, 0.1124	0.0532, 0.1670	0.0676, 0.2101
GOF on F^2	0.959	1.031	1.045	1.004

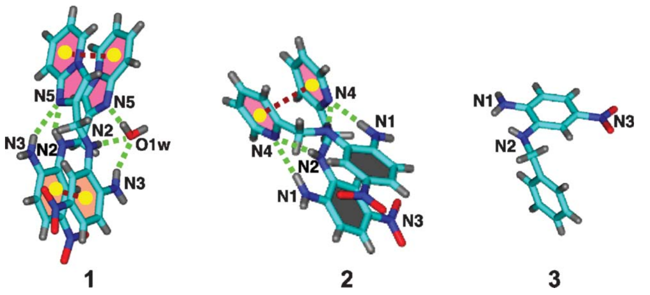


Fig. 1 "Scissors" like molecular dimers of compounds **1** and **2** and molecular structure of compound **3**.

In compound **3**, the phenyl ring and *o*-phenylenediamine containing the benzyl ring are approximately perpendicular to each other by an angle of 82.31°. It is noteworthy to mention that due to the absence of H-bond acceptor moieties (present in **1** and **2**), compound **3** does not exhibit any "scissors" like dimer (Fig. 1). However, an interesting intermolecular H-bonding polymer was observed. The primary amine (N1H1B) and secondary amine (N2H2A) were H-bonded with the next molecular unit containing O2 of nitro group (distances 3.127 and 3.212 Å, respectively, Table 3) and forms a 1D polymer (Fig. 4, top). The other N1H1A atom of the primary amine also forms an H-bond with another molecular unit nitro group containing O1 atom within the distance of 3.173 Å and leads to a 2D supramolecular network (Fig. 4, bottom).

According to the previous reported literature,[17] generally the dihydrogenphosphate ion can form a dimer through self-complementary (–OH and O$^-$ ion) H-bonding interaction. The remaining "–OH" group and "=O" atom are available as H-bond donor and H-bond acceptor, respectively, with the receptor or ligand. Our designed molecular systems have self-complementary H-bond donors and acceptors, which is suitable to interact with the dihydrogenphosphate molecule.

Table 2 Different types of H-bonding interactions in **2**

[a]D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
N1–H1A···O2	0.82(2)	2.49(2)	3.265(4)	160(2)
N1–H1B···N4	0.99(3)	2.22(3)	3.206(4)	175(2)
N2–H2A···N4	0.78(2)	2.45(2)	3.217(4)	165(2)

[a] D is donor and A is acceptor.

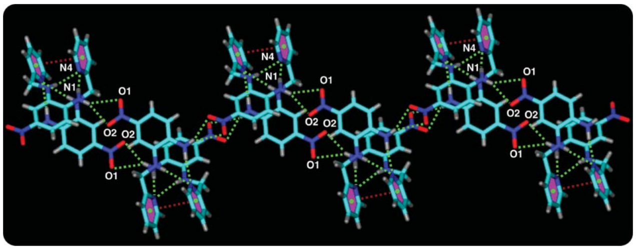


Fig. 2 1D polymer through intermolecular H-bonding/π interactions in compound **2**.

Compounds **2** and **3** interact with tetrabutylammonium dihydrogenphosphate to form complexes **2**·$H_2PO_4^-$ and **3**·$H_2PO_4^-$, respectively. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a mixture of an acetonitrile solution of each compound and tetrabutylammonium dihydrogenphosphate salt at room temperature.

The crystal analysis shows that mixture of compound **2** and dihydrogenphosphate (*n*-$Bu_4N·H_2PO_4$) was crystallized in space group *P*-1 with molecular formula [**2**·H_2PO_4·(*n*-Bu_4N)·H_2O] (Fig. 5, middle). In the presence of dihydrogenphosphate ion, H-bond donors N1 and N2 atoms of the *o*-phenylenediamine

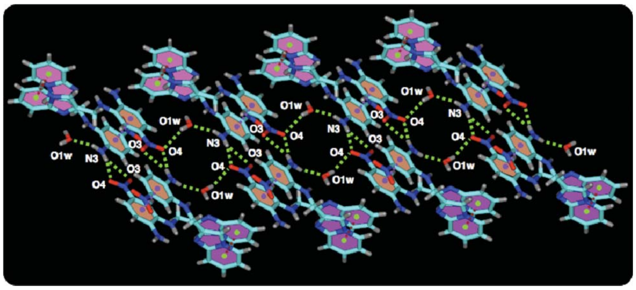


Fig. 3 Polymeric chain of "scissor" like structure of compound **1**.

Table 3 Different types of H-bonding interactions in **3**

[a]D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
N1–H1A···O1	0.90(2)	2.51(2)	3.173(2)	131.0(16)
N1–H1B···O2	0.86(3)	2.31(3)	3.127(19)	159(2)
N2–H2A···O1	0.78(2)	2.50(2)	3.212(2)	152.6(17)

[a] D is donor and A is acceptor.

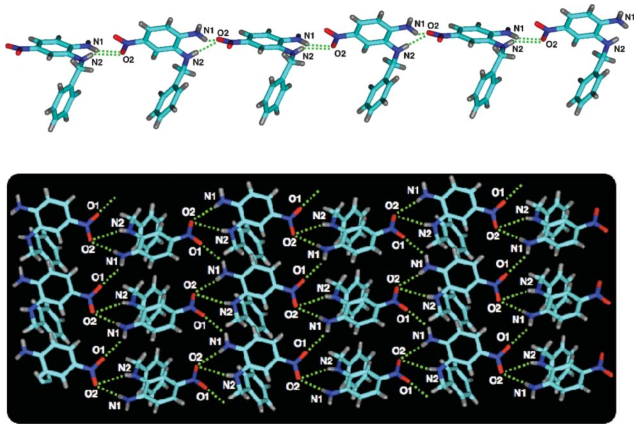


Fig. 4 1D polymer through intermolecular H-bonding (top) and 2D polymer through intermolecular H-bonding (bottom) of compound **3**.

moiety and the H-bond acceptor N4 atom of pyridine molecule are twisted by an angle of 90.18° and are pointing to opposite directions. As a result, the N4 atom of the pyridine moiety does not take part in H-bond formation but facilitates the incoming dihydrogenphosphate ion for dimerization with the other dihydrogenphosphate unit (Fig. 6, middle). Crystal structure analysis shows that primary amine (N1H1B) and secondary amine (N2H2A) forms a hydrogen bond with O7 of the dihydrogenphosphate ion (distances 3.043 and 2.976 Å respectively). Interestingly, one water molecule O3H3B is also H-bonded with the O7 atom (distance 2.662 Å) (Fig. 5 middle, Table 4).

In contrast, for the **1**·$H_2PO_4^-$ complex,[14] dihydrogenphosphate ion reinforces the N3 atom of imidazo[1,2-*a*]pyridine moiety pointing unidirectionally with respect to the N1 and N2 atoms of the amine group. As a result, O3 and O5 of $H_2PO_4^-$ ion form H-bonds with N3, N1 and N2 atoms of **1**. These types of H-bonding interactions "locked" the free rotation of imidazo[1,2-*a*]pyridine moiety of compound **1** (Fig. 5, left).[14]

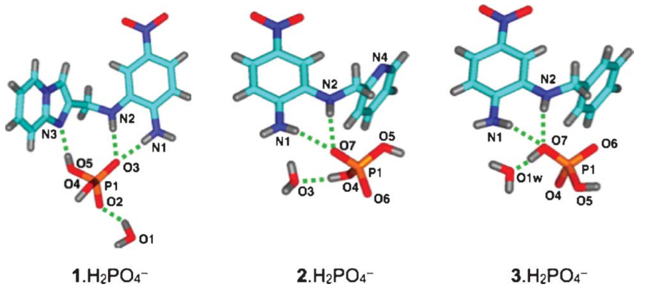


Fig. 5 Molecular structures of **1**·H_2PO_4, **2**·H_2PO_4 and **3**·H_2PO_4 (tetrabutylammonium cations, Bu_4N^+) omitted for clarity

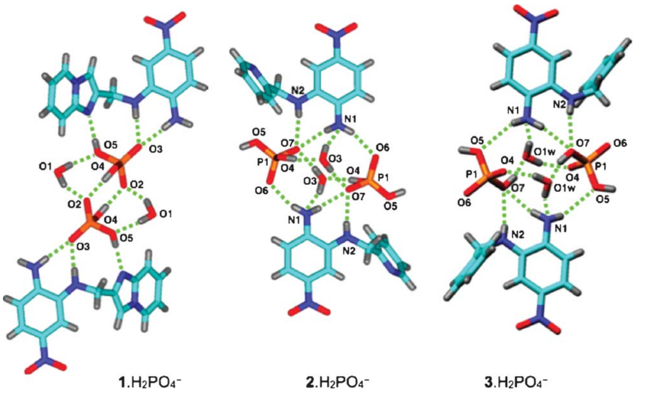


Fig. 6 Dimers of **1**·H_2PO_4·H_2O, **2**·H_2PO_4·H_2O and **3**·H_2PO_4·H_2O (tetrabutylammonium cations, Bu_4N^+) omitted for clarity.

Table 4 Different types of H-bonding interactions in **2**·H_2PO_4

[a]D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
O3(w)–H3A···N1	0.84(5)	2.44(5)	3.162(4)	145(4)
O3(w)–H3B···O7	0.85(3)	1.86(3)	2.707(3)	176(4)
O4–H4A···O3(w)	0.85(4)	1.81(4)	2.663(4)	173(3)
O5–H5A···O6	0.89(5)	1.64(5)	2.527(3)	177(5)
N1–H1A···O6	0.87(4)	2.19(4)	3.008(4)	157(4)
N1–H1B···O7	0.83(3)	2.23(3)	3.043(4)	166(3)
N2–H2A···O7	0.83(3)	2.15(3)	2.975(3)	171(3)

[a] D is donor and A is acceptor.

However, the crystal packing of **2**·$H_2PO_4^-$ shows that the O6 atom of dihydrogenphosphate ion is H-bonded with the next molecular unit containing the N1H1A atom and thus constructs a dihydrogenphosphate bridge dimer. The water O3 atom acts as H-bond acceptor and O4H4A atom of dihydrogenphosphate acts as H-bond donor (distance 2.663 Å) and water molecules act as a bridging agent between two dihydrogenphosphate dimers. Interestingly, the water molecule (O3H3A) is also H-bonded with the N1 atom of a primary amine (Table 4, 3.162 Å). Furthermore, the O5H5A atom of one dihydrogenphosphate acts as a H-bond donor and the other dihydrogenphosphate O6 atom acts as an H-bond acceptor and *vice versa* and forms a 1D polymer (Fig. 7). The 1D polymer is further connected by C–H –π interaction between two layers and forms a 2D supramolecular architecture (Fig. 8). Such type of dihydrogenphosphate–water polymer is hardly reported in the literature.[18]

Thus, the water molecule in **1**·H_2PO_4 (Fig. 6, left) and in **2**·H_2PO_4 (Fig. 6, middle) are H-bonded with dihydrogenphosphate

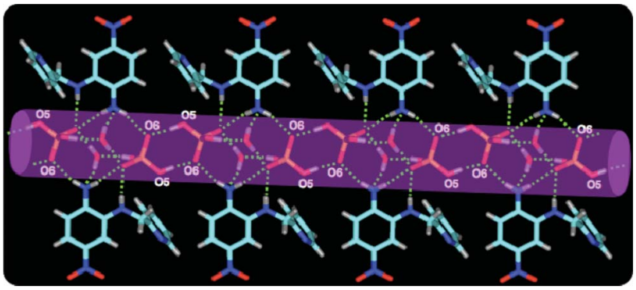


Fig. 7 1D framework through intermolecular H-bonding interactions in **2**·$H_2PO_4^-$ with 1D dihydrogenphosphate–water polymer.

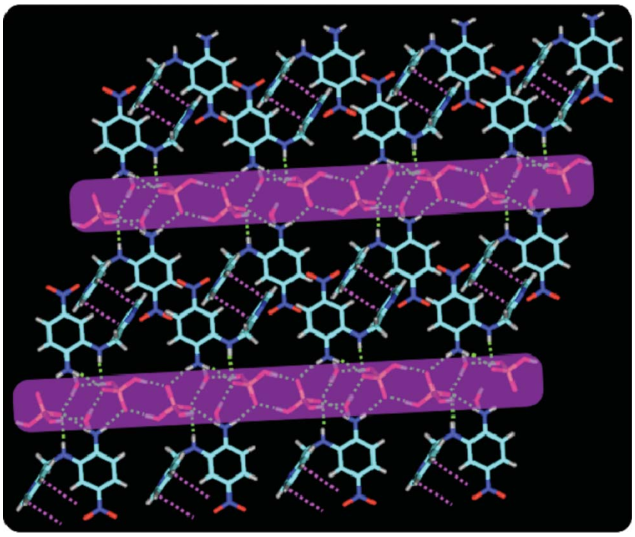


Fig. 8 2D architecture through intermolecular H-bonding/π interactions in $2{\cdot}H_2PO_4^-$ with 1D dihydrogenphosphate–water polymer.

in two different ways. In $1{\cdot}H_2PO_4$ the water molecule acts as a H-bond donor with two dihydrogenphosphate ions but in $2{\cdot}H_2PO_4$ the water molecule acts as an H-bond donor with one dihydrogenphosphate ion and an H-bond acceptor with the other dihydrogenphosphate ion. Furthermore, in $1{\cdot}H_2PO_4$ a dihydrogenphosphate–water cluster (Fig. 9 and 10) is formed through the water molecule, where the water O1 acts as a H-bond acceptor from the primary amine of N1 but in $2{\cdot}H_2PO_4$ a dihydrogenphosphate–water polymer is formed through a dihydrogenphosphate bridge, where the O5H acts as H-bond donor and O6 atom of another molecule acts as H-bond acceptor and *vice versa* (Fig. 7).

To examine the necessity of a pyridine/imidazo[1,2-*a*]pyridine] moiety as an H-bond acceptor for the formation of a dihydrogenphosphate complex we have designed and synthesized compound **3**, where one H-bond acceptor is absent compared to **1** and **2**. Interestingly, we also obtained single crystals from a 1 : 1 mixture of **3** and dihydrogenphosphate ion. The crystal structure analysis shows that complex crystallized in space group $P2_1/n$ with molecular formula $[3{\cdot}H_2PO_4(n\text{-}Bu_4N){\cdot}H_2O]$. The crystal structure shows that the *o*-phenylenediamine and benzyl moieties were deviated by an angle of ~83.96° from one another and form a stable conformer (Fig. 5, right). Additionally, the H-bonding interactions between compound **3** and dihydrogenphosphate ion are also similar with that of the H-bonding interactions between compound **2** and dihydrogenphosphate ion.

Table 5 Different types of H-bonding interactions in $3{\cdot}H_2PO_4$

[a]D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
O1w–H1w1···O4	0.8500	1.8300	2.584(5)	147.00
O1w–H2w1···N1	0.8500	2.2900	3.072(5)	153.00
O7–H7···O1w	0.8200	1.9200	2.633(4)	145.00
O5–H5A···O6	0.93(3)	1.57(3)	2.496(4)	178(3)
N1–H1A···O5	0.77(4)	2.58(4)	3.253(5)	147(3)
N1–H1B···O7	0.92(4)	2.19(4)	3.074(5)	161(3)
N2–H2A···O7	0.73(4)	2.28(4)	2.998(5)	171(4)

[a] D is donor and A is acceptor.

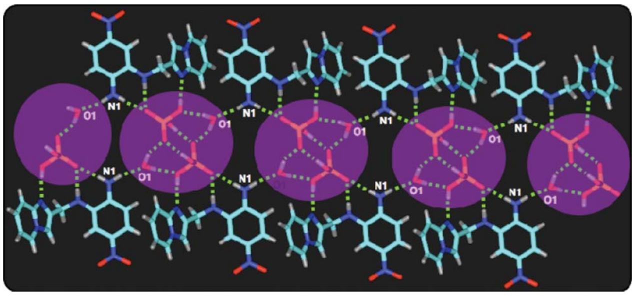


Fig. 9 Discrete dihydrogenphosphate–water cluster through intermolecular H-bonding interactions in $1{\cdot}H_2PO_4^-$.

In the complex $3{\cdot}H_2PO_4^-$, primary amine (N1H1B), and secondary amine (N2H2A) act as H-bond donors and form hydrogen bond with O7 of dihydrogenphosphate ion (distances 3.074 and 2.998 Å, respectively, Fig. 6, right and Table 5). Interestingly, one water molecule (O1wH1) is also H-bonded with the O4 atom of dihydrogenphosphate ion (distance 2.584 Å, Table 5).

The lattice diagram shows that the N1H1A atom is further H-bonded with another dihydrogenphosphate ion containing O5 atom (distance 3.253 Å). The O7H7 atom of dihydrogenphosphate acts as H-bond donor and O1w (water molecule) acts as H-bond acceptor. Importantly, here the water molecule (O1wH2) forms an H-bond with the primary amine (N1, distance 3.072 Å). Furthermore, dihydrogenphosphate ions form dimers through intermolecular H-bonding interactions, where the O5H5A atom of one dihydrogenphosphate ion acts as an H-bond donor and O6 atom of another dihydrogenphosphate ion acts as H-bond acceptor and *vice versa* (distance 2.496 Å) and forms a 1D dihydrogenphosphate–water polymer (Fig. 11).

In summery, we have structurally characterized reduced Schiff bases having a common nitro-*o*-phenylenediamine moiety, which form interesting supramolecular architectures. Among these, Schiff bases containing pyridyl/imidazole moieties form molecular "scissors". Moreover, these compounds act as efficient hosts to interact with biologically important dihydrogenphosphate guest, therefore, in all compounds (**1**, **2** and **3**) the *p*-nitro-*o*-phenylenediamine moiety plays an important role for the

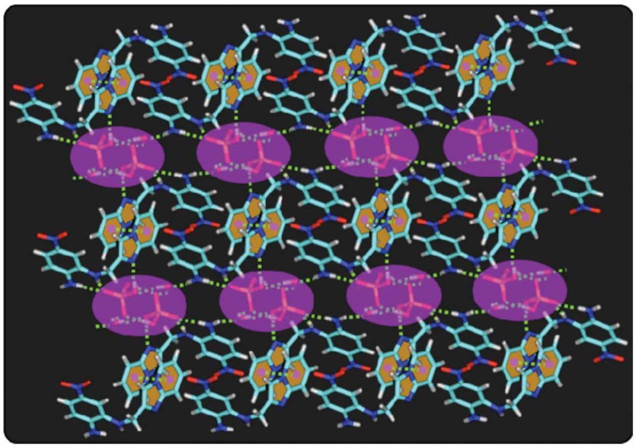


Fig. 10 2D architecture through intermolecular H-bonding/π interactions in $1{\cdot}H_2PO_4^-$ with discrete dihydrogenphosphate–water cluster.

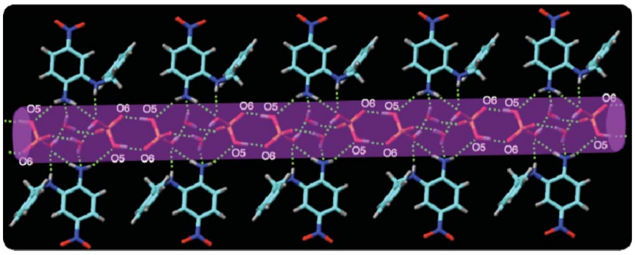


Fig. 11 1D framework through intermolecular H-bonding interactions in **3**·$H_2PO_4^-$ with 1D dihydrogenphosphate–water polymer.

formation of water–dihydrogenphosphate self-assemblies. Importantly, 'host–guest' complexation occurs through intermolecular H-bonding interaction and results in an unprecedented 1D dihydrogenphosphate–water polymer $(H_2PO_4\cdot H_2O)_n^{n-}$. In the present studies we try to explore how to construct an efficient host for the recognition of dihydrogenphosphate guest and the results clearly shows that *p*-nitro-*o*-phenylenediamine moiety is an effective recognizing unit in crystal engineering for preparing dihydrogenphosphate–water hybrid supramolecular polymers.

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