

Hydrogen-Bonded Self-Assembly of Pyridinium and Anilinium Bisphenols Mediated by the Hydrogen Difluoride Ion: Towards Control of C–H... π (Aromatic) Interactions

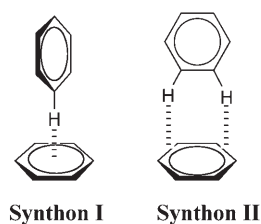
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Abstract: The role of C–H... π and C–H...O interactions in HF₂[−]-assisted self-assembly of nitrogen-containing bisphenols are investigated. Unusual control on the end–face and edge–face geometries of aromatic C–H... π interactions by a water molecule in the 4-[(4-hydroxy-3,5-dimethylphenyl)methyl]pyridinium difluoride lattice is observed. The bis(4-hydroxy-3,5-dimethylphenyl)(4-ammoniohenyl)-methane·HF₂[−] self-assembles through the formation of hydrogen-bonded cyclic hexamers.

Keywords: bisphenols • fluorides • hydrogen bonds • pi interactions • self-assembly

Introduction

The ability to design and control the self-assembly process in molecules through weak intermolecular interactions^[1–2] is intrinsically related to the understanding of molecular recognition. In particular, the weak C–H... π interactions^[3–8] are crucial in determining the conformation of organic molecules, in chiral recognition, and in protein structure. Anion-assisted molecular assembly and anion coordination^[9–13] are influenced by hydrogen bonding. This forms the basis for studying selective binding of anions by natural and artificial molecular receptors.^[14–17] Halides can also assist in the formation of directed self-assemblies from different organic^[18,19] and organometallic species.^[20–23] The coordination ability of fluoride,^[24] and the influence of both fluorine and the fluoride ion in molecular assemblies through hydrogen bonding and electrostatic interactions is actively being investigated.^[18,19,24–29] In this report, we show the effect of HF₂[−] ion on the hydrogen-bonded assembly of pyridinium and anilinium bisphenols. The most remarkable feature of the HF₂[−]-assisted assembly of pyridinium bisphenol is the recognition of two distinct aromatic C–H... π interactions involving the aromatic units corresponding to end–face and edge–face geometries (synthons **I** and **II**). We found unusual control on the aromatic C–H... π interactions by a water mole-

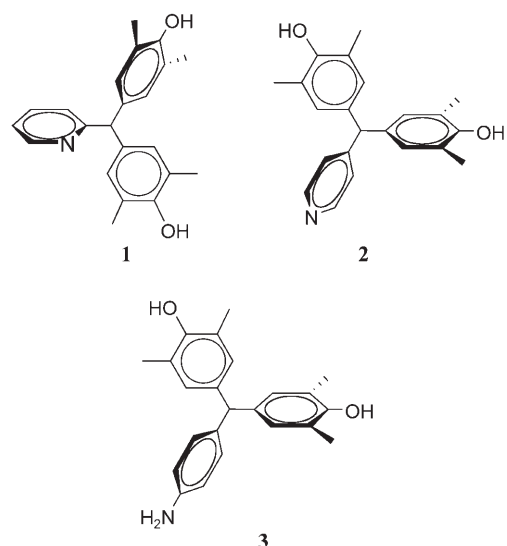


cule in the 4-[(4-hydroxy-3,5-dimethylphenyl)methyl]pyridinium difluoride lattice, given the fact that such interactions are extremely important in physiological environment.

Results and Discussion

To understand the role of weak interactions in HF₂[−]-assisted assembly, we have taken up structural study of HF₂[−] salts of nitrogen-containing bisphenols (**1–3**). It was recently shown that selective guest–host binding can be achieved in such motifs controlled by donor–acceptor interactions.^[30] The chloride- and bromide-assisted assemblies in the protonated form of **2** have T-shaped hydrogen-bonding environments around the halides.^[31] Out of compounds **1–3** we already know the structures of **2** and **3**,^[30,31] therefore, we determined the crystal structure of **1** to understand its packing pattern and the contribution of weak interactions to the crystal packing. We found that the molecules of **1** have a propeller-like shape and self-assemble into a structure with noncovalent interactions. The molecules are interconnected

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with each other by O–H...N and O–H...O interactions as shown in Figure 1. The self-assembled structure is further held by a C–H...O interaction between a phenolic O–H and C–H group of the ring containing methyl substituents. The

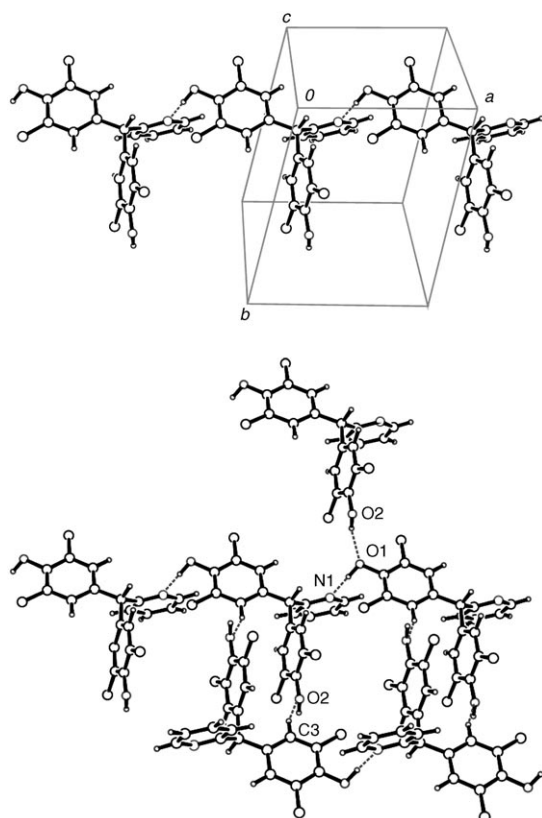


Figure 1. Top: Intermolecular O–H...N hydrogen bonding in **1** leads to one-dimensional chains that run parallel to the crystallographic *a* axis. Bottom: Intermolecular C3–H...O2 interactions in **1** connect two one-dimensional hydrogen-bonded chains that run parallel to the crystallographic *a* axis.

donor–acceptor bond lengths and angles contributing to the self-assembly are listed in Table 1.

Table 1. Hydrogen-bond geometry [distances in Å, angles in °] for compound **1**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠D–H...A
O2–H...O1 ^[a]	0.87	1.98	2.802	157.8
O1–H...N1 ^[b]	0.90	1.89	2.734	153.6

[a] Symmetry transformation: *x*+1, *y*+1, *z*. [b] Symmetry transformation: *x*–1, *y*, *z*.

Compounds **1–3** can be easily protonated in solution by hydrofluoric acid and the salts are obtained in the form of HF₂[–]. The crystal structure of each of the HF₂[–] salts has been determined. The proton NMR spectra of the compound **1** and **1**·H₂F₂ (**1a**) in methanol (Figure 2) show that

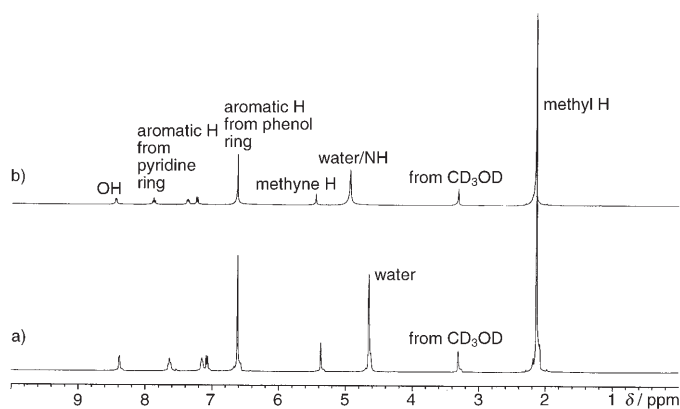


Figure 2. ¹H NMR spectra of a) **1** and b) **1a** in [D₄]methanol at room temperature.

there is a clear difference in the aromatic signals that arise from the pyridine rings in these two cases. This difference indicates the effect of protonation of the nitrogen atom, which reduces the electron density of the ring. The reduction in electron density at *ortho*-position shifts the signal of the hydrogen atom in the *ortho*-position with respect to the nitrogen atom towards a higher value.

Crystals of compound **1a** were obtained upon slow evaporation of a solution of compound in aqueous methanol containing aqueous hydrofluoric acid; it crystallizes in the space group *P2₁/n*. The HF₂[–] ions are held in the lattice through a network of five intermolecular hydrogen bonds (Figure 3); apart from the N⁺–H...F1 (*d*(N...F1) 2.618 Å, ∠169.5°) and O1–H...F1 (*d*(O1...F1) 2.649 Å, ∠143.9°) hydrogen bonds, the F1 atom is involved in a weak C–H...F (*d*(C7...F1) 3.390 Å, ∠139°) interaction with C7–H as the hydrogen-bond donor. It is observed that the three hydrogen bonds involving F1 adopt a pyramidal geometry. The HF₂[–] ion has a slightly bent geometry (171.8°) and the two H...F bond lengths are found to be 1.01 Å and 1.28 Å; the F...F distance is 2.295(2) Å, which is within the normal range of 2.20–2.30 Å^[32] for HF₂[–] ions. Important donor–acceptor bond

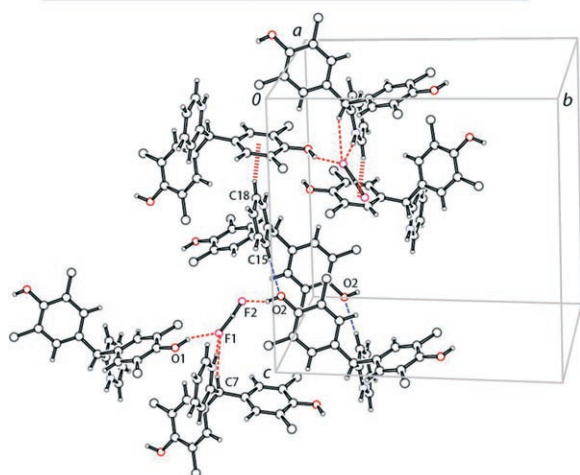
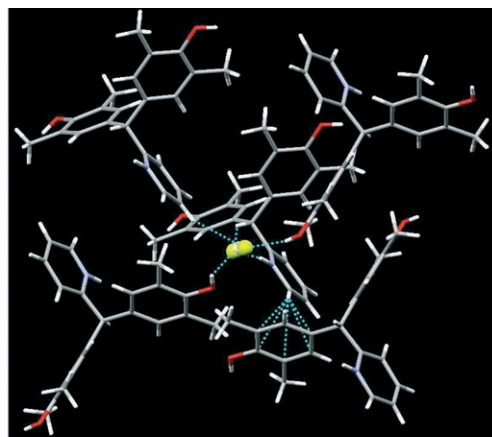


Figure 3. Top: Interactions between the HF_2^- ion and its four neighbors in **1a**. Bottom: Hydrogen-bonding interactions involving the hydroxy groups, the pyridinium $\text{N}^+\text{-H}$ group of **1**, and the weak $\text{C18-H}\cdots\pi$ interaction.

lengths and bond angles contributing to the assembly are listed in Table 2.

Two hydrogen bonds involving the HF_2^- ion are centered on F2, and include a strong $\text{O2-H}\cdots\text{F2}$ ($d(\text{O2}\cdots\text{F2})$ 2.759 Å, \angle 154.4°) hydrogen bond and a weak $\text{C17-H}\cdots\text{F2}$ ($d(\text{C17}\cdots\text{F2})$ 3.504 Å, \angle 155.6°) interaction. Thus, each of the HF_2^- ions is hydrogen bonded to four neighboring molecules of **1** as shown in Figure 3.

The remarkable feature of the structure of $\mathbf{1}\cdot\text{H}_2\text{F}_2$ is the presence of an aromatic $\text{C18-H}\cdots\pi$ interaction ($d(\text{C}\cdots\pi)$ 3.364 Å, \angle 148.6°) involving the C18-H as the donor and the aromatic ring of the 4-hydroxy-2,6-dimethylphenyl unit as the acceptor (Figure 3). Apparently, protonation of the pyridine nitrogen atom causes the hydrogen atom of the adjacent C18-H bond to behave as a soft acid thereby inducing the $\text{C-H}\cdots\pi$ (aromatic) interaction. The geometrical parameter for this aromatic $\text{C-H}\cdots\pi$ interaction ($d(\text{H}\cdots\pi)$ 2.49 Å) is in accordance with the reported values described

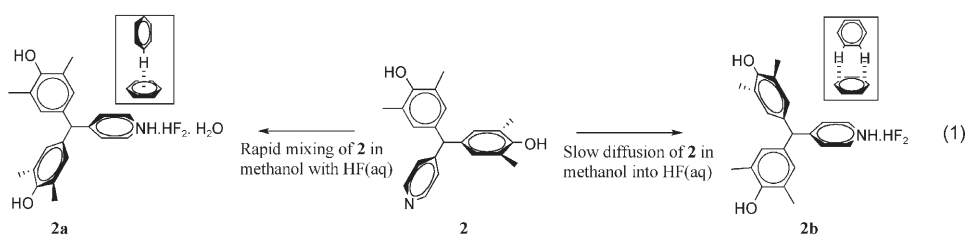


Table 2. Hydrogen bond geometry [distances in Å, angles in °] for compound **1a**.

D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{D-H}\cdots\text{A}$
F2-H...F1	1.01	1.28	2.295	171.9
N1-H...F1	0.92	1.70	2.618	169.5
O1-H...F1 ^[a]	0.91	1.86	2.649	143.9
O2-H...F2 ^[b]	0.87	1.98	2.795	154.4

[a] Symmetry transformation: $-x+0.5, y+0.5, -z+1.5$. [b] Symmetry transformation: $-x+0.5, y-0.5, -z+1.5$.

elsewhere.^[3-8] Similar aromatic $\text{C-H}\cdots\pi$ interactions are absent in the structure of **1**, which shows that the molecules assemble into one-dimensional chains that run along the a axis through $\text{O-H}\cdots\text{N}$ and $\text{C-H}\cdots\text{O}$ hydrogen bonds.

Protonation of **2** with hydrofluoric acid in aqueous methanol led to the formation of two polymorphic compounds [Eq. (1)]. It was found that rapid addition of a warm solution of **2** in methanol to a cold solution hydrofluoric acid in water results in the formation of a white crystalline solid (**2a**), which crystallizes in the monoclinic $P2_1/c$ space group. Compound **2a** contains the protonated form of **2**, the HF_2^- ion, and a molecule of water in 1:1:1 stoichiometry. The compound can be distinguished from **2** by the solid-state IR spectrum, in which a broad absorption band at 3280 cm^{-1} due to O-H stretching is observed for **2a**.

The presence of aromatic $\text{C-H}\cdots\pi$ interactions in **2a** is reflected as an additional absorption at 3085 cm^{-1} (marked as * in Figure 4). It should be pointed out that the presence of $\text{C-H}\cdots\text{O}$ ^[33-37] or aromatic $\text{C-H}\cdots\pi$ interactions in molecular assemblies can be recognized^[38-41] by a blue-shift of the IR absorption frequencies arising from C-H stretching. Analogous hydrogen-bonded assemblies of 4-[(4-hydroxy-3,5-dimethylphenyl)methyl]pyridinium chloride and bromide in the solid-state^[31] have shown that presence of the chloride

and bromide ions lead to the formation of hydrogen-bonded ribbons that are, however, devoid of significant aromatic $\text{C-H}\cdots\pi$ interactions involving the pyridinium units.

In contrast slow diffusion of a solution of **2** in methanol into aqueous hydrofluoric acid results in the 1:1 salt of **2** with H_2F_2 . This compound, **2b** is a polymorph of **2a** and crystallizes from the aqueous methanol in monoclinic space group $P2_1/n$. The packing structures of the two polymorphs are shown in Figure 5. In case of **2a**, the presence of the water molecules and the HF_2^- ion leads to the formation of one-dimensional channels running along the crystallographic c axis, while in **2b** the molecules self-assemble through hydrogen bonding to give two-dimensional molecular sheets.

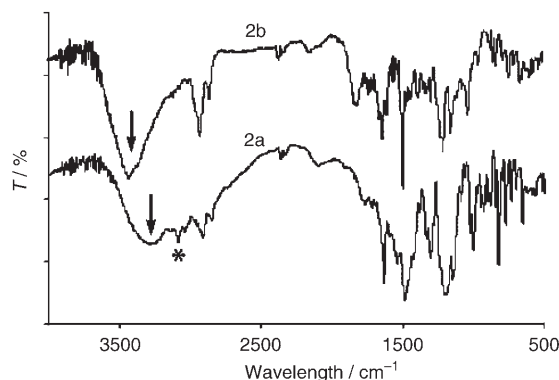


Figure 4. Solid-state FTIR spectra (KBr) of **2a** and **2b** showing the differences in the O–H and the C–H stretching regions.

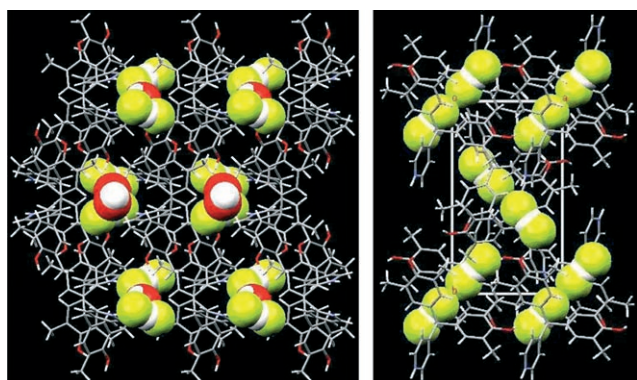


Figure 5. Packing structures of the two polymorphs, **2a** (left) and **2b** (right) viewed along the crystallographic *c* axis.

In the structure of **2a**, the HF_2^- ion is hydrogen bonded to three molecules of **2** and a molecule of water. As shown in Figure 6, the pyridinium $\text{N}^+\text{--H}$ moiety forms a strong hydrogen bond with F1 ($d(\text{N}\cdots\text{F}1)$ 2.656 Å, \angle 161.9°), which is slightly longer than in **1a**. The water molecule is strongly hydrogen bonded to F1 ($d(\text{O}3\cdots\text{F}1)$ 2.355 Å, \angle 168.5°) and $\text{O}1\text{--H}$ ($d(\text{O}3\cdots\text{O}1)$ 2.729 Å, \angle 145.3°) of **2**. The HF_2^- ion is also hydrogen bonded to $\text{O}2\text{--H}$ through F2 ($d(\text{O}2\cdots\text{F}2)$ 2.749 Å, \angle 148.6°) as the acceptor. The donor–acceptor bond lengths and angles for **2a** are listed in Table 3. Moreover, two weak $\text{C--H}\cdots\text{F}$ interactions involving C7–H and C15–H as donors and F2 as the acceptor are observed; the respective hydrogen bond geometries of the two interactions are $d(\text{C}\cdots\text{F}2)$ 3.351 (\angle 153.8) and 3.366 Å (140°), respectively. The intriguing aspect in this structure is the presence of an end–face aromatic $\text{C--H}\cdots\pi$ interaction ($d(\text{O}3\cdots\text{F}2)$ 3.292 Å, 144.6°), which is shown in Figure 6; this interaction involves C16–H as the hydrogen-bond donor and the aromatic ring of the 2,6-dimethylphenol group as the acceptor. In this case, the $\text{H}\cdots\pi$ (ring centroid) distance is found to be 2.49 Å, which is indicative of a reasonably strong interaction. In the lattice of the **2a**, a cooperative chain of hydrogen bonds involving the HF_2^- ions the pyridinium $\text{N}^+\text{--H}$ moiety, the hydroxy group, and the water molecule are

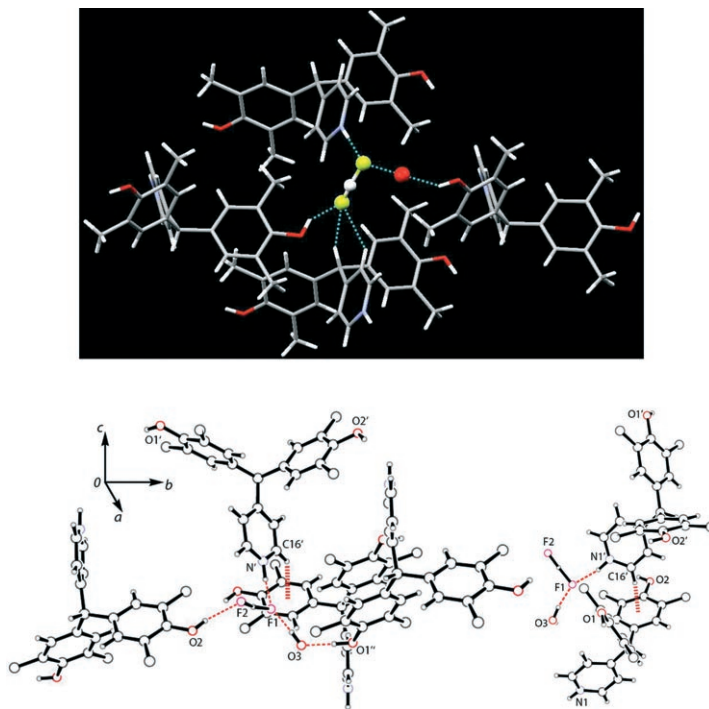


Figure 6. Top: Cooperative chain of hydrogen bonds in **2a** involving the HF_2^- ion, the pyridinium $\text{N}^+\text{--H}$ moiety, the hydroxy group, and the water molecule. Bottom left: Intermolecular $\text{N--H}\cdots\text{F}$ and $\text{O--H}\cdots\text{F}$ hydrogen-bonding interactions in **2a** involving the hydroxy groups, the pyridinium ion of **2**, and the HF_2^- ion (shown as red broken lines) and water. Bottom right: Weak aromatic $\text{C--H}\cdots\pi$ interactions.

Table 3. Hydrogen bond geometry [distances in Å, angles in °] for compound **2a**.

D–H...A	$d(\text{D--H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{D--H}\cdots\text{A}$
F2–H...F1	1.02	1.26	2.358	158.7
N1–H...F1	0.95	1.73	2.656	161.9
O2–H...F2 ^[a]	0.87	1.98	2.749	148.6
O1–H...O3 ^[b]	0.88	1.96	2.729	145.3
O3–H...F1 ^[c]	0.80	1.57	2.355	167.6

[a] Symmetry transformation: $-x+1, y+0.5, -z+0.5$. [b] Symmetry transformation: $x, y-1, z$. [c] Symmetry transformation: $-x+1, y+0.5, -z+0.5$.

formed, as shown in the Figure 6 (top). It should be mentioned that the hydrogen atoms bound to the water molecule are disordered and only one of them could be located. The donor–acceptor bond lengths that contribute to the formation of the self-assembled structure of **2a** are given in Table 3.

Absence of the water molecule in **2b** has a dramatic effect on the coordination environment of the HF_2^- ion as shown in Figure 7. The striking feature of the assembly in **2b** is the symmetrical disposition of hydrogen bonds about the HF_2^- ion. Each of the pyridinium $\text{N}^+\text{--H}$ moieties forms bifurcated hydrogen bonds with two HF_2^- ions, which are related by a mirror plane. Similarly the hydroxy groups of protonated **2** interact with F1 alone through $\text{O--H}\cdots\text{F}$ hydrogen bonds. The important distinction of the structure of **2b**

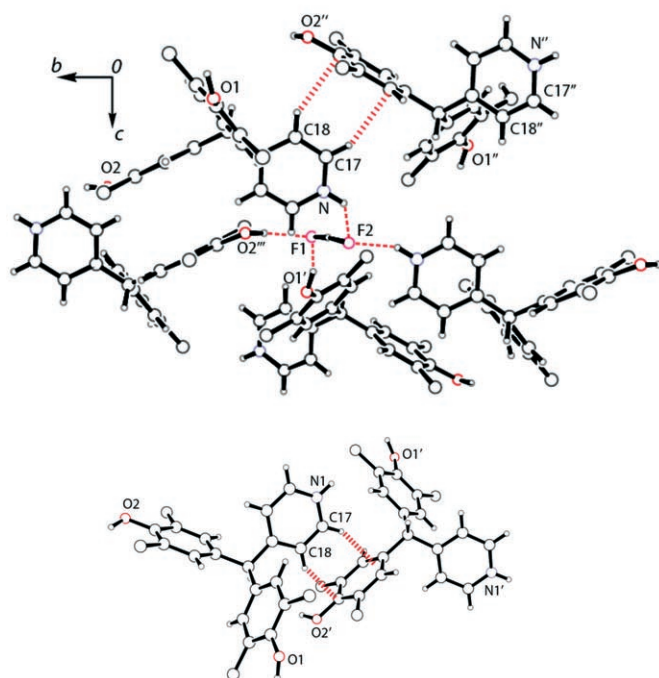
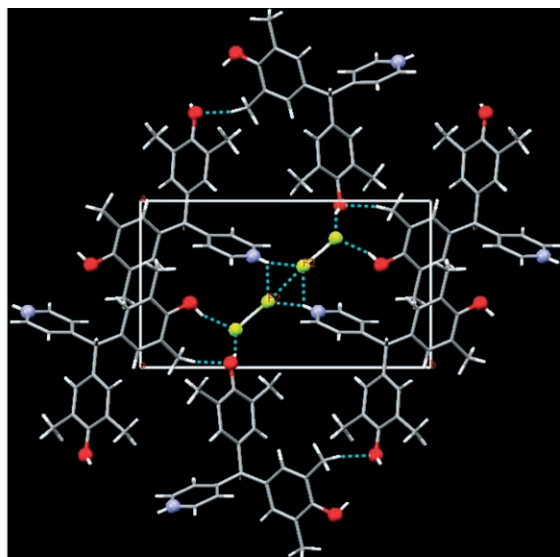


Figure 7. Top: Two-dimensional sheets in **2b**, in which the HF_2^- ion is symmetrically bonded to the hydroxy groups of the phenol and the pyridinium $\text{N}^+\text{-H}$ groups. Bottom left: Intermolecular $\text{N-H}\cdots\text{F}$ and $\text{O-H}\cdots\text{F}$ hydrogen bonding in **2b**. Bottom right: Aromatic $\text{C-H}\cdots\pi$ interactions between the pyridinium bisphenol molecules.

compared to that of either **1a** or **2a** is the presence of an edge-to-face approach (synthon **II**) of the pyridinium ring to the aromatic ring of the 2,6-dimethylphenol units. The centroid \cdots centroid distance in this case is 3.563 Å, and the geometry is apparently stabilized by two aromatic $\text{C-H}\cdots\pi$ interactions as shown in Figure 7. In the case of **1a** and **2a** the aromatic $\text{C-H}\cdots\pi$ interactions involving an end-to-face approach result in the T-shaped geometry (synthon **I**). The donor-acceptor bond lengths and angles in **2b** are listed in Table 4. The synthons **I** and **II** have been identified earlier in organic systems^[3] and different terminology has been

Table 4. Hydrogen bond geometry [distances in Å, angles in °] for compound **2b**.

D-H \cdots A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{D-H}\cdots\text{A}$
F1-H \cdots F2	0.97	1.26	2.234	171.6
N1-H \cdots F2	0.85	1.87	2.649	151.4
N1-H \cdots F2 ^[a]	0.86	2.34	2.891	122.6
O1-H \cdots F1 ^[b]	0.89	1.74	2.596	157.2
O2-H \cdots F1 ^[c]	0.87	1.89	2.729	160.4

[a] Symmetry transformation: $-x+1, -y+1, -z$. [b] Symmetry transformation: $-x+2.5, y-0.5, -z+0.5$. [c] Symmetry transformation: $x, y-1, z$.

used to represent them. For example alternative names for synthon **I** are point-to-face or T-shape aromatic $\text{C-H}\cdots\pi$ interaction and for synthon **II**, L-shape aromatic π interactions. However, since the orbital overlaps in these cases are between hydrogen and π -clouds and direction oriented, we prefer to refer to synthon **I** as having end-face and synthon **II** as having edge-face $\text{C-H}\cdots\pi$ interactions.

To rationalize the effect of the pyridinium ion on the occurrence of aromatic $\text{C-H}\cdots\pi$ interactions, we studied the crystal structure of the analogous 4-[bis-(4-hydroxy-3,5-dimethyl-phenyl)]methylanilinium difluoride, **3a**. The compound **3a** crystallizes as pink needles (space group $P\bar{1}$) from aqueous methanol containing hydrogen fluoride. In this compound, the HF_2^- ion is extensively hydrogen bonded to five protonated molecules of **3** (Figure 8), and is characterized by a short F \cdots F distance of 2.195(3) Å relative to the anion of **1a** described earlier.^[32] It is held in the lattice through three hydrogen bonds involving O1-H, O2-H and $\text{N}^+\text{-H}$ as donors and F1 as the acceptor. A weak $\text{C-H}\cdots\text{O}$ interaction ($d(\text{C}\cdots\text{O})$ 3.348 Å, \angle 159.7°) between the hydrogen atom of the methyl group and O2-H is observed; presumably, this interaction acts in a cooperative manner to increase the stability of the cyclic hexameric network of hydrogen bonds in the structure. Another hydrogen-bonding interaction involving the $\text{N}^+\text{-H}$ group as a donor and the F2 of the HF_2^- ion as an acceptor is also observed ($d(\text{N}\cdots\text{F2})$ 2.736 Å, \angle 168.9°). In this case, the $\text{N-H}\cdots\text{F}$ interaction is probably more electrostatic in nature, as expected in systems involving charged anions. These interactions lead to a cyclic hydrogen-bonded hexamer (synthon **III**) as shown in Figure 8. The donor-acceptor bond lengths and angles are listed in Table 5. To the best of our knowledge this is the first observation of the HF_2^- ion being involved in a cyclic hexameric system of hydrogen bonds. However, in this case $\text{C-H}\cdots\pi$ interactions are not observed,^[41-43] presumably because the activating effect of the $-\text{NH}_3^+$ ion is not extended into the aromatic ring system. Nonetheless $\text{N-H}\cdots\pi$ interactions are reported in the inclusion compound of **3** with toluene.^[30]

Conclusion

In conclusion, we have been able to show through crystallographic analysis that $\text{C-H}\cdots\pi$ interactions involving weakly

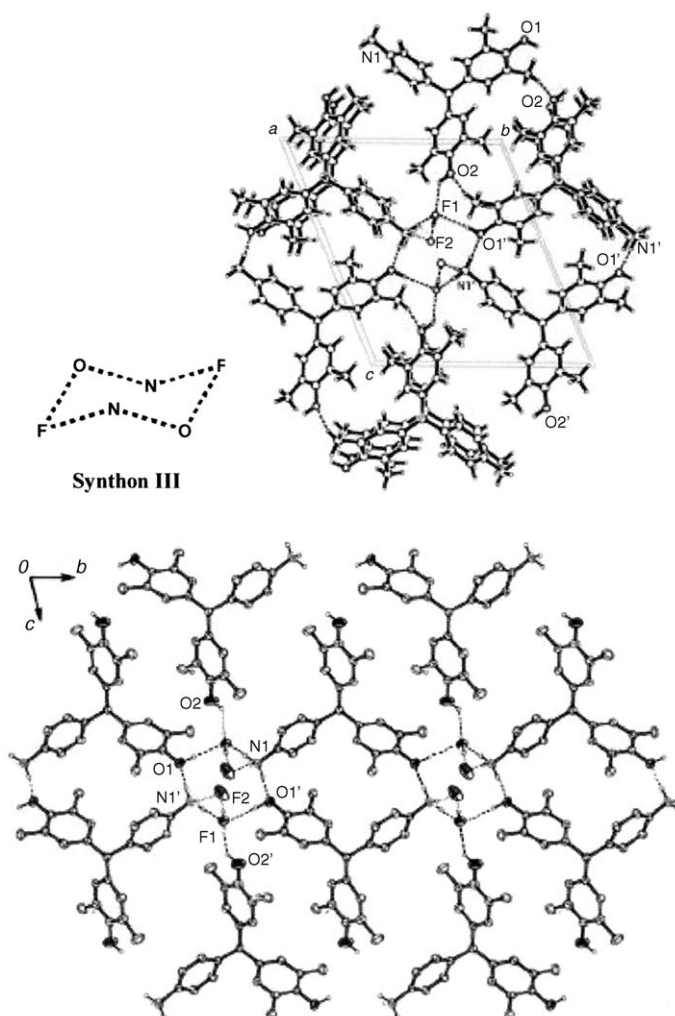


Figure 8. Top: Intermolecular N–H...F and O–H...F hydrogen-bonding between the hydroxy, the anilinium groups, and the HF₂⁻ ion leading to cyclic hydrogen bonded hexamers; weak C–H...O interactions in **3a** are shown. Bottom: Two-dimensional hydrogen-bonded assembly in **3a** incorporating synthon **III**.

Table 5. Hydrogen bond geometry [distances in Å, angles in °] for compound **3a**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠D–H...A
F1–H...F2	0.98	1.25	2.195	158.2
N1–H...F2 ^[a]	0.93	1.71	2.736	168.9
N1–H...F1 ^[b]	1.03	1.64	2.678	173.5
N1–H...O1 ^[c]	0.94	2.15	3.064	164.1
O1–H...F1 ^[d]	0.81	2.22	2.942	144.4
O2–H...F1 ^[e]	0.93	1.99	2.669	127.6

[a] Symmetry transformation: $-x+2, -y+1, -z+1$. [b] Symmetry transformation: $-x+1, -y+1, -z+1$. [c] Symmetry transformation: $-x+1, -y+2, -z+1$. [d] Symmetry transformation: $-x+1, -y+2, -z+1$. [e] Symmetry transformation: $x, y, z+1$.

acidic C–H groups are crucial factors in determining molecular self-assembly in the solid-state. From the study it transpires that these interactions are effective in the presence of water, and manifests itself in two distinct geometries. One of

them corresponds to an end–face approach of the aromatic rings, while the other invokes an edge–face approach, both of which were observed in the two polymorphic forms of 4-[(4-hydroxy-3,5-dimethylphenyl)]methylpyridinium difluoride. The ability to recognize these two distinct geometries for the C–H... π interactions in the two polymorphs **2a** and **2b** provides a new dimension to the understanding of weak intermolecular interactions in self-assembly, vis-à-vis in molecular recognition. The compound **3a** self-assembles through the formation of hydrogen-bonded cyclic hexamers and is in fact an important supramolecular synthon; however C–H... π interactions are not observed in this structure.

Experimental Section

The compounds **1–3** were prepared by a reported procedure^[31,44] and the corresponding difluoride salts were obtained from aqueous methanol containing hydrofluoric acid. The difluoride salts of **1–3** were prepared by adding a solution of the parent compound (0.5 mmol) in methanol (0.5 mL) into an aqueous HF (45%, 0.5 mL); the product could be subsequently obtained as a crystalline solid. Compound **2a** was prepared by adding a warm solution of **2** (0.17 g, 0.5 mmol) in methanol (0.5 mL; -45°C) to hydrofluoric acid (45%, 0.5 mL; $10\text{--}15^{\circ}\text{C}$). This on standing led to formation of **2a** as white crystalline solid. Compound **2b** was prepared by slow diffusion of a solution of **2** in methanol into hydrofluoric acid. For this purpose the solution of **2** (0.17 g, 0.5 mmol) in methanol (0.5 mL) was placed in a tube with a capillary end. This tube was placed in a solution of aqueous hydrofluoric acid (45%, 0.5 mL). Slow diffusion took place and on standing for two days resulted in the formation of **2b** in crystalline form. The crystals were collected and the structure was determined.

The X-ray data were collected at 296 K with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) by using a Bruker Nonius SMART CCD diffractometer equipped with graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated by using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations by using SHELXTL software. All the non-hydrogen atoms were refined in the anisotropic approximation against F^2 of all reflections. The hydrogen atoms, except those attached to N, O, and F were placed at their calculated positions and refined in the isotropic approximation; those attached to heteroatoms (N, O, and F) were located in the difference Fourier maps, and refined with isotropic displacement coefficients. Crystal parameters for the compounds reported here are as follows:

Compound 1: Pale yellow ($0.38 \times 0.32 \times 0.21 \text{ mm}^3$); C₂₂H₂₃NO₂; $M_r = 333.41$; triclinic $P\bar{1}$; $a = 8.9105(4)$, $b = 9.9939(6)$, $c = 11.8570(6) \text{ \AA}$; $\alpha = 113.398(3)$, $\beta = 101.408(3)$, $\gamma = 103.448(3)^{\circ}$; $Z = 2$; $V = 891.29(8) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.242 \text{ Mg m}^{-3}$; $\mu(\text{MoK}\alpha) = 0.079 \text{ mm}^{-1}$; Goof = 1.025; final $R1 = 0.0482$ for 5060 reflections with $I > 2\sigma(I)$; $R1 = 0.0754$, $wR2 = 0.1452$ for all data.

Compound 1a: Colorless ($0.43 \times 0.30 \times 0.23 \text{ mm}^3$); C₂₂H₂₅NO₂F₂; $M_r = 373.43$; monoclinic $P2_1/n$; $a = 8.4962(18)$, $b = 15.598(4)$, $c = 15.013(3) \text{ \AA}$; $\beta = 105.997(13)^{\circ}$; $Z = 4$; $V = 1912.6(7) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.297 \text{ Mg m}^{-3}$; $\mu(\text{MoK}\alpha) = 0.095 \text{ mm}^{-1}$; Goof = 1.035; final $R1 = 0.0557$ for 5775 reflections with $I > 2\sigma(I)$; $R1 = 0.0929$, $wR2 = 0.1768$ for all 25637 reflections.

Compound 2a: Colorless plates ($0.45 \times 0.25 \times 0.23 \text{ mm}^3$); C₂₂H₂₇NO₂F₂; $M_r = 391.45$; monoclinic $P2_1/c$; $a = 9.1686(14)$, $b = 15.999(3)$, $c = 14.899(2) \text{ \AA}$; $\beta = 107.603(9)^{\circ}$; $Z = 4$; $V = 2083.2(5) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.248 \text{ Mg m}^{-3}$; $\mu(\text{MoK}\alpha) = 0.094 \text{ mm}^{-1}$; Goof = 0.933; final $R1 = 0.0512$ for 5552 reflections with $I > 2\sigma(I)$; $R1 = 0.0926$, $wR2 = 0.1688$ for all 17436 reflections.

Compound 2b: Light pink (0.56 × 0.35 × 0.30 mm³); C₂₂H₂₅NO₂F₂; M_r = 373.43; monoclinic P2₁/n; a = 8.7837(16), b = 14.931(3), c = 15.672(3) Å; β = 102.987(11)°; Z = 4; V = 2002.8(7) Å³; ρ_{calcd} = 1.238 Mg m⁻³; μ(MoKα) = 0.089 mm⁻¹; Goof = 1.020; final R1 = 0.0591 for 5215 reflections with I > 2σ(I); R1 = 0.1031, wR2 = 0.1649 for all 19588 reflections.

Compound 3a: Pink (0.80 × 0.31 × 0.09 mm³); C₂₅H₂₇NO₂F₂; M_r = 387.46; triclinic P1̄; a = 5.4090(3), b = 13.6451(9), c = 15.2259(10) Å; α = 67.573(4), β = 89.159(4), γ = 85.682(4)°; Z = 2; V = 1035.70(11) Å³; ρ_{calcd} = 1.242 Mg m⁻³; μ(MoKα) = 0.09 mm⁻¹; Goof = 1.045; final R1 = 0.0621 for 3931 reflections with I > 2σ(I); R1 = 0.0741, wR2 = 0.1818 for all 9597 reflections.

CCDC-291996–292000 (**1**, **1a**, **2a**, **2b**, **3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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