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A Combined Experimental and Theoretical Study of Anion–π Interactions in Bis(pyrimidine) Salts

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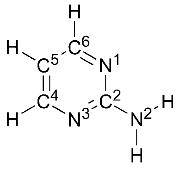
We report the synthesis and X-ray characterization of an *N*,*N′*-tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate salt that exhibits anion–π interactions that are responsible for the crystal packing. The anion forms a sandwich complex with two pyrimidine rings. When the anion is nitrate, the crystal packing is governed by anion–π interactions and hydrogen bonds, and the sandwich complex is not formed. Finally, a theoretical study of the anion–π interactions in charged pyrimidine rings is in good agreement with the experimental findings.

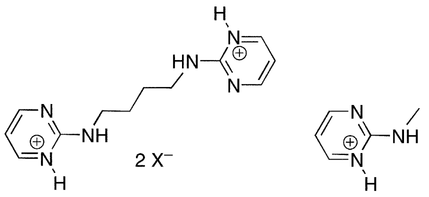
Introduction

Noncovalent interactions are very important in modern chemistry, especially in the fields of supramolecular chemistry and molecular recognition.[1] In particular, interactions involving aromatic rings[2] are key processes in both chemical and biological recognition, since aromatic rings are omnipresent in these systems. Interaction of cations with aromatic systems, namely cation–π interactions,[3] are important for the binding of acetylcholine to the active site of the enzyme acetylcholine esterase[4] and for the ion selectivity of potassium channels.[5] In addition, they also play an important role in transport of nitrogen through the membrane by the ammonia transport protein.[6] Anion–π interactions[7] are also important noncovalent forces that have attracted considerable attention. They have been observed experimentally, supporting the theoretical predictions and the promising proposal for the use of anion receptors based on anion–π interactions in molecular recognition.[8] In addition, π-acidic oligonaphthalenediimide rods have recently been proposed as transmembrane anion–π slides.[9] A recent review by P. Gamez et al. deals with anion-binding involving π-acidic heteroaromatic rings.[10] Anion–π interactions are energetically less favorable than their cation–π counterparts, because anions have larger van der Waals radii than cations and the binding energies strongly depend upon distance. To solve this issue, the use of charged aromatic rings is a good strategy[11] to improve the interaction.



2-aminopyrimidine

In this paper we report the synthesis and X-ray characterization of *N*,*N′*-tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate (**1**; Figure 1). We also analyze the effect of the anion on the crystal packing by comparing the solid-state structure of **1** with that of the previously reported *N*,*N′*-tetramethylenebis(2-aminopyrimidinium) nitrate (**2**). Relevant anion–π interactions are present in both structures and are responsible for the differences in the crystal packing.



1: X = BF_4^-

2: X = NO_3^-

3

Figure 1. *N*,*N′*-Tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate (**1**) and nitrate (**2**), and the 2-(methylamino)pyrimidinium cation.

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We also report a high-level ab initio study of the anion-binding affinity of the protonated 2-aminopyrimidine **3** through hydrogen bonding and anion–π interactions, with the aid of Molecular Interaction Potential with polarization (MIPp)[12] calculations for compound **3**. The MIPp is a convenient tool for predicting binding properties. It has been successfully used to explain molecular interactions such us hydrogen bonding and ion–π interactions and for predicting molecular reactivity.[13] In particular, it has been found useful for predicting the binding energies of a variety of π-acidic rings, such as hexafluorobenzene,[7a] *s*-triazine,[13f] *s*-tetrazine,[13g] tricyanobenzene,[13h] isocyanuric acid,[8e] etc.[13i] The MIPp partition scheme is an improved generalization of the Molecular Electrostatic Potential (MEP), in which three terms contribute to the interaction energy: (i) an electrostatic term identical to the MEP,[14] (ii) a classical dispersion-repulsion term,[15] and (iii) a polarization term derived from perturbation theory.[16] We have found a good agreement between the theoretical calculations and the solid-state structures. Anion–π interactions involving pyrimidine rings have been observed previously.[17]

Results and Discussion

The geometry of compound **3**, as a theoretical model of **1**, was fully optimized by use of the MP2/6-31++G** level of theory in the Gaussian 03 package.[18] Calculation of the MIPp maps of **3** interacting with F^- and O^- was performed by use of the HF/6-31++G**//MP2/6-31++G** wavefunction with the aid of the MOPETE-98 program.[19] The ionic van der Waals parameters for F and O were taken from the literature.[13f,20]

We synthesized compound **1** by the procedure shown in Scheme 1. The precursor of **1**, *N*,*N′*-tetramethylenebis(pyrimidine), is easily prepared in good yield (70%) from 2-chloropyrimidine and butane-1,4-diamine in *n*BuOH/Et_3N at reflux. Although dissolution of this compound in HBF_4 (1 M) yields the corresponding salt **1**, crystals were only obtained from the crude reaction mixture of *N*,*N′*-tetramethylenebis(pyrimidine) and $AgBF_4$ in an attempt to obtain the corresponding Ag^I complex. Compound **2**, as described previously,[21] was obtained by dissolution of *N*,*N′*-tetramethylenebis(pyrimidine) in HNO_3 (0.1 M).

The solid-state structures of compounds **1** and **2** are shown in Figures 2 and 3, respectively. In the X-ray structure of **1**, the anion is disordered between two positions. In the figure, only the most occupied position is represented. It can be observed that the BF_4^- anion participates in two relevant anion–π interactions through two fluorine atoms, with the anion sandwiched between two pyrimidine rings. It is worth mentioning that the distance between the fluorine atom and the ring centroid is in one case very short (i.e., 2.97 Å), indicating that the anion–π interaction is strong. A likely explanation is that the aromatic ring is positively charged and the electrostatic interaction is important. The anion also interacts with the pyrimidine ring, establishing two hydrogen bonds through one fluorine atom.

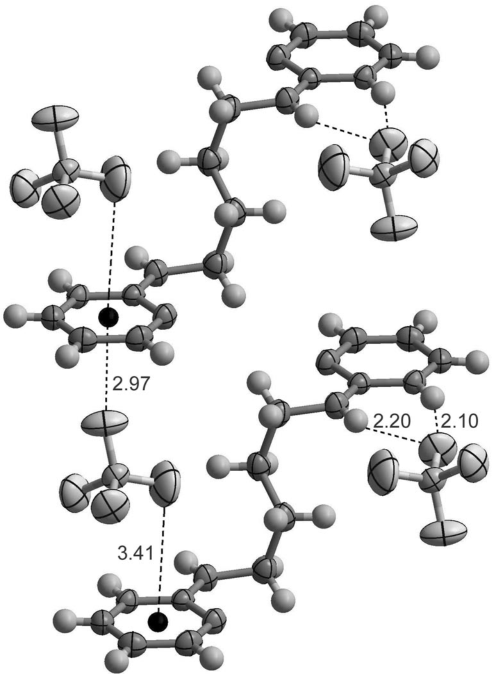
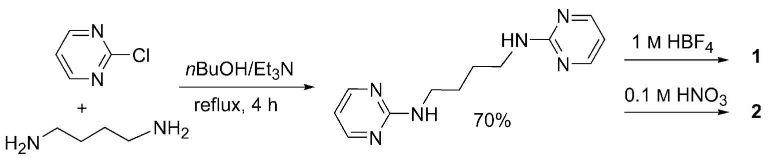


Figure 2. ORTEP drawing of **1**; the probability of the thermal ellipsoids is 50%. The ring centroids are represented by black spheres. Distances in Å.

The X-ray structure of compound **2** is represented in Figure 3. This compound was previously reported by some of us as an intermediate for the generation of Ag^I complexes,[21] but its geometric features were not carefully examined. In comparison with compound **1**, some differences provoked by the dual σ/π-anion-binding affinity of the protonated pyrimidine ring can be observed. In **2** the planar nitrate anion interacts through two hydrogen bonds with the 2-aminopyrimidine ring through two oxygen atoms. The anion also participates in an anion–π interaction with other bis(pyrimidine) molecule (3.32 Å), through one oxygen atom.

Some interesting points arise from comparison of the solid-state structures of **1** and **2**. Firstly, the BF_4^- anion shows a preference for π-interaction and the NO_3^- for σ-interaction. Secondly, the geometry of the sandwich complex of



Scheme 1. Synthetic route to **1** and **2**.

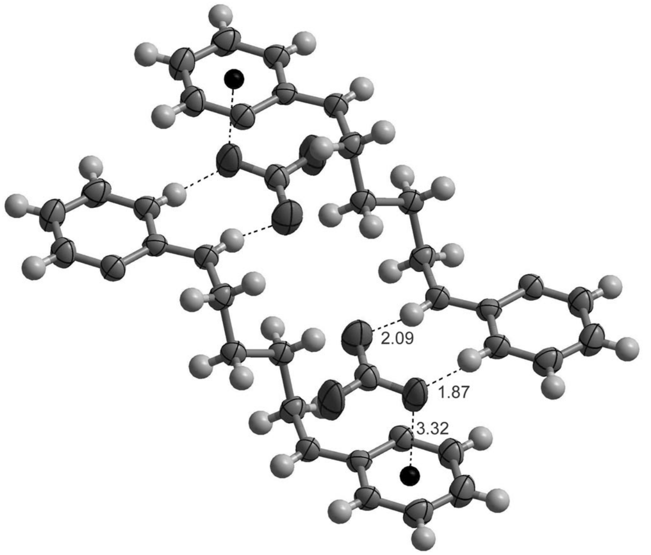


Figure 3. ORTEP drawing of **2**; the probability of the thermal ellipsoids is 50%. The ring centroids are represented by black spheres. Distances in Å.

BF_4^- with two pyrimidine rings observed in **1** is in agreement with a previous study that demonstrated that the anion–π interaction is additive and the most favorable geometry in 1:2 complexes is sandwich-like.[13e] Thirdly, the anion–π interaction has a strong influence on the crystal packing in the two structures.

With the purpose of comparing the anion-binding affinities of compound **3** as a model of **1** and **2** through hydrogen bonding and anion–π bonding, we computed the two-dimensional (2D) MIPp energy maps. We obtained the 2D-MIPp maps at the molecular plane, in order to study the spatial regions where the σ-interaction with F^- is more favorable, and at 3.0 Å above the molecular plane, in order to study where the π interaction with F^- is more favorable. The 2D-MIPp maps computed for the interaction of **3** with O^- are topologically very similar to those computed for F^-, and they have been included in the Supporting Information (Figure S1).

In addition, we compared the 2D-MIPp maps with the corresponding X-ray structures. In Figure 4, we show the 2D-MIPp maps calculated for **3** interacting with F^- and the X-ray structures of **1** and **2** (partial view). From inspection of the maps, the following results are remarkable. Firstly, the global minimum at the molecular plane arises from the interaction of the anion with the hydrogen atoms bonded to N^1 and N^2 (the location of the minimum is represented by a star in the 2D-MIPp maps of Figures 4 and S1). The distances from the minimum to H^1 and H^2 are 2.02 Å and 2.08 Å, respectively, in agreement with the solid-state structure (see Figure 2). Secondly, the 2D-MIPp map computed 3.0 Å above the molecular plane indicates a wide zone in which the interaction is favorable, and the minimum is located approximately above the region of N^1. The location of the MIPp minimum strongly agrees with the X-ray structures. The fluorine atom of the BF_4^- anion that points to-

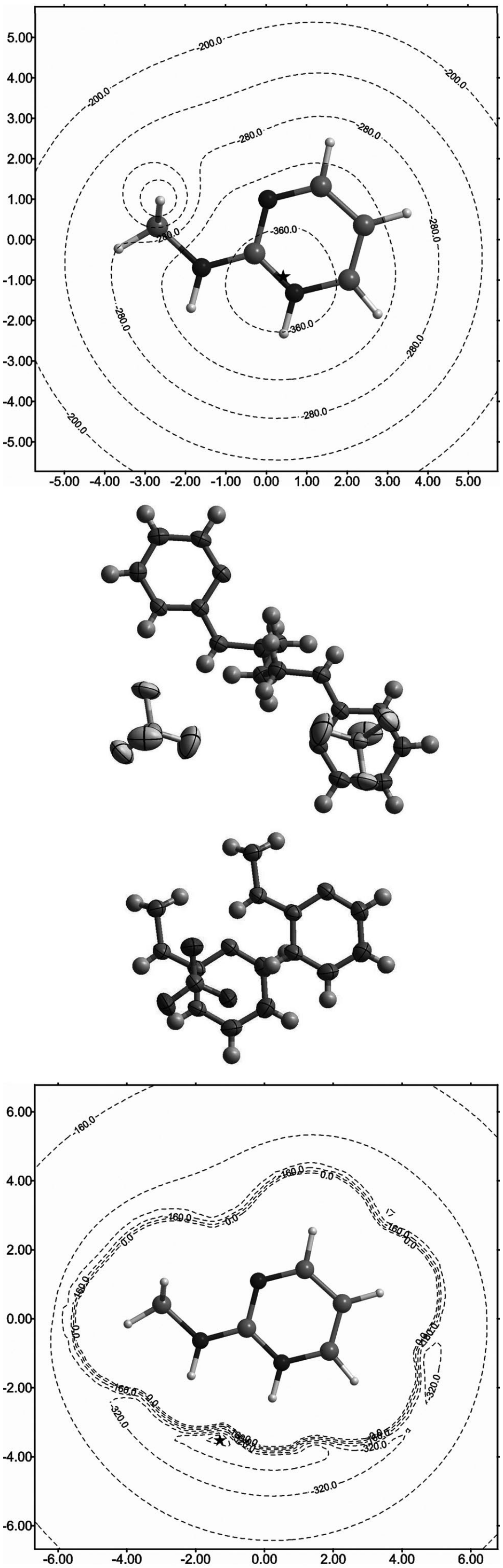


Figure 4. 2D-MIPp(F) energy maps computed at the molecular plane (bottom) and 3.0 Å above it (top). Isocontour lines are plotted every 80 kJ mol^{-1} in the bottom plane and every 40 kJ mol^{-1} in the top plane. The minimum is represented by a star. Axes units are Å. In the middle, zenithal views of the X-ray structures of compounds **1** and **2** (partial view) are shown.

ward the aromatic ring in **1** is positioned over the region of the protonated aromatic nitrogen atom. In addition, the position of the NO_3^- anion in the solid-state structure of **2** is also positioned at the MIPp minimum.

Conclusions

We have synthesized and X-ray-characterized a new compound, *N*,*N*′-tetramethylenebis(2-aminopyrimidinium) tetrafluoroborate, that illustrates the importance of anion–π interactions in supramolecular chemistry. Both hydrogen-bond and anion–π interactions involving the protonated 2-aminopyrimidine molecule are energetically very favorable, and both determine the geometric features of the crystal structures. The 2D-MIPp energy maps are in good agreement with the X-ray structures, since they are able to predict the spatial regions where the interaction of the anion with the ring is more favorable.

Experimental Section

General Methods: Elemental analyses were carried out with Carlo–Erba models 1106 and 1108 and Thermo Finnigan Flash 1112 microanalysers. Infrared spectra (KBr pellets) were recorded with a Bruker IFS 66 instrument. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AMX 300 spectrometer. ^{1}H and ^{13}C chemical shifts in dimethyl sulfoxide solution ([D$_6$]DMSO) were referenced to [D$_6$]DMSO itself [^{1}H: δ(DMSO) = 2.50 ppm; ^{13}C:, δ(DMSO) = 39.5 ppm]. All organic and inorganic (Sigma and Aldrich) reagents were used without further purification. Melting points were taken with a capillary melting point apparatus and are reported uncorrected.

***N*,*N*′-Bis(2-pyrimidyl)-1,4-tetramethylenediamine:**[21] A suspension of 2-chloropyrimidine (1.1 g, 9.6 mmol) in *n*-butyl alcohol (20 mL) and triethylamine (3 mL) was heated at reflux in butane-1,4-diamine (4.8 mmol) for 4 h. The resulting solid was filtered off and washed with cold water and cold acetone to remove the impurities of triethylammonium hydrochloride that contaminate the crude materials. Further purification can be achieved by recrystallization from boiling water in 65–70% yield. M.p. 182–184 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 8.25 [d, J = 4.8 Hz, 4 H, H(4)/H(6)/H(4′)/H(6′)], 7.16 [br. t, 2 H, NH], 6.51 [t, $J_{\text{est.}}$ = 4.8 Hz, 2 H, H(5)/H(5′)], 3.26 [4 H, m, H(7)/H(7′)], 1.55 [br. m, 4 H, H(8)/H(8′)] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 162.3 [C(2)/C(2′)], 157.8 [C(4)/C(6)/C(4′)/C(6′)], 109.6 [C(5)/C(5′)], 26.5 [C(8)/C(8′)] ppm. ^{13}C NMR (CDCl$_3$): δ = 162.5 [C(2)/C(2′)], 158.0 [C(4)/C(6)/C(4′)/C(6′)], 110.5 [C(5)/C(5′)], 41.08 [C(7)/C(7′)], 27.0 [C(8)/C(8′)] ppm. IR: $\tilde{\nu}_{\max}$ = 3257 (s), 2939 (s), 1599 (vs), 1542 (vs), 1463 (vs), 1416 (vs), 1369 (s), 1347 (s), 1278 (m), 1229 (m), 1183 (m), 1113 (w), 1088 (w), 1071 (w), 993 (w), 802 (m), 735 (m), 642 (w), 617 (w) cm^{-1}. $C_{12}H_{16}N_6$ (244.14): calcd. C 59.00, H 6.60, N 34.40; found C 58.85, H 6.88, N 34.17.

***N*,*N*′-Tetramethylenebis(2-aminopyrimidinium) Tetrafluoroborate (1):** The previously described *N*,*N*′-tetramethylenebis(2-aminopyrimidine) (100mg, 0.41 mmol) was dissolved in HBF$_4$ (1 M, 20 mL). The solution was heated under reflux for 15 min and then filtered. The compound was obtained in 43% yield. M.p. 189–194 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 8.46 [d, J = 5.1 Hz, 4 H, H(4)/H(6)/H(4′)/H(6′)], 6.80 [t, J = 5.1 Hz, 2 H, H(5)/H(5′)], 3.35 [br. t, 4 H, H(7)/H(7′)], 1.60 [br. t, 4 H, H(8)/H(8′)] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 157.3 [br., C(2)/C(2′)], 155.8 [C(4)/C(6)/C(4′)/C(6′)], 109.6 [C(5)/C(5′)], 40.7 [C(7)/C(7′)], 25.6 [C(8)/C(8′)] ppm. IR: $\tilde{\nu}_{\max}$ = 3253 (m), 2718 (s), 1654 (vs), 1616 (vs), 1572 (m), 1546 (w), 1467 (m), 1376 (w), 1331 (s), 1211 (m), 1062 (br. s), 984 (m), 873 (w), 844 (W), 808 (m), 764 (s), 638 (m), 599 (w), 521 (m) cm^{-1}. $C_{12}H_{18}B_2F_8N_6$ (420,17): calcd. C 34.32, H 4.32, N 20.01; found C 34.11, H 4.36, N 19.68. Crystals suitable for X-ray studies were obtained as a first crystalline material (13%) in an attempt to obtain the corresponding Ag$^{\text{I}}$ complex of *N*,*N*′-tetramethylenebis(2-aminopyrimidine).

X-ray Crystallographic Studies: A suitable crystal of **1** was selected and mounted on the tip of a glass fiber for single-crystal X-ray diffraction experiments with an Enraf–Nonius CAD4 diffractometer producing graphite-monochromated Mo-K_α radiation (λ = 0.71073). After a random search of 16 reflections, the indexation procedure gave the cell parameters (see Table 1 for a summary of the crystal data). Data were collected in the ω-2θ scan mode. The structural resolution procedure was carried out with the WinGX package.[22] Solution of the structure factor phases was performed by SIR2004,[23] and the full-matrix refinement by SHELXL97.[24] Non-H atoms were refined anisotropically and H atoms were located from difference Fourier syntheses. A summary of refinement parameters can also be seen in Table 1. The tetrafluoroborate anion exhibits disorder and was split between two locations (80% and 20% occupancy). CCDC-658781 contains 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.

Table 1. Crystal data and structure refinement parameters for compound **1**.

Compound	**1**
Empirical formula	$C_{12}H_{18}B_2F_8N_6$
Formula mass	419.94
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a [Å]	5.4012(12)
b [Å]	7.4263(16)
c [Å]	11.6010(10)
α [°]	82.876(11)
β [°]	83.619(12)
γ [°]	75.55(2)
Volume [Å^3]	445.57(14)
Z	1
Density (calcd.) [Mg m^{-3}]	1.565
Absorption coefficient [mm^{-1}]	0.155
F(000)	214
Crystal size [mm]	0.35 × 0.29 × 0.23
θ range for data collection [°]	1.78–29.97
Index ranges	$-7 \le h \le 7$
	$-10 \le k \le 10$
	$0 \le l \le 16$
Reflections collected	2723
Independent reflections	2601 [R(int) = 0.0177]
Completeness to final θ [%]	100.0
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	2601/0/200
Goodness-of-fit on F^2	1.126
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0524
	$wR2$ = 0.1649
R indices (all data)	$R1$ = 0.0848
	$wR2$ = 0.1832
Largest diff. peak/hole [e Å^{-3}]	0.289/–0.294

Supporting Information (see footnote on the first page of this article): IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses of synthesized compounds; Cartesian coordinates of optimized compound **3** and Figure S1.

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