

Two significantly different conformations in crystal: formation of a molecular dimer governed by cation– π interactions

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Received 17 April 2006; revised 15 May 2006; accepted 19 May 2006

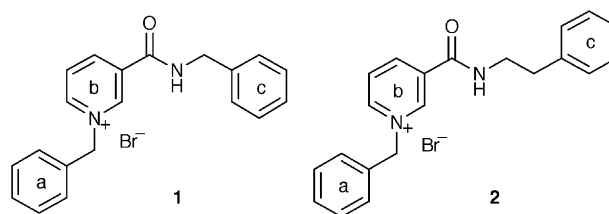
Abstract—Two significantly different conformations were observed in crystal of **1**, which form an unsymmetrical molecular dimer governed by cation– π interactions between a pyridinium cation and a phenyl ring, whereas compound **2** forms a head-to-tail type of dimer.

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It has been well documented that various non-covalent intermolecular interactions dramatically affect the crystal structure, and, therefore, elucidation of the relationship of the interaction types with the molecular packing modes is one of the most important subjects¹ in supramolecular chemistry and in crystal engineering. Among attractive interactions, cation– π interaction² between a pyridinium cation and an aromatic ring has become of interest in the recent years because it plays a key role for the formation of a wide variety of complexes, such as folded,^{3,4} dimeric,⁴ oligomeric,⁵ zipper-like⁶ and helical⁷ architectures as well as inclusion complexes⁸ in crystal or in solution.

We have previously reported the formation of a head-to-tail type of dimer for an *N*-methylpyridinium compound in crystal through cation– π interactions.⁴ In this letter, we describe that two significantly different conformations were observed in crystal of **1**, which form an unsymmetrical molecular dimer governed by pyridinium– π interactions, whereas compound **2** forms a head-to-tail type of dimer.⁴

1-Benzyl-3-benzylcarbamoylpyridinium bromide (**1**) and 1-benzyl-3-phenethylcarbamoylpyridinium bromide (**2**) were prepared to investigate the chain length effect on their geometries. These compounds comprise three rings a, b and c; the central ring b is a pyridinium ring and



both a and c correspond to the phenyl rings of the *N*-benzyl group attached to the pyridinium and the amide functional group, respectively.

Recrystallization of compound **1** from acetonitrile–hexane gave crystals suitable for X-ray analysis. A remarkable feature in the X-ray structure of **1**⁹ is that the asymmetric unit contains two independent molecules, **A** and **B**, having significantly different conformations from each other, as shown in Figure 1. The two phenyl rings, a and c, of **A** are located on the same side of the pyridinium ring b, whereas those of **B** are located on the opposite side of the pyridinium ring. Another significant feature is that these molecules, **A** and **B**, form a perpendicularly twisted molecular dimer through two cation– π interactions between the phenyl and the pyridinium rings. Rings Aa and Bb are very close to each other and are arranged face-to-face with an interplanar separation of about 3.44 Å, which is close to the sum of van der Waals radii. The two rings Ab and Bc also exhibit pyridinium– π stacking; the angle between the two planes is about 36° with 3.45 Å of interatomic distance between C(3) and C(16'). It should be noted that 2.91 Å of interatomic contact between the carbonyl

Keywords: Cation– π interaction; Pyridinium– π interaction; Pyridinium salt; Molecular dimer; Crystal structure.

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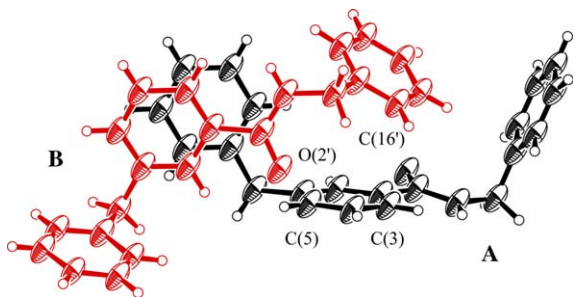


Figure 1. ORTEP drawing for compound **1** containing two independent molecules **A** and **B**. Bromide ions and hydrogen atoms are omitted for clarity.

oxygen O(2') and C(5) of the pyridinium ring suggests the existence of C=O...Py⁺ type of cation- π interaction that we have previously reported.¹⁰

Superimposition of the molecules, **A** and **B**, where their pyridinium rings are fixed at the same position, clearly shows the distinct differences in the geometries between them (Fig. 2). The torsion angles around the phenyl rings are significantly different from each other; the N(1)-C(7)-C(8)-C(9) and N(2)-C(14)-C(15)-C(16) angles for molecules **A** and **B** are 32.9° and 76.8°, and 61.4° and 41.7°, respectively. The angles of 32.9° and 41.7° for rings Aa and Bc indicate nearly coplanar orientation of them with respect to the pyridinium ring and the amide moiety, respectively, suggesting the existence of torsional strain around them. Furthermore, considerable strain was also observed in molecule **A** at the bond angles around the *N*-benzyl pyridinium moiety; the N(1)-C(7)-C(8) angle of 113.5(2)° in molecule **A** is much larger than that of 110.0(2)° in molecule **B**. In addition, the C(7)-C(8)-C(9) angle of 122.8(2)° in **A** is also larger than that of 120.5(3)° in **B**. These observations strongly suggest that the formation of a twisted dimer is accompanied with significant steric strain.

Optimized geometries of **1** and single point energies for the cationic parts of **A** and **B** were predicted by DFT calculations at B3LYP/6-31G* level to evaluate the de-

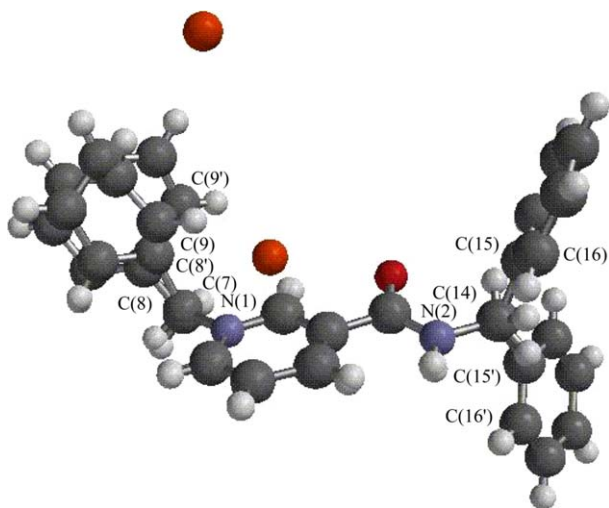


Figure 2. Superimposition of molecules **A** and **B**.

gree of distortion of **A** and **B**.¹¹ The optimized structure is very different from the X-ray structures of **A** and **B**, and has an extended geometry, as shown in Figure 3. The single point energies of **A** and **B** are much higher than the optimized energy,¹¹ suggesting the existence of significant strain in both of them. Comparison of the energies between **A** and **B** clarifies 13.48 kcal/mol of instability of **A** than **B**, which is in agreement with the severe deformation in torsion angles and bond angles in **A** as described above.

X-ray packing diagram revealed the formation of infinite columns along the *a* axis by self-assembling of the dimeric units, where the interplanar separation between rings Aa and B'b of the neighboring dimer is about 3.46 Å (Fig. 4). Moreover, the columns are arranged in an oppositely parallel manner with an interaction between Ab and B'a rings along the *c* axis, the interplanar separation of which is 3.50 Å. These features clearly show that the cation- π interaction governs not only the formation of the dimer, but also the arrangement of the dimeric units so as to promote cation- π interactions as much as possible in the crystal structure. Although the dimeric unit has considerable steric strain as described above, the stabilization energy resulting from the formation of the network of cation- π interactions would more than compensate for the strain energy of the dimer.



Figure 3. Optimized geometry of the cationic part of **1** predicted by DFT calculations at B3LYP/6-31G* level.

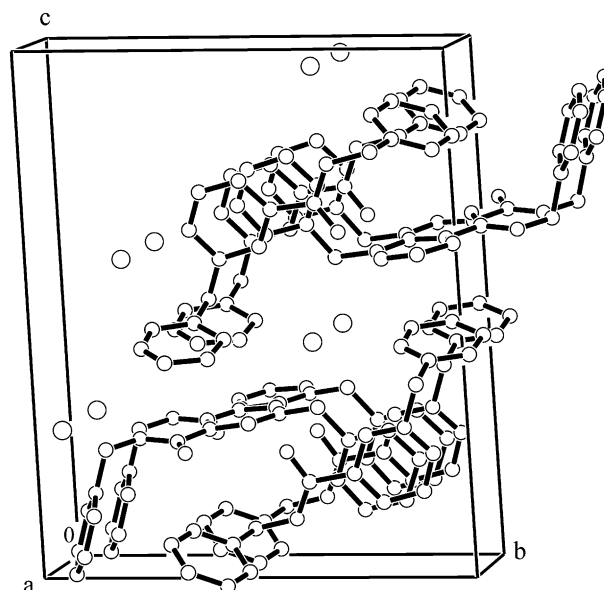


Figure 4. Packing diagram of **1** viewed along *a* axis. The hydrogen atoms are omitted for clarity.

X-ray structural analysis of **2**, having a longer chain length than **1**, was carried out to clarify the chain length effect on the packing structure.¹² Since crystals of **2** were not obtained until addition of chloroform, using a chloroform–methanol solvent system performed the recrystallization. The packing diagram shows face-to-face and head-to-tail type of dimeric arrangement with centrosymmetry, as shown in Figure 5. This obviously indicates the existence of cation– π interaction between rings 2b and 2c. The interplanar separation between a pyridinium and a phenyl ring is about 3.34 Å. On the other hand, no cation– π interaction was observed in ring 2a. The packing diagram also shows no network structure of the cation– π interactions because chloroform molecules surround the dimer. The geometry of this dimeric complex is very close to that of the corresponding *N*-methyl pyridinium salt that we have previously reported,⁴ suggesting the generality for the geometry of this type of compounds.

The significant difference in the interaction modes between **1** and **2** is definitely dependent on their chain lengths. The relatively smaller difference in the distances between Aa–Ab and Bb–Bc in **1** allows the two cation– π interactions of Aa···Bb and Ab···Bc to give an unsymmetrical dimer, which enables the construction of an efficient stacking network of cation– π interactions despite having considerable strain. On the other hand, formation of such dimer is geometrically difficult in compound **2** due to having a longer chain length than **1**; as a result, centrosymmetric dimer may be alternatively produced.

In solution, the existence of intermolecular cation– π interactions in **1** and **2** was evidenced by the $\Delta\delta$ values, which are the differences in the ¹H NMR chemical shifts of **1** and **2** with 1-benzyl-3-methylcarbamoylpyridinium bromide as a reference compound:¹³ $\Delta\delta$ values for **1**: H2, 1.37; H4, 0.10; H5, –0.36; H6, –1.57; $\Delta\delta$ values for **2**: H2, 1.46; H4, 0.07; H5, –0.30; H6, –1.72. Both $\Delta\delta$ values for **1** and **2** are very close each other; in addition, the trend of the $\Delta\delta$ values are similar to that of the previously reported 1-methyl-3-phenethylcarbamoylpyridinium bromide.⁴ These studies strongly suggest

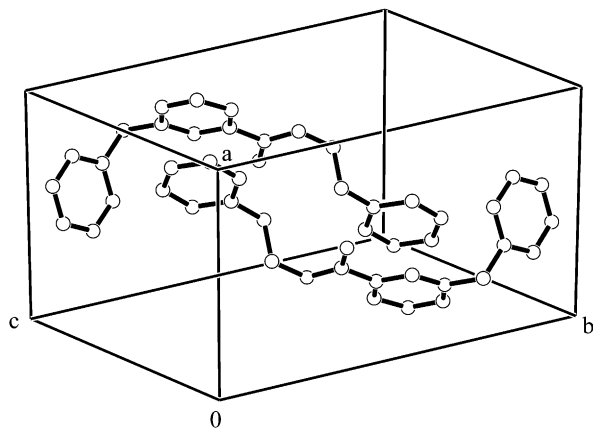


Figure 5. Dimeric structure of compound **2**. The hydrogen atoms, bromide ions and chloroform molecules are omitted for clarity.

that **1** and **2** would form dimeric structures close to the X-ray geometry of **2**.

The occurrence of more than one independent molecule in the asymmetric unit of the crystals is not uncommon. Hydrogen bonding is known to be a main factor for such phenomenon.¹⁴ However, there is no example caused by cation– π interactions. In addition, to the best of our knowledge, there has been little known about molecular dimers composed by two significantly different conformers.

In summary, we have found that the asymmetric unit of compound **1** contains two independent molecules having significantly different conformations from each other, and they form an unsymmetrical twisted molecular dimer. The origin of these unusual structural features would be the stabilization of the crystal by formation of a network structure of pyridinium– π interactions. The results reported here will provide an insight into the system of conformation controlling in various pyridinium compounds.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 17350046) from the Japan Society for the Promotion of Science.

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- X-ray crystal data for **1**: C₂₀H₁₉BrN₂O, *M* = 383.28, triclinic, *P*-1, *a* = 7.343(7), *b* = 14.591(3), *c* = 17.809(5) Å, *a* = 93.75(2), *b* = 98.08(4), *g* = 92.13(4), *V* = 1883(2) Å³, *T* = 298 K, *Z* = 4, *D*_c = 1.352 g cm⁻³, *m* = 3.029 mm⁻¹. A total of 8592 reflections were collected and 6825 were unique (*R*_{int} = 0.0572). *R*1 = 0.0623 [*I* > 2*s*(*I*)], *wR*2 = 0.1925 (all data). CCDC 293709.
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11. DFT calculations were carried out by using PC SPARTAN '02. The single point energies of **A** and **B** are -600901.987 and -600915.462 kcal mol $^{-1}$, respectively. The optimized energy of **1** is -601177.983 kcal mol $^{-1}$.
12. X-ray crystal data for **2**: C $_{23}$ H $_{23}$ BrCl $_6$ N $_2$ O, $M = 636.04$, triclinic, $P-1$, $a = 11.511(3)$, $b = 13.763(3)$, $c = 9.891(2)$ Å, $\alpha = 106.948(17)$, $\beta = 107.899(18)$, $\gamma = 97.734(17)$, $V = 1386.8(5)$ Å 3 , $T = 230$ K, $Z = 2$, $D_c = 1.523$ g cm $^{-3}$, $\mu = 13.067$ mm $^{-1}$. A total of 6982 reflections were collected and 4884 are unique ($R_{\text{int}} = 0.0716$). $R1 = 0.0833$ [$I > 2\sigma(I)$], $wR2 = 0.2287$ (all data). CCDC 293710.
13. The chemical shifts of **1**, **2** and 1-benzyl-3-methylcarbamoyl-pyridinium bromide measured at 400 MHz in 2 mM of CDCl $_3$ solutions are as follows: The δ values for **1**: H2, 10.78; H4, 9.01; H5, 7.88; H6, 8.66; The δ values for **2**: H2, 10.87; H4, 8.98; H5, 7.94; H6, 8.51; The δ values for the reference compound: H2, 9.41; H4, 8.91; H5, 8.24; H6, 10.23.
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