^{1}H NMR Analysis and Crystal Structures of 1,1′,3,3′-Tetramethyl-2,2′-bi-1*H*-imidazolium Bis(tetraphenylborate): Ion-Associative Interactions Containing Ketone, Aldehyde, and Nitrile

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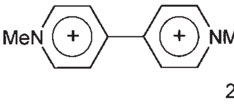
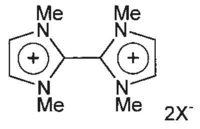
The title dication interacts with ion-associable tetraphenylborate (BPh_4) anions in an acetone or acetonitrile solution, and crystals of the salt included some kinds of ketone, aldehyde, and nitrile as guest molecules to afford unique molecular aggregations.

Much research attention has been focused on host-guest chemistry and supramolecular chemistry since these studies are applicable to development of material science, biochemistry, crystal engineering, and chemical synthesis.[1] Intermolecular forces utilized for molecular aggregations are mostly hydrogen bonds, coordination bonds, charge-transfer (CT) interactions, and van der Waals forces.[1,2] On the other hand, ion-association reagents such as tetraphenylborate salts, which are used for separation and analysis of ion species in analytical chemistry,[3] are also expected as a building block for supramolecular chemistry because they form ion pairs and ion complexes in solution and solid states. According to ^{1}H NMR analysis of 1,1′-dimethyl-4,4′-bipyridylium salts (**1**) and (**2**) in acetone-d_6, high magnetic field shifts of the chemical shifts were observed in tetraphenylborate **1**.[4] In this connection, we found significant differences of ^{1}H NMR chemical shifts between tetraphenylborate (**3**) and trifluoromethanesulfonate (**4**) in acetone-d_6 and acetonitrile-d_3. We report herein the ^{1}H NMR analysis and inclusion compounds of **3** with ketone, aldehyde, and nitrile.



1 X = BPh_4
2 X = PF_6



3 X = BPh_4
4 X = CF_3SO_3

Trifluoromethanesulfonate **4** (mp 291–295 °C) was obtained by methylation of 1,1′-dimethyl-2,2′-bi-1*H*-imidazole[5] with methyl trifluoromethanesulfonate in dichloromethane. Tetraphenylborate **3** (mp 234–236 °C) was prepared by a counter anion exchange reaction of **4** and sodium tetraphenylborate in hot water. ^{1}H NMR chemical shifts of **3** and **4** in 0.10 M solutions of acetone-d_6 are summarized in Table 1. The chemical shifts of **3** are shifted to higher magnetic fields than those of **4**, and their differences ($\Delta\delta$) are more remarkable compared with those between dimethylbipyridylium salts **1** and **2** (NCH_3: $\Delta\delta = 0.15$, CH: $\Delta\delta = 0.33, 0.40$).[4] In addition, a spectrum of a 1 : 1 mixture of **3** and **4** showed the chemical shifts around averages of **3** and **4**, indicating that the chemical shifts of the dication move within some range depending on concentration of the BPh_4 counter anion. A similar phenomenon was observed in acetonitrile-d_3 although $\Delta\delta$ values are not as large as those in acetone-d_6 (Table 1). However, $\Delta\delta$ values measured in DMSO-d_6 do not demonstrate significant differences. Table 2 reveals dependence of the chemical shifts of **3** with concentration in the each solvent. The chemical shifts in acetone-d_6 and acetonitrile-d_3 move to higher magnetic fields with increasing concentration, and both maximum shifts of the chemical shifts (Δ_{max}) are almost same. On the other hand, Δ_{max} values in DMSO-d_6 are smaller, suggesting a different type of solvation. As a result, the high magnetic field shifts in acetone-d_6 and acetonitrile-d_3 are ascribable to ion association between the dication and BPh_4 anions and solvation,[6] while the ion complex would be decomposed or loose in DMSO-d_6 due to its strong solvation.

Table 1. ^{1}H NMR chemical shifts (δ) of salts **3** and **4** in 0.10 M solutions

Salt	Acetone-d_6		Acetonitrile-d_3		DMSO-d_6	
	Me	CH	Me	CH	Me	CH
3	3.77	7.80	3.60	7.59	3.82	8.22
4	4.20	8.33	3.85	7.92	3.87	8.28
$\Delta\delta^a$	0.43	0.53	0.25	0.33	0.05	0.06

[a]Difference between **3** and **4**.

Table 2. Dependence of ^{1}H NMR chemical shifts (δ) of **3** with concentration

Conc[a]	Acetone-d_6		Acetonitrile-d_3		DMSO-d_6	
	Me	CH	Me	CH	Me	CH
0.01	4.08	8.19	3.75	7.80	3.85	8.26
0.05	3.92	7.99	3.60	7.62	3.82	8.23
0.15	3.73[b]	7.77[b]	3.43	7.40	3.75	8.14
0.20	—	—	3.36[b]	7.31[b]	3.71[b]	8.09[b]
$\Delta_{max}{}^c$	0.35	0.42	0.39	0.49	0.14	0.17

[a]Concentration in M. [b]Measured in a saturated solution. [c]Maximum shift of chemical shift with concentration.

Crystals of **3**, which were recrystallized from acetone and hexane, turned white in air, suggesting inclusion of acetone molecules in the crystals. Furthermore, organic salt **3** made cocrystals with other various ketones, aldehyde, and nitrile (Table 3), and molar ratios of the two guest molecules per one salt were demonstrated by elemental analyses. The cocrystals with 4-methyl-2-pentanone or benzonitrile melted to release the ketone or the nitrile. The other cocrystals also released the ketones or the aldehyde to turn white by heating. The releasing temperatures are not directly related to boiling points of the solvents. The cocrystals seem to release the molecules up to around 140 °C. Stretching frequencies (ν) of $C=O$ and $C\equiv N$ bonds were observed and are not different from those of the ketones, the aldehyde, and the nitrile (Table 3). These results indicate that coordination bonds of the guest molecules to the dication are not strong. Recrystallization of **4** in a similar way as **3** provided crystals without guest molecules, suggesting that the inclusion phenomenon of **3** with guest molecules is in relation to the interactions between the dication and BPh_4 anions in solution.

Table 3. Releasing temperatures and C = O and C ≡ N stretching frequencies of cocrystals of **3**

Compound (bp/°C)	Releasing temp/°C	ν/cm^{-1}
2-butanone (80)	103–107	1714
4-methyl-2-pentanone (117)	130–135	1705
cyclopentanone (130)	119–125	1725
cyclohexanone (155)	133–139	1702
benzaldehyde (178)	143–151	1693
benzonitrile (191)	139–165	2228

A single crystal of **3** with cyclohexanone was grown for an X-ray crystal analysis.[7] The biimidazolium dication is surrounded by four BPh_4 anions and is in a specific cyclic environment arising from eight phenyl groups (Figure 1a). Methyl groups and hydrogen atoms of the dication exist in the front of the phenyl groups. The crystal structure is essentially the same as found in the cocrystals of 2-butanone,[8] but the molecular aggregation is distorted because of a steric hindrance between cyclohexanone molecules (Figure 1b).

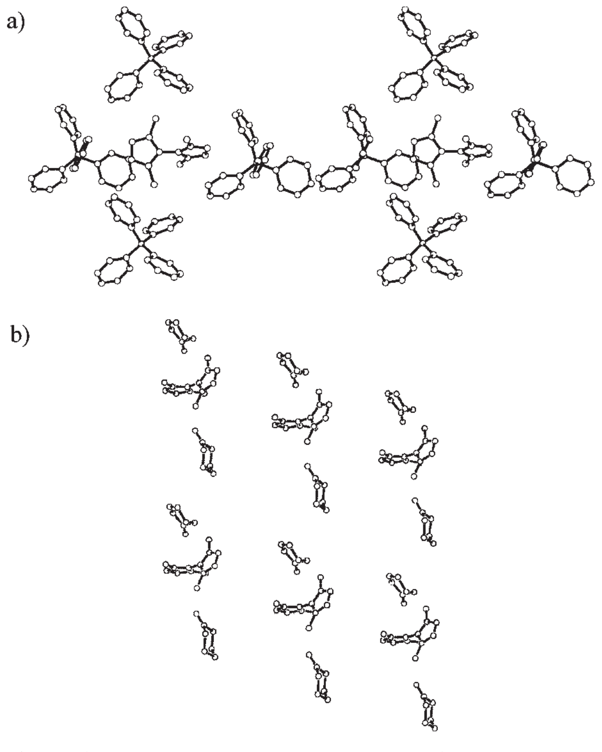


Figure 1. Crystal structures of cocrystals of **3** with cyclohexanone: a) packing mode (stereo view), b) molecular arrangement (BPh_4 anions are omitted).

An X-ray crystal analysis of **3** with benzonitrile was also carried out.[9] The crystal structure is shown in Figure 2. The two nitriles interact with the dication from a same side and exist almost in parallel with the dication resulted in partial distortion of the cyclic environment formed by BPh_4 anions. The intermolecular N···N distances are 3.15–3.39 Å and a dihedral angle of the dication is 73°. These values are similar to 3.02–4.55 Å of O···N distances and 69° of the dihedral angle found in Figure 1b. It is noteworthy that the crystal structures are changed depending on the used guest molecules. These results are ascribable to the intermolecular interaction modes. Thus, the dication forms a zigzag molecular string (Figure 2). According to an X-ray crystal analysis of the cocrystals with benzaldehyde, the crystal structure was much similar to that shown in Figure 2. Therefore, functional groups to interact with the dication may be not important for controlling the crystal structures. Further investigation on relationship of crystal structures with guest molecules is in progress.

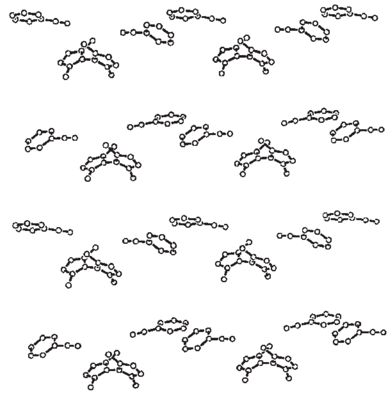


Figure 2. Crystal structure of cocrystals of **3** with benzonitrile (BPh_4 anions are omitted).

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References and Notes

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6 Reduction potential of the dication is too low to explain the shifts as increased electron density by a CT interaction ($E_{\mathrm{red}} = -1.48$ V (ir) vs SCE in CH_3CN).

7 Crystal data for **3**•2(cyclohexanone): colorless plate, $C_{70}H_{76}B_2N_4O_2$, $M = 1026.97$, triclinic, space group $P\bar{1}$, $a = 14.174(2)$, $b = 15.911(3)$, $c = 14.026(3)$ Å, $\alpha = 102.668(15)°$, $\beta = 90.867(17)°$, $\gamma = 76.685(15)°$, $V = 3001.1(9)$ Å^3, $Z = 2$, $D_c = 1.136$ g cm^{-3}, $\mu = 0.67$ cm^{-1}, $F(000) = 1100$. The final R_1 value was 0.0585 for 8602 reflections with $I > 2\sigma(I)$. CCDC 184420.

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9 Crystal data for **3**•2(benzonitrile): colorless block, $C_{72}H_{66}B_2N_6$, $M = 1036.97$, orthorhombic, space group $P2_12_12_1$, $a = 14.793(2)$, $b = 19.141(2)$, $c = 21.247(2)$ Å, $V = 6016(1)$ Å^3, $Z = 4$, $D_c = 1.145$ g cm^{-3}, $\mu = 0.66$ cm^{-1}, $F(000) = 2200$. The final R_1 value was 0.069 for 7415 reflections with $I > 2\sigma(I)$. CCDC 184421.