Bull. Chem. Soc. Jpn., 78, 867–872 (2005)

Molecular Arrangement in the Cocrystals of 1,1′,3,3′-Tetramethyl-2,2′-bi-1*H*-imidazolium Bis(tetraphenylborate) with Ketone, Aldehyde, and Nitrile as Guest Molecules

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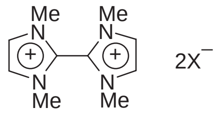
1,1′,3,3′-Tetramethyl-2,2′-bi-1*H*-imidazolium bis(tetraphenylborate), an ion-association compound, afforded inclusion crystals with a variety of guest molecules, such as ketone, aldehyde, and nitrile. X-ray crystallographic analyses revealed intermolecular interactions between the biimidazolium dication and the guest molecules in the inclusion crystals. Their contact modes depended on the molecular structures of the guest molecules, resulting in various molecular arrangements.

Supramolecular chemistry has been a subject of great research interest in various fields, such as material science, biochemistry, crystal engineering, and chemical synthesis, since molecular aggregations present novel properties and unique functionalities.[1–11] The most convenient methods for forming molecular aggregations include designing hydrogen bonds and/or metal–ligand (chelate) bonds, and much research work on supramolecular synthons involving these intermolecular interactions has been conducted.[7–11] On the other hand, ion-association compounds, such as tetraphenylborate salts, are used as reagents for separation and analysis in analytical chemistry because they form ion pairs and ion complexes in solution and the solid state.[12–15] The application of ion-association phenomena to supramolecular chemistry has also been conducted.[16–20] Since intermolecular interactions arising from ion association are fundamentally Coulomb forces, these are difficult to design and control in the aggregation structures formed as building blocks in solution and the solid state. In addition, their structures are closely related to solvation and are modified depending on the association modes, such as the solvent-separated type, the solvent-shared type, and the contact type.[13] We recently reported on the behavior of 1,1′,3,3′-tetramethyl-2,2′-bi-1*H*-imidazolium bis(tetraphenylborate) (**1**) in solution and the solid state.[21,22] The structure of the biimidazolium dication is similar to that of 1-alkyl-3-methyl-1*H*-imidazolium, which has attracted much attention as an ionic liquid.[23–26] According to ^{1}H NMR analyses of **1** in acetone-d_6 and acetonitrile-d_3, an upfield shift in the dication moiety was observed compared to the corresponding trifluoromethanesulfonate (**2**), indicating the formation of ion complexes in solutions. Furthermore, organic salt **1** was recrystallized from solutions containing ketone, aldehyde, and nitrile to afford inclusion compounds with a variety of crystal structures. In this context, we investigated the inclusion properties of the ion-association compound and the intermolecular interactions with a variety of guest molecules to build crystal structures using guest molecules as templates. We report herein on the X-ray crystallographic analyses of these inclusion compounds.



1 X = BPh_4
2 X = CF_3SO_3

Chart 1.

Results and Discussion

Inclusion Crystals with Aliphatic Ketone (3–7). Trifluoromethanesulfonate **2** was obtained in 92% yield by the methylation of 1,1′-dimethyl-2,2′-bi-1*H*-imidazole[27] with methyl trifluoromethanesulfonate in dichloromethane. Tetraphenylborate **1** was prepared in quantitative yield by a counter anion exchange reaction of organic salt **2** with sodium tetraphenylborate in hot water. Recrystallization of organic salt **1** from 2-butanone (**3**) afforded colorless crystals, which according to an elemental analysis contained two molecules of the guest per salt molecule. This phenomenon is attributable to the ion association arising from the tetraphenylborate anions because organic salt **2** did not produce inclusion crystals under identical conditions. The inclusion crystals with 2-butanone decomposed between 103–107 °C to release the guest molecules. The decomposition point was slightly higher than the boiling point of 2-butanone (bp 80 °C).[21] The intermolecular force between the host and the guest molecules is not strong. Figure 1a shows the structure of the inclusion crystal. Two guest molecules are solvated by coordination to the biimidazolium dication, where the distances between the carbonyl oxygen atom

Published on the web May 6, 2005; DOI 10.1246/bcsj.78.867

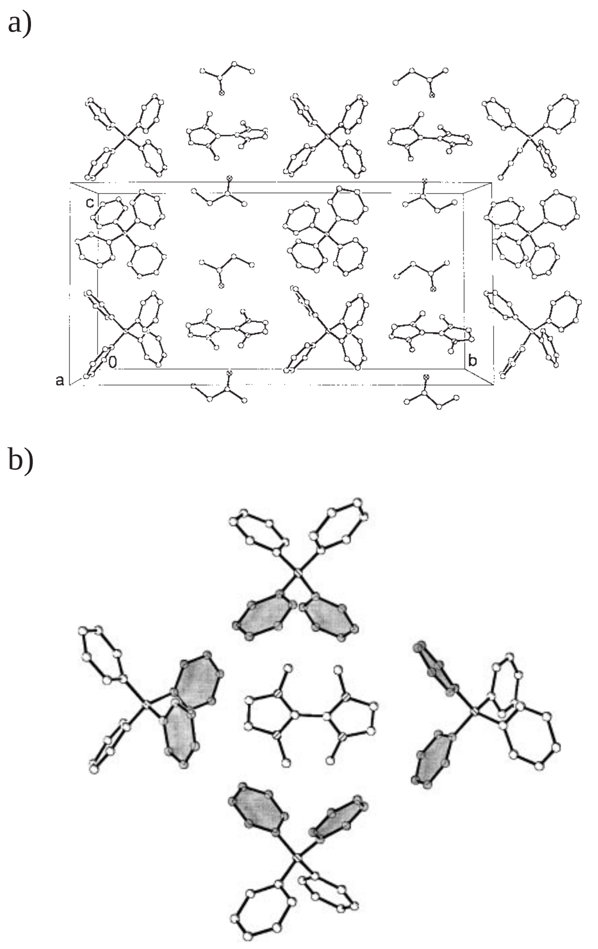


Fig. 1. Structure of inclusion crystal with **3**: a) columnar structure, b) packing mode.

of **3** and the biimidazolium nitrogen atoms are in the range of 2.97–3.26 Å. These values are similar to the sum of the van der Waals radii ($N\cdots O = 3.07$ Å).[28] The dication is surrounded by four tetraphenylborate anions and is in a specific cyclic environment arising from eight phenyl rings (Fig. 1b), indicating supplementary $CH\cdots\pi$ interactions between the dication and the tetraphenylborate anions in addition to the Coulomb forces. The crystal structure is thus formed by two types of columns, composed of ketone–dication–ketone units and the tetraphenylborate anions (Fig. 1a). In other words, the dication and guest molecules are packed in a straight cylinder formed by the tetraphenylborate anions.

Inclusion crystals were obtained by the recrystallization of organic salt **1** from cyclohexanone (**4**). The crystal structure was identified to have a 1:2 molar ratio of **1** to **4**. Figure 2 shows the structure of the cocrystal; the tetraphenylborate anions are omitted for clarity. The intermolecular distances between the carbonyl oxygen atoms of **4** and the biimidazolium nitrogen atoms range between 3.02 and 4.55 Å. The crystal also has a columnar structure containing ketone–dication–ketone units and tetraphenylborate anions. The unit cell has a triclinic shape and the columnar structure is different from the monoclinic one shown in Fig. 1a. This result implies that a columnar structure with a monoclinic shape is more unstable than that with a triclinic shape, due to a steric hindrance between the cyclohexane rings. Therefore, the crystal has a triclinic structure without any steric hindrance. The structures of selected guest molecules affect the molecular aggregation of ion complexes involving them and the biimidazolium dication.

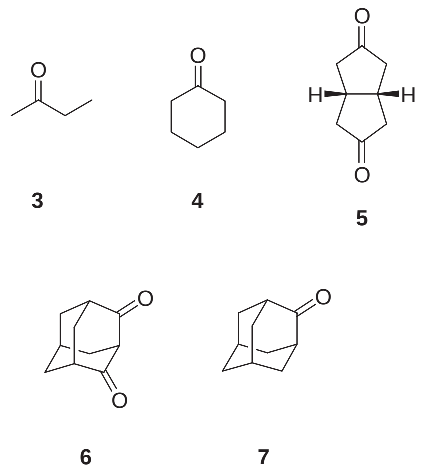


Chart 2.

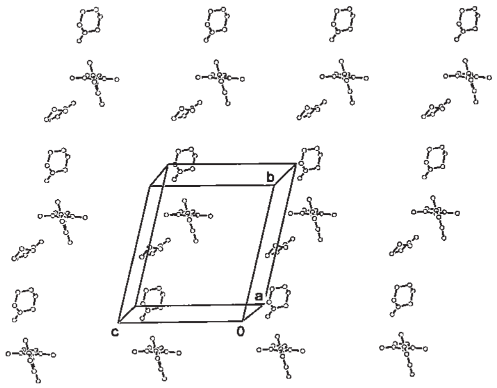


Fig. 2. Columnar structure of inclusion crystal with **4** (BPh_4 anions are omitted).

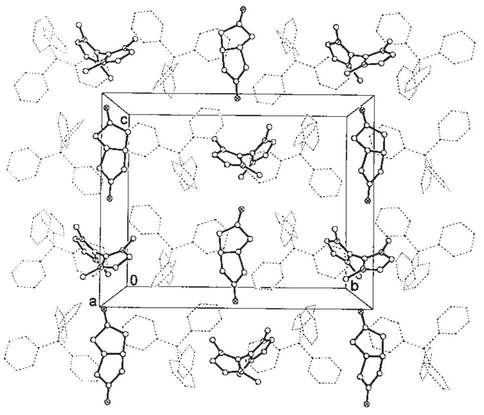


Fig. 3. Columnar structure of inclusion crystal with **5** (MeOH molecules are omitted).

In order to investigate cocrystals containing diketone as guest molecules, *cis*-bicyclo[3.3.0]octane-3,7-dione (**5**) was employed to prepare inclusion crystals. Figure 3 displays the columnar structure of the cocrystal, having one molecule of di-

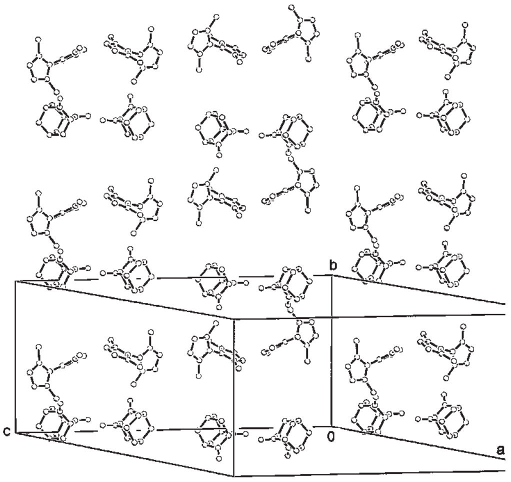


Fig. 4. Structure of inclusion crystal with **6** (BPh_4 anions and H_2O molecules are omitted).

ketone **5** per biimidazolium dication, which is solvated by one molecule of methanol. This structure demonstrates that the diketone can behave like two molecules of ketone. However, diketone **5** is disordered due to its relatively flexible skeleton. In addition, its molecular size is small for the distance between the two dications. The distances between the carbonyl oxygen atoms of **5** and the biimidazolium nitrogen atoms are in the range of 3.53–3.93 Å. These facts suggest that the intermolecular interaction is not strong enough to connect the diketone with the two dications in the columns.

Guest molecules, 2,4-adamantanedione (**6**) and 2-adamantanone (**7**), were applied to the preparation of inclusion crystals, since they have rigid skeletons. Cocrystals with a 1:1 molar ratio of **1** to **6**/**7** were obtained. These two cocrystals are isomorphic and their molecular arrangements are very similar to each other. The structure of a cocrystal with **1** and **6** is shown in Fig. 4. One carbonyl oxygen atom of **6** comes in contact with the biimidazolium nitrogen atom ($N\cdots O = 3.79$ Å), while the other is not used for coordination with the tetraphenylborate anion.

Inclusion Crystals with Aromatic Compounds (8 and 9). The role of aromatic compounds as guest molecules was investigated for the preparation of inclusion crystals. Single crystals were grown from a mixture of organic salt **1** and benzonitrile (**8**). Cocrystals with a 1:2 molar ratio of **1** to **8** were obtained; their structure is displayed in Fig. 5. The distances between the nitrogen atom of **8** and the biimidazolium nitrogen atoms are between 3.15 and 3.39 Å. These values are comparable to the sum of the van der Waals radii ($N\cdots N = 3.10$ Å).[28] Two nitrile molecules are in contact with the dication on the same side. This interaction mode differs from those observed in inclusion crystals with aliphatic guest molecules. Furthermore, a column composed of the tetraphenylborate anions was not found in the crystal. In order to investigate the interaction mode observed in inclusion crystals with benzonitrile (**8**), benzaldehyde (**9**) was used as a guest molecule for crystallization. The crystal structure resembles that shown in Fig. 5, indicating that the moieties of the aromatic guest molecules are able to modify the contact mode and not the functional groups. These results were elucidated by increasing the number of aromatic moieties, which afforded additional $CH\cdots\pi$ interactions. These resulted in interaction modes different from those of crystals with aliphatic guest molecules.

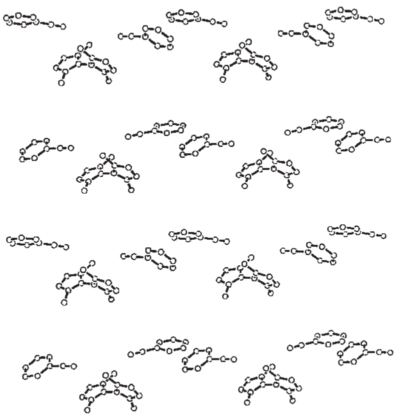
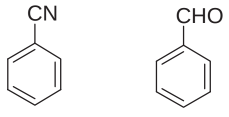


Fig. 5. Structure of inclusion crystal with **8** (BPh_4 anions are omitted).



8 **9**

Chart 3.

Inclusion Crystals with a π-Extended Aromatic Dicarbonitrile (10 and 11). In order to investigate the utility of π-extended aromatic systems as guest molecules, 4,4′-biphenyldicarbonitrile (**10**) was employed for the crystallization of inclusion crystals. The obtained crystals had one guest molecule per two salt molecules. Dication–guest–dication units were observed in the crystal structure. A top view of the components is shown in Fig. 6a. The nitrogen atoms of the cyano groups overlap the imidazolium five-membered rings with intermolecular distances in the range of 3.35–3.77 Å. These values are approximately equal to the sum of the van der Waals radii ($C\cdots N = 3.25$ Å, $N\cdots N = 3.10$ Å).[28] During crystal formation, this component is alternately packed, as shown in Fig. 6b. Inclusion crystals were grown with 3,3′-biphenyldicarbonitrile (**11**), a regioisomer of **10**. A single crystal with a molar ratio of 2:1 for organic salt **1** to **11** was obtained. Figure 7a shows the arrangement of the dication and the guest molecules. The intermolecular distances in this case are not as close ($N\cdots N = 4.39$, 6.45 Å) as those of the inclusion crystal with **10**. This is because the rotational vibration in the biphenyl moiety may decrease the intermolecular contact between the biimidazolium dication and the cyano groups in the crystal growth in addition to the inherent, weak intermolecular force. The biimidazolium dication forms a dimer through the $CH\cdots\pi$ interactions between the methyl group and the imidazolium five-membered ring. The dimer is packed to build the inclusion crystal, as shown in Fig. 7b.

Conclusion

Inclusion crystals of organic salt **1** were prepared with a variety of guest molecules, such as ketone, aldehyde, and nitrile,

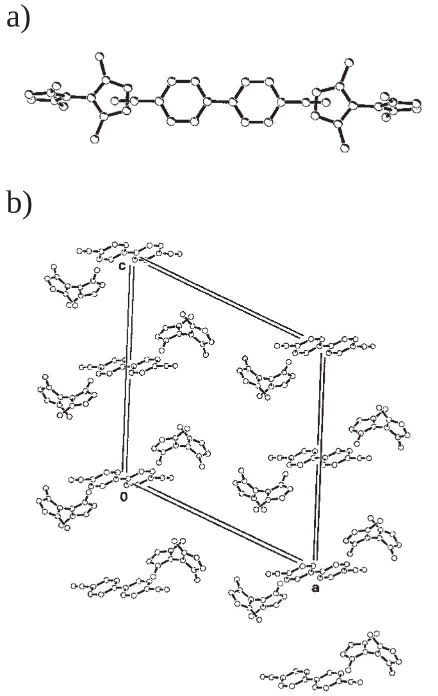


Fig. 6. Structure of inclusion crystal with **10**: a) overlap mode, b) packing (BPh_4 anions are omitted).

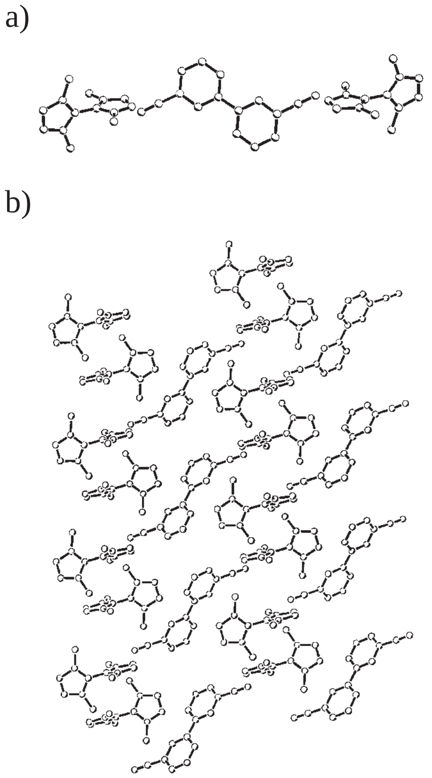
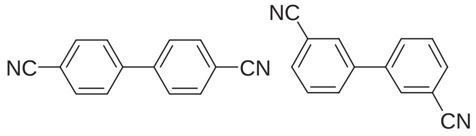


Fig. 7. Structure of inclusion crystal with **11**: a) arrangement, b) packing (BPh_4 anions are omitted).



10 **11**

Chart 4.

and their intermolecular interactions were studied. We identified two types of intermolecular contact modes between the biimidazolium dication and the aliphatic as well as aromatic guest molecules. These crystals were formed by molecular columns, which depended on the structures of the selected guest molecules. The intermolecular force between the dication and the guest molecules is not strong enough to govern the entire crystal structure as a template. However, a possibility exists that organic salt **1** could be studied in supramolecular chemistry. Furthermore, organic salt **1** is of interest in green chemistry, since the biimidazolium dication has the skeleton of 1-alkyl-3-methyl-1*H*-imidazolium, which has recently been focused upon as an ionic liquid. The intermolecular interactions arising from the ion association may be used for constructing unique molecular assemblies of liquids.

Experimental

General. Melting points were measured on a Yanaco micro melting-point apparatus and were uncorrected. IR spectra were obtained with a JASCO FT/IR-5300 spectrometer. ^{1}H NMR spectra were recorded with a Varian GEMINI spectrometer (300 MHz) with tetramethylsilane as an internal standard. Guest compounds **6**[29] and **10**, **11**[30] were prepared by following procedures previously reported in the literature. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Preparation of Trifluoromethanesulfonate Salt 2. To a solution of 1,1′-dimethyl-2,2′-biimidazole[27] (1.42 g, 8.8 mmol) in dry dichloromethane (3 mL) in an ice-cold water bath under nitrogen was added dropwise methyl trifluoromethanesulfonate (2.2 mL, 19.5 mmol). The reaction mixture was stirred at room temperature for 3 h. After the addition of ether (120 mL), the white precipitate was filtered. Recrystallization from 1-propanol afforded organic salt **2** (3.95 g, 92%) as colorless crystals: mp 285–287 °C; ^{1}H NMR (acetone-d_6, 0.10 mol dm^{-3}) δ 4.20 (s, 12H, CH_3), 8.33 (s, 4H, CH). Found: C, 29.59; H, 3.31; N, 11.50%. Calcd for $C_{12}H_{16}F_6N_4O_6S_2$: C, 29.39; H, 3.29; N, 11.43%. Slow diffusion of *n*-hexane (1.5 mL) into a solution of organic salt **2** (2.5 mg, 0.005 mmol) in 2-butanone (0.5 mL) afforded colorless prisms. Crystal data for **2**: $0.20 \times 0.25 \times 0.10$ mm^3, $C_{12}H_{16}F_6N_4O_6S_2$, $M = 490.39$, orthorhombic, space group *Pbca*, $a = 15.151(1)$, $b = 12.0180(8)$, $c = 21.954(2)$ Å, $V = 3997.6(5)$ Å^3, $Z = 8$, $D_c = 1.629$ g cm^{-3}, $\mu = 0.359$ mm^{-1}, $F(000) = 2000$. A total of 4554 reflections for $2\theta_{max} = 55°$ were collected [$I > 2\sigma(I)$] using a Rigaku MSC MercuryCCD diffractometer (Mo Kα radiation, $\lambda = 0.71070$ Å) at 296 K. The structure was solved using the direct method (SHELXS-97),[31] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.098$, $R = 0.127$, $R_w = 0.194$, GOF = 1.68, $\rho_{max}/\rho_{min} = 0.74/-0.64$ e Å^{-3}. CCDC 237604.

Preparation of Tetraphenylborate Salt 1. A solution of organic salt **2** (1.98 g, 4.0 mmol) in water (60 mL) was added to a solution of sodium tetraphenylborate (2.81 g, 8.2 mmol) in boiling water (240 mL). The reaction mixture was stirred for 30 min. The white precipitate was filtered and washed with water and ethanol to afford organic salt **1** (3.35 g, 100%). mp 233–235 °C; ^{1}H NMR (acetone-d_6, 0.10 mol dm^{-3}) δ 3.77 (s, 12H, CH_3), 6.85 (t, 8H, $J = 7.4$ Hz, Ph), 7.00 (t, 16H, $J = 7.4$ Hz, Ph), 7.43 (m, 16H, Ph), 7.80 (s, 4H, CH). Found: C, 83.65; H, 6.90; N, 6.67%. Calcd for $C_{58}H_{56}N_4B_2$: C, 83.86; H, 6.80; N, 6.75%.

Inclusion Crystals with 2-Butanone 3. Organic salt **1** (20 mg, 0.024 mmol) was dissolved in 2-butanone (5 mL). Slow vapor diffusion of *n*-hexane into the solution afforded colorless blocks;[33] decomp 103–107 °C; IR (KBr) 1714 cm^{-1} (C=O). Crystal data for **1**$\cdot$2(**3**): $0.78 \times 0.65 \times 0.60$ mm^3, $C_{66}H_{72}B_2N_4O_2$, $M = 974.90$, monoclinic, space group $P2_1/n$, $a = 12.934(1)$, $b = 29.803(2)$, $c = 14.612(1)$ Å, $\beta = 92.65(1)°$, $V = 5626.5(7)$ Å^3, $Z = 4$, $D_c = 1.151$ g cm^{-3}, $\mu = 0.07$ mm^{-1}, $F(000) = 2088$. A total of 6539 reflections for $2\theta_{max} = 50°$ were collected [$I > 2\sigma(I)$] using a Siemens P4 four circle diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at 150 K. The structure was solved using the direct method (SHELXS-86),[34] and refined by a full-matrix least-squares analysis (SHELXL-93),[35] giving values of $R_1 = 0.0564$, $wR_2 = 0.1529$, GOF $= 1.011$, $\rho_{max}/\rho_{min} = 0.37/-0.36$ e Å^{-3}. CCDC 135517.

Inclusion Crystals with Cyclohexanone 4. Organic salt **1** (10 mg, 0.012 mmol) was dissolved in cyclohexanone (2.5 mL). Slow vapor diffusion of *n*-hexane into the solution afforded colorless plates;[33] decomp 133–139 °C; IR (KBr) 1702 cm^{-1} (C=O). Found: C, 81.63; H, 7.48; N, 5.52%. Calcd for $C_{70}H_{76}B_2N_4O_2$: C, 81.86; H, 7.46; N, 5.42%. Crystal data for **1**$\cdot$2(**4**): $0.35 \times 0.20 \times 0.10$ mm^3, $C_{70}H_{76}B_2N_4O_2$, $M = 1026.97$, 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}, $\mu = 0.067$ mm^{-1}, $F(000) = 1100$. A total of 8602 reflections for $2\theta_{max} = 50°$ were collected [$I > 2\sigma(I)$] using a Rigaku MSC AFC-7R diffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å) at 296 K. The structure was solved using the direct method (SIR97),[36] and refined by a full-matrix least-squares analysis (SHELXL-97),[37] giving values of $R_1 = 0.0585$, $wR_2 = 0.2081$, GOF $= 0.946$, $\rho_{max}/\rho_{min} = 0.260/-0.297$ e Å^{-3}. CCDC 184420.

Inclusion Crystals with *cis*-Bicyclo[3.3.0]octane-3,7-dione 5. Organic salt **1** (10 mg, 0.012 mmol) was dissolved in methanol (12 mL). Then, diketone **5** (10 mg, 0.012 mmol) was dissolved in the solution. Evaporating the solvent slowly afforded colorless blocks; decomp > 180 °C. Found: C, 80.18; H, 6.78; N, 5.70%. Calcd for $C_{67}H_{70}B_2N_4O_3$: C, 80.40; H, 7.05; N, 5.60%. Crystal data for **1**$\cdot$**5**$\cdot$$CH_4O$: $0.70 \times 0.55 \times 0.50$ mm^3, $C_{67}H_{70}B_2N_4O_3$, $M = 1000.89$, monoclinic, space group $P2_1/c$, $a = 19.7322(14)$, $b = 19.0567(13)$, $c = 14.5189(11)$ Å, $\beta = 91.523(4)°$, $V = 5457.6(7)$ Å^3, $Z = 4$, $D_c = 1.218$ g cm^{-3}, $\mu = 0.07$ mm^{-1}, $F(000) = 2136$. A total of 5124 reflections for $2\theta_{max} = 46°$ were collected [$I > 2\sigma(I)$] using a Siemens P4 four circle diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at 130 K. The structure was solved using the direct method (SHELXS-86),[34] and refined by a full-matrix least-squares analysis (SHELXL-93),[35] giving values of $R_1 = 0.0546$, $wR_2 = 0.1527$, GOF $= 1.030$, $\rho_{max}/\rho_{min} = 0.48/-0.36$ e Å^{-3}. CCDC 135518.

Inclusion Crystals with 2,4-Adamantanedione 6. Organic salt **1** (20 mg, 0.024 mmol) was dissolved in methanol (14 mL). Then, diketone **6** (79 mg, 0.48 mmol) was dissolved in the solution. Evaporating the solvent slowly afforded colorless blocks; decomp > 85 °C; IR (KBr) 1699 cm^{-1} (C=O). Crystal data for **1**$\cdot$**6**$\cdot$0.5H_2O: $0.70 \times 0.30 \times 0.10$ mm^3, $C_{68}H_{70}B_2N_4O_{2.5}$, $M = 1004.94$, monoclinic, space group $C2/c$, $a = 32.913(2)$, $b = 13.633(1)$, $c = 28.354(1)$ Å, $\beta = 117.857(5)°$, $V = 11247(1)$ Å^3, $Z = 8$, $D_c = 1.187$ g cm^{-3}, $\mu = 0.548$ mm^{-1}, $F(000) = 4288$. A total of 7631 reflections for $2\theta_{max} = 115°$ were collected [$I > 2\sigma(I)$] using an Enraf Nonius CAD-4 diffractometer (Cu Kα radiation, $\lambda = 1.54178$ Å) at 296 K. The structure was solved using the direct method (SHELXS-97),[31] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.073$, $R = 0.165$, $R_w = 0.193$, GOF $= 1.36$, $\rho_{max}/\rho_{min} = 0.59/-0.65$ e Å^{-3}. CCDC 237605.

Inclusion Crystals with 2-Adamantanone 7. Organic salt **1** (20 mg, 0.024 mmol) was dissolved in methanol (14 mL). Then, ketone **7** (72 mg, 0.48 mmol) was dissolved in the solution. Evaporating the solvent slowly afforded colorless blocks; decomp > 115 °C; IR (KBr) 1698 cm^{-1} (C=O). Crystal data for **1**$\cdot$**7**$\cdot$0.5H_2O: $0.50 \times 0.20 \times 0.15$ mm^3, $C_{68}H_{72}B_2N_4O_{1.5}$, $M = 990.96$, colorless block, monoclinic, space group $C2/c$, $a = 32.982(4)$, $b = 13.653(1)$, $c = 28.232(3)$ Å, $\beta = 117.899(9)°$, $V = 11235(2)$ Å^3, $Z = 8$, $D_c = 1.172$ g cm^{-3}, $\mu = 0.527$ mm^{-1}, $F(000) = 4240$. A total of 5718 reflections for $2\theta_{max} = 100°$ were collected [$I > 2\sigma(I)$] using an Enraf Nonius CAD-4 diffractometer (Cu Kα radiation, $\lambda = 1.54178$ Å) at 296 K. The structure was solved using the direct method (SIR97),[36] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.072$, $R = 0.213$, $R_w = 0.190$, GOF $= 1.19$, $\rho_{max}/\rho_{min} = 0.65/-0.85$ e Å^{-3}. CCDC 237606.

Inclusion Crystals with Benzonitrile 8. Organic salt **1** (5 mg, 0.006 mmol) was dissolved in benzonitrile (0.7 mL). Slow vapor diffusion of *n*-hexane into the solution afforded colorless blocks;[33] decomp 139–165 °C; IR (KBr) 2228 cm^{-1} (C≡N). Found: C, 83.41; H, 6.59; N, 8.10%. Calcd for $C_{72}H_{66}B_2N_6$: C, 83.39; H, 6.42; N, 8.11%. Crystal data for **1**$\cdot$2(**8**): $0.70 \times 0.40 \times 0.40$ mm^3, $C_{72}H_{66}B_2N_6$, $M = 1036.97$, 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}, $\mu = 0.066$ mm^{-1}, $F(000) = 2200$. A total of 7415 reflections for $2\theta_{max} = 55°$ were collected [$I > 2\sigma(I)$] using a Rigaku MSC MercuryCCD diffractometer (Mo Kα radiation, $\lambda = 0.71070$ Å) at 296 K. The structure was solved using the direct method (SIR97),[36] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.069$, $R = 0.088$, $R_w = 0.142$, GOF $= 1.37$, $\rho_{max}/\rho_{min} = 0.28/-0.23$ e Å^{-3}. CCDC 184421.

Inclusion Crystals with Benzaldehyde 9. Organic salt **1** (2.5 mg, 0.003 mmol) was dissolved in benzaldehyde (0.4 mL). Slow vapor diffusion of *n*-hexane into the solution afforded colorless blocks;[33] decomp 143–151 °C; IR (KBr) 1693 cm^{-1} (C=O). Crystal data for **1**$\cdot$2(**9**): $0.25 \times 0.15 \times 0.10$ mm^3, $C_{72}H_{68}B_2N_4O_2$, $M = 1042.97$, orthorhombic, space group $P2_12_12_1$, $a = 14.8033(8)$, $b = 18.949(2)$, $c = 21.330(2)$ Å, $V = 5983.2(9)$ Å^3, $Z = 4$, $D_c = 1.158$ g cm^{-3}, $\mu = 0.529$ mm^{-1}, $F(000) = 2216$. A total of 6694 reflections for $2\theta_{max} = 149°$ were collected [$I > 2\sigma(I)$] using an Enraf Nonius CAD-4 diffractometer (Cu Kα radiation, $\lambda = 1.54178$ Å) at 296 K. The structure was solved using the direct method (SIR97),[36] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.059$, $R = 0.109$, $R_w = 0.161$, GOF $= 1.28$, $\rho_{max}/\rho_{min} = 0.46/-0.57$ e Å^{-3}. CCDC 237607.

Inclusion Crystals with 1,1′-Biphenyl-4,4′-dicarbonitrile 10. Organic salt **1** (10 mg, 0.012 mmol) was dissolved in methanol (12 mL). Then, dicarbonitrile **10** (2.5 mg, 0.012 mmol) and acetone (4 mL) were dissolved in the solution. Evaporating the solvent slowly afforded colorless blocks; decomp 119–125 °C; IR (KBr) 2222

$\mathrm{cm^{-1}}$ (C≡N). Crystal data for **1**•0.5(**10**): $0.50 \times 0.50 \times 0.25$ $\mathrm{mm^3}$, $C_{65}H_{60}B_2N_5$, $M = 932.84$, monoclinic, space group $P2_1/c$, $a = 19.358(4)$, $b = 14.889(2)$, $c = 20.078(4)$ Å, $\beta = 113.396(4)^\circ$, $V = 5311(1)$ $\mathrm{Å^3}$, $Z = 4$, $D_c = 1.167$ $\mathrm{g\,cm^{-3}}$, $\mu = 0.067$ $\mathrm{mm^{-1}}$, $F(000) = 1980$. A total of 12034 reflections for $2\theta_{max} = 55^\circ$ were collected $[I > 2\sigma(I)]$ using a Rigaku MSC MercuryCCD diffractometer (Mo Kα radiation, $\lambda = 0.71070$ Å) at 296 K. The structure was solved using the direct method (SHELXS-97),[31] and refined by a full-matrix least-squares analysis (teXsan),[32] giving values of $R_1 = 0.098$, $R = 0.144$, $R_w = 0.186$, GOF = 1.13, $\rho_{max}/\rho_{min} = 0.34/-0.28$ $\mathrm{e\,Å^{-3}}$. CCDC 237608.

Inclusion Crystals with 1,1′-Biphenyl-3,3′-dicarbonitrile 11. Organic salt **1** (10 mg, 0.012 mmol) was dissolved in methanol (12 mL). Then, dicarbonitrile **11** (4.9 mg, 0.024 mmol) and acetone (2 mL) were dissolved in the solution. Evaporating the solvent slowly afforded colorless blocks; decomp 145–151 °C; IR (KBr) 2230 $\mathrm{cm^{-1}}$ (C≡N). Crystal data for **1**•0.5(**11**): $0.40 \times 0.40 \times 0.25$ $\mathrm{nm^3}$, $C_{65}H_{60}B_2N_5$, $M = 932.84$, monoclinic, space group $P2_1/c$, $a = 12.712(3)$, $b = 25.302(5)$, $c = 17.333(4)$ Å, $\beta = 106.929(4)^\circ$, $V = 5333(2)$ $\mathrm{Å^3}$, $Z = 4$, $D_c = 1.162$ $\mathrm{g\,cm^{-3}}$, $\mu = 0.067$ $\mathrm{mm^{-1}}$, $F(000) = 1980$. A total of 12163 reflections for $2\theta_{max} = 55^\circ$ were collected $[I > 2\sigma(I)]$ using a Rigaku MSC MercuryCCD diffractometer (Mo Kα radiation, $\lambda = 0.71070$ Å) at 296 K. The structure was solved using the direct method (SIR97),[36] and refined by a full-matrix least-squares analysis (SHELXL-97),[37] giving values of $R_1 = 0.1610$, $wR_2 = 0.2980$, GOF = 1.602, $\rho_{max}/\rho_{min} = 0.721/-0.448$ $\mathrm{e\,Å^{-3}}$. CCDC 237609.

We would like to thank Prof. H. Bock and Dr. N. Nagel (J. W. Goethe University) for helpful discussions and suggestions, and the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science, for the crystal analyses. K. O. thanks the Saneyoshi Scholarship Foundation for financial support.

References

1 J.-M. Lehn, "Supramolecular Chemistry: Concepts and Perspectives," VCH, Weinheim (1995).

2 F. Vögtle, "Supramolecular Chemistry: An Introduction," Wiley, Chichester (1991).

3 "Comprehensive Supramolecular Chemistry," ed by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vögtle, Pergamon Press, Oxford (1996), Vol. 1–11.

4 M. Miyata, M. Shibakami, S. Chirachanchai, K. Takemoto, N. Kasai, and K. Miki, *Nature*, **343**, 446 (1990).

5 M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, and K. Biradha, *Chem. Commun.*, **2001**, 509.

6 T. Suzuki, T. Fukushima, Y. Yamashita, and T. Miyashi, *J. Am. Chem. Soc.*, **116**, 2793 (1994).

7 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, **34**, 2311 (1995).

8 F. Toda, "Diol, Bisphenol, and Diamide Host Compounds," in "Comprehensive Supramolecular Chemistry," ed by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vögtle, Pergamon Press, Oxford (1996), Vol. 6, p. 465.

9 G. M. Whitesides, J. P. Mathias, and C. T. Seto, *Science*, **254**, 1312 (1991).

10 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990).

11 M. Tadokoro and K. Nakasuji, *Coord. Chem. Rev.*, **198**, 205 (2000).

12 K. Tôei, *Anal. Sci.*, **3**, 479 (1987).

13 S. Motomizu, *Bunseki Kagaku*, **48**, 151 (1999).

14 G. J. Moody, R. K. Owusu, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, J. D. R. Thomas, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **26**, 890 (1987).

15 S. Tachiyashiki and H. Yamatera, *Inorg. Chem.*, **25**, 3209 (1986).

16 H. Bock, K. Gharagozloo-Hubmann, M. Sievert, T. Prisner, and Z. Havlas, *Nature*, **404**, 267 (2000).

17 P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, **40**, 486 (2001).

18 K. Tanaka and F. Toda, "Onium Salt Hosts," in "Comprehensive Supramolecular Chemistry," ed by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vögtle, Pergamon Press, Oxford (1996), Vol. 6, p. 517.

19 D. M. M. Farrell, G. Ferguson, A. J. Lough, and C. Glidewell, *Acta Crystallogr.*, **B58**, 530 (2002).

20 K. F. Bowes, G. Ferguson, A. J. Lough, and C. Glidewell, *Acta Crystallogr.*, **B59**, 100 (2003).

21 K. Ono, K. Saito, H. Uchiumi, and M. Tomura, *Chem. Lett.*, **2002**, 622.

22 N. Nagel, H. Bock, and P. Eller, *Z. Kristallogr.*, **215**, 39 (2000).

23 T. Welton, *Chem. Rev.*, **99**, 2071 (1999).

24 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, **39**, 3772 (2000).

25 R. Sheldon, *Chem. Commun.*, **2001**, 2399.

26 D. Zhao, M. Wu, Y. Kou, and E. Min, *Catal. Today*, **74**, 157 (2002).

27 P. Melloni, E. Dradi, W. Logemann, I. De Carneri, and F. Trane, *J. Med. Chem.*, **15**, 926 (1972).

28 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

29 D. M. Shen, U. S. Patent 5298666 (1994); *Chem. Abstr.*, **120**, 322827d (1994).

30 H. Kageyama, O. Furusawa, and Y. Kimura, *Chem. Express*, **6**, 229 (1991).

31 G. M. Sheldrick, "SHELXS-97, Program for the Solution of Crystal Structures," University of Göttingen, Göttingen, Germany (1997).

32 "teXsan, Crystal Structure Analysis Package," Molecular Structure Corporation (1985, 1999).

33 P. G. Jones, *Chem. Br.*, **17**, 222 (1981).

34 G. M. Sheldrick, "SHELXS-86, Program for the Solution of Crystal Structures," University of Göttingen, Göttingen, Germany (1986).

35 G. M. Sheldrick, "SHELXL-93, Program for the Refinement of Crystal Structures," University of Göttingen, Göttingen, Germany (1993).

36 SIR97, Program for the Solution of Crystal Structures: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, **32**, 115 (1999).

37 G. M. Sheldrick, "SHELXL-97, Program for the Refinement of Crystal Structures," University of Göttingen, Göttingen, Germany (1997).