CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901848

Specific Interaction between Chloroform and the Pockets of Triangular Annulene Derivatives Providing Symmetry Carry-Over Crystallization

Ichiro Hisaki,*[a] Hirofumi Senga,[a] Yuu Sakamoto,[a] Seiji Tsuzuki,*[b]
Norimitsu Tohnai,[a] and Mikiji Miyata*[a]

Hexadehydrotribenzo[12]annulene derivatives (DBAs)[1] are molecules that have the following structural characteristics: 1) delocalized π-electron clouds on the conjugated cycle and 2) a well-defined triangle geometry.[2] Because of these aspects, DBAs have been recently investigated from such viewpoints as optoelectronic materials[3] and building blocks for supramolecular assemblies.[4] DBAs are also attractive building blocks for crystalline superstructures.[5] In this context, we designed C_3-symmetric DBAs **1** and **2**, as well as **3** for a control (Figure 1 a), because **1** and **2** are expected to undergo symmetry carry-over crystallization (SCC)[6] through weak hydrogen bonds between the electron-donating substituents and aromatic hydrogen atoms as acceptors (Figure 1 b). Furthermore, the rotationally flexible substituents of the DBAs can fine-tune special noncoincidence when the molecules are packed into the crystals.

During this study on crystal engineering of the DBAs, we serendipitously found exotic complexes of the DBAs with chloroform in crystals of **1** and **2** (Figure 1 c). In the complexes, a hydrogen atom of the chloroform fits into the DBA's "pocket" surrounded by π electrons, which is actually another structural feature of the DBAs in addition to the two mentioned above. Such a complex of DBA with a neutral molecule has been hitherto unknown, although excellent organometallic complexes of DBAs using the pocket were reported by Youngs and co-workers.[7] Furthermore, the complexation seems to play a significant role for SCC in the present system.[8] Namely, chloroform assists the DBAs to form 2D layered networks with C_3-symmetric inclusion

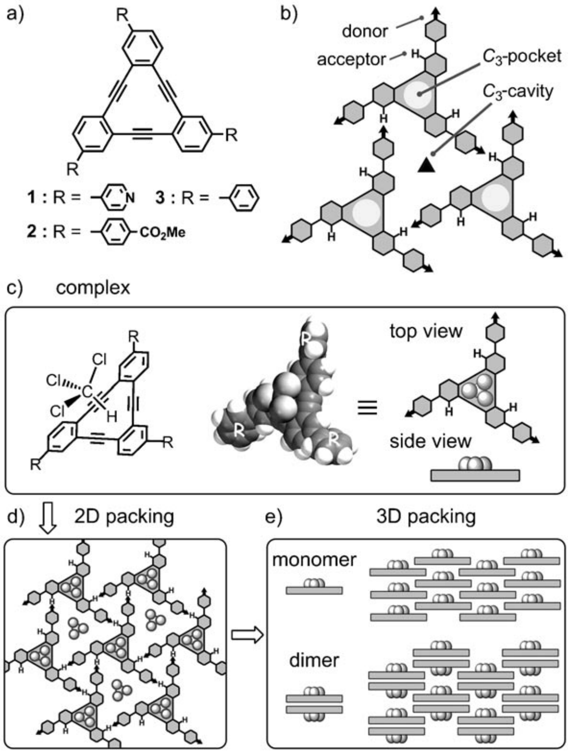

Figure 1. a) Structures of DBA derivatives **1**–**3**. b) A possible molecular arrangement with C_3 symmetry, in which electron donors interact with positively charged aromatic hydrogen atoms. c) Complexation of chloroform with DBA's pocket. Schematic representations of 2D (d) and 3D (e) packing of DBA and chloroform. For 3D packing, the complex can pile up either monomerically or dimerically.

---

[a] Dr. I. Hisaki, H. Senga, Y. Sakamoto, Dr. N. Tohnai,
Prof. Dr. M. Miyata
Department of Material and Life Science
Graduate School of Engineering
Osaka University, 2-1 Yamadaoka
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7406
E-mail: hisaki@mls.eng.osaka-u.ac.jp
miyata@mls.eng.osaka-u.ac.jp

[b] Dr. S. Tsuzuki
Research Institute of Computational Sciences
National Institute of Advanced Industrial Science and Technology
Tsukuba Ibaraki 305-8568 (Japan)
Fax: (+81) 29-851-5426
E-mail: s.tsuzuki@aist.go.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901848.

space (Figure 1 d), and subsequently the complexation between the chloroform and the DBA allows one layer to fit in the adjacent ones with aligning their C_3-rotational axes (Figure 1 e). Herein, we describe crystal structures of DBAs **1** and **2**, roles of chloroform for SCC, and quantitative evaluation for the origin of attractive interactions in the complexes.

Syntheses of the DBAs were performed according to Scheme S1 in Supporting Information. Crystallographic analysis revealed that **1** and **2** gave coplanar structure with C_3-axes, while **3**, which has no electron-donating groups, gave no coplanar but zigzag β-type[9] structure.[10]

DBA **1** crystallized into the space group of $R3c$ with accompanying inclusion of chloroform in a 1:1 molar ratio as shown in Figure 2 a–d.[11] DBA molecules in green color are arranged on the *ab* plane coplanar, and the molecules in orange on the neighbor plane are inverted (Figure 2 a). The distance between the layers composed of green and orange molecules is 2.28 Å (Figure 2 b). Since the substituents of **1** are not long enough to interact with the neighbors on the same plane, they interact with the DBAs on the adjacent layer; the nitrogen atoms of the pyridines form C−H···N bonds (i–iii) with the aromatic hydrogen atoms of the DBA on the adjacent layer (N···C distance of 3.38 Å and C-H-N angle of 133.3° in Figure 2 d).[12] Chloroform molecules are laid in C_3-symmetric inclusion spaces surrounded by the pyridine rings staggered by 35.2° from the DBA plane, though directional, strong interactions are not observed between the chloroform and the pyridine rings. However, the chloroform forms a complex with **1** as described above. The distance between the carbon atom of the chloroform and the DBA plane is 2.99 Å (Figure 2 b). Figure 2 c shows a schematic sectional view along the (110) plane. Chloroform molecules on the DBAs fit into the C_3-symmetric cavities sophisticatedly to pile up the layers along the *c* axis with the chloroform molecules facing to the same direction, constructing the 3D crystal structure.

DBA **2** crystallized into the space group of $R\bar{3}c$ with accompanying inclusion of chloroform in a 2:3 molar ratio as shown in Figure 2 e–h.[11] Contrary to **1**, compound **2** forms a π-stacked dimer (a pair of green and orange molecules) with an interplanar distance of 3.19 Å, probably due to dipole interactions between the carboxylate moieties. Both faces of the dimer are occupied by chloroform to form the complex (Figure 2 f). The distance between the carbon atom of the chloroform and the DBA plane in the complex is 3.29 Å. The dimers are then hexagonally packed to form the coplanar structure, which is stabilized by intermolecular C−H···O interactions between the hydrogen atoms in the benzene ring and the carbonyl oxygen atoms (i: O1···H−C8A, ii: O1A···H−C8B, and iii O1B···H−C8 with C···O distance of 3.44 Å and C-H-O angle of 147.0° in Figure 2 h).[12] The benzene rings, staggered by 20.7° from the DBA plane, interact with the chloroform (iv: C13−H···Cl1, v: C13A−H···Cl1A, and vi: C13B−H···Cl1B with the C···Cl distance of 3.64 Å and Cl-H-C angle of 132.8°). The sectional view (Figure 2 g) shows that the complexes pile up along the *c* axis, and in one cavity, totally three chloroform molecules are included on a line.

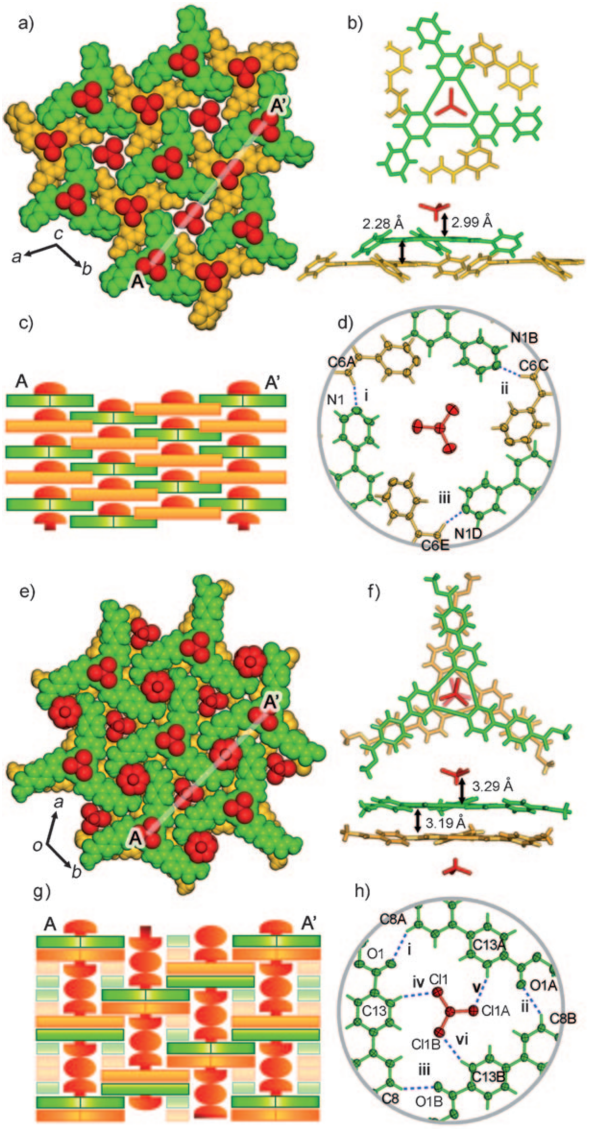

Figure 2. Crystal structures of $\mathbf{1}\cdot\mathrm{CHCl_3}$ (a–d) and $\mathbf{2}\cdot\mathrm{CHCl_3}$ (e–h). a,e) Molecular arrangements in the layered motifs, where the DBAs are colored in green and orange and chloroform in red. b,f) Complexes of the DBA and chloroform molecule. c,g) Schematic sectional views along the (110) plane. In the view g), one of the three chloroform molecules in the cavity are disordered. d,h) Intermolecular interactions around the included chloroform molecules with thermal ellipsoids at the 50 % probability. Symmetry codes for d) A: $5/3-y$, $4/3-x$, $1/6+z$; B: $1-x+y$, $1-x$, z; C: $2/3-x+y$, $-2/3+y$, $-1/6+z$; D: $1-y$, $x-y$, z: E: $-1/3+x$, $1/3+x-y$, $-1/6+z$. Symmetry codes for h) A: $1-y$, $x-y$, x; B: $1-x+y$, $1-x$, z.

Crystallization of **2** from THF also gave a $R\bar{3}c$ crystal, a void space of which accommodates three disordered THF molecules (crystal **2**·THF).[10] This indicates that strict C_3-symmetric guest molecule is not necessary for **2** to experience C_3-SCC probably due to relatively robust network of the DBA.[13] A solution of **1** in CH_2Cl_2/hexane , on the other hand, gave a crystal of the hydrate, instead of CH_2Cl_2 solvate, with the space group of $C2/c$, although the DBAs were arranged coplanar on the (40$\bar{4}$) plane.[10] These indicate that chloroform molecules must contribute to C_3-SCC of DBAs, at least in the case of crystal **1**$\cdot$$CHCl_3$. Chloroform molecules can act as a template of the C_3-void space. Furthermore, specific interaction between chloroform in the C_3-void space and the C_3-pocket of DBA allows the C_3-rotation axes in one layer to align with those in the adjacent layers, leading to the construction of C_3-symmetric crystals.

In an early stage of this study, we believed that the attractive interaction to form the complexes should be the electrostatic one between the acidic hydrogen atom of the chloroform and π-electron clouds of three acetylene units: namely, a CH/π interaction with a hydrogen bond character. However, Tsuzuki and co-workers suggested us another possible candidate: dispersion force between the benzene rings of the DBA and the chlorine atoms.[14] To certify the origin of the affinity between the DBA core and chloroform molecule quantitatively, we applied ab initio molecular orbital calculations for the following four model complexes (Figure 3): A) a DBA–chloroform complex in which the hydrogen atom of the chloroform is directed into the center of the pocket, and the chlorine atoms are located above the benzene rings (the complexes experimentally observed in the crystals correspond to the complex A); B) a DBA–methane complex in which the chlorine atoms of the chloroform molecule are replaced by hydrogen atoms although the geometry is same as the complex A; C) a DBA–chloroform complex in which the hydrogen atom of the chloroform is facing in the opposite direction to that of the complex A; and D) a DBA–chloroform complex in which the chlorine atoms are located over the acetylene units. The intermolecular distance (R) between the carbon atom of the chloroform and the DBA plane is indicated for each model in Figure 3.

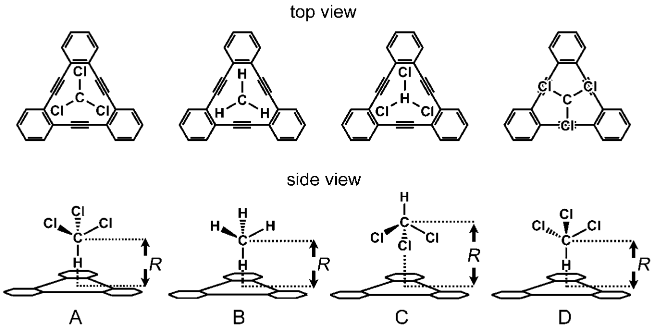

Figure 3. Four model complexes for the ab initio computational study. R denotes the distances between the carbon atom of the chloroform and the DBA plane.

Figure 4 shows the interaction energy (E) plotted versus R at the HF and MP2 levels using the cc-pVTZ basis set. It can be seen from Figure 4a that the HF level potential of the complex A has a very shallow minimum, while that of the MP2 level is deep. This indicates that the contribution of the electrostatic interaction to the attractive force is small and the major source of the attractive force is the dispersion force.[15] Figure 4b demonstrates that the HF level potential of the complex B has no minimum, indicating that almost no electrostatic attraction works in the complex B. The MP2 level potential of the complex B has a much shallower minimum than that of the complex A. Therefore, in the complex A, the chlorine atoms strongly contribute to the dispersion interaction.

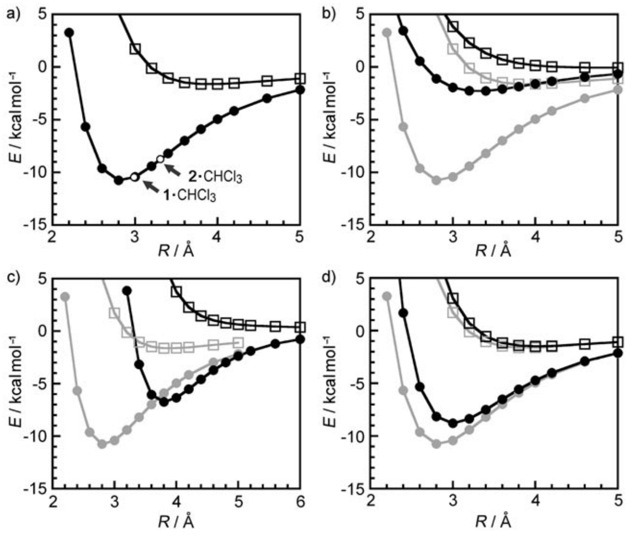

Figure 4. Intermolecular interaction potential curves of complexes a) A, b) B, c) C, and d) D calculated by the HF (open square) and MP2 (solid circle) method with cc-pVTZ basis set. Small open circles in a) correspond to the complexes observed in crystals **1**$\cdot$$CHCl_3$ and **2**$\cdot$$CHCl_3$. In b)–d), the curves for complex A are described in gray for easy comparison.

Next, the orientation effects of the chloroform were investigated by comparing the potentials of the complex A with those of the complexes C and D. Instead of shallow minimum in the HF potential of the complex A, that of the complex C has no minimum (Figure 4c), indicating that the electrostatic interaction is attractive when the C–H bond of chloroform points toward the DBA. The potential of the complex D (Figure 4d) is slightly shallower than that of the complex A. The dispersion interactions of chlorine atoms with the benzene rings are larger than those with the triple bonds.

The interaction energies at the potential minima are summarized in Table 1. The MP2/cc-pVTZ level interaction en-

Table 1. Intermolecular interaction energies [kcal mol^{-1}] of complexes A, B, C, and D at interaction potential minimum.

	R[a]	E_{MP2}[b]	E_{HF}[c]	E_{corr}[d]	E_{es}[e]
A	2.8	−10.75	5.11	−15.86	−1.97
B	3.4	−2.26	1.31	−3.57	0.17
C	3.8	−6.73	6.46	−13.20	0.51
D	3.0	−8.79	3.08	−11.87	−1.44

[a] Distance [Å] between the carbon atom of the chloroform and DBA plane. [b] The MP2 level interaction energy. [c] The HF level interaction energy. [d] The correlation interaction energy ($E_{corr}=E_{MP2}-E_{HF}$), which is mainly the dispersion energy. [e] The electrostatic energy, calculated as an interaction between distributed multipoles of monomers obtained from the MP2/6-311G** wave functions of isolated molecules.

ergies (E_{MP2}) for the complexes A–D are −10.75, −2.26, −6.73, and −8.79 kcal mol^{-1}, respectively. Complex A has the largest (most negative) interaction energy among them, supporting the validity of the experimentally observed structures, in which the hydrogen atom of chloroform fits into the pocket of the DBA. The correlation interaction energy of the complex A ($E_{corr} = -15.86$ kcal mol^{-1}) is significantly larger than that of the complex B, indicating that the chlorine atoms particularly contribute to the dispersion. The electrostatic interaction (E_{es}) also acts as an attractive force in the complex A, although its magnitude is smaller by a factor of eight than that of the dispersion forces, that is, E_{corr}.

In Figure 4 a, two open circles correspond to the complexes experimentally observed in crystals **1**•$CHCl_3$ and **2**•$CHCl_3$. The *R* value for **1**•$CHCl_3$ (2.99 Å) is close to that at the potential minimum and the *R* value for **2**•$CHCl_3$ (3.29 Å) is slightly larger. Their E_{MP2} at these distances are −10.4 and −8.8 kcal mol^{-1}, respectively. These calculations are consistent with their crystallization behaviors. Namely, crystallization of **1** was significantly dependent on the solvent and the molecular arrangement in crystal **1**•$CHCl_3$ results from specific strong interaction with chloroform. Meanwhile, the molecular arrangement in crystal **2**•$CHCl_3$ was achieved even when THF was adopted as the solvent, implying that interaction between the DBA and chloroform is not significantly specific for controlling the crystal structure.

In conclusion, we described that C_3-symmetric DBAs **1** and **2** underwent SCC into the space groups of $R3c$ and $R\bar{3}c$, respectively. In the crystals, the DBA core and chloroform form the complex, in which a hydrogen atom of the chloroform molecule fits into a "pocket" of the DBA. The complex is the first example for complexation between DBA and an organic molecule. The calculations of the chloroform–DBA complexes show that most of the affinity was produced by the dispersion forces between the benzene rings of the DBA and the chlorine atoms (−15.86 kcal mol^{-1}), while contribution of the electrostatic interaction was only −1.97 kcal mol^{-1}.

Finally, we suggest that the SCC of planer π-conjugated molecules should require the following two key steps: 1) construction of highly-symmetric layer assembly and 2) stacking of the layer with orienting its symmetrical axes to those of adjacent ones. In this study, the former step was accomplished by rational design of the DBAs and inclusion of chloroform into the void space. The latter was done by specific interaction between chloroform and the pocket of the DBA. However, many unsettled issues still remain concerning SCC, such as what crucially controls the symmetry of molecular assemblies. Further investigation is continuing in our laboratory.

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research and the Cooperation for Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) program by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Keywords: ab initio calculations • annulenes • crystal engineering • dispersion energy • supramolecular chemistry

---

[1] a) H. A. Staab, F. Graf, *Tetrahedron Lett.* **1966**, *7*, 751–757; b) I. D. Campbell, G. Eglinton, W. Henderson, R. A. Raphael, *Chem. Commun.* **1966**, 87–89.

[2] a) C. S. Jones, M. J. O'Connor, M. M. Haley in *Acetylene Chemistry* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**, pp. 303–385; b) U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107–119; c) E. L. Spitler, C. A. Johnson II, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344–5386.

[3] a) J. J. Pak, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 8182–8192; b) A. Sarkar, J. J. Pak, G. W. Rayfield, M. M. Haley, *J. Mater. Chem.* **2001**, *11*, 2943–2945; c) J. A. Marsden, J. J. Miller, M. M. Haley, *Angew. Chem.* **2004**, *116*, 1726–1729; *Angew. Chem. Int. Ed.* **2004**, *43*, 1694–1697; d) M. Sonoda, Y. Sakai, T. Yoshimura, Y. Tobe, K. Kamada, *Chem. Lett.* **2004**, *33*, 972–973; e) J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476.

[4] Examples for molecular assemblies, see: a) H. Enozawa, M. Hasegawa, D. Takamatsu, K. Fukui, M. Iyoda, *Org. Lett.* **2006**, *8*, 1917–1920; b) S. H. Seo, T. V. Jones, H. Seyler, J. O. Peters, T. H. Kim, J. Y. Chang, G. N. Tew, *J. Am. Chem. Soc.* **2006**, *128*, 9264–9265; c) S. H. Seo, J. Y. Chang, G. N. Tew, *Angew. Chem.* **2006**, *118*, 7688–7692; *Angew. Chem. Int. Ed.* **2006**, *45*, 7526–7530; d) K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T, Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.* **2006**, *128*, 16613–16625.

[5] a) A. J. Matzger, M. Shim, K. P. C. Vollhardt, *Chem. Commun.* **1999**, 1871–1872; b) I. Hisaki, Y. Sakamoto, H. Shigemitsu, N. Tohnai, M. Miyata, S. Seki, A. Saeki, S. Tagawa, *Chem. Eur. J.* **2008**, *14*, 4178–4187; c) K. Tahara, T. Fujita, M. Sonoda, M. Shiro, Y. Tobe, *J. Am. Chem. Soc.* **2008**, *130*, 14339–14345.

[6] One of the interesting issues for crystal engineering is how molecular symmetry effects on that of molecular aggregation motifs, and then, hole crystals. To answer this question, G. R. Desiraju proposed the importance of symmetry carry-over crystallization (SCC), pointing to C_3-symmetric molecules as examples, see: a) A. Anthony, G. R. Desiraju, R. K. R. Jetti, S. S. Kuduva, N. N. L. Madhavi, A. Nangia, R. Thaimattam, V. R. Thallad, *Cryst. Eng.* **1998**, *1*, 1–18; b) P. K. Thallapally, K. Chakraborty, A. K. Katz, H. L. Carrell, S. Kotha, G. R. Desiraju, *CrystEngComm* **2001**, *31*, 1–3.

[7] Complexation with metals such as Ni was reported, see: a) J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *J. Am. Chem. Soc.* **1985**, *107*, 6719–6721; b) J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *Organometallics* **1987**, *6*, 676–678; c) A. Djebli, J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *J. Chem. Soc. Chem. Commun.* **1988**, 548–549; d) J. D. Ferrara, A. A. Tanaka, C. Fierro, C. A. Tessier-Youngs, W. J. Youngs, *Organometallics* **1989**, *8*, 2089–2098; e) W. J. Youngs, J. D. Kinder, J. D. Bradshaw, C. A. Tessier, *Organometallics* **1993**, *12*, 2406–2407.

[8] To date only three crystal structures are reported for SCC of DBAs in reference [5a–c], although the last one has pseudo C_3-symmetry.

[9] G. R. Desiraju, A. Gavezzotti, *Acta. Crystallogr. Sect. B* **1989**, *45*, 473–482.

[10] For the details of crystallographic analyses, see the Supporting Information.

[11] Crystal data for **1**•$CHCl_3$: $(C_{39}H_{21}N_3)(CHCl_3)$, $M_r = 650.99$, $a = b = 19.8463(4)$ Å, $c = 13.7227(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 4680.87(16)$ Å^3, $T = 213$ K, trigonal, space group $R3c$ (no. 161), $Z = 6$, $\mu(Cu_{K\alpha}) = 2.929$ mm^{-1}, $\rho_{calcd} = 1.386$ g cm^{-3}, 15 269 collected, 1903 unique ($R_{int} = 0.084$) reflections, the final $R1$ and w$R2$ values 0.050 [$I > 2.0\sigma(I)$] and 0.124 (all data), respectively. Crystal data for

2•$CHCl_3$: $(C_{48}H_{30}O_6)_4(CHCl_3)_6$, $M_r = 3527.31$, $a = b = 18.7299(5)$ Å, $c = 40.0102(14)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 12\,155.5(6)$ Å^3, $T = 123$ K, trigonal, space group $R\bar{3}c$ (no. 167), $Z = 3$, $\mu(Cu_{K\alpha}) = 3.395$ mm^{-1}, $\rho_{calcd} = 1.445$ g cm^{-3}, 42736 collected, 2486 unique ($R_{int} = 0.130$) reflections, The final $R1$ and w$R2$ values 0.097 [$I > 2.0\sigma(I)$] and 0.300 (all data), respectively. CCDC-745440 (**1**•$CHCl_3$) and CCDC-745441 (**2**•$CHCl_3$) 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.

[12] In connection with a weak hydrogen bond such as C−H···X (X = O or N), a distance between C and X atoms can range from 3.0 to 4.0 Å, which is longer and more widely distributed than the distance observed in stronger hydrogen bond such as O−H···X (X = O or N) bond. The hydrogen bond angle C-H-X (X = O or N) of the weak hydrogen bond is also widely distributed in the range of 90 to 180°, although Desiraju and Steiner recommend a lower limit of 110° when accepting a C−H···O geometry as a hydrogen bond. See: a) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**; b) T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; c) G. R. Desiraju, *Chem. Commun.* **2005**, 2995–3001.

[13] Similar rhombohedral symmetry systems of chloroform solvate and disordered solvate have been reported, see: R. Thaimattam, F. Xue, J. A. R. P. Sarma, T. C. W. Mak, G. R. Desiraju, *J. Am. Chem. Soc.* **2001**, *123*, 4432–4445.

[14] a) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Phys. Chem. A* **1999**, *103*, 8265–8271; b) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2000**, *122*, 3746–3753; c) K. Shibasaki, A. Fujii, M. Mikami, S. Tsuzuki, *J. Phys. Chem. A* **2007**, *111*, 753–758; d) S. Tsuzuki, A. Fujii, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2584–2594.

[15] The HF calculation can evaluate the electrostatic and exchange–repulsion interactions but cannot do the dispersion interaction, while the MP2 calculation can evaluate the dispersion interaction, since the dispersion interaction has its origin in electron correlation. Thus, the HF calculation underestimates the attraction significantly compared to the MP2 calculation when the dispersion interaction is mainly responsible for the attraction in the complex: see reference [14].

Received: July 3, 2009