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Difference in guest-inclusion abilities of *anti*- and *syn*-rotamers

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Guest inclusion abilities of two rotamers, *anti*- and *syn*-*N*,*N*′-bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimides **1** and **2**, were investigated. Rotamers **1** and **2** were synthesised from 2-*tert*-butylaniline and naphthalene-1,4,5,8-tetracarboxylic dianhydride and separated by conventional column chromatography on silica gel. Recrystallisation of **1** from chloroform in the presence of a guest molecule (3 mole equivalents) was performed, and 15 guest molecules were included with a variety of host : guest ratios, 1 : 1 (chloroform, pyridine, 4-picoline, benzene, quinoline, diphenylacetylene, naphthalene, and *p*-toluidine), 1 : 2 (phenol, 3-ethylphenol, 4-methoxyphenol, indole, 5-methylindole, and tetrathiafulvalene), and 1 : 4 (benzothiazole). In contrast, **2** showed no inclusion of guest molecules under the same conditions as those applied to **1**. In order to investigate the intermolecular interaction in the crystalline state of **1**, **2** and **1**·(indole)$_2$, X-ray diffraction of single crystals was measured and these structures were compared.

Introduction

Recently, clathrate compounds have been utilised for studying molecular channels,[1] organic networks,[2] molecular recognition[3] and stereoselective reactions.[4] In these studies, conformation of the host molecule was one of the most important factors affecting the guest-inclusion ability, and flexible changes into a suitable host were required to generate a stable host–guest complex. An example of molecular recognition in solution using two stable rotamers was reported by Rebek, Jr., and co-workers. They described the difference in inclusion abilities between the two rotamers and found no difference in host : guest ratio; both rotamers gave 1 : 2 clathrate compounds with ethyl acetate.[5] On the other hand, the construction of differently hydrogen-bonded networks using the same guest was reported by Miyata and co-workers, in polymorphic cholic acid crystals, in which the conformational change of the host was observed, depending on the specific polymorphs, in their X-ray structures.[6] However, there is no report on guest-inclusion ability dependent on the host conformation in clathrate chemistry. In this paper, we report on the difference in the inclusion abilities between the two stable rotamers, *anti*- and *syn*-*N*,*N*′-bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimides **1** and **2**. This is the first example of a clathrate host which exhibits quite different guest-inclusion ability from its conformational isomer. Compound **1** has a broad inclusion ability, though its isomer **2** does not include any guest molecules.

The *N*-phenylimide derivatives are easily available and are useful compounds for studying conformational isomerisation because of their simple structure and thermal stability.[7] In order to examine the different inclusion abilities, the conformers **1** and **2** are designed as follows. 1) A large electron-deficient π-system is introduced at its centre so that strong π–π interaction with electron-rich aromatic compounds is possible (Fig. 1). 2) *N*-(2-Substituted phenyl) groups are put at both edges of the π-system to change the capacity of the space above the π-system. 3) Each of the rotamers **1** and **2** is stabilised by the large rotational barrier of the *N*-2-*tert*-butylphenyl groups with the N–C single bond. The rotational barrier is supposed to be more than 28 kcal mol^{-1}.†[5,7c]

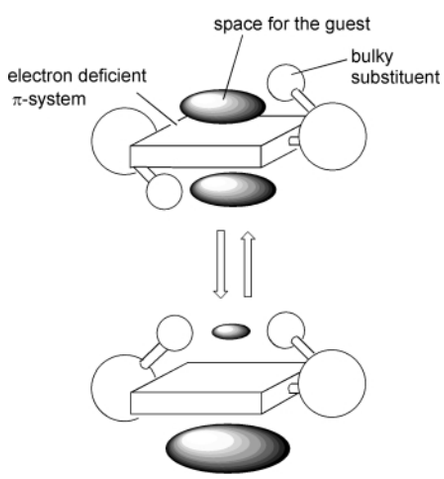

Fig. 1 Rotational isomerisation changes the capacities of the space above the π-system.

Fig. 2 shows the space-filling models[8] (side view) of **1** and **2**, and the dimensions (*a*–*e*) of the concave surfaces are indicated. Isomer **1** [Fig. 2(a)] has a space on both sides of the naphthalene ring. The length *a* (4.0 Å) is longer than the thickness of aromatic π-planes (3.55 Å[9]), and *c* (6.2 Å) is similar to the width of a benzene ring. Therefore, concave surfaces of **1** should be suitable for inclusion of aromatic compounds. While, in the case of **2** [Fig. 2(b)], the width of concave surface *d* (4.1 Å) is too narrow to include an aromatic compound using π–π interaction, dimension *b* is shorter than the thickness of aromatic π-planes although the length *e* (7.5 Å) is sufficient for inclusion. From these observations, the isomer **2** is unsuitable for inclusion of a guest molecule.

† 1 cal = 4.184 J.

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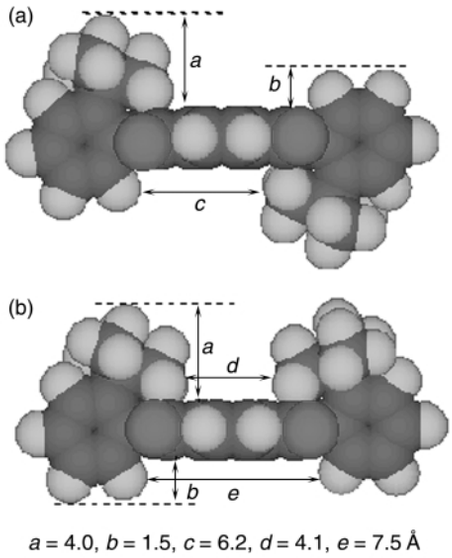
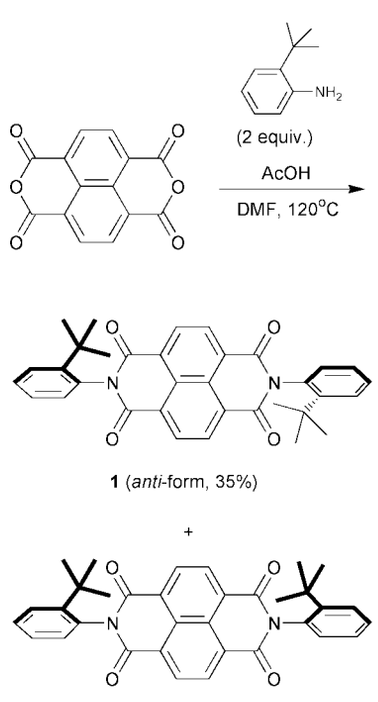


Fig. 2 Space-filled models of **1** (a) and **2** (b).

Results and discussion

Condensation of 2-*tert*-butylaniline and naphthalene-1,4,5,8-tetracarboxylic dianhydride by heating at 120 °C in DMF in the presence of acetic acid for 3 h gave the two stable rotational isomers, *anti*- and *syn*-*N*,*N*′-bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide (**1** and **2**) which were separated by conventional column chromatography on silica gel and elution with benzene–chloroform (Scheme 1). Recrystallisation of **1** and **2** from benzene–chloroform gave yellow and pale red prismatic crystals, respectively.



Scheme 1 Synthetic route to the rotamers.

We attempted to make clathrate compounds of **1** with various aromatic molecules by recrystallisation of **1** from chloroform in the presence of a guest molecule (3 mole equivalents). As a result, 15 guest molecules were included in a variety of host : guest ratios, 1 : 1, 1 : 2, and 1 : 4, which were determined by ^{1}H NMR spectroscopy and elemental analysis (Table 1). Chloroform, pyridine, 4-methylpyridine (4-picoline), benzene, quinoline, diphenylacetylene, naphthalene, and *p*-toluidine, which have no acidic proton (the atomic net charge[10] < +0.181) in the molecule and/or a low HOMO energy level,[10] are included with a host : guest ratio 1 : 1. A host : guest ratio of 1 : 2 was observed with phenol, 3-ethylphenol, 4-methoxyphenol, indole, 5-methylindole, and tetrathiafulvalene, which have an acidic proton (the atomic net charge: +0.215 to +0.247) in the molecule and/or a high HOMO energy level. Furthermore, benzothiazole was included with a ratio 1 : 4. From the results of inclusion experiments, chloroform has the lowest insertion ability in this series.

Table 1 Included guest molecules and host : guest ratios in the clathrate host **1**

Ratio of host : guest[a]	Guest molecules (HOMO energy level, eV[b])
1 : 1	chloroform (−12.9), pyridine (−9.9), 4-picoline (−9.9), benzene (−9.7), quinoline (−9.2), diphenylacetylene (−8.8), naphthalene (−8.7), *p*-toluidine (−8.4)
1 : 2	phenol (−9.1), 3-ethylphenol (−9.0), 4-methoxyphenol (−8.6), indole (−8.4), 5-methylindole (−8.4), tetrathiafulvalene (−8.1)
1 : 4	benzothiazole (−9.0)

[a] The ratios were determined by ^{1}H NMR spectroscopy and elemental analysis. [b] The HOMO energy levels were calculated by AM1.

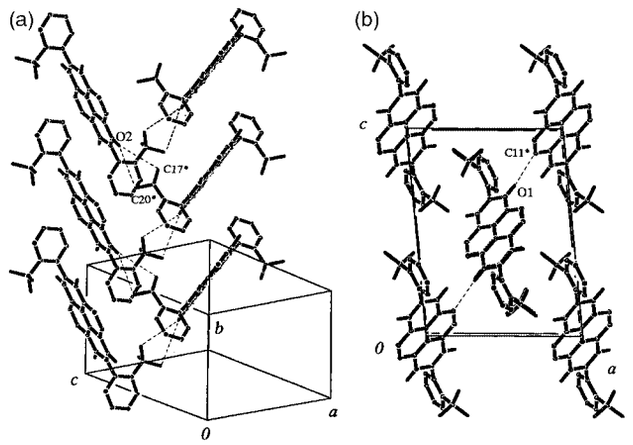


Fig. 3 Crystal structure of **1**. Hydrogen atoms are omitted for clarity. (a) CH···π interaction between the carbonyl and *tert*-butyl groups. O(2)···C(17*) = 3.60, O(2)···C(20*) = 3.63 Å. (b) CH···O interaction of the carbonyl group with the hydrogen of the naphthalene ring. O(1)···C(11*) = 3.39 Å.

In order to investigate the intermolecular interaction in the crystalline state of **1**, X-ray diffraction of a single crystal was measured. Inspection of the crystal structure of **1** [Fig. 3(a)] revealed that only the following weak CH···O interactions [<4 kJ mol^{-1},[11a] 2–20 kJ mol^{-1} (ref. 11b)] were responsible for creation of the network structure. CH···O interactions between the carbonyl oxygen and *tert*-butyl group [O(2)···H–C(17*) and O(2)···H–C(20*)] were observed [O(2)···C(17*): 3.60 Å, O(2)···C(20*): 3.63 Å]. The interaction was estimated to be weak since the observed distances were longer than the typical interatomic distance between an oxygen and a carbon atom, which is in the range 3.20–4.00[11a] (3.00–4.00[11b]) Å. Another CH···O interaction occurs between the other carbonyl oxygen and the naphthalene hydrogen [O(1)···H–C(11*), Fig. 3(b)], which is supposed to be stronger than the above mentioned [O(1)···C(11*): 3.39 Å]. Thus, CH···O

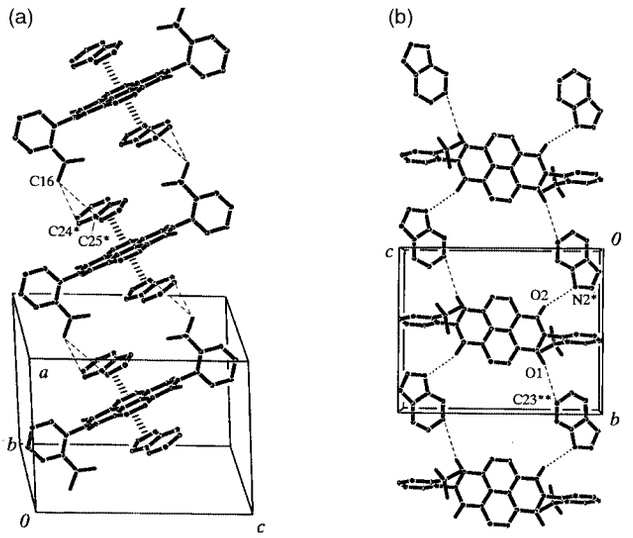


Fig. 4 Crystal structure of **1**·(indole)$_2$. Hydrogen atoms are omitted for clarity. (a) π···π (IIIII) and CH···π interactions (------) between **1** and indole. Distance between each atom of the indole molecule and the naphthalene plane is in the range 3.3–3.7 Å. C(16)···C(24*) = 3.91, C(16)···C(25*) = 3.84 Å. (b) NH···O (·····) CH···O (------) hydrogen bonding. O(2)···N(2*) = 2.80, O(1)···C(23*) = 3.19 Å.

interaction is the main force that maintains the crystal structure of **1**. Accordingly, the weak network of **1** implies it has the possibility to include guest molecules, if the interaction between the host and guest is stronger than that between the host molecules themselves.

The following features are characteristic in the X-ray crystal structure of **1**·(indole)$_2$ complex (Fig. 4), which gave the most stable single crystal in this series of clathrate compounds. Two indole molecules lie on both sides of the naphthalene ring of **1**, and the *tert*-butyl hydrogens of **1** are in contact with the π-face of the indole molecule [C(16)···C(24*): 3.91, C(16)···C(25*): 3.84 Å, Fig. 4(a)]. The crystal colour of **1**·(indole)$_2$ complex is dark red due to the charge-transfer complexation of indole and the electron-poor naphthalene ring of **1**. The distance between each atom of the indole molecule and the naphthalene plane is in the range of 3.2–3.7 Å. A UV spectrum of a chloroform solution of indole and **1** showed a charge-transfer band at λ_{max} 407 nm. Typical hydrogen bonding [2.5–3.2 [11a] (2.50–3.00 [11b] Å, the energy range is 4–15 kcal mol^{-1} (ref. 11a)) (20–40 kJ mol^{-1} (ref. 11*b*))] and CH···O hydrogen bonding were observed between N(2*)–H and O(2) [N(2*)···O(2): 2.80 Å], and between C(23**)–H and O(1) [C(23**)···O(1): 3.19 Å] in the crystal [Fig. 4(b)]. The stabilisation energy from the charge transfer and the hydrogen bonding in this complex is larger than that from the CH···O interactions in the host crystal. This energy difference is the driving force for the construction of the clathrate compounds of **1** with the guests. Mixing of indole (white powder) and **1** (pale yellow powder) gave a red solid, which showed peaks of **1**·(indole)$_2$ complex in the powder X-ray diffraction. This means that the indole molecules insert into the crystal lattice of **1** to produce **1**·(indole)$_2$ complex in the solid phase because of the stabilisation from the complexation.

On the other hand, the single-crystal X-ray crystallography of **2** (Fig. 5) showed a quite different network structure compared with that of **1**. The four molecules in the unit cell form a pinwheel shape using the several CH···O interactions between the two carbonyl oxygen atoms and hydrogen atoms of the two *tert*-butyl groups; [O(4)···H–C(22*), O(4)···H–C(24*), O(2**)···H–C(32), O(2**)···H–C(33), and O(2**)···H–C(34). O(4)···C(22*): 3.64, O(4)···C(24*): 3.62, O(2**)···C(32): 3.77, O(2**)···C(33): 3.66, and O(2**)···C(34): 3.80 Å, Fig. 5(a)]. Each of the CH···O hydrogen bonds is weak. However, the total amount of the interaction energy

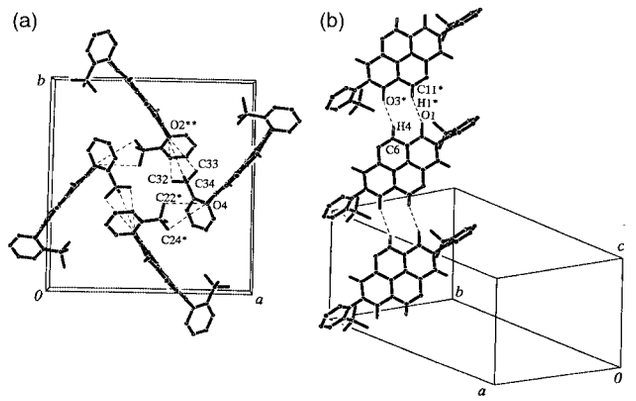


Fig. 5 Crystal structure of **2**. Hydrogen atoms are omitted for clarity. (a) CH···O interaction between the carbonyl and *tert*-butyl groups. O(2**)···C(32) = 3.77, O(2**)···C(33) = 3.66, O(2**)···C(34) = 3.80, O(4)···C(22*) = 3.64, O(4)···C(24*) = 3.62 Å. (b) CH···O (·····) interaction between the molecules. O(1)···C(11*) = 3.26, O(3*)···C(6) = 3.31 Å.

must be large, because several hydrogen atoms of the *tert*-butyl groups simultaneously interact with a carbonyl oxygen. The four molecules are strongly assembled into the pinwheel shape and this interaction makes a rigid two-dimensional network in the *ab* plane using interaction with two of the four carbonyl groups in the molecule. Furthermore, the molecules are stacked in the direction of the *c* axis [Fig. 5(b)]. The other two carbonyl oxygen atoms have a CH···O interaction with the hydrogen atoms at the naphthalene ring [O(1)···H(1*)–C(11*) and O(3*)···H(4)–C(6)]. The interactions are estimated to be extremely strong from their short interatomic distances [O(1)···C(11*): 3.26, O(3*)···C(6): 3.31 Å]. The parallel geometry of the molecules is effective for making the strong CH···O hydrogen bonding. The above-mentioned two-dimensional networks are firmly bonded to each other by strong CH···O interactions to generate a rigid three-dimensional network.

From these X-ray structural studies, we propose the following explanation for the difference between the inclusion abilities of isomers **1** and **2**. The clathrate host **1** includes the various guest molecules using strong interactions: NH···O=C or OH···O=C hydrogen bonding and/or charge-transfer complexation, because the network in the host crystal is only constructed from the weak CH···O interactions. In other words, the network of the host–guest complex is more rigid and stable than that in crystal of **1**.[12] Furthermore, the spaces on both faces of the naphthalenetetracarboxylic diimide of **1**, produced by an *anti*-conformation of the two *tert*-butyl groups, are suitable for the size of the guest molecules. In the case of isomer **2**, the *syn*-conformation of the two *tert*-butyl groups makes different kinds of spaces on each side of the π-system which are not an appropriate size for guest inclusion, and isomer **2** generates the rigid three-dimensional network by itself in its crystal. Accordingly, crystallisation of only compound **2** proceeds, regardless of the presence of other aromatic compounds.

Conclusions

As the results of this study, we found the following facts. 1) The guest-inclusion ability of a clathrate host can be changed by its rotational isomerisation, if the conformations are fixed during the crystal-packing process. 2) In this system, the charge-transfer and hydrogen bonding are the driving force for generating the 1 : 2 complex of **1**. 3) A good fit between the shape of guest and the available space above the π-system of the host is important for complexation with aromatic guests. 4) The network formed by CH···O interactions in the crystal of **2** is more stable than that in the crystal of **1**.

Experimental

^{1}H NMR spectra were obtained on a JEOL LA400 spectrometer. Microanalysis was performed with a Perkin-Elmer 240 elemental analyser. Infrared spectroscopy was performed with Hitachi I-2000 spectrometer. Melting points were measured on a Yanako MO-S3. Single crystal X-ray diffraction was measured on a Rigaku AFC7 diffractometer. In microanalytical data, compound **2** and inclusion compounds of **1** with guest molecules (chloroform, pyridine, 4-picoline, benzene, quinoline, diphenylacetylene, naphthalene, phenol, 3-ethylphenol and benzothiazole) include small amounts of water as hygroscopic water.

Synthesis of *anti*- and *syn*-*N*,*N*′-bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimides (1 and 2)

2-*tert*-Butylaniline (0.58 cm^3, 3.7 mmol), naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (500 mg, 1.8 mmol), and acetic acid (3.9 cm^3, 68 mmol) were heated in DMF (10 cm^3) for 5 h at 120 °C. The solution was cooled to room temperature, diluted with chloroform (100 cm^3), and washed with water (3 × 100 cm^3). The organic solution was concentrated *in vacuo* to give a red solid. The products were separated by column chromatography on silica gel and elution with benzene–chloroform to give the two isomers [**1**; 0.33 g (35%), **2**; 0.29 g (30%)].

Compound 1. Pale yellow crystals (Found: C, 76.98; H, 5.60; N, 5.13. Calc. for $C_{34}H_{30}N_2O_4$: C, 76.96; H, 5.70; N, 5.28%); mp >300 °C (from toluene–chloroform); ν_{max} (KBr)/cm^{-1} 2970 (C–H), 1720 (C=O), 1680 (C=O), 1450, 1350, 770; δ_H (400 MHz; $CDCl_3$) 1.31 (s, 18H), 7.02 (dd, *J* 8.0, 1.5 Hz, 2H), 7.38 (ddd, *J* 8.0, 7.5, 1.5 Hz, 2H), 7.49 (ddd, *J* 8.2, 7.5, 1.5 Hz, 2H), 7.70 (dd, *J* 8.2, 1.5 Hz, 2H), 8.87 (s, 4H).

Crystal data.‡ $C_{34}H_{30}N_2O_4$, $M = 530.62$, yellow, prismatic, monoclinic, $a = 11.061(2)$, $b = 8.602(1)$, $c = 14.653(3)$ Å, $\beta = 95.80(2)°$, $V = 1387.1(4)$ Å^3, $T = 296$ K, space group $P2_1/n$ (no. 14), $Z = 2$, μ(CuKα) = 7.61 cm^{-1}, 2362 reflections measured, 2234 unique ($R_{int} = 0.027$) which were used in all calculations. The final *R* and *wR* were 0.050 and 0.053.

Compound 2. Clear red crystals (Found: C, 74.98; H, 5.59; N, 5.24. Calc. for $C_{34}H_{30}N_2O_4 \cdot H_2O$: C, 74.97; H, 5.54; N, 5.04%); mp >300 °C (from chloroform); ν_{max} (KBr)/cm^{-1} 2970, 1680, 1450, 1350, 775 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.30 (s, 18H), 7.06 (dd, *J* 7.7, 1.4 Hz, 2H), 7.39 (ddd, *J* 7.7, 7.7, 1.5 Hz, 2H), 7.49 (ddd, *J* 8.2, 7.7, 1.4 Hz, 2H), 7.71 (dd, *J* 8.2, 7.7, 1.4 Hz, 2H), 8.87 (s, 4H).

Crystal data.‡ $C_{34}H_{30}N_2O_4$, $M = 530.62$, red, prismatic, monoclinic, $a = 9.326(1)$, $b = 16.890(3)$, $c = 18.301(4)$ Å, $\beta = 102.06°$, $V = 2819.1(9)$ Å^3, $T = 296$ K, space group $P2_1/n$ (no. 14), $Z = 4$, μ(CuKα) = 6.59 cm^{-1}, 4669 reflections measured, 4369 unique ($R_{int} = 0.028$) which were used in all calculations. The final *R* and *wR* were 0.062 and 0.063.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·chloroform 1 : 1 complex

Found: C, 64.67; H, 4.81; N, 4.31. Calc. for $C_{35}H_{31}N_2O_4 \cdot 0.2H_2O$: C, 64.32; H, 4.84; N, 4.29%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·pyridine 1 : 1 complex

Found: C, 76.35; H, 5.69; N, 6.41. Calc. for $C_{39}H_{35}N_3O_4 \cdot 0.4H_2O$: C, 75.93; H, 5.85; N, 6.81%.

‡ CCDC reference number 207/436.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·4-picoline 1 : 1 complex

Found: C, 75.68; H, 5.95; N, 6.71. Calc. for $C_{40}H_{37}N_3O_4 \cdot 0.5H_2O$: C, 75.93; H, 6.05; N, 6.64%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·benzene 1 : 1 complex

Found: C, 78.54; H, 5.90; N, 4.18. Calc. for $C_{40}H_{36}N_2O_4 \cdot 0.2H_2O$: C, 78.46; H, 5.99; N, 4.57%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·quinoline 1 : 1 complex

Found: C, 77.93; H, 5.51; N, 6.29. Calc. for $C_{43}H_{37}N_3O_4 \cdot 0.2H_2O$: C, 77.85; H, 5.68; N, 6.33%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·diphenylacetylene 1 : 1 complex

Found: C, 80.46; H, 5.42; N, 3.98. Calc. for $C_{48}H_{40}N_2O_4 \cdot 0.3H_2O$: C, 80.72; H, 5.73; N, 3.92%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·naphthalene 1 : 1 complex

Found: C, 78.42; H, 5.56; N, 4.40. Calc. for $C_{44}H_{38}N_2O_4 \cdot 0.8H_2O$: C, 78.50; H, 5.93; N, 4.16%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·*p*-toluidine 1 : 1 complex

Found: C, 77.23; H, 5.95; N, 6.35. Calc. for $C_{41}H_{39}N_3O_4$: C, 77.21; H, 6.16; N, 6.59%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·phenol 1 : 2 complex

Found: C, 75.78; H, 5.83; N, 3.80. Calc. for $C_{46}H_{42}N_2O_6 \cdot 0.5H_2O$: C, 75.91; H, 5.95; N, 3.85%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·3-ethylphenol 1 : 2 complex

Found: C, 75.51; H, 6.46; N, 3.51. Calc. for $C_{50}H_{50}N_2O_6 \cdot 1.1H_2O$: C, 75.56; H, 6.62; N, 3.52%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·4-methoxyphenol 1 : 2 complex

Found: C, 74.08; H, 5.88; N, 3.49. Calc. for $C_{48}H_{46}N_2O_8$: C, 74.02; H, 5.92; N, 3.60%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·indole 1 : 2 complex

Found: C, 78.51; H, 5.80; N, 7.33. Calc. for $C_{50}H_{44}N_4O_4$: C, 78.30; H, 5.75; N, 7.14%.

Crystal data.‡ $C_{50}H_{44}N_4O_4$, $M = 764.92$, red, prismatic, monoclinic, $a = 11.262(2)$, $b = 11.874(9)$, $c = 14.727(3)$ Å, $\beta = 95.28(2)°$, $V = 1961.1000(4)$ Å^3, $T = 296$ K, space group $P2_1/c$ (no. 14), $Z = 2$, μ(MoKα) = 0.83 cm^{-1}, 2097 reflections measured, 1654 reflections which were used in all calculations. The final *R* and *wR* were 0.060 and 0.066.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·5-methylindole 1 : 2 complex

Found: C, 78.76; H, 6.10; N, 7.07. Calc. for $C_{52}H_{48}N_4O_4$: C, 78.71; H, 5.99; N, 6.98%.

anti-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·tetrathiafulvalene 1 : 2 complex

Found: C, 59.18; H, 4.13; N, 2.90. Calc. for $C_{46}H_{38}N_2O_4S_8$: C, 58.82; H, 4.08; N, 2.98%.

***anti*-*N*,*N*′-Bis-(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxylic diimide 1·benzothiazole 1 : 4 complex**

Found: C, 68.69; H, 4.60; N, 7.66. Calc. for $C_{62}H_{50}N_6O_4S_4 \cdot 0.5H_2O$: C, 68.93; H, 4.76; N, 7.78%.

References

1 (*a*) K. Sada, N. Shiomi and M. Miyata, *J. Am. Chem. Soc.*, 1998, **120**, 10543; (*b*) M. Gdaniec and T. Polonski, *J. Am. Chem. Soc.*, 1998, **120**, 7353; (*c*) N. Hayashi, K. Kuruma, Y. Mazaki, T. Imakubo and K. Kobayashi, *J. Am. Chem. Soc.*, 1998, **120**, 3799; (*d*) K. A. Udachin and J. A. Ripmeester, *J. Am. Chem. Soc.*, 1998, **120**, 1080.

2 (*a*) K. Kishikawa, S. Tsubokura, S. Kohmoto, M. Yamamoto and K. Yamaguchi, *J. Org. Chem.*, 1999, **64**, 7568; (*b*) K. Biradha, D. Dennis, V. A. MacKinnon, C. V. Krishnamohan Sharma and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 11894; (*c*) H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622; (*d*) P. Bhyrappa, S. R. Wilson and K. S. Suslick, *J. Am. Chem. Soc.*, 1997, **119**, 8492; (*e*) K. Biradha and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 6431; (*f*) J. A. Swift, A. M. Pivovar, A. M. Reynolds and M. D. Ward, *J. Am. Chem. Soc.*, 1998, **120**, 5887; (*g*) P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, 1997, **119**, 2737; (*h*) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar and D. Venkataraman, *J. Am. Chem. Soc.*, 1996, **118**, 6946.

3 (*a*) T. Dewa, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1998, **120**, 8933; (*b*) L. R. MacGillivray and J. L. Atwood, *J. Am. Chem. Soc.*, 1997, **119**, 6931; (*c*) D. R. Evans, T. Drovetskaya, R. Bau, C. A. Reed and P. D. W. Boyd, *J. Am. Chem. Soc.*, 1997, **119**, 3633; (*d*) L. R. MacGillivray and J. L. Atwood, *J. Am. Chem. Soc.*, 1997, **119**, 2592; (*e*) K. Tanaka, A. Moriyama and F. Toda, *J. Org. Chem.*, 1997, **62**, 1192.

4 (*a*) F. Toda, H. Miyamoto, H. Koshima and Z. Urbanczyk-Lipkowska, *J. Org. Chem.*, 1997, **62**, 9261; (*b*) F. Toda, H. Miyamoto and H. Koshima, *J. Am. Chem. Soc.*, 1996, **118**, 11315.

5 K. D. Shimizu, T. M. Dewey and J. Rebek, Jr., *J. Am. Chem. Soc.*, 1994, **116**, 5145.

6 K. Nakano, K. Sada and M. Miyata, *Chem. Commun.*, 1996, 989.

7 (*a*) K. Kishikawa, R. Takeuchi, S. Kohmoto, M. Yamamoto, K. Yamaguchi and K. Yamada, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1143; (*b*) K. Kishikawa, K. Yoshizaki, M. Yamamoto, S. Kohmoto, K. Yamaguchi and K. Yamada, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 1233; (*c*) K. Kishikawa, I. Tsuru, S. Kohmoto, M. Yamamoto and K. Yamada, *Chem. Lett.*, 1994, 1605; (*d*) A. Srivastava, V. Srivastava and S. Verma, *J. Org. Chem.*, 1994, **59**, 3560; (*e*) D. P. Curran, S. J. Geib and N. C. DeMello, *J. Am. Chem. Soc.*, 1994, **116**, 3131.

8 Chem3D (Cambridge software corporation) representations of the most stable forms for compounds **1** and **2**.

9 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 443.

10 The AM1 semiempirical molecular orbital method implemented by WinMOPAC version 1.0a (Fujitsu Limited) was used for all calculations. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

11 (*a*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, in *Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999; (*b*) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997; (*c*) G. R. Desiraju and C. V. Krishnamohan Sharma, in *The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, John Wiley and Sons, New York, 1996.

12 R. Thaimattam, D. S. Reddy, F. Xue, T. C. W. Mak, A. Nangia and G. R. Desiraju, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 1783.