Non-hydroxylic clathrate hosts of [4 + 2]π cycloadducts of phencyclone and *N*-arylmaleimides: recognition of aromatic guests †

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A series of non-hydroxylic crystalline host compounds, [4 + 2]π cycloadducts of phencyclone and *N*-arylmaleimides having a bicyclo[2.2.1]heptene-7-one system, was synthesized and their inclusion behavior investigated. X-Ray crystal analyses of the inclusion compounds of the *N*-(1-naphthyl) derivative with butan-2-one, the *N*-(*m*-tolyl) derivative with *p*-xylene, together with the guest-free host and the *N*-(*p*-tolyl) derivative with *m*-xylene indicate that the "space" surrounded by the phenanthrene ring, two phenyl rings and bridge carbonyl of the 1,3-diphenyl-1,3-dihydrocyclopenta[*l*]phenanthren-2-one moiety plays an important role, not only in the formation of inclusion complexes with the aromatic guests but also in host–host interactions. In every case, the *N*-aryl succinimide assists complex formation with the guests, in which the weak lattice forces due to C–H ··· π and C–H ··· O interactions are operative. Methyl-substituted benzenes are effectively recognized by the C–H ··· π interactions between the guest molecules and the phenanthrene ring of the hosts.

Introduction

Crystalline inclusion compounds between simple organic molecules are useful models for studying weak interatomic interactions in molecular recognition and self-organization of molecules.[1a,b] As hosts, organic compounds having various functional groups have been designed and their clathrate forming abilities tested.[1c–h] Characteristic examples are diol or dicarboxylic host molecules, in which the hydroxy groups act as H-bond sites for the guest, as well as assisting host–host interactions.

In the course of studies of the pericyclic reaction behavior of cyclopentadienones, the authors encountered the formation of crystalline inclusion complexes with recrystallization solvents (host : benzene : MeOH = 1 : 1 : 1) in the [4 + 2]π cycloadducts (Diels–Alder adducts) derived from the cycloaddition reactions of phencyclone with *p*-bromostyrene and cyclooctatetraene.[2] Inspection of the crystal data suggests that the phenanthrene ring fused to the bicyclo[2.2.1]hepten-7-one moiety plays an important role in the inclusion of the guest molecule. In connection with this, we have published a communication describing a non-hydroxylic clathrate host of the [4 + 2]π adduct of phencyclone and *N*-(1-naphthyl)maleimide.[3] The inclusion behavior of the several [4 + 2]π adducts of phencyclone and *N*-(1-aryl)maleimides are discussed here with newly obtained data to clarify the overall character of the non-hydroxylic hosts.

† Electronic supplementary information (ESI) available: X-ray crystal reports for **3c**·butan-2-one (1 : 1), **3g**, **3g**·*p*-xylene (1 : 1) and **3h**·*m*-xylene (1 : 1) in .cif format; the distances between host and guest for **3c**·butan-2-one and distances between hosts for **3g**; numbering sequences of the compounds analyzed by X-ray crystallography; the PM3 structures of the model inclusion compounds (host : guest = 1 : 1 and 3 : 1). See http://www.rsc.org/suppdata/p2/b2/b201915a/

Results

Synthesis

The cycloadducts **3a**–**k** were synthesized by the cycloaddition reaction of phencyclone **1a** with *N*-substituted maleimides except for the [4 + 2]π adduct of *N*-(1-naphthylmethyl)-maleimide **3e**. The cycloadduct **3e** was synthesized by the reaction of the [4 + 2]π cycloadduct of maleic anhydride and phencyclone with 1-aminomethylnaphthalene (Scheme 1).

The configurations of the cycloadducts **3a**–**k** were determined to be *endo* on the basis of the NMR spectroscopic analysis of the C ··· H correlation between the bridge carbonyl carbon and the methine protons derived from the dienophiles.

Conformation of the *N*-aryl group of 3

In the cycloadducts **3c**, **3f**, **3i** bearing unsymmetrical *N*-aryl groups, but not the 3-methylphenyl derivative **3g**, the ^{1}H NMR spectra were observed as mixtures of the isomers derived from the restricted rotation about the *N*–Ar bond. The preferred conformations of the unsymmetrical *N*-aryl groups of the cycloadducts **3c**, **3f**, **3i** were determined by ^{1}H NMR spectroscopy. In the 2-methyl derivative **3f**, the methyl proton resonates at −0.03 (55%) and 2.03 (45%) ppm, remarkably high-field shifts due to the phenanthrene-ring current effect. Compounds **3c** and **3i** also showed similar high-field shifted spectral patterns. The 8′-H aromatic proton of **3c** resonates at 4.62 ppm and the ethyl protons of **3i** appeared at −0.15 (CH_3CH_2–) and 0.13 ppm (CH_3CH_2–). The populations (inner : outer) in $CDCl_3$ at room temperature are listed in Fig. 1. The 1-naphthyl, 2-methylphenyl and 2-ethylphenyl derivatives prefer the inner orientation despite the steric repulsion between the *endo*-orientated substituent and the phenanthrene moiety. AM1 and PM3 molecular orbital (MO) calculations[4a] could

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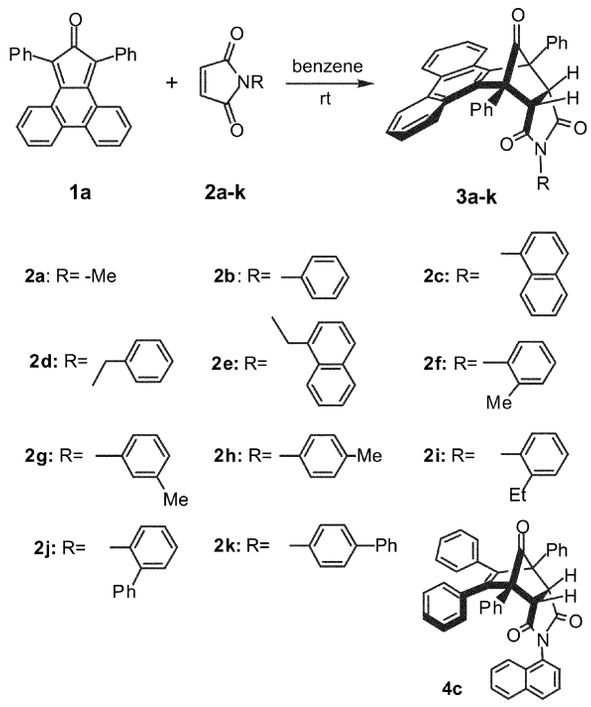

Scheme 1

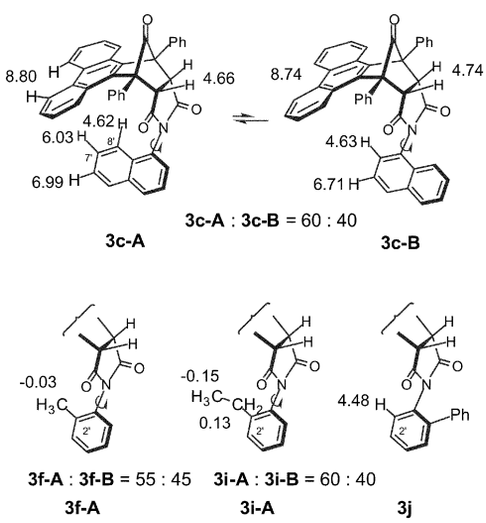

Fig. 1 ^{1}H NMR spectral data for conformational isomers due to restricted rotation about the N–Ar bond in **3c**, **3f** and **3i**.

not reproduce the conformational preference of the inner orientation in **3c**.[4b]

The ^{1}H NMR spectrum of the 2-phenylphenyl derivative **3j** indicates that the 2-phenyl ring is forced to adopt the outer conformation due to the serious steric repulsion in the inner orientation.

Inclusion properties

A variety of solvents (10 solvents of three types: ketone, ether, aromatic) were used to test the inclusion properties of the host compounds **3a**–**k**. Alcoholic solvents were not tested because of the insolubility of the hosts. The inclusion compounds were obtained by slow concentration of the solution of the host compounds in the respective guest solvents under atmospheric conditions. The results are summarized in Table 1. The host : guest ratios were evaluated by ^{1}H NMR spectral integration.

Compounds **3c**, **3f** and **3h** are efficient inclusion hosts. Compounds **3d**, **3g** and **3i** allow fewer inclusions, while compound **3b** afforded no clathrates with solvents tested. Of the DA adducts **3a**–**k**, **3c**, **3j** formed crystalline inclusion compounds with some polar solvents.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) data for some important clathrates are summarized in Table 2. The TG curve confirmed the host : guest stoichiometry. For example, in the **3c**·butanone complex, the total weight loss was observed to be 10.6% in agreement with the expected loss of 10.8% for a 1 : 1 ratio. The DSC data of **3c**·butanone showed a broad endothermic pattern corresponding to guest loss at 136 °C, followed by an endothermic peak at 272 °C caused by melting of the host. The desolvation temperature is high in comparison to the boiling point of pure guest liquid, indicating that the guest molecules are strongly held within the host lattice. In contrast, aromatic guest compounds form loose inclusion complexes, in which the desolvation temperatures are lower than the boiling points of pure guests.

Single crystal X-ray analysis

In order to clarify the structures of the inclusion compounds, the single crystal X-ray analyses were performed.

3c·Butan-2-one complex. A computer-generated drawing of the packing arrangement of the **3c**·butan-2-one inclusion compound is shown in Fig. 2. The important distances between the butan-2-one and the host are presented in Fig. 3 and further

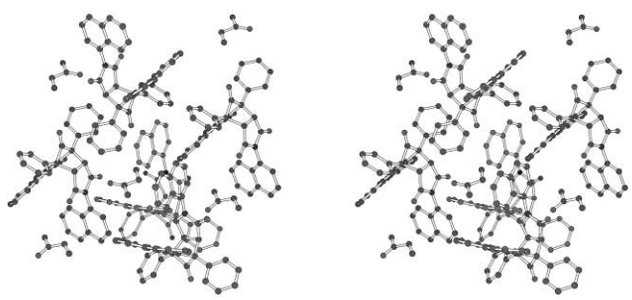

Fig. 2 Stereoview of the crystal packing of the **3c**·butanone complex.

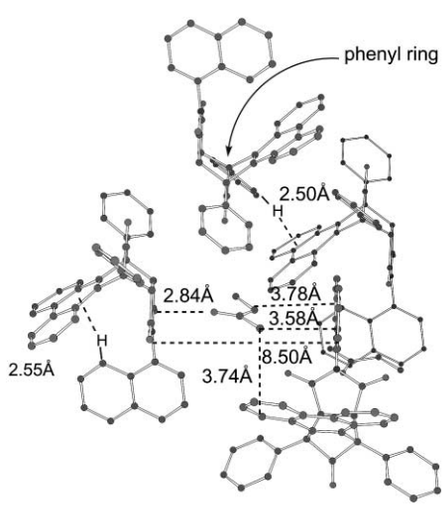

Fig. 3 Intermolecular atom–plane distances (Å) of the **3c**·butanone complex.

details are depicted in the electronic supporting information (ESI-1 †). The plane of the naphthalene ring is almost perpendicular to the maleimide ring and is covered with the phenanthrene ring in an 'edge-to-face' manner,[5] in which the 8′-H proton on the 1-naphthyl ring is located at a close-contact perpendicular distance of 2.54 Å above the face of the phenanthrene ring (Fig. 3).[6] As described above, this special geometrical feature is also observed in solution (see Fig. 1), indicating that **3c** prefers to adopt a congested T-shaped conformation with an attractive intramolecular Ar–H ··· π interaction[5] between the aromatic rings.

Table 1 Crystalline inclusion compounds (host : guest molar ratio)

Guest solvent	Host compound										
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**
Acetone	–	–	1 : 1	1 : 1	–	2 : 1	–	–	–	1 : 1	–
Butan-2-one	–	–	1 : 1	–	–	1 : 1	–	2 : 1	–	2 : 1	–
Pentan-3-one	–	–	1 : 1	–	3 : 2	1 : 1	–	2 : 1	–	2 : 1	–
THF	2 : 1	–	1 : 1	–	–	2 : 1	–	–	–	1 : 1	–
1,4-Dioxane	2 : 1	–	1 : 1	–	1 : 1	1 : 1	–	–	1 : 1	–	1 : 1
Benzene	1 : 1	–	1 : 1	–	–	1 : 1	–	2 : 1	–	–	1 : 1
Toluene	1 : 1	–	1 : 1	–	–	1 : 1	1 : 1	1 : 1	–	–	–
o-Xylene	–	–	1 : 1	–	–	–	–	1 : 1	–	–	1 : 1
m-Xylene	1 : 1	–	1 : 1	–	–	1 : 1	–	1 : 1	–	–	–
p-Xylene	1 : 1	–	1 : 1	–	1 : 1	1 : 1	1 : 1	1 : 1	–	–	–

Table 2 Differential scanning calorimetry (DSC) and thermogravimetry (TG) data

	Host molecule				
	3c	**3g**	**3h**	**3j**	**3j**
Guest molecule	Butanone	*p*-Xylene	*m*-Xylene	Acetone	Butanone
Host : guest ratio	1 : 1	1 : 1	1 : 1	1 : 1	2 : 1
Bp (guest)/°C	80	138	138	56	80
DSC:					
Desorption endotherm onset temperature/°C	136	110	98	143	135
Host melting endotherm onset temperature/°C	272	287	277	284	284
TG:					
Weight loss expected (%)	10.8	15.6	15.6	8.2	5.2
Weight loss observed (%)	10.6	13.0	15.7	8.4	5.4

The DA adduct (**4c**) of 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) having a stilbene moiety did not show a clear stoichiometric host–guest ratio with butan-2-one, which cannot form the T-shaped conformation that the 1-naphthyl ring is able to (see Scheme 1 for the structure of **4c**).

As can be seen in Figs. 2 and 3, butan-2-one is located between the parallel stacked walls of the neighboring naphthyl and maleimide rings. The distance between the guest carbonyl oxygen and the host maleimide-ring plane is 2.84 Å.[7a] The distances between the naphthyl-ring plane and the methyl and methylene carbons of the guest are 3.58 Å and 3.78 Å, respectively [see also the supplementary informationESI-1 †]. The guest methylene protons and carbonyl oxygen form C–H ··· O hydrogen bonds[8] with the host carbonyl oxygen and the naphthyl proton, respectively.[7b]

As an important host–host interaction, the phenyl ring of the adjacent host molecule is located above the phenanthrene ring (see Fig. 3).

3g and 3g·*p*-xylene complex. A computer-generated drawing of the crystal structure of the free host **3g** is depicted in Fig. 4a,b. The crystal packing of the free host **3g** is interesting. The molecules occur in the crystal as pairs of enantiomers bonded together *via* an attractive π–π interaction between the 1,3-diphenylpropanone moieties across a center of symmetry. The closest contact (3.02 Å) is found between the ketonic oxygen atom and the carbon at the 2′-position of the facing phenyl group. In addition, other short C ··· C contacts (3.42 Å) are found between the 2′-positions of the phenyl group and the 4′-positions of the one opposite.

These dimeric host molecules are intermolecularly linked by a C–H ··· O hydrogen bond and edge-to-face type interactions between aromatic rings of the host molecules. The C–H ··· O hydrogen bonds are evident between the imide carbonyls and the phenanthrene ring [C–(H) ··· O, 3.30 Å] and phenyl ring [C–(H) ··· O, 3.32 Å] of neighboring host molecules. These C–H ··· O hydrogen bonds together with the close contacts described above play a leading role in the construction of the host framework.

The edge-to-face type interaction is found between the diphenyl rings and the adjacent phenanthrene rings in which the distance between the phenyl hydrogen atom and the least-squares plane of the phenanthrene ring is 2.46 Å [the distance C–(H) ··· plane = 3.55 Å]. The plane of the phenanthrene ring of the free host **3g** is remarkably distorted, in which the dihedral angle (τ) C4–C4a–C4b–C5 is 7.00°.[9a,b] Distortion of the phenanthrene ring from the ideal planar structure may be accounted for by the closest approach[10] of the phenyl hydrogen atom to the phenanthrene ring plane constrained by other crystal packing forces, wherein the back-side C–(H) ··· O interaction between the phenanthrene ring and the imide carbonyl is operative (see Fig. 4b).

This distorted dihedral angle is reduced to 2.90° by inclusion of the guest molecule. This may be attributable to the relief of the strain due to the edge-to-face interactions between the host molecules. This geometrical feature seems to be important in connection with the recognition mode of aromatic guests by the phenanthrene-condensed bicyclo[2.2.1]heptenone moiety.

Computer-generated drawings of the crystal structure of the inclusion complex (**3g**·*p*-xylene) are depicted in Figs. 5 and 6 (see also ESI-2 †). Comparison of the packing diagrams of the guest-free host **3g** and **3g**·*p*-xylene complex indicates that the arrangement mode of the host molecules in the complex is almost the same as that of the free host **3g**. In the **3g**·*p*-xylene complex, the guest molecules intrude into the spaces occupied by the edge-to-face interaction (phenanthrene ring–phenyl ring) in the crystal structure of the free host **3g** (Fig. 5). The guest molecule is located almost parallel with both the succinimide ring and the plane of the bridge carbonyl group of the neighboring host molecules. The geometry of the two 1,3-diphenylpropanone moieties is not largely altered by the inclusion of the guest. This reflects the dimensions of the crystal lattice constants: the *b* and *c* axes of the inclusion complex are longer than those of the host by 2.5 Å and 1.5 Å, respectively.

One of the methyl groups of *p*-xylene makes a C–H ··· O hydrogen bond with a carbonyl group of the succinimide moiety [C–(H) ··· O, 3.52 Å] and an aromatic proton of

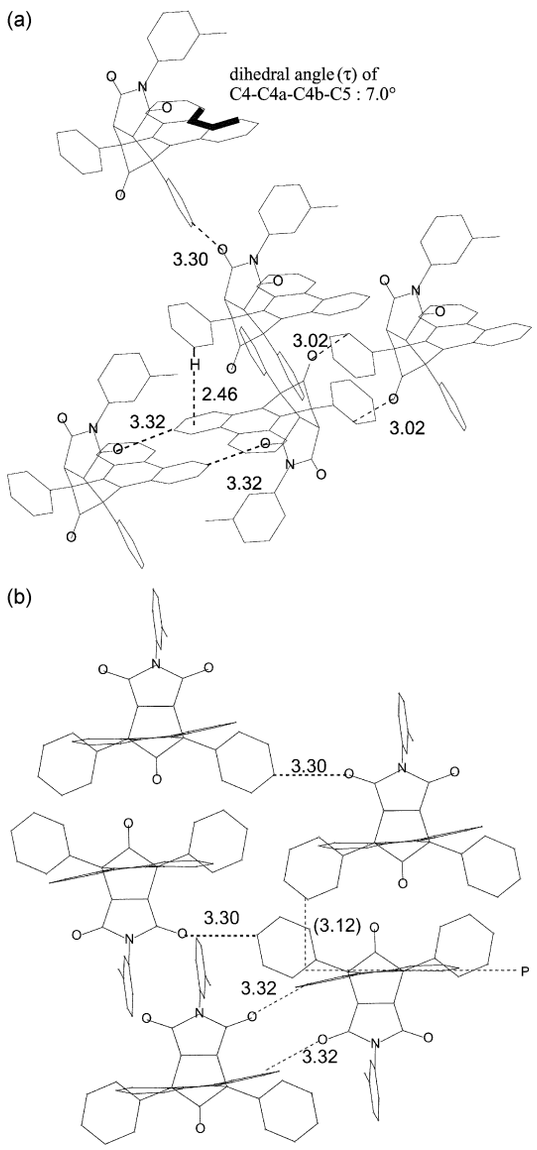

Fig. 4 (*a*) Short contacts in the crystal structure of the guest-free host (**3g**). (*b*) Distortion of the phenanthrene ring in the crystal structure of the guest-free host (**3g**). The horizontal dotted line (P) is the undistorted phenanthrene plane (see ref. 10).

p-xylene also hydrogen-bonds with the bridge carbonyl [C–(H) ··· O, 3.34 Å] (see Fig. 6).

The plane of *p*-xylene makes the angle of 47.50° with the phenanthrene ring and the "space" created by phenanthrene ring, the bridge carbonyl and diphenyl groups hold a *p*-xylene molecule which faces the succinimide ring with an interplane distance of 3.6 Å. The importance of the role of the "space" is also observed in the *m*-xylene·**3h** (*p*-tolyl derivative) complex described below.

The host **3g** included only toluene and *p*-xylene. This inclusion behavior is attributable to the nature of the cavity and the strict steric requirement due to the different types of CH ··· O interaction.

3h·*m*-Xylene complex. The computer-generated drawings of the inclusion complex **3h**·*m*-xylene are depicted in Figs. 7 and 8. As the case of **3g**·*p*-xylene, the "space" on the phenanthrene ring plays an important role in the holding of the guest. The interplanar distance between the phenanthrene rings is 7.21 Å. The intermolecular room created by the two "spaces" enclathrates two molecules of *m*-xylene (Me ··· Me, 4.32 Å). The distance between a methyl carbon of *m*-xylene and the phenanthrene-ring plane is 3.70 Å. On the other hand, along

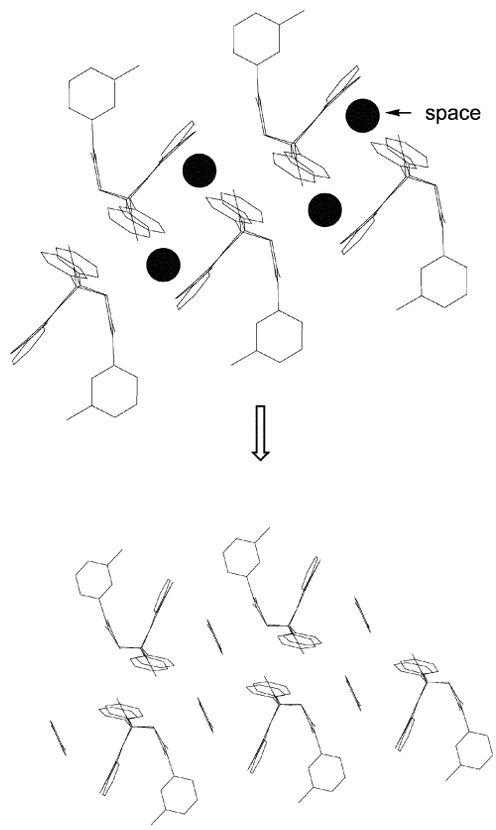

Fig. 5 Comparison of the crystal packings for **3g** (top) and **3g**·*p*-xylene (bottom).

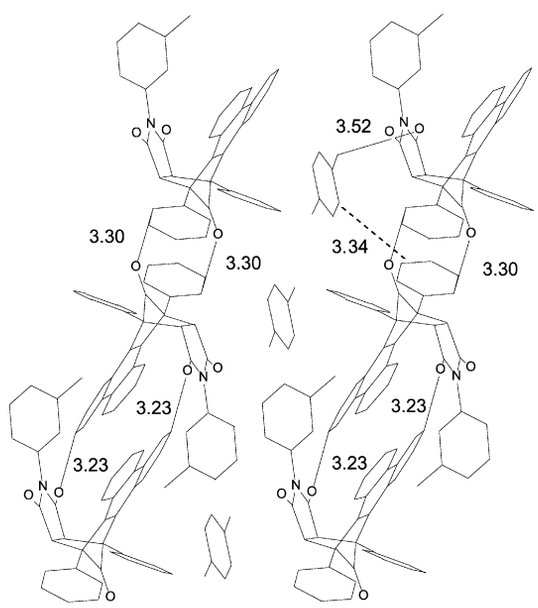

Fig. 6 Crystal structure of the **3g**·*p*-xylene complex.

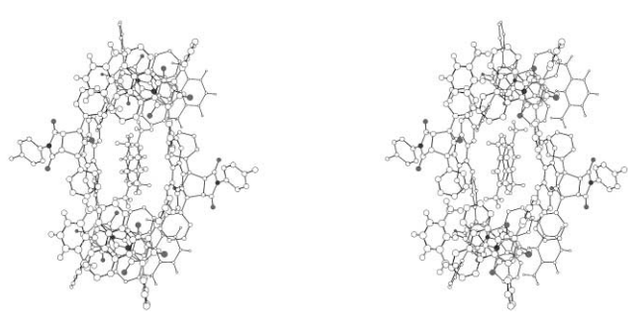

Fig. 7 Stereoview of the crystal packing of the **3h**·*m*-xylene complex.

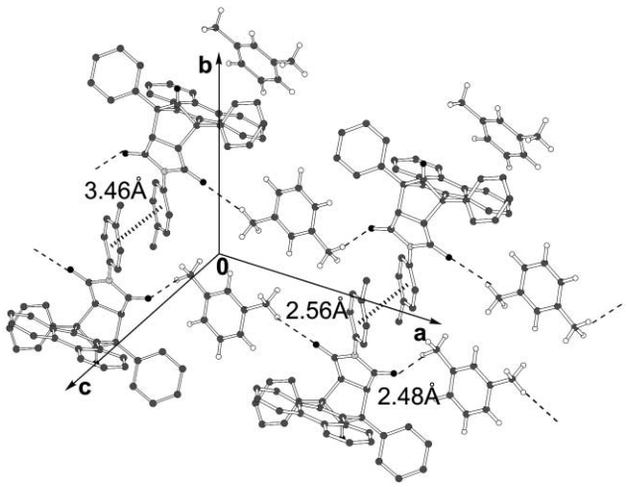

Fig. 8 Location of the guest in **3h**·*m*-xylene.

the rectangular direction of this interaction, the methyl hydrogens of the guests are linked with the carbonyl oxygens of the succinimide rings by a >C=O ··· H–$CH_2C_6H_4H_2C$–H ··· O= C< type interaction (see Fig. 8). The distance between the carbonyl oxygen atom of the maleimide and the methyl carbon atom of the guest is *ca.* 3.5 Å, in which the C–H ··· O distance is *ca.* 2.5 Å and the angle is 170–177°. The *p*-tolyl ring makes the angle of 45° with the plane of the maleimide ring and makes face-to-face interaction with an adjacent *p*-tolyl ring at intervals of 3.46 Å (the intermolecular distance between the carbon atoms at the 2- or 3-position), stabilizing the host framework.

The guest molecules are enclathrated in the enclosure of the aromatic rings of the hosts assisted by the C–H ··· O interactions.

Discussion

As a characteristic feature of the [4 + 2]π cycloadducts of phencyclone as a clathrate host, we point out that the hosts do not have any hydroxylic substituents which may act as hydrogen-bond sites for the guest, as well as assisting host–host interactions. The "space" above the phenanthrene plane is occupied by the aromatic guest or the aryl group of the hosts.

The inclusion ability seems to depend upon the rigidity of the *N*-aryl moiety of the hosts. Those hosts having conformationally free *N*-phenyl (**3b**) or *N*-arylmethyl (**3d**, **3e**) or *N*-(substituted aryl) (**3g**, **3i**, **3j**, **3k**) groups afford few inclusion compounds. In the cases of **3c** and **3f**, whose rotations about *N* ··· aryl bonds are restricted by the σ–π interaction, a wide range of inclusions were found. The *N*–Me derivative (**3a**) did not include ketones.

In butan-2-one·**3c**, the combination of the naphthalene ring and the succinimide ring derived from the dienophile plays a leading role in the inclusion of the guest molecule. The ketone is considered to be included by coulomb interactions between the carbonyl oxygen of butan-2-one and the electron-deficient carbonyl carbons of the succinimide ring, assisted by the C–H ··· π interaction between the α-hydrogen atoms of butan-2-one and the naphthalene ring (see ESI-1†), in which the rotation about the *N*–naphthyl bond is restricted by the edge-to-face interaction between the naphthalene and phenanthrene rings. As stated above, the host **3a** bearing an *N*–Me group did not afford inclusion compounds with ketones, indicating that the interaction with the *N*-aryl moiety is essential for inclusion of ketones.

As can be seen in Table 1, the host **3f** also enclathrates butan-2-one. The inclusion mode of **3c** seems to be applicable to the host **3f** in which the conformation of the 2-methylphenyl ring may be fixed by the CH ··· π interaction between the phenanthrene ring and the methyl protons. In the *N*-(2-phenylphenyl) derivative **3j**, this structural feature cannot be attained because of the serious steric interference between the phenanthrene ring and the 2-phenyl substituent, in which **3j** adopts a conformation having the *exo*-oriented phenyl substituent showing different inclusion behavior for ketones, *i.e.*, 2 : 1 complex formation.

From the X-ray analyses of the inclusion complexes of *p*- and *m*-xylenes, an important inclusion mode becomes clear wherein the "space" created by the phenanthrene ring, bridge carbonyl and two phenyl groups of the bicyclo[2.2.1]heptenone moiety plays a crucial role for inclusion of aromatic guest molecules. In the **3c**·butan-2-one complex, this "void space" is occupied by the aromatic ring of the neighboring host molecule for the stabilization of the host framework (Fig. 3). Therefore, the opposite space (below the phenanthrene ring and by the side of the naphthalene ring of the bicyclo[2.2.1]heptenone moiety) is used for the inclusion of ketones. Similarly, in the guest-free host **3g**, the "space" is used for self-inclusion complex formation stabilizing the host frame work.

In the cases of aromatic guests, the succinimide rings also play an important role in formation of the host ··· guest ··· host ··· sequence, *i.e.*, the face-to-face interaction in the **3g**·*p*-xylene complex and the >C=O ··· H–CH_2– bond formation in **3h**·*m*-xylene complex.

In connection with computer modeling technique in the field of clathrate chemistry, we examined the usability of semi-empirical MO calculations on the structural features of the inclusion compounds. The partial structures extracted from the host–guest complex were used for AM1 or PM3 calculations. The PM3 MO method roughly reproduced the geometrical features of the inclusion compounds of aromatic guests. The stabilization energy due to C–H ··· π interactions between *m*-xylene and **3h** was calculated to be 3.64 kcal mol^{-1}. The PM3-calculated stabilization energy is assumed to be greater than the actual value because the PM3 method is known to overestimate non-bonding H ··· H interaction energy. The calculated energies and geometries of the 1 : 1 (host : guest) models are shown in ESI-6–8† together with the geometries of the 3 : 1 complex.

Reinvestigation of the previously reported X-ray crystal structures of the (benzene and methanol)-included [4 + 2]π cycloadduct (**3l**) of **1a** and *p*-bromostyrene[2a] and the 2 : 1 cycloadduct (**3m**) of **1a** and bicyclo[4.2.0]octa-2,4,7-triene (a valence isomer of cyclooctatetraene)[2b] indicates that the inclusion behavior of these cycloadducts belongs to the category of the present cases. In **3l**, the guest molecule (benzene) is held on the opposite side of the phenanthrene ring to the bridge carbonyl group (Fig. 9).

Inspection of the X-ray structures indicated that the methyl-substituted benzenes are recognized by three-point interactions with the phenanthrene ring and benzene is located on the phenanthrene ring with two-point interactions. The aryl (host)–aryl (host) interactions in guest-free **3g** and butan-2-one·**2c** are also caused by similar recognition mechanisms.

The information of the present study seems to be very useful for the design of clathrate hosts bearing aromatic rings. The synthesis of some hosts which can enclathrate alcoholic guests is in progress.

Experimental

Melting points were uncorrected. The IR spectra were taken with a Hitachi 270–30 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were taken with JEOL JNM-EX 270 (270 MHz) and JNM-A 500 (500 MHz) spectrometers for *ca.* 10% solutions ($CDCl_3$) with TMS as an internal standard; chemical shifts are expressed as δ values and the coupling constants (J) are expressed in Hz. Mass spectra were obtained using a JEOL JMS-DX 303 instrument. UV spectra were recorded on a Shimadzu UV-2500PC spectrophotometer. Thermal analyses

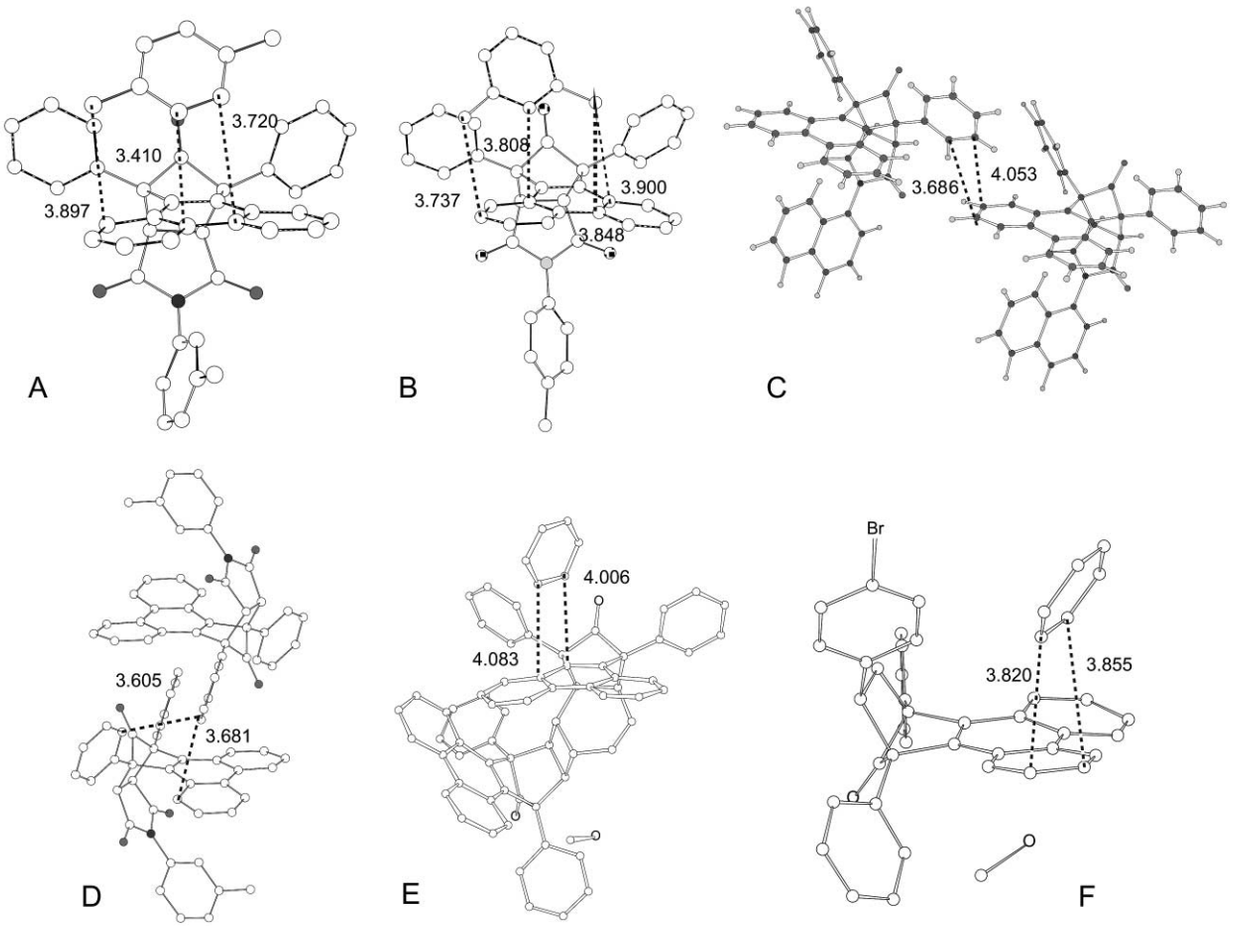

Fig. 9 Recognition of aromatic ring in guest–host and host–host interactions for the DA adducts of phencyclone: A, *p*-xylene·**3g**; B, *m*-xylene·**3h**; C, **3c**–**3c** interaction; D, guest-free **3g**–**3g** interaction; E, benzene–**3m**–MeOH; F, benzene–**3l**–MeOH.

were performed on a Perkin Elmer 7 Series/UNIX DSC 7 (differential scanning calorimeter DSC), a Perkin Elmer 7 Series/UNIX TGA 7 (thermogravimetric analysis TG) and a Shimadzu DTG-50/50H simultaneous TG/DTA instrument.

Materials

Phencyclone (mp 245–255 °C) was prepared according to the previously reported method using potassium hydroxide. The product was washed with ethanol, yield 73%.[11]

Preparation of maleanilic acids (general procedure)

1-Aminonaphthalene (4.44 g, 0.03 mol) dissolved in small amount of ether was added to a solution of maleic anhydride (3.00 g, 0.03 mol) in ether with stirring. The crystals precipitated were collected, washed with ether and dried under vacuum to give pure crystals.

Preparation of maleimides (general procedure)

A mixture of maleanilic acid (3.34 g, 0.01 mol), acetic anhydride (16 ml) and anhydrous sodium acetate (0.55 g) was stirred at 90–100 °C for 30 min. After being cooled, the reaction mixture was poured onto ice–water and stirred until the precipitates appeared. The crystals were collected and washed with 2 × 10 ml of water and then with *n*-hexane (5 ml). The crystals were dried under vacuum.

The [4 + 2]π cycloadduct (1a–MA) of 1a and maleic anhydride (MA)

A solution of **1a** (3.82 g, 0.01 mol), maleic anhydride (1.28 g, 11 mmol) in toluene (10 ml) was refluxed at 110 °C until the dark green color had faded out (about 5 min). After cooling, the precipitated crystals were collected and washed with cold ether. The product was dried under vacuum to give a colorless powder (4.3 g, yield 90%, mp 289 °C). IR (KBr)/cm^{-1} 1784 (bridge >C=O). δ_H (500 MHz) 4.75 (2H, s, methine), 7.12–7.76 (16H, m, aromatic H), 8.69 (2H, d, *J* 8.43, protons at the 4,5-positions of the phenanthrene moiety (H_a)). MS (*m*/*z*) 480 (M^+), 452 ($M^+ - CO$). Anal. Calcd. for $C_{33}H_{20}O_4$: C, 82.49; H, 4.20. Found: C, 82.33; H, 4.11%.

Preparation of the [4 + 2]π cycloadduct of 1a and 1-aminomethylnaphthalene (3e)

A mixture of **1a**–**MA** (0.5 g, 1.04 mmol) and 1-aminomethylnaphthalene (0.16 g, 1.02 mmol) in DMF was heated at 150 °C for 5 h. After cooling, the reaction product was poured onto ice–water. The precipitate was collected and recrystallized from acetone to give colorless needles **3e** (0.62 g, yield 96%); mp 287–288 °C (from acetone). IR (KBr)/cm^{-1} 1786 (bridge >C=O), 1702 (amide C=O). δ_H (270 MHz) 4.55 (2H, s, methylene), 4.46 (2H, s, methine), 6.57 (2H, m, aromatic H), 6.95–7.74 (19H, m, aromatic H), 8.25 (2H, d, *J* 8, aromatic H), 8.35 (2H, d, *J* 7.9, H_a). MS (*m*/*z*) 619 (M^+), 591 ($M^+ - CO$). Anal. Calcd. $C_{44}H_{29}O_3N$: C, 85.28; H, 4.72; N, 2.26. Found: C, 85.10; H, 4.65; N, 2.38%.

[4 + 2]π Cycloadducts (3a–k) of 1a and maleimides (2a–k)

The cycloadducts were obtained according to the method described in the [4 + 2]π cycloadduct of **1a** and maleic anhydride using **1a** (1.01 g, 0.03 mol), maleimide (0.03 mol) and benzene (6 ml) as solvent.

3a: with **2a**, 74%, colorless needles; mp 292–293 °C (from acetone). IR (KBr)/cm^{-1} 1792 (bridge >C=O), 1702 (amide >C=O). δ_H (270 MHz) 2.21 (3H, s, methyl), 4.43 (2H, s,

methine), 7.12–7.75 (14H, m, aromatic H), 8.33 (2H, d, *J* 7.9, aromatic H), 8.64 (2H, d, *J* 8.3, H_a). MS (*m*/*z*) 493 (M^+) 465 ($M^+ - CO$). Anal. Calcd. $C_{34}H_{23}O_3N$: C, 82.74; H, 4.70; N, 2.84. Found: C, 82.60; H, 4.67; N, 3.05%.

3b: with **2b**, 72%, colorless prisms; mp 295–296 °C (from acetone). IR (KBr)/cm^{-1} 1776 (bridge >C=O), 1718 (amide >C=O). δ_H (270 MHz) 4.60 (2H, s, methine), 5.88 (2H, d, *J* 6.9, C2′-H), 6.91–7.74 (17H, m, aromatic H), 8.36 (2H, d, *J* 7.9, aromatic H), 8.58 (2H, d, *J* 8.6, H_a). MS (*m*/*z*) 555 (M^+) 527 ($M^+ - CO$). Anal. Calcd. $C_{39}H_{25}O_3N$: C, 84.31; H, 4.53; N, 2.52. Found: C, 84.05; H, 4.68; N, 2.58%.

3c: with **2c**, 71%, colorless powder; mp 272–273 °C (from benzene). IR (KBr)/cm^{-1} 1780 (bridge >C=O), 1718 (amide >C=O). δ_H (270 MHz) 4.62 (0.6 of 1H, d, *J* 7.3, inner C8′-H), 4.63 (0.4 of 1H, d, *J* 7.3, outer C2′-H), 4.66 (1.2 of 2H, s, inner methine), 4.74 (0.8 of 2H, s, outer methine), 6.03 (0.6 of 1H, t, *J* 7.3, inner C7′-H), 6.71 (0.4 of 1H, t, *J* 7.3, outer C3′-H), 6.99 (0.6 of 1H, t, *J* 7.3, inner C6′-H), 7.12–7.69 (16H, m, aromatic H), 8.35 (0.8 of 2H, d, *J* 8.1, aromatic H), 8.37 (1.2 of 2H, d, *J* 8.1, aromatic H), 8.74 (0.8 of 2H, d, *J* 8.6, outer H_a), 8.80 (1.2 of 2H, d, *J* 8.6, inner H_a). MS (*m*/*z*) 604 ($M^+ + 1$), 576 ($M^+ + 1 - CO$). Anal. Calcd. $C_{43}H_{27}O_3N$: C, 85.27; H, 4.49; N, 2.31. Found: C, 85.15; H, 4.49; N, 2.48%.

3d: with **2d**, 84%, colorless needles; mp 286–287 °C (from benzene). IR (KBr)/cm^{-1} 1786 (bridge >C=O), 1704 (amide >C=O). δ_H (270 MHz) 4.07 (2H, s, methylene), 4.45 (2H, s, methine), 6.25 (2H, d, *J* 6.9, C2′-H), 6.46 (2H, t, *J* 7.8, C3′-H), 6.79 (1H, t, *J* 7.5, C4′-H), 7.02–7.74 (14H, m, aromatic H), 8.35 (2H, d, *J* 7.6, aromatic H), 8.47 (2H, d, *J* 8.3, H_a). MS (*m*/*z*) 569 (M^+), 541 ($M^+ - CO$). Anal. Calcd. $C_{40}H_{27}O_3N$: C, 84.34; H, 4.78; N, 2.46. Found: C, 84.58; H, 4.78; N, 2.63%.

3f: with **2f**, 91%, colorless prisms; mp 285–286 °C (from *p*-xylene). IR (KBr)/cm^{-1} 1788 (bridge >C=O), 1712 (amide >C=O). δ_H (270 MHz) −0.03 (1.64 of 3H, s, inner methyl), 2.03 (1.36 of 3H, s, outer methyl), 4.36 (0.46 of 1H, d, *J* 7.3, C6′-H), 4.64 (2H, s, methine), 6.49 (0.46 of 1H, t, *J* 7.3, C5′-H), 6.76 (0.54 of 1H, d, *J* 7.3, C3′-H), 6.86–7.70 (15H, m, aromatic H), 8.37 (2H, t, *J* 8.6, aromatic H), 8.66 (1.08 of 2H, d, *J* 8.6, inner H_a), 8.71 (0.92 of 2H, d, *J* 8.6, outer H_a). MS (*m*/*z*) 569 (M^+), 541 ($M^+ - CO$). Anal. Calcd. $C_{40}H_{27}O_3N$: C, 84.34; H, 4.78; N, 2.46. Found: C, 84.52; H, 4.73; N, 2.54%.

3g: with **2g**, 86%, colorless prisms; mp 286–287 °C (from *m*-xylene). IR (KBr)/cm^{-1} 1792 (bridge >C=O), 1710 (amide >C=O). δ_H (270 MHz) 1.89 (3H, s, methyl), 4.57 (2H, s, methine), 5.33 (1H, s, C2′-H), 5.88 (1H, d, *J* 6.9, C6′-H), 6.84 (1H, d, *J* 7.9, C4′-H), 6.87 (1H, t, *J* 7.6, C5′-H), 7.15–7.74 (14H, m, aromatic H), 8.36 (2H, d, *J* 7.9, aromatic H), 8.68 (2H, d, *J* 8.6, Ha). MS (*m*/*z*) 569 (M^+), 541 ($M^+ - CO$). Anal. Calcd. $C_{40}H_{27}O_3N$: C, 84.34; H, 4.78; N, 2.46. Found: C, 84.37; H, 4.49; N, 2.70%.

3h: with **2h**, 81%, colorless powder; mp 277–278 °C (from acetone). IR (KBr)/cm^{-1} 1788 (bridge >C=O), 1712 (amide >C=O). δ_H (270 MHz) 2.10 (3H, s, Me), 4.58 (2H, s, methine), 5.75 (2H, d, *J* 8.6, C2′-H), 6.75 (2H, d, *J* 8.3, C3′-H), 7.15–7.74 (14H, m, aromatic H), 8.39 (2H, d, *J* 7.5, aromatic H), 8.68 (2H, d, *J* 8.6, H_a). MS (*m*/*z*) 569 (M^+), 541 ($M^+ - CO$). Anal. Calcd. $C_{40}H_{27}O_3N$: C, 84.34; H, 4.78; N, 2.46. Found: C, 84.36; H, 4.77; N, 2.46%.

3i: with **2i**, 73%, colorless prisms; mp 279–280 °C (from toluene). IR (KBr)/cm^{-1} 1788 (bridge >C=O), 1712 (amide >C=O). δ_H (270 MHz) −0.15 (1.8 of 3H, t, *J* 7.6, inner CH_2CH_3), 0.13 (1.2 of 2H, q, *J* 7.6, inner CH_2CH_3), 1.10 (1.2 of 3H, t, *J* 7.6, outer CH_2CH_3), 2.35 (0.8 of 2H, q, *J* 7.6, outer CH_2CH_3), 4.27 (0.4 of 1H, d, *J* 7.9, C6′-H), 4.65 (2H, s, methine), 6.45 (0.4 of 1H, t, *J* 7.3, C5′-H), 6.82–7.73 (16H, m, aromatic H), 8.37 (2H, t, *J* 8.3, aromatic H), 8.70 (0.8 of 2H, d, *J* 7.9, outer H_a), 8.73 (1.2 of 2H, d, *J* 7.9, inner H_a). MS (*m*/*z*) 582 ($M^+ - 1$), 554 ($M^+ - 1 - CO$). Anal. Calcd. $C_{41}H_{29}O_3N$: C, 84.37; H, 5.01; N, 2.40. Found: C, 84.65; H, 5.13; N, 2.53%.

Table 3 Crystal data and intensity measurements for **3c**·butan-2-one(1 : 1)

Formula	$C_{43}H_{27}O_3N \cdot C_4H_8O$
Mp/°C	272–273
Formula weight	677.80
Crystal system	Monoclinic
Lattice type	Primitive
Lattice parameters	
a	10.843(3) Å
b	13.916(2) Å
c	23.573(1) Å
β	91.144(10)°
V	3556.1(10) Å^3
Space group	$P2_1/n$(No. 14)
Z	4
D_c/g cm^{-3}	1.266
Solvent	Butan-2-one
Radiation	Mo-Kα (λ = 0.71069 Å)
Scan range	$2\theta < 55.0°$
Reflections collected	8937
Unique data collected	8499
Unique data used [$I > 2.00\ \sigma(I)$]	4589
R	0.063
R_w	0.099

3j: with **2j**, 94%, colorless needles; mp 284–285 °C (from toluene). IR (KBr)/cm^{-1} 1788 (bridge >C=O), 1714 (amide >C=O). δ_H (270 MHz) 4.32 (2H, s, methine), 4.48 (1H, d, *J* 7.6, C6′-H), 6.62–6.68 (1H, m, C5′-H), 7.09–7.70 (16H, m, aromatic H), 8.22 (2H, d, *J* 7.9, aromatic H), 8.73 (2H, d, *J* 8.2, H_a). MS (*m*/*z*) 630 ($M^+ - 1$), 602 ($M^+ - 1 - CO$). Anal. Calcd. $C_{45}H_{29}O_3N$: C, 85.56; H, 4.63; N, 2.22. Found: C, 85.30; H, 4.74; N, 2.29%.

3k: with **2k**, 86%, colorless powder; mp 268–270 °C (from *p*-xylene). IR (KBr)/cm^{-1} 1788 (bridge >C=O), 1712 (amide >C=O). δ_H (270 MHz) 4.62 (2H, s, methine), 5.96 (2H, dd, *J* 1.96 and 6.6, C2′-H), 7.13–7.75 (21H, m, aromatic H), 8.39 (2H, d, *J* 7.9, aromatic H), 8.69 (2H, d, *J* 8.3, H_a). MS (*m*/*z*) 631 (M^+), 603 ($M^+ - CO$). Anal. Calcd. $C_{45}H_{29}O_3N$: C, 85.56; H, 4.63; N, 2.22. Found: C, 85.52; H, 4.47; N, 2.19%.

Preparation of inclusion complexes

The host compound was dissolved under heating in the minimum amount of a guest solvent. The solution was allowed to cool in a water bath to ensure crystallization of the inclusion compounds. After standing for several days at 25 ± 3 °C, the crystals were collected by suction filtration and dried.

Single crystal X-ray analysis‡

The crystal structure of **3c**·butan-2-one (1 : 1) was determined as follows. The reflection data (see Tables 3–5) were measured on a Rigaku AFC7R four-circle autodiffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) and a rotating anode generator. The structures were solved by direct methods. The hydrogen atoms were placed in calculated positions. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The final residuals for reflections with $I_0 > 2.00\sigma I$) were R = 0.063 and R_w = 0.099.

Similarly, the X-ray analyses of **3g**, **3g**·*p*-xylene and **3h**·*m*-xylene were performed. The X-ray analysis data (crystal data, final atomic coordinates, distance and angles) are summarized in the supporting information. All calculations were performed on a Silicon Graphics O2 WS with the teXsan[12] crystal structure analysis package.

‡ The crystal data have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference numbers 180113–180116. See http://www.rsc.org/suppdata/p2/b2/b201915a/ for crystallographic data in .cif or other electronic format.

Table 4 Crystal data and intensity measurements for **3g** and **3g**·*p*-xylene (1 : 1)

Compound	**3g**	**3g**·*p*-xylene(1 : 1)
Formula	$C_{40}H_{27}O_3N$	$C_{40}H_{27}O_3N{\cdot}C_8H_{10}$
Mp/°C	290–291	290–291
Formula weight	569.66	675.83
Crystal system	Triclinic	Triclinic
Lattice type	Primitive	Primitive
Lattice parameters		
a	11.667(3) Å	11.385(4)Å
b	14.264(3) Å	16.895(5)Å
c	9.053(2) Å	10.483(4)Å
a	90.09(2)°	101.11(3)°
β	100.01(2)°	114.33(2)°
γ	77.15(2)°	95.93(3)°
V	1445.5(6) Å^3	1764(1) Å^3
Space group	*P*1(−) (No. 2)	*P*1(−) (No. 2)
Z	2	2
D_c/g cm^{-3}	1.309	1.272
Solvent	*o*-Xylene	*p*-Xylene
Radiation	Mo-Kα (λ = 0.71069 Å)	
Scan range	$2\theta < 55.0°$	
Reflections collected	6963	8513
Unique data collected	6637	8103
Unique data used [$I > 3.00\ \sigma$(I)]	3632	4962
R	0.052	0.050
R_w	0.075	0.078

Table 5 Crystal data and intensity measurements for **3h**·*m*-xylene (1 : 1)

Formula	$C_{40}H_{27}O_3N{\cdot}C_8H_{10}$
Mp/°C	280–281
Formula weight	675.83
Crystal system	Monoclinic
Lattice type	Primitive
Lattice parameters	
a	14.802(2)Å
b	14.302(2)Å
c	16.739(2)Å
β	94.052(8)°
V	3534.9(6)Å^3
Space group	$P2_1/n$ (No. 14)
Z	4
D_{calc}/g cm^{-3})	1.270
Solvent	*m*-Xylene
Radiation	Mo-Kα (λ = 0.71069 Å)
Scan range	$2\theta < 55.0°$
Reflections collected	8768
Unique data collected	8452
Unique data used [$I > 3.00\ \sigma(I)$]	5390
R	0.053
R_w	0.081

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7 (*a*) The distances between the guest carbonyl oxygen and two maleimide carbonyl carbons are 3.00 and 3.20 Å. A similar short contact[7c] was found between the oxygen atom of a formamide (guest) and the phthalimide carbonyl carbon of *N*-[2-(3,5-dinitrobenzoylamino)-6-methylphenyl]phthalimide (host) K. Kishihara, R. Takeuchi, S. Kohmoto, M. Yamamoto, K. Yamaguchi and K. Yamada, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1143; (*b*) the H ··· O=C bond distances and angles are as follows: $CH_3COCH(CH_3)$–H ··· O=C(CH_2)N–, 2.52 Å, 139.5° and naphthyl-C2–H ··· O=C< of butan-2-one, 2.57 Å, 161.3°; (*c*) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 3rd edn., 1960.

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9 (*a*) Similar twisted or puckered structures of the phenanthrene ring were observed in several cases: the torsion angles of C4–C4a–C4b–C5 of the DA adducts from the reactions of phencyclone with

p-bromostyrene[2a] and cyclooctatetraene[2b] are 12.40 and 4.90, respectively; (*b*) In **3g**, the angles between the central benzene ring of the phenanthrene moiety and the benzene rings on both sides are 7.00 and 6.50. The interplanar angle between the benzene rings of either end of the phenanthrene ring is 12.5°, in which the C7 carbon deviates 0.35 Å from the central benzene ring of the phenanthrene moiety.

10 If the bending of the phenanthrene ring did not occur, the edge-to-face (Ph–H ··· phenanthrene ring) distance is estimated to be 3.12 Å from the best plane of the central benzene ring of the phenanthrene moiety.

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