

## Phencyclone Diels-Alder Adducts as a New Crystalline Host. Role of C-H $\cdots\pi$ and C-H $\cdots$ O Interactions

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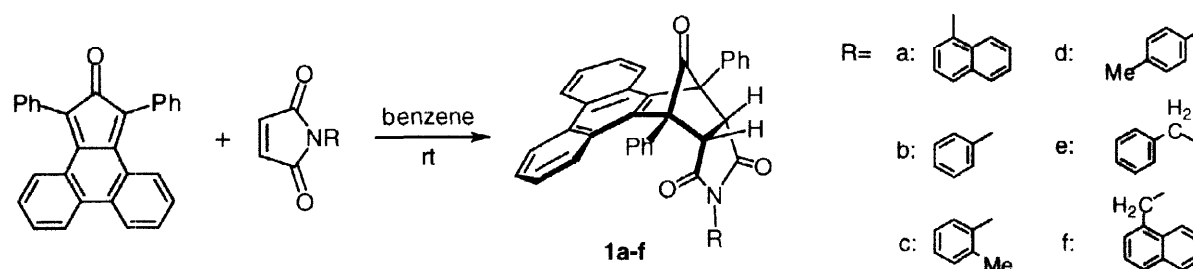
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**Abstract:** A series of crystalline host compounds, which have a bicyclo[2.2.1]heptene-7-one system, has been synthesized and their inclusion behavior has been investigated. The cycloadduct of phencyclone and *N*-naphthylmaleimide forms a 1:1 crystalline inclusion complex with 2-butanone. The crystal structure indicates the presence of weak lattice forces supported by C-H $\cdots\pi$  and C-H $\cdots$ O interactions. © 1998 Elsevier Science Ltd. All rights reserved.

Crystalline inclusion compounds between simple organic molecules are useful models for studying weak interatomic interactions in molecular recognition and self-organization of molecules.<sup>1</sup> In the course of studies of the pericyclic reaction behavior of cyclopentadienones, one of the authors observed that the Diels-Alder adduct of phencyclone and *p*-bromostyrene or cyclooctatetraene forms a crystalline inclusion complex with recrystallization solvents (host : benzene : MeOH = 1 : 1 : 1).<sup>2</sup>

We now report the inclusion behavior of nonhydroxylic hosts of a new type, which have a phenanthrene-condensed bicyclo[2.2.1]heptene-7-one framework.

The cycloadducts were synthesized by the Diels-Alder (DA) reaction of phencyclone with *N*-substituted maleimides. Of the DA adducts (**1a-f**), **1a** and **1c** formed crystalline inclusion compounds with some polar solvents (Table).<sup>3</sup>

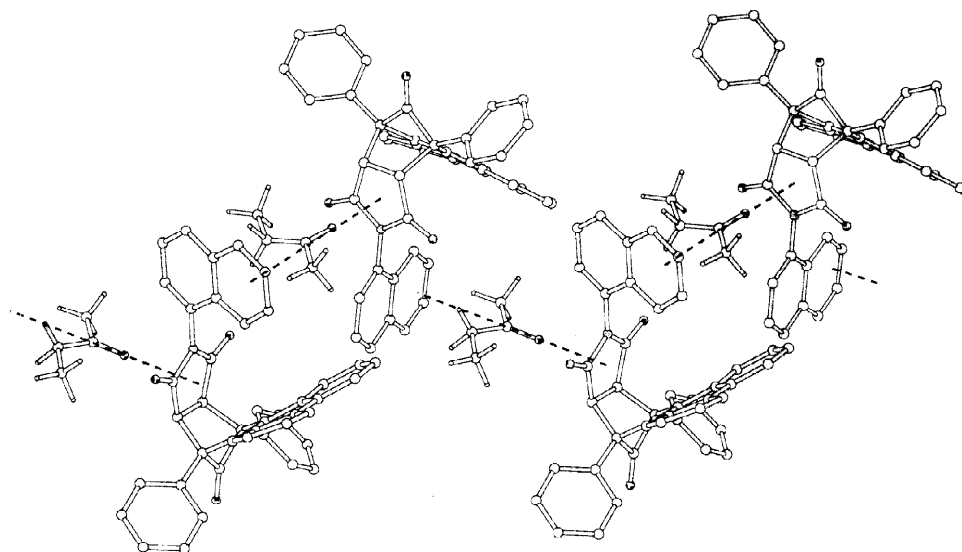


**Table** Crystalline inclusion compounds (host : guest stoichiometric ratio<sup>a</sup>)

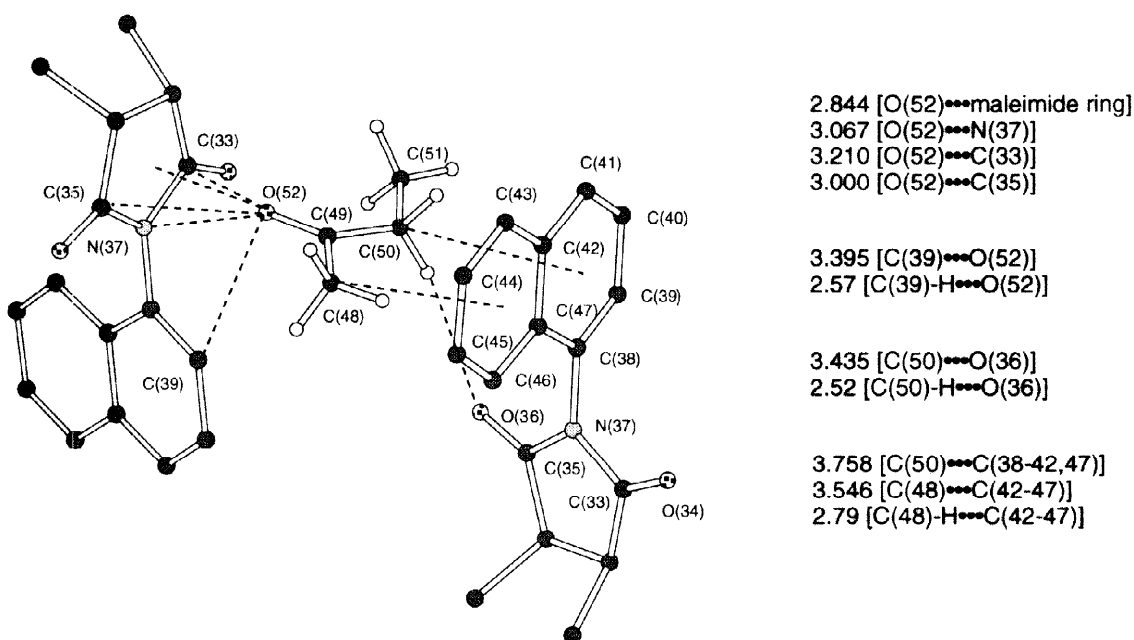
| Guest solvent    | Host compound |           |           |
|------------------|---------------|-----------|-----------|
|                  | <b>1a</b>     | <b>1c</b> | <b>1d</b> |
| Benzene          | -             | -         | -         |
| Toluene          | -             | 2 : 1     | 1 : 1     |
| <i>o</i> -Xylene | -             | -         | 1 : 1     |
| <i>m</i> -Xylene | -             | -         | 1 : 1     |
| <i>p</i> -Xylene | 1 : 1         | 1 : 1     | 2 : 1     |
| THF              | 2 : 1         | -         | -         |
| Dioxane          | 4 : 3         | 1 : 1     | -         |
| Acetone          | 3 : 1         | -         | -         |
| Butanone         | 1 : 1         | 3 : 2     | -         |
| 3-Pentanone      | 1 : 1         | 1 : 1     | -         |

a) Determined by <sup>1</sup>H NMR integration.

Interestingly, **1a** gave the complex with *p*-xylene but failed to enclathrate *o*- and *m*-xylene. On the other hand, hosts **1b**, **1e** and **1f** could not form inclusion complexes. Host **1d** showed a different inclusion ability and selectivity. These facts indicate that the inclusion complex formation is strongly influenced by the geometry of the *N*-aryl moiety. The crystal structure of the butanone (host **1a** : guest = 1 : 1) inclusion compound<sup>4</sup> is shown in Figure 1. The packing arrangement of **1a**•butanone is presented in Figure 2.



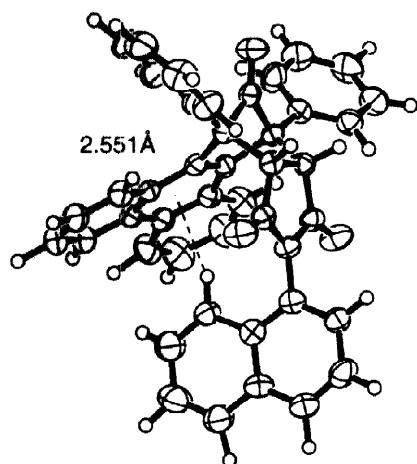
**Figure 1** A characteristic packing pattern in the **1a**•butanone complex  
Dotted lines indicate the face-to-face disposition of rings.



**Figure 2** Intermolecular atom-plane and atom-atom distances (Å) of the **1a**•butanone complex

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 (T-shaped conformation).<sup>5</sup> The H8' proton on the 1-naphthyl

ring is located at close-contact perpendicular distance of 2.551 Å above the face of the phenanthrene ring (Figure 3). This fact indicates that **1a** prefers to take a congested conformation with an attractive intramolecular



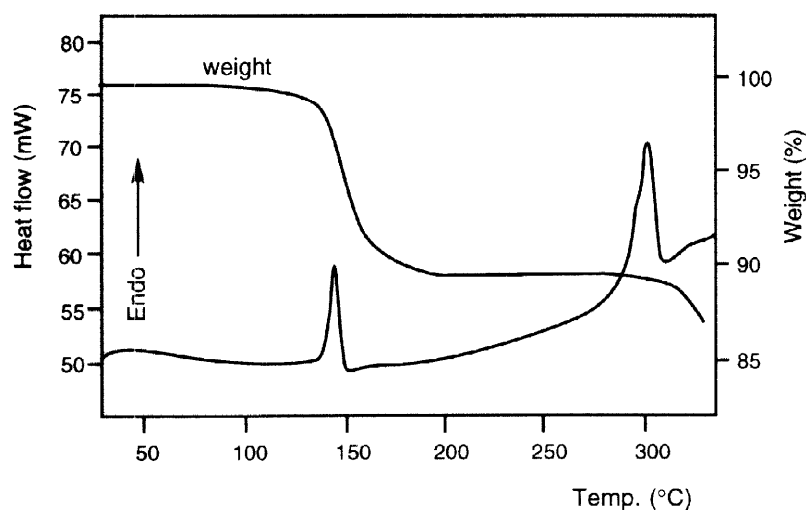
**Figure 3** ORTEP drawing of host **1a** in **1a**•butanone complex

C-H... $\pi$  interaction<sup>6</sup> between the aromatic rings. This special geometrical feature is also observed in solutions.<sup>7a</sup> On the other hand, the tetracyclone analogue (**2a**) having a stilbene moiety, which could not form T-shaped conformation<sup>7b</sup>, did not show a clear stoichiometric host-guest ratio with butanone.

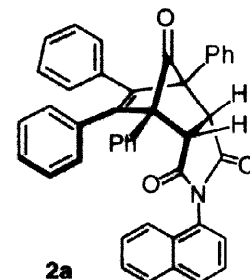
As can be seen in Figure 1, butanone located between the parallel stacked walls of the neighboring naphthyl and maleimide rings. The interatomic distances between the center of C(38-42, 47) plane in the naphthyl ring and C(50) of the guest is 3.758 Å, and the distance between C(42-47) and C(48) is 3.546 Å (Figure 2). The methyl protons are close to the naphthyl ring [C(48)-H...C(42-47) : 2.79 Å]. The guest methylene proton and carbonyl oxygen form hydrogen bondings with the host carbonyl oxygen and the naphthyl proton, respectively [C(50)-H...O(36) : 2.52 Å, 139.5° and C(39)-H...O(52) : 2.57 Å, 161.3°]. The distances between the guest carbonyl oxygen and maleimide carbonyl carbons are 3.000 and 3.067 Å, which are *ca.* 0.1-0.2 Å shorter than sum of the van der Waals radii of O and C [O(52)...maleimide ring : 2.844 Å]. These intermolecular contacts shorter than 3.6 Å in the crystal show the presence of weak lattice forces supported by electrostatic C-H...O<sup>8</sup> and C-H...aryl<sup>6b</sup> interactions.

Differential scanning calorimetry (DSC) of **1a**•butanone showed a broad endothermic pattern corresponding to the guest loss at 136°C, followed by an endothermic peak at 272°C caused by melting of the host (Figure 4). The thermogravimetry (TG) curve supported the host:guest stoichiometry derived from the crystal structure. The total weight loss was observed to be 10.6 % in agreement with the expected loss of 10.8 % for a 1:1 ratio. In conclusion, T-shaped interaction between the naphthalene and phenanthrene rings plays a leading role in the solid-state inclusion complex formation.

The inclusion mode of aromatic solvents by **1a**, **1b** and **1d** is under investigation.

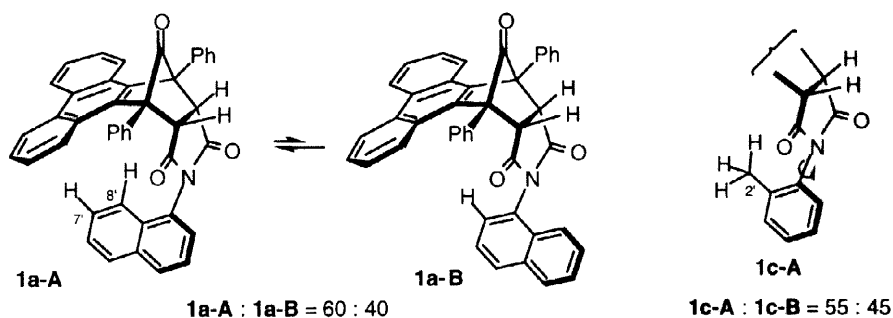


**Figure 4** DSC and TG curves for **1a**•butanone



## References and Notes

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3. The host compound was dissolved under heating in a 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  $25\pm 3^\circ\text{C}$ , the crystals were collected by suction filtration and dried.
4. Crystal data for **1a**•butanone. *M* 677.8, monoclinic, space group  $P2_1/n$ ,  $a=10.843(3)$ ,  $b=13.916(2)$ ,  $c=23.573(1)$  Å,  $\beta=91.14(1)^\circ$ ,  $V=3556(1)$  Å<sup>3</sup>,  $Z=4$ ,  $D_c=1.266$  g cm<sup>-3</sup>,  $D_m=1.268$  g cm<sup>-3</sup>. The reflection data were measured on a RIGAKU AFC7R four-circle autodiffractometer with a graphite monochromated Mo-K $\alpha$  radiation ( $\lambda=0.7107$  Å) and a rotating anode generator. The structures were solved by direct method. The hydrogens atoms were placed in calculated positions. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The final cycle of full-matrix least-square refinement was based on 4056 observed reflections ( $I_o>3.00\sigma I$ ) and 609 variable parameters and converged with unweighted (*R*) and weighted agreement factors (*R*<sub>w</sub>) of 0.061 and 0.036, respectively. All calculations were performed on a Silicone Graphics IRIS Indigo WS with *teXsan*<sup>8</sup> Crystal Structure Analysis Package.
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7. a) The <sup>1</sup>H NMR spectra of the host **1a** and **1c** show duplicated signal patterns due to restricted rotation about the Csp<sup>2</sup>(aryl)-Nsp<sup>2</sup> bond on the NMR time scale.



The chemical shift of H8' ( $\delta$  4.62) of an atropisomer **1a-A** is extremely high. The population of the atropisomers determined by <sup>1</sup>H NMR integration is 60:40. Similar upfield shift of methyl protons ( $\delta$  -0.03) was observed in the major atropisomer (A) of **1c** (A:B=55:45). These upfield shifts are ascribable to a shielding effect of the phenanthrene ring current, suggesting that a C-H $\cdots\pi$  interaction between the naphthyl or methyl proton and the phenanthrene ring is operative. b) **2a-A:2a-B=33:67**

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9. *teXsan*: Crystal Structure Analysis Package, Molecular Structure Corporation, 1989.