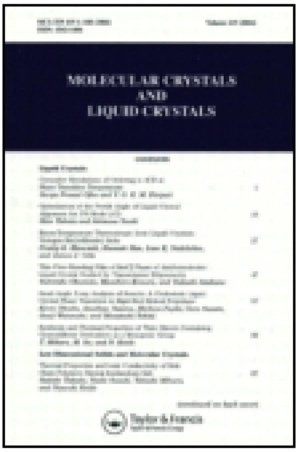

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INCLUSION CRYSTALS FROM NAPHTHALENOPHANES IN AROMATIC SOLVENTS

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Abstract The inclusion crystal formation of naphthalenophanes with polar substituents was investigated in comparison with that of naphthalenophanes without substituents. In contrast with the latters, the naphthalenophane with two methoxycarbonyl groups (**2a**) afforded rather stable inclusion crystals, in which the benzene molecules were accommodated in the channels along the b-axis. The formation of the channels is ascribable to the strong intermolecular dipole-dipole interaction between the methoxycarbonyl groups. On the other hand, no inclusion crystals were obtained from the naphthalenophane with four ethoxycarbonyl groups (**2b**).

INTRODUCTION

Naphthalenophanes with two naphthalene rings almost in parallel have attracted much interest with respect to their synthesis,[1,2] reactivities,[2d,3] and photophysical properties.[4] They are also intriguing compounds from the viewpoints of the intermolecular interaction with some aromatic molecules, especially in crystalline states, though such studies have been hardly made toward naphthalenophanes, probably due to the difficulty of their synthesis.

We have succeeded in the systematic synthesis of [2.n]naphthalenophanes by intra-[2a–d] or intermolecular[2e] [2 + 2] photocycloaddition of vinylnaphthalene derivatives. Interestingly, these methods enabled the selective synthesis of *syn*-naphthalenophanes.[2] In a series of (1,4)naphthalenophanes, [2.3]- and [2.4]-ones, (**1a** and **1b**), were found to give 1:1 inclusion crystals as needle ones with aromatic compounds, such as benzene, toluene, pyridine, furan, and thiophene, whereas the corresponding [2.5]-one (**1c**) was not.[2d] The obtained inclusion crystals, however, readily decompose within a short period due to efflorescence. This instability is considered to be ascribable to the weak lattice energy, mainly the van der Waals dispersion force between the T-shape-arranged benzene and two naphthalene rings, as shown in Figure 1.[2d]

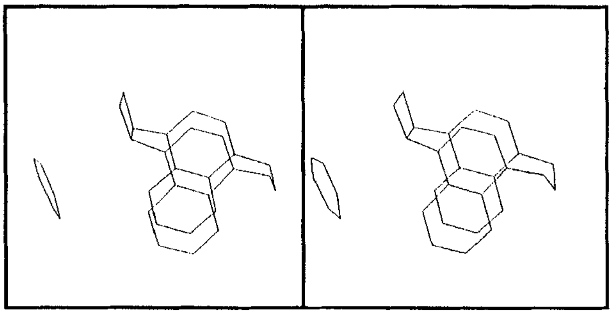
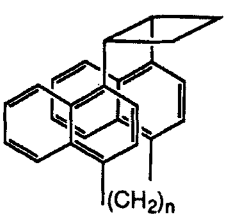
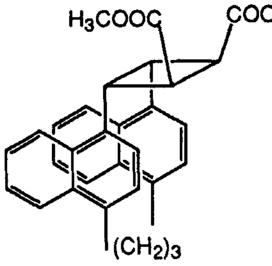


FIGURE 1 Stereoview of **1a**-benzene pair

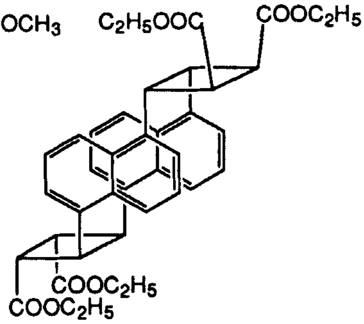
Thus, we were prompted to examine the inclusion behavior of the naphthalenophanes possessing some polar substituents such as alkoxycarbonyl groups. The strong intermolecular dipole-dipole interaction between the substituents is expected to produce rather stable inclusion crystals. We report an explanation for the selectivity observed in the **1a**-aromatic molecule crystal formation and also the inclusion behavior of the two naphthalenophanes, **2a**[2c,d] and **2b**,[2e] mainly on the basis of the X-ray crystallographic analysis.



1a (n=3)
1b (n=4)
1c (n=5)



2a



2b

RESULTS AND DISCUSSION

The inclusion crystal formation of **1a** with the aromatic solvent molecules presents an interesting selectivity; i.e., toluene was included, but chlorobenzene wasn't. The selectivity may be due to the molecular size of the solvents, because the crystal may recognize the subtle difference between them, or it may be due to their electronic interactions, because naphthalenophane **1a** has the thick π-electron cloud, which usually works as an electron-donor site, and also because it has the closely situated two-naphthalene edges, which provides a rather strong working site of van der Waals dispersion force with the benzene-face of aromatic solvent molecule,[5] even in solution. Although the latter possibility is now being investigated by the sophisticated molecular orbital theory, the former one has been studied by the Molecular Mechanics, using CRIUS2, POYGRAF with Dreiding II force field.[6]

Using the coordinate of **1a**–benzene inclusion crystal and replacing the benzene molecule by toluene or chlorobenzene one, the lattice energy was calculated and is summarized in Table 1. The calculation gives only a slight difference between those of benzene, toluene, and chlorobenzene-including crystals. Their packings are depicted in Figure 2. The results clearly suggest that the selectivity shown at the inclusion formation does not depend on the subtle size effect caused by changing a hydrogen atom to a methyl-group or chlorine atom.

TABLE 1 Lattice energy of naphthalenophane-arene inclusion crystal by MM calculation.[a)]

Phane-Arene	Phane-Benzene		Phane-Toluene		Phane-Chlorobenzene	
(kcal/mol)	vdW	vdW & ES	vdW	vdW & ES	vdW	vdW & ES
a pair in a cell	103.0	104.3	107.8	108.8	105.8	107.1
a pair of independent species	129.4 12.1	130.9 12.6	130.3 14.9	131.8 15.0	130.3 12.7	131.8 13.1
lattice energy per a pair	-38.5	-39.2	-37.4	-38.0	-37.2	-37.8
ΔLE	0 .0	0.0	1.1	1.2	1.3	1.4

a) Program: CRIUS2, POLYGRAF with Dreiding II force field (MSI, Inc.). The abbreviations, vdW and vdW & ES, mean the values calculated for only van der Waals interaction and for both van der Waals and electrostatic interactions, using Gasteiger's charge.

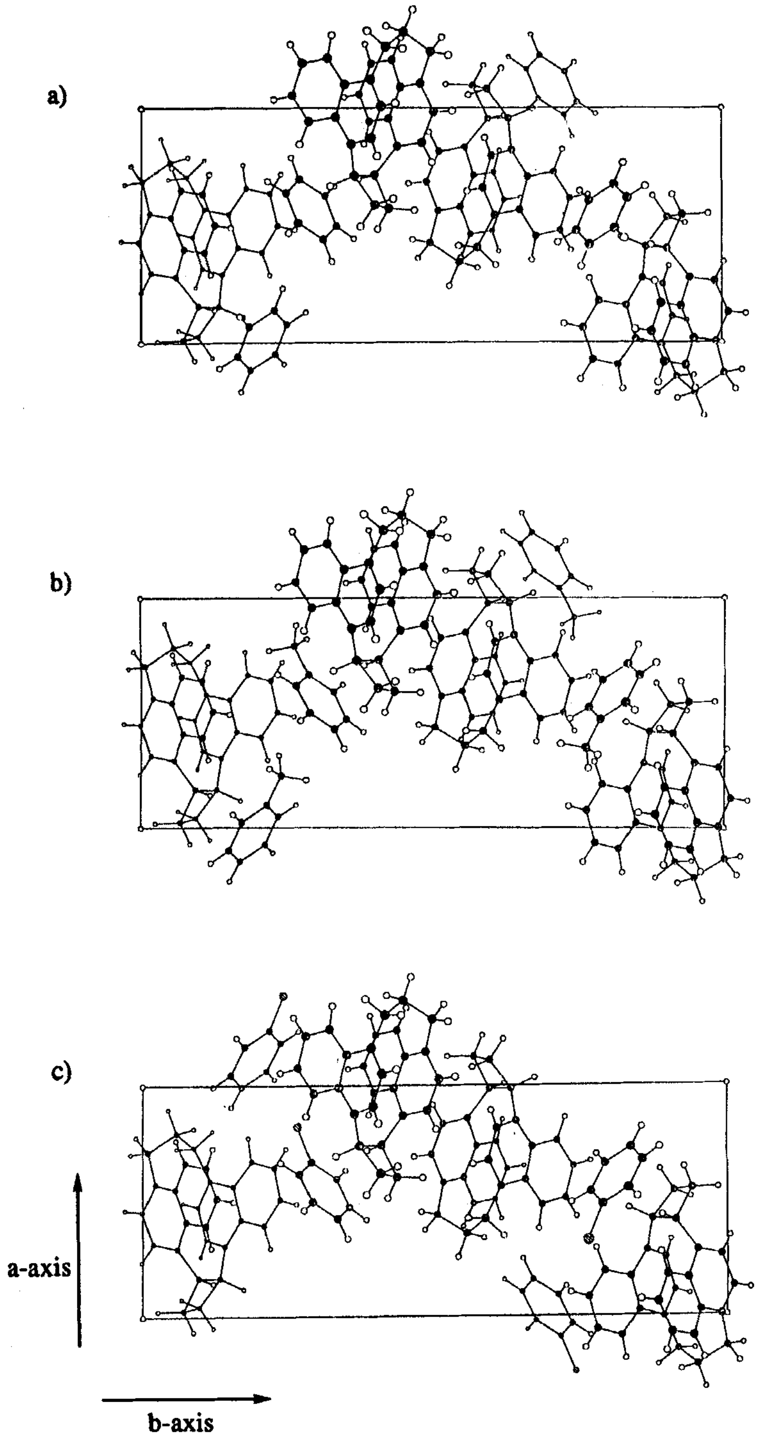


FIGURE 2 Packing diagrams of a) **1a**-benzene, b) **1a**-toluene, and c) **1a**-chlorobenzene.

Naphthalenophanes **2a**[2c,d] and **2b**[2e] were synthesized by the intra- and intermolecular [2 + 2] photocycloaddition of the corresponding vinylnaphthalene derivatives, respectively, in the manner reported previously. The inclusion behavior of **2a** and **2b** was investigated with various solvents. The results for **2a** are summarized in Table 2. Naphthalenophane **2a** was found to give inclusion crystals with aromatic solvents with a 5- or 6-membered ring (benzene, pyridine, furan, and thiophene), though the composition depended on the solvents, according to the ^{1}H NMR spectroscopy. In aromatic solvents with a substituent (toluene and aniline) or an aliphatic one (cyclohexane), however, no inclusion crystals were obtained, but **2a** itself was crystallized alone. Interestingly, in most cases, the obtained plate-like inclusion crystals were rather stable, in contrast with the unstable needles in the case of **1a**.

TABLE 2 Inclusion crystal formation of **2a** with various solvents.

Solvent	Remarks	Inclusion Crystal Formation	Ratio[a)]
benzene	plate	yes	1:1
pyridine	needle	yes	ca. 1:0.5
furan	plate	yes	ca. 1:1.5
thiophene	plate	yes	ca. 1:0.5
toluene	plate	no	–
aniline	plate	no	–
cyclohexane	plate	no	–

a) Ratio = **2a** : solvents.

The X-ray crystallographic analysis of the 1:1 inclusion crystal of **2a** with benzene was successful, as illustrated in Figure 3. The quality of the inclusion crystal was almost unchanged, at least during the measurement, even though it was done under the usual conditions. According to the crystal structure, the benzene molecules are apparently accommodated in the channels along the b-axis. The great stability of the inclusion crystals is ascribable to this arrangement; the benzene molecules can less easily leave from the crystals under the circumstances than those in **1a**. The formation of the channels is considered to be brought about by the presence of the polar substituents on the cyclobutane ring. The methoxycarbonyl groups of one molecule of **2a** are located close to those of the adjacent molecule in the c-axis direction, probably due to the intermolecular dipole-dipole interaction, and the naphthalene moiety is close to that of

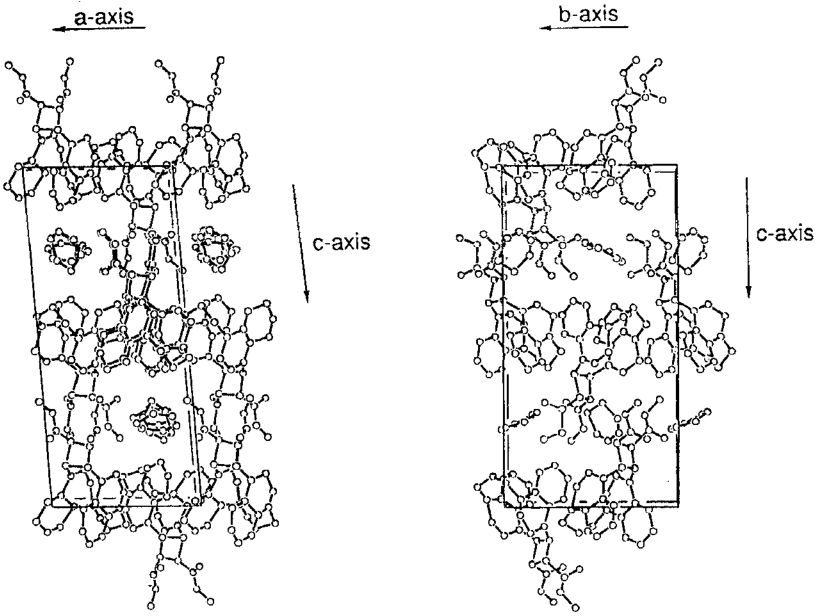


FIGURE 3 Crystal structure of **2a**-benzene inclusion crystal.

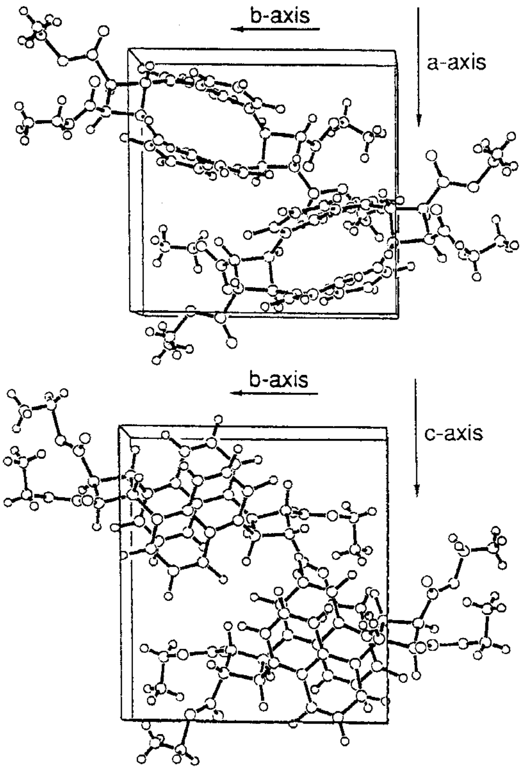


FIGURE 4 Crystal structure of naphthalenophane **2b**.

another molecule. These arrangements lead to the formation of the channels, in which benzene molecules can be suitably accommodated. The inclusion crystals were found to become white and decompose in about a month, because of the gradual release of the benzene. The inclusion crystals obtained from other solvents, though the X-ray structural analysis was unsuccessful yet, are also expected to possess a similar structure to that of **2a**–benzene. The inclusion crystals with furan and thiophene were relatively unstable, probably resulting from the fact that these solvents with a smaller size can readily leave from the channels. From larger toluene than benzene, the crystals of **2a** itself were obtained. This result suggests that it is energetically less favorable for naphthalenophanes **2a** to generate channels which can accommodate toluene molecules than to form the crystals by itself. Benzene may be the solvent with the critical size for the formation of the channels in **2a**.

On the other hand, no inclusion crystals of naphthalenophane **2b** were obtained from the solvents examined. The X-ray crystallographic analysis of **2b** recrystallized from benzene is shown in Figure 4. The arrangement between the naphthalenophanes is remarkably different from that in **2a**–benzene, although the ethoxycarbonyl groups of the neighboring molecules are as close to each other as the methoxycarbonyl groups in **2a**–benzene. Apparently, the channels to accommodate another molecule are not detectable. Such arrangement is caused either by the presence of the alkoxycarbonyl groups on the both sides of the naphthalenophanes or by the presence of the sterically crowded ethyl groups in **2b** instead of the methyl groups in **2a**. It is ambiguous at the present stage, which factor is more dominant.

In summary, the inclusion crystal formation of the naphthalenophanes is found to greatly depend on their structures, and the number and position of the substituents on the cyclobutane rings. Further examination of the substituent effect on the molecular packing is of great interest and in progress.

EXPERIMENTAL

Inclusion Crystal Formation of 2a

Naphthalenophanes **2a** (30–50 mg), dissolved in a solvent, was allowed to stand at room temperature for several days. The crystals were filtrated and washed with hexane rapidly. The composition of **2a** and the solvent in the inclusion crystals was determined by ^{1}H NMR spectroscopy after dissolved in $CDCl_3$.

X-ray Crystallographic Analysis

All the measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated MoKα or Cu-Kα radiation. The data were collected at a temperature of

20 ± 1 °C using the ω-2θ scan technique. The crystallographic data for **2a** and **2b** are as follows:

2a: formula: $C_{31}H_{28}O_4 \cdot C_6H_6$; formula weight: 542.67; crystal dimensions: 0.20 x 0.20 x 0.20 mm; crystal system: monoclinic; space group: $P2_1$; lattice parameters: a=10.344(7), b=11.926(7), c=23.088(3) Å, β=94.40(2) °, V=2839(2) $Å^3$; Z value: 4; Dcalc: 1.269 g/cm^3; μ(MoKα): 0.81 cm^{-1}; unique reflections: 6850. The structure was solved by direct methods (SAPI91). The final cycle of full-matrix least-squares refinement was based on 1658 observed reflections (I>3.00σ(I)), and converged with R=0.090 and R_w=0.064.

2b: formula: $C_{40}H_{40}O_8$; formula weight: 648.75; crystal dimensions: 0.20 x 0.20 x 0.15 mm; crystal system: monoclinic; space group: $P2_1$; lattice parameters: a=11.358(6), b=11.501(4), c=12.734(3) Å, β=99.54(3) °, V=1640(1) $Å^3$; Z value: 2; Dcalc: 1.313 g/cm^3; μ(CuKα): 7.40 cm^{-1}; unique reflections: 2594. The structure was solved by direct methods (MULTAN88). The final cycle of full-matrix least-squares refinement was based on 2277 observed reflections (I>3.00σ(I)), and converged with R=0.065 and R_w=0.057.

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