JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 368–371

Controlled host:guest ratio in an inclusion compound

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Received 4 January; revised 1 March; accepted 3 March

ABSTRACT: The host 2,2′-dihydroxy-1,1′-binaphthyl forms two distinct inclusion compounds with the guest 1,4-dioxane at different crystallization temperatures. The crystal structures, thermal stabilities and activation energies of desolvation of the compounds were determined. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: inclusion compound; controlled host: guest ratio; 2,2′-dihydroxy-1,1′-binaphthyl; 1,4-dioxane

INTRODUCTION

Inclusion compounds may be formed by dissolving a solid organic host, H, in a liquid guest, G, and crystallizing the solid inclusion compound:

$$\mathrm{H}(s) + \mathrm{G}(l) \longrightarrow \mathrm{H}\cdot\mathrm{G}_n(s)$$

When the guest is volatile, the stoichiometry of the inclusion compound may be readily ascertained by employing thermogravimetry (TG) to monitor the mass loss upon heating. The thermal decomposition of the inclusion compound, however, may involve more than one step:

$$\mathrm{H}\cdot\mathrm{G}_n(s) \longrightarrow \mathrm{H}\cdot\mathrm{G}_{n-m}(s) + m\mathrm{G}(g)\uparrow \qquad \text{(step 1)}$$

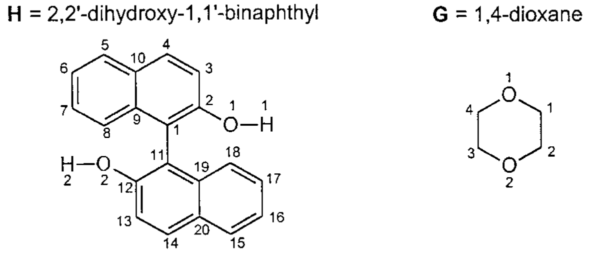
$$\mathrm{H}\cdot\mathrm{G}_{n-m}(s) \longrightarrow \mathrm{H}(s) + (n-m)\mathrm{G}(g)\uparrow \qquad \text{(step 2)}$$

The intermediate $\mathrm{H}\cdot\mathrm{G}_{n-m}(s)$ may be stable over a wide temperature range.[1] Single crystals of the inclusion compound $\mathrm{H}\cdot\mathrm{G}_n(s)$ generally break up to form a fine powder of the intermediate compound $\mathrm{H}\cdot\mathrm{G}_{n-m}(s)$, making it impossible to subject the latter to single-crystal structure analysis.

Previous reports have appeared detailing the possibility of growing inclusion compounds with various host:guest ratios by changing the crystallization temperature.[2–4] This technique has also been employed to control the selectivity of isomers of xylene by a dicarboxylic host.[5] We now present the results of variable-temperature crystallization experiments carried out on inclusion compounds formed between the host, H = 2,2′-dihydroxy-1,1′-binaphthyl, and the guest, G = 1,4- dioxane.

EXPERIMENTAL

The host H was dissolved in excess guest G. When allowed to crystallize at 25 °C by slow evaporation, it yielded compound **1**, $\mathrm{H}\cdot\mathrm{G}_{3.5}$. We then carried out the crystallization at elevated temperatures by inserting the crystallization vial in a brass block maintained at controlled temperature in a sand-bath. Suitable single crystals of compound **2**, $\mathrm{H}\cdot\mathrm{G}_{1.5}$, were obtained after 2 days at a fixed temperature of 60 ± 1 °C. The host:guest ratio for both compounds was established by TG. Preliminary unit cell dimensions and space groups for both compounds were obtained photographically and the unit cell parameters were subsequently refined by standard procedures on a Nonius KappaCCD diffractometer. Relevant crystal and experimental data are given in Table 1. Both structures were solved by direct methods using SHELX-86[6] and refined employing full-matrix least-squares using SHELX-93,[7] refining on F^2. The numbering scheme is shown in Scheme 1. For both structures, all non-hydrogen atoms were treated anisotropically. The aromatic and methylene hydrogens were geometrically constrained and refined with isotropic



Compound **1**: $\mathrm{H}\cdot\mathrm{G}_{3.5}$

Compound **2**: $\mathrm{H}\cdot\mathrm{G}_{1.5}$

Scheme 1. The crystallographically independent guest molecules are assigned letteried suffixes A, B, C, etc

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Table 1. Crystal data, experimental and refinement parameters for inclusion compounds **1** and **2**

	1	**2**
Molecular formula	$C_{34}H_{42}O_9$ $[C_{20}H_{14}O_2 \cdot 3.5(C_4H_8O_2)]$	$C_{26}H_{26}O_5$ $[C_{20}H_{14}O_2 \cdot 1.5(C_4H_8O_2)]$
Formula mass (g mol^{-1})	594.68	418.47
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.322(1)	8.938(1)
b (Å)	12.023(1)	28.013(2)
c (Å)	13.432(1)	9.137(1)
α (°)	111.651(3)	90
β (°)	91.955(3)	110.213(5)
γ (°)	90.716(3)	90
Volume (Å^3)	1547.8(2)	2146.8(4)
Z	2	4
D_c (g cm^{-3})	1.276	1.295
μ(Mo K$_\alpha$) (cm^{-1})	0.92	0.89
F(000)	636	888
Data Collection (173 K)		
Range scanned, θ(°)	2.72–26.13	2.48–27.48
Range of indices, h,k,l	0–12, ±14, ±15	±10, ±36, ±11
Reflections collected	10436	18862
Unique reflections	4474	4395
R(int)	0.037	0.068
Number of parameters	397	289
Final R indices [$I > 2\sigma I$], $R1$	0.0464	0.0766
$wR2$	0.114	0.2268
R indices (all data)	0.0752	0.1114
Goodness of fit on F^2	1.025	1.062
Max./min. height in difference electron map (e Å^{-3})	0.303/−0.245	0.807/−0.522

temperature factors set at 1.2 times the U_{eq} of the parent atoms. The hydroxyl hydrogens were located in difference electron density maps and refined with independent temperature factors and simple bond length constraints.

Thermal analyses were conducted on a Perkin-Elmer PC7 Series instrument. Finely powdered specimens were placed in open platinum pans for TG and in crimped, but vented, aluminium pans for differential scanning calorimetry (DSC). The sample mass in each case was 2–8 mg, and the sample was purged with a stream of nitrogen flowing at ca 40 ml min^{-1}. Data for the kinetics of desolvation were obtained from isothermal TG experiments carried out at selected temperatures.

RESULTS AND DISCUSSION

Structures

For compound **1**, $\mathbf{H \cdot G_{3.5}}$, the space group is $P\bar{1}$ with $Z = 2$. Hence the host molecule and three of the dioxane guests, A, B and C, are located in general positions, while one dioxane, D, lies on a centre of inversion at Wyckoff position *f*. Only two of the dioxane guests, A and B, are stabilized by (**H**)O—H···(**G**) hydrogen bonds, details of which are given in Table 2. The packing is shown in Fig. 1(a). There are two channels running through the structure. Dioxane guests A, B and C lie in a channel running parallel to [100], whereas guest D is located in a channel running parallel to [001].

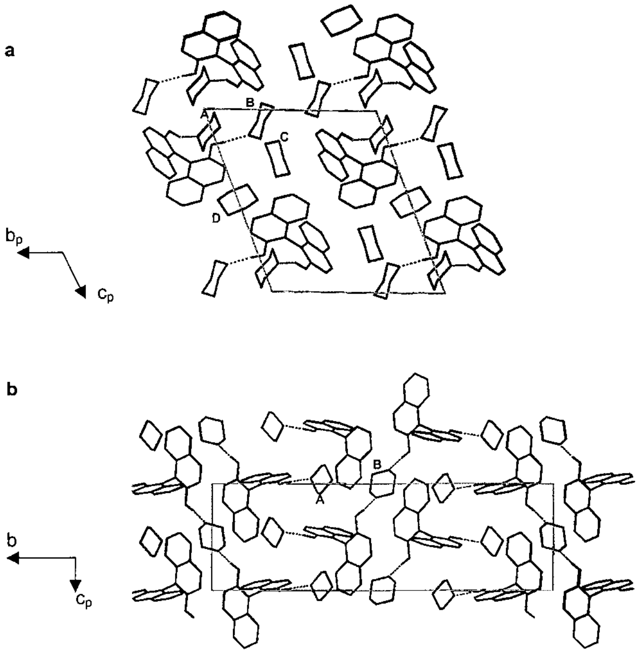

Figure 1. Projection along [100] for (a) compound **1** and (b) compound **2** with guest molecules marked. The hydrogen bonding is shown as dotted lines. All hydrogen atoms except the hydroxyl hydrogens on the host are omitted

Table 2. Hydrogen bond details for inclusion compounds **1** and **2**[a]

Compound	Donor (D)	Acceptor (A)	D—H (Å)	D···A (Å)	D···H—O (°)
1	O1	O1B[1]	0.973(7)	2.685(2)	176(3)
	O2	O1A[2]	0.971(9)	2.679(2)	146(2)
2	O1	O1B[3]	0.975(14)	2.676(3)	172(4)
	O2	O1A[4]	0.949(14)	2.760(3)	170(3)

[a] Symmetry codes: 1, $\bar{x}+1, \bar{y}, \bar{z}$; 2, $\bar{x}+2, \bar{y}, \bar{z}$; 3, $\bar{x}, \bar{y}, \bar{z}$; 4, $x, \bar{y}+1/2, \bar{z}-1/2$.

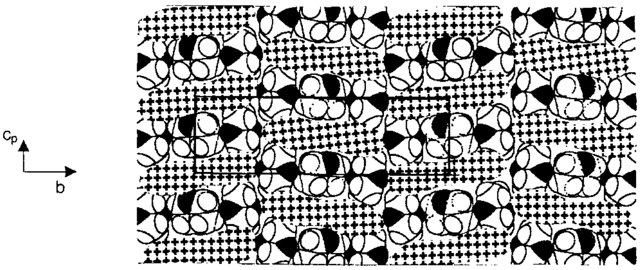

Figure 2. Cross-sectional area at *x*/*a* = 0.5 for compound **2**. The host molecules are shown as hatched areas. The guests are shown in van der Waals radii with oxygen atoms shaded

For compound **2**, $\mathbf{H}\cdot\mathbf{G}_{1.5}$, the space group is $P2_1/c$ with $Z = 4$. The host molecules and guest dioxane A are in general positions, while dioxane B is located in a centre of inversion at Wyckoff position *d*. Both guests are hydrogen bonded, details of which are shown in Table 2.

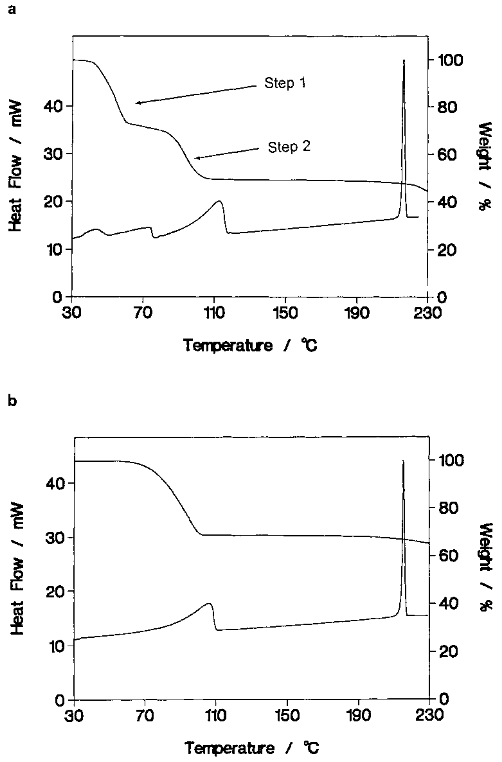

Figure 3. TG/DSC traces for (a) compound **1** and (b) compound **2**

Dioxane A is stabilized by a single hydrogen bond and dioxane B by two centrosymmetrically arranged (**H**)O—H···O(**G**) interactions, as displayed in Fig. 1(b). The dioxanes lie in the [011] and [01 $\bar{1}$] directions at *x*/*a* = 1/2. These are shown in Fig. 2, which was drawn with the program SECTION.[8]

In both structures, the conformation of the host molecules remains virtually constant. This is seen from the value of the torsion angle C(2)— C(1)— C(11)— C(12), which has a value of 101.4° for compound **1** and 99.9° for compound **2**. This is in general agreement with all the known crystal structures containing this host. A search of the Cambridge Structural Database System (CSDS)[9] gave 27 entries for this host molecule, with this torsion angle varying from 75° to 110° and averaging 91°.

Thermal analysis

The TG and DSC traces for compound **1** are shown in Fig. 3(a). There is a first mass change, step 1, which corresponds to the loss of two molecules of guest dioxane. This occurs between 40 and 75 °C and is followed by step 2, which corresponds to the loss of the remaining 1.5 dioxanes. The DSC curve is more

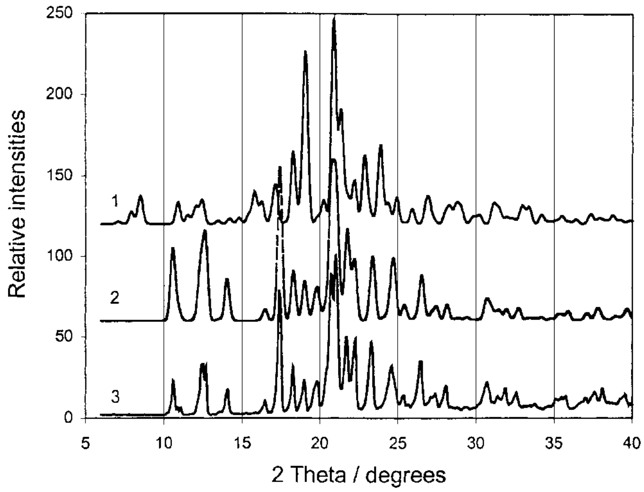

Figure 4. XRD patterns: (1) calculated for compound **1**, (2) calculated for compound **2** and (3) experimental from powder obtained by fast stirring

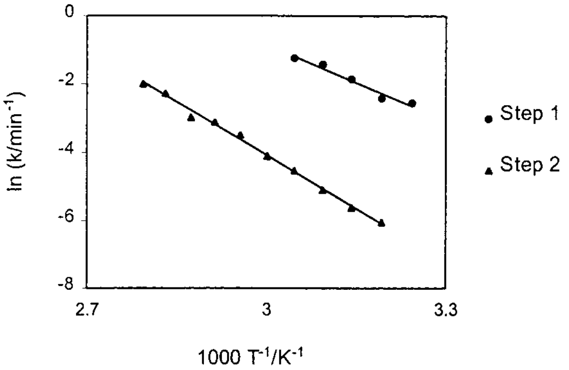

Figure 5. Arrhenius plot of ln*k* *vs* 1/*T* for the desolvation reactions of steps 1 and 2

complex, yielding the first two endotherms for step 1 and a larger endotherm for step 2. These have peaks at 43, 73 and 112 °C. The final sharp endotherm at 216 °C corresponds to the melting of the host. The TG/DSC traces for compound **2** are much simpler, showing a one-step mass loss for desolvation, with a concomitant endotherm peaking at 106 °C and the melting endotherm at 216 °C, as shown in Fig. 3(b).

It is interesting to note that compound **1** can only be synthesized by slow evaporation of the host solution at room temperature. If the evaporation is carried out fast and with vigorous stirring, we invariably obtained compound **2**. This was checked by XRD analysis of the compound obtained and is shown in Fig. 4. The XRD pattern of the powder obtained by fast stirring is very similar to that calculated using coordinates of the structure of compound **2**, employing the LAZY PULVERIX programe.[10]

Kinetics

We analysed the kinetics of desolvation of both compounds by carrying out a series of isothermal TG runs.

For step 1, in which two portions of guest dioxanes were lost, crystals of compound **1** were crushed and immediately inserted into the TG pan. Five individual kinetic traces were obtained in the temperature range 35–55 °C. The deceleratory desolvation curves fitted best to the R2, contracting area model[11]

$$1 - (1 - \alpha)^{1/2} = kt$$

where α is the extent of the desolvation reaction. The Arrhenius plot of ln*k* vs 1/*T* as shown in Fig. 5 yielded an activation energy of 61 ± 6 kJ mol^{-1} and a pre-exponential factor with ln $A = 21 \pm 2$.

We repeated the procedure for the analysis of step 2, in which 1.5 guest dioxanes were lost, by using compound **2** and carrying out 10 isothermal runs in the temperature range 40–85 °C. This desolvation also followed the R2 mechanism and yielded an activation energy of 86 ± 2 kJ mol^{-1} and a pre-exponential factor with ln $A = 27 \pm 1$, as also shown in Fig. 5.

In conclusion, we have successfully elucidated the structures of two distinct inclusion compounds formed between the host 2,2′-dihydroxy-1,1′-binaphthyl and the guest 1,4-dioxane. Their manner of desolvation was characterized by isothermal kinetics experiments. It was shown that temperature control and crystallization environments play an important role in determining the stoichiometry and structures of the inclusion compounds.

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