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# Complexation with diol host compounds, part 16[1]. Structure and thermal stability of 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl.diethyl ether

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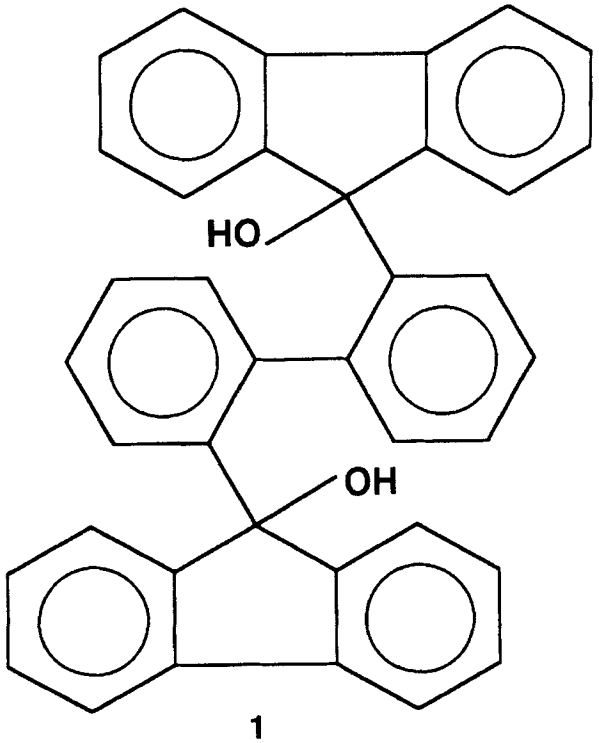
**The structure of the inclusion compound of 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl (1) with diethyl ether (2) (1:1) is reported. Crystal data: monoclinic, $P2_1/n$ with $a$ = 11.728(7), $b$ = 20.471(4), $c$ = 14.334(8) Å, β = 109.23(7)°, Z = 4, $D_c$ = 1.20 g cm$^{-3}$. The final R value was 0.045 for 3479 reflections. The inclusion compound displays a high thermal stability. The enthalpy of the guest release reaction and the activation energy of thermal decomposition have been measured. The crystal structure shows diethyl ether to be tightly packed in cavities formed by the host compound. The structure is further stabilized by host-guest hydrogen bonding.**

## INTRODUCTION

The molecule 2,2'-Bis(9-hydroxy-9-fluorenyl)biphenyl (**1**) has the properties required of a good host compound.[2] It is bulky, stiff and contains the hydroxyl moiety which acts as a hydrogen-bond donor in host-guest interactions. This host forms a variety of crystalline inclusion compounds and the structures of its clathrates with acetonitrile, cyclohexanone, di-n-propylamine and dimethylformamide have been reported.[3]

In general, inclusion compounds of highly volatile guests are unstable at room temperature and atmospheric pressure, and organic compounds which enclathrate volatile guests from the vapour phase are rare.[4] This host, however, forms a remarkably stable 1:1 inclusion compound (**2**) with diethyl ether from the vapour. We have elucidated its structure by X-ray diffraction methods on single crystals grown by slow evaporation of a solution of the host in diethyl ether.




**1**

**2 = 1 . $Et_2O$**

## RESULTS AND DISCUSSION

The stability of the **1** . $Et_2O$ 1:1 inclusion compound, **2**, is shown by the thermal analysis results given in Figure 1. The differential scanning calorimetry (DSC) curve (heating rate 10 °C min$^{-1}$, vented pans, purged in $N_2$ gas) is characterized by four peaks. The first endotherm, A, is

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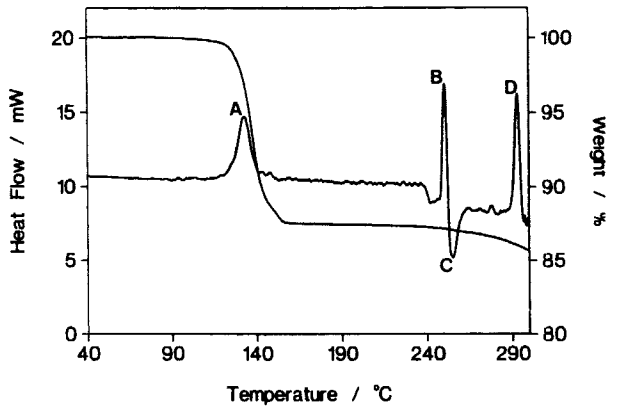


**Figure 1** TG and DSC traces

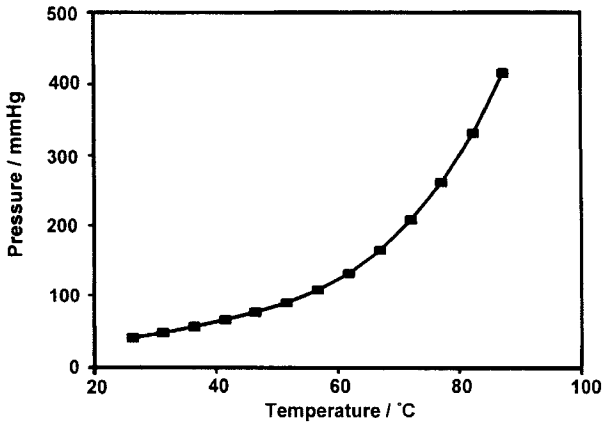


**Figure 2a** Plot of vapor pressure *versus* temperature

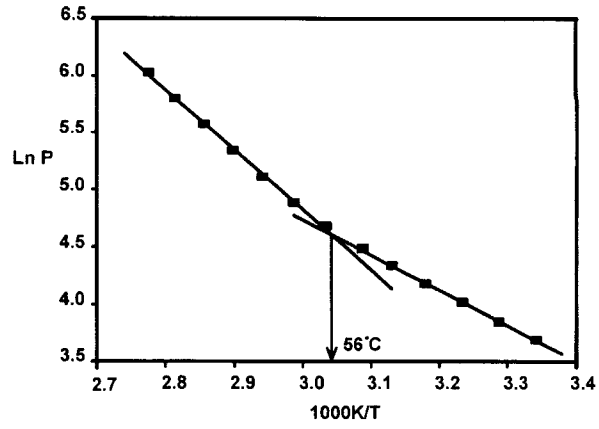


**Figure 2b** Corresponding plot of ln P *versus* 1/T

due to the guest release reaction and has an onset temperature of 125.8 °C, which is 91.3 °C above the normal boiling point of the diethyl ether. This is followed by endotherm B and exotherm C, occurring between 245 and 265 °C, which we attribute to a phase change in the desolvated host. Endotherm D is due to the final melting of the host. We have noted this sequence of events in other inclusion compounds, and the thermal decomposition of 1,1,2,2-tetraphenylethane . 2(3,5-lutidine) yields a similar decomposition pattern.[5]

In a previous publication[6] we suggested that the function $T_{on}$-$T_b$ ($T_{on}$ = onset temperature, $T_b$ = normal boiling point of the guest) may be a useful parameter describing the stability of the inclusion compound. For most inclusion compounds containing volatile guests, $T_{on} < T_b$, but there are some notable exceptions. We have reported the onset temperatures of 1,1′-binaphthyl-2,2′-dicarboxylicacid . 2(methanol)[7] and 9,10-dihydroxy-9,10-bis(4-tert-butylphenyl)-9,10-dihydroanthracene . 2(diethyl ether)[4] in which $T_{on}$-$T_b$ = +82 °C and +29.8 °C, respectively.

The equilibrium constant of the thermal decomposition reaction was investigated by measuring the vapour pressure of the diethyl ether at various temperatures (Figure 2a). The compound was heated at 0.3 °C $min^{-1}$ from 25 °C to 99 °C and the pressure recorded. This yielded the results shown in Figure 2b, which shows that the ln P versus 1/T curve has a distinct discontinuity at 56 °C and the two slopes correspond to $\Delta H_1$ = 24.7 $kJmol^{-1}$ and $\Delta H_2$ = 46.0 $kJmol^{-1}$ respectively. This method of measuring the equilibrium vapour pressure of the volatile guest gives more accurate values of the enthalpy of the guest-release reaction than that obtained by DSC. The latter method suffers from various experimental factors such as the heating rate, particle size and the geometry of the specimen holder.

Thermogravimetry at various heating rates allowed us to estimate the activation energy of the guest-release reaction. We used the method developed by Flynn and Wall[8], which has been applied to the decomposition of various systems, including inorganic complexes[9] and inclusion compounds.[10,11] The decomposition curves for **2**, recorded at various heating rates, β, ranging from 2.5 to 20 °C $min^{-1}$ are shown in Figure 3 and the corresponding semilogarithmic plots of log β versus reciprocal temper-

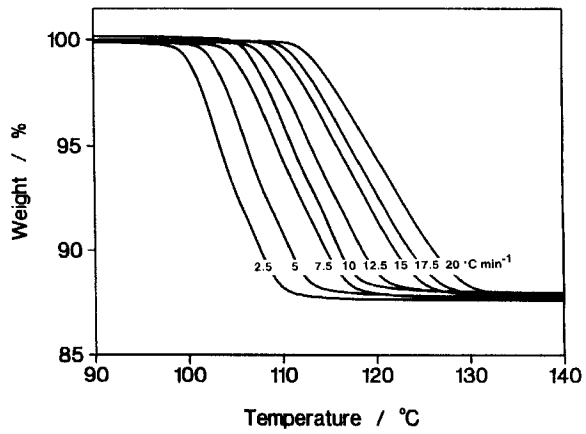


**Figure 3** TG curves at various heating rates

ature are shown in Figure 4. The latter corresponds to several degrees of decomposition varying between 2.5% and 10% of guest loss. The slopes of the lines correspond to a range of activation energies which vary from 107 to 137 kJmol$^{-1}$. Similar values were obtained from the desorption of acetonitrile from its inclusion compound with trans-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene.[10]

The crystal structure of compound **2** was determined by direct methods and refined by full-matrix least-squares routines using SHELXS-86 and SHELX76 .[12,13] Crystal data and other experimental details are given in Table 1. The molecular structure of host compound **1**, with atomic nomenclature, is shown in Figure 5, while the packing of the structure is shown in Figure 6. The hydroxyl hydrogens were located unequivocally in a difference electron density map and refined with a common isotropic temperature factor. The host structure is characterized by the twisting about the central bond C(20)-C(40) and the torsion angle C(15)-C(20)-C(40)-C(35) has a value of 93.2(4)°, which is similar to those found in other clathrate structures of this host.[3] This constant conformation is governed by the intramolecular hydrogen bond (O(14)...O(34)=2.727(3) Å). The second hydroxyl hydrogen is involved in the host-guest hydrogen bond, where O(34)...O(3G)=2.756(3) Å. The stability of this inclusion compound, however, cannot be attributed solely to the host-guest hydrogen bond but also to the tight packing of the guest in the structure. Thus the pack-

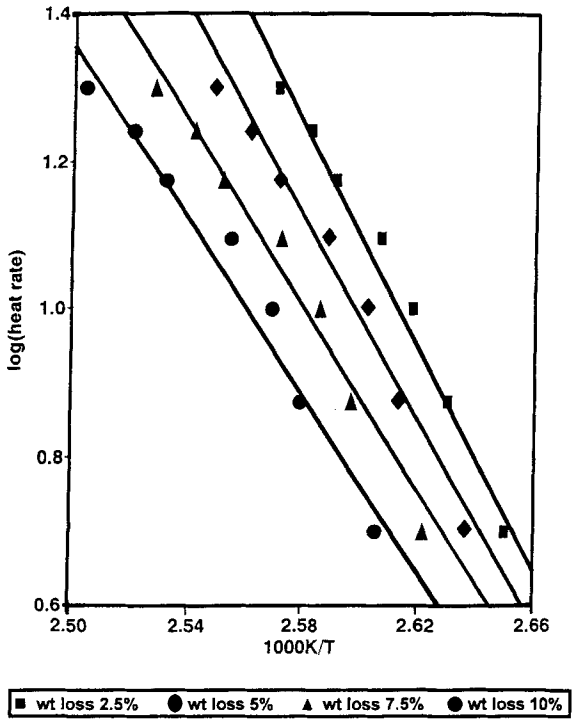


**Figure 4** Plot of log $\beta$ *versus* 1/T for several percentages of decomposition

**Table 1** Crystal data, details of data collection and final refinement.

| | |
|---|---|
| Molecular formula | $C_{38}H_{26}O_2 \cdot C_4H_{10}O$ |
| Mass (g mol$^{-1}$) | 588.75 |
| Space group | $P2_1/n$ |
| a (Å) | 11.728(7) |
| b (Å) | 20.471(4) |
| c (Å) | 14.334(8) |
| α(°) | 90 |
| β(°) | 109.23(7) |
| γ(°) | 90 |
| Volume (Å$^3$) | 3249(3) |
| Z | 4 |
| F(000) | 1248 |
| μ (Mo Kα) (cm$^{-1}$) | 0.69 |
| Crystal dimensions (mm) | 0.40 × 0.40 × 0.50 |
| $D_c$ (g cm$^{-3}$) | 1.20 |
| θ range scanned (°) | 1 – 25 |
| Range of *h,k,l* | ±13, 24, 17 |
| Decay during collection (%) | 0.8 |
| Number of reflections collected | 6125 |
| Number of reflections with $I_{rel}>2\sigma I_{rel}$ | 3479 |
| Number of parameters | 421 |
| Max LS shift to e.s.d. | 0.09 |
| R ($\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$) | 0.045 |
| $R_w$ | 0.055 |
| $W = (\sigma^2F + gF^2)^{-1}$ | 0.008 |
| Max/min residual electron density (eÅ$^{-3}$) | 0.14/-0.22 |

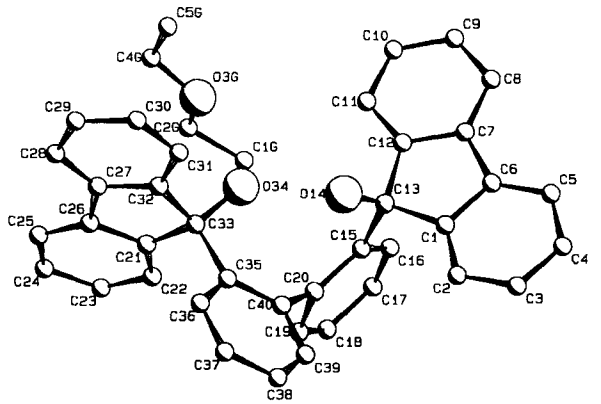


**Figure 5** Perspective view of the host

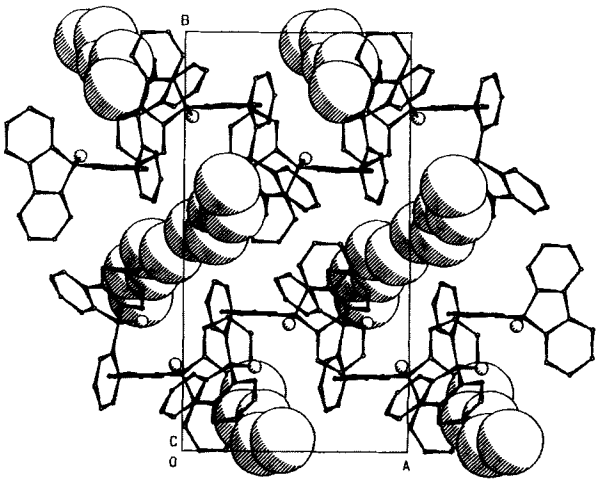


**Figure 6** Packing diagram viewed down [0 0 1] - guest drawn with van der Waals radii

ing factor, calculated as the volume per non-hydrogen atom, is 18.1 Å$^3$ in this structure, but rises to 21.0 Å$^3$ and 19.7 Å$^3$ in other organic clathrates containing diethyl ether as guest.[4,14] The geometry of the guest cavities is illustrated in Figure 7 which shows how pairs of diethyl ether molecules are located about centres of inversion in the structure.

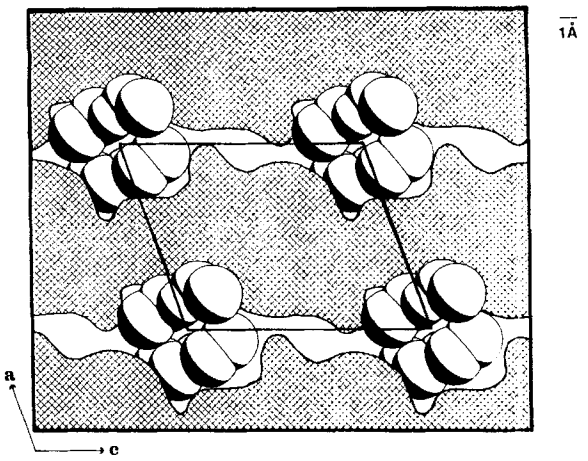


**Figure 7** Cross-section of the cell at y = 0.5 indicating the cavitites in which the guest is enclosed

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