Complexation with Diol Host Compounds, 12[1]

Synthesis and Solid-State Inclusion Properties of Bis(diarylhydroxymethyl)-Substituted 1,1′-Binaphthyls. Crystal Structures of a Host and Its Pyridine Clathrate

Edwin Weber*[a][+], Konstantinos Skobridis[a], Andreas Wierig[a], Leonard J. Barbour[b], Mino R. Caira[b], and Luigi R. Nassimbeni*[b]

Institut für Organische Chemie und Biochemie der Universität Bonn[a],
Gerhard-Domagk-Straße 1, W-5300 Bonn, F.R.G.

Department of Chemistry, University of Cape Town[b],
Private Bag, Rondebosch 7700, South Africa

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A series of new clathrate host molecules **1**–**8** containing two bis(diarylhydroxymethyl) groups attached to different positions (2,2′ or 8,8′) of a 1,1′-binaphthyl frame have been synthesized. Their clathrate formation properties with organic guests including alcohols, amines, ketones, and other dipolar aprotic compounds or aromatic hydrocarbons are reported (74 examples of clathrates) together with the results of solvent competition experiments for the parent host compound. The inclusion formation and the clathrate stoichiometries depend on the structure of the host molecules in a systematic manner. The crystal structures of the free parent host **1** and its pyridine clathrate (1:3) have been determined by X-ray diffraction. The molecular structure of the host is similar in the two species involving an intramolecular hydrogen bond between the host hydroxyls. No other hydrogen bond is involved in the free host case while in the pyridine inclusion compound the second host hydroxyl forms a hydrogen bond with the nitrogen of one pyridine guest which is surrounded by two unbound pyridine species such as to form clusters of three pyridine guests enclosed in the cavities between the host molecules. Thermal analysis corresponds with the two binding states of the pyridine molecules in the clathrate.

Organic compounds that form crystalline host-guest inclusions (clathrates)[2] with secondary molecules are attracting increasing attention[3] in view of their practical uses. These include chemical separation, stabilization and protection of labile species, topochemistry or development of new solid materials[1–7]. This has stimulated the development of new strategies in crystalline inclusion formation and motivated the design of novel host types[2,3]. The most consistent results refer to inclusion compounds which are based on coordination-assisted clathrate formation between functionalized and polar guest molecules[8]. The formation and stability of these crystalline complexes are affected by functional as well as by topological complementarity, and consequently are sensitive to small structural variations[9,10].

Among the many new types of polar host structures[1,2,8–10], the hydroxylic group-containing molecules, in particular those involving triarylmethanol and bridged triarylmethanol units, were found to be very effective clathrate formers[1,11–13]. From the geometric point of view, the scissor-type hosts based on the 1,1′-binaphthyl frame proved particular successful[8,14,15]. We report here on the synthesis of several specified compounds **1**–**8** that combine both characteristic features, namely the triarylmethanol and the 1,1′-binaphthyl construction elements. These compounds (**1**–**7**) have different polar and apolar substituents in different positions attached to the lateral aromatic rings. Moreover, linkage of the basic construction elements is also different (2,2′ or 8,8′ with reference to the binaphthyl unit, cf. **1** vs. **8**) making possible a comprehensive evaluation of the host structures. We describe in detail the crystal inclusion properties of **1**–**8**, including guest competition experiments for **1** and present crystal structures of the free host compound **1** and of its inclusion complex with pyridine having the uncommon host-to-guest stoichiometry 1:3.

1. Synthesis

The bis-carbinols **1**–**7** were synthesized by the reaction of dimethyl 1,1′-binaphthyl-2,2′-dicarboxylate (**9**)[15a] with the corresponding aryllithium reagents. These were prepared by treatment of the respective aryl bromides with *n*BuLi under usual conditions[16]. Analogously, the bis-carbinol **8** was synthesized from dimethyl 1,1′-binaphthyl-8,8′-dicarboxylate (**10**), bromobenzene, and BuLi. The dimethyl ester **10**[17] was obtained by the reaction of the corresponding dicarboxylic acid with diazomethane. All lithium organic reactions gave the bis-carbinols in high yield (70–90%). The inclusion compounds were obtained by recrystallization of

[+] New address: Institut für Organische Chemie der Technischen Universität – Bergakademie Freiberg, Leipziger Straße 29, O-9200 Freiberg, F.R.G.

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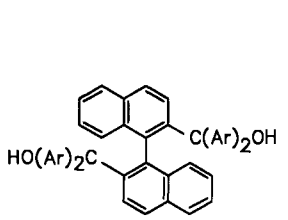
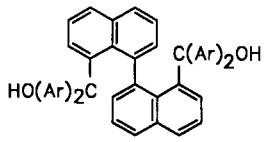
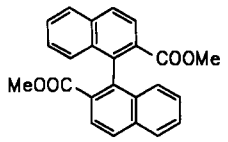
the host compound from the respective guest solvent. The drying conditions specified in the experimental section (1 h, 15 Torr, room temp.) refer to what we consider a "stable clathrate"[9,13,15].



	Ar
1	C_6H_5
2	4-MeC_6H_4
3	4-$(Me_3C)C_6H_4$
4	4-$(F_3C)C_6H_4$
5	4-$(MeO)C_6H_4$
6	3-MeC_6H_4
7	2-MeC_6H_4



8 Ar = C_6H_5



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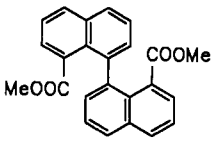

10

2. Inclusion Properties

A total of 74 different inclusion compounds are specified in Table 1, showing the efficiency of the new host design in general. Nevertheless, the individual bis-carbinols **1**–**8** are rather different in their inclusion ability and demonstrate a characteristic level of selectivity. Some of the compounds of which **6** and **7** are typical examples, form inclusions in the broad sense, i.e. with molecules belonging to different substance classes (alcohols, amines, aprotic dipolar and rather apolar compounds). These hosts have methyl groups in the 3- or 2-position of the lateral phenyls. Others, among them **1**, **3**, and **4**, which have no lateral substituents (**1**) or contain a bulky *tert*-butyl (**3**) or a polar trifluoromethyl group (**4**) in the 4-position of the lateral phenyls, provide a moderate number of inclusion compounds; **2** with methyl groups in the 4-positon of the lateral phenyls and **8**, which has the carbinol sustituents in the 8,8′-position of the binaphthyl frame, allow only few inclusions. There is also one example of the explored group of compounds which displays no host property under the experimental conditions, namely compound **5** which has a methoxy substituent attached to the 4-position of the lateral phenyls. These findings show that the nature and the position of the lateral substituents are important structural features of the present host design.

Host-to-guest stoichiometric ratios determined include 2:1, 3:2, 1:1, 1:2, 1:3, and 1:4, the most frequently observed ratio being 1:1, followed by 1:2. It is difficult however to draw conclusions from the individual stoichiometric data except for the inclusions of **3** where the high stoichiometric ratios in favor of the guest may relate to the presence of the bulky *tert*-butyl groups, and in the inclusion compounds of **7** the 1:1 stoichiometric ratio is possibly favored due to the possible shielding of the host hydroxyls by the 2-positioned methyls.

Table 1. Crystalline inclusion compounds (host-to-guest stoichiometric ratios)[a]

Guest solvent[b]	Host compound							
	1[c]	**2**	**3**	**4**	**5**	**6**	**7**	**8**
MeOH	—	—	—	—	—	2:1	1:1	—
EtOH	—	—	—	—	—	—	1:1	—
1-PrOH	—	—	1:3	—	—	—	1:1	—
2-PrOH	[d]	—	—	—	—	[d]	1:1	—
1-BuOH	[d]	—	[d]	—	[d]	[d]	1:1	—
2-BuOH	1:2	—	1:3	—	—	1:2	1:1	—
*t*BuOH	—	—	—	—	—	2:1	3:2	—
Acetone	1:1	—	1:3	—	—	1:1	1:1	—
Cyclohexanone	1:2	1:2	1:2	1:1	[d]	1:2	1:1	[d]
Ethyl acetate	1:1	—	1:1	1:1	—	1:1	1:1	—
DMF	1:1	1:1	1:3	1:3	—	1:1	1:1	[d]
DMSO	1:1	1:2	[d]	1:2	—	1:2	1:2	1:1
Dioxane	—	1:3	1:4	1:1	—	[d]	1:1	1:2
Morpholine	1:3	1:2	1:2	1:2	[d]	1:2	1:2	1:2
*n*PrNH$_2$	1:3	—	1:3	1:1	—	1:1	1:1	—
(*n*Pr)$_2$NH	1:1	—	—	1:1	—	1:1	1:1	[d]
*t*BuNH$_2$	1:3	1:3	—	1:1	—	1:1	1:1	1:3
Pyridine	1:3	—	1:2	[d]	—	—	1:1	—
Benzene	—	—	1:1	—	—	—	1:1	—
Toluene	—	—	1:1	—	—	—	—	—
Xylene	—	—	[d]	1:1	—	—	—	—

[a] See Experimental for methods of preparation, drying standard, and characterization. — [b] Acetonitrile, nitromethane, piperidine, and mesitylene, which were also tested as guest solvents, yielded no inclusion compounds. — [c] This host forms also crystalline inclusion compounds with 2-methylcyclohexanone (1:2), 3-methylcyclohexanone (1:2), and acetoin (1:1). — [d] Difficult to crystallize.

With reference to the solvent molecules included, the results show that, in general, the dipolar aprotic compounds and the amines form the highest number of inclusions, in particular morpholine. Most remarkably in this connection, piperidine forms no inclusion with any of the hosts. Compared to the amines and dipolar aprotic compounds, the alcohols and the aromatic hydrocarbons yield fewer inclusion compounds. Most of them are generated with the host compound **7** and among the alcohols, 2-BuOH is the preferred guest although it is not effective with all hosts. Actually, there are hosts that exhibit no inclusion behavior towards alcohols (**2**, **4**, **5**, **8**) or towards aromatic hydrocarbons (**1**, **2**, **5**, **8**) under the experimental conditions. Another remarkable finding is that host **3** forms alcohol inclusion compounds only with 1-PrOH and 2-BuOH both having stoichiometric ratios of 1:3; interestingly, both of these alcohols contain a hydroxypropane unit. On the other hand,

6 includes MeOH and *t*BuOH in a stoichiometric ratio of 2:1 but 2-BuOH in a stoichiometric ratio of 1:2, and in the case of **7**, the stoichiometric ratio for the alcohol inclusions is uniformly 1:1 except for *t*BuOH where it is 3:2. In the case of inclusions of aromatic hydrocarbons, a 1:1 stoichiometric ratio is exclusively found.

These results suggest a characteristic mode of selectivity for the different hosts and for a particular host when exposed to a solvent mixture. Table 2 shows the results of solvent competition experiments for host compound **1**. As can be seen: DMF and DMSO are the guests highly favored over the other solvents mentioned in Table 2. In the competition between DMSO and DMF, the former is superior.

Table 2. Selective crystalline inclusion formation of **1** from two component solvent mixtures

Solvent (1) / solvent (2) (equal volumes)	Ratios Host:(1):(2)
Acetone/BuOH	1:1:1
Acetone/DMF	1:0:1
Acetone/DMSO	1:0:1
Acetone/cyclohexanone	1:0:2
Acetone/ethyl acetate	1:1:0
DMF/DMSO	1:0:1
DMF/ethyl acetate	1:1:0
DMSO/ethyl acetate	1:1:0
Ethyl acetate/2-BuOH	1:1:0
$(n\text{Pr})_2\text{NH}/t\text{BuNH}_2$	1:1:0

In order to investigate the building principles of the new inclusion family and to increase experimental support to some of the mentioned problems, we have studied the crystal structures of a free host and of a corresponding inclusion compound, namely **1** and **1** · pyridine (1:3). Particular questions to be answered by these structures refer to the presence of a potential intramolecular hydrogen bond between the two hydroxy groups in **1** and the unusual 1:3 stoichiometric ratio (host-to-guest) in the pyridine inclusion compound of **1**.

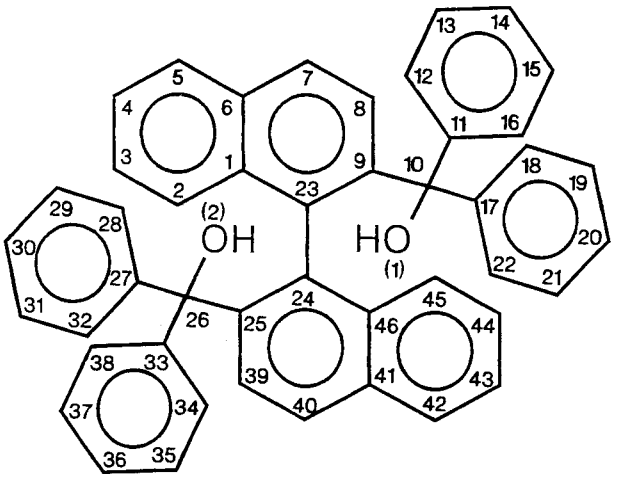

Figure 1. Structure diagram and numbering scheme for **1**

3. X-Ray Crystal Structure of 1 and 1 · Pyridine (1:3)

The structural diagram and numbering scheme are shown in Figure 1, and the atomic coordinates of compounds **1** and **1** · pyridine (1:3) are given in Tables 5 and 6. Complete lists of bond lengths, angles, anisotropic thermal parameters, and coordinates of calculated hydrogen positions have been deposited (see Experimental).

The molecular structure of the host compound is similar in the two compounds. The central bond C(23)–C(24), joining the two naphthyl moieties, and the bonds C(9)–C(10) and C(25)–C(26) have similar lengths in the two compounds and are recorded, together with other important molecular parameters, in Table 3. The conformation of the host compound remains remarkably constant when we compare the non-porous α phase, free host compound **1**, with the β phase of the pyridine inclusion compound.

Table 3. Selected molecular parameters of **1** and **1** · pyridine (1:3)

Distance [Å], Angle [°]	**1**	**1** · pyridine (1:3)
C(23)-C(24)	1.503(11)	1.498(5)
C(9)-C(10)	1.554(10)	1.546(3)
C(25)-C(26)	1.534(10)	1.547(4)
C(10)-O(1)	1.428(10)	1.425(3)
C(26)-O(2)	1.455(9)	1.437(3)
angle at C10	105.5-112.6	106.3-112.0
angle at C26	106.0-114.0	105.8-112.6
τ_1 = C(9)-C(23)-C(24)-C(25)	95	97
τ_2 = O(1)-C(10)-C(9)-C(23)	-31	-31
τ_3 = C(16)-C(11)-C(10)-C(9)	59	41
τ_4 = C(18)-C(17)-C(10)-C(9)	48	57
τ_5 = O(2)-C(26)-C(25)-C(24)	-48	-44
τ_6 = C(28)-C(27)-C(26)-C(25)	51	57
τ_7 = C(9)-C(33)-C(26)-C(25)	59	63
O(1)···O(2)	2.76(1)	2.68(1)
O(1)-H(1)	0.97(3)	1.03(3)
H(1)···O(2)	1.81(3)	1.65(3)
O(1)-H(1)···O(2)	167	175
O(2)···N(1G2)	—	2.78(1)
O(2)-H(2)	0.84(7)	0.97(2)
H(2)···N(1G2)	—	1.81(3)
O(2)-H(2)···N(1G2)	—	174
τ_8 = H(2)-O(2)-C(26)-C(25)	-148(5)	-169(2)

This can be seen directly by considering Figures 2a and 2b which give a perspective view of the molecular structures viewed along C(23)–C(24). We may take the intramolecular hydrogen bond as the most important feature which governs the conformation of the host molecule in both structures. The O(1)···O(2) distances of 2.76 and 2.68 Å in compounds **1** and **1** · pyridine (1:3) show these to be moderately strong hydrogen bonds.

The packing of compound **1** is shown in Figure 3 which views the structure along [100]. There is no intermolecular hydrogen bonding, but the structure is tightly packed, with a packing factor of 16.9 Å^3 per non-hydrogen atom. The hydrogen bond details are given in Table 3 and are similar for the two structures. In particular, the positions of H(2) correspond, as can be seen by the torsion angle τ_8 (Table 3). The overall effect is that the host molecule retains its con-

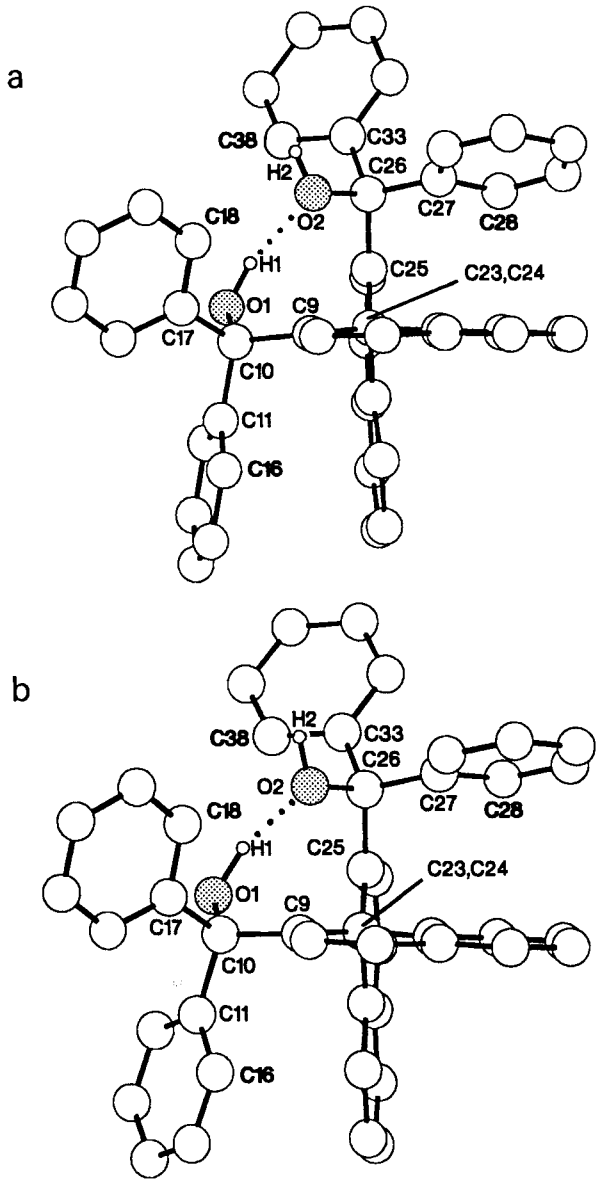

Figure 2. Perspective view of **1** along the central bond: (a) in the free host compound; (b) in the inclusion compound with pyridine. Oxygen atoms are shaded; the dotted lines indicate hydrogen bonds

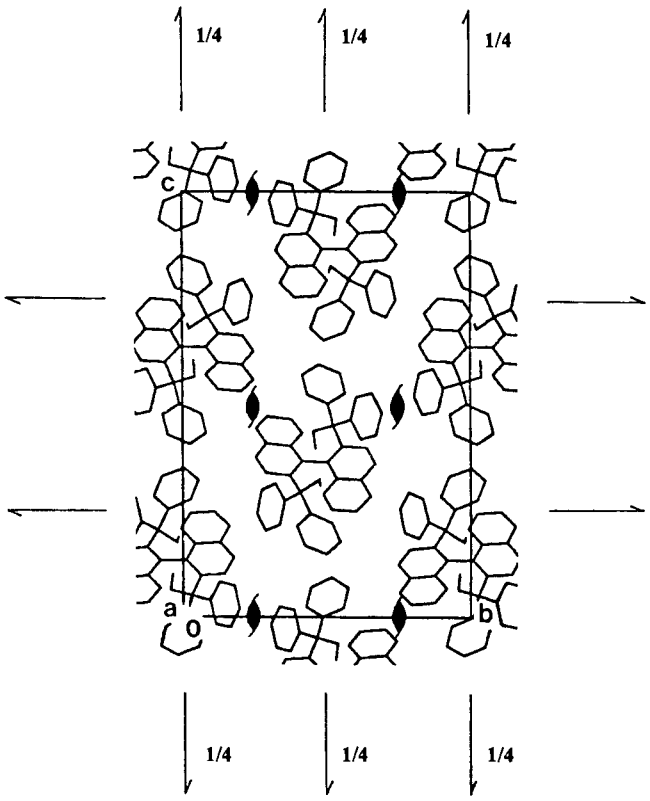

Figure 3. Packing structure of the free host compound **1** (α phase) viewed from the *bc* plane

formation when going from the α to the β phase, i.e. from the free host to the inclusion compound, displaying only slight changes in the torsion angles τ_1 to τ_7, listed in Table 3.

The packing of the pyridine inclusion compound is shown in Figure 4, where the structure is viewed perpendicular to the *bc* face. The host is only hydrogen-bonded to one pyridine guest with O···N = 2.78 Å. This is indicated by dotted lines. The three pyridine molecules lie in channels running parallel to *a**. This β phase has a packing factor of 18.0 Å^3 per non-hydrogen atom and is thus more loosely packed than the α form.

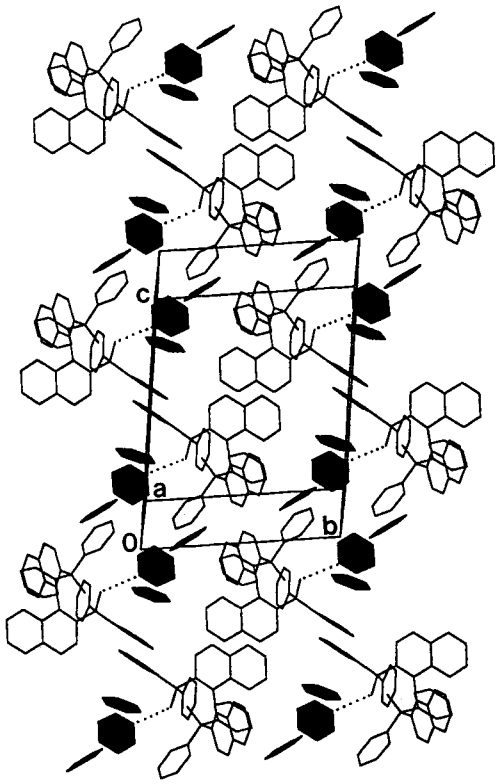

Figure 4. Packing structure of **1** · pyridine (1 : 3) (β phase) viewed from the *bc* plane. The pyridine guests are shaded; the dotted lines indicate hydrogen bonds

4. Thermal Analysis

We have carried out the thermal analysis of the pyridine inclusion compound **1** · pyridine (1 : 3). The results are shown

in Figure 5. It is interesting to note that the Thermal Gravimetry (TG) curve shows two distinct decomposition steps. The first step corresponds to the loss of two pyridine guests (weight loss: found 18.6%, calcd. 18.5%), while the second step shows the loss of the third pyridine (total weight loss: found 27.5%, calcd. 27.5%).

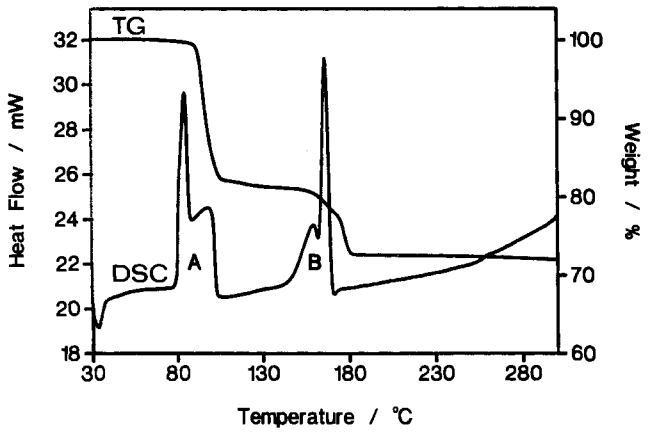

Figure 5. TG and DSC curves of **1** · pyridine (1 : 3)

The corresponding Differential Scanning Calorimetry (DSC) curve shows two complex endotherms which correspond to the two decompositon steps. The first endotherm (A) has an onset temperature T_{on} = 79.4 °C while the second endotherm (B) has T_{on} = 142.5 °C. Both endotherms show two peaks, implying complex mechanisms of decomposition. We surmise that the first decomposition step corresponds to the release of the two pyridine units which are not hydrogen-bonded, while the second step, occuring at the higher temperature, is due to the loss of the third hydrogen-bonded pyridine unit (cf. Figure 4). This is an excellent example of reconciling the results of crystal structure analysis with the thermal decomposition behavior of an inclusion compound.

5. Conclusions

The attachment of bulky diarylhydroxymethyl groups to a conformationally rigid 1,1′-binaphthyl frame provides new crystalline inclusion hosts with novel structures. They form clathrates with a variety of uncharged organic molecules ranging from protic dipolar to rather apolar compounds (74 different examples, Table 1) and show guest selectivity (Table 2). Inclusion formation depends on structural parameters of the host, the type and position of the lateral substituents, and the position of the diarylhydroxymethyl groups with reference to the 1,1′-binaphthyl frame being the most important.

The efficiency of clathrate formation increases in the order **2**→**6**→**7**, i.e. *ortho*-methyl as lateral substituent is more efficient than *meta*-, and *meta*- is more efficient than *para*-methyl. More bulky *tert*-butyl groups in *para*-position of the lateral aryls (**3**) are more efficient than less bulky methyl (**2**) and trifluoromethyl groups (**4**), while methoxy (**5**), is inefficient. With reference to the diarylhydroxymethyl groups, attachment to the 1,1′-binaphthyl frame is more efficient in the 2,2′- than in the 8,8′-positions (cf. **1** vs. **8**).

The X-ray analyses of **1** and its pyridine clathrate manifest a conformationally inflexible host structure with an intramolecular hydrogen bond between the two hydroxy groups, thus making the host to a single hydrogen bond donor.

From the practical point of view[2], these hosts are superior to other compounds in forming clathrates with remarkably high guest ratios (1 : 3 or 1 : 4). Moreover, the 1,1′-binaphthyl frame admits of separation into atropo enantiomers[11,14] which is promising in chiral guest discrimination[7,18].

E. W. is indebted to the *Deutsche Forschungsgemeinschaft* (SFB 334) and the *Fonds der Chemischen Industrie* for their generous support.

Experimental

Melting points: uncorrected, hot-stage apparatus (Reichert, Wien). – IR: SP-1100 (Pye-Unicam). – ^{1}H NMR: WH-90 (Bruker); standard TMS (int.). – ^{13}C NMR: AC-200 (Bruker); standard TMS (int.). – MS: MS-30 and MS-50 (A.E.I., Manchester). – Elemental Analysis: Microanalytical Laboratory of the Institut für Organische Chemie und Biochemie der Universität Bonn. – Chromatography: SiO_2 (0.063–0.1 mm, Merck). – Solvents were dried by standard procedures.

1-Bromo-4-*tert*-butylbenzene[19] and dimethyl 1,1′-binaphthyl-2,2′-dicarboxylate (**9**)[15a] were prepared according to literature procedures.

Dimethyl 1,1′-Binaphthyl-8,8′-dicarboxylate (**10**): To a suspension of 6.0 g (17.5 mmol) of 1,1′-binaphthyl-8,8′-dicarboxylic acid in 500 ml of dry Et_2O was dropped at room temp. a solution of diazomethane in dry Et_2O (freshly prepared from diazald) until the formation of gas ceased. Stirring of the mixture was continued for 1 h. The precipitate was filtered, the solution concentrated under reduced pressure and the residue chromatographed on a SiO_2 column (eluant $CHCl_3$) to yield an oil which crystallized on stirring with a little MeOH (14.3 g, 76%), pale yellow solid, m.p. 154 °C (see ref.[17]). – IR (KBr): = 1735 cm^{-1} (C=O), 1275, 1205 (C–O), 805, 780, 750 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 2.70 (s, 6H, OMe), 7.10–8.10 (m, 12 Ar-H).

$C_{24}H_{18}O_4$ (370.1) Calcd. C 77.82 H 4.90
Found C 77.82 H 5.13
Calcd. 370.1205 Found 370.1197 (MS)

Bis-carbinols **1–8**. – *General Procedure:* To a stirred solution of the respective aryl halide (50 mmol) in dry Et_2O (100 ml) was dropped during 0.5 h at 0 °C and under Ar a solution of *n*BuLi (35 ml, 55 mmol; 1.6 M in *n*-hexane). Stirring was continued for additional 2 h at the same temp., and the corresponding diester (10 mmol) was added in small portions during 0.5 h. The solution was diluted with 50 ml of Et_2O and allowed to warm up to room temp. After stirring for 2 h, the mixture was refluxed for 3 h, then cooled, and the reaction was quenched with a sat. aqueous NH_4Cl solution. Workup depended on the solubility of the product in the organic phase. Specific details for each compound are given below.

2,2′-Bis(hydroxydiphenylmethyl)-1,1′-binaphthyl (**1**): From bromobenzene and **9**. The precipitate which formed on quenching was collected. The organic layer was separated, washed with water, dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to give an oil, which was crystallized from methanol. For further

purification, the combined solids were digested with MeOH and Et_2O to remove starting compounds and byproducts; colorless solid (5.1 g, 82%), m.p. 299–302°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1520, 1510 (Ar), 1065, 1025 (C–O), 835, 760, 710 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 4.80 (s, 2H; OH), 5.80–6.05 (m, 2 Ar-H), 6.20–6.40 (m, 2 Ar-H), 6.80–7.35 (m, 24 Ar-H), 7.50–7.90 (m, 4 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 150.42, 142.39, 140.81, 136.50, 132.00, 131.29, 128.51, 127.83, 126.95, 126.76, 126.40, 126.24, 125.82, 124.59, 124.07, 82.84.

$C_{46}H_{34}O_2$ (618.3) Calcd. C 89.29 H 5.53
Found C 88.89 H 5.54
Calcd. 618.2558 Found 618.2526 (MS)

2,2'-Bis[hydroxybis(4-methylphenyl)methyl]-1,1'-binaphthyl (**2**): From 4-bromotoluene and **9**; workup as described for **1**; colorless solid (5.8 g, 86%), m.p. > 300°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1520 (Ar), 1200, 1070 (C–O), 830, 790 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 2.20 (s, 6H, Me), 2.35 (s, 6H, Me), 4.47 (s, 2H, OH), 5.95 (d, 2 Ar-H), 6.30 – 6.40 (m, 2 Ar-H), 6.68 and 8.82 (AA'BB', J = 8 Hz, 8 Ar-H), 7.05–7.37 (m, 12 Ar-H), 7.65 (d, 2 Ar-H), 7.77 (d, 2 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 146.08, 141.68, 140.21, 137.13, 135.71, 135.52, 132.60, 131.88, 128.83, 128.70, 128.48, 127.94, 127.13, 126.96, 126.62, 124.97, 124.87, 84.10, 21.11, 20.90.

$C_{50}H_{42}O_2$ (674.3) Calcd. C 88.99 H 6.27
Found C 88.61 H 6.32
Calcd. 674.3184 Found 674.3179 (MS)

2,2'-Bis[bis(4-tert-butylphenyl)hydroxymethyl]-1,1'-binaphthyl (**3**): From 1-bromo-4-*tert*-butylbenzene and **9**. The precipitate which formed on quenching was collected, washed with cold MeOH and dried ($MgSO_4$) to yield a colorless solid (6.9 g, 82%), m.p. > 300°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1520 (Ar), 1410 (*t*Bu), 1130 (C–O), 830, 760 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 18H, *t*Bu), 1.29 (s, 18H, *t*Bu), 4.52 (s, 2H, OH), 5.89–5.95 (m, 2 Ar-H), 6.25–6.33 (m, 2 Ar-H), 6.83–7.37 (m, 20 Ar-H), 7.33–7.80 (m, 2 Ar-H), 7.60–7.68 (m, 2 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 150.09, 148.72, 146.28, 141.77, 139.90, 135.56, 132.39, 131.89, 128.71, 128.38, 127.06, 126.56, 125.20, 125.10, 124.90, 124.18, 84.09, 34.51, 34.26, 31.49, 31.41.

$C_{62}H_{66}O_2$ (842.5) Calcd. C 88.32 H 7.89
Found C 88.09 H 7.92
Calcd. 842.5062 Found 842.5031 (MS)

2,2'-Bis{hydroxybis[4-(trifluoromethyl)phenyl]methyl}-1,1'-binaphthyl (**4**): From 1-bromo-4-(trifluoromethyl)benzene and **9**. After quenching, the organic layer was separated, washed with water, dried ($MgSO_4$) and the solvent evaporated. On treatment of the solid residue by stirring for 1 h at room temp. with 100 ml of petroleum ether (40–60°C) the byproducts dissolved. The product was collected by suction filtration, washed twice with petroleum ether (40–60°C), and dried to yield a pale yellow solid (8.5 g, 96%), m.p. > 300°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1630 (Ar), 1340 (C–F), 1200, 1140, 1090 (C–O), 860, 840 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 4.67 (s, 2H, OH), 5.85 (d, 2 Ar-H), 6.32–6.43 (m, 2 Ar-H), 6.98–7.41 (m, 16 Ar-H), 7.60 (d, 4 Ar-H), 7.70 (d, 2 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 152.06, 144.86, 138.53, 135.28, 130.97, 130.55, 128.16, 127.53, 127.14, 126.50, 126.36, 126.24, 125.59, 124.97, 123.98, 123.79, 123.72, 123.60, 122.81, 122.74, 120.21, 81.63.

$C_{62}H_{30}O_2$ Calcd. 890.2054 Found 890.2031 (MS)

2,2'-Bis[hydroxybis(4-methyoxyphenyl)methyl]-1,1'-binaphthyl (**5**): From 4-bromoanisole and **9**. The precipitate which formed on quenching was collected, washed with cold MeOH and dried ($MgSO_4$) to yield a colorless solid (5.2 g, 71%), m.p. > 300°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1630, 1520 (Ar), 1255, 1200, 1055 (C–O), 835 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 3.68 (s, 6H, OMe), 3.78 (s, 6H, OMe), 4.43 (s, 2H, OH), 5.94–6.02 (m, 2 Ar-H), 6.39–6.48 (m, 6 Ar-H), 6.77–6.89 (m, 8 Ar-H), 7.04–7.35 (m, 8 Ar-H), 7.63–7.80 (m, 4 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 158.72, 157.98, 141.78, 141.45, 135.59, 135.44, 132.58, 131.88, 129.94, 128.40, 128.09, 127.11, 126.68, 125.19, 124.92, 113.36, 112.65, 83.76, 55.27, 55.17.

$C_{50}H_{42}O_6$ Calcd. 738.2981 Found 738.2969 (MS)

2,2'-Bis[hydroxybis(3-methylphenyl)methyl]-1,1'-binaphthyl (**6**): From 3-bromotoluene and **9**. After quenching the organic layer was separated, washed with water, dried ($MgSO_4$), and the solvent evaporated. The residue was dissolved in 50 ml of MeOH and the solution cooled. The precipitate was collected, washed with cold MeOH, and dried to yield a colorless solid (5.5 g, 82%), m.p. 132°C. – IR (KBr): $\tilde{\nu} = 3600$ cm^{-1} (OH), 1620, 1510 (Ar), 1260, 1060 (C–O), 780, 755 (Ar). – ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 6H,

Table 4. Crystal data, experimental and refinement parameters

Compound	**1**	**1** · pyridine (1:3)
Molecular formula	$C_{46}H_{34}O_2$	$C_{46}H_{34}O_2 \cdot 3C_5H_5N$
Molecular mass [g mol^{-1}]	618.77	856.08
Crystal data		
Space group	$P2_12_12_1$	$P\bar{1}$
a[Å]	8.080(1)	12.541(3)
b [Å]	16.709(4)	12.643(5)
c [Å]	24.032(5)	15.684(2)
α [°]	90	82.78(2)
β [°]	90	76.05(1)
γ [°]	90	82.76(2)
Z	4	2
V [Å^3]	3245(1)	2382(1)
D_c [g cm^{-3}]	1.27	1.19
μ (MoK_α) [cm^{-1}]	0.71	0.76
F (000)	1304	904
Data collection (293 K)		
Crystal dimensions [mm]	0.16x0.16x0.38	0.41x0.41x0.47
Range scanned θ [°]	1-23	1-23
Range of indices *h,k,l*	0,18;0,8;0,26	±13;±13;0,17
Reflections for lattice parameters no., θ range [°]	24, 16-17	24, 16-17
Instability of standard reflections (%)	1.2	-1.8
Scan mode	ω-2θ	ω-2θ
Scan width [°]	(0.80 + 0.35tanθ)	(0.80 + 35tanθ)
Vertical aperture length [mm]	4	4
Aperture width [mm]	(1.12 + 1.05tanθ)	(1.12 + 1.05tanθ)
Number of reflections collected (unique)	2091	5457
Number of reflections observed with $I_{rel} > 2\sigma I_{rel}$	1434	3958
Final refinement		
Number of parameters	442	605
R	0.043	0.052
wR	0.038	0.059
w	$(\sigma^2 F)^{-1}$	$(\sigma^2 F + 1.83 \cdot 10^{-3} F)^{-1}$
S	2.17	1.68
Max. shift/e.s.d. (host)	0.04	0.60
Max. shift/e.s.d. (guest)	—	0.82
Max. height in difference electron density map [e Å^{-3}]	0.16	0.19
Min. height in difference electron density map [e Å^{-3}]	-0.18	-0.22

Me), 2.28 (s, 6H, Me), 4.45 (s, 2H, OH), 6.01 (d, 2 Ar-H), 6.37–6.45 (m, 2 Ar-H), 6.70 (s, 2 Ar-H), 6.75–6.90 (m, 6 Ar-H), 7.01–7.25 (m, 10 Ar-H), 7.33 (d, 2 Ar-H), 7.78 (d, 2 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 148.87, 142.97, 141.38, 137.60, 136.87, 135.62, 132.69, 131.95, 129.27, 128.61, 128.22, 128.14, 127.42, 127.06, 126.81, 126.65, 126.52, 126.18, 125.36, 124.81, 124.75, 84.26, 21.81, 21.46.

$C_{50}H_{42}O_2$ (674.3) Calcd. C 88.99 H 6.27
Found C 88.40 H 6.33
Calcd. 674.3184 Found 674.3173 (MS)

2,2'-Bis[hydroxybis(2-methylphenyl)methyl]-1,1'-binaphthyl (**7**): From 2-bromotoluene and **9**. Workup as described for **6** yielded a colorless solid (4.7 g, 70%), m.p. 166–168°C. – IR (KBr): $\tilde{\nu}$ = 3600 cm^{-1} (OH), 1615, 1510 (Ar), 1060 (C–O), 755 (Ar.). – ^{1}H NMR ($CDCl_3$): δ = 1.50–2.70 (m, 14H, Me, OH), 6.10–7.90 (m, 28 Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 146.10, 144.74, 142.72, 142.12, 141.87, 140.98, 139.81, 139.37, 139.19, 138.72, 136.31, 134.43, 134.13, 133.60, 133.17, 133.06, 132.71, 132.54, 132.34, 132.18, 131.90, 131.83, 131.49, 130.33, 129.90, 129.33, 129.02, 128.58, 128.25, 127.94, 127.88, 127.51, 127.28, 127.05, 126.76, 126.57, 126.42, 125.80, 125.50, 125.39, 125.26, 125.08, 124.83, 124.63, 85.83, 85.34, 76.45, 23.82, 23.67, 22.10.

$C_{50}H_{42}O_2$ (674.3) Calcd. C 88.99 H 6.27
Found C 88.92 H 6.42
Calcd. 674.3184 Found 674.3155 (MS)

8,8'-Bis(hydroxydiphenylmethyl)-1,1'-binaphthyl (**8**): From bromobenzene and **10**. Workup as described for **1** (digestion with Et_2O) yielded a cream-colored solid (4.9 g, 76%), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 1200, 1050 (C–O), 840, 770 (Ar). – ^{1}H NMR ([D$_6$]DMSO): δ = 5.75–5.80 (m, 2 Ar-H), 6.05–6.12 (m, 2 Ar-H), 6.80–6.90 (m, 10 Ar-H), 7.10–7.20 (m, 10 Ar-H), 7.21–7.30 (m, 4 Ar-H), 7.46–7.50 (m, 2 Ar-H), 7.80–7.85 (m, 2 Ar-H), 8.00 (s, 2H, OH). – ^{13}C NMR ([D$_6$]DMSO): δ = 154.75, 145.77, 142.69, 140.66, 135.82, 133.19, 130.85, 130.12, 128.19, 127.28, 127.16, 126.92, 126.34, 126.30, 122.47, 122.34, 84.58.

$C_{46}H_{34}O_2$ (618.3) Calcd. C 89.29 H 5.53
Found C 88.58 H 5.72
Calcd. 618.2558 Found 618.2546 (MS)

Crystalline Inclusion Compounds: The corresponding host compound was dissolved by heating in a minimum amount of the respective guest solvent. The solution was placed into a hot oil bath to prevent it from rapid cooling and to ensure crystallization of the inclusion compound. After storage for 12 h at 20°C, the crystals which formed were collected by suction filtration and dried (1 h, 15 Torr, room temp.). The host-to-guest stoichiometric ratios were determined by ^{1}H-NMR integration. Data for each compound are given in Table 1.

X-Ray Crystal Structures of **1** *and* **1** · pyridine (1:3). For both structures, unit cell parameters and space group assignments were first obtained photographically, and later by least squares analysis of 24 reflections measured on an Enraf-Nonius CAD4 diffractometer in the range $16 < \Theta < 17°$. Intensity data were collected on the diffractometer at 293 K by using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å) and the ω-2Θ mode. During each data collection three reference reflections were monitored periodically to check crystal stability. The data were corrected for Lorentz and polarization effects but not for absorption. Both structures were solved by direct methods by using SHELX-86[20] and refined by full matrix least squares by using SHELX-76[21]. Refinement proceeded in parallel for both structures. Non-hydrogen atoms were refined anisotropically, and the aromatic hydrogen atoms were subjected to constrained refinement. The hydroxy hydrogens were located in Fourier maps and allowed to refine independently. When they were involved in hydrogen bonding, they were constrained to fixed distances from their parent oxygens according to a function of OH versus O···O distance[22]. Crystal data and experimental parameters are given in Table 4. The fractional atomic coordinates and thermal parameters for the non-hydrogen atoms are listed in Tables 5 and 6. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe,

Table 5. Fractional atomic coordinates (·10^4) and thermal parameters (Å^2·10^3) with e.s.d.'s in parentheses for **1**

Atom	x/a	y/b	z/c	Uiso(*)/Uequiv
O(1)	1751(6)	9580(3)	4361(2)	39(2)
H(1)	1394(76)	9638(39)	3978(10)	43(24)*
O(2)	1227(7)	9788(3)	3236(2)	39(2)
H(2)	260(82)	9831(42)	3114(27)	33(25)*
C(1)	5722(9)	10409(4)	3261(3)	31(3)
C(2)	6700(9)	9923(5)	2907(3)	34(3)
C(3)	7799(10)	10252(5)	2542(3)	42(3)
C(4)	8011(10)	11079(6)	2507(4)	52(4)
C(5)	7128(10)	11578(5)	2849(3)	46(3)
C(6)	5973(9)	11252(5)	3231(3)	35(3)
C(7)	5097(10)	11744(5)	3599(3)	42(4)
C(8)	4022(10)	11421(4)	3980(3)	40(4)
C(9)	3731(9)	10598(5)	4013(3)	32(3)
C(10)	2597(9)	10305(5)	4494(3)	39(3)
C(11)	3675(10)	10118(5)	5007(3)	42(3)
C(12)	3684(11)	9370(5)	5224(4)	57(4)
C(13)	4671(13)	9196(7)	5683(4)	75(5)
C(14)	5628(13)	9780(7)	5930(4)	86(5)
C(15)	5601(13)	10528(7)	5713(4)	90(5)
C(16)	4655(11)	10700(6)	5252(4)	61(4)
C(17)	1224(9)	10924(4)	4619(3)	37(3)
C(18)	314(10)	11245(5)	4178(4)	58(4)
C(19)	-972(11)	11759(5)	4271(4)	62(4)
C(20)	-1458(12)	11945(5)	4810(4)	63(4)
C(21)	-585(12)	11625(5)	5247(4)	64(4)
C(22)	734(11)	11106(5)	5162(3)	52(4)
C(23)	4514(10)	10096(4)	3647(3)	27(3)
C(24)	4375(10)	9199(5)	3656(3)	34(3)
C(25)	3269(9)	8759(4)	3341(3)	31(3)
C(26)	2035(9)	9141(4)	2935(3)	37(3)
C(27)	2973(10)	9486(5)	2438(3)	37(3)
C(28)	4104(10)	8991(5)	2154(3)	47(3)
C(29)	4886(11)	9276(6)	1685(4)	62(4)
C(30)	4609(14)	10048(7)	1488(4)	79(5)
C(31)	3506(13)	10527(6)	1780(4)	65(5)
C(32)	2698(11)	10254(5)	2235(4)	48(3)
C(33)	652(10)	8578(4)	2746(3)	37(3)
C(34)	326(10)	8390(5)	2193(3)	43(3)
C(35)	-981(11)	7896(5)	2045(4)	52(4)
C(36)	-1967(11)	7579(5)	2445(5)	63(4)
C(37)	-1657(11)	7745(6)	3001(4)	61(4)
C(38)	-391(10)	8242(5)	3148(4)	50(4)
C(39)	3252(10)	7907(4)	3401(3)	40(3)
C(40)	4279(11)	7528(5)	3763(3)	44(3)
C(41)	5434(10)	7932(5)	4080(3)	38(3)
C(42)	6557(11)	7552(5)	4429(4)	53(4)
C(43)	7727(12)	7960(6)	4707(4)	67(4)
C(44)	7887(10)	8794(6)	4650(3)	56(4)
C(45)	6794(9)	9195(5)	4310(3)	46(3)
C(46)	5534(10)	8784(5)	4023(3)	37(3)

Table 6. Fractional atomic coordinates ($\cdot 10^4$) and thermal parameters ($Å^2 \cdot 10^3$) with e.s.d.'s in parentheses for **1** · pyridine (1 : 3)

Atom	x/a	y/b	z/c	Uiso(*)/Uequiv
N(1G1)	7253(9)	-1601(6)	2718(5)	173(4)
C(1G1)	6281(10)	-1338(10)	2647(8)	223(7)
C(2G1)	5823(10)	-405(16)	2383(11)	267(10)
C(3G1)	6537(15)	342(8)	2182(8)	222(8)
C(4G1)	7578(13)	111(10)	2250(7)	210(7)
C(5G1)	7887(8)	-867(11)	2550(7)	179(5)
N(1G2)	2179(3)	103(3)	2535(2)	77(2)
C(1G2)	2132(4)	-829(4)	3021(3)	98(2)
C(2G2)	1635(5)	-1662(4)	2841(4)	104(3)
C(3G2)	1209(4)	-1538(4)	2131(5)	110(3)
C(4G2)	1258(5)	-580(4)	1614(4)	118(3)
C(5G2)	1754(5)	219(4)	1849(3)	98(2)
N(1G3)	265(10)	1473(5)	9825(5)	169(5)
C(1G3)	-686(8)	1846(9)	10271(6)	156(5)
C(2G3)	-822(7)	2745(9)	10687(4)	146(4)
C(3G3)	99(11)	3220(6)	10678(5)	153(4)
C(4G3)	1062(9)	2843(7)	10229(5)	141(5)
C(5G3)	1192(7)	1993(8)	9803(5)	152(4)
O(1)	4687(2)	2752(2)	2613(1)	54(1)
H(1)	3951(22)	2408(30)	2764(26)	103(13)*
O(2)	2718(2)	1970(2)	3019(1)	50(1)
H(2)	2507(31)	1305(20)	2895(26)	90(13)*
C(1)	1645(2)	4866(2)	2647(2)	44(1)
C(2)	846(3)	5143(3)	3425(2)	53(1)
C(3)	-141(3)	5698(3)	3373(3)	60(2)
C(4)	-407(3)	6042(3)	2555(3)	67(2)
C(5)	337(3)	5805(3)	1795(3)	63(2)
C(6)	1374(3)	5228(2)	1826(2)	49(1)
C(7)	2169(3)	4982(3)	1052(2)	57(1)
C(8)	3151(3)	4428(3)	1102(2)	52(1)
C(9)	3444(2)	4056(2)	1914(2)	45(1)
C(10)	4626(2)	3502(2)	1864(2)	45(1)
C(11)	5426(2)	4331(3)	1849(2)	47(1)
C(12)	6253(3)	4089(3)	2307(2)	62(2)
C(13)	7001(3)	4823(3)	2267(3)	79(2)
C(14)	6937(3)	5794(3)	1773(3)	75(2)
C(15)	6115(3)	6046(3)	1324(3)	67(2)
C(16)	5367(3)	5317(3)	1364(2)	59(1)
C(17)	5004(3)	2874(2)	1048(2)	51(1)
C(18)	4374(3)	2084(3)	948(3)	69(2)
C(19)	4694(4)	1470(3)	245(3)	81(2)
C(20)	5658(4)	1618(3)	-369(3)	85(2)
C(21)	6293(4)	2390(3)	-287(3)	81(2)
C(22)	5966(3)	3013(3)	416(2)	64(2)
C(23)	2683(2)	4264(2)	2692(2)	41(1)
C(24)	2897(2)	4013(2)	3599(2)	41(1)
C(25)	2617(2)	3104(2)	4161(2)	43(1)
C(26)	2110(2)	2178(2)	3893(2)	44(1)
C(27)	900(2)	2518(2)	3893(2)	44(1)
C(28)	153(3)	2851(3)	4653(2)	53(1)
C(29)	-936(3)	3171(3)	4650(2)	59(1)
C(30)	-1307(3)	3191(3)	3896(3)	62(2)
C(31)	-585(3)	2874(3)	3140(2)	60(2)
C(32)	504(3)	2552(3)	3137(2)	52(1)
C(33)	2270(3)	1129(2)	4484(2)	49(1)
C(34)	1414(3)	580(3)	4992(2)	62(2)
C(35)	1625(4)	-381(3)	5475(3)	82(2)
C(36)	2685(4)	-825(3)	5452(3)	84(2)
C(37)	3551(4)	-296(3)	4942(3)	81(2)
C(38)	3346(3)	666(3)	4469(3)	65(2)
C(39)	2736(2)	3031(3)	5044(2)	50(1)
C(40)	3131(3)	3834(3)	5352(2)	56(2)
C(41)	3432(2)	4763(3)	4803(2)	51(1)
C(42)	3845(3)	5603(3)	5108(3)	62(2)
C(43)	4111(3)	6505(3)	4566(3)	70(2)
C(44)	3983(3)	6621(3)	3702(3)	70(2)
C(45)	3596(3)	5813(3)	3382(3)	58(1)
C(46)	3309(2)	4866(2)	3923(2)	48(1)

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[387/92]