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Design of New Host Compounds, 1,3-diphenyl-cyclohexane-1,3-diol, 1,4-, 1,3- and 1,2-bis(hydroxydiphenylmethyl)cyclohexanes, and 1,2-bis(hydroxydiphenylmethyl)cyclopropane

Fumio Toda[a]; Yuichi Fujii[a]; Zofia Stein[b]; Israel Goldberg[b]; Ikuko Miyahara[c]; Ken Hirotsu[c]
[a] Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime, Japan [b] School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, Israel [c] Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, Japan

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Design of New Host Compounds, 1,3-diphenylcyclohexane-1,3-diol, 1,4-, 1,3- and 1,2-bis(hydroxydiphenylmethyl)cyclohexanes, and 1,2-bis(hydroxydiphenylmethyl)cyclopropane

FUMIO TODA[a,*], YUICHI FUJII[a], ZOFIA STEIN[b], ISRAEL GOLDBERG[b], IKUKO MIYAHARA[c] and KEN HIROTSU[c,*]

[a]*Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790, Japan;* [b]*School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Ramat-Aviv, Israel;* [c]*Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan*

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The title host compounds were designed. The *cis*-1,3-diphenylcyclohexane-1,3-diol, its 2-methyl derivative, as well as the *cis*- and *trans*-isomers of 1,4- and 1,3-bis(hydroxydiphenylmethyl)cyclohexanes showed high inclusion ability for guest compounds. However, while the *trans*-1,2-bis(hydroxydiphenylmethyl)-cyclopropane showed also a good inclusion ability, *cis*-1,2-bis(hydroxydiphenylmethyl)cyclohexane showed none. In order to evaluate the structural features which control the inclusion behavior of the newly designed host compounds, molecular and crystal structures of inclusion complexes of *trans*-1,4-bis(hydroxydiphenylmethyl)cyclohexane with acetone and with MeOH, and of *cis*-1,3-diphenylcyclohexane-1,3-diol with EtOH were determined.

INTRODUCTION

Previously we reported that *cis*-1,4-diphenylcyclohexane-1,4-diol (**1**) is a very good host compound and readily yields inclusion complexes with a variety of guest species. However, its *trans*-isomer (**2**) is not, it forms a compact hydrogen-bonded network structure without incorporation of guest molecules into the crystalline lattice.[1] In order to clarify the relationship between the molecular shapes of diol host compounds containing the cyclohexane backbone, and their tendency to form inclusion compounds with other components, we designed the title series of potential hosts and studied their inclusion behavior.

RESULTS AND DISCUSSION

Reaction of cyclohexane-1,3-dione with PhLi gave *cis*-1,3-diphenylcyclohexane-1,3-diol in which the two OH groups are substituted at axial positions (**3**). By a similar reaction, *cis*-2-me

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*Corresponding author.

thyl-1,3-diphenylcyclohexane-1,3-diol (**4**) was derived form 2-methylcyclohexane-1,3-dione. *trans*-Isomers of **3** and **4** which should have one axial phenyl group and, therefore, a serious 1,3-interaction between Ph and OH groups, could not be prepared. By a Grignard reaction of the corresponding dimethyl cyclohexanedioate with PhMgBr, *cis*-(**5**) and *trans*-1,4-bis(hydroxydiphenylmethyl)cyclohexane (**6**), *cis*-(**7**) and *rac-trans*-1,3-bis(hydroxydiphenylmethyl)cyclohexane (**8**), and *cis*-1,2-bis(hydroxydiphenylmethyl)-cyclohexane (**9**) were prepared. The *trans*-isomer of **9** was not obtained. Nevertheless, *trans*-1,2-bis(hydroxydiphenylmethyl)cyclopropane (**10**) was obtained by a Grignard reaction of dimethyl 1,2-cyclopropanedioate with PhMgBr. The host compounds **3**–**9** are all colorless, crystalline materials.

Of these new hosts, **3**–**10**, all except **9** showed good inclusion ability for guest compounds and their inclusion tendencies for some typical guest compounds; their inclusion affinities for some typical guest compounds are shown in Table I. The corresponding inclusion complexes were prepared by recrystallization of the hosts from liquid guests. Most of the inclusion compounds which formed did not show sharp melting points. Single crystals of only three adducts were found for a detailed crystallographic analysis.

X-ray crystal structure analysis of a 1:1 inclusion compound of **3** and EtOH showed that two molecules of host **3** and two molecules of EtOH form a cyclic structure through hydrogen bond association around the crystallographic centers of inversion. The intermolecular organization in the crystal is illustrated in Figure 1. The tetrameric cluster of H-bonded species is also shown schematically in Figure 2. The cyclic pattern is similar to that observed in the 1:2 inclusion compound of *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (**11**) and MeOH (Figure. 3).[2] In the present structure, however, intramolecular hydrogen bonding occurs in addition to the intermolecular one, which adds to the rigidity of the host framework. This is not so in the inclusion compounds formed by the analogous 1,4-host derivatives (**1**) as the two hydroxyl groups in **1** are too distant to hydrogen bond to one another.[1] The parameters of hydrogen bonding in this structure are as follows (atom labeling scheme is shown in Figure 4): O---O bond lengths for O(1)-H(1)---O(5), O(5)-H(5)---O(21) and O(21)-H(21)---O(1) are 2.685(3), 2.749(5) and 2.734(5)Å, respectively, and bond angles for ∠O(1)-H(1)---O(5) and ∠O(5)-H(21)---O(21) are 148.7° and 171.7°, respectively.

It is interesting to note that the crystalline arrangement of **3**·EtOH is quite different from that of the inclusion compound of a similar host 2,6-dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol (**12**). The latter tends to form lattice inclusion compounds of the helical tubulate type with a wide variety of differently functionalized guest entities.[3] It is anticipated, however, that inclusion complexes of host **4** would be structurally similar to that of **3** described above, as the two hosts have the same spatial disposition of the H-bonding sites.

X-ray crystal structure analysis of **6**·MeOH showed that **6** has a crystallographic C_i symmetry with C4-O1 bond antiparallel to C1-H bond (O1-C4-C1-C2=58.5(3)°), and two OH groups of **6** are hydrogen bonded to two MeOH oxygens with the distance and angle of O1---O2=2.965(3)Å and ∠O1-H---O2=162° (Figure 5a). The crystal structure of **6**·MeOH is shown in Figure 6. The host molecules stack around the two-fold axes parallel to the *b*-axis to make the inclusion column. Each guest molecule is linearly arranged on the two-fold axis, going through the center of the column and is hydrogen bonded by two OH groups of the two host molecules related by the two-fold axis, although hydrogen of the MeOH does not participate in the hydrogen bonding.

X-ray crystal structure of **6** · 2acetone showed that the molecular conformation (O1-C4-C1-C2=64.8(2)°) and the hydrogen bonding interactions between the host and the guest (O1---

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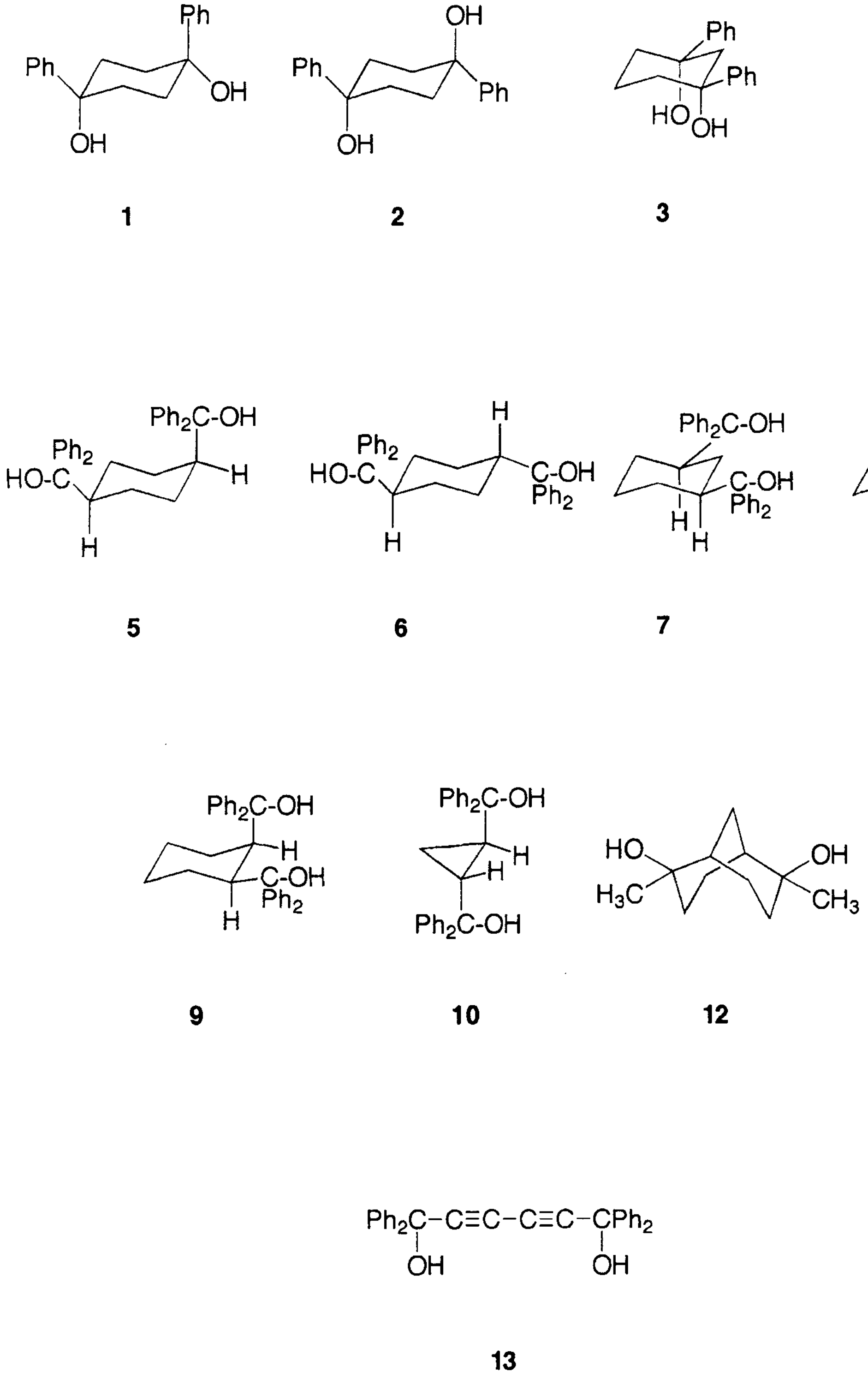
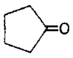


SCHEME 1

TABLE I Host:guest ratios in the inclusion compounds

Guest	Host							
	3	4	5	6	7	8	9	10
MeOH	1:1	1:1	1:1	1:1	—	1:1	—	—
EtOH	1:1	2:1	1:1	—	—	—	—	—
acetone	—	—	1:1	1:2	—	2:1	—	1:1
	—	—	1:1	1:2	—	1:1	—	1:1
THF	—	2:1	1:1	1:2	1:1	1:1	—	1:1
dioxane	2:1	2:1	1:1	1:1	1:1	1:1	—	1:1
MeCN	—	—	1:2	1:2	1:1	2:1	—	1:1
DMF	1:1	1:1	1:2	1:2	1:1	1:1	—	1:1
DMSO	1:1	1:1	1:1	1:2	1:1	1:2	—	1:1
benzene	—	—	2:1	2:1	—	—	—	—
CCl_4	—	—	1:1	2:1	1:1	1:1	—	1:1

O2=2.855(3)Å and ∠O1-H···O2=158°) are similar to those found in **6** · MeOH complex crystal (Figure 5b), but contrary to expection, the crystal structures of these two inclusion complexes are quite different as shown in Figures 6 and 7. This is due at least in part, to the small space of the inclusion column of **6** · MeOH complex to accommodate the more bulky acetone as the guest,

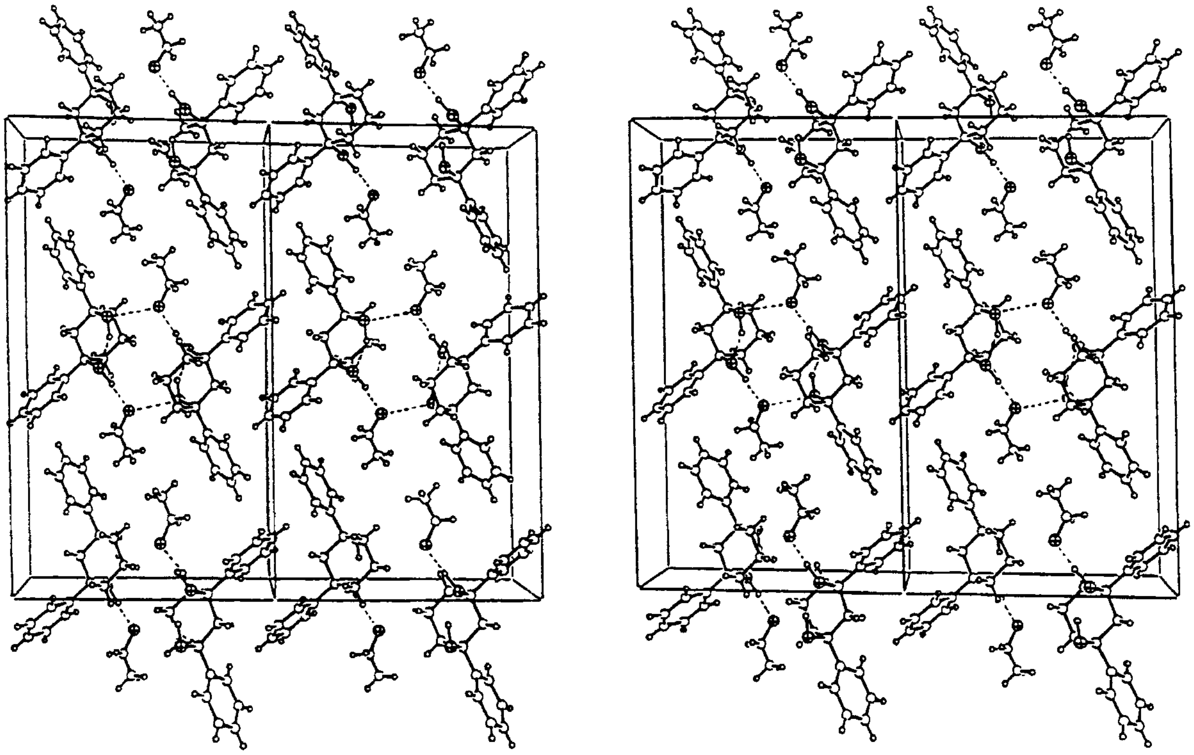


FIGURE 1 The crystal packing of **3**·EtOH stereoviewed down the short *b*-axis. Two unit cells are shown.

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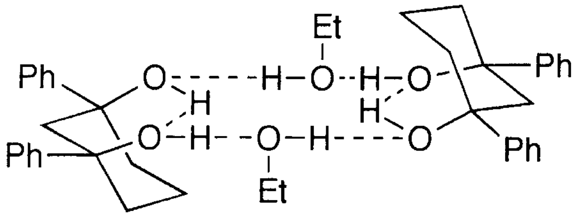

FIGURE 2 Schematic diagram of hydrogen bonding network in **3** · EtOH.

as can be seen the size of the thermal ellipsoid of C18 of the MeOH (Figure 5a). The host molecules lie on the crystallographic center of symmetry and stack along the *a*-axis to make the inclusion column. Interestingly, all the phenyl groups of the host molecules make van der Waals interactions with the guest molecules, in contrast to no participation of the phenyl groups of **6** · MeOH complex in host-guest interactions, reflecting the potential inclusion ability of **6** for various kinds of guest molecules.

In the 1,4-disubstituted derivatives of cyclohexane, the distances between the two OH groups is considerably larger than in **3**, and formation of an intramolecular hydrogen bonding is not feasible. Correspondingly, inclusion compounds of **5** and **6** are expected to have a different structure. Crystallographic analysis of the 1:1 inclusion complex of **6** with MeOH shows that each MeOH guest molecule (acting as proton acceptor) is hydrogen bonded to the OH groups of two different host molecules (Figure 6). The structure of the 1:2 inclusion compound of **6** with acetone is slightly different than that of **6** · MeOH. Here, as shown in Figure 7, two acetone species are bound to two OH groups of a single host entity. The observed structure is similar to structure of the 1:2 inclusion compound of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (**13**) and acetone.[4] The *trans*-1,4-disubstituted cyclohexane moiety in **6** appears to mimic the function of the linear and rigid diacetylene moiety in **13**, leading to the same pattern of intermolecular interaction in the two compounds. A somewhat different intermolecular hydrogen bonding acheme is expected in the 1:1 inclusion complex of the *cis*-isomer **5** with acetone, owing to the different host-guest stoichiometry (Table I).

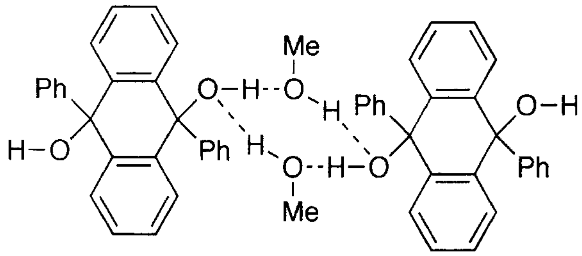

FIGURE 3 Schematic diagram of hydrogen bonding network in **11** · MeOH.

Hosts **7** and **8** exhibit also a good inclusion ability towards various guest compounds, the *trans*-isomer **8** being a more versatile host than the *cis*-isomer **7** (Table I). Among the 1,2-analogs of this series, the *cis*-isomer **9** did not form any inclusion complex with the guest compounds studied. The inclusion behavior of the *trans*-1,2-bis(hydroxydiphenylmethyl)cyclohexane derivative could not be tested in view of our fruitless attempts to synthesize this compound. Successful synthesis of an analogous *rac*-*trans*-1,2-bis(hydroxydiphenylmethyl)cyclopropane (**10**), instead, allowed to study the inclusion features of this *trans*-1,2-disubstituted diol derivative. As shown in Table I, host **10** is an excellent host for a variety of guest components (all good proton acceptors), forming exclusively inclusion complexes with a 1:1 host-guest ratio.

Examination of molecular models, and of the structural data obtained for **3** and **6**, allowed to estimate the distances between carbon atoms bearing the hydroxyl groups in the various hosts. These are 4.6 Å in **5**, 5.8 Å in **6**, 4.4 Å in **7**, 4.1 Å in **8**, 2.9 Å in **9** and 3.7 Å in **10**. When the distance between the two carbons in these host molecules is sufficiently short (e.g., <4 Å), the H-bonding capacity of the two OH groups attached to them could be utilized competitively in an *intra*molecular or an *inter*molecular hydrogen bond formation. Evidently, occurrence of in-

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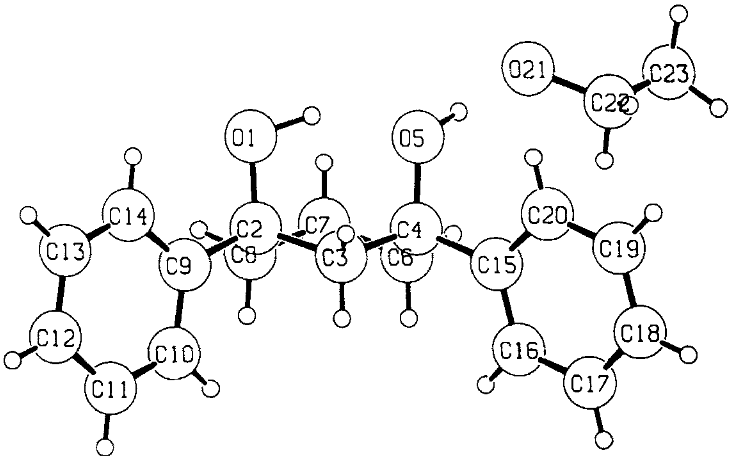

FIGURE 4 Atom labeling scheme of **3** · EtOH.

tramolecular associations is usually associated with a lower (e.g., 1 : 1) host-guest stoichiometry.

EXPERIMENTAL

General Procedure

IR and ^{1}H NMR spectra were measured in Nujol mull and $CDCl_3$, respectively.

Preparation of 3

To a PhLi solution in ether (150 ml) prepared from Li (6.1 g, 0.88 g atom) and PhBr (69.4 g, 0.44 mol), was added a solution of cyclohexane-1,3-dione (10 g, 89 mmol) in THF (50 ml) under N_2 and the mixture was stirred for 35 h at room temperature. The rection mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave 3-hydroxy-3-phenyl-1-cyclohexanone as colorless crystals (5.5 g, 33% yield). IR: 3350 (OH) and 1710 cm^{-1} (C=O). To a PhLi solution in ether (100 ml) prepared from Li (1.5 g, 0.22 g atom) and PhBr (16.5 g, 0.11 mol), was added a solution of 3-hydroxy-3-phenyl-1-cyclohexanone (4.7 g, 26 mmol) in THF (20 ml) under N_2 and the mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water and aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave **3** (mp 107–108 °C, 1.5 g, 22% yield). IR: 3520 and 3320 cm^{-1} (OH), ^{1}H NMR δ 1.7–2.4 (8H, m, cyclohexane), 3.7–4.2 (2H, s, OH) and 7.2–7.6 (10H, m, Ph). Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.37; H, 7.78%.

Preparation of 4

To a solution of PhLi in ether (100 ml) prepared from Li (2.4 g, 0.35 g atom) and PhBr (25 g, 0.16 mol), was added a solution of 2-methylcyclohexane-1,3-dione (4.9 g, 49 mmol) under N_2 and the mixture was stirred for 2 h at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water and aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave 2-methyl-3-hydroxy-3-phenyl-1-cyclohexanone as colorless crystals (3.15 g, 39% yield). IR: 3400 (OH) and 1685 cm^{-1} (C = O). To a solution of PhLi in ether (50 ml) prepared from Li (0.82 g,

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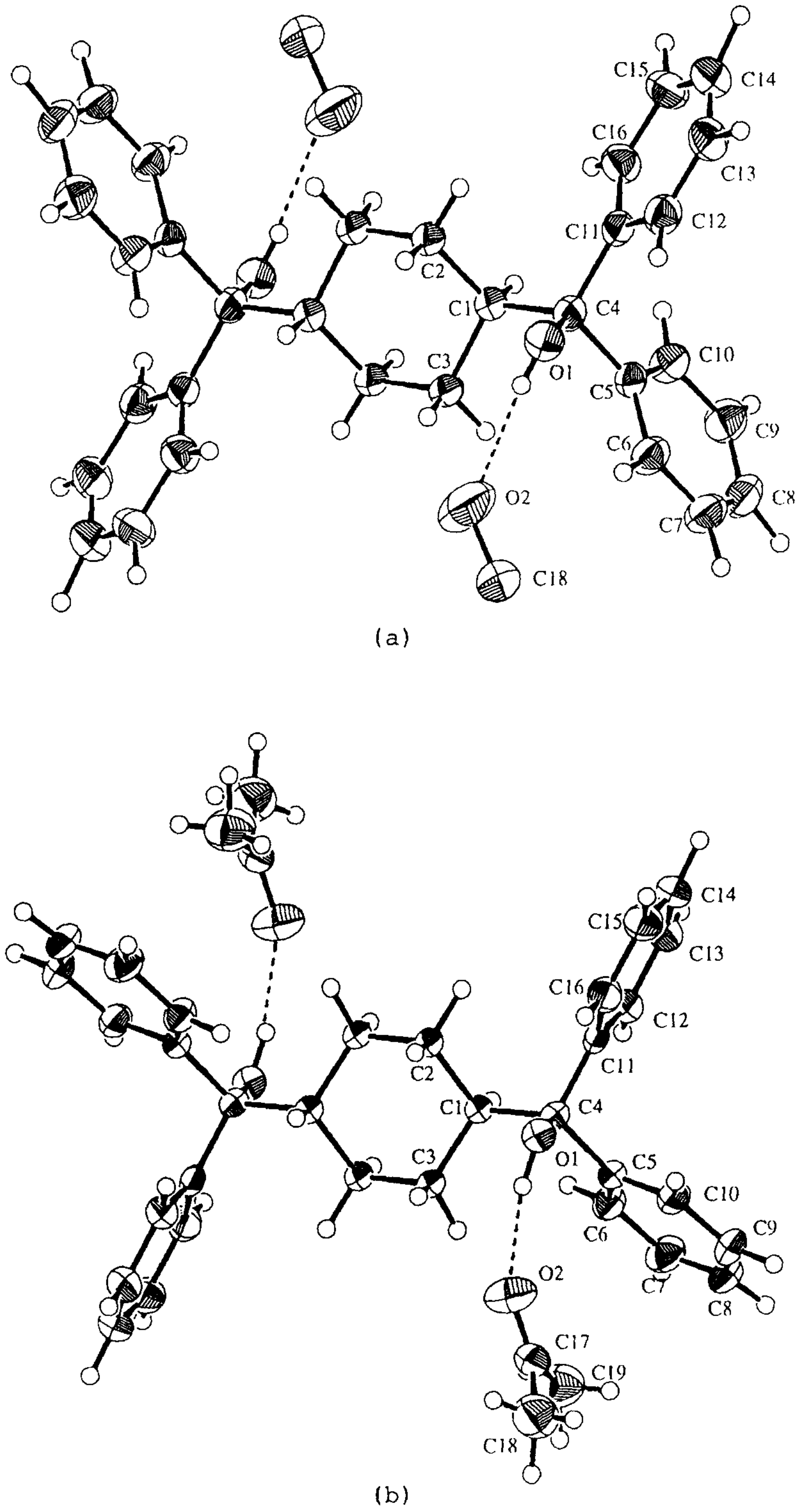

FIGURE 5 Hydrogen bonding and atom labeling scheme in (a) **6**· MeOH (b) **6** · 2acetone.

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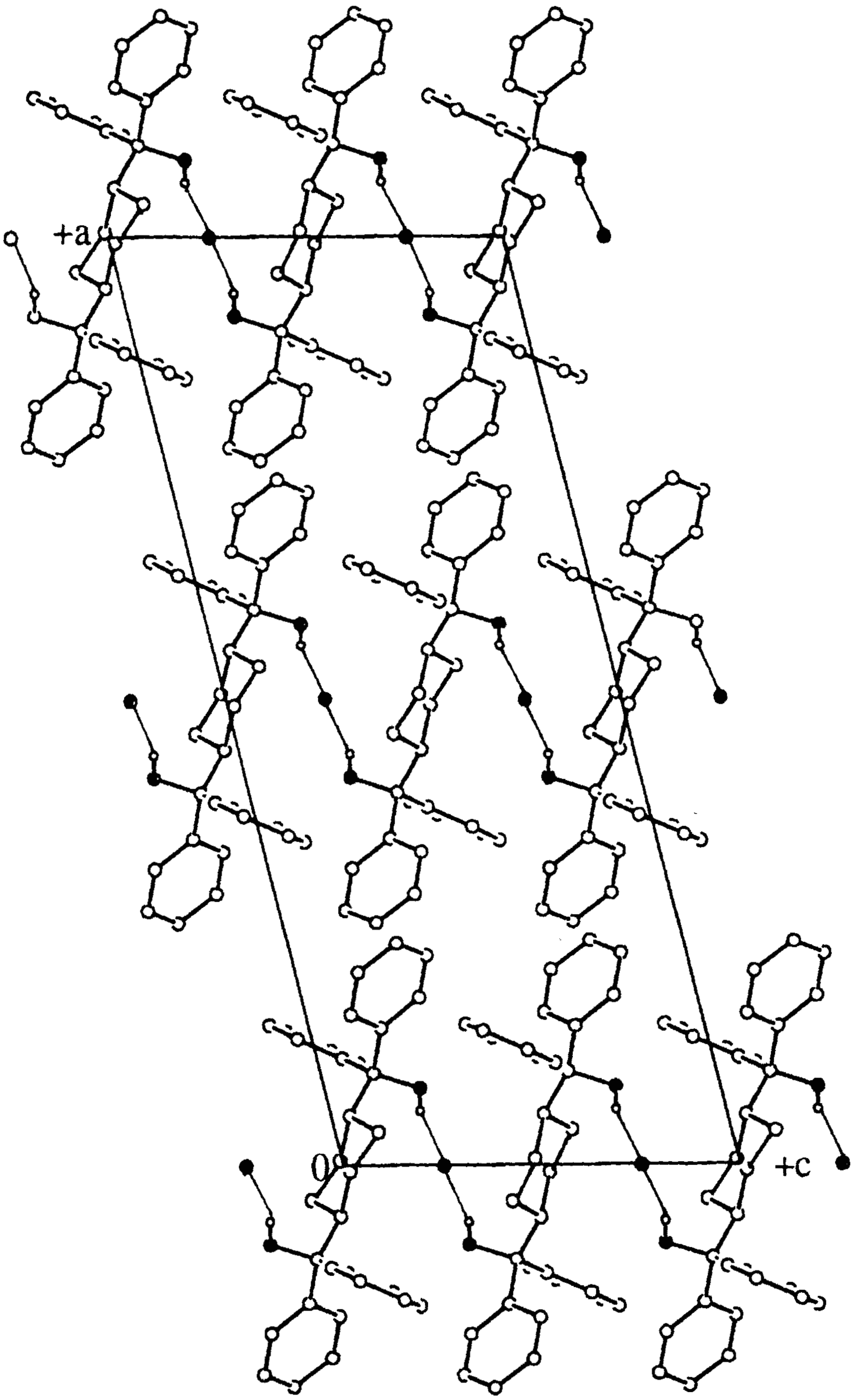

FIGURE 6 Packing diagram of **6** · MeOH.

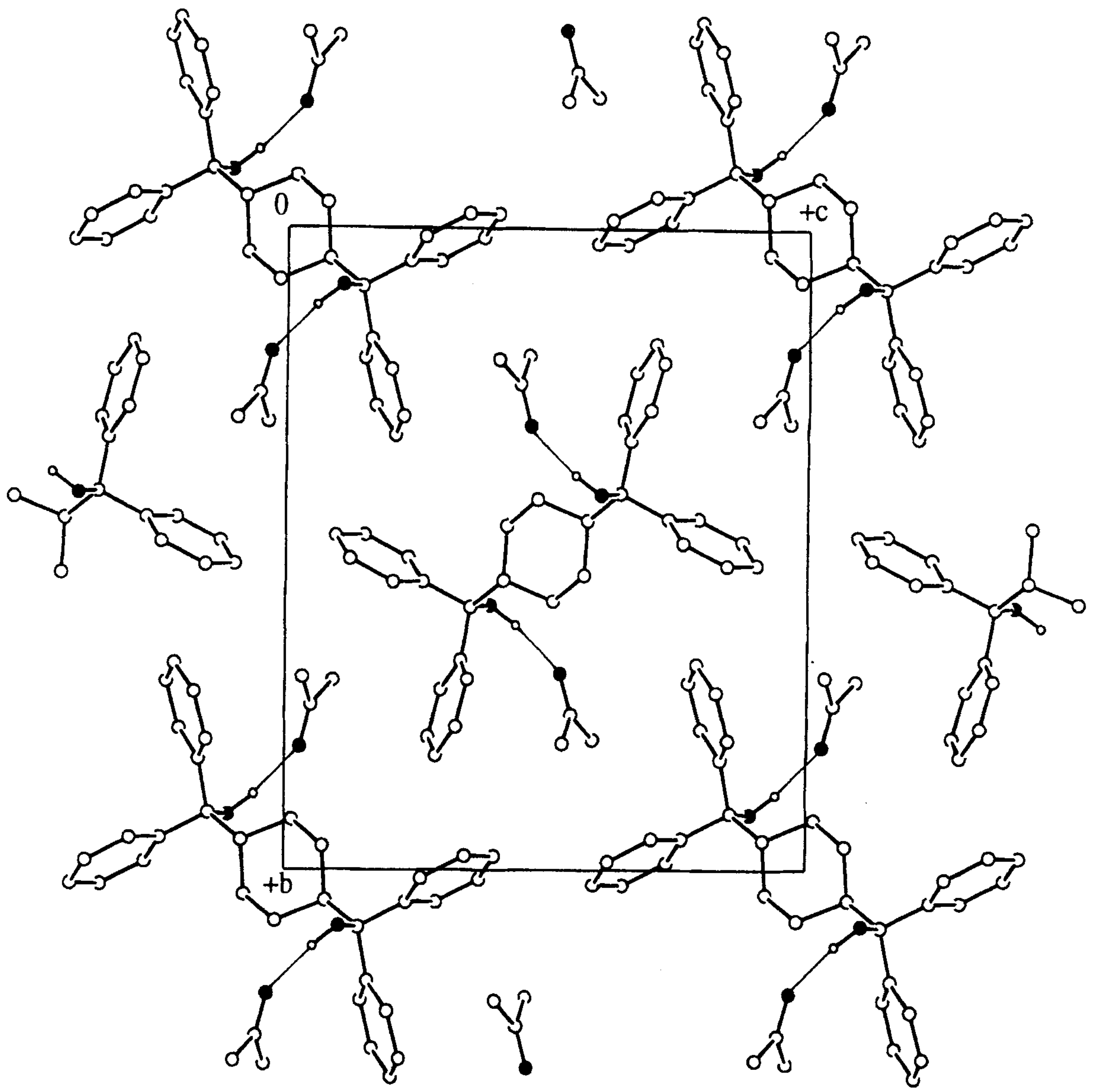

FIGURE 7 Packing diagram of **6** ·2 acetone.

0.12 g atom) and PhBr (9.4 g, 60 mmol) was added 2-methyl-3-hydroxy-3-phenyl-1-cyclohexanone (3 g, 15 mmol) in THF (5 ml) under N_2 and the mixture was stirred for 34 h at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water and aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave **4** as colorless crystals (mp 179–180 °C, 4.9 g, 91% yield). IR: 3600 and 3300 cm^{-1} (OH), ^1H NMR: δ 0.17 (3H, s, Me), 1.63 (2H, s, OH), 1.8–1.9 (3H, m, cyclohexane), 2.2–2.4 (4H, m, cyclohexane) and 7.2–7.6 (10H, m, Ph). Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85%. Found: C, 80.67; H, 7.78%.

Preparation of 5

To a Grignard reagent PhMrBr in ether (30 ml) prepared from Mg (10 g, 0.41 g atom) and PhBr

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(77.5 g, 494 mmol), was added a solution of dimethyl *cis*-1,4-cyclohexanedioate (8.5 g, 42 mmol) in ether (20 ml), and the mixture was stirred overnight at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave **5**. Recrystallization from acetone gave a 1:2 inclusion compound of **5** and acetone as colorless crystals, which upon heating in vacuo gave pure **5** (mp 189–190 °C, 9.3 g, 48% yield). IR: 3580, 3560 and 3520 cm^{-1} (OH), ^1H NMR: δ 1.41–1.46 (4H, m, cyclohexane), 1.56–1.67 (4H, m, cyclohexane), 2.14 (2H, s, OH), 2.70 (2H, bs, cyclohexane) and 7.1–7.5 (20H, m, Ph). Anal. Calcd. $C_{32}H_{32}O_2$: C, 85.68; H, 7.19%. Found: C, 85.45; H, 7.44%.

Preparation of 6

To a PhMgBr reagent in ether (30 ml) prepared from Mg (10 g, 0.41 g atom) and PhBr (77.5 g, 0.5 mol), was added a solution of dimethyl *trans*-1,4-cyclohexanedioate (10 g, 0.05 mol) in ether (20 ml), and the mixture was stirred overnight at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave **6**. Recrystallization from acetone gave a 1:2 inclusion compound of **6** and acetone as colorless crystals, which upon heating in vacuo gave pure **6** (mp 262–263 °C, 17.2 g, 78% yield). IR: 3580 and 3560 cm^{-1} (OH). ^1H NMR: δ 1.17–1.24 (4H, m, cyclohexane), 1.62–1.65 (4H, m, cyclohexane), 2.05 (2H, s, OH), 2.39 (2H, bs, cyclohexane) and 7.15–7.44 (20H, m, Ph). Anal. Calcd. for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19%. Found: C, 85.50; H, 7.34%.

Preparation of 7 and *Rac*-8

To a PhMgBr reagent in ether (30 ml) prepared from Mg (10 g, 0.41 g atom) and PhBr (77.5 g, 0.5 mol), was added a solution of 1:1 mixture of *cis*- and *trans*-dimethyl-1,3-cyclohexanedioate (10 g, 50 mmol) in ether (20 ml), and the mixture was stirred overnight at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave a mixture of **7** and *rac*-**8**. Column chromatography of the mixture on silica gel using hexane-ethyl acetate (95:1) as an eluent gave **7** and *rac*-**8** in pure state. **7** (mp 166–168 °C), IR: 3530 cm^{-1} (OH), ^1H NMR δ 0.94–1.10 (3H, m, cyclohexane), 1.34–1.83 (3H, m, cyclohexane), 1.67–1.83 (2H, m, cyclohexane), 2.02 (2H, s, OH), 2.54–2.62 (2H, m, cyclohexane) and 7.05–7.43 (20H, m, Ph). Anal. Calcd. for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19%. Found. C, 85.77, H, 7.35%. *rac*-**8** (mp 153–155 °C) showed two peaks of (+)- and (−)-enantiomer at 16.3 and 19.8 min points in HPLC using a column containing an optically active stationary phase CHIRALCEL OD (Daicel Chemical Industries, Ltd.) and hexane-AcOEt as an eluent by an elution speed 0.5 ml/min. IR: 3580 and 3540 cm^{-1} (OH), ^1H NMR δ 1.42–1.68 (8H, m, cyclohexane), 2.11 (2H, s, OH), 3.00–3.09 (2H, m, cyclohexane) and 7.05–7.46 (20H, m, Ph). Anal. Calcd. for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19%. Found: C, 85.77, H, 7.47%.

Preparation of 9

To a PhMgBr reagent in ether (30 ml) prepared from Mg (10 g, 0.41 g atom) and PhBr (77.5 g, 0.5 mol), was added a solution of dimethyl *cis*-1,2-cyclohexanedioate (10 g, 50 mmol) in ether (20 ml) and the mixture was stirred overnight at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from acetone gave **9** (mp 193–196 °C, 3.6 g, 16% yield). IR: 3400 and 3210 cm^{-1} (OH), ^1H NMR δ 1.16–1.19 (8H, m, cyclohexane), 3.12 (2H, s, OH), 3.70–4.80 (2H, m, cyclohexane) and 7.04–7.41 (20H, m, Ph). Anal. Calcd. for $C_{32}H_{32}O_2$: C, 85.68; H, 7.19%. Found: C, 85.91; H, 7.33%.

Preparation of 10

To a PhMgBr reagent in ether (35 ml) prepared from Mg (12.2 g, 0.5 g atom) and PhBr (77.5 g, 0.5 mol), was added a solution of dimethyl *trans*-1,2-cyclopropanedioate (15.8 g 0.1 mol) in ether (20 ml) and the mixture was stirred overnight at room temperature. The reaction mixture was decomposed with ice water containing HCl and extracted with toluene. The toluene solution was washed with water, aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from toluene gave **10** (mp 163–167 °C, 32.5 g, 80% yield). IR: 3540 and 3500 cm^{-1} (OH), ^1H NMR: 0.87–0.92 (2H, m, CH), 1.73–1.78 (2H, m, CH_2), 1.86 (2H, s, OH) and 6.97–7.31 (20H, m, Ph). Anal Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.46%. Found: C, 85.88; H, 6.57%.

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X-Ray Data

Crystal structure determination of **3** · EtOH. The X-ray diffraction measurements were carried out at room temperature (ca. 295K) using MoKα (λ = 0.7107 Å) radiation. Intensity data were collected on an automated CAD4 diffractometer, equipped with a graphite monochrometor, out to 2θ = 50° by the ω-2θ scan mode with a constant scan speed of 2 deg/min. The crystals of this inclusion compound diffract weakly and deteriorate slightly with time. Stability of the analyzed crystal during the experiment was ensured by covering its surface by an epoxy resin. A total of 2535 unique reflections with positive intensities were collected. No corrections for absorption or secondary extinction effects were applied.

Crystal data: 1:1 $C_{18}H_{20}O_2 \cdot C_2H_6O$, formula weight 314.42, monoclinic, space group $P2_1/c$, $a = 13.202(3)$, $b = 5.936(1)$, $c = 23.289(9)$ Å, $\beta = 90.98(3)°$, $V = 1824.8$ Å^3, $Z = 4$, $D_{calc} = 1.145$ g.cm^{-3}, $F(000) = 680$, μ(MoKα) = 0.70 cm^{-1}.

The structure was solved by direct method (SHELXS-86),[5] and refined by fullmatrix least-squares (SHELXL-93),[6] including the positional and anisotropic thermanl parameters of the non-hydrogen atoms. The final refinement, based on F^2, converged at R = 0.072 for 1356 observations having $1 > 2\sigma(I)$. The hydrogen atoms attached to carbon were introduced in calculated positions, the methyls being treated as rigid groups. Those of the hydroxyl groups in the host molecules were located in difference-Fourier maps; the hydroxyl proton of ethanol could not be located. The loosely packed ethyl residue is partly disordered in the structure, affecting the precision of the molecular parameters and giving rise to the somewhat high R value. At convergence, the peaks and troughs of the final difference density map did not exceed 0.17 and −0.22 e.Å^{-3}, respectively.

Crystal structure determination of ***6*** *· MeOH and* ***6*** *· 2acetone*. Intensity data were collected at room temperature (23 °C) on a Rigaku diffractometor with graphite monochromated Cu-Kα radiation and a 12KW rotating anode generator, using ω − 2θ scan technique. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by −2.4% for **6** · MeOH and by −24.7% for **6** · 2acetone. A linear correction factor was applied to the data of **6** · 2acetone to account for this phenomenon. The unit cell parameters were refined by the least-squares method, using 25 carefully centered reflections in the range 58.8 ° 2θ < 59.9 ° for **6** · MeOH and 57.74 ° < 2θ < 59.83 ° for **6** · 2acetone.

Crystal data and some experimental details are summarized in Table II.

The structures were solved by direct methods.[7] and expanded using Fourier techniques.[8] Full matrix least-squares refinements with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen converged to conventional crystallographic

TABLE II Crystal data and selected details of the refinement calculations

	6 · MeOH(1:1)	**6** · acetone(1:2)
Empirical formula	$C_{33}H_{36}O_3$	$C_{38}H_{44}O_4$
Formula weight	480.65	564.76
Space group	C2/c	$P2_1/c$
a(Å)	26.365(2)	6.122(2)
b(Å)	9.335(2)	17.646(2)
c(Å)	11.055(2)	14.766(1)
α(°)	90	90
β(°)	103.88(1)	92.30(1)
γ(°)	90	90
V(Å^3)	2641.3(6)	1593.9(5)
Z	4	2
D_c (g cm^{-3})	1.209	1.177
μ(cm^{-1})	5.92	5.86
F(000)	1032.00	608.00
Crystal size (mm)	1.04×0.42×0.36	0.53×0.32×0.26
2θ range (°)	6.0-113.6	6.0-113.6
h,k,l range	28,10,± 11	6,19,± 16
Unique reflections	1901	2229
Reflections with I>3σ(I)	1609	1813
Parameters	228	278
RI[I>3σ(I)]	0.063	0.056
wR2	0.122	0.078
Largest diff. peak and hole (e Å^{-3})	0.52, −0.38	0.20, −0.40

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discrepancy indexes (R1) of 0.063 and 0.056 for **6** · MeOH and **6** · 2acetone, respectively.[9] Further details of the final refinements are given in Table II.

All final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, tortional angles and observed and calculated structure factors have been deposited.

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