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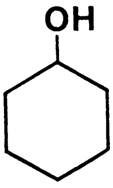
Separation of Cyclohexanol and Cyclohexanone by Complexation with 1,1-Di(p-hydroxyphenyl)cyclohexane and 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol, and Crystallographic Structural Studies of the Complexes with the Former Host Compound

Israel GOLDBERG,*# Zafra STEIN,# Akihiro KAI, and Fumio TODA*
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
#School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Ramat-Aviv, Israel

An efficient separation of cyclohexanol and cyclohexanone by selective complexations with the title host compounds has been achieved. Crystallographic analyses of the corresponding 1:1 complexes with the cyclohexane host derivative show a characteristic structure type which is dominated by continuous arrays of hydrogen bonds

Separation of cyclohexanol (1, bp 161 °C) and cyclohexanone (2, bp 155.6 °C) from their mixture has always been a difficult problem in the chemical industry due to the close boiling points of these two compounds. We have previously reported several successful applications of a new separation procedure of isomeric compounds by selective crystalline complexations with suitable hosts.1-4) More recent findings show that an effective separation of 1 and 2 can also easily be achieved by their complexation with 3 and with 4. We now report on the separation method and on crystallographic structural studies of the complexes: I. 1:1 3+1, and II. 1:1 3+2.



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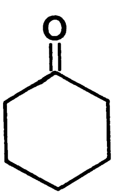

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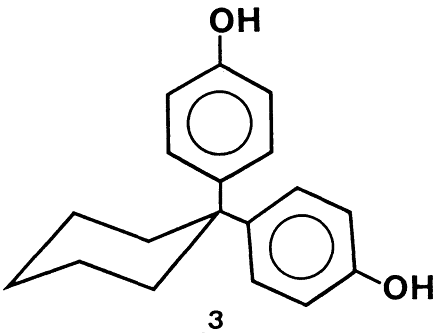

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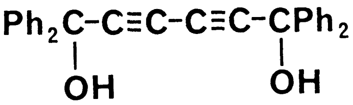

$\underset{\displaystyle OH}{Ph_2C}-C\equiv C-C\equiv C-\underset{\displaystyle OH}{CPh_2}$

4

The separation procedure for cyclohexanol and cyclohexanone by complexation with **3** is characterized by the following examples: When a solution of **3** (8.0 g, 30 mmol) and a 1:1 mixture of **1** and **2** (6.0 g) in ethyl acetate (50 ml) was kept at room temperature for 24 h, a 1:1 complex of **1** and **3** (5.8 g, 53% yield, mp 140-142 °C) was obtained as colorless crystals. Heating of the complex in vacuo gave crude **1** (1.44 g, 48% yield) which consists of 94.71% of **1** and 5.23% of **2**. Distillation of the filtrate left after separation of the complex gave crude **2** (2.5 g, 83% yield) which consists 73.41% of **2**, 23.67% of **1**, and 2.79% of water. Application of a similar procedure to a 0.85:99.15 mixture of **1** and **2** (1.0 g) and 2.7 g (10 mmol) of **3** dissolved in 10 ml of ethyl acetate gave 2.3 g (62% yield) of the complex. The guest mixture obtained from it upon heating in vacuo (0.35 g, 35% yield) contains 99.69% of **2** and 0.31% of **1**. The complex formed in the filtrate (1.05 g) after additional 24 h contains 0.29 g (29% yield) of the guest mixture (94.99% of **2** and 2.56% of **1**). The significant complexation of cyclohexanone with **3**, particularly at high concentrations of the former, is probably due to a lower solubility of this complex in ethyl acetate.

Host **4** was found to form stable complexes with carbonyl compounds.[5)] When a solution of **4** (4.2 g, 10 mmol) and a 1:1 mixture of **1** and **2** (4.0 g) in 30 ml of ethyl ether-petrol ether (1:1) solvent was kept at room temperature for 12 h, a 2:1 complex of **2** and **4** (5.3 g, 85% yield) was obtained as colorless prisms (mp 94-96 °C). Recrystallization of the complex from the same solvent gave pure crystals (4.3 g, 69% yield, mp 96-97 °C), which upon heating in vacuo gave almost pure **2** (1.22 g, 61% yield) containing 99.85% of **2** and 0.15% of **1**. From the remaining filtrate crude **1** (1.82 g, 91% yield) which contains 87.79% of **1** and 12.21% of **2** was obtained by distillation. Further experiment with a 0.85:99.15 mixture of **1** and **2** led to the following results: A solution of **4** (4.2 g, 10 mmol) and 1.0 g of the guest mixture in 10 ml of ethyl ether-petrol ether (1:1) solvent produced 2.52 g (82% yield) of the 2:1 complex of **2** and **4**. Heating of the complex in vacuo gave pure **2** (0.76 g, 77% yield) which does not contain any **1**. Recrystallization of the compound left in the filtrate gave a pure complex (2.11 g), which upon heating in vacuo gave crude **2** (0.11 g, 11% yield) containing 99.64% of **2** and 0.11% of **1**. The contents of the resolved compounds were determined by gas chromatography.

Diffraction data of complexes **I** and **II** were measured at ca. 18 °C on an CAD4 diffractometer equipped with a graphite monochrometor, using MoKα(λ=0.7107 Å) radiation. To avoid possible deterioration, the analyzed crystals were enclosed within a thin glass capillary. The intensities of reflections within $0<2\theta<50^\circ$ were collected by the ω-2θ scan technique with scan range of $0.9+0.3\tan\theta^\circ$. All data were recorded at a constant $2^\circ\ \mathrm{min}^{-1}$ scan rate. Frequent detection of the intensities of standard reflections showed only minor random variations during the measurements. The data sets were not corrected for absorption or secondary extinction effects. The crystal data are:

I. $C_{18}H_{20}O_2 \cdot C_6H_{12}O$ (FW 368.5), monoclinic, space group $P2_1/c$, Z=4, $\underline{a}$=6.226(3), $\underline{b}$=32.218(6), $\underline{c}$=10.810(3) Å, β=103.65(3)°, V=2107.1 $Å^3$, D_c=1.162 g cm^{-3}.

II. $C_{18}H_{20}O \cdot C_6H_{10}O$ (FW 366.5), monoclinic, space group $P2_1/n$, Z=4, $\underline{a}$=6.326(3), $\underline{b}$=30.663(5), $\underline{c}$=10.778(5) Å, β=100.38(3)°, V=2056.4 $Å^3$, D_c=1.184 g cm^{-3}.

The two structures were solved by a combination of direct methods and Fourier techniques (MULTAN80). Their refinements were carried out by full-matrix least-squares (SHELX76), including the positional and anisotropic thermal parameters of all the nonhydrogen atoms. To avoid unreliable distortions of the geometry due to a partially disordered conformation of the guest species, geometric constraints were applied to the guest cyclohexyl rings. Most hydrogens were included in the structure factor computations in calculated positions; those invloved in hydrogen bonds were located directly in difference-Fourier maps, but are not very reliable. The final refinements were based only on observations above the intensity threshould of $3\sigma(I)$. The final difference-Fourier maps showed no indication of incorrectly placed or missing atoms, the highest peak and deepest trough not exceeding 0.4 eÅ^{-3}. At convergence the discrepancy factors are: For example **I** - R=0.091 for 672 reflections above the intensity threshold, goodness-of-fit = 1.20e. For compound **II** - R=0.102 for 851 observations above threshold, g.o.f.=1.44e. The relative high R-values are due to the apparent partial disorder and the low number of significant reflections. The atomic coordinates for the two compounds have been deposited with the Cambridge Crystallographic Data Centre.

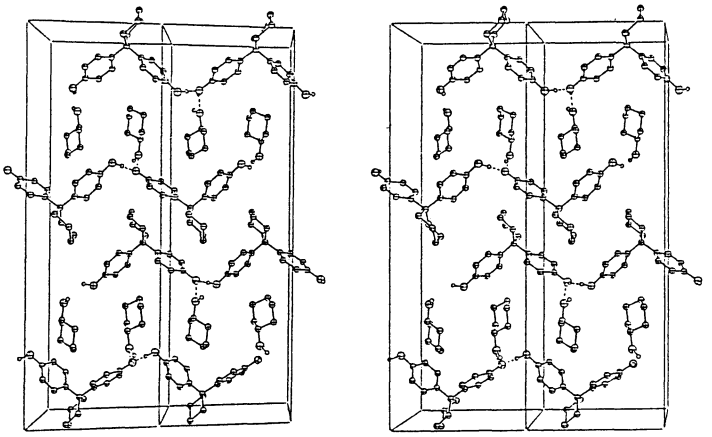

Fig. 1. Stereodrawing of the molecular packing in **I**. Hydrogen bonds are shown as broken lines.

The nearly isomorphous crystal structures of complexes **I** and **II** are shown in Figs. 1 and 2 (stereoviews down the *a*-axis, *c* is horizontal), respectively. In spite of the differences in periodicity and space symmetry, the observed patterns of intermolecular arrangement are very similar to those reported for related complexes of **3** with phenol and cresol derivatives.[4)] Thus, the structure of **I** can be described as composed of two-dimensional cross-linked arrays of H-bonded entities which are characterized by the general pattern host-host-host··· along *c*, and guest-(host-host)-guest-(host-host)··· along *a* (utilizing the dual capacity of a hydroxyl group for H-bonding). The OH···OH distances related to these interactions vary from 2.59(2) to 2.80(2) Å. The arrangement of the H-bonded layers along the *b* axis is stabilized, on the other hand, by weak van der Waals forces. The cyclohexyl fragments (one from the host and one from the guest) located on both sides of each such layer (conveniently fit in between the cyclohexyl groups of adjacent layers.

No major differences occur in the overall crystal packing arrangement when cyclohexanol is replaced by cyclohexanone in the structure. In the structure of **II** the host species form continuous chains of H-bonded moieties as in **I**, but each OH···OH site is further linked via an H-bond only to one guest (the two distinct O···O bonds are within 2.75-2.77 Å). The relative disposition of the molecular units with respect to the a axis, associated with a transformation of the space symmetry from $P2_1/c$ in **I** to $P2_1/n$ in **II**, is now modified to optimize other packing interactions. This is reflected in a marked contraction of the b axis by 1.56 Å, and an improved steric fit between neighboring chains of molecules. Evidently, the more extensively hydrogen bonding pattern in complex **I** makes it energetically more stable than **II**, giving rise to the preferential complexation of **3** with cyclohexanol.

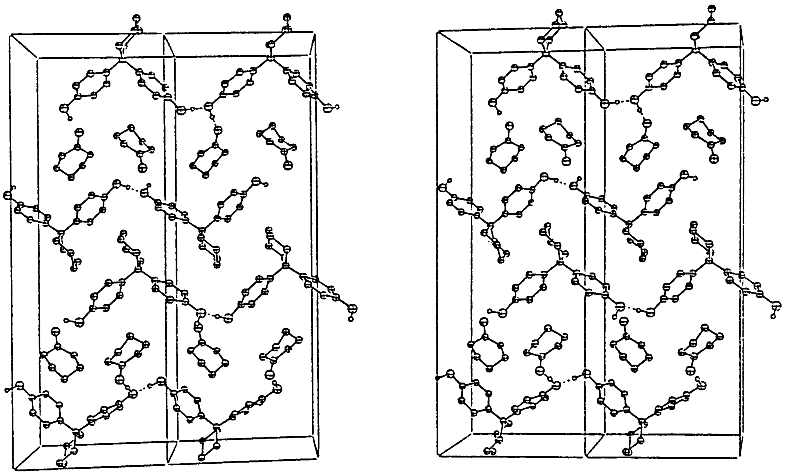

Fig. 2. Stereodrawing of the molecular packing in **II**. Hydrogen bonds are shown as broken lines.

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