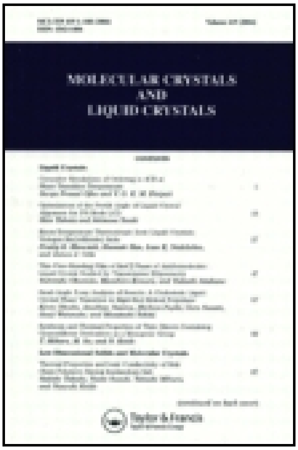

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Molecular Recognition in Inclusion Complexes and its Application to Isolation and Optical Resolution of Materials

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MOLECULAR RECOGNITION IN INCLUSION COMPLEXES AND ITS APPLICATION TO ISOLATION AND OPTICAL RESOLUTION OF MATERIALS

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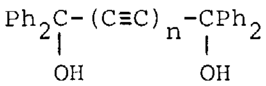
Abstract If a host compound includes only one isomer of a mixture of isomers selectively, it can be used for separation of isomers. This selective inclusion can also be used for isolation of inorganic and organic compounds from aqueous solution. We have designed several new host compounds and studied separation of isomers and isolation of materials from aqueous solution by using host compounds. When an optically active host compound is used, enantioselective inclusion of guest compounds can occur. Optical resolution of compounds according to this idea was also studied.

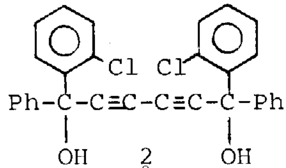
Several new host compounds (**1**-**17**) able to include a wide variety of guest compounds were designed. It was found that not only alcohols (**1**-**4**), phenols (**5**-**8**) and amides (**9**-**15**), but also simple hydrocarbons (**16**, **17**) work as host compound.[1]

The host and guest molecules recognize each other in their inclusion complexes. When the host compound can recognize isomerism of a guest compound, the inclusion phenomenum is useful for isolation of one isomer from a mixture of isomers. When the host compounds include water soluble material but not water, this can be used for isolation of the water



1

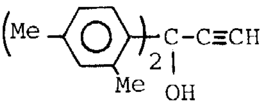
a: n=2; b: n=1; c: n=0



2

a: (-)-form

b: (+)-form



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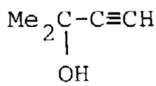

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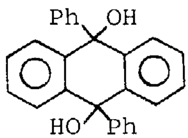

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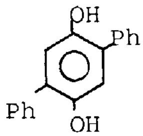

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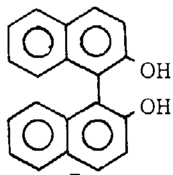

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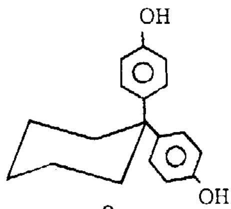
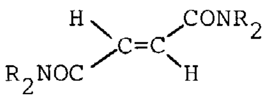


8

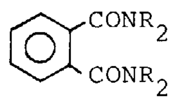
$(iPr)_2NCOCON(iPr)_2$

9

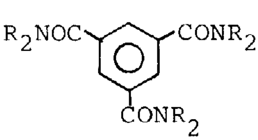


10

R=cyclohexyl



11



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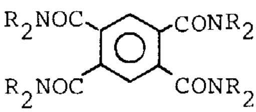
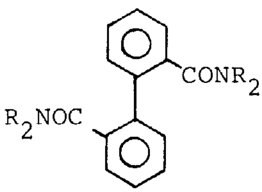


13

R=cyclohexyl

$(R_2NOC)_3CH$

14



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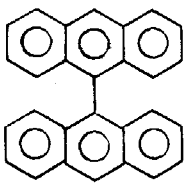

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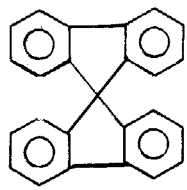

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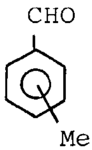

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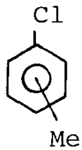

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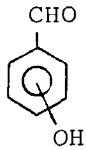

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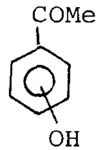

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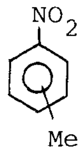
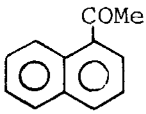
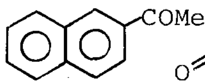


22

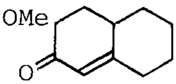
a: ortho; b: para



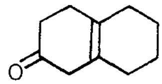
23a



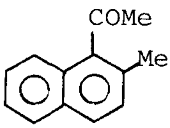
23b



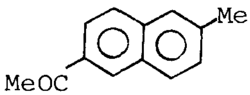
24a



24b



25a



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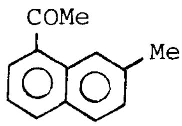
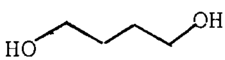
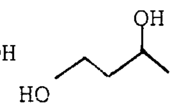


25c



26a



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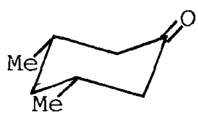
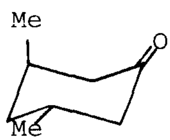


27a



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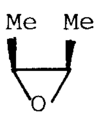

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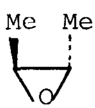
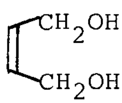
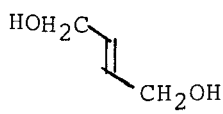


28b



29a



29b

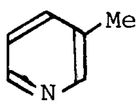
soluble material from aqueous solution. The most interesting recognition in the complex is that of chirality. By using the chiral recognition, optical resolution of compounds was carried out.

1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (1a) is very useful for separation of isomers. For example, when a solution of 1a and a 1:1 mixture of o- (18a) and p-tolualdehyde (18b) in ether-pet. ether (1:1) was kept at room temperature for 12 h, a 1:1 complex of 1a and 18b was formed as colorless crystals. Upon heating in vacuo these gave pure 18b at a 96% yield. From the filtrate left after separation of the complex of 1a and 18b, 95% pure 18a was obtained in 90% yield by distillation.[2] By a similar complexation method, the following separations were achieved easily:[2] 19a:19b, 20a:20b, 21a:21b, 22a:22b, 23a:23b, 24a:24b, 25a:25b:25c, 26a:26b, 27a:27b, 28a:28b, 29a:29b.

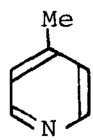
Separation of β- (30a) and γ-picoline (30b) was achieved by complexation with 1a or 1c.[3] Since 1c includes p-xylene but not m-xylene, separation of the two isomers can be done easily.[4] An X-ray crystal structure study of a 2:1 complex of 1c and p-xylene has been done.[4] Interestingly, 1,1,2,2-tetraphenylethane also includes p-xylene selectively and forms a 2:1 complex of the host and p-xylene.[4] X-Ray crystal structure analysis of the complex has also been done.[4] Since 1c includes various organic compounds, 1c could be used for separation of various isomers.[4]

The amide host compound 10 is effective for separation of isomeric alcohols such as 29a and 29b, and m- and p-cresol.[5] The effective molecular recognition in the complex was studied by X-ray structure analysis of a 1:2 complex of 10 and m-cresol.[5] The another amide host, compound 15, includes a wide variety of alcohols. It can be used for separation of various isomeric alcohols[6]. The structure of a 1:1 complex of 15 and phenol was studied by X-ray crystallography.[6]

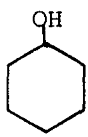
It was found that 8 is very effective for separation of cyclohexanol (31) and cyclohexanone (32) from their mixture.[7] The separation has been a difficult problem in the chemical industry due to close boiling points in these two compounds. Although 8 forms complex both with 31 and 32, the complex with the former is more easily formed. Thus 31 and 32 can be separated by the complexation with 8.[7] X-Ray crystal structures of both the complexes of 8 with 31 and with 32 have been reported.[7]



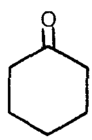
30a



30b

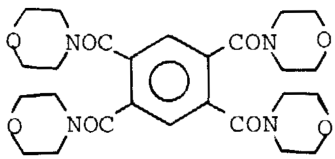


31



32

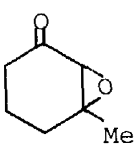
Extraction of ethanol from aqueous solution was carried out by complexation with 10.[8,9] Extraction of methanol was also achieved by complexation with 14[10] and 7.[11] Crystal structures of all the complexes obtained were studied by X-ray crystallography.[8-11] Interestingly, the amide host 33 predominantly includes water[12]. Extraction of sodium hydroxide, potassium hydroxide, amines, and ammonia from aqueous solution can be achieved by complex formation with 7.[13]



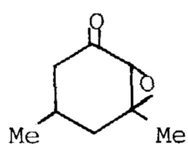
33

When an optically active host compound such as 2 is used for complexation with a guest compound, the guest compound is effectively resolved. For example, epoxycyclohexanones (34-36)[14] and bicyclic lactones (37-40)[15] were easily resolved by complexation with 2a or 2b to give optically pure enantiomers.

Optically active 7 is also useful for optical resolution of various organic compunds. For example, sulfoxides[16-18] and selenoxides[19] were easily resolved by complexation with optically active 7.



34



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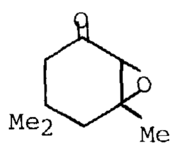

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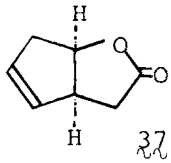

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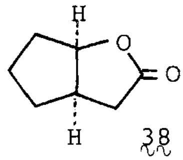
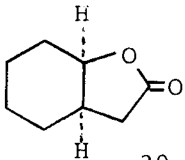


38



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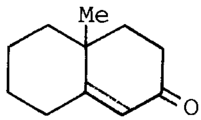

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