Preparation and X-ray Structures of *trans*-5,6-Diaryl-5,6-dihydro-1,10-phenanthroline-5,6-diols: Formation of Supramolecular Rod by Hydrogen Bonds

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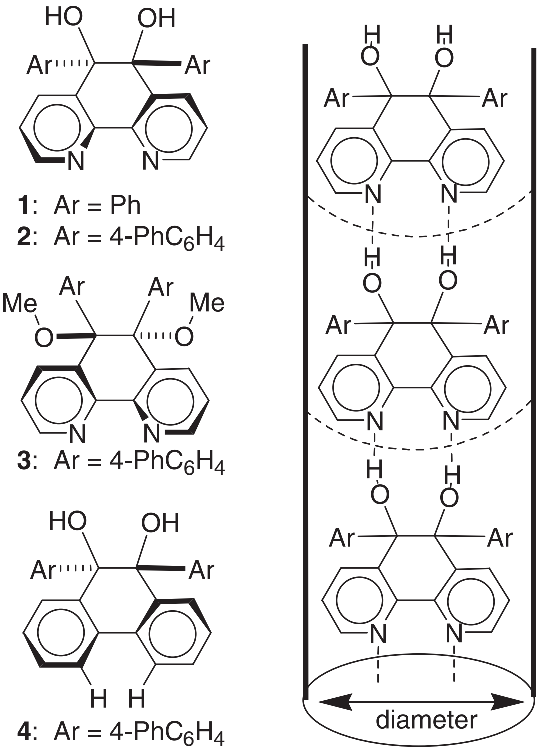
A series of X-ray analyses on the newly prepared title molecules have revealed that the one-dimensional rod-like structures are commonly present in the crystals of *trans*-dihydrophenanthrolinediols. The architecture is of interest from the viewpoint of supramolecular chirality because homochiral diol molecules with the same sense of helicity are connected in a head-to-tail fashion by a pair of N···H–O hydrogen bonds.

The hydrogen bond is one of the most important and effective tools to construct supramolecular architectures[1] as has been well established in the field of supramolecular polymers.[2] Infinite networks by hydrogen bonds are more frequently observed in the designed crystal of organic solids.[3] We have been interested in constructing one-dimensional infinite rod-like structures with a well-defined diameter from the viewpoint of possible application to molecular wire[4] in terms of molecular devices.[5] We have designed and prepared here the title diols **1** and **2** as promising candidates to form the desired network by hydrogen bonds (Scheme 1). Methyl ether **3** and phenanthrene derivative **4** are also included in this study as references, in which the hydrogen-bond donating groups or accepting sites are missing, respectively.

Double addition of PhMgBr to 1,10-phenanthroline-5,6-quinone[6] in refluxing THF gave phenyl-diol **1**[7] as colorless crystals in 51% yield. No cis isomer was formed, which can be accounted for by steric effects.[8] By using 4-PhC_6H_4MgBr, biphenyl-diol **2**[7] was obtained in 30% yield. Optical resolution of these racemic diols were successfully conducted by using chiral HPLC (OA-2000 column, recycled 2–3 times, CH_2Cl_2 elution). Each of the enantiomers obtained as the first fraction {(+)-**1** ($[\alpha]^D = +340°$, $c = 0.06$); (+)-**2** ($[\alpha]^D = +424°$, $c = 0.26$)} was later proven to have R,R configuration for C5 and C6 asymmetric centers.[9]

From biphenyl-diol (*R*,*R*)-(+)-**2** was obtained biphenyl-methyl ether (*R*,*R*)-(−)-**3**[7] ($[\alpha]^D = -60.5°$, $c = 0.21$) in 67% yield by successive treatment with NaH then MeI in THF at room temperature. Another reference compound, phenanthrene-type diol **4**,[7] was prepared in 66% yield by the reaction of phenanthrenequinone with 4-PhC_6H_4Li in THF at −78 °C.

Optically pure phenyl-diol (*R*,*R*)-(+)-**1** crystallizes in a chiral space group of $P2_12_12$ ($Z = 4$),[10] with two crystallographically independent molecules on the 2-fold axis. One-dimensional rod-like networks are formed along the *c* axis as designed (Figure 1), with a diameter of about 12 Å. In this supramolecular architecture, each molecule of (*R*,*R*)-(+)-**1** is connected with two neighbors in a head-to-tail fashion by a pair of hydrogen bonds of N···H–O [d(N···H) = 2.0, 2.0 Å, d(N···O) = 2.79, 3.09 Å, θ(N–H–O) = 155, 173°]. The hydroxy groups, which are involved in such intermolecular connection, occupy the pseudo equatorial positions, so that the dihydrophenanthroline skeleton adopts P helicity (Scheme 2). This is the successful transmission of point chirality to mobile helicity.[11]



Scheme 1.

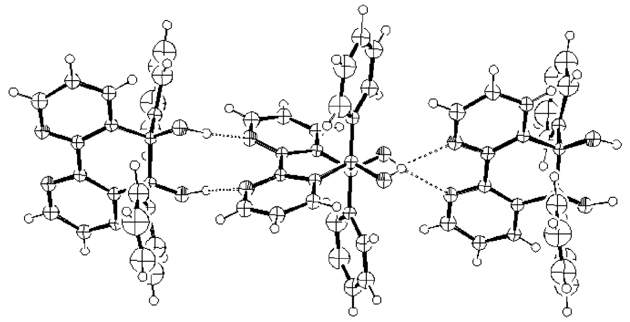
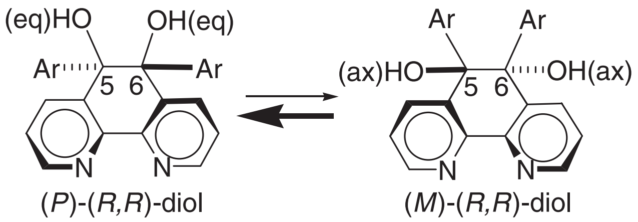


Figure 1. Supramolecular rod structure in (*R*,*R*)-(+)-**1** crystal.

Segregation of enantiomers is attained in the crystal of racemic phenyl-diol **1**. Thus, the chiral supramolecular rods consisting of only (*P*)-(*R*,*R*)-(+)-**1** (P rod) or (*M*)-(*S*,*S*)-(−)-**1** (M rod) are also formed in the crystal of *rac*-**1** (benzene solvate, $P4_2/n$, $Z = 4$)[10] (Figure S1)[7] as in the case of (*R*,*R*)-(+)-**1** crys-



Scheme 2.

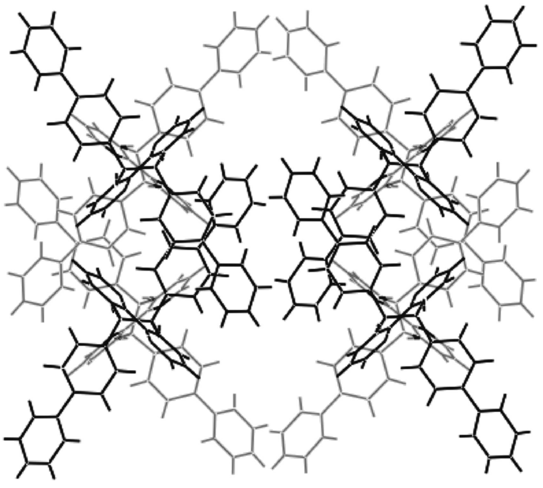


Figure 2. Supramolecular rod structure in (*R*,*R*)-(+)-**2** crystal (perspective view along the *c* axis).

tal. The P and M rods are extended along the *c* axis and packed in a side-by-side fashion on the *ab* plane. Crystallization solvent (benzene) is clathrated in the void formed between the rod structures.

Not only phenyl-diol **1** but also biphenyl-diol **2** was proven to form similar supramolecular rod structures as shown by the X-ray analysis of (*R*,*R*)-(+)-**2** ($P2_12_12$, $Z = 8$, two independent molecules)[10] (Figure 2). The long axis of biphenyl substituents is nearly perpendicular to the rod direction, thus expanding the diameter to ca. 20 Å. In the case of racemic crystal (*Ibca*, $Z = 8$, molecule on the two fold axis), molecules of **2** are again connected to form the rod-like structure although homogeneity of chiral sense in the rod is not well demonstrated due to the disorder around the C5–C6 bond in the crystal structure (Figure S2).[7]

The above crystallographic data clearly show that the supramolecular rod-structure is commonly present in those crystals irrespective to the aryl groups at C5 and C6.[12] Since their crystal structures are nonisomorphic, the observed structural motif is intrinsic to 5,6-diaryldihydrophenanthroline-5,6-diol skeleton having two hydrogen-bond donating groups (OH) on one side and two hydrogen-bond accepting sites (pyridine-N) on the other side.

In fact, phenanthrene-type diol **4** without pyridine-N sites cannot form the rod structure in the crystal although its molecular structure closely resembles that of **2**: the OH groups occupy the pseudo equatorial positions, and the R,R point chiralities are transmitted to P helicity of dihydrophenanthrene unit. Only the head-to-head centrosymmetric dyad is formed by the hydrogen bond in the crystal of *rac*-**4**[10] (Figure S3).[7] In the crystal of methyl ether **3**,[10] molecules are rather isolated from each other without any special intermolecular interactions (Figure S4).[7] Lack of inter/intramolecular hydrogen bonds may be the reason for the change in helicity preference of **3**, in which methoxy groups at C5 and C6 occupy the pseudo axial positions.[13] Such switching in helicity would be also related to the π–π interaction between two biphenyl groups of the pseudogauche arrangement.

In summary, we have found here that the title diols can serve as reliable motif for the supramolecular rod. Since the homochiral diols aggregate to form the one-dimensional network, the rod structure is also chiral, thus providing the chance to further study its supramolecular chirality.[14] Studies in this vein are now in progress and will be reported in due course along with detailed chiroptical properties of diols **1** and **2** in solution.

References and Notes

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9 Dimethyl ether (−)-**3** obtained from diol (+)-**2** reacted with 1,3-diiodopropane to give the diiodide salt of bis(quaternary) dication. Its absolute configuration at C5 and C6 was successfully determined to be R,R by the X-ray analysis using anomalous dispersion. The detail will be reported elsewhere.

10 Selected crystal data are as follows (ref. 7). (*R*,*R*)-(+)-**1**: $C_{24}H_{18}N_2O_2$, orthorhombic, $P2_12_12$, $a = 14.748(2)$, $b = 8.731(1)$, $c = 14.255(2)$ Å, $V = 1835.7(8)$ Å^3, $Z = 4$, CCDC-725934. *rac*-**1** benzene solvate: $C_{30}H_{24}N_2O_2$, tetragonal $P4_2/n$, $a = b = 12.196(3)$, $c = 14.114(3)$ Å, $V = 2099.5(8)$ Å^3, $Z = 4$, CCDC-725936. (*R*,*R*)-(+)-**2**: $C_{36}H_{26}N_2O_2$, orthorhombic, $P2_12_12$, $a = 26.610(5)$, $b = 15.281(3)$, $c = 14.146(2)$ Å, $V = 5752(1)$ Å^3, $Z = 8$, CCDC-725935. *rac*-**2**: $C_{36}H_{26}N_2O_2$, orthorhombic, *Ibca*, $a = 24.369(9)$, $b = 15.423(6)$, $c = 14.127(5)$ Å, $V = 5309(3)$ Å^3, $Z = 8$, CCDC-725937. *rac*-**3** methanol solvate: $C_{40}H_{38}N_2O_4$, monoclinic, $P2_1/c$, $a = 12.355(2)$, $b = 12.289(1)$, $c = 22.113(3)$ Å, $\beta = 105.1531(5)°$, $V = 3240.5(7)$ Å^3, $Z = 4$, CCDC-725938. *rac*-**4** dichloromethane solvate: $C_{38.5}H_{29}ClO_2$, monoclinic, $P2_1/n$, $a = 16.303(4)$, $b = 9.419(2)$, $c = 17.912(5)$ Å, $\beta = 91.368(2)°$, $V = 2749.7(1)$ Å^3, $Z = 4$, CCDC-725939.

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12 Diols with two 4-alkoxyphenyl groups at C5 and C6 positions were also prepared. Preliminary studies on their crystal structures showed the presence of similar supramolecular rod structure although difficulty in obtaining a sufficiently sized single crystal hampered full analyses.

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