

Experimental Section

X-ray structure analysis: Crystal dimensions $0.020 \times 0.015 \times 0.015$ mm. Monoclinic, space group $C2/c$, $a = 13.056(2)$, $b = 7.2941(9)$, $c = 15.162(2)$ Å, $\beta = 103.575(2)^\circ$, $V = 1403.6(3)$ Å³, $Z = 4$, $M_w = 784.2$ g mol⁻¹, $\rho_{\text{calc}} = 3.711$ g cm⁻³, $F(000) = 1464$. CCD Siemens diffractometer (sealed tube, 2.4 kW), $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu_{\text{K}\alpha} = 14.87$ mm⁻¹; of 2611 reflections measured, 1002 were independent ($R_{\text{int}} = 0.0547$), $2 < \theta < 23.5^\circ$. Structure determination and refinement software SHELXTL.^[25] All the hydrogen atoms were located in the difference Fourier maps. The 114 variables were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms and isotropic for hydrogen atoms. The final residuals were $R_F = 0.024$ for $F > 4\sigma(F)$ and 0.027 for all data, $\text{GOF}(F) = 1.167$. Further details of crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344, Eggenstein-Leopoldshagen (Germany), on quoting the depository number CSD-407222. Patent Registry No. (NH₄)₂Ge₇O₁₅ 9700705.

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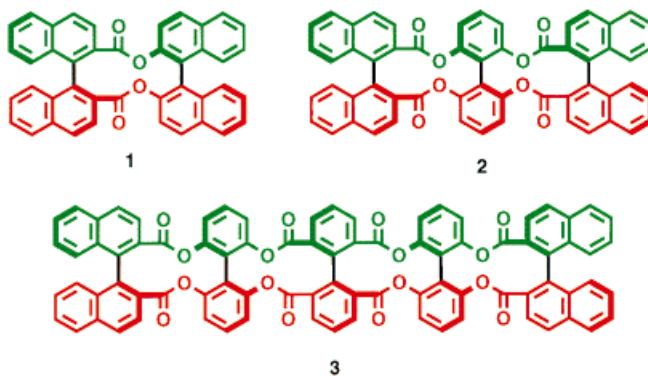
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Double-Helical Oligo Esters: Chiral Twist of Two Aromatic Ester Chains

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The double-helical structure is often found in nature, and artificial double-helical molecules are also of interest; for instance, in 1991 Lehn and co-workers prepared a double-helical structure by utilizing the coordination of nitrogen atoms of two chains to copper ions.^[1] In another example, two chains are bound by hydrogen bonds of an oligopeptide.^[2] However, in contrast to these approaches based on self-assembly, covalent bonds have been used less frequently in the synthesis of such molecules. Here we report the preparation of oligo esters **2** and **3**. In these molecules, biphenyl groups are sandwiched between two chiral binaphthyl groups. Through this “chiral twist”, the originally achiral biphenyl groups are fixed in the same absolute configuration as the two binaphthyl groups on both ends. As a result, the two oligo ester chains in one molecule (green and red in **1–3**) are twisted to form a double-helical structure.^[3]



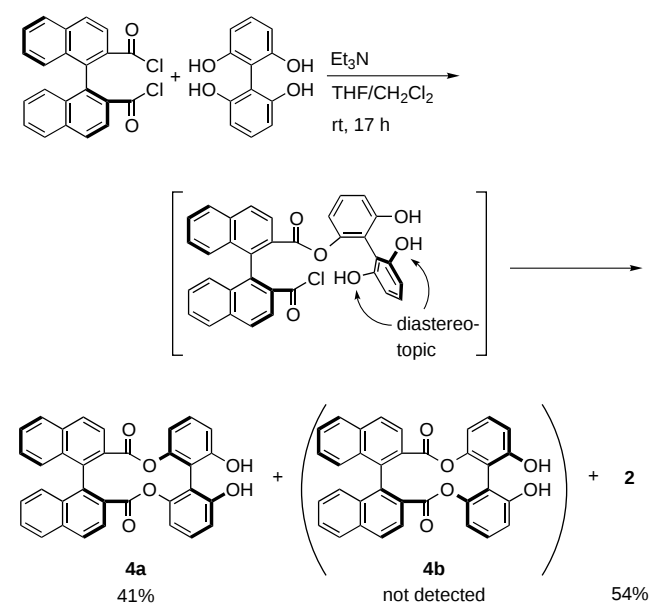
For the synthesis of these compounds (*S*)-1,1'-binaphthyl-2,2'-dicarbonyl dichloride was initially treated with biphenyl-2,2',6,6'-tetrol (Scheme 1), which gave the 1:1 coupling product **4a** and the 2:1 product **2** in 41% and 54% yield, respectively. It is noteworthy that **4a** was obtained as a single diastereomer although two diastereomers **4a** and **4b** could have formed. Biphenyl-2,2',6,6'-tetrol itself is an achiral molecule. After the first esterification of the 2-hydroxy group, the two hydroxy groups at the 2'- and 6'-positions are diastereotopic. Thus the second esterification step proceeds exclusively at one of these two hydroxy groups.

The absolute configuration of the biphenyl group was determined by the following method: The two hydroxy groups of **4a** were protected as methyl ethers, and then the compound was hydrolyzed to give the 2,2'-dimethoxybiphenyl-6,6'-diol (**5**) and 1,1'-binaphthyl-2,2'-dicarboxylic acid (Scheme 2). The

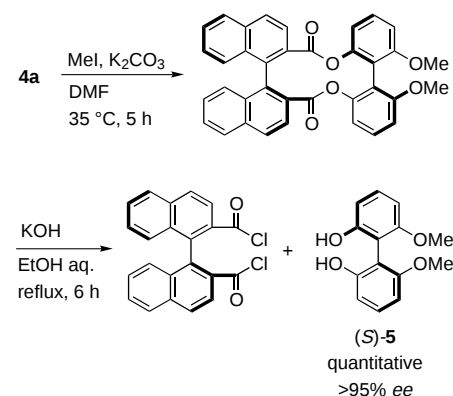
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Scheme 1.



Scheme 2.

enantiomeric excess of **5** was determined to be >95% by HPLC on a chiral column. By comparison of the optical rotation value of **5** to that in the literature,^[4] this compound was assigned the absolute configuration *S*. This indicates that the absolute configuration of the biphenyl group is controlled by that of the binaphthyl group. The 1,1'-binaphthyl-2,2'-dicarboxylic acid was recovered without racemization. Thus, the present method provides a novel synthetic route to optically active biphenyl compounds.^[5]

The following experiments also suggest that the biphenyl group in such cyclic esters prefers to adopt the same absolute configuration as the binaphthyl group. The condensation of (*S*)-1,1'-binaphthyl-2,2'-diol with (*S*)-1,1'-binaphthyl-2,2'-dicarboxylic acid dichloride gave the cyclic ester **1** as a single product in 92% yield, while a complex mixture of products was obtained from (*R*)-1,1'-binaphthyl-2,2'-diol and (*S*)-1,1'-binaphthyl-2,2'-dicarbonyl dichloride. In addition, Miyano and co-workers reported the asymmetric synthesis of a biphenyl group.^[6] In their work, two benzoic acid derivatives were linked to (*R*)-1,1'-binaphthyl-2,2'-diol through ester bonds, and then the two phenyl groups were connected to

each other at their 2-positions to form a (*R*)-biphenyl group.^[7, 8] In the 1:2 condensation product **2** (Scheme 1), one biphenyl group is sandwiched between the two binaphthyl groups. Only one diastereomer was formed. The absolute configuration of the central biphenyl group is assigned to be *S* on the basis of the above result. An optimized space-filling model of the oligo ester **2** is shown in Figure 1. In this model,

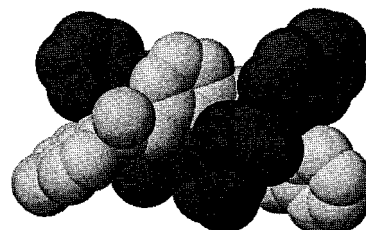
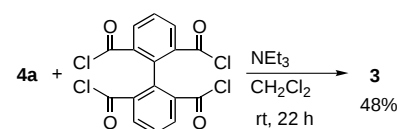


Figure 1. A model of **2** optimized with an MM2 force field (CACH system). One ester chain, “naphthyl-C(=O)OC₆H₃OC(=O)C₆H₃-naphthyl”, is depicted in light gray and the other in dark gray. The two chains form a double-helical structure.

two ester chains, which are depicted in light gray and dark gray in Figure 1, form the double-helical structure. The two chains are bound to each other by the covalent bond between the two benzene rings of each biaryl group.

The longer biphenyl ester **3** was synthesized from **4a** and biphenyl-2,2',6,6'-tetracarboxyl tetrachloride (Scheme 3). Again, a single coupling product was obtained. The product



Scheme 3.

was assigned as the aromatic oligo ester **3** with three *S* configured biphenyl groups and two binaphthyl groups.

The specific rotations of esters **1–3** [α]_D ($c = 1.00$ g 100 mL⁻¹) are shown in Table 1. The greater the number of biphenyl groups in the molecule, the more the specific rotation increases. This increase in specific rotation can be attributed to the double-helical structures of **1–3**. The CD absorption of the biaryl group at around 250–260 nm also increases in the series **1** → **2** → **3**. This is a further indication that all biphenyl groups in **3** are *S* configured. Unlike common

Table 1. Optical rotation and CD-spectroscopic data of the oligo esters **1–3**.

Ester	No. of biphenyl groups	$[\alpha]_D^{25}$	$\lambda_{\max}$	$\epsilon_{\max}$
1	0	–553 ^[a]	260	2
2	1	–589 ^[a]	254	–131
3 ^[d]	3	–821 ^[b]	252	–286

[a] $c = 1.00$ in CHCl₃. [b] $c = 1.00$ in CH₂Cl₂. [c] 2.05×10^{-5} M in 1,4-dioxane. [d] Because of the low solubility of **3**, other solvents that were clear at <240 nm were not used.

macrocyclic compounds, the conformation of the cyclic oligo esters **2** and **3** is much more restricted because the binaphthyl groups are not allowed to rotate around the 1,1' axis because of steric repulsion between the 8- and 8'-hydrogen atoms. Thus once the configuration of the biphenyl groups is regulated in **2** and **3**, the conformation of the whole molecule is restricted unequivocally except for the small changes in the torsion angles of the biaryl groups. Accordingly, a double-helical structure similar to that of **2** is suggested for **3**.

Experimental Section

2 and **4a**. A solution of biphenyl-2,2',6,6'-tetrol (1.10 mmol) in THF^[9] was added to a solution of the acid chloride derived from (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid^[10] (1.00 mmol) in CH₂Cl₂, and the resulting mixture was stirred at 20 °C for 22 h. Aqueous work-up followed by purification by silica-gel column chromatography (CH₂Cl₂/EtOAc, 9/1) gave **4a** (41 % yield) and **2** (54 % yield) as colorless solids. **4a**: Sublimed above 206.0 °C; ¹H NMR (CDCl₃): δ = 7.95–7.89 (m, 4H), 7.81 (d, 2H, J = 8.58 Hz), 7.52 (t, 2H, J = 6.93 Hz), 7.30–7.03 (m, 6H), 6.79 (d, 2H, J = 8.25 Hz), 6.60 (d, 2H, J = 8.25 Hz); ¹³C NMR (CDCl₃): δ = 166.76, 154.16, 149.27, 136.95, 134.39, 133.01, 129.60, 129.49, 128.57, 128.17, 127.71, 127.53, 127.22, 124.56, 115.44, 113.98, 111.32. **2**: M.p. (CH₂Cl₂/hexane) 274.3–274.9 °C; ¹H NMR (CDCl₃): δ = 7.97–7.91 (m, 8H), 7.81 (d, 4H, J = 8.58 Hz), 7.52 (t, 4H, J = 6.93 Hz), 7.31–7.24 (m, 4H), 7.05–6.99 (m, 6H), 6.75 (d, 4H, J = 7.92); ¹³C NMR (CDCl₃): δ = 166.34, 149.00, 136.35, 134.29, 132.96, 129.58, 128.57, 128.37, 128.18, 127.63, 127.42, 127.26, 124.56, 119.37, 116.17; HR-MS: m/z found for [M+H]⁺: 831.1975; calcd.: 831.2017.

3: Biphenyl-2,2',6,6'-tetracarboxylic acid^[11] (0.21 mmol) was converted into the corresponding acid chloride and condensed with **4a** (0.41 mmol) in the presence of triethylamine (21 mmol). Work-up followed by purification by column chromatography (CH₂Cl₂) gave **3** (48 % yield) as fine needles: Sublimed above 470.0 °C. ¹H NMR (CD₂Cl₂): δ = 8.02–7.78 (m, 16H), 7.58 (t, 4H, J = 7.92 Hz), 7.47 (t, 2H, J = 8.24 Hz), 7.32 (t, 4H, J = 8.24 Hz), 7.21–7.02 (m, 12H), 6.79 (d, 4H, J = 8.25 Hz); ¹³C NMR (CD₂Cl₂): δ = 166.54, 165.35, 149.65, 149.14, 137.39, 136.80, 134.77, 133.46, 133.40, 131.75, 129.88, 129.04, 128.77, 128.68, 128.52, 128.21, 127.71, 127.65, 124.63, 120.39, 120.14, 116.33; HR-MS: m/z found for [M+H]⁺: 1307.2607; calcd.: 1307.2548.

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From Molecular to One-Dimensional Polychalcogenides: Preparation, Structure, and Reactivity of NaNbS₆, the First Ternary Alkali Metal Niobium Polychalcogenide Exhibiting Infinite Anionic Chains**

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The preparation of multinary transition metal chalcogenides in reactive alkali polychalcogenide melts at temperatures between 250 and 500 °C is a fast-growing area of inorganic solid state chemistry.^[1,2] Owing to the relatively low reaction temperatures, compounds containing large Q_x²⁻ ions (x > 1) are accessible which cannot be obtained with classical high-temperature syntheses.

Recently we investigated new polychalcogenide compounds of niobium. There are only a few examples of such compounds prepared by the reactive flux method.^[3] Systematic variation of the preparation conditions yielded several novel niobium chalcogenides, all containing molecular [Nb₂Q₁₁]⁴⁻ subunits (Figure 1).^[4-7] These units occur as isolated anions, as in K₄Nb₂S₁₁,^[4] or are connected through terminal sulfur ligands, as in Rb₆Nb₄S₂₂ or Cs₆Nb₄S₂₂.^[5] Incorporation of additional S₃²⁻ fragments, which are present under the preparation conditions, can lead to an expansion of the [Nb₂Q₁₁]⁴⁻ subunits. In K₄Nb₂S₁₄^[6] the S₃²⁻ ion acts as a terminal ligand, and in K₆Nb₄S₂₅^[7] it connects two units to form the novel complex [Nb₄S₂₅]⁶⁻ ion.

By extending the synthetic conditions used for preparing the novel niobium compounds to sodium polysulfide melts, we succeeded in synthesizing transparent, orange-red needles.^[8] All crystals investigated were grown together, and a twin refinement had to be performed.^[9] Here we report on the synthesis, crystal structure, optical behavior, and reactivity of NaNbS₆, the first ternary niobium chalcogenide containing one-dimensional anionic polymeric chains.

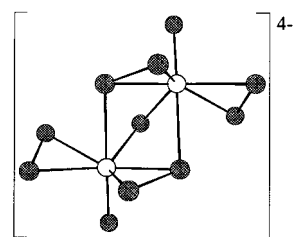


Figure 1. View of the [Nb₂Q₁₁]⁴⁻ unit (Nb = ○, Q = ●).

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