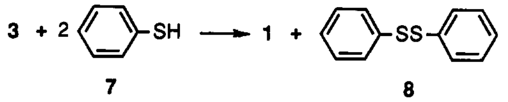
Scheme II

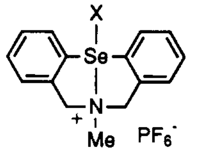


afforded selenane **3** in 85% yield (Scheme I).

The structure of **3** in solution was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se, and ^{31}P) spectroscopy. With regard to the conformational properties of heterocyclic analogues of dibenzocyclooctane, for eight-membered rings typically two different conformers, the boat-chair (BC) and the twist-boat (TB) and/or the boat-boat (BB) forms, can exist.[7] The conformers can be assigned by the ^{1}H NMR spectral data for benzylic protons of the eight-membered ring.[7] The ^{1}H NMR (500 MHz) spectrum of **3** in CD_3CN shows peaks at δ 3.12 (s, 3 H, CH_3), 4.59, 4.63 (AB q, J = 15.7 Hz, 4 H, CH_2), 7.49–7.54 (m, 2 H, Ar H), 7.68–7.75 (m, 4 H, Ar H), and 8.35–8.40 (m, 2 H, Ar H), which show downfield shifts relative to those of **1** and **2**,[3] while the ^{13}C NMR (125 MHz, CD_3CN) spectrum shows absorptions at δ 45.1, 62.4, 128.7, 130.7, 131.6, 132.6, 134.7, and 139.4. The ^{77}Se NMR spectrum of **3** in CH_3CN shows a singlet peak at δ 813.4 (relative to Me_2Se).[8] The ^{31}P NMR spectrum of the PF_6^- anion of **3** in CH_3CN shows a phosphorus absorption at δ −143.2 (sept, J_{PF} = 707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-. This spectroscopic evidence indicates that **3** is a single conformer, i.e., TB or BB form in solution. The selenane **3** exists solely as a single conformer from −40 to +70 °C as evidenced from the variable-temperature ^{1}H NMR spectral data, though the selenazocine **1** shows the existence of two conformers.[3]

The crystal structure of **3** was determined by X-ray diffraction analysis (Figure 1).[9] The Se–N distance is 2.191 Å, which is significantly shorter than the sum of the van der Waals radii (3.50 Å), indicating transannular bond formation between Se and N. The Se–Cl bond length (2.296 Å) is close to that of diphenylselenium dichloride (2.30 Å).[10] The Cl–Se–N bond angle of 174.3° is approximately collinear, and the C_{eq}–Se–C_{eq} bond angle is 101.7°. Thus, the configuration about the selenium atom is slightly distorted trigonal bipyramidal with two apical Se–N and Se–Cl bonds, two equatorial Se–C bonds, and the lone-pair electrons considered to occupy the third equatorial position. These structural features are consistent with a σ-selenane structure.

Treatment of the *Se*-chloro derivative **3** with lithium dimethylcuprate, $(CH_3)_2CuLi$, or lithium diphenylcuprate, $(C_6H_5)_2CuLi$[11] (1.2 equiv), in anhydrous tetrahydrofuran at −78 °C resulted in the formation of the *Se*-methyl- or *Se*-phenylammonioselenane (**5** or **6**), which was recrystallized from CH_3CN–Et_2O.[12,13] The selenanes of *Se*-methyl **5**, *Se*-phenyl **6**, and *Se*-methoxy **4**[5b] also show one type of absorption in the ^{1}H, ^{13}C, and ^{77}Se NMR spectra. The ^{1}H NMR spectra of **4–6** in CD_3CN did not show any temperature dependence between −40 and +70 °C. These results indicate that the conformations of **4–6** are fixed as the TB or BB form by a transannular bond between the selenio and amino groups, although normally the BC conformer has been shown to be more stable and rigid than TB and/or BB conformers.[7]



4 X = OMe
5 X = Me
6 X = Ph

Interestingly, the new σ-selenane **3** behaves as an oxidizing agent, as follow (Scheme II). Treatment of benzenethiol (**7**) (2 equiv) with **3** (1 equiv) in the presence of triethylamine (2 equiv) in CH_3CN under an Ar atmosphere at room temperature for 1 h gave diphenyl disulfide (**8**) as the oxidation product in 88% yield and the selenazocine **1** as the reduction product in 83% yield.

The selenanes **3–6** are a new type of hypervalent selenium compounds, since generally σ-selenanes bear two electronegative groups such as oxygen atoms or halogen atoms at the apical positions.[2]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency (No. 02247101) from the Ministry of Education, Science and Culture, Japan. H.F. gratefully acknowledges a Scientific Research Grant (No. 03640435) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Detailed information of the X-ray crystal structure of **3** and tables of positional parameters, bond distances and angles, and torsional angles (7 pages). Ordering information is given on any current masthead page.

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(8) The ^{77}Se NMR spectrum of **1** in CH_3CN shows a broad peak due to the existence of conformers.[3]

(9) Crystal data for **3**: $C_{15}H_{15}NClSePF_6$, orthorhombic, space group *Pbca*, a = 15.525 (5) Å, b = 16.970 (5) Å, c = 13.217 (3) Å, $\alpha = \beta = \gamma$ = 90°, V = 3482.015 Å^3, Z = 8, D_{calcd} = 1.788 g/cm^3, Cu Kα radiation (λ = 1.5418 Å), $F(000)$ = 1856, CAD4 diffractometer, 2296 reflections (2° < θ < 60°), 3069 observed with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically by full-matrix least squares using the SDP program package. The final R value was 0.050.

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(12) **5**: mp 225–228 °C dec; ^{1}H NMR (CD_3CN) δ 2.55 (s, 3 H, CH_3), 2.95 (s, 3 H, CH_3), 4.04 (s, 4 H, CH_2), 7.38–7.40 (m, 2 H, Ar H), 7.53–7.61 (m, 4 H, Ar H), 7.69–7.71 (m, 2 H, Ar H); ^{13}C NMR (CD_3CN) δ 18.9, 40.5, 57.4, 126.8, 129.2, 130.4, 131.2, 133.3, 140.5; ^{77}Se NMR (CH_3CN) δ 452.5 (s); ^{31}P NMR (CH_3CN) δ −145.5 (sept, J_{PF} = 707 Hz). Anal. Calcd for $C_{16}H_{18}NSePF_6$: C, 42.87; H, 4.05; N, 3.12. Found: C, 43.09; H, 4.02; N, 3.12. **6**: mp 263–266 °C dec; ^{1}H NMR (CD_3CN) δ 2.56 (s, 3 H, CH_3), 4.05, 4.19 (AB q, J = 15.7 Hz, 4 H, CH_2), 7.33–7.61 (m, 8 H, Ar H), 7.78–7.89 (m, 5 H, Ar H); ^{13}C NMR (CD_3CN) δ 40.2, 56.8, 127.0, 130.2, 131.0, 131.6, 133.5, 133.6, 134.3, 135.4, 135.6, 141.1; ^{77}Se NMR (CH_3CN) δ 554.5 (s); ^{31}P NMR (CH_3CN) δ −149.0 (sept, J_{PF} = 707 Hz). Anal. Calcd for $C_{21}H_{20}NSePF_6$: C, 49.42; H, 3.95; N, 2.74. Found: C, 49.37; H, 3.85; N, 2.72.

(13) The *N,N*-dimethylammonium salt of **1** shows the following ^{1}H NMR spectral data, which is similar to that of its sulfur analogue:[7b] mp 222.5–224 °C; ^{1}H NMR (CD_3CN) δ 2.61, 3.54 (s, CH_3; BC form), 2.97 (s, CH_3; TB form), 4.52, 5.63 (AB q, J = 13.5 Hz, CH_2; BC), 4.08, 4.67 (AB q, J = 13.5 Hz, CH_2; TB), 7.33–7.97 (m, Ar H); ^{13}C NMR (CD_3CN) δ 52.5, 64.7, 129.1, 129.5, 130.6, 130.7, 132.6, 137.3. Anal. Calcd for $C_{16}H_{18}NSePF_6$: C, 42.87; H, 4.05; N, 3.12. Found: C, 42.70; H, 3.90; N, 3.09.

Reversible Screw Sense Inversion of the 3_{10}-Helix in a Dehydropeptide

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Dehydro amino acid residues, that is, amino acid residues containing a C=C double bond in the α,β-position, are characterized by very peculiar geometric features, so their presence in a peptide sequence produces remarkable conformational consequences.[1]

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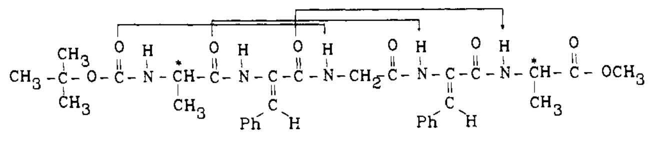
Scheme I



In this communication we report the conformation in solution of the dehydropeptide Boc-L-Ala-ΔPhe-Gly-ΔPhe-L-Ala-OMe containing two dehydrophenylalanine (ΔPhe) residues and provide unequivocal experimental evidence of an equilibrium between right-handed and left-handed 3_{10}-helical conformations. The equilibrium between the two "enantiomeric" helices may be shifted toward the right- or left-handed conformer, depending on solvent and temperature conditions.

In the solid state, the above dehydropentapeptide assumes a right-handed 3_{10}-helical conformation stabilized by two intramolecular hydrogen bonds.[2] The helix includes the three achiral residues ΔPhe(2), Gly(3), and ΔPhe(4), while the two chiral residues, Ala(1) and Ala(5), which govern the screw sense of the helix, are out of the spiralized segment of the peptide.

In methylene chloride solution, the chemical shifts of the various NH protons in the sequence undergo different perturbation degrees by addition of small amounts of the strongly hydrogen bond accepting solvent dimethyl sulfoxide (DMSO). Particularly, there is a marked distinction between the two NHs of Ala(1) and ΔPhe(2), which are significantly affected by DMSO, and the other NHs of Gly(3), ΔPhe(4), and Ala(5), which are relatively inaccessible to solvent, thus indicating that they must be involved in hydrogen bonding (Scheme I). Moreover, strong $N_iH \leftrightarrow N_{i+1}H$ NOEs were observed, between the NHs of ΔPhe(2), Gly(3), ΔPhe(4), and Ala(5), confirming the helical structure of the peptide.

As other ΔPhe-containing peptides, the subject pentapeptide exhibits an intense absorption maximum at 270–280 nm assigned to a charge-transfer transition from the highest occupied orbital localized on the styrene moiety to the vacant orbital of the electron-accepting carbonyl group.[3] In correspondence of this band, the CD spectra display intense couplets, typical of exciton splitting due to dipole–dipole interactions between the two dehydro chromophores (Figure 1). This provides a strong probe that the molecule assumes a rigid folded structure. Indeed, at least two hydrogen bonds, forming two consecutive type III β-bends, are necessary for maintaining the two ΔPhe residues in a mutual rigid disposition with a predominant chirality within the molecule, as occurring in a 3_{10}-helical conformation (Scheme I).

The most striking feature of the CD spectra is the sign of the couplet, which is positive in chloroform, methylene chloride, acetonitrile, and methanol, and negative in hexafluoro-2-propanol (HFP). This is a clear evidence that the helical peptide assumes opposite screw senses depending on the solvent.

Of course, "the stability of a conformation may be expressed as a ratio of internal attractive forces to the external attractive forces".[4] Moreover, in the present peptide a crucial role is played by the two alanine residues located at the opposite ends of the sequence. In fact, the preferred conformation imposed by the C-terminal L-Ala(5) has opposite screw sense with respect to that favored by the L-Ala(1) residue.[5-10] The actual conformation adopted is the balance of all these factors. In HFP, the high protonating solvent molecules probably replace the intermolecular hydrogen bonding of the crystal packing, so the peptide is likely to maintain the same right-handed sense as in the crystalline state.

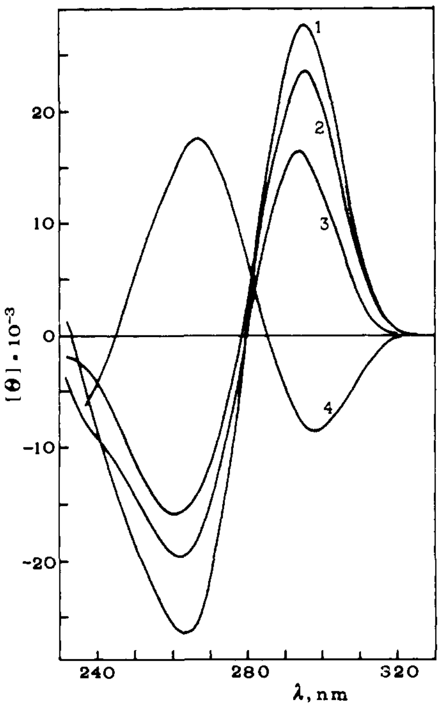


Figure 1. CD spectra of Boc-Ala-ΔPhe-Gly-ΔPhe-Ala-OMe in various solvents: (1) acetonitrile; (2) methylene chloride; (3) methanol; (4) hexafluoropropanol.

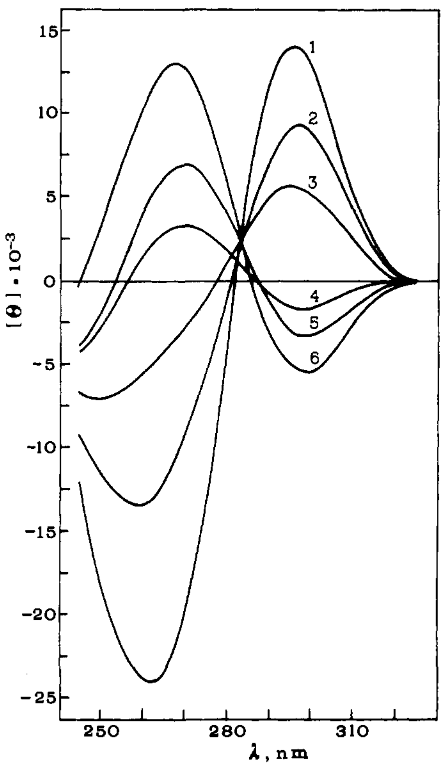


Figure 2. CD spectra of Boc-Ala-ΔPhe-Gly-ΔPhe-Ala-OMe at room temperature in chloroform/HFP solvent mixtures. $CHCl_3$/HFP: (1) 100/0; (2) 99/1; (3) 98/2; (4) 96.5/3.5; (5) 95/5; (6) 90/10 v/v.

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(2) The crystal structure was actually solved for the enantiomer Boc-D-Ala-ΔPhe-Gly-ΔPhe-D-Ala-OMe, which was found to adopt a left-handed 3_{10}-helix in the solid state (see ref 1).

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In the other more apolar solvents, the balance of the forces favors the opposite screw sense.

Addition of small amounts of HFP to the chloroform solution induces the progressive inversion of the helix, revealed by the decrease of the positive couplet and then by the gradual appearance of a couplet having opposite chirality (Figure 2).

At about 3% HFP concentration and 20 °C, the optical activity in the 280-nm region is practically zero, corresponding to a 50:50 composition of right-handed and left-handed helices. The temperature decrease shifts the equilibrium toward formation of the negative couplet, thus suggesting that the right-handed 3_{10}-helix is the more stable conformation at low temperature. At −11 °C the molar ellipticity was −8000 at 295 nm and +5800 at 265 nm.

3_{10}-Helices of both screw senses have been frequently found in homooligopeptides of aminoisobutyric acid, $(\mathrm{Aib})_n$, owing to the absence of chiral residues.[5,11,12] Indeed, Jung was able to reveal their interconversion in solution by freezing the equilibrium at very low temperature.[12] $(\mathrm{Aib})_n$ peptides, however, can be considered a "racemate" of the two enantiomeric helices at any conditions. The dehydropeptide described here, by contrast, was able to adopt preferentially either the left-handed or the right-handed 3_{10}-helix, the interconversion between the two enantiomeric helices depending on temperature and solvent conditions.

The result confirms the unique conformational features of dehydropeptides, which may be also of interest as models for conformational energy investigation of more complex biological structures.

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Peculiar Chirality in a Hydrothermally Synthesized One-Dimensional Molybdenum Phosphate Polymer: Structure of $(\mathrm{Et_4N})_2[\mathrm{Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2}]\cdot 2H_2O$

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Compared to the more familiar organic polymers, there is a relative paucity of structural data known for one-dimensional (1-D) inorganic systems. While inorganic polymers from the lighter main-group elements, such as S, N, and P, contain covalent bonds and often have structures reminiscent of their organic counterparts, metal–metal bonds can also connect the monomers as in the 1-D Chevrel phase materials and the well-known platinum chain compounds. Oxygen and the other chalcogens often lend themselves to the formation of extended chain materials like SiS_2, SeO_2, Sb_2O_3, and HgO as well as numerous types of silicates, especially those of the pyroxene group such as Na_2SiO_3.[1] Isolated one-dimensional chains are not common for transition-metal oxides, but examples are provided by $Mo(OH)_3PO_4$[2] and $VO(HPO_4)\cdot 4H_2O$.[3] We recently reported a 1-D sodium-bridged molybdenum phosphate polymer[4] as well as a new class of microporous solids based on the octahedral–tetrahedral framework molybdenum phosphates.[5-8] Molecular, layered, and nonporous 3-D molybdenum phosphates[9] are also known. In this paper we describe $(\mathrm{Et_4N})_2[\mathrm{Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2}\cdot 2H_2O]$ (**1**), a chiral, 1-D molybdenum phosphate polymer built up from Mo_4O_4 cubes and PO_4 tetrahedra.

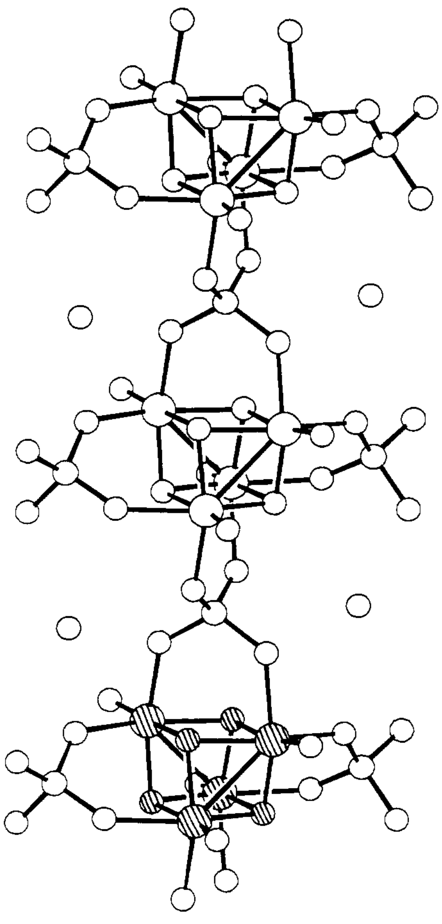

Figure 1. View of the 1-D chain which runs along [001]. The large circles represent the Mo atoms, the tetrahedrally coordinated circles the P atoms and the remaining circles the O atoms. The circles with no bonds drawn to them are the O atoms of water molecules. One of the Mo_4O_4 units has had the Mo and O atoms striped to emphasize the cubane-like geometry.

Phosphate **1**, which crystallizes as dark orange needles with a psuedohexagonal cross section, is isolated in 80% yield from the reaction of $Et_4N\cdot OH$, Mo(<2μ), MoO_3, H_3PO_4, and H_2O in a mole ratio of 15:1:5:20:250 at 200 °C for 112 h and is the only solid separating from solution. It is single phase as judged from comparison of the powder X-ray diffraction pattern to the pattern calculated from the fractional coordinates from the single-crystal study discussed below.

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