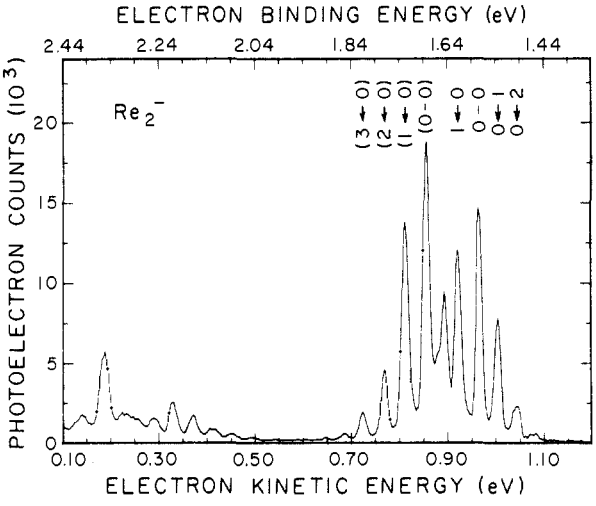

Figure 2. Photoelectron spectrum of Re_2^-. Labels indicate $Re_2 \leftarrow Re_2^-$ vibrational quantum numbers for transitions to the ground and (excited) Re_2 states. The low electron kinetic energy region was obtained at 457.9 nm, but the entire spectrum is displayed as for 488.0-nm (2.540 eV) excitation for clarity. Intensities of the bands below ~0.5 eV are suppressed by up to a factor of 3 by a decreasing instrumental sensitivity in this region.

electrons were energy-analyzed by a hemispherical electrostatic monochromator with multichannel detection. The instrumental resolution was 11 meV (90 cm^{-1}) in the electron kinetic energy region above 0.7 eV and up to ~20 meV at lower energies. A detailed description of the negative ion photoelectron spectrometer has recently appeared.[8]

The photoelectron spectrum of Re_2^-, shown in Figure 2, displays at least four vibronic band systems. The rightmost of these corresponds to the transition between the ground states of the anionic and neutral dimers, and its origin band position yields a Re_2 electron affinity of 1.571 ± 0.008 eV. The observed vibronic structure indicates fundamental vibrational frequencies of 340 ± 20 cm^{-1} for Re_2 and 320 ± 15 cm^{-1} for Re_2^-. The same vibrational frequencies are observed in a second band system 890 ± 30 cm^{-1} higher in energy. Harmonic Franck–Condon analyses of these intensity profiles indicate a change of 0.03 Å in the internuclear separation on electron attachment for both systems and a vibrational temperature of 1200 K. On the basis of this anion temperature and the similar intensities of the two band systems, we assign them to different states of Re_2 rather than Re_2^-. The small shifts in bond lengths and vibrational frequencies on electron attachment suggest that both Re_2 electronic states result from the detachment of a nonbonding or weakly antibonding electron. At least two additional band systems are observed in the low electron kinetic energy region of the spectrum, with intensity maxima approximately 5100 and 6200 cm^{-1} from that of the ground-state band system.

The Re_2 and Re_2^- vibrational frequencies observed here imply unusually large force constants of 6.4 ± 0.8 and 5.6 ± 0.5 mdyn $Å^{-1}$, respectively. Among the homonuclear transition-metal dimers, force constants of this magnitude have been reported[9] only for Mo_2 (6.44 mdyn $Å^{-1}$) and V_2 (4.34 mdyn $Å^{-1}$), which are multiply bonded.[10,11] In contrast, the single 6s–6s bond in Au_2 yields a vibrational force constant[9] only one-third that of Re_2. We conclude that these results provide strong evidence for multiple bonding in both Re_2 and Re_2^-. The bonding in this third row dimer thus differs dramatically from the van der Waals bonding[6] in the isoelectronic first-row molecule, Mn_2.

Acknowledgment. We are grateful to Dr. Amy E. S. Miller for stimulating our study of Re_2^-. This research was supported in part by the National Science Foundation under Grants CHE83-16628 and PHY82-00805 to the University of Colorado and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(9) DiLella, D. P.; Limm, W.; Lipson, R. H.; Moskovits, M.; Taylor, K. V. *J. Chem. Phys.* **1982**, *77*, 5263–5266.
(10) Hopkins, J. B.; Langridge-Smith, P. R. R.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1983**, *78*, 1627–1637. McLean, A. D.; Liu, B. *Chem. Phys. Lett.* **1983**, *101*, 144–148; Goodgame, M. M.; Goddard, W. A., III *Phys. Rev. Lett.* **1982**, *48*, 135–138. Atha, P. M.; Hillier, I. H. *Mol. Phys.* **1982**, *45*, 285–293.
(11) Langridge-Smith, P. R. R.; Morse, M. D.; Hansen, G. P.; Smalley, R. E. *J. Chem. Phys.* **1984**, *80*, 593–600. Walch, S. P.; Bauschlicher, C. W., Jr.; Roos, B. O.; Nelin, C. J. *Chem. Phys. Lett.* **1983**, *103*, 175–179.

Asymmetric Synthesis of Helical Metallocenes†

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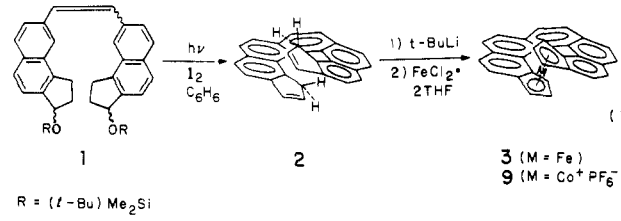
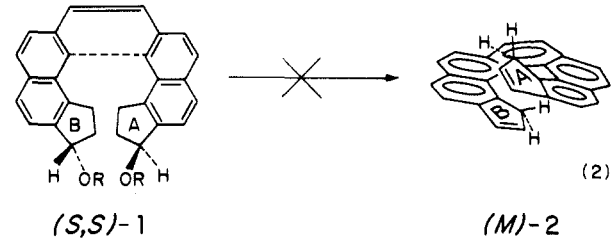
We report that the helical metallocene **3**, prepared previously by the steps summarized in eq 1,[1] can be obtained optically active



by a simple procedure that controls the direction in which the helix winds during photocyclization.[2] Consider the cyclization of diether (*S,S*)-**1**. If the steric bulk of the silyloxyls favored their placement outside the helix, ring A would stack above ring B, and the helix would wind to the left (eq 2).[3] In fact, however, when (*S,S*)-**1**,



synthesized from (*S*)-**4** (see below), is photocyclized as in eq 1, it gives helical hydrocarbon **2** that is largely racemic.[4] So does the isomer of **1** synthesized[5] from (*R*)-(−)-**5**, giving the isomer of **2** in which both double bonds are shifted one position.[7]

Supposing the scheme's failure to be a consequence of ROH having eliminated from the precursors, **1** and its isomer, *before* they cyclize, experiments were performed to prevent the eliminations. The discovery was that with propylene oxide added to consume HI as it forms,[8] with a full mole of I_2 to effect the

† Dedicated to Professor Harry H. Wasserman on his 65th birthday.
(1) Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* **1982**, *103*, 346.
(2) In winding hexahelicene esters of (−)-menthol and other chiral alcohols, Martin previously achieved such selection (usually small, except in one photocylization at −78 °C, and of unanalyzed origin). See: (a) Cochez, Y.; Jespers, J.; Libert, V.; Mislow, K.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1033 (b) Cochez, Y.; Martin, R. H.; Jespers, J. *Isr. J. Chem.* **1975**, *15*, 29. (c) Vanest, J.; Martin, R. H. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 113.
(3) *P* ≡ left-handed and *M* ≡ right-handed helix. See: Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(4) Synthesized from (*S*)-**4** [40% enantiomeric excess (ee)], it gave (*P*)-(+)-**2** in <3% ee.[5,6]
(5) As in ref 1.
(6) The chiral selectivity is (strangely) opposite to that expected according to eq 2. For absolute configurations see notes 31 and 37 below.
(7) Previously prepared by combining **2** with *t*-BuLi and then aqueous acetic acid;[1] its structure was confirmed by X-ray diffraction analysis of a sample prepared from racemic **5**. We thank Dr. Ian Williams of MIT for the analysis.

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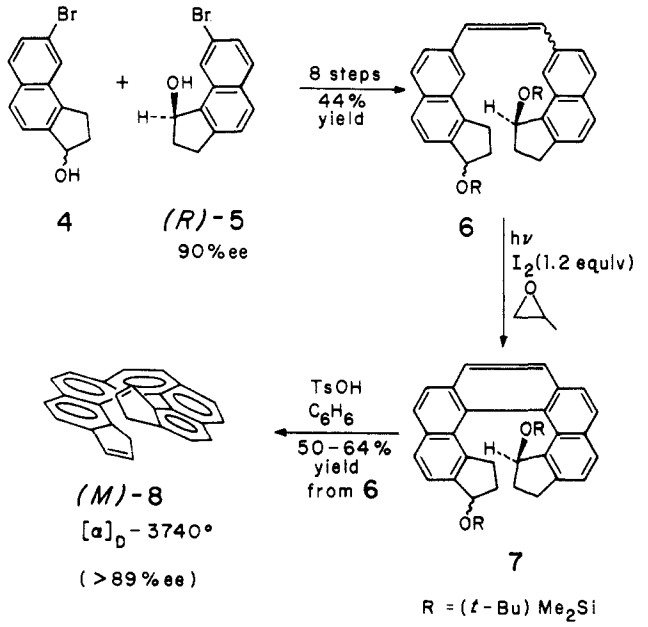
Scheme I



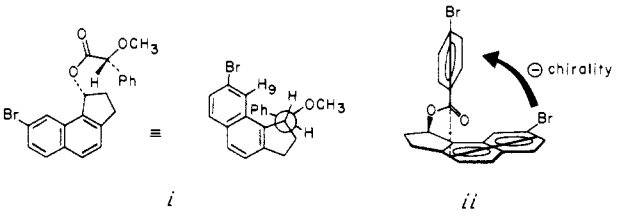
oxidation, and with the precursor **6**, derived from *racemic* **4** and (*R*)-**5**, the synthesis summarized in Scheme I could be carried out easily.[9,10] The product is the helical hydrocarbon **8**, in which one of the double bonds in **2** (or in the double-bond isomer described above) is shifted one position.[12] It is obtained in excellent enantiomeric purity.[13]

Two other experiments confirm that in stereoisomers of **6** it is the chiral center derived from **5** that dominates the direction in which the helix winds.[15] The configuration of **4** plays essentially no role.[17] Thus, if the configuration of **4** is fixed, while that of **5** is inverted, the configuration of the helicene is inverted.[18] Moreover, if optically active (*S*)-**4** [46% enantiomeric excess (ee)] and racemic **5** are carried through the steps in Scheme I, the resulting helicene **8** (in 51% yield from the stilbene) is largely racemic.[19]

When **8** in tetrahydrofuran (THF) is combined with *tert*-butyllithium at −78 °C and then with $FeCl_2$·2THF, the helical ferrocene **3** is obtained optically active (ca. 60% yield).[20] If $CoBr_2$–dimethoxyethane is substituted for the iron salt, the analogous cobaltocenium hexafluorophosphate **9**[21,23] can be obtained also [in 58% yield after acidification, oxidation (aqueous $FeCl_3$), and precipitation (aqueous NH_4PF_6)].[24]

To prepare **5**, the corresponding ketone was made from 2-bromonaphthalene and 3-chloropropionyl chloride ($AlCl_3$, at high concentration in CH_2Cl_2, 20 °C, >3 h;[25] then H_2SO_4–$AlCl_3$, 90 °C, 1 h; 55–80% yield).[26] To prepare the ketone corresponding to **4**,[27] the same procedure was applied to 2-bromo-7-(trimethylsilyl)naphthalene (−78 °C; this time the concentration was not high; yield 75%).[28] This last material was made in ca. 100% yield from 2,7-dibromonaphthalene [n-C_4H_9Li, then $(CH_3)_3SiCl$].[1,29]

The best procedure for reducing the ketones asymmetrically uses $LiAlH_4$, *N*-methylephedrine, and 3,5-dimethylphenol in ether (0–20 °C).[30] One crystallization gives (*R*)-(−)-**5**[30b] of 90% ee in 42% yield, and crystallization of the mother liquor gives an additional 21% of 81.5% ee.[31] Similarly, one crystallization gives



i *ii*

observation that the first Cotton effect of (*R*)-**5**'s p-bromobenzoate (see ii) is negative.[34,35] For **4** the assignment was based on analogy with reduction of indanones[36] and the observations that when comparing (*R*)-α-methoxyphenyl acetates of the (−) and (+) enantiomers in the former the proton adjacent to the methoxyl resonates at higher and that on the cyclopentane adjacent to the ester at lower field.[36]

(8) We thank Prof. Larry Overman for suggesting we try it. See: Barton, D. H. R.; Forbes, C. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1614. Best, W. M.; Wege, D. *Tetrahedron Lett.* **1981**, *22*, 4877. Gordon, E. M.; Chang, H. W.; Cimarusti, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 5504. Imai, I.; Ueda, M.; Iizawa, T.; Kudo, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2929. It has not been used to trap acids in photochemical transformations.

(9) All new compounds exhibited satisfactory NMR, IR, and (except for the salts) mass spectra (including, for key compounds, high-resolution mass spectra).

(10) Optically active **1** (a mixture of *S,S* and *S,R*) gives, after elimination, **2**, whose enantiomeric purity is less than that of **8**.[6] That isomer of **1** both halves of which are derived from **5** (the material was racemic) gives a non-helical product (^1H NMR δ 8.7–9.0, 8.2–8.4).[11]

(11) Maruyama, K.; Otsuki, T.; Mitsui, K. *J. Org. Chem.* **1980**, *45*, 1424.

(12) The ^1H NMR spectrum is a hybrid of the spectra of **2** and of the isomer in which both double bonds are shifted one position. See the supplementary material.

(13) Measured by analyzing the ^1H NMR resonances of one of its CH_2's when a solution (2 mg) in $CDCl_3$ (1 mL) contained Ag(fod) (6 mg) and $Eu(hfc)_3$ (18 mg).[14] The rotation of a sample having an ee of 95% (see note 18) implies that $[\alpha]_D^{max}$ = 4210° and $[\alpha]_{578}^{max}$ = 4470°.

(14) (a) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 382. (b) Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227.

(15) This accords with Dewan's analysis that the shortest C···H intramolecular contact in **2**, between the methylene H and the carbon on the inner core six away, splays the rings considerably.[16]

(16) Dewan, J. C. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1421.

(17) This is fortunate for three reasons: (1) **5** is easier than **4** to obtain in high optical purity; (2) the racemic material is carried through more steps, for the favored path involves converting the Br of **4** to $CH_2P^+(C_6H_5)_3Br^-$ and the Br of **5** to CHO (the silyloxyl appears to be lost more easily when the Br of **5** is converted to the phosphonium salt); (3) only one precursor need be obtained optically active.

(18) Subjecting (*S*)-**5** of 53% ee and (*S*)-**4** of 48% ee to Scheme I gave helicene **8** (in 58% yield from the stilbene) $[\alpha]_D$ +2770° (*c* 0.02 g/dL, CH_2Cl_2, ee 66%), whereas (*R*)-**5** of 51% ee gave **8** $[\alpha]_D$ −2550° (*c* 0.09, CH_2Cl_2). When the ee of the (*R*)-(−)-**5** in this last experiment was raised to 90% and that of the (*S*)-(−)-**4** was 40%, the ee of helix **8** (64% yield from the stilbene) was 95% [$[\alpha]_D$ −4000° and $[\alpha]_{578}$ −4250° (*c* 0.022, CH_2Cl_2)].

(19) Its $[\alpha]_{578}$ is +330° (*c* 0.017, CH_2Cl_2), implying an ee of ca. 8%.[6,13]

(20) Obtained from (−)-**8** of 62% ee, $[\alpha]_D$ −3700° (*c* 0.022, THF), implying $[\alpha]_D^{max}$ = −5970° (assuming no racemization occurred).

(21) The ^1H and ^{13}C NMR spectra, in the supplementary material, show under sharp peaks, broad resonances possibly due to polymeric cobaltocenium salts. The ^{13}C spectrum shows five intense (CH) and four weak (quaternary) aromatic resonances and three intense and two weak cyclopentadienyl resonances. The latter (δ 104–78) are at lower fields than in diindenylcobalt(III) hexafluorophosphate (δ 80–74).[22]

(22) Köhler, F. H. *Chem. Ber.* **1974**, *107*, 570.

(23) (−)-**8** of 95% ee gave (−)-**9** having $[\alpha]_{578}$ −7100° (*c* 4.5 × 10^{-3}, acetone). ($[\alpha]_{578}^{max}$ should thus be ca. 7450°.)

(24) Kölle, U.; Khouzami, F. *Chem. Ber.* **1981**, *114*, 2929.

(25) (a) For acetylation of 2-bromonaphthalene: Girdler, R. B.; Gore, P. H.; Hoskins, J. A. *J. Chem. Soc. C* **1966**, 518. (b) High concentration enhances α-substitution in acetylation of naphthalene: Andreou, A.; Bulbulian, R. V.; Gore, P. H.; Kamounah, F. S.; Miri, A. Y.; Waters, D. N. *J. Chem. Soc., Perkin Trans 2* **1981**, 376.

(26) See: (a) Woodward, R. B.; Hoye, T. R. *J. Am. Chem. Soc.* **1977**, *99*, 8007. (b) Mayer, F.; Müller, P. *Chem. Ber.* **1927**, *60*, 2278. (c) Hart, R. T.; Tebbe, R. F. *J. Am. Chem. Soc.* **1950**, *72*, 3286.

(27) The previous procedure is less effective.[1]

(28) See: (a) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058. (b) Dey, K.; Eaborn, C.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/1971**, *1*, 151.

(29) (a) Porzi, G.; Concilio, C. *J. Organomet. Chem.* **1977**, *128*, 95. (b) For the preparation of arylsilanes, see: Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.

(30) (a) Vigneron, J. P.; Jacquet, I. *Tetrahedron* **1976**, *32*, 939. (b) Reagent prepared from (1*R*,2*S*)-(−)-*N*-methylephedrine gives (*R*)-**4** and (*R*)-**5**.

(31) The ee's for **4** and **5** were measured by the ^1H NMR spectra of their (*R*)-(+)-α-methoxyphenyl acetates.[32] Their absolute configurations [(*S*)-**4** and (*R*)-**5** levorotatory] were deduced in a number of ways.[32] For **5** these include (1) analogy with reductions of indan-1-one,[36] (2) the expectation that H-9 in (*R*)-**5**'s (*R*)-α-methoxyphenyl acetate resonates at higher field than in (*S*)-**5**'s ester (see the extended Newman projection i),[32,33] and (3) the

(32) Yamaguchi, S. In "Asymmetric Synthesis"; Morrison, J. D.; Ed.; Academic Press: New York, 1983; Vol. 1, Chapter 7.

(33) See: Trost, B. M. *Chem. Soc. Rev.* **1982**, 141 and references cited therein.

(34) See: Koreeda, M.; Akhtar, M. N.; Boyd, D. R.; Neill, J. D.; Gibson, D. T.; Jerina, D. M. *J. Org. Chem.* **1978**, *43*, 1023.

(35) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy"; University Science Books: New York, 1983.

(*S*)-(−)-**4**[30b] in 57% yield and 48% ee.[31]

The absolute configurations[31,37] in Scheme I show that the helix **7** winds so as to place the silyloxyl derived from **5** on the outer face.

Acknowledgment. We are grateful to the National Science Foundation for support under Grant DMR-82-13794.

Supplementary Material Available: ^{1}H NMR spectra of **2**, **8**, their double-bond isomer, and **9**, the ^{13}C NMR spectrum of **9**, and CD and UV spectra of **3**, **8**, and **9** (8 pages). Ordering information is given on any current masthead page.

(36) Sudhakar, A. Ph.D. Dissertation, Columbia University, New York, 1985.

(37) The absolute configuration of **8** was assigned assuming that, like other helicenes, the *M* enantiomer is levorotatory at 578 nm and exhibits negative Cotton effects in methanol for the p bands (λ = 371 nm, $[\theta] = -2.45 \times 10^5$ deg cm^2 mol^{-1}; 354 nm, $[\theta] = -2.46 \times 10^5$ deg cm^2 mol^{-1}) and the β band (λ = 329 nm, $[\theta] = -5.50 \times 10^5$ deg cm^2 mol^{-1}).[38]

(38) (a) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63 and references cited therein (on page 91). (b) Groen, M. B.; Wynberg, H. *J. Am. Chem. Soc.* **1971**, *93*, 2970. (c) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 343. (d) Weigang, O. E., Jr.; Trouard Dodson, P. A. *J. Chem. Phys.* **1968**, *49*, 4248.

2,8-Dimethyl-4-(carboxymethyl)-6-(aminomethyl)phenoxathiin *S*-Dioxide: An Organic Substitute for the β-Turn in Peptides?

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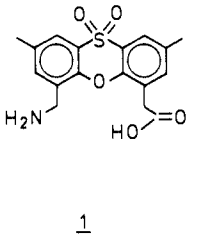
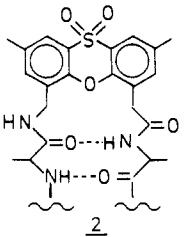
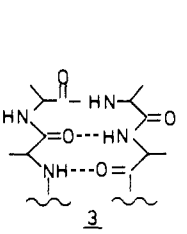
Cyclic peptides are known to adopt several conformations in solution; single rigid conformations are found only for small rings with a specific combination of amino acids. Attempts to stabilize specific peptide conformations incorporating nonpeptide residues are rare.[1] We propose the use of the spacer **1** to force hydrogen



1



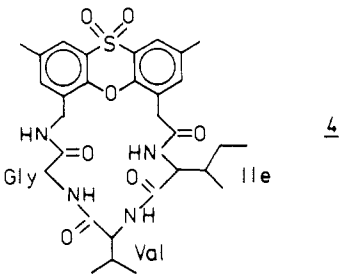
2



3

bridging between antiparallel peptide strains (**2**) in a similar manner as a β-turn (**3**).

Here we report the synthesis and conformational investigation of compound **4**, a cyclic peptide consisting of **1** and the amino acid sequence Ile-Val-Gly. Two low-energy conformations of **4** were found with the MM2 force field. One- and two-dimensional ^{1}H NMR experiments support **4A** as the prominent conformation in Me_2SO. **4A** contains a β-type hydrogen bridge and possibly a γ-loop, a situation that is found in several cyclic pentapeptides. Therefore, **1** may be used as an organic substitute simulating a pair of amino acids preferring the $i + 1$ and $i + 2$ positions of the β-reverse turn in peptides.



4

2,8-Dimethylphenoxathiin,[2] lithiated α to the oxygen, reacts with bromoacetic acid to form 2,8-dimethyl-4-(carboxymethyl)-phenoxathiin.[3] This was converted by H_2O_2 in acetic acid to the *S*-dioxide. Subsequent treatment with (hydroxymethyl)phthalimid in concentrated H_2SO_4 gave 2,8-dimethyl-4-(carboxymethyl)-6-(phthalimidomethyl)-phenoxathiin *S*-dioxide (**5**), the N-protected derivative of **1**. The tripeptide Ile-Val-Gly-OMe was coupled with **5** by propanephosphonic anhydride in CH_2Cl_2[4] (33%). Deprotection with hydrazine and cyclization by the Medzihradszky method yields **4** in 35% yield.[5]

The ^{1}H NMR spectrum of **4** in Me_2SO-d_6 was completely assigned with the aid of two-dimensional scalar correlated spectroscopy. The weak temperature coefficient of the chemical shift of the Ile-NH proton (Ile-NH, 0.5×10^{-3}; Val-NH, 3.3×10^{-3}; Gly-NH, 3.9×10^{-3}; **1**-NH, 4.7×10^{-3} ppm/deg) indicates that the proton is shielded from the solvent. This can be attributed to various types of intramolecular interactions—the most probably one is a hydrogen bridge to the Gly-CO (see below). Force-field calculations[6] revealed two basic low-energy conformations **4A** and **4B**, both possessing trans peptide bonds (Figure 1). Whereas **4A** has the expected "β-loop" with a hydrogen bridge from the Ile-NH to the Gly-CO (and in addition a γ-loop), conformation **4B** contains two γ-loops. It is possible to "invert" the phenoxathiin part in **4A** without significant change in the energy or distortion of the peptide moiety (see Figure 1). The NH–α-CH dihedral angles, derived from NMR coupling constants, support both conformations **4A**,**B** if fast inversion of the phenoxathiin part is assumed.[8] More definitive conclusions, however, can be drawn from the intramolecular distances measured by the nuclear Overhauser experiments.

We observed cross peaks due to chemical exchange in the 2D NOE spectra at 78 °C. Inspection of the 1D spectrum proves the presence of small amounts (4%) of a second conformation in slow exchange with the dominant form. To slow the exchange rate, in order to determine the NOE connectivity pattern of the main component, the experiments were run in a Me_2SO/CCl_4 solvent mixture at −3 °C. Here, the NOEs are negative and of medium size (2–18% in 1D experiments with 2.8-s presaturation).

(1) (a) Kellogg, R. M. *Angew. Chem.* **1984**, *96*, 769–781; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 782. (b) Mosberg, H. I.; Omnaas, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 2986–2987. (c) Ravi, A.; Balaram, P. *Tetrahedron* **1984**, *40*, 2577–2583. (d) Natural examples are some peptide antibiotics, e.g., ristocetin[11] or bouvardin: Jolad, S. D.; Hoffmann, J. J.; Torrance, S. J.; Wiedhopf, R. M.; Cole, J. R.; Arora, J. K.; Bates, R. B.; Gargiulo, R. L.; Kriek, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 8040–8044.

(2) Tomita, M. *J. Pharm. Soc. Jpn.* **1938**, *58*, 510. See also: Suter, C. M.; McKenzie, J. P.; Maxwell, C. E. *J. Am. Chem. Soc.* **1936**, *58*, 717–720.

(3) Addition at −100 °C, in THF; chromatography on Silica gel (CH_2Cl_2, 1% MeOH); yield 31%. For analogous reaction conditions, see: Neidlein, R.; Kramer, W. *Helv. Chim. Acta* **1981**, *64*, 939–942.

(4) BOC protection during peptide synthesis; coupling conditions: Wissmann, H.; Kleiner, H.-J. *Angew. Chem.* **1980**, *92*, 129–130; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 133–134.

(5) Azide cyclization in DMF at 6×10^{-2} mol/L; 4 °C; 6 days; after workup, 2 times recrystallization from MeOH; purity 98% by HPLC; Anal. ($C_{30}H_{38}N_4O_7S$) C, H, N. The monomeric structure of **4** is proved by its mass spectrum: EI 598 (M^+), most intense peak above mass 90; no peaks were detected at masses higher than 598.

(6) An undated version of the MM2 program of Allinger[7a]—obtained by courtesy of Molecular Design Ltd., Hayward, CA—was parametrized for amide functions giving reasonable energies and geometries for small *N*-alkyl amides as peptide models. H bonds are formed by the attraction of the NH and CO dipoles; the van der Waals repulsion of the NH proton was reduced in an interaction with a carbonyl oxygen.[7b] Six preconceived backbone conformations of **4** were used as starting points in the energy minimization; no attempts were made to explore the total conformational energy surface.

(7) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. (b) Hagler, A. T.; Huler, E.; Lifson, S. *J. Am. Chem. Soc.* **1974**, *96*, 5319–5327.

(8) Coupling constants $^3J_{NH,\alpha H}$, derived dihedral angles (Karplus), MM2 angles in **4A**,**B**: Ile 7.1 Hz, 25° or 130°, 139.5° and 133.6°; Val 7.6 Hz, 20° or 140°, 138.6° and 153.4°; Gly-α_1 8.1 Hz, 10° or 150°, 156.8° (*Pro-S*) and 24.4° (Pro-R); Gly-α_2 5.3 Hz, 130° or 30°, 38.3° (*Pro-R*) and 142.9° (*Pro-S*); **1**-α_1 and **1**-α_2 both 6 Hz, not compatible with Karplus equation.

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