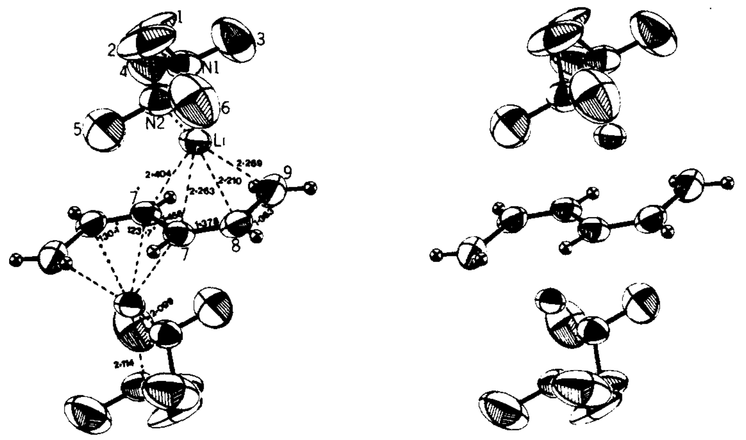


Figure 1. Stereoscopic view with selected bond lengths (Å) and angles (deg). Standard deviations in CC, LiC, and LiN lengths were 0.05, 0.07, and 0.07 Å, respectively, and in angles, 0.3°.

triene dianion would be **1**.[1] Recently, we prepared (hexatriene dianion)dilithium and obtained evidence from a ^1H NMR coupling constant that in solution this substance prefers the *Z,Z* shape as in **1**, but it was not clear whether a π-bonded ionic species like **1** or a σ-bonded covalent one like **2** was involved.[2] As this dilithiated substance apparently crystallized well from the tetramethylenediamine (TMEDA)-hexane solution in which it was generated, an X-ray study was initiated to gain further information regarding its structure.

1

2

The red twinned crystals were split and mounted in a capillary under argon. The space group is $P2_1/c$ with cell dimensions a = 8.614 (4) Å, b = 8.356 (4) Å, c = 15.975 (6) Å, β = 96.1°, d_c = 0.947 g/cm^3 for $C_6H_8Li_2 \cdot 2C_6H_{16}N_2$, and Z = 2. A set of 945 reflections $>3\sigma$ was obtained using a Picker FACS-I diffractometer with Cu Kα radiation. The structure was solved using MULTAN[3] and refined anisotropically to R = 0.065. Some disorder was not surprisingly[4] noted in the TMEDA and was compensated for partly by anisotropic thermal motion and partly by refining C1 in two positions, with occupancy factors of 0.78 and 0.22.

As can be readily seen in Figure 1, the crystals consist of *Z,Z-hexatriene dianions ion-paired with lithium-TMEDA*, with a center of symmetry at the dianion center. The structure is quite similar to that of the corresponding complex of naphthalene dianion.[5] The carbons and four of the hydrogens of the dianion **1** are within 0.02 Å of coplanarity; the C7 hydrogen is 0.17 Å and the internal C9 hydrogen is 0.87 Å out of this plane, both bending away from the nearest lithium atom. As expected from MO calculations, the C7-C8 and C8-C9 bonds in the dianion are about equally long and are noticeably shorter than the central bond. **1** can thus be roughly approximated as two allyl anions attached by a single bond, a situation reminiscent of butadiene (central bond, 1.483 Å).[6] As in butadiene, some delocalization energy is very likely gained in **1** by having the two π systems coplanar.

Knowledge of the geometry of dianion **1** permits more accurate calculation of the electron densities on its carbons: INDO calculations suggest charges of −0.18, +0.07, and −0.49 on C7, C8, and C9, respectively.

It has been proposed by Brooks and Stucky[4] that carbanion stability can be deduced in a complex of this sort from the Li-N bond lengths. If so, **1**, with Li-N bonds averaging 2.107 (7) Å, is about as stable as naphthalene dianion.[5]

The question remains why the dianion **1** prefers the *Z,Z* shape in the crystal and in solution.[2] MO calculations indicate this shape to be favored in the absence of cation due to attractive 1,4-overlaps.[1] However, another factor favoring this shape in the ion pair is coordination of each metal atom with *four* rather than three partially negatively charged carbons. It is not clear how much each of these factors contributes to making the observed shape the most stable.

Acknowledgments. We thank the National Science Foundation (GP-38070) for financial aid and the University of Arizona Computer Center for computer time.

Supplementary Materials Available. A packing diagram and tables of coordinates, temperature factors, bond distances, bond angles, least-squares plane, and structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6271.

References and Notes

(1) R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).
(2) R. B. Bates, W. A. Beavers, M. G. Greene, and J. H. Klein, *J. Am. Chem. Soc.*, **96**, 5640 (1974).
(3) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).
(4) J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7333 (1972).
(5) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7346 (1972).
(6) A. Almenninger, O. Bastiansen, and M. Traettenberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

Satish K. Arora, Robert B. Bates*
William A. Beavers, Robert S. Cutler
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received June 24, 1975

Asymmetric Titanium(IV) Metal. First Example of a Resolved Titanocene Derivative

Sir:

Dynamic stereochemistry of ligand substitution has been studied in many cases for square-planar and octahedral

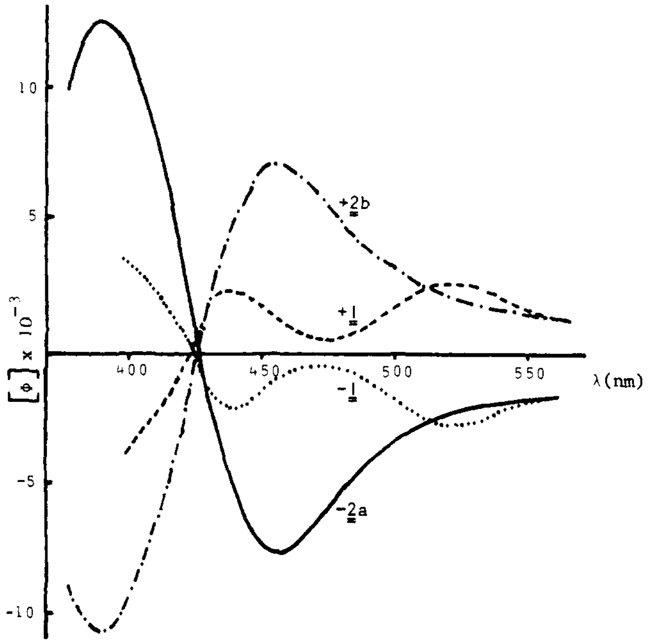


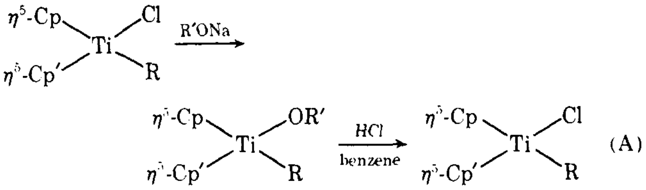
Figure 1. ORD curves of (+)-**1**, (−)-**1**, (+)-**2b**, and (−)-**2a**.

complexes. It is well known that the straightforward relationship between steric course and mechanism which characterizes substitutions at carbon centers is lost in octahedral systems. Such a relationship must be expected to be better in tetrahedral or quasi-tetrahedral systems, but examples of this kind have been limited until now to few complexes of groups 6, 7, and 8 transition elements.[1]

Preliminary results concerning chiral titanium complexes η^5-Cp-η^5-Cp′TiXY, where the titanium atom is surrounded by four different ligands, have been published. Chirality of these complexes has been detected by NMR analysis of diastereotopic groups and by isolation of diastereoisomeric pairs.[2-4] We have also described the formation of optically active titanocene compounds by asymmetric destruction of racemic forms.[5] We wish now to report the first separation of a chiral titanocene complex into its two enantiomeric forms.

We first tried this resolution through a classical manner by introducing on one ligand a functional group able to react with a chiral reagent. Our attempts to obtain such substrates have not been successful. Another possibility was to separate the diastereoisomers η^5-Cp-η^5-Cp′TiX*Y and to remove the chiral ligand X* in a selective and stereospecific way.

We first established,[6] that, in the transformation (A), where η^5-Cp′ bears a chiral group (η^5-Cp′ = η^5-$C_5H_4CHCH_3C_6H_5$), the first step gives a mixture of the two diastereoisomeric forms and that the second reaction is always selective and stereospecific (R = C_6F_5, OR′ = OCH_3, OC_6H_4-*o*-CH_3; R = CH_3, OR′ = OCH_3).[7]

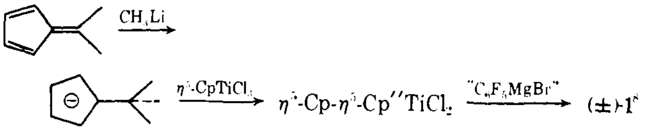


(A)

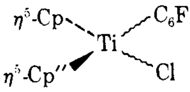
We used the stereospecificity of the second step to obtain the enantiomers of (±)-**1** [η^5-Cp = η^5-C_5H_5; η^5-Cp″ = η^5-$C_5H_4C(CH_3)_3$] which was prepared by the following reaction sequence:

Table I. Chemical Shifts (δ, 60 MHz in $CDCl_3$) of Protons Concerned in (−)-**2a** and (+)-**2b**

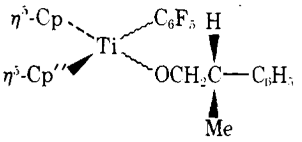
	$C(CH_3)_3$	η^5-C_5H_5	CH_3CH–	OCH_2CH–
(−)-**2a**	1.08	5.82	1.22	4.65
(+)-**2b**	0.98	5.98	1.25	4.50



(±)-**1** (1.0 mmol) in dry THF was cooled to −60°C and treated with the sodium salt of (−)-(*S*)-2-phenyl-1-propanol[9] (1.5 mmol). The mixture was allowed to warm and solvent evaporated. Preparative thin layer chromatography of the residue (ligroin/ether 9/1) afforded the two diastereoisomers[10] (overall yield 40%:ratio 1/1) **2a** (mp 90°C, $[\alpha]^{25}$D −146° (*c* 0.3 C_6H_6)) and **2b** (mp 120°C $[\alpha]^{25}$D +127° (*c* 0.24 C_6H_6)). Characteristic ^{1}H NMR data are listed in Table I.



(±)-**1**



2a

2b epimeric at titanium

The action of HCl in benzene solution affords finally the two enantiomeric forms of **1** in 20% yield:

(−)-**2a** $\xrightarrow{\text{HCl}}$ (−)-**1** (mp 137°C; $[\alpha]^{25}$D −193°; *c* 0.22. C_6H_6)

(+)-**2b** $\xrightarrow{\text{HCl}}$ (+)-**1** mp 137°C; $[\alpha]^{25}$D +190°; *c* 0.22. C_6H_6

Figure 1 reveals that the ORD spectrum of (+)-**2b** is nearly the mirror image of (−)-**2a**. This result establishes that in these regions the transitions are almost entirely those of the metal and are independent of the alkoxy group. Therefore, closely related compounds with similar properties should have the same absolute configuration.

This observation cannot be used to assign tentatively a steric filiation between (−)-**2a** and (−)-**1** (or between (+)-**2b** and (+)-**1**) because substitution of an halogen ligand by an OR ligand can alter dramatically the morphology of the ORD curves. However, it is known that HCl cleaves optically active α-phenethyl phenyl ether with a minimum of 85–90% retention of configuration.[11] Of course, one cannot conclude, a priori, that HCl cleavage of Ti–OR and C–OR bonds occurs with the same mechanism and dynamic stereochemistry.

Crystallographic analysis of both (−)-**2a** and (−)-**1** is under way and our aim is to use stereostability of these complexes to carry out substitution reactions in order to establish their stereochemical course.

Acknowledgments. We thank Dr. J. P. Guette for a generous gift of (+)-(*S*)-2-phenylpropanoic acid, and Dr. M. D. Rausch for critical comments of this manuscript.

References and Notes

(1) H. Brunner, *Angew. Chem., Int. Ed. Engl.*, **10**, 249 (1971).
(2) J. Tirouflet, A. Dormond, J. C. Leblanc, and F. Le Moigne, *Tetrahedron Lett.*, 257 (1973).
(3) F. Le Moigne, A. Dormond, J. C. Leblanc, C. Moïse, and J. Tirouflet, *J. Organomet. Chem.*, **54**, C13 (1973).
(4) H. Brunner and H. D. Schindler, *J. Organomet. Chem.*, **55**, C71 (1973).
(5) A. Dormond, J. Tirouflet, and F. Le Moigne, *J. Organomet. Chem.*, **69**, C7 (1974).
(6) J. C. Leblanc, C. Moïse, and Tep Bounthakna, *C. R. Acad. Sci., Ser. C*, **278**, 973 (1974); Tep Bounthakna, J. C. Leblanc, and C. Moïse, *C. R.*

Acad. Sci., Ser. C. **280**, 1431 (1975).

(7) In contrast, a partial epimerization is observed for methyl ligand substitution in the reaction

$$\eta^5\text{-Cp-}\eta^5\text{-Cp'TiYCH}_3 \xrightarrow{\text{HCl}} \eta^5\text{-Cp}\eta^5\text{-Cp'TiYCl}$$

($Y = C_6F_5$ or ortho $OC_6H_4CH_3$).

(8) NMR ($CDCl_3$): singlets at δ 1.22 ($-C(CH_3)_3$) and 6.30 (η^5-C_5H_5). Furthermore, the spectrum reveals traces of the bromo compound η^5-Cp-η^5-Cp'C_6F_5Br originated from Grignard's reagent (δ 6.35: η^5-C_5H_5). This impurity does not affect the following stages.

(9) This alcohol was prepared by $LiAlH_4$ reduction of (+)-(*S*)-2-phenylpropanoic acid (99% of optical purity).

(10) The racemic forms **2**a and **2b** (obtained from (±)-2-phenyl-1-propanol) melt respectively at 87 and 134°C. All new compounds gave satisfactory elemental analysis.

(11) H. Hart and R. J. Elia, *J. Am. Chem. Soc.*, **83**, 985 (1961).

C. Moïse, J. C. Leblanc, J. Tirouflet*
Laboratoire de Polarographie Organique, L.A. 33
Universite de Dijon, 21000 Dijon, France

Received June 16, 1975

Optical Rotatory Dispersion and Vacuum Ultraviolet Circular Dichroism of a Polysaccharide. ι-Carrageenan

Sir:

Many polysaccharides have no electronic transitions above 190 nm. Their optical rotatory dispersion (ORD) in the near-ultraviolet and visible regions is therefore of the normal type and Cotton effects are totally absent. Circular dichroism (CD) in that region is also completely absent. We report here the vacuum ultraviolet circular dichroism (VUCD) (155-200 nm) of ι-carrageenan; no polysaccharide CD has been reported previously below 190 nm. We also report a Drude equation analysis of the ORD of ι-carrageenan.

ι-Carrageenan was chosen for this study because it has been well-characterized by Rees and coworkers.[1-5] It approximates in structure an alternating copolymer $(A-B)_n$, in which B is a residue of β-D-galactose 4-sulfate and A of 3,6-anhydro-α-D-galactose 2-sulfate, with a mean residue weight of 271 for the potassium salts.[1,2] The glycoside linkages are A1→3B and B1→4A. In solution it undergoes a coil-to-helix transition as the temperature is decreased, with the helical form being more dextrarotatory than the unordered form.[3,4] Fiber X-ray studies indicated the presence of a helical structure.[5]

Figure 1 shows the ORD of a 0.5% ι-carrageenan solution in water at 22°C (curve 2) and in 0.05 *M* KCl at 24°C (curve 1) (measured on a Cary 60 spectropolarimeter). Curve 2 corresponds to the disordered form but in curve 1 the transition to helical form is not complete; the fully helical form is not achieved at temperatures above the freezing point of our solution (Chen and Yang, unpublished results). Both ORD spectra appear to be of the normal type[6] above 200 nm and obey the Drude equation: $[\alpha] = k/(\lambda^2 - \lambda_c^2)$ with $k = 18.9 \times 10^6$ and 13.9×10^6 when $\lambda_c = 155$ and 157 nm for curves 1 and 2, respectively. However, since the VUCD results (see below) show two bands, we can fit the same data with a two-term Drude equation:

$$[\alpha] = k_1/(\lambda^2 - \lambda_1^2) + k_2/(\lambda^2 - \lambda_2^2) \qquad (1)$$

A plot of $[\alpha](\lambda^2 - \lambda_1^2)$ vs. $(\lambda_2^2 - \lambda_1^2)/(\lambda^2 - \lambda_2^2)$ yields a straight line with λ_1 and λ_2 preset at 180 and 164 nm, respectively.[7] We find that $k_1 = -10.2 \times 10^6$ and -10.8×10^6 and $k_2 = 29.2 \times 10^6$ and 25.2×10^6, respectively, for curves 1 and 2. The fit is good over the wavelength range of 220-560 nm, except that the data points near 500 nm show some scatter. The fit is not unique; with $\lambda_1 = 180$ nm, lowering λ_2 to 160 or 150 nm would also give straight lines, but the magnitudes of both k_1 and k_2 decrease with decreasing λ_2; for instance, $k_1 = -5.9 \times 10^6$ and $k_2 = 24.9 \times 10^6$ with $\lambda_2 = 160$ nm (for curve 1).

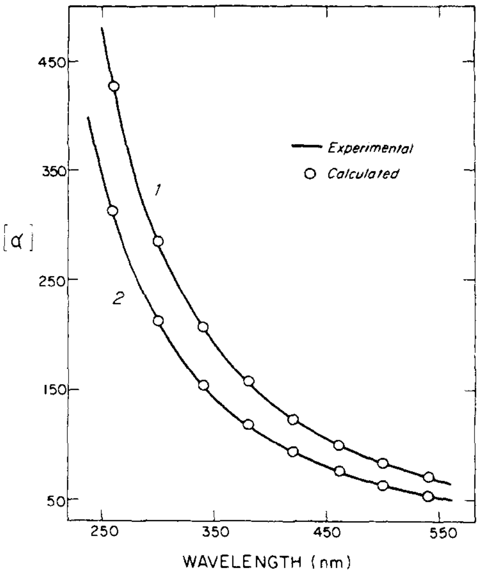


Figure 1. Optical rotatory dispersion of ι-carrageenan in solution: curve 1, 0.5% in 0.05 *M* KCl at 24°C, and 2, 0.5% in water at 22°C (pH 5). The circles are calculated values based on a two-term Drude equation. See text for details.

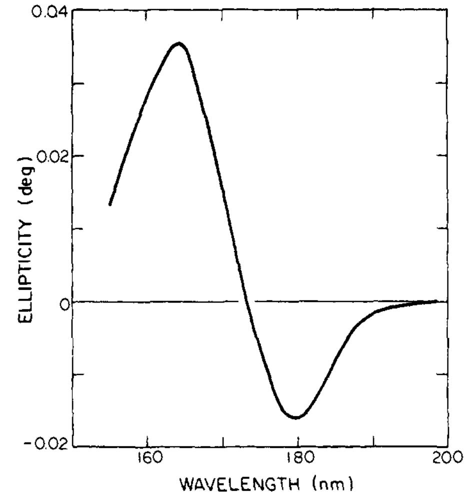


Figure 2. Vacuum ultraviolet circular dichroism of ι-carrageenan film prepared from aqueous solution.

ι-Carrageenan has no optical transitions above 190 nm and the CD spectrum measured on commercial instruments (not shown) indicates only the onset of negative dichroism as the instrumental wavelength limit is reached near 190 nm. Figure 2 shows the VUCD of ι-carrageenan from 155 to 200 nm. For the VUCD study a film of ι-carrageenan was prepared on a 1 mm CaF_2 disk by evaporation to dryness of an aqueous solution. The spectrometer[8] was operated with a spectral width of 1.66 nm, a time constant of 10 sec and a scan rate of 2 nm/min. Rotation of the film about the optical axis had no effect on the signal, and there was no indication of flattening of the CD bands. The data in Figure 2 have been corrected by subtraction of a wavelength dependent scattering contribution to the signal. The wavelength dependence of the correction was determined by measuring the scattering contribution to the signal measured with a film of poly(D,L-alanine). The wavelength positions of the two bands observed in the VUCD spectrum and the signs of those bands, together with the ORD data, are sufficient information to preclude the possibility that a third CD band at higher energy is contributing significantly