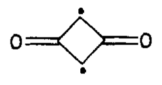
the parallel between *m*-quinomethane and *m*-xylylene and the spectra of Figures 1 and 2 is illuminating, it should also be noted that the effect of the oxygen in *m*-quinomethane makes the *D* value (0.0266 cm^{-1}) about twice as large as that of *m*-xylylene (0.011 cm^{-1}).[16] The same trend is not observed in the spectra of Figures 1 and 2 as might have been expected if III were the correct structure corresponding to the triplet of Figure 1. At the same time an accurate assessment of *D* values is unfortunately not at hand so this point cannot now be decided with finality.

It is attractive to hypothesize that the product of α-cleavage, dimethylenecyclobutadiene (I), is a consequence of $n \rightarrow \pi^*$ excitation while the diradical III arises by β-cleavage from a $\pi \rightarrow \pi^*$ excited state; both cleavage reactions would then be under stereoelectronic control.[13]

Curie law plots of the intensities of the $\Delta m = 2$ lines vs. $1/T$ lead to the conclusion that both I and III are ground-state triplets. This is intriguing because the next member of the series, the 1,3-cyclobutanedione diradical (VI), has been predicted to be a ground-state singlet.[15]



VI

Acknowledgment. We thank Philip Garner and Raymond Schappert for early exploratory studies, Celia Go for preparing starting materials, and, particularly, Professor David W. Pratt for helpful discussions and assistance with the ESR measurements. This research was generously supported by the National Science Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial suport of this research.

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[15] Gleiter, R.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 214. Schleyer, P. v. R.; Budzelaar, P. H. M.; Cremer, D.; Kraka, E. *Ibid.* **1984**, 23.

[16] Also kindly pointed out by Professors Matthew Platz and Dennis Dougherty.

Synthesis of a Helical Metallocene Oligomer

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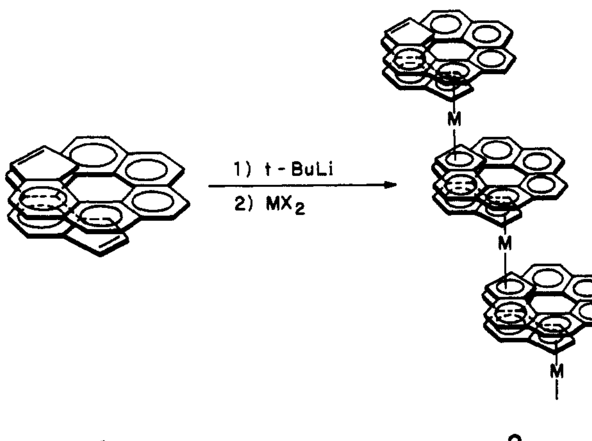
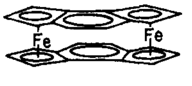
Received August 19, 1985

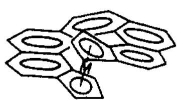
Helicenes that are sufficiently large and capped by unsaturated five-membered rings should yield previously unknown conjugated polymeric metallocenes (eq 1),[1] for, unlike planar hydrocarbons, helicenes cannot form dimers like **3**,[2,3] and they cannot form monomers like **4**[4,5] if their five-membered rings do not superimpose. If the polymeric metallocenes were optically active, their conductive, magnetic, and optical properties might be unusual. We are reporting the synthesis and optical properties of the first, an oligomer with 3–4 units.



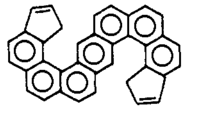
1 2 (1)



3



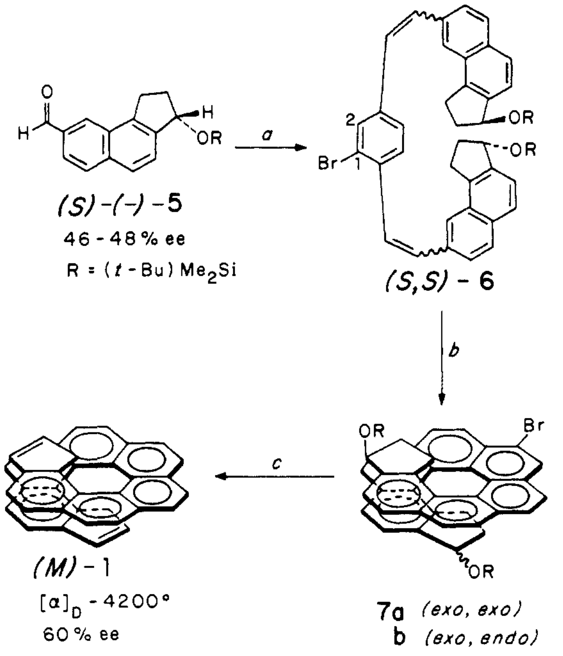
4a (M = Fe)
b (M = $Co^+ PF_6^-$)



8

The preparation of hydrocarbon **1** (Scheme I) is easy and has three features.[6-9] (1) A bromine directs the photocyclization by blocking both the position it occupies (C-1) and the one adjacent (C-2).[7] In its absence, the cyclization gives only the planar isomer **8**.[7a] (2) Propylene oxide consumes HI generated during photoirradiation, preventing ROH functions from being eliminated prior to cyclization.[5] In its absence, (*R*,*R*)-**6** gives helical product, but

Scheme I



[a] 1,4-*bis*[$(C_6H_5)_3P^+CH_2$]-2-Br-C_6H_3 $2Br^-$ (0.5 equiv wt),[7] LiOEt (1.1 equiv wt), EtOH, 25 °C, 5–12 h, 95–100% yield.

[b] $h\nu$, C_6H_6, I_2 (2.2 equiv wt), propylene oxide, 4–12 h.

[c] (1) *t*-BuLi, tetrahydrofuran, −78 °C; (2) H_2O; (3) *p*-toluenesulfonic acid, C_6H_6, 80 °C, 10 min (45–56% yield from **6**).

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[1] (a) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. *Organometallic Polymers*; Academic Press: New York, 1978. (b) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149.

[2] Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1979**, *101*, 4259.

[3] (a) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc.* **1964**, *86*, 3169. (b) Katz, T. J.; Balogh, V.; Schulman, J. *Ibid.* **1968**, *90*, 734.

[4] (a) Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* **1982**, *104*, 346. (b) Pesti, J. Ph.D. Dissertation, Columbia University, New York, NY, 1981.

[5] Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179.

[6] For (*S*)-(−)-**5**, see ref 5.

[7] (a) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.*, in press. (b) Contamination by material with skeletal structure **8** is ≤5%.

[8] New compounds exhibited satisfactory NMR, IR, and (except for the salts) mass spectra (including, for key compounds, high-resolution mass spectra). The olefinic and allylic proton resonances of **1** (supplementary material) are shifted, as expected, to higher field than in simpler indenes.[1,4b,5]

[9] Isomers of **6** in which both ether functions are in the other benzylic position do not give appreciable amounts of helical product. When the ethers are in the non-benzylic position the product is helical, but the ethers could not be eliminated.[10]

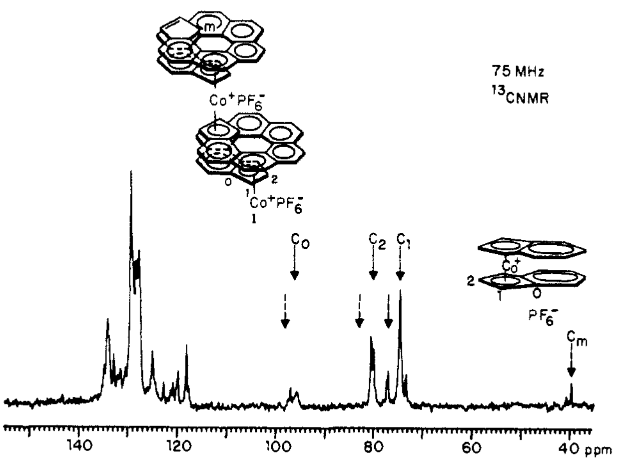

Figure 1. 75-MHz proton-noise-decoupled ^{13}C NMR spectrum of **2** in CD_3COCD_3. The spectrum, measured by using 90° pulses and no relaxation delay, is displayed with 5 Hz line broadening. The chemical shifts were measured assuming that of CD_3COCD_3 to be 29.8 ppm. Peaks assigned to metallocene carbons are pointed out, and the dotted arrows show where the corresponding resonances appear for the indene analogue (pictured). The peak marked C_m is attributed to the methylene carbon (labeled on the diagram).

it is racemic.[11] (3) The direction in which the helix winds is that favoring silyloxyls outside the helix.[12,13] Helicity is thus controlled by the stereochemistry of **5**.[5]

When the sample of helicene **1** in Scheme I is combined in tetrahydrofuran first with *tert*-butyllithium and then with $CoBr_2 \cdot DME$ (DME = 1,2-dimethoxyethane) and the product is oxidized in aqueous HCl with $FeCl_3$, addition of NH_4PF_6 precipitates a red cobaltocenium salt (64% yield after washing with water and ether and drying).[5,14,15] It is soluble in acetone and acetonitrile and is unaffected by heating in air at 260 °C.

Evidence that this material is a short polymer of structure **2** (M = $Co^+PF_6^-$) is the following. The ^{13}C NMR spectrum (Figure 1) shows how metal and hydrocarbon are linked. The spectrum consists only of resonances characteristic of benzenoid helicenes (including **1**)[16] (135–118 ppm),[17] diindenylcobalt(III) salts (80–74 ppm),[18] and the methylene group of **1** (40 ppm, this last one small, corresponding to ca. two end groups for every three to four cobalts).[16,18] The shift of the cyclopentadienyl resonances 2 ppm to higher field than in diindenylcobalt(III) corresponds to the shift of the carbon-2 resonance in [7]helicene[17] (where this carbon is above another ring) from that in [4]helicene.[19] The absence of resonances around 51.3 ppm, characteristic of 1,1′-bi-1*H*-indene ["bi(3-indenyl)"], is also significant, showing that the transition-metal ions do not couple the carbanions by oxidation.

The fast atom bombardment (FAB) mass spectrum,[20] measured by S. Naylor and D. H. Williams in Cambridge, identifies the material as a mixture of oligomers. Thus the only prominent peaks correspond to oligomers with the following compositions:[21] $HArCo^+ArH$ (*m/e* 965), $HArCo^+ArCo^+ArH$ (*m/e* 1476), and $HArCo^+ArCo^+ArCo^+ArH$ (*m/e* 1987). The conclusion that two to four units are linked is also supported by elemental analyses, which correspond to 3.13 hydrocarbons, 2.13 $CoPF_6$'s, and 3.45 ± 1.4 H_2O's,[16] and therefore a number average molecular weight of ca. 1.9×10^3.

The optical activity is very large, $[\alpha]_D$ −26 000° for 100% enantiomeric excess (ee),[23] 4.1 (±0.6) times greater than that of **1**. The molar ellipticities of the CD peaks at 474 and 263 nm (-8.4×10^5 and -3.3×10^6, assuming the molecular weight to be 1.9×10^3) are 7.2 and 6.0 times larger than for the corresponding peaks in **4b**.[5]

Acknowledgment. We are grateful to the National Science Foundation (DMR-82-13794) and the National Institutes of Health (GM-34737) for support, to Christopher Turner and Michael Zagorski for assistance in measuring NMR spectra, and to D. H. Williams and S. Naylor for the FAB mass spectrum.

Supplementary Material Available: Elemental analyses of **2**, ^{1}H and ^{13}C NMR spectra of **1**, and CD and UV spectra of **1** and **2** (5 pages). Ordering information is given on any current masthead page.

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[10] Sudhakar, A. Ph.D. Dissertation, Columbia University, New York, NY, 1985.

[11] Prepared from (*R*)-**5** [46–52% enantiomeric excess (ee)] and irradiated in the presence of traces of iodine, it gives helical bis(indene) (containing the bromine) whose $[\alpha]_D$ (+82°) corresponds to ca. 1% ee. The double bonds in this material are shifted from their position in **1**.[10]

[12] The absolute configurations of **1** and **5** and **1**'s ee were assigned as in ref 5.

[13] (*S,S*)-**6** gives 27% (*M*)-**7a** (recognized by the symmetry of the ^{1}H NMR after debromination), 12% **7b**, and no detectable (^{1}H NMR) endo,endo isomer. The major product cannot have the endo,endo structure since the *M* configuration requires more asymmetric carbons with R stereochemistry than are present in **6**.[10]

[14] Kölle, U.; Khouzami, F. *Chem. Ber.* **1981**, *114*, 2929.

[15] $FeCl_2 \cdot 2(THF)$ gives an elusive product. (Diindenyliron is similarly sensitive. See: Treichel, P. M.; Johnson, J. W.; Calabrese, J. C. *J. Organomet. Chem.* **1975**, *88*, 215.)

[16] See the supplementary material.

[17] Defay, N.; Zimmermann, D.; Martin, R. H. *Tetrahedron Lett.* **1971**, 1871.

[18] Köhler, F. H. *Chem. Ber.* **1974**, *107*, 570.

[19] The second protonated carbon in the first ring counting from the inside of the helix.

[20] (a) Barber, M.; Bordoli, R. S.; Elliott, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A. (b) Rinehart, K. L., Jr. *Science (Washington, D.C.)* **1982**, *218*, 254.

[21] 3-Nitrobenzyl alcohol matrix,[22] 8-keV Xe^+ beam. Ar is $C_{36}H_{20}$. It is the monocations, formed by reduction, that are detected.

[22] Meili, J.; Seibl, J. *Org. Mass Spectrom.* **1984**, *19*, 581.

[23] Measured by using a sample prepared from **1** whose ee was 60%.

Molecular Discrimination in the Formation of Mixed Crystals of Some Substituted Chlorocinnamic Acids

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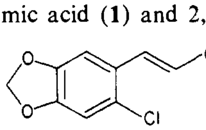
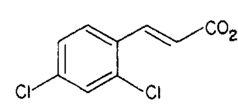
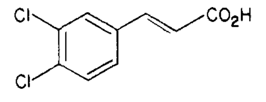
A study of the packing of mixed crystals is a valuable approach toward understanding weak intermolecular interactions in organic solids.[1] We have found that 6-chloro-3,4-(methylenedioxy)cinnamic acid (**1**) and 2,4-dichlorocinnamic acid (**1a**) form a distinct 2:1 complex, **2a**, which is neither a solid solution nor a mixture of **1** and **1a**.[2] Yet, acid **1** and 3,4-dichlorocinnamic acid (**1b**) cocrystallize from EtOH not only as a 1:1 complex, **2b** (mp 217–218 °C), but also as variable-melting solids with compositions between 7:1 and 1:3 of **1** and **1b**. These differences between the closely related acids **1a** and **1b** may be used to monitor the im-



1



1a



1b

2a = $(1)_2(1a)$ **2b** = (1)(1b)

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[1] Kitaigorodskii, A. I. *Mixed Crystals*; Springer-Verlag: Berlin, Heidelberg, 1984.

[2] Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1984**, 145.

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