hole over both macrocycles in Zn_2-I$^{+\cdot}$.[3a,b] The fluorescence lifetime of H_4-I is 8 ns, compared with 7.5 ns for monomer H_2-VII (CH_2Cl_2). The ESR spectra of the photoexcited triplet states of H_4-I and H_2-VII or Zn_2-I and Zn-VII are nearly indistinguishable.[15] Thus, it is evident that neither of these latter types of measurements distinguishes between monomers and dimers, in this case, although they have frequently been used to make this distinction in vivo.

Acknowledgment. We thank the Ribermag Corporation and Professor Djerassi for their generous assistance in obtaining the mass spectrum of H_4-I. This work was supported by NSF Grant PCM7926677. NMR spectra were obtained at the Stanford Magnetic Resonance Laboratory, supported by NIH and NSF grants RR00711 and GR23633, respectively. Fluorescence lifetimes were obtained at the Stanford Synchrotron Radiation Laboratory, supported by NIH Grant 01209-01. S.G.B. is a Sloan and Dreyfus Fellow.

(15) Measured in 2-MeTHF glasses at 80 K, 400-700-nm broadband excitation, 400-Hz light modulation.

Biosynthesis of Streptonigrin from [U-$^{13}C_6$]-D-Glucose. Origin of the Quinoline Quinone[1,2]

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Since the introduction of the use of [1,2-$^{13}C_2$]acetate to study terpenoid and polyketide metabolism,[5] precursors doubly labeled with carbon-13 have been used to investigate a host of complex biosynthetic problems.[6] This powerful method derives from the simple principle that two adjacent carbons simultaneously enriched in carbon-13 give rise to a pair of new coupled signals in the corresponding ^{13}C NMR spectrum. These coupled pairs appear as satellites about the natural abundance carbon signal, producing an easily recognized trio of resonances. Any intervening process which breaks an intact ^{13}C–^{13}C bond results instead in a simple enrichment of the appropriate sites in the resulting metabolite and a corresponding enhancement of the relevant natural abundance signals.

Recently Cane et al.[7] used a variation of the doubly labeled acetate technique in which uniformly ^{13}C-labeled glucose ([U-$^{13}C_6$]glucose) was used as an in vivo precursor of [1,2-$^{13}C_2$]-acetyl-CoA, leading to the demonstration of the mevalonoid origin of pentalenolactone and its precursor pentalenic acid by interpretation of the derived ^{13}C NMR spectra. Logically, this methodology should be applicable to the study of additional products of glucose metabolism.[8,9] Thus, the presence of a chain

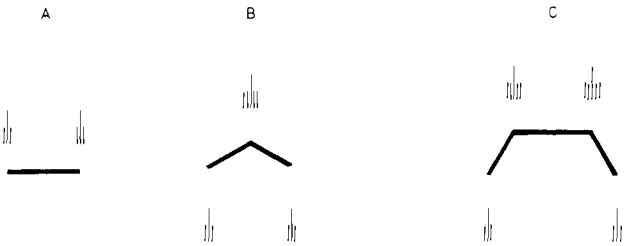

Figure 1. Schematic representation of carbon chains in which each carbon is enriched with carbon-13 and showing the expected NMR spin-coupled signal patterns. (A) A two-carbon unit; (b) a three-carbon unit; (C) a four-carbon unit.

of three labeled carbon atoms derived intact from glucose should yield a characteristic pattern consisting of two trios, corresponding to each end of the chain, and a quintet, resulting from the central carbon atom. The quintet would arise from the superposition of a triplet corresponding to those species in which both neighboring carbons are labeled and a doublet resulting from those species in which either one or the other of the adjacent carbons is enriched with ^{13}C.[10] Similarly, a four-carbon unit could be recognized by the resulting pattern of trio–quintet–quintet–trio. Each of these various coupling relationships, illustrated schematically in Figure 1, is easily recognized by the characteristic coupling constants and should be directly verifiable by the appropriate homonuclear ^{13}C–^{13}C decoupling experiments.

By way of example, the utility of such an approach can be readily envisioned for shikimic acid derived metabolites. Shikimic acid, the apparent precursor of numerous families of natural products, has been the subject of intensive investigations[11] and is now known to be derived from glucose by the combination of an intact four-carbon unit, erythrose 4-phosphate, and an intact three-carbon unit, phosphoenol pyruvate. However, studies of the biosynthesis of shikimate derived metabolites using singly labeled samples of glucose have frequently been difficult to interpret because of competition between alternative metabolic pathways which result in indirect labeling of numerous additional sites in the derived metabolites.[12]

We expected that the utilization of [U-$^{13}C_6$]glucose would be effectively transparent to scrambling processes while remaining opaque to the direct incorporation of intact biosynthetic units, regardless of the manner of their derivation from glucose. To test our proposal we have studied the antitumor antibiotic streptonigrin (**1**). The biosynthesis of this metabolite has been extensively investigated by Gould and his collaborators, who have shown that the 4-phenylpicolinic acid moiety is derived from tryptophan (**2**)—a shikimate metabolite—via a putative β-carboline intermediate.[13] These studies had failed, however, to implicate any known pathway in the formation of the remaining, quinoline, portion of **1**.[14] We have now obtained evidence from a single

(1) This is Part 5 in the series "The Biosynthesis of Streptonigrin".
(2) Reported at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 29–April 3, 1981.
(3) Career Development Awardee of the National Cancer Institute (CA 00627), 1979–1984.
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(6) For a review, see: McInnes, A. G.; Walter, J. A.; Wright, J. L. C.; Vining, L. C. In "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley-Interscience: New York, 1976; Vol. 2; pp 154–167.
(7) Cane, D. E.; Rossi, T.; Tillman, A. M.; Pachlatko, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 1838.
(8) White has used [U-$^{13}C_6$]glucose in an investigation of thiamine biosynthesis in which the distribution of label was examined by mass spectrometry: White, R. H. *Biochemistry* **1978**, *17*, 3833.
(9) Rinehart has recently independently reported the use of [U-$^{13}C_6$]-glucose to confirm the shikimate origin of the C_7N unit of pactamycin and used homonuclear decoupling to confirm the observed labeling patterns: Rinehart, K. L., Jr.; Potgieter, M.; Delaware, D. L.; Seto, H. *J. Am. Chem. Soc.* **1981**, *103*, 2099.
(10) (a) The doublets contributing to lines 2 and 4 of a quintet arise because the precursor is not 100% labeled at each site and from competing scrambling processes which reduce the percentage of intact biosynthetic units. (b) The predicted quintet pattern is based on the assumption that $J_{AB} \sim J_{BC}$. For the more general case a more complex pattern of up to nine lines would be expected. Such patterns have in fact been observed in some cases by expansion at high resolution, as illustrated in the supplementary material. (c) The center resonance of the quintet would be superimposed on both the natural abundance signal and an enhanced signal due to indirect enrichment by competing pathways.
(11) Haslam, E. C. "The Shikimate Pathway"; Halsted Press: New York, 1974; Ganem, B. *Tetrahedron* **1978**, *34*, 3353.
(12) Cf.: Srinivasan, P. R.; Shigeura, H. T.; Sprecher, M.; Sprinson, D. B.; Davis, B. D. *J. Biol. Chem.* **1956**, *220*, 447. Hornemann, U.; Kehrer, J. P.; Eggert, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 1045. Haber, A.; Johnson, R. D.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 3541.
(13) Gould, S. J.; Chang, C. C. *J. Am. Chem. Soc.* **1980**, *102*, 1702.

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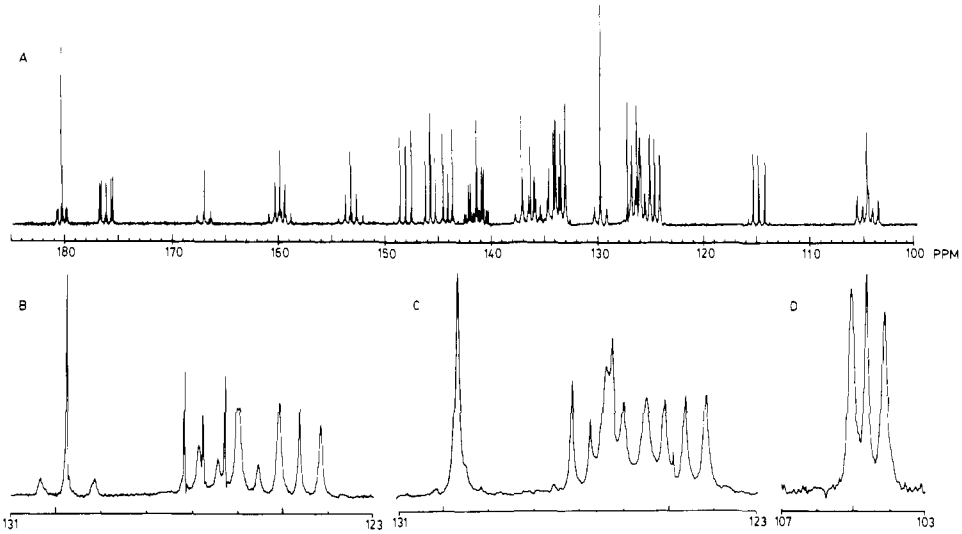
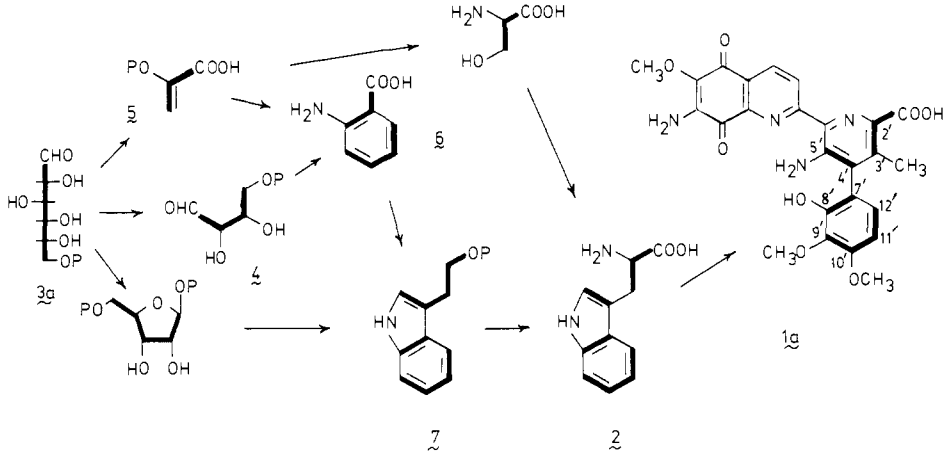


Figure 2. 62.85-MHz proton-noise decoupled ^{13}C NMR spectra of **1a**. Spectral parameters: Bruker WM 250, spectral width 11 904 Hz; 32K data points; quadrature detection; 25° pulse width; 0.54-s acquisition time; 12 857 data points zero fill; 12 mg in 0.5 mL of Me_2SO-d_6. (A) Fully ^{13}C-coupled spectrum (exclusive of the four methyl resonances): 62 500 transients, 2-Hz line broadening; (B) expansion of the 123–131-ppm region of (A) showing signals 16 (trio), 17 (trio), 18 (quintet), and 19 (trio); (C) same region as (B) upon irradiation of signal 4, showing collapse of signals 16 (to a singlet) and 18 (to a trio); (D) signal 21 of (A) upon irradiation of signal 5.

Scheme I



feeding experiment for the identity of all the primary precursors to the antibiotic. [U-$^{13}C_6$]Glucose (**3a**) has been fed to a culture of *Streptomyces flocculus*, resulting in the specific labeling of all carbon atoms of streptonigrin and revealing the size and location of each of the primary precursors by analysis of the ^{13}C–^{13}C spin-coupling patterns.

After preliminary studies with [6-^{14}C]glucose (**3b**), a mixture of 1.2 g of **3a** (80 atom % ^{13}C/position), 1.8 g of unlabeled glucose, and 10 μCi of **3b** was divided and added aseptically to three 500-mL fermentation broths[17] in 2-L Erlenmeyer flasks 24 h after inoculation with a growing seed culture.[18] The fermentations were then incubated an additional 48 h and worked up in standard fashion to afford 25 mg of pure, labeled streptonigrin **1a**.

Aside from the four upfield methyl signals, which appeared as enhanced singlets,[19] all of the remaining 21 carbons in the 62.85-MHz ^{13}C NMR spectrum of **1a** (Figure 2a) had been enriched and were spin coupled to at least one ^{13}C neighbor. Fourteen signals appeared as trios, while six resonances appeared as quintets.[20] Only one signal, corresponding to C-2′, was a multiplet whose pattern could not be clearly analyzed due to severe overlap with adjacent resonances. An additional noteworthy feature was a further 11-Hz splitting of the resonances centered at 176.2 and 141.4 ppm, apparently due to long-range coupling. Finally, the ratio of the satellites to the central lines of the trios at 180.3, 137.1, and 129.7 ppm were significantly smaller than the corresponding ratios for the remaining 11 trios, indicating a proportionally greater contribution of scrambling processes to the labeling of these three carbons.

Although the entire ^{13}C NMR spectrum of **1** had not been previously assigned unambiguously, the assignment of several key signals were already secure: the chemical shifts of C-2′, ^{16}C-3′,[13] and C-5′[15] had been assigned by feedings of specifically labeled tryptophans, those of C-3, C-4, C-11′, and C-12′ had been deduced

(14) No incorporation into the quinoline moiety of **1** was obtained in experiments with [β-^{14}C]tryptophan,[13] [7a-^{14}C]tryptophan,[15] [^{14}COOH]-anthranilate,[13] [β-^{14}C]tyrosine,[13] [β-^{14}C]phenylalanine,[13] [U-^{14}C]shikimate,[13] [2-^{14}C]pyruvate,[16] [2-^{14}C]acetate,[16] [1,2-$^{13}C_2$]acetate,[16] [4-^{14}C]aspartate,[16] [1-^{14}C]fumarate,[16] [3,4-^{14}C]glutamate,[16] and [1,4-^{14}C]succinate.[16]

(15) Gould, S. J.; Chang, C. C.; Darling, D. S.; Roberts, J. D.; Squillacote, M. *J. Am. Chem. Soc.* **1980**, *102*, 1707.

(16) Gould, S. J. et al., unpublished observations.

(17) The previously described fermentation conditions[13] were used except that the initial concentration of glucose in the nutrient medium was reduced to 7.0 g/L.

(18) Labeled glucose was added 12 h prior to the usually observed onset of antibiotic production.

(19) The four methyl carbons have previously been shown to be derived from methionine.[13] The lack of coupling between the aromatic C-methyl and C-3′ signals indicates sufficient dilution of the glucose pool so as to insure that observed couplings result only from intact biosynthetic units.

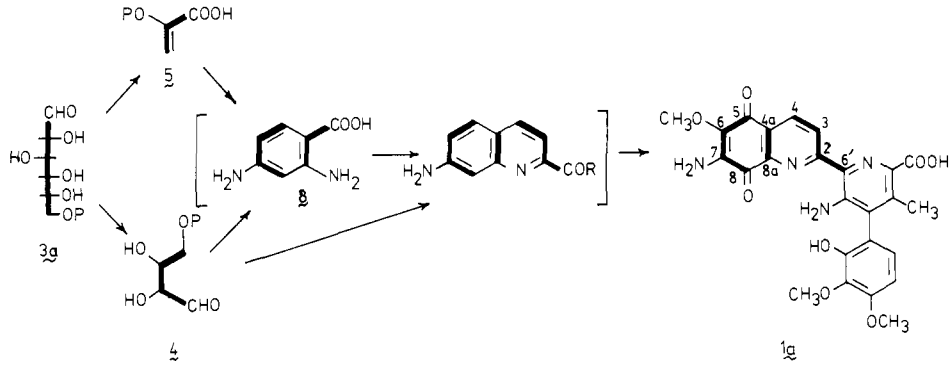
(20) The original ^{13}C NMR assignments of Lown and Begleiter (Lown, J. W.; Begleiter, A. *Can. J. Chem.* **1974**, *52*, 2331) were based exclusively on empirical chemical shift additivity parameters. The majority of these assignments must be revised in light of subsequent incorporation experiments[13,15] and the present study.

Table I. ^{13}C NMR Spectrum of 1a

carbon	chemical shift, δ	signal no.	method of assignment	multiplicity	J_{CC}, Hz	^{13}C–^{13}C decouplings: signal irrad	^{13}C–^{13}C decouplings: change obsd
9′	137.1	10	*d*	trio	75	5	trio → singlet
10′	153.2	5	*c, d*	quintet	78, 67	21	quintet → trio
11′	104.7	21	*b*	quintet	64, 58	5	quintet → trio
						19	quintet → trio
12′	124.6	19	*b, d*	trio	59	21	trio → singlet
4′	134.1	14	*d*	trio	64	7	trio → singlet[g]
5′	145.7	7	*e*	trio	60		
7′[f]	114.8	20	*d*	trio	68		
8′[f]	148.0	6	*c, d*	trio	68	20	trio → singlet
2′	134.6	13	*e*	m	*h*	3	*g*
3′	136.3	11	*e*	trio	70		
COOH	167.1	3	*a*	trio	77		
5	176.2	2	*a*	doublet of trios	70, 11		
6	136.0	12	*d*	quintet	70, 75	2	quintet → trio
7	141.4	9	*d*	doublet of quintets	72, 57, 11	2	d of quintet → quintet
						1	d of quintet → trio
8	180.3	1	*a*	doublet of trios	57, 7		
4a[f]	126.8	17	*c, d*	trio	56	8	trio → singlet
8a[f]	144.1	8	*c, d*	trio	56		
6′	129.7	16	*d*	trio	72	4	trio → singlet
2	159.9	4	*d*	quintet	74, 57		
3	126.0	18	*b*	quintet	57, 57	4	quintet → trio
4	133.5	15	*b*	trio	57		

[a] Assigned by chemical shift correlations. [b] Assigned by SFORD experiments on 1. [c] Assigned with help of $^3J_{CH}$ from gated decoupled spectrum of 1. [d] Assigned by ^{13}C–^{13}C homonuclear decouplings (spectrum of 1a). [e] Assigned by incorporation of specifically labeled tryptophans. [f] These pairs of signals may be interchanged. [g] Only signal that changed upon irradiation, but new line pattern not clean. [h] Not measurable.

Scheme II



by SFORD experiments, and C-5, C-8, and the carboxyl carbon had been recognized by correlation with typical quinones and acids. The remaining 11 carbon atoms were unambiguously assigned by detailed analysis, including homonuclear ^{13}C–^{13}C decoupling,[21] of the fully ^{13}C-coupled spectrum of **1a**. The data are summarized in Table I.

Since the biosynthesis of tryptophan (**2**) is well established,[11] that portion of streptonigrin derived from **2** was used as an internal control for the correct analysis of the spectrum of **1a**, as shown in Scheme I. Thus, the erythrose-4-phosphate (**4**) derived unit, C-9′–C-12′, exhibited the expected signal pattern (trio–quintet–quintet–trio). These coupling relationships were confirmed by ^{13}C–^{13}C homonuclear decoupling experiments.[22] Irradiation at 124.6 ppm (C-12′) collapsed the signal at 104.7 ppm (C-11′) from a quintet to a trio (Figure 2d); irradiation of C-11′ collapsed the signal for C-12′ (trio → singlet) and the signal at 153.2 ppm (C-10′, quintet → trio); irradiation of C-10′ collapsed the signals at 104.7 (quintet → trio) and 137.1 ppm (C-9′, trio → singlet). C-7′ and C-8′, which are derived from phosphoenol pyruvate (**5**), and have lost their labeled neighbor in the conversion from anthranilic acid (**6**) to indole glycerol phosphate (**7**), appear as a pair of coupled trios while the expected paired signals were observed for C-4′ and C-5′. The multiplicity expected for C-2′ was unambiguously deduced from the fact that each of its neighbors, C-3′ and COOH, appeared as trios.

Similar analysis revealed an intact four-carbon unit at C-5 to C-8. In addition to the usual pattern of trios and quintets, this relationship was further supported by the two-bond 11-Hz coupling between C-5 and C-7, which disappeared upon irradiation of the C-5 resonance. C-4a and C-8a appeared as a coupled pair of trios,[23] suggesting once again a shikimate origin with loss of the carboxyl carbon at some intermediate stage.

The remaining carbon atoms, C-4, C-3, C-2, and C-6′, were found to correspond to a third intact four-carbon unit, the center two carbons giving rise to quintets at 126.0 and 159.9 ppm, respectively. Irradiation of the C-2 quintet confirmed these relationships (see Figure 2b,c).

As shown in Scheme II, the observed labeling pattern of the quinoline moiety can be accounted for by a shikimate derived

(21) For an earlier example of the use of ^{13}C–^{13}C decoupling to interpret the spectrum of a multiply enriched polyketide, see: McInnes, A. G.; Smith, D. G.; Walter, J. A.; Vining, L. C.; Wright, J. L. C. *J. Chem. Soc., Chem. Commun.* **1975**, 66.

(22) Homonuclear ^{13}C–^{13}C decoupling was performed on a Bruker WM 250 NMR spectrometer by using a BSV-3X broadband amplifier and 62.85-MHz fixed frequency plugin and normal spectral acquisition parameters.

(23) The alternative placement of the two-carbon unit at C-6/C-7 is firmly excluded by the observation of long-range $^3J_{C-H}$ couplings for the resonances at 144.1 and 126.8 ppm in a gated decoupled spectrum of **1**.

4-aminoanthranilic acid (**8**)[24] condensing with a third erythrose-4-phosphate with loss of the carboxyl group of **8**. This new quinoline-generating pathway would be directly analogous to tryptophan biosynthesis (Scheme I) and is supported by the apparent excess enrichment of C-8, C-6′, and C-9′, each of which is apparently derived from C-1 of **4**. The previously observed[27] equilibrium between (glucose derived) fructose diphosphate and the triose phosphates would be expected to generate a subpopulation of labeled erythrose in which the aldehyde carbon is no longer coupled to its neighbor.

Although the identity of the precursors to streptonigrin will have to be confirmed by specific feeding experiments, the study reported here clearly demonstrates the value of [U-$^{13}C_6$]glucose in elucidating complex biosynthetic pathways.

Acknowledgment. This work was supported by grants from the NIH, CA 27339 (S.J.G.) and GM 22172 (D.E.C.). Initial ^{13}C NMR spectra were obtained by Peter Demou on a Bruker HX 270 spectrometer at the Northeast Regional NSF-NMR Facility, Yale University, partially supported by the National Science Foundation, Grant CHE 79-16210. The Bruker WM 250 spectrometer at Brown University was purchased with funds provided by the NSF and the Montedison Company. We thank Tzyy-Chyau Liang, Brown University, for carrying out the ^{13}C–^{13}C decoupling experiments. Strains of *S. flocculus* were a gift of Dr. John DeZeeuw of Chas. Pfizer, Inc.

Registry No. 1a, 80206-29-7; **2**, 80206-30-0; **3a**, 80206-31-1; **4**, 80206-32-2; **5**, 80206-33-3; **6**, 80206-34-4; **7**, 80206-35-5.

Supplementary Material Available: Additional ^{13}C NMR spectra of **1a**, including expansions of significant regions and additional ^{13}C–^{13}C decoupling experiments (5 pages). Ordering information is given on any current masthead page.

(24) The same C_6N_2 unit may also be involved in the formation of the structurally related metabolites, lavendamycin[25] and nybomycin.[26]
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(27) Ugurbil, K.; Brown, T. R.; den Hollander, J. A.; Glynn, P.; Shulman, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3742. den Hollander, J. A.; Brown, T. R.; Ugurbil, K.; Shulman, R. G. *Ibid.* **1979**, *76*, 6096.

Synthesis of a Helical Ferrocene

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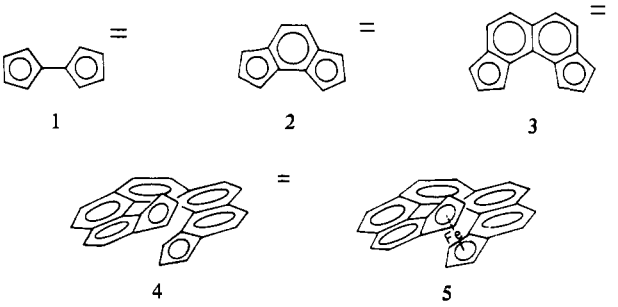
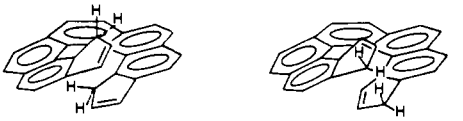
Hydrocarbon dianions comprised of a pair of conjugated cyclopentadienyl anions, such as **1**,[1] **2**,[2] or **3**,[3] as well as other examples,[3,4] react with transition-metal halides to yield dimeric sandwich molecules. However, were many more angularly fused rings than in **2** or **3** to separate the terminal rings, the hydrocarbon would be helical[5] and incapable of giving the analogous dimer,[3] and were the fused ring system to contain five benzene rings, a unique opportunity would arise.[6] The cyclopentadienyl rings would almost superimpose (structure **4**), and if a metal cation, say ferrous, were to unite them as in **5**, the product would be an unprecedented metallocene with unbroken conjugation between its planes.[7] We are reporting here the synthesis of the first example of such a structure.



1 2 3 4 5

The initial stage involved synthesizing the [7]-helicene analogue **6** and was carried out as outlined in Scheme I. Notable features



6 7

are the use of the abundant 2,7-dihydroxynaphthalene,[8] the vinyl ketone cyclization as a means for fusing an unsubstituted cyclopentenone to the 1,2-positions of a naphthalene,[9,10] the photocyclization uniting only the α carbons of the naphthalenes to give the helical structure despite the congesting saturated rings,[11,12] and the confirmation of the structure of hydrocarbon **6**[13] by X-ray diffraction.[16]

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(6) Šlusarek, W. Dissertation, Columbia University, New York, 1977.
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(9) This has been done before only with 2-naphthyl vinyl ketones that are substituted on the double bond.[10a-c] Unsubstituted 1-naphthyl vinyl ketone has been cyclized as well.[10d]
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(13) The ^1H NMR spectrum [(300 MHz, C_6D_6) δ 7.80 (d, J = 8.6 Hz), 7.78 (d, J = 8.2 Hz), 7.75 (s), 7.62 (d, J = 8.6 Hz), 7.62 (d, J = 8.6 Hz), 7.41 (d, J = 8.6 Hz) [total aromatic integration = 10.71 H], 6.42 (d of t, 1.52, J = 5.6 Hz, J' = 1.7 Hz), 5.72 (d of t, 1.61, J = 5.6 Hz, J' = 1.7 Hz), 2.35 d of t, 2.08, J = 24.1 Hz, J' = 1.9 Hz), 2.02 (d of br t, 2.08, J = 23.6 Hz, $J' \sim$ 1.4 Hz)[14]] supports the structure inasmuch as the olefinic signals are shifted upfield from their positions in simpler indenes[3] (in $CDCl_3$, by 0.5 and 0.8 ppm, respectively) by the shielding effect of the opposing rings[15a] and inasmuch as there are two different allylic proton resonances.
(14) The pattern of the aromatic resonances resembles that due to the corresponding protons in [7]helicene.[15]
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