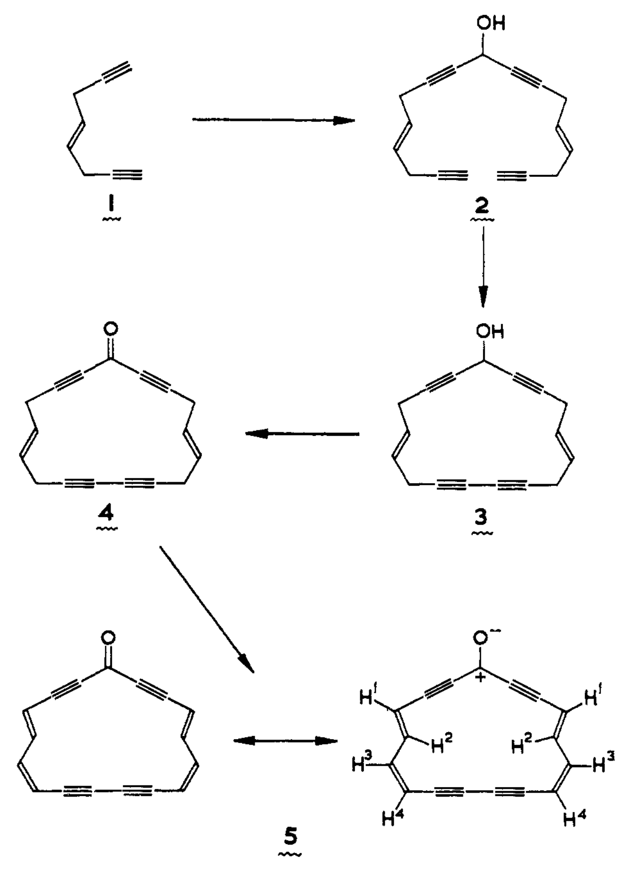
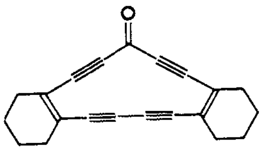
The Synthesis of 2,8,10,16-Tetradehydro[17]annulenone. The Demonstration of a Paramagnetic Ring Current in a [4*n* + 1]Annulenone Derivative[1]

Sir:

Planar monocyclic conjugated ketones (annulenones)[2] are expected to be aromatic if they contain a (4*n* + 3)-membered ring and nonaromatic if they contain a (4*n* + 1)-membered ring.[3] The most convenient method for studying aromaticity in the annulene series involves measurement of the nmr spectra, the aromatic [4*n* + 2]annulenes exhibiting a diamagnetic ring current and the nonaromatic [4*n*]annulenes a paramagnetic ring current.[4] There is already evidence for a diamagnetic ring current in the [4*n* + 3]annulenones cyclopropenone[5] and tropone.[6] We now report the synthesis of 2,8,10,16-tetradehydro[17]annulenone (4,6,12,14-cycloheptadecatetraene-2,8,10,16-tetrayn-1-one) (**5**), the nmr spectrum of which for the first time clearly shows the existence of a paramagnetic ring current in a [4*n* + 1]annulenone derivative. A similar effect could not be observed definitely in the case of the previously prepared substituted [13]annulenone derivative **6**,[2] also made up of a (4*n* + 1)-membered ring, since the molecule contains no protons bound directly to the conjugated ring.[7]

Treatment of *trans*-4-octene-1,7-diyne (**1**)[8] with 1 molar equiv of ethylmagnesium bromide and then with 0.5 molar equiv of ethyl formate in tetrahydrofuran at room temperature yielded 60% of *trans,trans*-4,13-heptadecadiene-1,7,10,16-tetrayn-9-ol (**2**),[9] mp 46–48°. This alcohol was coupled with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene at 60°. The resulting 17-membered ring cyclic alcohol **3**,[9,10] isolated in 40% yield by chromatography on silica gel, showed mp 123.5–125.5°; λ_{max}^{EtOH} 227 mμ (ϵ 340), 240 (350), and 253 (200); mass spectrum, molecular ion *m/e* 234. Oxidation of **3** with chromium trioxide (Jones reagent) led to over 90% of the rather unstable ketone **4** as pale yellow crystals, which decomposed on attempted melting point determination; λ_{max}^{EtOH} 233 mμ (ϵ 9300) and 250 sh (7600); $\nu_{max}^{CHCl_3}$ 1625 (s) cm^{-1} (C=O); mass spectrum, molecular ion *m/e* 232.





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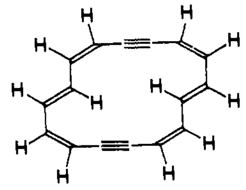

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The ketone **4** in undistilled tetrahydrofuran [reagent grade (stabilized with 0.1% of hydroquinone), dried over sodium] was treated with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol at −70 to −20° for 30 min. The only colored product, isolated in *ca.* 5% yield by chromatography on silica gel, proved to be the tetradehydro[17]annulenone **5**. Compound **5** was a very unstable dark red crystalline substance, which decomposed rapidly in the solid state; $\lambda_{max}^{Et_2O}$ 304 mμ

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[1] Unsaturated Macrocyclic Compounds. LXIV. For part LXIII, see G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 5611 (1968).

[2] See G. M. Pilling and F. Sondheimer, *ibid.*, **90**, 5610 (1968).

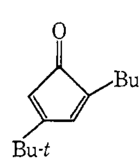
[3] See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

[4] J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967); Special Publication No. 21, The Chemical Society, London, 1967: F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, p 75; H. C. Longuet-Higgins, p 109.

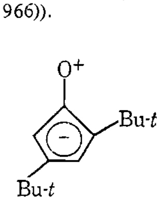
[5] See R. Breslow and L. J. Altman, *J. Amer. Chem. Soc.*, **88**, 504 (1966); N. J. McCorkindale, R. A. Raphael, W. T. Scott, and B. Zwanenburg, *Chem. Commun.*, 133 (1966); R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967).

[6] See D. J. Bertelli, C. Golino, and D. L. Dreyer, *ibid.*, **86**, 3329 (1964).

[7] The relatively high field positions of the ring proton resonances in the nmr spectrum of the [4*n* + 1]annulenone derivative 2,4-di-*t*-butylcyclopentadienone (i) may also be due to a paramagnetic ring current, although they were ascribed to contributions from ii (E. W. Garbisch and R. F. Sprecher, *ibid.*, **88**, 3433, 3434 (1966)).



i



ii

[8] Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *ibid.*, **90**, 4940 (1968).

[9] The structural assignment was supported by the ir and nmr spectra, as well as by the elemental analysis.

[10] The conversion of **1** to **3** is based on analogous syntheses carried out previously with 1,5-hexadiyne (C. C. Leznoff and F. Sondheimer, *ibid.*, **90**, 731 (1968)) and 1,2-diethynylcyclohexene.[2]

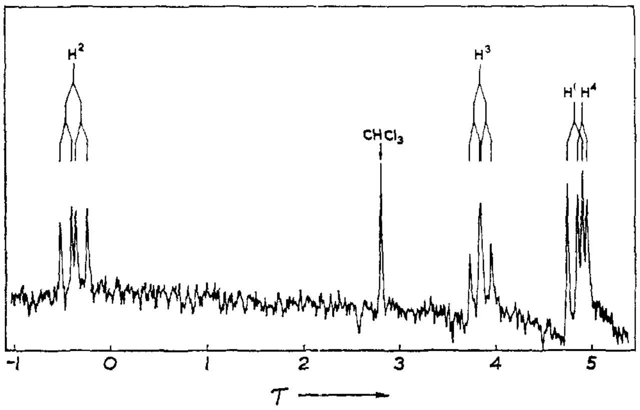


Figure 1. *Nmr spectrum at 35° of 2,8,10,16-tetradehydro[17]-annulenone* (**5**), *measured in deuteriochloroform at 100 MHz.*

(ϵ 48,000), 461 (710), *ca.* 500 sh (640), and *ca.* 550 sh (250);[11] $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2190 (s) ($C\equiv C$), 1628 (s) ($C=O$), 1585 (m) ($C=C$), and 980 (m) (*trans* $C=C$); mass spectrum, molecular ion *m/e* 228, base peak *m/e* 200 (M − CO). Catalytic hydrogenation of **5** in ethanol over 10% palladium-charcoal led to cycloheptadecanone (identified by mass spectral comparison with an authentic sample), showing the compound to be monocyclic.

The nmr spectrum of **5** at 35°[12] (Figure 1) confirms the structure. The 2H double doublet at τ −0.31 is assigned to the inner H^2 protons ($J_{2,1}$ = 16 Hz, $J_{2,3}$ = 12 Hz), the 2H incompletely resolved double doublet at τ 3.88 to the outer H^3 protons ($J_{3,2}$ = 12 Hz, $J_{3,4}$ = 10 Hz), the 2H doublet at τ 4.87 to the outer H^1 protons ($J_{1,2}$ = 16 Hz), and the 2H doublet at τ 4.95 to the outer H^4 protons ($J_{4,3}$ = 10 Hz). The assignments were confirmed by frequency-swept double-irradiation experiments. The low-field position of the inner protons and the high-field position of the outer protons resemble those of the similarly placed protons in 1,9-bisdehydro-[16]annulene (**7**) at −80° (inner protons, τ 0.2; outer protons, τ 3.92–4.55)[13] and clearly indicate the existence of a magnetically induced paramagnetic ring current in the annulenone **5**.

Dehydroannulenes have been prepared previously by isomerization of certain cyclic polyacetylenes with potassium *t*-butoxide in *t*-butyl alcohol, and this procedure usually yielded small amounts of dehydroannulenes containing two fewer protons than the precursors as by-products.[14] By comparison, the presently observed formation of **5** (containing four fewer protons than the precursor **4**) as sole product is unusual. However, treatment of **4** in freshly distilled tetrahydrofuran with potassium *t*-butoxide in *t*-butyl alcohol at −70 to −20° yielded two new unstable red substances (probably also dehydro[17]annulenones), and no **5**. Unfortunately, these compounds decomposed on attempted determination of the mass spectra, and the structures are still unknown.

Acknowledgments. We are indebted to the Science Research Council for financial support and to Dr. R. H. Mitchell for determining the mass spectrum of **5**.

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[11] The ϵ values are approximate and represent minimum values.

[12] The spectrum at −60° was essentially unchanged.

[13] I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4954 (1968).

[14] F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, **84**, 4595 (1962); R. Wolovsky, *ibid.*, **87**, 3638 (1965); F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966); I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, **90**, 4946 (1968).

A Dimeric Iron(III) Complex Containing Two Ethyl Mercaptide and Two Ethyl Thioxanthate Groups as Bridging Ligands

Sir:

Recently we have been investigating the coordination chemistry of iron–sulfur complexes of possible relevance to certain nonheme iron protein (NHIP) systems.[1,2] Since sulfur-bridged iron(III) dimers and higher oligomers have been postulated for the NHIP,[3,4] one objective of our research has been to prepare and characterize inorganic analogs of similar structure. The reaction shown in eq 1 ($R = C_6H_5CH_2$) was discovered

$$Fe(S_2CSR)_3 \xrightarrow[C_2H_5OH]{THF} [Fe(S_2CSR)_2(SR)]_2 + 2CS_2 \qquad (1)$$

by one of us[5] during the course of a systematic investigation of trithiocarbonate ester complexes of nickel.[6] The product was originally formulated as a μ-benzylthio-bis(benzyltrithiocarbonato)iron(III) dimer (isomer II below) by analogy to the nickel complexes, although no physical measurements were reported at that time.[5] Since the reaction shown in eq 1 provides an interesting route to possible NHIP analogs, we decided to study it and the products more carefully. The present communication reports the solid-state and solution structural characterization of the compound, $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$.

The ethyl complex was prepared according to eq 1[7] and recrystallized from carbon disulfide–pentane. *Anal.* Calcd for $C_8H_{15}S_7Fe$: C, 24.5; H, 3.86. Found: C, 24.4; H, 3.91. Dark red-brown prisms suitable for X-ray diffraction studies were obtained. Preliminary Weissenberg and precession photographs revealed the Laue symmetry, 2/m, with lattice constants $a = 12.19 \pm 0.01$ Å, $b = 8.47 + 0.01$ Å, $c = 19.82 \pm 0.01$ Å, $\beta = 130.1 \pm 0.1°$, and space group $P2_1/c$. The measured density, ρ = 1.64 g/cc, is in good agreement with the value calculated for four formula units of $C_8H_{15}S_7Fe$ per unit cell, 1.66 g/cc. Intensity data were collected on a Picker full-circle automated diffractom-

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[1] D. Coucouvanis and S. J. Lippard, *J. Am. Chem. Soc.*, **90**, 3281 (1968).

[2] D. Coucouvanis and S. J. Lippard, *ibid.*, **91**, 307 (1969).

[3] A. San Pietro, Ed., "Non-Heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.

[4] R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967).

[5] D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

[6] Work on the nickel complexes is actively being pursued in Professor J. P. Fackler's laboratory, Case-Western Reserve University.

[7] The complex $[Fe(S_2CSC_2H_5)_3]$ has been previously reported by Ewald and Sinn.[8]

[8] A. H. Ewald and E. Sinn, *Austral. J. Chem.*, **21**, 927 (1968).