mg) at room temperature and atmospheric pressure. The reaction was terminated after 8 min, when 8.5 cc (ca. 3.3 molar equiv) of hydrogen had been absorbed. The product was isolated as previously and chromatographed on alumina (150 g, Alcoa F-20). Pentane-ether (95:5) eluted [16]annulene (1.2 mg, 5%, estimated spectroscopically) and then dehydro[16]annulene, compound A (7.2 mg, 31%, estimated spectroscopically; 5.4 mg, mp 86–87°, isolated by crystallization). Each of these substances was identified with the respective authentic sample by mixed tlc and by ultraviolet spectroscopy.

C. By Partial Hydrogenation of Dehydro[16]annulene, Compound A. A solution of compound A (25 mg) in benzene (10 ml) was stirred in hydrogen with a 10% palladium–calcium carbonate catalyst (25 mg) at room temperature and atmospheric pressure. The reaction was terminated after 5 min, when 9.2 cc (ca. 3.3 molar equiv) of hydrogen had been absorbed. The catalyst was removed,

the solvent was replaced by pentane, and the solution was chromatographed on alumina (100 g, Alcoa F-20). Elution with pentane–ether (95:5) gave [16]annulene (2.8 mg, 11%, estimated spectroscopically) and then recovered dehydro[16]annulene, compound A (5.5 mg, 22%, estimated spectroscopically). Each of these substances was identified with the respective authentic sample by mixed tlc and by ultraviolet spectroscopy.

Unsaturated Macrocyclic Compounds. LX.[1] The Nuclear Magnetic Resonance Spectra of Dehydro[16]annulenes
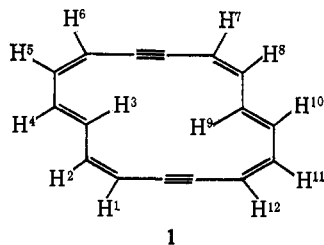
I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer[2]

Contribution from the Daniel Sieff Research Institute, the Weizmann Institute of Science, Rehovoth, Israel, and the University Chemical Laboratory, Cambridge, England. Received March 27, 1968

Abstract: The synthesis of several dehydro[16]annulenes was described in the previous paper. The nmr spectra of three of these substances have been determined, and it is shown that compound A is 1,9-bisdehydro[16]annulene (1), compound B is 1,3,9-tridehydro[16]annulene (4), and compound C is 1,3-bisdehydro[16]annulene (5). The nmr spectra are temperature dependent, due to exchange of the protons on the *trans* double bonds. Compounds 4 and 5 are the first dehydroannulenes in which interconversion between nonequivalent conformers is observed, and 4 is also the first example of a dehydroannulene in which the protons on a *trans* double band adjacent to an acetylene are being transferred between internal and external positions. The fact that the inner protons in all three compounds 1, 4, and 5 appear at considerably lower field than the outer protons provides evidence for the existence of a magnetically induced paramagnetic ring current, as predicted for dehydro[4n]annulenes.

The synthesis of four dehydro[16]annulenes (compounds A, B, C, and D) was described in the previous paper.[1] The nmr spectra of three of these substances are now discussed. The spectra show that compound A is 1,9-bisdehydro[16]annulene (1), compound B is 1,3,9-tridehydro[16]annulene (4), and compound C is 1,3-bisdehydro[16]annulene (5). Compound D was too unstable for a satisfactory nmr spectrum to be obtained (although an interesting low-field band at ca. τ −4 was apparent), and its structure is still unknown.

Compound A (1,9-Bisdehydro[16]annulene) (1). The nmr spectrum of compound A at 35° (Figure 1, top)

1

clearly established the 1,9-bisdehydro[16]annulene structure 1 (no conformation implied). It consists of a 4 H

quartet at τ 2.12 assigned to the equivalent H^3, H^4, H^9, H^{10} protons, a 4 H octet at τ 4.12 assigned to the equivalent H^2, H^5, H^8, H^{11} protons, and a 4 H doublet at τ 4.73 assigned to the equivalent H^1, H^6, H^7, H^{12} protons.[3–5] The equivalence of the various sets of protons is due to the fact that the H^3, H^4, H^9, H^{10} protons on the two *trans* double bonds are interchanging positions at such a rate that average values for the band positions result.[6–9] The spectrum is of the same type as the spectra of 1,5-bisdehydro[12]annulene (2)[4,5,9,10] and the "partially rearranged C_{14} cyclic monomer" (1,3,5,10-cyclotetradecatetraene-7,13-diyne) (3),[5,9,11] both of which contain the same yne-(*cis*)ene-(*trans*)ene-(*cis*)-

(1) For Part LIX, see I. C. Calder, Y. Gaoni, and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 4646 (1968).
(2) To whom inquiries should be addressed at the Chemistry Department, University College London, London W. C. 1, England.

(3) Extended nmr spectra of 1 (determined at 60 Mcps in carbon tetrachloride), in which the band patterns are more easily recognized, have been published by us.[4,5]
(4) F. Sondheimer, *Pure. Appl. Chem.*, 7, 363 (1963).
(5) F. Sondheimer, *Proc. Roy. Soc.* (London), A297, 173 (1967).
(6) The fact that the nmr spectra of various annulenes consists of a singlet at higher temperatures, but of widely separated bands at lower temperatures, is due to the same type of interchange process.[5,7–9]
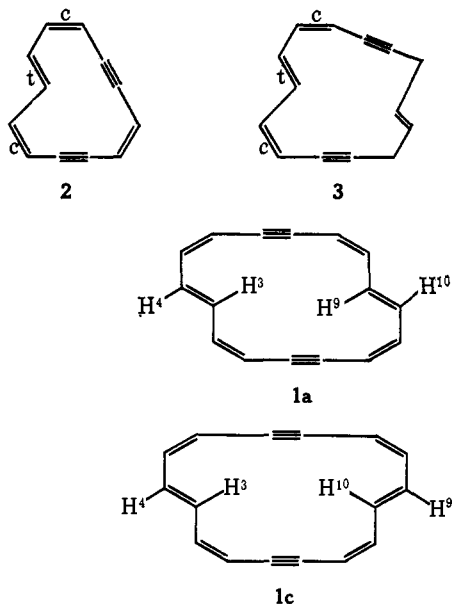(7) G. Schröder and J. F. M. Oth, *Tetrahedron Lett.*, 4083 (1966).
(8) I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).
(9) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75.
(10) R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, 87, 5720 (1965). The use of first-order analysis in the interpretation of the nmr spectrum of 2 reported in this paper is probably unjustified.
(11) Y. Gaoni and F. Sondheimer, to be published.

2   **3**

1a

1b

1c

1d

spectrum consists of a 2 H complex band at *ca.* τ 0.8 assigned to H³ and H⁸, a 1 H multiplet at τ 1.5 assigned to H⁴, a 1 H doublet at τ 2.65 ($J = 15$ cps) assigned to H⁷, and two complex groups of signals (3 H each) at τ 3.8–4.7 and 5.0–5.4. The band at τ 3.8–4.7 (see Figure 3) consists of three partially resolved overlapping double doublets at τ 3.95 ($J = 11$, 8 cps), 4.30 ($J = 11$, 9 cps),
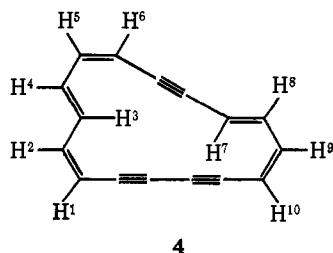
ene-yne chromophore as **1**, and in which the same interchange process occurs.

The explanation for the equivalence of the various sets of protons of **1** in the spectrum at 35° is confirmed by the effect on the spectrum of cooling an acetone-d_6 solution (see Figure 1). The H³, H⁴, H⁹, H¹⁰ quartet at τ 2.12 becomes progressively broader, until at $-70°$ it has coalesced. At $-80°$, a new 2 H band at τ 0.2 has appeared, assigned to the inner H³, H⁹ protons. In addition, a new 2 H resonance (H⁴, H¹⁰) is present in the same region (τ 3.92) as the outer H², H⁵, H⁸, H¹¹ protons. Clearly, the interchange of the protons on the *trans* double bonds is sufficiently slow at $-80°$ for discrete inner H³, H⁹ and outer H⁴, H¹⁰ protons to be seen. As expected, the location of the H³, H⁴, H⁹, H¹⁰ quartet at 35° (τ 2.12) is close to the average (τ 2.06) of the inner H³, H⁹ and outer H⁴, H¹⁰ band positions at $-80°$.

Four conformers of **1** are possible (**1a–d**),[12] of which **1a** is equivalent to **1b**, and **1c** is equivalent to **1d**. Analogous nmr spectral arguments to those made above can be applied to all of these conformers. With the data available, it is not possible to determine the relative importance of **1a,b** compared with **1c,d**.

An estimate of 9.0 kcal/mol has been made for the free-energy barrier for interconversion of the inner and outer protons in **1**.[13]

Compound B (1,3,9-Tridehydro[16]annulene) (4). Compound B was assigned the 1,3,9-tridehydro[16]-annulene structure **4** (no conformation implied) on the basis of the nmr spectrum (Figure 2). At 35°, the

4

and 4.55 ($J = 11$, 8.5 cps); the two lower field double doublets are together assigned to H² and H⁹, and the one at highest field to H⁵. The band at τ 5.0–5.4 (see Figure 3) appears to consist of a double doublet at *ca.* τ 5.15
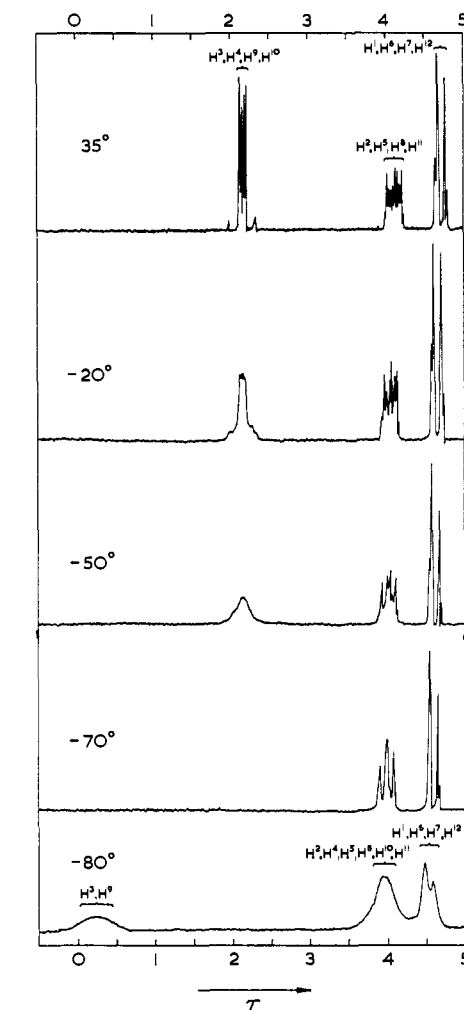

Figure 1. Nmr spectra at various temperatures of compound A (1,9-bisdehydro[16]annulene) (**1**), measured in acetone-d_6 at 100 Mcps.

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(12) The assumption is made that planar or near-planar conformers of **1**, **4**, and **5** are energetically favored. The large difference in the chemical shift of protons in an "internal" and an "external" environment suggest that this assumption is justified.

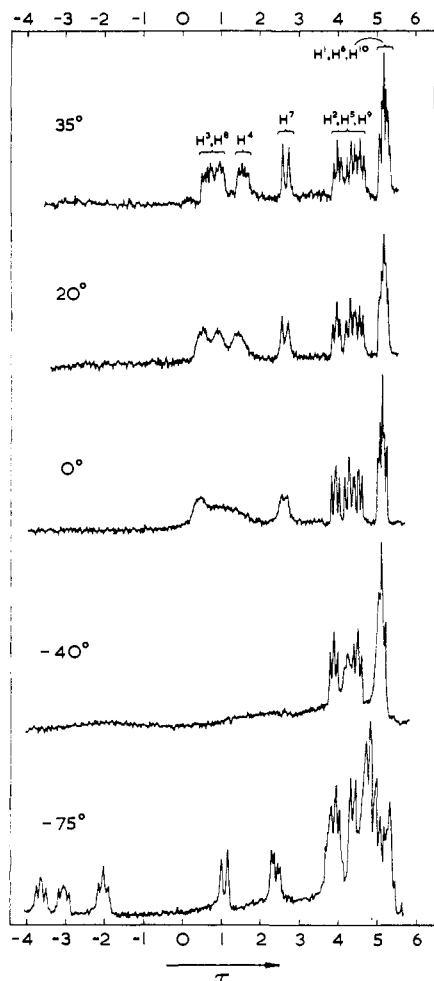(13) I. C. Calder and P. J. Garratt, *J. Chem. Soc., B*, 660 (1967).

Figure 2. Nmr spectra at various temperatures of compound B (1,3,9-tridehydro[16]annulene) (4), measured in acetone-d_6 at 100 Mcps.
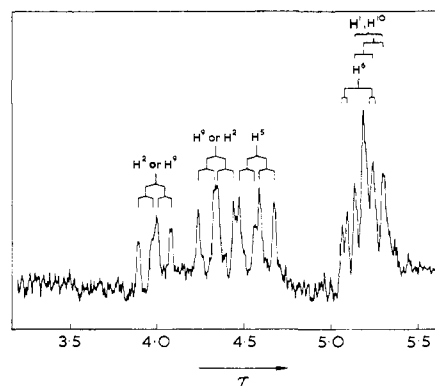

Figure 3. Nmr spectrum at 35° of compound B (1,3,9-tridehydro-[16]annulene) (4), measured in acetone-d_6 at 100 Mcps (expanded scale).

($J = 15$, 2.5 cps) assigned to H^6 and two doublets ($J = 11$ cps) assigned to H^1 and H^{10}.

The above assignments are based mainly on frequency-swept double-irradiation nmr experiments. Irradiation at τ 0.6 (H^3 or H^8, see below) caused the collapse of the double doublet at τ 3.95 (H^2 or H^9) to a doublet, while irradiation at τ 0.9 (H^3 or H^8, see below) caused the collapse of the double doublet at τ 4.30 (H^2 or H^9) to a doublet. Irradiation at τ 1.5 (H^4) caused the collapse of the double doublet at τ 4.55 (H^5) to a doublet. Irradiation of the 5.0–5.4 band at the position of the H^6 signal (*ca.* τ 5.15) again caused the collapse of the double doublet at τ 4.55 (H^5) to a doublet, while irradiation at the position of the H^1 and H^{10} protons caused the collapse of the H^2 and H^9 double doublets to doublets. Unfortunately, on irradiation at τ 2.65 (H^7) it was not possible to observe the behavior of the H^3, H^8 band, and it is therefore not possible to distinguish between the signals due to H^3 and H^8.

The nmr spectrum of 4 exhibits thermal effects of the same type as described above for 1. On cooling an acetone-d_6 solution of 4 (see Figure 2), the τ 0.8 signal due to H^3 and H^8 at first separates into two distinct bands (τ 0.6 and 0.9 at 20°). These bands broaden on further cooling, as do the bands at τ 1.5 (H^4) and 2.65 (H^7). At 0°, the H^3, H^8, and H^4 signals have merged to a single band at *ca.* τ 0–2, and the H^7 doublet has lost its

fine structure. At $-40°$, the H^3, H^8, H^4, and H^7 bands have coalesced, and the H^2 or H^9 signal at *ca.* τ 4.2 has lost its fine structure. On further cooling, new low-field signals appear. At $-75°$, the spectrum is well resolved, and consists of double doublets at τ -3.60 ($J = 15$, 12 cps), -3.05 ($J = 15$, 12 cps), and -2.00 ($J = 14$, 10 cps), a doublet at τ 1.10 ($J = 15$ cps), a double doublet at τ 2.40 ($J = 15$, 5 cps), and a complex signal at τ 3.5–5.6. The integration (*ca.* 0.4, 0.4, 0.6, 0.6, 0.6, and 7.5 H, respectively) shows that each of the bands except that at highest field is less than one proton in intensity, indicating that the spectrum is due to a "frozen" mixture of *conformers*.

Double irradiation at $-75°$ of the τ 2.40 signal caused the collapse of the doublet at τ 1.10 to a singlet and the disappearance[14] of the double doublet at τ -3.05.

The four conformers which can be considered for 4 are 4a–d,[12] but it is not possible to decide their relative importance. However, we assign the $-75°$ signals at τ -3.60, -2.00 to H^3, H^4, the signal at τ -3.05 to H^8,


4a

4b

4c

4d
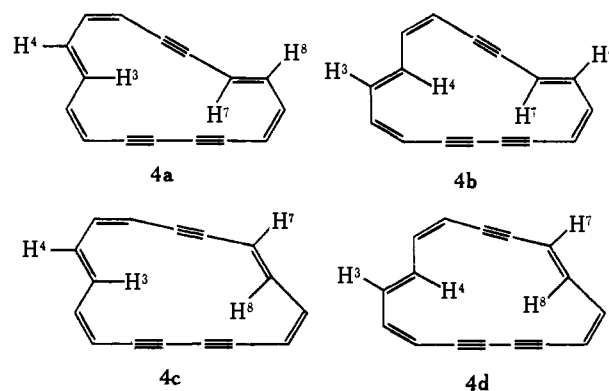
and the signal at τ 1.10 to H^7 when these protons are in an *internal* environment. The band at τ 2.40 is assigned to H^8 in an *external* environment, while the external H^3, H^4, and H^7 protons presumably occur as part of the τ 3.5–5.6 band. The relatively high-field position of the internal H^7 proton and the relatively low-field position of the external H^8 proton are attributed to these protons being in the cone of shielding and deshielding, respectively, of the lone acetylene. The disappearance of the signal at τ -3.05 on irradiation of the signal at τ 2.40 supports the view that both of these bands are due to

(14) See I. C. Calder, P. J. Garratt, and F. Sondheimer, *Chem. Commun.*, 41 (1967).

the same proton which is being transferred between two different environmental positions at a rate such that spin–spin relaxation has not completely occurred.[14]

From the above-described assignments and integration at −75°, it appears that a conformer in which H^7 is internal (4a,b) is slightly preferred to one in which H^7 is external (4c,d).

Compound C (1,3-Bisdehydro[16]annulene) (5). Compound C was assigned the 1,3-bisdehydro[16]-annulene structure 5 (no conformation implied) on the
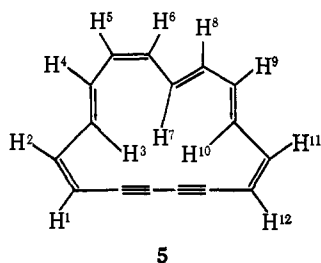
5

basis of the nmr spectrum (Figure 4). At 0°,[15] the spectrum consists of a 1 H double doublet at τ −3.05, a 2 H quintet at τ −0.50, a 2 H quintet at τ 1.85, a 5 H complex group of signals between τ 4.2 and 5.3, and a 2 H doublet at τ 5.50.

The spectrum is approximately first order and proved amenable to first-order analysis. The low-field double doublet at τ −3.05 is a unique proton coupled to two nonequivalent protons; it is on a "non-averaging" *trans* double bond and is assigned to the inner H^7 proton ($J_{7,8} = 15.5$ cps, $J_{7,6} = 11$ cps). The τ −0.50 quintet consists of two overlapping double doublets at τ −0.53 ($J = 15.5, 8.5$ cps) and τ −0.48 ($J = 15.5, 9.5$ cps) assigned to H^3, H^{10}; the positions of these bands are attributed to the protons being on "averaging" *trans* double bonds and which are spending a greater proportion of the time inside the ring. The τ 1.85 quintet consists of two overlapping double doublets at τ 1.80 assigned to H^4 ($J_{4,3} = 15.5$ cps, $J_{4,5} = 8$ cps) and τ 1.87 assigned to H^9 ($J_{9,10} = 15.5$ cps, $J_{9,8} = 9$ cps); the positions of these bands are again attributed to the protons being on "averaging" *trans* double bonds, but which are spending a greater proportion of the time outside the ring. The signals between τ 4.2 and 5.3 appear to consist of two overlapping double doublets at τ 4.42 ($J = 10.5, 9$ cps) and 4.55 ($J = 10.5, 10$ cps) assigned to H^2, H^{11}, two almost coincidental double doublets at *ca.* τ 4.8 assigned to H^6, H^8, and a double doublet at τ 5.22 assigned to H^5 ($J_{5,6} = 11$ cps, $J_{5,4} = 8$ cps). The doublet at τ 5.50 is assigned to H^1, H^{12} on the basis[9] of the high-field chemical shift and the presence of only one large coupling constant ($J = 10.5$ cps). Since the compound is a bisdehydro[16]annulene[1] and the nmr spectrum shows that only two protons are next to an acetylene, the molecule must contain the assigned 1,3-diacetylene linkage.

The assignments were supported by frequency-swept double-irradiation nmr experiments. Irradiation at the frequency of H^7 caused the collapse of the H^6, H^8 double doublets to two overlapping doublets. Irradiation at the frequency of H^3, H^{10} caused the collapse of both the H^4, H^9 and the H^2, H^{11} double doublets each to two overlapping doublets. Irradiation at the frequency of H^4, H^9 caused collapse of the H^3, H^{10}

(15) The interpretation of the 0° spectrum was used, since solutions at higher temperatures decomposed comparatively quickly.
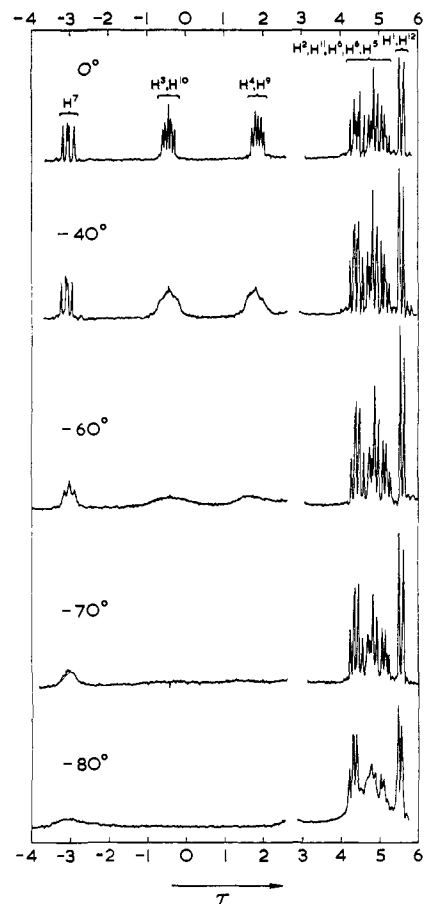
Figure 4. Nmr spectra at various temperatures of compound C (1,3-bisdehydro[16]annulene) (5), measured in acetone-d_6 at 100 Mcps.

double doublets to two overlapping doublets, the collapse of *one* of the double doublets at *ca.* τ 4.8 (H^8) to a doublet, and the collapse of the H^5 double doublet to a doublet. Irradiating the spectrum between τ 4.42 and 4.55 (H^2, H^{11}) caused a large change in the H^3, H^{10} signal, but complete decoupling could not be attained. Irradiation at the frequency of H^6, H^8 caused the H^7 double doublet to collapse to a singlet and the H^4, H^9 double doublets to a doublet superimposed on a double doublet.

The nmr spectrum of 5 exhibits the same type of thermal effects as described for 1 and 4. On cooling an acetone-d_6 solution of 5 to −40° (see Figure 4), the signals due to H^3, H^{10} and H^4, H^9 broaden and lose their fine structure, while the remainder of the spectrum is virtually unchanged. At −60°, the H^7 signal has become a triplet. At −70°, the H^3,H^{10} and H^4,H^9 bands have coalesced, and the H^7 resonance has now become broad. At −80°, the signals due to H^6, H^8, and H^5 have broadened and lost their fine structure.

The temperature effects are presumably due to the slowing down of the interchange of the H^3, H^4, H^9, and H^{10} protons between the internal and external environments. We consider that the H^7,H^8 protons are not interchanging between internal and external positions (although these protons are on a *trans* double bond), since H^8 in the 0° spectrum appears at the position of a normal nonexchanging vinyl proton. The broadening of the H^7, H^6, H^8, and H^5 bands is probably due to the
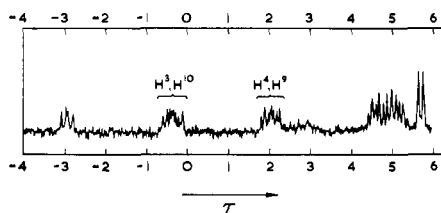
Figure 5. Nmr spectrum at 40° of compound C (1,3-bisdehydro-[16]annulene) (5), measured in carbon tetrachloride at 100 Mcps.

difference in environment of each of these protons in the conformers.

The four conformers of 5 are 5a–d,[12] only rotation about the H^3,H^4 and the H^9,H^{10} trans double bonds being considered. The chemical shifts suggest that H^3, H^{10} occupy an inner position about two-thirds of the

5a   5b

5c   5d
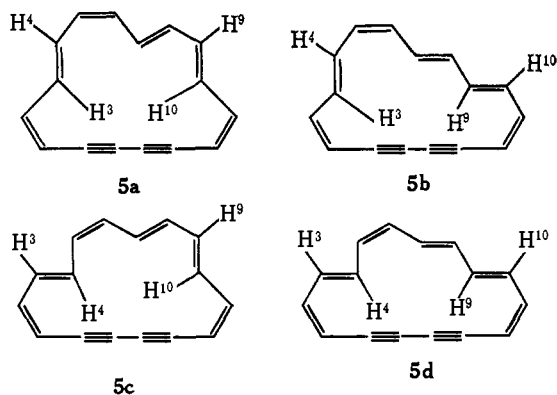
time, whereas H^4, H^9 occupy an inner position about one-third of the time. Cooling to lower temperatures

than −80° would presumably give information about the relative contribution of the various conformers.

On warming a carbon tetrachloride solution of 5, the chemical shifts of H^3 and H^{10} become different from each other, as do those of H^4 and H^9. As a result, at 40° (Figure 5) the H^3, H^{10} and H^4, H^9 bands each exhibit eight lines. The substance decomposed relatively quickly at 40°, and it was not possible to investigate the spectrum at higher temperatures.

Conclusion

The substances 4 and 5 are the first dehydroannulenes in which interconversion between *nonequivalent* conformers has been observed. Substance 4 is also the first example of a dehydroannulene in which the protons on a *trans* double band adjacent to an acetylene are being transferred between internal and external positions.

The fact that the inner protons in all three compounds 1, 4, and 5 appear at considerably lower field than the outer protons provides evidence for the existence of a magnetically induced paramagnetic ring current. Each of the three substances has 16 out-of-plane π electrons, and this finding (which parallels that made with [16]annulene)[7] is in accord with the predictions made for [4n]annulenes and dehydro[4n]annulenes.[16]

(16) 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); H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109.

The Mechanism of Hydrolysis of Methyl Pseudo-2-benzoylbenzoate in Aqueous Sulfuric Acid[1]

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Contribution from the Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079. Received February 28, 1968

Abstract: The hydrolysis of methyl pseudo-2-benzoylbenzoate (2) in 1 M aqueous sulfuric acid is characterized by a ΔS^* of −19.4 eu and a D_2O solvent isotope effect of $k_{H_2O}/k_{D_2O} = 0.50$. In 5 M sulfuric acid these values become −19.1 eu and 0.56, respectively. In moderately concentrated sulfuric acid a plot of log k_ψ vs. $−H_0$ is linear with a slope of 0.67. A plot of log k_ψ + H_0 vs. H_0 + log [H$^+$] shows downward curvature. The slopes, ϕ, are 0.66 at 1 M and 0.41 at 5 M. In 90% aqueous acetonitrile containing sulfuric acid (−)-menthyl pseudo-(−)-2-benzoylbenzoate undergoes racemization much faster than hydrolysis. Thus, the evidence supports a mechanism which is bimolecular.

Several attractive mechanisms can be written for the acid-catalyzed hydrolysis of partial acylals, 1. Since these compounds are the esters of hemiacetals they could choose to react, as most simple esters do,[3]

by the $A_{Ac}2$ mechanism shown in Scheme I. On the other hand 1 might prefer to react as most acetals do[4] (A1 mechanism, Scheme I). Considering 1 as an ester the A1 mechanism would correspond to the $A_{Al}1$ mecha-

(1) Presented, in part, at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S175.
(2) Taken in part from the M.S. Theses submitted by A. G. (1966) and R. F. (1967) to Seton Hall University.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 767; M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).
(4) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).