Unsaturated Macrocyclic Compounds. LIX.[1] The Synthesis of Four Dehydro[16]annulenes and [16]Annulene

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Abstract: Oxidation of *trans*-4-octene-1,7-diyne (1) with oxygen, cuprous chloride, and ammonium chloride led to the cyclic dimer 2, the linear dimer 3, the linear trimer 4, the linear tetramer 5, and a chloro compound of unknown constitution. Treatment of the cyclic dimer 2 with potassium *t*-butoxide gave mainly phenylsuccindene-10 (6), as well as smaller amounts of three dehydro[16]annulenes (compounds A, B, and C). The data given in the present paper, together with the nmr spectra described in the following one, show that compound A is 1,9-bis-dehydro[16]annulene (7), compound B is 1,3,9-tridehydro[16]annulene (8), and compound C is 1,3-bisdehydro-[16]annulene (9). Oxidation of the linear dimer 3 with cupric acetate in pyridine and ether resulted in rearrangement as well as coupling, giving rise in low yield to three dehydro[16]annulenes (compounds A, B, and D); in addition, conjugated linear material consisting of hexadecahexaenediyne(s) (type 10) was formed. Compound D is probably another bisdehydro[16]annulene, but its structure could not be determined because of its instability. Catalytic partial hydrogenation of compound A and of compound D, as well as of the mixture of compounds A, B, and D, led to [16]annulene (12) in poor yield. The [16]annulene is identical with that prepared subsequently by Schröder and Oth. The low-temperature nmr spectrum determined by these workers confirms the configuration 12 and provides evidence for the existence of a magnetically induced paramagnetic ring current, as predicted for [4n]annulenes.

In 1961, our group reported in preliminary form the synthesis of several dehydro[16]annulenes and of [16]annulene.[3] This work (which was carried out without the benefits of thin layer chromatography, nmr spectroscopy, or mass spectroscopy) was complicated by the facts that the yields of the dehydro[16]annulenes were low, the mixtures were difficult to separate, and several of these substances are very unstable. Some of the experiments have now been repeated, and the use of the above-mentioned techniques has been found of great help in the separation and structure elucidation of the products. The results have been mentioned in part in several lectures[4-6] and are now reported in detail. The synthetic work is described in the present paper, while the nmr spectra are discussed in the following one.[7]

The starting material was *trans*-4-octene-1,7-diyne (1), the synthesis of which is described in the previous paper.[1] Oxidation of 1 with oxygen, cuprous chloride, and ammonium chloride (Glaser conditions) in ethanol and dilute hydrochloric acid at 55°[8,9] led to a mixture of substances, separated by crystallization and chromatography on alumina. The products proved to be the cyclic dimer 2 (3.0%), the linear dimer 3 (23%), the linear trimer 4 (1.8%), the linear tetramer 5 (1.5%), and a chloro compound of unknown constitu-

tion (Chart I). The structures were assigned on the basis of the spectral data and catalytic hydrogenation experiments, which gave the corresponding known saturated hydrocarbons.

Chart I

3, n=2
4, n=3
5, n=4
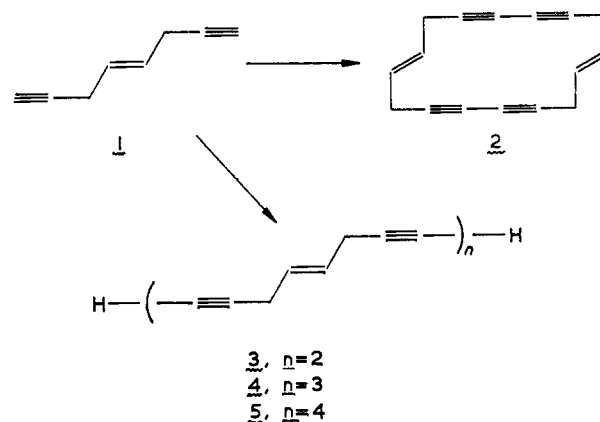
Recently, we have found that it is advantageous to carry out the oxidation of 1 under the Glaser conditions in the presence of benzene.[10-12] These conditions resulted in an increased yield of the cyclic dimer 2 (11%), the yield of the linear dimer 3 (22%) being essentially unchanged. The addition of benzene also has the advantage that the yields of 2 and 3 were reproducible, while the yields of these substances obtained under the original conditions were not constant in repeated experiments.

The oxidation of 1 with cupric acetate in pyridine (Eglinton conditions)[13] has also been studied. This re-

(1) For Part LVIII, see Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 4940 (1968).

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(3) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, 83, 4863 (1961).

(4) F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963).

(5) F. Sondheimer, *Proc. Roy. Soc.*, (London), A297, 173 (1967).

(6) 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.

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

(8) These conditions have been used to convert the related 1,7-octadiyne to the corresponding cyclic dimer, linear dimer, and linear tetramer.[9]

(9) F. Sondheimer and Y. Amiel, *J. Amer. Chem. Soc.*, 79, 5817 (1957).

(10) The finding that this type of oxidation is best carried out in the presence of benzene was made in the coupling of 1,5-hexadiyne to the corresponding cyclic dimer.[11,12]

(11) (a) R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, 87, 5720 (1965); (b) F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, 88, 2610 (1966).

(12) See also R. H. Mitchell and F. Sondheimer, *Tetrahedron*, 24, 1397 (1968).

action led to products derived from the cyclic trimer, tetramer, and pentamer, but no cyclic dimer 2 or derived substances were isolated.[14] These experiments will be reported elsewhere.

It has been shown that linear 1,5-diynes are rearranged to conjugated linear polyenynes with potassium *t*-butoxide in *t*-butyl alcohol,[15] and this reaction has been applied to the synthesis of dehydroannulenes (conjugated macrocyclic polyenynes) containing 12-,[11] 18-,[16,17] 20-,[18] 24-,[16] and 30-membered[16,18] rings from the corresponding cyclic 1,5-diynes. In the preceding paper[1] the rearrangement of linear 1,4-enynes (*e.g.*, 1) to conjugated linear polyenynes was described, and it was shown that this reaction takes place under considerably milder conditions than those used with linear 1,5-diynes. The cyclic dimer 2 is made up of 1,4-enyne units, and we therefore expected that it could be isomerized to a dehydro[16]annulene even more readily than the above-mentioned cyclic 1,5-diynes. This proved to be the case, although the reaction was more complex than anticipated and the yields were poor.

Treatment of the cyclic dimer 2 with potassium *t*-butoxide in *t*-butyl alcohol and benzene at 40° for 1 min effected almost complete conversion of the starting material and gave a solution colored red by the presence of dehydro[16]annulenes. Chromatography on alumina and examination of the various fractions by thin layer chromatography showed that three highly colored dehydro[16]annulenes (compounds A, B, and C) had been formed in poor yield; each of these could be obtained in pure form by careful rechromatography, including chromatography on alumina coated with silver nitrate.[17] In addition, a pale yellow benzenoid compound was isolated. The latter, which was the major product (*ca.* 20% yield), proved to be the known diphenylsuccindene-10 (3,6-dihydro-1,2:4,5-dibenzpentalene, 6),[19] identified by direct comparison with an authentic sample. Similar transannular reactions

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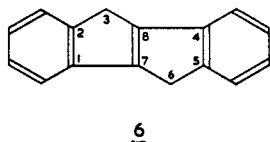
leading to benzenoid compounds have been effected by potassium *t*-butoxide treatment of the cyclic dimer and cyclic trimer of 1,5-hexadiyne, which led to biphenylene[11a] and triphenylene,[16,20] respectively.

Rearrangement of the cyclic dimer 2 ($C_{16}H_{12}$) was expected to give rise to bisdehydro[16]annulenes ($C_{16}H_{12}$). The assumption was therefore made that the three dehydroannulenes were isomeric bisdehy-

dro compounds, named isomers A, B, and C in a previous report.[4] More recently we have found that potassium *t*-butoxide can effect dehydrogenation as well as rearrangement, and dehydroannulenes in the 12-,[11] 14-,[21] and 18-membered[17] ring series have been obtained which contain two fewer protons than the corresponding precursors. The above-mentioned assumption is therefore not justified, and it was necessary to determine accurately the empirical formula of each of the three dehydro compounds.[22] This was done conveniently by mass spectrometry, which showed that "isomers" A and C are indeed bisdehydro[16]annulenes (molecular ion, m/e 204), but "isomer" B is a tridehydro[16]annulene (molecular ion, m/e 202).[23] Consequently these substances are now called compounds A, B, and C, instead of isomers A, B, and C.

Compound A was shown to be 1,9-bisdehydro[16]annulene (7). This substance, formed in *ca.* 2% yield as large brown plates, was considerably more stable
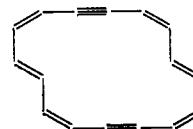
7 (Compound A,
1,9-Bisdehydro[16]annulene)

than the other dehydro[16]annulenes and exhibited a normal melting point (90–91°).[24] The infrared spectrum (KBr) showed bands at 4.65 μ (w) (acetylene) and 10.15 (s), 10.26 μ (s) (*trans* double bond), but no allene band at *ca.* 5.1 μ. The ultraviolet spectrum in isooctane (Table I and Figure 1) exhibited a shoulder at *ca.* 270 mμ (ϵ 40,300), and maxima at 283 mμ (ϵ 54,200) and 296 mμ (ϵ 38,500), with absorption beyond 600 mμ.[25,26] Catalytic hydrogenation in ethyl acetate over a platinum catalyst led to cyclohexadecane, confirming the monocyclic nature of the substance. The properties of compound A clearly demonstrate that it is a bisdehydro[16]annulene. The 1,9-bisdehydro formulation 7 follows from the nmr spectrum, discussed in the following paper.[7]

Compound B[27] was shown to be 1,3,9-tridehydro-

(13) *Inter alia*, see G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); G. Eglinton and W. McCrae, *Advan. Org. Chem.*, 4, 225 (1963).

(14) By comparison, oxidation of 1,7-octadiyne under these conditions has been found to give the corresponding cyclic dimer, in addition to higher cyclic oligomers (F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, 81, 4600 (1959)).

(15) F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *ibid.*, 83, 1682 (1961).

(16) F. Sondheimer and R. Wolovsky, *ibid.*, 84, 260 (1962).

(17) R. Wolovsky, *ibid.*, 87, 3638 (1965).

(18) F. Sondheimer and Y. Gaoni, *ibid.*, 84, 3520 (1962).

(19) K. Brand and K. O. Müller, *Ber.*, 55, 601 (1922); S. Wawzonek, *J. Amer. Chem. Soc.*, 62, 745 (1940); L. Fieser and M. M. Pechet, *ibid.*, 68, 2577 (1946).

(20) Y. Amiel and F. Sondheimer, *Chem. Ind.* (London), 1162 (1960).

(21) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, 82, 5765 (1960); F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, 84, 4595 (1962).

(22) Microanalysis was of little use, since compounds B and C were too unstable for significant analyses to be obtained, and this technique had led us to assign incorrect empirical formulas to related compounds (1,5,9-tridehydro[12]annulene,[11] 1,8-bisdehydro[14]annulene[21]). In the preliminary communication,[3] compound A had also been assigned a wrong empirical formula on the basis of an incorrect microanalysis.

(23) A possible mechanism for the dehydrogenation leading to this compound is given in ref 5, Figure 17.

(24) In the preliminary communication,[3] this substance was obtained from a partial hydrogenation experiment, and considered to be monodehydro[16]annulene on the basis of an incorrect microanalysis. A satisfactory analysis in agreement with the bisdehydro[16]annulene structure has now been obtained (see Experimental Section).

(25) By comparison, the main ultraviolet maxima of mono-, di- and tridehydro[14]annulenes occur at 304–314 mμ,[4,5,21,26] while those of tri- and tetradehydro[18]annulenes occur at 327–335 mμ.[16,17] For a comparison of the ultraviolet spectra of the various dehydroannulenes and annulenes, see P. J. Garratt and K. Grohmann in Houben–Weyls "Methoden der organischen Chemie," Vol. V/IB, E. Müller, Ed., G. Thieme Verlag, Stuttgart, in press.

(26) J. Mayer and F. Sondheimer, *J. Amer. Chem. Soc.*, 88, 602 (1966); Y. Gaoni and F. Sondheimer, unpublished experiments.

(27) In the preliminary communication,[3] this was the only dehydroannulene isolated from this reaction and was tentatively assigned the 1,9-bisdehydro[16]annulene structure 7.

Table I. Ultraviolet Maxima of Dehydro[16]annulenes and [16]Annulene in Isooctane[a]

Compound A (7)	Ca. 270 (40.3),[b] 283 (54.2), 296 (38.5)
Compound B (8)	279 (49.5), 290 (51.5)
Compound C (9)[c]	281 (55.5), 291 (55.0)[d]
Compound D	Ca. 260 (42.2),[b] 272 (62.7), 278 (61.7), 290 (41.7)
[16]Annulene (12)	284 (77.3), ca. 430–450 (0.70)[b]

[a] λ_{max} in millimicrons; ϵ values × 10^{-3} (in parentheses). [b] Shoulder. [c] In pentane. [d] See ref 29.

[16]annulene (8). This substance was obtained in *ca.* 5% yield as dark brown plates, mp 59–60° dec.[28] It was
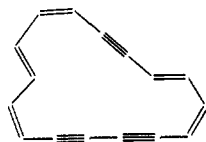
8 (Compound B,
1,3,9-Tridehydro(16)annulene)

very unstable in the solid state, but reasonably stable in solution. The infrared spectrum (chloroform) exhibited bands at 4.58 μ (w) (acetylene) and 10.13 (s), 10.29 μ (m) (*trans* double bond), but no allene bands. The ultraviolet spectrum in isooctane (Table I and Figure 2) showed maxima at 279 mμ (ϵ 49,500) and 290 mμ (ϵ 51,500), with absorption beyond 600 mμ.[25] Catalytic hydrogenation in ethyl acetate over platinum again yielded cyclohexadecane. The properties and the above-mentioned mass spectrum indicate compound B to be a tridehydro[16]annulene. The 1,3,9-tridehydro formulation 8 is based on the nmr spectrum, discussed in the following paper.[7]

Compound C was shown to be 1,3-bisdehydro-[16]annulene (9). This substance was obtained in *ca.* 8% yield in the form of violet solutions. The com-
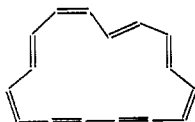
9 (Compound C,
1,3-Bisdehydro[16]annulene)

pound was very unstable; it could not be handled in the neat state due to ready polymerization, and it decomposed fairly rapidly even in solution (see Experimental Section). The infrared spectrum (carbon tetrachloride) exhibited bands at 4.60 μ (w) (acetylene) and 10.12 (m), 10.29 μ (s) (*trans* double bond), but no allene bands. The ultraviolet spectrum in pentane (Table I and Figure 3) showed maxima at 281 mμ (ϵ 55,500) and 291 mμ (ϵ 55,000), with absorption beyond 600 mμ.[25,29] Catalytic hydrogenation over platinum again led to cyclohexadecane. The 1,3-bisdehydro[16]annulene formulation 9 follows from the nmr spectrum, discussed in the following paper.[7]

(28) The sample was placed on an open cover slide on a rapidly heated block just below this temperature; only decomposition occurred when the melting point was determined in the usual way.

(29) The ϵ values are approximate, and are based on the weight of the residue obtained by evaporation of the solvent after determination of the ultraviolet spectrum.

Treatment of compound A, B, or C with potassium *t*-butoxide under the conditions used for their formulation resulted in the recovery of starting material (or in decomposition), but no detectable amounts of one of the other dehydroannulenes or of diphenylsuccindene-10 (6) were produced. These experiments show that compounds A, B, and C are formed from the cyclic dimer 2 by independent paths, and that they are not intermediates in the conversion of 2 to 6.

The rearrangement of the cyclic dimer 2 with other bases was studied, but the dehydro[16]annulenes could not be obtained in increased yield. It was found that treatment of 2 with boiling ethanolic potassium hydroxide gave rise to diphenylsuccindene-10 (6) in greatly increased yield, *ca.* 60% of this substance being formed.

It will be recalled that the oxidative coupling of the monomer 1 under Glaser conditions had given the linear dimer 3 in larger amounts than the cyclic dimer 2, but only the latter substance has been used so far for the synthesis of dehydro[16]annulenes. In order to utilize the linear dimer 3, this substance was oxidized with cupric acetate in pyridine and ether (Eglinton conditions)[13] in relatively dilute solution at 55°. Rather surprisingly, this reaction resulted in rearrangement as well as coupling, and led directly to conjugated cyclic and linear compounds. Chromatography on alumina first gave a mixture of dehydro[16]annulenes (*ca.* 2% yield), and then yellow-orange solutions exhibiting principal ultraviolet maxima (in ether) at 362 and 392 mμ. The last mentioned material presumably consists of conjugated hexadecahexaenediyne(s) (10, rela-

$$H\text{—}(CH\text{=}CH)_6\text{—}(C\text{≡}C)_2\text{—}H$$
10

$$CH_3\text{—}(CH\text{=}CH)_3\text{—}(C\text{≡}C)_2\text{—}(CH\text{=}CH)_3\text{—}CH_3$$
11

tive positions of acetylenic and ethylenic bonds unknown), formed from the linear dimer 3 by prototropic rearrangement. This formulation was confirmed by the fact that treatment of 3 with potassium *t*-butoxide in *t*-butyl alcohol and benzene at room temperature for 1 min gave similar material (principal ultraviolet maxima in ether at 364 and 394 mμ). By comparison, the principal ultraviolet maxima (in ether) of the related 2,4,6,-12,14,16-octadecahexaene-8,10-diyne (11), which contains two additional alkyl substituents, occur at 370 and 400 mμ.[30]

Thin layer chromatographic examination of the dehydroannulenes derived from the linear dimer 3 showed that three different substances had been found, two of which were identical with the above-described compounds A and B. The major dehydroannulene was new, and is named compound D.[31] Red solutions of pure compound D (estimated yield, *ca.* 1.2%) were obtained by rechromatography on alumina. Although the substance was comparatively stable in dilute solution (isooctane), it decomposed rapidly in concentrated solution. The infrared spectrum (chloroform) showed bands at 4.60 μ (w) (acetylene) and 10.13 (m), 10.31 μ (s) (*trans* double bond), but no allene bands. The ultraviolet spectrum in isooctane (Table I

(30) F. Bohlmann, H. Bornowski, and P. Herbst, *Chem. Ber.*, 93, 1931 (1960); see also F. Bohlmann and H. J. Mannhardt, *ibid.*, 89, 1307 (1956).

(31) In the preliminary communication,[3] this was the only dehydroannulene isolated from this reaction, and was tentatively assigned the 1,3-bisdehydro structure 9.

and Figure 4) exhibited a shoulder at *ca.* 260 mμ (ε 42,200), and maxima at 272 mμ (ε 62,700), 278 (61,700), and 290 (41,700), with absorption beyond 600 mμ.[25] It is of interest that each of the dehydro[16]annulenes, compounds A, B, C, and D (as well as [16]annulene, see below), could be recognized by the characteristic shape of the ultraviolet spectra (Figures 1–4), despite the general similarity of these spectra.

It was generally not possible to obtain compound D free of solvent, only black polymer being obtained on careful evaporation of the solvent at 0° under reduced pressure. However, in some cases the substance was obtained as dark brown needles, mp 79–80° dec.[28] The solid was very unstable; it was almost completely decomposed after standing for 15 min, and in one case it detonated with a flash on being touched with a spatula.

Compound D decomposed on attempted determination of the mass spectrum. No satisfactory nmr spectrum could be obtained, since the solution (carbon tetrachloride) deposited insoluble polymeric material during the measurement. The lack of these data made it impossible to assign a definite structure to the substance, although it is probably another bisdehydro[16]annulene. A dehydro[16]annulene formulation follows from the infrared and ultraviolet spectra, from the results of partial hydrogenation (see below), as well as from the fact that full hydrogenation in ethyl acetate over platinum again led to cyclohexadecane. A bisdehydro structure is indicated by an elemental analysis, which gave satisfactory figures for a $C_{16}H_{12}$ formula. However, the latter evidence must be treated with some reserve (see ref 22).

The sequence of events leading from the linear dimer **3** to the bisdehydro[16]annulenes, compounds A, B, and D, has not been determined in detail. The reaction cannot involve the cyclic dimer **2** as an intermediate, since **2** was recovered essentially unchanged on treatment with cupric acetate in pyridine and ether under the conditions used for the coupling of **3**. Presumably, some isomerization of **3** takes place before ring formation, and this is supported by the fact that the coupling of **3** gives rise to the conjugated hexadecahexaenediyne(s) (type **10**) in addition to dehydro[16]annulenes. It was established that cupric acetate is necessary for the rearrangement, since **3** was unaffected by treatment under the conditions used for the coupling, but omitting the cupric acetate.

A number of catalytic partial hydrogenation experiments with the various dehydro[16]annulenes were carried out, in order to obtain [16]annulene (*e.g.*, **12**).
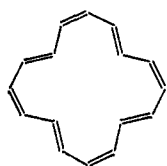
12 ([16]Annulene)

The first experiments were performed with the mixture of dehydro[16]annulenes, compounds A, B, and D, as obtained by the cupric acetate coupling of the linear dimer **3**. This mixture in benzene solution was hydrogenated over a 10% palladium–calcium carbonate catalyst until *ca.* 2.5–3.0 molar equiv of hydrogen had been absorbed.[32] Chromatography on alumina then
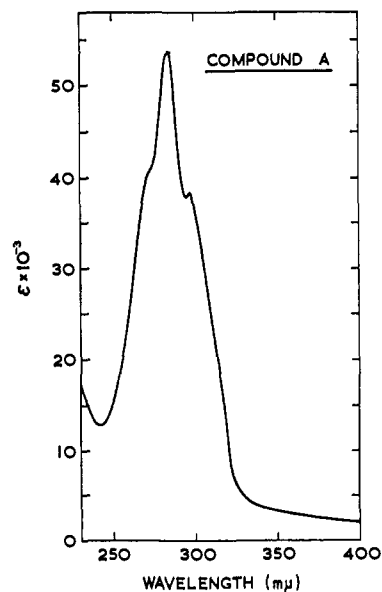

Figure 1. Ultraviolet absorption spectrum of compound A (1,9-bisdehydro[16]annulene) (**7**), in isooctane.

yielded three substances, which proved to be (in order of elution) [16]annulene (**12**, *ca.* 8%), compound A (**7**, *ca.* 30%),[24] and diphenylsuccindene-10 (**6**, *ca.* 30%). The source of the last-mentioned substance was not investigated. The amount of compound A was greater than that present originally, and this indicated that compound A had been formed in the hydrogenation from compound D (the major component of the original mixture). Indeed, a separate partial hydrogenation experiment carried out with pure compound D led to compound A in *ca.* 30% yield in addition to 5% of [16]annulene. If compound D is really a bisdehydro[16]annulene, its conversion to compound A under the hydrogenation conditions involves an isomerization; however, this apparent isomerization was not studied further in view of the instability of compound D. Finally, compound A was also subjected to partial hydrogenation, a reaction which led to *ca.* 10% of [16]annulene.

The various partial hydrogenation experiments yielded the same [16]annulene, which crystallized as dark brown crystals, mp 92–93°. The crystalline substance was comparatively stable, but it gradually decomposed in dilute isooctane solution without protection from diffuse daylight. A [16]annulene structure was assigned to the compound, since the elemental analysis indicated the formula $C_{16}H_{16}$, the infrared spectrum no longer showed an acetylene band at *ca.* 4.60 μ, and hydrogenation in ethyl acetate over platinum led to cyclohexadecane. The ultraviolet spectrum in isooctane (Table I and Figure 5) resembled those of the various dehydro[16]annulenes (Figures 1–4), showing a maximum at 284 mμ (ε 77,300) and a broad shoulder at *ca.* 430–450 mμ (ε *ca.* 700), with absorption beyond 600 mμ.[33] The nmr spectrum of [16]annulene (60

(32) It has been found in related hydrogenation experiments that it is advantageous to allow more than the theoretical amount of hydrogen to be absorbed (see F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Amer. Chem. Soc.*, **84**, 274 (1962)).

(33) By comparison, the main ultraviolet maximum of [14]annulene (both conformers) occurs at 317 mμ,[4,5,34] and that of [18]annulene at 369 mμ.[4,5,32] For a comparison of the ultraviolet spectra of the various annulenes, see ref 25.
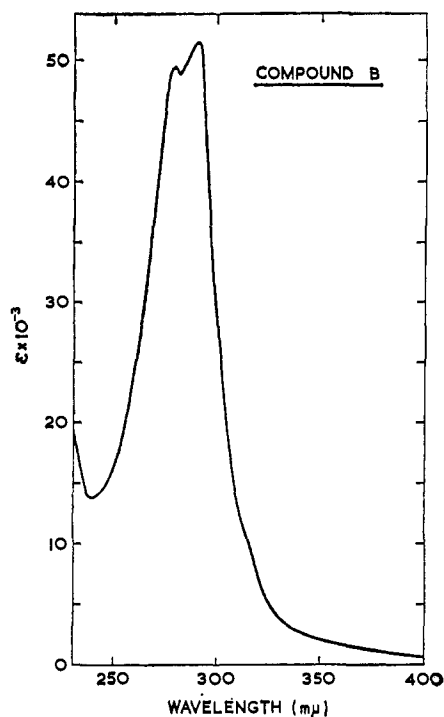
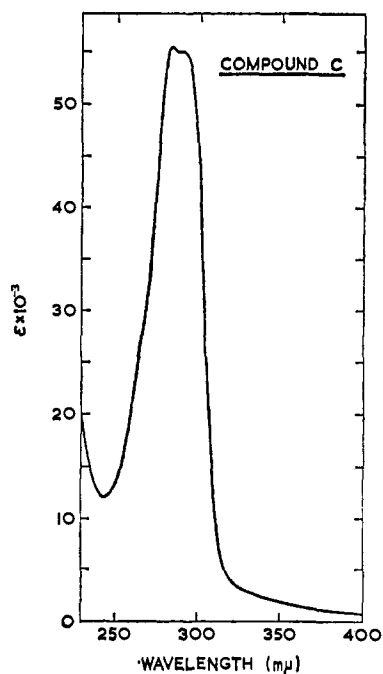Figure 2. Ultraviolet absorption spectrum of compound B (1,3,9-tridehydro[16]annulene) (8), in isooctane.

Figure 3. Ultraviolet absorption spectrum of compound C (1,3-bisdehydro[16]annulene) (9), in pentane.

Figure 4. Ultraviolet absorption spectrum of compound D, in isooctane.
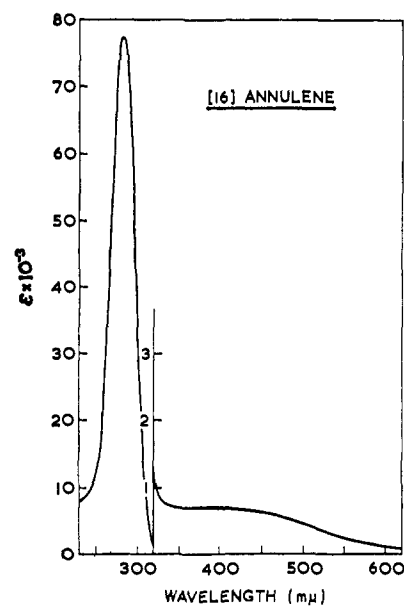
Figure 5. Ultraviolet absorption spectrum of [16]annulene (12), in isooctane.

Mcps, 37°, carbon tetrachloride) consisted of a singlet at τ 3.27.[35]

[16]Annulene can exist in a number of different configurations.[36,37] In previous publications,[3-5] we have assumed that the compound obtained by us possesses structure 12. This configuration contains

alternating *cis* and *trans* double bonds, and the clash of the internal protons has been minimized. Unfortunately, no information regarding the configuration could be obtained from the above nmr spectrum.

In 1964, our group reported[38] that the nmr spectra of the $(4n + 2)$ π electron systems [14]annulene (main conformer) and [18]annulene consist of a singlet at higher temperatures, but of widely separated bands corresponding to the outer (low-field) and inner (high-field) protons at lower temperatures. The reason advanced for the singlet at higher temperatures was that at these temperatures the protons change position at such a rate that an average value results for the band location. We suspected that a similar averaging process was responsible for the room-temperature nmr singlets

(34) Y. Gaoni and F. Sondheimer, *Proc. Chem. Soc.*, 299 (1964).
(35) For the spectrum, see ref 4, Figure 18, and ref 5, Figure 11.
(36) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 87, 685 (1965).
(37) G. Schröder and J. F. M. Oth, *Tetrahedron Lett.*, 4083 (1966).
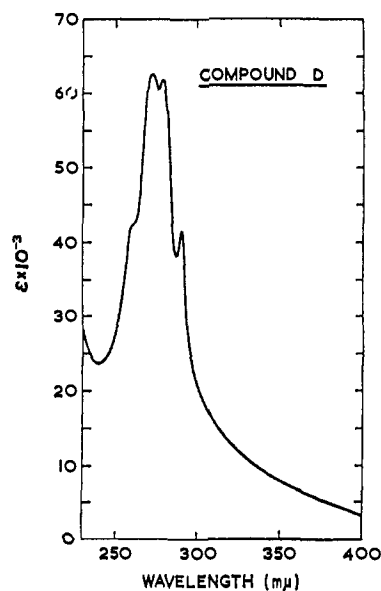
(38) Y. Gaoni, A. Melera, F. Sondheimer, and R. Wolovsky, *Proc. Chem. Soc.*, 397 (1964); see also ref 5 and 6.

of the $4n$ π electron systems [16]annulene and [24]annulene.[4,6,39] It was obviously of interest to determine the nmr spectra of these compounds at lower temperatures, and in the case of [24]annulene we have shown recently that the spectrum at $-80°$ in fact consists of a low-field band due to the inner protons and a high-field band due to the outer protons.[40] On the other hand, we were not able to study the low-temperature nmr spectrum of [16]annulene, since we no longer had a sample available.

Fortunately, a new synthesis of [16]annulene (12) has been reported recently by Schröder and Oth,[37] involving photolysis of the cyclooctatetraene dimer 13. This synthesis is much superior to ours in yield, and [16]annulene has been prepared in gram quantities in this manner. The resulting [16]annulene appeared to be identical with ours in view of the close correspondence of the melting points, ultraviolet spectra, and nmr spectra (see Experimental Section), and identity was confirmed by direct comparison of the infrared spectra, kindly carried out by Dr. Schröder. The fact that the same substance is formed by the two routes indicates

Chart II

13   12

14   15
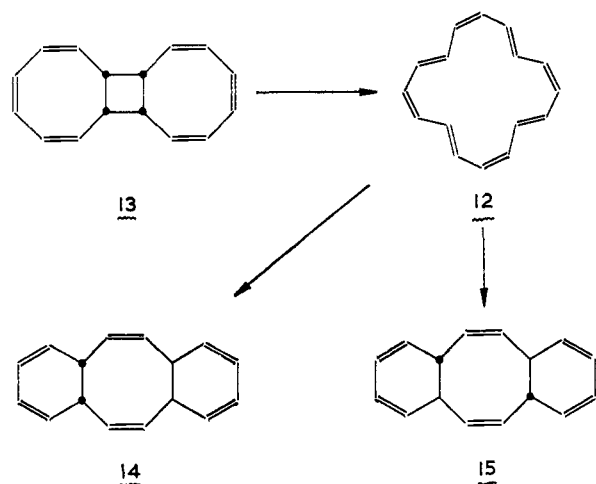
that [16]annulene exists in the thermodynamically most favored configuration and that the configuration is not dependent on the precursor. A similar conclusion has already been made by us[5] for [18]annulene, since the same annulene was again obtained from different precursors.[17,32]

The nmr spectrum of [16]annulene at low temperatures has now been determined by Schröder and Oth.[37] At $-110°$, the spectrum (in carbon disulfide and dideuteriomethylene chloride) consists of a triplet at τ -0.43 (inner protons) and a multiplet at τ 4.60 (outer protons), with relative intensities of ca. 4:12. This spectrum shows that [16]annulene indeed possesses the configuration 12 assigned by us, containing four inner and twelve outer protons. The finding that the inner protons appear at low field and the outer protons at high field parallels the results obtained subsequently with [24]annulene[40] and provides experimental evidence for the existence of a magnetically induced paramagnetic ring current in annulenes containing $4n$ π electrons.[41] This is a reversal of the behavior of [14]-

(39) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **84**, 4307 (1962).

(40) I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).

annulene (major conformer) and [18]annulene, containing ($4n$ + 2) π electrons, in which the low-temperature nmr spectra indicate the existence of a diamagnetic ring current.[6] The fact that the nmr spectrum of [16]annulene at higher temperatures consists of a singlet has been interpreted as being due to both rotation about the carbon–carbon bonds (conformational isomerism) and movement of the π bonds (valence isomerism).[37] An estimate of 8.6 kcal/mol has been made for the free-energy barrier for interconversion of the inner and outer protons in [16]annulene.[42]

Very recently, Schröder, *et al.*,[43] have reported the interesting observation that heating [16]annulene (12) gives rise to the tricyclic compound 14, while irradiation with ultraviolet light yields the isomer 15.

It is important to investigate the degree of coplanarity of the carbon skeleton of [16]annulene and whether bond alternation occurs. The outcome of an X-ray crystallographic analysis which is being carried out by Professor I. C. Paul, *et al.*, University of Illinois, is awaited with interest.

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 137 Infracord recording spectrophotometer (s = strong, m = medium, w = weak) and ultraviolet spectra with a Cary Model 14 spectrophotometer. Nmr spectra (100 Mcps) were determined with a Varian HA-100 spectrometer, and 60-Mcps nmr spectra with a Varian A-60 spectrometer, tetramethylsilane being used as internal reference. Mass spectra were measured with an AEI MS-9 mass spectrometer (direct inlet system). Microanalyses were carried out in the microanalytical department of the Weizmann Institute of Science under the direction of Mr. Erich Meier and Mr. Raoul Heller. Thin layer chromatograms were carried out as described by Wolovsky and Sondheimer.[11a] All solvents were evaporated under reduced pressure, the bath temperature being kept below 40°.

Oxidation of *trans*-4-Octene-1,7-diyne (1) with Oxygen, Cuprous Chloride, and Ammonium Chloride. A. Without Benzene. Ammonium chloride (32 g), cuprous chloride (20 g), water (85 ml), and concentrated hydrochloric acid (0.2 ml) were introduced into a flask fitted with a mechanical stirrer, gas inlet tube, and reflux condenser. The mixture was heated to 55°, a vigorous stream of oxygen was bubbled in, and a solution of *trans*-4-octene-1,7-diyne (1)[1] (10 g) in ethanol (50 ml) was added in one portion, with vigorous stirring. The reaction was allowed to proceed at 55° for 80 min, with continuous stirring and passage of oxygen. The mixture was then cooled, filtered through Celite, and extracted repeatedly with warm benzene. The extract was washed with water, dried, and evaporated to small volume. The solution was then allowed to stand at ca. 10° for 24 hr. The resulting precipitate on recrystallization from benzene yielded *trans,trans*-1,9-cyclohexadiene-4,6,12,14-tetrayne (cyclic dimer) (2, 180 mg) as colorless plates, which decomposed explosively at ca. 215°;[28] infrared bands (KBr) at 4.43 (w) 4.58 μ (w) (1,3-diyne) and 10.39 (s) (*trans* double bond), no terminal acetylene band at ca 3.03 μ; λ_{max}^{ether} 232 mμ (ϵ 740), 245 (780), and 258 (490); nmr spectrum (100 Mcps, CDCl$_3$), 4 H multiplet at τ 4.10 (olefinic protons) and 8 H multiplet at τ 7.12 (methylene protons); mass spectrum, molecular ion peak at *m/e* 204.

Anal. Calcd for C$_{16}$H$_{12}$: C, 94.08; H, 5.92. Found: C, 94.44; H, 5.96.

Substance 2 gradually decomposed on standing. Full hydrogenation of 2 (platinum, ethyl acetate; product crystallized from aqueous methanol) yielded cyclohexadecane, mp 61–62°. This substance was identified by the mass spectrum (molecular ion peak

(41) 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.

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

(43) G. Schröder, W. Martin, and J. F. M. Oth, *Angew. Chem.*, **79**, 861 (1967).

at m/e 224) and nondepression of the melting point on admixture with an authentic sample (mp 61–62°).[9]

The combined mother liquors were chromatographed on alumina (1 kg, Merck acid-washed) into *ca.* 150 fractions. Elution with pentane–ether (95:5) gave unchanged **1** (510 mg, 5%). Further elution with this solvent mixture led to an oil (150 mg), which partially crystallized; crystallization from pentane yielded a chloro compound (73 mg) as colorless plates, mp 64–65° (Cl, 15.02). This substance was not investigated further.

Elution with pentane–ether (90:10) yielded *trans,trans*-4,12-hexadecadiene-1,7,9,15-tetrayne (linear dimer) (**3**), admixed with a small amount of cyclic dimer **2**. Evaporation led to crystals (2.70 g), which were treated with warm pentane. The insoluble residue consisted of the cyclic dimer **2** (110 mg, explodes at *ca.* 215°, after crystallization from benzene; total yield, 290 mg, 3.0%). The pentane solution on evaporation to small volume and cooling gave the linear dimer **3** (2.25 g, 23%) as colorless plates, mp 80–81°, homogeneous on tlc; infrared bands (KBr) at 3.02 (s), 4.69 μ (w) (terminal acetylene), 4.41 (w), 4.58 μ (w) (1,3-diyne), and 10.29 μ (s) (*trans* double bond); $\lambda_{max}^{isooctane}$ 225 mμ (ϵ 430), 239 (390), and 253 (240); nmr spectrum (100 Mcps, CDCl$_3$), 4 H multiplet at τ 4.28 (olefinic protons), 8 H multiplet at τ 6.99 (methylene protons), and 2 H multiplet at τ 7.94 (acetylenic protons); mass spectrum, molecular ion peak at m/e 206.

Anal. Calcd for C$_{16}$H$_{14}$: C, 93.16; H, 6.84. Found: C, 93.29; H, 6.79.

Substance **3** gradually became yellow on standing. Full hydrogenation of **3** (platinum, ethyl acetate; product crystallized from methanol–ethyl acetate) gave *n*-hexadecane (cetane), mp 17–18°, undepressed on admixture with an authentic sample (mp 17–18°).[9]

Elution with pentane–ether (80:20) yielded fractions, which on concentration to small volume and filtration gave *all-trans*-4,12,20-tetracosatriene-1,7,9,15,17,23-hexayne (linear trimer) (**4**, 180 mg, 1.8%) as colorless leaflets, mp 110–112° (unchanged on recrystallization from ether–pentane), homogeneous on tlc; infrared bands (KBr) at 3.03 (s), 4.69 μ (w) (terminal acetylene), 4.41 (w), 4.58 μ (w) (1,3-diyne), and 10.28 μ (s) (*trans* double bond).

Anal. Calcd for C$_{24}$H$_{20}$: C, 93.46; H, 6.54. Found: C, 93.36; H, 6.56.

Full hydrogenation of **4** (platinum, ethyl acetate; product crystallized from methanol–ethyl acetate) led to *n*-tetracosane, mp 50–51°, undepressed on admixture with an authentic sample (mp 50–51°).[44]

Elution with pentane–ether (20:80) yielded fractions, which on concentration, addition of pentane, and cooling gave *all-trans*-4,12,20,28-dotriacontatetraene-1,7,9,15,17,23,25,31-octayne (linear tetramer) (**5**, 150 mg, 1.5%), mp 118–121° dec, mp 120–121° (sample put on block just before), homogeneous on tlc; infrared bands (KBr) at 3.03 (s), 4.71 μ (w) (terminal acetylene), 4.41 (w), 4.60 μ (w) (1,3-diyne), and 10.29 μ (s) (*trans* double bond). Full hydrogenation of **5** (platinum, ethyl acetate; product crystallized from methanol) yielded *n*-dotriacontane (dicetyl), mp 69–70°, undepressed on admixture with an authentic sample (mp 69–70°).[9]

This experiment on being repeated under apparently identical conditions was found to give irreproducible yields, the yield either of the cyclic dimer **2** or the linear dimer **3** at times being considerably lower than indicated.

B. With Benzene. The oxidation of **1** (10 g) was carried out exactly as described under A, except that benzene (250 ml) was added initially to the reaction mixture, and the reaction was allowed to proceed for 2 hr. Isolation as before then gave the cyclic dimer **2** (1.05 g, 11%; mainly by direct crystallization) and the linear dimer **3** (2.15 g, 22%), as well as the other substances described under A. In this case, the yields were found to be reproducible.

Conversion of Cyclic Dimer 2 to Dehydro[16]annulenes (Compounds A, B, C) and Diphenylsuccindene-10 (6). A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (5 ml) was added to a solution of the cyclic dimer **2** (500 mg) in benzene (250 ml). The mixture was shaken at 40° for 1 min and was then poured into ice–water. The mixture was extracted with ether, and the organic extract was washed with water and dried. The resulting red solution (main λ_{max}^{ether} 288 mμ) was concentrated to *ca.* 25 ml under reduced pressure and chromatographed on alumina (500 g, Camag activity I). The extraction, concentration, and chromatography were carried out as rapidly as possible (2–3 hr) to keep decomposition of the products to a minimum.

The column was eluted with pentane and then with pentane–ether mixtures, containing increasing amounts of ether. A colored band was seen to move down the column, which gradually separated into a violet (lower) and an orange (upper) band; 30-ml fractions were collected during the elution of the colored bands, while otherwise 250-ml fractions were collected. Tlc analysis of the fractions showed that dehydro[16]annulenes, compounds A, B and C, had been formed, as well as diphenylsuccindene-10 (**6**); on tlc plates, compound C was eluted first, followed by compound B and **6** (about equal R_f values), followed by compound A.

The fractions given in Table II were collected, all being examined by tlc and ultraviolet spectroscopy. Subsequently, yellow solutions were eluted, which were not examined further.

Table II

Fraction no.	Pentane–ether ratio	Color	Products
10–12	95:5	Violet	C only
13–14	95:5	Violet-orange	C, B, 6
15–17	95:5	Orange	C, B, A, 6
18–23	95:5	Orange	B, A, 6
23–30	90:10 to 75:25	Colorless	6 only

Fractions 10–12 were combined, concentrated to *ca.* 15 ml, and rechromatographed on alumina (100 g, Camag activity I). Elution with pentane–ether (97:3) gave pure compound C (**1,3-bisdehydro-[16]annulene (9)**) (*ca.* 40 mg, 8%, estimated spectroscopically) as violet solutions, homogeneous on tlc; ultraviolet spectrum, see Discussion, Table I, and Figure 3; mass spectrum, molecular ion peak at m/e 204. The carbon tetrachloride solution used for determination of the infrared spectrum (see Discussion) and nmr spectrum (see following paper[7]) was obtained by evaporation of the pentane–ether solutions to small volume, addition of carbon tetrachloride, chromatography on alumina (100 g, Camag activity I), elution with carbon tetrachloride to remove the pentane and ether, and finally evaporation to small volume under reduced pressure. All these operations were carried out as rapidly as possible to prevent decomposition. Compound C was very unstable. Only 10–20% remained when chromatography fractions were allowed to stand in a refrigerator at 0° for 24 hr, and all solutions were kept in liquid nitrogen for storage purposes. When taken to dryness at 0° under reduced pressure, solutions of compound C yielded a residue which rapidly turned to a brown polymer. Full hydrogenation in pentane and ether over platinum gave cyclohexadecane, identified by the mass spectrum (molecular ion peak at m/e 224).

Fractions 13–17 were allowed to stand for 48 hr at 0° in a refrigerator to remove most of isomer C through decomposition. These fractions were then added to fractions 18–23, concentrated to small volume, and rechromatographed on alumina (100 g, Camag activity II). Pentane eluted a mixture of compounds A and B, admixed with small amounts of compound C and **6** (tlc and ultraviolet spectral examination). This mixture was then concentrated and chromatographed on alumina coated with silver nitrate, prepared from alumina (100 g, Camag activity I) and silver nitrate (20 g).[17] Elution with pentane–ether (80:20) yielded mainly compound B, pentane–ether (70:30 to 60:40) gave mainly compound A, while pentane–ether (50:50 to 30:70) gave a little remaining compound C (tlc and ultraviolet spectral examination).

The fractions containing compound B were concentrated and rechromatographed on alumina (100 g, Camag activity II). Elution with pentane then yielded pure compound B (**1,3,9-tridehydro[16]-annulene (8)**) (*ca.* 25 mg, 5%, estimated spectroscopically) as red-brown solutions, homogeneous on tlc. The substance was best stored in solution, but through evaporation to small volume and collection of the resulting crystals could be obtained as very unstable dark brown plates, mp 59–60° dec;[28] infrared and ultraviolet spectra, see Discussion, Table I, and Figure 2; nmr spectrum, see following paper;[7] mass spectrum, molecular ion peak at m/e 202. The crystalline substance had almost completely decomposed after 15-min standing at room temperature, but it could be kept in pentane solution at 0° in the refrigerator for several weeks with little change. Full hydrogenation (platinum, ethyl acetate) yielded cyclohexadecane, mp 58–61°, identified by the mass spectrum (molecular ion peak at m/e 224) and nondepression of the melting point on admixture with an authentic sample (mp 61–62°).[9]

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(44) *Inter alia*, F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, 79, 6263 (1957).

The fractions containing compound A were concentrated and rechromatographed on alumina (100 g, Camag activity II). Elution with pentane then yielded pure compound A (**1,9-bisdehydro[16]annulene (7)** (*ca.* 10 mg, 2%, estimated spectroscopically) as red-brown solutions, homogeneous on tlc. Evaporation and crystallization from pentane gave large brown plates, mp 90–91°; infrared and ultraviolet spectra, see Discussion, Table I, and Figure 1; nmr spectrum, see following paper;[7] mass spectrum, molecular ion peak at *m/e* 204.

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.18; H, 5.80.

Compound A was considerably more stable than compounds B or C. The solid after 4-days standing without protection from diffuse daylight had suffered only *ca.* 30% decomposition, while solutions at 0° in the refrigerator were essentially unchanged after 3 months. Full hydrogenation (platinum, ethyl acetate) gave cyclohexadecane, mp 59–61°, identified by the mass spectrum (molecular ion peak at *m/e* 224) and nondepression of the melting point on admixture with an authentic sample (mp 61–62°).[9]

Fractions 23–30 from the original chromatogram were evaporated and the crystalline residue was sublimed at 150° (1 mm). Crystallization from pentane then gave **diphenylsuccindene-10 (6)** (70 mg, 14%; total estimated yield, *ca.* 20%) as very pale yellow plates, mp 212–213°; $\lambda_{max}^{isooctane}$ 230 mμ (ϵ 12,800), 236 (14,700), 243 (12,000), 303 (24,500), 314 (28,800), 323 (20,800), and 330 (17,800). The melting point was undepressed on admixture with an authentic sample (mp 211–212°),[19] and the infrared and ultraviolet spectra were identical.

Conversion of Cyclic Dimer 2 to Diphenylsuccindene-10 (6) with Potassium Hydroxide. Potassium hydroxide (1.8 g) in ethanol (20 ml) was added to a boiling solution of the cyclic dimer **2** (20 mg) in ethanol (50 ml), and the reaction mixture was boiled gently under reflux for 20 min. Cooling, addition of water, and extraction with ether gave an ether solution, which showed the typical ultraviolet spectrum of **6** (spectroscopic yield, 60%). Evaporation, sublimation at 150° (1 mm), and crystallization from pentane then gave **6** (mp 211–212°), identified with the previously described material in the usual way.

Oxidation and Rearrangement of Linear Dimer 3 to Dehydro[16]-annulenes (Compounds A, B, D). A solution of linear dimer **3** (5 g) in ether (250 ml) was added dropwise during 2 hr to a stirred mixture of cupric acetate monohydrate (25 g), pyridine (1.5 l.), and ether (1.25 l.) at 55°. The mixture was then stirred for a further 1 hr at 55°. It was cooled, diluted with ether, and poured into 5% hydrochloric acid (6 l.). The aqueous layer was extracted with ether, and the combined ether extracts were washed with 5% hydrochloric acid, water, and saturated sodium chloride solution. The resulting red solution (λ_{max}^{ether} 252, 285, 311, 330, 362, and 392 mμ) was dried evaporated to small volume, diluted with benzene (*ca.* 10 ml), and chromatographed on alumina (1 kg, Alcoa F-20). Elution with pentane–ether (95:5) gave red solutions (main λ_{max}^{ether} 270–290 mμ). These consisted of incompletely separated mixtures of dehydro[16]-annulene, compounds A, B, and D (*ca.* 100 mg, estimated spectroscopically, ϵ 60,000 being assumed for the main ultraviolet maximum), as determined by tlc (order of elution on tlc plate: compound D, followed by compound B, followed by compound A). Subsequently, elution with pentane–ether (95:5 to 90:10) yielded yellow-orange solutions containing hexadecahexaenediyne(s) (main λ_{max}^{ether} 362 and 392 mμ). These solutions on standing gradually deposited an insoluble polymer. Later chromatography fractions were not investigated in detail.

The solutions containing dehydro[16]annulenes were evaporated to small volume and rechromatographed on alumina (300 g, Alcoa F-20). All fractions were examined by tlc and ultraviolet spectral analysis. Pentane–ether (95:5) first gave fractions containing only compound D (estimated yield, 60 mg, 1.2%) and then mixtures of compounds D, B, and A. The mixed fractions were not separated preparatively. The identities of compounds B and A with the corresponding substances obtained from the cyclic dimer **2** were established by mixed tlc and by comparison of the ultraviolet spectra of the spots obtained from tlc plates.

Careful evaporation of the fractions containing pure compound D to small volume and cooling gave compound D (35 mg in two crops) as dark brown needles (red in solution): mp 79–80° dec;[28] homogeneous on tlc; infrared and ultraviolet spectra, see Discussion, Table I, and Figure 4.

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.13; H, 5.67.

Compound D was very unstable in the solid state (see Discussion). However, it could be kept in dilute solution, and a dilute

solution in isooctane had suffered only *ca.* 10% decomposition after 2-weeks standing at room temperature in the dark. Generally, evaporation of solutions of compound D did not lead to the crystalline substance, but resulted in complete decomposition to a black insoluble polymer. Full hydrogenation of compound D (platinum, ethyl acetate) gave cyclohexadecane, mp 57–59°, identified by the mass spectrum (molecular ion peak at *m/e* 224) and nondepression of the melting point on admixture with an authentic sample (mp 61–62°).[9]

Rearrangement of Linear Dimer 3 with Potassium *t*-Butoxide (with W. H. Okamura). A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (10 ml) was added to a solution of the linear dimer **3** (50 mg) in benzene (10 ml). The solution was allowed to stand at room temperature for 1 min. Addition of water and isolation with ether then gave a yellow-orange solution, which was concentrated and subjected to preparative tlc. The three products, in order of elution, showed the following principal ultraviolet maxima (in ether): (a) 364, 394 mμ; (b) 376, 398 mμ; (c) 360, 379, 404 mμ.

Treatment of Cyclic Dimer 2 with Cupric Acetate and Pyridine. A solution of the cyclic dimer **2** (50 mg) in ether (15 ml) was added to cupric acetate monohydrate (250 mg) in pyridine (15 ml), and the mixture was stirred at 55° for 3 hr. Isolation with ether then led to impure starting material as sole product, no trace of a dehydro[16]annulene being detected.

Treatment of Linear Dimer 3 with Ether and Pyridine. A solution of the linear dimer **3** (100 mg) in ether (30 ml) and pyridine (30 ml) was heated at 55° for 3 hr. Evaporation then led only to recovered starting material.

[16]Annulene. A. By Partial Hydrogenation of Dehydro[16]-annulenes, Mixture of Compounds A, B, and D. A mixture of dehydro[16]annulenes, compounds A, B, and D (*ca.* 100 mg, estimated spectroscopically; obtained from the linear dimer **3** with cupric acetate and subsequent chromatography, as described above), in benzene (25 ml) was stirred in hydrogen with a 10% palladium-calcium carbonate catalyst (50 mg) at room temperature and atmospheric pressure. The reaction was terminated after 7 min, when 32 cc (*ca.* 2.8 molar equiv) of hydrogen had been absorbed. The hydrogenation was then repeated on the same scale, and the reaction mixtures were combined. The catalyst was removed, the solvent was replaced by pentane, and the solution was chromatographed on alumina (500 g, Alcoa F-20). The fractions (100 ml each) were examined by tlc and ultraviolet spectroscopy.

Fractions 31–39 [eluted with pentane–ether (95:5)] contained **[16]annulene (12)** (17 mg, *ca.* 8%, estimated spectroscopically). Evaporation of these orange fractions and crystallization from pentane gave dark brown crystals (11.5 mg in two crops), mp 92–93°; homogeneous on tlc; infrared bands (KBr) at 3.33 (m), 6.35 (w), 7.06 (w), 7.62 (m), 8.07 (w), 9.03 (w), 10.04 (m), 10.13 (m), 10.26 (m), 10.56 (m), 10.67 (s), 11.49 (w), 11.65 (w), 12.81 (s), 13.00 (m), 13.09 (m), 13.42 (w), and 14.24 μ (w); $\lambda_{max}^{isooctane}$ 284 mμ (ϵ 77,300) and broad shoulder at *ca.* 430–450 (*ca.* 700) (see Table I and Figure 5); nmr spectrum (60 Mcps, 37°, CCl$_4$), singlet at τ 3.27[35] [lit.[37] mp 90–91°; $\lambda_{max}^{cyclohexane}$ 282 mμ (ϵ 81,000) and 440 (660); nmr spectrum (30°, CS$_2$ and CD$_2$Cl$_2$), singlet at τ 3.29].

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.56; H, 7.62.

Crystals of [16]annulene were comparatively stable, but the substance gradually decomposed when a dilute isooctane solution was allowed to stand at room temperature without protection from diffuse daylight. Full hydrogenation (platinum, ethyl acetate) gave cyclohexadecane, identified with an authentic sample by glpc analysis.

Fractions 44–54 [also eluted with pentane–ether (95:5)] contained bisdehydro[16]annulene, compound A (7) (61 mg, *ca.* 30%, estimated spectroscopically). Evaporation and crystallization from pentane gave 46 mg (in two crops), mp 90–91°. It was identified with the previously described compound by tlc, ultraviolet, infrared, and nmr spectral comparison.

Fractions 65–74 [eluted with pentane–ether (90:10 to 75:25)] contained diphenylsuccindene-10 (6) (62 mg, *ca.* 30%, estimated spectroscopically). Evaporation and crystallization from pentane led to 51 mg (in two crops), mp 210–212°; it was identified with the previously described compound by tlc and ultraviolet spectral comparison, as well as by the nondepression of the melting point on admixture.

B. By Partial Hydrogenation of Dehydro[16]annulene, Compound D. A solution of compound D (23 mg) in benzene (10 ml) was stirred in hydrogen with a Lindlar palladium catalyst[45] (30

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(45) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952); H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

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
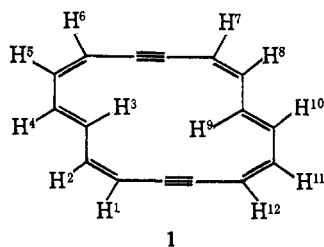
I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer[2]

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*)-

(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.

(1) For Part LIX, see I. C. Calder, Y. Gaoni, and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 4646 (1968).

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