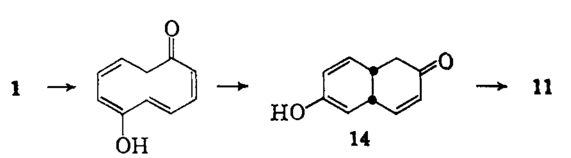
Mcps, CCl_4), 6-H multiplet at τ 3.0–4.6 (olefinic protons) and 4-H multiplet at 6.5–7.0 (methylene protons). The monocyclic nature of **1** was confirmed by catalytic hydrogenation in ethyl acetate over palladium–charcoal. This reaction smoothly led to cyclodecane-1,6-dione (mp 96–98°), identified by direct comparison with an authentic sample (mp 95–97°).[12]

So far, it has not been possible to convert the two keto groups of **1** to the corresponding bis(enol acetate) (1,6-diacetoxy[10]annulene) or bis(vinyl chloride) (1,6-dichloro[10]annulene).[13] Addition of dilute aqueous potassium hydroxide to **1** resulted in the instantaneous formation of a bright red solution (principal λ_{max}^{EtOH} 374 mμ), acidification of which did not regenerate the starting material.

Substance **1** was unaffected by dilute mineral acids or *p*-toluenesulfonic acid at room temperature. However, reaction of **1** with *p*-toluenesulfonic acid in boiling acetone for 30 min yielded *ca.* 25% *cis*-1,2,5,6,9,10-hexahydronaphthalene-2,6-dione (**11**) as crystals, mp 149–151°;[7] λ_{max}^{EtOH} 220 mμ (ϵ 16,500); ν_{max}^{Nujol} 1674 (s) and 1617 (w) cm^{-1}; nmr spectrum (60 Mcps, $CDCl_3$), 2-H double doublet (J = 10 and 4 cps) at τ 3.09 (β-olefinic protons), 2-H doublet (J = 10 cps) at 3.84 (α-olefinic protons), and 6-H multiplet at 6.4–7.7 (methylene and methine protons). The structure and stereochemistry of **11** was established by catalytic hydrogenation in ethanol over palladium–charcoal. The resulting *cis*-decahydronaphthalene-2,6-dione (**12**) (mp 72–73°) proved to be identical with an authentic sample (mp 72–74°).[14]

It is tempting to speculate that the conversion of **1** to **11** involves 1,6-dihydroxy[10]annulene (*e.g.*, **2**) as an intermediate, formed by enolization of both keto groups. However, we believe that most probably only one keto group in **1** is enolized to give **13**, which then undergoes valence tautomerism to **14**, a monoenol of **11**.



13 **14**

The structure of **1** follows unequivocally from the above-described data, but the stereochemistry has not yet been elucidated. The reasonable assumption has been made that the isolated Δ^8-double bond retains the *cis* stereochemistry. The remaining two conjugated double bonds cannot be accommodated in the ten-membered ring if they were both *trans*, and the compound therefore possesses either the *cis,trans,cis* configuration **1a** or the all-*cis* configuration **1b**. The infrared spectra of **1** and of its ten-membered ring precursors all exhibit medium or strong bands in the 990–940-cm^{-1} region; however, this cannot be considered as definite evidence for the presence of a *trans* double bond,[15] since certain oxygenated derivatives of *cis*-cyclodecene (*e.g.*, **7**) and of cyclodeca-1,6-diene (*cis,cis*)[16] also show medium or strong bands in this region. An X-ray crystallographic analysis of **1** is now being carried out by Mrs. O. Kennard, *et al.*, in order to elucidate the stereochemistry.

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(12) *Inter. al.*, W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *Ann.*, **474**, 121 (1929).
(13) For the synthesis of the corresponding 2,7-dihydro compound, see K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, 3121 (1967).
(14) R. L. Clarke and C. M. Martini, *J. Am. Chem. Soc.*, **81**, 5716 (1959).
(15) See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.
(16) K. Grohmann, P. J. Mulligan, and F. Sondheimer, unpublished observations.
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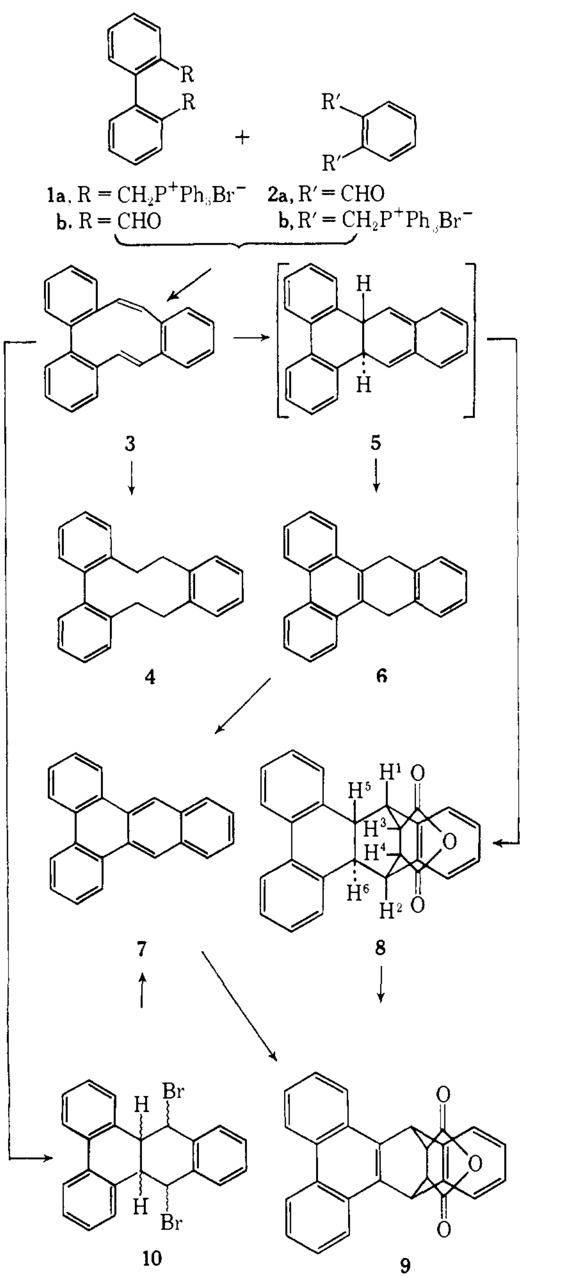
Mono-*trans*-1,2:3,4:7,8-tribenz[10]annulene[1]

Sir:

We report the synthesis of mono-*trans*-1,2:3,4:7,8-tribenz[10]annulene (**3**). This is the first annelated derivative of the ($4n + 2$) π-electron system, [10]annulene,[2] for which a Kekulé structure incorporating the cyclodecapentaene system can be written.

Wittig reaction of 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**1a**)[5] and *o*-phthalaldehyde (**2a**) with lithium methoxide in ether and methanol at room temperature under nitrogen gave a mixture of substances, separated by chromatography on silica gel. The products derived by ring formation proved to be **3** (15% yield) and 9,10-dihydro-1,2:3,4-dibenzanthracene (**6**) (1.5% yield, see below). The same tribenz[10]annulene **3** was also obtained by the Wittig reaction of biphenyl-2,2′-dicarboxaldehyde (**1b**)[6] and *o*-xylylenebis(triphenylphosphonium bromide) (**2b**)[7] with lithium methoxide, although the yield was only 1.5%.

(1) Unsaturated Macrocyclic Compounds. LVII. For part LVI, see P. J. Mulligan and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 7118 (1967).
(2) Other annelated [10]annulenes have been prepared ([2.2]metacyclophane-1,9-diene derivatives: V. Boekelheide, *et al.*, *ibid.*, **87**, 130 (1965); **89**, 1695, 1704, 1709 (1967); 1,2,3:6,7,8-di(1′,8′-naphth)-[10]annulene: R. H. Mitchell and F. Sondheimer, *ibid.*, in press). 1,6-Bridged [10]annulenes have been synthesized by E. Vogel, *et al.* (*Angew. Chem.*, **76**, 145, 785 (1964); **78**, 754 (1966); *Tetrahedron Letters*, 3613, 3625 (1965)), and by our own group (F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964); A. Shani and F. Sondheimer, *ibid.*, **89**, 6310 (1967)). Very recently, evidence has been obtained that all-*cis*- or 1,5-di-*trans*-[10]annulene is formed as a very unstable substance in the photolysis of *trans*-9,10-dihydronaphthalene at −190°,[3] while mono-*trans*-[10]annulene has been postulated as an unstable intermediate in the conversion of bicyclo[6.2.0]deca-2,4,6,9-tetraene to *trans*-9,10-dihydronaphthalene.[4]
(3) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).
(4) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967).
(5) D. M. Hall and B. Prakobsantisukh, *J. Chem. Soc.*, 6311 (1965); H. J. Bestmann, H. Häberlein, H. Wagner, and O. Kratzer, *Chem. Ber.*, **99**, 2848 (1966); E. D. Bergmann, P. Bracha, I. Agranat, and M. A. Kraus, *J. Chem. Soc., Sect. C*, 328 (1967).
(6) P. S. Bailey and R. E. Erickson, *Org. Syn.*, **41**, 41 (1961).
(7) C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); C. E. Griffin and J. A. Peters, *ibid.*, **28**, 1715 (1963).



1,2:3,4:7,8-Tribenz[10]annulene (3)[8] formed colorless prisms, mp 121–122°; mass spectrum, molecular ion at *m/e* 280.121 (base peak; calcd for $^{12}C_{22}{}^{1}H_{16}$: 280.125); λ_{max}^{EtOH} 242 mμ (ϵ 33,900) and 286 (10,700); ν_{max}^{KBr} 958 (s) cm^{-1}. The nmr spectrum (100 Mcps, CCl_4) showed a 12-H multiplet at τ 2.48–3.22 (aromatic protons), a 3-H six-line multiplet at 3.27–3.75, and a 1-H doublet (J = 17 cps) at 4.58 (olefinic protons). Substance **3** was reasonably stable in the solid state, but a solution in petroleum ether gradually became cloudy on standing in light and air.

Catalytic hydrogenation of **3** in ethanol over platinum on charcoal led to 70% 1,2:3,4:7,8-tribenzcyclodecane (**4**),[8] mp 94–95°; mass spectrum, molecular ion at *m/e* 284.153 (base peak; calcd for $^{12}C_{22}{}^{1}H_{20}$: 284.156); λ_{max}^{EtOH} 266 mμ (ϵ 1110) and 274 (980); ν_{max}^{KBr} 948 (m) cm^{-1}; nmr spectrum (60 Mcps, CCl_4), 8-H broad singlet at τ 2.92 (biphenyl protons), 4-H broad singlet at 3.04 (benzene protons), and 8-H broad singlet at 7.29 (aliphatic protons).

(8) Satisfactory microanalytical data were obtained for this compound.

Thermal rearrangement of **3** at 190° for 5 min gave 85% 9,10-dihydro-1,2:3,4-dibenzanthracene (**6**), mp 200–201° (lit. mp 202–203°),[9] which was identical with the minor product obtained from the Wittig reaction. Structure **6** was confirmed by the ultraviolet and nmr spectral data, as well as by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ; boiling benzene, 5 hr). The resulting 1,2:3,4-dibenzanthracene (**7**, mp 204–205°) was identified by direct comparison with an authentic sample (mp 204–205°).[10]

The thermal rearrangement of **3** to **6** probably involves the *o*-xylylene derivative **5** as an intermediate, from which **6** is obtained by the shift of two hydrogens. The rearrangement of **3** to **5** is a disrotatory process[11] and is analogous to the postulated conversion of mono-*trans*-[10]annulene to *trans*-9,10-dihydronaphthalene.[4] In order to trap the intermediate **5**, the thermal isomerization of **3** in the presence of maleic anhydride was studied.[12] This reaction (boiling xylene, 3 hr) yielded 75% of adduct **8**,[8] mp 262–263°; mass spectrum, molecular ion at *m/e* 378; λ_{max}^{EtOH} 265 mμ (ϵ 15,900) and 295 (5000);[13] ν_{max}^{KBr} 1870 (s), 1850 (m), and 1780 (s) cm^{-1}. The nmr spectrum (100 Mcps, $CDCl_3$) showed a 2-H multiplet at τ 2.14–2.44 and a 10-H multiplet at 2.44–2.95 (aromatic protons), a 1-H doublet (J = 4 cps) at 5.82 and a 1-H doublet (J = ~2 cps) at 5.94 (H^1, H^2), a 2-H eight-line band at 6.47 (H^3, H^4), as well as a 2-H AB quartet (J = 14 cps) at 7.50 (H^5, H^6). The observed $J_{5,6}$ value and the complexity of the nmr spectrum indicate the *trans* relationship of H^5 and H^6. The *endo* configuration of the anhydride grouping to the lone benzene ring follows from the rule of maximum overlap of unsaturation in the transition state,[14] although the possibility of inversion to the corresponding *exo* configuration under the vigorous reaction conditions cannot definitely be excluded. Structure **8** was confirmed by dehydrogenation with DDQ (boiling benzene, 5 hr). The resulting dehydro compound **9** (mp 255–257° dec) proved to be identical with one of the adducts (mp 257–259° dec) of 1,2:3,4-dibenzanthracene (**7**) and maleic anhydride described by Clar and Lombardi.[10b]

Adducts analogous to **8** were obtained by reaction of **3** with dimethyl acetylenedicarboxylate (adduct[8] mp 202–203°; nmr spectrum, $J_{5,6}$ = 19 cps) and with tetracyanoethylene (adduct[8] mp >300°). The formation of the adducts provides evidence for the intermediate **5**, although other pathways cannot be excluded.

Treatment of **3** with ~1 equiv of bromine in carbon tetrachloride at room temperature led to 70% of the dibromotetrahydrodibenzanthracene **10**, mp 174–176° dec. The nmr spectrum (100 Mcps, $CDCl_3$) exhibited broad bands at τ 4.48 (–C*H*Br–) and 6.00 (benzylic protons) of equal area, as well as a multiplet at ~2.2–

(9) W. E. Bachmann and L. H. Pence, *J. Am. Chem. Soc.*, **59**, 2339 (1937).

(10) (a) E. Clar, *Ber.*, **62**, 350, 1574 (1929); (b) E. Clar and L. Lombardi, *ibid.*, **65**, 1411 (1932).

(11) See R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(12) For a related trapping experiment, see I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1795 (1960).

(13) The related 9,10-dihydrophenanthrene shows λ_{max}^{EtOH} 264 mμ (ϵ 17,000) and 296 (5000) (R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941); R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 168).

(14) K. Alder and G. Stein, *Angew. Chem.*, **47**, 837 (1934); **50**, 510 (1937); K. Alder and R. Schmitz-Josten, *Ann.*, **595**, 1 (1955).

3.0 (aromatic protons). The dibromide **10** was contaminated with **7** and was easily converted to this substance by dehydrobromination with boiling ethanolic potassium hydroxide.

The properties and reactions of **3** provide clear evidence for the assigned structure. At least one of the double bonds must have the *trans* configuration, in view of the presence of a strong band at 958 cm^{-1} in the infrared spectrum and the observed J value of 17 cps in the nmr spectrum. The di-*trans* stereochemistry is excluded by the complexity of the olefinic pattern of the nmr spectrum. The mono-*trans* configuration **3** is confirmed by the fact that H^5 and H^6 (see **8**) in the adducts are *trans*-oriented (J = 14–19 cps). The corresponding protons in the precursor **5** are therefore also *trans*, the stereochemistry expected to be formed from the mono-*trans* compound **3** by a thermal disrotatory cyclization process.[4,11,15] On the other hand, all-*cis*-1,2:3,4:7,8-tribenz[10]annulene or the corresponding di-*trans* compound should have given *cis*-fused adducts.[3,11,16]

It appears that the ten-membered ring in **3** is nonplanar and does not represent a delocalized ten-π-electron system. A reason for the greatly increased stability of **3**, as compared with [10]annulene itself,[3,4] is presumably that the isomerization to the 9,10-dihydronaphthalene derivative in this case involves disruption of the cyclic delocalization of a benzene ring.

Acknowledgment. We are indebted to the Royal Society (London) for generous financial support and to Drs. P. J. Garratt and D. H. Williams for valuable discussions.

(15) See E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Letters*, 391 (1965).
(16) See D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, 377 (1965); E. J. Corey and A. G. Hortmann, *J. Am. Chem. Soc.*, **87**, 5736 (1965).
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Nuclear Magnetic Resonance and Superconductivity in the Clathrate Salt $[Ag_7O_8]^+HF_2^-$

Sir:

The electrical conductivity, superconductivity, and crystal structure of a number of silver oxide clathrate salts having the formula $[Ag_7O_8]^+X^-$ have been reported recently.[1] Among them was the material Ag_7O_8F, a black metallic substance having a cubic crystal structure as shown in Figure 1.[2,3] As can be seen from this figure, the structure consists of face-sharing Ag_6O_8 polyhedra enclosing alternately Ag^+ and F^- ions, with interatomic distances as given in the figure caption. By virtue of its structure, the lack of any abundant silver or oxygen nuclear species of sizable nuclear magnetic moment, and the large F^-–F^- separation, the nuclear dipole magnetic fields acting on an F^- ion in Ag_7O_8F will be quite small, the expected root-

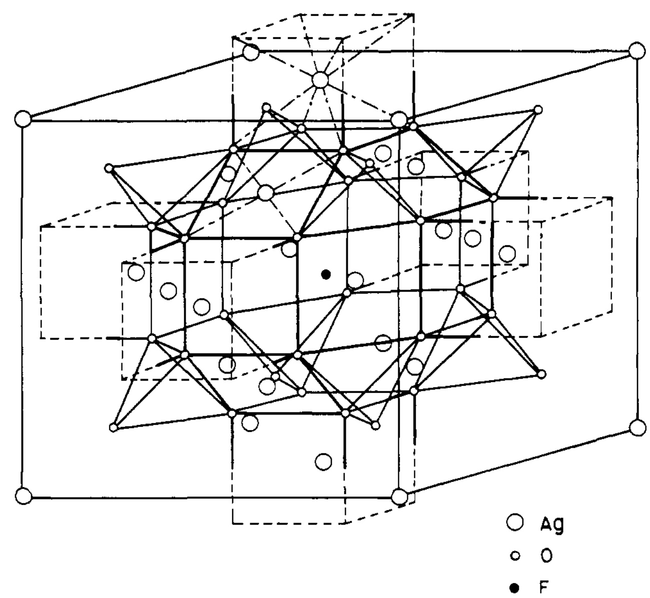

Figure 1. The crystal structure of Ag_7O_8F. In this structure, the distance from one fluoride ion to the next in an adjacent cage is 6.97 Å and to the twelve nearest neighbor silver ions is 3.49 Å; the distance to the nearest neighbor oxide ions is 4.09 Å.

mean-square second-moment broadening being approximately 0.2 G. It was then with some surprise that the 22-G-wide ^{19}F nmr spectrum shown in Figure 2 was observed at 4.2°K in material of nominal composition Ag_7O_8F. In addition, a proton nuclear resonance with two satellites was also seen. Our work suggests that these spectra are characteristic of the HF_2^- ion, and that preparation of the compound Ag_7O_8F is accompanied by the formation of more or less $Ag_7O_8HF_2$. This explains in part the variability of composition of "Ag_7O_8F" reported by Náray-Szabó and Popp.[4]

The unusually good resolution of the four ^{19}F lines in $Ag_7O_8HF_2$ is attributed to the low extraionic dipolar magnetic fields mentioned above. By contrast, in measurements made on $NaHF_2$ and KHF_2, the four components of the ^{19}F resonance could not be individually resolved.[5] The four-line pattern centered near the unperturbed fluorine resonance and three transitions near the unperturbed proton resonance are those expected for a system of randomly oriented, linear symmetric HF_2^- ions.[5] The peaks in the spectrum arise from absorption by nuclei in those ions lying in a plane perpendicular to the applied magnetic field. The assumption of an end-to-end distance of 2.26 Å[6] in a linear, symmetric HF_2^- ion leads to predicted resonances[5] at the positions shown in Table I. The agreement between the calculated and experimentally observed splittings confirms that the resonances are those of the HF_2^- ion, the small differences between calculated and observed values being attributed to the combined effects of vibrational or torsional zero-point motions of the ion, indirect nuclear exchange or nuclear pseudo-dipolar coupling, and the possibilities that the over-all length of the ion is greater than 2.26 Å or that the ion is

(1) M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, and D. B. McWhan, *Phys. Rev. Letters*, **17**, 917 (1966).
(2) C. Kung-Du, *Sci. Sinica* (Peking), **12**, 139 (1963).
(3) I. Náray-Szabó, G. Argay, and P. Szabó, *Acta Cryst.*, **19**, 180 (1965).
(4) I. Náray-Szabó and K. Popp, *Z. Anorg. Allgem. Chem.*, **322**, 286 (1963).
(5) J. S. Waugh, F. B. Humphrey, and D. M. Yost, *J. Phys. Chem.*, **57**, 486 (1953).
(6) L. Helmholz and M. T. Rodgers, *J. Am. Chem. Soc.*, **61**, 2590 (1939).