Fig. 1.—Absorbancies (A) at 260 mμ of fractions obtained by chromatography of pancreatic ribonuclease digests of 1.5 mg. each of the purified alanine-acceptor RNA (bottom curve), valine-acceptor RNA (middle curve), and tyrosine-acceptor RNA (top curve) on DEAE-Sephadex. (The column, 0.25 × 50 cm., was eluted with an increasing gradient of ammonium carbonate produced by using 120 ml. of water, 120 ml. of water, and 116 ml. of 0.75 M ammonium carbonate respectively, in three chambers of a Varigrad (see ref. 4). The volume of the fractions was 2.2 ml.)

fraction 90, very pronounced in the digest of the alanine RNA, is believed to be GpUp, the last of the dinucleotides to be eluted.

Comparison of the three curves in Fig. 1 indicates that there is hardly a single oligonucleotide that occurs to the same extent in any two of the RNAs. The chromatographic analyses on DEAE-Sephadex are highly reproducible and even the smaller differences in the curves are believed to be real.

It is clear that the alanine-, valine-, and tyrosine-acceptor "soluble" RNAs of yeast differ greatly in structure. The differences between these three RNAs are much more complex than would be required by simple hypotheses of information transfer by nucleic acids.

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RECEIVED NOVEMBER 8, 1961

MOLECULAR STRUCTURE OF $C_8H_8Fe(CO)_3$

Sir:

There have been a number of suggestions[1,2,3,4,5,6] that the cyclooctatetraene (COT) ring in $C_8H_8Fe(CO)_3$ is planar, and one suggestion[7] that the tub form, like that established for free cyclooctatetraene[8,9,10] and its silver complex,[11,12] occurs in this compound. A similarly large number and greater variety of suggestions for the geometry of the C_8H_8 ring in $(OC)_3FeC_8H_8Fe(CO)_3$ were shown to be incorrect, when the unsuspected chair form was proved.[13] We show here that yet another geometry, a dihedral form not included in any of the above predictions, occurs for the cyclooctatetraene ring in $C_8H_8Fe(CO)_3$.
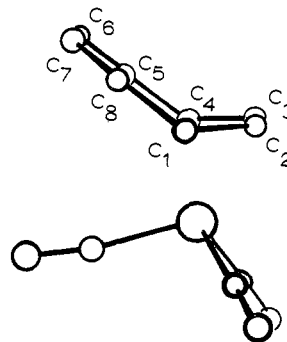

Fig. 1.—The structure of $C_8H_8Fe(CO)_3$: bond distances are $C_1-C_2 = C_3-C_4 = 1.42$, $C_2-C_3 = 1.42$, $C_4-C_5 = C_1-C_8 = 1.45$, $C_5-C_6 = C_7-C_8 = 1.34$, $C_6-C_7 = 1.49$, $Fe \cdot C_1 = Fe-C_4 = 2.18$, $Fe-C_2 = Fe-C_3 = 2.05$, $Fe-C$ (carbonyl) $= 1.80$ (av.), $C-O = 1.13$ (av.) all ± about 0.02 Å. Bond angles are $C_1-C_2-C_3 = C_2-C_3-C_4 = 124.6°$, $C_3-C_4-C_5 = C_2-C_1-C_8 = 132.4°$, $C_4-C_5-C_6 = C_1-C_8-C_7 = 133.2$, $C_5-C_6-C_7 = C_8-C_7-C_6 = 131.8°$, all ± about 1°, and to be compared with 135° in the regular plane octagon. The angle between normals to the two planes in C_8H_8 is 41° in $C_8H_8Fe(CO)_3$.

A total of 856 observed X-ray diffraction maxima from a single crystal of symmetry Pnam with four molecules in a unit cell of dimensions $a = 6.54$, $b = 13.46$ and $c = 11.51$ Å. has yielded an agreement factor of $R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.091$. The molecular structure (Fig. 1) shows that the $Fe(CO)_3$ group is attached to a "buta-

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diene" part of the C_8H_8 ring in a structural unit which is proving increasingly neatly general,[14,15,16,17] and which was suggested[18] for $C_4H_6Fe(CO)_3$, and employed[19] in interpreting closely related compounds and associated reactions. The structure also shows that six of the eight atoms of the ring are very nearly coplanar, and that six of the eight bond angles of the ring are within about 3° of the 135° angle of a completely regular and planar ring. The nature and extent of these distortions from the tub form of uncomplexed cyclooctatetraene make it possible that the $(COT)^-$ and $(COT)^{-2}$ ions may achieve planarity without great difficulty, as has long been anticipated from molecular orbital theory, and recently proposed[20,21] in connection with the preparation and properties of these ions, but distortions from planarity cannot yet be ruled out. Aside from these large bond angle distortions, the distances in the uncomplexed half of the ring in $C_8H_8Fe(CO)_2$ are very suggestive of a butadiene residue, but a comparison of overlap integrals[22] which are 0.25 between C_4–C_5 or C_1–C_8 in $C_8H_8Fe(CO)_3$ and 0.04 between corresponding atoms in $(OC)_3$-$Fe(C_8H_8)Fe(CO)_2$, indicates that the butadiene halves of the C_8H_8 ring interact more strongly in $C_8H_8Fe(CO)_3$ than in $(OC)_3FeC_8H_8Fe(CO)_3$.

It is not known whether the equivalence of H^1 nuclear magnetic resonances, previously incorrectly attributed[18] to $(OC)_3FeC_8H_8Fe(CO)_3$, observed[1,2] for $C_8H_8Fe(CO)_3$ is indicative of negligible relative chemical shifts, a dynamical effect, or some difference of molecular geometry upon solution in carbon disulfide. A study of the temperature dependence of this spectrum may be of some help in elucidating this problem.

We wish to thank Dr. T. A. Manuel and Dr. F. G. A. Stone for their courtesy in supplying us with a sample, and we acknowledge support of this research by the Office of Naval Research.

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UNSATURATED MACROCYCLIC COMPOUNDS. XXIV.[1] SYNTHESIS OF FOUR COMPLETELY CONJUGATED SIXTEEN-MEMBERED RING CYCLIC SYSTEMS

Sir:

We have synthesized four completely conjugated sixteen-membered ring monocyclic hydrocarbons, namely, cyclohexadecaoctaene ([16]annulene[2]), cyclohexadecaheptaenyne (monodehydro-[16]annulene[2]) and two isomers of cyclohexadeca-

(1) Part XXIII, F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc.*, in press.

(2) For the nomenclature employed, see Part XXI of this Series (F. Sondheimer and R. Wolovsky, *ibid.*, in press).

hexaenediyne (bis-dehydro[16]annulene[2]). These 16 π-electron systems were expected to be nonaromatic, since they do not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π-electrons].

Reaction of trans-1,4-dibromo-2-butene with an excess of ethynylmagnesium bromide in tetrahydrofuran in the presence of cuprous chloride yielded besides other products[3] ca. 25% of trans-4-octene-1,7-diyne (I) [m.p. 15°, b.p. 59–60° (25 mm.), $n^{19}D$ 1.4718; C_8H_8 (found: C, 92.28; H, 7.80; act. H, 2.01); no high-intensity absorption

$$HC{\equiv}CCH_2CH{\overset{t}{=}}CHCH_2C{\equiv}CH$$
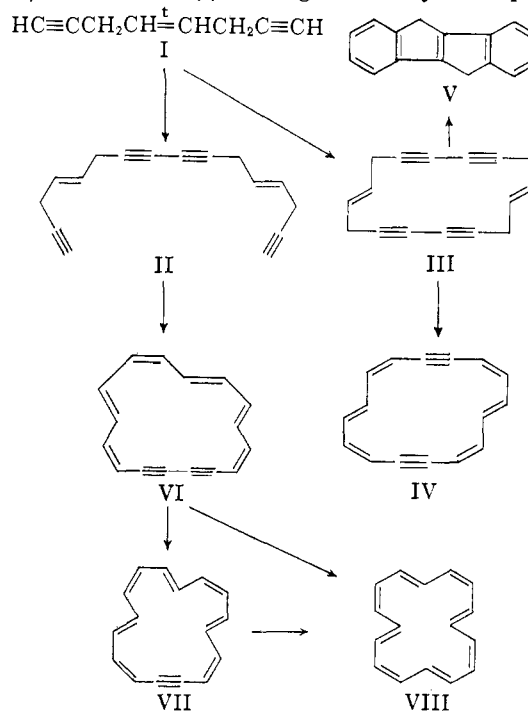
in the ultraviolet]. Coupling of I by passing oxygen into a mixture containing this hydrocarbon, ammonium chloride, cuprous chloride, ethanol and dilute hydrochloric acid[4] at 55° for 80 minutes produced ca. 25% of the linear dimer trans-trans-4,12-hexadecadiene-1,7,9,15-tetrayne (II) [colorless plates, m.p. 79–80°; $C_{16}H_{14}$ (found: C, 93.29; H, 6.79); $\lambda_{max}^{isooctane}$ 225, 239 and 253 mμ (ϵ 430, 390 and 240); converted by full hydrogenation to n-hexadecane, m.p. and mixed m.p. 17→18°] and 3 per cent. of the cyclic dimer trans-trans-1,9-cyclohexadecadiene-4,6,12,14-tetrayne (III) [colorless plates decomposing explosively at ca. 215°; $C_{16}H_{12}$ (found: C, 94.44; H, 5.96); λ_{max}^{ether} 232, 245 and 258 mμ (ϵ 740, 780 and 490); no terminal acetylene (infrared); converted by full hydrogenation to cyclohexadecane, m.p. and mixed m.p. 61–62°].

Treatment of the cyclic dimer III in benzene with a saturated solution of potassium t-butoxide in t-butyl alcohol at 40° for 1 minute yielded an isomeric mixture of bisdehydro[16]annulenes, chromatography on alumina giving violet and then orange solutions with main ultraviolet maxima

(3) See F. Sondheimer and Y. Gaoni, *ibid.*, **82**, 5765 (1960); **83**, 1259 (1961).

(4) See F. Sondheimer, *et al.*, *ibid.*, **79**, 5817, 6263 (1957); **81**, 6301 (1959).