must contain bromo-I, which although originally covalent, may ionize in appropriate solvents to give III.

For cations obtained by protonation of carotenoids an upper limit for λ_{max} has been calculated by Wassermann.[6] For two double bonds, conjugated with a positive charge, this limit is 484 mμ, indicating that III is not itself the magenta species, but rather a precursor to it.

From the magenta solutions three dimeric hydrocarbons are recovered, with ultraviolet spectra, characteristic of polyenes. Each upon protonation regenerates the magenta color instantaneously with high ϵ. This indicates that in its simplest form the magenta species is also dimeric. The absence of chromophores of different length, corresponding to progressive extension, follows from the observation of only a single peak at 552 mμ.

The acetic acid solvent was evaporated *in vacuo* at 25° from a magenta solution obtained by protonation of II. The remaining viscous magenta residue was triturated repeatedly with pentane so as to extract all but the most strongly protonated compounds. Ice cold aqueous potassium hydroxide then was added. Extraction of the resulting suspension with pentane, then evaporation of the solvent, gave an orange viscous residue. Sublimation at 0.1 mm. (Dry Ice in condenser) yielded: (1) at 80°, a yellow hydrocarbon (VI), after resublimation, partially crystallizable from a minimum of pentane at −10° to give yellow needles, m.p. 66–75° (prob. impure with VII). *Anal.* C, 88.85; H, 11.03; mass spec. mol. wt., 296 ($C_{22}H_{32}$). $\lambda_{max}^{isooctane}$, 333.6, 370.0, 390.0 (sh) mμ; $\epsilon_{max} \times 10^{-4}$, 2.165, 3.020, 2.890, 0.62[7]; $\lambda_{max}^{CH_3COOH, CH_3SO_3H(0.05\ M)}$, 552 m$\mu$; ϵ_{max} 48,800. Carr–Price reaction,[8] $\lambda_{max}^{CHCl_3, SbCl_3}$ 563, 602 mμ. (2) at 100–110°, an orange hydrocarbon (VII); after resublimation and recrystallization from pentane at −10°, orange needles m.p. 140–145°. *Anal.* C, 89.03; H, 10.97; mass spec. mol. wt., 296 ($C_{22}H_{32}$). $\lambda_{max}^{isooctane}$, 350.0, 369.0, 390.0 m$\mu$; $\epsilon_{max} \times 10^{-4}$, 1.88, 2.66, 2.32.[7] $\lambda_{max}^{CH_3COOH,CH_3SO_3H(0.05\ M)}$, 552 m$\mu$; ϵ_{max} 49,600. Carr–Price reaction: $\lambda_{max}^{CHCl_3, SbCl_3}$, *563*, 602 m$\mu$. (3) at 130°, an orange hydrocarbon (VIII); after resublimation and crystallization from pentane at −10°, m.p. 151–153°, orange needles. *Anal.* C, 89.23; H, 10.72; mass spec. mol. wt., 296 ($C_{22}H_{32}$). $\lambda_{max}^{isooctane}$, 350.0, 369.0, 390.0 m$\mu$; $\epsilon_{max} \times 10^{-4}$, 1.88, 1.27, 1.66, 1.41; [7]$\lambda_{max}^{CH_3COOH,CH_3SO_3H(0.05\ M)}$, 552 m$\mu$; ϵ_{max} 49,300. Carr–Price reaction; $\lambda_{max}^{CHCl_3, SbCl_3}$ *563*, 602 mμ.

The ultraviolet spectra especially of VI and VII, with three intense maxima, are characteristic of conjugated polyenes with unhindered coplanarity.[9]

II may add to III either as IIIa or IIIb. Dreiding stereomodels[10] indicate that crowding in the primary addition product of II to IIIa is prohibitive in all steric configurations.
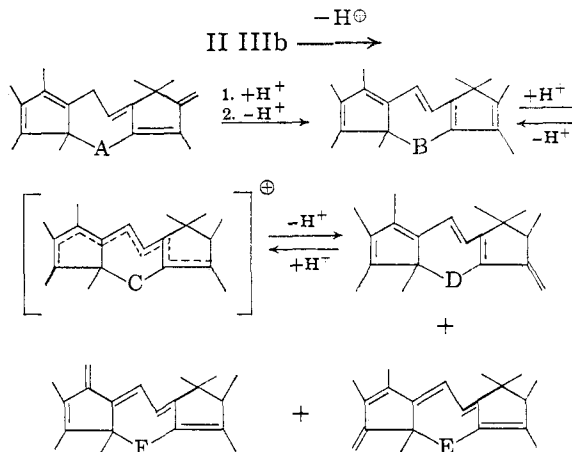
(6) A. Wassermann, *J. Chem. Soc.*, 979 (1959).

(7) Initially the hydrocarbon was dissolved in a minimum of isooctane.

(8) E. H. Carr and E. A. Price, *Biochem. J.*, **31**, 497 (1926).

(9) W. Oroshnik, *et al.*, *J. Am. Chem. Soc.*, **74**, 295 (1952); **76**, 5719 (1959).

(10) Rinco Instrument Company, Greenfield, Illinois.

On the other hand, hindrance is absent in A, the addition product of II to IIIb, as well as in the secondary rearrangement products E and F with double "retro" structure[9] (B and D show some crowding).

In VI and VII bands at: 858 (mw), 1720 (w) (overtone of 858), 3078 (vw) cm.$^{-1}$ indicate vinyl-methylene exocyclic to a strained ring such as in II. The low relative intensities indicate a ratio of vinyl-methylene to CH_3 considerably less than half that in II (2:4). A sharp band at 800 cm.$^{-1}$

(mw) $\begin{bmatrix} R \\ R \end{bmatrix} C{=}C \begin{matrix} H \\ R \end{matrix}$ in VI and VII is absent

in VIII, which instead exhibits a sharp band at

958 cm.$^{-1}$ (m) $\begin{bmatrix} R \\ H \end{bmatrix} C{=}C \begin{matrix} H \\ R \end{matrix}$ In the 1600–1700

cm.$^{-1}$ region, all three exhibit complex absorption with a main band at 1620 cm.$^{-1}$ (s).

These spectra are consistent with the assignments VI = F, VII = E, VIII = B + D. The exceptionally stable magenta species then is presumably the ion C, which is similar to certain carotenoid ions.[6]

Thanks are due to Professor S. Winstein for constructive criticisms.

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DIPOLE MOMENTS OF BIS-CYCLOPENTADIENYL TITANIUM AND ZIRCONIUM DICHLORIDES

Sir:

Metal compounds involving π-bonded bis-cyclopentadienyl groups have evoked a great amount of interest in the past decade, and a recent review[1] has critically surveyed the bonding aspects and inorganic and physical chemistry of these materials. The relative positions of the cyclopentadienyl rings have been elucidated by crystal structure and dipole moment determinations for ferrocene and a few other similar materials, but no conclusive evidence as to the structure of bis-cyclopentadienyl

(1) G. Wilkinson and F. A. Cotton in "Progress in Inorganic Chemistry," Vol. I, edited by F. A. Cotton, Interscience Publishers Inc., New York, N. Y., 1959, pp. 1–124.

titanium dichloride (I) or its zirconium analog (II) has been found. Wilkinson and Birmingham[2] demonstrated from infrared data that a monomeric π-bonded "sandwich" structure exists for I and II. Sloan and Barber[3] reinforced these observations by proton magnetic resonance data on I and II, but no mention has been made of the spatial configuration of the rings.

"Angular" sandwich structures have been postulated for bis-cyclopentadienyl tin and lead on the basis of dipole moments and other measurements,[4] and X-ray measurements on $(C_5H_5)_2TiCl_2 \cdot Al(C_2H_5)_2$ (III).[5]

We wish to report that the *high* values of the dipole moments obtained, 6.3 and 5.9 D for I and II, respectively, indicate that there are four essentially equivalent bond angles and that the structure is similar to the $[(C_5H_5)_2TiCl_2]$ grouping in III, *i.e.*, approaching the tetrahedral configuration as depicted in Fig. A. It is of interest that the structure appears to be independent of the oxidation state.
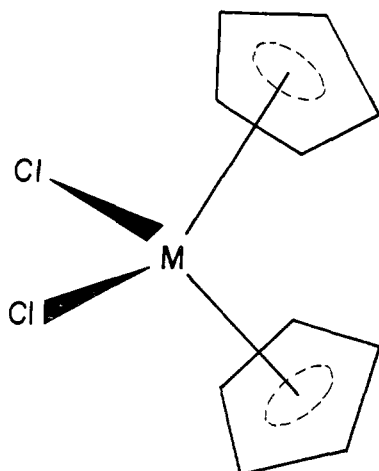

Fig. 1.

The measurements were conducted in benzene using the "dielectric constant–refractive index" method for I and II, and the "dielectric constant–density" method for I. Measurements made both on freshly prepared solutions and on solutions one day old were identical, suggesting that changes in solution, if any, had no effect on the dielectric constant. The results are shown in Table I.

Dielectric constant measurements were made at 30.0° using a heterodyne-beat circuit consisting of two electron coupled oscillators, one controlled with a quartz crystal at 576.5 kc. and the frequency of the other one controlled by the variable capacitance. A Balsbaugh model cell made of Pyrex and monel metal was used. The volume was 50 ml., and the interplate air capacitance was 49.4 $\mu\mu f$. Refractive index was measured with a Bausch and Lomb Precision Abbe refractometer,

(2) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

(3) C. L. Sloan and W. A. Barber, *ibid.*, **81**, 1364 (1959).

(4) L. D. Dave, D. F. Evans and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(5) G. Natta, P. Corradini and I. W. Bassi, *J. Am. Chem. Soc.*, **80**, 755 (1958).

BIS-CYCLOPENTADIENYL TITANIUM DICHLORIDE

Concn. (wt. fract.)	Dielectric constant ϵ	Density (g./cc.)	$\eta^{30}D$	$(\eta_D)^2$
0.000869	2.284	...	1.49440	2.23323
.001929	2.300	...	1.49448	2.23347
.002870	2.313	...	1.49457	2.23374
.00169	2.290	0.8695	...	...
.000615	2.279	.8690	...	...
.000327	2.269	.8689	...	...
Solvent	2.265	.8684	...	...

BIS-CYCLOPENTADIENYL ZIRCONIUM DICHLORIDE

Concn. (wt. fract.)	ϵ	$\eta^{30}D$	$(\eta_D)^2$
0.002978	2.303	1.49459	2.23379
.001951	2.291	1.49454	2.23365
.001052	2.276	1.49448	2.23347
.000472	2.273	1.49440	2.23323
Solvent	2.265	1.49439	2.23320

temperature controlled to 0.05°. Densities were measured in a 25 ml. pycnometer.[6]

The data were interpreted by the method of Guggenheim and Prue[7] and of Halverstadt and Kumler.[8] A least squares analysis was applied with these results.

	μ(Debyes)	Method
Ti Compound I	6.26 ± 0.39	Refractive index
	6.22 ± 0.39	Density
Zr Compound II	5.90 ± 0.38	Refractive index

The uncertainty given represents the 95% confidence interval of the data.

(6) The dielectric constant, refractive index and density measurements were performed by J. R. Murray of these Laboratories.

(7) E. A. Guggenheim and J. E. Prue, "Physicochemical Calculations," Interscience Publishers, Inc., New York, N. Y., 1955, pp. 106, *et seq.*

(8) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

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THE CONFORMATION OF METAL-ADENOSINE TRIPHOSPHATE COMPLEXES IN SOLUTION

Sir:

The fact that adenosine triphosphate (ATP) forms strong complexes with divalent metal ions is well known and quantitative equilibrium[1,2] and kinetic studies[3] have been caried out by several workers. The most important metal binding sites are undoubtedly the phosphate groups, but the role of the rest of the molecule in forming the metal complex has given rise to much speculation (*cf.* reference 4 for a review of this subject and pertinent literature citations). Solid state infrared studies,

(1) A. E. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

(2) R. A. Alberty and R. M. Smith, *J. Am. Chem. Soc.*, **78**, 2376 (1956).

(3) H. Diebler, M. Eigen and G. G. Hammes, *Z. für Naturforsch.*, **15B**, 554 (1960).

(4) M. R. Atkinson and R. K. Morton in "Comparative Biochemistry," M. Florikin and H. S. Mason, ed.), **2**, Academic Press, New York, N. Y., 1960, pp. 1-82.