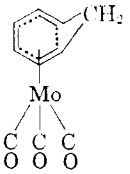
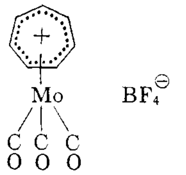
triene and molybdenum hexacarbonyl vapors through a hot tube at 150–250°, was identical in all respects with the previously reported material made by an unspecified method[3] (orange-red plates by


I


II

sublimation or from pentane, m.p. 100.5–101.5°; ultraviolet ($\lambda_{max}$, $\epsilon_{max}$, $CH_2Cl_2$): 252 (sh., 12,300), 324 (7450), 383 (4200), 482 mμ (600); infrared (KBr): 3.02 w, 5.15 s, 5.30 s, 5.36 (sh.) s, 6.90 w, 7.01 w, 10–10.75 w, 11.93 w, 12.77 w. Equivalent quantities of I and trityl fluoroborate in methylene chloride react immediately to give a crystalline precipitate of π-tropenium-molybdenum-tricarbonyl fluoroborate (II) and evaporation of the filtrate, then chromatography on alumina, furnishes tritane, both in 98–100% yields; recrystallization of the precipitate from methylene chloride yields II as light orange fine needles, m.p. >270° (gradual darkening from 140°), insoluble in water or pentane, slightly soluble in methylene chloride, very soluble in acetone, acetonitrile or 96% sulfuric acid, stable in air but slow decomposition with liberation of tropenium fluoroborate occurs in these organic solvents; *anal.* Calcd. for $C_{10}H_7O_3BF_4Mo$: C, 33.55; H, 1.97. Found: C, 33.20; H, 2.09; u. v. ($\lambda_{max}$, $\epsilon_{max}$, $CH_2Cl_2$ or 96% $H_2SO_4$): 238 (sh., 14,700), 299 (29,000), 380 mμ (1,300); i.r. (KBr): 3.02 w, 4.93 (sh.) w, 5.03 s, 5.13 s, 7.00 w, 8.5–10.0 s ($BF_4^-$), 9.70 m, 12.52 m.

Ultraviolet and infrared spectra, by differing markedly from those for tropenium fluoroborate,[4] clearly establish II as a molecular complex. The presence of two intense carbonyl stretching bands in its infrared spectrum, as found in analogous aromatic complexes, $(\pi\text{-}C_6H_6)Mn(CO)_3$ and $(\pi\text{-}C_6H_6)Cr(CO)_3$, of similar symmetry but in contrast to the three carbonyl bands shown by the cycloheptatriene complex (I) with lower symmetry, and of a single proton resonance band in its high resolution nuclear magnetic resonance spectrum in $D_2SO_4$ are only consonant with a structural assignment of a fully aromatic structure to II in which the molybdenum atom is complexed with the cyclic π-molecular orbital encompassing all seven carbon atoms of the tropenium ion ligand.

Additional studies on this and other metal-tropenium ion complexes are in progress.

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RECEIVED SEPTEMBER 15, 1958

## THE $B_8Cl_8$ STRUCTURE: A NEW BORON POLYHEDRON IN SMALL MOLECULES

*Sir:*

Samples of a boron chloride hitherto known[1] only as $(BCl_{0.9})_x$ have been supplied to us through the courtesy of H. I. Schlesinger, T. Wartik and G. Urry. In a preliminary X-ray diffraction study, completed about three years ago, M. Atoji and W. N. Lipscomb obtained 1175 diffraction maxima, and showed that there were four molecules in an orthorhombic unit cell having symmetry $P2_12_12_1$ and dimensions $a$ = 13.64, $b$ = 7.85 and $c$ = 12.91 Å. A density of 1.75 g. cm.$^{-3}$, measured with difficulty, agrees best with the formula $B_8Cl_8$, but this formula was then regarded as highly uncertain.

We have now solved the complete molecular structure with the use of point-by-point Patterson superposition techniques on the UNIVAC SCIENTIFIC 1103 Computer. Present values of $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.20$ and $r = \Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma w|F_0|^4 = 0.18$ indicate that refinement is nearly complete. The resulting molecular structure is shown in Fig. 1. A polyhedron of boron atoms is surrounded by Cl atoms, each of which is joined to B by a single bond, as is true in the $B_4Cl_4$ structure.[2] Although no molecular symmetry is required by the space group, the isolated molecule apparently has $D_{2d}$ symmetry.

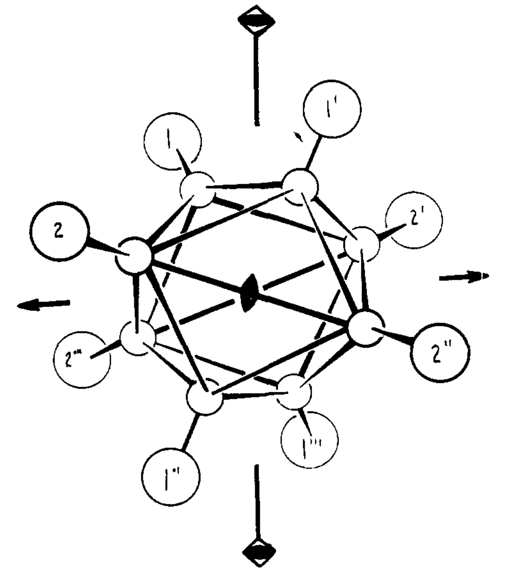

Fig. 1.—The $B_8Cl_8$ structure: small circles represent B and large circles represent Cl. Average Cl . . . Cl distances (±0.04 Å.) are 4.05 Å. for the 8 symmetry-equivalent distances of type 1–2, 3.51 Å. for the other 4 of type 1–2, 4.45 Å. for the 4 of type 2–2, and 3.94 Å. for the two of type 1–1. Corresponding average B–B distances (±0.05 Å.) are, respectively, 1.79, 1.85, 2.07 and 1.78 Å. The average B–Cl distance is 1.70 ± 0.04 Å.

As usual in such a compact structure, the use of three-center bonds is not a very satisfactory descrip-

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[5] We are indebted to the Office of Ordnance Research, U. S. Army, Contract No. DA-04-200-ORD-715, for financial support, and to the Shell Chemical Corporation and to the Climax Molybdenum Company, respectively, for samples of cycloheptatriene and molybdenum hexacarbonyl.

[1] G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **76**, 5293 (1954).

[2] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953); *Acta Crystallographica*, **6**, 547 (1953).

tion[3] unless a number of resonance structures is hybridized. However, the LCAO orbitals are reasonable, and indicate that the compound has filled valence orbitals. Local hybridization is conveniently assumed to be sp along the BCl direction. The eight sp orbitals pointing inward form two strongly bonding orbitals and, in the one-electron approximation, a vacant doubly degenerate pair which may interact with the lone pairs on the Cl atoms.[4] The $\pi$ orbitals of the boron atoms form six pairs of bonding orbitals, thus giving a total of eight bonding pairs for the B . . . B interactions. A more detailed discussion of the structure determination and valence theory will be presented elsewhere. This molecule, like other known boron hydrides and halides, has high enough symmetry to prevent reactive regions, and low enough symmetry that unfilled electronic levels do not occur near the highest filled levels. The occurrence of this new polyhedron has suggested a study, now under way, of LCAO molecular orbitals in other polyhedra, and a comparison with orbitals in $Mo(CN)_8^{-4}$, which also has $D_{2d}$ symmetry.[5]

We wish to thank Dr. M. Atoji for his help in the early stages, and to thank the Office of Naval Research, the Office of Ordnance Research and the Computing Center of the University for aid in this investigation. We are also indebted to the Shell Oil Company for a fellowship to Robert Jacobson.

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[3] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[4] H. C. Longuet-Higgins, *Quarterly Reviews*, **11**, 121 (1957).

[5] J. L. Hoard and H. H. Nordsieck, THIS JOURNAL, **61**, 2853 (1939).

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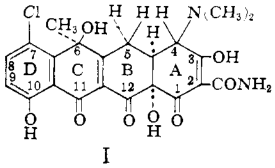
RECEIVED AUGUST 25, 1958

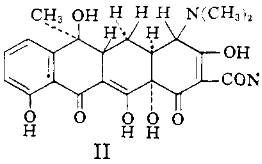
## TWO NEW TETRACYCLINE-RELATED COMPOUNDS: 7-CHLORO-5a(11a)-DEHYDROTETRACYCLINE AND 5a-*epi*-TETRACYCLINE. A NEW ROUTE TO TETRACYCLINE

*Sir:*

We wish to report the isolation. characterization, and structure proof of two new tetracycline-related compounds: 7-chloro-5a(11a)-dehydrotetracycline (I), accumulated by *Streptomyces aureofaciens* Duggar mutant S-1308, and 5a-*epi*-tetracycline (II), prepared from I by catalytic hydrogenation.[1]



I



II

7-Chloro-5a(11a)-dehydrotetracycline hydrochloride: $[\alpha]^{25}_D$ +15.5° (0.65% in 0.03N HCl); $\lambda_{max}$ 221 m$\mu$, $\epsilon$ 27,500; $\lambda_{max}$ 251 m$\mu$, $\epsilon$ 23,000; $\lambda_{max}$ 375 m$\mu$ (very broad), $\epsilon$ 4,300. *Anal.* Found for $C_{22}H_{22}N_2Cl_2O_8$: C, 51.23; H, 5.12; N, 5.21; Cl, 13.82; 0 (Unterzaucher), 24.54; loss on drying, 0; ash, 0. The origin and composition of I implied a close relationship to 7-chlorotetracycline. Upon catalytic hydrogenation (Pd–C), I rapidly absorbed two moles of hydrogen, yielding two chlorine-free organic products. They were tetracycline and II, an isomer of tetracycline differing from tetracycline, on the basis of the ultraviolet absorption spectrum (300–400 m$\mu$), in the Rings B–C–D chromophore region. 5a-*epi*-Tetracycline hydrochloride monohydrate: $[\alpha]^{25}_D$ +147° (0.50% in 0.1 *N* $H_2SO_4$); $\lambda_{max}$ 220 m$\mu$, $\epsilon$ 15,000; $\lambda_{max}$ 265 m$\mu$, $\epsilon$ 19,200; $\lambda_{max}$ 336 (broad), $\epsilon$ 12,000. *Anal.* Found for $C_{22}H_{25}N_2ClO_8.H_2O$: C, 53.12; H, 5.33; N, 5.36; Cl, 7.41; 0 (Unterzaucher), 28.75; loss on drying, 3.43; ash, 0. The hydrogen uptake, the fact that tetracycline is a major reduction product, and the difference between the ultraviolet absorption spectrum of I and of 7-chlorotetracycline, especially in the region attributed solely to the Rings B-C-D chromophore (300–400 m$\mu$), suggested that I is a dehydrochlorotetracycline, the additional unsaturation being associated with the Rings B-C-D chromophore. The presence in I of non-hydrogen-bonded carbonyl absorption in the infrared (5.8 $\mu$) favors 5a(11a) as the position of the additional double bond.

The isomeric relationship of II and tetracycline was established by analysis and by the conversion of II in essentially quantitative yield under established dehydration conditions to anhydrotetracycline. These facts, together with the fact that tetracycline and II maintain their different identities under conditions expected to bring about tautomeric equilibrium, established II as 5a-*epi*-tetracycline.

Further confirmation of the relationship between tetracycline and II was found in their relative rates of dehydration. In 1*N* sulfuric acid at 100°, the half reaction times for dehydration of tetracycline and II were <1 min. and 67 min., respectively. This is consistent with the structural assignment of 5a($\alpha$)H,6($\beta$)OH (therefore *trans*) for tetracycline[1] and 5a($\beta$)H,6($\beta$)OH (therefore *cis*) for II.

Paper chromatography gave these $R_f$ values for I in the systems: 0.3*M* sodium phosphate (*p*H 3.0)/*n*-butanol, 0.49; MacIlvaine's buffer (*p*H 4.7)/ethyl acetate, 0.87; 0.3*N* phosphoric acid, 0.1% trichloroacetic acid/9:1 chloroform-*n*-butanol, 0.39. II ih the phosphate/butanol system had an $R_f$ value of 0.65.

The organism, S-1308, accumulating I is a mutant descended from the original 7-chlorotetracycline-producing *S. aureofaciens* A-377 soil isolate of Duggar.

Neither 7-chloro-5a(11a)-dehydrotetracycline nor 5a-*epi*-tetracycline possesses *in vitro* antibacterial activity toward *Staphylococcus aureus* in excess of 0.5% that of 7-chlorotetracycline.

It is now known that the antibacterial activity of tetracycline (toward *S. aureus*) is substantially unaltered by replacement of 5-H with OH, of 6-$CH_3$ with H, or of 7-H with Cl or Br. In contrast, other small changes reducing this antibacterial activity

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[1] The configurations in this paper are based on the stereochemistry suggested by Hochstein, *et al.* (THIS JOURNAL, **75**, 5467 (1953)) for 5-hydroxytetracycline.