$H_{34-6}O_4$,[1] but attempts to prepare derivatives led to complex mixtures of products.

Good single crystals of harunganin were grown by slow crystallization from methylene chloride-cyclohexane. These were monoclinic needles, cell dimensions: $a = 32.90$ Å., $b = 9.30$ Å., $c = 17.80$ Å., $\beta = 101° 17'$; and from the systematic extinctions belonged to one of the space groups Cc or C2/c. The density (1.150) indicated the presence of eight molecules of molecular weight 464, definitely favoring the formula $C_{30}H_{36}O_4$ (460.6).

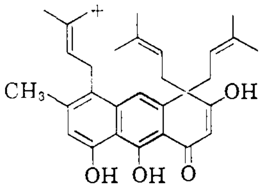
Data were collected on a G.E. counter diffractometer, 5821 reflections being scanned with 3086 measurably above background, and a three-dimensional sharpened Patterson function was calculated.

Patterson superpositions were at first based on C2/c symmetry and revealed the presence of several six-membered rings in harunganin, but the apparent molecules consistently approached each other too closely. Since the symmetry operations of Cc form a subset of those of C2/c, later superpositions were therefore based on Cc in the expectation that any higher symmetry would be revealed in the final structure. However, two molecules (68 non-hydrogen atoms) instead of only one had then to be located in the asymmetric unit of the superposition map.

Repeated superpositions and extensive testing of individual atoms revealed first one and then a second anthracene-like skeleton of six-membered rings, together with some of the atoms joined directly to the rings, 36 atoms in all. Structure factors were calculated using these and examination of a three-dimensional Fourier synthesis based on the calculated phases showed the location of thirty more side chain atoms. One more round of structure factor calculations and Fourier synthesis revealed the last two atoms of the 68. At this point, the asymmetric unit appeared to consist of two identical molecules related by the additional symmetry of C2/c, and subsequent calculations were therefore performed in this space group. Refinement by full-matrix least squares,[2] identified the oxygen atoms through the behavior of their individual temperature factors, and showed the molecular structure to be I.

When anisotropic temperature factors were introduced, it was found that one of the side chain methyl groups (starred in I) showed excessive anisotropy (r.m.s. amplitudes of vibration along the principal axes, 0.76, 0.28, and 0.42 Å.). Such behavior was found to be consistent with a crystal structure in which the side chain may lie in two slightly different positions in the cell. Despite extensive investigation, it is not yet possible to say whether this represents a slight randomization of a C2/c structure or whether harunganin in fact crystallizes in a very nearly centrosymmetric Cc form.

At the present stage of refinement, the residual index R is 11.9% on the observed reflections. The bond lengths found indicate that the predominant direction of enolization of the β-diketone system is as shown in I, but it appears possible from the packing that it is not the same in all molecules.



I

The structure of harunganin, although highly unusual, is not without analogy. *gem*-Diisopentenyl substitution on phenolic precursors also has been found in the hop principle lupulon.[3] Furthermore, in view of the close botanical relationship of *Harungana* and the genus *Hypericum*, it is of interest that both harunganin and hypericin[4] are based on emodin related skeletons.

Acknowledgments.—This work was supported in part by grants from the National Institutes of Health and by generous gifts of computer time from the Research Computer Laboratory of the University of Washington.

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(1) Harunganin has been isolated independently by Dr. Walter C. Taylor, University of Sydney, who kindly communicated his findings to us.

(2) A Crystallographic Least Squares Refinement Program for the IBM 704, W. R. Busing and H. A. Levy, Oak Ridge National Laboratory, 1959.

(3) M. Verezele and F. Govaert, *Bull. soc. chim. Belg.*, **58**, 432 (1949).

(4) H. Brockmann, E. H. F. v. Falkenhausen, R. Neeff, A. Dorlars and G. Budde, *Ber.*, **84**, 865 (1951).

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A NEW SYSTEM OF STABLE FREE RADICALS[1]

Sir:

We wish to report the first members in a series of complex free radicals, stable at ambient temperatures, containing only boron and chlorine. The first has been completely characterized by analysis, molecular weight determinations and the electron spin resonance spectrum as $B_{12}Cl_{11}$. The second has been obtained so far in quantities too small for adequate characterization but has a composition in the range $(B_{1.0}Cl_{0.9-1.1})_x$ and a molecular weight in the range from 650–750.

Both of the new radicals are formed in the spontaneous disproportionation of diboron tetrachloride.

Other volatile materials formed in this disproportionation are boron trichloride, tetraboron tetrachloride in trace quantities, and a moderate amount of a clear yellow solid slightly volatile at room temperature *in vacuo*. A refractory white solid having the composition $(B_{1.0}Cl_{0.6})_x$ also is formed.

The radical $(B_1Cl_{0.9-1.1})_x$ is a dark purple crystalline solid, volatile at 45° *in vacuo*, melting sharply at 185°. It exhibits a broad paramagnetic resonance absorption resolved into four lines centered at a g value of 2.034 with a breadth of approximately 50 gauss between outermost points of extreme slope.

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(1) The research herein reported was supported by the Public Health Service under a National Institutes of Health grant.

A solution of the purple substance exhibits a simple infrared spectrum with a broad band from 8.5 to 11.0 μ possessing two poorly resolved peaks at 9.4 and 9.95 μ, respectively. One other weak band centered at 13.05 μ is observed.

Dodecaboron undecachloride, $B_{12}Cl_{11}$, is a deep red crystalline solid which sublimes *in vacuo* at 100° and melts with little apparent decomposition at 115 ± 1°. The formula was established by elemental analysis: *Anal.* Found with a 99.1% material balance: B, 24.7; Cl, 74.4; Cl/B, 0.918; calculated for $B_{12}Cl_{11}$: B, 24.9; Cl, 75.1; Cl/B, 0.916, and by molecular weight determinations using the isopiestic method. Found: 523 ± 12; calculated for $B_{12}Cl_{11}$: 520.1.

In cyclopentane the red subchloride exhibits a single broad paramagnetic resonance at a *g* value of 2.011 with a breadth of 25 gauss between points of extreme slope. Unlike the purple subchloride, no hyperfine splittings could be observed in this case although various attempts were made using the spectrometer at high resolution with the probe at low temperatures.

The infrared spectrum of a similar solution exhibited a band from 8.75 to 10.7 μ with a peak at 9.85 μ. A sharp peak at 11.02 μ also was observed. The latter is a characteristic absorption of the BCl_2 group in B_2Cl_4.[2]

The red subchloride, $B_{12}Cl_{11}$, absorbs in the visible and ultraviolet regions of the spectrum with a broad strong band centered at 420 mμ and a weak band at 310 mμ.

The strong infrared band in the region of 9.3 to 10.0 μ common to both of the new radical species appears to be characteristic of boron cage structures since similar absorptions have been reported for $B_{10}H_{10}^{=}$, $B_{12}H_{12}^{=}$,[3] $B_{10}Cl_{10}^{=}$ and $B_{12}Cl_{12}^{=}$.[4] We also have observed a similar band in the case of the simpler boron cage in B_4Cl_4.

Acidic hydrolysis of $B_{12}Cl_{11}$ occurs slowly even at 80° with the reaction virtually ceasing when 9.5 moles of hydrogen have been evolved per mole of initial $B_{12}Cl_{11}$. In basic solution hydrolysis proceeds according to the equation

$$2B_{12}Cl_{11} + 14\ OH^- = 3H_2 + 4BO_2^- + 2B_{10}Cl_8(OH)_2^{=} + 2H_2O + 6Cl^-$$

Ions similar to $B_{10}Cl_8(OH)_2^{=}$ already have been reported.[5]

Potassium and tetramethylammonium salts can be precipitated from the alkaline hydrolysis solution. The infrared spectra of these indicate retention of the cage structures.

Treatment of $B_{12}Cl_{11}$ in cyclopentane with an excess of trimethylamine results in a complete discharge of the red color with the formation of the 2:1 complex, $[B_{12}Cl_{11} \cdot 2N(CH_3)_3]_n$. In this case also an infrared spectrum characteristic of cage compounds is obtained.

The new radical species are unusual in that the boron cage resonance forms probably contribute to their stability.

Further characterization of the purple species is being undertaken. Similarly, an investigation of the clear yellow crystalline solid is underway since in many of its reactions free radicals of limited stability can be observed.

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[3] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

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BOOK REVIEWS

Polyelectrolyte Solutions. A Theoretical Introduction. By STUART A. RICE, University of Chicago, and MITSURU NAGASAWA, Nagoya University. With a contribution by HERBERT MORAWETZ, Polytechnic Institute of Brooklyn. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 568 pp. 16 × 23.5 cm. Price, $16.50.

Polyelectrolytes have, during the last decade or so, become one of the most active and fruitful fields of research in physical chemistry, as a consequence of advances in two superficially unrelated fields, synthetic polymers and biochemistry. Pioneer work by Kern, A. Katchalsky and Fuoss on synthetic polymers which were designed to be simultaneously polymers and electrolytes gradually built up a store of descriptive information about these hybrid substances, from which a qualitatively useful molecular model was deduced. The polyelectrolytic nature of many biochemical substances was then recognized, and naturally occurring compounds such as nucleic acids and proteins began to be investigated as polyelectrolytes. Furthermore, E. Kachalski, Doty and others commenced the deliberate synthesis of polyelectrolytes which were designed to be chemical as well as electrochemical models of natural substances. Meantime, attempts were made to construct a theory which would correlate the observed macroscopic properties of polyelectrolytes with molecular parameters. The difficulty the theoretician faced was in the working model to use as his starting point: if it were made simple enough to be amenable to mathematical treatment, it departed too far from reality; if it were made elaborate enough to realistically describe all the details of behavior which one would like to account for, it became too complicated for mathematical analysis.

Rice and Nagasawa have summarized in this first book to appear on polyelectrolytes the various theoretical approaches to the problem, together with sufficient experimental examples to show how far the theory in its present state of development can go in accounting for observations. The development is presented in logical sequence, so that a graduate student with a firm background of thermody-