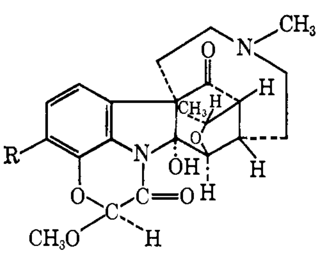
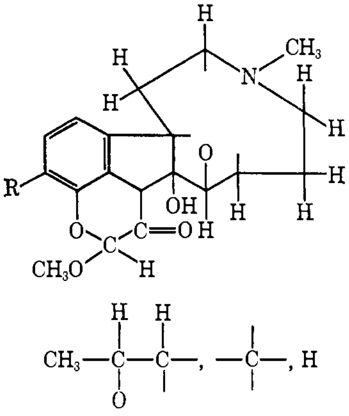
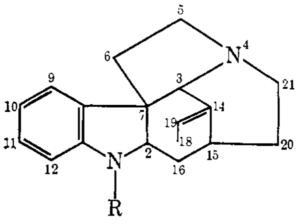


I

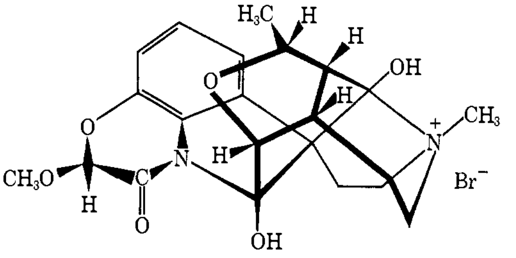


II



III

reflections, of which 2757 were not systematically extinct. The unique bromine position was determined from a sharpened three-dimensional Patterson function. The reliable image method,[6] a new systematic and objective analysis of the Patterson function, was used to derive a trial image of the remaining 33 light atoms. However, 2 of the 33 atoms were eliminated by the least-squares refinement, but their new positions were located in the difference Fourier map. After several full-matrix least-squares refinements with all the data, the discrepancy factor ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) was lowered to 12.6%.



A

A three-dimensional projection of dichotine hydrobromide, showing its relative configuration, is presented (A). In the free base the N_b nitrogen is bonded to the carbonyl carbon to give a zwitterion. This zwitterionic character has precedence in the Strychnos alkaloids such as (+)-vomicine,[7] (−)-novacine,[8] and (−)-icajine.[9] As a result, the hydrobromide of dichotine is protonated on the carbonyl oxygen instead of the N_b nitrogen and a full-fledged carbon-nitrogen bond is formed between the N_b nitrogen and the carbonyl carbon.

Biogenetically, the overall skeleton of dichotine (I, R = H) and 11-methoxydichotine (I, R = OCH_3) can be derived from aspidospermatidine[10] (III, R = H) by oxidative cleavage of the 3,4 bond,[11] followed by N-methylation. This biosynthetic route is supported by the isolation of N-acetylaspidospermatidine[2] (III, R = $COCH_3$) from the same plant. While relatively simple steps can be envisaged for the biogenetic introduction of the tetrahydrofuran ring, the most unusual feature in these two alkaloids is the six-membered acetal amide ring which has not been encountered as yet in any indole alkaloids.

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(6) J. W. Becker and P. G. Simpson, paper in preparation.

(7) H. Wieland and G. Oertel, *Ann. Chem.*, **469**, 193 (1929); R. Huisgen, H. Eder, L. Blazejewicz, and E. Mergenthaler, *ibid.*, 573, 121 (1951).

(8) W. F. Martin, H. R. Bentley, J. A. Henry, and F. S. Spring, *J. Chem. Soc.*, 3603 (1952).

(9) H. Bisset, *C. R. Acad. Sci., Paris*, **261**, 5237 (1965).

(10) K. Biemann, A. L. Burlingame, and D. Stauffacher, *Tetrahedron Lett.*, 527 (1962); K. Biemann, M. Friedmann-Spiteller, and G. Spiteller, *ibid.*, 485 (1961).

(11) For numbering system see M. Hesse, "Indoalkaloide in Tabellen," Vol. I, Springer-Verlag, Berlin–Gottingen–Heidelberg, 1964, p 41.

A Higher Oxidation State for a Coupled Icosahedral Borane Anion[1]

Sir:

The only known compounds having two B_{12} or $B_{10}C_2$ icosahedra linked directly are biscarborane ($(B_{20}C_4H_{22})$)[2] and some partially halogenated derivatives of the as yet unobserved $B_{24}H_{22}^{4-}$ ion, which would be isoelectronic with biscarborane. In addition, the known $B_{24}H_{23}^{3-}$ ion (and its partially halogenated derivatives) can be regarded as protonated $B_{24}H_{22}^{4-}$.[3] All of these compounds can be represented as resulting from a one-electron oxidation of the icosahedral $B_{12}H_{12}^{2-}$ or $B_{10}C_2H_{12}$, followed by dimerization and elimination of H^+. Although the $B_{24}H_{23}^{3-}$ ion is itself resistant to further oxidation without degradation, some of its partially halogenated derivatives are more easily oxidized.[3] We wish to report the oxidation of $B_{24}H_{21}I_2^{3-}$ to $B_{24}H_{20}I_2^{2-}$, a derivative of the higher oxidation state ion, $B_{24}H_{22}^{2-}$, which has not yet been observed.

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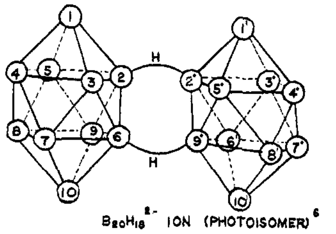
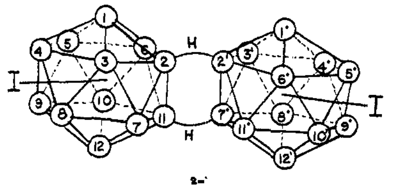
(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) taken in part from the Ph.D. thesis of R. J. Wiersema, University of Kansas, 1969.

(2) J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1643 (1964).

(3) R. J. Wiersema and R. L. Middaugh, *Inorg. Chem.*, **8**, 2074 (1969).



$B_{20}H_{18}{}^{2-}$ ION (PHOTOISOMER)[6]



$B_{24}H_{20}I_2{}^{2-}$ ION

Figure 1. Circles represent boron atoms. Each boron of $B_{20}H_{18}{}^{2-}$ except 2,6,2′,9′ is bonded to a terminal H. Each boron in the proposed structure of $B_{24}H_{20}I_2{}^{2-}$ except 2,11,2′,7′ is bonded to a terminal H or I.

A sample of $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$ (2.44 g, 2.64 mmol) was dissolved in 50 ml of acetonitrile (0.1 *M* tetraethylammonium perchlorate as supporting electrolyte). The solution was exhaustively electrolyzed under nitrogen at +1.3 V (sce), using a graphite cloth electrode. The current was monitored and corresponded to the value $n = 2.04$ equiv per mol of $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$. The electrolyzed solution was added to 400 ml of H_2O and titrated with standardized NaOH solution. The titration indicated that 0.92 mol of H^+ per mol of $B_{24}H_{21}I_2{}^{3-}$ was formed in the oxidation process. The aqueous solution was heated to boiling to remove the acetonitrile. The precipitate which formed as the acetonitrile evaporated was collected by filtration of the hot solution and recrystallized from an acetonitrile–water mixture. Almost quantitative yields of the product were obtained by this procedure. *Anal.* Calcd for $[(C_2H_5)_4N]_2B_{24}H_{20}I_2$: B, 32.68; I, 31.97; equiv wt, 398.0. Found: B, 31.0; I, 31.6; equiv wt, 400. The ir spectrum included absorptions at 2510 and 2200 cm^{-1}. The 32-MHz ^{11}B nmr spectrum of $[(C_2H_5)_4N]_2B_{24}H_{20}I_2$ in acetonitrile consisted of a single poorly resolved doublet 34.1 ppm upfield from external methyl borate. The ^1H nmr spectrum of aqueous $Na_2B_{24}H_{20}I_2$ with ^{11}B decoupled consisted of at least three signals at 1.17, 1.30, and 1.55 ppm downfield from internal sodium 3-(trimethylsilyl)-1-propanesulfonate. Only end absorption was observed near 200 nm in the uv spectrum.

A one-electron oxidation of $B_{10}H_{10}{}^{2-}$ yields either $B_{20}H_{19}{}^{3-}$ or $B_{20}H_{18}{}^{4-}$, depending on the pH of the medium. Under slightly more vigorous conditions, a higher oxidation state results, $B_{20}H_{18}{}^{2-}$.[4] In $B_{20}H_{18}{}^{4-}$, there is a direct B–B bond between B_{10} cages, and that bond is apparently protonated to form a BHB bridge bond in $B_{20}H_{19}{}^{3-}$.[4b,c] In the higher oxidation state, $B_{20}H_{18}{}^{2-}$, two B_{10} cages are linked by a pair of BBB three-center bonds.[4b,5] Uv irradiation of $B_{20}H_{18}{}^{2-}$ gives a photoisomer in which two B_{10} cages are linked by a pair of BHB bridge bonds.[6] The $B_{24}H_{23}{}^{3-}$ ion is analogous to $B_{20}H_{19}{}^{3-}$, and the new $B_{24}H_{20}I_2{}^{2-}$ should be analogous to $B_{20}H_{18}{}^{2-}$.

The transfer of two electrons and liberation of one H^+ per $B_{24}H_{21}I_2{}^{3-}$ support this analogy (eq 1). The equivalent weight and analyses for boron and iodine lead to the formulation $B_{24}H_{20}I_2{}^{2-}$. The lack of a uv absorption maximum (observed for the stable isomer of $B_{20}H_{18}{}^{2-}$ and not for the photoisomer) and the presence of an ir band at 2200 cm^{-1} (BHB bridge, absent in the stable isomer of $B_{20}H_{18}{}^{2-}$ and present in the photoisomer) suggest a structure for $B_{24}H_{20}I_2{}^{2-}$ analogous to that of the photoisomer of $B_{20}H_{18}{}^{2-}$ (see Figure 1). Unfortunately, the nmr spectra do not provide an unambiguous indication of the structure of the $B_{24}H_{20}I_2{}^{2-}$ ion. The presence of at least three environments in the ^1H nmr spectrum and a poorly resolved doublet in the ^{11}B nmr spectrum indicate either that the oxidized ion is a mixture of isomers with respect to the iodine substituents due to a lack of stereospecificity in the reactions, or that the positions of the iodine atoms lower the symmetry of the ion to the point that no unique structure can be assigned on the basis of the spectral data. Models based on the stable isomer of $B_{20}H_{18}{}^{2-}$ suggest that H-H repulsions between cages will be more severe for coupled B_{12} cages than for coupled B_{10} cages. These steric repulsions can be significantly reduced by the formation of BHB bridge bonds between cages instead of direct BB or BBB bonds.

$$B_{24}H_{21}I_2{}^{3-} \longrightarrow B_{24}H_{20}I_2{}^{2-} + H^+ + 2e^- \qquad (1)$$

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[4] (a) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **48**, 729 (1962); (b) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964); (c) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Amer. Chem., Soc.*, **87**, 1893 (1965); (d) R. L. Middaugh and F. Farha, Jr.. *ibid.*, **88**, 4147 (1966).

[5] C. H. Schwalbe and W. N. Lipscomb, *ibid.*, **91**, 194 (1969).

[6] (a) M. F. Hawthorne and R. L. Pilling, *ibid.*, **88**, 3873 (1966); (b) B. G. Deboer, Z. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **7**, 1085 (1968).

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Evaluation of Fast Homogeneous Electron-Exchange Reaction Rates Using Electrochemistry and Reflection Spectroscopy

Sir:

We wish to report the evaluation of the kinetic rates of fast homogeneous reactions involving electrogenerated species using the technique of internal reflection spectroscopy (irs) at optically transparent electrodes (ote). This technique has not been previously applied successfully to kinetic measurements. Moreover, we wish to demonstrate that fast homogeneous rates approaching diffusional control are determinable, taking advantage of the repetitiveness of the process for improvement of the signal to noise ratio.

Although this technique can be applied in general to follow any species whose concentration is perturbed through a heterogeneous electrochemical reaction, the reaction scheme[1,2]

$$A \longrightarrow B \pm e^- \qquad E_1{}^0 \qquad (1)$$

$$B \longrightarrow C \pm e^- \qquad E_2{}^0 \qquad (2)$$

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[1] J. W. Strojek, T. Kuwana, and S. W. Feldberg, *J. Amer. Chem. Soc.*, **90**, 1353 (1968).

[2] T. Kuwana and J. W. Strojek, *Discuss. Faraday Soc.*, **45**, 134 (1968).