

OCEANOGRAPHY

Challenger Centenary

from a Correspondent

AFTER two or three centuries of fits and starts, followed by more continuous growth during the Second World War and the subsequent period of advancing marine technology, oceanography has settled down to earn its living and recent attempts to learn more from its past seem to be one of the signs of maturity. The first international congress on the History of Oceanography was held at Monaco in 1966, partly to celebrate the work of Prince Albert I of Monaco, who made extensive studies from his own research ships and built and endowed his own research centre—the Musée Océanographique—at Monaco. The second congress was held at Edinburgh from September 12–20, 1972, to celebrate the centenary of the sailing of HMS Challenger round the world on a voyage of scientific exploration. It was also the 50th anniversary of the death of Prince Albert I.

At the opening session Sir Maurice Yonge spoke on the inception and significance of the Challenger Expedition and Dr Daniel Merriman, former Master of Davenport College, Yale University, gave a graphic account of the personalities of the youngest and oldest scientists in the ship, and of life and work on board. Dr Harold Burstyn, of the Carnegie-Mellon University, Pittsburgh, showed how the scientists of the day negotiated with the Royal Society, the Admiralty and the Government and how the problems which still face marine science were dealt with 100 years ago. Eighty papers were presented on the following days, one of which by Dr D. E. Cartwright of the National Institute of Oceanography at Wormley showed how the results of a continuous series of tidal observations, made with remarkable perseverance of effort and accuracy at Brest from 1711 to 1716 by Cassini, were lost for 50 years before being found, with great difficulty, incomplete and without relevant meteorological information by Lalande, who published the data, which were afterwards used by Laplace, who pioneered rigorous methods of tide prediction.

One of the most telling coloured slides was shown at the congress by Mr P. Foxton of the National Institute of Oceanography. It showed one of the twelve, charred, surviving pages of the late Dr Stanley Kemp's revision of the *Acanthephyra*, which was recovered after the disastrous bombing of the Plymouth laboratory during the Second World War. All the presented papers have been published in volumes 72 and 73 of the Proceedings (Section B) of the Royal Society of Edinburgh. A feature of the congress was the different way the

historians and scientists approached the history of oceanography. The historians tended to have a systematic approach whereas the scientists' approach could be called subjective dabbling. But the scientists did give some of the most effective contributions and it was clear that they are finding historical studies well worth while.

The congress was made possible by collaboration between the Royal Societies of Edinburgh and London, with generous support from the City and University of Edinburgh, and donations from many people and industrial organizations. The descendants of Sir John Murray, who succeeded Sir Wyville Thomson as Director of the Challenger Expedition Commission, were among the congress members.

CHEMISTRY

Probing Decaborane (14)

from a Correspondent

ONE of the most complex computer calculations of the electronic properties of a molecule yet attempted concerns the basket-shaped molecule $B_{10}H_{14}$ (Laws, Stevens and Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4467; 1972). The molecule has little symmetry to simplify the calculation but an important advantage over calculations on more symmetrical large molecules, such as octahedral chromium hexacarbonyl and cage-shaped boron compounds (see *Molec. Phys.*, **22**, 1025; 1971; and *J. Amer. Chem. Soc.*, **92**, 4158; 1970), is that a wealth of experimental information is already available on the chemical reactivity of its various parts.

The ten boron atoms lie near corners of a regular icosahedron, omitting two corners which define a single edge, and each bears a single, terminal hydrogen atom. The remaining hydrogen atoms each bridge a pair of boron atoms, so as to "stitch up" the open face of the basket, the overall symmetry being that of V-shaped molecules such as water (point group C_{2v}). There are consequently nine distinct types of atom, namely the four sets (B_1, B_3), (B_2, B_4), (B_5, B_7, B_8, B_{10}) and (B_6, B_9) and their

respective terminal hydrogen atoms and, lastly, the set of bridging atoms ($H_{56}, H_{67}, H_{89}, H_{910}$).

In the calculation of Laws *et al.* a minimum basis set of Slater-type atomic orbitals was first chosen. These are convenient mathematical functions used to describe the electronic properties of individual component atoms of the molecule; their significance is that, if the functions "occupied" by electrons are squared and added together, the sum will be an electron density map for the atom. Linear combinations of these atomic orbitals give rise to a set of molecular orbitals (MOs), from which an electron density map of the molecule may be calculated after allocating the electrons available, usually in pairs, to the MOs of lowest calculated energy. The relevant coefficients are unknown at the start of the calculation and so a trial set has to be chosen and successively refined in accord with each calculated electron density map until successive iterations lead only to insignificant changes in both the calculated molecular orbital coefficients and the density map. This is known as the Hartree-Fock self-consistent field procedure.

The $B_{10}H_{14}$ calculation required no less than 18 h of computing time (the number of integrals calculated was 560,000), and the total energy of the molecule and that of the most readily ionized electron were predicted accurately. Conversely, and typically for such calculations, the dipole moment was overestimated by 40 per cent, but the calculated electron density agrees well qualitatively with data available from X-ray and neutron diffraction experiments. From the calculated electron density contour maps it was possible to establish the presence of a strong single bond between B_2 and B_6 , whereas the connexion between B_5 and B_6 apparently involves only hydrogen bridge bonding. The electron density in the plane $B_1B_2B_3$ was found to be almost symmetrical, which establishes the presence of a closed three-centre bond in this face (that is the face is bound by a single, symmetrically arranged pair of electrons). In the plane $B_2B_5B_7$ there is an open three-centre bond with no connexion between B_5 and B_7 . It is, however, still uncertain whether the bonding in the plane $B_1B_5B_{10}$ is closed or whether B_5 and B_{10} are disjoint. The effective static atomic charges and the electron populations of frontier orbitals (the highest occupied and lowest unoccupied MOs) are in good agreement with the experimental order of reactivity in electrophilic and nucleophilic substitution reactions—electron densities calculated for the unique boron atoms follow the sequence $2 > 1 > 5 > 6$ (Lipscomb, *Boron Hydrides*, W. A. Benjamin, New York, 1963).

