teride present in sample I or II in Table I can be computed to be less than 0.7%. No usual bands were observed in the n.m.r. spectra of these samples.

TABLE I

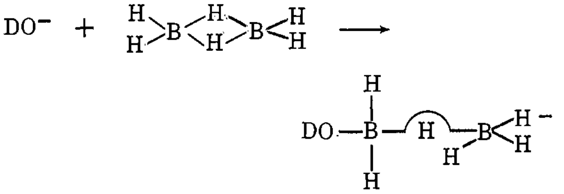
HYDROLYSIS IN H_2O

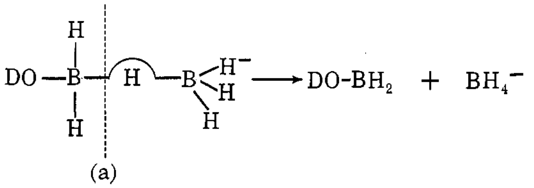
	I^a	II^b	III^c
H_2	98.4	98.6	99.980
HD	1.6	1.4	0.020^d
D_2	0.00	0.00	0.000

[a] Trials on the material from diborane into basic heavy water, ±0.05%. [b] Trials using another sample prepared at a different flow rate of diborane. [c] Hydrolysis of sodium borohydride in a light water buffer, ±0.0007%. [d] Natural abundance of deuterium.

The infrared spectra of samples I and II in potassium bromide pellets and in Nujol mulls showed only the infrared-active bands of the borohydride. Kenson and Davis[11] have computed infrared spectra to be expected from $BH_xD_{4-x}^-$ ions using the F and G matrix method and the force constants reported by Taylor[12] from the analysis of BH_4^- and BD_4^-. None of the bands of BH_3D^- was seen at 2261 (e), 2200 (a_1), 1697 (a_1), 1168 (e), 1075 (a_1), or 955 (e) cm.$^{-1}$, which are the values computed for this ion.

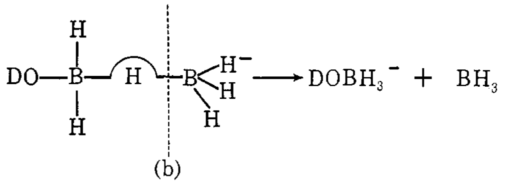
Parry[13] has reviewed numerous reactions and suggested that many occur by nonsymmetrical cleavage of the double bridge bond of diborane and other boron hydrides.[14] This suggestion is supported by the present data in which even the isotopic integrity of the boron hydrogens is maintained. The minor reaction of deuterioxide with diborane producing BH_4^- can be postulated[15] as occurring with rupture of bond (a) about 14% of the time.


(5)


(6)

$$DOBH_2^- \xrightarrow[\text{fast hydrolysis}]{D_2O} D_3BO_3 + 2HD \qquad (7)$$

Heavy water could also function as a nucleophile. If $B_2H_6OD^-$ is an intermediate then cleavage of the (a) boron–hydrogen bond could occur to produce borohydride. If the other bond cleaves to produce BH_3OD^- and BH_3 only total hydrolysis products[3] would result.


(8)

$$BH_3 + DOBH_3^- \xrightarrow[\text{fast hydrolysis}]{D_2O} D_3BO_3 + HD\uparrow \qquad (9)$$

Further experimental work is required to provide further information.

Experimental

Materials.—All materials were analytical reagents. Diborane was generated from sodium borohydride and methanesulfonic acid. Borate analysis was made by electrometric titration in the presence of mannitol. The iodate technique[3] was used for borohydride. The kinetic techniques have been discussed.[3]

Matched infrared cells (0.1 mm.) of IRtran-2 were obtained from the Connecticut Instrument Corp. The spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer. Salt plates were also used to obtain the spectra.

The n.m.r. spectra were recorded using a Varian A-60. Mass spectral analyses were determined using both a Bendix Model 12-1-1 time-of-flight mass spectrometer and a Consolidated-Nier Model 21-201 isotope-ratio mass spectrometer.

Acknowledgments.—The present study was supported by a Frederick Gardner Cottrell grant from the Research Corporation and the Sloan Foundation. The support of J. A. G. by the National Science Foundation is also greatly appreciated.

---

(11) R. E. Kenson, Ph.D. Thesis, Purdue University, June 1965.

(12) R. C. Taylor, D. R. Schultz, and A. R. Emery, *J. Am. Chem. Soc.*, **80**, 27 (1958); A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, **28**, 1029 (1958).

(13) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(14) A latter review of the literature is given by W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, pp. 154–197.

(15) Postulated by analogy from the data of R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

The Dipole Moments of the Isomers of Dicarbadecaborane, $B_{10}H_{10}C_2H_2$[1]

BY A. W. LAUBENGAYER AND W. R. RYSZ

Received May 10, 1965

The recent synthesis[2] of *p*-dicarbadecaborane has completed the list of the three isomeric forms possible for this remarkable three-dimensional aromatic framework and sets the stage for much interesting research on the physical and chemical characteristics of such icosahedral structures. In order to further substantiate the assignments[3,4] of the structures shown in Figure 1 we have measured the dipole moments of the three isomers.

---

(1) Based on part of a thesis submitted by W. R. Rysz to the Graduate School of Cornell University, Feb. 1965, in partial fulfillment of the requirements for the M.S. degree.

(2) S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

(3) J. A. Potenza and W. N. Lipscomb, *ibid.*, **86**, 1874 (1964).

(4) H. Schroeder and G. D. Vickers, *Inorg. Chem.*, **2**, 1317 (1963).

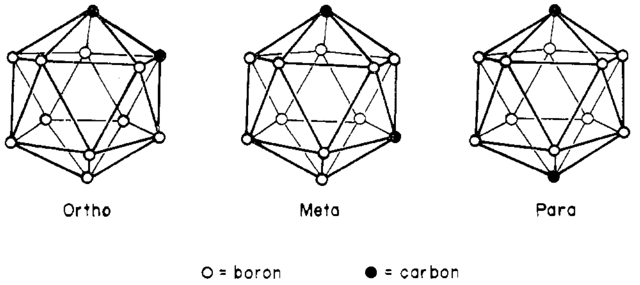


Figure 1.—Structures of the dicarbadecaboranes (hydrogen not shown).

Experimental

Very pure samples of the dicarbadecaboranes were obtained through the courtesy of Dr. T. L. Heying of the Olin Research Center, New Haven, Conn. The benzene employed as solvent was dried by refluxing over potassium and then was distilled and stored over molecular sieves. Duplicate runs were made for each dicarbadecaborane at four different dilutions. All manipulations necessary in preparing a solution were carried out in a glove bag under an atmosphere of dry nitrogen. The dielectric constants of the solutions were measured by the heterodyne-beat oscillator method using a Model DM 01 Dipolmeter with a Type DFL 1 cell.[5] All measurements were made at 25°.

Results

The dipole moments given in Table I were calculated using a modification of the Guggenheim method.[6] The errors indicated are experimental. There are possible errors of up to 10% inherent in the method of calculation.

TABLE I

DIPOLE MOMENTS OF THE DICARBADECABORANES

Compound	Slope $\Delta\epsilon/w$[a]	μ[b], D.
o-$B_{10}H_{10}C_2H_2$	15.33	4.53 ± 0.05
m-$B_{10}H_{10}C_2H_2$	6.07	2.85 ± 0.05
p-$B_{10}H_{10}C_2H_2$	0.00	0.00

[a] Experimental value of slope. $\Delta\epsilon$ is the difference of the dielectric constants of the solutions and benzene, and w is the weight fraction of solute. [b] Calculated from $\mu^2 = (27kT/4\pi N)\cdot(1/d_1(\epsilon_1 + 2)^2)(\text{slope } \Delta\epsilon/w - \text{slope } \Delta n^2/w)M_2$. The contribution of the electronic polarization has been assumed to be negligible when compared to the total polarization because in all cases the slope $\Delta n^2/w$, as measured by an Abbé refractometer, was found to be zero.

Discussion

The values for the dipole moments obtained are in good accord with the structures which have been assigned. The variation in dipole moments for the dicarbadecaboranes shows the same trend as is found in going from the *ortho* to the *para* isomers of disubstituted benzene derivatives. It is of interest also to compare the dicarbadecaboranes with decaborane, whose structure is based on an incompleted boron icosahedron. Decaborane has a dipole moment of about 3.4 D., this being consistent with its open asymmetric structure. Since dicarbadecaboranes are closed icosahedral structures, the dipole moments we have observed indicate fairly large B–C bond moments.

Acknowledgments.—We are indebted to the National Science Foundation and the Advanced Research Projects Agency for financial support for this research.

---

[5] Wissenschaftlich-Technische Werkstätten Gmbh., Weilheim/obb., Germany. Kahl Scientific Instrument Corp., El Cajon, Calif.

[6] (a) J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955; (b) F. Oehme and H. Wirth, "The Determination of the Molecular Dipole Moment," Kahl Scientific Instrument Corp., El Cajon, Calif.; (c) J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950); (d) E. A. Guggenheim, *ibid.*, **47**, 573 (1951).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

The Chloramination of Bis(2,2-dimethylhydrazino)phosphines

BY HARRY H. SISLER AND JOSEPH WEISS

Received May 13, 1965

It has recently been established that mono(hydrazino)phosphines react with chloramine to yield aminohydrazinophosphonium salts[1] in which the chloramine nitrogen has become attached to the phosphorus atom, *e.g.*, $[(C_6H_5)_2P(NH_2)[NHN(CH_3)_2]]^+[Cl]^-$. The nitrogen atoms in the mono(hydrazino)phosphines appear to be inert to the attack of the chloramine molecule under the usual chloramination conditions. Further, even in the hydrazinophosphine oxide in which the attachment of an oxygen atom to the phosphorus atom prevents amination of the phosphorus atom, no attack of the hydrazino nitrogen atoms occurs.

In view of the well-known susceptibility of the hydrazine N–N linkage to destructive action by chloramine,[2] the above facts are, to say the least, surprising. We were, therefore, interested in examining this effect further, by studying the chloramination of bis(hydrazino)phosphine derivatives. The present communication reports the results of studies of the reactions of bis(2,2-dimethylhydrazino)phenylphosphine and of bis(2,2-dimethylhydrazino)methylphosphine with the gaseous mixture of chloramine, excess ammonia, and nitrogen obtained by the Sisler–Mattair process.[3,4] The chloramination of bis(2,2-dimethylhydrazino)phenylphosphine oxide was likewise attempted.

Experimental

Materials.—Phenyldichlorophosphine, Victor Chemical Co., practical grade, was purified as described earlier.[5] Methyldichlorophosphine, F.M.C. Corp., industrial grade, was distilled in a vacuum line prior to use. Phenylphosphonic dichloride, Victor Chemical Co., practical grade, was distilled under vacuum; b.p. 88° at 1 mm. 1,1-Dimethylhydrazine, Eastman Kodak, practical grade, was refluxed over calcium hydride for 48 hr. and then distilled from it under dry nitrogen; b.p. 63–64° at

---

[1] R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *Inorg. Chem.*, **2**, 760 (1963).

[2] F. N. Collier, H. H. Sisler, J. G. Calvert, and F. Hurley, *J. Am. Chem. Soc.*, **81**, 6177 (1959).

[3] R. Mattair and H. H. Sisler, *ibid.*, **73**, 1619 (1951).

[4] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Young, *ibid.*, **76**, 3906 (1954).

[5] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).