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The Boron-11 Nuclear Magnetic Resonance Spectrum of $B_{20}H_{18}^{-2}$ at 60 Mc./sec.

Sir:

We have recently had occasion to employ an experimental nuclear magnetic resonance (n.m.r.) spectrometer for the observation of ^{11}B spectra at 60 Mc./sec. (43.9 kgauss). The experimental spectrometer employed a cryogenic solenoid and was recently described elsewhere.¹ The very high level of resolution obtained prompts us to present results bearing on the structure of the $B_{20}H_{18}^{-2}$ ion.

The known chemistry of the $B_{20}H_{18}^{-2}$ ion and its electron balance suggest that this ion is formally composed of two $B_{10}H_9^-$ ions joined by two bonds of the three-center type.²⁻⁷ The simplest suggested structure in keeping with the known centrosymmetric³ character of $B_{20}H_{18}^{-2}$ and previously recorded³ ^{11}B n.m.r. spectra (19.3 Mc./sec.) employed two B-H-B bridge bonds as the required three-center linkages between $B_{10}H_9^-$ units.^{2,3} Each B-H-B bridge bond in this postulated structure linked an apical boron atom in one polyhedral B_{10} unit with an equatorial boron of the other B_{10} unit as in Fig. 1. The presence of a low-

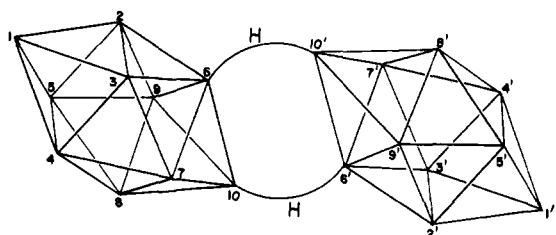


Fig. 1.—Structure of the $B_{20}H_{18}^{-2}$ ion previously proposed^{2,3} on the basis of the 19.3 Mc./sec. ^{11}B n.m.r. spectrum and the centrosymmetric character of the ion.

field singlet of area 2 in the earlier ^{11}B n.m.r. spectra was attributed to the apical boron atoms (10 and 10') involved in these B-H-B bridge bonds.³ Following this suggestion further, one would expect to observe a similar singlet of area 2 due to the B-H-B bonded equatorial boron atoms (6 and 6') in the high-field array if sufficient resolution were obtained. In addition, the high-field region should also contain four doublets of area 2:4:4:4 due to the 8-8', 7-9-7'-9', 2-3-2'-3',

- (1) *Chem. Eng. News*, **42**, No. 23, 55 (1964).
- (2) W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961).
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- (4) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).
- (5) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963.
- (6) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963).
- (7) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3704 (1963).

and 4-5-4'-5' boron atoms, respectively. Figure 2 presents the ^{11}B spectrum of $B_{20}H_{18}^{-2}$ obtained at 60 Mc./sec. in which the high-field resonances are well resolved. Also included in Fig. 2 is the similar spectrum of $B_{20}D_{18}^{-2}$. These two spectra clearly show the high-field group to be composed of *five* doublets with areas 2:4:4:4:2 reading upfield. The greater apparent height of the area 4 singlet f in $B_{20}D_{18}^{-2}$ is attributed to a smaller line width and not to a greater intensity. The presence of only one singlet of area 2 in the spectrum of $B_{20}H_{18}^{-2}$ is not compatible with the simplest proposed structure^{2,3} unless the bridge hydrogen atoms are strongly coupled only with one type of boron atom involved in the B-H-B bridge bonds. Such strong and specific coupling interactions have not been previously observed, and it appears likely that $B_{20}H_{18}^{-2}$ may contain two B-B-B three-center linkages.

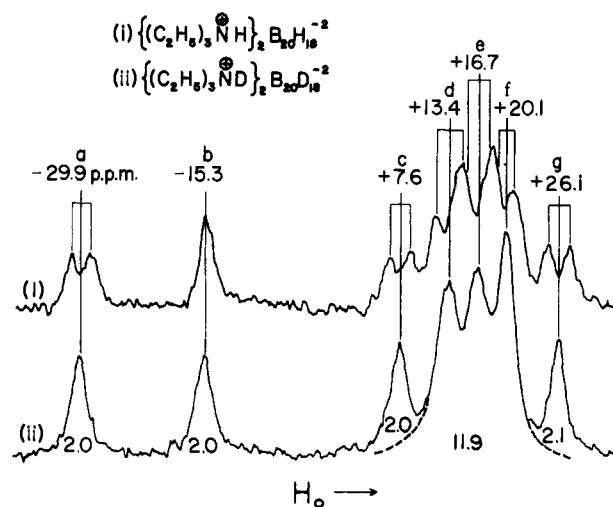


Fig. 2.— ^{11}B n.m.r. spectra at 60 Mc./sec. in acetonitrile of (i) $\{(C_2H_5)_3NH\}_2B_{20}H_{18}^{-2}$, and (ii) $\{(C_2H_5)_3ND\}_2B_{20}D_{18}^{-2}$. Chemical shifts in parts per million (p.p.m.) from $BF_3 \cdot O(C_2H_5)_2 = 0$ were extrapolated from chemical shift values obtained at 32.1 Mc./sec. for the doublet a and the singlet b. Integrated areas, normalized to give a total of 20 atoms, are indicated below the peaks.

The low-field singlet b of area 2 could equally well represent an apical or equatorial set of boron atoms which carry no terminal hydrogens, and thus two other possible $B_{20}H_{18}^{-2}$ structures based upon B-B-B linkages could be considered. Each of these structures might utilize a pair of three-center interactions, each of which involves a terminal apical or terminal equatorial orbital and an edge of the other B_{10} polyhedral located between apical and equatorial boron atoms. Thus, atoms 10 and 10' might be bonded to the 6'-10' and 6-10 edges, respectively, with preservation of the required center of symmetry.⁵ Alternatively, boron atoms 6 and 6' could be bonded with the 6'-10' and 6-10 edges, respectively. The latter model is much preferred due to the presence of more favorable angles between bonding orbitals. Either of these models would provide a strong basis for the framework fusion observed in the $B_{18}H_{22}$ hydrides^{4,8-10} and the ultra-

- (8) P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1490 (1962).
- (9) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963).
- (10) P. G. Simpson, K. Folting, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 1879 (1963).

violet absorption bands^{3,11} at 230 and 292 $m\mu$ which are not seen in $B_{10}H_{10}^{-2}$ itself. In addition, the absence of B-H-B bands in the infrared spectrum of $B_{20}H_{18}^{-2}$ is now rationalized.

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(11) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

(12) Alfred P. Sloan Research Fellow.

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A 2,3-Diazacyclopropanone (Di-*t*-butyldiaziridinone)

Sir:

We wish to report the preparation of a new small-ring heterocycle, a diaziridinone (I, R = *t*-butyl) possessing a number of properties of special interest and of considerable potential as a synthetic intermediate.

Treatment of N,N'-di-*t*-butyl-N-chlorourea,¹ m.p. 30–31°, with potassium in pentane or with potassium *t*-butoxide in *t*-butyl alcohol² affords di-*t*-butyldiaziridinone (I, 40–80% yield), m.p. 0–1° (*Anal.* Found: C, 63.38; H, 10.74; N, 16.47), mol. wt. 178 (cryoscopic in cyclohexane), n.m.r. (in CCl_4), single peak at τ 8.80, infrared absorption in the carbonyl region (in CCl_4), maximum at 1880 and 1862 cm^{-1} with shoulders at 1926 and 1800 cm^{-1} . Chemical evidence in support of structure I³ is found in: (1) cleavage of the N–N bond by hydrogenation (palladium on carbon) with formation of N,N'-di-*t*-butylurea in 96% yield; (2) cleavage of the C–N bond by sodium borohydride with formation of N,N'-di-*t*-butyl-N-formylhydrazine (60% yield), m.p. 42–43°, n.m.r. (in CCl_4), τ 8.92 (singlet, 9 H's), 8.63 (singlet, 9 H's), 5.80 (broad, 1 H), and 1.43 (singlet, 1 H).

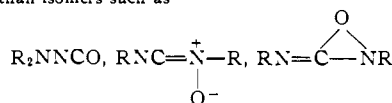
Compound I is reactive toward acids. Treatment of I with dry hydrogen chloride followed by water gives 2,3-di-*t*-butylcarbazyl chloride, II. Treatment of II with potassium *t*-butoxide in *t*-butyl alcohol yields a mixture of I (45%) and *t*-butyl 2,3-di-*t*-butylcarbazate (III, 25%).

Among the unusual properties of I are the high thermal stability (only slight decomposition in 2 hr. at 175°)

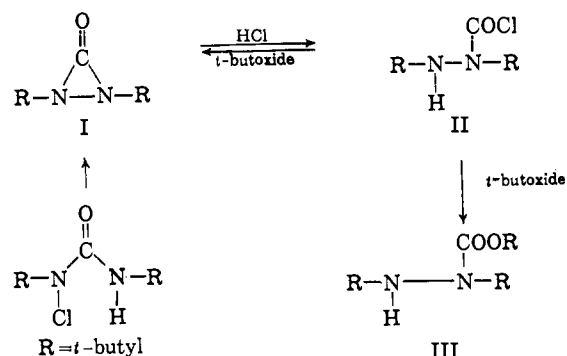
(1) Satisfactory combustion data and proof of structure have been obtained for new compounds.

(2) These methods are analogous to those used to prepare α -lactams: H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Am. Chem. Soc.*, **85**, 3303 (1963); J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 1356 (1964).

(3) The physical and chemical evidence appears in strong favor of structure I rather than isomers such as



X-Ray evidence on the structure and particularly on the interesting question of the location of the substituents relative to the plane of the ring will be forthcoming.



and the stability toward nucleophiles⁴ (50% conversion of I to III by potassium *t*-butoxide (0.3 *M*) in *t*-butyl alcohol in 16 hr. at reflux; no reaction of I with aniline in ether for 6 days at 25°).

The *t*-butyl carbazate, III, is readily cleaved by hydrogen chloride; the resulting N,N'-di-*t*-butylhydrazine may be directly oxidized to azo-*t*-butane (one of several procedures for the conversion of I to the azo compound). Thus the work described here represents a method for the formation from ureas of substituted⁵ hydrazines with like or unlike substituents and of symmetrical and unsymmetrical azo compounds.

A full account of the synthetic aspects and of the physical and chemical properties of compounds of type I will be reported at a later date.

(4) These properties are more reminiscent of the cyclopropanones [R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960); R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963)] than of the α -lactams (ref. 2).

(5) E.g., *t*-alkyl; primary and secondary N,N'-disubstituted hydrazines are accessible from the corresponding azines.

(6) National Science Foundation Predoctoral Fellow, 1961–1964.

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Potassium Perxenate Nonahydrate¹

Sir:

Several salts of the unstable perxenic acid have been isolated and identified. Sodium perxenate^{2,3} exists in several crystalline forms, and the structures of $Na_4XeO_6 \cdot 8H_2O$ ^{4,5} and $Na_4XeO_6 \cdot 6H_2O$ ⁶ have been determined. Perxenate salts of barium^{7,8} and of calcium, lithium, and cesium⁸ have been prepared, but their structures are unknown. We have now prepared a potassium salt and characterized it as $K_4XeO_6 \cdot 9H_2O$ by determination of its crystal structure.

The solubility of potassium perxenate appears to be much greater than that of the sodium perxenates at a given concentration of OH^- . The disproportionation reaction of xenic acid in potassium hydroxide solution failed to give crystals under conditions analogous to those at which $Na_4XeO_6 \cdot 8H_2O$ was easily crystallized.

(1) Work done in part under the auspices of the U. S. Atomic Energy Commission.

(2) J. G. Malm, B. D. Holt, and R. W. Bane, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167.

(3) S. Siegel and E. Gebert, ref. 2, p. 193.

(4) W. C. Hamilton, J. A. Ibers, and D. R. Mackenzie, *Science*, **141**, 532 (1963).

(5) J. A. Ibers, W. C. Hamilton, and D. R. Mackenzie, *Inorg. Chem.*, to be published.

(6) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *Science*, **142**, 501 (1963).

(7) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(8) C. W. Koch and S. M. Williamson, unpublished work.