

absorbed without laborious amino acid analyses, a feature which has virtue in studies of amino acid residue reactivities.

It is clear that the general principles allow various permutations. Thus, compounds can be made having other spectral properties, *e.g.*, compounds that absorb in other regions of the spectrum or that fluoresce. Similarly, variation of the reactive group may produce compounds which are specific for other residues, *e.g.*, tyrosine. The application of this and similar reagents will be reported in subsequent publications.

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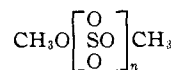
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Effect of Distant Atoms in a Molecule on Nuclear Magnetic Resonance Chemical Shifts

Sir:

Proton nuclear magnetic resonance (n.m.r.) spectra of methyl groups terminating long chains of atoms have been found to be unusually sensitive to structural changes far distant¹ from the methyl group in the molecule, when sulfur or selenium is incorporated in the molecular backbone. For example, careful assignment of proton nuclear magnetic resonances in the product obtained by reaction of dimethyl sulfate with sulfur trioxide shows that separate resonance peaks can be observed for n as great as 6 in the following molecule



As n increases, the difference in chemical shift, $\Delta\delta$, diminishes from 0.23 p.p.m. for molecules having values of $n = 1$ and $n = 2$ to the nearly indistinguishable difference of 0.005 p.p.m. for the molecules with $n = 5$ and $n = 6$.

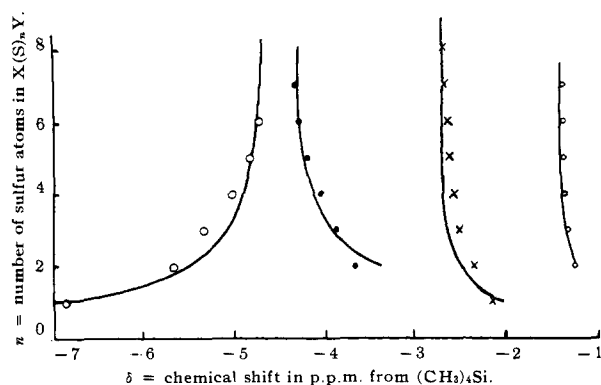


Fig. 1.—Proton n.m.r. chemical shifts of the CH_2 or CH_3 hydrogen atoms in the substituent X of polysulfide molecules of the type $\text{X}(\text{S})_n\text{Y}$ as a function of the chain length: O, $\text{X} = \text{CH}_3$ and $\text{Y} = \text{Cl}$; ●, $\text{X} = \text{Y} = \text{CH}_2(\text{C}_6\text{H}_5)$; X, $\text{X} = \text{Y} = \text{CH}_3$; ○, $\text{X} = \text{Y} = \text{C}(\text{CH}_3)_3$.

(1) The major applications of "seeing-in-depth" within molecules by n.m.r. have been in the sequence distribution of polymers [references given in *Chem. Eng. News*, **41**, No. 16, 36 (1963)] and the interpretation of molecular-size distributions in novel families of compounds [K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802, 807, 814 (1964)]. In most cases, n.m.r. chemical shifts are affected by atoms no more than four or five positions removed in the structure. For this effect in C^{13} spectra, see E. G. Paul and D. M. Grant, *ibid.*, **85**, 1701 (1963), who show that their additive shift parameters become constant for butyl and longer n -alkyl groups.

Similar long-range effects are observed with sulfur chains having the structure $\text{X}(\text{S})_n\text{Y}$ and selenium chains having the structure $\text{X}(\text{Se})_n\text{X}$, where the proton resonance of the X group is observed and X has been chosen to be CH_3 , $\text{C}(\text{CH}_3)_3$, or $\text{CH}_2(\text{C}_6\text{H}_5)$. Typical data for four different polysulfide reaction mixtures² are shown in Fig. 1.

These data may be fitted to an approximation based on the theory for the so-called "neighbor anisotropy effect."³ If it is assumed that the local magnetic susceptibility tensor on the distant group or atom is axially symmetric, one has the following equation for its contribution $\Delta\sigma$ to the magnetic screening constant, σ , of the nucleus being observed

$$\Delta\sigma = [(\Delta\chi/3N_0) (1 - 3 \cos^2\gamma)_{\text{av.}}]/R^3 \quad (1)$$

where $\Delta\chi/3N_0$ is a constant, R is the distance between the center of the contributing group and the nucleus in question, and γ is the angle between the axis of anisotropy of this group and the vector R . In order to avoid problems with bulk magnetic susceptibility and other contributions to the over-all screening constant, we have treated our data in terms of the difference in chemical shift between molecules having $(n + 2)$ units in the chain and those of infinite length, assuming that eq. 1 can be reduced to the form C/R^3 , where C is a constant. Thus, for the molecule $\text{X}(\text{Z})_n\text{Y}$, we have the following equation for the difference in chemical shift, $\Delta\delta$, in which C_y is the shift contribution of the terminal group Y separated from the group X, containing the magnetic nucleus, by n Z atoms or moieties and C_z is the shift contribution of each Z

$$\Delta\delta = \delta_n - \delta_\infty = C_y/R_{n+1}^3 + C_z \left(\sum_{j=1}^n 1/R_j^3 - \sum_{j=1}^{\infty} 1/R_j^3 \right) \quad (2)$$

A reasonable *a priori* assumption for estimating the value of R is to use the random-flight calculation of the end-to-end distance for a chain having free rotation at tetrahedral bond angles.⁴

$$R = j - \sum_{k=1}^{j-1} 2(j-k)/3^k \quad (3)$$

where

$$\sum_{j=1}^{\infty} 1/R_j^3 = 1.750 \quad (4)$$

Application of eq. 2 and 3 to the data of Fig. 1 gives curves of the correct general shape. The lines in Fig. 1 were calculated on the basis of $C_y = +9$ for $\text{X} = \text{Y} = \text{CH}_3$, -17 for $\text{X} = \text{CH}_3$ and $\text{Y} = \text{Cl}$, $+30$ for $\text{X} = \text{Y} = \text{CH}_2(\text{C}_6\text{H}_5)$, $+9$ for $\text{X} = \text{Y} = \text{C}(\text{CH}_3)_3$, and $+18$ for S in the molecule $\text{X}(\text{S})_n\text{Y}$. The fit between the data and the theoretical curves is reasonably good but far from perfect. It can be improved by allowing the value of the shift constant for sulfur to be somewhat dependent on the end groups in the $\text{X}(\text{S})_n\text{Y}$ molecules, thereby allowing in part for chain-

(2) Proof of the existence and structure of the new compounds reported in Fig. 1 (particularly the series $\text{CH}_3(\text{S})_n\text{Cl}$) is presented in a forthcoming paper.

(3) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957); J. A. Pople, *Proc. Roy. Soc. (London)*, **A239**, 550 (1957).

(4) H. Eyring, *Phys. Rev.*, **39**, 746 (1932); F. T. Wall, *J. Chem. Phys.*, **11**, 67 (1943); see also P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 414.

transmitted inductive effects not buried in the mathematics of eq. 2 and 3. Likewise, inclusion of restricted rotation will act in the direction of giving better fit.

According to this simple approximation, it appears that each atom or group makes a more-or-less fixed contribution to the chemical shift, with this contribution being attenuated in proportion to $1/R^3$, where R is the distance of separation measured through space, not through the molecular chain. Refinement of the C_γ values into the respective $\Delta\chi$ contributions⁵ of eq. 1 is not given here because of the approximation involved in eq. 2 and 3. A more complete theory should include electronic effects propagated through the molecular chain itself.

(5) *E.g.*, A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958); R. W. Lenz and J. D. Heeschen, *J. Polymer Sci.*, **51**, 247 (1961); J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961); see also J. Guy and J. Tillieu, *J. Chem. Phys.*, **24**, 1117 (1956).

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Preparation, Isolation, and Structure of B_8H_{12}

Sir:

One of the important predictions^{1,2} of the valence theory of boron hydrides is the existence of B_8H_{12} and its structural possibilities. We report here the isolation of this thermally unstable material in pure crystalline form in small yields from the electric discharge of a mixture of diborane-6 and pentaborane-9, and the proof of chemical composition and structural formula from a complete three-dimensional X-ray diffraction study of single crystals at low temperatures (Fig. 1).

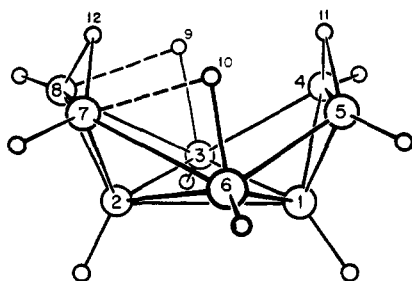


Fig. 1.—Molecular structure of B_8H_{12} . The B_8 unit is an icosahedral fragment. The B-B distances are 1-3 = 1.793, 1-6 = 1.783, 1-4 = 1.684, 1-5 = 1.696, 2-3 = 1.791, 2-6 = 1.796, 2-7 = 1.718, 2-8 = 1.721, 3-4 = 1.790, 5-6 = 1.787, 3-8 = 1.800, 6-7 = 1.793, 1-2 = 1.803, 4-5 = 1.672, and 7-8 = 1.706, all ± 0.003 Å. Average B-H (terminal) is 1.10 ± 0.03 Å. Some other B-H distances are 3-9 = 1.30, 6-10 = 1.27, 8-9 = 1.48, 7-10 = 1.46, 4-9 = 1.98, and 5-10 = 1.99 Å.

Diborane-6 and pentaborane-9 in a 2:1 ratio were swept in a carrier of H_2 at 12 mm. into a cylindrical discharge tube containing two parallel circular electrodes of copper, 90 mm. in diameter and 80 mm. apart maintained at 2700 v. a.c. The product gases were passed through traps at -80 , -131 , -196 , and -196° , and the material condensing at -80° was then repeatedly slowly passed through two -57° traps until the sample was free of pentaborane-9. A series of rapid fractionations through a -45° trap passed hexaborane-10, at first mixed with pentaborane-9 and later with octa-

borane-12. After a sufficient number of fractionations, small amounts of pure octaborane-12 passed through the trap, but rapid passes were necessary in order to ensure that the nonaborane-15 and the decaborane-16 were retained in the -45° trap. All fractionations were carefully followed by mass spectrometric measurements, which indicated a final product showing a maximum mass number of 100 atomic units (Fig. 2).

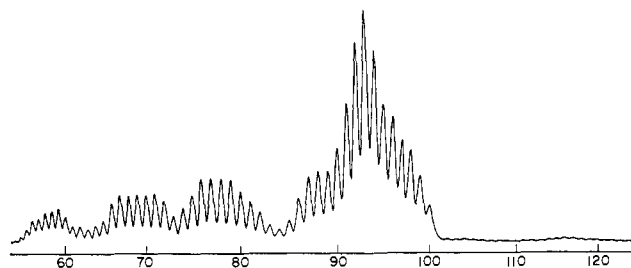


Fig. 2.—Mass spectrum of B_8H_{12} ; intensities are plotted on the vertical scale and mass numbers on the horizontal scale.

Each single crystal examined by X-ray diffraction methods was grown in a thin-walled cylindrical capillary maintained at about -20° or lower by a cold nitrogen stream. Complete Weissenberg photographs taken about two axes indicated the space group $Pbca$ and the unit cell dimensions, $a = 13.61$, $b = 10.41$, and $c = 10.41$, all ± 0.01 Å. The structure shown in Fig. 1 was obtained from three-dimensional superposition procedures, and all H atoms were located without chemical assumptions in three dimensional electron density maps from which the B atoms had been subtracted. The present value of $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ is 0.11 for the 1571 reflections.

The three very similar probable structures² have symmetries C_{2v} , C_s , and C_2 . Of these, the structure of symmetry C_s is the correct one, and is, moreover, the structure which is most closely related to that³ of $C_2H_5NH_2B_8H_{12}NHC_2H_5$. There are two symmetrical H bridges across the B_4-B_5 and the B_7-B_8 distances which differ from one another by ten times their standard deviations. The bridges across the B_3-B_8 and B_6-B_7 distances are unsymmetrically displaced toward B_3 and B_6 , respectively, probably in order to prevent the $H_9 \cdots H_{12} = 1.87$ Å. and $H_{10} \cdots H_{12} = 1.95$ Å. distances from becoming too short. For comparison, we note that the $H_9 \cdots H_{11}$ and $H_{10} \cdots H_{11}$ contacts of 2.20 and 2.23 Å., respectively, indicate a very significant distortion from an idealized C_{2v} symmetry toward the observed structure of C_s symmetry. Theoretical studies of the energies involved in these distortions are underway.

An early report⁴ of a possible B_8 hydride has been reconsidered recently⁵ to favor B_9H_{15} . Vapor pressure anomalies in the B_9H_{15} preparation^{6,7} as well as mass spectroscopic studies⁸⁻¹⁰ have supported the probable

(3) R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 478 (1963); *J. Chem. Phys.*, **39**, 1532 (1963); also ref. 2, pp. 52-53 (Principle 7).

(4) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).

(5) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

(6) R. Schaeffer, private communication, 1953.

(7) R. E. Dickerson, P. J. Wheatley, P. A. Howell, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **25**, 606 (1956).

(8) I. Shapiro and B. Kellin, *J. Am. Chem. Soc.*, **76**, 3864 (1954).

(9) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

(10) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, "Borax to Boranes," Advances in Chemistry Series, American Chemical Society, Washington, D. C., 1961, p. 127.

(1) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(2) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, p. 59.