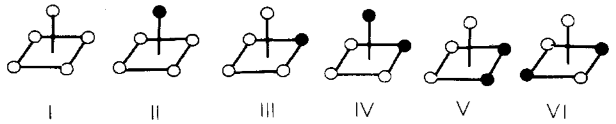

Figure 1.

Table I. Isotopic Isomer Abundances for B_5H_9

Stoichiometry of isotopic isomer	Structure of isomer	σ_i	Fractional abundance
$^{11}B_5H_9$	I	4	$\frac{4}{4}(0.804)^5 = 0.336$
$^{10}B^{11}B_4H_9$	II	4	$\frac{4}{4}(0.804)^4(0.196) = 0.082$
$^{10}B^{11}B_4H_9$	III	1	$\frac{4}{1}(0.804)^4(0.196) = 0.328$
$^{10}B_2{}^{11}B_3H_9$	IV	1	$\frac{4}{1}(0.804)^3(0.196)^2 = 0.080$
$^{10}B_2{}^{11}B_3H_9$	V	1	$\frac{4}{1}(0.804)^3(0.196)^2 = 0.080$
$^{10}B_2{}^{11}B_3H_9$	VI	2	$\frac{4}{2}(0.804)^3(0.196)^2 = 0.040$
$^{10}B_3{}^{11}B_2H_9$	VI	2	$\frac{4}{2}(0.804)^2(0.196)^3 = 0.010$
$^{10}B_3{}^{11}B_2H_9$	V	1	$\frac{4}{1}(0.804)^2(0.196)^3 = 0.019$
$^{10}B_3{}^{11}B_2H_9$	IV	1	$\frac{4}{1}(0.804)^2(0.196)^3 = 0.019$
$^{10}B_4{}^{11}BH_9$	III	1	$\frac{4}{1}(0.804)(0.196)^4 = 0.005$
$^{10}B_4{}^{11}BH_9$	II	4	$\frac{4}{4}(0.804)(0.196)^4 = 0.001$
$^{10}B_5H_9$	I	4	$\frac{4}{4}(0.196)^5 = 0.0003$

symmetry numbers.

The general formula to be used for the fractional abundance of a particular isotopic isomer, denoted f_i, is

$$f_i = \frac{\sigma}{\sigma_i} a^w b^x c^y \ldots \tag{1}$$

where σ is the symmetry number[2] of the parent molecule considered as isotopically pure, σ_i is the symmetry number of the particular isotopic isomer, a is the natural abundance of an isotope occurring w times in the isomeric species, b is the natural abundance of isotope occurring x times, etc.

As an example, the NMR spectrum of B_5H_9 may be considered to consist of the spectra of all of the possible isotopic isomers drawn in Figure 1[3], where the darkened circles represent either ^{10}B (fractional natural abundance 0.196, nuclear spin quantum number 3) or ^{11}B (fractional natural abundance 0.804, spin $^3/_2$). The results of applying eq 1 to these data are given in Table I. The boron-11 NMR spectrum of B_5H_9 is a weighted average of the spectra of the isomers given in Table I.

Derivation. A necessary and sufficient assumption for the derivation of eq 1 is that the probability of a particular isotope occupying any particular site is given by its fractional natural abundance—i.e., it is assumed that no isotopic fractionation has occurred in the course of compound formation and that random distribution of the isotopes over the various sites occurs. Under this assumption the abundance of any particular isotopic isomer will be the product of the fractional isotopic abundance for a given stoichiometry (denoted as f_s) with the ratio of the distinguishable[7] configurations which a given isomer may have (denoted as c_i) to the total number of distinguishable configurations for the given stoichiometry (denoted as c_t). Algebraically this is given by

$$f_i = \frac{c_i}{c_t} f_s = \frac{\sigma}{\sigma_i} a^w b^x c^z \ldots \tag{2}$$

where

$$c_t = P_1{}^n \tag{3}$$

$$c_i = \sigma/\sigma_i \tag{4}$$

$$f_s = P_1{}^n a^w b^x c^y \ldots \tag{5}$$

$P_1{}^n$ is the number of distinguishable permutations possible for the isotopic atoms among the n sites and is found by evaluating $n!/w!x!y!\ldots$. The rotation group of the isotopic isomer is a subgroup of the rotation group of the parent geometry. The ratio σ/σ_i is simply the index of this subgroup and gives the number of distinct cosets plus one for the subgroup itself.[6] This is the number of operations producing distinguishable configurations of a given isomer. Equation 5 is commonly used by mass spectroscopists to calculate relative abundances of isotopic species from the stoichiometry alone but has also been used in spectral synthesis in cases where each stoichiometry leads to a single isomer.[1a]

References and Notes

(1) See (a) W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, **34**, 147 (1962), for an example involving NMR spectroscopy, or (b) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967), for an example involving ir spectroscopy.
(2) The number of equivalent orientations of the molecule available by rotations alone, hence the order of the rotation group of the species (excluding all operations associated with C_∞).
(3) These may readily be drawn by inspection. For more complex cases, the complete expansion of the Polya cycle index provides both an enumeration[4] and a guide to formulation[5] of the isomers.
(4) B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *Inorg. Chem.*, 3, 265 (1964).
(5) D. H. McDaniel, *Inorg. Chem.*, **11**, 2678 (1972).
(6) M. Tinkham, "Group Theory and Quantum Mechanics", McGraw-Hill, New York, N.Y., 1964, pp 9–10.
(7) Distinguishable in a fixed-coordinate system.

Department of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221
Darl H. McDaniel

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Additions and Corrections

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R. Romeo*, D. Minniti, and M. Trozzi: Uncatalyzed Cis–Trans Isomerization and Methanol Solvolysis of Arylbromobis(triethylphosphine)platinum(II) Complexes. A Different Role for Steric Hindrance in Dissociative and Associative Mechanisms.

Page 1136. Equation 4 should read $k_1 = k_s k_Y[Y]/(k_{-s}[X^-] + k_Y[Y])$.—R. Romeo

Motoharu Tanaka: Solvent Exchange at Some Bivalent Metal Ions.

Page 2325. In the left column, first line of third paragraph, "dissociation" should read "dissociative".

Page 2327. Reference *h* in Table II should read: H. Levanon and Z. Luz, *J. Chem. Phys.*, **49**, 2031 (1968).—M. Tanaka