served if the carbon atom 2s orbital contained one unit of unpaired spin density. The difficulty with this approach is that there is very likely a contribution to $a^{C^{13}}$ from the 1s orbital of the carbon atom. Karplus and Fraenkel[24] have estimated this contribution for sp^2-hybridized carbon atoms and found that it is approximately two-thirds as large as the 2s contribution and of opposite sign. For tetrahedral carbon atoms there is undoubtedly a similar contribution, although not necessarily of the same magnitude. As a result the estimate of ρ_{2s} by Stock and Suzuki is likely to be too low, perhaps by as much as a factor of 2. Spin densities produced in the C^{13} 1s orbital will not affect significantly the proton hfs so we are correct in using the value of ρ_Z determined in our Hückel calculations to estimate Q_t.

Finally, we have examined the effect of *t*-butyl substituents on the ring proton hyperfine splittings from the point of view of the additivity rules of Venkataraman and Fraenkel.[3] These rules work reasonably well for methyl substitution in *p*-benzosemiquinones. We have attempted to fit our data on 2-*t*-butyl-*p*-, 2,5-di-*t*-butyl-*p*-, and 2,6-di-*t*-butyl-*p*-benzosemiquinone and have found that it is not possible to obtain a set of additivity constants which give good agreement with the experimental values of the splitting constants. This may be a further indication of a direct interaction between the *t*-butyl groups and the carbonyl group.

Conclusions

We have obtained the esr spectra of seven *t*-butyl-substituted semiquinones and have resolved the *t*-butyl proton splittings in six of these radicals. In the *p*-benzosemiquinones this splitting is 0.060 gauss and in the *o*-benzosemiquinones it is 0.3 gauss in the fourth and fifth ring position but less than 0.03 gauss in the third and sixth position. The most reasonable mechanism whereby *t*-butyl proton splittings may arise is a transfer of spin density to the β-carbon atoms *via* carbon–carbon hyperconjugation and thence to the *t*-butyl protons *via* the usual spin-polarization mechanism. Based on this model we estimate that the Q value for the spin-polarization mechanism is approximately 44 gauss. This quite reasonable value for Q probably indicates the essential correctness of the model and provides the expected result that tetrahedral obitals are more effective than p_z orbitals in polarizing hydrogen 1s orbitals. The parameters used in our HMO calculations indicate that carbon–carbon hyperconjugation is somewhat less effective than carbon–hydrogen hyperconjugation. In addition the HMO calculations suggest that the *t*-butyl group has a larger inductive effect upon the aromatic ring than the methyl group and that an interaction between the substituent (either methyl or *t*-butyl) and adjacent carbonyl groups may occur, although the nature of this interaction is somewhat uncertain. The fact that the additivity relationships of Venkataraman and Fraenkel do not apply to *t*-butyl substitution in *p*-benzosemiquinones may suggest a stronger interaction of the carbonyl group with the *t*-butyl group than with the methyl group.

Acknowledgment. We thank the National Science Foundation for a departmental equipment grant, GP-2104.

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(24) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

Carbon-13 Magnetic Resonance. XI.[1a] Structural and Electronic Effect on the Carbon-13 Nuclear Magnetic Resonance Spectra of the Halogen-Substituted Methanes[1b]

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Abstract: The carbon-13 chemical shifts of the halomethanes exhibit anomalous trends which cannot be explained by any simple additive relationship in the number of halogen substituents. The addition of a pair-interaction term in a linear expression, however, allows reasonable correlation of the chemical shift data. These parameters are discussed theoretically in terms of charge polarization, the steric influence of halogen substituents on the effective orbital radii, and deviations from the classical bond structure. Polarization effects upon the chemical shift are attributed to changes in the effective nuclear charge and its accompanying alteration of the $\langle 1/r^3 \rangle$ term in the paramagnetic screening expression. Steric effects produce changes in the bond lengths which are reflected in the effective radius of the electron as shown by further changes in the $\langle 1/r^3 \rangle$ term. Deviation from perfect pairing alters the extent of spin pairing of two interacting electrons on the same carbon, and this affects the preferential admixture by the magnetic field of excited states having intrinsic angular momentum into the ground state of the molecules.

The carbon-13 chemical shifts of the halogen-substituted methanes were reported quite early by Lauterbur,[2] but a satisfactory theoretical explanation of the somewhat anomalous experimental values has been needed. The chemical shifts of the iodine and chlorine series, $CH_{4-n}X_n$, were found[2] to exhibit values above and below, respectively, that of methane, while the trend in chemical shift values reverses itself at CH_2Br_2 in the

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(1) (a) Previous paper in this series: R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, 90, 697 (1968). (b) This is an essential portion of a thesis submitted to the Department of Chemistry, University of Utah, in partial fulfillment of the requirements for a Ph.D. degree.

(2) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, 70, 841 (1958).

bromine series. It is understandable that this divergence in the chemical shifts might be considered to be unusual. While this paper reports more accurate shift values for some of the compounds by using the proton-decoupling technique,[3] the central purpose of this work is concerned with a discussion of the chemical shift features reported earlier.[2]

Since Ramsey[4] presented an expression for the chemical shift Hamiltonian, several investigations have dealt with the calculation of the chemical shift parameter using both MO[1,5–11] and VB[11,12] approximations. In addition, much discussion has been based on the anisotropy[7,13–15] of remote groups and the importance of inductive terms ensuing from electronegativity considerations.[15] It is felt, however, that none of these previous approaches offers an adequate explanation of the trends noted in the halogenated methanes.

Cheney and Grant[12] have extended the VB formulation of Jameson and Gutowsky[11] to include canonical structures other than the principle bond structure. In this formulation substituent group effects arise from minor perturbations of the electronic structure of the carbon-13 atom, and in addition to normal inductive effects a linear parameterization of the chemical shift data becomes possible for minor deviations from perfect pairing. Thus, part of the anomalous trends in the carbon-13 chemical shifts of the halomethanes can be rationalized in terms of bond delocalization. The perturbation approach, used here for the evaluation of chemical shifts, suffers from the limitations of the average energy approximation. The work of McLachlan[16] and of Karplus,[17] however, lends validity to this approximation for the class of compounds considered in this paper.

The concept of "bond effective nuclear charge" used in our previous work to rationalize the directly bonded C^{13}–H coupling constants[18] found for this class of compounds is incorporated in our calculations to account for important inductive effects upon the average orbital radius on which the paramagnetic screening constant depends. The use of a variable effective nuclear charge is similar to that employed in previous papers[1,5,12] in this series.

Experimental Section

The halogen-substituted methanes were all obtained from standard commercial sources and with the exception of iodoform were run as neat liquids. Iodoform was dissolved in pyridine to the extent of saturation. The samples were sealed in tubes after being degassed by a vacuum-freezing technique.

A Varian V-4311 high-resolution spectrometer and a Varian V-4320 proton decoupler were used with the decoupling techniques described by Paul and Grant[3] to obtain the carbon-13 chemical shifts of many of the compounds considered in this study. The carbon-13 chemical shifts are calculated from eq 1,[19] where $\Gamma_i = f_i/\nu_i$ with f_i and ν_i representing the decoupler and transmitter

$$\delta_{C^{13}} \cong \frac{\Gamma_i - \Gamma_0}{\Gamma_i} - (\delta_{H_i} - \delta_{H_0}) \qquad (1)$$

frequencies, respectively, for the most favorable decoupling conditions. The proton chemical shift measured from tetramethylsilane (TMS) is δ. The subscript "i" represents the sample and "0" denotes the reference with $\Gamma_0 = 3.9764492 \pm 0.00000004$ and $\delta_{H_0} = 7.17$ ppm for benzene.

The chemical shifts of those compounds studied after receiving delivery of our new Varian AFS-60 were obtained on this field-frequency lock instrument. Operating in the frequency sweep mode the chemical shift is obtained directly from the difference in frequency of a proton-decoupled benzene singlet and the corresponding peaks in the sample compound. A 50% benzene solution was investigated in each of these samples.

Results

The chemical shift values for various substituted methanes considered in this investigation are given in Table I. The value of Γ, the proton chemical shifts with reference to TMS, and the carbon-13 chemical shifts with respect to benzene are presented along with previous literature values.[2,15]

Table I. Carbon-13 Chemical Shifts for Selected Halomethanes

	Molecule	Γ_i	δ_{H_i}	$\delta_{C^{13}}$	Lit values[a]
1.	CH_4				130.8[b]
2.	CH_3Cl	3.97684451	2.99	103.5_9	103.8,[b] 107
3.	CH_3Br	3.97690244	2.64	118.5_0	119.3,[b] 115
4.	CH_3I	3.97702264	2.16	149.2_0	151.0,[b] 148
5.	CH_2Cl_2	3.97673815	5.31	74.5_4	74
6.	CH_2ClBr	3.97679264	4.91	88.6_5[c]	89
7.	CH_2Br_2	3.97686644	4.98	107.1_1	106
8.	CH_2I_2	3.97716218	3.92	182.5_2	190
9.	$CHCl_3$	3.97665242	7.27	51.0_1	48
10.	$CHCl_2Br$	3.97673230	7.01	71.3_4[c]	70
11.	$CHClBr_2$	3.97681804	6.47	94.1_4[c]	93
12.	$CHBr_3$	3.97691075	6.86	116.3_7	118
13.	CHI_3	3.97750761	4.89	268.3_8	266
14.	CCl_4			32.0_3[c]	31
15.	CCl_3Br			60.9_2[c]	59
16.	CCl_2Br_2			. . .[e]	92
17.	$CClBr_3$			123.5_9[c]	120
18.	CBr_4			157.1_6[c,d]	155

[a] Taken from ref 2 and converted to benzene reference by subtracting 50 ppm. [b] Taken from ref 15. [c] Determined with AFS-60 spectrometer. [d] 106.15 ppm from $CHCl_3$. [e] Sample was not available.

Additive relations for the alkanes and some of their derivatives have been observed in many kinds of chemical data such as heats of reaction,[20] parachor,[21] the coupling constant,[22] and carbon-13 chemical shifts.[23] These results have suggested that additive substituent effects might also exist for the carbon-13 chemical shifts of the halomethanes. However, the observed reversal in shift values in the $CH_{4-n}Br_n$ series as the number of bromine atoms increases emphasizes that a simple additive relationship in the number of substituents does

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(3) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964).
(4) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1952).
(5) T. D. Alger, D. M. Grant, and E. C. Paul, *J. Am. Chem. Soc.*, **88**, 5397 (1966).
(6) M. Fixman, *J. Chem. Phys.*, **35**, 679 (1961).
(7) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 541, 550 (1957).
(8) F. Prosser and L. Goodman, *J. Chem. Phys.*, **38**, 374 (1963).
(9) M. Karplus and T P. Das, *ibid.*, **34**, 1683 (1961).
(10) M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).
(11) C. J. Jameson and H. S. Gutowsky, *ibid.*, **40**, 1714 (1964).
(12) B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5319 (1967).
(13) J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961).
(14) H. M. McConnell, *ibid.*, **27**, 226 (1957).
(15) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722, 731 (1961).
(16) A. D. McLachlan, *ibid.*, **32**, 1263 (1960).
(17) M. Karplus, *ibid.*, **33**, 941 (1960).
(18) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).
(19) W. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).
(20) S. Glasstone "Textbook of Physical Chemistry," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1946, p 202.
(21) Reference 20, pp 526–527.
(22) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961).
(23) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964).

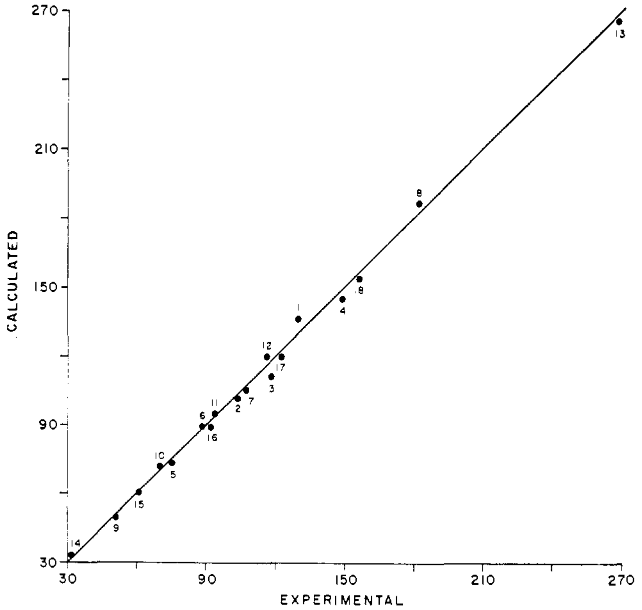

Figure 1. Predicted chemical shift values are plotted against the experimental quantities. The correlation indicates the general success of the linear expression represented by eq 2. The points are designated by the item number given in Table I.

not exist and that additional terms must be considered if a linear relationship is to be found.

A simple linear expression which might be used to correlate the chemical shift data is

$$\delta_{C_{13}}(m) = k + \sum_{i,\nu} p_i\delta_i + \sum p_{ij}\delta_{ij} \quad (2)$$

where $\delta_{C_{13}}(m)$ is the chemical shift of the *m*th halomethane, *k* is an arbitrary scale factor which can be adjusted to accommodate the shifts to any reference value, p_i and p_{ij} are populational factors, and δ_i and δ_{ij} are substituent parameters representing the direct effect of a substituent group and the effect of pair interactions of such groups, respectively. Implicit relationships existing between the halomethane molecules prevent eq 2 from yielding values for all of the parameters. Thus, the chemical shifts for methane and for all of the halomethanes are more appropriately represented with the following set of linearly independent expressions

$$\delta_{C^{13}}(CH_4) = \delta_0 \quad (3)$$

$$\delta_{C^{13}}(CH_3X) = \delta_0 + \Delta(X) \quad (4)$$

$$\delta_{C^{13}}(CH_2XX') = \delta_0 + \Delta(X) + \Delta(X') + \Delta(X\text{-}X') \quad (5)$$

$$\delta_{C^{13}}(CHXX'X'') = \delta_0 + \Delta(X) + \Delta(X') + \Delta(X'') + \Delta(X\text{-}X') + \Delta(X\text{-}X'') + \Delta(X'\text{-}X'') \quad (6)$$

$$\delta_{C^{13}}(CXX'X''X''') = \delta_0 + \Delta(X) + \Delta(X') + \Delta(X'') + \Delta(X''') + \Delta(X\text{-}X') + (X\text{-}X'') + \Delta(X\text{-}X''') + \Delta(X'\text{-}X'') + \Delta(X'\text{-}X''') + \Delta(X''\text{-}X''') \quad (7)$$

where the above substituent parameters are defined in eq 8–10 in terms of the more fundamental constants given in eq 2.

$$\delta_0 = k + 4\delta_H + 6\delta_{H-H} \quad (8)$$

$$\Delta(X) = (\delta_X - \delta_H) + 3(\delta_{HX} - \delta_{HH}) \quad (9)$$

$$\Delta(X\text{-}X') = \delta_{XX'} + \delta_{HH} - \delta_{HX} - \delta_{HX'} \quad (10)$$

The population matrix for both the direct substituent parameters, Δ(X), as well as the cross-correlated terms, Δ(X–X′), is taken from eq 3–7, and these are given in Table II for all of the halogen-substituted methanes considered in this study. A regressional analysis performed on these parameters yielded the results given in Table III. The success of the least-squares fit is exhibited both by the high multiple correlation coefficient and by the relatively small standard deviation between the predicted and the experimental quantities which are plotted in Figure 1. While the standard deviation of 4 ppm is considerably greater than the experimental error, it should be noted that this value is less than 2% of the total chemical shift range (32–268 ppm) exhibited by the halomethanes. Figure 1 also portrays the experimental shifts with predicted values obtained from the information contained in Tables II and III. To allow a more flexible analysis of the data, the dependent variable, δ_0, was not constrained to equal the methane chemical shift value, $\delta_{C^{13}}(CH_4)$. Even so, the value of 136.33 ppm obtained for δ_0 is only about one standard deviation from the experimental value for $\delta_{C^{13}}(CH_4)$, and within the over-all accuracy of the fit the two quantities can be considered to be in fair agreement. The values for the Δ(X) and Δ(X–X′) parameters vary in an orderly manner as one traverses the halogen family from chlorine to iodine. The change in Δ(X) is probably due to the variation in electronegativity[24] while in-

Table II. Population Matrix Used in Chemical Shift Calculation

Molecule	p_{Cl}	p_{Br}	p_I	p_{ClCl}	p_{BrBr}	p_{II}	p_{ClBr}
CH_3I			1				
CH_3Br		1					
CH_3Cl	1						
CH_2I_2			2			1	
CH_2Br_2		2			1		
CH_2BrCl	1	1					1
CH_2Cl_2	2			1			
CHI_3			3			3	
$CHBr_3$		3			3		
$CHBr_2Cl$	1	2			1		2
$CHBrCl_2$	2	1		1			2
$CHCl_3$	3			3			
CBr_4		4			6		
CBr_3Cl	1	3			3		3
CBr_2Cl_2	2	2		1	1		4
$CBrCl_3$	3	1		3			3
CCl_4	4			6			

Table III. Results of Least-Squares Regressional Analysis

Number of independent variables		7
Number of pieces of data		17
Multiple correlation coefficient *R* squared		0.9968
Standard error of estimate		4.0660
Constant term		136.33
Δ(Cl)	−33.98 ± 3.04	
Δ(Br)	−24.18 ± 3.04	
Δ(I)	+7.83 ± 4.15	
Δ(Cl–Cl)	+5.44 ± 1.87	
Δ(Cl–Br)	+11.29 ± 1.52	
Δ(Br–Br)	+18.88 ± 1.87	
Δ(I–I)	+35.67 ± 3.94	

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[24] G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **67**, 2430 (1963).

creased steric involvement for the larger halogens as well as changes in spin pairing are suggested as reasons for the increase in the Δ(X–X′) parameters. It is of interest to note that Δ(Cl–Br) is the mean, within experimental fluctuations, of the Δ(Cl–Cl) and Δ(Br–Br) values. Thus, trends which reflect the periodic properties of the halogen family exist for these empirical parameters.

Theoretical Considerations

The screening parameter, usually separated into diamagnetic and paramagnetic terms, is separated along other lines in this study to emphasize certain conceptual features. Using the VB formalism it is possible to subdivide the shielding expression into terms attributed solely to the principal bond structure, σ_{11}, and terms, $\sigma_{1\mu}{}^{(\mathrm{del})}$, arising from cross terms between the principal bond structure and the μth canonical structure. The expression[25] obtained in this manner is

$$\sigma = \sigma_{11} + \sum_{\mu} \sigma_{1\mu}{}^{(\mathrm{del})} \tag{11}$$

This equation is valid only if deviations from perfect pairing are minor. Equation 11 is affected only by those structures in the canonical set which alter the spin-pairing features of two electrons centered on the particular carbon-13 under consideration. Thus, a summation of the type given in eq 11 is similar in form to the pairwise summation given in eq 2 as two separate bonds on the same carbon-13 must be involved in the spin-delocalized structure if the chemical shift is to be affected. Any sizable variation in the spin-pairing features will, therefore, become important in discussing those parameters given in Table III which represent pairwise interactions.

Important variations in the value of σ_{11} will result also from the degree of charge polarization and of steric repulsion realized for the various halogens. Charge-polarization effects upon the chemical shift are associated with a contraction or expansion of the orbital radius when the electron density is decreased or enhanced, respectively. As charge transfer is especially pronounced for the very electronegative halogens, the polarization effect is of major consideration and is used to account for the gross shift features which spread the resonance positions of the halomethanes over two-thirds of the total carbon-13 shift range of about 300 ppm.

While it is not possible at the present time to discuss in exact terms the effect of steric repulsion between larger geminal halogens, this feature is considered in a semiquantitative manner. It is proposed that sizable repulsive interactions may be expected to lead to bond elongation and therefore a greater average orbital radius. This increase in the average orbital radius will decrease the $\langle 1/r^3 \rangle$ term in the paramagnetic shielding expression, and the chemical shift may be expected to move to higher fields. While the charge polarization effects can be expected to influence more directly the Δ(X) parameters, steric repulsion between halogens should affect the Δ(X–X′) parameter more significantly.

A. Charge Polarization Effects on the Chemical Shift. The evaluation of the chemical shift parameter, σ_{11}, for the principal bond structure proceeds in a straightforward manner if one employs a wave function[26] of the form

$$\psi_0 = \left[\frac{(2n)!}{2^n}\right]^{-1/2} \sum_{P} (-1)^P P[\psi_{aw}(1,2)\psi_{bx}(3,4)\cdots] \tag{12}$$

where

$$\psi_{aw}(1,2) = (1/2)^{1/2} u_{aw}(1,2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{13}$$

This function, used also by Jameson and Gutowsky,[11] offers a particularly attractive form since ionic terms are explicitly included in the bond function which is given as

$$u_{aw}(1,2) = n_{aw}[\varphi_a(1)\varphi_w(2) + \varphi_w(1)\varphi_a(2) + \lambda_a\varphi_a(1)\varphi_a(2) + \lambda_w\varphi_w(1)\varphi_w(2)] \tag{14}$$

where the individual atomic hybrid orbitals are written as linear combinations of Slater-type atomic orbitals

$$\varphi_a(1) = c_s{}^a s + c_x{}^q p_x + c_y{}^a p_y + c_z{}^a p_z + c_{xy}{}^a d_{xy} + \cdots \tag{15}$$

Grant and Cheney[12] omitted ionic terms in their consideration of the alkanes as only minor contributions result from the inclusion of ionic terms in the chemical shift expression for the relatively nonpolar alkanes. In the haloalkanes, polarization effects are more than minor perturbations, and ionic terms cannot be properly ignored. It should be pointed out, however, that their inclusion alters the screening expression in a way which predicts a charge dependence of carbon-13 chemical shifts which is opposite to the experimentally determined relationship unless the radial distribution of electrons is also varied with the degree of polarization by varying the effective nuclear charge.

Using the same procedure as Jameson and Gutowsky, the diamagnetic part of σ_{11} can be written as

$$\sigma_{11}{}^{(\mathrm{d})} = 2\sum_a n_a{}^2 \langle \varphi_a(i) | Q(i) | \varphi_a(i) \rangle \tag{16}$$

where "*a*" denotes the *a*th bond on the atom, $Q(i)$ is $e^2/3mc^2r_i$, λ_a is the ionic coefficient of the carbon in the *a*th bond, and S_a is the overlap of the *a*th bond. The paramagnetic term can be expressed as

$$\sigma_{11}{}^{(\mathrm{p})} = 2\sum_a n_a{}^2 \{[(1 + 2\lambda_a S_a + \lambda_a{}^2)\langle \varphi_a(i) | Q(i,i) | \varphi_a(i)\rangle + \lambda_a{}^2 \langle \varphi_a(i)\varphi_a(j) | Q(i,j) | \varphi_a(i)\varphi_a(j)\rangle + (1 + 2\lambda_a S_a + \lambda_a{}^2)\sum_{b>a} n_b{}^2(1 + 2\lambda_b S_b + \lambda_b{}^2)[4\langle \varphi_a(i)\varphi_b(j) | Q(i,j) | \varphi_a(i)\varphi_b(j)\rangle - 2\langle \varphi_a(i)\varphi_b(j) | Q(i,j) | \varphi_b(i)\varphi_a(j)\rangle]\} \tag{17}$$

where

$$Q(i,j) = \frac{-e^2}{3m^2c^2\Delta}\frac{\mathrm{L}_j \cdot \mathrm{L}_k}{r_j{}^3}$$

By substituting the Slater orbitals into the expressions for the diamagnetic and paramagnetic terms, the following expression for the chemical shift parameter is obtained[27]

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(25) Equation 34 of ref 12.

(26) A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc.* (London), **A220**, 446 (1953); J. M. Parks, and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958).

(27) This expression is comparable to eq 21 and 22 of Cheney and Grant.[12] The two equations become equivalent when $\mu = \nu = 1$, $C_1 = 1$, $f_{11}(p_{ab}) = -1/2$, $\lambda_a = \lambda_b = 0$, and $n_a{}^2 = n_b{}^2 = 1/2$. The paramagnetic part of this expression is also comparable with eq 20 of Jameson and Gutowsky.[11]

Table IV. Calculated Parameters in the Chemical Shift Calculation[a]

Molecule	ξ_{CH}	ξ_{CX}	η_{CH}^2	η_{CX}^2	λ_{CH}	S_{CH}	S_{CX}	$\Delta\sigma_{11}^{(p)}$
CH_4	3.7400	...	0.26742	...	0.3559	0.6100	...	[130.8]
CH_3Cl	3.9185	3.7400	0.27448	0.44903	0.3586	0.5826	0.3369	93.21
CH_3Br	3.9045	3.7400	0.27393	0.44390	0.3584	0.5847	0.3555	96.28
CH_3I	3.8905	3.7400	0.27338	0.43672	0.3582	0.5869	0.3807	99.34
CH_2Cl_2	4.0970	3.9185	0.28146	0.45331	0.3617	0.5558	0.3209	53.12
CH_2ClBr	4.0830	Cl 3.9045	0.28091	Cl 0.45297	0.3615	0.5579	Cl 0.3222	56.39
		Br 3.9185		Br 0.44883			Br 0.3377	
CH_2Br_2	4.0690	3.9045	0.28037	0.44845	0.3612	0.5600	0.3391	59.64
CH_2I_2	4.0410	3.8905	0.27928	0.44098	0.3607	0.5642	0.3658	66.14
$CHCl_3$	4.2755	4.0970	0.28828	0.45750	0.3652	0.5299	0.3048	10.56
$CHCl_2Br$	4.2615	Cl 4.0830	0.28776	Cl 0.45718	0.3649	0.5319	Cl 0.3060	14.03
		Br 4.0970		Br 0.45361			Br 0.3198	
$CHClBr_2$	4.2475	Cl 4.0690	0.28723	Cl 0.45686	0.3646	0.5339	Cl 0.3073	17.49
		Br 4.0830		Br 0.45324			Br 0.3212	
$CHBr_3$	4.2335	4.0690	0.28669	0.45287	0.3643	0.5359	0.3226	20.93
CHI_3	4.1915	4.0410	0.28509	0.44501	0.3635	0.5420	0.3515	31.24
CCl_4	...	4.2755	...	0.46113	...	...	0.2903	−34.40
CCl_3Br	...	Cl 4.2615	...	Cl 0.46087	...	...	Cl 0.2914	−30.73
		Br 4.2755		Br 0.45830	...	...	Br 0.3016	
CCl_2Br_2	...	Cl 4.2475	...	Cl 0.46061	...	...	Cl 0.2924	−27.08
		Br 4.2475		Br 0.45751			Br 0.3048	
$CClBr_3$	...	Cl 4.2355	...	Cl 0.46035	...	...	Cl 0.2935	−23.44
		Br 4.2475		Br 0.45751			Br 0.3048	
CBr_4	...	4.2335	...	0.45715	...	...	0.3062	−19.82

[a] Values obtained from eq 18 were adjusted to the benzene chemical shift scale by offsetting the theoretical values so as to get exact agreement between the theoretical and experimental values for methane. The calculated values for σ_{11} can be obtained from $\Delta\sigma_{11}$ by subtracting 416.80 ppm.

Table V. Bond Distances in the Halomethanes[a]

Formula	Chlorides		Bromides		Iodides	
	R_{CH}	R_{CCl}	R_{CH}	R_{CBr}	R_{CH}	R_{CI}
CH_4	1.0938	...	1.0938	...	1.0938	...
CH_3X	1.0959	1.78123	1.0954	1.9388	1.0958	2.1387
CH_2X_2	1.068	1.7724	1.093[c]	1.907	...[b]	2.12
CHX_3	1.073[c]	1.762	1.068	1.930	...[b]	2.12
CX_4	...	1.766	...	1.942	...	2.15

[a] Obtained from L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958, Supplement, 1956–1959, The Chemical Society, London, 1965. [b] Not available. [c] Assumed values.

$$\sigma_{11} = A\sum_a\langle 1/r\rangle_a n_a^2(1 + 2\lambda_a S_a + \lambda_a^2) - 2B[\sum_a\langle 1/r^3\rangle_a \times n_a^2(1 + 2\lambda_a S_a + \lambda_a^2)P^a - \sum_{a,b>a}\langle 1/r^3\rangle_{ab} n_a^2 n_b^2(1 + 2\lambda_a S_a + \lambda_a^2)(1 + 2\lambda_b S_b + \lambda_b^2)P^{ab}] \quad (18)$$

where $A = e^2/3mc^2a_0 = 17.75$ ppm, $B = 2e^2h^2/3m^2\cdot c^2a_0^3\Delta = 965.4$ ppm/Δ, $P^a = \Sigma_{i=x,y,z}(c_i^a)^2$, $P^{ab} = (c_z^ac_y^b - c_y^ac_z^b)^2 + (c_x^ac_z^b - c_z^ac_x^b)^2 + (c_y^ac_x^b - c_x^ac_y^b)^2$, $\langle 1/r\rangle_a = \xi_a/4$, $\langle 1/r^3\rangle_a = \xi_a^3/24$, and $\langle 1/r^3\rangle_{ab} = (\xi_a\xi_b)^{5/2}/6(\xi_a + \xi_b)^2$. The geometry of the compounds considered in this study is very closely approximated by the tetrahedral configuration, and under this assumption $P^a = {}^3/_4$ and $P^{ab} = {}^1/_2$.

The overlap integral, S_a, was obtained theoretically using atomic orbitals of the following form

$$\Phi_a = NY_{l,m}(\theta,\varphi)R_{an}(r) \quad (19)$$

and

$$R_{an}(r) = r^{n-1}\exp(-\xi_a r/na_0) \quad (20)$$

where N is a normalization constant and ξ is a bond effective nuclear charge. These values are tabulated in Table IV for both C–H and C–X bonds. Values for n_a and n_b were obtained by normalizing the appropriate wave functions. The effective nuclear charge, ξ_a, and ionic coefficient, λ_a, were calculated from polarization charges using, respectively, the expressions 21 and 22,

$$\xi_a = \xi_0\beta - 0.35\sum_{k\neq a}(q_k - 1) \quad (21)$$

$$q_k = \frac{2\lambda_k S_k + \lambda_k^2}{2 + 2S_k^2 + 4\lambda_k S_k + \lambda_k^2} \quad (22)$$

where $\xi_0 = 3.25$, $\beta = 1.15$,[28] and q_k is the charge density in electron units in the carbon orbital of the kth valence bond. Thus, several parameters used in eq 18 depend upon the choice of values for q_k. Approximate values of q_k for various carbon–halogen bonds can be related to q_{CH} with the following empirical relationship[18]

$$q_{CX} = q_{CH}(\mu_{CX}R_{CH}/\mu_{CH}R_{CX}) \quad (23)$$

where μ and R are dipole moments and bond distances, respectively. Suggested values for q_{CH} have ranged from 0.04 to 0.33 electron. However, previous work[1,5,18,29,30] indicates that values from 0.1 to 0.2 electron lead to reasonable theoretical correlation of carbon-13 chemical shifts and C^{13}–H coupling constants.

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(28) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(29) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U.S.*, **45**, 1269 (1959).

(30) See also the extended HMO work of R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

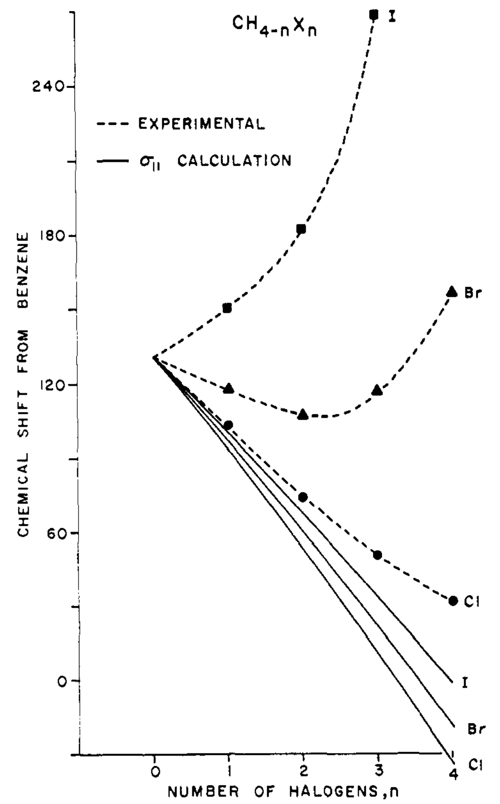

Figure 2. The experimental chemical shifts are compared with the theoretical values predicted by a charge polarization model utilizing only the principal bond structure.

To be consistent with the previous VB work on chemical shift calculations,[12] we shall use 0.15 electron for q_{CH}. Using literature values for μ[31a] and R,[31b] values for q_{CCl}, q_{CBr}, and q_{CI} are calculated from eq 23 to be -0.36, -0.32, and -0.28, respectively. The bond effective nuclear charges calculated from the q_k's by means of eq 26 are given in Table IV along with the values for the ionic coefficient. The values of σ_{11} obtained from the respective parameters given in Table IV were calculated with eq 18 and then scaled by $+416.80$ ppm so that the experimental and theoretical values for methane would agree. A comparison of predicted and experimental values is given in Figure 2 for the compounds in which the halogens are not mixed. The mixed compounds have intermediate values between the extremes and are not included in Figure 2 for the sake of clarity. It is obvious from Figure 2 that the application of charge polarization in the "perfect pairing" approximation (only σ_{11} considered) is not adequate to explain the upward trends present in both the Br and I series. The essential features of the Cl series are rationalized with charge-transfer effects, and it is concluded that other effects, spin delocalization and steric repulsion, are less important in the chlorine series.

B. Steric Effects on the Chemical Shift. Steric changes in the bond distance between two atoms can be expected to alter the effective orbital radius of the electrons associated with bonded atoms, and these changes should then affect the chemical shift parameter through the $\langle 1/r^3 \rangle$ terms. Bond distances given in Table V are available for some of the halogenated methanes, and these distances are used to approximate the average orbital radius of the bonding electron in the following manner. First, an improved covalent radius in atomic units is obtained from

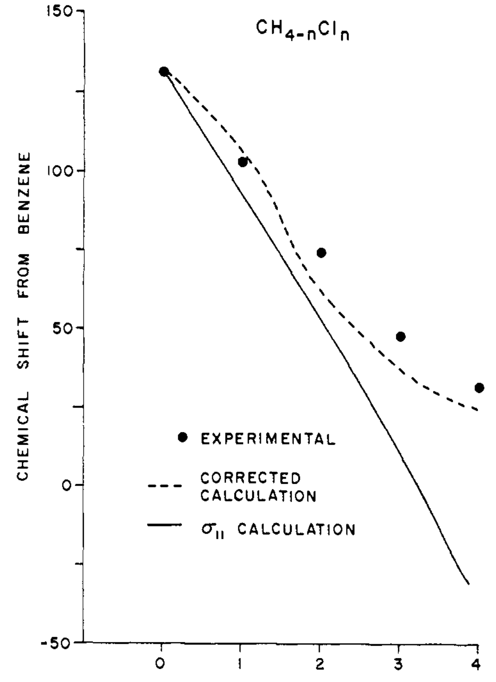

Figure 3. Steric corrections upon the $\langle 1/r^3 \rangle$ term improve the agreement between theoretical and experimental shifts for the chloromethanes.

$$r_C(CX) = R_{CX}\left(\frac{\rho_C}{\rho_C + \rho_X}\right) \qquad (24)$$

where $r_C(CX)$ is the covalent radius, R_{CX} is the bond distance, and ρ_C and ρ_X are standard covalent radii.[32] It is understood, of course, that these standard covalent radii are in themselves averages obtained from bond distances in a variety of molecules so that the values obtained from these calculations are, admittedly, only approximations for estimating relative changes in bond distances for a particular family of halogens.

The chemical shift parameter can then be changed to include the effects of varying bond distances by the inclusion of an additional term given by

$$l_a = \frac{r_C(CH_4)}{r_C(CX)} \qquad l_{ab} = (l_a l_b)^{1/2} \qquad (25)$$

so that the radial components are altered in eq 18 with the following substitutions.

$$\begin{aligned} \langle 1/r^3 \rangle_a &= l_a^3 \langle 1/r^3 \rangle_a \\ \langle 1/r^3 \rangle_{ab} &= l_{ab}^3 \langle 1/r^3 \rangle_{ab} \\ \langle 1/r \rangle_a &= l_a \langle 1/r \rangle_a \end{aligned} \qquad (26)$$

The result of correcting eq 18 with the concepts embodied in eq 26 are shown in Figures 3 and 4 for the chlorine and bromine series. The distance data for the iodine compounds are not complete and cannot be considered at present. The effect of steric alterations

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(31) (a) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd revised ed, Pergamon Press, New York, N. Y., 1961, p 530, but using the value of 0.4 D for the CH bond from ref 27; (b) *ibid.*, p 1042.

(32) As given by Moelwyn-Hughes in ref 31, p 25, the values are: $\rho_C = 0.771$, $\rho_H = 0.3707$, $\rho_{Cl} = 0.994$, $\rho_{Br} = 1.1415$, $\rho_I = 1.3333$.

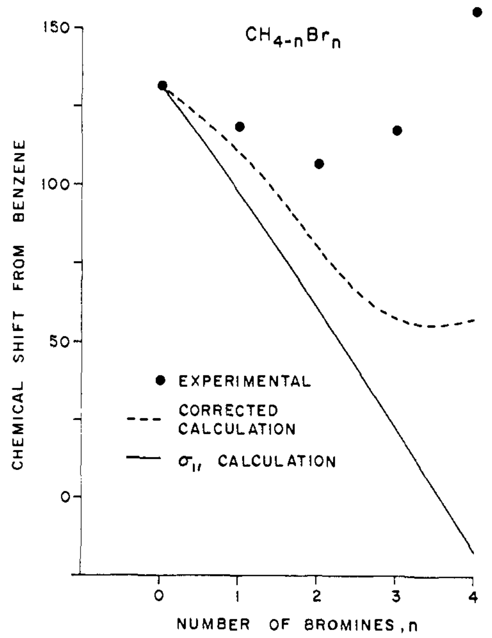

Figure 4. Steric corrections upon the $\langle 1/r^3 \rangle$ term for the bromomethanes reflect some of the anomalous trends noted in the experimental values.

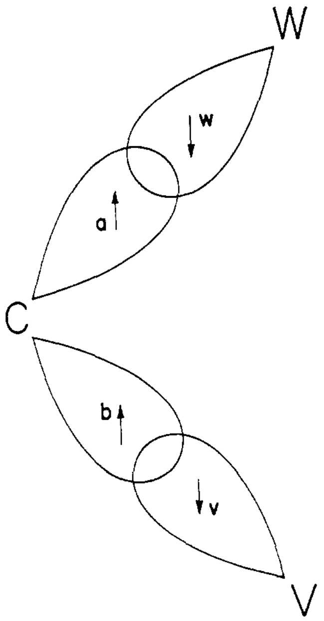

Figure 5. Schematic representation of orbitals used in VB treatment of electron delocalization.

of the bond distances is to raise the calculated curve closer to the actual experimental values in both instances. In the bromine series this correction results in the σ_{11} curve reversing itself as does the experimental data. Table VI lists the values of the terms used in this calculation. Admittedly the assumptions are quite crude, but the calculation does substantiate the position that sterically induced variations in the bond distance are sufficiently large that they may account for some of the anomalous trends noted in the carbon-13 chemical shift parameter in the halomethanes. Furthermore, the terms of l_a and l_{ab} exhibit a similar populational relationship in their effect upon the chemical shift as was noted for the substituent parameters $\Delta(X)$ and $\Delta(X-X')$, respectively.

Table VI.[a] Calculated Steric Parameters Affecting the Chemical Shift

Molecule	l_a^3 CH	l_b^3 CX	l_{ab}^3 CHCX	σ	Chemical shift[b]
CH_4	1.0000	...	...	−286.00	[130.8]
CH_3Cl	0.9940	0.8558	0.9223	−310.62	106.18
CH_3Br	0.9955	0.8442	0.9167	−307.23	109.57
CH_2Cl_2	1.0741	0.8683	0.9657	−356.44	60.36
CH_2Br_2	1.0021	0.8870	0.9428	−337.14	79.66
$CHCl_3$	1.0590	0.8839	0.9675	−376.83	39.97
$CHBr_3$	1.0741	0.8558	0.9587	−360.46	56.34
CCl_4	...	0.8778	...	−390.56	26.24
CBr_4	...	0.8399	...	−359.64	57.16

[a] The values for all other terms in the calculation are given in Table IV. [b] Values obtained from eq 18 were adjusted to the benzene chemical shift scale by offsetting the theoretical values so as to get exact agreement between the theoretical and experimental values for methane. The calculated values for σ_{11} can be obtained from $\Delta\sigma_{11}$ by subtracting 416.80 ppm.

While good structural data for the iodine series are not available at present, it is expected that steric effects will be more pronounced with iodine than either bromine or chlorine. Pending additional theoretical work with better structural information it is proposed that the positive iodine substituent parameter, $\Delta(I)$, arises primarily from a steric interaction. Equation 9 indicates that the simple substituent parameters do have a proton halogen interaction term which could reflect interactions between geminal groups. The pair correlation parameters should always be positive when dominated by repulsive steric terms as can be seen from eq 10.

C. Electron Delocalization Effects on the Chemical Shift. Bartell[33] has pointed out that it is not possible to separate nonbonded repulsive effects of the type considered in the last section from electron delocalization effects which are characterized in the VB formalism with deviations from perfect pairing. Relief of steric repulsions was proposed as a principal reason for the existence of unusual long-range bond structures. This being the case, steric and delocalization effects upon the chemical shift would properly be considered as two different expressions of the same structural feature. Even so, the chemical shift equation is affected in two distinct ways and the discussion is subdivided into two parts for convenience. The previous section considered changes in the $\langle 1/r^3 \rangle$ term which results from variations in the actual molecular geometry. This section deals with changes in the chemical shift arising from differences in the spin-pairing features associated with electron delocalization. The effect of electron delocalization has been given for the μth canonical structure in eq 11 with

$$\sigma_{1\mu}^{(\mathrm{del})} = -BC_1C_\mu 2^{-n+i_{1\mu}} \sum_{a,b>a} \langle 1/r^3 \rangle_{ab} P^{ab}[2f_{1\mu}(p_{a,b}) + 1] \tag{27}$$

where the various terms are defined in ref 12. A four-electron structure of importance in discussing delocalization in the halomethanes is given in Figure 5. The coefficients C_1 and C_μ for this four-electron system have been

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[33] L. S. Bartell, *Tetrahedron*, 17, 177 (1962).

given[12] as follows.

$$C_1 \cong 1 \tag{28}$$

$$C_\mu = \frac{K_{ab} + K_{vw} - K_{av} - K_{bw}}{2(K_{aw} + K_{bv})} \tag{29}$$

When w and v are both hydrogens, the negative H–H integral K_{vw} is of comparable magnitude with the positive Hund exchange integral, K_{ab}, and thus these two terms tend to cancel one another, thereby increasing the importance of the smaller K_{av} and K_{bw} integrals. Substitution of a halogen for a hydrogen might be expected to decrease the negative K_{vw} integral relative to the methylene case as the halogen σ-bond orbital has more directional characteristics than does the 1s hydrogen orbital. As the denominator in eq 29 is a negative quantity the effect of this change in K_{vw} with halogen substitution is to make C_μ more negative. This will result in an upfield shift as indicated by eq 27 as all other terms $[f_{1\mu}(p_{ab}) = +1, P^{ab} = +{}^1/_2]$ are positive quantities. If both v and w are halogens, even greater parallel spin correlation might be expected for the same reasons given above. The effect of altering electron spin pairing in this manner can be expected to result in an even greater upfield shift. Experimentally, this is the trend which is observed. The unavailability of values for the pertinent exchange integrals prevents, for the present, a quantitative calculation of the magnitude of this effect, but shifts of several parts per million were calculated in the alkanes[12] and the effects may be even greater in the halomethanes.

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Iodo- and Fluoropentaboranes. Nuclear Magnetic Resonance Comparison of 2-Pentaborane(9) Derivatives[1]

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Abstract: Pentaborane(9) derivatives of the type 1-XB_5H_8 are more stable when X = heavier halogen, whereas 2-XB_5H_8 compounds are more stable when X = lighter halogen. The reason may be found in the different π-type interactions with the B_5 cage, and similar ideas explain some otherwise anomalous ^{11}B nmr chemical shifts. The catalytic isomerization of 1-IB_5H_8 to the far less stable new isomer 2-IB_5H_8 (mp −39°; bp 167° est) requires steady removal of this more volatile product. It is argued that halogen exchanges on the B_5 skeleton are done best by gas-flow processes at minimal pressure, as when $HgCl_2$ converts 1-IB_5H_8 to 1-ClB_5H_8 or SbF_3 converts 2-IB_5H_8 to the new 2-FB_5H_8 (mp −63°; bp 71° est). However, the analogous synthesis of 1-FB_5H_8 gave a product too unstable to be isolated. The ^{11}B nmr comparisons include all four of the 2-halogenated pentaboranes and 2-CH_3-B_5H_8, and accurate vapor-phase infrared spectra are reported for the five known XB_5H_8 compounds not previously so recorded.

Pentaborane derivatives of formula-type RB_5H_8 so far have been limited to R = hydrocarbon or halogen other than F. They usually are formed by substitution at the 1 (pyramid-peak) position, by methods suggestive of proton replacement by other positive ions (*e.g.*, CH_3^+ or X^+); then a catalytic skeletal rearrangement may lead to the 2-RB_5H_8 isomer. Replacement of one R by another apparently has been done only with halogens, often with yields far short of 100%.

The difficulty of such replacement may relate to the character of the pentaborane skeleton. The boron sites can be invaded only by strong bases, which tend to remove BH_3 groups[2] rather than displace hydride or halide. If X^+ were removed by some means, the remaining lone-pair electrons on boron would have strong-base character leading to extensive reaction with other pentaborane units. Or, if X^- were taken off, the opened boron site would have almost a hemisphere empty of electrons, with only strong Lewis-acid reactivity to relieve the strain; then an attack upon the XB_5H_8 substrate would be likely.

By the latter argument, replacement of halide in XB_5H_8 should be most effective if a strong halide-exchange reagent were employed at pressures so low as to make XB_5H_8 only very poorly available to the $B_5H_8^+$ unit remaining after removal of halide. Otherwise, the reaction of $B_5H_8^+$ with XB_5H_8 must lead to a variety of polyboranes and resinous products.

In agreement with this hypothesis, a 105° sealed-tube reaction of 1-IB_5H_8 with $HgCl_2$ gave only a 7% yield of 1-ClB_5H_8 (with other volatiles and resins), whereas the same reactants in a 100° flow process at minimal pressure gave a 58% yield of 1-ClB_5H_8.

A similar low-pressure flow process was applied to the new isomer 2-IB_5H_8 with SbF_3, giving a 40% yield of the

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[1] It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the U. S. Government. I am deeply grateful also to my colleague Dr. K. L. Servis for instruction and assistance in the use of the Varian HA-100 instrument, and to Dr. R. E. Williams of Space-General Corp., for full access to his experience with boron nmr spectra and the loan of a 32.1-Mc radiofrequency unit and probe.

[2] A. B. Burg, *J. Am. Chem. Soc.*, 79, 2129 (1957).