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Alkenylboranes. II. Improved Preparative Methods and New Observations on Methylvinylboranes[1]

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Reaction of chlorovinylboranes with dimethyl zinc gave the methylvinylboranes and trivinylborane. A disproportionation reaction gave chloromethylvinylborane. Ultraviolet and nuclear magnetic resonance (n.m.r.) spectra were observed. An approximate linear combination of atomic orbitals–molecular orbital (l.c.a.o.–m.o.) computation was used as a model to correlate the postulated delocalization with some of the physical properties.

Introduction

The original method for obtaining the methylvinylboranes gave low yields and many side reaction products[2a,b] which interfered seriously with purification even by gas liquid chromatography (g.l.c.), methods. This paper describes a better preparative method employing chlorovinylboranes[3] and dimethyl zinc, which gives good yields of rather pure products. Using the larger amounts of substances thus made available, revised values of physical constants have been obtained. An extensive spectroscopic survey has been made to obtain data on infrared, ultraviolet, mass and n.m.r. spectra,[4] and an approximate l.c.a.o.–m.o. correlation has been made between some of these properties and the C–B π-bonding.

Experimental

The manipulative methods were those in general use for work in high vacuum.[5]

Ultraviolet spectra were measured on a Cary Model 14 recording spectrophotometer. All samples were vapor in 1 cm. cells at a low pressure obtained by expansion of gas. The data obtained for some alkenylboranes are given in Table I.

Table I

Ultraviolet Spectra of Some Alkenylboranes

Substance	λ_{max}, mμ Obsd.	λ_{max}, mμ Calcd.	$\epsilon_{max} \times 10^{-4}$	Relative intensity Obsd.	Relative intensity Calcd.
$(C_2H_3)_3B$	234	238	1.90	1.2	1.3
$(C_2H_3)_2BCH_3$	220	225	1.33	1.0	1.0
$C_2H_3B(CH_3)_2$	196	192	0.98	0.4	0.7
$(C_2H_3)_2BCl$	222		1.67		
$C_2H_3B(CH_3)Cl$	206		1.07		
$(C_2H_3)_4Sn$	<187				

Proton nuclear magnetic resonance spectra were determined on a Varian model 4311 high resolution n.m.r. spectrometer operating at 60 megacycles. The compounds were observed in 5% carbon tetrachloride solution containing either 2% tetramethylsilane or cyclohexane as the internal standard. The sample tubes were prepared on the vacuum apparatus, and they were stored in liquid nitrogen to prevent decomposition. The values for chemical shift recorded in Table II are relative to tetramethylsilane as the standard.

Table II

N.m.r. Spectra of Vinylboranes and Comparison Substances

Substance	Chemical shift, δ^a H^1	Chemical shift, δ^a B^{11}
$(C_2H_3)_3B$	−6.55 (m8) Vi^b	−55.2^c
$(C_2H_3)_2BCH_3$	−6.48 (m14) Vi, 10.9 cm.^{2} −0.86 (s) Me, 5.3 cm.^{2}	−64.4^c
$C_2H_3B(CH_3)_2$	−6.35 (mb8) Vi 2.9 cm.^{2} −0.82 (s) Me, 5.9 cm.^{2}	−74.5^c
$(C_2H_3)_2BCl$	−6.52 (mb3) Vi	−54.8^c
$C_2H_3BCl_2$	−6.51 (b) Vi	−52.4^c
$(CH_3)_3B$	−0.79 (s) Me	−85 ± 1^d
$(C_2H_5)_3B$	−1.09 (m5) Et	−85 ± 1^d
$(C_2H_3)_4Sn$	−6.20 (m13) Vi	
$B(C_6H_5)_3$		−60.2 ± 4.0^c
$C_6H_5BCl_2$		−54.1^e
BCl_3		−45.6^e
BBr_3		−40.1^f
$B(OC_2H_5)Cl_2$		−32.5^f
$B[N(C_2H_5)_2]_3$		−31.1^e
$C_6H_5B(OC_2H_5)_2$		−28.6^e
$HB(OCH_3)_2$		−26.1^f
$B(OC_2H_5)_2Cl$		−23.3 ± 1.0^f
$B(OH)_3$ (aq.)		−18.8 ± 1.0^f
$B(OCH_3)_3$, $B(OC_2H_5)_3$		−18.1^f
$B(O\text{–}n\text{-}C_3H_7)_3$		−17.7^e
$B(OCH_2CH{=}CH_2)_3$		−17.5^f
BF_3 (*g*)		− 9.4 ± 1.0^f

[a] P.p.m., relative to tetramethylsilane for H^1 and to boronfluoride etherate for B^{11}. [b] Read (*m* 8) as multiplet of 8 peaks; (s) singlet; (b) broad, Vi, Me, group characteristic of chemical shift; values in cm.^{2} are areas under bands. [c] Ref. 6. [d] Private communication, see ref. 6. [e] W. D. Phillips, H. C. Miller and H. C. Muetterties, *J. Am. Chem. Soc.*, 81, 4496 (1959). [f] I. Shapiro and J. F. Ditter, *J. Chem. Phys.*, 26, 799 (1957).

The B^{11} nuclear magnetic resonance spectra were determined on a Varian V-4300 high resolution NMR spectrometer[6] operated at 12.3 megacycles. Using the vacuum apparatus the samples were loaded neat into short 3 mm. diameter tubes. For centering in the spectrometer they were placed inside 5 mm. tubes. The measurements were made without an internal reference substance using an operating procedure described previously.[7] The values in Table II are those relative to the B^{11} resonance of boron trifluoride diethyletherate.

Preparations of the following substances were made in accordance with previously published directions: divinyl mercury,[8] tetravinyl tin,[9a,b] dimethylzinc and diethylzinc,[10]

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contracts No. AF18(600)-1541 and AF49(638)-937. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] (a) T. D. Parsons and D. M. Ritter, *J. Am. Chem. Soc.*, **76**, 1710 (1954). (b) T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

[3] F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

[4] Physical properties and data on infrared and mass spectra are reported in *J. Chem Eng. Data*, **7**, in press (1962).

[5] As developed by Alfred Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, New York, 1933, and by H. I. Schlesinger and his co-workers, described by R. T. Sanderson "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948,

[6] The determinations were made by Dr. R. E. Williams of the National Engineering Science Corp., Pasadena, California, an assistance for which the authors extend their thanks.

[7] T. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[8] B. Bartocha and F. G. A. Stone, *Z. Naturforsch.*, **13b**, 347 (1958).

difluorovinylborane,[3] chlorodivinylborane and dichlorovinylborane.[3]

Methylvinylboranes and trivinylborane were prepared by reaction between dimethylzinc and the chlorovinylboranes. In one experiment chlorodivinylborane, 1.38 mmole, and dimethylzinc, 0.60 mmole, were condensed in a 500 ml. vessel, and the mixture was warmed to room temperature. A white solid formed at the site of the reactants, which in about 1 minute decomposed depositing a grey-white solid over the entire vessel. The volatile products were separated on g.l.c. column B[4], and there was obtained chlorodivinylborane, 0.48 mmole; trimethylborane, 0.06 mmole; dimethylvinylborane, 0.27 mmole; methyldivinylborane, 0.32 mmole; and trivinylborane, 0.11 mmole, a yield of 85% based on the chlorodivinylborane consumed. Smaller proportions of dimethylzinc gave lower yields. From 0.87 mmole dichlorovinylborane and 0.83 mmole dimethylzinc there was obtained 0.03 mmole recovered dichlorovinylborane, 0.19 mmole trimethylborane, 0.48 mmole dimethylvinylborane, 0.04 mmole methyldivinylborane, but no trivinylborane, an over-all yield of 83%. Each of the products was identified or characterized by its g.l.c. properties, its physical properties, infrared spectrum and n.m.r. spectrum.

Chloromethylvinylborane was prepared from a mixture of boron trichloride, 0.082 mmole; and methyldivinylborane 0.305 mmole; permitted to stand for 1 hr. at 25° in a 500 ml. volume. From this was obtained chloromethylvinylborane, 0.015 mmole and recovered methyldivinylborane, 0.280 mmole, a product yield of 5%. A mixture originally containing trimethylborane, 0.205 mmole; dimethylvinylborane, 0.414 mmole; trivinylborane, 0.134 mmole; and chlorodivinylborane, 0.289 mmole stood for two months at 25° in a 150 ml. storage flask. The mixture then contained chloromethylvinylborane, 0.046 mmole; trimethylborane, 0.131 mmole; dimethylvinylborane, 0.288 mmole; methyldivinylborane, 0.125 mmole; trivinylborane, 0.196 mmole; chlorodivinylborane, 0.074 mmole; chlorodimethylborane, 0.037 mmole; and dichloromethylborane, 0.043 mmole.

An attempt to prepare the ethylvinylboranes from 0.57 mmole chlorodivinylborane and 0.24 mmole diethylzinc gave a recovery of 0.19 mmole unreacted chlorodivinylborane and 0.07 mmole each of triethylborane and trivinylborane. An attempt to prepare methylvinylboranes from difluorovinylborane, 5.0 mmole, and dimethylzinc, 7.9 mmole, gave after 20 hr. a mixture of ethylene, trimethylborane, unreacted difluorovinylborane and a trace of material having the same g.l.c. retention volume as dimethylvinylborane.

Amine adducts were formed between trivinylborane and ammonia or trimethylamine. Trivinylborane, 0.106 mmole was condensed at −196° with ammonia, 0.114 mmole. A white solid formed, stable at room temperature, from which there was distilled at −80° 0.009 mmole of unreacted ammonia, identified by its vapor pressure in comparison with an ammonia vapor pressure thermometer. Similarly trivinylborane, 0.158 mmole, reacted with trimethylamine, 0.222 mmole, yielding 0.055 mmole trimethylamine recovered, identified by its vapor pressure 6.5 mm. at −78°. Both the adducts were slowly volatile but the vapor pressures were less than 0.1–0.3 mm. at 25°. When the ammonia adduct, 0.106 mmole, was treated with 0.133 mmole of dry hydrogen chloride at room temperature a dark glass-like solid formed. The volatile products contained 0.044 mmole % unreacted hydrogen chloride, 0.007 mmole of trivinylborane, each identified by its infrared spectrum, and a small quantity of unknown material. This represented a 6.9% recovery of trivinylborane from the original adduct.

To test the acidity of trivinylborane a reaction was carried out between that substance and the adduct prepared from 0.189 mmole of trimethylborane and 0.209 mmole of trimethylamine, from which 0.02 mmole of trimethylamine was recovered. This was treated with 0.099 mmole of trivinylborane and the mixture was heated at 60° briefly. There was recovered from the reaction 0.098 mmole % trimethylborane. Treatment of the solid with boron trichloride, 0.413 mmole, gave 0.048 mmole of trivinylborane.

Interconversion reactions of the methylvinylboranes were observed by maintaining the substances under appropriate conditions for various time intervals after which the mixtures were separated, and the components were identified by means of their g.l.c. properties. The information pertinent to the experiments is given in Table III.

TABLE III

INTERCONVERSION OF THE METHYLVINYLBORANES

Reactants, mmole		Time, hr.	Substances, recovered, mmole			
			B-$(CH_3)_3$	$(CH_3)_2$-BC_2H_3	CH_3B-$(C_2H_3)_2$	B-$(C_2H_3)_2$
$(CH_3)_2BC_2H_3$						
0.81		6[a]	0.02	0.78	0.02	...
0.78		361[a]	.10	.55	.06	0.002
$CH_3B(C_2H_3)_2$						
0.42		5[a]	...	.02	.38	.02
.89		90[a]	...	.04	.80	.04
.80		1[b]	...	...	.80	...
.80		85[b]	.006	.05	.63	.02
.80		102[b]	.005	.06	.61	.04
$B(CH_3)_3 + B(C_2H_3)_3$						
0.19	0.13	90[a]	[c]	.005	.004	.07
.19	.13	467[a]	[c]	.006	.005	.05
.19	.13	1.25[b]	[c]	.007	.004	.03

[a] 25°. [b] 100°. [c] Not determined.

Results and Discussion

The preparative methods which have served to give the methylvinylboranes and trivinylborane in improved yields are extensions of the well known reaction between the zinc alkyls and the boron halides and the disproportionation reactions of the haloalkylboranes. The chlorides were used in these reactions; presumably the bromides would work also, but the fluorides seemed not to give the desired products; thus with dimethylzinc the product was trimethylborane; a great deal of polymerization occurred, and no vinylmethylborane was obtained. Similarly diethylzinc failed to give ethylvinylboranes even with the chlorovinylboranes; instead the small amount of trivinylborane and triethylborane was that which would be expected from a complete disproportionation of whatever products escaped polymerization.

From mixtures of methylvinylboranes and chlorovinylboranes there was obtained the mixed derivative chloromethylvinylborane, together with trivinylborane, leading to the conclusion that in this case not only did methyl groups and chlorine atoms exchange as might be expected, but also there was a migration of vinyl groups from one boron atom to another, a result different from that observed with the halovinylboranes alone.[11] Apparently the methyl and halogen substituents exerted a synergistic influence upon the exchange.

When the idea of delocalization was originally suggested as a feature of bonding in vinylboranes,[2a] the effect on Lewis acid strength and stability were cited as key properties for evaluating the proposal. To these can be added the data from optical and n.m.r. spectroscopy. All can be summarized within the conceptual scheme provided by molecular orbital theory.[12] Accordingly an l.c.a.o–

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(9) (a) D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957). (b) A sample was also supplied by Metal and Thermit Corp.

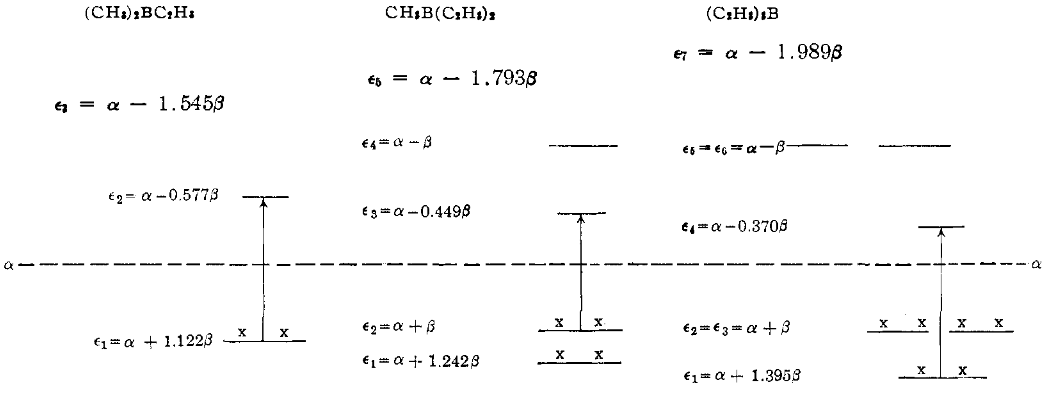
(10) C. R. Noller, *J. Am. Chem. Soc.*, **51**, 594 (1929).

(11) F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6235 (1960).

(12) The authors acknowledge the assistance of Dr. G. R. Seely, present address: Shell Development Co., who earlier solved a tentative secular equation for a vinylborane model.

TABLE IV

RELATIVE π-ORBITAL ENERGIES



Molecular orbital coefficients

$(CH_3)_2BC_2H_3$

$$\varphi_1 = 0.646\psi_1 + 0.725\psi_2 + 0.239\psi_3$$
$$\varphi_2 = 0.668\psi_1 - 0.385\psi_2 - 0.638\psi_3$$

$CH_3B(C_2H_3)_2$

$$\varphi_1 = 0.419(\psi_1 + \psi_5) + 0.325\psi_3 + 0.521(\psi_2 + \psi_4)$$
$$\varphi_2 = .500(\psi_1 + \psi_2 - \psi_4 - \psi_5)$$
$$\varphi_3 = .519(\psi_1 - \psi_5) - 0.593\psi_3 - 0.233(\psi_2 + \psi_4)$$

$(C_2H_3)_3B$

$$\varphi_1 = 0.316(\psi_1 + \psi_5 + \psi_7) + 0.383\psi_3 + 0.430(\psi_2 + \psi_4 + \psi_6)$$
$$\varphi_2 = .289(\psi_1 + \psi_2 + \psi_4 + \psi_5) - 0.577(\psi_6 + \psi_7)$$
$$\varphi_3 = .500(\psi_1 + \psi_2 - \psi_4 - \psi_5)$$
$$\varphi_4 = .450(\psi_1 + \psi_5 + \psi_7) - 0.555\psi_3 - 0.167(\psi_2 + \psi_4 + \psi_6)$$

m.o. computation was made using the approximation developed by Pauling and Wheland[13] in which $\alpha_{C_1} = \alpha_{C_2}$ and $\alpha_B = \alpha_C - \beta_{C-C}$. The exchange integrals were fixed at $\beta_{B-C} = 0.7\ \beta_{C-C}$. This was equivalent to setting $\zeta = -1$ and $\eta = 0.7$ in the Pauling and Wheland treatment, which involved reassigning electronegativity values 0.2 unit higher for carbon and lower for boron than the values for those elements in their standard valence states. Considering that the hybridization of carbon is sp^2 and the boron is postulated to have hybridization somewhere between sp^2 and sp^3 in the vinylboranes, this is perhaps a justifiable assumption.[14] This relationship of β values is the one found to apply in a similar computation on the vinylboronic esters.[15] Overlap integrals were set equal to zero, and hyperconjugation was assumed to be absent. In Table IV are given the solutions to the secular equations as the relative π-orbital energies in terms of α and the coefficients of β, with the molecular orbital coefficients for the ground state and the first excited state for trivinylborane and each of the methylvinylboranes. In Table V are recorded the quantities calculated from the molecular orbital coefficients. The π-electron densities at the various atoms and the total bond orders are those for a model in which the postulated delocalization of electron density into the p_z orbital of the boron atom has occurred. The various resonance stabilization energies show that the effect is one of modest degree, the smallness arising doubtless from the hetero-atom character of the boron atom, since in the isoelectronic vinyl carbonium ions the resonance energies are 16.2, 27.0 and 35.2 kcal./mole.[16] The closeness with which the model describes the physical properties of the vinylboranes can be judged by comparing the observed and calculated absorption maxima and intensities for the ultraviolet spectra, the principal bands of which probably represent the π-π^* transitions depicted in Table IV. Though the fit is doubtless fortuitous, it does generate confidence that the delocalization phenomenon exists

TABLE V

QUANTITIES DERIVED FROM M.O. COEFFICIENTS

Compound	R.e.[a]	π-Electron density			Total bond order	
		C(1)	C(2)	B	C(1)–C(2)	C(2)–B
$(CH_3)_2BC_2H_3$	0.24	0.84	1.05	0.11	1.94	1.35
$CH_3B(C_2H_3)_2$	.48	.85	1.04	.21	1.94	1.34
$(C_2H_3)_3B$	.72	.87	1.04	.29	1.94	1.33

[a] Resonance stabilization energy in units of β. If β is 16.5 kcal., r. e. = 4.0, 8.0, 11.8 kcal./mole for the respective methylvinylboranes.

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(13) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chapt. 4.

(14) C. A. Coulson, "Valence," Oxford Univ. Press, London, 1952, p. 207.

(15) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

(16) Y. K. Syrkin and M. E. Diatkina, *Acta Physico. Chim. U.S.S.R.*, XXI, No. 4, p. 5 (1946).

and that the molecular orbital computation can be used to correlate other properties. Thus, from the C—C bond order 1.94, close to that in 1,3-butadiene, application of Gordy's rule[17] should give a stretching frequency close to 1597 cm.$^{-1}$ observed for that substance. The C—C stretching frequencies observed[4] for the methylvinylboranes and trivinylborane were 1603, 1605, 1605 cm.$^{-1}$, not far from the predicted value. In the absence of dependable assignments, no such correlation can be made for the C–B stretching frequencies.

Consider also the acidity of trivinylborane, which toward amines is greater than that of trimethylborane and less than that of boron trichloride. The acid strength of a borane, as judged by the heat of formation of its adduct with a base, has been shown clearly to be divisable into two parts, a σ part responsive to electronegativity and a π part responsive to delocalization. The relative acid strengths of a series of similarly substituted boranes toward a particular base becomes the resultant of the two contributing factors as has been amply demonstrated for the boron trihalides.[18] To apply this reasoning to the vinylboranes, there needs to be considered that among the organic groups the vinyl group is more electronegative than the saturated alkyl groups.[19] In contrast the resonance stabilization energy is relatively low, making it not difficult to understand how trivinylborane can stand relatively higher in the acidity scale than do the alkyl boranes.

Slowness of disproportionation is one of the remarkable properties of the methylvinylboranes. Only the very roughly determined data in Table V are available for estimation of a rate, but from these an approximate activation energy can be calculated using the collision theory of bimolecular reactions. Assuming a collision diameter of 3 Å., the value calculated for dimethylvinylborane was 7 kcal. This value can be considered to consist of the resonance stabilization energy of $\sim$4 kcal. and $\sim$0.5 kcal. required for conversion from sp^2 to sp^3 hybridization in the transition state. From comparison with the rapid rates of disproportion found for dimethylethylborane[2b] the activation energy for bridge formation in the transition state can be considered negligible. Considering how approximate is each calculation the agreement is fair.

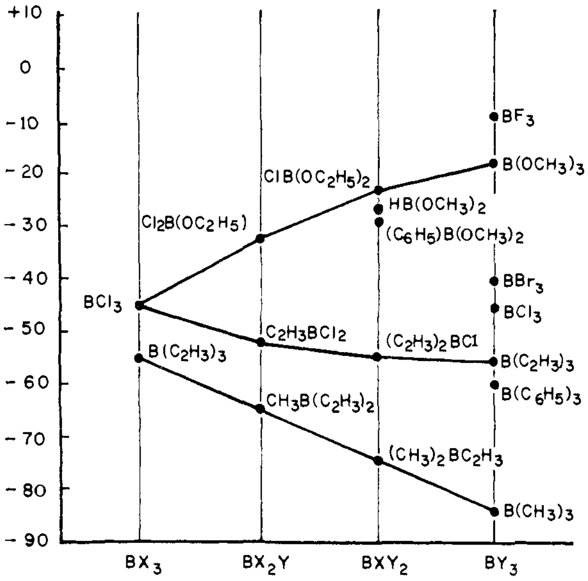

Fig. 1.

Though the magnetic shielding which gives rise to the chemical shift in n.m.r. spectra stems from electric currents induced by the external magnetic field, the current strength and therefore the shielding appear to be approximately proportional to the electron density around the shielded nucleus. Thus a correlation has been made between proton chemical shifts and electronegativity of neighbouring atoms,[20] and the C^{13} chemical shifts in C^{13}—X bonds have been found linearly related to the electronegativities of X.[21] The boron halides, as seen in Table II and in Fig. 1, show an opposite ordering reminiscent of that for relative acid strength, and similarly, π-donation has been invoked to qualitatively explain the sequence.[7] Applying this analogy to the B^{11} chemical shifts in the ternary boranes, there can be written

$$\delta = \delta_\sigma + \delta_\pi \qquad (1)$$

where δ_σ should be a function of the electronegativity belonging to the substituent atom or group, and δ_π should represent an increment in shielding arising from delocalization, proportional to π-electron density on the boron atom, and to resonance stabilization energy.

A linear relation between δ_σ and electronegativity is known,[20] and chemical shift values for two purely σ-bonded compounds are required to permit calculation of the two constants in the equation.[22] Ternary boron compounds free from π-bonding are limited to the alkyl boranes and the inaccessible borane, BH_3. For the latter an estimate can be made of the B^{11} chemical shift by reference to those of some related compounds. Fig. 1 shows the relation of B^{11} chemical shifts for compounds BX_nY_{3-n}, where it is seen that for compounds containing strong π-donor groups the relation is not linear, but when the substituents are weak π-donors linearity is approached. This makes uncertain an effort to estimate δ_σ for BH_3 by extrapolation of the series $B(OCH_3)_3$, $BH(OCH_3)_2$, BH_3. Interpolation may be more reliable using the series: (a) $CH_3OB(OCH_3)_2$, (b) $ClB(OCH_3)_2$, (c) $HB(OCH_3)_2$, (d) $C_6H_5B(OCH_3)_2$, in comparison with the series: $B(OCH_3)_3$, BCl_3, $B(C_6H_5)_3$. The vertical scale in Fig. 1 corresponding to the first

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[17] W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

[18] F. A. Cotton and J. R. Leto, *ibid.*, **30**, 993 (1959).

[19] The relative electronegativity of the vinyl group can be estimated by use of the polar substituent function σ^*, *cf.* R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, New York, N. Y., 1956, pp. 618, 619. If the principle of vinylogy is invoked, it can be seen that in compounds R—CH=CH—X the effect of interposing a vinyl group between phenyl, hydrogen or methyl and the function X will be to compress the σ^* scale without changing the relative ordering. Interpolation of the compressed scale gives $\sigma^* = 0.400$ for the vinyl group.

[20] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

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

[22] For more detailed discussion see C. D. Good, Thesis, Univ. of Washington, 1961.

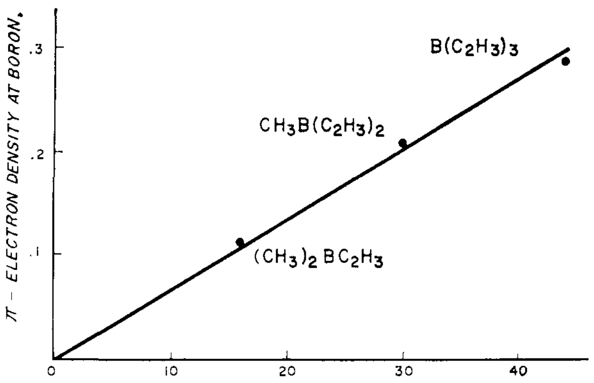

Fig. 2.

Table VI

Calculated B^{11} Chemical Shifts

Compound	X^a	Chemical shifts, p.p.m. $\delta\sigma^b$	δ, obsd.	$\delta\pi$
BF_3	3.90	−183	− 9.4	174
$B(OR)_3$	3.5	−155	−18.1	137
BCl_3	3.15	−131	−45.6	85
$B(NR_2)_3$	3.05	−124	−31.1	93
BBr_3	2.95	−117	−40.1	77
$B(C_6H_5)_3$	2.70	− 99	−60.2	39
$B(C_2H_3)_3$	2.70	−99	−55.2	44
$B(C_2H_3)_2CH_3$	2.63[c]	−94	−64.4	30
$B(CH_3)_2C_2H_3$	2.57[c]	−90	−74.5	16
$B(CH_3)_3$	2.50	−85	−85	0

[a] X electronegativity of atoms bonded directly to boron. [b] Calculated from the equation $\delta_\sigma = 90 - 70X$. [c] Average of three X value

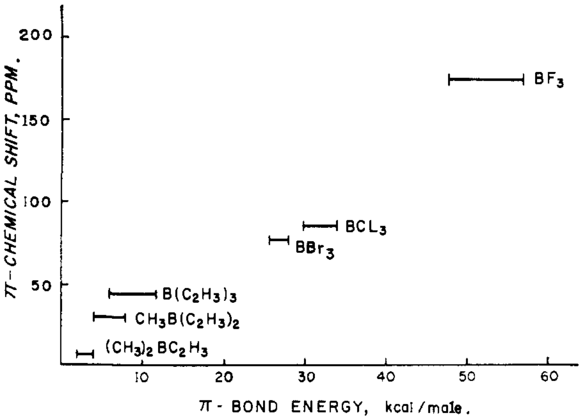

Fig. 3.

series is compressed compared with the second, which will lead to inaccuracy as will the fact that the two scales deviate somewhat from linear proportionality. Interpolating b, c, d gives $\delta_{BH_3} = -53.3$ and a, b, c gives $\delta_{BH_3} = -60.4$. If the average value −57 is adopted, the δ values in Table VI are found.

This empirical method of accounting quantitatively for the ordering of B^{11} chemical shifts for ternary boron compounds is found to have the expected correlation with the molecular orbital model. In Fig. 2 is shown the graphical relationship between the π-chemical shifts and the π-electron densities on the boron atom for the vinylboranes, and in Fig. 3 is shown the relation to the resonance stabilization energies for these substances and in addition for the boron halides. The cord spans represent the estimated uncertainty in the π-bond energies for the vinylboranes arising from uncertainty in the value for β, and for the boron halides the lower value on the cord span for each substance is the one calculated for sp hybridization of the halogen atoms, and the higher value is for pure p-bonding.[18]