References and Notes

(1) This work is the 11th publication in the series "Nmr Studies of Heterocyclic Compounds." For previous papers in this series, see ref 50. The part of this research done at the California Institute of Technology was supported by the National Science Foundation.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Tetraalkylammonium Tetraalkylborides

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Received August 24, 1973

Chemical shifts in carbon-13 nuclear magnetic resonance spectra of tetraalkylammonium ions, tetraalkylboride ions, and trialkylboranes correlate linearly with calculated chemical shifts of the corresponding isoelectronic hydrocarbons. Additive substituent effects on chemical shifts for charged and neutral nitrogen and charged and neutral boron also are reported. Aromatic solvent induced shifts of tetraalkylammonium tetraalkylborides in parts per million are smaller in carbon-13 nmr spectra than in proton nmr spectra.

As part of a broad investigation of the properties of tetraalkylammonium tetraalkylborides we have obtained carbon-13 nmr spectra of some tetraalkylammonium halides and tetraalkylborides, as well as some trialkylboranes. Because the effects of substituents on carbon-13 chemical shifts are largely additive,[1,2] it is usually possible to predict new ^{13}C nmr spectra from previous spectra of similar compounds. In this paper we report correlations of ^{13}C chemical shifts which may be used to predict chemical shifts of tetraalkylammonium ions, tetraalkylboride ions, and trialkylboranes. An extensive correlation of primary, secondary, and tertiary amine ^{13}C chemical shifts is already available.[3]

Experimental Section

Tetraethylammonium iodide (Eastman) was dried at 50° for 5 hr at 10^{-5} Torr. Other tetraalkylammonium salts and trialkylboranes were obtained and purified as described elsewhere.[4]

Carbon-13 nmr spectra were obtained at 25.2 MHz with a Varian XL-100 spectrometer equipped with 15-in. magnet and Digilab Model FTS-NMR-3 Fourier transform accessory and controlled by a Nova 1200 computer. Fourier transforms of 100–800 transients used 16K data points for completely proton decoupled spectra and 32K data points for off-resonance decoupled spectra. Solutions of 2.6–22.6 mol % tetraalkylammonium salt or 41–53 mol % trialkylborane in $CDCl_3$ or C_6D_6 were used at 35°. Deuterium in the solvent served as the lock signal, and TMS was used as an internal reference.

Results and Discussion

Chemical Shifts. Carbon-13 chemical shifts of tetraalkylammonium salts and trialkylboranes are in Tables I and II. Assignments of the individual carbon resonances in tetraalkylammonium halides were made by correlation of the data for the six cations in Table I with previously reported substituent parameters for hydrocarbons. Assignments for the tetraalkylborides were made by the same method after the tetraalkylammonium ion chemical shifts were established. Off-resonance decoupled spectra were employed to resolve a few otherwise ambiguous assignments.

There are two discrepancies between our assignments and literature data. The chemical shifts of tri-*n*-propylborane reported by Weigert and Roberts[5] are in error. They[5] concur with our assignments which are based on the width of the C_α resonance from coupling to boron and an off-resonance decoupled spectrum which distinguishes C_β from C_γ. For trimethyl-*n*-hexylammonium bromide ($N_{1116}Br$)[6] our assignments of C_β and C_γ in the *n*-hexyl group reverse the assignments of Cordes and coworkers.[7] Otherwise their chemical shifts in water and ours in $CDCl_3$ agree well. Their assignments are based on the principle that the ^{13}C spin-lattice relaxation time (T_1) for C_β should be less than T_1 for C_γ, but their measured values of T_1 for the two carbon atoms in question are within experimental error of one another. Our assignment is based on the fit of experimental data to chemical-shift correlations. Use of their assignments with our data results in much larger standard deviations in linear chemical-shift correlations and additive substituent parameters reported later in this paper. Consequently, we believe that the C_β and C_γ assignments of all three trimethyl-*n*-alkylammonium bromides reported by Cordes and coworkers[7] should be reversed.

Spectra of two samples of $N_{1116}B_{1116}$ in $CDCl_3$ which differ in concentration by a factor of 4.7 are nearly identical; all chemical shifts agree within 0.2 ppm. Most chemical shifts of our tetraalkylammonium ions are essentially independent of the counterion except for the two C_α resonances of N_{1116}, which appear at higher field with the smaller Br^- counterion than with the larger B_{1116}, and the C_β resonance in the ethyl group of N_{2226}, which appears at lower field with Br^- than with B_{2226}.

Aromatic Solvent Induced Shifts. The proton resonances of tetraalkylammonium and tetraalkylboride ions experience large aromatic solvent induced shifts (ASIS), defined as the difference in chemical shifts of a given nucleus X relative to an internal standard in benzene and in $CDCl_3$ (eq 1). A comparison of carbon-13 and proton ASIS

$$\text{ASIS} = \delta_X(\text{CDCl}_3) - \delta_X(\text{C}_6\text{H}_6) \qquad (1)$$

values for 20 mol % solutions of tetraalkylammonium tetraalkylborides is in Table III. For CH_2 groups attached to charged nitrogen or boron, ASIS values are consistently larger in proton spectra than in carbon-13 spectra. Carbon chemical shifts in general are no more sensitive to solvent diamagnetic anisotropy than are proton chemical shifts, although sensitivities of both nuclei depend on their site factors.[8] Carbon chemical shifts are also insensitive to intramolecular diamagnetic anisotropies.[9]

Coupling Constants. The α-carbon resonances of all tetraalkylammonium ions in Table I exhibit coupling to ^{14}N of J_{CN} = 2.0–4.5 Hz. In some spectra no discrete 1:1:1 triplets appear, but the α-carbon resonances are 6–8 Hz wide at half-height. Similar J_{CN} values in tetraalkylammonium ions have been observed before.[5,7]

All of the α- and γ-carbon resonances of the tetraalkylboride ions in Table I appear as 1:1:1:1 quartets because of coupling to ^{11}B with $J(C_\alpha B)$ = 39.7–40.8 and $J(C_\gamma B)$ = 3.6–4.2 Hz. One and three bond C–B couplings of comparable sizes were reported earlier for tetraphenylboride ion[10] and 1-methylpentaborane (9);[11] two and four bond C–B couplings were reported also for tetraphenylboride ion.[10b] The α-carbon resonances of the trialkylboranes in Table II are all very broad (41–96 Hz at half height) as reported previously,[5] presumably because of the large B–C coupling which is incompletely relaxed by the quadrupole mechanism.

Chemical-Shift Correlations and Substituent Parameters. We have employed two independent methods to correlate the data in Tables I and II. The first, or linear correlation, method was used earlier to correlate chemical-shift data for aliphatic alcohols[12] and aliphatic amines.[3] It assumes that the chemical shifts of carbon atoms in tetraalkylammonium and tetraalkylboride ions are linearly related to the chemical shifts of the corresponding carbon atoms in isoelectronic hydrocarbons in which N^+ or B^- is replaced by C. An analogous replacement of B by CH designates the isoelectronic hydrocarbon for trialkylboranes. For example, the hydrocarbon isoelectronic with tetraethylammonium ion is 3,3-diethylpentane, and the hydrocarbon isoelectronic with tri-*n*-propylborane is 4-propylheptane. Since the ^{13}C nmr spectra of most of these branched hydrocarbons are unknown, we have calculated their chemical shifts by the method of Lindeman and Adams.[13] Results of these correlations are in Table IV. Use of all the data in Table I to construct Table IV results in smaller standard deviations of observed chemical shifts from calculated chemical shifts than would be obtained if each ion were included in the correlation only once. However, each line of data in Table I represents a unique experiment which differs from all the others in structure, counterion, solvent, or concentration. Table IV and the Lindeman and Adams[13] parameters may be used to calculate chemical shifts of other tetraalkylammonium ions, tetraalkylboride ions, and trialkylboranes with reasonable accuracy.

Our second, or additive substituent parameter, method of correlating the data in Tables I and II uses parameters similar to those reported earlier by Grant and Paul.[14] It assumes that the various effects of functional groups and branching are additive, as described by eq 2, in which

$$\delta_C{}^X(k) = \delta_C(k) + \sum_l A_l n_{kl} + \sum B + S \qquad (2)$$

$\delta_C{}^X(k)$ is the ^{13}C chemical shift of the kth carbon of species X (tetraalkylammonium ion, tetraalkylboride ion, or trialkylborane), $\delta_C(k)$ is the ^{13}C chemical shift of the kth carbon of the *n*-alkane corresponding to the longest carbon chain in species X, n_{kl} is the number of branching carbon atoms in the lth position relative to the kth carbon, A_l is the additive chemical shift parameter assigned to the lth carbon atom, B is a branching correction term for the kth carbon, and S is a substituent parameter term. Additive chemical shift parameters, A_l, were reported by Grant and Paul[14] as α +9.1, β +9.4, γ −2.5, δ +0.3, and ϵ +0.1, but their limited data on branching corrections, B, was inadequate for our purposes. Consequently, we com-

Table I
Carbon-13 Chemical Shifts of Tetraalkylammonium and Tetraalkylboride Ions in $CDCl_3$[a]

		Short alkyl group				n-Hexyl group					
Registry no.	Compd	α	β	γ	δ	α	β	γ	δ	ε	ζ
					Tetraalkylammonium Ions						
68-05-3	$N_{2222}I$	54.4	9.5								
1941-30-6	$N_{3333}Br$	60.8	16.0	10.9							
1643-19-2	$N_{4444}Br$	59.1	24.3	19.8	13.8						
311-28-4	$N_{4444}I$	59.3	24.4	19.8	13.8						
2650-53-5	$N_{1116}Br$	53.2				66.5	23.0	25.8	31.2	22.3	13.9
13028-71-2	$N_{2226}Br$	53.5	8.2			57.5	22.0	26.0	31.1	22.3	13.9
37026-90-7	$N_{4446}Br$	59.1	24.3	19.8	14.0	59.4	22.4	26.1	31.3	22.4	13.7
41724-50-9	$N_{1116}B_{1116}$[b]	53.8				67.4	23.2	25.8	31.2	22.4	13.9
	$N_{1116}B_{1116}$[c]	54.0				67.6	23.0	25.6	31.1	22.3	13.9
41724-45-2	$N_{2226}B_{2226}$	53.5	7.7			57.8	21.9	26.0	31.1	22.4	13.9
	$N_{2226}B_{2226}$[d]	53.1	7.3			57.3	21.7	26.1	31.3	22.7	14.0
4172-447-4	$N_{3333}B_{3336}$	60.9	15.9	10.8							
	$N_{3333}B_{3336}$[d]	60.7	15.7	10.7							
41724-48-5	$N_{3333}B_{4446}$	61.0	16.0	10.8							
41724-49-6	$N_{4446}B_{4446}$	59.1	24.2	19.8	13.7	59.1	22.5	26.1	31.3	22.2	13.8
					Tetraalkylboride Ions						
	$N_{1116}B_{1116}$[b]	17.1				e	29.1	35.7	32.9	23.2	14.4
	$N_{1116}B_{1116}$[c]	17.3				36.3	29.1	35.7	32.9	23.0	14.4
	$N_{2226}B_{2226}$	18.5	11.7			27.9	28.2	36.2	33.0	23.2	14.4
	$N_{2226}B_{2226}$[d]	18.8	12.3			28.2	28.7	36.6	33.4	23.6	14.7
	$N_{3333}B_{3336}$	33.6	21.2	20.5		28.3	28.2	36.1	33.0	23.2	14.4
	$N_{3333}B_{3336}$[d]	33.6	21.6	21.2		e	28.5	36.6	33.3	23.5	14.6
	$N_{3333}B_{4446}$	29.4	30.8	29.0	15.0	29.8	28.1	36.2	33.0	23.3	14.5
	$N_{4446}B_{4446}$	29.4	30.8	29.1	15.0	29.8	28.1	36.4	33.1	23.3	14.4

[a] Subscripts refer to the number of carbon atoms in the *n*-alkyl groups, and α refers to the carbon atoms bound directly to nitrogen or boron. [b] Concentration in $CDCl_3$ of 3 mol %. [c] Concentration in $CDCl_3$ of 14 mol %. [d] Concentration in C_6D_6 of 20 mol %. [e] Resonances could not be distinguished with certainty from base line noise in available spectra.

Table II
Carbon-13 Chemical Shifts of Trialkylboranes

Registry no.	Compd	α	β	γ	δ
97-94-9	Triethylborane	19.7	7.9		
1116-61-6	Tri-*n*-propylborane	31.1	18.1	17.6	
122-56-5	Tri-*n*-butylborane	27.8	27.0	26.2	14.1

Table III
Comparison of ^{13}C and ^1H Aromatic Solvent Induced Shifts

		ASIS, ppm	
Ion	Group	^{13}C	^1H
N_{2226}	NCH_2 of ethyl	+0.4	+0.82
	NCH_2 of hexyl	+0.5	+0.82
N_{3333}	NCH_2 of propyl	+0.2	+0.55
B_{2226}	BCH_2 of ethyl	−0.3	−0.37
	BCH_2 of hexyl	−0.3	−0.37
B_{3336}	BCH_2 of propyl	0.0	−0.22

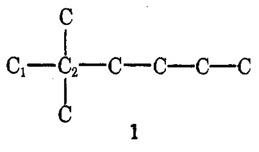
Table IV
Linear Correlations of the Carbon Chemical Shifts of Tetraalkylammonium Ions, Tetraalkylboride Ions, and Trialkylboranes and Their Corresponding Hydrocarbons

Carbon atom X	No. of observations[a]	A	B	σ[b]	r[c]
		Tetraalkylammonium Ions			
α	23	0.849	28.27	0.94	0.977
β	20	0.880	0.41	0.70	0.994
γ	16	0.977	−3.43	0.39	0.998
δ	12	0.937	0.84	0.10	0.99993
		Tetraalkylboride Ions			
α	14	1.406	−22.75	1.32	0.978
β	14	1.013	3.21	0.57	0.996
γ	12	0.999	5.99	0.32	0.9986
δ	10	0.975	1.49	0.16	0.9998
		Trialkylboranes			
α	3	1.103	−9.77	0.21	0.9996
β	3	1.025	−3.36	0.61	0.998
γ	2	0.935	4.23		

[a] All data in Tables I and II were used for these correlations. [b] Standard deviation in parts per million of calculated chemical shifts from observed chemical shifts. [c] Correlation coefficient.

piled the more extensive list of branching corrections in Table V from all of the applicable data in three papers.[3,12,13]

An example will illustrate how the branching corrections in Table V were calculated. The *n*-alkane corresponding to the longest carbon chain in the branched structure is chosen as a starting point. For 2,2-dimethylhexane (1), whose observed chemical shifts are 29.2 ppm



$$C_1-\underset{C}{\overset{C}{C_2}}-C-C-C-C$$

1

for C_1 and 30.1 ppm for C_2,[13] the starting point is hexane. Without the branching corrections, the chemical shift of C_1 would be calculated as the sum of the chemical shift of C_1 of *n*-hexane (13.7 ppm) and two β-carbon effects (2 × 9.4 ppm), which equals 32.5 ppm. The difference between the observed chemical shift and the calculated chemical shift is 29.2 − 32.5 = −3.3 ppm. This is the branching correction, denoted $1°(4°_{112})$, for a primary carbon (1°) which is bonded to a quaternary carbon (4°), which is bonded in turn to two other primary carbons and a secondary carbon ($4°_{112}$). A similar calculation for the chemical shift of C_2 of 1 from the chemical shift of C_2 of *n*-hexane (22.7 ppm) plus two α-carbon effects (2 × 9.1 ppm) leads to $4°_{1112}$ = (30.1) − (22.7 + 18.2) = −10.8 ppm, where $4°_{1112}$ is the branching correction for the chemical shift of

Table V
Branching Corrections for Calculation of Carbon Chemical Shifts in Alkyl Groups[a]

System	No. of observations	B	σ^b
$1^\circ(3^\circ_{12})$	18	−0.7	0.3
$1^\circ(3^\circ_{22})$	12	−1.4	0.4
$1^\circ(4^\circ_{112})$	8	−3.1	0.3
$1^\circ(4^\circ_{122})$	3	−3.3	0.3
$2^\circ(3^\circ_{11})$	14	−2.2	0.3
$2^\circ(3^\circ_{12})$	25	−2.2	0.5
$2^\circ(3^\circ_{22})$	9	−3.7	0.6
$2^\circ(4^\circ_{111})$	7	−6.6	0.6
$2^\circ(4^\circ_{112})$	6	−6.8	0.6
$2^\circ(4^\circ_{222})$	1	−8.9	
3°_{112}	15	−3.8	0.3
3°_{122}	20	−6.6	0.4
3°_{222}	5	−9.9	0.2
4°_{1112}	7	−9.3	1.6
4°_{1122}	4	−17.3	2.3

[a] Data was taken from ref 3, 12, and 13. Method of calculation and nomenclature are described in the text. [b] Standard deviation of branching correction.

a quaternary carbon which is bonded to three primary carbons and one secondary carbon. Similarly, 3°_{122} denotes the branching correction for the chemical shift of a tertiary carbon which is bonded to one primary carbon and two secondary carbons.

In the substituent parameter method, calculation of carbon chemical shifts for hydrocarbons isoelectronic with tetraalkylammonium ions, tetraalkylboride ions, and trialkylboranes proceeded as follows. The *n*-alkane corresponding to the longest carbon chain in the model was chosen as a starting point, the corrections of Grant and Paul[14] for α, β, γ, δ, and ϵ carbon atoms were applied, and finally the branching corrections in Table V were applied. The substituent parameters S in Table VI are differences between observed chemical shifts of our heteroatom species and calculated chemical shifts of the isoelectronic hydrocarbons. All the data in Tables I and II were used to compile Table VI. Data of Simeral and Maciel[15] for trimethylammonium compounds give substituent parameters α, +19.9 ppm, and β, −3.0 ppm, in reasonable agreement with Table VI.

The substituent parameters represent formally the changes in chemical shifts effected by replacement of C by N^+ or B^- and replacement of CH by B. Charged nitrogen shifts α carbon downfield and all other carbons upfield, while charged boron shifts α carbon upfield and all other carbons downfield. Substituent parameters for primary, secondary, and tertiary amines calculated by the same method from the data of Eggert and Djerassi[3] are α, +20.2 ppm; β, +0.8; γ, −2.0; δ, +0.1; ϵ, 0.0; and ζ, +0.1. Comparisons of substituent parameters of tetraalkylammonium ions and amines and of tetraalkylboride ions and trialkylboranes reveal that the effects of charge on chemical shifts of carbon atoms one to three bonds away are real but not large. In both tetraalkylammonium and tetraalkylboride ions the α-substituent parameters for charged nitrogen and boron are not greatly different from the parameters for neutral nitrogen and boron, respectively.

Which method do we recommend for correlation of carbon chemical shifts? If quantitative predictions of chemical shifts are desired, the linear correlations provide more accurate results, as can be seen from the standard deviations in Tables IV and VI. However, for most purposes additive substituent parameters provide only slightly less accurate results, are easier to calculate, and are more recognizable to organic chemists as simple substituent effects.

Table VI
Substituent Parameters for Tetraalkylammonium Ions, Tetraalkylboride Ions, and Trialkylboranes[a]

Carbon atom	No. of observations	S, ppm	σ^a
	Tetraalkylammonium Ions		
α	23	+23.7	1.1
β	20	−2.8	1.2
γ	16	−4.3	0.3
δ^b	4	−0.4	0.1
δ^c	8	−1.4	0.1
ϵ	8	−0.7	0.1
ζ	8	−0.2	0.1
	Tetraalkylboride Ions		
α	14	−7.6	2.6
β	14	+2.7	0.8
γ	12	+5.6	0.3
δ^b	2	+0.7	0.0
δ^c	8	+0.5	0.2
ϵ	8	+0.3	0.2
ζ	8	+0.4	0.1
	Trialkylboranes		
α	3	−5.5	0.7
β	3	−3.2	0.4
γ	2	+3.0	0.4

[a] Standard deviation in parts per million of chemical shifts calculated with substituent parameters from observed chemical shifts. [b] CH_3 groups. [c] CH_2 groups.

Acknowledgments. We thank R. Thrift and S. Silber for running the carbon-13 spectra, G. M. Bodner for helpful discussions, and the National Science Foundation for the support of Grant GP 38493. The National Science Foundation provided partial funding for the Fourier transform ^{13}C nmr system.

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