were obtained in 18.5 and 22.1% yields based on the consumed H_3PO_5, respectively.

n-Butyl alcohol was trapped by using acetic acid, the yields of *n*-butyl acetate (**8**), *n*-butyl alcohol, and *n*-butyl butyrate (**7**) being estimated by GLC (Table III).

Reaction of THF and CH_3CO_3H. THF (100 mL) was treated with CH_3CO_3H (0.18 M) at 25 °C in the presence of 0.15 M H_3PO_4 under conditions analogous to those above or in the absence of H_3PO_4, but no appreciable amount of peracetic acid was decomposed after 30 h, and no product was detected by GLC.

Registry No. 1, 109-99-9; **2**, 96-48-0; **4**, 5371-52-8; **5**, 25714-71-0; **6**, 142-96-1; **7**, 109-21-7; **8**, 123-86-4; *n*-BuOH, 71-36-3; H_3PO_5, 13598-52-2.

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^1H and ^{13}C NMR Spectra of Substituted Borylbenzenes

Brian G. Ramsey*[1a] and Kenneth Longmuir[1b]

Department of Chemistry, The University of Oregon, Eugene, Oregon

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In an earlier paper,[2] an analysis, based upon modified CNDO/2 calculations, was presented of BX_2 substituent effects on benzene π orbital energies and atomic charge densities in the series $PhBX'_2$ (X′ is F, Cl, OH, and Me). Agreement was found between the results of these calculations and photoelectron ionization energies, as well as UV transition energies of $PhBX_2$ (X is F, Cl, OH, OMe, and X_2 = 9-bicyclononane). No correlation was found between changes in calculated (π or total) charge densities at carbon and reported[2,3] ^1H NMR (60 MHz) chemical shifts of $PhBX_2$ (X is Cl, F, OMe), and it was suggested[2] that the ortho and meta proton assignments[3a] in the NMR spectra of $PhBF_2$ and $PhBCl_2$ should be reversed. We report a redetermination of the ^1H NMR spectra of the series $PhBX_2$ at 100 MHz which confirms our earlier suggestion and corrects the previous misassignments in the ^1H NMR spectra of $PhBF_2$ and $PhBCl_2$.

The ^{13}C aromatic carbon NMR chemical shifts relative to benzene were also determined for each member of the series $PhBX_2$ by proton-decoupled 25.2-MHz FT NMR spectroscopy. In this series, only the ^{13}C NMR spectra of $PhB(OH)_2$ and $PhB(OMe)_2$ have been previously reported by Niedenzu and co-workers.[4] The ortho and meta carbon assignments in the ^{13}C NMR spectra of $PhBCl_2$, $PhBF_2$, and other phenylboranes by Niedenzu are, however, in conflict with later assignments by Brown and co-workers[5] for similar molecules in a series of phenylalkoxy- and aminoboranes. The assignments of Brown were made by off-resonance-decoupled, selectively decoupled, and undecoupled ^{13}C NMR spectroscopy and must be regarded as correct for the molecules studied. In agreement with the results of Brown and co-workers, our results support assignment of the ortho carbon ^{13}C NMR chemical shifts as downfield with respect to those of meta or para carbons for all members of the series $PhBX_2$.

Table I. ^1H and ^{13}C NMR Chemical Shifts (δ) of $PhBX_2$ Relative to Benzene

	δ ortho		δ meta		δ para	
BX	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
BCl_2[a]	0.75	8.57	0.07	−0.13	0.23	6.76
BF_2[a]	0.49[b]	8.02	0.08	0.05	0.22	5.80
BR_2[g]	0.60	6.33	(0.1)[d]	−0.27	(0.1)[d]	4.46
$B(OH)_2$[c]	0.40	5.91	(0.0)[d]	−0.29	(0.0)[d]	2.38
$B(OMe)_2$[a,e]	0.22	5.08	(−0.1)[d]	−0.64	(−0.1)[d]	1.31
BPh_2[f]		9.9		−1.2		2.7

[a] Solvent $CDCl_3$. [b] J [^{13}C,F (ortho)] = 4.70 Hz. [c] Solvent CD_3OD. [d] Multiplet center. [e] OCH_3 δ^{CH} C 25.48, δ^{CH} H 3.73 (cyclohexane internal reference). [f] Reference 7. [g] R is 9-bicyclononane.

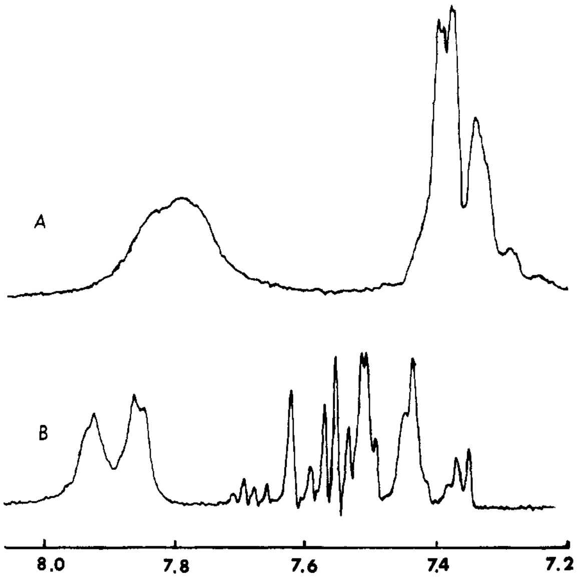

Figure 1. ^1H NMR spectrum at 100 MHz of (a) $PhB(OH)_2$ in CD_3OD and (b) $PhBF_2$ in $CDCl_3$ in parts per million downfield from Me_4Si.

Proton and ^{13}C NMR chemical shifts downfield relative to benzene for the compounds investigated appear in Table I. In the ^1H spectra, the aromatic protons divide into two multiplets of two (low field) and three (high field) protons, each separated by 0.3 to 0.5 ppm. Figure 1 provides ^1H NMR spectra of $PhBF_2$ and $PhB(OH)_2$ as representative. The low-field multiplet of two protons, which is broadened by coupling to boron, is assigned to the ortho protons in each case. Ortho shifts are reported as the average of the two most intense inner lines in the multiplet, a procedure supported by computer analysis of the spectra of $PhBCl_2$ and $PhBF_2$ which were very similar in appearance.

The observed ^1H NMR spectra of $PhBCl_2$ and $PhBF_2$ can be adequately computer similated to extract meta and para ^1H chemical shifts (Table I) by using the following coupling constants (Hz): $J_{2,3} = J_{5,6} = 7.0$, $J_{3,4} = J_{4,5} = 7.5$, $J_{2,4} = J_{4,6} = 1.3$, $J_{3,5} = 1.4$, $J_{3,6} = J_{2,5} = 0.6$. Remaining ^1H NMR spectra of $PhBX_2$ were not subjected to computer analysis because of poor resolution of structure, and combined meta–para ^1H NMR shifts are therefore reported as the center of the high-field multiplet.

Proton-decoupled ^{13}C NMR shifts were assigned on the basis of intensity and an assumed larger downfield shift for ortho than meta carbon, as found for ortho and meta H, and in agreement with Brown and co-workers's assignments in similar molecules.[5]

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[1] (a) Department of Chemistry, San Francisco State University, San Francisco, CA 94132. (b) Department of Physiology, California College of Medicine, University of California, Irvine, CA 92717.

[2] B. G. Ramsey and S. J. O'Neill, *J. Organomet. Chem.*, **141**, 257 (1977).

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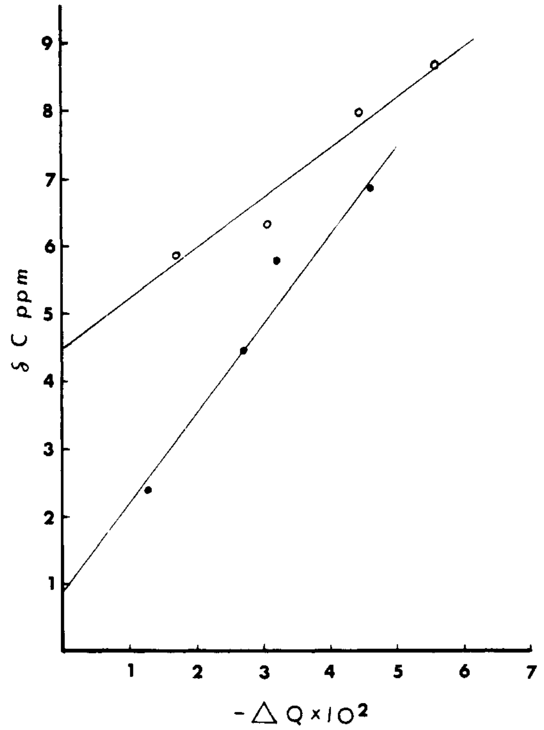

Figure 2. ^{13}C NMR chemical shifts of $PhBX_2$ (X is F, Cl, OH, and 9-BBN), referenced to benzene, as a function of change in total electron charge density, ΔQ, relative to benzene: ○ ortho; ● para.

As may be seen from the combined NMR data in Table I, there is now the expected trend in correlation between para ^{13}C and ^1H NMR shifts within the series $PhBX_2$ and an absence of such correlations at the meta and ortho positions.

In the series $PhBX'_2$, previously calculated[2] changes in benzene carbon electron density on BX'_2 substitution ranged from -0.016 to -0.065, para; 0.011 to 0.020, meta; and -0.017 to -0.055, ortho (electrons). Figure 2 demonstrates that very reasonable linear correlations are found to exist between both para and ortho ^{13}C chemical shifts relative to benzene and changes in total electron density, ΔQ_T, at carbon on BX_2 substitution. The least-squares regression lines are given by (1) and (2) for these correlations. Similar but somewhat less satisfactory correlations

$$\delta^{\mathrm{PhH}}\ {}^{13}\mathrm{C}\ (\mathrm{para}) = -136\Delta Q_{\mathrm{T}} + 0.86\ \mathrm{ppm}\ (\mathrm{SD}\ 0.22\ \mathrm{ppm}) \qquad (1)$$

$$\delta^{\mathrm{PhH}}\ {}^{13}\mathrm{C}\ (\mathrm{ortho}) = -75\Delta Q_{\mathrm{T}} + 4.45\ \mathrm{ppm}\ (\mathrm{SD}\ 0.30\ \mathrm{ppm}) \qquad (2)$$

between ortho and para δ ^{13}C and changes in π charge density are also obtained.

There is no correlation found between ΔQ and δ ^{13}C NMR of $PhBX_2$ for meta carbons. However, the modified CNDO/2 calculations do predict an *increase* in electron density at meta carbons for all $PhBX_2$, in qualitative agreement with the observed near zero or upfield ^{13}C shifts.

For unknown reasons, both ortho and meta carbon ^{13}C shifts are less sensitive to charge-density changes than para carbon. The large nonzero intercept (ΔQ_T is 0.0) of (2) suggests a substantial, but relatively constant, deshielding anisotropy associated with the BX_2 group or perhaps the B-C/sp^2 bond. The ortho δ ^{13}C shifts are also unusual in that they are further downfield than the para, unlike analogous substituents such as NO_2 or COR.[6]

Table II. σ Substituent Constants for BX_2

BX_2	BCl_2	BF_2	BR_2[a]	$B(OH)_2$	$B(OMe)_2$
σ^0_{R}[b]	0.28	0.24	0.22	(0.13)[d]	0.12
σ_{I}[b]	0.31	0.26	0.03	(-0.05)[d]	-0.27
σ^+_{p}[c]	0.86	0.76	0.61	(0.38)[d]	0.26

[a] R is 9-bicyclo[3.3.1]nonane (9-BBN). [b] Error limits are estimated as $\sigma^0_R \pm 0.02$; $\sigma_I \pm 0.05$. These are based upon uncertainty in the last place figure reported for values of ρ_I and ρ_R (ref 7) and upon an experimental error in ^{13}C chemical shifts of 0.01 ppm. [c] Error limits on σ^+_p (Swain-Lupton) are estimated as ±0.01. [d] These σ values were determined from ^{13}C chemical shifts measured in CH_3OD and therefore assume a negligible solvent effect in a change from CH_3OD to carbon tetrachloride.

From relationships provided by Hehre, Taft, and Topsom,[7] and by Nelson, Levy, and Cargioli,[8] the ^{13}C NMR chemical shifts may be used to calculate values of the Hammett-type substituent constants σ^0_R, σ_I and σ^+ found in Table II.[9] The NMR results and derived substituent constants are now consistent with the previously published[2] interpretations of BX_2 substituent interaction mechanisms in the $PhBX_2$ system, which were based on photoelectron (PE) and UV spectra and modified CNDO/2 calculations. It must however be kept in mind that substituent effects on UV and PE spectra may largely reflect changes in orbital energy, whereas *local charge* density at carbon appears to play a major and often dominant role in determining the change in ^1H and ^{13}C NMR chemical shifts of monosubstituted benzenes relative to benzene.[10]

All BX_2 substituents donate electron density, ΔQ_σ, to the benzene ring through the σ framework in the modified CNDO/2 calculations (BF_2 -0.14; BCl_2 -0.08; $B(OH)_2$ -0.17; BR_2 -0.15, electrons) and withdraw π-electron density, δQ_π (BF_2 0.07; BCl_2 0.11; $B(OH)_2$ 0.05; BR_2 0.09 electron).[2]

At the para position, and to a lesser extent at the meta position, changes in benzene ^{13}C and ^1H NMR chemical shifts on BX_2 substitution may now be rationalized in terms of changes in carbon charge density. It is not necessary or even likely that the same order of substituent effects will be obtained in a series comparing PE (or UV) spectra and NMR chemical shifts.

Para ^1H and ^{13}C NMR chemical shifts of $PhBCl_2$ are greater than those of $PhBF_2$, primarily because of the large π-electron-withdrawing effect of BCl_2, added to a strong field effect. Because 2p-π back-bonding by fluorine to boron reduces the ability of BF_2 to otherwise withdraw π electrons from the benzene ring, the strongest interaction mode of the BF_2 group is the field effect. This BF_2 field effect operates more effectively in determining orbital energy than meta or para carbon electron density, with the

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(6) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 200.

(7) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, 12, 159 (1976).

(8) (a) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, 94, 3089 (1972). (b) The σ^+p values obtained by this correlation are based upon a derived synthetic set of σ^+p values of C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, 90, 4328 (1968). R. T. C. Brownlee and R. D. Topsom, *Tetrahedron Lett.*, 5187 (1972), have criticized this correlation of σ^+p with para ^{13}C chemical shifts. Nevertheless, the BX_2 σ^+p values are provided here as the best estimate presently available for these substituent constants.

(9) Substituent σ^0_R values derived from infrared intensity measurements have been reported for BCl_2 (0.30) and $B(OH)_2$ (0.23) by A. Katritzky and R. D. Topsom, *Chem. Rev.*, 77, 654 (1977).

(10) The theory behind and extent to which correlations exist between charge density at carbon and ^1H, ^{19}F, and ^{13}C NMR chemical shifts have been the subject of recent reviews; see ref 6; also, D. G. Farnum, *Adv. Phys. Org. Chem.*, 11, 22 (1975); G. Nelson and E. Wilson, *Prog. Phys. Org. Chem.*, 12, 229 (1976). For a discussion of the correlation of NMR chemical shifts in monosubstituted benzenes with "ab initio" calculated charge densities see ref 7; correlation of ^{13}C NMR shifts in substituted benzenes with CNDO/2 calculated charge densities is discussed in ref 8.

result that the first and second π ionization energies of $PhBF_2$ are greater than those of $PhBCl_2$. There is, therefore, a reversal of the substituent effect order based on NMR chemical shifts. The postulate of a dominant BF_2 field effect also offers a rationale for the observation that although according to the CNDO/2 calculation the BF_2 group withdraws less π-electron density from the benzene ring than even BR_2, the ^{13}C NMR derived $\sigma^0{}_R$ and $\sigma^+{}_p$ values of BF_2 are more positive than those of BR_2.

Still greater p–π back-bonding to boron by oxygen in $PhB(OH)_2$ and $PhB(OCH_3)_2$ reduces π-electron withdrawal from benzene by BX_2 to the point that the electron-donating inductive effect in the sigma framework finds expression in the negative σ_I values, Table II. The small calculated π-electron withdrawal of 0.05 electron from the ring by $B(OH)_2$ is however sufficient to account for the observed para ^{13}C NMR chemical shifts when a shift factor of the order of 2×10^2 ppm/electron[7] is assumed.

It is interesting to compare the ^{13}C NMR chemical shifts of the monoarylboranes $PhBX_2$ with recently reported[11] NMR data for triphenylborane (Table I) and with trimesitylborane ^{13}C NMR shifts relative to mesitylene, which we have also measured.

The small δ ^{13}C para and negative δ ^{13}C meta NMR shifts relative to benzene reported[10] for Ph_3B seem in keeping with the known twisted propeller conformation of the triarylboranes which reduces 2p–π interactions between boron and the benzene ring. Comparable ^{13}C chemical shifts were measured for trimesitylboron relative to mesitylene (δ para 2.5 δ meta 1.7). The ortho carbons of Ph_3B, however, show an exceptionally large downfield shift of almost 10 ppm, which is even more surprising in view of the small ortho ^{13}C shift of trimesitylborane, relative to mesitylene, δ ^{13}C ortho 2.9, when compared to the other ortho ^{13}C NMR shifts of the $PhBX_2$ series. (The ortho and para methyl carbons of trimesitylborane exhibit downfield shifts of 2.0 and 0.1 ppm, respectively, relative to mesitylene.) It would appear that ortho carbon ^{13}C chemical shifts of triarylboranes may be sensitive functions of the aryl group twist angle relative to the plane of the boron–carbon bonds. This propeller twist angle is greater in trimesitylborane, because of the steric bulk of the ortho methyl groups, than in triphenylborane.[12] At small twist angles, ortho positions of triarylboranes will be deshielded by adjacent aromatic rings,[12] as well as by the deshielding anisotropy which seems to be associated with B–sp^2 bonds in the $PhBX_2$ sereis. At twist angles approaching 45°, the ortho ring positions may move into shielding regions of both B–sp^2 bonds, analogous to those of C=O or NO_2, and of the adjacent aromatic rings.[13]

If magnetic anisotropy, associated with adjacent rings and the central boron atom, does play a significant role in the ^{13}C NMR shifts of triarylboranes, the role of similar effects will have to be reevaluated in the spectra of the isoelectronic and isosteric triarylcarboniums, where they have been neglected[6,13] in favor of charge density effects. There is, in general, a parallel between NMR shifts observed for carbonium ions and corresponding boranes, for example, $PhCF_2{}^+$,[13,14] $PhCMe_2{}^+$,[15,16] and $PhC(OMe)_2{}^+$.[16,17]

Following submission of this manuscript, an extensive study appeared[17] of the ^{13}C spectra of phenylboranes and boron-substituted aromatic heterocycles. Between this most recent paper and our own there is no disagreement as to experimental details; in the interpretation of the results we differ most in drawing attention to the strong inductive-field effects of BCl_2, BF_2, and $B(OR)_2$ groups.

Experimental Section

Details of the synthesis of $PhBX_2$ (X is F, OCH_3) and of the modified CNDO/2 calculations (X is Cl, F, OH, and CH_3) are provided in ref 2.

All NMR spectra were run in either the CW (for ^{1}H NMR) or FT (^{13}C NMR) mode on a Varian XL-100 spectrometer with internal D lock; ^{1}H (100 MHz), ^{13}C (25.2 MHz).

Both ^{1}H and ^{13}C NMR spectra of $PhBX_2$ (X is F, Cl, OCH_3, and 9-BBN) were run on 15% v/v solutions in $DCCl_3$ with internal cyclohexane as a reference. Conversions to chemical shifts relative to benzene were made with the following shift conversions: $\delta^{CH}{}_{PhH}$ ^{1}H 5.94 ppm; $\delta^{CH}{}_{PhH}$ ^{13}C 101.16 ppm; in $DCCl_3$, ref 8a.

Spectra of $PhB(OH)_2$ were run in CD_3OD (saturated solution) referenced to internal tetramethylsilane and converted to benzene reference by $\delta^{Me_4Si}{}_{PhH}$ ^{1}H 7.37 ppm; $\delta^{Me_4Si}{}_{PhH}$ ^{13}C 128.50 ppm, ref 8a.

Spectra of trimesitylborane were run in C_6D_6 referenced to internal tetramethylsilane. Chemical shifts of mesitylene, δ^{13}C, were taken from ref 6, corrected to $\delta^{Me_4Si}{}_{PhH}$ ^{13}C 128.6 ppm. Chemical shifts, δ^{13}C, relative to tetramethylsilane, of trimesitylborane were 21.23 (p-CH_3), 23.07 (o-CH_3), 129.02 (m-C), 140.25 (p-C), and 140.57 (o-C) ppm.

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Registry No. $PhBCl_2$, 873-51-8; $PhBF_2$, 368-98-9; $PhBR_2$, 72826-88-1; $PhB(OH)_2$, 98-80-6; $PhB(OMe)_2$, 13471-35-7.

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Isolation and Structure of Bohemamine, (1aβ,2α,6aβ,6bβ)-3-Methyl-*N*-(1a,6,6a,6b-tetrahydro-2,6a-dimethyl-6-oxo-2*H*-oxireno[*a*]pyrrolizin-4-yl)-2-butenamide

Terrence W. Doyle,* Donald E. Nettleton, David M. Balitz,
John E. Moseley, and Robert E. Grulich

*Research Division, Bristol Laboratories, Division of
Bristol-Myers Company, Syracuse, New York 13201*

Terry McCabe and Jon Clardy*

*Department of Chemistry, Baker Laboratory, Cornell
University, Ithaca, New York 14853*

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While screening cultures of actinomycetes for novel antitumor substances we have isolated an anthracycline mixture, bohemic acid complex, from *Actinosporangium* sp. strain C36145 (ATCC 31127).[1] In addition to the known antibiotics cinerubins A and B[2] and pyrromycin,[3]

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[1] It is the practice of this laboratory (B.L.) to give trivial names to antibiotic complexes based on operas. This complex is named for La Bohême and compounds subsequently isolated from the complex are given trivial names based on characters in the opera.

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