

A COMPARISON OF MODIFIED CNDO/2 CALCULATIONS AND THE PHOTOELECTRON, NMR AND UV SPECTROSCOPIC PROPERTIES OF BORON-SUBSTITUTED MONOPHENYLBORANES

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Summary

Substituted boryl, BX_2 , substituent effects on the ultraviolet, hydrogen NMR and photoelectron spectra of benzene are compared with the results of modified CNDO/2 calculations. The substituents BF_2 , BCl_2 , $B(OR)_2$ and BR_2 are characterized by the relative degree of the electronegativity of X and π bonding to boron. Intramolecular charge transfer UV transitions are identified where BX_2 is BCl_2 or BR_2 . In contrast to other groups, $B(OR)_2$ leads to a decrease in the first two benzene π ionization energies.

Introduction

The generally accepted importance of the boron virtual valence shell $2p$ orbital in the description of physical and chemical properties of organometallic derivatives of trivalent boron, RBX_2 , as compared to the present controversy concerning the role of valence "d orbitals" in other organometalloids, makes it important to establish the origin, magnitude and direction of BX_2 substituent effects on the physical and chemical properties of fundamental organic π -electron functional groups such as benzene.

Photoelectron spectra of trivinylborane [1] have failed to establish the importance of ground state boron $2p$ π -bonding to hydrocarbon π systems, and photoelectron spectra (PES) of simpler molecules have not yet been reported, so the importance of boron to carbon π -bonding remains to be established in ground states of neutral molecules.

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TABLE 2
ELECTRONIC TRANSITION ENERGIES AND SUGGESTED ASSIGNMENTS IN SUBSTITUTED PHENYLBORANES

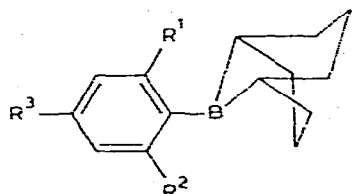
Phenylborane	E_1^f	(log ϵ)	Assignment	E_2^f	(log ϵ)	Assignment	E_3^f	(log ϵ)	Assignment	Ref.
$C_6H_5BF_2$ ^a	4.61	—	L_b	5.70	—	I_{1g}	>6.2	—	$B_{u,b}$	c
$C_6H_5BCl_2$ ^a	4.39	—	L_b	5.00	—	CT(A_1)	>6.2	—	$B_{u,b}$	c
$C_6H_5B(OR)_2$ ^b	4.64	(2.52)	L_b	5.64	(4.01)	I_{1g}	6.46	(4.82)	$B_{u,b}$	24
$C_6H_5B(OH)_2$	4.66	(2.66)	L_b	5.69	(3.93)	I_{1g}	6.53	(4.70)	$B_{u,b}$	24
$C_6H_5BR_2$ ^d	4.59	(3.01)	L_b	5.27	(4.10)	CT(A_1)	6.26	(4.45)	$B_{u,b}$	c
4-MeC ₆ H ₄ BR ₂ ^d	4.43	(3.00)	L_b	5.01	(3.90)	CT(A_1)	6.11	(4.11)	$B_{u,b}$	c
2,4,6-Me ₃ C ₆ H ₂ BR ₂ ^d	4.89	(3.23)	L_b	5.74	(3.02)	CT	6.18	(3.77)	$B_{u,b}$	c
$C_6H_5BR_2 \cdot Pip$ ^d	4.84	(2.65)	L_b	5.75	(3.15)	I_{1g}			B_u	c

^a Gas phase spectra; ^b not determined. ^c This work. ^d R is n-butyl. ^e BR₂ is 9-borabicyclo[3.3.1]nonane.

With respect to electronically excited states of vinyl- and aryl-boranes, a question [2-4] remains as to the relative energies of localized hydrocarbon and borane BX_2 π^* orbitals, as well as the magnitude of their interaction, in perturbation models treating electronic transition energies. Molecular orbital calculations on vinyl- and phenyl-boranes have been limited to π electrons only. In this paper we wish to report the results of a comparison of some spectroscopic properties of selected phenylboranes with all valence shell molecular orbital calculations.

II. Results and discussion

The two lowest π photoelectron ionization energies of four representative phenylboranes, $PhBCl_2$ (I), $PhB(OCH_3)_2$ (II), $PhBR_2$ (IIIa), and $PhBF_2$ (IV), and the ultraviolet spectra of I and IV in the gas phase, as well as solution phase UV spectra of the monophenyldialkylboranes IIIa-IIIc, are reported here for the first time (Tables 1 and 2).



(IIIa) $R^1, R^2, R^3 = H$

(IIIb) $R^1, R^2 = H; R^3 = CH_3$

(IIIc) $R^1, R^2, R^3 = CH_3$

Modified CNDO/2 calculations were made on phenyldichloroborane (I), phenylboronic acid (as a model for II), and phenyldimethylboron (as a model for IIIa) and phenyldifluoroborane (IV). The modifications of the original Pople-Segal-Santry CNDO/2 program [6] are essentially those of Jaffe and Del Bene [6] and are described in detail elsewhere [7-9]. However, it is important to note at this point that the modifications were specifically developed [6] to reproduce elec-

TABLE 1

FIRST TWO π VERTICAL IONIZATION ENERGIES OF PHENYLBORANES, CNDO/2 CALCULATED CHANGES IN BENZENE π ORBITAL ENERGIES, $\delta\epsilon$, AND CHANGES IN BORANE-SUBSTITUENT ELECTRON DENSITY, $\delta(Q)$

$PhBX_2$	$I^V(a_2)$	$\delta\epsilon(a_2)^a$	$I^V(b_1)$	$\delta\epsilon(b_1)^a$	$\delta(Q_{BX_2}^T)^b$	$\delta(Q_{BX_2}^a)^b$
$PhBF_2$	9.61	-0.28	10.0 ^c	-0.48	-0.071	-0.142
$PhBCl_2$	9.52	-0.54	9.8 ^c	-0.74	0.033	-0.079
$PhB(OR)_2^e$	9.25 ^c	0.08	8.97	0.12	-0.119	-0.167
$PhBR_2^f$	9.16	0.16	(9.4) ^d	-0.12	-0.059	-0.145

^a $\delta\epsilon$ are relative to calculated π orbital energies of -10.64 eV; the measured Jahn-Teller corrected I^V of benzene π is taken as 9.35 eV (first adiabatic 9.25 eV). ^b $\delta(Q)$ is net gain in total- (T) or σ -electron density by substituent BX_2 . ^c Resolved shoulder, estimated probable error ± 0.05 eV. ^d PES band overlapped and unresolved, estimate within ± 0.2 eV. ^e Calculations on $B(OH)_2$, PES of $B(OCH_3)_2$. ^f Calculations on $B(CH_3)_2$, PES of 9-borabicyclo[3.3.1]nonane (9-bbn).

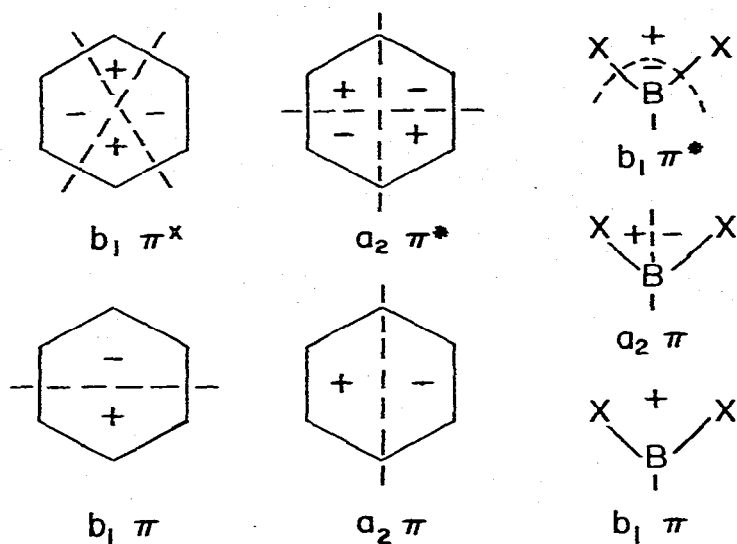


Fig. 1. Symmetry assignments in the C_{2v} point group for phenyl and BX_2 π orbitals as used in a perturbation or linear combination of molecular orbitals model.

tronic transition energies in an all valence shell electron calculation, and the procedure has enjoyed previous success in calculation of vertical ionization energies, I^v , of boron containing molecules [8].

In the following discussion, assignment in the C_{2v} point group has been adopted for the initial localized benzene π and vacant BX_2 π^* orbitals (Fig. 1), which in a perturbation model, can be used to generate the delocalized π -molecular orbitals of $PhBX_2$ of corresponding symmetry.

Ionizations associated with a_2 and b_1 π -orbitals lead to 2A_2 and 2B_1 radical cation states. Electronic transitions from benzene b_1 and a_2 π -orbitals to the BX_2 b_1 π^* orbital are associated with 1A_1 and 1B_2 charge transfer excited states.

The first two lowest vertical PES determined ionization energies of I, II, IIIa, and IV, as well as results of the CNDO/2 calculations are given in Table 1. Ultraviolet transition energies of monophenylboranes, $PhBX_2$, are given in Table 2. A comparison of ionization energies, I^v , and electronic transition energies, E_t , in Tables 1 and 2 reveals no correlation between the two, although for corresponding UV transitions we might expect that an increase in I^v would lead to a proportional increase in E_t . Modified CNDO/2 calculations however provide an interpretation of this result in keeping with earlier [2] π -electron only PPP-SCF-LCAO-CI calculations of UV transition energies in phenylboronic acids, and phenyldialkylboranes.

Photoelectron spectra. To understand the net effect of BX_2 substituents on benzene electronic transitions and ionization energies, it is necessary to first consider the PES determined I^v of I, II, IIIa and IV (Fig. 2).

In benzene the a_2 and b_1 degenerate filled π -molecular orbitals have a CNDO/2 calculated energy of -10.64 eV. The degenerate lowest vacant benzene π^* are calculated at 0.496 eV. In Table 1 are listed the calculated changes in these a_2 and b_1 π -orbital energies, $\delta\epsilon$, on BX_2 substitution, where X is F, Cl, CH, and CH_3 .

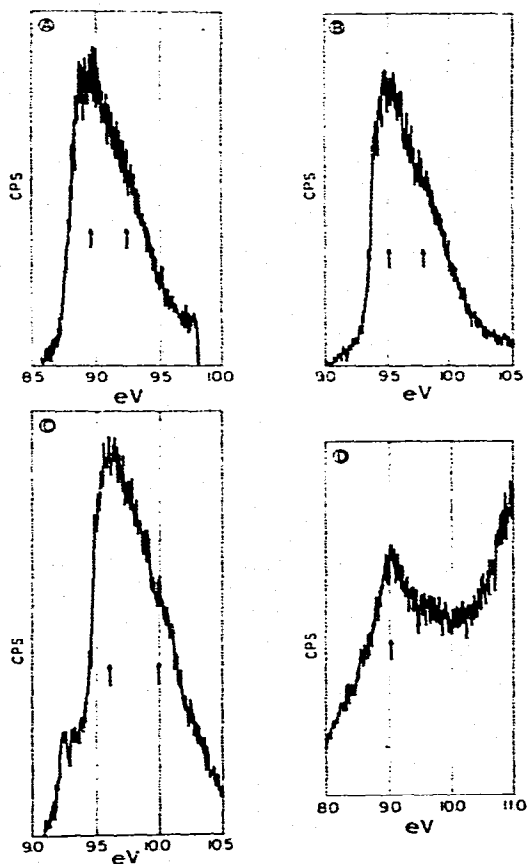


Fig. 2. Photoelectron spectra of PhBC₂ in 8.0 to 11.0 eV range: A is PhB(OMe)₂, B is PhBCl₂, C is PHBF₂, D is PhB(Me)₂. Arrows † indicate vertical ionization energies.

Within the limitations of the approximations of Koopmans' Theorem [10], changes in I^v should be proportional to $-\delta\epsilon(\text{SCF})$, and experience indicates a proportionality constant of the magnitude 0.90 to 0.95. The first I^v of benzene is accurately known at 9.25 eV [11]. After correction for Jahn-Teller splitting of the degenerate states associated with degenerate a_2 and b_2 π -orbitals, a vertical reference I^v of 9.35 eV is, however, more appropriate for discussion of substituent effects on benzene the degenerate π -orbital energies [11-13].

As described by the CNDO/2 calculations, only the BCl₂ group is net electron withdrawing ($\delta(Q^T)$ Table 1), although as in all BX₂ substituents there is a calculated electron donation to the σ framework of the benzene ring. The net electron-withdrawing character of the BCl₂ group is the result of a significant resonance interaction between phenyl πb_1 and $\pi^* b_1$ of the BX₂ moiety such that the atomic orbital mixing coefficient of boron in πb_1 is 0.1564 for I. Since resonance, net inductive, and field effects on the π -orbital energies are all in the same direction, and since these effects are felt more strongly by the b_1 function rather than the a_2 , which is nodal at the substituent site, the CNDO/2 model predicts a

decrease in both a_2 and b_1 orbital energies (increase in I^v) with the a_2 π -energy decrease in both a_2 and b_1 orbital energies (increase in I^v) with the a_2 π -energy decrease the largest. If we equate vertical ionization energies, I^v , with minus SCF orbital energies, $-\epsilon(\text{SCF})$, and thus invoke Koopmans' theorem [10], the predicted increase in I^v and expected splitting is found in the PES of I (Table 1, Fig. 2).

For the $\text{B}(\text{OH})_2$ substituent, which serves as a model for $\text{B}(\text{OCH}_3)_2$ in the modified CNDO/2 calculation, $\text{B}(\text{OR})_2$ is net electron donating, more so even than BR_2 . The origin of this net electron donation is the strong boron-oxygen π -bonding which effectively reduces the interaction between the boron $2p_z$ vacant orbital and the benzene ring, and allows σ -electron donation to dominate over π -electron withdrawal. The boron $2p_z$ orbital mixing coefficient in πb_2 of II is appropriately reduced by one half to 0.0845 from its value in I.

Again in agreement with the modified CNDO/2 calculation the first I^v of II is considerably lower than that of benzene, 9.35 eV. In the CNDO/2 model the net inductive effect of $\text{B}(\text{OR})_2$, increasing the b_1 π orbital energy, predominates over a small resonance interaction between b_1 π and b_1 π^* (BX_2) and the first I^v of II is assigned to the ${}^2\text{B}_1$ radical cation state. This does seem to be the most reasonable assignment, since a very large inductive effect indeed would be required to move the nodal a_2 π orbital to the observed 8.97 eV E^v , and an even more unlikely BX_2 resonance effect would be required to reverse an expected still larger inductive effect on the b_1 π orbital and return it to an energy of -9.25 eV.

The first band of the PES of IIIa is broad and overlapped on the high energy side by ionizations probably associated with the boron-carbon bonds. Only the first I^v can therefore be obtained with confidence, although a second ionization is clearly present within the 9.4 ± 0.2 eV region. The first ionization in the PES of IIIa is quite reasonably assigned by the CNDO/2 calculation to the ${}^2\text{A}_2$ radical cation state as a result of a modest net electron-donating effect into the benzene system by BR_2 (methyl was taken as a CNDO/2 model for the 9-bbn fragment). Again a substantial boron $2p_z$ mixing coefficient (0.1603) in the b_1 IIIa π orbital, reflects the $\pi-\pi^*$ interaction between phenyl and BX_2 groups which leads to a predicted 0.1 eV increase in the I^v to the ${}^2\text{B}_1$ state of the radical cation.

In spite of the fact that within the CNDO/2 model, the inductive effects of BF_2 are close to those of BR_2 in terms of net electron charge donation. There is a predicted increase with respect to benzene I^v in both the a_2 and b_1 π -ionization energies of PhBF_2 , which is observed in the PES of IV. The observed increase in the a_2 π -ionization energy of IV must largely be ascribed to a substantial radical cation destabilizing field effect of the BF_2 substituent. Unlike typical CX_3 organic substituents, the inductive and field effects of the BF_2 substituent are in opposite directions with respect to charge stabilization. Examination of the diagonal elements of the final SCF Hartree-Fock matrix of the modified CNDO/2 calculation on IV support the conclusion that even the increased I^v associated with the b_1 π -orbital is largely due to the BF_2 field effect with only approximately 25% of the increase in I^v the result of carbon to boron π bonding, i.e. resonance effects.

NMR spectra. Substituted benzene ${}^{13}\text{C}$ NMR chemical shifts relative to benzene are largely determined by charge density at carbon, and the observation of a linear relationship between *para* ${}^1\text{H}$ and *para* ${}^{13}\text{C}$ chemical shifts in monosub-

TABLE 3

CALCULATED CHANGES, $\delta(Q) \times 10^4$, IN π AND TOTAL (T) CARBON AND HYDROGEN BENZENE RING ELECTRON DENSITIES ON BX_2 SUBSTITUTION

$PhBX_2^a$	$\delta(Q_\pi^2)$	$\delta(Q_\pi^3)$	$\delta(Q_\pi^4)$	$\delta(Q_T^2)$	$\delta(Q_T^3)$	$\delta(Q_T^4)$	$\delta(Q_H^1)$	$\delta(Q_H^3)$	$\delta(Q_H^4)$
$PhB(OH)_2$	-283	114	-163	-170	108	-125	81	29	15
$PhBF_2$	-611	203	-453	-435	177	-324	-73	-28	-32
$PhBCl_2$	-764	237	-647	-554	202	-454	-140	-71	-68
$PhBR_2$	-538	203	-367	-305	188	-265	-42	8	-2

^a Positions 2, 3, 4 correspond to *ortho*, *meta* and *para*; a minus sign indicates loss of electron density from the indicated atom as compared to electron density in benzene.

stituted benzenes has served to justify the use of *para* H NMR shifts as a direct measure of changes in the aromatic carbon charge density [14].

In both "ab initio" and modified CNDO/2 calculations [15,16] there is a pronounced tendency towards the development of charge alternation between atoms in substituted benzene, and in apparent agreement with this result, a roughly two-thirds majority of the *meta* and *para* carbon ¹³C NMR chemical shifts tabulated by Stothers [14] for monosubstituted benzenes are in the opposite direction, whereas *meta* and *para* hydrogen chemical shifts * seem almost without exception to all be in the same direction. As a corollary, *meta* ¹³C and ¹H NMR chemical shifts are most often in the opposite direction relative to benzene [17], nitrobenzene and benzaldehyde being notable exceptions. In somewhat simplified terms, the *meta* hydrogens often seem to respond as required to the demand of charge alternation between *ortho* and *para* carbons by accepting or donating electron density.

In general, *ortho* hydrogen chemical shifts are too strongly affected by magnetic anisotropies associated with the substituent group to provide reasonable correlations with simple charge density considerations.

Before proceeding further it needs to be established whether in the $PhBX_2$ series, modified CNDO/2 calculations of charge density changes, as provided in Table 3, are consistent within themselves.

Within the $PhBX_2$ series, a number of linear relationships between changes, $\delta(Q)$, in charge density exist. As may be seen from Fig. 3, the three substituents where boron is bonded to heteroatom lone pair electron donors (F, Cl, O) define straight-line correlations between calculated changes in *ortho*- and *para*-electron densities at carbon, $\delta(Q_\pi)$ and $\delta(Q_T)$, and hydrogen, $\delta(Q_H)$ on BX_2 substitution of benzene. The points for BR_2 deviate from these correlation lines through perhaps not significantly. The correlation lines do not, however, pass through the origin so that for example $B(OR)_2$ substitution of benzene is predicted to actually increase the electron density at the *para* hydrogen, in disagreement with an observed downfield shift of the *para*-benzene hydrogen in the NMR spectrum of II.

At the *meta* positions, all BX_2 substituents produce increases in π -electron density at carbon which correlate with a decreasing electron density at hydrogen for BCl_2 , BF_2 and $B(OR)_2$ substituents. Again, within the calculations, $B(CH_3)_2$

* Ref. 17 provides an extensive compilation of ¹H NMR data for substituted benzenes.

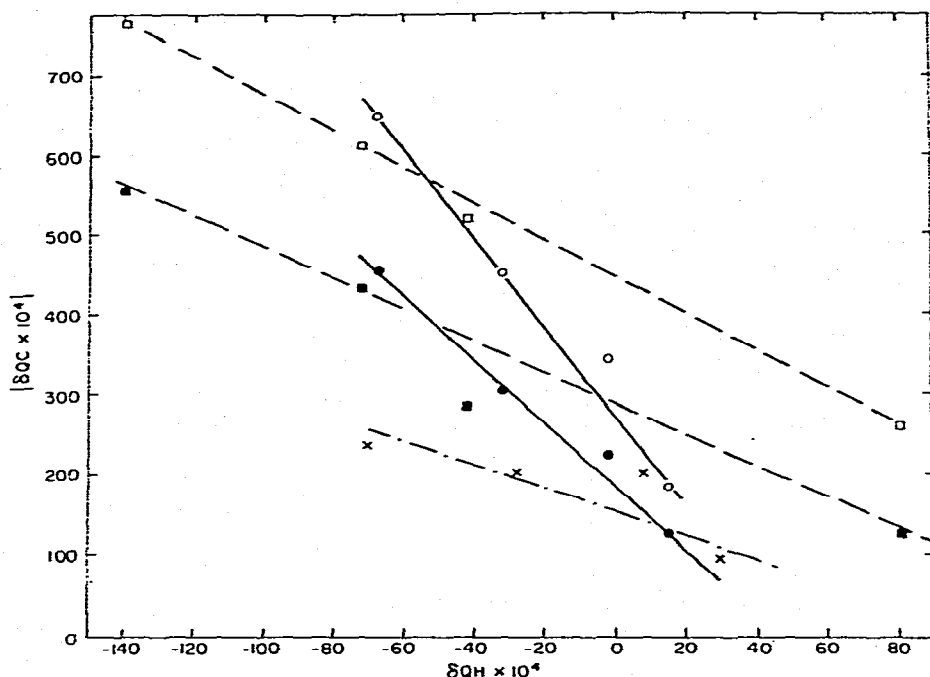


Fig. 3. The correlation between calculated changes in electron density at carbon, $\delta(Q_C)$, and hydrogen, $\delta(Q_H)$, on substitution of benzene by BX_2 : Total *para* $\delta(Q_C)$, closed circles ●; total *ortho* $\delta(Q_C)$, closed square ■; π only *para* $\delta(Q_C)$, open circles ○; π only *ortho* $\delta(Q_C)$, open squares □; π only *meta* $\delta(Q_C)$ X.

appears to be somewhat anomalous. Finally, for the substituents BF_2 , BCl_2 and $B(OMe)_2$, changes in *meta*-carbon π -electron density, $\delta(Q_\pi^3)$, are linear functions of either $\delta(Q_\pi^4)$ or $\delta(Q_\pi^2)$ or their sum. Experimentally, correlations between *meta*- and *para*-carbon π -charge density have already been noted in the close linear relationships between *meta*- and *para*-fluorine NMR chemical shifts [18] in monosubstituted benzenes where the substituents are analogous in structure.

The modified CNDO/2 calculated electron densities do seem therefore to be reasonable and consistent internally if not in absolute magnitude.

On the basis of the preceding discussion, we would expect to find first of all a linear relationship between observed and *para*-H NMR chemical shifts calculated on the basis of charge density, and secondly parallel *para*- and *meta*-H NMR chemical shifts. If magnetic anisotropies of the BX_2 substituents were constant *ortho*-H NMR shifts might also be a linear function of carbon charge density charges.

Observed and calculated aromatic hydrogen NMR chemical shifts of the phenylboranes are compared in Table 4. The original *ortho* and *meta* assignments [19] of phenyldichloro- and phenyldifluoro-borane have been interchanged on the basis of the *ortho* shifts of IIIa–IIIb, and the downfield chemical shifts of *ortho* relative to *meta* and *para* hydrogens in analogous molecules such as benzaldehyde, nitromethane and the phenyldimethylcarbonium ion [17]. The NMR chemical shifts of the piperidine complex of IIIa serve as useful refer-

TABLE 4

OBSERVED AND CALCULATED HYDROGEN NMR CHEMICAL SHIFTS, δ (ppm), OF MONOPHENYLBORANES RELATIVE TO BENZENE^{a,b}

Compound	δ (<i>Ortho</i>)		δ (<i>Para</i>)		δ (<i>Meta</i>)	Primary ref. and solvent
	obsv.	calcd.	obsv.	calcd.	obsv.	
IIIa	0.90	0.57	(0.33)	0.39	(0.33)	ext. TMS, neat
IIIb	0.60	—	—	—	0.03	ext. TMS CCl ₄
IIIc	—	—	—	—	-0.58	ext. TMS, neat
IIIa · Pip ^c	-0.02	—	-0.02	—	-0.02	ext. TMS CS ₂
PhBCl ₂ ^d	(1.48)	0.82	(1.48)	0.69	0.83	ext. TMS, neat
PhBF ₂ ^d	(0.28)	0.66	(0.28)	0.38	-0.14	ext. TMS, neat
PhB(OR) ₂ ^e	(0.23)	0.27	(0.23)	0.14	(0.23)	int. TMS, DCCl ₃

^a Values in parentheses are multiplets assigned to two or more sets of hydrogens. ^b Benzene ref: external TMS 7.27 ppm; int. TMS 7.24 ppm. ^c Piperidine adduct. ^d Ref. 14 *o* and *m* assignments interchanged. ^e Ref. 18, R is methyl.

ence points for the effect of removal of the boron vacant $2p$ orbital from conjugation with the aromatic ring. The calculated *ortho*- and *para*-hydrogen chemical shifts are based on a shift factor [20] of 10.7 ppm per unit of π charge at carbon and benzene chemical shifts of 7.27 ppm (external tetramethylsilane) [21] or 7.24 ppm (internal tetramethylsilane). The calculated chemical shifts due to charge density at carbon are given by the expression $(10.7 \delta(Q_\pi) - \delta_{\text{PhH}}^{\text{TMS}})$ (Table 3).

As may be seen from Table 4 there is fair qualitative agreement between the calculated and experimental *para*- and *ortho*-hydrogen NMR shifts of the boryl-substituted benzenes. No linear relationships between chemical shifts and calculated charge density changes at carbon or hydrogen, Table 3, exist however, The downfield chemical shifts of PhBCl₂ hydrogen are much larger than would be expected solely on the basis of changes in calculated charge density, whereas by contrast those of PhBF₂ are at unexpectedly high fields. Indeed the *meta* hydrogens in the NMR spectrum of IV, PhBF₂, are uniquely upfield shifted with respect to benzene itself, a result unaccounted for in the CNDO/2 charge density model.

Taken together, the NMR and PES results for IV are consistent with a model in which the predominating interaction mechanisms for the BF₂ group are σ -electron releasing inductive and cation destabilizing field effects. The field effect alone could qualitatively account for the development of positive charge at the *para* (and *ortho*) carbons and therefore the observed *ortho*- and *para*-H NMR downfield shifts. The NMR spectrum of phenyldifluoroborane may be an excellent example of the appearance of the "perfluoro effect", first recognized in the PES of aryl and alkenyl fluorides, wherein the strong electron withdrawing effects of fluorine in a σ -orbital system are almost completely counterbalanced by fluorine $2p$ π back bonding to orbitals of π symmetry [22]. The resulting vacant BF₂ π^* orbital then interacts only weakly with the benzene π system in terms of p π bonding.

A difficulty with the foregoing rationalization of the upfield position of the *meta* hydrogens of IV, is that the inductive effects should be even larger in the case of PhB(OMe)₂ for which the *meta* hydrogen are by contrast downfield shif-

ted with respect to benzene. We therefore conclude, that changes in carbon charge density, at least as calculated by the modified CNDO/2 method, are of limited utility in rationalizing the ^1H NMR spectra of phenylboranes, and conversely great caution must be exercised in interpreting the ^1H NMR spectra of phenyl-(or vinyl)-boranes as evidence in favor of, or opposed to, simple models for BX_2 interactions with π systems.

Ultraviolet spectra. The π -molecular orbitals of PhBX_2 may be generated by a perturbation model which unites the phenyl and boryl (BX_2) fragments utilizing the six π -molecular orbitals of benzene and the three of BX_2 (or single vacant boron $2p$ where R is alkyl). The interaction between the vacant BX_2 $b_1 \pi^*$ orbital and the $b_1 \pi^*$ orbital of the vacant degenerate benzene pair, serves to create two vacant $\pi^* b_1$ molecular orbitals, one of which is lower in energy than the original degenerate benzene π^* pair. This low energy $b_1 \pi^*$ molecular orbital of PhBX_2 will be largely localized on BX_2 or within the benzene ring, depending upon whether the initial BX_2 $b_1 \pi^*$ function was respectively lower or higher in energy than the benzene degenerate pair (see Fig. 6), according to the well known principles of perturbation theory [2,4].

Excluding high energy transitions associated with X, the principle effect of BX_2 substitution on the ultraviolet spectrum of benzene then is to introduce, in addition to the usual $^1\text{L}_b$, $^1\text{L}_a$ and $^1\text{B}_{a,b}$ transitions, two new π electronic transitions in the near UV ($b_1 \rightarrow b_1$, $^1\text{A}_1(\text{CT})$ and $a_2 \rightarrow b_1$, $^1\text{B}_2(\text{CT})$) which have as their origin intramolecular electron transfer to BX_2 .

After configuration interaction, CI, the $^1\text{L}_b$ transition is expected and observed at lowest energy in the UV spectra of monophenylboranes, PhBX_2 [2]. The second lowest energy transition is then to a $^1\text{A}_1$ state and may be characterized as either $^1\text{L}_a$ or CT depending on the dominant character of the $b_1 \pi^*$ orbital. We have previously demonstrated [2] that this $^1\text{A}_1$ transition will be charge transfer after CI only when the initial BX_2 $b_1 \pi^*$ orbital is lower in energy than the benzene π^* pair in the perturbation model.

Because of a less favorable charge distribution in the benzene ring after electron transfer to BX_2 , the $^1\text{B}_2(\text{CT})$ configuration is about one eV higher in energy than the $^1\text{A}_1(\text{CT})$ configuration [23]. Strong configuration interaction may then be expected to distribute the $^1\text{B}_2$ CT character into the final $^1\text{L}_b$, $^1\text{B}_2(\text{CT})$ and $^1\text{B}_b$ states in roughly equal proportions [4].

In any semiempirical SCF calculation of PhBX_2 transition energies the assignment of the first $^1\text{A}_1$ transition as $^1\text{L}_a$ or CT is found to be a sensitive function of the choice of energy for the boron $2p$ function [2]. Not unexpectedly then, there has been some disagreement [2,3,4] in the past concerning the most appropriate characterization of this transition in the UV spectra of PhBX_2 . However, we have previously shown [2] that in π only PPP-SCF-CI or variable electronegativity calculations, reasonable choices of boron $2p_z$ orbital valence state energies equal to or less than -2.0 eV lead to the $^1\text{L}_a$ and $^1\text{A}_1(\text{CT})$ assignments for $\text{PhB}(\text{OR})_2$ and PhBR_2 as indicated in Table 2.

The data in Table 2 represent the first reported UV spectra of monoaryldialkylboranes, and it is especially satisfying that the predicted [2] transition energies, (4.68 B_2 ; 5.30 $^1\text{A}_1(\text{CT})$; $^1\text{B}_2$ 6.16; $^1\text{A}_1$ 6.27), made in the absence of prior knowledge, now agree so well with the experimental result. The CNDO/2 calculated boron $2p$ mixing coefficient in the lowest vacant π^* orbital of energy, -0.334 eV, is 0.6100.

A simple proportionality constant [23] of 0.72 exists between differences in UV charge transfer transition energies of triarylboranes and aryl group PES ionization energies. The PES determined difference in first I^v between benzene (Jahn-Teller corrected) and toluene of 0.46 eV leads to a predicted 0.33 eV red shift of the $^1A(CT)$ transition from IIIa to IIIb. The observed shift is 0.27 eV.

A second prediction made by our earlier calculations [2] was that twisting of the phenyl π system 45° out of coplanarity with the vacant boron $2p$ orbital should lead to an increase of 0.4 eV in the $^1A_1(CT)$ transition energy. There should also be substantial loss in intensity as in the limit of a 90° rotation, the $^1A_1(CT)$ transition becomes 1A_2 symmetry forbidden when the vacant boron $2p$ orbital lies in the plane of the benzene ring.

In the mesityl-9-bbn (IIIc), the *ortho*-methyl groups are strongly eclipsed by the bridge head bicyclononane C-H groups and steric models indicate that in IIIc a twisted geometry should be preferred. Appropriately then, the UV spectrum of IIIc consists of a typically benzenoid 1L_b band with sharp vibrational structure (λ_{max} 253 nm, 4.89 eV), perched on the tail of a broad band descending from a shoulder near λ_{max} 216 nm. Assignment of this shoulder (216 nm, 5.74 eV) or the maximum at 6.18 eV in the UV spectrum of IIIc is not straightforward. Previous calculations [4] suggest correlation with $^1A(CT)$ and $^1B_\alpha$, but the $^1B_\alpha$, but the $^1A_1(CT)$ transition of IIIa and IIIb may be buried beneath what are now the $^1B_2(CT)$ and $^1B_\alpha$ transitions of IIIc.

In any case the results are very analogous to the effects of *ortho* substitution on the UV spectra of *N,N*-dimethylaniline [24] where the charge transfer occurs in the reverse sense from nitrogen to phenyl ring.

Finally, complexation of the boron by piperidine with the removal of the boron vacant $2p$ function causes the disappearance of the 5.27 eV charge transfer transition, and reappearance of the typical vibration structure of the 1L_b transition.

Both the validity and utility of an intramolecular charge transfer description of the second and intense UV transition in triaryl- and arylalkyl-boranes would not seem well established, and the ultraviolet spectrum of IIIb is given in Fig. 4 as typical of a monoaryldialkylborane. The red shift, increase in intensity, and loss of vibrational structure in the 1L_b transition evident in Fig. 4 may be attributed to charge transfer character acquired by mixing with the $^1B_2(CT)$ configuration.

The results of PES and the modified CNDO/2 calculations in which the lowest vacant π^* orbital at 0.2442 eV has a negligible boron $2p$ atomic mixing coefficient serve to confirm earlier characterizations [2,25] of the 5.5 to 5.6 eV transition of phenylboronic acids and their esters as $^1L_\alpha$ rather than charge transfer [2]. Strong boron-oxygen $2p-\pi$ bonding interactions place the vacant $b_1 \pi^*$ orbital of $B(OR)_2$ higher in energy than the benzene π^* orbitals. It is only the third lowest energy π^* orbital of phenylboronic acid at 2.37 eV which has a large boron $2p$ contribution (0.7435).

The UV transition energies of phenyldichloro- and phenyldifluoro-borane have been reported, by Armstrong and Perkins [26], as being virtually identical, with intense transitions near 5.24 and 5.44 eV. Unfortunately the spectra and details of the conditions under which the spectra were obtained were not provided, and the reported transition energies are suspiciously close to that of the

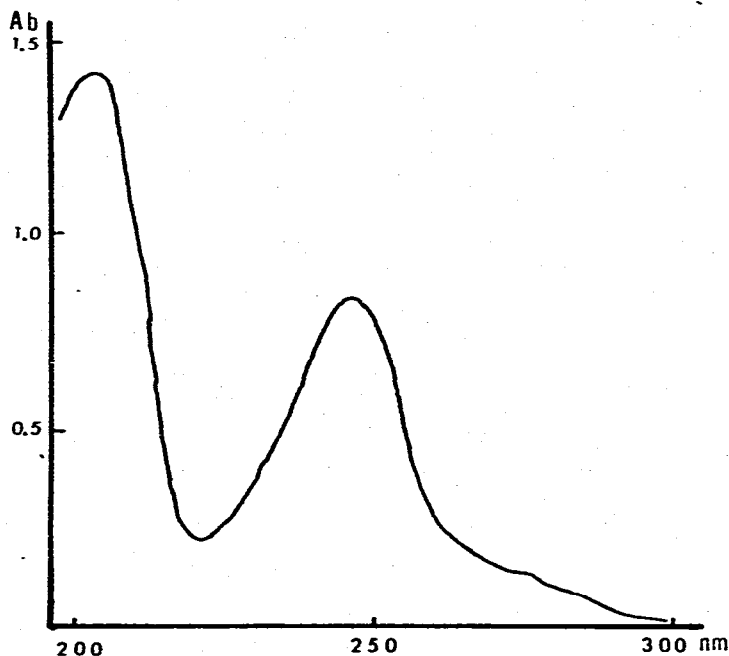


Fig. 4. The ultraviolet spectrum of β -*p*-tolyl-9-borabicyclo[3.3.1]nonane in hexane: 1.03×10^{-3} molar.

equilibrium mixture of phenylboronic acid and its anhydride [27] which would result from hydrolysis of the phenylboron halides in a typical hydrocarbon solvent such as heptane unless extreme precautions are taken to obtain and maintain a dry solvent. (To obtain the UV spectrum of phenylboronic acid anhydride in hexane, Santucci and Triboulet [27] required the use of vacuum line techniques in which the solvent was distilled from phosphorous pentoxide.) As normally used, saturated hydrocarbon solvents contain more than enough water to hydrolyze a 10^{-4} to 10^{-5} molar solution of boron anhydride or halide.

We have circumvented this problem by obtaining the UV spectra of I and IV in the gas phase utilizing high vacuum line water and oxygen free techniques (Fig. 5). Since the gas phase spectra of I and IV are quite dissimilar and show no transitions near 5.44 eV we believe the spectra reported by Armstrong and Perkins to be incorrect.

The all valence shell modified CNDO/2 calculations lead to very different interpretations of the phenyldichloro- and phenyldifluoroborane UV spectra. Although the replacement of alkyl by chlorine at boron in III has the effect of decreasing the b_1 π -orbital energy by as much as 0.4 to 0.6 eV, the calculated lowering of the BCl_2 b_1 π^* orbital energy from -0.334 to -1.260 eV, as a result of the strong chlorine inductive effect on the boron $2p$ orbital energy, readily accounts for a net decrease in the first 1A_1 transition energy and an increase in its charge transfer character. The boron $2p$ mixing coefficient in the lowest π^* orbital of I has increased to 0.6796. This leads to a new assignment of the second UV transition in II as ${}^1A_1(\text{CT})$ rather than 1L_a as indicated by Armstrong

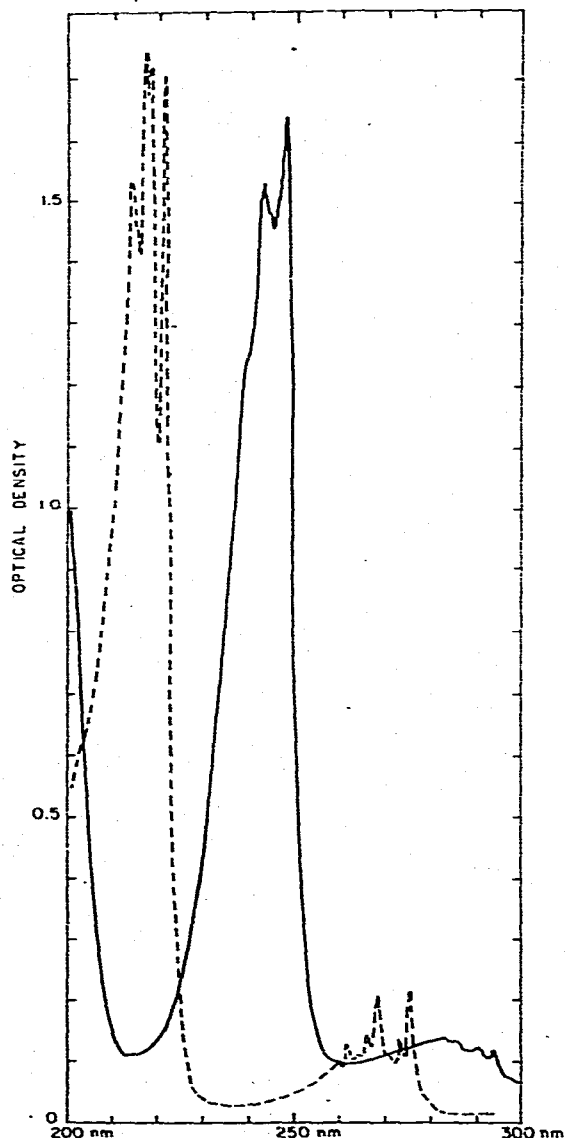


Fig. 5. Ultraviolet spectra of PhBCl₂ (solid line —) and PhBF₂ (dashed line - - -) in the gas phase.

and Perkins [26], whose calculated transition energies for I are now in error by as much as 0.6 eV. The absence of pronounced vibrational structure in even the gas phase spectrum of the PhBCl₂ ¹L_b transition suggest strong mixing with the ¹B₂(CT) configuration (Fig. 4).

The result of the "perfluoro effect", commented upon in the NMR discussion, in the BF₂ substituent is to place the vacant *b*₁ π* orbital of BF₂ higher in energy than the benzene degenerate π* pair. As a result, in the modified CNDO/2

calculation the lowest energy (-0.393 eV) π^* orbital of phenyldifluoroborane (IV) has a negligible contribution from boron, and it is only the 3rd lowest π^* orbital at 1.69 eV which contains a large boron $2p$ contribution (0.763). This result is consistent with the experimental observations from PES spectra of BF_3 and $\text{B}(\text{OMe})_3$, that B-F π -bonding interactions are actually greater than B-O π -bonding interactions [28]. In sharp contrast to the conclusion reached for I, the second transition in the ultraviolet spectrum of phenyldifluoroborane can be best characterized as 1L_a transition energy of IV is 0.7 eV greater than the ${}^1A(\text{CT})$ transition energy of I, although the differences in their b_1 π -ionization energies are only 0.2 eV. Furthermore there is a reemergence of the typical vibrational structure in the 1L_b transition of IV as compared to I. Thus, the UV spectrum of phenyldifluoroborane is more comparable to that of phenylboronic acids and esters than phenyldichloroborane, Table 2, and there is very good agreement between the observed transition energies, and those calculated by Arm-Armstrong and Perkins [26] in a π electron only LCAO-MO-PPP-SCF-CI calculation (1L_b 4.76; 1L_a 5.58 eV).

Concluding comments. The perturbation by substituted boryl groups (BX_2) of the benzene electronic structure, and by implication the electronic structure of other unsaturated hydrocarbon moieties, is determined by the competition between X and the hydrocarbon π system for the vacant boron $2p$ orbital as well as electronegativity differences which produce a reorganization of σ electron density.

The substituents X studied here are examples of four types which may be categorized as follows with respect to boron: (1) strongly electronegative and π bonding, e.g. F; (2) moderately to weakly electronegative but strongly π bonding, e.g. OH, OR, SR, NR_2 , etc.; (3) both weakly electronegative or electropositive and π bonding, e.g. alkyl, silyl, PR_2 , H, etc. and (4) strongly electronegative but weakly π bonding, e.g. Cl, Br, CF_3 , etc.

Substituents in categories 1 and 2 probably will not give rise to low energy charge transfer transitions, although the normal $\pi \rightarrow \pi^*$ transitions of the substituted hydrocarbon will be shifted to lower energy. On the other hand, substituents in categories 3 and 4 may be expected to give rise to low energy charge transfer transitions in aromatic, alkenyl and alkynyl systems.

A combination of inductive, field and resonance effects of BX_2 substituents in categories 1 and 4 should lead to increases in ionization energies, particularly those originating from π orbitals, and except for BF_2 large downfield hydrogen NMR chemical shifts.

Electron releasing σ inductive effects should be important for substituents in categories 2 and 3, producing for example decreases in ionization energy, particularly if the ionization is associated with an orbital nodal at the substituent site. Compensating π -electron-withdrawing resonance effects may however increase some ionization energies and downfield H NMR chemical shifts of unsaturated hydrocarbons substituted by BX_2 groups in category 3. Substituents in category 4 should produce the largest effects on chemical and spectroscopic properties to be associated with net inductive electron withdrawal and boron $2p-\pi$ bonding to the hydrocarbon unsaturated system.

These points and the effect of BX_2 substitution on benzene π -orbital energies are graphically summarized in Fig. 6.

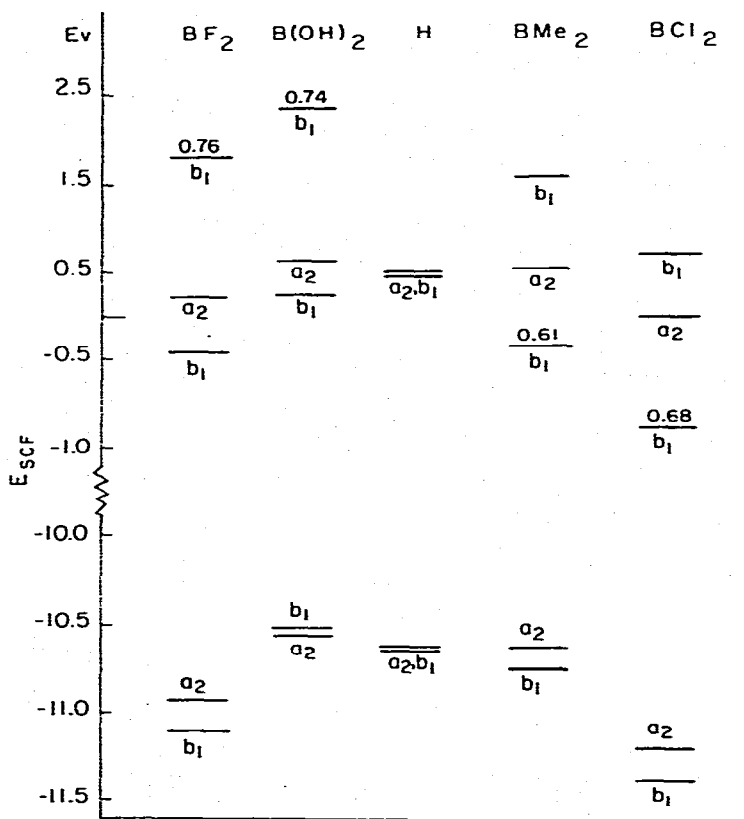


Fig. 6. The effect of boryl, BX₂, substitution on benzene π -orbital energies and boron 2p atomic orbital mixing coefficients in molecular orbitals. Numbers above b₁ π^* orbitals indicate the boron 2p atomic orbital mixing coefficient in that orbital.

Experimental

Calculations

Modified CNDO/2 calculations were carried out at the University of Frankfurt Computing Center using the program modified CNDO/2 made available by the research group of Professor Hans Bock. Details of the program are published elsewhere [6–9]. Bond angles and bond lengths were taken from ref. 29.

Compounds

Phenyldichloroborane (I). Compound I was obtained commercially and purified by distillation under an inert atmosphere, b.p. 177°C. All manipulations were carried out with the exclusion of oxygen and moisture by vacuum line techniques. Gas phase UV λ_{\max} , 1st band 282.5, 289.7, 292.9 nm; 2nd band 240(sh), 242.8, 247.9 nm.

Phenyldimethoxyborane (II). II was prepared by the addition of phenylboron dichloride to an equimolar amount of sodium methoxide in anhydrous methanol

at ice bath temperatures, followed by fractional distillation of the product under dry nitrogen, after filtration to remove sodium chloride.

β -Phenyl-9-borabicyclo[3.3.1]nonane (IIIa). This compound was synthesized by the method of Brown and Rogic [31] from the reaction of phenyllithium with 9-borabicyclo[3.3.1]nonane followed by decomposition of the resultant borohydride with methane sulfonic acid.

After a preliminary vacuum distillation under nitrogen, the final product was purified by vacuum distillation under nitrogen on a spinning band column (b.p. 105°C/0.3 Torr) into ampules which were sealed for later use. Gas phase chromatographic analysis and infrared spectroscopic analysis indicated the varying presence of one or two percent by weight biphenyl impurity in the samples. This did not require correction of the observed UV absorption maxima.

β -p-Tolyl-9-borabicyclo[3.3.1]nonane (IIIb). Compound IIIb was synthesized from *p*-tolyllithium by the procedure used for IIIa, b.p. 72°C/0.05 Torr. Purification was by repetitive fractional distillation under nitrogen, after which no significant amounts of bitolyl were detected.

β -Mesityl-9-borabicyclo[3.3.1]nonane (IIIc). IIIc was synthesized from mesityllithium by the procedure used for IIIa, b.p. 120°C/0.25 Torr. Purification was by repetitive fractional distillation under nitrogen.

Phenyldifluoroborane (IV). IV was synthesized from I and resublimed antimony trifluoride, by the method of McCusker and Kakowski [31] and distilled at atmospheric pressure under argon, b.p. 95°C. Gas phase λ_{\max} 1st band 261.9, 266.7, 268.7, 273.5, 275.8 nm; 2nd band 214.2, 215.0, 217.4, 218.5, 221.8 nm.

Ultraviolet spectra of IIIa, IIIb and IIIc. These were determined in hexane which had been dried over phosphorus pentoxide and degassed by high vacuum line techniques. Spectra were recorded on a Cary Model 14. Solutions were prepared and cells were filled in an oxygen free inert atmosphere glove box. After running UV spectra, solutions were exposed briefly to air and changes in UV spectra appropriate for oxidation of the organoborane were noted. The ultraviolet spectra of the pyridine adduct of IIIa was determined in acetonitrile. The UV spectra of I and IV were obtained in the gas phase by filling the gas cells on a greaseless high vacuum line with vapor at ambient room temperature followed by reduction of the pressure to a convenient level for obtaining the spectra. Facilities were not available for measurement of the final pressure.

Photoelectron spectra. PES were determined at the Institute for Inorganic Chemistry, University of Frankfurt on a Perkin-Elmer Model 18 using a heated inlet. Spectra were referenced to argon 15.75 eV and methyl iodide 9.54 eV.

Nuclear magnetic resonance spectra. The NMR spectra of IIIa and IIIc were run on the pure liquid samples without solvent, that of IIIb in carbon tetrachloride. Chemical shifts are reported as ppm downfield from external tetramethylsilane. NMR spectra were determined on a 60 MHz JEOL spectrometer.

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