arise solely from decreases in the N–C_α bond orders. Charge polarization shifts are all downfield as the charge densities in these compounds have not been decreased below the minimum point in the curve given in Figure 4.

It is obvious that an additional proton in the protonated species is going to affect the whole molecule and not just the nitrogen atom. For this reason, the effect of various intermediate values of Δ_{NH} upon the chemical shift were investigated. Values of Δ_{NH} between 0 and 1.0 in steps of 0.1 were employed and the best visual fit, given in Figure 8, was realized for $\Delta_{NH} = 0.3$ and $\Delta_N = 0$. The predicted C-2 shift in diprotonated pyrimidine is significantly improved by the choice of this intermediate value as is also the carbon resonance in diprotonated pyrazine and the C-2 shift in monoprotonated pyrimidine. The calculated charge densities and bond orders in diprotonated pyrimidine are given in Figure 7 for $\Delta_{NH} = 0.3$ to allow a convenient comparison with the results of the two previous calculations using $\Delta_{NH} = 0$ and $\Delta_{NH} = 1.0$. It is felt that these new charge densities are more reasonable than those observed for the case of $\Delta_{NH} = 1.0$. Furthermore the predicted shift values in Figure 8 for the parent compound and their protonated derivatives continue to reflect the correct α-protonation parameter, and at the same time, the scatter in the plot is reduced from that found in Figures 5 and 6. In all three calculations the predicted value for C-4 in the pyridinium ion deviates significantly from the agreement line. Here we see a failure of the HMO approach to properly characterize the long-range polarization effects in the *para* position which are suggested experimentally as being important by the relatively large γ-protonation parameter. To properly treat polarization effects at β and γ positions one should vary the effective electronegativities of all atoms in the ring in some self-consistent manner. Qualitatively one can see how such a treatment would improve Figure 8. If all β positions were made slightly more "electronegative" (larger ionization potential), their charges would increase and the predicted shift values for these atoms would move upfield and onto the line. Likewise C-4 in pyridine hydrochloride and C-4,6 in pyrimidine and its cationic species would have charge removed and shift down onto the line. Such additional quantum mechanical improvements, however, were considered to be beyond the scope of this study as the essential chemical shift features have been discussed and identified with certain important aspects of the electronic structure of these molecules. It is felt, however, that theoretical workers interested primarily in refined molecular wave functions of the SCF variety will want to check their results against carbon-13 chemical shift data. σ and π densities and bond orders are given in Figure 9 for the $\Delta_N = 0$ and $\Delta_{NH} = 0.3$ approximation for all the molecules considered in this study. In every instance one notes a charge depletion at α carbons with protonation. This result is at variance with the calculations of Adam and Grimson[11] in which an increase in electronic charge at α carbons was found and then proposed as an explanation for the upfield protonation shifts. The change in bond order terms is suggested as a preferable explanation of the upfield α-protonation parameter.

Acknowledgment. This investigation was supported primarily by the Public Health Service under Grant GM 0-8521 awarded by the National Institutes of Health. The University of Utah Computer Center allowed us complimentary time to complete a large part of our calculations. Our gratitude is extended to Professor R. Hoffmann for making his program available through the Quantum Chemistry Program Exchange.

New Heteroaromatic Compounds. XXVII.[1] Boron-11 Chemical Shifts of Some Heteroaromatic Boron Compounds[2]

Franklin A. Davis,[3] Michael J. S. Dewar, and Richard Jones[3]

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received September 1, 1967*

Abstract: ^{11}B nmr spectra have been measured for 19 of the heteroaromatic boron compounds whose preparation was reported in an earlier paper of this series. The results provide further evidence that these compounds are indeed aromatic, and also throw light on the relationship between chemical structures and ^{11}B chemical shifts.

Previous papers of this series[1,4] have described the preparation and properties of a number of novel heteroaromatic compounds, isoconjugate with "normal" aromatic systems and derived from them by replacing pairs of carbon atoms with boron and nitrogen, or boron and oxygen. The physical and chemical properties of these novel compounds seemed to indicate that they too are aromatic; for example, they show a resistance to oxidation or hydrolysis of a different magnitude from that displayed by organoboron compounds of more conventional types.

It seemed to us that a study of the ^{11}B chemical shifts in the nmr spectra of these boron-containing heteroaromatics would not only provide additional informa-

---

[1] Part XXVI: K. M. Davies, M. J. S. Dewar, and P. Rona, *J. Am. Chem. Soc.*, **89**, 6294 (1967).

[2] This work was supported by a grant from the Robert A. Welch Foundation.

[3] Robert A. Welch Postdoctoral Fellow.

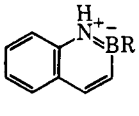
[4] See M. J. S. Dewar, *Progr. Boron Chem.*, 1, 235 (1964), and papers referred to in ref 1.

tion about the bonding in them, but might also lead to a better understanding of the factors that determine ^{11}B resonance frequencies. We have therefore measured the ^{11}B nmr spectra of compounds I–X, the preparations of which have been described in earlier papers of this series, apart from Ib whose preparation will be reported elsewhere.[5] The esters Ib, IIIb, IVb, and VII were prepared *in situ* by dissolving the corresponding B-hydroxy derivatives in ethanol; compounds of this type undergo exchange of RO groups attached to boron very rapidly.[4] The ^{11}B nmr spectra were measured by the procedures described previously.[6] The results are listed in Table I. Note that the chemical shifts appear to be almost independent of the solvent, so that the chemical shifts of different compounds can be compared even if the spectra were measured in different solvents.

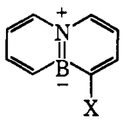
Table I. ^{11}B Chemical Shifts for Compounds I–X

Compd	Ref	Solvent	Chemical shift[a]	Line width,[b] Hz
Ia	*c*	Carbon disulfide	−37.5	97
Ib	*c*	Ethanol	−29.7	223
IIa	*d*	*n*-Hexane	−28.4	85
		Acetic acid	−27.9	113
IIb	*e*	Acetic acid	−27.5	175
IIIa	*f*	Benzene	−36.5[g]	140
		Ethanol	−38.5[g]	247
		Acetic acid	−37.5[g]	305
IIIb	*f*	Acetic acid	−30.0[g]	290
IIIc	*h*	Acetic acid	−37.5[g]	308
IVa	*i*	Benzene	−39.0	250
IVb	*i*	Ethanol	−29.3[j]	221
		Carbon disulfide	−29.5[j]	266
IVc	*i*	Tetrahydrofuran	−36.5	226
IVd	*i*	Benzene	−33.7	224
		Carbon disulfide	−34.4	178
IVe	*k*	Carbon disulfide	−41.9	350
V	*l*	Carbon disulfide	−38.1	181
VI	*l*	Carbon disulfide	−31.0	142
		Benzene	−30.4	150
VII	*m*	Acetonitrile	−27.7	115
VIII	*m*	Carbon disulfide	−31.9	111
IX	*n*	Ethanol	−30.0	290
Xa	*n*	Ethanol	−28.8	233
Xb	*n*	Carbon disulfide	−36.9	127

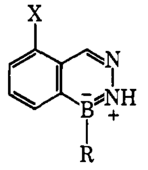
[a] In ppm, relative to boron trifluoride etherate. Estimated error ±0.5 ppm for line widths <300 Hz, ±1 ppm for wider lines. [b] At half-height; estimated error ±5%. [c] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959). [d] M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Amer. Chem. Soc.*, **86**, 5698 (1964). [e] Reference 5. [f] M. J. S. Dewar and R. C. Dougherty, *J. Amer. Chem. Soc.*, **86**, 433 (1964). [g] Values taken from part XXV.[6] [h] M. J. S. Dewar and J. L. Von Rosenberg, *J. Amer. Chem. Soc.*, **88**, 358 (1966). [i] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958). [j] This value was previously reported as −36.8. The reason for this discrepancy is not known, but is believed to be due to a fault in the frequency counter used in the previous determination. No other discrepancy was observed between the values in Table I and in ref 6. [k] M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959). [l] G. C. Culling, M. J. S. Dewar, and P. A. Marr, *J. Amer. Chem. Soc.*, **86**, 1125 (1964). [m] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958). [n] M. J. S. Dewar and R. Dietz, *ibid.*, 1344 (1960). [o] Reference 6.



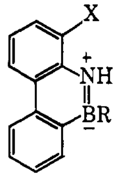
Ia, R = CH$_3$
b, R = OEt



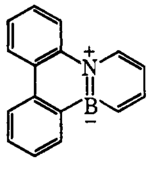
IIa, X = H
b, X = Br



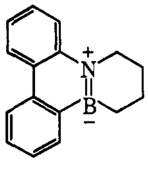
IIIa, R = CH$_3$; X = H
b, R = OEt; X = H
c, R = CH$_3$; X = Br



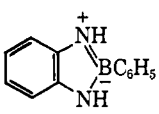
IVa, R = CH$_3$; X = H
b, R = OEt; X = H
c, R = Ph; X = H
d, R = Cl; X = H
e, R = CH$_3$; X = NO$_2$



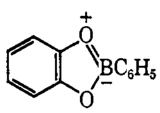
VI



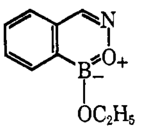
V



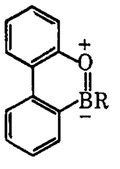
VII



VIII



IX



Xa, R = OEt
b, R = Cl

Discussion

There is compelling evidence[7] that ^{11}B chemical shifts are largely controlled by the degree of occupancy of the vacant p_z orbital on boron. Thus compounds containing trivalent boron absorb at much lower fields than do quadrivalent boron complexes, and the shift to low field is greatest for compounds in which trivalent boron is attached to groups lacking p or π electrons. Trimethylboron, for example, has the lowest known chemical shift (−86.4 ppm[8]) relative to boron trifluoride etherate (EBT),[9] while compounds in which —E groups are attached to boron absorb at much higher fields (*e.g.*, −18.1 ppm for trimethyl borate[7]).

If this were the sole factor involved, one would expect the chemical shifts of boron to depend on the π-donating ability of the groups attached to it; in particular, one would expect dimethylamino to be more effective than methoxy, Me$_2$N being a more active —E group than MeO. In aliphatic boron compounds, however, the reverse seems to be the case; thus tris(dimethylamino)boron absorbs at much lower field (−27.1 ppm[10]) than does trimethyl borate. A similar anomaly is seen in the boron trihalides. Thus boron trifluoride absorbs at much higher field (−11.6 ppm[8]) than either trimethyl borate or tris(dimethylamino)boron, although fluorine is a very much poorer donor for forming dative π bonds than either nitrogen or oxygen. Again, the absorption of boron trichloride (−47.4 ppm[8]) appears far upfield from that for triphenylboron (−60.8 ppm[11]), although chlorine is more electronegative than carbon and a less effective π-donating agent than phenyl. The same is true even

---

(5) M. J. S. Dewar and R. Jones, submitted for publication.

(6) M. J. S. Dewar and R. Jones, *J. Amer. Chem. Soc.*, **89**, 2408 (1967).

(7) P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 476.

(8) W. D. Phillips, H. C. Miller, and E. L. Muetterties *J. Amer. Chem. Soc.*, **81**, 4496 (1959).

(9) All chemical shifts reported in this paper are given relative to EBT.

(10) J. K. Ruff, *J. Org. Chem.*, **27**, 1020 (1962).

(11) C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962).

more forcefully for boron tribromide (−40.9 ppm[8]) and triodide (+5.1 ppm[8]), the latter absorbing at higher field even than some quadricovalent boron compounds (*e.g.*, tetrahydrofuran–BH_3, +0.8 ppm[8]). Unless and until these very large anomalies can be explained, it would be futile to try to use ^{11}B nmr as a quantitative measure of π bonding to boron.

We believe that a second major factor in determining ^{11}B chemical shifts is the presence of additional pairs of unshared electrons on the atoms adjacent to boron, over and above those needed for π bonding. A similar effect has been observed[12] in the ^{19}F nmr spectra of aryl fluorides, where a substituent carrying p or π electrons in a position *ortho* to fluorine produces an upfield shift of *ca.* 10 ppm. Dewar and Kelemen[12] interpreted these results in terms of the Karplus–Goodman theory of chemical shifts in π systems.[13] If their final expression is simplified by neglecting differential overlap, it can be shown that the chemical shift (δv_i) of the nucleus of atom i is given by

$$\delta v_i = Aq_i + \sum_{j \neq i} Bq_j/r^3{}_{ij} \qquad (1)$$

when q_k is the π-electron density of atom i, r_{ij} is the internuclear distance between atoms i and j, and A and B are constants. In the case of σ-bonded systems, a similar expression should hold, with q_h now representing the total electron density on atom k. Atoms (j) with unshared pairs of electrons adjacent to boron should then make especially large contributions to the chemical shift, q_j being large and r_{ij} small. On this basis, one can account for the observed pattern of shifts in the series $B(NMe_2)_3$, $B(OMe)_3$, BF_3, BCl_3, BBr_3, and BI_3 in terms of two distinct factors: first, π bonding, which decreases along the series; second, the lone pair effect, which increases along the series.

The compounds listed in Table I all absorbed at about the field expected for analogous open-chain compounds; for example, the chemical shifts of IX and Xa (−30.0 and −28.8 ppm, respectively) are very similar to that of diethyl phenylboronate ($PhB(OEt)_2$, −28.6 ppm[8]). While, however, oxygen appears to be more effective than nitrogen in shifting the ^{11}B resonance upfield in the aliphatic series (*cf.* $B(NMe_2)_3$, −27.1 ppm;[10] $B(OMe)_2$, −18.2 ppm;[8] $PhB(NMe_2)_2$, −32.4 ppm; $PhB(OEt)_2$, −28.6 ppm[8]), this is no longer true when the boron atom forms part of an aromatic ring. In cases where the boron-containing ring is six membered, nitrogen and oxygen appear to be equally effective (*cf.* IVb with Xa, and IIIb with IX), while in the compounds with five-membered rings (VII and VIII), it is the nitrogen-containing analog that absorbs at higher field. If our arguments are correct, this must imply that π bonding between boron and the heteroatom adjacent to it in the ring is more important in compounds I–X than it is in open-chain analogs, as of course would be expected if the former are aromatic[4] since here aromaticity depends on enchanced π bonding to boron.

The remaining results in Table I also follow the expected pattern. Thus introduction of a nitro group into the 8 position of 10-methyl-10,9-borazarophenanthrene (*cf.* IVa with IVe) leads to a significant downfield shift (2.9 ppm); here mutual conjugation between the nitro and imino groups should reduce the ability of the latter to form a dative π bond to boron. One would on this basis also expect IVe to be less aromatic than IVa, as indeed appears to be the case.[4]

Further support for this interpretation is provided by a comparison of the relative effects of different groups attached to boron. Replacement of chloro by ethoxy leads to an upfield shift of 8.1 ppm in the boroxarophenanthrene series (X), but only 4.7 ppm in the borazarophenanthrene series (IV). Since the upfield shift is undoubtedly due to π bonding between oxygen and boron, such π bonding must be less efficient in X than in IV. Now π bonding to boron will be less facile, the greater the p-electron density on boron, and this in turn would be expected to be greater, the more aromatic the compound in question. Indeed, both theory and experiment indicate[4] that X is a less aromatic system than IV, as would be expected from our comparison of the corresponding >BOEt and >BCl derivatives.

One final point concerns the shapes of the ^{11}B nmr lines. All the signals were observed as singlets; this would be expected, since multiplets have been observed only for boron linked directly to hydrogen. The line widths at half-height are in accordance with the hypothesis[6] that charge symmetry about boron produces sharper lines. Thus the smallest line width was that for 10,9-borazaronaphthalene (IIa) and even monobromination to IIb led to a significant increase in line width. The line widths also seemed to increase with increasing solvent polarity (*cf.* the results for IIIa in Table I); this would be expected.[6] Polar solvents will tend to cluster round the polar heteroatoms and so lead to fluctuating electrostatic fields at the boron nucleus; the resulting quadrupole relaxation should lead to an increase in line width. For the same reason, line widths are systematically less for compounds with the grouping >BMe than those with the grouping >BOR; in the latter case solvation effects should again be more important.

---

(12) M. J. S. Dewar and J. Kelemen, submitted for publication.

(13) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961); F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963).