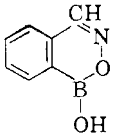
to be a more stable ring system than boroxarophenanthrene,[3] it seemed likely that aza analogs of I might show unusual properties. We now have prepared several derivatives of this novel ring system and find them to show typical aromatic stability.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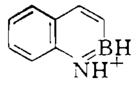
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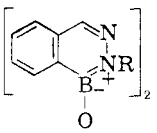
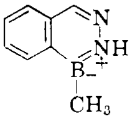

III


IV

a, R = H
b, R = Ph

Reaction at room temperature of *o*-formylphenylboronic acid in ether with anhydrous hydrazine in absolute ethanol yielded bis-(4,3-borazaro-4-isoquinolinyl) ether, IIIa, (80%) m.p. 234–234.5°; $\lambda_{\text{max}}^{\text{EtOH}}$ 300, 280, 269 mμ (log ϵ = 3.64, 3.85, 4.26); $\nu_{\text{max}}^{\text{KBr}}$ (salient absorptions) 3340, 1603, 1563, 1502, 1445, 1382, 772 cm.$^{-1}$; *anal.* Calcd. for $C_{14}H_{12}B_2N_4O$: C, 61.39; H, 4.42; B, 7.90; N, 20.46. Found: C, 61.29; H, 4.48; B, 7.61; N, 20.22. This compound may be recovered after boiling for 2 hours in 15% potassium hydroxide or concentrated hydrochloric acid. Aliphatic hydrazones or aromatic boronic acids would be destroyed by this treatment. IIIa is not deboronated by bromine in refluxing acetic acid. To our knowledge this is the first example of a borazaro compound containing more than two heteroatoms that withstands such treatment.

When *o*-formylphenylboronic acid was added to an aqueous solution of phenylhydrazine hydrochloride, bis-(3-phenyl-4,3-borazaro-4-isoquinolinyl) ether (IIIb) (m.p. 196–186.5°) separated immediately as colorless needles in almost quantitative yield; $\lambda_{\text{max}}^{\text{EtOH}}$ 303, 284 mμ (log ϵ = 4.38, 4.45); $\nu_{\text{max}}^{\text{KBr}}$ (salient absorptions) 3052, 1597, 1494, 1406, 1383, 1334, 893, 757, 695 cm.$^{-1}$; n.m.r. complex multiplet between 2.98 and 1.63 τ only; *anal.* Calcd. for $C_{26}H_{20}B_2N_4O$: C, 73.98; H, 4.78; B, 513; N, 12.33; mol. wt., 422. Found: C, 73.76; H, 4.74; B, 5.05; N, 12.50; mol. wt. (Rast), 399.

The spectra of these compounds and their hydrolytic stability suggest that the hetero ring is aromatic. The stability and ease of preparation of 4-methyl-4,3-borazaroisoquinoline (IV) provide additional evidence for this. Reaction of excess of methylmagnesium bromide with IIIa in ether at 0° yielded IV (60%), m.p. 97.0–97.5°; $\lambda_{\text{max}}^{\text{EtOH}}$ 301, 290, 265, 210 mμ (log ϵ = 3.53, 3.46, 3.88, 4.55); $\nu_{\text{max}}^{\text{KBr}}$ (salient absorptions) 3280, 1597, 1557, 1494, 1430, 1315, 1211, 902, 764 cm.$^{-1}$; n.m.r., sharp singlet, 9.10 τ, multiplets 2.90 to 1.67 τ (relative areas 3:5); *anal.* Calcd. for $C_8H_9BN_2$: C, 66.73; H, 6.30; B, 7.51; N, 19.46; mol. wt., 144; found: C, 66.56; H, 6.35; B, 7.54; N, 19.75; mol. wt. (Rast), 136. This compound is recovered unchanged from boiling 10% hydrochloric acid or boiling 10% potassium hydroxide and may indeed be purified by extracting an aqueous solution of its hydrochloride with ether, followed by neutralization to precipitate the neutral compound. 4-Methyl-4,3-borazaroisoquinoline reacts with fuming nitric acid in acetic anhydride, at −30°, to yield a mixture of boron containing compounds, the infrared and n.m.r. spectra of which indicate that they are probably nitro isomers of IV with predominant retention of the B methyl group.

Snyder and his co-workers were unable to characterize the reaction product of *o*-formylphenylboronic acid and 2,4-dinitrophenylhydrazine.[1] It seems likely in this case that the destabilizing effect of an electron withdrawing group adjacent to boron in the molecule promotes hydration to form the acyclic 2,4-dinitrophenylhydrazone.[4]

We also have re-examined the boroxaroisoquinoline (I). If I is aromatic, it should behave as a protic acid, in contrast to non-aromatic boron compounds which behave as Lewis acids.[2] We found that the ultraviolet spectrum of I showed a small bathochromic shift on solution in alkali, unaffected by addition of mannitol. This implies that I is indeed a protic acid.[5] However, attempts to replace the hydroxyl group in I by methyl have so far failed, suggesting that I is less aromatic than the nitrogen analog (III) (*cf.* ref. 3).

In the light of our studies of I and III, amides of *o*-aminophenylboronic acid which have been reported as semianhydrides[6] may well be 4,3-boroxaroquinolines. If so, the corresponding 4,3-borazaroquinolines should be stable.

This work has been supported by a grant from the National Science Foundation.

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(3) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960).

(4) Similar problems have been encountered in studies of 9,10-borazarophenanthrene (M. J. S. Dewar and P. M. Maitlis, *Tetrahedron*, **15**, 35 (1961).

(5) The ultraviolet spectrum of boronophthalide in ethanol shows a small hypsochromic shift on addition of alkali or mannitol and aromatic boronic acids behave likewise.

(6) C. G. Clear and G. E. K. Branch, *J. Org. Chem.*, **2**, 522 (1938); A. H. Soloway, *J. Am. Chem. Soc.*, **82**, 2442 (1960).

(7) Woodrow Wilson Fellow 1960–1961; National Science Foundation Predoctoral Fellow, 1961–1962.

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SUBSTITUENT EFFECTS. II. C^{13}-PROTON COUPLINGS IN CARBON sp^2 SYSTEMS[1]

Sir:

An additivity relation for C^{13}-proton couplings in substituted methanes was reported recently.[1] Gutowsky and Juan[2] have attempted to explain the additivity relation by means of a valence bond approach. These investigations, however, have been restricted to substituted sp^3 carbon atoms. The present communication reports some of our findings on substituted sp^2 carbon atoms.

For the substituted methanes, CHXYZ, the C^{13}-H coupling constants have been found[1] to obey the equation

$$J_{CH} = \Sigma\zeta_X. \tag{1}$$

where ζ_X is a numerical constant associated with substituent X, the sum being taken over all the substituents except the proton in question. Zeta

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(1) Part I, E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961).

(2) H. S. Gutowsky and C. S. Juan, *ibid.*, **84**, 307 (1962).

values obtained from the data of substituted methanes are directly related to J_{CH} of substituted aldehydes, XCHO. A plot of $J_{CH}(XCHO)$ *versus* ζ_x is a straight line with a slope = 4.01 and an intercept = 5.3, as determined by a method of least squares. Consequently, any J_{CH} of the substituted aldehydes can be predicted from the equation

$$J_{CH}(XCHO) = 5.3 + 4.01\,\zeta_x \tag{2}$$

Calculated and experimental coupling constants of various substituted aldehydes, along with corresponding zeta values, are presented in Table I.

TABLE I

CALCULATED AND OBSERVED C^{13}-H COUPLING CONSTANTS OF SUBSTITUTED ALDEHYDES

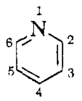
Substituent	ζ,[a] cps.	J_{CH}, cps., calcd.	J_{CH},[e] cps., exptl.	Diff.
$-H$	41.7	172.5	172[3]	−0.5
$-C(CH_3)_3$	40.6	168.1	168.6	−0.5
$-CH(CH_3)_2$	39.0[b]	161.7	168.9	+7.2
$-CH_2CH_3$	41.0[c]	169.7	170.6	+0.9
$-CH_3$	42.6	176.1	172.4	−3.7
$-C_6H_5$	42.6	176.1	173.7	−2.4
−*p*-C_6H_4Cl	42.9	177.3	175.2	−2.1
−*m*-C_6H_4Cl	43.4	179.3	177.5	−1.8
−*o*-C_6H_4Cl	44.1	182.1	182.8	+0.7
$-CCl_3$	50.6	208.2	207.2	−1.0
$-N(CH_3)_2$	47.6	196.2	191.2	−5.0
$-OCH_3$	54.6[4]	224.2	226.2	+2.0
$-OCH_2CH_3$	53.4[d]	219.4	225.6	+6.2
$-F$	65.6	268.4	267[5]	−1.4

[a] Calculated from data for methyl derivatives except where indicated otherwise, see ref. 1. [b] Calculated from $J_{CH}((CH_3)_2CH\mathbf{CH_2}Cl)$ = 147.3 cps. [c] Calculated from $J_{CH}(CH_3CH_2\mathbf{CH_2}Cl)$ = 149.3 cps. [d] Calculated from $J_{CH}(CH_3\mathbf{CH_2})_2O)$ = 137.7 cps. [e] From proton spectra using a Varian Associates DP-60 Spectrometer.

We believe the additivity rule can be accounted for if overlap integrals are retained in calculations based on the Fermi contact term.[6] The ζ values determined from the methanes appear in eq. 2 for the aldehydes because the overlap integrals are essentially, at least to our approximation, independent of the state of hybridization of the carbon atoms. The coefficients in eq. 2 arise because of the difference in the state of hybridization of the carbon atom in the methanes, sp^3, as compared to its hybridization in the aldehydes, sp^2. Previous investigators[7,8] have shown that J_{CH} depends upon the state of hybridization of the carbon atom; similar arguments are held to be true here. Obviously since the carbonyl oxygen is common to all aldehydes its contribution to the coupling must be essentially a constant and, therefore, an additivity relation analogous to eq. 1 must be expected for the aldehydes.

Benzene (I), pyridine (II) and pyrimidine (III) represent a series of compounds which also contain sp^2 carbon atoms. Table II shows very clearly that this series does obey the additivity relation. For convenience in notation the coupling components are expressed as ζ_{ij}', where the prime indicates that the carbon orbital is sp^2 rather than sp^3 and the subscripts ij indicate only the first and second atoms of the substituent group. For example, consider the C–H bond in the 2 position in pyridine. N_1 is α and C_6 is β to the C_2–H bond, so we write ζ_{NC}' for the component of this group. Again C_3 is α and C_4 is β to the C_2–H bond, so we write ζ_{CC}' for the component of this group. In this series it is not necessary to define the substituent group beyond the β position because of the negligible effect of any atom further removed. From the available data self-consistent ζ' values have been assigned and are listed in Table II. This table clearly shows that these values well account for the data and, thereby, illustrates the extensibility of the additivity rule for substituents on C^{13}–H coupling for carbon in its various states of hybridization.

I



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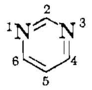

III

TABLE II

CALCULATED AND OBSERVED C^{13}-H COUPLING CONSTANTS OF BENZENE, PYRIDINE AND PYRIMIDINE, USING ζ'_{CC} = 77.5 CPS., ζ'_{CN} = 84.5 CPS. AND ζ'_{NC} = 103.0 CPS.

C–H bond	J_{CH}, calcd.	J_{CH}, exptl.	Diff.
Benzene	$\zeta'_{CC} + \zeta'_{CC} = 155.0$	158	−3.0
2, pyridine	$\zeta'_{CC} + \zeta'_{NC} = 180.5$	179	+1.5
3, pyridine	$\zeta'_{CC} + \zeta'_{CN} = 162.0$	163	−1.0
4, pyridine	$\zeta'_{CC} + \zeta'_{CC} = 155.0$	152	+3.0
2, pyrimidine	$\zeta'_{NC} + \zeta'_{NC} = 206.0$	206.0[9]	0
4, pyrimidine	$\zeta'_{CC} + \zeta'_{NC} = 180.5$	181.8[9]	−1.3
5, pyrimidine	$\zeta'_{CN} + \zeta'_{CN} = 169.0$	168.0[9]	+1.0

Further work along these lines is being conducted in this laboratory.

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[10] National Defense Fellow (Department of Health, Education, and Welfare).

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RECEIVED MAY 11, 1962

NEW LOWER LIMIT FOR THE BINDING ENERGY OF THE HELIUM MOLECULE ION[1]

Sir:

The literature contains three *experimental* values for the binding energy[2] of He_2^+. D_e = 3.1 e.v. obtained[3] by an extrapolation of the Rydberg spectrum of He_2, $D_e \geq 1.4$ e.v. from[4] electron impact experiments and D_e = 2.16 e.v. from[5] the analysis of scattering data.

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[1] This research was supported by the Robert A. Welch Foundation of Houston, Texas, and Air Force Office of Scientific Research.

[2] The zero-point energy ~0.2 e.v. has been neglected in this discussion.

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