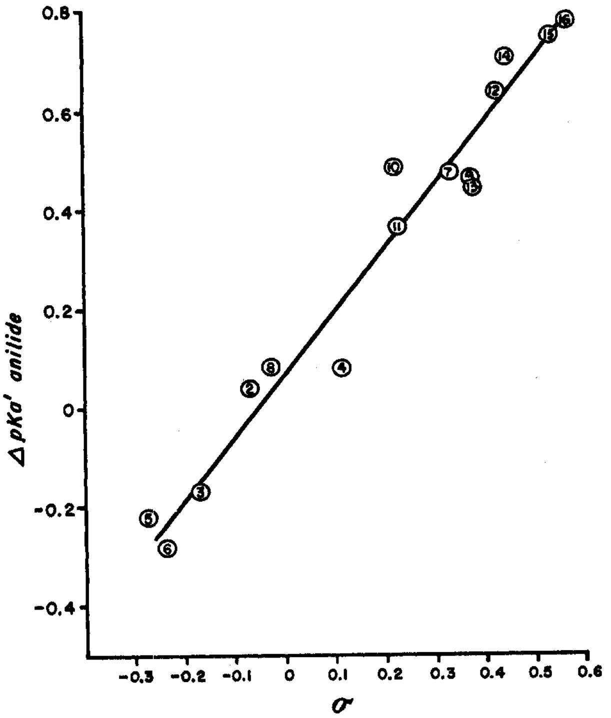

Figure 1.—Correlation of relative anilide pK_a' values with σ (ref 7). The equation for this linear relationship is $\Delta pK_a' = 1.25\sigma + 0.06 \pm 0.136$ (95% confidence), $r = 0.982$, $n = 15$. Numbers refer to compounds in Table I.

(III) remains unanswered. Topping and Tutt,[8] in reporting an almost 100-fold increase in acidity obtained when comparing the pK_a' value of salicylamide with that of *N*-salicoylmesitamide, favored an explanation based upon hydrogen bonding of the phenolate anion to the imide proton. The importance of the hydrogen on the anilide nitrogen and, therefore, of the likely meaningful contribution of the hydrogen bonded species III is also attested to by the failure of the *N*-methylanilide–aniline pair (Table I, no. **17**) to fit the relationship described by eq 1.

The amide moiety, therefore, does appear to be capable of transmitting electronic effects, apparently on a "one-way" basis, depending upon the location of the substituents *vis-à-vis* the anilide nitrogen.

Experimental Section

Melting points are uncorrected. pK_a' determinations were performed at 25° in 1:2 (v/v) water–dioxane using a Metrohm automatic potentiograph (Model E436) which had been standardized against both phthalate and phosphate buffers. Isocyanates used were commercial materials.

Method A.—A solution of appropriate aryl isocyanate in THF was added dropwise to a refluxing solution of equimolar amounts of triethylamine and 2-methylisoquinoline-1,3-(2*H*,4*H*)-dione[9] in THF. Reaction completion, usually in *ca.* 2 hr, was determined by tlc. Work-up included pouring the clear reaction solution into aqueous acid, filtering and drying the resulting precipitate, and recrystallization.

Method B.—A solution of equimolar quantities of ethyl 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxylate and appropriate aniline in xylene was heated at reflux for 2–4 hr, during which time solvent was slowly removed by means of a still head. The product precipitated during the reflux period and, after cooling, was filtered, dried, and recrystallized.

Registry No.—**1**, 21389-75-3; **2**, 22367-26-6; **3**, 22416-10-0; **4**, 27799-74-2; **5**, 22367-28-8; **6**, 22367-30-2; **7**, 27669-98-3; **8**, 21925-91-7; **9**, 22367-24-4; **10**, 21925-90-6; **11**, 22351-31-1; **12**, 27670-01-5; **13**, 22351-45-7; **14**, 22351-36-6; **15**, 22351-19-5; **16**, 27670-04-8; **17**, 21389-81-1.

Acknowledgment.—The author thanks Professor D. S. Kemp for many helpful discussions.

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[8] R. M. Topping and D. E. Tutt, *J. Chem. Soc. B*, 1346 (1967).

[9] S. Gabriel, *Ber.*, **19**, 2363 (1886).

Borylation of 2,5-Heterosubstituted 1,4-Benzoquinoid Systems

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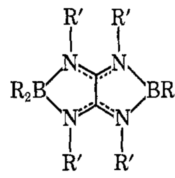
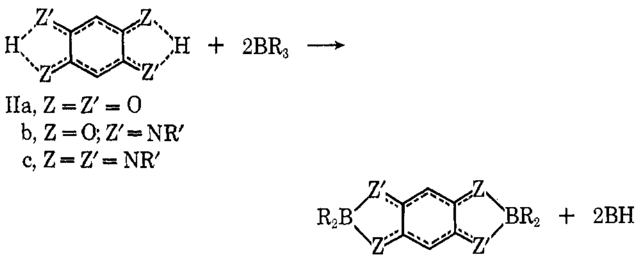
The facile reaction of *sym*-tetraalkyl- or *sym*-tetraaryloxamidine with trialkyl- or triarylboranes to yield the highly stable, symmetrical heterocycles I, doubly bridged with BR_2 groups,[2] prompted an investigation of the benzologous system II. Its borylation should give rise to analogous doubly bridged heterocycles, III.



I



IIa, Z = Z′ = O
b, Z = O; Z′ = NR′
c, Z = Z′ = NR′

IIIa, Z = Z′ = O
b, Z = O; Z′ = NR′
c, Z = Z′ = NR′

The types of II most thoroughly studied in this reaction were 2,5-bis(alkylamino)-1,4-benzoquinones (IIb).

The reaction of triethylborane with 2,5-bis(ethylamino)-1,4-benzoquinone proceeded in refluxing xylene with evolution of ethane. However, gas evolution did not stop at the theoretical point and proceeded further necessitating quenching of the reaction by cooling. The product was isolated by chromatography in 7% yield. It was an air-stable, yellow solid; the analytical and spectral data were in accord with structure IIIb

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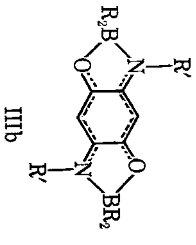
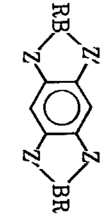
[2] S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 7014 (1967).

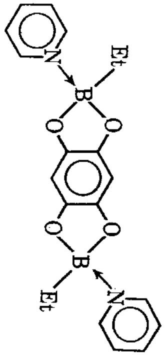
(R = R′ = Et). The low yield contrasts with the almost quantitative formation of diboryloxamidines, I.



IIIb



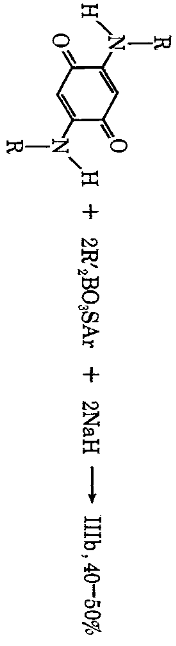
IVa, Z = Z′ = O
b, Z = O; Z′ = NR′



V

This may be ascribed to the inability of IIb to react with BR_3 *via* a cyclic, low-energy transition state involving not a four-membered ring but rather a six-membered ring as is possible with *sym*-tetraalkyloxamidines.[2] In the present case, the reaction could be then diverted toward the formation of hydroquinone derivatives as has been reported[3] for the reaction of BR_3 with 1,4-quinone. Alternatively, IIIb could decompose during the reaction to form the reduced system IVb plus, *e.g.*, butane. Mass spectrographic analysis of the emanating gas at several stages of the reaction indicated it to be essentially pure ethane with no butane or ethylene present. The exact fate of the remaining 93% of the starting material remains unknown. Compounds IIIb were themselves stable under the reaction conditions of their formation.

Other 2,5-bis(alkylamino)-1,4-benzoquinones reacted in the same fashion with triethylborane and yields were comparably low. The yield was substantially improved by letting the 2,5-bis(alkylamino)-1,4-benzoquinone react with a borylsulfonate[4,5] in the presence of sodium hydride (see Table I). Similar results were obtained



with 3,6-dichloro-2,5-bis(alkylamino)-1,4-benzoquinones. In general, most compounds IIIb (R = alkyl) were stable to storage in air and to hydroxylic solvents, although prolonged boiling in alcohols led to regeneration of the starting quinone IIb. Some, such as IIIb, where R = Et and R′ = *n*-octyl, were formed readily enough, but were air-sensitive, especially in solution (even in hydrocarbons) being converted to IIb (R′ = *n*-octyl).

By contrast, compounds IIIb, where R = phenyl, were not only formed in excellent yields but also ex-

Table I.—Compounds of Structure 1

R	R′	X	Z	Registry no.	Mp, °C	% yield[a]	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Miscellaneous	Nmr[b]	Uv λ_{max} (ϵ)
C_6H_5	C_6H_5	H	NC_6H_5	27669-88-1	306–308 dec	90 (C)	84.3	5.47		85.0	5.67			m 2.79, m 3.00, s 4.24 (10:10:1)	464 (50,800), 350 (8920), 273 (33,700), 247 (35,400)
C_6H_5	C_3H_7	H	O	27669-89-2	300–305 dec	91 (C)	78.5	6.55	5.09	78.5	6.92	5.29			
C_6H_5	n-C_4H_9	H	O	27724-53-4	230–231	88 (C)	78.1	6.82	4.84	79.1	7.09	4.93	B^{11}, ∼+2 ppm[c] (very broad)	s 2.65, s 3.89, t (7.0) 6.30, m 8.77, m 9.17 (10:1:2:4:3)	
C_6H_5	*n*-Octyl	H	O	27724-54-5	131–132	99 (C)	80.0	8.12	4.06	80.3	8.14	4.58	B^{11}, nmr +2.6 ppm	s 2.62, s 3.89, m 6.32, m ∼9 (10:1:2:15)	
C_6H_5	Benzyl	H	O	27724-55-6	255–257	85 (C)	81.5	5.55	4.32	81.8	5.68	4.30			
C_2H_5	CH_3	H	O	27724-56-7	150–152 dec	9 (A)	63.6	9.28		63.6	9.19			s 4.12, s 6.80, s 9.37 (1:3:16)	
C_2H_5	C_2H_5	H	O	27724-57-8	146–147 dec	7 (A) 46 (B)	65.5	9.71	8.48	65.6	10.2	8.40	B^{11}, ∼+2 ppm (very broad)	s 4.13 q, (7.0) 6.48, t (7.0) 8.69, s 9.39 (1:2:3:10)	
C_2H_5	*tert*-C_4H_9	H	O	27724-58-9	178–179	45 (B)	68.3	10.4	7.25	68.5	10.7	7.37		s 3.80, s 8.42, s 9.33 (1:9:10)	
C_6H_5	C_2H_5	Cl	O	27724-59-0	233–235	40 (C)	69.1	5.08	4.74	69.1	5.39	4.97	B^{11}, nmr +2.6 ppm	s 2.58, q (7.0) 5.72, t (7.0) 9.00 (10:2:3)	
C_2H_5	C_3H_7	Cl	O	27669-90-5	133–134	43 (B)	56.2	7.98	6.57	55.9	7.44	6.70	Cl, 16.6; Cl, 16.6		
n-C_4H_9	C_2H_5	H	O	27669-91-6	93–94	58 (B)	70.7	10.9	6.34	71.1	11.4	6.32		s 4.17, q (7.5) 6.45, m 8.5–9.5 (1:2:12)	

[a] A, B, and C refer to method of synthesis (see Experimental Section). [b] Listed are multiplicity (J), chemical shift in τ (area ratios). [c] From $B(OMe)_3$.

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(3) (a) M. F. Hawthorne and M. Reintjes, *J. Amer. Chem. Soc.*, **87**, 4585 (1965); (b) B. M. Mikhailov, G. S. Ter-Sarkisian, and N. A. Mikolaeva, *Izv. Akad. Nauk SSSR, Ser. Khim*, **541** (1968).

(4) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 2139 (1969).

(5) S. Trofimenko, *Inorg. Chem.*, **8**, 1714 (1969).

hibited great oxidative, thermal, and hydrolytic stability.

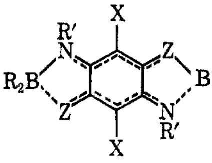
At the other extreme, compounds IIIb, where R = H, which were formed as primary products of the reaction of IIb with borane in tetrahydrofuran and characterized by the usual color transition from red to bright yellow, were the least stable of all. They could not even be isolated as such, but lost further hydrogen yielding the reduced species IVb. These were quite air sensitive and reacted with alcohols evolving hydrogen and yielding the starting material IIb. While this instability precluded analysis, their structure follows from the stoichiometry of hydrogen evolution and the presence of a BH singlet in the infrared spectrum (rather than of a more complex pattern characteristic of a BH_2 group). Thus both the ease of preparing and the stability of compounds IIIb decrease in the order R = aryl > alkyl > H.

When 2,5-dihydroxy-1,4-benzoquinone was heated with triethyl- or triphenylborane, reduction of the quinoid system took place leading to compounds IVa (R′ = ethyl or phenyl). While the phenyl derivative was an air-stable white solid, the ethyl derivative was air sensitive. Nevertheless, it could be characterized as the bispyridine adduct V.

The only example of an available IIc system was azophenin. Its reaction with triphenylborane gave a high yield of the bisborylated derivative IIIc (R = R′ = phenyl) thermally stable beyond 300°.

The stability order IIIc > IIIb ≫ IIIa probably mirrors the superior nucleophilicity of an NR′ group as compared with O as well as the screening effect of the substituent R′. The same general order of hydrolytic stability would be anticipated for the transition metal chelates derived from dianions of IIa–c.

Table I lists data for compounds of structure 1.



1

Experimental Section

The 2,5-bis(alkylamino)-1,4-benzoquinones were prepared in good yield by the copper-catalyzed oxidative addition of a primary amine to quinone,[6] the 3,6-dichloro-2,5-bis(alkylamino)-1,4-benzoquinones by the reaction of primary amines with chloranil.[7] Azophenin was synthesized by the published method.[8]

The following new 2,5-bis(alkylamino)-1,4-benzoquinones were prepared by the published method.

A. **2,5-Bis(octylamino)-1,4-benzoquinone** was prepared in 51% yield on 1-mol scale and purified by recrystallization from a 9:1 heptane–toluene mixture. It was obtained as red platelets, mp 135–136°. *Anal.* Calcd for $C_{22}H_{38}N_2O_2$: C, 72.9; H, 10.6. Found: C, 73.2; H, 10.6.

B. **2,5-Bis(benzylamino)-1,4-benzoquinone** was obtained in 35% yield after two recrystallizations from DMF, mp 258–259°.

C. **2,5-Bis(*tert*-butylamino)-1,4-benzoquinone** was obtained in 33% yield, mp 241–242° after recrystallization from toluene. It sublimes *in vacuo*: nmr broad singlet at τ 3.31, sharp singlet τ 4.46, and sharp singlet at τ 8.60 in 1:1:9 ratio; uv λ_{max} 338 mμ (ϵ 28,600), 490 (242).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 76.2; H, 8.86; N, 11.2. Found: C, 76.2; H, 8.91; N, 11.3.

D. **2,5-Bis(1-adamantylamino)-1,4-benzoquinone** was prepared from 1-adamantylamine hydrochloride and 1,4-benzoquinone. It was obtained in poor yield as red crystals (from toluene) which darken gradually from 395° on and decompose above 400°. The nmr spectrum has broad bands around τ 3.3, a singlet at τ 4.3, and adamantyl hydrogens as two broad bands at τ 7.9 and 8.2 in 1:1:15 ratio.

Anal. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.8; H, 8.43; N, 6.89. Found: C, 76.8; H, 8.12; N, 7.22.

The following three specific examples illustrate the procedures used to prepare bisborylated 2,5-bis(alkylamino)quinones. For other data see Table I.

Procedure A. 2,5-Bis(*N*-diethylborylethylamino)-1,4-benzoquinone.—A mixture of 19.4 g (0.1 mol) of 2,5-bis(ethylamino)-1,4-benzoquinone and 28.2 ml (0.2 mol) of triethylborane in 200 ml of xylene was refluxed. Ethane was evolved briskly and continued to be evolved even after the theoretical amount was obtained; the reaction was quenched by cooling at this point. The reaction mixture was chromatographed on alumina collecting the bright yellow band. After stripping and trituration with ether there was obtained 2.3 g (7%) of bright yellow solid which was recrystallized from hexane, mp 146–147° dec.

Procedure B. 2,5-Bis(*N*-diethylborylethylamino)-1,4-benzoquinone.—A mixture of 19.4 g (0.1 mol) of 2,5-bis(ethylamino)-1,4-benzoquinone and 8.7 g (0.2 mol) of sodium hydride (55% suspension in mineral oil) in 200 ml of tetrahydrofuran was stirred and refluxed overnight at which time about 2.6 l. of hydrogen had been evolved. A solution of 0.2 mol of Et_2BOTs in toluene was added whereupon more hydrogen was evolved and the mixture turned yellow and thickened. When no more unreacted starting material was noted and gas evolution ceased, the reaction mixture was filtered and the cake was washed with methylene chloride. The filtrate was stripped to dryness and the residue was chromatographed on alumina, eluting with hexane. The yellow band was stripped yielding 20 g of crude product which, after recrystallization from hexane, yielded 15.2 (46%) of bright yellow crystals identical in all respects with those from the preceding experiment.

Procedure C. 2,5-Bis(*N*-diphenylborylbutylamino)-1,4-benzoquinone.—A mixture of 2.5 g (0.01 mol) of 2,5-bis(butylamino)-1,4-benzoquinone and 7.0 g (0.029 mol) of triphenylborane in 50 ml of *o*-dichlorobenzene was refluxed overnight. On cooling, the amber solution deposited crystals. They were filtered and washed with ether, yielding 4.1 g (71%) of product. An additional 1.0 g (17%) was obtained by chromatographing the filtrate. The product was purified by recrystallization from toluene, mp 230–231°.

1,2,4,5-Bis(phenylborylenedioxy)benzene.—A mixture of 7.0 g (0.05 mol) of 2,5-dihydroxybenzoquinone and 26 g (0.1 mol) of triphenylborane in 100 ml of *o*-dichlorobenzene was refluxed for 3 hr. The reaction mixture was cooled and filtered, and the solid was recrystallized from toluene. There was obtained 6.8 g (44%) of white fluffy crystals, mp 310–312°. They can be sublimed *in vacuo*.

Anal. Calcd for $C_{18}H_{12}B_2O_4$: C, 71.0; H, 3.95. Found: C, 71.0; H, 4.09.

1,2,4,5-Bis(ethylbornylenedioxy)benzene–Dipyridine Complex.—A mixture of 14.0 g (0.1 mol) of 2,5-dihydroxybenzoquinone and 28 ml (0.2 mol) of triethylborane in 250 ml of toluene was refluxed under nitrogen until ethane ceased to be evolved. The solution was stirred with Darco and filtered, and the filtrate was stripped at 70° (1 mm). The residue was taken up in 400 ml of hexane and 60 ml of pyridine was added. A yellow precipitate separated. It was recrystallized from 1,2-dimethoxyethane and was obtained in two crops of 7.6 and 4.3 g (total yield 11.9 g or 32%). The product melts at 108–112° to a red melt which starts gassing above 220°. The material is sublimable *in vacuo*.

Anal. Calcd for $C_{20}H_{22}B_2N_2O_4$: C, 63.9; H, 6.85; B, 5.74. Found: C, 64.5; H, 6.36; B, 5.60.

Registry No.—2,5-Bis(octylamino)-1,4-benzoquinone, 23419-93-4; 2,5-bis(benzylamino)-1,4-benzoquinone, 1521-00-2; 2,5-bis(*tert*-butylamino)-1,4-benzoquinone, 19617-94-8; 2,5-bis(1-adamantylamino)-1,4-benzoquinone, 27724-50-1; 1,2,4,5-bis(phenylborylenedioxy)benzene, 27724-51-2; 1,2,4,5-bis(ethylborylenedioxy)benzene–dipyridine complex, 27724-52-3.

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[6] R. E. Covey, U. S. Patent 3,114,755 (1963).

[7] K. Wallenfels and W. Draber, *Justus Liebigs Ann. Chem.*, **667**, 65 (1963).

[8] V. P. Ruggli and F. Buchmeier, *Helv. Chim. Acta*, **28**, 850 (1945).