The residue from the steam distillation was allowed to cool to room temperature and was filtered to remove a small amount of a yellow substance. The clear filtrate was extracted with a 100-ml portion of ether. Evaporation of the ether left no residue.

The aqueous phase from the ether extraction was made strongly basic with potassium hydroxide pellets until a yellow oil separated on the surface of the aqueous phase. The mixture was extracted with three 40-ml portions of benzene. The combined benzene extract was dried by stirring for 2 hr over potassium hydroxide pellets. The benzene phase was decanted into a 250-ml beaker and was evaporated on a hot plate under a stream of anhydrous nitrogen until approximately 1 ml of a viscous yellow oil remained. The beaker was placed in a vacuum desiccator and the residue was evacuated under full pump vacuum overnight.

The yellow oil was transferred into a 3-ml distilling flask which had been previously tared. The yield of crude methylethylphenylphosphine oxide was 0.91 g (80%). Distillation *in vacuo* gave a colorless oil which solidified in an ice bath, mp 52-54° (lit.[25] mp 52-56°).

Reaction of (+)-Methylethylphenylbenzylidenephosphorane with *p*-Methylbenzonitrile, Benzonitrile, and *p*-Chlorobenzonitrile. Experiments identical in every respect with those described under the previous heading were carried out, proportional quantities of the three nitriles specified in the heading being used. The results are tabulated in Table III.

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N,N'-Diboryloxamidines[1]

S. Trofimenko

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Abstract: A new class of bicyclic, boron-bridged compounds has been prepared from *sym*-tetrasubstituted oxamidines and diverse boranes. Their synthesis and properties are discussed.

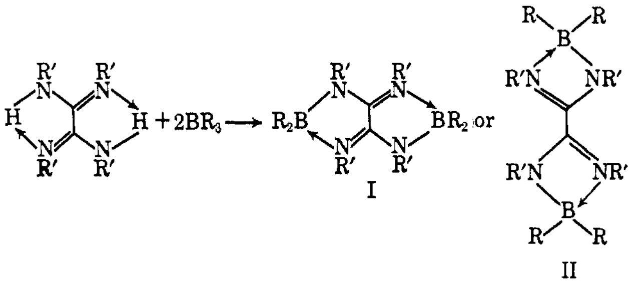
Numerous examples are known of a BR_2 group replacing the hydrogen bridge in chelating agents. In most of these cases only one such bridge was involved; the few examples containing two BR_2 bridges are pyrazaboles,[2] some transition metal dipyrazolylborates,[3] and the BR_2-bridged Ni(II)[4] and Co(II)[5] dimethylglyoximates.

We now report the synthesis and properties of a new class of metal-free compounds containing two intramolecular BR_2 bridges. These compounds, of general structure I, were prepared by the reaction of diverse boranes with *sym*-tetraalkyl- and *sym*-tetraaryloxamidines.

Results and Discussion

When a 2:1 mixture of triethylborane and *sym*-tetraethyloxamidine was refluxed in toluene, 2 equiv of ethane were rapidly evolved and compound I (R = R' = Et), mp 165°, was obtained in 96% yield. The structure assignment was consistent with the following data.

Elemental analysis, molecular weight determination, and the stoichiometry of hydrogen evolution indicated replacement of both active hydrogens by diethylboryl groups. The infrared spectrum lacked the NH band of the starting material and contained a very strong and broad band at 1675 cm^{-1} (C-N multiple bonding). The nmr spectrum indicated two types of ethyl groups present in equal numbers: one, displaying a normal quadruplet and triplet pattern at τ 6.71 and 8.76 (J = 7 cps), respectively, assigned to the N-ethyl groups, the other, a narrow (~10 cps) "triplet" at τ 9.5, assigned to the B-ethyl groups. Such shift of the methylene hydrogens to overlap with those of the methyl group has been noted in bridging BEt_2 groups before.[6] The B^{11} nmr peak fell likewise into the range of "chelated" BEt_2 groups.[6]



Of the two possible structures (I and II) satisfying these data, structure I appears more plausible for steric reasons.

The fact that only two types of ethyl groups are discernible in the nmr implies either an interconversion of the two tautomers of I at a rate faster than the nmr time scale or a resonance hybrid of charge-separated structures such as III. The molecule is given the representation IV, which shows the D_{2h} symmetry apparently present.

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[1] Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April, 1967.

[2] S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966); **89**, 3165 (1967).

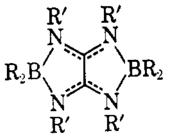
[3] S. Trofimenko, *ibid.*, **89**, 3170 (1967).

[4] G. Schrauzer, *Ber.*, **95**, 1438 (1962).

[5] G. Schrauzer, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

[6] L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *Inorg. Chem.*, **4**, 1649 (1965).

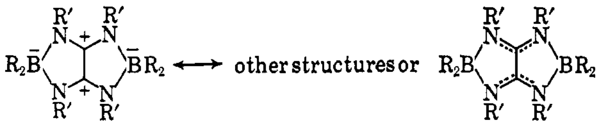
Table I. Compounds of Type



R	R′	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found	X, % Calcd	X, % Found	Ultraviolet[g] λ_{max}, mμ	Ultraviolet[g] ϵ	H¹ nmr[i]	B¹¹ nmr[j]
Et	Me	88	160–161[a]	60.4	59.8 61.0	11.5	11.6			280	18,100	s, 6.95 (3) m, 9.5 (5)	
Et	Et	96	164–165[a]	64.7	65.1	12.0	11.9	B 6.46 N 16.7 Mol wt, 334	B 6.49 N 16.7 Mol wt, 348[f]	279	18,200	q, 6.71, 7 (2) t, 8.76, 7 (3) "t," 9.5 (5)	+10.3 (sharp)
Et	Ph	67	244–245[b]	77.7	77.5	7.61	7.71	N 10.6	N 10.7			s, 3.08 (5) m, 9.28 (5)	+2 (broad)
Ph	Me	86	281–282[c]	76.6	76.5	6.82	6.64	N 11.9	N 11.9	292 sh 278 270	>40,000[h] >36,200 >16,900	s, 2.77 (5) s, 5.99 (3)	+11.7 (broad)
Ph	Et	92	250–251[d]	77.7	78.0	8.62	7.65			293 sh 280 270	>27,100[h] >24,400 >11,600	d, 2.67 (5) q, 6.65, 7 (2) t, 9.22, 7 (3)	
Ph	Pr	90	189–190[e]	78.5	78.5	8.26	8.52	N 9.62	N 9.37	293 sh 280 270	28,000 25,300 12,100	d, 2.68 (5) m 6.83 (2) m, 8.5–9.0 (5)	+10 (broad)
Ph	Ph	88	285–286[d]	83.5	83.7	5.57	5.77					m, 2.4–2.9 (5) s, 3.40 (5)	+2 (broad)

[a] Recrystallized from ethanol. [b] Sublimed. [c] Recrystallized from *o*-dichlorobenzene. [d] Recrystallized from toluene. [e] Recrystallized from *n*-heptane. [f] By vapor pressure osmometry in $CHCl_3$. [g] Spectra determined in isooctane. [h] Compounds incompletely dissolved in isooctane. [i] Multiplicity, chemical shift in τ, J (cps), relative intensity. [j] The data are given in ppm and are referred to external trimethyl borate.

Other compounds of this general structure were prepared by heating the appropriate borane and *sym*-tetrasubstituted oxamidine components, preferably in an aromatic hydrocarbon solvent. The compounds prepared are shown in Table I.



III IV

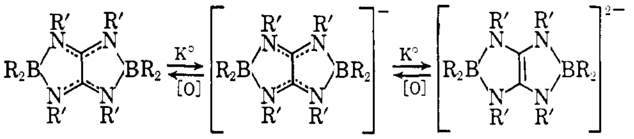
When an asymmetrically substituted oxamidine (N,N′′-dipropyl-N′,N′′′-diphenyloxamidine) reacted with triphenylborane, the product melted over a relatively wide range, suggesting a mixture of *cis* and *trans* isomers that were partially separated by chromatography.

In addition to dialkylboryl and diphenylboryl bridges, compounds containing BH_2 or BBr_2 bridges were prepared starting, respectively, with tetrahydrofuran–borane complex or boron tribromide. From *o*-phenylenedioxyborane, prepared *in situ* from pyrocatechol and borane in tetrahydrofuran, the analogous product containing two *o*-phenylenedioxyboryl bridges was obtained.

All these compounds were colorless, high-melting solids, some of exceptional thermal stability. For instance, the melt of IV (R = R′ = Et) showed no sign of decomposition even when kept above 310° in air for hours. The compound IV (R = R′ = Ph) started to decompose (by DTA) at 353°.

The facile formation of the bicyclic products of structure IV contrasts with the reaction of tetrakis(dimethylamino)ethylene with BF_3 where only one BF_2 bridge could be introduced.[7] In fact, the reaction of equimolar amounts of triphenylborane with *sym*-tetramethyloxamidine gave primarily (44.4%) the bis-bridged compound and only 4% of the monobridged derivative.

Compounds of structure IV (R = R′ = Et and R = R′ = Ph) react with 2 equiv of potassium metal in tetrahydrofuran to yield first a deep green intermediate and ultimately a red solution. These colored products are thought to be the anion radical V and the dianion VI, respectively. Support for the radical nature of the green species has been obtained from epr studies.[8] With oxidizing agents or merely upon exposure to air, the red species is reconverted to starting material, the reaction proceeding again through the green intermediate. The air sensitivity of VI resembles that of the tetraaminoethylenes of which VI may be considered a derivative.



colorless green V red VI

The mechanism of the reaction of boranes with *sym*-tetrasubstituted oxamidines presumably involves coordination of the borane moiety to the imino nitrogen, followed by intramolecular elimination of the appropriate HX molecule. Of the two possibilities, concerted four-center reaction (VII) and concerted but involving a six-membered ring in the transition state, VIII, the latter is more plausible. It is analogous to the mechanism for the reaction of boranes with car-

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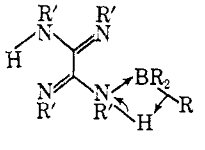
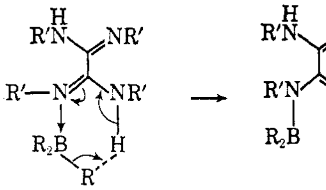
(7) N. Wiberg and J. W. Buchler, *J. Am. Chem. Soc.*, **85**, 244 (1963).
(8) R. E. Dessy, private communication.



VII



VIII IX

boxylic acids proposed by Brown[9] and confirmed by Toporcer, Dessy, and Green.[10] The BR_2 group of the resulting intermediate, IX, will coordinate to give the thermodynamically more stable five-membered ring (assuming no significant barriers for rotation around the C–C and C–N bonds).

Experimental Section

Triethylborane, triphenylborane, and borane in tetrahydrofuran are commercially available. *sym*-Tetraphenyloxamidine[11] and *sym*-tetraalkyloxamidines[12] were prepared by published methods. Merck acid-washed alumina was used for chromatography.

Preparation of N,N′-Bis(diethylboryl)-*sym*-tetrasubstituted Oxamidines. These compounds were prepared by refluxing under nitrogen a mixture of 2 equiv of triethylborane and 1 equiv of the appropriate *sym*-tetrasubstituted oxamidine in toluene (about 200 ml/0.1 mole) until the theoretical amount of ethane had been evolved. The solvent was then removed *in vacuo* and the residue purified by recrystallization or by sublimation (see Table I).

Preparation of N,N′-Bis(diphenylboryl)-*sym*-tetrasubstituted Oxamidines. These compounds were prepared by heating, under nitrogen, a 2:1 mixture of triphenylborane and the appropriate *sym*-tetrasubstituted oxamidine in *o*-dichlorobenzene and distilling out the benzene evolved through a small Vigreux column. When the theoretical amount of benzene was evolved, the solvent was removed *in vacuo* and the residue was purified (see Table I).

N-Diphenylboryl-*sym*-tetramethyloxamidine. A mixture of 14.2 g (0.1 mole) of *sym*-tetramethyloxamidine and 29 g (0.12 mole) of triphenylborane was refluxed in 250 ml of *o*-dichlorobenzene until benzene ceased to distil. The solution was stripped *in vacuo*, and the residue was recrystallized from dimethylformamide. The solid that crystallized (6.4 g) was identified as N,N′′-bis(diphenylboryl)tetramethyloxamidine. The filtrate was chromatographed on alumina. A solid fraction (2.2 g) was eluted with ether; a second fraction (1.2 g, 4%) was eluted with methylene chloride. It has an NH band at 3250 cm^{-1}. Elution with methanol gave an additional 4.0 g of N,N′′-bis(diphenylboryl)tetramethyloxamidine for its total yield of 10.4 g (44.4%).

The fraction showing the NH band was recrystallized from toluene and melted at 230–231°; it was then sublimed at 230° (1 mm). *Anal.* Calcd for $C_{18}H_{23}BN_4$: C, 70.6; H, 7.53. Found: C, 70.5; H, 7.03.

N,N′′-Bis(dihydroboryl)tetramethyloxamidine. A mixture of 7.1 g (0.05 mole) of tetramethyloxamidine and 100 ml of 1.0 *M* borane in tetrahydrofuran and 200 ml of dry tetrahydrofuran was refluxed overnight. About 2.5 l. of hydrogen was evolved. The solution was concentrated at 65° and aspirator vacuum yielding a taffy-like residue which was purified by sublimation. The product was obtained as shiny white needles in 2.1 g. (25%) yield. The sublimed product was recrystallized from *n*-heptane; mp 169–170° (*Anal.* Calcd for $C_6H_{16}B_2N_4$: C, 43.4; H, 9.65; N, 33.7. Found: C, 43.6; H, 9.59; N, 33.3); ultraviolet analysis (isooctane): λ_{max} 302 mμ (sh) (ϵ 17,400), 288 (sh) (ϵ 15,100), and 280 (ϵ 6840).

N,N′′-Bis(dibromoboryl)tetrapropyloxamidine. To a solution of 10 ml of boron tribromide (26.4 g, 0.105 mole) in 200 ml of carbon tetrachloride was added a solution of 12.7 g (0.05 mole) of tetrapropyloxamidine in 300 ml of toluene. A solid precipitated during the addition. The reaction mixture was left standing for 2 days at room temperature. It was then filtered yielding 26.4 g (89%) of white solid. A small sample was purified by sublimation above 200° (1 mm), another by recrystallization from chlorobenzene. Both purified products had identical infrared spectra (*Anal.* Calcd for $C_{14}H_{28}B_2Br_4N_4$: C, 28.3; H, 4.72; Br, 53.8. Found: C, 28.9; H, 4.84; Br, 53.5); ultraviolet analysis (isooctane): λ_{max} 265 mμ (ϵ >11,500) (limited solubility in isooctane).

N,N′′-Bis(*o*-phenylenedioxyboryl)tetrapropyloxamidine. A solution of 11.0 g (0.1 mole) of pyrocatechol in 100 ml of tetrahydrofuran was added slowly to 100 ml of 1 *M* borane in tetrahydrofuran. Hydrogen (4.8 l.) was evolved. A solution of 12.7 g (0.05 mole) of *sym*-tetrapropyloxamidine in the least amount of tetrahydrofuran necessary to effect solution was added, and the resulting solution was refluxed overnight. Tetrahydrofuran was then distilled out and replaced by xylene, and refluxing was continued for several hours. The crude reaction mixture was chromatographed on alumina (packing and eluting with ether). The first fraction (3.9 g, 16%) was a solid which gave a negative ferric chloride test; subsequent fractions gave a positive test and were discarded.

The product was purified by sublimation at 200° (1 mm) and melted at 245–246°. *Anal.* Calcd for $C_{26}H_{36}B_2N_4O_4$: C, 63.7; H, 7.35. Found: C, 63.8; H, 7.43. Its B^{11} nmr spectrum consisted of a sharp singlet at +5.4 ppm.

N,N′′-Diphenyl-N′,N′′′-dipropyloxamidine. A solution of 277 g (1 mole) of N,N′-diphenyloxamidoyl chloride in 1500 ml of benzene was added slowly and with cooling to a solution of 425 g (7 moles) of *n*-propylamine in 2 l. of benzene. The reaction mixture was left standing overnight. It was then filtered, and the filtrate was stripped to dryness yielding an oil which was stirred with 500 ml of hexane. A solid precipitated. It was filtered, washed with pentane, and air dried to give 270 g (91%) of a solid, mp 65–67°. *Anal.* Calcd for $C_{18}H_{26}B_2N_4$: C, 72.5; H, 8.73. Found: C, 75.2; H, 8.13. The nmr spectrum had a complex multiplet centered at τ 2.80 (five protons), triplet at 7.10 (two protons), multiplet at 8.72 (two protons), and triplet at 9.28 (three protons).

N,N′′-Bis(diphenylboryl)-N,N′′-diphenyl-N′,N′′′-dipropyloxamidine. A mixture of 15 g (0.05 mole) of N,N′′-diphenyl-N′,N′′′-dipropyloxamidine and 27 g (0.11 mole) of triphenylborane was refluxed in 150 ml of *o*-dichlorobenzene until benzene ceased to distil. The solution was evaporated to dryness, and the residue was rapidly chromatographed on alumina, packing and eluting with ether. The two main fractions were recrystallized from heptane-benzene; mp 203–216 and 220°, respectively.

The nmr spectrum supports the assigned structure with a 15-proton multiplet around τ 2.8, and two-proton multiplets around τ 7.2 and 9.5, respectively (the methyl was beyond the tetramethylsilane signal). *Anal.* Calcd for $C_{44}H_{44}B_2N_4$: C, 81.3; H, 6.78. Found (fraction 1): 81.4; H, 6.92. (Fraction 2): C, 81.6; H, 7.14.

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[9] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 66.

[10] L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *J. Am. Chem. Soc.*, 87, 1236 (1965).

[11] R. Bauer, *Ber.*, 40, 2650 (1907).

[12] H. M. Woodburn, B. A. Morehead, and C. M. Chih, *J. Org. Chem.*, 15, 541 (1950).