(2)

OFFICE OF NAVAL RESEARCH

Contract No. N00014-83-K-0611

R & T Code 4135003-1
Replaces old
Task No. NR 053-842

TECHNICAL REPORT NO. UK/DC/TR-25

New Boron–Nitrogen Analogues of Uracil Derivatives

by

L. Komorowski and K. Niedenzu

Prepared for publication in

ZEITSCHRIFT FUER NATURFORSCHUNG

University of Kentucky
Department of Chemistry
Lexington, KY 40506

July 1989

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT prepared for publication in ZEITSCHRIFT FUER NATURFORSCHUNG
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UK/DC/TR-25	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Kentucky	6b. OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Lexington, KY 40506-0055	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / R&T Code 4135003-1 / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
NEW BORON-NITROGEN ANALOGUES OF URACIL DERIVATIVES (unclassified)

12. PERSONAL AUTHOR(S)
Ludwik Komorowski and Kurt Niedenzu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
interim technical	FROM _____ TO _____	89/7	16

16. SUPPLEMENTARY NOTATION

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	boron-nitrogen compounds, isoelectronic species, azaborauracils, 1,3,5-triaza-2-boracyclohexa-4,6-diones

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The reaction of N,N′-dimethylurea with 1,5-dimethyl-2,4-bis-(dimethylamino)-1,5-diaza-2,4-dibora-3-oxacyclohexan-6-one (**2**) in the melt proceeds with condensation of the urea to yield two major products: the acid 1,3,5-trimethyl-2-hydroxy-1,3,5-triaza-2-boracyclohexa-4,5-dione (**1a**); and a mixture of the methylammonium (**4a**) and dimethylammonium (**4b**) of the anion $[\{CH_3N(\mu\text{-}CONCH_3)_2\}_2B]^-$. Analogous product were obtained from the reaction of **2** with N, N′, N″-triorganylbiurets. The 2-hydroxy derivatives of type **1** form 1:1 molar adducts with amines (**3**) of variable thermal stability. The anhydride of **1a** was obtained as the bis(dimethylamine) adduct $[CH_3N(\mu\text{-}CONCH_3)_2B]_2O \cdot 2(CH_3)_2NH$ (**6**) from the reaction of $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ with N, N′, N″-trimethylbiuret.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kurt Niedenzu	22b. TELEPHONE (Include Area Code) (606) 257-7073 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
unclassified

New Boron-Nitrogen Analogues of Uracil Derivatives [1]

Ludwik Komorowski and Kurt Niedenzu*

*Reprint requests to Prof. K. Niedenzu.

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506–0055, USA

Z. Naturforsch.....; received.....

Boron–Nitrogen Compounds, Isoelectronic Species, Azaborauracils, 1,3,5–Triaza–2–boracyclohexa–4,6–diones

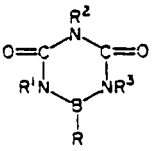
Abstract:

The reaction of N, N′–dimethylurea with 1,5–dimethyl–2,4–bis–(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (2) in the melt proceeds with condensation of the urea to yield two major products: the acid 1,3,5–trimethyl–2–hydroxy–1,3,5–triaza–2–boracyclohexa–4,5–dione (1a); and a mixture of the methylammonium (4a) and dimethylammonium (4b) of the anion $[\{CH_3N(\mu\text{–}CONCH_3)_2\}_2B]^-$. Analogous product were obtained from the reaction of 2 with N, N′, N″–triorganylbiurets. The 2–hydroxy derivatives of type 1 form 1:1 molar adducts with amines (3) of variable thermal stability. The anhydride of 1a was obtained as the bis(dimethylamine) adduct $[CH_3N(\mu\text{–}CONCH_3)_2B]_2O{\cdot}2(CH_3)_2NH$ (6) from the reaction of $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ with N, N′, N″–trimethylbiuret.

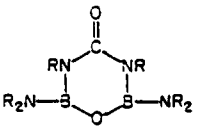
Introduction

The CC and BN moieties are a classical example of a pair of isoelectronic and isosteric species [2]. Although the physical properties of many boron–nitrogen and isosteric organic compounds, *e.g.*, borazine, $(-BH-NH-)_3$, and benzene, are very similar, the chemical behavior is usually greatly influenced by the differences in the polarities of the isosteric units. On the other hand, the chemical properties of an organic species may be altered to a small extent only by the selective incorporation of a single BN unit into an organic framework, as has been documented for iminoboranes of the type RB≡NR′ and acetylenes [3]. Nevertheless, the physiological and pharmacological properties of such isoelectronic species may still differ considerably. This has prompted an interest in boron–nitrogen analogues of biologically active materials, *e.g.*, boron analogues of amino acids and derivatives thereof have been studied extensively [4].

Uracil is an important constituent of many nucleic acids, but very few boron–nitrogen analogues of uracil derivatives, *i.e.*, 1,3,5–triaza–2–boracyclohexa–4,6–diones containing the principal framework **1**, are known. The limited literature on such species has been summarized earlier [5] and only three relevant studies have appeared since [6–8].



1



2

a: R = OH, $R^1 = R^2 = R^3 = CH_3$

b: R = OH, $R^1 = R^2 = CH_3$, $R^3 = C_2H_5$

c: R = OH, $R^1 = R^2 = CH_3$, $R^3 = C_6H_5$

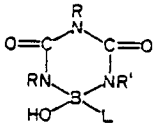
R = CH_3

Within the course of a general study of the synthesis of boron heterocycles and their interaction with nitrogen donor molecules, reactions of N, N′–dimethylurea with some simple boron–nitrogen derivatives have recently been investigated [8]. In a continuation of this latter work, the reaction of 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (**2**) with N, N′–dimethylurea as well as N, N′, N″–triorganylbiurets has been found to give access to the azaborauracil derivatives **1a–1c**. Relevant results are described here.

Results and Discussion

No reaction was observed when 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (2) was treated with N, N′–dimethylurea in refluxing toluene, and the starting materials were recovered unchanged. However, when 2 was reacted with excess molten N, N′–dimethylurea at 190–200 °C, two major types of boron–containing products were obtained. Approximately one half of the boron content of the originating 2 was found as the Lewis acid 1,3,5–trimethyl–2–hydroxy–1,3,5–triaza–2–boracyclohexa–4,6–dione (1a); and a mixture of the salts 5a and 5b was the other major boron–containing product (see below).

The acid **1a** is a thermally stable material that melts and can be sublimed under vacuum without condensation. It is a Lewis acid and adducts of type 3 could be obtained from the interaction of **1b** with methylamine (3a) or with dimethylamine (3b).



3

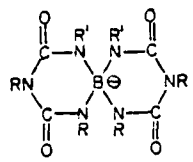
a: R = R^1 = CH_3, L = CH_3NH_2

b: R = R^1 = CH_3, L = $(CH_3)_2NH$

c: R = CH_3, R^1 = C_6H_5, L = CH_3NH_2

With triethylamine, however, only minor complexation was observed in solution as indicated by a ^{11}B NMR signal at δ = 2.2, and most of **1b** remained in free state; the acid **1b** was recovered quantitatively after solvent evaporation and drying of the remaining solid under vacuum at ambient temperature. These observations imply that steric factors may control the thermal stability of adducts of type 3.

As noted above, the remainder of the boron of the starting material 2 from its interaction with N, N′–dimethylurea was found as a mixture of the methylammonium (4a) and dimethylammonium salt (4b) of the anion $[\{CH_3N(\mu\text{–}CONCH_3)_2\}_2B]^-$.



4

a: R = R^1 = CH_3; cation: $[CH_3NH_3]^+$

b: R = R^1 = CH_3; cation: $[(CH_3)_2NH_2]^+$

c: R = R^1 = CH_3; cation: $[(CH_3)_3NH]^+$

d: R = CH_3, R^1 = C_2H_5; cation: $[CH_3NH_3]^+$

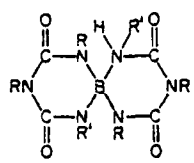
e: R = CH_3, R^1 = C_2H_5; cation $[(CH_3)_2NH_2]^+$

f: R = CH_3, R^1 = C_6H_5; cation: $[CH_3NH_3]^+$

g: R = CH_3, R^1 = C_6H_5; cation: $[(CH_3)_2NH_2]^+$

The formation of these salts presents one of the relatively rare cases where a B–O bond is being broken in favor of a B–N bond formation.

On heating of the salts **4a–4c** under vacuum, the betaine **5a** was obtained.



5

a: R = R^1 = CH_3

b: R = CH_3, R^1 = C_2H_5

c: R = CH_3, R^1 = C_6H_6

However, the thermal decomposition proceeded readily (at 165 °C/10^{-3} Torr) only in the case of **4c**. The salt **4a** showed some decomposition at the melting point, but required much more forcing conditions (300 °C/10^{-3} Torr) than **4c** in order to obtain **5a** (which was extracted from the thermolysis product with chloroform), and the process was accompanied by the formation of unidentified by–products. The same holds true for the thermolysis of **4b**.

The betaine **5a** interacted, in turn, with primary, secondary, or tertiary amines to give salts of type **4**. (The salts **4b** and **4c** (only impure) of the spiroboron anion as well as **5a** have previously been obtained from the interaction of N, N′, N″–trimethylbiuret with tris(dimethylamino)borane or trimethylamine–borane, respectively [5].)

In summary, the interaction of **2** with N, N′–dimethylurea in the melt can be described by equation (1).

$$\mathbf{2} + 5OC(NHCH_3)_2 \rightarrow \mathbf{1a} + \mathbf{4a} + 2(CH_3)_2NH + 2CH_2NH_3 \quad (1)$$

However, some of the generated dimethylamine can take the place of methylamine in **4a** leading to the observed formation of **4b**. In addition, a noticeable amount of the dimethylamine also interacted with the N, N′–dimethylurea to form N, N, N′–trimethylurea. This corresponds to an earlier observation that on heating of dimethylaminoboranes, $(CH_3)_2NBR_2$, with N, N′–dimethylurea an amino group exchange occurs with the formation of the corresponding monomethylaminoboranes and N, N, N′–trimethylurea [9].

As noted above, **1a** is thermally stable and can be sublimed without condensation. However, the anhydride $[CH_3N(\mu\text{–}CONCH_3)_2B]_2O$ was obtained as the bis(dimethylamine) adduct $[CH_3N(\mu\text{–}CONCH_3)_2B]_2O{\cdot}2(CH_3)_2NH$ (**6**) from the reaction of $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ with N, N′, N″–trimethylbiuret. The boron in **6** is four–coordinate (^{11}B NMR), illustrating the binding of the dimethylamine moieties at the two boron atoms. Surprisingly, **6** decomposed on thermal treatment with the formation **4b** rather than a simple loss of dimethylamine; the thermolysis may be described by equation (2).

$$[CH_3N(\mu\text{–}CONCH_3)_2B]_2O{\cdot}2(CH_3)_2NH \rightarrow [\{CH_3N(\mu\text{–}CONCH_3)_2\}_2B]^-(CH_3)_2NH_2^+ + 1/3\,[-BN(CH_3)_2\text{–}O\text{–}]_3 \quad (2)$$

As was to be expected on the basis of the above results, **2** interacted with N, N′, N″–trimethylbiuret in a fashion analogous to the reaction with N, N′–dimethylurea. The reaction proceeded extremely sluggish in boiling toluene and after 8 h reflux less than one half of the biuret had been consumed. The reaction in boiling xylene proceeded somewhat more readily but offered no advantage as compared to the reaction in the melt. Again approximately one half of the boron of the originating **2** was found as the acid **1a**, and the remainder was obtained as a mixture of the salts **4a** and **4b**. The urea moiety of **2** was recovered as N, N′–dimethylurea but some N, N, N′–trimethylurea was also formed.

N, N′–Dimethyl–N″–ethylbiuret reacted with 2 to give the acid **1b** besides a mixture of ammonium salts of **4d** and **4e**. The reaction of 2 with N, N′–dimethyl–N″–phenylbiuret gave identical products and in about the same ratio in toluene solution or in the melt, *i.e.*, the acid **1c** and the salt **4g**; surprisingly, no formation of the salt **4f** was observed in this case.

The acid **1b** did not form isolable complexes with either methylamine or dimethylamine. If the reagents were combined in chloroform solution, only a very small signal four four–coordinate boron was observed in the ^{11}B NMR spectrum at room temperature, besides the signal of the free acid. At –40 °C, however, only one signal at 1.0 or 2.1 ppm, respectively, was observed for mixtures of **1b** with methylamine or dimethylamine, indicative of complete complexation at low temperatures.

The acid **1c** formed an isolable adduct with methylamine (**3c**). Essentially no interaction was observed at room temperature between **1c** and dimethylamine, trimethylamine, or pyridine (as based ^{11}B NMR studies).

The thermal decomposition of the salt **4g** did not proceed cleanly and the free betaine **5c** could not be obtained in pure state. However, the ^{1}H NMR spectrum of the thermolysis product suggested that the mixture contained **5c** as two isomers with the (N)H located at either a $N(C_6H_5)$ (majority) or a $N(CH_3)$ site (minor product) adjacent to the boron. However, the mixture contained additional thermolysis products; no effort was made to separate these.

Experimental Section

Reactions and transfers were carried out in an inert atmosphere. 1,5–Dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexane–6–one (**2**) was obtained from the reaction of N, N′–dimethylurea with either tris(dimethylamino)borane [7] or tetrakis(dimethylamino)–1,3,2–diboroxane [10]; N, N′, N″–trimethylbiuret and N, N′–dimethyl–N″–ethylbiuret were prepared by reaction of 3,5–dimethyl–1,3,5–oxadiazacyclohexa–2,4,6–trione (obtained by a modified [11] reaction of carbon dioxide with methyl isocyanate [12]) with anhydrous methylamino or ethylamine, respectively [12]; and N, N′–dimethyl–N″–phenylbiuret was prepared from phenyl isocyanate and N, N′–dimethylurea [13].

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined in sealed capillaries on a Mel–Temp block. NMR spectra were recorded on solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL–200 or VXR–400 (^{11}B) or GEMINI–200 (^{1}H, ^{13}C)

instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet; an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. All ^{13}C NMR spectra were recorded in the proton decoupled mode. EI mass spectral data were obtained on a VG ZAB–2F instrument; data are given to *m/z* = 30 for 5% or greater relative abundances (in parentheses) only.

The reaction of 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (2) *with N, N′–dimethylurea*:

(a) 1,3,5–Trimethyl–2–hydroxy–1,3,5–triaza–2–boracyclohexa–4,6–dione (1a)

A mixture of 2.0 g (19.4 mmol) of **2** and 6.6 g (70 mmol) of N, N′–dimethylurea was slowly heated to give a clear melt, which was subsequently kept at a bath temperature of 190–200 °C for 15 h. Unreacted N, N′–dimethylurea (and a small amount of N, N, N″–trimethylurea as well as N, N′, N″–trimethylbiuret) was sublimed off under vacuum and 4.0 g of solid residue remained. This latter was extracted with 400 mL of boiling toluene to leave 2.6 g of insoluble residue, m.p. 215–235 °C. The toluene solution was evaporated and the resultant solid material (1.3 g, 39%) was recrystallized from acetonitrile to give **1b**, m.p. 172–173 °C.

Analysis for $C_5H_{10}BN_3O_3$ (170.96).

Found	C, 35.50	H, 6.29	N, 24.03,
Calcd	C, 35.13	H, 5.89	N, 24.58.

NMR data: δ ^1H = 6.05* (1 H, s), 3.29 (3 H, s), 3.05 (6 H, s); δ ^{11}B = 23.3 (s, $h_{1/2}$ = 300 Hz); δ ^{13}C = 155.5, 29.7, 28.6. – Mass spectrum: *m/z* = 172 (6), 171 (100), 170 (23), 143 (20), 115 (5), 114 (34), 113 924), 112 (6), 99 (9), 87 (8), 86 (24), 85 (24), 84 (5), 72 (10), 70 (19), 69 (8), 58 (21), 57 (12), 56 (47), 55 (11), 42 (12), 30 (16).

(b) Methylammonium bis(N, N′, N″–trimethylbiuret–1,5–diyl)borate (**5a**)

The toluene–insoluble material of the preceding experiment (a) was extracted with cold acetonitrile to leave 1.3 g (20%) of insoluble material. This latter residue, m.p. 253–258 °C, was recrystallized from acetonitrile/methanol (4:1 by volume) to give pure **5a**, m.p. 260–262 °C decomp.

Found	C, 40.76	H, 7.40	N, 29.40,

Calcd C, 40.14 H, 7.35 N, 29.79.

NMR (solution in CD_3OD): δ ^1H = 3.19 (2 H, s), 2.55 (1 H, s), 2.51 (4 H, s); δ ^{11}B = 0.2 (s, $h_{1/2}$ = 15 Hz); δ ^{13}C = 158.8, 29.6, 29.0, 25.5. Mass spectrum (13 eV): *m/z* = 298 (35), 297 (8), 185 (9), 184 (86), 183 (21), 171 (6), 145 (23), 127 (9), 88 (52), 41 (5), 31 (100), 30 (53).

The same compound **5a** was obtained on treatment of the betaine 1,3,5–trimethyl–2–(N, N′, N″–trimethylbiuret–1–yl)–1,3,5–triaza–2–boracyclohexa–4,6–dione **6a** [5] with anhydrous methylamine in chloroform solution as follows: Anhydrous methylamine was bubbled for a few minutes through a solution of **6a** in chloroform. A precipitate formed in an exothermic reaction. Excess amine and chloroform were evaporated to leave an essentially quantitative yield of crude **5a**, m.p. 248–257 °C. (A m.p. 276–278 °C has been reported for **6a** [5]; this seems to be a printing error and the correct datum should be 296–298 °C.)

(c) Dimethylammonium N, N′, N″–trimethylbiuret–1,5–diyl)–borate (**5b**)

The acetonitrile solution from the preceding experiment (b) was evaporated to leave 1.1 g (16%) of residue. This was recrystallized from acetonitrile/benzene (1:1 by volume) to give **5b**, m.p. 252–253 °C. (A m.p. of 232 °C has previously been reported for **5b** as obtained from tris(dimethylamino)borane and N, N′, N″–trimethylbiuret [5].)

NMR data: δ ^1H = 9.45* (1 H, s), 3.17 (3 H, s), 2.83 (3 H, s), 2.46 (6 H, s); δ ^{11}B = –1.3 (s, $h_{1/2}$ = 20 Hz). In CD_3OD: δ ^1H = 3.17 (3 H, s), 2.68 (3 H, s), 2.50 (two closely spaced s, 6 H); δ ^{11}B = 0.2 (s, $h_{1/2}$ = 15 Hz); δ ^{13}C = 158.8, 35.5, 29.6, 29.0. – Mass spectrum (14 eV): *m/z* = 298 (14), 184 (6), 45 (100), 44 (87), 30 (8). – Lit. [5]: δ ^1H = 9.2* (1 H, s), 3.03 (3 H, s), 2.69 (3 H, s), 2.36 (6 H, s); δ ^{11}B = –1.0; δ ^{13}C = 156.3, 35.5, 28.8, 28.3.

The same compound **5b** was also obtained in essentially quantitative yield on treatment of the betaine **6a** [5] with anhydrous dimethylamine in chloroform solution. After evaporation of excess amine and solvent, the residue was recrystallized from acetonitrile to give a pure product, m.p. 252–253 °C.

The reaction of 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (**2**) *with N, N′, N″–trimethylbiuret:*

(a) 1,3,5–Trimethyl–2–hydroxy–1,3,5–triaza–2–boracyclohexa–4,6–dione (**1a**)

A mixture of 1.0 g (4.7 mmol) of **2** and 3.0 g (20.7 mmol) of N, N′, N″–trimethylbiuret was slowly heated in an

The reaction of 1,5-dimethyl-2,4-bis(dimethylamino)-1,5-diaza-2,4-dibora-3-oxacyclohexan-6-one (**2**) *with N, N', N''-trimethylbiuret*:

(a) 1,3,5-Trimethyl-2-hydroxy-1,3,5-triaza-2-boracyclohexa-4,6-dione (**1a**)

A mixture of 1.0 g (4.7 mmol) of **2** and 3.0 g (20.7 mmol) of N, N', N''-trimethylbiuret was slowly heated in an oil bath. Vigorous gas evolution started at about 150 °C with the formation of syrupy material. The mixture was kept at 200 °C for 2 h. After cooling to room temperature the glassy product was extracted with 300 mL of boiling toluene to leave 2.4 g of colorless residue. The clear toluene solution was evaporated and the residue was sublimed under vacuum. The sublimate was recrystallized from acetonitrile (in order to remove N, N'-dimethylurea) to give 0.4 g (25%) of **1b** (see above).

(b) Methylammonium bis(N, N', N''-trimethylbiuret-1,5-diyl)borate (**5a**)

The 2.4 g of (toluene-insoluble) residue from the preceding experiment (a) was treated with 60 mL of acetonitrile to leave 1.2 g (38%) of a colorless residue. The latter was recrystallized from acetonitrile/methanol (4:1 by volume) to give **5a** (see above).

(c) Dimethylammonium bis(N, N', N''-Trimethylbiuret-1,5-diyl)borate (**5b**)

The acetonitrile solution from the preceding experiment (b) was evaporated to leave 1.0 g (30%) of solid material which was recrystallized from acetonitrile/benzene (1:1 by volume) to give 0.6 g of pure **5b** (see above).

2-Methylamine-1,3,5-Trimethyl-2-hydroxy-1,3,5-triaza-2-boracyclohexa-4,6-dione (**3a**)

Approximately 0.1 g of **1b** was dissolved in a minimal amount chloroform and anhydrous methylamine was slowly bubbled through the solution for 10–15 min. Volatile material was evaporated under vacuum to leave **3a**, m.p. 158–160 °C, in essentially quantitative yield.

NMR data: δ ^{1}H = 3.14 (3 H, s), 2.65 (6 H, s), 2.51 (3 H, s); δ ^{11}B = –0.1 (s, $h_{1/2}$ = 10 Hz); δ ^{13}C = 159.9, 29.5, 28.4, 25.5. – Mass spectrum (13 eV): *m/z* = 171 (35), 170 (12), 31 (100), 30 (23).

2-Dimethylamine-1,3,5-trimethyl-2-hydroxy-1,3,5-triaza-2-boracyclohexa-4,6-dione (**3b**)

This compound, m.p. 180–183 °C, was obtained in a fashion analogous to the preparation of the preceding compound employing **1b** and anhydrous dimethylamine.

NMR data: δ ^{1}H = 5.8* (1 H, s), 3.26 (3 H, s), 3.00* (6 H, s), 2.54 (6 H, s); δ ^{11}B = 0.5 (s, $h_{1/2}$ = 120 Hz). – Mass spectrum (13 ev): *m/z* = 199 (19), 172 (6), 171 (100), 170 (24), 145 (17), 88 (29), 85 (7), 83 (8), 45 (91), 44 (19).

Bis(1,3,5–trimethyl–1,3,5–triaza–2–boracyclohexa–4,6–dion–2–yl)oxide–Bis(dimethylamine) (**6**)

A mixture of 1.5 g (7 mmol) of $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ [10], 2.0 g (14 mmol) N, N′, N″–trimethylbiuret, and 20 mL of toluene was stirred at room temperature for 7 days. The mixture was then heated in an oil bath of 50–60 °C for 7 h and finally refluxed overnight. An additional 50 mL of toluene was added and the insoluble material was collected, washed with toluene, and dried under vacuum to give 2.5 g (86%) of crystalline **6**, m.p. 170–230 °C decomp.

Analysis for $C_{14}H_{32}B_2N_8O_5$ (414.08)

Found	C, 40.68	H, 8.02	N, 26.80,
Calcd	C, 40.61	H, 7.79	N, 27.05.

NMR data: δ ^{1}H = 9.3* (1 H, s), 3.14 (3 H, s), 2.71 (6 H, s), 2.45 (6 H, s); δ ^{11}B = –1.4 (s, $h_{1/2}$ = 25 Hz); δ ^{13}C = 156.8, 35.1, 28.9, 28.5.

The mass spectrum of the product showed only traces at *m/z* = 324 (for the oxide) and a small cluster at *m/z* = 211 (for B–tris(dimethylamino)boroxin); the spectrum was dominated by *m/z* = 298 (for the betaine **5a**) and its fragmentation as well as strong peaks at *m/z* = 45, 44 (for dimethylamine). Indeed, heating (150–160 °C) of the material under vacuum gave the salt **4b** and, ultimately, the betaine **5a** besides some unidentified by–products.

Reaction of 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (**2**) *with N, N′–dimethyl–N″–ethylbiuret*:

(a) 1,5–Dimethyl–2–hydroxy–3–ethyl–1,3,5–triaza–2–boracyclohexa–4,6–dione (**1b**)

A stirred mixture of 1.1 g (5.2 mmol) of **2** and 2.7 g (16 mmol) of N, N′–dimethyl–N″–ethylbiuret was heated in an oil bath of 200 °C for 2 h. After cooling to room temperature, the glassy product was treated with three 60–mL portions of hot toluene. Evaporation of the toluene from the combined solutions gave 0.7 g (36%) of crude **1b**, containing a small amount of its anhydride. Recrystallization of the product from toluene at the air gave pure **1b**, m.p. 150–151 °C.

Analysis for $C_6H_{12}B_3N_3O_3$ (184.99)

Found	C, 39.58	H, 6.62	N, 23.04,
Calcd	C, 38.95	H, 6.54	N, 22.71.

NMR data: δ ^{1}H = 5.3* (1 H, s), 3.59 (2 H, q, J = 7), 3.27 (3, H, s), 3.05 (3 H, s), 1.16 (3 H, t, J = 7); δ ^{11}B = 23.6 (s, $h_{1/2}$ = 260 Ha); δ ^{13}C = 155.6, 155.0, 38.9, 39.6, 28.5, 14.9. – Mass spectrum: m/z = 186 (12), 185 (89), 184 (23), 170 (44), 169 (11), 157 (16), 156 (5), 129 (6), 127 (7), 114 (14), 113 (100), 112 (25), 100 (20), 99 (13), 86 (20), 85 (13), 72 (6), 70 (41), 69 (15), 58 (13), 57 (7), 56 (57), 55 (16), 42 (27).

(b) Methylammonium bis(N, N′–dimethyl–N″–ethylbiuret–1,5–diyl)borate (**5d**)

All volatiles were removed from the toluene–insoluble oily residue from the preceding reaction under vacuum at room temperature. On standing for 3 days, the remaining syrupy material crystallized partially. Acetonitrile was then added to dissolve the oily part, and 0.75 g (21%) of colorless crystalline material remained. It was collected and recrystallized from acetonitrile/methanol (10:1 by volume) to give 0.4 g of **5d**, m.p. 240–244 °C.

NMR data (solution in CD_3OD): δ ^{1}H = 3.19 (6 H, s), 3.06 (4 H, unresolved q), 2.56 (3 H?, s) + 2.53* (6 H?, s) 9 H total), 1.04 (6 H, t, J = 7); δ ^{11}B = –0.9 (s, $h_{1/2}$ = 20 Hz). – Mass spectrum (14 eV): m/z = 326 (4), 325 (17), 324 (3), 198 (8), 31 (100), 30 (60).

The acetonitrile solution was evaporated to leave ca. 1.2 g of viscous liquid. NMR data showed it to consist primarily of the salt **5e** (δ ^{11}B = –1.3 (s, $h_{1/2}$ = 30 Hz); no effort was made to purify the species).

Reaction of 1,5–dimethyl–2,4–bis(dimethylamino)–1,5–diaza–2,4–dibora–3–oxacyclohexan–6–one (**2**) *with N, N′–dimethyl–N″–phenylbiuret*

(a) 1,5–Dimethyl–2–hydroxy–3–phenyl–1,3,5–triaza–2–boracyclohexa–4,6–dione (**1c**)

A stirred mixture of 1.0 g (4.7 mmol) of **2**, 3.0 g (14.5 mmol) of N, N′–dimethyl–N″–phenylbiuret, and 60 mL of toluene was heated to reflux for 18 h. Some precipitate formed and, after cooling the mixture to room temperature, the clear solution was decanted. The toluene was evaporated to leave 2 g of colorless solid. This was heated in a sublimator under vacuum to remove some N, N′–dimethylurea and N, N, N′–trimethylurea. The sublimation residue was recrystallized from toluene to give 0.7 g (32%) of **1c**, m.p. 197–199 °C.

Analysis for $C_{10}H_{12}BN_3O_2$ (233.03)

Found	C, 51.12	H, 5.35	N, 17.70,
Calcd	C, 51.54	H, 5.19	N, 18.03.

NMR data: δ ^{1}H = 7.5 (3 H, unresolved m), 7.2 (2 H, unresolved m), 3.99* (1 H, s), 3.34 (3 H, s), 3.10 (3 H, s); δ ^{11}B = 23.6 (s, $h_{1/2}$ = 200 Hz). – Mass spectrum: *m/z* = 234 (11), 233 (100), 232 (28), 176 (50), 175 (9), 119 (36), 118 (7), 93 (10).

(b) Dimethylammonium bis(N, N'–dimethyl–N''–phenylbiuret–1,5–diyl)borate (5e)

Some N, N'–dimethylurea and N, N, N'–trimethylurea was sublimed off the toluene–insoluble material from the preceding experiment (a). The sublimation residue was then recrystallized from acetonitrile to give 1.1 g (25%) of 5e, m.p. 250–252 °C.

Analysis for $C_{22}H_{30}BN_7O_4$ (467.33)

Found	C, 54.96	H, 6.40	N, 20.87,
Calcd	C, 56.54	H, 6.47	N, 20.98.

NMR data: δ ^{1}H = 7.27 (5 H, m), 2.92 (3 H, s), 2.58 (3 H, s), 1.95 (3 H, s); δ ^{11}B = –1.0 (s, $h_{1/2}$ = 40 Hz); δ ^{13}C = 156.6, 156.2, 142.5, 128.9, 127.7, 126.2, 34.8, 29.2, 28.8. – Mass spectrum (13 eV): *m/z* = 246 (23), 207 (15), 119 (26), 93 (14), 88 (20), 45 (100), 44 (80), 30 (42).

2–Methylamine–1,5–Dimethyl–2–hydroxy–3–phenyl–1,3,5–triaza–2–boracyclohexa–4,6–dione (3c)

This compound was obtained in a manner analogous to the preparation of 3a (see above) using the B–hydroxy compound 1c. The product, m.p. 105 °C decomp, was obtained in essentially quantitative yield.

NMR data (solution in CD_3OD): δ ^{1}H = 7.23 (5 H, m), 3.20 (3 H, s), 2.72* (3 H, s), 2.37 (3 H, s); δ ^{11}B = 2.5 (s, $h_{1/2}$ = 15 Hz). – Mass spectrum: *m/z* = 261 (24), 233 (14), 208 (12), 207 (100), 204 (8), 93 (7), 88 (15), 85 (10), 83 (17), 45 (6), 31 (45), 30 (9).

Acknowledgments. This work was supported in part by the U.S. Office of Naval Research and the Alexander von Humboldt Foundation (K.N.). L. K. acknowledges a leave of absence from the Technical University Wrocław, Wrocław, Poland.

References:

[1] Boron–Nitrogen Compounds. Part 122. For Part 121 of this series, see: K. Niedenzu and K. R. Woodrum, Inorg. Chem., in hand of editor.

[2] H. Schmidbaur, Fortschr. Chem. Forsch. (Top. Curr. Chem.) **13**, 167 (1969).

[3] P. Paetzold, Adv. Inorg. Chem. **31**, 123 (1987).

[4] B.F. Spielvogel, F. U. Ahmed, and A. M. McPhail, Inorg. Chem. **25**, 4395 (1986), and references cited therein.

[5] J. Bielawski, K. Niedenzu, A. Weber, and W. Weber, Z. Naturforsch. **36b**, 470 (1981), and references cited therein.

[6] W. Maringgele, J. Organomet. Chem. **222**, 17 (1981).

[7] W. Maringgele, Chem. Ber. **115**, 3271 (1982).

[8] J. Bielawski, K. Niedenzu, and J. S. Stewart, Z. Naturforsch. **40b**, 389 (1985).

[9] L. Komorowski and K. Niedenzu, Inorg. Chem. **28**, 804 (1989).

[10] M. Komorowska, K. Niedenzu, and W. Weber, to be published.

[11] D. Etienne, B. Boute, and D. Druet, Bull. Soc. Chim. Fr. **1972**, 242.

[12] K. I. Slotta and R. Tschesche, Ber. Dtsch. Chem. Ges. **60**, 295 (1927).

[13] P. L. Salzberg, U. S. Patent 3,189,431 (1965).

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1

ORGANOELEMENT CHEMISTRY - Distribution List

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214
R&T Code 4135002

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907
R&T Code 4135011

Professor Steven L Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
R&T Code 4135014

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
R&T Code 4135007

Professor M. Frederick Hawthorne
Department of Chemistry
405 Hilgard Avenue
University of California
Los Angeles, CA 90024
R&T Code 4135004

Professor Robert H. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, TX 76843
R&T Code 4135005

Professor Kurt Niedenzu
Department of Chemistry
University of Kentucky
Lexington, KY 40506
R&T Code 4135003

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706
R&T Code 4135008