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

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited
**NEW BORON-NITROGEN ANALOGUES OF URACIL DERIVATIVES** (unclassified)

Ludwik Komorowski and Kurt Niedenzu

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$_3$)$_2$N(2-CONCH$_3$)$_2$B$]_2$O. Analogous products were obtained from the reaction of 2 with N,N',N"-trimercuriureas. The 2-hydroxy derivatives of 1a was obtained as the bis(dimethylamine) adduct [(CH$_3$)$_2$N(2-CONCH$_3$)$_2$B$]_2$O-2(CH$_3$)$_2$NH (6) from the reaction of [(CH$_3$)$_2$N]BOB[N(CH$_3$)$_2$]$_2$ with N,N',N"-trimethylurea. K.
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 ........................................................................................................

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 \([\text{CH}_3\text{N(\mu-CONCH}_3\text{)}_2\text{B}]^-\). 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 \([\text{CH}_3\text{N(\mu-CONCH}_3\text{)}_2\text{B}]_2\text{O}+2(\text{CH}_3)_2\text{NH}\) (6) from the reaction of \([\text{CH}_3\text{N}_2\text{BOB(N(CH}_3\text{)_2}])\) 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=N=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].

\[
\begin{align*}
  &1 \\
  &2 \\
  a: & R = \text{OH}, R^1 = R^2 = R^3 = \text{CH}_3 & R = \text{CH}_3 \\
  b: & R = \text{OH}, R^1 = R^2 = \text{CH}_3, R^3 = \text{C}_2\text{H}_5 \\
  c: & R = \text{OH}, R^1 = R^2 = \text{CH}_3, R^3 = \text{C}_6\text{H}_5
\end{align*}
\]

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).

\[
\begin{align*}
3 \\
a: R &= R^l = CH_3, L = CH_3NH_2 \\
b: R &= R^l = CH_3, L = (CH_3)NH \\
c: R &= CH_3, R^l = C_6H_5, L = CH_3NH_2
\end{align*}
\]

With triethylamine, however, only minor complexation was observed in solution as indicated by a $^{11}$B NMR signal at $\delta = 2.2$, 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 \(\{CH_3N(\mu-CONCH_3)_2\}_2B\)\(^-\).
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.

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).

\[
2 + 5OC(NHCH_3)_2 \rightarrow 1a + 4a + 2(CH_3)_2NH + 2CH_2NH_3
\]  

(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(μ-CONCH_3)_2B]_2O was obtained as the bis(dimethylamine) adduct [CH_3N(μ-CONCH_3)_2B]_2O·2(CH_3)_2NH (6) from the reaction of [(CH_3)_2N]_2BOB[N(CH_3)_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).

\[
[CH_3N(μ-CONCH_3)_2B]_2O·2(CH_3)_2NH \rightarrow [(CH_3N(μ-CONCH_3)_2B)]^+(CH_3)_2NH_2^+ + 1/3 [-BN(CH_3)_2-O-]_3
\]  

(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(C₆H₅) (majority) or a N(CH₃) 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'-trimehylbiuret 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 CDCl₃ (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$_3$)$_4$Si for $^1$H and $^{13}$C NMR, external (C$_2$H$_5$)$_2$O-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-dirrethvy-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$_5$H$_{10}$BN$_3$O (170.96).

<table>
<thead>
<tr>
<th>Found</th>
<th>C, 35.50</th>
<th>H, 6.29</th>
<th>N, 24.03,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>C, 35.13</td>
<td>H, 5.89</td>
<td>N, 24.58.</td>
</tr>
</tbody>
</table>

NMR data: $\delta ^1$H = 6.05* (1 H, s), 3.29 (3 H, s), 3.05 (6 H, s); $\delta ^{11}$B = 23.3 s, $\delta ^{13}$C = 300 Hz; $\delta ^{13}$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.

<table>
<thead>
<tr>
<th>Found</th>
<th>C, 40.76</th>
<th>H, 7.40</th>
<th>N, 29.40,</th>
</tr>
</thead>
</table>
Calcd C, 40.14  H, 7.35  N, 29.79.

NMR (solution in CD$_3$OD): $\delta$ $^1$H = 3.19 (2 H, s), 2.55 (1 H, s), 2.51 (4 H, s); $\delta$ $^{11}$B = 0.2 (s, $\nu_{112}$ = 15 Hz); $\delta$ $^{13}$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: $\delta$ $^1$H = 9.45* (1 H, s), 3.17 (3 H, s), 2.83 (3 H, s), 2.46 (6 H, s); $\delta$ $^{11}$B = -1.3 (s, $\nu_{112}$ = 20 Hz). In CD$_3$OD: $\delta$ $^1$H = 3.17 (3 H, s), 2.68 (3 H, s), 2.50 (two closely spaced s, 6 H); $\delta$ $^{11}$B = 0.2 (s, $\nu_{112}$ = 15 Hz); $\delta$ $^{13}$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]: $\delta$ $^1$H = 9.2* (1 H, s), 3.03 (3 H, s), 2.69 (3 H, s), 2.36 (6 H, s); $\delta$ $^{11}$B = -1.0; $\delta$ $^{13}$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 15-dimethyl-2,4-bis(dimethylamino)-15-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: \( \delta^1H = 3.14 \) (3 H, s), 2.65 (6 H, s), 2.51 (3 H, s); \( \delta^{11}B = -0.1 \) (s, \( h_{11} = 10 \) Hz); \( \delta^{13}C = 159.9, 29.5, 28.4, 25.5 \). – 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 1H = 5.8* (1 H, s), 3.26 (3 H, s), 3.00* (6 H, s), 2.54 (6 H, s); δ 11B = 0.5 (s, h1/2 = 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 [CH3]2N2BOB[N(CH3)2]z [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 C14H32B2N8O5 (414.08)

<table>
<thead>
<tr>
<th>Found</th>
<th>C, 40.68</th>
<th>H, 8.02</th>
<th>N, 26.80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>C, 40.61</td>
<td>H, 7.79</td>
<td>N, 27.05</td>
</tr>
</tbody>
</table>

NMR data: δ 1H = 9.3* (1 H, s), 3.14 (3 H, s), 2.71 (6 H, s), 2.45 (6 H, s); δ 11B = -1.4 (s, h1/2 = 25 Hz); δ 13C = 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 C₉H₁₂B₃N₃O₃ (184.99)

<table>
<thead>
<tr>
<th>Found</th>
<th>C, 39.58</th>
<th>H, 6.62</th>
<th>N, 23.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>C, 38.95</td>
<td>H, 6.54</td>
<td>N, 22.71</td>
</tr>
</tbody>
</table>

NMR data: \( \delta \) \(^1\)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, \( J = 7 \)); \( \delta ^{11}\)B = 23.6 (s, \( h_{1,2} = 260 \) Ha); \( \delta ^{13}\)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 CD₃OD): \( \delta ^1\)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, \( J = 7 \)); \( \delta ^{11}\)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 (\( \delta ^{11}\)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 C₁₀H₁₃BN₃O₂ (233.03)
Found  C, 51.12  H, 5.35  N, 17.70,
Calcd  C, 51.54  H, 5.19  N, 18.03.

NMR data: $\delta^1H = 7.5$ (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); $\delta^{11}B = 23.6$ (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 $\text{C}_{22}\text{H}_{39}\text{BN}_{7}\text{O}_{4}$ (467.33)

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calcd</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54.96</td>
<td>56.54</td>
</tr>
<tr>
<td>H</td>
<td>6.40</td>
<td>6.47</td>
</tr>
<tr>
<td>N</td>
<td>20.87</td>
<td>20.98</td>
</tr>
</tbody>
</table>

NMR data: $\delta^1H = 7.27$ (5 H, m), 2.92 (3 H, s), 2.58 (3 H, s), 1.95 (3 H, s); $\delta^{11}B = -1.0$ (s, $h_{1/2} = 40$ Hz); $\delta^{13}C = 156.6, 156.2, 142.5, 128.9, 127.7, 126.2, 34.8, 29.2, 28.8$. – 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 (3e)

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$_3$OD): $\delta^1H = 7.23$ (5 H, m), 3.20 (3 H, s), 2.72* (3 H, s), 2.37 (3 H, s); $\delta^{11}B = 2.5$ (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 Wroclaw, Wroclaw, Poland.
References:


<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry Division, Code 1113</td>
<td>Dr. Ronald L. Atkins</td>
</tr>
<tr>
<td>800 North Quincy Street</td>
<td>Chemistry Division (Code 385)</td>
</tr>
<tr>
<td>Arlington, VA 22217-5000</td>
<td>Naval Weapons Center</td>
</tr>
<tr>
<td>Chief of Naval Research</td>
<td>1</td>
</tr>
<tr>
<td>Commanding Officer</td>
<td>Special Assistant</td>
</tr>
<tr>
<td>Naval Weapons Support Center</td>
<td>for Marine Corps Matters</td>
</tr>
<tr>
<td>Attn: Dr. Bernard E. Douda</td>
<td>Code 00MC</td>
</tr>
<tr>
<td>Crane, IN 47522-5050</td>
<td>800 North Quincy Street</td>
</tr>
<tr>
<td>Arlington, VA 22217-5000</td>
<td>Arlington, VA 22217-5000</td>
</tr>
<tr>
<td>Dr. Richard W. Drisko</td>
<td>1</td>
</tr>
<tr>
<td>Naval Civil Engineering Laboratory</td>
<td>Dr. Bernadette Eichinger</td>
</tr>
<tr>
<td>Code L52</td>
<td>Naval Ship Systems</td>
</tr>
<tr>
<td>Fort Hueneme, California 93043</td>
<td>Engineering Station</td>
</tr>
<tr>
<td>Defense Technical Information Center</td>
<td>2</td>
</tr>
<tr>
<td>Building 5, Cameron Station</td>
<td>Code 053</td>
</tr>
<tr>
<td>Alexandria, Virginia 22314</td>
<td>Philadelphia Naval Base</td>
</tr>
<tr>
<td>high quality</td>
<td>Philadelphia, PA 19112</td>
</tr>
<tr>
<td>David Taylor Research Center</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Eugene C. Fischer</td>
<td>Dr. Sachio Yamamoto</td>
</tr>
<tr>
<td>Annapolis, MD 21402-5067</td>
<td>Naval Ocean Systems Center</td>
</tr>
<tr>
<td>Dr. James S. Murday</td>
<td>Code 52</td>
</tr>
<tr>
<td>Chemistry Division, Code 6100</td>
<td>San Diego, CA 92152-5000</td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td>1</td>
</tr>
<tr>
<td>Washington, D.C. 20375-5000</td>
<td>David Taylor Research Center</td>
</tr>
<tr>
<td>Dr. Harold H. Singerman</td>
<td>1</td>
</tr>
<tr>
<td>Annapolis, MD 21402-5067</td>
<td>ATTN: Code 283</td>
</tr>
</tbody>
</table>
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