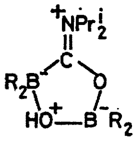
Reaction of Di-n-hexylbromoborane with Di-isopropylcarbamoyl-lithium: *X*-Ray Crystal Structure of 2,2,5,5-Tetra-n-hexyl-4,6-bis(di-isopropyliminio)-2,5-diborata-1,3-dioxacyclohexane, a New Organoborane which is Remarkably Resistant to Oxidation

By Andrew S. Fletcher, Walter E. Paget, Keith Smith,* and Kalyanaraman Swaminathan
(*Department of Chemistry, University College of Swansea, Swansea* SA2 8PP)

and Martin J. Haley
(*Department of Chemistry, University of Nottingham, Nottingham* NG7 2RD)

Summary 5-Di-isopropyliminio-2,2,4,4-tetra-n-hexyl-2,4-diborata-1-oxa-3-oxoniacyclopentane (**1**, R = n-hexyl) and 2,2,5,5-tetra-n-hexyl-4,6-bis(di-isopropyliminio)-2,5-diborata-1,3-dioxacyclohexane (**2**) have been obtained from reactions of di-n-hexylbromoborane with di-isopropylcarbamoyl-lithium; compound (**2**) is the first example of a new class of organoboranes and is remarkably resistant to oxidation, being unaffected by 50% hydrogen peroxide and base.

We have previously reported the reaction of di-isopropylcarbamoyl-lithium with diphenylbromoborane, and have fully characterized 5-di-isopropyliminio-2,2,4,4-tetraphenyl-2,4-diborata-1-oxa-3-oxoniacyclopentane (**1**, R = Ph).[1] It was of interest to know whether di-n-alkylbromoboranes reacted to give analogous products.



(**1**)

Addition of di-n-hexylbromoborane to LiCONPr$^i_2$ in tetrahydrofuran (THF)[2] or THF–ether–pentane,[3] at −78 °C or below, followed by warming to ambient temperature, removal of solvent, treatment with water, and passage through deoxygenated silica gave an oil, with ν_{max} 1550 cm^{-1}. The properties of the oil indicated that it contained primarily the same compound type as that obtained in the reaction of diphenylbromoborane, *i.e.*, (**1**, R = n-hexyl). However, although oxidation of the reaction mixture with alkaline hydrogen peroxide destroyed the bulk of the organoboron material, giving hexan-1-ol and HCONPr$^i_2$, a small amount of a white, crystalline solid, m.p. 58 °C, survived this treatment. This is a different product of novel structure (**2**).

The new product shows the following physical and spectroscopic properties: ν_{max} 1510 and 1490 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$), τ 5·42 (m, 2H), 6·63 (m, 2H), and 8·5—9·3 (complex m, 76H); ^{13}C n.m.r. (CDCl$_3$), δ 48·8, 47·2, 33·8 (2 lines detectable), 32·2 (2 lines), 29·1, 25·6, 22·8, 21·3, 20·3, and 14·2 (2 lines) p.p.m.; ^{11}B n.m.r. (CDCl$_3$; BF$_3$·OEt$_2$ = 0; downfield shifts positive†), δ −18·0 (sh s) and −13·8 (br); *m/e* 533 (base peak, M^+ −C$_6$H$_{13}$·); microanalysis consistent with the formula $C_{38}H_{80}B_2N_2O_2$. These data indicate at least two different types of n-hexyl group

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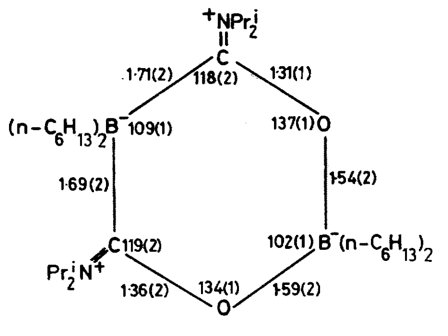
† Using the new convention adopted at the International Meeting on Boron Chemistry, IME Boron 3, Ettal, 1976.

and show that both boron atoms are four-co-ordinate, but they do not permit unequivocal formulation of (**2**). The structure was therefore determined by *X*-ray crystallography, and shown to be 2,2,5,5-tetra-n-hexyl-4,6-bis(diisopropyliminio)-2,5-diborata-1,3-dioxacyclohexane (Figure 1).



(2)

FIGURE 1. Bond lengths (Å) and angles (°) in the heterocyclic molecule.

Crystal data: (**2**), $C_{38}H_{80}B_2N_2O_2$, $M = 618{\cdot}69$, triclinic, $a = 9{\cdot}938(5)$, $b = 15{\cdot}191(4)$, $c = 17{\cdot}715(5)$ Å, $\alpha = 111{\cdot}63(10)$, $\beta = 99{\cdot}05(9)$, $\gamma = 111{\cdot}60(10)°$, $U = 2644$ Å^3, $Z = 2$, $D_c = 0{\cdot}78$ g cm^{-3}, $F(000) = 696$, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) $= 0{\cdot}6$ cm^{-1}, space group $P\bar{1}$.

A Hilger and Watts four-circle diffractometer was used to measure 3056 reflection intensities in the range $0 \leqslant \theta \leqslant 22°$ with graphite-monochromated Mo-K_α radiation. The structure was solved directly using MULTAN 77.[4] *E*-values, calculated by the *K*-curve method, had statistics which indicated a centrosymmetric cell and 410 reflections with $E > 1{\cdot}4$ were used in Σ_2 relationships. Three origin-fixing reflections and six reflections with permuted signs were used to generate phase sets and an *E*-map based on the set with the lowest ψ_0 figure of merit enabled 37 of the atomic positions to be located. The remaining atoms (excluding hydrogens) were found from a difference Fourier synthesis computed after isotropic refinement with 1873 independent, observed reflections using the CRYSTALS[5] set of programs. Full-matrix, least-squares refinement in two blocks each containing one-half of the molecule gives an *R* value which, at present, is 12%. The molecular structure of (**2**) is illustrated in Figure 2 and bond lengths and angles data for the approximately planar heterocyclic ring are given in Figure 1.‡

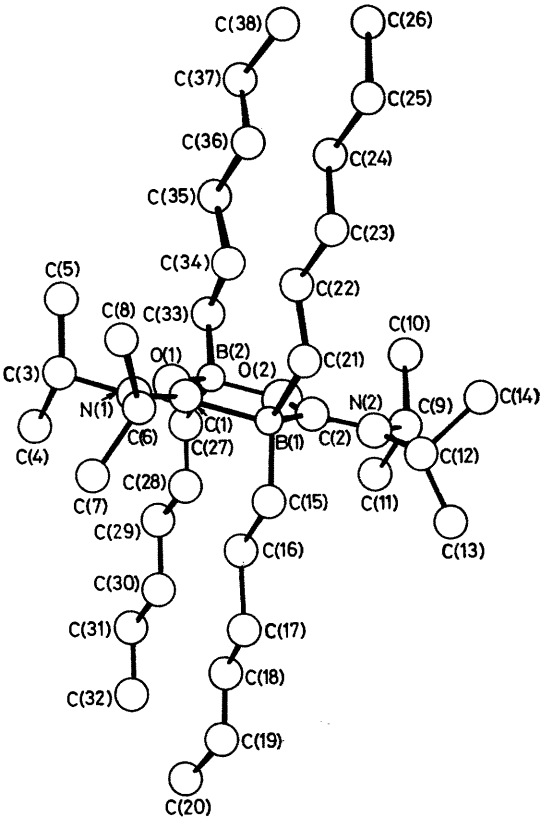


FIGURE 2. The molecular structure of (**2**).

Compound (**2**) is the first example of a new class of compounds. It shows remarkable resistance to oxidation, even by 50% hydrogen peroxide and alkali. The yield of (**2**) varies from 0—20%, depending upon the way in which the experiment is carried out. Surprisingly, its yield is highest (*ca.* 20%) when the reaction is carried out in THF, using LiCONPr$^i_2$ prepared from HCONPr$^i_2$ and Bu^{t}Li in the same solvent. Under these conditions, only *ca.* 30% of the theoretical amount of LiCONPr$^i_2$ is formed,[3b] so in terms of this reagent, the yield is relatively high.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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