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X-RAY STRUCTURE OF 1,2'-DIBORAZINE-2,6-DICHLORO-4,4',6'-TRI(DIISOPROPYLAMINO) TOLUENE SOLVATE

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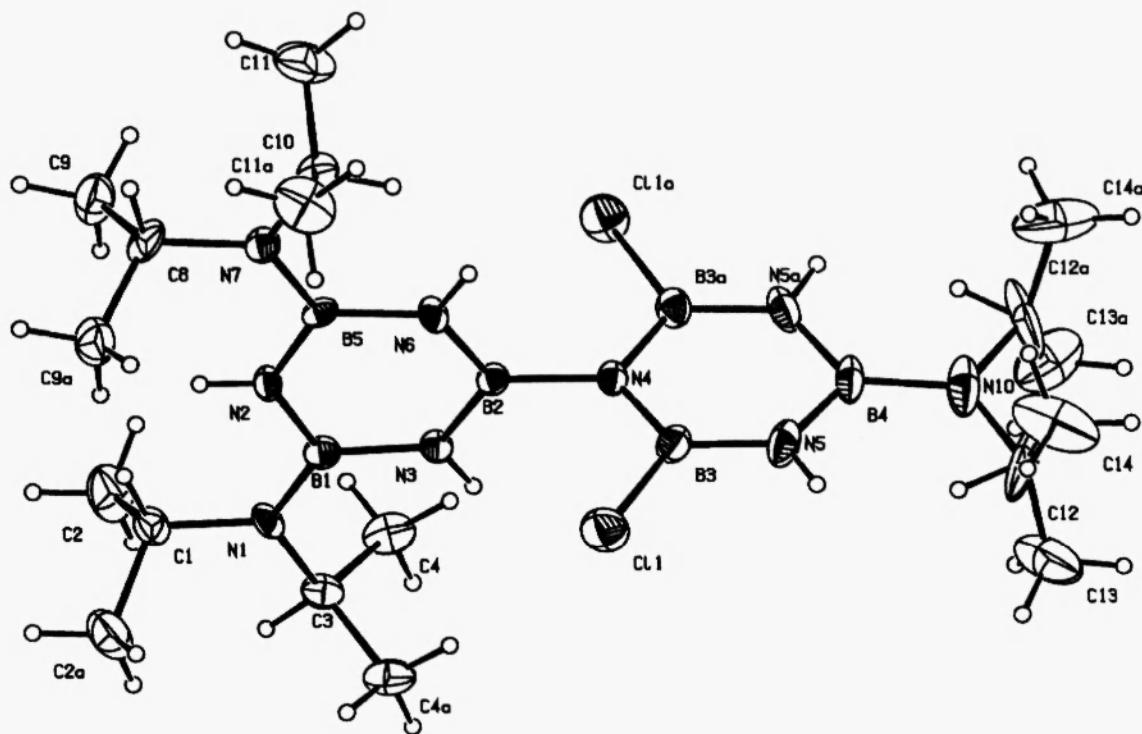


Figure 1. Molecular structure of the diborazine 1,2'-[(2,6-Cl)-4-(Prⁱ₂N)B₃N₃H₃](4',6'-(Prⁱ₂N)₂B₃N₃H₃) **1** in the structure of the title compound. Selected bond distances (Å) and angles (°) for **1**: B-Cl 1.782(6), N(4)-B(2) 1.501(8), N(3)-B(2) 1.42(1), N(3)-B(1) 1.45(1), N(2)-B(1) 1.44(1), N(2)-B(5) 1.46(1), N(5)-B(3) 1.388(7), N(5)-B(4) 1.450(6), N(4)-B(3) 1.429(6), N(10)-B(4) 1.42(1), N(1)-B(1) 1.42(1), N(1)-C(1) 1.459(9), N(1)-C(3) 1.49(1), N(7)-B(5) 1.427(9), N(7)-C(8) 1.46(1), N(7)-C(10) 1.46(1), N(10)-C(12) 1.471(3), B(2)-N(3)-B(1) 123.4(6), B(5)-N(6)-B(2) 123.9(4), B(3)-N(4)-B(2) 122.6(3), B(3a)-N(4)-B(3) 114.7(5), N(3)-B(2)-N(4) 120.0(6), N(6)-B(2)-N(4) 121.4(6), B(3)-N(5)-B(4) 125.0(4), B(1)-N(2)-B(5) 125.0(5), N(1)-B(1)-N(2) 123.4(7), N(2)-B(1)-N(3) 114.2(6), N(2)-B(5)-N(7) 122.6(7), N(1)-B(1)-N(3) 122.3(7), N(3)-B(2)-N(6) 118.6(5), N(6)-B(5)-N(7) 122.5(6), N(2)-B(5)-N(6) 114.9(5), N(10)-B(4)-N(5) 124.7(3), N(4)-B(3)-N(5) 122.1(4), N(5)-B(4)-N(5a) 110.7(6).

Comment

The unit cell contains four molecules of toluene and four molecules of the compound **1**. The latter is a diborazine displaying a linked ring structure. The *endo*-rings B-N distances are between 1.388(7) and 1.46(1) Å falling within the range of the distances found in other borazines [1, 2]. It should be noted that this large range is also observed in the other previously described diborazine 1,2'-(B₃N₃H₃)₂ [3]. As expected, the *exo*-rings B-N_(amino) bond lengths [av. 1.42(1) Å] are consistent with a B-N double-bond character [4]. The B-Cl bond lengths [1.782(6) Å] agree within experimental error with the values reported for 2,4,6-trichloroborazine, 1.76(2) Å [2] and for boron trichloride, ~1.73-1.76 Å [4]. The significant feature of this structure is the orthogonal arrangement of the borazine rings planes unlike in the diborazine 1,2'-(B₃N₃H₃)₂ [3]. In the latter, the two rings are coplanar, as biphenyl in the solid state, and the inter-ring B-N bond is short [1.464(7) Å] mirroring its double-bond character. By contrast, in **1** the relative twist of the B₃N₃ planes

[90.00(1)°] precludes any interaction between the lone pair of the N(4) nitrogen atom and the vacant *p*-orbital of the B(2) boron atom. Thus, this distance [1.502(8) Å] is longer than in 1,2'-(B₃N₃H₅)₂ and resembles B-N single-bonds [~1.58 Å] rather B-N double-bond distances [~1.41 Å]. This phenomenon is presumably related to the steric bulk of the borazine substituents in ortho and meta positions of both rings which precludes their coplanarity.

Experimental

Preparation. All experiments were performed under atmosphere of pure argon and anhydrous conditions using vacuum line and schlenk techniques with solvents purified by standard techniques. 2,4,6-trichloroborazine [5] and chloro(diisopropylamino)borane [6] were prepared as previously described and purified by vacuum sublimation and distillation, respectively. Triethylamine (17.8 mmol) was added to a solution of 2,4,6-trichloroborazine (5.94 mmol) and chloro(diisopropylamino)borane (17.8 mmol) in toluene (20 mL). The mixture was stirred for 24h at room temperature then heated under reflux conditions for 2h. Under cooling, suitable crystals for X-ray analysis were obtained. ¹¹B NMR (C₆D₆): δ 30.1 (2B), 24.6 (3B). ¹H NMR (CDCl₃): δ 1.12, 1.13 (CH₃); 3.05 (NH); 3.32, 3.39 (CH).

Table 1. Crystal data for 1,2'-[(2,6-Cl₂-4-(Prⁱ₂N)B₃N₃H₂)(4',6'-(Prⁱ₂N)₂B₃N₃H₃)]·(C₆H₅)CH₃

Formula	C ₂₅ H ₅₅ B ₆ Cl ₂ N ₉	Formula weight	617.54
Crystal system	orthorhombic	Crystal size, mm	0.30 × 0.22 × 0.15
Space group	Cmc21	<i>a</i> , Å	11.871(2)
<i>b</i> , Å	18.919(4)	<i>c</i> , Å	16.251(3)
<i>V</i> , Å ³	3650(1)	<i>Z</i>	4
Diffractometer	Nonius Kappa CCD	Temperature, K	123
μ(Mo-Kα), cm ⁻¹	2.08	Trans. factors	0.940-0.970
D _{calcd.} , g cm ⁻³	1.124	<i>F</i> (000)	1328
θ _{max.} , °	24.7	Reflns meas.	3028
Reflns unique	3028	Reflns with <i>I</i> > 2.0σ(<i>I</i>)	2119
<i>R</i> (<i>F</i> ²), <i>R</i> _w (<i>F</i> ²) [<i>I</i> ≥ 2.0σ(<i>I</i>)]	0.084, 0.232	ρ, e Å ⁻³	0.51 and -0.49
Weighting scheme	1/[σ ² (<i>F</i> _o ²) + (0.1420 <i>P</i>) ² + 5.8540 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3		
Programs used	Denzo & Scalepak [7], PLATON [8], SHELXL97 [9].		
Deposition number	CCDC 166376		
No absorption correction was applied			

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