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Structure of 1,5-Diisopropyl-4-phenyl-4,5-dihydrotetraazaborole

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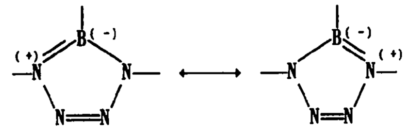
Abstract. $C_{12}H_{19}BN_4$, $M_r = 230{\cdot}12$, monoclinic, $P2_1/n$, $a = 5{\cdot}914\,(1)$, $b = 21{\cdot}225\,(3)$, $c = 11{\cdot}207\,(2)$ Å, $\beta = 102{\cdot}74\,(1)°$, $V = 1372{\cdot}1\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}114$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}6$ cm^{-1}, $F(000) = 496$, room temperature, final $R = 0{\cdot}054$ for 1292 observed reflections. The molecule shows extensive π delocalization throughout the dihydrotetraazaborole ring indicated by equivalent B—N bonds, shortened N—N single bonds and a lengthened N═N double bond. Intramolecular steric interactions are minimized by twisting the phenyl group by an interplanar angle of 44·4° relative to the five-membered ring.

Introduction. Boron–nitrogen groups are isosteric to the analogous carbon–carbon groups (Langmuir, 1919; Wiberg, 1948). Therefore, the title compound can be considered as a triazole with the two possible resonance structures (I) and (II):


(I) (II)

It has been pointed out that B—N bonds are nearly 0·05 Å (for single bonds) and 0·08 Å (for double and triple bonds) longer than the corresponding C—C bonds with standard values for B—N bonds of 1·58 Å for a single, 1·41 Å for a double and 1·26 Å for a triple bond (Paetzold, 1987).

Our investigation of 1,5-diisopropyl-4-phenyl-4,5-dihydrotetraazaborole is the first structure analysis of the BN_4 ring by X-ray diffraction. Only an electron diffraction study on 1,4-dimethyl-4,5-dihydrotetraazaborole is known (Chang, Porter & Bauer, 1969). Thus, quantitative information on the dimensions of the dihydrotetraazaborole ring system should be provided. Also the question should be answered whether π delocalization in the five-membered ring or a reduction of the symmetry of the ring by conjugation with the phenyl group occurs.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$), *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	2495 (4)	9081 (1)	2249 (2)	52 (1)
N(2)	1416 (5)	8906 (1)	1081 (3)	64 (1)
N(3)	195 (6)	8413 (1)	1128 (3)	62 (1)
N(4)	442 (5)	8236 (1)	2331 (2)	50 (1)
B(5)	1922 (6)	8663 (2)	3117 (3)	48 (1)
C(6)	3903 (6)	9659 (2)	2346 (4)	60 (1)*
C(7)	−859	7715	2569	50 (1)*
C(8)	−3181	7661	1965	66 (1)*
C(9)	−4518	7163	2240	89 (2)*
C(10)	−3533	6718	3119	93 (2)*
C(11)	−1211	6772	3722	82 (2)*
C(12)	125 (3)	7270 (1)	3447 (2)	62 (1)
C(13)	2456 (8)	10223 (2)	1901 (5)	95 (2)
C(14)	5898 (7)	9576 (2)	1731 (5)	95 (2)
C(15)	2630 (7)	8672 (2)	4552 (3)	62 (1)
C(16)	1944 (8)	9276 (2)	5104 (4)	90 (2)
C(17)	5175 (9)	8517 (3)	5050 (4)	108 (2)

* Atoms in rigid groups have standard deviations only for the pivot atom.

Experimental. Crystals of the title compound were provided by Professor P. Paetzold (Meier, Paetzold & Schröder, 1984). Crystal size 0·50 × 0·21 × 0·03 mm, Nicolet *R*3*m*/V four-circle diffractometer, ω scan (scan width 0·9°), lattice parameters determined with 30 reflections (2θ range $20° \le 2\theta \le 25°$), no absorption correction applied, maximum value of $(\sin\theta)/\lambda = 0{\cdot}54$ Å^{-1}, *hkl* range $h = -6$ to 6, $k = 0$ to 22 and $l = -10$ to 12, two standard reflections (*hkl* = $00\overline{2}$ and $\overline{2}5\overline{2}$) with no significant variation throughout the experiment, 3223 measured reflections, 1810 unique reflections, $R_{\text{int}} = 0{\cdot}011$, 518

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unobserved reflections [$F_o < 4\sigma(F)$], structure solved by direct methods and refined by full-matrix least squares (on F) with *SHELXTL-Plus* (Sheldrick, 1988), with rigid-group refinement for phenyl C atoms (C—C 1·396 Å, C—C—C 120°). H atoms located from difference Fourier map, refined as rigid groups only for methyl and phenyl with unique isotropic temperature factors each for methyl and phenyl H atoms (C—H 0·96 Å, H—C—H 109·5° for methyl, C—C—H 120° for phenyl), 155 parameters, $R = 0{\cdot}054$ and $wR = 0{\cdot}069$ with $w^{-1} = \sigma^2(F_o) + 0{\cdot}0089F_o^2$, $(\Delta/\sigma)_{\max} = 0{\cdot}009$, maximum and minimum electron densities based on final difference Fourier synthesis 0·14 and $-0{\cdot}19$ e Å^{-3}, atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1988) and Cromer & Mann (1968), f' and f'' values from Cromer & Liberman (1970).

Table 2. *Selected bond distances* (Å) *and angles* (°) *for 1,5-diisopropyl-4-phenyl-4,5-dihydrotetraazaborole* (*A*) *with some comparative values for 1,4-dimethyl-4,5-dihydrotetraazaborole* (*B*), *and torsion angles* (°) *for A, with e.s.d.'s in parentheses*

	A	*B**
N(1)—B(5)	1·411 (5)	1·413 (10)
N(1)—N(2)	1·375 (4)	1·375 (5)
N(2)—N(3)	1·279 (4)	1·291 (6)
N(3)—N(4)	1·376 (4)	1·375 (5)
N(4)—B(5)	1·422 (4)	1·413 (10)
N(4)—C(7)	1·407 (4)	
B(5)—C(15)	1·571 (5)	
C(15)—H(15)	0·961 (37)	
C(15)—C(16)	1·517 (6)	
C(15)—C(17)	1·521 (6)	
N(1)—N(2)—N(3)	109·2 (3)	109·1
N(1)—B(5)—N(4)	100·5 (3)	101·8 (6)
N(1)—B(5)—C(15)	130·4 (3)	
N(2)—N(1)—B(5)	110·8 (3)	110·0
N(2)—N(3)—N(4)	108·9 (3)	
N(3)—N(4)—B(5)	110·6 (3)	
N(3)—N(4)—C(7)	117·1 (2)	
N(4)—B(5)—C(15)	129·1 (3)	
B(5)—N(4)—C(7)	132·2 (3)	
B(5)—C(15)—C(16)	113·1 (3)	
B(5)—C(15)—C(17)	113·1 (4)	
H(15)—C(15)—C(16)	108·3 (22)	
H(15)—C(15)—C(17)	102·6 (19)	
C(16)—C(15)—C(17)	111·4 (3)	
N(1)—N(2)—N(3)—N(4)	−0·8 (4)	
N(2)—N(1)—B(5)—N(4)	0·5 (4)	
N(2)—N(1)—B(5)—C(15)	−177·7 (4)	
N(2)—N(3)—N(4)—B(5)	1·1 (4)	
N(2)—N(3)—N(4)—C(7)	177·4 (3)	
N(3)—N(2)—N(1)—B(5)	0·2 (4)	
N(3)—N(2)—N(1)—C(6)	−177·8 (3)	
N(3)—N(4)—B(5)—N(1)	−0·9 (4)	
N(3)—N(4)—B(5)—C(15)	177·3 (3)	
N(3)—N(4)—C(7)—C(8)	−43·8 (3)	
N(3)—N(4)—C(7)—C(12)	139·4 (2)	
C(6)—N(1)—B(5)—N(4)	177·9 (3)	
C(6)—N(1)—B(5)—C(15)	−0·3 (6)	
C(7)—N(4)—B(5)—N(1)	−176·4 (3)	
C(7)—N(4)—B(5)—C(15)	1·8 (6)	

* Chang *et al.* (1969).

Discussion. Table 1* gives the final atomic coordinates and the equivalent isotropic thermal parameters. Table 2 summarizes selected bond lengths and angles for the title compound and for 1,4-dimethyl-4,5-dihydrotetraazaborole for comparison (Chang *et al.*, 1969). The molecular conformation and the atomic numbering are shown in Fig. 1. The BN_4 ring system was the main subject of this investigation into whether C_{2v} symmetry is maintained or whether the double bonds are localized according to one of the two mesomeric structures (I) and (II). We found a strictly planar five-membered ring (maximum torsion within the ring = 0·2°) with alternating N—N bonds and almost equivalent B—N bonds. The structure parameters agree well with those of the BN_4 ring of 1,4-dimethyl-4,5-dihydrotetraazaborole, determined by electron diffraction (see Table 2). Both B—N

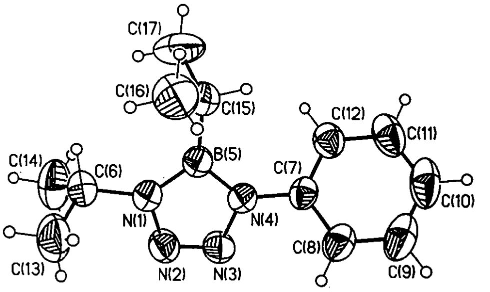

Fig. 1. Perspective view of the molecular geometry showing the atom labelling with thermal ellipsoids of 50% probability for non-H atoms.

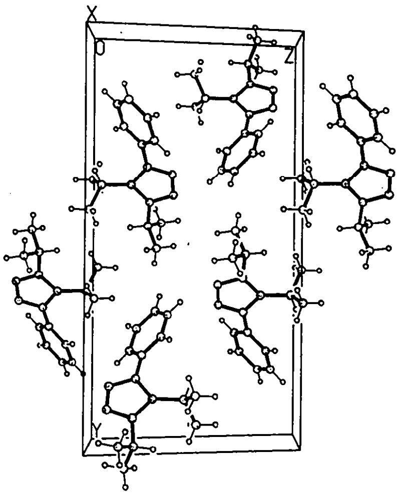

Fig. 2. Crystal packing viewed along the x axis.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52513 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond lengths are in the normal range of B—N double bonds (Paetzold, 1987). In contrast, the N—N single bonds are almost 0·04 Å shorter than the standard $N(sp^2)$—$N(sp^2)$ single-bond length at 1·41 Å (Patai, 1975). On the other hand, the N—N double bond was found to be 0·03 Å longer than the standard value of 1·25 Å (Rademacher, 1987). The structure determination confirms C_{2v} symmetry of the BN_4 unit within standard deviations. This indicates extensive π delocalization in the BN_4 ring. All atoms in α position to the BN_4 unit are located in the ring plane. To reduce interference between the isopropyl groups, the BN_4 ring and the phenyl group, the last is twisted by an interplanar angle of 44·4° relative to the five-membered ring, as shown in Fig. 2.

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Structural Refinement of Low-Temperature Copper(II) Pyrophosphate

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Abstract. α-$Cu_2P_2O_7$, $M_r = 301{\cdot}02$, monoclinic, $C2/c$, $a = 6{\cdot}895\,(2)$, $b = 8{\cdot}113\,(3)$, $c = 9{\cdot}164\,(3)$ Å, $\beta = 109{\cdot}62\,(2)°$, $V = 482{\cdot}9$ Å^3, $Z = 4$, $D_x = 4{\cdot}14$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 9{\cdot}2$ mm^{-1}, $F(000) = 576$, room temperature, $R = 0{\cdot}036$ for 1757 unique observed reflections. CuO_5 polyhedra are connected to form sheets in (001), which are linked by P_2O_7 groups; $P—O_{\rm terminal} = 1{\cdot}497\,(1)$, 1·514 (1) and 1·540 (1), $P—O_{\rm bridging} = 1{\cdot}579\,(1)$ Å, P—O—P = 156·8 (2)°. Crystals were synthesized under hydrothermal conditions up to some tenths of a millimeter; they are colourless.

Experimental. Crystals of the title compound were obtained during synthesis of $Cu_3(PO_4)_2$ under hydrothermal conditions: 1 g elemental Cu (wire), 1 g Cu_2O (powder), 2 ml H_3PO_4 85%, and 1 ml HNO_3 65% were sealed in a 'teflon' lined stainless steel autoclave with ~7 ml capacity. H_2O was added to approximately 80% degree of filling. After heating to 500 (10) K for five days crystals of $Cu_3(PO_4)_2$ and α-$Cu_2P_2O_7$ were obtained. The latter compound was up to some tenths of a millimeter in size; the crystallographic forms $\{\bar{1}12\}$, $\{110\}$, $\{011\}$ and $\{\bar{2}21\}$ were observed. It is conspicuous that the crystals of α-$Cu_2P_2O_7$ obtained during the present studies are colourless; in contrast, Robertson & Calvo (1967) described them as 'small blue-green crystals'.

Synthetic crystal, 0·09 × 0·10 × 0·37 mm, Stoe four-circle diffractometer AED2, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 75 reflections ($40 \le 2\theta \le 53°$); $2\theta/\omega$ scan mode, 55 steps (increased for $\alpha_1 - \alpha_2$ dispersion, nine steps each side for background correction), step width 0·03°, step time 0·5 to 1·5 s, $2\theta \le 90°$, three standard reflections, max. variation 5·6%, 4502 reflections measured (h: $-13 \rightarrow 13$, k: $-16 \rightarrow 0$, l: $-18 \rightarrow 18$), 1999 reflections in unique data set ($R_{\rm int} = 0{\cdot}046$),

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