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Acta Cryst. (1996). C**52**, 3248-3250

An Inorganic *N*-Amino Analogue of Pyrrole: a Five-Membered Ring with Methylhydrazine and Two B Atoms as Building Blocks

UDO ENGELHARDT* AND SEUNG SOON PARK

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany. E-mail: udoengel@blume.chemie.fu-berlin.de

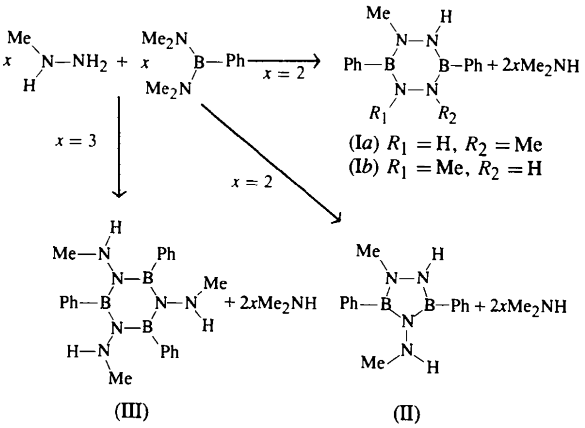
(*Received 18 March 1996; accepted 1 August 1996*)

Abstract

The compound 1-methyl-4-methylamino-3,5-diphenyl-1,2,4-triaza-3,5-diborole, $C_{14}H_{18}B_2N_4$, has been synthesized from bis(dimethylamino)phenylborane and methylhydrazine. The molecular structure of the planar ring system is best described as an inorganic *N*-methylaminopyrrole with two rather short and two normal B—N bonds [1.40 (1) and 1.44 (1) Å, mean] and a short N—N bond [1.414 (5) Å] in the ring [exocyclic N—N 1.441 (4) Å].

Comment

Inorganic rings containing boron atoms and hydrazine building blocks have long been known (Nöth & Regnet, 1969; Nöth, Reichenbach & Winterstein, 1977; Nölle & Nöth, 1978; Barlos & Nöth, 1980; Dirschl, Nöth & Wagner, 1984; Kumpfmüller, Nölle, Nöth, Pommerenning & Staudigl, 1985; Boese & Klingebiel, 1986). Since boron is capable of exchanging different amino moieties in aminoboranes, we began several years ago to prepare phosphorus(V) hydrazine heterocycles with boron in the ring starting from the corresponding dihydrazido derivatives of phosphoric acid and bis(dimethylamino)phenylborane (Scheffler, 1989; Engelhardt & Park, 1995). The transamination reaction may lead to equilibria involving several different compounds. In this context, we now have tested the reaction of methylhydrazine with bis(dimethylamino)phenylborane (see scheme below).



Of the most probable reaction products (I), (II) and (III), only (II) could be isolated from the hexane solution (yield 91% based on methylhydrazine) besides some insoluble material. The molecular peak at m/e = 264 is the strongest signal in the mass spectrum, the isotope pattern corresponding to two B atoms in the molecule. The constitution in solution ($CDCl_3$) is confirmed by the NMR spectral data (see *Experimental*). The X-ray structure analysis reveals the same constitution in the solid phase. The asymmetric unit contains one molecule (Fig. 1). The central inorganic five-membered ring is essentially planar (Table 2). The N1—N2 distance in the ring of 1.414 (5) Å is not exceptionally short and compares well with other values in non-planar hydrazine rings with Nsp^2 atoms (Engelhardt & Hartl, 1975, 1976). This is in contrast, however, to the longer exocyclic N3—N4 distance of 1.441 (4) Å, where N3 has a trigonal pyramidal coordination [the sum of the bond angles around N3 is 326 (4)°]. There are two rather short B—N distances [B2—N1 1.399 (6) and B3—N2 1.404 (6) Å] and two significantly longer ones [B2—N4 1.446 (6) and B3—N4 1.432 (6) Å]. Out of several resonance forms (Fig. 2), the aromatic form (*b*), analogous to pyrrole, is apparently the most important. The phenyl rings bonded to B2 and B3 are almost coplanar with and normal to the central inorganic ring, respectively [interplanar angles 5.0 (2) and 84.3 (2)°].

It is remarkable that only the five-membered ring product (II) is obtained in this study. In the case of the

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

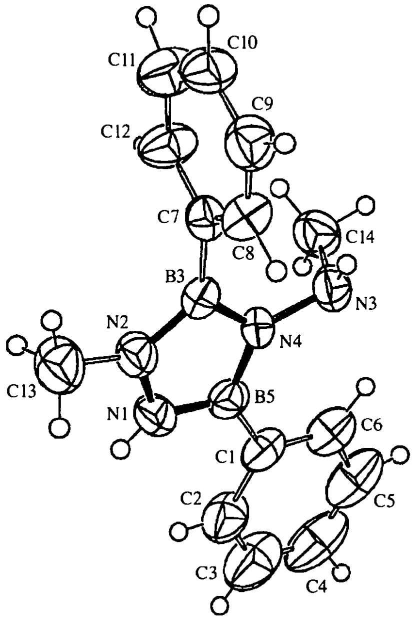


Fig. 1. The molecular structure and numbering scheme for the asymmetric unit which contains one molecule of (II). The crystallographic numbering does not follow that in the chemical formula (methyl group at N1). The numbering of H atoms follows that of their parent C or N atoms. Displacement ellipsoids are plotted at the 25% probability level.

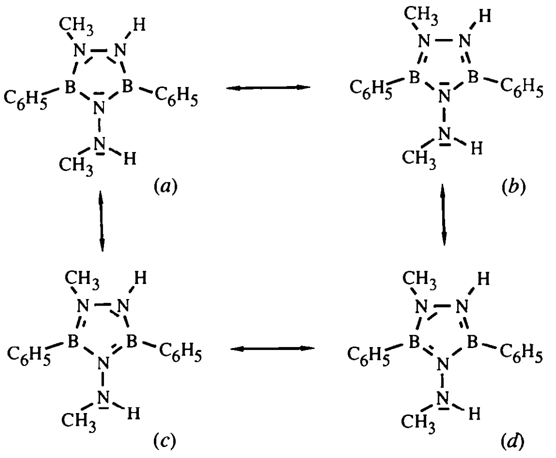


Fig. 2. Resonance forms of the title molecule (II).

corresponding Si compounds five- and six-membered rings and even four-membered rings have been reported; depending on the substitution at silicon and/or nitrogen, either the six-membered or the five-membered ring is formed (He & Harrod, 1994; Dielkus, Drost, Herbst-Irmer, Klingebiel & Pauer, 1994).

Experimental

Compound (II) was synthesized in our laboratory according to the reaction scheme. To a solution of 4.6 g (0.026 mol) of bis(dimethylamino)phenylborane in 30 ml *n*-hexane, a solution of 1.21 g (0.026 mol) of methylhydrazine in 100 ml *n*-hexane was added dropwise. The mixture was stirred at 333 K for 2 d and the dimethylamine formed was removed under slightly reduced pressure during this time. Crystals of (II) were obtained from *n*-hexane solution.

^{1}H NMR: δ 2.54 (doublet, 3 H, methyl protons at N1), δ 4.02 [quartet, 1 H, proton at N2, ^4J(HNNCH) = 5 Hz], δ 3.22 (singlet, 3H, exocyclic NCH$_3$ protons), δ 5.88 (singlet, 1 H, exocyclic NH proton), the protons at the non-equivalent phenyl groups give multiplets at δ 7.41, 7.55 and 7.80 (all values in p.p.m.). The $\{^1\text{H}\}$ ^{13}C NMR shows signals for two different *N*-methyl C atoms: δ 33.45 and 43.07; detected signals for the phenyl C atoms are: δ 133.11, 133.02, 128.91, 128.41 127.97 and 127.86.

Crystal data

$C_{14}H_{18}B_2N_4$
M_r = 263.946
Orthorhombic
Pbca
a = 21.86 (2) Å
b = 12.48 (2) Å
c = 11.047 (8) Å
V = 3013 (6) Å^3
Z = 8
D_x = 1.165 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 22 reflections
θ = 6–13°
μ = 0.070 mm^{-1}
T = 293 K
Needle
0.65 × 0.30 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2650 measured reflections
2650 independent reflections
1108 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max}$ = 25°
$h = -25 \rightarrow 0$
$k = 0 \rightarrow 14$
$l = -13 \rightarrow 0$
2 standard reflections monitored every 100 reflections
intensity decay: <1.5 %

Refinement

Refinement on F
R = 0.080
wR = 0.030
S = 1.99
1852 reflections including unobserved reflections with $|F_c| > |F_o|$
254 parameters
H atoms refined isotropically
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max}$ = 0.057

$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
$\Delta\rho_{\min}$ = −0.52 e Å^{-3}
Extinction correction: isotropic (Larson, 1967)
Extinction coefficient: 0.29 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.5601 (2)	0.2594 (3)	0.4404 (3)	0.060 (3)
N2	0.6127 (2)	0.1945 (2)	0.4266 (3)	0.059 (2)
N3	0.5484 (2)	0.0880 (3)	0.7062 (3)	0.055 (3)
N4	0.5644 (1)	0.1452 (2)	0.5974 (2)	0.048 (2)
B3	0.6165 (2)	0.1218 (4)	0.5233 (4)	0.048 (3)

B5	0.5280 (1)	0.2302 (4)	0.5450 (1)	0.051 (3)
C1	0.4682 (2)	0.2837 (3)	0.5864 (4)	0.057 (3)
C2	0.4456 (3)	0.3707 (4)	0.5218 (5)	0.083 (4)
C3	0.3921 (3)	0.4212 (5)	0.5542 (6)	0.110 (5)
C4	0.3588 (3)	0.3867 (6)	0.6508 (7)	0.110 (5)
C5	0.3798 (3)	0.3015 (5)	0.7164 (5)	0.096 (5)
C6	0.4339 (2)	0.2495 (4)	0.6862 (4)	0.073 (3)
C7	0.6688 (2)	0.0401 (3)	0.5427 (3)	0.050 (3)
C8	0.7198 (2)	0.0626 (3)	0.6134 (4)	0.062 (3)
C9	0.7674 (2)	−0.0088 (4)	0.6287 (4)	0.071 (4)
C10	0.7649 (2)	−0.1048 (4)	0.5695 (4)	0.071 (4)
C11	0.7159 (2)	−0.1308 (4)	0.4991 (4)	0.082 (4)
C12	0.6682 (2)	−0.0582 (4)	0.4865 (4)	0.071 (3)
C13	0.6522 (3)	0.2197 (5)	0.3263 (5)	0.086 (4)
C14	0.5090 (3)	−0.0034 (4)	0.6776 (5)	0.069 (4)
H1	0.553 (2)	0.303 (3)	0.385 (3)	0.07 (2)
H7	0.585 (1)	0.071 (2)	0.734 (3)	0.04 (1)

Table 2. *Selected geometric parameters (Å, °)*

N1—N2	1.414 (5)	N3—C14	1.463 (7)
N1—B5	1.399 (6)	N3—H7	0.88 (3)
N1—H1	0.83 (3)	N4—B5	1.446 (6)
N2—B3	1.404 (6)	N4—B3	1.432 (6)
N2—C13	1.440 (7)	B5—C1	1.538 (6)
N3—N4	1.441 (4)	B3—C7	1.547 (6)
N2—N1—B5	110.3 (3)	N3—N4—B5	124.3 (3)
N2—N1—H1	117 (2)	N3—N4—B3	124.7 (3)
B5—N1—H1	132 (2)	B5—N4—B3	110.9 (3)
N1—N2—B3	109.6 (3)	N1—B5—N4	104.2 (4)
N1—N2—C13	116.4 (4)	N1—B5—C1	124.0 (4)
B3—N2—C13	133.8 (4)	N4—B5—C1	131.8 (4)
N4—N3—C14	110.4 (3)	N2—B3—N4	104.9 (4)
N4—N3—H7	101 (2)	N2—B3—C7	125.1 (4)
C14—N3—H7	115 (2)	N4—B3—C7	130.0 (4)
B5—N1—N2—B3	−0.7 (4)	B5—N1—N2—C13	−176.5 (4)
N1—N2—B3—N4	−0.4 (4)	N4—B3—N2—C13	174.4 (4)
N2—N1—B5—N4	1.4 (4)	C7—B3—N2—C13	−3.0 (7)
B3—N4—B5—N1	−1.7 (4)	C1—B5—N1—N2	−179.3 (4)
B5—N4—B3—N2	1.3 (4)	B5—N4—N3—C14	87.4 (4)
N3—N4—B5—N1	−178.6 (3)	B3—N4—N3—C14	−89.1 (4)
N3—N4—B3—N2	178.2 (3)	N4—B3—C7—C8	−83.7 (6)
N3—N4—B5—C1	2.3 (6)	N1—B5—C1—C2	−4.1 (6)
N3—N4—B3—C7	−4.6 (6)		

The structure was solved by direct methods using *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Refinement was by full-matrix least-squares methods; heavy atoms were refined anisotropically and H atoms isotropically using *Xtal*3.0 (Hall & Stewart, 1990). Molecular graphics were drawn using *ORTEP*II (Johnson, 1976).

The authors thank the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1263). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3250-3252

3,7-Bis(2-thienyl)-1,5,2,4,6,8-dithiatetrazocine

Tosha M. Barclay,[a] A. Wallace Cordes,[a] Richard T. Oakley[b] and Kathyrn E. Preuss[b]

[a]*Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA, and* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada. E-mail: wcordes@comp.uark.edu*

(*Received 12 June 1996; accepted 3 September 1996*)

Abstract

The title molecule, 3,7-bis(2-thienyl)-1,5,2,4,6,8-dithiatetrazocine, $C_{10}H_6N_4S_4$, is planar within 0.069 (5) Å and crystallizes in the monoclinic space group $P2_1/c$. There are two centrosymmetric molecules in the cell; these are stacked such that each eight-membered $C_2N_4S_2$ ring has a thienyl ring above and below it. The mean interplanar separation is 3.55 (2) Å.

Comment

The 1,5,2,4,6,8-dithiatetrazocine ring system is known for the structural dichotomy it displays as a function of the exocyclic 3,7-ligands (Ernst *et al.*, 1981): aryl substituents afford planar central rings, while amine groups induce a folding of the ring and the formation of a transannular S···S contact (Oakley, 1988). The thienyl group of the title compound, (I), results in a planar central ring with distances and angles [S—N = 1.556 (3),

Acta Crystallographica Section C
ISSN 0108-2701 © 1996