

Structure of the Triphenylboroxin–*N,N*-Dimethylethylenediamine 1:1 Adduct

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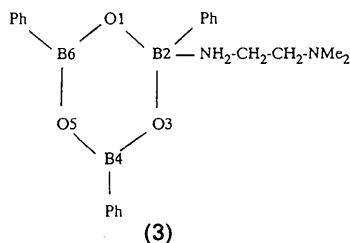
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Abstract. $C_{22}H_{27}B_3N_2O_3$, $M_r = 399.9$, orthorhombic, $P2_12_12_1$, $a = 13.429$ (3), $b = 14.125$ (2), $c = 11.964$ (3) Å, $V = 2269$ (2) Å³, $Z = 4$, $D_x = 1.17$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.7$ cm⁻¹, $F(000) = 848$, $T = 294$ K, $R = 0.044$ for 1279 observed reflections. The B_3O_3 ring is almost planar but a small fold distortion exists across the ring to yield a shallow boat conformation. Two B atoms have sp^2 trigonal planar coordination and the third achieves sp^3 tetrahedral coordination by bonding to the NH_2 group of *N,N*-dimethylethylenediamine. The Me_2N group does not interact with any B atom. Three distinct B–O distances are observed in the B_3O_3 ring with mean values $B(sp^2)–O[B(sp^3)]$ 1.338 (5), $B(sp^2)–O[B(sp^2)]$ 1.381 (5) and $B(sp^3)–O[B(sp^2)]$ 1.460 (6) Å.

Introduction. We have recently found that the reaction of $PhB(OSiR_3)_2$ [$R_3 = Me_3$ (1) or $MePh_2$ (2)] with *N,N*-dimethylethylenediamine (DMED) in a 1:1 molar ratio in dichloromethane solvent for 1 h at room temperature affords the DMED adduct (3) of triphenylboroxin (Sheehan, 1989). The molecular structures of uncomplexed $(PhBO)_3$ (Brock, Minton & Niedenzu, 1987) and two amine adducts, $2(PhBO)_3 \cdot 3(p-NH_2C_6H_4NH_2)$ (4) and $2(PhBO)_3 \cdot N-(CH_2CH_2)_3N$ (5) (Yalpani & Boese, 1983), have also been reported. No 1:1 amine adducts have been reported previously and we describe here the crystal and molecular structure of $(PhBO)_3 \cdot DMED$ (3).



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Experimental. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the range $9 < \theta < 17^\circ$. Crystal dimensions $0.63 \times 0.50 \times 0.33$ mm; intensities of reflections with indices $h0$ to 17, $k0$ to 18, $l-15$ to 15, with $2 < 2\theta < 54^\circ$ measured (the space group is chiral and we measured both sets of Friedel reflections), $\omega-2\theta$ scans, ω scan width $(0.6 + 0.35 \tan \theta)^\circ$; graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 5487 reflections measured, 4922 unique, only 2370 with $I > 3\sigma(I)$ labelled observed and used in structure solution and initial refinement. Data corrected for Lorentz and polarization effects. Space group $P2_12_12_1$ was determined uniquely by the systematic absences ($h00$ absent if $h = 2n + 1$; $0k0$ absent if $k = 2n + 1$; $00l$ absent if $l = 2n + 1$). The structure was solved with the aid of MULTAN82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. A difference map showed maxima in positions consistent with the expected locations of all H atoms. In the final rounds of calculations, the H atoms were positioned on geometrical grounds (C–H, 0.95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 7.0 Å². Parallel refinement with the chirality of the molecule reversed gave no significant difference in R factors or molecular geometry (presumably because the small $\Delta f''$ contributions to the structure factors were not enough to yield sufficiently different values for Friedel pairs; there were no significant differences in F_c values for hkl and $h\bar{k}l$ reflections). In the final cycles of refinement we averaged the hkl and $h\bar{k}l$ reflections ($R_{int} = 0.019$) to yield 1279 observed reflections and included 272 variable parameters, $R = 0.0438$, $wR = 0.0600$, goodness of fit = 1.83, $w = 1/[\sigma^2(F_o) + 0.055(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle

Table 1. Positional and thermal parameters and their *e.s.d.*'s
$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
O1	0-1629 (2)	0-3953 (2)	0-3220 (2)	5-06 (6)
O3	0-2597 (2)	0-4931 (2)	0-4490 (2)	4-81 (6)
O5	0-3308 (2)	0-3585 (2)	0-3625 (2)	5-36 (6)
N1	0-1463 (2)	0-5669 (3)	0-3143 (3)	5-19 (8)
N2	0-2714 (2)	0-6974 (3)	0-2202 (4)	6-38 (9)
C3	0-1491 (3)	0-6628 (3)	0-3639 (5)	6-8 (1)
C4	0-1867 (4)	0-7323 (4)	0-2796 (5)	8-3 (1)
C5	0-2824 (5)	0-7477 (5)	0-1180 (6)	10-4 (2)
C6	0-3626 (4)	0-7040 (5)	0-2828 (7)	10-1 (2)
C11	0-0751 (3)	0-4733 (3)	0-4884 (3)	4-65 (9)
C12	-0-0099 (3)	0-4204 (3)	0-4746 (4)	6-0 (1)
C13	-0-0877 (3)	0-4215 (4)	0-5525 (5)	7-4 (1)
C14	-0-0800 (4)	0-4761 (4)	0-6465 (4)	6-9 (1)
C15	0-0033 (4)	0-5279 (4)	0-6626 (4)	6-8 (1)
C16	0-0807 (3)	0-5272 (3)	0-5869 (4)	5-8 (1)
C21	0-4324 (3)	0-4460 (3)	0-5088 (3)	4-82 (9)
C22	0-4476 (3)	0-5267 (3)	0-5721 (3)	5-2 (1)
C23	0-5292 (3)	0-5336 (4)	0-6423 (4)	6-3 (1)
C24	0-5958 (3)	0-4606 (4)	0-6501 (4)	7-1 (1)
C25	0-5815 (3)	0-3821 (4)	0-5869 (4)	8-2 (1)
C26	0-5042 (3)	0-3741 (4)	0-5180 (4)	6-6 (1)
C31	0-2431 (3)	0-2625 (3)	0-2121 (3)	4-46 (9)
C32	0-3342 (3)	0-2167 (3)	0-1828 (4)	6-0 (1)
C33	0-3337 (3)	0-1462 (4)	0-1031 (4)	6-6 (1)
C34	0-2486 (4)	0-1207 (3)	0-0527 (4)	6-7 (1)
C35	0-1615 (3)	0-1634 (3)	0-0788 (4)	6-4 (1)
C36	0-1594 (3)	0-2342 (3)	0-1570 (4)	5-1 (1)
B2	0-1627 (4)	0-4764 (4)	0-3977 (4)	4-9 (1)
B4	0-3355 (3)	0-4331 (3)	0-4372 (4)	4-5 (1)
B6	0-2445 (3)	0-3429 (3)	0-3029 (4)	4-3 (1)

< 0.005 ; density in final difference map $\pm 0.24 e \text{ \AA}^{-3}$; there were no chemically significant features. Scattering factors and initial anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1984). Atomic coordinates* and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *ORTEPII* (Johnson, 1976).

Discussion. The B_3O_3 ring in (3) is almost planar but is distorted slightly towards a boat conformation [atoms O3 and B6 are 0.087 (3) and 0.053 (5) Å respectively from the best plane through atoms O1, B2, B4 and O5]; an alternative description is that the ring is slightly folded from planarity (6.6°) about an axis through atoms B6 and O3. This distortion contrasts with those found in $(PhBO)_3$ and $[Ph_4B_3O_3]^-$ (Kliigel, Motzkus, Rettig & Trotter, 1985), both of which have an envelope distortion in the B_3O_3 rings with one atom out of the plane containing the other five.

* Lists of structure factors, anisotropic thermal parameters, mean-planes data, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53003 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and bond angles ($^\circ$)

O1—B2	1.460 (6)	C15—C16	1.378 (7)
O1—B6	1.342 (5)	C21—C22	1.384 (6)
O3—B2	1.460 (5)	C21—C26	1.405 (6)
O3—B4	1.333 (5)	C21—B4	1.568 (6)
O5—B4	1.383 (6)	C22—C23	1.384 (6)
O5—B6	1.378 (5)	C23—C24	1.369 (7)
N1—C3	1.480 (6)	C24—C25	1.355 (8)
N1—B2	1.636 (6)	C25—C26	1.330 (7)
N2—C4	1.429 (7)	C31—C32	1.428 (6)
N2—C5	1.422 (8)	C31—C36	1.363 (5)
N2—C6	1.437 (7)	C31—B6	1.572 (6)
C3—C4	1.495 (8)	C32—C33	1.379 (7)
C11—C12	1.373 (6)	C33—C34	1.342 (7)
C11—C16	1.406 (6)	C34—C35	1.352 (7)
C11—B2	1.601 (6)	C35—C36	1.370 (6)
C12—C13	1.400 (7)	N1...N2	2.737 (5)
C13—C14	1.368 (7)	HN2...N2	2.18
C14—C15	1.350 (7)		
B2—O1—B6	122.6 (3)	C24—C25—C26	121.7 (5)
B2—O3—B4	122.3 (3)	C21—C26—C25	121.6 (5)
B4—O5—B6	119.7 (3)	C32—C31—C36	117.1 (4)
C3—N1—B2	117.9 (4)	C32—C31—B6	119.1 (3)
C4—N2—C5	109.7 (4)	C36—C31—B6	123.8 (4)
C4—N2—C6	113.4 (5)	C31—C32—C33	119.5 (4)
C5—N2—C6	109.1 (4)	C32—C33—C34	120.6 (4)
N1—C3—C4	109.8 (4)	C33—C34—C35	120.9 (4)
N2—C4—C3	112.2 (4)	C34—C35—C36	120.1 (4)
C12—C11—C16	116.1 (4)	C31—C36—C35	121.8 (4)
C12—C11—B2	123.0 (4)	O1—B2—O3	112.7 (4)
C16—C11—B2	120.9 (4)	O1—B2—N1	103.6 (4)
O1—C12—C13	122.3 (4)	O1—C12—C11	113.6 (4)
C12—C13—C14	119.8 (5)	O3—B2—N1	104.5 (3)
C13—C14—C15	119.0 (5)	O3—B2—C11	112.0 (4)
C14—C15—C16	121.9 (5)	N1—B2—C11	109.7 (3)
C11—C16—C15	120.9 (4)	O3—B4—O5	121.2 (4)
C22—C21—C26	116.8 (4)	O3—B4—C21	120.1 (4)
C22—C21—B4	121.2 (4)	O5—B4—C21	118.7 (4)
C26—C21—B4	121.9 (4)	O1—B6—O5	120.7 (4)
C21—C22—C23	120.5 (4)	O1—B6—C31	120.4 (4)
C22—C23—C24	120.4 (5)	O5—B6—C31	118.9 (4)
C23—C24—C25	119.0 (4)	N1—HN2...N2	116

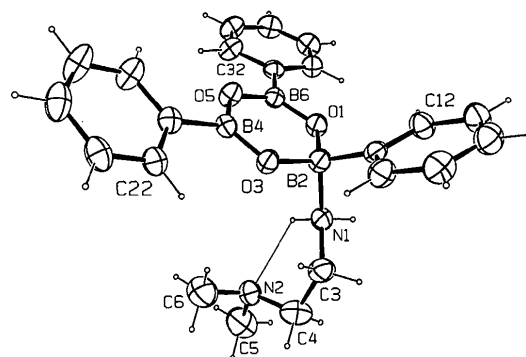


Fig. 1. A view of $(PhBO)_3.NH_2-CH_2-CH_2-NMe_2$ with the numbering scheme. Ellipsoids are at the 50% level for non-H atoms; H atoms are shown as small spheres.

The B—O distances in (3) vary systematically around the ring. Those involving $B(sp^3)$ are both the same [1.460 (5) Å] and typical of $B(sp^3)$ —O bonds which are reported to range from 1.43 to 1.49 Å (Singh, Rupani, Singh, Rai, Mehrotra, Rogers & Atwood, 1986); the $B(sp^2)$ —O bonds adjacent to $B(sp^3)$ are much shorter [1.333 (5) and 1.342 (5) Å] while the other $B(sp^2)$ —O bonds are 1.378 (5) and 1.383 (5) Å. These values may be compared with a mean $B(sp^2)$ —O distance in $(PhBO)_3$ of 1.386 (2) Å.

The variation in B—O distances in (3) reflects the relative contributions of B—O π bonding in the bonds. Atoms B4 and B6 compete for π -electron density most effectively when interacting with O3 and O1 respectively. When both B4 and B6 compete for electron density from the same O atom, O5, the π component is reduced. The same situation was observed in [Ph₄B₃O₃]⁻ and both the amine adducts of (PhBO)₃ previously reported.

Only the primary amine group of DMED interacts with (PhBO)₃ in (3). The B—N distance of 1.636 (6) Å is shorter than that in 2(PhBO)₃·3(*p*-NH₂C₆H₄NH₂) [1.663 (8) Å], and much shorter than that reported for 2(PhBO)₃·N(CH₂CH₂)₃N [1.714 (10) Å] (Yalpani & Boese, 1983). In both of the latter adducts an N atom was bonded to B atoms in separate (PhBO)₃ rings. In (3) there is an intramolecular hydrogen-bonding interaction N1—H...N2 [N1...N2 2.737 (5) Å, N—H...N 116°]; the large deviation of the N—H...N angle from the 180° value often found is a consequence of the intramolecular nature of this hydrogen bond. Another point of difference between (3) and (4) or (5) was that space-filling molecules [two *p*-NH₂C₆H₄NH₂ in (4) and three benzene molecules in (5)] were present in the crystal lattices of the latter two adducts; compound (3) does not have this feature.

The B—C(Ph) distances [B(*sp*³)—C 1.601 (6) and mean values of B(*sp*²)—C 1.570 (6) Å in (3)] are comparable with mean values of B(*sp*²)—C [1.541 (8) Å] in (PhBO)₃ and B(*sp*³)—C [1.626 (10) Å]

and B(*sp*²)—C [1.566 (9) Å] in [Ph₄B₃O₃]⁻. The C—C and C—N distances in (3) are all normal. There are no untoward intermolecular contacts; surprisingly, while one amino H atom is involved in intramolecular hydrogen bonding, the other is involved in neither intra- nor intermolecular hydrogen bonding.

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Phenyl(*p*-tolylsulfonylamino)(*p*-tolylsulfonylimino)- λ^4 -sulfane, a Reaction Product of Diphenyl Disulfide and Chloramine-T

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Abstract. *N*¹-Tosyl-*N*²-tosylbenzenesulfinamidine, C₂₀H₂₀N₂O₄S₃, *M*_r = 448.59, triclinic, *P* $\bar{1}$, *a* = 10.140 (1), *b* = 12.465 (2), *c* = 9.665 (2) Å, α = 101.88 (1), β = 114.57 (1), γ = 81.18 (1)°, *V* =

1084.0 (6) Å³, *Z* = 2, *D*_x = 1.37 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 3.5 cm⁻¹, *F*(000) = 468, *T* = 294 K, *R* = 0.035 for 3376 observed reflections. The analysis establishes that the reaction product is PhS(=NSO₂C₆H₄CH₃)(NHSO₂C₆H₄CH₃). The S^{VI}—N and S^{VI}—N(H) distances are 1.611 (2) and 1.630 (2) Å respectively, the S^{IV}—N and S^{IV}—N(H)

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