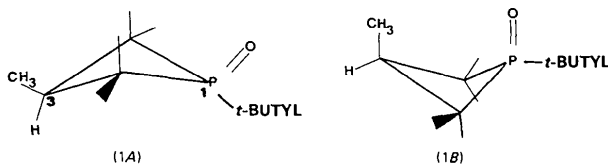


and *cis* to one another with respect to the phosphetane ring system. The C(5)–C(8) distance in TPPO is 3.010 (6) Å, which is substantially less than a 3.4 Å distance based on van der Waals radii (Bondi, 1964). The C(5)–O(1) distance is 3.019 (5) Å, which is also less than the sum of van der Waals radii (Bondi, 1964). Fitzgerald *et al.* (1978) found the amount of puckering to be in the range 19.6–24° for similar compounds with two methyl–methyl interactions. The amount of puckering in TPPO is very close to this range and may, in fact, represent a lower limit for compounds with two *cis* methyl–methyl interactions.

With respect to puckering direction or conformation preferences for TPPO, the following conformers may be considered.



TPPO exists in form (1A), and the C(8)–O distance of 4.69 (6) Å agrees well with similar compounds in which there is a single methyl group *trans* to a substituent on P (Fitzgerald *et al.*, 1978) and with distances measured from the molecular model of (1A).

We thank G. D. Smith and K. Emerson for many helpful discussions and assistance.

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Structure of Tri-1-naphthylborane–Benzene (1/1) Complex, C₃₀H₂₁B.C₆H₆

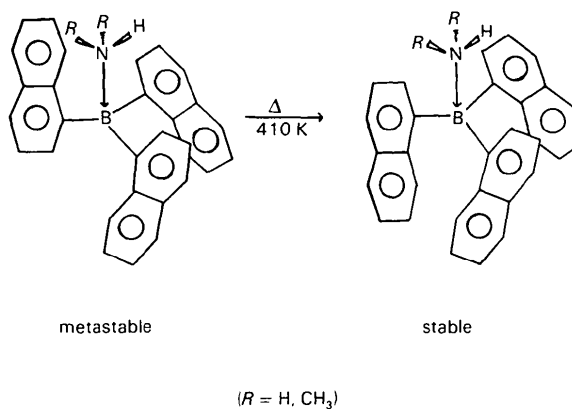
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Abstract. $M_r = 470.46$, rhombohedral, $R3$, $a = 8.710$ (4) Å, $\alpha = 91.10$ (3)°, $V = 660.4$ (9) Å³, $Z = 1$, $D_m = 1.170$ (floatation in KI solution), $D_x = 1.183$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.033$ mm⁻¹, $F(000) = 248.0$, $T = 293$ K, $R = 4.6\%$ (481 unique reflections). The molecule has C_3 symmetry and is propeller shaped, the angle of twist about the B–C bond being 41.5 (7)°. The space group being chiral, this is yet another example of spontaneous resolution. The results of a thermal-motion analysis are discussed.

Introduction. Brown & Sujishi (1948) reported that a metastable complex formed between amines NH₃, NH₂CH₃ and NH(CH₃)₂ and tris-1-naphthylborane (TNB) upon heating undergoes a conformational change to give a stable complex. In connection with our interest in finding any possible correlation between the dynamic properties of molecules, such as methyl migration, rearrangements *etc.*, on heating the crystals and the thermal motion of the relevant groups, this investigation of TNB was undertaken.



Experimental. TNB prepared as reported by Brown & Sujishi (1948), recrystallized from benzene. Crystals became opaque upon exposure to atmosphere. From the calculated molecular weight, it was clear that one molecule of TNB and one molecule of benzene were present in the unit cell. Crystal mounted in Lindemann capillary tube with a trace of mother liquor. Crystal

Table 1. Final positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^2$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
B(1)	0	0	0	6.48 (16)
C(1)	1443 (9)	-278 (10)	-1006 (9)	6.23 (18)
C(2)	2371 (10)	944 (10)	-1269 (11)	8.43 (24)
C(3)	3781 (11)	826 (12)	-2006 (13)	9.91 (32)
C(4)	4229 (11)	-545 (13)	-2500 (11)	10.13 (35)
C(5)	3730 (13)	-3336 (13)	-2887 (10)	10.14 (36)
C(6)	2840 (13)	-4585 (13)	-2660 (11)	11.25 (35)
C(7)	1448 (13)	-4477 (11)	-1932 (12)	9.93 (29)
C(8)	993 (11)	-3093 (10)	-1378 (10)	7.64 (23)
C(9)	1923 (9)	-1737 (9)	-1552 (8)	5.83 (17)
C(10)	3290 (9)	-1916 (11)	-2327 (9)	7.54 (20)
C(11)	2345 (24)	4240 (16)	2307 (24)	15.00 (71)
C(12)	3607 (21)	3600 (25)	1711 (19)	14.82 (63)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

Bond lengths corrected for rigid-body motion are given alongside their uncorrected values.

	Corrected		Corrected
C(1)-B(1)	1.566 (5)	C(10)-C(5)	1.384 (11)
C(2)-C(1)	1.350 (8)	C(6)-C(5)	1.344 (13)
C(9)-C(1)	1.422 (7)	C(7)-C(6)	1.383 (13)
C(3)-C(2)	1.401 (10)	C(8)-C(7)	1.359 (10)
C(4)-C(3)	1.330 (11)	C(9)-C(8)	1.431 (8)
C(10)-C(4)	1.447 (11)	C(10)-C(9)	1.390 (7)
C(1)-B(1)-C(1)	119.8 (4)	C(8)-C(7)-C(6)	119.6 (8)
C(2)-C(1)-B(1)	117.4 (6)	C(9)-C(8)-C(7)	121.1 (7)
C(9)-C(1)-B(1)	125.0 (5)	C(8)-C(9)-C(1)	121.5 (4)
C(9)-C(1)-C(2)	117.3 (5)	C(10)-C(9)-C(1)	122.0 (5)
C(3)-C(2)-C(1)	123.2 (7)	C(10)-C(9)-C(8)	116.5 (5)
C(4)-C(3)-C(2)	119.1 (7)	C(5)-C(10)-C(4)	122.1 (7)
C(10)-C(4)-C(3)	121.9 (7)	C(9)-C(10)-C(4)	116.4 (7)
C(10)-C(5)-C(6)	119.9 (8)	C(9)-C(10)-C(5)	121.5 (7)
C(7)-C(6)-C(5)	121.3 (8)		

Symmetry code: (i) z, x, y.

dimensions $0.5 \times 0.5 \times 0.5$ mm. Intensity data collected on Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode; scan speed 1° min^{-1} ; $\theta < 23.5^\circ$. 9 reflections used for calculating lattice parameters. 1504 reflections collected, equivalent reflections merged to give 635 unique reflections of which 481 were judged significant $|F_o| \geq 3\sigma|F_c|$. $R_{int} = 7.8\%$; intensities not corrected for absorption. h 0 ± 6 , k 0 ± 6 , l 0 ± 9 . Structure solution with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). E map computed with phases from best set ($R_{Karle} = 19.2\%$; ABSFOM = 1.171; PSIZERO = 1.159; combined figure of merit = 2.633) in R3 gave atomic positions of one naphthalene ring in asymmetric unit and boron situated on threefold axis. After five cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters $R = 25.9\%$. Difference Fourier map revealed two more atoms, recognized as benzene carbons, benzene on threefold axis. $R = 11.4\%$

with these two atoms included in isotropic refinement. All atoms refined anisotropically, $R = 7.4\%$. Difference Fourier map revealed all hydrogens. In final cycles of refinement, all non-hydrogens refined anisotropically and hydrogens isotropically. Max. $\Delta/\sigma \sim 0.02$. Final $R = 4.56\%$ ($R_w = 4.82\%$; $S = 0.9722$). Difference Fourier map did not reveal any significant peak. Max. and min. heights in final difference map 0.18 and -0.10 e \AA^{-3} . Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 0.85/(\sigma^2|F_o| + 0.002|F_o|^2)$. Scattering factors from International Tables for X-ray Crystallography (1974). Full-matrix least-squares refinement with SHELX76 (Sheldrick, 1976).*

Discussion. The final positional and equivalent thermal parameters are listed in Table 1; bond lengths and angles are given in Table 2. The structure viewed along the threefold axis of symmetry is shown in Fig. 1 and the packing diagram in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and the results of the thermal-motion analysis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39640 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

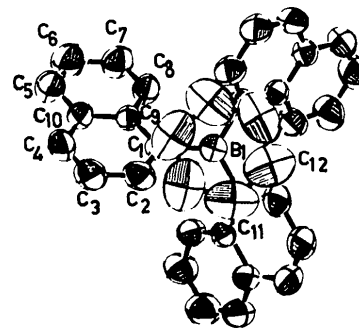


Fig. 1. Perspective view of the molecular complex down the threefold symmetry axis.

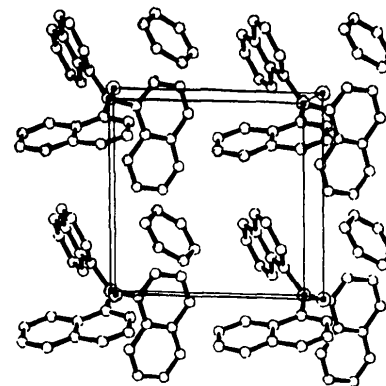


Fig. 2. Packing of the molecular complex.

Geometry of the molecule. The B—C bond length 1.566 (5) Å, after rigid-body-motion correction to 1.570 Å, is close to the mean value of 1.576 (4) Å observed in trimesitylborane (TMB), 1.580 (4), 1.573 (4) Å (Blount, Finocchiaro, Gust & Mislow, 1973), and slightly less than the mean value of 1.580 (4) Å observed in triphenylborane (TPB), 1.589 (5), 1.571 (3) Å (Zettler, Hausen & Hess, 1974). The molecular symmetry in the crystal being C_3 , naphthalene is twisted by 41.3° about the B—C bond. This conformational angle is more than in the less crowded TBP (30°), but less than in the more crowded TMB ($49.6, 51.1^\circ$). Unlike the other triarylboranes, TPB, TMB, where boron is in the plane of the three carbons bonded to it, boron in the present molecule is out of the plane of the three covalent neighbours by 0.078 (8) Å. The boron, which reveals small pyramidality, might be expected to move towards the benzene ring in view of the acidic and basic nature of TNB and benzene, respectively. But, surprisingly, the boron atom moves away from the benzene ring. A plausible explanation for this could be as follows. It is known that the ionization potential of naphthalene (8.26 eV) is smaller than that of benzene (9.38 eV) (Wacks & Diblen, 1959). The smaller value for naphthalene may be expected to facilitate the HOMO—LUMO interaction between naphthalene and the electron deficient boron, which would change the hybridization of boron towards sp^3 . The deviation of boron in the opposite direction to that of benzene may be due to the repulsion between the π -electrons of benzene and the partially occupied p -orbital of the boron atom.

The centre of the benzene ring is 4.39 Å from boron. The shortest C...C distances between the atoms of the benzene ring and surrounding naphthalene ring atoms are: C(12^b)...C(2^b) = 3.58 (2) Å; C(12^b)...C(6^h) = 3.70 (2) Å [symmetry code: (i) x, y, z ; (ii) $y, z + 1, x$].

Thermal-motion analysis. Both the benzene molecule and TNB were subjected to thermal-motion analysis using THMB, developed by Trueblood (1982). The major libration axes* L_1 (88.04 deg^2) and L_2 (88.04 deg^2) for benzene are nearly in the plane of the benzene ring and the minor one L_3 (73.43 deg^2) perpendicular to the ring, very close to the crystallographic threefold axis. Owing to the high temperature factors, the bond length of benzene was underestimated at 1.350 (17) Å; the corrected bond length is 1.383 Å. As for the TNB molecule, it has librations exactly coinciding with three libration axes of benzene ($L_1 = 13.47$, $L_2 = 13.47$ and $L_3 = 4.76 \text{ deg}^2$). Further, it was detected that the

molecule exhibits two non-rigid librations: (a) a libration about the B—C(10) vector with an amplitude of $24.0 (2.4) \text{ deg}^2$ and (b) a motion about the axis perpendicular to the naphthalene ring, the axis being located at C(9) with an amplitude of $14.8 (17) \text{ deg}^2$ (Fig. 1).

Spontaneous resolution. Blount *et al.* (1973) have studied the kinetics of isomerization of triaryl boranes using a dynamic NMR technique. They concluded that the half-life of any possible diastereoisomer of TNB in solution, even at 208 K, is at the most 5–10 min. This indicates that at room temperature there would be rapid equilibrium among the various possible conformers. The two propeller borane molecules investigated crystallographically, TPB (Zettler *et al.*, 1974) and TMB (Blount *et al.*, 1973), form racemic crystals. However, in our case, the molecule goes into a chiral space group, in the presence of benzene. It seems likely that the benzene molecule tends to associate itself with TNB even in the solution phase in the same way as in the crystals and this encourages crystallization of the enantiomers separately. We attempted to crystallize the TNB molecules from other solvents such as dimethoxyethane, ethyl acetate/methanol, carbon tetrachloride and acetone, in the hope of getting crystals without solvent molecules in the lattice, but we could not obtain crystals suitable for further study.

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* Further details of thermal-motion analysis have been deposited.