more marked extent, the C(8)–P bond turns away from the bicyclic skeleton: C(6)–C(8)–P and C(7)–C(8)–P are augmented by 7·7 and 6·8° compared with the *exo*-phosphonate isomer.
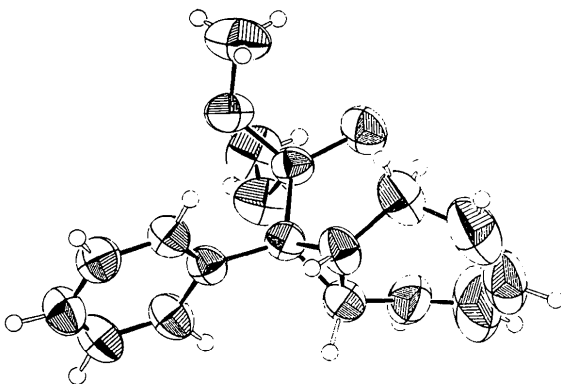

Fig. 1. An *ORTEP* plot of dimethyl 8-*exo*-phenylbicyclo[5.1.0]-octa-2,4-diene-8-phosphonate.
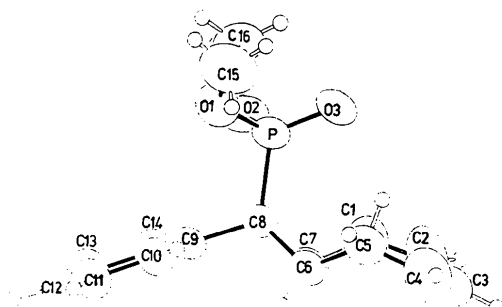

Fig. 2. Possible steric interactions between the phosphonate group and the bicyclic system become evident from this plot.

In the diene moiety of the bicyclic ring, differences between single- and double-bond lengths are more distinct than in the *endo*-phenyl isomer (Table 3). However, a C(2)–C(3) contact of 1·366 Å is again found; even for a Csp^2–Csp^2 single bond, this is a surprisingly short distance: the normal single-bond length between Csp^2 atoms in unsaturated seven-membered rings is 1·40–1·46 Å (for some examples see Bürgi, 1975).

Another uncommon feature concerns the torsion angle of 29° about one of the two double bonds in the cycloheptadiene ring. Dihedral angles about double bonds in cyclic polyenes do not exceed *ca* 18° (*e.g.* Gramaccioli, Mimun, Mugnoli & Simonetta, 1973) and structures with a nearly planar conjugated π system are known, *e.g.* cycloheptatriene–Mo(CO)₃ (Dunitz & Pauling, 1960). The dihedral angle between the two double bonds approaches 21°. This lack of planarity may be one reason why the 1,3-diene system is not prone to a Diels–Alder reaction, even at elevated temperature.

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3,4-Dihydro-3,4,4-trimethyl-4,3-borazaroisoquinoline

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Abstract. $C_{10}H_{15}N_2B$, orthorhombic, $P2_12_12_1$, $a = 13\cdot177\,(1)$, $b = 12\cdot115\,(1)$, $c = 6\cdot392\,(1)$ Å, $V = 1020\cdot3$ Å³, $Z = 4$, F.W. 174·05 g mol⁻¹, $D_x = 1\cdot13$ g cm⁻³, $\mu(\text{Cu }K\alpha) = 4\cdot4$ cm⁻¹. The structure was determined from diffractometer data and refined to $R = 0\cdot037$ for 836 observed reflexions. The B atom has a tetrahedral environment with four approximately equal lengths to three C (1·62 Å) and one N (1·65 Å). The hetero-atomic ring has a twist conformation with the methyl group on N equatorial.

Introduction. Dewar & Dougherty (1964) first synthesized and examined the properties of the heteroaromatic 4-methyl-4,3-borazaroisoquinoline (I). The naming convention used here is that of Dewar & Dietz (1959). The π-bonding is achieved through donation of the N

lone pair to the B–N bond. As the formula is written, there is a formal positive charge on N and a negative charge on B. However, the dipole moment of the B–N bond in aminoboranes has been found to be practically zero (Coates & Livingstone, 1961).

(I)   (II)   (III)
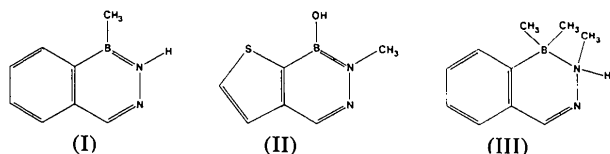
Aurivillius & Löfving (1974), in an X-ray study of 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-c]pyridine (II) (Gronowitz & Namtvedt, 1967), confirmed that the ring system is planar and found a B–N distance, 1·435 (6) Å, equal to that in borazine (Harshberger, Lee, Porter & Bauer, 1969).

Maltesson (1974) studied the syntheses and reactions of 3,2-borazaropyridines. During that work the title compound (III) was also obtained (Maltesson, 1976).

The crystals are colourless needles. Weissenberg photographs showed the symmetry to be orthorhombic, space group $P2_12_12_1$ from systematic extinctions.

A crystal, $0·24 \times 0·07 \times 0·05$ mm, was used for determination of cell dimensions and collection of intensities on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromatized Cu $K\alpha$ radiation was used. For the θ values of 44 reflexions in the range 15 to 50° the cell dimensions were refined to $a = 13·177$ (1), $b = 12·115$ (1) and $c = 6·392$ (1) Å ($\lambda = 1·54056$ Å). Intensities were collected for one octant of reciprocal space to $\theta = 70°$. The peak scan width was $0·7° + 0·5°$ tan θ

and the background counts were taken by extending the scan 25% on each side. 1140 reflexions were examined and of these. 836 were considered observed, with $I > 2·6\sigma(I)$. A standard reflexion measured periodically showed a linear intensity decrease which amounted to 12% at the end. Data were corrected for Lorentz, polarization and absorption effects and for

Table 2. *Interatomic distances and angles*

B——C(7)	1·624 (4) Å	C(7)—B——N(1)	102·0 (2)°
C(8)	1·612 (5)	–C(8)	113·7 (3)
C(9)	1·616 (5)	–C(9)	111·2 (2)
N(1)	1·645 (4)	N(1)—B——C(8)	107·1 (2)
N(1)—C(10)	1·485 (4)	–C(9)	108·9 (2)
H(N1)	0·89 (3)	C(8)—B——C(9)	113·1 (3)
N(2)	1·463 (3)	B——N(1)-N(2)	116·8 (2)
N(2)—C(1)	1·282 (3)	–C(10)	115·2 (2)
C(1)—H(C1)	0·98 (3)	–H(N1)	106 (2)
C(2)	1·460 (4)	N(2)—N(1)-C(10)	106·5 (2)
C(2)—C(7)	1·398 (4)	N(2)—N(1)-H(N1)	103 (2)
C(3)	1·399 (4)	C(10)-N(1)-H(N1)	108 (2)
C(3)—H(C3)	0·98 (4)	N(1)—N(2)-C(1)	113·9 (2)
C(4)	1·366 (5)	N(2)—C(1)-C(2)	128·2 (3)
C(4)—H(C4)	1·03 (3)	C(1)—C(2)-C(7)	118·7 (2)
C(5)	1·381 (5)	–C(3)	118·9 (3)
C(5)—H(C5)	0·87 (4)	C(7)—C(2)-C(3)	122·4 (3)
C(6)	1·386 (5)	C(2)—C(3)-C(4)	119·6 (3)
C(6)—H(C6)	0·90 (3)	C(3)—C(4)-C(5)	119·3 (3)
C(7)	1·387 (4)	C(4)—C(5)-C(6)	120·8 (3)
C(8)—H(C8A)	1·00 (4)	C(5)—C(6)-C(7)	121·8 (3)
H(C8B)	0·85 (5)	C(6)—C(7)-C(2)	116·1 (2)
H(C8C)	0·95 (3)	C(6)—C(7)-B	125·3 (2)
C(9)—H(C9A)	0·92 (5)	C(2)—C(7)-B	118·5 (2)
H(C9B)	1·02 (3)		
H(C9C)	0·90 (5)		
C(10)-H(C10A)	1·10 (3)		
H(C10B)	1·00 (5)		
H(C10C)	1·02 (4)		

Table 1. *Positional and thermal parameters*

The form of the anisotropic temperature factor is exp $(-\beta_{11}h^2 \cdots -2\beta_{12}hk \cdots)$. The positional parameters have been multiplied by 10^4 for B, N and C; by 10^3 for H. The β_{ij}'s have been multiplied by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B	630 (2)	9091 (2)	2009 (5)	38 (2)	58 (2)	172 (8)	−3 (2)	−12 (3)	4 (4)
N(1)	1517 (2)	9808 (2)	3204 (3)	39 (1)	49 (2)	158 (6)	−1 (1)	−1 (2)	6 (3)
N(2)	2110 (2)	9232 (2)	4801 (4)	49 (1)	60 (2)	158 (6)	−4 (1)	−23 (3)	4 (3)
C(1)	2332 (2)	8233 (2)	4321 (5)	47 (2)	61 (2)	196 (8)	−2 (2)	−26 (3)	17 (4)
C(2)	2053 (2)	7623 (2)	2437 (4)	42 (2)	52 (2)	193 (7)	−8 (1)	−5 (3)	2 (3)
C(3)	2595 (2)	6666 (2)	1927 (6)	53 (2)	53 (2)	305 (10)	0 (2)	0 (4)	−2 (4)
C(4)	2368 (3)	6110 (3)	127 (6)	60 (2)	63 (2)	341 (11)	0 (2)	16 (4)	−30 (4)
C(5)	1591 (3)	6486 (3)	−1132 (6)	72 (2)	77 (3)	232 (9)	−18 (2)	19 (4)	−44 (4)
C(6)	1040 (2)	7418 (3)	−589 (5)	54 (2)	74 (2)	180 (8)	−8 (2)	−5 (3)	−7 (4)
C(7)	1256 (2)	8018 (2)	1204 (4)	38 (1)	54 (2)	168 (7)	−9 (1)	3 (3)	8 (3)
C(8)	196 (3)	9850 (3)	142 (6)	58 (2)	80 (3)	252 (10)	0 (2)	−39 (4)	25 (5)
C(9)	−228 (3)	8748 (3)	3695 (6)	46 (2)	82 (3)	270 (10)	−2 (2)	24 (4)	6 (5)
C(10)	1170 (3)	10858 (3)	4165 (6)	65 (2)	58 (2)	258 (9)	9 (2)	−8 (4)	−20 (4)

	x	y	z	B (Å²)		x	y	z	B (Å²)
H(N1)	198 (2)	997 (2)	224 (5)	3·2 (6)	H(C8C)	−20 (2)	937 (2)	−71 (5)	4·0 (8)
H(C1)	273 (2)	783 (2)	537 (5)	4·2 (7)	H(C9A)	−78 (4)	844 (3)	303 (8)	8·3 (1·2)
H(C3)	313 (3)	636 (3)	283 (6)	6·3 (1·0)	H(C9B)	−66 (2)	937 (3)	429 (5)	4·1 (7)
H(C4)	281 (3)	546 (3)	−38 (6)	6·0 (9)	H(C9C)	−1 (4)	830 (4)	473 (8)	9·2 (1·4)
H(C5)	141 (3)	616 (3)	−229 (6)	5·4 (8)	H(C10A)	77 (2)	1141 (2)	308 (5)	4·2 (7)
H(C6)	52 (2)	753 (2)	−146 (5)	4·4 (7)	H(C10B)	76 (3)	1075 (3)	547 (7)	6·7 (1·0)
H(C8A)	−28 (3)	1041 (3)	73 (7)	7·1 (1·0)	H(C10C)	173 (3)	1138 (3)	468 (7)	6·6 (9)
H(C8B)	67 (3)	992 (4)	−74 (8)	8·4 (1·3)					

the intensity decrease with *DATACC* (previous version called *DATAPC*; Svensson, 1974).

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The H atoms were located from difference maps. Positional parameters were refined together with anisotropic thermal parameters for the non-H and isotropic for the H atoms by full-matrix least squares. The form factors were those of Doyle & Turner (1968) for C, N and B, and Stewart, Davidson & Simpson (1965) for H. The function minimized was $\sum w_i(|F_o|-|F_c|)^2$, where $w_i^{-1}=\sigma^2(|F_o|^2)/4|F_o|^2+0.002|F_o|^2+0.1$. The refinement converged to $R=0.037$, $R_w=0.049$ and $S=0.77$ for 836 reflexions. The averages of $w_i(|F_o|-|F_c|)^2$ were approximately constant as a function of both $|F_o|$ and $\sin\theta$. A refinement with H(N1) excluded converged to $R=0.042$, $R_w=0.056$ and the largest residual in the following difference map appeared at the H(N1) position.

Final values of positional and thermal parameters are given in Table 1,* interatomic distances and angles in Table 2. Fig. 1 shows a stereoscopic view of the molecule.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31955 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The molecule has an asymmetric N atom and thus exists in two configurations. The crystal examined contained only one of these, though no attempt was made to determine which. Deviations from the least-squares plane through the aromatic ring are given in Table 3. The conformation (Fig. 1) can be described as a twist or half-chair with N(1) most out of the plane. Some torsion angles are listed in Table 4. The methyl group on N(1) is equatorial. The other possible staggered conformation, with the methyl axial, would result from flipping over N(1).

Table 3. *Deviations* (Å) *from the least-squares plane through the six atoms of the aromatic ring*

C(2)	0.010	B	−0.068
C(3)	−0.011	N(1)	0.790
C(4)	0.003	N(2)	0.383
C(5)	0.006	C(1)	0.048
C(6)	−0.008	C(8)	0.687
C(7)	0.000	C(9)	−1.587
		C(10)	0.894

The B atom has a tetrahedral environment (Table 2) with an average of 1.617 (3) Å for three B–C distances and a B–N distance of 1.645 (4) Å. The B–C distances are somewhat shorter than in the tetraphenylborate ion (Sime, Dodge, Zalkin & Templeton, 1971) with an average 1.640 (4) Å, and the B–N distance is consider-
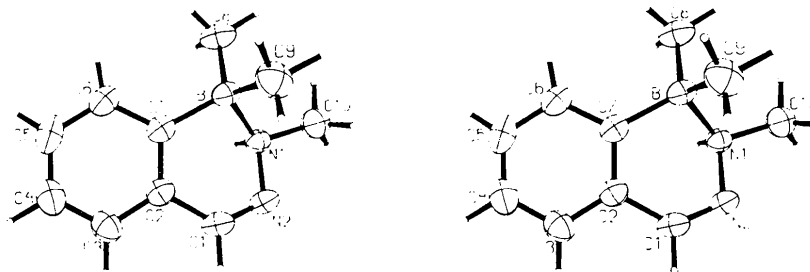

Fig. 1. Stereo view of the molecule (III) perpendicular to the plane of the aromatic ring. The thermal vibration ellipsoids are scaled to include 50% probability. The H atoms have arbitrarily been given radii of 0.05 Å.
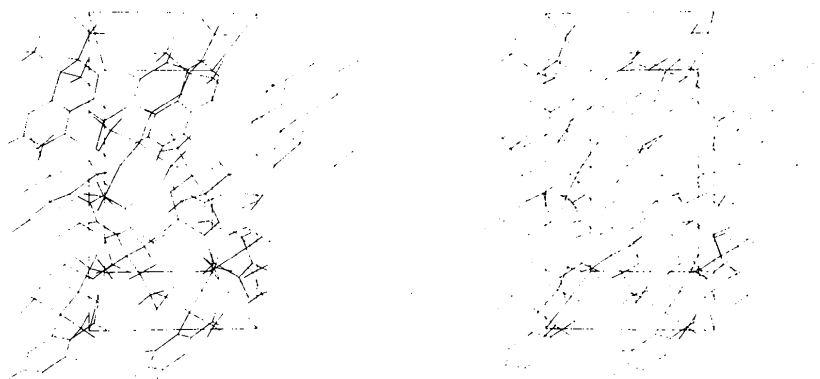

Fig. 2. Packing of the molecules in the crystal (III). The weak hydrogen bonds are indicated by dashed lines.

Table 4. *Torsion angles in the heteroatomic ring* (°)

C(2)—C(7)–B——N(1)	33·8 (3)		C(10)—N(1)–B–C(7)	−179·1 (2)
C(7)—B——N(1)–N(2)	−52·9 (3)		H(N1)–N(1)–B–C(8)	−59 (2)
B——N(1)–N(2)–C(1)	39·4 (3)		H(N1)–N(1)–B–C(9)	179 (2)
N(1)—N(2)–C(1)–C(2)	−1·0 (4)		H(N1)–N(1)–B–C(7)	61 (2)
N(2)—C(1)–C(2)–C(7)	−17·8 (4)		C(2)——C(7)–B–C(8)	148·8 (3)
C(1)—C(2)–C(7)–B	−4·0 (4)		C(2)——C(7)–B–C(9)	−82·2 (3)
C(10)-N(1)–N(2)–C(1)	169·7 (2)		N(2)——N(1)–B–C(8)	−172·7 (2)
C(10)-N(1)–B——C(8)	61·2 (3)		N(2)——N(1)–B–C(9)	64·7 (3)
C(10)-N(1)–B——C(9)	−61·4 (3)			

ably longer than those found in addition compounds between boron trihalides and amines, *e.g.* 1·575 (11) Å in (CH₃)₃NBCl₃ (Hess, 1969). A cyclization similar to that in the title compound is found in *B,B*-diphenyl-boroxazolidine (Rettig & Trotter, 1973) with a five-membered ring. Its two B–C distances average 1·611 (2) and the B–N distance is 1·653 (3), while the fourth distance, to O, is 1·484 (3) Å. These distances agree well with those in the present compound. C(7)–B–N(1) is only 102·0 (2)° which can be compared to the small O–B–N angle 99·7 (1)° in the boroxazolidine.

N(1)–C(10), 1·485 (4) Å, is normal for four-coordinated N. N(1)–N(2), 1·463 (3), and C(1)–N(2), 1·282 (3) Å, correspond closely to an N–N single bond and a C–N double bond. These bonds are coplanar with C(1)–C(2) (Table 4). The heteroatomic ring seems to be strained as C(2)–C(1)–N(2) and C(1)–N(2)–N(1) deviate considerably from the expected 120°.

The packing of the molecules is shown in Fig. 2. Weak hydrogen bonds N(1)–H· · ·N(2) link the molecules to form chains along **c**. N(1)–N(2) and N(2)–H are 3·058 (3) and 2·19 (3) Å and N(1)–H–N(2) is 164 (3)°. Most likely, the hydrogen bonds N–H· · ·N are also present in (I) as shown by the high melting point, 97°C, compared with that for the corresponding 3,4-dimethyl compound, 20°C (Dewar & Dougherty, 1964).

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A Monoclinic High-Temperature Modification of Potassium Carbonate

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Abstract. β-K₂CO₃, monoclinic, $C2/c$; $a=5\cdot675$ (3), $b=9\cdot920$ (4), $c=7\cdot018$ (4) Å, $\beta=96\cdot8$ (1)° at 310°C from powder photographs, $V=392\cdot3$ Å³, $Z=4$, $D_x=2\cdot34$ g cm⁻³; final $R=0\cdot077$ for 170 reflexions on precession and powder photographs. Crystals were taken from the melt. The main difference from the hexagonal high-temperature form is that the CO₃ groups are rotated around one of the C–O bonds. Upon cooling, the room-temperature structure ($P2_1/c$) is formed at 250°C. It is a superstructure of the present one.

Introduction. Little is known of the structure of the anhydrous alkali carbonates. Crystals of these substances are highly hygroscopic and easily twinned.

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