

## The Crystal and Molecular Structure of Bis-9-borabicyclo[3,3,1]nonane: a Study of the Boron–Carbon Bond

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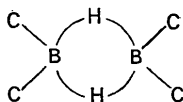
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The crystal structure of bis-9-borabicyclo[3,3,1]nonane has been determined from three-dimensional single-crystal X-ray data collected at room temperature by counter methods. The compound crystallizes in the monoclinic space group  $C2/m$  with  $a = 14.5351$  (8),  $b = 15.492$  (1),  $c = 6.8847$  (5) Å,  $\beta = 92.737$  (8)°,  $Z = 4$ . The calculated density is  $1.047$  g cm<sup>-3</sup>. Full-matrix least-squares refinement yielded an  $R$  of 0.079 based on 1121 observed reflexions. The unit cell contains two independent hydride-bridged dimers centred at  $C_{2h}$  ( $2/m$ ) symmetry sites. The molecular symmetry does not deviate significantly from  $D_{2h}$  ( $mmm$ ). Corrections to bond lengths due to librational motion have been applied although the molecules do not exhibit rigorous rigid-body motion. The B–C(1) distance is  $1.567$  (2) Å (corrected  $1.573$  Å), the B–B' bond length is  $1.818$  (3) Å (corrected  $1.821$  Å), and the C(1)–B–C(8) angle is  $111.8$  (3)°. The above bond lengths are compared with the corresponding values in diborane, trimethylborane and tetramethyldiborane.

### Introduction

While interest continues in the bonding of diborane and its derivatives, accurate structural dimensions exist for only two of these compounds. Diborane (Bartell & Carroll, 1965*a*) and tetramethyldiborane, TMDB (Carroll & Bartell, 1968) have been studied by gas-phase electron diffraction techniques. The structure of diborane was also investigated by low-temperature X-ray diffraction methods (Smith & Lipscomb, 1965; Jones & Lipscomb, 1970). The B–B' distances in diborane,  $1.775$  (4) Å, and TMDB,  $1.840$  (10) Å, differ by  $0.065$  (11) Å. This difference has been rationalized in terms of hyperconjugation (B–C  $\pi$  bonding) and in terms of non-bonded repulsion effects (Carroll & Bartell, 1968). Both arguments were consistent with the slight difference of the B–C bond lengths in trimethylborane,  $1.578$  (1) Å (Bartell & Carroll, 1965*b*) and TMDB,  $1.590$  (3) Å.

Bis-9-borabicyclo[3,3,1]nonane, BBBN, was prepared originally by hydroboration of cycloocta-1,5-diene (Köster, 1960) with tetra-*n*-propyldiborane *via* propyl-BBN. In BBBN the boron atoms are bonded to two secondary carbon atoms as well as to two bridging hydrogen atoms. Since a secondary carbon atom should not be able to participate in B–C hyperconjugative bonding as effectively as a methyl carbon atom, accurate molecular parameters for the



fragment of BBBN should be useful in the formation of qualitative bonding schemes for diborane derivatives.

### Experimental

Air-stable crystals of BBBN were prepared from cycloocta-1,5-diene and ethyldiborane *via* 9-ethyl-BBN (Köster & Grassberger, 1968) and were supplied by Drs R. Köster & M. A. Grassberger of this institute. One of the crystals was sealed inside an argon-filled glass capillary. Preliminary precession and Weissenberg photographs showed the crystal to be monoclinic. The systematic absences ( $hkl$ ,  $h+k=2n+1$ ) are consistent with the space groups  $C2/m$ ,  $C2$  and  $Cm$ ; subsequent analysis indicated the space group to be  $C2/m$ . The lattice constants at 22°C were obtained by a least-squares analysis of 42  $2\theta$  angles [Cu  $K\alpha$  ( $\lambda = 1.54178$  Å), Cu  $K\alpha_1$  ( $\lambda = 1.54051$  Å) and Cu  $K\alpha_2$  ( $\lambda = 1.54433$  Å)] of intensity maxima which were measured on an automated diffractometer (PDP-8/S + Siemens-Hoppe) equipped with a vertical slit in front of the detector. Crystallographic data are given in Table 1.

Table 1. *Crystal data for bis-9-borabicyclo[3,3,1]nonane*

$C_{16}H_{30}B_2$ , M.W. 244.04
Colourless
M.p. 148°C
Crystal faces and interfacial distances
[100], $[\bar{1}00]$ 0.232 mm
[010], $[0\bar{1}0]$ 0.638
[001], $[00\bar{1}]$ 0.377
Systematic absences $hkl$ , $h+k=2n+1$
Space group $C2/m$
$a = 14.5351$ (8) Å*
$b = 15.492$ (1)
$c = 6.8847$ (5)
$\beta = 92.737$ (8)°
$V = 1548.5$ Å <sup>3</sup>
$Z = 4$ , $D$ (calc) = $1.047$ g cm <sup>-3</sup>
$\mu$ (Cu $K\alpha$ ) = $3.888$ cm <sup>-1</sup> , $T = 22^\circ\text{C}$

\* Numbers in parentheses here and in succeeding tables and discussions represent the standard deviations in the least significant digit.

The crystal was mounted on the diffractometer with  $\mathbf{b}^*$  coincident with the  $\varphi$  axis. The faces were identified and the interfacial distances were measured with the aid of a microscope.  $\omega$  and  $\theta$  scans of several reflexions indicated that the crystal was suitable for intensity measurement. An orientation matrix was obtained from the refined unit-cell constants. Photographs of several reflexions ensured that the diffracted beams were entering the centre of the detector, which was mounted 17 cm from the crystal, and that the receiving collimator size was satisfactory. Intensities were collected by the five-value  $\theta-2\theta$  scan technique with nickel pre-filtered Cu  $K\alpha$  radiation, at 22 (1)°C. The size of the symmetrical scans about the Bragg maxima were chosen as a function of  $\theta$  and ranged from 0.80 to 1.00°. In the five-value technique integrated intensities of the left half of the peak *PL*, left background *BL*, full peak *P*, right background *BR* and right half of the peak *PR* are measured. Each background counting time equalled the time used to scan the corresponding half of the peak. Before the intensity for each peak was collected, the counter was positioned at the reflexion maximum, and a sampling of diffracted flux was made. Based on the strength of this flux, one of four scanning speeds was selected (1.25, 2.50, 5.00, 10.00°/min) in order to obtain the most efficient counting rates. When necessary, additional nickel filters were inserted into the primary beam to minimize coincident counting losses. Every 20 reflexions, the intensity of a reflexion (400) was measured with and without an occluder covering the lower half of the detector window. Thus movements and decomposition of the crystal as well as the stability of the diffractometer system could be monitored. No evidence for crystal decomposition was observed. One form of data (*hkl*,  $\bar{h}k\bar{l}$ ) was collected with  $\theta \leq 70^\circ$ .

The diffraction data were reduced to intensities,  $I = 0.5(P + PL + PR) - (BL + BR)$ , which were corrected for absorption and monitor reflexion fluctuations and then converted to structure factor amplitudes  $|F_o|$  by correction for Lorentz and polarization effects. Of the 1511 unique data, 1121 satisfied the condition  $I > \sigma(I)$ , where  $\sigma^2(I) = 0.25(P + PL + PR) + BL + BR$ . The observed  $|F_o|$ 's were assigned standard deviations  $\sigma(|F_o|) = k[\sigma^2(I) + (0.02I)^2]^{1/2}/2LpA|F_o|$ , where  $k$  is a scale factor and  $A$  is the absorbance. Statistical  $|F_o|$ 's were assigned to unobserved reflexions (Hamilton, 1955).

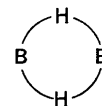
### Solution and refinement

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966). A set of  $|E|$ 's was generated, and since their distribution compares better with that expected for a theoretical centric structure (Table 2), the space group was assumed to be  $C2/m$ . The signs of two  $|E|$ 's were fixed in order to define the origin, and four other large  $|E|$ 's were given symbolic signs. The program of Dewar & Stone (1968) was used to determine signs for the other 174  $|E|$ 's  $> 1.50$ . An

Table 2. Normalized  $|E|$  distribution for bis-9-borabicyclo[3,3,1]nonane

	Calculated	Theoretical	
		Centric	Acentric
$\langle  E  \rangle$	0.798	0.798	0.886
$\langle  E ^2 \rangle$	1.000	1.000	1.000
$\langle  E ^2 - 1 \rangle$	1.011	0.968	0.736

*E* map, calculated with the sixth most probable combination of signs, clearly revealed the structure. Peaks for the 11 non-hydrogen atoms in the asymmetric unit were found among the 14 largest peaks in the *E* map. Later it was found that 18 of 180  $|E|$ 's had been given incorrect signs. The unit cell was found to contain two independent BBBN dimers centred at  $2/m$  ( $C_{2h}$ ) symmetry sites  $c$  ( $0\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) and  $b$  ( $0\frac{1}{2}0, \frac{1}{2}00$ ). For molecules at site  $c$ , the unit



lies on the crystallographic mirror plane; for molecules at site  $b$ , the B-B' vector lies on the 2 ( $C_2$ ) axis.

The structure was refined by full-matrix least-squares techniques. The function minimized was  $\sum w\Delta^2$ ,  $\Delta = ||F_o| - |F_c||$ , where  $w = 1/\sigma^2(|F_o|)$  or  $w = 0.0$  for the 'observed' and 'unobserved' reflexions respectively. The scattering factors for B and C were those of Cromer & Waber (1965), and the best spherical scattering factors were used for H (Stewart, Davidson & Simpson, 1965). No corrections for anomalous dispersion were made. The initial values for the discrepancy indices were 0.242 and 0.244 for  $R_1 = \sum \Delta / \sum |F_o|$  and  $R_2 = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2}$ , respectively. Three isotropic least-squares cycles yielded  $R_1 = 0.178$  and  $R_2 = 0.170$ . All 18 hydrogen atoms in the asymmetric unit were located in a difference Fourier synthesis, and three more cycles of isotropic refinement on the non-hydrogen atoms afforded  $R_1 = 0.124$  and  $R_2 = 0.098$ . After anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms, a comparison of  $|F_o|$  with  $|F_c|$  revealed that, for a few reflexions which had the largest intensities,  $|F_o|$  was less than  $|F_c|$ . Therefore, the 16  $|F_o|$ 's with the largest intensities were given zero weights. The final values for  $R_1$  and  $R_2$  were 0.079 and 0.043 respectively.

A difference Fourier map confirmed the structural analysis. The map contained densities in the range  $-0.31$  to  $0.20 \text{ e } \text{\AA}^{-3}$ , the maximum peak being about half as large as that for an average hydrogen atom in this structure. Plots of  $\langle w\Delta^2 \rangle$  versus  $|F_o|$ ,  $\sin \theta/\lambda$  and the Miller indices, indicate that the relative weights used were satisfactory. The final value for the error of fit, 1.572, shows that the  $\sigma(|F_o|)$ 's were somewhat underestimated. Final positional and thermal parameters are given in Table 3, the standard deviations being calculated from the diagonal elements of the inverse matrix. The numbering scheme is shown in Fig. 1.

Observed and calculated structure factors are listed in Table 4.

### Thermal motion analysis

The anisotropic thermal parameters for the two independent BBN molecules were fitted to a rigid-body

motion model of  $2/m$  symmetry (Schomaker & Trueblood, 1968). The r.m.s.  $\Delta u$  for molecules 1 and 2 are 0.008 and 0.005 respectively; thus the derived results must be treated with caution. The principal axes of libration of each molecule lie close to the molecular  $C_2(2)$  symmetry axes, not only because of the imposed

Table 3. Positional and thermal parameters for bis-9-borabicyclo[3.3.1]nonane

The form of the anisotropic thermal ellipsoid is:

$$\exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

The form of the isotropic thermal ellipsoid is:

$$\exp[-8\pi^2 U \sin^2 \theta / \lambda^2].$$

The numbering scheme for the hydrogen atoms is based on the carbon or boron atoms to which they are attached. For the methylene hydrogen atoms, the equatorial and axial atoms are designated with a '1' and '2' respectively.

Molecule 1	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{13}$
B	0.4395 (2)	0.5000	0.4602 (5)	0.044 (2)	0.050 (2)	0.045 (2)	0.000	0.000	0.002 (2)
C(1)	0.3814 (1)	0.4163 (1)	0.4207 (3)	0.052 (1)	0.046 (1)	0.062 (1)	0.006 (1)	0.000 (1)	-0.003 (1)
C(2)	0.3019 (2)	0.4171 (2)	0.5610 (4)	0.062 (1)	0.067 (2)	0.065 (2)	-0.011 (1)	0.011 (1)	0.001 (1)
C(3)	0.2457 (3)	0.5000	0.5627 (6)	0.061 (2)	0.078 (3)	0.054 (2)	0.000	0.000	0.006 (2)
C(7)	0.3017 (3)	0.5000	0.1354 (6)	0.104 (3)	0.079 (3)	0.043 (2)	0.000	0.000	-0.013 (2)
C(8)	0.3491 (2)	0.4173 (2)	0.2046 (4)	0.076 (2)	0.065 (2)	0.067 (2)	0.001 (2)	-0.016 (1)	0.002 (1)
HB	0.487 (2)	0.500	0.623 (3)	0.051 (8)					
HC(1)	0.418 (1)	0.363 (1)	0.441 (3)	0.060 (6)					
H(1)C(2)	0.260 (2)	0.371 (1)	0.525 (3)	0.081 (8)					
H(2)C(2)	0.330 (1)	0.407 (1)	0.698 (3)	0.083 (8)					
H(1)C(3)	0.210 (2)	0.500	0.686 (5)	0.072 (10)					
H(2)C(3)	0.206 (2)	0.500	0.447 (4)	0.043 (8)					
H(1)C(7)	0.298 (2)	0.500	-0.010 (5)	0.082 (11)					
H(2)C(7)	0.233 (3)	0.500	0.170 (6)	0.127 (17)					
H(1)C(8)	0.310 (2)	0.365 (2)	0.178 (3)	0.098 (10)					
H(2)C(8)	0.405 (2)	0.412 (1)	0.133 (3)	0.081 (8)					
Molecule 2									
B	0.5000	0.0587 (2)	0.000	0.043 (2)	0.037 (2)	0.052 (2)	0.000	0.000	0.000 (2)
C(1)	0.4736 (1)	0.1158 (1)	0.1773 (3)	0.061 (1)	0.044 (1)	0.046 (1)	-0.001 (1)	0.002 (1)	0.012 (1)
C(2)	0.3892 (2)	0.1702 (2)	0.1122 (4)	0.066 (2)	0.056 (2)	0.068 (2)	0.008 (1)	-0.001 (1)	0.018 (1)
C(3)	0.3974 (2)	0.2196 (2)	-0.0783 (4)	0.064 (2)	0.061 (2)	0.074 (2)	0.016 (1)	0.005 (1)	0.006 (1)
C(4)	0.4403 (2)	0.1686 (2)	-0.2408 (3)	0.077 (2)	0.060 (2)	0.056 (1)	0.007 (2)	0.010 (1)	0.004 (1)
HB	0.446 (1)	0.000	-0.037 (3)	0.041 (7)					
HC(1)	0.457 (1)	0.082 (1)	0.292 (3)	0.054 (6)					
H(1)C(2)	0.378 (1)	0.211 (1)	0.219 (3)	0.079 (8)					
H(2)C(2)	0.337 (1)	0.128 (1)	0.087 (3)	0.076 (8)					
H(1)C(3)	0.338 (2)	0.240 (1)	-0.122 (3)	0.079 (8)					
H(2)C(3)	0.436 (1)	0.273 (1)	-0.054 (3)	0.066 (7)					
H(1)C(4)	0.458 (1)	0.210 (1)	-0.346 (3)	0.079 (7)					
H(2)C(4)	0.393 (1)	0.127 (2)	-0.298 (3)	0.084 (8)					

Table 4. Observed structure factor amplitudes and calculated structure factors ( $\times 100$ )

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	0	1000	1000	0	0	0	1000	1000	0	0	0	1000	1000	0	0	0	1000	1000	0	0	0	1000	1000
1	0	0	1000	1000	1	0	0	1000	1000	1	0	0	1000	1000	1	0	0	1000	1000	1	0	0	1000	1000
2	0	0	1000	1000	2	0	0	1000	1000	2	0	0	1000	1000	2	0	0	1000	1000	2	0	0	1000	1000
3	0	0	1000	1000	3	0	0	1000	1000	3	0	0	1000	1000	3	0	0	1000	1000	3	0	0	1000	1000
4	0	0	1000	1000	4	0	0	1000	1000	4	0	0	1000	1000	4	0	0	1000	1000	4	0	0	1000	1000
5	0	0	1000	1000	5	0	0	1000	1000	5	0	0	1000	1000	5	0	0	1000	1000	5	0	0	1000	1000
6	0	0	1000	1000	6	0	0	1000	1000	6	0	0	1000	1000	6	0	0	1000	1000	6	0	0	1000	1000
7	0	0	1000	1000	7	0	0	1000	1000	7	0	0	1000	1000	7	0	0	1000	1000	7	0	0	1000	1000
8	0	0	1000	1000	8	0	0	1000	1000	8	0	0	1000	1000	8	0	0	1000	1000	8	0	0	1000	1000
9	0	0	1000	1000	9	0	0	1000	1000	9	0	0	1000	1000	9	0	0	1000	1000	9	0	0	1000	1000
10	0	0	1000	1000	10	0	0	1000	1000	10	0	0	1000	1000	10	0	0	1000	1000	10	0	0	1000	1000
11	0	0	1000	1000	11	0	0	1000	1000	11	0	0	1000	1000	11	0	0	1000	1000	11	0	0	1000	1000
12	0	0	1000	1000	12	0	0	1000	1000	12	0	0	1000	1000	12	0	0	1000	1000	12	0	0	1000	1000
13	0	0	1000	1000	13	0	0	1000	1000	13	0	0	1000	1000	13	0	0	1000	1000	13	0	0	1000	1000
14	0	0	1000	1000	14	0	0	1000	1000	14	0	0	1000	1000	14	0	0	1000	1000	14	0	0	1000	1000
15	0	0	1000	1000	15	0	0	1000	1000	15	0	0	1000	1000	15	0	0	1000	1000	15	0	0	1000	1000
16	0	0	1000	1000	16	0	0	1000	1000	16	0	0	1000	1000	16	0	0	1000	1000	16	0	0	1000	1000
17	0	0	1000	1000	17	0	0	1000	1000	17	0	0	1000	1000	17	0	0	1000	1000	17	0	0	1000	1000
18	0	0	1000	1000	18	0	0	1000	1000	18	0	0	1000	1000	18	0	0	1000	1000	18	0	0	1000	1000
19	0	0	1000	1000	19	0	0	1000	1000	19	0	0	1000	1000	19	0	0	1000	1000	19	0	0	1000	1000
20	0	0	1000	1000	20	0	0	1000	1000	20	0	0	1000	1000	20	0	0	1000	1000	20	0	0	1000	1000
21	0	0	1000	1000	21	0	0	1000	1000	21	0	0	1000	1000	21	0	0	1000	1000	21	0	0	1000	1000
22	0	0	1000	1000	22	0	0	1000	1000	22	0	0	1000	1000	22	0	0	1000	1000	22	0	0	1000	1000
23	0	0	1000	1000	23	0	0	1000	1000	23	0	0	1000	1000	23	0	0	1000	1000	23	0	0	1000	1000
24	0	0	1000	1000	24	0	0	1000	1000	24	0	0	1000	1000	24	0	0	1000	1000	24	0	0	1000	1000
25	0	0	1000	1000	25	0	0	1000	1000	25	0	0	1000	1000	25	0	0	1000	1000	25	0	0	1000	1000
26	0	0	1000	1000	26	0	0	1000	1000	26	0	0	1000	1000	26	0	0	1000	1000	26	0	0	1000	1000
27	0	0	1000	1000	27	0	0	1000	1000	27	0	0	1000	1000	27	0	0	1000	1000	27	0	0	1000	1000
28	0	0	1000	1000	28	0	0	1000	1000	28	0	0	1000	1000	28	0	0	1000	1000	28	0	0	1000	1000
29	0	0	1000	1000	29	0	0	1000	1000	29	0	0	1000	1000	29	0	0	1000	1000	29	0	0	1000	1000
30	0	0	1000	1000	30	0	0	1000	1000	30	0	0	1000	1000	30	0	0	1000	1000	30	0	0	1000	1000
31	0	0	1000	1000	31	0	0	1000	1000	31	0	0	1000	1000	31	0	0	1000	1000	31	0	0	1000	1000
32	0	0	1000	1000	32	0	0	1000	1000	32	0	0	1000	1000	32	0	0	1000	1000	32	0	0	1000	1000
33	0	0	1000	1000	33	0	0	1000	1000	33	0	0	1000	1000	33	0	0	1000	1000	33	0	0	1000	1000
34	0	0	1000	1000	34	0	0	1000	1000	34	0	0	1000	1000	34	0	0	1000	1000	34	0	0	1000	1000
35	0	0	1000	1000	35	0	0	1000	1000	35	0	0	1000	1000	35	0	0	1000	1000	35	0	0	1000	1000
36	0	0	1000	1000	36	0	0	1000	1000	36	0	0	1000	1000	36	0	0	1000	1000	36	0	0	1000	1000
37	0	0	1000	1000	37	0	0	1000	1000	37	0	0	1000	1000	37	0	0	1000	1000	37	0	0	1000	1000
38	0	0	1000	1000	38	0	0	1000	1000	38	0	0	1000	1000	38	0	0	1000	1000	38	0	0	1000	1000
39	0	0	1000	1000	39	0	0	1000	1000	39	0	0	1000	1000	39	0	0	1000	1000	39	0	0	1000	1000
40	0	0	1000	1000	40	0	0	1000	1000	40	0	0	1000	1000	40	0	0	1000	1000	40	0	0	1000	1000
41	0	0	1000	1000	41	0	0	1000	1000	41	0	0	1000	1000	41	0	0	1000	1000	41	0	0	1000	1000
42	0	0	1000	1000	42	0	0	1000	1000	42	0	0	1000	1000	42	0	0	1000	1000	42	0	0	1000	1000
43	0	0	1000	1000	43	0	0	1000	1000	43	0	0	1000	1000	43	0	0	1000						



ficant, 0.0–0.2°. Bond distances before and after corrections for libration are listed in Table 5. Only the uncorrected bond angles are given in Table 6.

Table 5. Bond distances (Å) in bis-9-borabicyclo[3.3.1]nonane

Bond lengths in the second molecule, which is centred at site *c*, are marked with an asterisk. Bond distances given in parentheses have been corrected for rigid-body librations. Primed atoms are related to unprimed atoms by a centre of inversion. The standard deviations of the average values are calculated either by  $[\sum(l_i - \bar{l})^2/n(n-1)]^{1/2}$  or  $1/n[\sum\sigma_i^2]^{1/2}$ , the larger value being reported.

B–B'	1.817 (4)	(1.819)
*B–B'	1.820 (4)	(1.823)
Ave	1.818 (3)	(1.821)
B–C(1)	1.565 (2)	(1.572)
*B–C(1)	1.569 (3)	(1.574)
Ave	1.567 (2)	(1.573)
C(1)–C(2)	1.541 (3)	(1.548)
C(1)–C(8)	1.538 (3)	(1.546)
*C(1)–C(2)	1.537 (3)	(1.543)
*C(1)–C(8)	1.542 (3)	(1.547)
Ave	1.540 (2)	(1.546)
C(2)–C(3)	1.523 (3)	(1.529)
C(7)–C(8)	1.521 (4)	(1.528)
*C(2)–C(3)	1.528 (4)	(1.533)
*C(3)–C(4)	1.527 (4)	(1.532)
Ave	1.525 (2)	(1.530)
B–HB	1.28 (2)	
B–HB'	1.24 (3)	
*B–HB	1.23 (1)	
Ave	1.25 (2)	
Ave C–H	1.00 (1)	

Table 6. Selected bond angles (°) in bis-9-borabicyclo[3.3.1]nonane

C(1)–B–C(5)	112.0 (1)	C(2)–C(3)–C(4)	115.1 (3)
*C(1)–B–C(5)	111.5 (2)	C(6)–C(7)–C(8)	114.9 (3)
ave*	111.8 (3)	*C(2)–C(3)–C(4)	114.9 (2)
		Ave	115.0 (1)
B–C(1)–C(2)	107.4 (2)	B–HB–B'	92 (2)
B–C(1)–C(8)	107.3 (2)	*B–HB–B'	95 (1)
*B–C(1)–C(2)	107.7 (2)	Ave	94 (2)
*B–C(1)–C(8)	107.1 (2)	HB–B–HB'	88 (2)
Ave	107.4 (3)	*HB–B–HB'	85 (1)
C(2)–C(1)–C(8)	113.8 (2)	Ave	86 (2)
*C(2)–C(1)–C(8)	114.7 (2)	Ave H–C–H	109 (3)
Ave	114.2 (6)		
C(1)–C(2)–C(3)	115.5 (2)		
C(1)–C(8)–C(7)	115.1 (2)		
*C(1)–C(2)–C(3)	115.5 (2)		
*C(3)–C(4)–C(5)	114.9 (2)		
Ave	115.2 (3)		

\* The bond angles are not assumed to be strictly averageable.

## Results and discussion

The structure of BBBN is illustrated in Fig. 1. The highest possible symmetry for BBBN is  $D_{2h}$  ( $mmm$ ), the  $C_2(2)$  axes lying along the above defined vectors  $V_1$ ,  $V_2$  and  $V_1 \times V_2$ . Clearly three unique orientations of the molecule with respect to  $C_2(2/m)$  crystallographic symmetry are possible. Indeed two unique orientations were found in this investigation. The high  $D_{2h}$  symmetry is also indicated by the excellent agreement between the chemically equivalent bond distances and angles of the two crystallographically independent dimers (Tables 5 and 6). From a different point of view, the good agreement between chemically equivalent

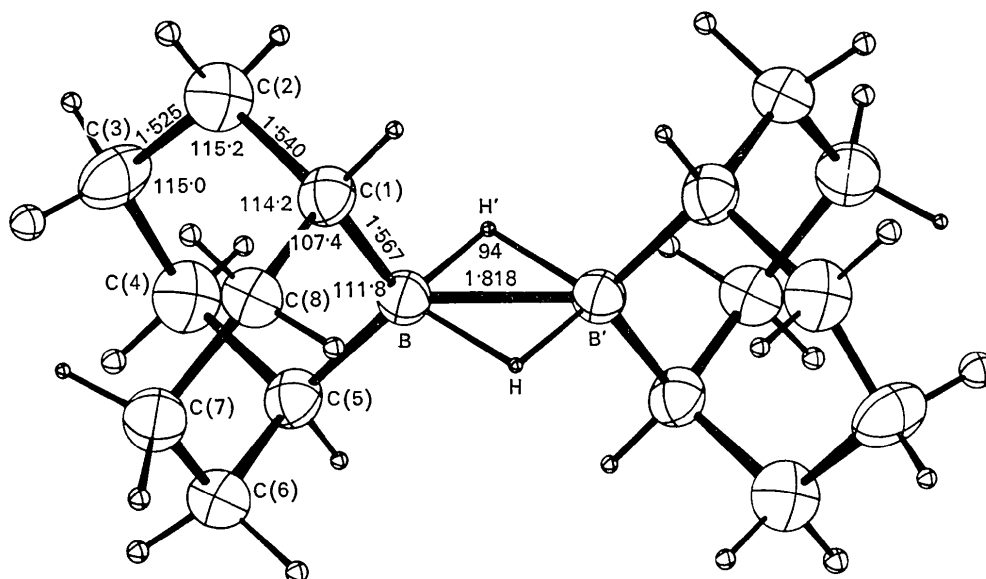


Fig. 1. A perspective drawing of bis-9-borabicyclo[3.3.1]nonane including average values of selected bond distances and angles.

bond lengths indicates that the standard deviations of the atomic positional parameters as estimated from least-squares refinement are adequate.

The bis-9-borabicyclo[3,3,1]nonane skeleton exists in the twin-chair form. The average value for the angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4),  $115.1^\circ$ , is larger than the  $111^\circ$  value in cyclohexane and indicates that the six-membered rings are flattened. The reason for the flattening of the rings, repulsion between methylene groups C(3) and C(7) as well as C(2) and C(8), has been thoroughly discussed by other authors (Webb & Becker, 1967; Brown, Martin & Sim, 1965; Dobler & Dunitz, 1964). All C–C–C, B–C–C, and C–B–C angles in BBBN are in good agreement with those found in other bicyclo[3.3.1]nonane derivatives.

The C–C bond lengths show an interesting trend. The bonds C(2)–C(3) average  $1.525(2) \text{ \AA}$  (corrected  $1.530 \text{ \AA}$ ) and compare well with C–C bond lengths found for cyclohexane and its derivatives,  $1.527(5) \text{ \AA}$  (Luger, Plieth & Ruban, 1972; Altona & Sundaralingam, 1970). The bonds C(1)–C(2) are significantly longer, averaging  $1.540(2) \text{ \AA}$  (corrected  $1.546 \text{ \AA}$ ). Whether this lengthening is due to the steric strain of the bicyclic ring system or to the presence of the boron atom in this structure is difficult to decide since previous investigations of bicyclo[3,3,1]nonane systems are not of the highest precision. However, the average value of this bond in 2-chlorobicyclo[3,3,1]nonane-9-one ( $1.522 \text{ \AA}$ ) (Webb & Becker, 1967) supports the idea that the bond lengthening is peculiar to the boron derivative. The slight lengthening may be understood in terms of a hybridization effect on C(1) resulting from its linkage to the boron atom; that is, C(1) would use more  $2s$  character in its bond to B than in its bonds to C(2), C(8) and HC(1) (Walsh, 1947).

The geometry about the boron atoms is of principal interest. The average C(1)–B–C(8) angle of  $111.8(3)^\circ$  is smaller than the  $120.0(26)^\circ$  value found in TMDB, probably because of the constraints of the bicyclic ring system (Webb & Becker, 1967). The B–C(1) distance,  $1.567(2) \text{ \AA}$  (corrected  $1.573 \text{ \AA}$ ), is slightly shorter than the B–C distance of trimethylborane,  $1.578(1) \text{ \AA}$  (Bartell & Carroll, 1965*b*), and is significantly shorter than the B–C distance,  $1.590(3) \text{ \AA}$  (electron diffraction), in TMDB (Carroll & Bartell, 1968). The B–B' distance,  $1.818(3) \text{ \AA}$  (corrected  $1.821 \text{ \AA}$ ), is longer than

the value reported for diborane,  $1.762(10) \text{ \AA}$  (corrected  $1.776 \text{ \AA}$ ; Jones & Lipscomb, 1970), and only marginally shorter than the length in TMDB,  $1.840(10) \text{ \AA}$  (electron diffraction; Carroll & Bartell, 1968). The average B–H bond length,  $1.25(2) \text{ \AA}$ , and H–B–H' bond angle,  $86(2)^\circ$ , compare well with those reported in the spherical atom refinement of diborane (Smith & Lipscomb, 1965; Jones & Lipscomb, 1970).

Owing to the differences in the definition of X-ray and electron diffraction bond lengths, an X-ray B–C or B–B bond length, which has been corrected for librational shortening, should be somewhat shorter ( $0.002\text{--}0.005 \text{ \AA}$ ) than its electron diffraction counterpart (Kuchitsu, 1968; Jones & Lipscomb, 1970; Lipscomb, 1972). Despite this consideration the B–C(1) bond length in BBBN is significantly shorter than the corresponding bond length in TMDB. If hyperconjugation effects were important in determining the B–C bond length, the opposite effect would have been expected.

Since the C(1)–B–C(1') angle is smaller in BBBN than in trimethylborane or TMDB, BBBN should be more strained than the latter two molecules. Once again the relatively short B–C bond length in BBBN is not to be expected, if nonbonded repulsions were dominant. In addition, since the B–C(1)–C(2) angles are smaller than the tetrahedral value, and since the C(1)–B–C(8) angle is smaller than the trigonal value, hybridization theory based on bond angles would have predicted a longer B–C distance for BBBN. A bent-bond effect might be used in rationalizing the observed trend. In addition, the short B–C bond can be rationalized by a chelate effect of the bicyclic ring system which might tend to diminish non-bonded repulsions in the boron-atom coordination sphere by distributing them throughout the ring system and thus allow a closer approach of C(1) and C(8).

A unit-cell packing diagram is shown in Fig. 2. Three intermolecular H...H contacts are less than  $2.60 \text{ \AA}$ ; and the shortest, between molecule I atoms H(1)C(3)–H(1)C(7) ( $x, 1+y, 1+z$ ), is  $2.40(5) \text{ \AA}$ . All other intermolecular contacts are normal.

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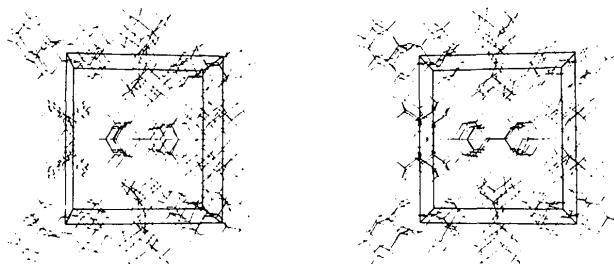


Fig. 2. A stereodrawing of the unit-cell contents of bis-9-borabicyclo[3,3,1]nonane.

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## The Crystal Structure of 9-Isobutylthioxanthene\*

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The crystal structure of 9-isobutylthioxanthene,  $C_{17}H_{18}S$ , has been determined by the heavy-atom method. The refinement was carried out by the least-squares method with anisotropic temperature factors based on three-dimensional data to give a final  $R$  value of 0.059 for 1736 reflections. The space group is  $P2_1/n$  with  $Z=4$ , and the unit-cell parameters are:  $a=6.188 \pm 0.002$ ,  $b=28.024 \pm 0.005$ ,  $c=8.426 \pm 0.002$  Å, and  $\beta=101.97 \pm 0.03^\circ$ . All the hydrogen atoms were located on a difference Fourier synthesis. The crystal contains both enantiomorphs in equal amounts. The best planes of the benzene rings make a dihedral angle of  $138.9^\circ$ . The *meso* atoms C(9) and S are significantly displaced from the benzene ring. The isobutyl group is 'boat axial' with respect to the central thioxanthene ring. All interatomic distances and angles are normal. The sulfur-carbon bond distance is  $1.768 \pm 0.003$  Å. The average carbon-carbon bond distance is  $1.522 \pm 0.006$  Å for carbon-carbon single bonds,  $1.386 \pm 0.006$  Å for carbon-carbon bonds in benzenoid rings and  $1.511 \pm 0.005$  Å for carbon-carbon bonds involving C(9) and the benzenoid ring. The packing of the molecules in the crystal is determined mainly by the van der Waals interaction.

### Introduction

9-Isobutylthioxanthene is one of a series of thioxanthene derivatives under study in this laboratory. The objectives of these studies are to determine the conformation of thioxanthene derivatives, the effect of different *meso*- and *peri*-substituents on the stereochemistry of these compounds, and to compare the conformation of thioxanthene derivatives in crystals with that in solution deduced from nuclear magnetic resonance studies. Also, the accurate determination of the C-S bond lengths and the C-S-C bond angles in thioxanthene derivatives will provide information on the bonding characteristic of the sulfur atom.

### Experimental

Single crystals of 9-isobutylthioxanthene were obtained through the courtesy of Dr A. L. Ternay of the

Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms, elongated along the  $a$  axis. Accurate cell parameters were measured with Mo  $K\alpha$  radiation on a Picker FACS-1 automatic diffractometer. The density of the crystals was determined by the flotation equilibrium method in a mixture of *n*-propyl alcohol and carbon tetrachloride. The crystal data is summarized in Table 1.

Table 1. *Crystal data of 9-isobutylthioxanthene*

Chemical formula $C_{17}H_{18}S$ , M.W. 254.40	
Monoclinic, space group $P2_1/n$ from the systematic extinctions:	
$h0l$ absent for $h+l=2n+1$ and $0k0$ absent for $k=2n+1$ .	
$a = 6.188 \pm 0.002$ Å	$Z = 4$
$b = 28.024 \pm 0.005$	$D_m = 1.202$ g cm $^{-3}$
$c = 8.426 \pm 0.002$	$D_x = 1.182$
$\beta = 101.97 \pm 0.03^\circ$	$\mu(\text{Mo } K\alpha) = 2.06$ cm $^{-1}$
	$\lambda(\text{Mo } K\alpha) = 0.7107$ Å

The integrated intensity data were collected on a Picker FACS-1 automatic diffractometer. The crystal

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