

The Crystal and Molecular Structure of 1,2:3,4:5,6-Tris-(*o,o'*-biphenylene)borazine, $C_{36}H_{24}B_3N_3$

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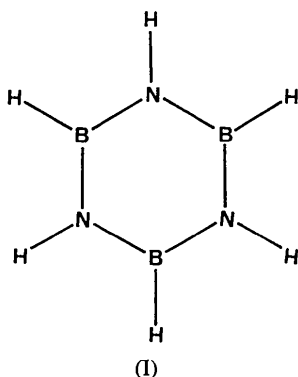
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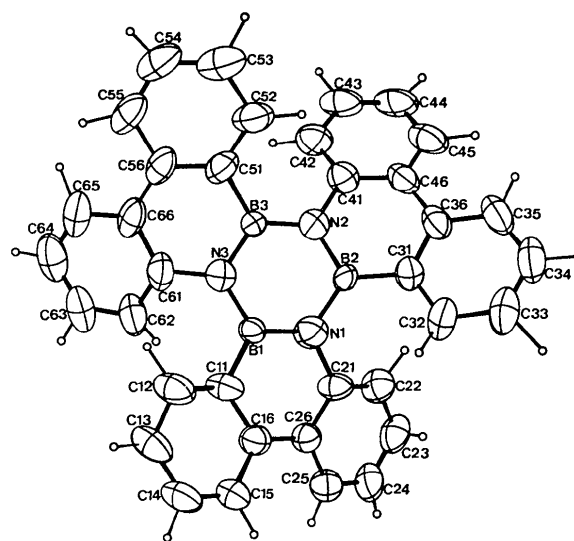
1,2:3,4:5,6-Tris-(*o,o'*-biphenylene)borazine, $C_{36}H_{24}B_3N_3$, is monoclinic, space group $P2_1/c$, with $a=20.066$ (6), $b=7.090$ (1), $c=19.656$ (4) Å, $\beta=104.28$ (4)°, $Z=4$. The structure was solved by weighted multi-solution tangent formula phase refinement from diffractometer data collected with Cu radiation. Block-diagonal least-squares refinement resulted in a final R of 0.084 for 4137 reflexions. The central borazine ring suffers severe distortion from planarity as a result of the crowding of the biphenyl groups. B-N lengths are shorter (mean 1.430 Å) when bridged by a biphenyl group than when not (mean 1.488 Å). Mean B-C and N-C lengths are 1.490 and 1.464 Å respectively.

Introduction

A recent electron diffraction determination of the geometrical parameters of borazine (I) (Harshbarger, Lee, Porter & Bauer, 1969*a*) could be interpreted equally well by models with D_{3h} , C_2 or C_{3v} symmetry. It was later pointed out (Blick, Dawson & Niedenzu, 1970) that only D_{3h} symmetry was compatible with spectral observations (Niedenzu, Sawodony, Watanabe, Dawson, Totani & Weber, 1967). The borazine molecule is therefore planar with a B-N length of 1.435 Å (Harshbarger, Lee, Porter & Bauer, 1969*a*), intermediate between the values expected for single and double B-N bonds. It is thus generally recognized that the B-N bond in such compounds possesses some multiple-bond character as the result of donation of electron density by the nitrogen atom to a π -bonding orbital between the two atoms. Because of the difference in electronegativity of boron and nitrogen, however, this delocalization is not as extensive as in the case of benzene, which is considered to have approximately twice the aromatic character of borazine (Pauling, 1962).



1,2:3,4:5,6-Tris-(*o,o'*-biphenylene)borazine (II) (TBB) was first synthesized by the pyrolysis of *N,N,N*-trisbiphenyl-(2)-borazine (Köster, Hattori & Morita, 1965; Köster, Iwasaki, Hattori & Morita, 1968).



(II)

Examination of a model of TBB shows that a completely planar structure is impossible because of steric interactions between hydrogen atoms on adjacent biphenyl groups. To explore this overcrowding and to determine which part of the molecule loses its aromaticity to relieve the strain, an X-ray structure analysis was undertaken.

Experimental

Crystal data

1,2:3,4:5,6-Tris-(*o,o'*-biphenylene)borazine, $C_{36}H_{24}B_3N_3$, F.W. 531.04, monoclinic, $a=20.066$ (6), $b=7.090$ (1), $c=19.656$ (4) Å, $\beta=104.28$ (4)°, $V=2709.9$ Å³, $Z=4$, $D_x=1.30$ g cm⁻³, $\mu(\text{Cu } K\alpha)=5.86$ cm⁻¹, $F(000)=1104$, $\lambda(\text{Cu } K\alpha)=1.5418$ Å. Space group $P2_1/c$ (C_{2h}^5).

The space group and cell parameters were determined by photographic methods. The cell dimensions were refined by least-squares analysis of θ values measured for 51 reflexions on a Siemens AED diffractometer with Cu $K\alpha$ radiation. Intensities were measured by our standard five-value method (Krüger, 1970; Brauer & Krüger, 1973) with a platy crystal of dimensions $0.20 \times 0.99 \times 0.49$ mm mounted with **b** parallel to the φ axis of the diffractometer. The standard deviation of an intensity was calculated from $\sigma^2(I) = S + B + (dS)^2$ where S = scan count, B = background, $I = S - B$ and d = an empirical constant to allow for instrumental instability, taken as 0.03. Of 4860 independent reflexions with 2θ (Cu $K\alpha$) $\leq 140^\circ$ (minimum interplanar spacing 0.82 Å), 723 had $I/\sigma(I) \leq 2.0$ and were classified as unobserved. Lorentz and polarization factors were applied and the structure amplitudes and normalized structure amplitudes (E 's) were derived. No absorption correction was made.

The structure was solved by multi-solution tangent formula refinement (Germain, Main & Woolfson, 1970) of 227 reflexions with $|E| \geq 2.1$. The starting set shown in Table 1 was successful in producing one solution with $R\alpha$ (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) = 0.167 while values of this parameter for all other permutations exceeded 0.335. Considerable difficulty was encountered in several attempts at achieving a solution with other direct methods programs. We attribute this to the effect on the E 's and Σ_2 probabilities of the large number of atoms in the unit cell and to their decidedly non-random locations. The E map based on this solution of low $R\alpha$ revealed directly the positions of the 42 non-hydrogen atoms among the 46 highest peaks. The positions of these 42 atoms (all treated as carbon at this stage) were subjected to two cycles of isotropic full-matrix least-squares refinement followed by one cycle of anisotropic

refinement. The 24 hydrogen atoms were found on two successive difference maps and the entire structure was refined to convergence in eight cycles of block-diagonal least-squares refinement. The function minimized was $\sum w|F_o - kF_c|^2$ where statistical weights were used for observed reflexions while unobserved had $w = 0.0$. Scattering factors were those of Cromer & Waber (1965). The boron and nitrogen atoms were assigned by refinement of the two possible models, giving R values of 0.084 and 0.094. The model with the lower R also gave a more reasonable and consistent set of bond lengths. The final value of $R_w = [\sum w|F_o - kF_c|^2 / \sum wF_o^2]^{1/2}$ was 0.135. Final positional and thermal parameters are given in Tables 2 and 3 with their standard deviations calculated from the final refinement cycle.* The molecular structure is shown in Fig. 1. Bond lengths, valency angles and torsion angles are given in Tables 4 and 5 and Fig. 2. Fig. 3 shows the unit cell viewed down $-b$.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30562 (43 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Reflexions in the starting set, with their initial values ($^\circ$)

-4	1	2	0
-5	1	3	0
0	4	13	0
0	1	4	0.180
-1	3	13	0.180
-1	2	2	0.180
-15	2	10	0.180

Table 2. Final coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$) for the non-hydrogen atoms

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
B(1)	3366 (1)	3047 (6)	3613 (1)	C(36)	1542 (2)	-1210 (4)	4038 (1)
N(1)	3122 (1)	1997 (5)	4112 (1)	C(41)	1218 (1)	1658 (5)	3299 (2)
C(11)	4124 (1)	3247 (5)	3712 (1)	C(42)	739 (1)	3003 (6)	2995 (2)
C(12)	4413 (1)	3617 (6)	3153 (2)	C(43)	62 (2)	2882 (7)	3046 (2)
C(13)	5117 (2)	3499 (6)	3229 (2)	C(44)	-130 (2)	1448 (7)	3416 (2)
C(14)	5536 (2)	3044 (6)	3865 (2)	C(45)	345 (2)	84 (6)	3736 (2)
C(15)	5265 (2)	2672 (5)	4424 (2)	C(46)	1026 (1)	155 (5)	3684 (1)
C(16)	4554 (1)	2731 (4)	4362 (2)	B(3)	2205 (2)	3004 (5)	2799 (2)
C(21)	3563 (1)	1794 (5)	4828 (1)	N(3)	2846 (1)	3995 (5)	3042 (1)
C(22)	3283 (2)	1438 (5)	5396 (2)	C(51)	1823 (1)	3244 (5)	2052 (1)
C(23)	3681 (2)	1485 (5)	6072 (2)	C(52)	1370 (2)	1866 (6)	1713 (2)
C(24)	4364 (2)	1921 (6)	6194 (2)	C(53)	1069 (2)	1990 (6)	996 (2)
C(25)	4644 (2)	2324 (6)	5651 (2)	C(54)	1236 (2)	3459 (7)	621 (2)
C(26)	4256 (1)	2260 (4)	4948 (1)	C(55)	1695 (2)	4838 (6)	946 (2)
B(2)	2450 (1)	1001 (5)	3868 (2)	C(56)	2006 (1)	4752 (5)	1670 (1)
N(2)	1946 (1)	1935 (5)	3326 (2)	C(61)	2956 (2)	5711 (5)	2677 (2)
C(31)	2241 (1)	-755 (4)	4175 (2)	C(62)	3426 (2)	7081 (5)	3016 (2)
C(32)	2728 (2)	-2090 (5)	4505 (2)	C(63)	3483 (2)	8798 (5)	2715 (2)
C(33)	2531 (2)	-3815 (5)	4713 (2)	C(64)	3050 (2)	9193 (6)	2057 (3)
C(34)	1854 (3)	-4268 (6)	4590 (2)	C(65)	2587 (2)	7929 (6)	1732 (2)
C(35)	1358 (2)	-2984 (6)	4249 (2)	C(66)	2514 (2)	6145 (5)	2025 (2)

Table 2 (cont.)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B(1)	31 (1)	92 (3)	32 (1)	-17 (1)	6 (1)	12 (1)
N(1)	47 (1)	117 (3)	61 (2)	0 (1)	13 (1)	23 (2)
C(11)	38 (1)	86 (2)	51 (2)	-6 (1)	11 (1)	-13 (1)
C(12)	46 (2)	123 (3)	55 (2)	-13 (2)	18 (1)	-16 (2)
C(13)	52 (2)	93 (3)	86 (2)	-16 (2)	35 (2)	-21 (2)
C(14)	38 (2)	93 (3)	113 (3)	-3 (2)	17 (2)	11 (2)
C(15)	43 (1)	81 (2)	96 (2)	-9 (2)	8 (2)	20 (2)
C(16)	44 (1)	54 (2)	58 (2)	-3 (1)	5 (1)	-3 (1)
C(21)	45 (1)	71 (2)	41 (1)	3 (1)	8 (1)	-4 (1)
C(22)	61 (2)	81 (2)	47 (1)	6 (2)	14 (1)	1 (1)
C(23)	102 (3)	64 (2)	43 (2)	-6 (2)	13 (2)	1 (1)
C(24)	109 (3)	95 (3)	48 (2)	-41 (2)	-7 (2)	13 (2)
C(25)	73 (2)	95 (3)	61 (2)	-28 (2)	-12 (2)	11 (2)
C(26)	53 (1)	52 (2)	52 (2)	-2 (1)	1 (1)	2 (1)
B(2)	31 (1)	71 (2)	53 (2)	-1 (1)	10 (1)	30 (2)
N(2)	50 (1)	89 (2)	85 (2)	-8 (1)	11 (1)	27 (2)
C(31)	60 (2)	54 (2)	60 (2)	-7 (1)	22 (1)	8 (1)
C(32)	82 (2)	56 (2)	76 (2)	8 (2)	30 (2)	19 (2)
C(33)	122 (3)	54 (2)	73 (2)	-4 (2)	36 (2)	3 (2)
C(34)	139 (4)	62 (2)	80 (2)	-34 (2)	24 (2)	5 (2)
C(35)	94 (3)	84 (3)	73 (2)	-45 (2)	26 (2)	-2 (2)
C(36)	67 (2)	60 (2)	47 (1)	-21 (1)	18 (1)	-7 (1)
C(41)	45 (1)	76 (2)	62 (2)	-6 (1)	17 (1)	6 (2)
C(42)	42 (2)	97 (3)	81 (2)	5 (2)	15 (1)	9 (2)
C(43)	46 (2)	137 (4)	71 (2)	-1 (2)	19 (2)	-5 (2)
C(44)	40 (2)	152 (4)	71 (2)	-13 (2)	16 (1)	-5 (2)
C(45)	57 (2)	130 (3)	62 (2)	-36 (2)	18 (1)	-6 (2)
C(46)	53 (2)	83 (2)	43 (1)	-28 (2)	14 (1)	-9 (1)
B(3)	39 (1)	71 (2)	45 (2)	-13 (1)	-5 (1)	25 (2)
N(3)	69 (2)	104 (2)	60 (2)	-23 (2)	11 (1)	22 (2)
C(51)	54 (2)	82 (2)	41 (1)	5 (1)	9 (1)	10 (1)
C(52)	58 (2)	98 (3)	50 (2)	1 (2)	0 (1)	0 (2)
C(53)	60 (2)	121 (3)	54 (2)	16 (2)	7 (1)	-10 (2)
C(54)	70 (2)	141 (4)	41 (2)	31 (2)	13 (1)	10 (2)
C(55)	66 (2)	118 (3)	49 (2)	30 (2)	24 (1)	23 (2)
C(56)	53 (2)	78 (2)	48 (1)	21 (1)	21 (1)	18 (1)
C(61)	71 (2)	64 (2)	57 (2)	-6 (2)	26 (1)	12 (1)
C(62)	90 (2)	68 (2)	76 (2)	-21 (2)	33 (2)	4 (2)
C(63)	96 (3)	63 (2)	118 (3)	-7 (2)	66 (2)	4 (2)
C(64)	98 (3)	65 (2)	136 (4)	7 (2)	62 (3)	31 (2)
C(65)	84 (2)	84 (3)	92 (3)	23 (2)	45 (2)	39 (2)
C(66)	62 (2)	71 (2)	60 (2)	19 (2)	32 (1)	20 (1)

Table 3. Final coordinates ($\times 10^3$) and isotropic temperature factors ($\times 10^2$) for hydrogen atoms

	x/a	y/b	z/c	U
H(12)	408 (2)	415 (5)	267 (2)	9 (1)
H(13)	532 (1)	365 (4)	284 (2)	5 (1)
H(14)	603 (2)	281 (6)	388 (2)	10 (1)
H(15)	562 (2)	224 (4)	487 (2)	6 (1)
H(22)	278 (2)	86 (5)	532 (2)	8 (1)
H(23)	352 (2)	133 (6)	654 (2)	10 (1)
H(24)	463 (2)	223 (6)	671 (2)	10 (1)
H(25)	510 (2)	274 (5)	587 (2)	9 (1)
H(32)	322 (1)	-186 (4)	448 (1)	5 (1)
H(33)	290 (2)	-508 (7)	505 (3)	13 (2)
H(34)	173 (2)	-557 (5)	477 (2)	8 (1)
H(35)	90 (2)	-343 (5)	407 (2)	8 (1)
H(42)	92 (2)	406 (6)	275 (2)	9 (1)
H(43)	-32 (2)	389 (5)	277 (2)	7 (1)
H(44)	-63 (2)	116 (5)	353 (2)	8 (1)
H(45)	14 (2)	-115 (6)	402 (2)	8 (1)
H(52)	121 (2)	62 (5)	196 (2)	7 (1)
H(53)	70 (2)	90 (5)	69 (2)	8 (1)
H(54)	112 (2)	371 (6)	17 (2)	10 (1)
H(55)	192 (2)	601 (6)	75 (2)	11 (1)
H(62)	359 (2)	685 (5)	347 (2)	9 (1)
H(63)	382 (2)	1004 (5)	302 (2)	8 (1)
H(64)	305 (2)	1056 (5)	185 (2)	8 (1)
H(65)	217 (2)	821 (5)	124 (2)	9 (1)

Table 4. Bond lengths (\AA) with standard deviations in parentheses

B(1)-N(1)	1.412 (4)	B(1)-N(3)	1.491 (4)
B(2)-N(2)	1.437 (4)	B(2)-N(1)	1.494 (4)
B(3)-N(3)	1.442 (4)	B(3)-N(2)	1.478 (4)
B(1)-C(11)	1.493 (4)	N(1)-C(21)	1.474 (4)
B(2)-C(31)	1.488 (5)	N(2)-C(41)	1.461 (4)
B(3)-C(51)	1.488 (4)	N(3)-C(61)	1.457 (5)
C(11)-C(12)	1.389 (4)	C(41)-C(42)	1.382 (5)
C(11)-C(16)	1.403 (4)	C(41)-C(46)	1.414 (4)
C(12)-C(13)	1.385 (4)	C(42)-C(43)	1.390 (3)
C(13)-C(14)	1.363 (6)	C(43)-C(44)	1.360 (6)
C(14)-C(15)	1.367 (5)	C(44)-C(45)	1.395 (6)
C(15)-C(16)	1.403 (4)	C(45)-C(46)	1.397 (4)
C(16)-C(26)	1.462 (4)	C(51)-C(52)	1.389 (5)
C(21)-C(22)	1.391 (4)	C(51)-C(56)	1.408 (4)
C(21)-C(26)	1.392 (4)	C(52)-C(53)	1.393 (5)
C(22)-C(23)	1.371 (4)	C(53)-C(54)	1.364 (6)
C(23)-C(24)	1.368 (6)	C(54)-C(55)	1.388 (5)
C(24)-C(25)	1.355 (5)	C(55)-C(56)	1.408 (4)
C(25)-C(26)	1.410 (5)	C(56)-C(66)	1.467 (4)
C(31)-C(32)	1.401 (4)	C(61)-C(62)	1.404 (5)
C(31)-C(36)	1.401 (4)	C(61)-C(66)	1.403 (5)
C(32)-C(33)	1.378 (5)	C(62)-C(63)	1.371 (5)
C(33)-C(34)	1.360 (7)	C(63)-C(64)	1.399 (7)
C(34)-C(35)	1.395 (6)	C(64)-C(65)	1.335 (6)
C(35)-C(36)	1.402 (5)	C(65)-C(66)	1.413 (5)
C(36)-C(46)	1.463 (4)		

Table 5. Valency angles ($^\circ$) with standard deviations in parentheses

N(1)-B(1)-C(11)	118.4 (3)	B(1)-N(1)-B(2)	117.8 (3)
N(1)-B(1)-N(3)	117.6 (2)	B(1)-N(1)-C(21)	119.0 (2)
C(11)-B(1)-N(3)	123.9 (3)	B(2)-N(1)-C(21)	123.0 (3)
N(2)-B(2)-C(31)	118.0 (3)	B(2)-N(2)-B(3)	116.8 (2)
N(2)-B(2)-N(1)	115.9 (3)	B(2)-N(2)-C(41)	118.7 (3)
C(31)-B(2)-N(1)	126.0 (3)	B(3)-N(2)-C(41)	124.3 (3)
N(3)-B(3)-C(51)	118.2 (3)	B(3)-N(3)-B(1)	115.6 (3)
N(3)-B(3)-N(2)	117.2 (3)	B(3)-N(3)-C(61)	118.3 (3)
C(51)-B(3)-N(2)	124.4 (3)	B(1)-N(3)-C(61)	125.8 (3)
B(1)-C(11)-C(12)	121.8 (3)	N(2)-C(41)-C(42)	120.4 (3)
B(1)-C(11)-C(16)	118.2 (3)	N(2)-C(41)-C(46)	118.9 (3)
C(12)-C(11)-C(16)	119.1 (3)	C(42)-C(41)-C(46)	119.9 (3)
C(11)-C(12)-C(13)	121.1 (3)	C(41)-C(42)-C(43)	121.0 (3)
C(12)-C(13)-C(14)	119.8 (3)	C(42)-C(43)-C(44)	119.7 (4)
C(13)-C(14)-C(15)	120.3 (3)	C(43)-C(44)-C(45)	120.5 (3)
C(14)-C(15)-C(16)	121.5 (3)	C(44)-C(45)-C(46)	121.0 (3)
C(11)-C(16)-C(15)	118.1 (3)	C(41)-C(46)-C(45)	117.9 (3)
C(11)-C(16)-C(26)	119.9 (2)	C(41)-C(46)-C(36)	119.9 (3)
C(15)-C(16)-C(26)	122.0 (3)	C(45)-C(46)-C(36)	122.1 (3)
N(1)-C(21)-C(22)	121.1 (2)	B(3)-C(51)-C(52)	120.7 (3)
N(1)-C(21)-C(26)	118.7 (2)	B(3)-C(51)-C(56)	118.4 (3)
C(22)-C(21)-C(26)	119.4 (3)	C(52)-C(51)-C(56)	120.3 (3)
C(21)-C(22)-C(23)	121.2 (3)	C(51)-C(52)-C(53)	120.8 (3)
C(22)-C(23)-C(24)	119.7 (3)	C(52)-C(53)-C(54)	119.5 (3)
C(23)-C(24)-C(25)	120.1 (3)	C(53)-C(54)-C(55)	120.9 (3)
C(24)-C(25)-C(26)	121.9 (3)	C(54)-C(55)-C(56)	120.9 (3)
C(21)-C(26)-C(25)	117.6 (3)	C(51)-C(56)-C(55)	117.7 (3)
C(21)-C(26)-C(16)	120.4 (3)	C(51)-C(56)-C(66)	120.0 (3)
C(25)-C(26)-C(16)	122.0 (3)	C(55)-C(56)-C(66)	122.3 (3)
B(2)-C(31)-C(32)	121.3 (3)	N(3)-C(61)-C(62)	120.7 (3)
B(2)-C(31)-C(36)	118.9 (3)	N(3)-C(61)-C(66)	119.7 (3)
C(32)-C(31)-C(36)	119.1 (3)	C(62)-C(61)-C(66)	118.8 (3)
C(31)-C(32)-C(33)	121.3 (3)	C(61)-C(62)-C(63)	121.9 (4)
C(32)-C(33)-C(34)	120.3 (4)	C(62)-C(63)-C(64)	118.6 (4)
C(33)-C(34)-C(35)	119.7 (4)	C(63)-C(64)-C(65)	120.6 (4)
C(34)-C(35)-C(36)	121.3 (4)	C(64)-C(65)-C(66)	122.4 (4)
C(31)-C(36)-C(35)	118.3 (3)	C(61)-C(66)-C(65)	117.6 (3)
C(31)-C(36)-C(46)	119.9 (3)	C(61)-C(66)-C(56)	119.8 (3)
C(35)-C(36)-C(46)	121.8 (3)	C(65)-C(66)-C(56)	122.6 (3)

Discussion

The molecular geometry (Fig. 1) can be visualized as distortion of a planar molecule by H \cdots H contacts on adjacent biphenyl moieties, resulting in the loss of aromaticity in the central borazine ring. Interactions between hydrogen atoms whose numbers (modulus 10) equal 2 cause twisting of the biphenyl groups around the bond between carbon atoms whose numbers (modulus 10) equal 6. In this manner all such H \cdots H contacts are increased to the values shown in Table 6 which also gives H \cdots C distances in these regions of the molecule. Similar means for the relief of overcrowding have been observed in tetrabenzonaphthalene (Herbstein & Schmidt, 1954) and 1,2-bis-(*o,o'*-biphenylene)-diborane (Köster & Willemsen, 1974; Brauer & Krüger, 1974). The phenyl rings remain aromatic, the strain being transferred to the borazine ring which adopts a shallow chair conformation with a mean dihedral angle of 34.8°. The six-membered rings between the borazine and biphenyl fragments are forced into conformations consistent with these features (Fig. 2), *i.e.* dihedral angles equivalent to B(1)–C(11)–C(16)–C(26) reflect the planarity of the benzene ring, those equivalent to C(11)–B(1)–N(1)–C(21) are large because of the chair conformation of the borazine ring and those equivalent to C(11)–C(16)–C(26)–C(21) indicate the relative twist of the two benzene rings of the biphenyl group. The molecule possesses only very approximate C₃ symmetry. Although valency angles generally are consistent with this symmetry, bond lengths reveal severe deviations, particularly in those parts of the biphenyl groups most remote from the centre of the molecule, *e.g.* C(13)–C(14), C(14)–C(15).

Table 6. Important intermolecular contacts (Å)

H(12)–H(62)	2.81 (5)	H(42)–H(52)	3.03 (5)
H(12)–C(62)	2.64 (4)	H(42)–C(52)	2.89 (4)
H(22)–H(32)	2.82 (5)	H(52)–C(42)	2.97 (3)
H(22)–C(32)	2.62 (4)	H(62)–C(12)	2.97 (4)
H(32)–C(22)	2.94 (3)		

B–C lengths average 1.490 Å (r.m.s. deviation from the mean=0.002 Å) compared with 1.52 ± 0.01 Å in *B*-trimethylborazine (Anzenhofer, 1966). N–C bonds average 1.464 Å (r.m.s. deviation=0.007 Å) compared

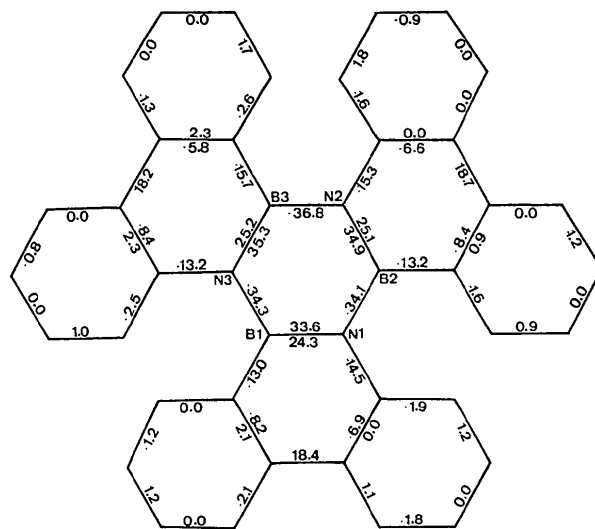


Fig. 2. Torsional angles.

with 1.48 ± 0.03 Å in *N*-trimethylborazine (Coffin & Bauer, 1955). For both B–C and N–C distances, values for tris(biphenyl)borazine are shorter by 0.02–0.03 Å as a result of the difference in bonding radii between *sp*² and *sp*³ hybridized carbon atoms (Bartell & Bonham, 1960). C–C lengths within the benzene rings average 1.387 Å (r.m.s. deviation=0.018 Å) while those between the two halves of the biphenyl groups average 1.464 Å (r.m.s. deviation=0.002 Å). Table 7 shows some geometrical parameters of a collection of substituted borazines. B–N lengths in these compounds range from 1.39 to 1.451 Å. In each compound except hexachloroborazine, B–N lengths were shown or assumed to be equivalent. In hexachloroborazine, two independent investigations showed that two types of B–N bond alternate around the ring. This result has since been disputed by theoretical considerations and by a recalculation of the least-squares refinement (Gopinathan, Whitehead, Coulson, Carruthers & Rollett, 1974) to give a structure in which the borazine ring has equal B–N lengths of 1.424 (1) Å. In tris(biphenyl)borazine B–N lengths show genuine alternation; those bridged by the biphenyl groups average 1.430 Å (r.m.s. deviation=0.013 Å) while the others are considerably

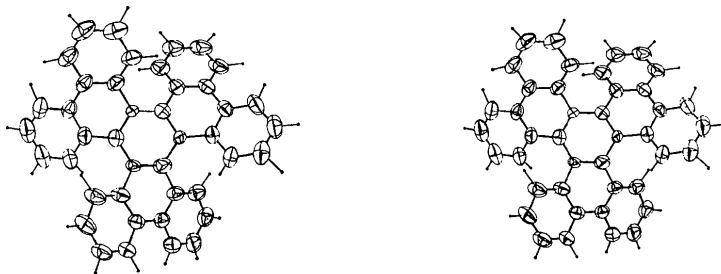


Fig. 1. A stereoscopic view of the TBB molecule.

longer (mean 1.488 Å, r.m.s. deviation = 0.007 Å). The most reasonable explanation of this feature is the large steric interaction between biphenyl groups mentioned previously; van der Waals forces in these areas could be imagined to cause stretching of the B–N bond. In fact, patterns in the H···H and H···C distances in Table 6 can clearly be correlated with the B–N lengths. Contacts between rings 1 and 6 are roughly equal to those between rings 2 and 3 while rings 4 and 5 are more widely separated. In the event that steric repulsions were responsible for the increase in alternate B–N lengths, B(3)–N(2) would then be expected to be less extended than B(1)–N(3) and B(2)–N(1) which should be approximately equivalent. This situation in fact occurs (Table 4).

It would be tempting to draw two conclusions about the structures of borazines from the data in Table 7. First, in all cases except the present work the B–N distance is always shorter than that reported for borazine itself. That this occurs is possibly a consequence of the reduction of the polarity of the B–N bond upon substitution, allowing a greater donation by the nitrogen atom to a multiple-bonding system in the ring. Secondly, as a rule, N–B–N angles are smaller and B–N–B angles are larger than 120°. However, estimated errors in structural parameters are sufficiently large that firm conclusions regarding neither of these trends are justified.

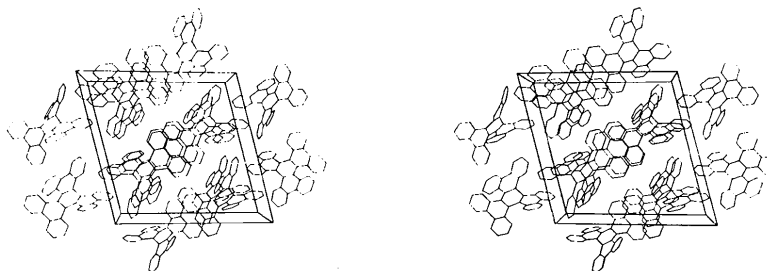
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Table 7. Geometrical parameters of some substituted borazines

	B–N (ring)	B–R	N–R'	N–B–N	B–N–B	Method	Reference
[HNBH] ₃	1.435 ± 0.002	1.26 ± 0.01	1.05 ± 0.01	117.7 ± 1.2	121.1 ± 1.2	e.d.	a
[HNBF] ₃	1.432 ± 0.01	1.361 ± 0.01	1.04 ± 0.02	119 ± 1	121	e.d.	b
[HNBCl] ₃	1.413 ± 0.01	1.76 ± 0.02		119 ± 1	121 ± 1	X-ray	c
	1.41 ± 0.02	1.78 ± 0.03	1.01			e.d.	d
[HNBCH ₃] ₃	1.39 ± 0.02	1.52 ± 0.01		120.9 ± 0.5	119.8 ± 1.0	X-ray	e
[HNBN(CH ₃) ₂] ₃	1.433 ± 0.005	1.429 ± 0.015		116.9 ± 0.6	123.4 ± 0.8	X-ray	f
B ₃ N ₄ H ₇	1.418 ± 0.004	1.498 ± 0.008	1.03 ± 0.02		119.0, 122.8	e.d.	g
[CH ₃ NBH] ₃	1.42 ± 0.02	1.20	1.48 ± 0.03			e.d.	d
[C ₂ H ₅ NBC ₂ H ₅] ₃	1.423 ± 0.015					X-ray	h
[ClNBCl] ₃	1.43 (3), 1.40 (3)	1.76 (3)	1.73 (2)	120 (3)	119 (3)	X-ray	i
	1.398 (8), 1.451 (8)	1.724 (9)	1.749 (8)	118 (1)	122 (1)	X-ray	j
	1.424 (1)						k
[C ₆ H ₄ NBC ₆ H ₄] ₃	1.430, 1.488	1.490	1.464	116.9	116.7	X-ray	l

References: (a) Harshbarger, Lee, Porter & Bauer (1969a). (b) Bauer, Katada & Kimura (1968). (c) Coursen & Hoard (1952). (d) Coffin & Bauer (1955). (e) Anzenhofer (1966). (f) Hess & Reiser (1971). (g) Harshbarger, Lee, Porter & Bauer (1969b). (h) Viswamitra & Vaidya (1965). (i) Mueller (1971). (j) Haasnoot, Verschoor, Romers & Groeneveld (1972). (k) Gopinathan, Whitehead, Coulson, Carruthers & Rollett (1974). (l) This work.

Fig. 3. A stereoscopic view of the cell contents viewed down *b*.

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Structure Cristalline de l'Orthofluorobéryllate $\text{Na}_3\text{Li}(\text{BeF}_4)_2$

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The crystal structure of sodium lithium orthofluoroberyllate, $\text{Na}_3\text{Li}(\text{BeF}_4)_2$, has been determined by the symbolic addition method with data collected on a single-crystal diffractometer (Mo $K\alpha$ radiation). The compound is monoclinic, space group $P2_1/c$ with $a = 6.542$ (2), $b = 9.634$ (2), $c = 9.939$ (2) Å, $\beta = 93.83^\circ$ (1), $Z = 4$. A least-squares refinement was carried out with anisotropic temperature factors. The final R value is 0.06 for 2188 reflexions. The structure consists of rings of fluorine tetrahedra filled with Be(1) and Li cations lying on the (100) plane. The rings contain either eight or four tetrahedra and pack together so as to form a two-dimensional framework. Be(2) tetrahedra are linked to the Li tetrahedra of the eight-membered rings. The two-dimensional frameworks are linked by the sodium polyhedra.

Introduction

L'étude du système NaF–LiF– BeF_2 a mis en évidence l'existence des quatre composés $\text{NaLi}(\text{BeF}_3)_2$, $\text{Na}_2\text{LiBe}_2\text{F}_7$, NaLiBeF_4 et $\text{Na}_3\text{Li}(\text{BeF}_4)_2$. Les trois premiers se sont révélés isotopes respectivement de la diopside $\text{CaMg}(\text{SiO}_3)_2$ (Boucherle, 1973), de l'akermanite (Le Roy, 1970; Brunton, 1972) et de la monticellite (Le Roy, 1970). Quant au dernier, isolé pour la première fois par Jahn (1954), ses caractéristiques cristallographiques n'ont été déterminées que récemment (Pontonnier & Aléonard, 1972).

L'objet du présent travail est la détermination de la structure cristalline de ce composé.

Partie expérimentale

La méthode de préparation des cristaux de $\text{Na}_3\text{Li}(\text{BeF}_4)_2$ a été décrite précédemment (Pontonnier & Aléonard, 1972): se présentant sous forme d'aiguilles épaisses prismatiques, ils ne s'obtiennent qu'au début de la cristallisation de solutions concentrées (portées à environ 60°C) contenant les deux orthofluorobéryllates de lithium et de sodium en quantité équimoléculaire.

Le cristal choisi pour l'étude cristallographique

n'ayant pu être rendu sphérique, avait la forme d'un cylindre de longueur et diamètre égaux à 0,25 mm.

Nous avons redéterminé ses caractéristiques à partir de 15 observations sur le diffractomètre automatique quatre cercles Hilger & Watts du Laboratoire (la radiation utilisée est celle du molybdène $K\alpha$): groupe spatial $P2_1/c$; $a = 6,542 \pm 0,0015$; $b = 9,634 \pm 0,002$; $c = 9,939 \pm 0,002$ Å; $\beta = 93,83 \pm 0,01^\circ$; $Z = 4$. Elles sont légèrement différentes de celles trouvées par L. Pontonnier à l'aide de clichés de chambre de Guinier.

Les intensités des réflexions ont été enregistrées à l'aide du diffractomètre quatre cercles en utilisant la méthode des mesures rapides indiquée par Bassi (1973).

Elles ont été mesurées directement au maximum de la réflexion, après ajustement pour compenser le manque de rigidité de l'ensemble cristal-tête goniométrique et les légères imprécisions pouvant survenir dans la matrice d'orientation. Cet ajustement n'a pas été fait pour les intensités très faibles ou nulles (au-dessous de 20 c.p.s.). La mesure intégrée de 30 réflexions, dans un domaine angulaire θ allant de $6,5$ à 25° , nous a permis de déterminer expérimentalement la loi de variation du rapport de taux de comptage au maximum de la raie sur l'intensité corrigée des facteurs de Lorentz-polarisation. La détermination de cette loi a permis de calculer directement le facteur de structure au carré (F^2) pour toutes les observations, à partir des mesures au sommet.

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