Acta Cryst. (1978). B**34**, 2990–2993

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

V.* Spiro[9*H*-borepino[2,3-*b*:7,6-*b'*]dithiophene-9,2'-[1,3,2]oxazaborolidine]

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(*Received* 5 *October* 1977; *accepted* 28 *January* 1978)

$C_{12}H_{14}BNOS_2$ crystallizes in the monoclinic space group $P2_1/n$, with $a = 8{\cdot}625$ (1), $b = 8{\cdot}969$ (1), $c = 16{\cdot}892$ (2) Å, $\beta = 103{\cdot}03$ (1)° (87 K), $Z = 4$. The structure was refined to $R = 0{\cdot}029$ for 2130 counter reflections. The seven-membered ring is in a boat conformation, the oxazaborolidine ring is a half-chair. The angle between the normals to the planes of the thiophene rings is 48°. The B—N distance is 1·635 (3) Å. The molecules are held together by N—H···O hydrogen bonds.

Introduction

This study is part of an investigation of a series of tricyclic compounds with two thiophene aromatic rings fused to a central seven-membered ring. Our primary interest is in the conformation of the seven-membered ring as a function of the mode of attachment of the side rings. Some compounds of analogous structure also have pharmacological activity, and a knowledge of the structures involved is of significance in understanding such activity.

Although Rettig & Trotter (1973) had reported the structure of *B,B*-diphenyloxazaborolidine, it was not clear whether the present compound actually contained the oxazaborolidine ring (Jeffries & Gronowitz, 1973).

Experimental

Crystals were grown from an ethanol–water mixture as colorless, rectangular needles. Photographs indicated monoclinic symmetry. Systematically absent reflections determine the space group to be $P2_1/n$. Cell dimensions were determined from a set of Cu $K\alpha$ axial reflections measured on a Picker four-circle diffractometer with the crystal at 87 K. The results are given in Table 1 together with other crystallographic data.

Intensities were collected on a Picker automatic diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The crystal, 0·42 × 0·11 × 0·05 mm, was mounted with its longest direction (**b**) about 7° from the instrument φ axis, and cooled to about 87 K with a modified Enraf–Nonius gas-stream device.

Table 1. *Crystal data*

$C_{12}H_{14}BNOS_2$	$M_r = 263{\cdot}1$

Space group $P2_1/n$ (absent reflections: $h0l$ for $h + l$ odd, $0k0$ for k odd)

$a = 8{\cdot}625$ (1) Å	$V = 1273$ Å^3
$b = 8{\cdot}969$ (1)	$D_m = 1{\cdot}40$ g cm^{-3}
$c = 16{\cdot}892$ (2)	$D_x = 1{\cdot}37$
$\beta = 103{\cdot}03$ (1)°	$Z = 4$

The intensities of 2130 unique reflections with $2\theta < 130°$ were measured with the θ–2θ scan method at a 2θ scan speed of 2° min^{-1}, with scan ranges given by $[2\theta(\alpha_1) - 0{\cdot}8°]$–$[2\theta(\alpha_2) + 0{\cdot}8°]$. Stationary background counts were taken for 20 s at each end of the scan.

A monitor reflection was remeasured every 200 reflections, yielding an observed variance (s^2) in intensity of $s^2 = I + (0{\cdot}005I)^2$. This expression was used to assign e.s.d.'s to all observations in conjunction with Lorentz and polarization corrections (Hope, 1971). No absorption correction was made ($\mu = 35{\cdot}6$ cm^{-1}). All reflections were considered observed and used in later refinement.

Solution and refinement

The signs of 184 E's > 1·75 were determined with Long's (1965) sign-determining program. The solution with the highest consistency index led to an E map which was readily interpreted in terms of a reasonable structure, although a few false peaks were present.

From an initial R of 0·28 full-matrix least-squares refinement with isotropic temperature factors reduced

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* Part I: Aurivillius (1974*a*); part II: Aurivillius (1974*b*); part III: Andersson (1975); part IV: Cynkier (1976).

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R to 0·08. At this point all H atoms were added at calculated positions. Further refinement for all atom parameters (isotropic) led to convergence with R = 0·042, R_w = 0·041 for reflections with $I > 3\sigma(I)$. Additional cycles with anisotropic temperature factors for atoms other than H converged with R = 0·030 and R_w = 0·029 for all reflections.* The final atomic parameters are given in Table 2.

Table 2. *Final positional* ($\times 10^4$; *for* H $\times 10^3$) *and hydrogen isotropic thermal parameters*

	x	y	z	B (Å^2)
S(1)	4444·6 (6)	4555·1 (5)	1386·9 (3)	
S(2)	4060·3 (6)	2279·0 (5)	4286·3 (3)	
C(1)	4906 (2)	4971 (2)	2409 (1)	
C(4)	6101 (2)	5445 (2)	1216 (1)	
C(5)	6971 (2)	6047 (2)	1915 (1)	
C(6)	6300 (2)	5776 (2)	2596 (1)	
C(7)	7032 (2)	6255 (2)	3457 (1)	
C(8)	7690 (2)	4946 (2)	4014 (1)	
C(9)	6487 (2)	3871 (2)	4219 (1)	
C(10)	6968 (2)	2861 (2)	4883 (1)	
C(11)	5791 (2)	1942 (2)	4999 (1)	
C(14)	4918 (2)	3681 (2)	3818 (1)	
C(15)	1267 (2)	5331 (2)	3266 (1)	
C(16)	987 (2)	4256 (2)	2558 (1)	
O	2469 (1)	3488 (1)	2637 (1)	
B	3841 (2)	4450 (2)	3018 (1)	
N	2903 (2)	5882 (2)	3286 (1)	
H(4)	632 (2)	542 (2)	69 (1)	2·1 (4)
H(5)	794 (2)	655 (2)	194 (1)	1·9 (4)
H(10)	802 (2)	281 (2)	518 (1)	1·4 (4)
H(11)	581 (2)	122 (2)	539 (1)	2·2 (5)
H(71)	624 (2)	678 (2)	370 (1)	1·3 (4)
H(72)	789 (2)	697 (2)	345 (1)	1·8 (4)
H(81)	836 (2)	537 (2)	457 (1)	2·5 (5)
H(82)	844 (2)	433 (2)	378 (1)	2·5 (5)
H(151)	127 (2)	482 (2)	379 (1)	1·4 (4)
H(152)	51 (2)	618 (2)	319 (1)	1·9 (4)
H(161)	71 (2)	484 (2)	203 (1)	2·2 (5)
H(162)	13 (2)	355 (2)	259 (1)	1·0 (4)
H(1N)	335 (2)	622 (2)	377 (1)	2·1 (5)
H(2N)	286 (2)	667 (2)	293 (1)	2·1 (5)

All calculations were performed on a CDC 7600 computer with programs developed in this laboratory. The function minimized was $S = \sum [\Delta F/\sigma(F_o)]^2$. For S, O, N, C the form factors of Doyle & Turner (1968) and for H the bonded form factor of Stewart, Davidson & Simpson (1965) were used. For S the f' and f'' values were those of Cromer & Liberman (1970).

The very smooth refinement with only isotropic temperature factors is common with low-temperature data. For standard determinations of molecular geometry it appears that refinements with anisotropic temperature factors tend to add expense for which there is little return in the form of added information or increased reliability.

Description and discussion of the structure

A stereoview of the molecule is shown in Fig. 1, which also gives the atomic numbering. The structure contains the five-membered oxazaborolidine ring, spiro to the central seven-membered borepin ring. The central ring with attached thiophene moieties consists of two nearly planar portions, folded along B···C(7). The angle between the normals to the planar thiophene rings is 48·3°. B, C(7) and C(8) are close to the respective neighboring thiophene planes, and C(7) is also only 0·35 Å away from the plane of the S(2) ring. The seven-membered ring can be described as a boat with C(1), C(6), C(8), C(9) defining the bottom, C(7) the bow and B, C(14) the stern. The bottom is very nearly planar, whereas the stern atoms deviate by about 0·1 Å from their mean plane (Table 3). The bottom–bow and bottom–stern dihedral angles are 24 and 57°, respectively.

The oxazaborolidine ring is practically at right angles to the seven-membered ring. The coordination around B is essentially tetrahedral, with the O atom near the mean plane of C(1), C(6), C(9) and C(14), and B–N nearly normal to this plane.

Distances to the least-squares planes through different sections of the molecule are listed in Table 3. Neither thiophene ring shows a significant deviation from planarity. The geometry of the oxazaborolidine ring is in

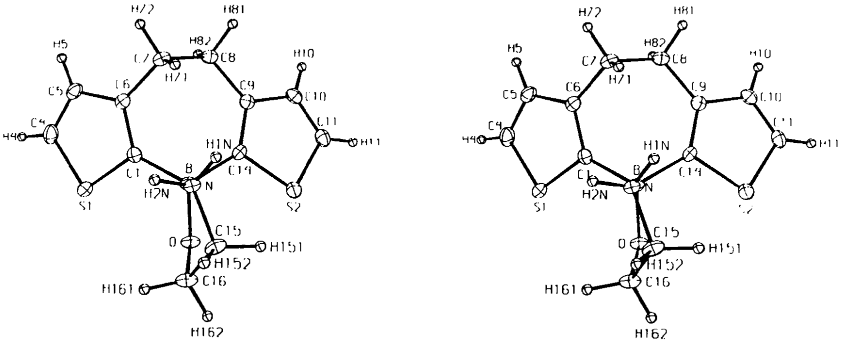

Fig. 1. A stereoscopic view of one molecule of $C_{12}H_{14}BNOS_2$ showing the atom labelling.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33417 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances of atoms* (Å ×10³) *from some least-squares planes*

Plane I: borepin, plane I*a*: bottom, plane I*b*: stern, plane I*c*: bow, planes II and III: thiophenes, plane IV: oxaborolidine (atoms OBN define the plane).

Plane I		Plane I*a*		Plane I*b*		Plane I*c*
C(1)	−94	C(1)	−13	C(1)	−46	C(6)
C(6)	77	C(6)	16	C(9)	70	C(7)
C(7)	816	C(8)	−15	C(14)	−130	C(8)
C(8)	54	C(9)	12	B	105	
C(9)	−77					
C(14)	93					
B	440					

Plane II		Plane III		Plane IV	
C(1)	1	C(14)	−6	O	0
C(6)	−1	C(9)	7	B	0
C(5)	2	C(10)	−5	N	0
C(4)	−2	C(11)	1	C(15)	432
S(1)	2	S(2)	3	C(16)	−190

Angles between planes (°)

Plane I–Plane II	35·0	Plane I*a*–Plane I*c*	57
Plane I–Plane III	13·5	Plane I*b*–Plane I*c*	81
Plane I–Plane IV	89·9	Plane II–Plane III	48·3
Plane I*a*–Plane I*b*	24		

reasonable agreement with that reported by Rettig & Trotter (1973) for *B*,*B*-diphenyloxazaborolidine.

The oxazaborolidine ring has a half-chair conformation, with C(15) and C(16) displaced to opposite sides of the OBN plane by 0·43 and 0·19 Å respectively. The sum of the interior angles (524°) is 23·5° less than the sum of five tetrahedral angles, suggesting a strained ring. Rettig & Trotter (1973) have suggested this strain as the cause for some deviant structural features (shortened C—C and lengthened B—N). The short C—C bond is more realistically interpreted as the result of a failure to allow for thermal-motion effects, which are substantial for both atoms even with our low-temperature data. The B—N distance (1·635 Å) is probably normal for this type of bond, whether in a strained ring or not. A similar B—N distance was found in an azaboraisoquinoline structure (Svensson, 1976). The N—C (1·488), O—B (1·488) and C—O (1·431 Å) bonds are of standard length (see, for example, Sime, Dodge, Zalkin & Templeton, 1971).

The B—C distances (mean: 1·606 Å) are similar to those given by Rettig & Trotter (1973), and somewhat shorter than the mean B—C distances of 1·64 Å found in the tetraphenylborate anion (Sime *et al.*, 1971). There is no significant difference in geometry between the two thiophene moieties. The average S—C(borepin) distance (1·731 Å) is slightly longer than the average S—C (thiophene) distance (1·719 Å).

Bond lengths and angles are given in Tables 4 and 5, torsion angles in Table 6.

Fig. 2 shows a stereoscopic view of the packing. Some intermolecular contacts are given in Table 7. All intermolecular distances apart from O···H are normal for van der Waals interactions.

Table 4. *Bond lengths* (Å) *and angles* (°) *between non-hydrogen atoms in* $C_{12}H_{14}BNOS_2$

S(1)–C(4)	1·717 (2)	C(1)–S(1)–C(4)	93·2 (1)
S(1)–C(1)	1·724 (2)	S(1)–C(4)–C(5)	110·8 (1)
C(4)–C(5)	1·360 (3)	C(4)–C(5)–C(6)	112·9 (2)
C(5)–C(6)	1·419 (3)	C(5)–C(6)–C(1)	113·5 (2)
C(6)–C(1)	1·377 (3)	C(6)–C(1)–S(1)	109·6 (1)
C(6)–C(7)	1·512 (3)	C(14)–S(2)–C(11)	93·2 (1)
C(7)–C(8)	1·531 (3)	S(2)–C(11)–C(10)	110·6 (1)
C(8) C(9)	1·513 (3)	C(11)–C(10)–C(9)	113·9 (2)
C(9)–C(14)	1·381 (3)	C(10)–C(9)–C(14)	112·8 (2)
C(14)–B	1·611 (3)	C(9)–C(8)–C(7)	116·8 (2)
C(1)–B	1·596 (3)	C(8)–C(7)–C(6)	113·0 (2)
C(9)–C(10)	1·428 (3)	C(9)–C(14)–S(2)	109·6 (1)
C(11)–C(10)	1·356 (3)	C(1)–B–C(14)	111·0 (2)
S(2)–C(14)	1·738 (2)	B–C(14)–C(9)	132·5 (2)
S(2)–C(11)	1·720 (2)	C(14)–C(9)–C(8)	127·8 (2)
O–B	1·488 (2)	C(7)–C(6)–C(1)	121·5 (2)
N–B	1·635 (3)	C(6)–C(1)–B	127·3 (2)
O–C(16)	1·431 (2)	O–B–N	100·4 (1)
C(16)–C(15)	1·513 (3)	B–N–C(15)	105·0 (1)
C(15)–N	1·488 (2)	N–C(15)–C(16)	102·2 (2)
		C(15)–C(16)–O	104·7 (2)
		C(16)–O–B	111·6 (1)

Table 5. *Bond lengths* (Å) *and angles* (°) *involving hydrogen atoms*

C(4)–H(4)	0·948 (20)	S(1)–C(4)–H(4)	120·0 (1·2)
		C(5)–C(4)–H(4)	129·1 (1·2)
C(5)–H(5)	0·943 (20)	C(4)–C(5)–H(5)	122·3 (1·1)
		C(6)–C(5)–H(5)	124·7 (1·1)
		C(6)–C(7)–H(71)	111·0 (1·1)
C(7)–H(71)	0·989 (19)	C(8)–C(7)–H(71)	107·5 (1·1)
C(7)–H(72)	0·978 (20)	C(6)–C(7)–H(72)	109·5 (1·1)
		C(8)–C(7)–H(72)	109·0 (1·2)
		C(7)–C(8)–H(81)	108·7 (1·2)
C(8)–H(81)	1·051 (20)	C(9)–C(8)–H(81)	107·1 (1·1)
C(8)–H(82)	0·994 (21)	C(7)–C(8)–H(82)	111·6 (1·2)
		C(9)–C(8)–H(82)	106·3 (1·2)
C(10)–H(10)	0·932 (19)	C(9)–C(10)–H(10)	122·1 (1·2)
		C(11)–C(10)–H(10)	123·9 (1·2)
C(11)–H(11)	0·914 (20)	C(10)–C(11)–H(11)	129·4 (1·3)
		S(2)–C(11)–H(11)	120·0 (1·3)
C(15)–H(151)	0·996 (19)	C(16)–C(15)–H(151)	112·1 (1·1)
		N–C(15)–H(151)	108·8 (1·1)
C(15)–H(152)	0·993 (20)	N–C(15)–H(152)	109·8 (1·2)
		C(16)–C(15)–H(152)	113·7 (1·1)
C(16)–H(161)	1·012 (20)	O–C(16)–H(161)	111·0 (1·2)
		C(15)–C(16)–H(161)	109·3 (1·2)
C(16)–H(162)	0·983 (21)	C(15)–C(16)–H(162)	110·9 (1·1)
		O–C(16)–H(162)	110·5 (1·2)
N–H(1N)	0·878 (21)	C(15)–N–H(1N)	110·8 (1·4)
		B–N–H(1N)	112·9 (1·4)
N–H(2N)	0·927 (21)	C(15)–N–H(2N)	109·8 (1·3)
		B–N–H(2N)	111·4 (1·3)
		H(1N)–N–H(2N)	106·9 (1·9)

Table 6. *Torsion angles* (°)

S(1)–C(1)–B–C(14)	130·8 (1)	C(8)–C(9)–C(14)–B	1·0 (3)	S(2)–C(14)–C(9)–C(8)	178·6 (2)
S(1)–C(1)–B–N	−108·1 (1)	C(9)–C(14)–B–C(1)	28·9 (2)	C(8)–C(9)–C(10)–C(11)	−178·9 (2)
S(1)–C(1)–B–O	3·8 (2)	C(14)–B–C(1)–C(6)	−48·3 (2)	S(2)–C(14)–C(9)–C(10)	1·6 (2)
S(1)–C(1)–C(6)–C(5)	0·1 (2)	C(14)–B–O–C(16)	123·9 (1)	C(5)–C(6)–C(7)–C(8)	−108·8 (2)
C(1)–C(6)–C(7)–C(8)	69·0 (2)	C(14)–B–N–C(15)	−99·9 (1)	S(2)–C(14)–B–N	90·0 (2)
C(6)–C(7)–C(8)–C(9)	−69·0 (2)	B–O–C(16)–C(15)	−30·5 (2)	S(2)–C(14)–B–O	−20·1 (2)
C(7)–C(8)–C(9)–C(14)	18·5 (3)	O–C(16)–C(15)–N	40·4 (2)	S(2)–C(14)–B–C(1)	−148·5 (1)
C(7)–C(8)–C(9)–C(10)	−164·6 (2)	C(16)–C(15)–N–B	−34·9 (2)		

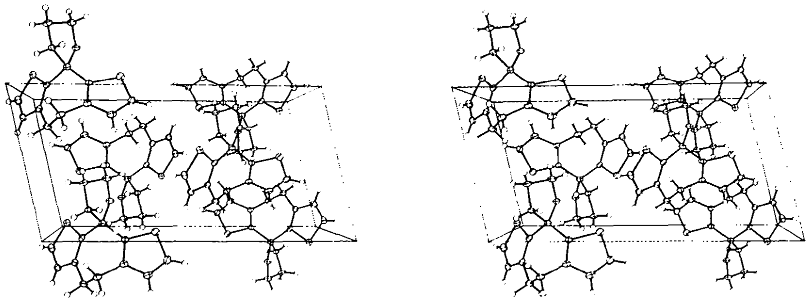

Fig. 2. A stereoscopic view of the crystal packing.

Table 7. *Intermolecular distances* (Å)

C(11)–N″	3·464	C(10)–N″	3·269
C(11)–H(1N″)	2·623	O‴–N	2·788
C(15)–O‴	3·505	O‴–H(2N)	1·880

An N–H···O hydrogen bond of 2·788 Å links molecules related through the twofold screw axis to form continuous spirals. The O···H distance is 1·88 Å. The angle N–H···O is 167°.

We are grateful to Dr A. Jeffries for supplying the material. This study was supported by the National Science Foundation.

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