

Fig. 4. The rearrangement of the nearest *A* neighbours to a subtracted *A* atom (a) connected with the coordination change from eight to seven (b).

sequences will be  $\overline{44,43434}$ ,  $\overline{343343}$  and so on. Thus, the structure of  $Zr_7O_9F_{10}$  is the second member of this series and the  $U_3O_8$  structure the end member, Table 7.

To reduce the anion to cation ratio below  $\frac{8}{3}$  ( $M_3A_8$ ) requires the introduction of six coordination by removing *A* atoms with the sequence 2, which very likely occurs in the oxygen deficient non-stoichiometric  $U_3O_8$  (Sato, Doi, Ishii & Ushikoshi, 1961). This con-

cept will be further discussed in a forthcoming article on the structure of  $Nb_5O_{12}F$ .

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## Aminoboranes. The Crystal Structure of 1, 3-Di-*p*-chlorophenyl-2-triethylcarbinyl-4-ethyl-5,5-diethyl-1,3-diaza-2,4-diborolidine, $C_{26}H_{38}N_2B_2Cl_2$ \*

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The structure of 1,3-di-*p*-chlorophenyl-2-triethylcarbinyl-4-ethyl-5,5-diethyl-1,3-diaza-2,4-diborolidine,  $C_{26}H_{38}N_2B_2Cl_2$ , has been determined by a three-dimensional single-crystal X-ray diffraction study. The crystals are tetragonal, space group  $P4_2/m$ ,  $a = 16.943 \pm 0.008$ ,  $c = 9.599 \pm 0.005$  Å at approximately  $-125^\circ\text{C}$  with four molecules per unit cell. The structure was solved independently by Patterson map analysis and by the direct method. The molecule contains a heterocyclic five-membered ring which is isoelectronic with cyclopentadiene. Bond lengths in this ring are  $N(1)-B(2) = 1.433$  (10),  $B(2)-N(3) = 1.489$  (9),  $N(3)-B(4) = 1.421$  (10),  $B(4)-C(5) = 1.576$  (11) and  $C(5)-N(1) = 1.492$  (10) Å. Crystal symmetry requires the molecule to have  $m(C_s)$  symmetry which is, however, pseudosymmetry due to disorder of one of the ethyl groups. The residual is 0.072 for 1814 observed data.

### Introduction

The heterocyclic compound,  $C_{26}H_{38}N_2B_2Cl_2$ , was synthesized by Casanova & co-workers (Casanova, Kiefer, Kuwada & Boulton, 1965; Casanova, 1966; Casanova & Kiefer, 1969) who suggested the problem to us as one which needed structural proof and as part of a con-

tinuing collaboration to determine fundamental chemical and structural information about aminoboranes. Our preliminary communication (Tsai & Streib, 1968) reported the correct structure to contain a diazadiborolidine ring. We present here the completed study and a more detailed interpretation of our results.

### Experimental

The colorless crystals grew as needles of square cross-section when recrystallized from methanol. Preliminary

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Weissenberg and precession photographs established that the crystals were tetragonal with the  $c$  axis along the needle axis. The systematic extinction of  $00l$  for  $l$  odd restricted the space group to  $P4_2$  or  $P4_2/m$ . The approximate cell dimensions and density ( $1.11 \text{ g.cm}^{-3}$  at room temperature, measured by flotation) indicated four molecules per unit cell. All subsequent data were collected with Mo  $K\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ) at low temperature on a Datex automated General Electric diffractometer with quarter-circle orienter. The improved cell constants were obtained by least-squares fit with diffractometer  $2\theta$  data (Heaton, Gvildys & Mueller, 1964) and were found to be  $a=16.943 \pm 0.008$  and  $c=9.599 \pm 0.005 \text{ \AA}$  at approximately  $-125^\circ\text{C}$ . With four molecules in the unit cell the calculated density is  $1.135 \text{ g.cm}^{-3}$  at approximately  $-125^\circ\text{C}$ .

The intensity data were collected from a  $0.4 \times 0.4 \times 0.5$  mm crystal using the moving crystal, moving counter technique (Furnas, 1966). Data were collected to a maximum  $2\theta_{\text{Mo}}=55^\circ$ , equivalent to the complete copper sphere. The scan rate was  $2^\circ \text{ min}^{-1}$  over an average scan of  $2.4^\circ$ , and 20 sec background counts were collected at both the upper and lower scan limits. A  $0.03\text{mm}$  Zr  $\beta$ -filter was used on all intensity measurements and a second filter made up of Al and Zr foils was used to give an order of magnitude attenuation where needed to keep the strongest reflections below the saturation counting rate. The intensities were calculated using the formula

$$I = Lp q [N - k(b_1 + b_2)], \quad (1)$$

where  $Lp$ =Lorentz and polarization corrections,  $q$ =filter factor,  $N$ =scan count,  $k$ =factor to scale each of the background counts to one-half the scan time, and  $b_1$  and  $b_2$  are the background counts. A 5% error was assigned to the filter factor based on a manual calibration. Counting statistics [ $\sigma(x)=\sqrt{x}$ ] were assumed valid. By standard propagation of errors, the expression used to calculate standard deviations was

$$\sigma(I) = Lp q [0.0025 C^2 + N + k^2(b_1 + b_2)]^{1/2}.$$

where  $C=N-k(b_1+b_2)$ . At 2% probability of  $I$  being significant,  $I \geq 2.33 \sigma(I)$ . On this basis, 1814 of our 3345 unique intensities were considered to be observed. 'Unobserved' data were given the intensity obtained from equation (1) for  $I > 0$ , and were given the intensity = 0 for  $I \leq 0$ . No correction for absorption was made ( $\mu_{\text{Mo}}=2.536 \text{ cm}^{-1}$ ). A Wilson plot (Wilson, 1942) was used to determine the initial values of the overall temperature factor and absolute scale factor.

### Structure determination

For reasons described below, our first computation of the statistical distribution of normalized structure factor magnitudes was inconclusive in determining whether or not the structure was centrosymmetric. We therefore did not attempt to use the direct method initially, but rather proceeded with the interpretation of Patter-

son maps and Patterson superposition maps. From these it was apparent that the benzene rings were perpendicular to the  $ab$  plane and that the dihedral angle between them corresponded to a five-membered ring. From the proposed mechanism for the formation of this compound (Casanova & Kiefer, 1969) it then seemed likely that the structure was a diazadiborolindane. An electron density map computed assuming space group  $P4_2$  with phases based on the above atoms then revealed trial positions for the remaining carbon atoms of the ethyl groups. Several cycles of least-squares refinement in space group  $P4_2/m$  as well as  $P4_2$  indicated the crystal to be centrosymmetric. The residuals,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , were nearly the same for the two space groups; however, the centrosymmetric structure refinement converged better and the resulting coordinates were more chemically reasonable. The terminal atom, C(14), of the B(4) ethyl group, which had been placed in the plane of the heterocyclic ring, was unreasonably close to a benzene ring, at a distance of C(14) . . . C(19) =  $2.13 \text{ \AA}$ , in both space groups. Difference electron density maps computed after all other atoms had refined to a reasonable structure, established all hydrogen atom positions except on the B(4) ethyl group and showed that the C(14) atom should be well out of the plane of the heterocyclic ring. This C(14) position was chemically reasonable and quite acceptable in space group  $P4_2$ , however in  $P4_2/m$  it required a disordered structure. The space group assignment was therefore again in question and we began to reevaluate our normalized structure factor magnitude statistics.

Since the explanation (Karle, 1967) of our difficulty with the  $|E|$  statistics was only obvious in retrospect, we feel it is worth brief mention here. First of all, it is important that the  $\langle |E|^2 \rangle$  be very close to the theoretical value of 1.00, within one or two per cent. Secondly, if a  $K$  curve (Karle & Hauptman, 1953) is used in calculating the normalized structure factor magnitudes, the shape of the  $K$  curve is very important. The futility of simply shifting a poorly shaped curve is illustrated by Fig. 1 and Table 1 (columns I and II) where  $\langle |E| \rangle$  and  $\langle |E^2 - 1| \rangle$  appear to be extrapolating toward values of 0.82 and 0.93 at  $\langle |E|^2 \rangle = 1.0$ , in between the theoretical centrosymmetric and non-centrosymmetric values. In our case the curve needed to be much flatter in the region of small  $\sin \theta / \lambda$ . When the correct curve was used, there was a clear indication that the crystal structure was centrosymmetric (Table 1, column III).

Phase determination for centrosymmetric structures is almost a routine computation if one makes use of a multiple-solution computer program such as that of Long (1965), which generates signs using the Sayre (1952) equation, which we will refer to as  $\sum_2$  (Hauptmann & Karle, 1953). We therefore decided to confirm the disordered structure by the direct method. The program implements the sign determination by using a set of six normalized structure factor magnitudes (Table 2) which are chosen so as to have large magnitudes and a relatively large number of  $\sum_2$  interaction

pairs. For  $P4_2/m$ , two of these must be linearly independent modulo 2 (Hauptman & Karle, 1953) to establish the origin. The sign combination  $+ -$  for these in Table 2 corresponds to the origin in our earlier results. For 240  $|E|$  values with  $h \leq 18$ ,  $k \leq 18$ ,  $l \leq 9$ ,  $(hkl) \neq 0$ , and  $|E| \geq 1.7$ , the solution obtained from the starting set  $+ - + - - +$  was clearly the best choice. It was later found that all 240 signs agreed with those of  $F_{\text{calc}}$  after final refinement. A three-dimensional  $E$  map computed using these signs revealed essentially the same trial structure and clearly showed the *p*-chlorophenyl groups and the two nitrogen atoms. An electron density map then revealed trial positions for all remaining non-hydrogen atoms and nearly the same false position for C(14) in the plane of the heterocyclic

ring and very close to one of the benzene rings, at a distance of C(14) . . . C(19) = 2.15 Å. A second electron density map using signs derived from all non-hydrogen positions except the ethyl group on B(4) again revealed the disordered structure.

Table 2. Starting set for the application of  $\Sigma_2$

<i>h</i>	<i>k</i>	<i>l</i>	$ E $	Sign
6	11	4	4.72	+
3	1	3	3.21	-
5	10	4	3.69	$\pm$
1	5	8	3.05	$\pm$
3	1	5	2.97	$\pm$
4	13	1	2.94	$\pm$

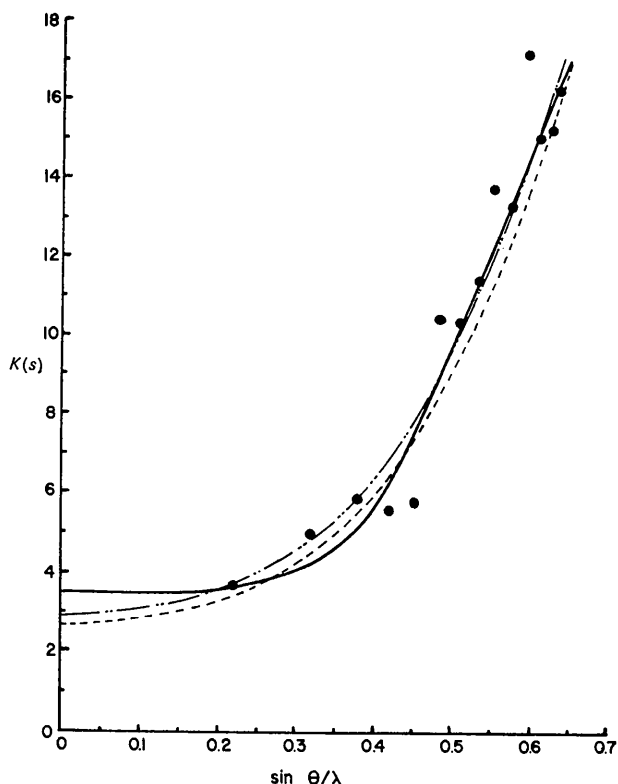


Fig. 1.  $K$  curves used to compute the structure factor magnitudes whose statistics are shown in Table 1.

Only observed data were used (Vand, 1965) in the refinements. The refinement of the structure was completed by: (1) three cycles of isotropic refinement of the non-hydrogen atoms,  $R=0.15$ , (2) two cycles of refinement with anisotropic Cl, isotropic B, N, C, and constant H atoms from our previous results,  $R=0.11$ , (3) two cycles of anisotropic refinement of all non-hydrogen atoms, hydrogen atoms were again included and held constant,  $R=0.092$ , (4) two cycles of anisotropic refinement of all non-hydrogen atoms,  $R=0.081$ , (5) anisotropic refinement of B(4), C(5), C(6), C(7), C(13), and C(14) with isotropic refinement of positional parameters of hydrogen atoms (except hydrogen atoms of the C(13)–C(14) ethyl group),  $R=0.076$ , (6) two cycles of anisotropic refinement of all non-hydrogen atoms. The final residuals were 0.072 for the 1814 observed data and 0.122 for the 3345 complete data. A final difference Fourier synthesis showed no significant electron density. The observed and calculated structure factors are given in Table 3. The function minimized during the least-squares refinements was

$$\sum w(|F_o|^2 - |F_c|^2)^2$$

with  $w=1/\sigma^2(F_o)^2$ . No corrections were included for extinction or anomalous dispersion. For the final cycle of refinement, the maximum coordinate shifts were 0.23 estimated standard deviations and the maximum thermal parameter shifts were 0.65 e. s. d. for the Cl, B, N, C, atoms [except C(13) and C(14)]. The standard deviation of an observation of unit weight was 2.01.

Table 1. Experimental and theoretical distributions and statistical averages of normalized structure factors

	Experimental			Theoretical	
	I*	II*	III*	Centro-symmetric	Non-centro-symmetric
$ E  > 3$	0.8%	0.5%	0.6%	0.3%	0.01%
$ E  > 2$	5.7%	4.9%	4.7%	5.0%	1.8%
$ E  > 1$	33.7%	31.8%	29.2%	32.0%	37.0%
$\langle  E ^2 \rangle$	1.181	1.096	1.011	1.000	1.000
$\langle  E  \rangle$	0.883	0.852	0.798	0.798	0.886
$\langle  E^2 - 1  \rangle$	1.049	0.994	1.000	0.968	0.736

\*  $|E|$  values were scaled using the  $K$  curves shown in Fig. 1, (I) dash dot dot dash (---) curve, (II) dash (---) curve, (III) solid (—) curve.

Computations

All calculations were performed on a CDC 3400/3600 computer. Patterson and electron density maps were

computed using special programs written at this laboratory. The Busing, Martin & Levy (1962) full-matrix least-squares program ORFLS was used for refinement, and their function and error program ORFFE (Busing,

Table 3. Observed and calculated structure factors

Columns contain values of h, 10|Fo| and 10F<sub>c</sub>.

Unobserved data are designated by an asterisk.

Table with multiple columns containing numerical data for h, 10|Fo|, and 10F\_c. The table is organized into several vertical sections, with some columns containing asterisks to denote unobserved data. The data points are arranged in a grid-like pattern across the page.

Continuation of the data table from the previous block, containing numerical values for h, 10|Fo|, and 10F\_c. The layout continues the grid-like structure of the data points.

Final section of the data table, containing numerical values for h, 10|Fo|, and 10F\_c. The table concludes with the final set of data points in the grid.



and the molecular packing in the unit cell is shown in Fig. 4.

Table 4. Fractional atomic coordinates for the Cl, B, N and C atoms

Standard deviations (in parentheses) correspond to the least significant digits.

	x	( $\sigma$ )	y	( $\sigma$ )	z	( $\sigma$ )
N(1)	0.7322	(3)	0.3297	(3)	0.0000	
B(2)	0.7652	(5)	0.2518	(5)	0.0000	
N(3)	0.8524	(3)	0.2625	(3)	0.0000	
B(4)	0.8723	(5)	0.3440	(5)	0.0000	
C(5)	0.7933	(5)	0.3931	(5)	0.0000	
C(6)	0.7845	(4)	0.4485	(5)	0.1250	(12)
C(7)	0.8011	(5)	0.4042	(5)	0.2696	(11)
C(8)	0.7209	(4)	0.1684	(4)	0.0000	
C(9)	0.6294	(4)	0.1743	(4)	0.0000	

Table 4 (cont.)

	x	( $\sigma$ )	y	( $\sigma$ )	z	( $\sigma$ )
C(10)	0.5852	(5)	0.0939	(5)	0.0000	
C(11)	0.7477	(3)	0.1214	(3)	0.1311	(5)
C(12)	0.7286	(4)	0.1620	(4)	0.2693	(6)
C(13)	0.9468	(9)	0.3741	(7)	-0.0489	(47)*
C(14)	0.9985	(10)	0.3896	(11)	0.0863	(23)*
C(15)	0.6504	(4)	0.3511	(4)	0.0000	
C(16)	0.6087	(3)	0.3623	(3)	0.1245	(6)
C(17)	0.5304	(3)	0.3816	(3)	0.1270	(6)
C(18)	0.4926	(4)	0.3904	(4)	0.0000	
C(19)	0.9141	(4)	0.2042	(4)	0.0000	
C(20)	0.9461	(3)	0.1776	(3)	0.1250	(5)
C(21)	1.0104	(3)	0.1272	(3)	0.1249	(5)
C(22)	1.0409	(4)	0.1025	(4)	0.0000	
Cl(23)	1.1240	(1)	0.0400	(1)	0.0000	
Cl(24)	0.3913	(1)	0.4150	(1)	0.0000	

\* The z coordinate refers to 'half-atom', the z coordinate for the other 'half-atom' being of the opposite sign.

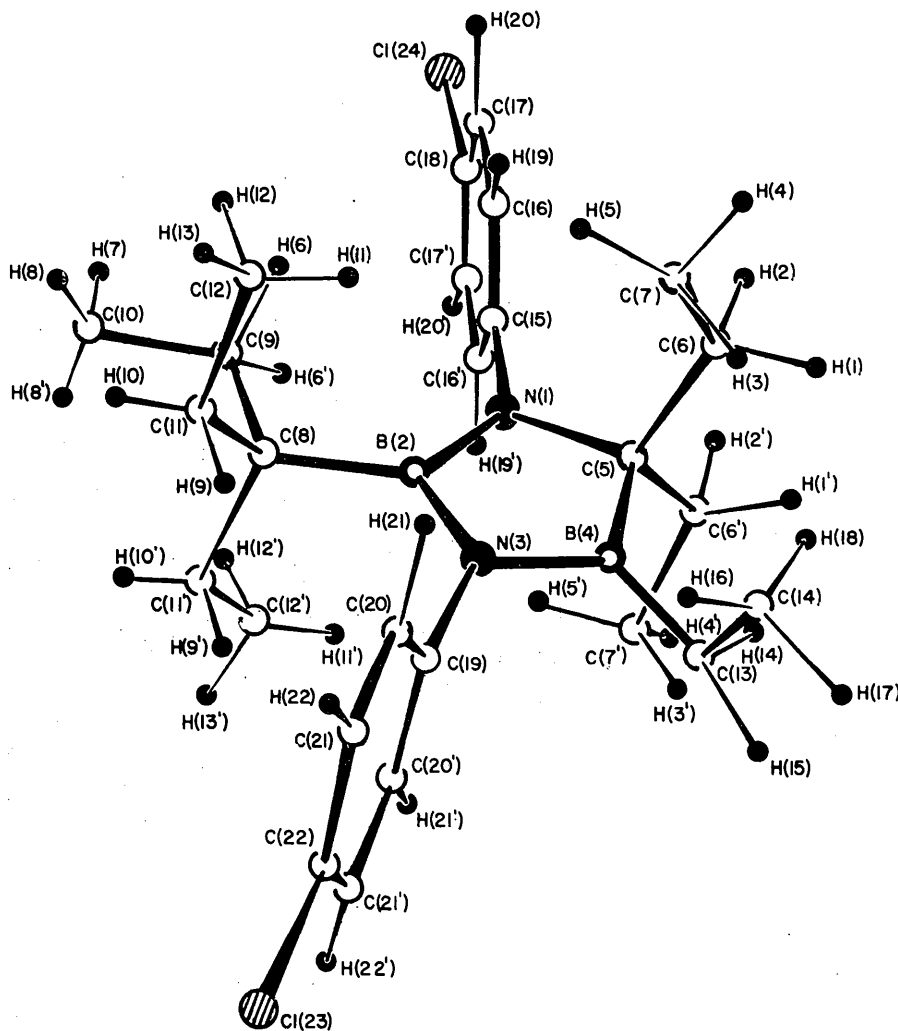


Fig. 2. The molecular structure and the labeling convention used for the designation of atoms.

The shortest intermolecular distances for the different atomic contacts are Cl...C=3.66, C...C=3.72, Cl...H=3.02, C...H=2.72, and H...H=2.49 Å and are all close to normal van der Waals contacts. The average bond lengths for N-C=1.436, B-C=1.588,

Cl-C=1.764, and aromatic C-C=1.383 Å, are all normal. The C(6)-C(7) bond is somewhat long,  $1.603 \pm 0.013$  Å, which we believe is due to correlation with the disordered ethyl group during refinement as was indicated by the correlation matrix of the least-squares

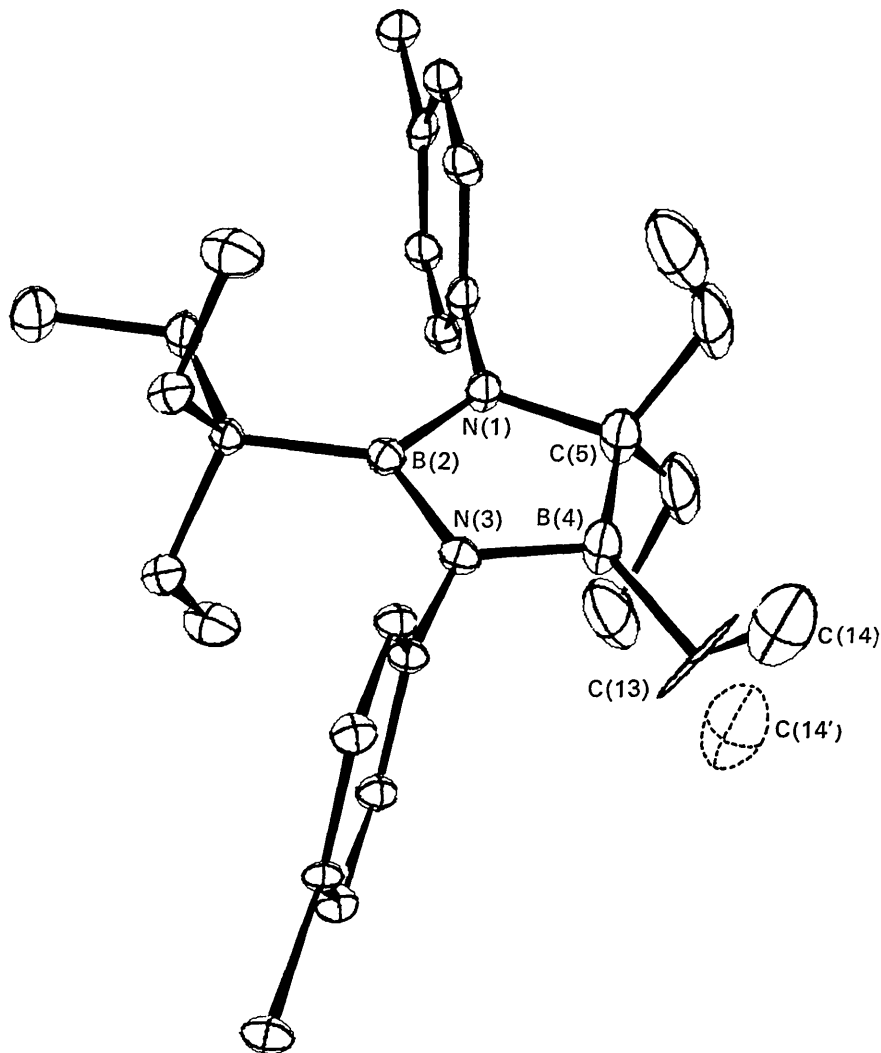


Fig. 3. Plot of the thermal ellipsoids showing also the disordered positions for atom C(14) above and below the plane of the heterocyclic ring. Ellipsoids enclose 25% probability.

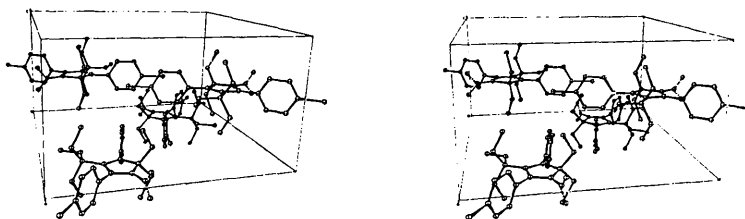


Fig. 4. Stereoscopic view of the unit cell. Hydrogen atoms have been deleted for clarity.

output. The thermal parameters suggest that atom C(13) of the disordered ethyl group is also undergoing large thermal motion primarily in the *c*-axis direction (Table 6 and Fig. 3). In fact our best refinement was obtained when C(13) was also allowed to be disordered during which time it moved to a position 0.47 Å out of

the *ab* plane (Table 4). If the C(6)–C(7) bond and the disordered C(13)–C(14) bond are excluded, the average C–C single bond length is 1.545 Å, which is normal within experimental error. One other discrepancy was noted, this with regard to the *p*-chlorophenyl groups and the nitrogen atoms to which they are bonded. The

Table 5. Fractional atomic coordinates of the hydrogen atoms and the isotropic thermal parameters\* assigned during the final cycle of refinement

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Bonded to
H(1)	0.8259	0.5053	0.1030	5.0 Å <sup>2</sup>	C(6)
H(2)	0.7323	0.4794	0.1290	5.0	C(6)
H(3)	0.8829	0.3766	0.2690	5.0	C(7)
H(4)	0.7923	0.4402	0.3456	5.0	C(7)
H(5)	0.7602	0.3496	0.2793	5.0	C(7)
H(6)	0.6156	0.2039	0.0892	2.0	C(9)
H(7)	0.5363	0.1121	0.0000	2.0	C(10)
H(8)	0.5931	0.0635	0.0895	2.0	C(10)
H(9)	0.8061	0.1163	0.1261	2.0	C(11)
H(10)	0.7214	0.0728	0.1290	2.0	C(11)
H(11)	0.7491	0.2152	0.2715	2.0	C(12)
H(12)	0.6622	0.1637	0.2769	2.0	C(12)
H(13)	0.7450	0.1302	0.3391	2.0	C(12)
H(14)	0.9458	0.4284	−0.0938†	5.0	C(13)
H(15)	0.9791	0.3390	−0.1088†	5.0	C(13)
H(16)	0.9917	0.3333	0.1583†	5.0	C(14)
H(17)	1.0598	0.4008	0.0642†	5.0	C(14)
H(18)	0.9668	0.4374	0.1432†	5.0	C(14)
H(19)	0.6355	0.3515	0.2069	2.0	C(16)
H(20)	0.4973	0.3863	0.2217	2.0	C(17)
H(21)	0.9264	0.1974	0.2232	2.0	C(20)
H(22)	1.0306	0.1100	0.2026	2.0	C(21)

\* The isotropic thermal parameters are in the form  $\exp(-B \sin^2 \theta/\lambda^2)$ .

† The *z* coordinate refers to 'half-atom', the *z* coordinate for the other 'half-atom' being of the opposite sign.

Table 6. Anisotropic thermal parameters\* for the Cl, B, N and C atoms

	$\beta_{11}(\sigma)$ ( $\times 10^4$ )	$\beta_{22}(\sigma)$ ( $\times 10^4$ )	$\beta_{33}(\sigma)$ ( $\times 10^4$ )	$\beta_{12}(\sigma)$ ( $\times 10^4$ )	$\beta_{13}(\sigma)$ ( $\times 10^4$ )	$\beta_{23}(\sigma)$ ( $\times 10^4$ )
N(1)	14 (2)	18 (2)	112 (10)	1 (2)	0	0
B(2)	20 (3)	20 (3)	56 (10)	1 (2)	0	0
N(3)	18 (2)	18 (2)	76 (8)	7 (2)	0	0
B(4)	14 (3)	16 (3)	227 (20)	5 (3)	0	0
C(5)	19 (3)	21 (3)	213 (17)	3 (3)	0	0
C(6)	32 (3)	42 (3)	425 (23)	−9 (2)	−5 (7)	−72 (7)
C(7)	64 (5)	60 (4)	272 (18)	0 (4)	−32 (7)	−64 (7)
C(8)	16 (2)	15 (2)	67 (9)	1 (2)	0	0
C(9)	20 (3)	19 (3)	127 (12)	−1 (2)	0	0
C(10)	23 (3)	31 (4)	202 (17)	0 (3)	0	0
C(11)	23 (2)	25 (2)	68 (7)	3 (2)	1 (3)	8 (3)
C(12)	50 (3)	39 (3)	81 (8)	15 (2)	8 (4)	11 (4)
C(13)†	46 (7)	23 (5)	1239 (176)	21 (5)	235 (31)	125 (24)
C(14)†	52 (8)	61 (9)	305 (39)	−7 (7)	−6 (15)	33 (13)
C(15)	14 (2)	16 (3)	131 (13)	0 (2)	0	0
C(16)	22 (2)	20 (2)	104 (8)	6 (2)	−3 (3)	−6 (3)
C(17)	18 (2)	21 (2)	113 (8)	3 (2)	−2 (3)	−6 (3)
C(18)	11 (2)	19 (3)	144 (13)	2 (2)	0	0
C(19)	14 (2)	19 (3)	56 (9)	4 (2)	0	0
C(20)	18 (2)	22 (2)	46 (6)	1 (1)	0 (3)	−3 (3)
C(21)	20 (2)	23 (2)	35 (6)	1 (1)	−3 (2)	1 (2)
C(22)	9 (2)	17 (2)	48 (8)	4 (2)	0	0
Cl(23)	17 (1)	23 (1)	51 (2)	7 (1)	0	0
Cl(24)	14 (1)	32 (1)	124 (3)	5 (1)	0	0

\* The anisotropic thermal parameters are in the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

† Half-atoms.



Table 7. Bond distances and their standard deviations (in Å)

Bond	Distance	Bond	Distance
B(2)—N(1)	1.433 ± 0.010	C(9)—C(10)	1.555 ± 0.011
B(2)—N(3)	1.489 ± 0.009	C(8)—C(11)	1.557 ± 0.006
N(3)—B(4)	1.421 ± 0.010	C(11)—C(12)	1.529 ± 0.008
C(5)—B(4)	1.576 ± 0.011	C(13)—C(14)	1.588 ± 0.046
N(1)—C(5)	1.492 ± 0.010	C(15)—C(16)	1.401 ± 0.006
C(15)—N(1)	1.433 ± 0.008	C(16)—C(17)	1.367 ± 0.007
C(19)—N(3)	1.438 ± 0.008	C(18)—C(17)	1.385 ± 0.006
B(2)—C(8)	1.600 ± 0.010	C(19)—C(20)	1.392 ± 0.006
B(4)—C(13)	1.440 ± 0.017	C(21)—C(20)	1.384 ± 0.006
	(1.635 ± 0.025)*	C(22)—C(21)	1.371 ± 0.005
C(5)—C(6)	1.531 ± 0.009	C(22)—Cl(23)	1.762 ± 0.006
C(6)—C(7)	1.603 ± 0.013	C(18)—Cl(24)	1.766 ± 0.007
C(8)—C(9)	1.554 ± 0.010	C—H <sub>average</sub>	1.05†

\* Value corrected for thermal motion with the second atom assumed to be riding on the first. Although the riding model is not applicable in general to the correction of the lengths of bonds in rings or chains (Brown, 1968) it is appropriate for terminal groups. We therefore applied this correction to the B(4)—C(13) bond to indicate the approximate correction to this abnormal bond length.

† The C—H bond distances are in the range 0.87–1.21 Å except for C(7)—H(3) = 1.47 Å.

Table 8. Bond angles and their estimated standard deviations (in degrees)

	Angle		Angle
B(2)—N(1)—C(5)	113.1 (0.6)	B(2)—C(8)—C(11)	108.4 (0.4)
B(2)—N(1)—C(15)	127.6 (0.6)	C(9)—C(8)—C(11)	108.9 (0.4)
C(5)—N(1)—C(15)	119.3 (0.6)	C(11)—C(8)—C(11')	107.9 (0.5)
N(1)—B(2)—N(3)	106.0 (0.6)	C(8)—C(9)—C(10)	115.1 (0.6)
N(1)—B(2)—C(8)	129.1 (0.6)	C(8)—C(11)—C(12)	114.2 (0.4)
N(3)—B(2)—C(8)	125.0 (0.6)	B(4)—C(13)—C(14)	106.0 (2.8)
B(2)—N(3)—B(4)	110.7 (0.6)	N(1)—C(15)—C(16)	121.5 (0.3)
B(2)—N(3)—C(19)	129.6 (0.6)	C(16)—C(15)—C(16')	117.1 (0.6)
B(4)—N(3)—C(19)	119.7 (0.6)	C(15)—C(16)—C(17)	122.5 (0.5)
N(3)—B(4)—C(5)	108.2 (0.7)	C(16)—C(17)—C(18)	117.3 (0.5)
N(3)—B(4)—C(13)	123.5 (0.9)	C(17)—C(18)—Cl(24)	118.3 (0.3)
C(5)—B(4)—C(13)	123.9 (0.9)	C(17)—C(18)—C(17')	123.3 (0.7)
B(4)—C(5)—N(1)	102.1 (0.6)	N(3)—C(19)—C(20)	120.4 (0.3)
B(4)—C(5)—C(6)	114.0 (0.5)	C(20)—C(19)—C(20')	119.1 (0.6)
N(1)—C(5)—C(6)	112.0 (0.5)	C(19)—C(20)—C(21)	120.4 (0.5)
C(6)—C(5)—C(6')	103.2 (1.0)	C(20)—C(21)—C(22)	119.0 (0.4)
C(5)—C(6)—C(7)	112.0 (0.6)	C(21)—C(22)—Cl(23)	119.0 (0.3)
B(2)—C(8)—C(9)	114.3 (0.6)	C(21)—C(22)—C(21')	122.0 (0.6)

group associated with N(1) is coplanar as expected, with small random deviations from the mean plane

Table 9. Shortest non-bonded interatomic contacts (in Å)

## (a) Intramolecular contacts

All intramolecular contacts less than 4 Å were calculated. Only the most significant contacts are listed.

Distance		Distance	
C(6)····C(15)	3.05	H(1)····H(1')	1.98
C(9)····C(15)	3.02	H(3')····H(14)	2.18
C(13)····C(19)	2.97	H(3')····H(15)	2.33
C(13)····H(3')	2.37	H(3)····H(16)	2.25
C(15)····H(6)	2.70	H(3)····H(18)	2.13
C(16)····H(6)	2.71	H(5)····H(19)	2.22
C(19)····H(9)	2.65	H(6)····H(12)	2.08
C(20)····H(9)	2.65	H(8)····H(10)	2.21

## (b) Intermolecular contacts

All distances less than 4 Å between the asymmetric unit (I) and neighboring units were calculated. Only the most significant contacts are listed.

Table 9 (cont.)

I	····	II	Distance	I	····	III	Distance
C(16)	····	Cl(24)	3.66	Cl(24)	····	C(18)	3.84
C(17)	····	Cl(24)	3.70	Cl(24)	····	H(2)	3.02
H(19)	····	Cl(24)	3.02	C(18)	····	C(18)	3.72
H(20)	····	Cl(24)	3.06				
C(16)	····	C(17)	3.72				
C(17)	····	C(17)	3.76				
C(16)	····	H(20)	2.72				
C(17)	····	H(20)	2.82				
H(4)	····	H(7)	2.73				
H(2)	····	H(20)	2.49				
H(19)	····	H(20)	2.59				

Molecule	I at	x	y	z
II		1 - y	x	½ - z
III		1 - x	1 - y	z

(Table 10); however, N(3) and its *p*-chlorophenyl group are significantly non-coplanar, N(3) being 0.080 Å from the mean plane and 0.13 Å from the plane defined by the six carbon atoms.

Table 10. *Least-squares planes (referred to tetragonal coordinates) through the phenyl rings and certain out-of-plane distances*

Plane (1) defined by C(15), C(16), C(16'), C(17), C(17'), C(18):  
 $4.089x + 16.442y - 0.000z = 8.440 \pm 0.008$

	Deviation
N(1)	-0.026 Å
C(15)	-0.009
C(16)	0.005
C(16')	0.005
C(17)	0.003
C(17')	0.003
C(18)	-0.007
Cl(24)	-0.016

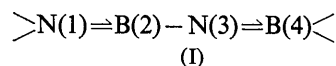
Plane (2) defined by C(19), C(20), C(20'), C(21), C(21'), C(22):  
 $10.549x + 13.258y - 0.000z = 12.341 \pm 0.008$

	Deviation
N(3)	0.130 Å
C(19)	0.009
C(20)	-0.007
C(20')	-0.007
C(21)	0.004
C(21')	0.004
C(22)	-0.002
Cl(23)	0.045

Angle between plane (1) and plane (2) =  $155.5^\circ$ .

At the suggestion of a referee, we have carefully examined the intramolecular non-bonded distances (Table 9) to see if the departure of N(3) from coplanarity with the C(19)–C(22) phenyl ring could be explained by overcrowding within the molecule. Indeed there does seem to be a correlation. As seen in Figs. 2 and 3, the intramolecular environment of the phenyl ring contains two ethyl groups to the left and only a single disordered ethyl group to the right. The nearest carbon-carbon contact, C(13)–C(19) = 2.97 Å, to the right is quite significantly shorter than the corresponding contact, C(8)–C(19) = 3.33 Å, to the left, as one would expect if the phenyl ring were experiencing significantly greater repulsion from the two ethyl groups. If one attributes the displacement of the phenyl ring to a bend in the N(3)–C(19) bond, the plane of the phenyl ring does in fact shift so as to cause a positive deviation for N(3), approximately a  $10^\circ$  bend being required to account for the full 0.13 Å deviation shown in Table 10. A similar situation exists for N(1) relative to the C(15)–C(18) phenyl ring. The crowding is much less severe and the displacement is correspondingly small, but again it is in the right direction. We do not feel it establishes an error in the N(3) position, for two reasons. First, the standard deviations for the positional parameters for N(3) are very small (Table 4), and secondly, the B–N bond distances that can be compared agree very well. Our N(1)–B(2) and N(3)–B(4) distances of 1.43 and 1.42 Å agree with each other and with the average distances of 1.44 in borazine (Bauer, 1938), 1.42 in trimethylborazine (Coffin & Bauer, 1955), and 1.42 triazaboradecalin (Bullen & Clark, 1967). To the best of our knowledge this work is the

first determination of a B(2)–N(3) bond in a compound of type (I)



The B–N bond distances are intermediate between the assumed values of 1.58 Å for a single bond (Lipscomb & Lewin, 1964) and 1.35 Å for a double bond (Watanabe, Ito & Kubo, 1960; Cartmell & Fowles, 1961), indicating the presence of resonance and delocalized  $\pi$ -bonding among the tricoordinate boron and nitrogen atoms. The bond distances predicted from simple Hückel molecular orbital calculations are given in Table 11. The Hückel procedure for  $\pi$ -systems that we used is described in standard texts (*e.g.* Daudel, Lefebvre & Moser, 1959; Streitwieser, 1961). The calculations were carried out using the following approximations for the boron and nitrogen diagonal Coulomb integrals,  $\alpha$ , and off-diagonal resonance integrals,  $\beta$ , in terms of the corresponding integrals for carbon:

$$\begin{aligned} \alpha_B &= \alpha_C - h\beta_{CC} \\ \alpha_N &= \alpha_C + h\beta_{CC} \\ \beta_{BN} &= k\beta_{CC} \end{aligned}$$

The values  $h=1$  (Roothaan & Mulliken, 1948) and  $k=0.87$  (Watanabe *et al.*, 1960) were used. The B–N bond distances were obtained from the mobile bond order (Roberts, 1962) using the expression,

$$d_{P_{ij}} = 1.58 - 0.28 P_{ij} \quad (2)$$

where  $d_{P_{ij}}$  is the bond distance of a bond with  $P_{ij}$  bond order. This expression was obtained by assuming a linear dependence of the form  $d_{P_{ij}} = s - cP_{ij}$ , where  $s$  is the 'single bond' distance. The constant,  $c=0.28$ , was evaluated from the observed bond length and our calculated  $P_{ij}=0.508$  for borazine. Although not quantitative, two different B–N bond lengths are clearly indicated for the heterocyclic ring. If the  $\beta$ 's are adjusted accordingly (Streitwieser, 1961),

$$\begin{aligned} \beta_{B(2)-N(1)} &= \beta_{B(4)-N(3)} \\ \beta_{B(2)-N(3)} &= 0.890 \beta_{B(2)-N(1)}, \end{aligned} \quad (3)$$

the results shown in Table 12 and Fig. 5 are obtained. A better straight line fit is seen to be

$$d_{P_{ij}} = 1.58 - 0.26 P_{ij} \quad (4)$$

giving predicted values which are within approximately  $\pm 0.02$  Å of the observed data. The predicted B–N 'double bond' length is then a somewhat shorter 1.32 Å.

Table 11. *Results of molecular orbital calculations*

Bond	Bond order $P_{ij}$	Predicted bond length (equation 2)
N(1)–B(2)	0.576	1.42 Å
B(2)–N(3)	0.451	1.45
N(3)–B(4)	0.576	1.42

Table 12. Bond lengths and bond orders of B-N bonds

Compound	Bond order $P_{ij}$	Predicted bond length (equation 4)	Observed bond length
$C_{26}H_{38}N_2B_2Cl_2$	0.588*	1.43 Å	1.433 Å
$C_{26}H_{38}N_2B_2Cl_2$	0.419*	1.47	1.489
$C_{26}H_{38}N_2B_2Cl_2$	0.588*	1.43	1.421
$B_3N_3H_6$	0.508†	1.45	1.44§
$B_3N_3(NCH_3)_3$	0.532‡	1.44	1.42

\* This work, using  $\beta$ 's modified according to equation (3).

† This work. Perkins & Wall (1966) calculate 0.509 using SCMO.

‡ Perkins & Wall (1966).

§ Bauer (1938).

|| Coffin & Bauer (1955).

If we take the B(2)-N(3) length of 1.489 Å to be significantly shorter than a single bond, then a substantial degree of resonance stabilization is indicated. This could partially account for the unusual thermal stability of the compound (Casanova, 1969). In this connection it is of interest to estimate the delocalization energy. There are two obvious cases to consider, the one relative to unshared electrons on the nitrogen atoms, and the other relative to isolated double bonds analogous to the situation in 1,3-butadiene. The energy of four electrons in the extended molecular orbitals would be

$$E_{\pi} = 4\alpha_C + 2\{[(h/k)^2 + 0.422]^{1/2} + [(h/k)^2 + 2.370]^{1/2}\}k\beta_{CC},$$

the energy of four electrons localized on the nitrogen atoms of two B-N bonds would be

$$E_{\pi}^N = 4\alpha_C + 4h\beta_{CC},$$

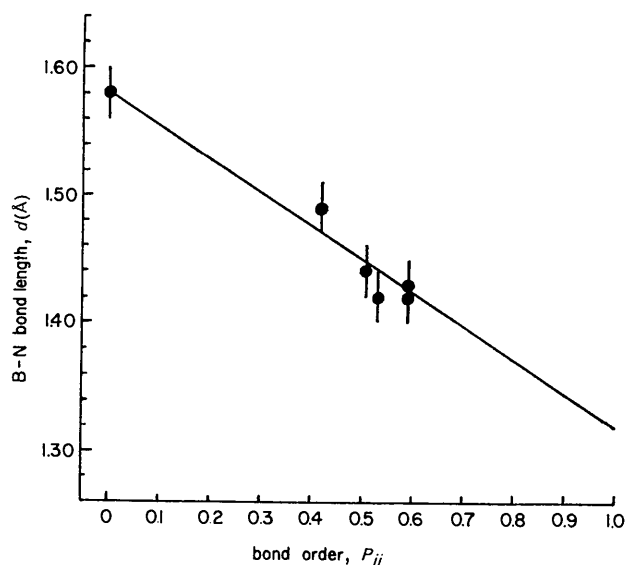


Fig. 5.  $\pi$ -bond order vs. observed B-N bond lengths. Solid line represents the values predicted by equation (4).

and the energy of four electrons localized on two B=N bonds would be

$$E_{\pi}^{B=N} = 4\alpha_C + 4[(h/k)^2 + 1]^{1/2} k\beta_{CC}.$$

For  $h = 1.0$ , and  $k = 0.87$ , the delocalization energy is then either

$$DE_{\pi}(I) = E_{\pi} - E_{\pi}^N = 1.64 \beta_{CC}$$

or

$$DE_{\pi}(II) = E_{\pi} - E_{\pi}^{B=N} = 0.34 \beta_{CC}.$$

The latter is to be compared with  $DE_{\pi} = 0.36\beta_{CC}$  for 1,3-butadiene (Streitwieser, 1961). While calculations such as these are undoubtedly oversimplified, they do indicate the existence of delocalization energy for the B-N system depicted by (I). Finally, since attempts to synthesize simple non-cyclic molecules of type (I) generally produce polymeric material (Niedenzu & Dawson, 1965), we feel the 1,3-diaza-2,4-diborolidine derivatives will play an important role in the study of conjugated aminoboranes.

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## The Crystal Structure and Absolute Configuration of (+)-Methyl *p*-Tolyl Sulfoxide

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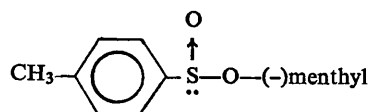
The crystal structure of (+)-methyl *p*-tolyl sulfoxide has been solved by the heavy-atom method and refined by Fourier and least-squares techniques. The absolute configuration has been determined by the anomalous phase displacement technique with the sulfur atom acting as the anomalous scatterer. The space group is  $P2_12_12_1$  with four molecules per unit cell of dimensions  $a = 5.826$  (6),  $b = 8.621$  (8) and  $c = 16.435$  (3) Å. Three-dimensional data (Cu  $K\alpha$ ) were collected with a Picker automatic diffractometer. The final  $R$  indices obtained for the two configurations are 0.034 and 0.044 respectively, for 832 observed reflections. In the notation of Cahn, Ingold & Prelog the correct absolute configuration at sulfur is  $R$ ; the same assignment had been made earlier on the basis of chemical evidence.

### Introduction

One of the most fruitful approaches to the elucidation of a specific reaction mechanism lies in the study of the reaction stereochemistry which in turn may yield clues concerning the geometry of the transition state. In general, knowledge of the dynamic stereochemistry of carbon centers has played a key role in the evolution of our present detailed picture of the reaction mechanisms of such centers. The importance of sulfur as a reaction center in biological processes is well documented; however, relative to the corresponding situation for carbon centers, fundamental mechanistic studies of sulfur centers are rare. The work reported here is part of an effort to rigorously settle the question of absolute and relative configuration for a number of optically active compounds with asymmetric sulfur centers.

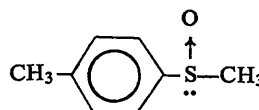
At the time this study was started the conversion of (-)-*p*-tolyl (-)-menthyl sulfinate (I) to (+)-methyl *p*-tolyl sulfoxide (II) by treatment with methyl Grignard reagent was thought to proceed *via* inversion of configuration, based on optical rotatory dispersion and

circular dichroism studies by Mislow, Green, Lauer, Melillo, Simmons & Ternay (1965).



m.p. 105-106°  
 $[\alpha]_D = -198^\circ$  (acetone)

(I)



m.p. 73-74.5°  
 $[\alpha]_D = +146^\circ$  (acetone)

(II)