LITERATUR

1. Sonesson A.: Acta Chem. Scand. *12*, 165, 1937 (1958).
2. Kolat R. S., Powell J. E.: Inorg. Chem. *1*, 193 (1962).
3. Veselý F.: diese Zeitschrift *28*, 444 (1963).
4. Veselý F.: *Dissertation*. Technische Hochschule für Chemie, Prag 1962.
5. Veselý F., Petrů F., Mader K.: Chem. zvesti *20*, 792 (1966).

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CHEMISTRY OF BORANES. XXIV.*
THE CRYSTAL STRUCTURE OF $B_9H_{12}OCH_3S(CH_3)_2$

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The objective of this study was to determine the structure of methoxy-6-dimethylsulphido-dodecahydrononaborane*** by X-ray analysis and to specify the position of the methoxyl group with respect to the boron skeleton.

EXPERIMENTAL AND RESULTS

Colourless, transparent, cylindrical crystals (diameter 0·2 mm, length 0·5 mm) were measured in a Weissenberg goniometer (Nonius, Niederlandische Roentgenapparatenfabrik Evershed Enraf - Delft - Holland). As a source of unfiltered copper radiation Mikrometa 2 (Chirana, Czechoslovakia) was employed. From the rotational, oscillation and Weissenberg photographs, taken in the directions of the three crystallographic axes, the crystals have been found to be monoclinic and have the following lattice constants: $a = 12{\cdot}94$ Å, $b = 9{\cdot}10$ Å, $c = 11{\cdot}40$ Å, $\beta = 97{\cdot}80°$. From the systematic absence of reflexions of the types $h\,0\,l$ for $l = 2n + 1$ and $0\,k\,0$ for $k = 2n + 1$ the space group has been determined as $P2_1/c$. The calculated density $d_{\text{calc}} = 1{\cdot}014$ g cm^{-3}, the density determined experimentally by the method of heavy liquids (a mixture of bromoform and hexane) $d_{\text{exp}} = 1{\cdot}015$ g cm^{-3}, which corresponds to four molecules in a unit cell.

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** The greater part of this work was performed at the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague - Řež.

*** Monocrystals of this compound were prepared by J. Plešek and B. Štíbr, Department of the Chemistry of Boron, Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague - Řež.

By photographing on a multiple film we have obtained layers hKl for $0 < K < 4$ and Hkl for $0 < H < 6$. The intensities were evaluated visually by comparison with a standard intensity scale, obtained with reflexions of the same crystal. The linear absorption coefficient of the studied compound was 17·18 cm^{-1}. In view of the small size of the crystals the correction for absorption could be neglected. After correction with Lorenz and polarization factors the intensities were recalculated for one scale. In this way 960 independent structure factors have been obtained.

Analysis of the three-dimensional Patterson function revealed the position of the sulphur atom, which was then employed to calculate the three-dimensional Fourier maps of electron densities. From these maps it was possible to determine the orientation of the molecules, the position of the oxygen atom and of the two carbon atoms bound to sulphur. By repeating the calculations we have successively determined the positions of all the atoms of boron and of the methoxyl carbon. Thus we have obtained the complete configuration of the molecule $B_9H_{12}OCH_3S(CH_3)$ except for the hydrogen atoms. The calculations were performed using the computer Gier (Regnecentralen, Copenhagen, Denmark) at Řež.

The coordinates of the individual atoms were refined by the least square method. First we used the programme for isotropic refinement of the structure of monoclinic centrosymmetrical crystals[1] for a computer NE 503 (National Elliott, Great Britain). Further, anisotropic refinement was performed by the ORFLS programme according to Busing, Martin and Levy[2], with a complete matrix of normal equations using a computer IMB 7040. After these refinements the factor $R = \Sigma|Fo - kF_c|/\Sigma|Fo|$ (where the scale factor k was also refined) decreased to 13·7%. When the set of reflexions was enlarged by another 102 very weak reflexions (not evaluated photographically), for which $F_{o\min}/2$ was substituted, the factor R reached a value of 14·1%.

The resulting values of the coordinates and their standard deviations are listed in Table I, the coefficients from the expression for the anisotropic temperature factor $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$ are given in Table II.

TABLE I

Fractional Coordinates of the Atoms in the Molecule $B_9H_{12}OCH_3S(CH_3)_2$

Atom	x	y	z
S	0·164 ± 0·0004	0·185 ± 0·001	0·406 ± 0·0003
O	0·336 ± 0·001	0·512 ± 0·001	0·603 ± 0·001
C 1	0·082 ± 0·001	0·161 ± 0·002	0·271 ± 0·002
C 2	0·274 ± 0·001	0·276 ± 0·002	0·356 ± 0·002
C 3	0·444 ± 0·001	0·490 ± 0·002	0·665 ± 0·002
B 1	0·302 ± 0·002	0·827 ± 0·002	0·639 ± 0·002
B 2	0·202 ± 0·001	0·940 ± 0·002	0·580 ± 0·002
B 3	0·183 ± 0·001	0·747 ± 0·002	0·594 ± 0·002
B 4	0·301 ± 0·001	0·658 ± 0·003	0·571 ± 0·002
B 5	0·333 ± 0·001	0·976 ± 0·002	0·559 ± 0·001
B 6	0·222 ± 0·002	0·990 ± 0·002	0·436 ± 0·002
B 7	0·128 ± 0·002	0·844 ± 0·002	0·470 ± 0·002
B 8	0·178 ± 0·001	0·660 ± 0·002	0·459 ± 0·002
B 9	0·402 ± 0·002	0·803 ± 0·002	0·550 ± 0·002

TABLE II

Anisotropic Temperature Factors of the Individual Atoms and their Standard Deviations ($\beta \cdot 10^4$)

Atom	11	22	33	12	13	13
S	88 ± 3	182 ± 7	122 ± 5	21 ± 5	15 ± 3	6 ± 5
O	92 ± 11	183 ± 19	162 ± 13	12 ± 12	1 ± 9	11 ± 14
C 1	102 ± 17	381 ± 47	177 ± 22	−27 ± 23	−62 ± 16	124 ± 27
C 2	58 ± 14	232 ± 33	201 ± 24	−2 ± 16	38 ± 14	−16 ± 22
C 3	72 ± 16	264 ± 35	210 ± 24	47 ± 19	−45 ± 16	46 ± 24
B 1	101 ± 20	200 ± 37	136 ± 24	−6 ± 23	28 ± 17	−82 ± 26
B 2	70 ± 16	169 ± 32	99 ± 19	22 ± 18	−16 ± 13	9 ± 19
B 3	89 ± 19	281 ± 40	76 ± 18	25 ± 22	4 ± 14	34 ± 21
B 4	54 ± 16	194 ± 36	118 ± 21	−20 ± 19	−8 ± 13	37 ± 22
B 5	28 ± 13	174 ± 30	111 ± 18	25 ± 16	0 ± 12	22 ± 19
B 6	79 ± 17	167 ± 33	134 ± 23	−43 ± 20	4 ± 16	−16 ± 22
B 7	101 ± 18	165 ± 36	150 ± 23	35 ± 22	15 ± 17	−15 ± 23
B 8	40 ± 15	241 ± 48	140 ± 23	−79 ± 22	9 ± 15	−47 ± 27
B 9	104 ± 18	161 ± 31	94 ± 18	−6 ± 20	7 ± 14	−2 ± 19

We have also attempted to determine the positions of the hydrogen atoms by means of the difference Fourier synthesis. However, only some of the hydrogen atoms have thus been located, *viz.* the two hydrogens forming hydrogen bonds between atoms B 7 and B 8 and between B 5 and B 9, and the terminal hydrogens H 5, H 7, H 8 and H 9. The numbering of the hydrogens is identical with the numbering of the boron atoms to which these hydrogens are bound. The non-refined coordinates of the hydrogen atoms are listed in Table III.

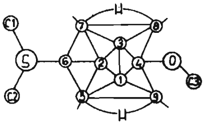

FIG. 1

Projection of the Determined Structure

TABLE III

Coordinates of the Hydrogen Atoms Obtained by Differential Synthesis

Atom	x	y	z
H 5,9	0·405	0·900	0·526
H 7,8	0·138	0·750	0·400
H 5	0·383	0·046	0·845
H 7	0·046	0·845	0·438
H 8	0·231	0·630	0·404
H 9	0·424	0·733	0·470

The calculated bond lengths and bond angles in the molecule $B_9H_{12}OCH_3S(CH_3)_2$ are in a reasonably good agreement with those determined for structurally similar derivatives of higher boron hydrides. The differences between some interatomic distances (*e.g.* between B 5—B 9 and B 7—B 8) may be caused by the rather heavy methoxy group bound to B 4. Since the skeleton LB_9H_{12} (where L is a ligand on B 6) is not so rigid as, *e.g.*, the decaborane skeleton, the atoms

TABLE IV

Bond Lengths and Angles

Atoms	$B_9H_{12}OCH_3S(CH_3)_2$	Average	$B_9H_{13}(CH_3CN)$ (ref.[4])	$B_{10}H_{12}(S(CH_3)_2)_2$ (ref.[3])
		Bond lengths, Å		
S—C 1	$1{\cdot}78_7$	1·79	—	1·82
S—C 2	$1{\cdot}80_5$			
S—B 6	$1{\cdot}93_9$	—	—	1·92
O—C 3	$1{\cdot}49_1$	—	—	
O—B 4	$1{\cdot}43_5$	·	—	
B 1—B 2	$1{\cdot}71_7$	1·75	1·77	1·73
B 2—B 3	$1{\cdot}78_4$			
B 1—B 3	$1{\cdot}71_8$		1·83	1·82
B 1—B 4	$1{\cdot}72_2$	1·75	1·76	1·77
B 3—B 4	$1{\cdot}77_9$			
B 1—B 5	$1{\cdot}71_2$	1·71	1·72	1·78
B 3—B 7	$1{\cdot}71_7$			
B 1—B 9	$1{\cdot}76_3$	1·74	1·72	1·78
B 3—B 8	$1{\cdot}72_4$			
B 2—B 5	$1{\cdot}77_4$	1·74	1·75	1·74
B 2—B 7	$1{\cdot}71_4$			
B 2—B 6	$1{\cdot}75_6$	-	1·73	1·74
B 4—B 8	$1{\cdot}90_0$	1·90	1·87	—
B 4—B 9	$1{\cdot}89_5$			
B 5—B 9	$1{\cdot}82_0$	1·81	1·85	1·91
B 7—B 8	$1{\cdot}80_6$			
B 5—B 6	$1{\cdot}87_0$	$1{\cdot}87_5$	1·87	1·86
B 6—B 7	$1{\cdot}88_0$			
B 5—H 5	0·96	—	1·17	1·13
B 7—H 7	1·07	—	1·17	1·15
B 8—H 8	1·03	—	1·02	—
B 9—H 9	1·18	—	1·08	—
B 5—H 5,9	1·26	—	1·21	1·15
B 9—H 5,9	0·93	—	1·35	1·17
B 7—H 7,8	1·19	—	1·20	1·19
B 8—H 7,8	1·14	—	1·35	1·19

TABLE IV
(*Continued*)

Atoms	$B_9H_{12}OCH_3S(CH_3)_2$	$B_9H_{13}(CH_3CN)$ (ref.[4])	$B_{10}H_{12}(S(CH_3)_2)_2$ (ref.[3])
		Angles[a]	
C 1—S—C 2	101°18′	—	104°02′ 100°41′
C 1—S—B 6	102°22′	—	102°16′
C 2—S—B 6	100°00′	—	101°46′
B 8—B 4—O	112°43′	—	—
B 9—B 4—O	118°32′	—	—
B 4—O—C 3	114°28′	—	—
O—C 3—B 4	31°32′	—	—
C 3—B 4—O	33°59′	—	—

[a] The bond angles between the boron atoms in the borane skeleton correspond to an icosahedron; they range from 58 to 66°.

B 8 and B 9, as well as other atoms, can occupy positions somewhat different from those in the non-substituted molecule. The bond lengths and angles are given in Table IV together with the corresponding values for the molecules $B_{10}H_{12}[S(CH_3)_2]_2$ (ref.[3]) and $B_9H_{13}CH_3CN$ (ref.[4]).

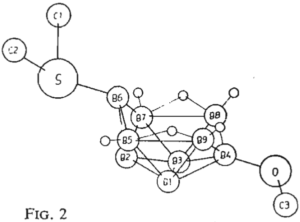

FIG. 2

A Perspective View of the Molecule $B_9H_{12}OCH_3S(CH_3)_2$

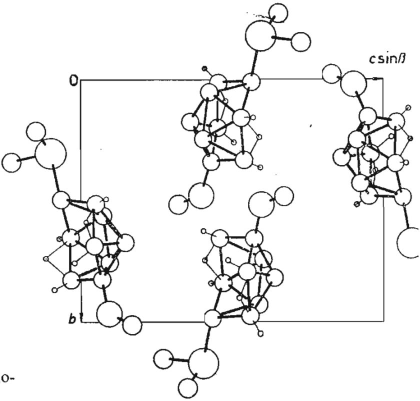

FIG. 3

Arrangement of the Molecules in a Monoclinic Unit Cell

DISCUSSION

Methoxy-6-dimethylsulphidododecahydrononaborane was produced by solvolysis of 5-Br-6,9-$B_{10}H_{11}[S(CH_3)_2]_2$ with methanol. The same product was obtained by methanolysis of 8-Br-6-$S(CH_3)_2B_9H_{12}$. It has been assumed[5] that alkoxyl replaces the halogen, so that it can be attached to the molecule at position 5 (low probability) or position 8 (Fig. 1).

Determination of the structure of $B_9H_{12}OCH_3S(CH_3)_2$ by X-ray analysis has refuted either assumption. The methoxy group has proved to be bound to B 4.* This result is in full accordance with the study by other authors[6], who found that methanolysis of 2-Br-6,9-$B_{10}H_{11}[S(CH_3)_2]_2$ and of the optically active (1)5-Br-6,9-$B_{10}H_{11}[S(CH_3)_2]_2$ led in either case to the inactive $B_9H_{12}OCH_3S(CH_3)_2$.

In the molecule investigated the boron atoms form a skeleton, which, like in most higher hydrides of boron, represents an icosahedral fragment. The dimethylsulphide group, is bound to the boron atom in position 6, the oxygen of the methoxyl to B 4 the bond length being $1{\cdot}43_5$ Å. The bond length $O-C_3$ in the methoxy group has been found to be $1{\cdot}49_1$ Å. As can be seen from Fig. 2, the carbon atom of this group reduces the overall symmetry of the molecule. Why this carbon does not lie in the plane of atoms B 6, B 2, B 4 and O has not been revealed by the X-ray analysis and to find some chemical reason for this anomaly does not seem possible either. The angles B 4—O—C 3, O—C 3—B 4 and C 3—B 4—O are 114°28′, 31°32′ and 33°59, respectively. It can be assumed that if the CH_3 group rotates freely these angles do not change. The arrangement of the molecules in a monoclinic elementary cell is illustrated in Fig. 3.

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REFERENCES

1. Očenášková D.: Českoslov. čas. fys. *17*, 280 (1967).
2. Busing W. R., Martin K. O., Levy H. A.: ORFLS, A Fortran Crystallographic Least-Squares Program, Oak Ridge National Laboratory, Oak Ridge, Tennesee 1962.
3. Sands D. E., Zalkin A.: Acta Cryst. *15*, 410 (1962).
4. Wang F. E., Simpson P. G., Lipscomb W. N.: J. Chem. Phys. *35*, 1335 (1961).
5. Štíbr B., Plešek J., Heřmánek S.: This Journal *34*, 3241 (1969).
6. Plešek J., Heřmánek S., Štíbr B.: This Journal *35*, 344 (1970).

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* For the system of numbering of the borane skeleton see part XVII, This Journal *34*, 3244 (1969).