
**THE CRYSTAL AND ELECTRON STRUCTURE
OF 3-BENZYL BENZOTHAZOLIUM BROMIDE**

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3-benzylbenzothiazolium bromide forms colourless needle-like crystals of monoclinic system, space group $P2_1/c$, with cell parameters $a = 8.315(6)$, $b = 12.323(9)$, $c = 13.140(11) \cdot 10^{-10}$ m, $\beta = 103.79(6)^\circ$, and $Z = 4$. The phase problem was solved by heavy atom method and structure was refined by full matrix least-squares method with anisotropic thermal parameters to final $R = 0.105$ and $wR = 0.113$. The crystal structure is formed by monomer non-centrosymmetric units, among them weak non-bonding interactions of type Br...S, Br...N and also intermolecular interactions of van der Waals type C...S, C...N, C...C, and C...H—C are observed. Values of angles C6N1C8 $122.2(6)^\circ$, C7N1C8 $122.5(7)^\circ$, and C6N1C7 $115.4(7)^\circ$ correspond to sp^2 type of nitrogen hybridization and they support its trigonal planar configuration. The CNDO/2 quantum chemistry method for electron structure calculation was used. Calculations were concentrated to partial optimization of two dihedral angles and to evaluation of indices describing the electron density distribution in the molecule of the title compound. The torsion angles for the most stable conformation are in a good agreement with the X-ray structure analysis results.

In the recent years, the plant growth regulators have become increasingly important with respect to their application in practice. They exhibit special effects as they interfere directly with physiological processes in the plant, thus affecting its technological parameters¹. The title compound seems to be just of this type. It has an influence on technological parameters of sugar beet, *i.e.* it increases the sugar content in sugar beet and decreases that of amidic nitrogen². The aim of this work has been crystal and electron structure determination for this new preparation. Structural and electron properties here presented will be a basis for further study of relations between molecular structure and its biological activity.

EXPERIMENTAL

Preparation of the Substance and its Basic Crystallographic Data

0.11 mol of benzylbromide was added at 50–55°C with stirring to 0.1 mol of benzothiazole in 70 ml of acetone and 30 ml of dimethylformamide. The stirring continued for 6 hours at the same temperature. After cooling the precipitated crystalline product was separated by filtration and washed with acetone. As a result, colourless needle-like crystals of the title compound with 70% yield are obtained; these were purified by recrystallization from ethyl alcohol. The purity of the compound was confirmed by elemental analysis for C, H, and N elements on a Carlo Erba Model 1102 instrument (see Table I). For $C_{14}H_{12}BrNS$ (306.2) calculated: 54.91% C, 3.95% H, 4.57% N, 26.10% Br, 10.47% S; found: 54.99% C, 4.01% H, 4.53% N, 26.23% Br, 10.49% S.

For the intensity data collection the crystal with dimensions $0.3 \times 0.15 \times 0.1$ mm was chosen. From preliminary oscillation and Weissenberg patterns the monoclinic system was determined. Systematic extinctions of type $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the $P2_1/c$ space group. The lattice parameters were refined by the least squares method from diffractometer settings for 15 reflections. The crystal density was determined by flotation in chloroform–ethylbromide mixture and it is in a good agreement with the calculated one with an assumption of four formula units in the unit cell.

Integral intensities were measured on SYNTEX $P2_1$ automated diffractometer with Ni-filter monochromated $CuK\alpha$ radiation ($\lambda = 1.5418 \cdot 10^{-10}$ m) with HV-generator 50 kV/20 mA working conditions. Reflections in the range $0^\circ \leq 2\theta \leq 100^\circ$ of diffraction angle 2θ were measured. After every 100 reflections, standard reflections were measured for experiment stability monitoring. From 1345 symmetrically independent reflections measured, 1228 were with $I > 1.96 \sigma(I)$ and they were classified as observed (91.3% of all reflections). Corrections for Lorentz and polarization factors were made, not for absorption ($\mu = 5.9 \text{ mm}^{-1}$). For structure determination and refinement, all 1228 observed reflections were used.

TABLE I

Basic crystallographic data for 3-benzylbenzothiazolium bromide

Formula	$C_{14}H_{12}BrNS$
Relative molecular mass	306.2
Crystallographic system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions and the corresponding estimated standard deviations	$a = 8.315(6) \cdot 10^{-10}$ m $b = 12.323(9)$ $c = 13.140(11)$ $\beta = 103.79(6)^\circ$
Unit cell volume	$V = 1308(2) \cdot 10^{-30} \text{ m}^3$
Number of formula units per unit cell	$Z = 4$
Number of electrons per unit cell	$F(000) = 616$
Density measured	$D_q = 1.55(1) \cdot 10^3 \text{ kg m}^{-3}$
Density calculated	$D_c = 1.56$
Linear absorption coefficient	$\mu(CuK\alpha) = 5.9 \text{ mm}^{-1}$
Melting point	190.4°C

RESULTS AND DISCUSSION

Structure Determination and Refinement

Positions of Br and S atoms were found from Patterson function. Fourier synthesis on the basis of these positions revealed positions of N-atom and some of C-atoms. By subsequent use of Fourier synthesis of electron density all non-H atoms of the title compound have been found. The structure was subjected to 8 cycles of refinement in diagonal approximation of least squares method with thermal coefficients $4.0 \cdot 10^{-20} \text{ m}^2$ for all non-H atoms and with the unit weight ($w = 1$) for all observed reflections. In next 5 cycles of refinement the function minimized was $M = \sum w(|F_o| - |F_c|)^2$, where $w = 1$ for $|F_o| < 110$ and $w = 110/F_o$ for $|F_o| > 110$. For all non-H atoms anisotropic thermal vibrations were considered and 9×9 block diagonal approximation of least squares method gave $R = 0.14$.

From difference Fourier synthesis of the residual electron density positions of H-atoms were localized; their introduction to F_c calculation dropped the values of R and wR factors defined as $R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$ and $wR = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}$ to the final values $R = 0.105$ and $wR = 0.113$. In the last cycle of refinement the shifts of all positional and thermal parameters were less than 0.2σ . All calculations were made by XTL modul from SYNTEX and on EC1033 computer.

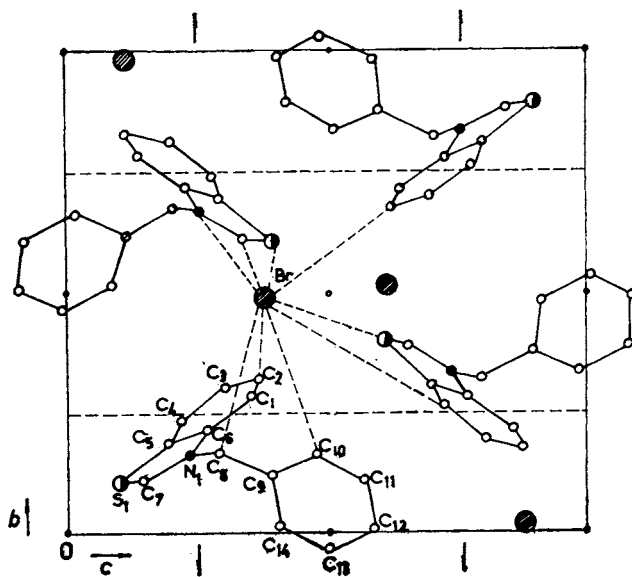


FIG. 1

Projection of the structure of 3-benzylbenzothiazolium bromide onto (100) plane

The atomic scattering factors for neutral atoms were taken from tables³. Refined positions of non-H atoms are given in Table II, positions of H-atoms refined isotropically are given in Table III, and anisotropic thermal parameters of non-H atoms are given in Table IV. Bond distances and bond angles of the title compound are given in Table V and intermolecular contacts $\sim 4 \cdot 10^{-10}$ m are given in Table VI. Distances of some atoms from selected mean planes are given in Table VII. Projection of the structure to the plane (100) can be seen in Fig. 1. For electron structure calculation of the title compound the quantum chemistry method^{4,5} was used. Calculations were concentrated to partial optimization of selected torsion angles and to evaluation of indices characterizing the electron density distribution.

Structure Description and Discussion

Projection of the structure of the title compound to the plane (100) can be seen in Fig. 1. In the unit cell there are four molecules. The crystal structure consists of monomer non-centrosymmetric units, among them on the one hand weak non-

TABLE II

Positional parameters ($\cdot 10^4$) and equivalent isotropic thermal parameters for non-H atoms of 3-benzylbenzothiazolium bromide with estimated standard deviations in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \bar{a}_i \cdot \bar{a}_j$$

Atom	x/a	y/b	z/c	$B_{\text{eq}} \cdot 10^{-20} \text{ m}^2$
S(1)	4 360(3)	1 065(2)	1 018(2)	4·21
N(1)	2 806(8)	1 652(5)	2 373(4)	3·68
C(1)	4 861(10)	2 829(6)	3 574(6)	4·17
C(2)	6 443(9)	3 253(6)	3 750(6)	4·50
C(3)	7 484(10)	3 023(7)	3 065(7)	4·85
C(4)	6 954(11)	2 379(7)	2199(7)	5·11
C(5)	5 344(9)	1 911(6)	2 021(6)	3·55
C(6)	4337(9)	2176(6)	2716(6)	3·48
C(7)	2 636(10)	1 103(8)	1 536(6)	4·36
C(8)	1 472(10)	1 766(7)	2 924(6)	4·36
C(9)	1 882(9)	1 204(7)	3 974(6)	4·13
C(10)	1 339(11)	1 632(8)	4 795(7)	5·49
C(11)	1 586(12)	1 083(9)	5 768(7)	6·45
C(12)	2 388(12)	89(9)	5 876(7)	6·68
C(13)	2 899(15)	-336(9)	5 063(9)	8·06
C(14)	2 629(12)	192(9)	4 086(6)	6·47
Br(1)	1 485(1)	4 869(1)	3 848(1)	4·60

TABLE III

Positional parameters ($\cdot 10^4$) and isotropic thermal parameters for H-atoms of 3-benzylbenzo-thiazolium bromide with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B_{eq} \cdot 10^{-20} \text{ m}^2$
H(1)	4 109(78)	3 000(53)	4 232(50)	2·6(15)
H(2)	6 987(72)	3 609(56)	4 407(46)	1·3(13)
H(3)	8 526(99)	3 592(77)	3 064(71)	6·1(25)
H(4)	7 293(99)	2 413(99)	1 621(99)	13·0(44)
H(5)	1 582(99)	750(82)	740(76)	10·6(27)
H(6)	1 069(99)	2 395(91)	2 874(82)	7·0(31)
H(7)	435(73)	1 237(51)	2 516(43)	2·7(14)
H(8)	657(82)	2 292(57)	4 656(52)	2·1(16)
H(9)	930(89)	1 540(60)	6 262(56)	4·1(18)
H(10)	2 549(99)	−149(99)	6 821(99)	9·7(42)
H(11)	6 434(99)	945(95)	5 049(87)	9·8(34)
H(12)	3 026(93)	−172(64)	3 356(59)	3·5(19)

TABLE IV

Anisotropic thermal parameters ($\cdot 10^4$) for non-H atoms from expression $T = \exp - (B_{11} \cdot h^2 + \dots + B_{12} \cdot hk + \dots)$ with estimated standard deviations in parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	152(4)	81(2)	64(2)	−29(4)	86(4)	−24(3)
N(1)	173(13)	80(6)	31(4)	2(14)	74(12)	−34(8)
C(1)	165(15)	64(6)	59(6)	−15(16)	5(15)	−29(10)
C(2)	160(14)	62(6)	74(6)	−41(16)	−18(15)	−69(11)
C(3)	181(17)	66(7)	85(7)	−18(17)	31(18)	−18(12)
C(4)	185(18)	67(7)	98(8)	16(19)	61(20)	23(13)
C(5)	127(13)	48(6)	61(6)	−69(15)	2(14)	−47(10)
C(6)	103(13)	65(6)	54(6)	−14(15)	6(14)	−25(10)
C(7)	165(16)	108(9)	46(6)	58(19)	113(16)	46(12)
C(8)	175(16)	93(8)	53(6)	2(18)	103(16)	6(11)
C(9)	108(13)	85(7)	69(6)	−48(16)	50(15)	−4(11)
C(10)	222(19)	95(8)	88(7)	−18(20)	147(19)	−1(13)
C(11)	275(22)	123(10)	81(7)	−142(25)	130(21)	−39(14)
C(12)	255(20)	124(10)	87(8)	−119(24)	53(20)	34(15)
C(13)	332(27)	129(11)	127(11)	48(28)	150(28)	63(18)
C(14)	262(21)	111(10)	106(9)	47(24)	180(23)	18(16)
Br(1)	153(1)	80(1)	76(1)	14(2)	52(2)	13(1)

-bonding interactions of type Br...S, Br...N, Br...H—C, Br...C and on the other intermolecular interactions of type C...S, C...C, and C...H—C of van der Waals character are observed. In Table VI some intermolecular interactions $\sim 4 \cdot 10^{-10}$ m are given, which determine as a main factor the crystal lattice stability and molecular packing in the crystal structure.

Trigonal planar configuration at the N-atom is supported by values of bond angles C6—N1—C8 122.2(6)°, C7—N1—C8 122.5(7)°, and C6—N1—C7 115.4(7)° and also by distances of atoms C6, C7, C8, and N1 from mean plane defined by atoms of benzothiazolic part of the molecule (see Table VII). Bond distances N1—C8

TABLE V
Interatomic distances ($\cdot 10^{-10}$ m) and bond angles (°) in an asymmetric part of unit cell of 3-benzylbenzothiazolium bromide with estimated standard deviations in parentheses

Distances		Distances	
C1—C2	1.383(11)	N1—C7	1.270(10)
C2—C3	1.418(12)	N1—C8	1.460(10)
C3—C4	1.372(13)	C8—C9	1.507(11)
C4—C5	1.424(12)	C9—C10	1.370(12)
C5—C6	1.417(11)	C10—C11	1.417(13)
C6—C1	1.369(11)	C11—C12	1.386(15)
C6—N1	1.402(10)	C12—C13	1.346(15)
C5—S1	1.726(8)	C13—C14	1.408(15)
S1—C7	1.728(9)	C14—C9	1.386(14)
C8...Br	4.011(9)	Br...H1	3.129(7)
C10...Br	4.188(9)	Br...H6	3.292(10)
		Br...H8	3.469(7)
Bond angles		Bond angles	
C2—C1—C6	117.6(7)	N1—C8—C9	112.0(7)
C1—C2—C3	121.2(7)	C8—C9—C10	119.0(7)
C2—C3—C4	121.3(8)	C9—C10—C11	121.5(8)
C3—C4—C5	118.3(8)	C10—C11—C12	118.5(9)
C4—C5—C6	118.5(7)	C11—C12—C13	119.8(10)
C5—C6—C1	123.1(7)	C12—C13—C14	122.2(11)
C5—C6—N1	108.5(6)	C14—C9—C10	119.1(8)
C6—N1—C7	115.4(7)	C14—C9—C8	120.5(8)
C7—N1—C8	122.5(7)	C8—N1—C6	122.2(6)
C7—N1—C6	115.4(7)		

TABLE VI

Intermolecular interactions in crystal structure^a of 3-benzylbenzothiazolium bromide $\sim 4 \cdot 10^{-10}$ m

Br...S1 ^{II}	3·721(2)	C2 ...S1 ^{II}	3·555(8)
Br...S1 ^{III}	3·452(2)	C2 ...S1 ^{III}	3·878(9)
Br...N1 ^{II}	4·172(6)	C10...C7 ^{III}	3·607(12)
Br...C2 ^I	3·961(8)	C10...N1 ^{III}	3·933(11)
Br...C7 ^{II}	3·673(9)	C11...N1 ^{III}	3·500(12)
Br...H7 ^{II}	2·692(6)	C11...C6 ^{III}	3·688(12)
Br...H5 ^{III}	2·583(10)	C11...C7 ^{III}	3·658(14)
Br...H3 ^{IV}	2·896(9)	C3 ...H12 ^{II}	2·870(8)

^a Transformations of atoms from different symmetrically related units with respect to the basic one (with positions x, y, z) given in Table II and III. I $-x, -y, -z$; II $-x, y + 1/2, 1/2 - z$; III $x, 1/2 - y, z + 1/2$; IV $1 + x, y, z$.

TABLE VII

Values of least squares coefficients of plane-equation $AX + BY + CZ = D$ for planes defined by selected atoms

Plane	Atoms	A	B	C	D
1	C1C5C3C4C2C6	-0·2385	0·7982	-0·5532	-0·4410
2	S1C5C6N1C7	-0·2206	0·8010	-0·5565	-0·3929
3	C9C10C11C12C13C14	-0·8331	-0·4558	-0·3134	-2·5154
4	C1C2C3C4C5C6C7S1N1	-0·2329	0·7987	-0·5548	-0·4229

Deviations ($\cdot 10^{-10}$ m) of some atoms from the above defined planes. For numbering of atoms see Fig. 1

Plane 1	C1C2C3C4C5C6
Deviations	C4 0·013(9); C5 -0·014(7); C7 0·033(9); S1 -0·019(2);
Plane 2	S1C5C6N1C7
Deviations	C7 0·013(9); N1 -0·012(6); C4 0·055(9);
Plane 3	C9C10C11C12C13C14
Deviations	C9 -0·017(8); C14 -0·018(10); C8 0·097(8);
Plane 4	C1C2C3C4C5C6C7S1N1
Deviations	C4 0·021(9); C7 0·022(9); S1 -0·020(2); C8 0·018(8);

$1.469 \cdot 10^{-10}$ m, $\text{N1—C6 } 1.402(10) \cdot 10^{-10}$ m, and $\text{N1=C7 } 1.270(10) \cdot 10^{-10}$ m are single, single, and double C—N bonds, respectively, and they are in an interval defined by a sum of Pauling⁶ covalent radii for single and double bond ($\text{N—C } 1.47 \cdot 10^{-10}$ m and $\text{N=C } 1.29 \cdot 10^{-10}$ m, resp.).

In the rest of the benzothiazole part of the molecule there are no anomalies in C—C bonds; their lengths are in the interval from $1.369(11)$ to $1.424(12) \cdot 10^{-10}$ m, and also the bond length $\text{C—S } 1.728(9) \cdot 10^{-10}$ corresponds to a single bond. Similar results were obtained for the second part of the molecule, where all bond lengths C—C and bond angles C—C—C of the benzene ring (Table V) correspond to values characteristic of this conjugated system.

In addition to above mentioned intramolecular bonds of covalent character, there are bonds of ionic character to the bromide anion. As free electron pair of nitrogen atom takes part in conjugation with π -electrons of N1=C7 bond, there is a delocalization of π -electrons in the whole benzothiazole part of molecule and as a consequence of this fact the interactions of bromide anion with atoms C8, C10, H1, H6, and H8 occur with distances close to the sum of Pauling ion radii.

Different parts of molecule were tested for planarity. In case of 5-membered thiazole ring the maximum distance from the mean plane had atom C4 ($0.055(9) \cdot 10^{-10}$ m), as reported in Table VII. The presence of N1—C8 and C8—C9 single σ -bonds in the molecule allows a rotation of separate parts of the molecule around them. For this reason, the isolated molecule may exist in different conformations. A twist of the benzene ring around C8—C9 and that of benzothiazole fragment around C8—N1 is given by an energy barrier of rotation of part of molecule which is influenced by intra- and intermolecular interactions in solid state, *i.e.* in crystal structure. Values of torsion angles $\text{N1C8—C9C10 } (\alpha) 146(1)^\circ$ or $\text{N1C8—C9C14 } -42(1)^\circ$, and $\text{C6N1—C8C9 } (\beta) -67(1)^\circ$ or $\text{C7N1—C8C9 } 113(1)^\circ$ represent probably the most stable conformation of the molecule and they are in a good agreement with the results of electron structure calculations (see below). Some differences in results obtained by the two methods can be explained by the fact that an isolated molecule is assumed in the case of electron structure calculations, *i.e.* an influence of the crystal field is neglected.

Optimization of Geometry of the Title Compound

The optimal geometry of a molecule may be found by calculation of the total energy for different geometries. The complexity of here discussed molecule does not allow an optimization of many geometry parameters. For this reason, all bond lengths and bond angles were fixed at values obtained by X-ray structure determination and the optimization was performed for torsion angles only, mainly for torsion angles α and β . Both angles characterize the twist of parts of molecule from plane N1, C8, C9 (Fig. 1). The torsion angle α describes the twist of the phenyl group; the optimal value was obtained in the interval $\alpha = 135$ to 150° . The torsion

angle β describes the twist of the benzothiazole group; the minimal energy was obtained for β in the range -40 to -60° . The most stable conformation of a free molecule of the title compound has both its parts twisted in an opposite way. Position determination of bromide anion from quantum chemistry calculations is more problematic. It might be necessary to optimize its position in a relatively large parameter space and this requires a huge amount of further calculations. Moreover, this position is strongly influenced by the environment of the molecule (solution, solid state).

Calculation of Indices of the Electron Structure

For optimal geometry of the title compound with torsion angles $\alpha = 150^\circ$ and $\beta = -45^\circ$, indices of the electron structure were calculated. Only cation of 3-benzylbenzothiazolium (with total charge $+1$) was taken into account, as the optimal position of Br^- was not determined with sufficient precision. Nevertheless, values of net charges and Wiberg indices (Table VIII) present a good approximation of electron distribution and bond characters in the molecular cation of the title compound.

The charge distribution in the 3-benzylbenzothiazolium cation shows that the positive charge is localized not only at the nitrogen atom, but is distributed over the

TABLE VIII
Values of net charges at individual atoms and Wiberg bonding indices I_w

Atom	Charge, q	Bond	I_w
C8	0.17	N1—C8	1.09
N1	0.23	N1—C7	1.49
C7	0.19	N1—C6	1.26
S1	-0.09	C7—S1	1.32
C5	0.16	S1—C5	1.29
C4	0.03	C5—C4	1.39
C3	0.11	C4—C3	1.35
C2	0.12	C3—C2	1.31
C1	0.05	C2—C1	1.36
C6	0.10	C1—C6	1.32
C9	-0.03	C8—C9	1.06
C10	0.06	C9—C10	1.43
C11	-0.07	C10—C11	1.46
C12	0.05	C11—C12	1.42
C13	-0.04	C12—C13	1.43
C14	0.08	C13—C14	1.43
		C5—C6	1.38

whole benzothiazolium part and carbon C8. The phenyl group is practically neutral. Hence, it is possible to conclude that important coulombic interactions also exist between the bromide anion and the whole benzothiazolium part plus atom C8. The Wiberg indices indicate that N1—C8 and C9—C8 bonds are single bonds; this corresponds with the possibility of rotation around these bonds (angles α and β determined above). A lower I_w in benzothiazole ring in comparison with those in phenyl group is caused by a lower electron density at benzothiazole ring. Values of Wiberg indices are in a good agreement with bond lengths obtained in a preceding part of this paper.

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