

Benzothiazole Derivatives. 48. Synthesis of 3-Alkoxy-carbonyl-methyl-6-bromo-2-benzothiazolones and 3-Alkoxy-carbonyl-methyl-6-nitro-2-benzothiazolones as Potential Plant Growth Regulators

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Abstract: 3-Alkoxy-carbonylmethyl-6-bromo- and 3-alkoxy-carbonylmethyl-6-nitro-2-benzothiazolones were synthesized by reaction of alkylesters of halogenoacetic acids with 6-bromo-2-benzothiazolones and 6-nitro-2-benzothiazolones respectively. The compounds were tested for plant growth stimulating activity on wheat (*Triticum aestivum*). The bromo derivatives manifested 25.4 % average stimulating activity in comparison with the control. The stimulation activity of the nitro derivatives was not significant. Optimal structures of the compounds were obtained by a MMPI method, atomic charges and dipole moments were calculated by a semiempirical AM1 method. On the basis of molecular electrostatic potential it has been found that the biological activity of synthesized compounds depends on charge distribution in the molecules.

Keywords: 3-Alkoxy-carbonylmethyl-6-bromo-2-benzothiazolones, 3-alkoxy-carbonylmethyl-6-nitro-2-benzothiazolones, plant growth regulators, AM1 calculations, lipophilicity.

Introduction

Good plant growth stimulating activity of benzothiazole derivatives [1-13] has been a challenge for synthesis of further compounds of this type. 4-Chloro-3-(3-oxa-5-pentenyloxycarbonylmethyl)-2-benzothiazolone [16] has been found to manifest 68 % activity of stimulation in comparison with the control, which is 17 % higher than the activity of 2,4-dichlorophenoxyacetic acid used as standard. 3-Phenoxy carbonylmethyl-2-benzothiazolone showed 32.7 % activity [13], but its 4-chloro derivative manifested 60 % efficiency [13]. High stimulating activity has been found for 3-(2-methoxyphenoxy carbonylmethyl)-2-benzothiazolone (53.76 %) [13] and for 4-chloro-3-(2-fluoroethoxy carbonyl-methyl)-2-benzothiazolone (62 %) [16] as well.

3-Benzyloxycarbonylmethyl-2-benzothiazolone [6,7,9], referred to as RASTIM 30 DKV has been tested in large scale field tests on sugar beet, grapevine, maize, rape, barley, paprika, roses, clove - pink and chrysanthemum.

The compound after application does not cumulate and leave undesirable residues in the soil. It stimulates germination and sprouting, it helps to promote a richer crop, quickens ripening of the crop and improves its quality. It heightens the resistance of products against diseases caused by fungi. In the case of vegetative propagation, it stimulates the formation of the callus and root system and improves the yield of gardening products as well.

Many 4-chloro-3-alkoxycarbonylmethyl-2-benzothiazolones in tests on wheat (*Triticum aestivum* L.) showed significantly higher stimulating activity than the corresponding derivatives unsubstituted at position 4, which means that the substitution at position 4 by chlorine heightens stimulating efficiency. It can be supposed that other than charge distribution in the molecule, the possible intramolecular donor - acceptor interaction between chlorine atom and the methylene or carbonyl group can also influence efficiency by means of raising lipophilicity [13-16]. This hypothesis will be subjected to further study.

Results and Discussion

To gain further proof in favour of this hypothesis, 13 new 3-alkoxycarbonylmethyl-6-bromo-2-benzothiazolones and 9 new 3-alkoxymethyl-6-nitro-2-benzothiazolones were synthesized (Scheme 1) and tested for stimulating activity on wheat (*Triticum aestivum*) (Table 1). The average stimulating activity in comparison to the control was 25.43 % for the bromo derivatives and only 5.53% for the nitro derivatives, which is near to the range of experimental error.

Table 1. Growth regulation activity of the synthesized compounds tested on *Triticum aestivum L.* (concentration of the compounds is 10^{-5} mol dm⁻³).

Compound	Stimulation		Compound	Stimulation	
	Δl (mm)	Δ (%)		Δl (mm)	Δ (%)
1	1.59	26.04 ^a	13	0.26	5.71
2	0.26	5.78	14	1.01	22.19 ^a
3	1.64	27.37 ^a	15	1.61	26.87 ^a
4	0.12	2.63	16	0.42	9.23
5	1.50	25.04 ^a	17	1.12	22.73 ^a
6	-0.04	-0.67	18	0.02	0.43
7	1.50	25.04	19	1.80	29.10 ^a
8	0.56	12.30	20	1.72	27.31 ^a
9	1.79	29.88 ^a	21	0.92	20.21 ^a
10	0.50	9.34	22	0.29	4.84
11	1.60	26.11 ^a	IAA^b	5.93	100.33
12	1.37	22.87 ^a	2,4-D^c	2.56	51.09

^a) Highly significant activity; ^b) **IAA** - Indolylacetic acid; ^c) **2,4-D** - 2, 4- Dichlorophenoxyacetic acid.

The synthesized compounds were studied from the viewpoint of influence of bromo and nitro substituents upon their plant growth stimulating activity.

Optimal structures of the compounds were obtained by the method MMPI [20]. Atomic charges and dipole moments of the optimal structures were calculated by the semiempirical AM1 method [21] with standard parametrization (Table 2). The theoretical values of logP were gained by Crippen's method [22].

Table 2. Calculated atomic charges and dipole moments by AM1 method and theoretical values log P.

Compound	$Q_1(S).10^3$	$Q_2(C).10^3$	$-Q_6(C).10^3$	$\mu.10^{30} / \text{Cm}$	log P
1	299	184	181	11.6	1.41
2	325	179	226	11.6	0.58
3	298	184	182	11.0	1.76
4	324	178	227	11.1	0.92
5	298	183	182	11.2	2.22
6	325	178	227	10.9	1.39
7	296	182	182	11.8	2.17
8	323	177	227	12.0	1.33
9	299	185	182	10.8	2.15
10	325	180	227	10.2	1.32
11	299	182	181	11.4	1.69
12	298	185	182	9.9	2.62
13	324	180	227	10.7	1.78
14	296	181	181	11.6	2.64
15	297	184	181	10.6	3.02
16	324	180	227	10.6	2.15
17	297	185	181	10.0	3.02
18	324	180	227	10.5	2.11
19	298	184	182	10.6	3.41
20	297	184	181	10.5	3.81
21	293	184	182	9.5	3.19
22	319	178	227	11.0	2.35

Table 3. Correlation analysis for experimental and theoretical data.

$$\Delta I\% = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2$$

x_1	x_2	$a_0 \pm s_a^a$	$a_1 \pm s_a^a$	$a_2 \pm s_a^a$	R^b	s^c	F^d	n^e
Q ₁ (S)	-	(2.4385.10 ² ± 2.0024.10 ¹)	(-7.3541.10 ² ± 6.4939.10 ¹)	-	0.930	3.9864	128.2	22
Q ₂ (C)	-	(-6.2665.10 ² ± 8.4834.10 ¹)	(3.5473.10 ³ ± 4.6729.10 ²)	-	0.862	5.5090	57.6	22
Q ₆ (C)	-	(1.0545.10 ² ± 6.7573)	(4.4095.10 ² ± 3.3591.10 ¹)	-	0.947	3.4999	172.3	22
Q ₁ (S)	μ	(-8.4264.10 ² ± 6.9879.10 ¹)	(4.3124.10 ³ ± 3.4233.10 ²)	(7.0989.10 ³⁰ ± 1.3712.10 ³⁰)	0.945	3.6403	79.4	22

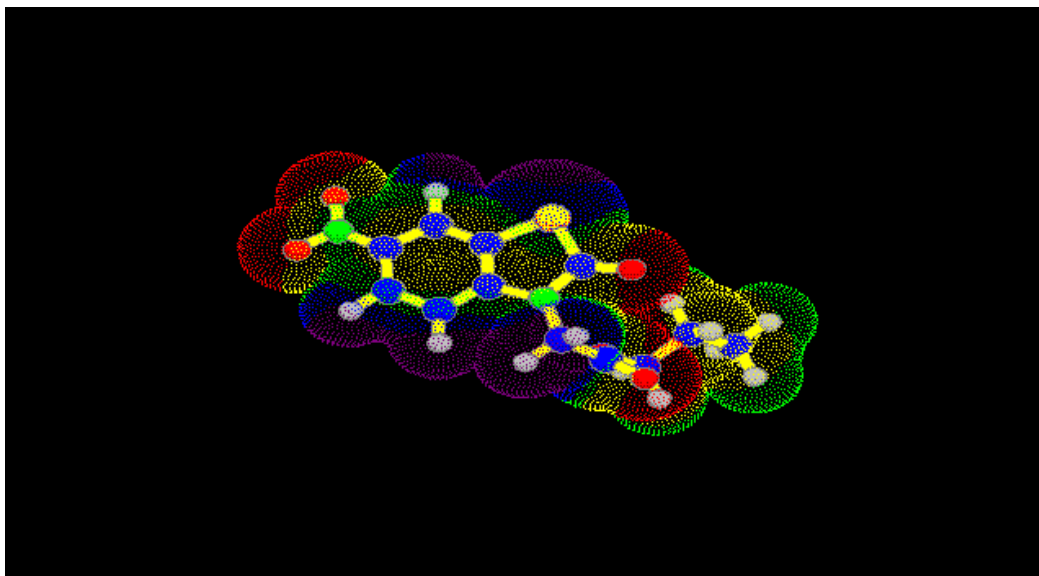
^a) Standard deviation of the slope. ^b) Correlation coefficient. ^c) Standard deviation of the correlation. ^d) The value of Fisher - Snedecor test for parameters significant at 99.5 % level. ^e) Number of compounds used in correlation.

The above data was correlated with the stimulation expressed as the percentage increase of growth caused by the tested compounds in comparison to the control (Table 1).

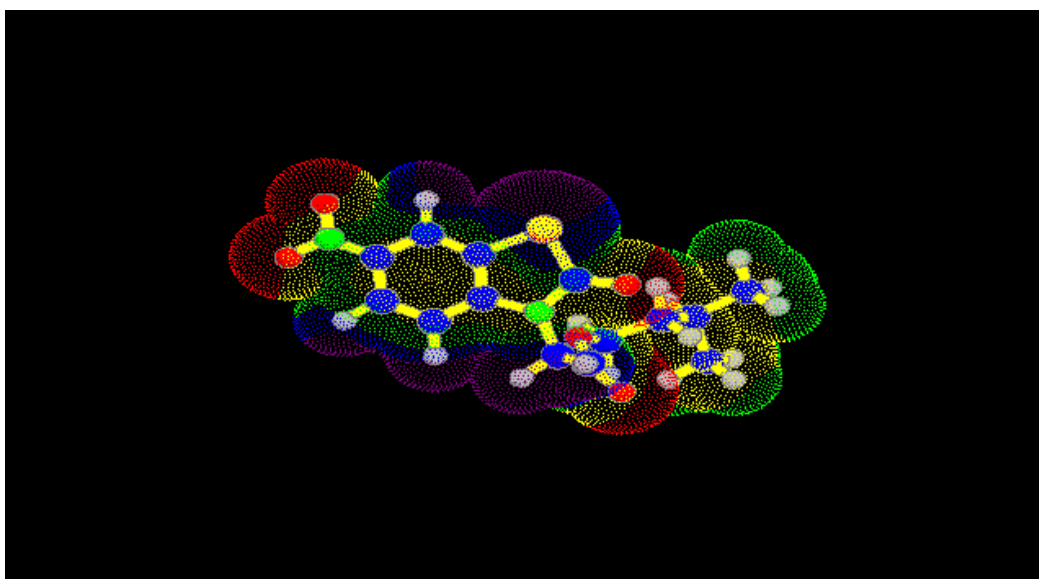
A low correlation coefficient resulted (0.556), which means that lipophilicity probably did not influence the studied stimulating efficiency of the synthesized compounds. Correlation of the charge distribution on the carbon atom at position 6, as well as of dipole moments obtained by quantum chemical methods have given statistically significant correlations (Table 3).

It has been concluded from the values of F-tests that the statistical significance of all regression equations is higher than 99.5 %. The results show that the biological activity of these compounds depends on the charge distribution in the molecules which also can be characterised by the distribution of the molecular electrostatic potential on the van der Waals surface of the molecule (Figure 1 and Figure 2).

Due to the influence of the substituent at position 6, an essential change occurs in the distribution of the negative charge in the molecule. In the case of a nitro group the electrons are drawn off from the aromatic ring and so two divided centres of negative charge are created (red area in Figure 1). In the case of a bromo substituent at position 6 there is only one centre of negative charge in the molecule (Figure 2). These results enable the prediction, from dipole moment values, of the influence of other substituents at position 6 on the studied biological efficiency of this type of compounds. The presence of a NO₂ group causes a decrease of stimulating activity from a significant to an insignificant level.

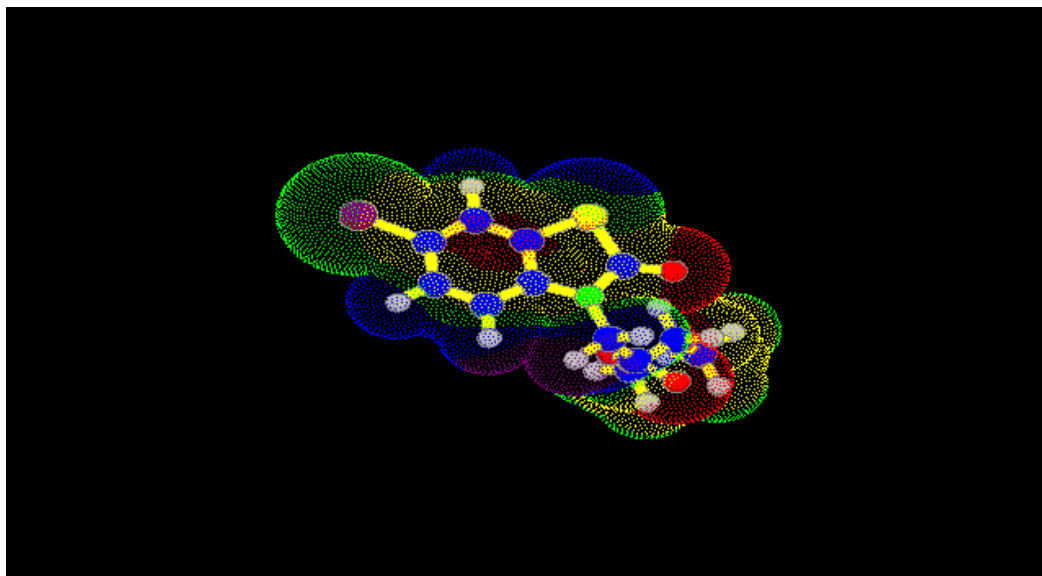


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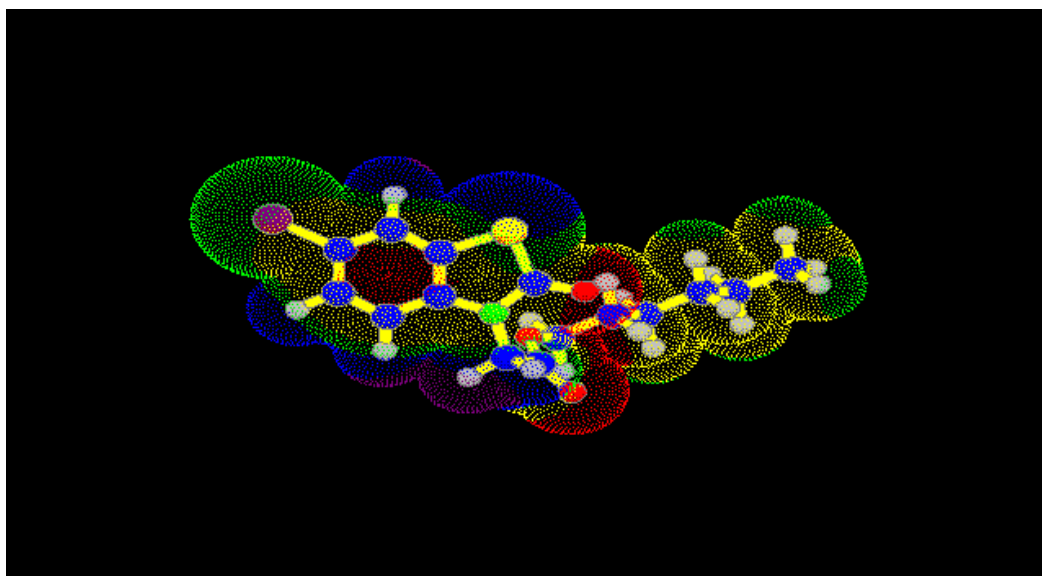


18

Figure 1. Structure and MEP on the van der Waals surface of 6-nitro (**6** and **18**) derivatives.



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19

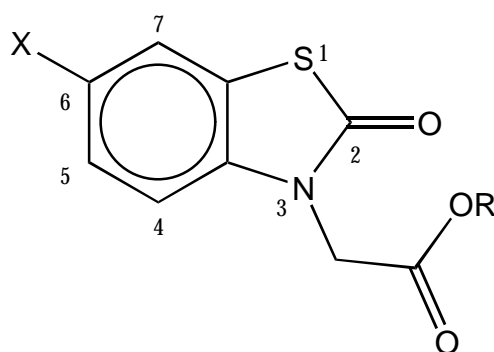
Figure 2. Structure and MEP on the van der Waals surface of 6-bromo (**5** and **19**) derivatives.

Experimental

General

6-Nitro-2-benzothiazolone and 6-bromo-2-benzothiazolone were prepared according to [17] and [18] respectively. Melting points were determined on a Kofler hotstage apparatus and are uncorrected (Analytical data are listed in Table 4). ^1H NMR spectra were obtained in CDCl_3 solution on TESLA BS 587 spectrometer (80 MHz). Tetramethylsilane (TMS) was used as inner standard.

Plant growth regulating activity has been tested on wheat (*Triticum aestivum* L) by measuring the primary roots according to [23]. The values have been compared with the primary root lengths obtained for the control as well as with values obtained for the standards 2-indolylacetic acid (IAA) and 2,4-dichlorophenoxyacetic acid (2, 4-D) in concentration $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ (Table 1).



	X	R		X	R
1	Br	CH_3	12	Br	C_4H_9
2	NO_2	CH_3	13	NO_2	C_4H_9
3	Br	C_2H_5	14	Br	sec. C_4H_9
4	NO_2	C_2H_5	15	Br	C_5H_{11}
5	Br	C_3H_7	16	NO_2	C_5H_{11}
6	NO_2	C_3H_7	17	Br	i- C_5H_{11}
7	Br	i- C_3H_7	18	NO_2	i- C_5H_{11}
8	NO_2	i- C_3H_7	19	Br	C_6H_{13}
9	Br	$\text{CH}_2\text{CH}=\text{CH}_2$	20	Br	C_7H_{15}
10	NO_2	$\text{CH}_2\text{CH}=\text{CH}_2$	21	Br	$\text{CH}_2\text{C}_6\text{H}_5$
11	Br	$\text{CH}_2\text{C}\equiv\text{CH}$	22	NO_2	$\text{CH}_2\text{C}_6\text{H}_5$

Scheme 1.

Table 4. Characterisation of the synthesized compounds.

	R	X	Formula M _r	W _i (calc.) %				Yield %	M.p.(°C) Solvent(φ _r)
				W _i (found) %					
				C	H	N	S		
1	CH ₃	Br	C ₁₀ H ₈ BrNO ₃ S 302.15	39.77 39.86	2.67 2.78	4.96 4.82	10.61 10.50	72	165-167 acetone-water (3:1)
2	CH ₃	NO ₂	C ₁₀ H ₈ N ₂ O ₅ S 268.24	44.76 44.82	3.00 2.89	10.45 10.32	11.96 12.04	59	182-184 acetone- heptane (4:1)
3	C ₂ H ₅	Br	C ₁₁ H ₁₀ BrNO ₃ S 316.18	41.81 41.89	3.18 3.31	4.43 4.32	10.14 10.10	63	95-98 ethanol - water (3:1)
4	C ₂ H ₅	NO ₂	C ₁₁ H ₁₀ N ₂ O ₅ S 282.27	46.84 46.71	3.57 3.60	9.92 8.81	11.37 11.35	56	161-164 acetone - heptane (5:1)
5	C ₃ H ₇	Br	C ₁₂ H ₁₂ BrNO ₃ S 330.20	43.67 43.55	3.66 3.80	4.24 4.18	9.71 9.60	62	67-69 acetone - ether (3:1)
6	C ₃ H ₇	NO ₂	C ₁₂ H ₁₂ N ₂ O ₅ S 296.30	48.69 48.87	4.08 3.90	9.46 9.41	10.83 10.92	57	105-108 acetone - water (2:1)
7	<i>i</i> -C ₃ H ₇	Br	C ₁₂ H ₁₂ BrNO ₃ S 330.20	43.67 43.82	3.66 3.54	4.24 4.41	9.71 10.02	55	73-76 ether
8	<i>i</i> -C ₃ H ₇	NO ₂	C ₁₂ H ₁₂ N ₂ O ₅ S 296.30	48.69 48.82	4.08 4.16	9.46 9.29	10.83 10.61	49	126-129 acetone - heptane (3:1)
9	CH ₂ CH=CH ₂	Br	C ₁₂ H ₁₀ BrNO ₃ S 328.19	43.94 44.11	3.07 3.16	4.27 4.22	9.77 9.66	61	106-107 ether - acetone (4:1)
10	CH ₂ CH=CH ₂	NO ₂	C ₁₂ H ₁₀ N ₂ O ₅ S 294.28	49.02 49.19	3.42 3.30	9.52 9.47	10.90 10.86	57	93-94 acetone - heptane (3:1)
11	CH ₂ C≡CH	Br	C ₁₂ H ₈ BrNO ₃ S 326.17	44.21 44.08	2.47 2.33	4.29 4.41	9.83 9.79	54	110-113 acetone - ether (2:1)

Continuation of the Table 2.

	R	X	Formula M _r	W _i (calc.) %				Yield %	M.p.(°C) Solvent(φ _r)
				W _i (found) %					
				C	H	N	S		
12	C ₄ H ₉	Br	C ₁₃ H ₁₄ BrNO ₃ S 344.23	45.39 45.45	4.10 3.92	4.06 4.15	9.32 9.25	45	63-65 ether
13	C ₄ H ₉	NO ₂	C ₁₃ H ₁₄ N ₂ O ₅ S 310.33	50.36 50.51	4.55 4.41	9.35 9.48	10.34 10.41	53	81-84 acetone - heptane (3:1)
14	sec-C ₄ H ₉	Br	C ₁₃ H ₁₄ BrNO ₃ S 344.23	45.39 45.51	4.10 4.04	4.06 3.94	9.32 9.20	43	83-85 ether
15	C ₅ H ₁₁	Br	C ₁₄ H ₁₆ BrNO ₃ S 358.26	46.97 47.13	4.50 4.32	3.91 3.80	8.95 8.92	48	70-72 ether
16	C ₅ H ₁₁	NO ₂	C ₁₄ H ₁₆ N ₂ O ₅ S 324.35	51.86 51.70	4.97 5.11	8.64 8.72	9.89 10.18	51	67-70 acetone - water (3:1)
17	<i>i</i> -C ₅ H ₁₁	Br	C ₁₄ H ₁₆ BrNO ₃ S 358.26	46.96 46.74	4.50 4.33	3.91 4.10	8.95 8.94	51	74-75 ether
18	<i>i</i> -C ₅ H ₁₁	NO ₂	C ₁₄ H ₁₆ N ₂ O ₅ S 324.35	51.86 51.95	4.97 4.76	8.64 8.74	9.89 9.85	47	72-73 acetone - heptane (3:1)
19	C ₆ H ₁₃	Br	C ₁₅ H ₁₈ BrNO ₃ S 372.28	48.45 48.72	4.87 4.69	3.76 3.70	8.61 8.50	52	59-61 acetone - heptane (1:1)
20	C ₇ H ₁₅	Br	C ₁₆ H ₂₀ BrNO ₃ S 386.31	49.78 49.59	5.24 5.11	3.62 3.74	8.30 8.55	49	60-62 isohexane
21	CH ₂ C ₆ H ₅	Br	C ₁₆ H ₁₂ BrNO ₃ S 378.25	50.84 50.74	3.19 3.02	3.70 3.52	8.48 8.61	59	130-132 acetone - heptane (3:1)
22	CH ₂ C ₆ H ₅	NO ₂	C ₁₆ H ₁₂ N ₂ O ₅ S 344.34	55.86 55.68	3.51 3.54	8.14 8.03	9.32 9.41	64	122-123 acetone - water (3:1)

Results of ^1H NMR analysis (80 MHz; CDCl_3):

6-Bromobenzothiazole skeleton

δ 7.57 (H-7, d, $^4\text{J} = 2.0$ Hz), 7.41 (H-5, dd, $^3\text{J} = 8.5$ Hz, $^4\text{J} = 2.0$ Hz), 6.73 (H-4, d, $^3\text{J} = 8.5$ Hz) and 4.62 - 4.69 (NCH₂, s).

6-Nitrobenzothiazole skeleton

δ 8.38 (H-7, d, $^4\text{J} = 2.2$ Hz), 8.22 (H-5, dd, $^3\text{J} = 8.8$ Hz, $^4\text{J} = 2.2$ Hz), 7.00 (H-4, d, $^3\text{J} = 8.8$ Hz), 4.72 - 4.78 (NCH₂, s).

-CH₂-COOR substituents

1 (R = CH₃) δ 3.77 (s, 3H, CH₃), 4.67 (s, 2H, N-CH₂-CO), 6.72 - 7.58 (m, 3H, H_{arom.})

2 (R = CH₃) δ 3.81 (s, 3H, CH₃), 4.77 (s, 2H, N-CH₂-CO), 6.96 - 8.41 (m, 3H, H_{arom.})

3 (R = C₂H₅) δ 1.27 (t, 3H, CH₃), 4.33 (q, 2H, -O-CH₂-), 4.65 (s, 2H, N-CH₂-CO), 6.72 - 7.58 (m, 3H, H_{arom.})

4 (R = C₂H₅) δ 1.30 (t, 3H, CH₃), 4.27 (q, 2H, -O-CH₂-), 4.76 (s, 2H, N-CH₂-CO), 6.98 - 8.40 (m, 3H, H_{arom.})

5 (R = C₃H₇) δ 0.89 (t, 3H, CH₃), 1.64 (sextet, 2H, -CH₂-), 4.17 (t, 2H, -O-CH₂-), 4.66 (s, 2H, N-CH₂-CO), 6.72 - 7.57 (m, 3H, H_{arom.})

6 (R = C₃H₇) δ 0.918 (t, 3H, CH₃), 1.68 (sextet, 2H, -CH₂-), 4.17 (t, 2H, -O-CH₂-), 4.77 (s, 2H, N-CH₂-CO), 6.99 - 8.40 (m, 3H, H_{arom.})

7 (R = *i*-C₃H₇) δ 1.25 (d, 6H, (CH₃)₂), 4.62 (s, 2H, N-CH₂-CO), 5.08 (septet, 1H, -O-CH), 6.70 - 7.58 (m, 3H, H_{arom.})

8 (R = *i*-C₃H₇) δ 1.28 (d, 6H, (CH₃)₂), 4.72 (s, 2H, >N-CH₂-), 5.11 (septet, 1H, -O-CH<), 6.96 - 8.40 (m, 3H, H_{arom.})

9 (R = CH₂CH=CH₂) δ 4.66 (s, 2H, N-CH₂-CO), 4.40 - 5.86 (m, 5H, O-CH₂-CH=CH₂), 6.72 - 7.59 (m, 3H, H_{arom.})

10 (R = CH₂CH=CH₂, X = NO₂) δ 4.78 (s, 2H, N-CH₂-CO), 4.70 - 6.10 (m, 5H, O-CH₂-CH=CH₂), 6.96 - 8.41 (m, 3H, H_{arom.})

12 (R = C₄H₉) δ 0.90 - 1.67 (m, 7H, C₃H₇), 4.15 (t, 2H, O-CH₂), 4.65 (s, 2H, N-CH₂-CO), 6.71 - 7.51 (m, 3H, H_{arom.})

13 (R = C₄H₉) δ 0.912 - 1.64 (m, 7H, C₃H₇), 4.21 (t, 2H, O-CH₂-), 4.76 (s, 2H, N-CH₂-CO), 6.97 - 8.40 (m, 3H, H_{arom.})

14 (R = *sec*-C₄H₉) δ 0.845 (t, 3H, -CH₂-CH₃), 1.22 (d, 3H, -CH-CH₃), 1.52 (quartet, 2H, -CH-CH₂-CH₃), 4.63 (s, 2H, -N-CH₂-CO)

15 (R = *sec*-C₅H₁₁) δ 0.80 - 1.70 (m, 9H, -C₄H₉), 4.16 (t, 2H, -O-CH₂-), 4.66 (s, 2H, -N-CH₂-CO),

6.72 - 7.59 (m, 3H, H_{arom.})

16 (R = C₅H₁₁) δ 0.81 - 1.73 (m, 9H, -C₄H₉), 4.20 (t, 2H, -O-CH₂-), 4.75 (s, 2H, -N-CH₂-CO), 6.96 - 8.41 (m, 3H, H_{arom.})

17 (R = i-C₅H₁₁) δ 0.81 - 1.61 (m, 9H, -CH₂-CH(CH₃)₂), 4.20 (t, 2H, -O-CH₂-), 4.65 (s, 2H, -N-CH₂-CO), 6.71 - 7.59 (m, 3H, H_{arom.})

18 (R = i-C₅H₁₁) δ 0.83 - 1.62 (m, 9H, -CH₂-CH(CH₃)₂), 4.23 (t, 2H, -O-CH₂-), 4.75 (s, 2H, -N-CH₂-CO), 6.96 - 8.41 (m, 3H, H_{arom.})

19 (R = C₆H₁₃) δ 0.802 - 1.68 (m, 11H, -C₅H₁₂), 4.24 (t, 2H, -O-CH₂-), 4.66 (s, 2H, -N-CH₂-CO), 6.72 - 7.58 (m, 3H, H_{arom.})

20 (R = C₇H₁₅) δ 0.81 - 1.68 (m, 13H, -C₆H₁₃), 4.16 (t, 2H, -O-CH₂-), 4.66 (s, 2H, -N-CH₂-CO)

21 (R = CH₂C₆H₅) δ 4.69 (s, 2H, -N-CH₂-CO), 5.20 (s, 2H, -O-CH₂-H_{arom.}), 6.65 - 7.5 (m, 3H, H_{arom.})

22 (R = CH₂C₆H₅) δ 5.22 (s, 2H, -N-CH₂-CO), 4.78 (s, 2H, CH₂-H_{arom.}), 6.87 - 8.38 (m, 3H, H_{arom.})

The signals of the alkyl substituents are in accordance with the values of δ given in literature [19]

3-Alkoxy carbonylmethyl-6-bromo-2-benzothiazolones **1, 3, 5, 7, 9, 11, 12, 14, 15, 17, 19, 20, 21**

6-Bromo-2-benzothiazolone (2.30 g, 0.01 mol), triethylamine (0.01 g, 0.01 mol) and chloroacetic acid alkylester (0.015 mol) were added to acetone (15 cm³). After 3 h reflux the cooled reaction mixture was poured out onto crushed ice, the crystalline product was filtered off, dried at room temperature and crystallized from the solvent given in Table 4.

3-Alkoxy carbonylmethyl-6-nitro-2-benzothiazolones **2, 4, 6, 8, 10, 13, 16, 18, 22**

6-Nitro-2-benzothiazolone (1.96 g, 0.01 mol) was dissolved in methanol (20 cm³) under heating. Subsequently potassium hydroxide (0.84 g, 0.015 mol) or pyridine (1.17 g, 0.015 mol) and the corresponding chloroacetic acid alkylester were added. After refluxing for 4 h and cooling the reaction mixture was poured onto crushed ice. The solid was filtered off, dried at room temperature and crystallized from the solvent given in Table 4.

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Samples Availability: Available from the authors.