

# Benzothiazole Compounds

## XLV. Compounds Based on 3-Phenoxy carbonylmethyl-2-benzothiazolinone as Potential Plant Growth Regulators

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3-Phenoxy carbonylmethyl-2-benzothiazolinones and their 4-chloro derivatives have been synthesized by the reaction of (2-oxobenzothiazolin-3-yl)acetyl chloride and (4-chloro-2-oxobenzothiazolin-3-yl)acetyl chloride, respectively, with phenols. Tests performed on *Triticum aestivum* L. have proved the stimulation activity of 7.6 % to 52.18 %. UV and IR spectra of the synthesized compounds have been measured. On the basis of them, an existence of intramolecular donor-acceptor interaction has been considered.

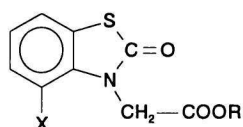
This work represents a continuation of the systematic research of benzothiazole derivatives as plant growth stimulators. Starting from the previously achieved results [1–6], the work has been oriented towards the synthesis of new substituted 3-phenoxy carbonylmethyl-2-benzothiazolinones and their 4-chloro derivatives and the study of the influence of phenoxy group substitution on the plant growth stimulation. The compounds have been synthesized from (2-oxobenzothiazolin-3-yl)acetyl chloride or from (4-chloro-2-oxobenzothiazolin-3-yl)acetyl chloride and the appropriate phenol derivatives in acetone in the presence of pyridine. The reactions afforded yields from 46 to 81 % (Table 1).

In UV spectra of the synthesized compounds, an absorption of medium intensity can be observed in the region of  $\lambda = 250\text{--}300$  nm and an intensive band at  $\lambda = 212\text{--}220$  nm, in analogy to UV spectra of 3-methyl-2-benzothiazolinone [7]. This implies the origin of the bands in electron transitions of benzothiazolinone skeleton. The substituent in the position 3 practically does not influence the shape of the electronic spectra. The substitution on the benzothiazolinone moiety in the position 4 with chlorine leads to bathochromic shift. On the other hand, the substitution on phenoxy group influences the UV spectra only to a very little extent (Table 2).

Certain exception is represented by some nitro and formyl derivatives (XIV–XVII) (Table 2), where a change of the spectrum shape occurs. The change is given by the superposition of the benzothiazolinone spectrum and of that of nitro- or formyl-substituted phenoxy groups. These conclusions are in good agreement with the quantum chemistry calcula-

tion of 3-phenoxy carbonylmethyl-2-benzothiazolinone and its 4-chloro derivative [6] where both the aromatic systems are almost perpendicular with respect to each other. The calculations proved for both molecules the existence of two approximately equally stable conformers differing in the twisting of the phenoxy carbonyl moiety. The analysis of IR spectra led to similar conclusions. In the region of  $\tilde{\nu} = 1677\text{--}1799$   $\text{cm}^{-1}$ , absorption of C=O group in the position 2 has been observed as well as that of the C=O group in the ester part of the molecule. Apart from the shift of the absorption bands due to substitution, which is connected to the change of electron-donating properties of substituents, also a modification of the shape of  $\nu(\text{C=O})$  absorption bands occurs. In the area of wavenumbers around  $1680$   $\text{cm}^{-1}$  ( $\nu(\text{C=O})$  position 2) of the spectra of compounds without chlorine substitution in the position 4, a low-resolution doublet in the form of a "shoulder" from the side of higher wavenumbers can be clearly observed. The substitution of the benzothiazolinone skeleton in the position 4 with chlorine leads to the shift of this "shoulder" to the side of lower wavenumbers.

On the other hand, this substitution exhibits a substantially lower influence on the  $\nu(\text{C=O})$  band of the ester group at  $\tilde{\nu} = 1800$   $\text{cm}^{-1}$ . Here as well, a low-resolution doublet can be recorded. The changes in IR spectra of the studied compounds may be explained by different population of conformers of particular compounds in a solution depending on the substitution. As the shift of the absorption maxima of C=O group in the position 2, dependent on the substituent in the position 3, is small — the

**Table 1.** Characterization of the Synthesized Compounds


Compound	R	X	Formula	$M_r$	$w_i(\text{calc.})/\%$				Yield %	M.p./°C Solvent ( $\varphi$ )
					$w_i(\text{found})/\%$					
					C	H	N	S		
I	2-Cl—C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> ClNO <sub>3</sub> S	319.76	56.30 56.16	3.14 3.08	4.37 4.44	10.02 9.95	48	137—140 Acetone—petroleum ether (2 : 1)
II	2-Cl—C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>3</sub> S	354.21	50.89 50.71	2.56 2.42	3.95 4.07	9.05 9.04	53	143—145 Acetone
III	3-Cl—C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> ClNO <sub>3</sub> S	319.76	56.30 56.18	3.14 3.21	4.37 4.26	10.02 9.99	51	143—144 Acetone
IV	3-Cl—C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>3</sub> S	354.21	50.89 50.73	2.56 2.41	3.95 3.85	9.05 9.18	62	152—154 Acetone
V	4-Cl—C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> ClNO <sub>3</sub> S	319.76	56.30 56.51	3.14 3.02	4.37 4.46	10.02 10.01	58	147—148 Acetone—hexane (1 : 1)
VI	4-Cl—C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>3</sub> S	354.21	50.89 50.79	2.56 2.39	3.95 3.86	9.05 8.88	56	138—140 Acetone—hexane (2 : 1)
VII	2,4-Cl <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	H	C <sub>15</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>3</sub> S	354.21	50.89 50.76	2.56 2.39	3.92 4.10	9.05 9.01	46	149—151 Acetone—petroleum ether (3 : 1)
VIII	2,4-Cl <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	Cl	C <sub>15</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>3</sub> S	388.56	46.31 46.13	2.09 2.22	3.60 3.51	8.24 8.19	50	120—122 Acetone—petroleum ether (2 : 1)
IX	2-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> S	330.32	54.59 54.74	3.05 3.16	8.48 8.62	9.71 9.88	78	130—131 Acetone
X	2-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>5</sub> S	364.76	49.35 49.18	2.48 2.57	7.67 7.49	8.78 8.86	68	166—167 Acetone
XI	3-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> S	330.32	54.59 54.41	3.05 3.18	8.48 8.32	9.71 9.54	52	155—156 Acetone—ether (2 : 1)
XII	3-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>5</sub> S	364.76	49.35 49.40	2.48 2.36	7.67 7.52	8.78 8.72	61	145—148 Acetone
XIII	4-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	H	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> S	330.32	54.59 54.78	3.05 2.91	8.48 8.60	9.71 9.67	81	155—157 Acetone—ether (3 : 1)
XIV	4-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>5</sub> S	364.76	49.35 49.47	2.48 2.67	7.67 7.52	8.78 8.86	73	160—163 Acetone—ether (3 : 1)
XV	2,4-(NO <sub>2</sub> ) <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	H	C <sub>15</sub> H <sub>9</sub> N <sub>3</sub> O <sub>7</sub> S	375.31	48.04 48.16	2.41 2.35	11.20 11.09	8.55 8.44	76	176—179 Acetone
XVI	2,4-(NO <sub>2</sub> ) <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	Cl	C <sub>15</sub> H <sub>8</sub> ClN <sub>3</sub> O <sub>7</sub> S	409.76	43.94 43.81	1.96 2.05	10.24 10.29	7.82 7.80	72	200—203 Acetone
XVII	4-Cl-2-NO <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	H	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>5</sub> S	364.76	49.35 49.24	2.48 2.37	7.67 7.72	8.78 8.70	57	187—189 Acetone—DMF (2 : 1)
XVIII	4-Cl-2-NO <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	Cl	C <sub>15</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	399.21	45.15 44.93	2.02 2.14	7.02 6.86	8.03 8.07	52	204—207 Acetone—DMF (3 : 1)
XIX	3-Cl-4-NO <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	H	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>5</sub> S	364.76	49.35 49.21	2.48 2.40	7.67 7.74	8.78 8.81	70	180—181 Acetone
XX	3-Cl-4-NO <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	Cl	C <sub>15</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	399.21	45.15 45.31	2.02 2.11	7.02 6.84	8.03 7.81	73	171—173 Acetone
XXI	3-CH <sub>3</sub> -4-NO <sub>2</sub> —C <sub>6</sub> H <sub>3</sub>	H	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub> S	344.34	55.84 55.98	3.51 3.39	8.14 8.27	9.32 9.19	57	166—168 Acetone
XXII	3-CH <sub>3</sub> -4-Cl—C <sub>6</sub> H <sub>3</sub>	H	C <sub>16</sub> H <sub>12</sub> ClNO <sub>3</sub> S	333.80	57.53 57.41	3.62 3.50	4.19 4.31	9.60 9.72	69	164—167 Acetone—hexane (2 : 1)
XXIII	3-CH <sub>3</sub> -4-Cl—C <sub>6</sub> H <sub>3</sub>	Cl	C <sub>16</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>3</sub> S	368.24	52.22 52.37	3.01 2.90	3.83 3.71	8.71 8.56	68	126—127 Acetone—hexane (2 : 1)
XXIV	3-CHO—C <sub>6</sub> H <sub>4</sub>	H	C <sub>16</sub> H <sub>11</sub> NO <sub>4</sub> S	313.33	61.39 61.51	3.54 3.41	4.49 4.57	10.24 10.20	57	133—134 Ether—acetone (2 : 1)
XXV	3-CHO—C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>16</sub> H <sub>10</sub> ClNO <sub>4</sub> S	347.77	55.22 55.06	2.89 3.72	4.02 3.87	9.21 9.10	51	148—149 Acetone—hexane (2 : 1)
XXVI	4-CHO—C <sub>6</sub> H <sub>4</sub>	H	C <sub>16</sub> H <sub>11</sub> NO <sub>4</sub> S	313.33	61.39 61.52	3.54 3.41	4.49 4.69	10.24 10.30	60	151—152 Acetone—hexane (2 : 1)
XXVII	4-CHO—C <sub>6</sub> H <sub>4</sub>	Cl	C <sub>16</sub> H <sub>10</sub> ClNO <sub>4</sub> S	347.77	55.22 55.36	2.89 2.74	4.02 4.13	9.21 9.08	53	143—146 Acetone—petroleum ether (1 : 1)

electron transition *via*  $\sigma$  bonds is small — a stabilization of the conformers by intramolecular donor-ac-

ceptor interaction probably occurs. The population of the conformers depends on the stabilization or on

Table 2. IR and UV Spectral Data of the Synthesized Compounds

Compound	$\tilde{\nu}(\nu(\text{C}=\text{O}))/\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$ (log ( $\epsilon/(\text{m}^2 \text{mol}^{-1})$ ))		
I	1678, 1787	214 (3.70)	282 (2.56)	288 (2.55)
II	1682, 1785	218 (3.51)	284 (2.24)	282 (2.28)
III	1678, 1779	212 (3.59)	282 (2.37)	288 (2.37)
IV	1680, 1778	218 (2.93)	286 (1.65)	292 (1.70)
V	1678, 1779	216 (3.47)	282 (2.36)	288 (2.36)
VI	1682, 1777	220 (3.55)	284 (2.21)	292 (2.23)
VII	1679, 1789	204 (3.54)	282 (2.26)	288 (2.20)
VIII	1682, 1786	220 (3.58)	284 (2.25)	292 (2.23)
IX	1677, 1790	216 (3.50)	280 (2.64)	288 (2.58)
X	1682, 1789	220 (2.90)	284 (1.72)	292 (1.69)
XI	1678, 1783	214 (2.98)	280 (1.92)	290 (1.73)
XII	1687, 1783	218 (3.28)	284 (2.13)	292 (2.06)
XIII	1678, 1786	216 (3.40)	252 (2.98)	272 (2.98)
XIV	1678, 1787	218 (3.46)	284 (2.76)	294 (2.59)
XV	1677, 1799	216 (3.49)	280 (2.74)	290 (2.58)
XVI	1681, 1793	220 (3.43)	284 (2.44)	294 (2.33)
XVII	1678, 1796	214 (3.63)	280 (2.53)	288 (2.50)
XVIII	1682, 1792	218 (2.96)	284 (1.90)	292 (1.91)
XIX	1678, 1786	216 (3.54)	280 (2.66)	288 (2.61)
XX	1681, 1786	218 (3.39)	284 (2.33)	292 (2.29)
XXI	1679, 1783	214 (3.45)	250 (2.87)	280 (2.76)
XXII	1678, 1778	216 (3.47)	280 (2.31)	288 (2.30)
XXIII	1682, 1777	222 (3.45)	284 (2.19)	292 (2.22)
XXIV	1678, 1779	216 (3.48)	242 (3.10)	288 (2.52)
XXV	1681, 1778	218 (2.76)	284 (1.40)	292 (1.39)
XXVI	1678, 1781	212 (3.47)	280 (2.54)	290 (2.38)
XXVII	1681, 1781	218 (3.00)	284 (1.99)	292 (1.90)

the donor-acceptor pair interaction with its surroundings. Therefore in most cases in chloroform, the modification of  $\nu(\text{C}=\text{O})$  bands cannot be so clearly observed as it can be in carbon tetrachloride. The donor-acceptor interaction can represent one of the factors influencing the biological activity of the studied compounds.

The biological tests of the synthesized compounds have been aimed at the growth regulation of *Triticum aestivum* L. in the concentration of  $10^{-5} \text{ mol dm}^{-3}$ . In the same concentration, parallel tests of the standards — 3-indolylacetic acid (IAA) and 2,4-dichlorophenoxyacetic acid (2,4-D) — have been performed for comparison. From 27 tested compounds, 21 have exhibited highly significant activity whereby the compound XXVII has achieved an efficiency (52.18 %) comparable to that of 2,4-D (51.09 %) and for further four compounds (IV, VI, XIV, and XXV), close values have been recorded. In all the synthesized compounds, a substituent with electron-withdrawing effect has been introduced to the phenoxy group in order to assess the structure—activity relationship. In the previous paper [6], the stimulation effects of 3-phenoxy carbonylmethyl-2-benzothiazolinone (32.71 %) and its 4-chloro derivative (60.18 %) were discussed. The structural change consisting in the introduction of chlorine into the position 2 of phenoxy group (I) caused an increase of activity from 32.71 % to 44.11 %; while for another derivative (II)

it meant a decrease from 60.18 % to 26.99 % (Table 3).

The introduction of chlorine into the positions 3 or 4 of phenoxy group (III and V) caused a decrease of stimulation effect in comparison to compound I; and for compounds IV and VI with chlorine also on benzothiazolinone skeleton in the position 4, the stimulation activity substantially increased in comparison with that of compound II. An analogous effect has been observed for compounds VII and VIII. The presence of nitro group (IX—XVI) has not influenced the stimulation activity significantly with the exception of compound XIV. The materials with combined substitution on phenoxy group — nitro and chloro (XVIII—XX), methyl and nitro, and methyl and chloro (XXI—XXIII) have not shown noticeable activity. The introduction of formyl group meant significant increase of activity for compounds XXV and XXVII. No principle or regularity for the influence of chloro or nitro groups, or for that of their combinations, has been observed, confirming the complexity of the acting factors.

## EXPERIMENTAL

The characterization of the synthesized compounds is given in Table 1. UV spectra were measured using methanolic solutions ( $c = 10^{-4} \text{ mol dm}^{-3}$ ) in 1 cm thick

**Table 3.** Growth Regulation Activity of the Synthesized Compounds Tested on *Triticum aestivum* L.

Compound	Stimulation ( $c = 10^{-5}$ mol dm $^{-3}$ )		Compound	Stimulation ( $c = 10^{-5}$ mol dm $^{-3}$ )	
	$\Delta l/mm$	$\Delta l/\%$		$\Delta l/mm$	$\Delta l/\%$
I	2.36	44.11*	XVI	0.62	11.78
II	1.42	26.99*	XVII	0.73	13.64
III	1.20	22.42*	XVIII	1.29	23.76*
IV	2.44	46.38*	XIX	0.40	7.60
V	1.45	22.98*	XX	1.09	20.72*
VI	2.55	48.47*	XXI	0.94	16.46*
VII	0.89	16.63*	XXII	0.49	9.31
VIII	2.09	36.60*	XXIII	1.29	24.52*
IX	1.94	34.76*	XXIV	1.42	24.86*
X	1.29	24.52*	XXV	2.78	48.68*
XI	0.64	11.01	XXVI	1.54	26.97*
XII	1.18	25.10*	XXVII	2.98	52.18*
XIII	1.32	25.09*	IAA	5.93	100.33
XIV	2.58	49.04*	2,4-D	2.56	51.09
XV	0.43	8.17			

\*Highly significant activity.

cuvette on HP 8452 A spectrophotometer. The positions of the absorption maxima were determined from the fourth derivation of the spectra. IR spectra were measured on PE 180 apparatus in NaCl cuvettes of 0.1 mm thickness, the compounds being dissolved in  $\text{CHCl}_3$ . The spectra were corrected for polystyrene absorption. The starting (2-oxobenzothiazolin-3-yl)acetyl chloride was synthesized according to [8] and (4-chloro-2-oxobenzothiazolin-3-yl)acetyl chloride according to [6]. The plant growth regulation tests were performed only on the prolongation growth of primary roots of wheat (*Triticum aestivum* L.) according to the methodology of [9] and were compared to the growth regulation activity of standards — 3-indolylacetic acid (IAA) and 2,4-dichlorophenoxyacetic acid (2,4-D) in the concentration of  $10^{-5}$  mol dm $^{-3}$ .

### 3-Phenoxy carbonylmethyl-2-benzothiazolinones

To the solution of (2-oxobenzothiazolin-3-yl)acetyl chloride or its 4-chloro derivative (0.01 mol) in 15 cm $^3$  of dry acetone, dry pyridine (0.79 g; 0.01 mol) and phenol derivative (0.01 mol) were added. After

24 h of standing at room temperature, the reaction mixture was refluxed for 1 h, followed by addition of 30–40 cm $^3$  of cold water. The precipitated crystalline portion was dried and crystallized from the solvent mixture.

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