

# Synthesis and biological properties of dithiocarbamic acid esters

## XI.\* Pesticidal activity of *N*-(alkyl or aryl)-3,4-bis(*N'*,*N'*-dialkylthiocarbamoylthio)maleimides

V. KONEČNÝ

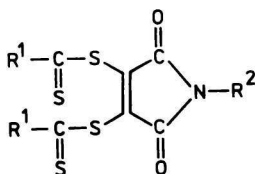
Research Institute of Chemical Technology,  
CS-831 06 Bratislava

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A synthesis of novel dithiocarbamic acid esters prepared by the reaction of *N*-(alkyl or aryl)-3,4-dichloromaleimide with alkaline salts of *N,N*-dialkyl-dithiocarbamic acid is described. The prepared compounds were tested on contact and systemic insecticidal, acaricidal, ovicidal, fungicidal, and herbicidal activities. The structure of compounds prepared was proved by infrared and ultraviolet spectrometry.

Описан синтез новых эфиров дитиокарбамовой кислоты посредством реакции *N*-(алкил или арил)-3,4-дихлормалеинимида со щелочными солями *N,N*-диалкилдитиокарбамовой кислоты. У полученных соединений были проверены их контактная и системная инсектицидная, акарицидная, овицидная, фунгицидная и гербицидная активности. Строение полученных соединений было подтверждено с помощью ИК- и УФ-спектрометрии.

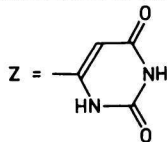
Continuing the study of the synthesis and biological activity of dithiocarbamic acid esters we prepared novel compounds of the formula



by the reaction of *N*-(alkyl or aryl)-3,4-dichloromaleimide with sodium or potassium dithiocarbamate.

\* For Part X see *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 25, 37 (1977).

Table 1. Characterization of the synthesized compounds

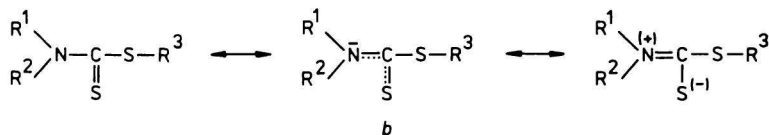


Compound	R <sup>1</sup>	R <sup>2</sup>	Formula	M <sub>r</sub>	w <sub>i</sub> (calc.)/% w <sub>i</sub> (found)/%		Yield/%	M.p./°C
					N	S		
I	(CH <sub>3</sub> ) <sub>2</sub> N	CH <sub>3</sub>	C <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	349.49	12.00	36.70	88.4	145—147
					11.70	37.06		
II	(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>4</sub> H <sub>9</sub>	C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	391.55	10.74	32.80	79.1	144—146
					10.63	32.68		
III	(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>13</sub>	C <sub>16</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	419.59	10.01	30.56	77.7	124—127
					10.12	31.00		
IV	(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>12</sub> H <sub>25</sub>	C <sub>22</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	503.74	8.34	25.46	81.2	112—114
					8.16	25.13		
V	(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>16</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	417.58	10.06	30.71	70.9	160—162
					10.42	30.85		
VI	(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	411.56	10.21	31.18	91.0	155—157
					10.09	30.98		
VII	(CH <sub>3</sub> ) <sub>2</sub> N	4-F—C <sub>6</sub> H <sub>4</sub>	C <sub>16</sub> H <sub>16</sub> FN <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	429.56	9.78	29.87	81.0	157—159
					10.01	29.75		
VIII	(CH <sub>3</sub> ) <sub>2</sub> N	4-Cl—C <sub>6</sub> H <sub>4</sub>	C <sub>16</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	446.01	9.42	28.75	78.3	161—163
					9.61	28.42		
IX	(CH <sub>3</sub> ) <sub>2</sub> N	4-NO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> S <sub>4</sub>	456.56	12.27	28.09	76.0	155—157
					12.26	28.10		
X	(CH <sub>3</sub> ) <sub>2</sub> N	CH <sub>2</sub> CH <sub>2</sub>	C <sub>22</sub> H <sub>28</sub> N <sub>6</sub> O <sub>4</sub> S <sub>8</sub>	696.97	12.06	36.80	70.9	153—158
					12.03	36.97		
XI	(CH <sub>3</sub> ) <sub>2</sub> N	2-CH <sub>2</sub> —furyl	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S <sub>4</sub>	415.55	10.11	30.86	77.7	130—133
					10.09	31.04		

Table 1 (Continued)

Compound	R <sup>1</sup>	R <sup>2</sup>	Formula	M <sub>r</sub>	w <sub>i</sub> (calc.)/% w <sub>i</sub> (found)/%		Yield/%	M.p./°C
					N	S		
XII	(CH <sub>3</sub> ) <sub>2</sub> N	CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	C <sub>17</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	425.58	9.87 9.84	30.14 30.11	80.0	142—145
XIII	(CH <sub>3</sub> ) <sub>2</sub> N	Z	C <sub>14</sub> H <sub>15</sub> N <sub>5</sub> O <sub>4</sub> S <sub>4</sub>	445.53	15.72 15.63	28.78 28.71	70.9	220—224
XIV	(CH <sub>3</sub> ) <sub>2</sub> N	NH-C <sub>6</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> S <sub>4</sub>	426.57	13.14 13.35	30.06 30.00	69.7	148—150
XV	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>20</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	473.70	8.87 8.64	27.07 27.01	74.2	168—170
XVI	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	C <sub>21</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	481.69	8.72 8.76	26.62 26.92	79.2	149—151
XVII	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	C <sub>21</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> S <sub>4</sub>	497.69	8.44 8.68	25.77 25.63	71.3	148—150
XVIII	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	3-HO-C <sub>6</sub> H <sub>4</sub>	C <sub>20</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> S <sub>4</sub>	483.67	8.69 8.41	26.51 26.58	62.3	123—125
XIX	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	4-COOH-C <sub>6</sub> H <sub>4</sub>	C <sub>21</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> S <sub>4</sub>	511.68	8.21 7.81	25.06 24.70	64.3	171—174
XX	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	1,4-C <sub>6</sub> H <sub>4</sub>	C <sub>34</sub> H <sub>44</sub> N <sub>6</sub> O <sub>4</sub> S <sub>8</sub>	857.22	9.80 9.73	29.92 30.19	60.6	183—185
XXI	(CH <sub>2</sub> =CH-CH <sub>2</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>24</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	521.75	8.05 7.88	24.58 24.32	86.6	92—94
XXII	[(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>24</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub> S <sub>4</sub>	529.81	7.93 7.69	24.20 23.94	80.4	127—129
XXIII	O(CH <sub>2</sub> -CH <sub>2</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>20</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> S <sub>4</sub>	501.68	8.38 8.40	25.25 25.48	84.6	170—172
XXIV	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> N	C <sub>6</sub> H <sub>11</sub>	C <sub>36</sub> H <sub>55</sub> N <sub>3</sub> O <sub>2</sub> S <sub>4</sub>	690.06	6.09 6.20	18.58 18.74	74.2	185—187

The influence of substituents  $R^1$  and  $R^2$  (Table 1) on the synthesis was not observed. From up-date published literature data [1, 2] it is known that not only salts but also dithiocarbamic acid esters (*a*) can occur in "thioureidic structure" (*c*)



In consequence of this it is possible in infrared spectra to detect an intermediate structure (*b*). The medium intensity bands occurring in the spectra in the region of  $1515\text{--}1500\text{ cm}^{-1}$  and  $980\text{--}971\text{ cm}^{-1}$  can be assigned to the stretching vibrations of the  $C\cdots N$  and  $C\cdots S$  bands, respectively (Table 2). Ultraviolet spectral data of the compounds prepared are summarized in Table 3.

As the synthesized compounds were in tests on insecticidal, acaricidal, ovicidal, and herbicidal activity in the first screening substantially less active than the standards used, the results are not reported. In tests on fungicidal activity some compounds showed a relatively good activity. As mordants on *Fusarium nivale* the most active compounds were *I*, *XIII*, *XXII*, *XXIII* but none of them was more active than the Dithiocyanatomethan standard. In the Sharvell test on fungi *Aspergillus niger* and *Cladosporium cucumerinum* compounds *V*, *VII*, *VIII*, *XIII*, *XIV*, and *XXII* were active but they did not reach the activity of the Captan standard. In the glass slide test on *Sclerotinia fructicola* compound *XIV* was substantially more active ( $ED_{50} = 0.009\text{ ppm}$ ) than the Captan standard ( $ED_{50} = 0.7\text{ ppm}$ ) while other compounds *I*, *III*, *V*—*VIII*, *X*, *XI*, *XXII*, and *XXIII* were less active than the standard. Against *P. infestans* (on tomatoes) only compound *IV* approached the activity of the used standard Dithane M-45. Similarly against *E. graminis* (on barley) only compound *V* came close to the level of the Karathane standard (Table 4). None of the prepared and pesticidally examined compounds was included into technological research even though compounds *XIV* and *V* were quite promising. The disadvantage of compound *XIV* was its very narrow selectivity in activity, which in this case was not convenient in praxis. Compound *V* showed from the point of the practical use to have no advantage in comparison with the used standards.

## Experimental

Infrared spectra of compounds prepared were recorded with a UR-20 (Zeiss, Jena) instrument in KBr tablets (300 mg/1 g) in the wavenumber region of  $400\text{--}2000\text{ cm}^{-1}$ . The wavenumber calibration was checked against the spectrum of polystyrene.

Table 2

IR spectral data ( $\tilde{\nu}/\text{cm}^{-1}$ ) of some compounds prepared

Compound	$\nu_s(\text{C}=\text{O})$	$\nu_{as}(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}\cdots\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\overset{\text{  }}{\underset{\text{S}}{\text{C}}}-\text{S})$		$\nu(\text{C}\cdots\text{S})$	$\nu(\text{C}=\text{S})$
II	1767	1708	1575	1511	1380	1221	1152	974	653
III	1773	1714	1620	1515	1387	1249	1155	974	655
VI	1757	1708	1610	1503	1381	1250	1128	971	657
VII	1757	1710	1612	1511	1382	1228	1126	979	645
VIII	1758	1714	1610	1500	1379	1248	1124	971	632
XV	1777	1714	1582	1506	1368	1278	1150	980	690
XVI	1779	1726	1575	1506	1382	1277	1195	976	635

Table 3

## UV spectra of some compounds prepared

Compound	$\lambda_{\max}/\text{nm}; \log(\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}))$	
II	278 (4.12)	238 (4.02)
III	267 (4.16)	218 (3.98)
VI	272 (4.11)	240 (4.00)
VII	271 (4.12)	236 (3.96)
VIII	274 (4.16)	225 (4.00)
XV	280 (4.10)	240 (4.06)
XVI	280 (4.13)	229 (3.96)

Table 4

## Fungicidal activity of compounds prepared

Compound	$m/(\text{g} (100 \text{ kg})^{-1})$		Sharvell test		Glass slide method Sf	<i>P. infestans</i> w/%		<i>E. graminis</i> w/%	
	100	10	As	Cc		0.5	0.1	0.1	0.04
	I	88	39	B		C	b	3.5	1
II	0	0	C	C	c	2	1.5	2	0
III	46	1	B	C	b	1.5	0	0.5	0
IV	36	0	C	C	c	4	3.5	2.5	1
V	0	0	B	B	b	+	+	3.5	3
VI	0	0	C	C	b	+	2.5	3	1.5
VII	0	0	B	B	b	3	1.5	2.5	2
VIII	0	0	B	B	b	3	1.5	1	0
IX	0	0	B	D	c	+	1	2	1
X	4	0	C	D	b	1	0	0	0
XI	25	2	C	C	b	1.5	0	1	0
XII	0	0	C	C	d	3.5	1.5	0	0
XIII	79	39	B	B	c	3.5	2	0	0
XIV	0	0	A	B	a	3.5	1.5	1.5	0.5
XV	0	0	D	D	d	2	0	1	0
XVI	0	0	D	D	d	0	0	1	0
XVII	0	0	D	D	d	0	0	0	0
XVIII	0	0	D	D	d	1.5	0.5	0	0
XIX	31	0	D	D	c	0	0	1.5	0
XX	0	0	D	D	d	2.5	0	0	0
XXI	0	0	D	D	d	0.5	0	0	0
XXII	82	52	B	B	b	0.5	0	0.5	0

Table 4 (Continued)

Compound	$m/(g(100\text{ kg})^{-1})$		Sharvell test		Glass slide method Sf	<i>P. infestans</i> w/%		<i>E. graminis</i> w/%	
	100	10	As	Cc		0.5	0.1	0.1	0.04
XXIII	78	34	C	C	b	1	0	0	0
XXIV	13	0	D	D	d	2	0	0	0
Dithio- cyanato- methan	100	88	—	—	—	—	—	—	—
Captan	—	—	A	A	a	—	—	—	—
Dithane	—	—	—	—	—	—	—	—	—
M-45	—	—	—	—	—	4	4	—	—
Karathane	—	—	—	—	—	—	—	4	4

As — *Alternaria* sp., Cc — *Cladosporium cucumerinum*, Sf — *Sclerotinia fructicola* A < 10 ppm, B = 10—100 ppm, C = 100—1000 ppm, D > 1000 ppm, a < 2 ppm, b = 2—20 ppm, c = 20—200 ppm, d > 200 ppm. The values express the activity /%: 4 — 0—15 % of attacked area, 3 — 16—40 %, 2 — 41—60 %, 1 — 61—80 %, 0 — 81—100 %, + — phytotoxic, — not tested.

Ultraviolet spectra were recorded with a UV VIS (Zeiss, Jena) instrument in 1.0 cm cells in ethanol within concentrations of 10—100  $\mu\text{mol dm}^{-3}$ .

Fungicidal activity of compounds prepared was followed by both the *in vitro* and *in vivo* methods. Inherent activity was followed by the glass slide method on spores of fungi *Sclerotinia fructicola* (WINT.) and on *Aspergillus niger* TIEGH and *Cladosporium cucumerinum* ELL. et ARRTH. by the Sharvell method using Captan ((*N*-trichloromethylthio)-1,2,3,6-(tetrahydrophthalimide)) as standard. Antipowdery mildew activity was followed on *Erysiphe graminis* (on the living plants of spring barley, sort Dunajský trh) using Karathane (2,4-dinitrophenyl-6-isooctyl-2-butenate) as standard and on tomatoes (*Phytophthora infestans* DE BY) using Dithane M-45 (a mixture of manganese(II) and zinc(II) 1,2-ethanediybis(carbamodithioates)) as standard according to the known methods [3].

The mordant activity was determined on dead caryopsis of rye infected by conidia of *Fusarium nivale* using Dithiocyanatomethan as standard after known methods [4].

Herbicidal activity was followed on *Avena sativa* L., *Polygonum persicaria* L., *Fagopyrum sagittatum* L. and *Sinapis alba* L. using a preemergence application (into the soil) as well as a postemergence application (to the leaf) according to the known methods [5].

According to the published methods [3, 6] compounds prepared were tested on contact insecticidal activity (*Musca domestica* L., *Sitophilus granarius*, and *Aphis fabae* SCOP) using Fenitrothion (*O,O*-dimethyl *S*-(3-methyl-4-nitrophenyl)phosphorothioate), on systemic insecticidal activity (*Aphis fabae* SCOP on *Chrysanthemum indicum*) using Thiometon (*O,O*-dimethyl *S*-(2-ethylthiomethyl)phosphorodithioate), on acaricidal activity (females of *Tetranychus urticae* KOCH), and on ovicidal activity (eggs of *T. urticae*) using Carbophen-thion (*O,O*-diethyl *S*-(4-chlorophenylthiomethyl)phosphorodithioate) as a standard.

*N*-(Alkyl or aryl)-3,4-bis(*N,N'*-dialkylthiocarbamoylthio)-maleimides (I—XIII, XV—XXIV)

To *N*-(alkyl or aryl)-3,4-dichloromaleimide (0.05 mol) in 2-butanone (120 cm<sup>3</sup>) a sodium or potassium salt of *N,N*-dialkyldithiocarbamic acid (0.11 mol) was gradually added during 15 min at 10—15 °C under stirring. The stirring was continued at the same temperature for 30 min and then at 40 °C for 30 min. The reaction mixture was poured into ice water (500 cm<sup>3</sup>) under stirring. The excluded solid compound was separated by filtration, dried and purified by crystallization from acetonitrile, *N,N*-dimethylformamide or from ethanol.

*N*-Phenylamino-3,4-bis(*N,N'*-dimethylthiocarbamoylthio)maleimide (XIV)

To *N*-Phenylamino-3,4-dichloromaleimide (0.06 mol) in propanone (120 cm<sup>3</sup>) a sodium salt of *N,N*-dimethyldithiocarbamic acid (0.12 mol) was added at 15—30 °C during 20 min under stirring. The stirring was continued for 3 h at 40 °C. After cooling the reaction mixture was poured into ice water (600 cm<sup>3</sup>). The excluded solid compound was separated by filtration, dried and purified by crystallization from ethanol.

### References

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