Phosphorylated isothioureas. II. Preparation and properties of *N*-(*O*,*O*-dialkyl and -diphenylphosphoryl)-*S*-alkyl substituted isothioureas

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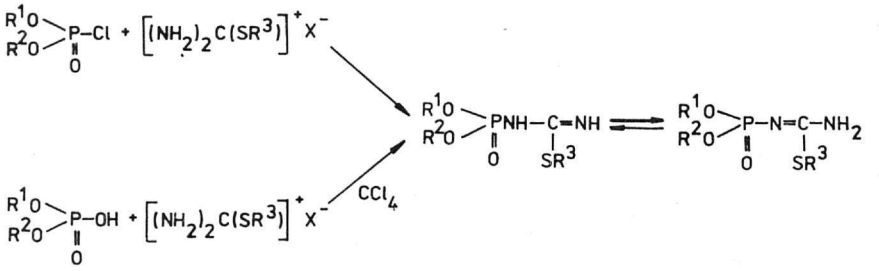
The synthesis of trisubstituted phosphorylisothioureas by the reaction of *O*,*O*-dialkyl and *O*,*O*-diphenyl chlorophosphates with thiouronium salts in the presence of different agents binding hydrogen halogenide or by the reaction of the corresponding phosphites with thiouronium salts in carbon tetrachloride in the presence of triethylamine is described. The i.r., u.v., and ^{1}H-n.m.r. spectra as well as pesticidal activities of the prepared compounds are discussed.

Описан синтез трехзамещенных производных фосфорилизотиомочевины при помощи реакции *O*,*O*-диалкил- и *O*,*O*-дифенилхлорфосфатов с солями тиоурония в присутствии разных реактивов, связывающих галогенводород, или при реакции соответствующих фосфитов с солями тиоурония в среде четыреххлористого углерода в присутствии триэтиламина. Обсуждаются ИК, УФ, и ^{1}Н-ЯМР спектры полученных соединений и также их пестицидные свойства.

Synthesis, properties, and structures of *N*-(*O*,*O*-dialkyl and -diphenylthiophosphoryl)-*S*-alkyl substituted isothioureas were described in our previous paper [1]. *Cramer* and *Vollmar* [2] described the preparation of some *N*-(*O*,*O*-diarylphosphoryl)-*S*-methyl(ethyl)isothioureas by the reaction of *O*,*O*-diaryl chlorophosphates with methylthiouronium sulfate or ethylthiouronium bromide in a heterogeneous mixture (benzene—water) in the presence of sodium hydroxide. They described also the preparation of *N*-(*O*,*O*-dibenzylphosphoryl)-*S*-methyl(ethyl)isothioureas by the reaction of dibenzyl phosphite with methylthiouronium sulfate or ethylthiouronium bromide in the mixture of carbon tetrachloride and water in the presence of sodium hydroxide.

It was found that substituted phosphorylisothioureas, similarly as substituted thiophosphorylisothioureas, were decomposed by treatment with alkali hydroxide. Therefore, it has evolved a need for a more suitable method of preparation. As



Scheme 1

seen from Scheme 1, the compounds can be isomeric with respect to the position of the double C=N bond. Therefore, it was necessary to determine their structures and physicochemical properties. The investigated compounds were tested also for pesticidal activity as they were structurally similar to some pesticidal preparations.

Experimental

Dimethyl [3], diethyl [4], dipropyl [3], diisopropyl [3], dibutyl [5], diisobutyl [6], diphenyl [7], dibenzyl [8], bis(2-chloroethyl) [9], and diallyl [10] phosphites were prepared by known procedure, *i.e.* from phosphorus chloride and the appropriate alcohol. Ethyl butyl phosphite was prepared by treatment of diethyl phosphite with butanol at 150°C [11]. The corresponding chlorophosphates were prepared by treatment of phosphites with freshly distilled sulfuryl chloride in carbon tetrachloride at 20—30°C [3, 12] or by the reaction of phosphite with carbon tetrachloride in the presence of triethylamine [13, 14]. Thiouronium salts were prepared from thiourea and the appropriate alkyl halogenide and dimethyl sulfate, respectively, in ethanol [15, 16].

The compounds listed and characterized in Table 1 were prepared by the above-mentioned general methods, some of them by two methods.

Infrared spectra of the investigated compounds were measured on UR-20 and IR-71 Zeiss spectrophotometers in carbon tetrachloride and chloroform. The apparatuses were calibrated with polystyrene foil and the reading accuracy was ± 1 cm^{-1}.

Ultraviolet spectra were taken with a Unicam SP 8000 spectrophotometer ($d = 1$ cm, $c = 10^{-4}$—10^{-5} M in methanol).

^{1}H-n.m.r. spectra were measured on a Tesla BS-487 C apparatus in $CDCl_3$ (99.5% D-isotope), CCl_4, and DMSO at 25°C. The working frequency was 80 MHz and TMS was used as internal standard.

Thin-layer chromatography and purification of the compounds were provided similarly as in the previous work [1].

Pesticidal activity was investigated under conditions described in [1] according to the methods published in [17, 18].

Table 1

Compound	R^1	R^2	R^3	Formula	*M*
I	CH_3	CH_3	CH_3	$C_4H_{11}N_2O_3PS$	198.19
II	CH_3	CH_3	$PhCH_2$	$C_{10}H_{15}N_2O_3PS$	274.33
III	CH_3	CH_3	$C_2H_5COOCH_2CH_2$	$C_8H_{17}N_2O_5PS$	284.28
IV	C_2H_5	C_2H_5	CH_3	$C_6H_{15}N_2O_3PS$	226.24
V	C_2H_5	C_2H_5	$PhCH_2$	$C_{12}H_{19}N_2O_3P$	302.34
VI	C_2H_5	C_2H_5	4-Cl—Ph—S—CH_2	$C_{12}H_{18}ClN_2O_3PS_2$	368.55
VII	C_2H_5	i-C_3H_7	$PhCH_2$	$C_{13}H_{21}N_2O_3PS$	316.37
VIII	CH_2=$CHCH_2$	CH_2=$CHCH_2$	CH_3	$C_8H_{15}N_2O_3PS$	252.30
IX	CH_2=$CHCH_2$	CH_2=$CHCH_2$	$PhCH_2$	$C_{14}H_{21}N_2O_3PS$	328.38
X	C_2H_5	C_4H_9	$PhCH_2$	$C_{14}H_{23}N_2O_3PS$	330.40
XI	C_3H_7	C_3H_7	CH_3	$C_8H_{19}N_2O_3PS$	254.30

Characterization of the synthesized compounds

Calculated/found			Yield	Method of	Reaction	T, °C	n_D^{20}	T.l.c.
% N	% P	% S	%	preparation	time, h		M.p., °C Solvent	R_f
14.14	15.63	16.18	29.9	*C*	1.5	20	74—76	0.22[a]
								0 [b]
14.5	15.28	16.49					Cyclohexane	0.08[c]
10.12	11.28	11.66	84.5	*C*	1	20	55—58	0.21[a]
								0 [b]
10.5	11.41	11.96					Heptane	0.25[c]
9.86	10.90	11.28	61.3	*C*	6	25	1.5012	0.40[a]
								0 [b]
9.53	11.00	11.59						0.54[c]
12.38	13.69	14.17	74.5	*C*	2	19	1.5050	0.44[a]
								0 [b]
12.59	13.32	13.85						0.34[c]
9.26	10.25	10.60	65.6	*C*	4	80	1.5515	0.15[a]
								0.01[b]
8.98	10.31	11.1						0.54[c]
7.60	8.40	17.40	92.9	*C*	3	25	77—79	0.40[a]
								0 [b]
7.91	8.74	17.21					Hexane	0.54[c]
8.87	9.77	10.13	84.2	*B*	4	80	1.5530	0.38[a]
								0.01[b]
9.30	9.85	10.15						0.40[c]
11.10	12.28	12.7	71.5	*C*	8	18	1.5359	0.40[a]
								0 [b]
10.89	12.45	12.98						0.37[c]
8.53	9.43	9.76	72.6	*C*	6	18	1.5609	0.49[a]
								0.02[b]
8.87	9.66	9.89						0.42[c]
8.48	9.38	9.71	92.1	*C*	3	23	1.5318	0.47[a]
								0.01[b]
8.15	9.02	9.24						0.53[c]
11.02	12.19	12.6	86.6	*A*	2	22	1.4921	0.17[a]
								0 [b]
11.09	12.37	12.38						0.17[c]

Table 1 (Continued)

Compound	R^1	R^2	R^3	Formula	*M*
XII	C_3H_7	C_3H_7	C_2H_5	$C_9H_{21}N_2O_3PS$	268.32
XIII	C_3H_7	C_3H_7	C_2H_5	$C_{10}H_{23}N_2O_3PS$	282.35
XIV	C_3H_7	C_3H_7	C_4H_9	$C_{11}H_{25}N_2O_3PS$	296.38
XV	C_3H_7	C_3H_7	C_8H_{17}	$C_{15}H_{33}N_2O_3PS$	352.49
XVI	C_3H_7	C_3H_7	$CH_2=CHCH_2$	$C_{10}H_{21}N_2O_3PS$	280.33
XVII	C_3H_7	C_3H_7	$CH\equiv CCH_2$	$C_{10}H_{19}N_2O_3PS$	278.30
XVIII	C_3H_7	C_3H_7	$PhCH_2$	$C_{14}H_{23}N_2O_3PS$	330.40
XIX	C_3H_7	C_3H_7	$C_2H_5SCH_2$	$C_{10}H_{23}N_2O_3PS$	314.42
XX	C_3H_7	C_3H_7	$C_2H_5SCH_2CH_2$	$C_{11}H_{25}N_2O_3PS_2$	328.44
XXI	C_3H_7	C_3H_7	$BrCH_2$	$C_8H_{18}BrN_2O_3PS$	333.20
XXII	C_3H_7	C_3H_7	$ClCH_2CH_2$	$C_9H_{20}ClN_2O_3PS$	302.77

Table 1 (Continued)

Calculated/found			Yield %	Method of preparation	Reaction time, h	T, °C	n_D^{20} M.p., °C Solvent	T.l.c. R_f
% N	% P	% S						
10.43	11.55	11.93	83.6	*A*	3	16	1.4960	0.16[a]
								0 [b]
10.85	11.37	12.2						0.37[c]
9.92	10.97	11.36	86.5	*A*	2	21	1.4898	0.16[a]
								0 [b]
10.24	10.69	11.70						0.42[c]
9.45	10.46	10.8	88.5	*A*	1	30	1.4842	0.16[a]
								0 [b]
9.10	10.80	10.75						0.71[c]
7.95	8.82	9.10	76.7	*A*	1.5	30	1.4860	0.36[a]
								0.04[b]
8.31	8.50	9.70						0.83[c]
9.99	11.05	11.44	85.7	*A*	3	17	1.5031	0.17[a]
								0 [b]
10.25	10.90	11.88						0.37[c]
10.06	11.12	11.49	76.2	*A*	2.5	18	1.5208	0.17[a]
								0 [b]
10.28	10.92	11.76						0.43[c]
8.48	9.38	9.71	81.1	*A*	0.5	24	1.5318	0.41[a]
								0 [b]
8.15	9.02	9.24						0.39[c]
8.92	9.85	20.2	79.6	*A*	4	25	1.5150	0.61[a]
								0.03[b]
9.15	9.99	20.23						0.66[c]
8.54	9.44	19.54	75	*A*	4	16	1.5162	0.16[a]
								0 [b]
8.89	9.18	20.03						0.39[c]
8.42	9.29	9.61	57.2	*A*	11	20	1.4820	0.02[a]
								0 [b]
8.78	9.09	9.98						0.01[c]
9.21	10.17	10.50	43.1	*A*	16	20	115—116.5	0.07[a]
								0 [b]
9.53	10.48	10.88						0.08[c]

Table 1 (Continued)

Compound	R^1	R^2	R^3	Formula	*M*
XXIII	C_3H_7	C_3H_7	$C_2H_5OCOCH_2CH_2$	$C_{12}H_{20}N_2O_5PS$	340.39
XXIV	C_3H_7	C_3H_7	4Cl—Ph—CH_2	$C_{14}H_{22}ClN_2O_3PS$	364.84
XXV	i-C_3H_7	i-C_3H_7	CH_3	$C_8H_{19}N_2O_3PS$	254.30
XXVI	i-C_3H_7	i-C_3H_7	C_3H_7	$C_{10}H_{23}N_2O_3PS$	282.35
XXVII	i-C_3H_7	i-C_3H_7	$PhCH_2$	$C_{14}H_{23}N_2O_3PS$	330.40
XXVIII	C_4H_9	C_4H_9	CH_3	$C_{10}H_{23}N_2O_3PS$	282.35
XXIX	C_4H_9	C_4H_9	$PhCH_2$	$C_{16}H_{27}N_2O_3PS$	358.45
XXX	C_4H_9	C_4H_9	3,4-diCH_3PhCH_2	$C_{18}H_{21}N_2O_3PS$	386.50
XXXI	C_4H_9	C_4H_9	4-Cl—Ph—CH_2	$C_{16}H_{26}ClN_2O_3PS$	378.86
XXXII	i-C_4H_9	i-C_4H_9	CH_3	$C_{10}H_{23}N_2O_3PS$	282.35
XXXIII	i-C_4H_9	i-C_4H_9	$PhCH_2$	$C_{16}H_{27}N_2O_3PS$	358.45

Table 1 (Continued)

Calculated/found			Yield	Method of	Reaction	T, °C	n_D^{20}	T.l.c.
% N	% P	% S	%	preparation	time, h		M.p., °C Solvent	R_f
7.99	9.12	9.42	42.3	*A*	14	22	1.4745	0.38[a]
								0.03[b]
7.52	9.60	8.95						0.41[c]
8.15	8.53	8.69	91.8	*A*	1.5	24	1.5403	0.29[a]
								0.01[b]
8.51	8.35	9.1						0.29[c]
11.02	12.19	12.93	72.4	*A*	8	19	45—46.5	0.14[a]
								0 [b]
11.41	11.94	12.93					Heptane	0.18[c]
9.90	10.97	11.36	90.1	*A*	8	19	45.5—47	0.18[a]
								0 [b]
10.31	10.80	11.71					Heptane	0.22[c]
8.48	9.38	9.71	91.4	*A*	7	19	1.5311	0.22[a]
								0.01[b]
8.87	9.28	10.14						0.21[c]
9.92	10.97	11.36	96.8	*A*	5	19	1.4895	0.25[a]
								0 [b]
10.3	10.53	11.74						0.28[c]
7.82	8.64	8.95	91.9	*A*	5	19	29—32	0.30[a]
								0.01[b]
8.19	8.32	9.26						0.28[c]
7.25	8.02	8.30	88.6	*A*	2.5	40	1.5405	0.21[a]
								0.02[b]
6.98	8.22	8.09						0.91[c]
7.40	8.18	8.46	95.7	*A*	2.5	40	1.5335	0.23[a]
								0.01[b]
7.45	7.85	8.80						0.90[c]
9.92	10.97	11.36	94.9	*A*	7	20	1.4839	0.25[a]
								0 [b]
10.24	10.61	11.63						0.28[c]
7.82	8.64	8.95	97.6	*A*	6	20	42.5—45 Hexane	0.32[a]
								0 [b]
8.11	8.86	9.21						0.19[c]

Table 1 (Continued)

Compound	R^1	R^2	R^3	Formula	*M*
XXXIV	$ClCH_2CH_2$	$ClCH_2CH_2$	CH_3	$C_6H_{13}Cl_2N_2O_3PS$	295.14
XXXV	$ClCH_2CH_2$	$ClCH_2CH_2$	$PhCH_2$	$C_{12}H_{17}Cl_2N_2O_3PS$	371.24
XXXVI	Ph	Ph	CH_3	$C_{14}H_{15}N_2O_3PS$	322.33
XXXVII	Ph	Ph	C_3H_7	$C_{16}H_{19}N_2O_3PS$	350.38
XXXVIII	Ph	Ph	$PhCH_2$	$C_{20}H_{19}N_2O_3PS$	398.43
XXXIX	$PhCH_2$	$PhCH_2$	C_2H_5	$C_{17}H_{21}N_2O_3PS$	364.41
XL	$PhCH_2$	$PhCH_2$	$PhCH_2$	$C_{22}H_{23}N_2O_3PS$	426.48

Mobile phase: *a*) $CHCl_3$:C_2H_5OH 95:5; *b*) benzene; *c*) petroleum ether:acetone 7:3.

Compounds I—VI, VIII—X, XXXIX, XL prepared in CCl_4; *VII* in ethyl methyl ketone; *XI, XIII, XVI, XVIII, XXI, XXV—XXIX, XXXVIII* in benzene:water 2:1; *XII, XVII, XX* in acetonitrile:water 2:1; *XIX, XXX* in acetonitrile:water 3:2; *XIV, XV, XII, XXIV, XXX, XXXI* in acetonitrile:water 1:1.

Physical properties of the compounds *XXXVI* and *XXXIX* are identical with those of the compounds prepared according to [2].

Table 1 (Continued)

Calculated/found			Yield	Method of	Reaction	T, °C	n_D^{20} M.p., °C	T.l.c.
% N	% P	% S	%	preparation	time, h		Solvent	R_f
9.49	10.49	10.86	46.9	*A*	9	20	1.5289	0.13[a]
								0 [b]
9.87	10.76	11.22						0.11[c]
7.55	8.34	8.64	80.5	*A*	8	18	1.5672	0.19[a]
7.57	8.75	9.01						0.01[b]
								0.14[c]
8.69	9.61	9.93	96.9	*A*	7	18	77—78	0.28[a]
								0.02[b]
8.91	9.54	10.4					Heptane	0.16[c]
7.99	8.84	9.15	82.8	*A*	8	18	45—46.5	0.28[a]
								0.02[b]
8.08	8.91	9.60					Cyclohexane	0.20[c]
7.03	7.77	8.05	87.9	*A*	7	19	87—88	0.29[a]
								0.04[b]
7.32	7.92	8.13					Cyclohexane	0.24[c]
7.70	8.50	8.80	54.4	*C*	3	20	46—47	0.25[a]
								0.41[b]
7.39	8.78	9.10					Cyclohexane	0.51[c]
6.57	7.26	7.52	55.9	*C*	4	23	1.6049	0.58[a]
								0.09[b]
6.81	7.53	7.80						0.92[c]

N-(O,O-Dialkyl and -diphenylphosphoryl)-S-alkyl substituted isothioureas

Method A

Into the reaction mixture containing the appropriate chlorophosphate (0.1 mole), thiouronium salt (0.1 mole), potassium carbonate (0.1 mole), and acetonitrile (benzene, acetone) (100 ml), water (50 ml) was added under stirring. Stirring was continued at the temperature given in Table 1 and the course of the reaction was followed by t.l.c. At the end of the reaction the product was extracted with chloroform (benzene) (3 × 40 ml) and dried. The solvent was distilled off under reduced pressure. The formed solids were purified by crystallization and the oily compounds by column chromatography.

Method B

The reaction mixture of chlorophosphate (0.1 mole), thiouronium halogenide (0.1 mole), triethylamine (0.2 mole), and the solvent (ethyl methyl ketone, acetone, acetonitrile) (100 ml)) was heated to reflux. The salt formed was filtered off and the filtrate was evaporated under reduced pressure. Chloroform (benzene) (100 ml) was added to the distillation residue, washed with water and dried. The solvent was distilled off under reduced pressure and the obtained crude product was purified by column chromatography.

Method C

Into the reaction mixture containing the appropriate disubstituted phosphite (0.1 mole), thiouronium salt (0.1 mole), and carbon tetrachloride (150 ml), triethylamine (0.2 mole) was added within 10 min under stirring while the temperature increased by 20—40°C. Then water (100 ml) was added and after separation the water layer was extracted with chloroform (2 × 50 ml). The combined organic layers were dried and the solvent was distilled off under reduced pressure. The formed solids were purified by crystallization and the oily compounds by column chromatography.

N-Diisobutylphosphoryl-N,N',S-trimethylisothiourea

To diisobutyl chlorophosphate (11.4 g; 0.05 mole), *N,N',S*-trimethylthiouronium iodide (12.5 g; 0.05 mole), and toluene (100 ml), sodium carbonate (5.3 g; 0.05 mole) dissolved in water (50 ml) was added at room temperature under stirring which was continued for 16 h. The toluene layer was separated, dried and the solvent was distilled off. After purification of the liquid residue by column chromatography a white yellow viscous liquid (6.5 g; 41.9%) of $n_D^{20} = 1.4429$ was obtained.

For $C_{12}H_{27}N_2O_3PS$ (310.4) calculated: 9.03% N, 9.98% P, 10.33% S; found: 8.71% N, 9.61% P, 10.56% S.

Results and discussion

The suitability of individual methods for preparation of the studied compounds depends on the alkoxy groups bound to phosphorus. In the case of methyl, ethyl, allyl, benzyl, and propyl derivatives it is advantageous to use the reaction of the appropriate phosphite with thiouronium salt in carbon tetrachloride in the presence of triethylamine (method *C*). In fact, it is only a different way of obtaining chlorophosphate. The phosphite with carbon tetrachloride gives chlorophosphate which then reacts with the appropriate isothiourea liberated from thiouronium salt by treatment with triethylamine [13, 14]. The advantage of this method is that a preparatively difficult step is omitted and that the unstable chlorophosphates have not to be prepared. The phosphites, contrary to chlorophosphates, are stable. The method of Cramer and Vollmar, where hydrogen halogenide was bound with aqueous solution of sodium hydroxide, gave low yields of contaminated phosphoryl-isothioureas with by-products due to their decomposition in alkali medium. The modified method gave very pure products in spite of the fact that triethylamine was added into the reaction mixture without cooling and the temperature increased to 50°C.

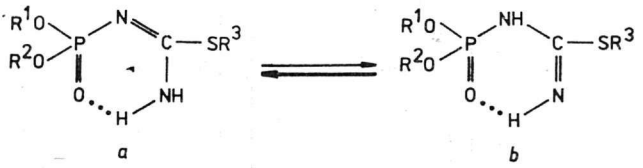
The compounds with higher number of carbons in the alkoxy groups should be prepared by the method *A* and *B*. At the method *A* the reaction time is shorter and purer products are obtained than at the method *B* where the reaction proceeds in polar organic solvent at increased temperature. Generally, the purity of products grows worse with the increasing temperature regardless the method used.

The yields of the investigated compounds are rather influenced by their solubility in water which decreases with the increasing number of carbons in the alkoxy groups bound to phosphorus. Therefore, at the method *C*, the methyl and ethyl derivatives should be washed with less amounts of water and extracted several times. The solubility in water was affected also by the chain length on sulfur though essentially less than on phosphorus. The most soluble compound was *N*-dimethyl-phosphoryl-*S*-methylisothiourea (*I*) and consequently, it was obtained in the least yield.

In the i.r. spectra (Table 2) of the studied compounds four absorption bands were observed in the region of 3200—3500 cm^{-1} which could be attributed to the stretching vibration of N—H bonds in the amido and imido groups.

The relatively strong bands at ~3270 and ~3470 cm^{-1} could be attributed to the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ vibrations. The differences in the wavenumbers of these bands (~200 cm^{-1}) could be explained by that the hydrogen of the amido group was involved in the hydrogen bond with oxygen atom of the P=O group.

The relatively weak bands at ~3200 and ~3350 cm^{-1} belonged to ν(=NH) and ν(—NH) vibrations. It is evident from the i.r. spectra that the investigated compounds can exist in two taoutomeric forms



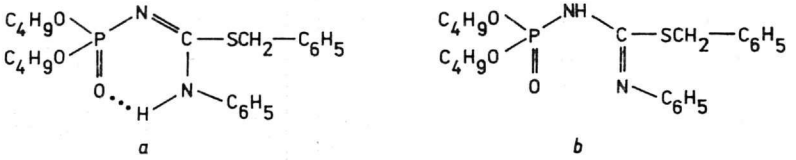
a *b*

$\nu_s(NH_2) \sim 3270\ cm^{-1}$
$\nu_{as}(NH_2) \sim 3470\ cm^{-1}$

$\nu(-NH) \sim 3350\ cm^{-1}$
$\nu(=NH) \sim 3200\ cm^{-1}$

the amido form *a* being the dominant one.

The attribution of bands in this region of the spectra was proved by the spectrum of the deuterated compound *XVIII* where bands belonging to N—D bonds were observed at 2570, 2481, 2418, and 2374 cm^{-1}. The appearance of these bands proved that the above-mentioned bands belonged to stretching vibrations of the N—H bonds. Also the comparatively low wavenumbers of bands belonging to $\nu(P=O)$ at $\sim 1205\ cm^{-1}$ supported the attribution of bands to N—H vibrations. The attribution of bands in the region of 3200—3500 cm^{-1} was verified by the i.r. spectrum of a model compound where only one band was observed at 3200 cm^{-1}. This indicated that the compound had the structure *a*



a *b*

It was found that the intensity of the band $\nu_s(NH_2)$ at 3288 cm^{-1} (compound *XXXIII*) practically did not change ($\varepsilon = 97$—$96\ l\ mol^{-1}\ cm^{-1}$) in the concentration range 5.6×10^{-3}—4.75×10^{-2} M in chloroform, however, the intensity of the band $\nu_{as}(NH_2)$ decreased ($\varepsilon = 162 - 141\ l\ mol^{-1}\ cm^{-1}$). This fact can be explained by intermolecular interactions.

The bands $\nu_s(NH_2)$ measured in chloroform were observed at higher wavenumbers (by about 20 cm^{-1}) than those in carbon tetrachloride and the bands $\nu_{as}(NH_2)$ at lower wavenumbers (by about 10 cm^{-1}). The intensity of bands differed only negligibly under these conditions. In the proton-accepting solvents (tetrahydrofuran, dioxan) significant changes were observed both in the wavenumbers and intensities of bands belonging to N—H bond vibrations. The band at 3470 cm^{-1} was not observed in the spectrum of these compounds but a very strong band appeared at 3350 cm^{-1}.

The i.r. spectra of all compounds studied showed strong absorption bands $\nu(C=N)$ in the region of 1615—1630 cm^{-1}, which also indicated the conjugation

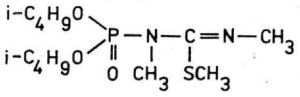
Table 2

Infrared spectral data of the studied compounds

Compound	$\tilde{\nu}$, cm^{-1}						
	ν(P=O)	$\delta(NH_2)$	ν(C=N)	ν(=NH)	$\nu_s(NH_2)$	ν(NH)	$\nu_{as}(NH_2)$
I[a]	1217	1560	1620	3205	3276	3358	3470
II	1225	1566	1623	3212	3290	3370	3460
III	1226	1566	1622	3205	3272	3349	3470
IV	1205	1577	1623	3205	3270	3359	3473
V	1205	1566	1624	3205	3270	3355	3472
VI	1205	1573	1630	3205	3262	3349	3470
VII	1205	1568	1630	3205	3267	3350	3470
VIII	1210	1563	1625	3205	3275	3350	3475
IX[a]	1205	1558	1620	3200	3273	3358	3470
X	1210	1564	1622	3205	3269	3358	3471
XI	1205	1570	1629	3204	3271	3354	3470
XIII	1207	1565	1620	3205	3271	3354	3476
XIV	1204	1566	1620	3206	3274	3359	3477
XV	1204	1564	1620	3207	3265	3357	3470
XVI	1207	1567	1622	3204	3269	3358	3471
XVIII	1205	1552	1622	3205	3285	3350	3470
XIX	1208	1567	1625	3205	3270	3349	3470
XX	1209	1568	1627	3204	3268	3350	3470
XXIII	1206	1572	1626	3202	3260	–	3475
XXIV	1205	1567	1623	3205	3265	3350	3470
XXV	1205	1570	1631	3206	3270	3350	3472
XXVI	1210	1567	1628	3205	3275	3350	3470
XXVII	1205	1568	1629	3205	3265	3350	3470
XXVIII	1204	1565	1628	3204	3268	3354	3472
XXIX	1205	1566	1623	3205	3268	3350	3472
XXX	1205	1568	1628	3206	3270	3349	3471
XXXI	1205	1551	1628	3204	3274	3356	3470
XXXII	1205	1569	1629	3210	3270	3360	3475
XXXIII	1205	1568	1624	3205	3269	3370	3476
XXXIV	1210	1567	1628	3204	3270	3361	3469
XXXV	1210	1567	1628	3205	3275	3350	3470
XXXVI	1207	1560	1626	3205	3277	3359	3470
XXXVII[a]	1205	1595	1626	3205	3300	3350	3470
XXXVIII[a]	1198	1552	1623	3204	3310	–	3470
XXXIX	1210	1566	1619	3204	3268	3350	3471
XL	1212	1564	1621	3205	3274	3355	3474

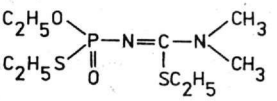
Spectra were recorded in CCl_4; *a*) measured in $CHCl_3$.

of the C=N double bond with π electrons of the P=O group. This followed from the fact that the spectrum of the model compound *C*, with an isolated system of double bonds, revealed the ν(C=N) band at higher wavenumber than the spectrum of the model compound *D* with a conjugated system of double bonds



C

ν(C=N) = 1684 cm^{-1}



D

ν(C=N) = 1594 cm^{-1}

The bands belonging to deformational vibrations of N—H in NH_2 groups were found at ~1560 cm^{-1}. With the compounds containing aromatic rings, these bands were overlapped by the ν(C=C) bands.

The ^{1}H-n.m.r. spectra of the investigated compounds (Table 3) showed broad double-proton signals at ~7 p.p.m., which also proved the predominance of the amido form in these compounds. The resonance signals of protons of NH_2 groups were observed in dimethyl sulfoxide at higher values, which indicated an interaction of the solvent with the NH_2 group, for instance in the spectrum of the

Table 3

^{1}H–n.m.r. spectral data of the studied compounds

Compound	δ(p.p.m.)						Solvent
XXV	NH_2	CH_3CH	$CHCH_3$	CH_3S			
	6.87 (2H, bs)	1.32 (d)	4.56 (d7)	2.37 (s)			$CDCl_3$
XXXII	NH_2	CH_3CH	$CHCH_3$	CH_2S	CH_3O		
	7.02 (2H, bs)	0.95 (d)	1.92 (m)	2.36 (dd)	3.72 (s)		$CDCl_3$
XXXIII	NH_2	CH_3CH	$CHCH_3$	CH_2O	CH_2S	Ph	
	6.87 (2H, bs)	0.92 (d)	1.91 (m)	3.68 (dd)	4.23(s)	7.30 (m)	$CDCl_3$
XXXIII	NH_2	CH_3CH	$CHCH_3$	CH_2O	CH_2S	Ph	
	—	0.91 (d)	1.91 (m)	3.68 (dd)	4.21 (s)	7.30 (m)	$CDCl_3+D_2O$
XXXIII	NH_2	CH_3CH	$CHCH_3$	CH_2O	CH_2S	Ph	
	7.53 (2H, bs)	0.90 (d)	1.88 (m)	3.60 (dd)	4.16 (s)	7.25 (m)	CCl_4
XXXVIII	NH_2	CH_2S	Ph				
	6.95 (2H, bs)	4.10 (s)	7.25 (m)				$CDCl_3$
XXXVIII	NH_2	CH_2S	Ph				
	8.07 (2H, bs)	4.14 (s)	7.26 (m)				DMSO

Observed multiplicities: s – singlet, d – doublet, bs – broad singlet, m – multiplet.

compound *XXXVIII*: $\delta = 7.25$ p.p.m. ($CHCl_3$) and $\delta = 8.07$ p.p.m. (DMSO). At increased temperature (25→130°C) the resonance signal of the NH_2 protons was observed at lower values (8.07→7.76 p.p.m.) in the spectrum of the compound *XXXVIII* measured in DMSO.

The tautomer *a* was thermodynamically more stable than the tautomer *b* because of the present conjugated system O=P—N=C. This is evident also from the u.v. spectra of the compounds investigated which revealed very strong absorption bands at 209—214 nm (log $\varepsilon \sim 4$) indicating the presence of a conjugated system. The enlargement facilitated the formation of an intramolecular hydrogen bond with hydrogen of the amido group (Table 4).

None of the synthesized compounds showed so high pesticidal activity as the used standards malathion, fenitrothion, and carbophenothion. The compound *XXI* was most active when tested for acaricidal activity against *Tetranychus urticae* KOCH and the highest ovicidal activity on eggs of *Tetranychus urticae* KOCH was found with the compounds *XIX, XXXI, XXXVI, XXXVII, XXXVIII,* and *XL.* The studied group of compounds did not show herbicidal and fungicidal activities. The only exception was the compound *XXIX* which was found to be a growth regulator. However, the activity was not high and it would be worthless to test this compound in detail.

Table 4

Ultraviolet spectral data of the studied compounds (in methanol)

Compound	λ_{max} nm	log ε	λ_{max} nm	log ε
I	212.5	4.102	225.5	4.098
II	213	4.161	226	3.983
III	213	4.057	225.5	4.016
V	210	4.127	224.5	3.986
VI	213.5	4.264	262	4.187
IX	214	4.170	224	4.064
XVIII	209	4.084	225	3.781
XXII	213	4.074	225	4.031
XXV	212	4.003	225	3.984
XXVIII	210	4.114	225	4.031
XXIX	210	4.117	225	3.925
XXXII	210	4.097	225	4.003
XXXIII	209	4.009	225	3.764
XXXVII	213	4.198	229	3.913

ε in l mol^{-1} cm^{-1}.

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