Synthesis, spectral properties, and hydrogen bonds of phosphoryl- and thiophosphorylhydrazines

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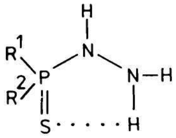
A synthesis of substituted thiophosphorylhydrazines and of *O,O*-dialkylphosphorylhydrazines prepared by the reaction of hydrazine hydrate with dialkyl(diaryl) or alkyl (alkylamino, dialkylamino)chlorothiophosphates and with dialkyl phosphonates, respectively, in the presence of potassium carbonate and triethylbenzylammonium chloride is described. Infrared, ultraviolet, and ^{1}H NMR spectra of the prepared compounds forming strong intramolecular hydrogen bonds are interpreted.

Описан синтез замещенных тиофосфорилгидразинов и *O,O*-диалкилфосфорилгидразинов посредством реакции гидразингидрата с диалкил(диарил)- или алкил(алкиламино, диалкиламино)хлортиофосфатами и с диалкилфосфонатами в присутствии карбоната калия и хлорида триэтилбензиламмония. Обсуждаются инфракрасные, ультрафиолетовые и ^{1}H ЯМР спектры полученных соединений, образующих прочные внутримолекулярные водородные связи.

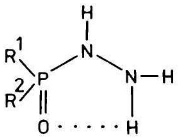
There are several papers in the literature dealing with the synthesis of some thiophosphorylhydrazines [1] and substituted phosphorylhydrazines [2—5].

The aim of the present work was a study of the synthesis and properties of substituted thiophosphoryl- and phosphorylhydrazines. The prepared compounds were used as starting compounds in the synthesis of pesticides. In the present work substituted thiophosphorylhydrazines were prepared by the reaction of chlorothiophosphates with hydrazine hydrate. Substituted phosphorylhydrazines were prepared by the reaction of dialkyl phosphonates with hydrazine hydrate using the solid—liquid phase-transfer catalysis in the presence of anhydrous potassium carbonate and triethylbenzylammonium chloride in the mixture of solvents (dichloromethane and tetrachloromethane) [2]. The prepared compounds could be distilled without decomposition only under high vacuum.

In the IR spectra of the prepared substituted thiophosphoryl- (*I—XIX*) and phosphorylhydrazines (*XX—XXI*) three bands in the region of $\tilde{\nu} = 3200—3430\ \text{cm}^{-1}$ (Table 1) are observed. The bands at the largest and smallest wavenumbers belong to the vibrations of the NH_2 groups involved in the intramolecular hydrogen bonding with the sulfur and oxygen atoms of the P=S and P=O groups, respectively.



I-XIX

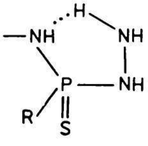


XX-XXI

$\nu_{as}(NH_2)$, $\tilde{\nu}/\text{cm}^{-1}$:	3400—3423	3416—3423
$\nu_s(NH_2)$, $\tilde{\nu}/\text{cm}^{-1}$:	3162—3307	3216—3226
$\nu(NH)$, $\tilde{\nu}/\text{cm}^{-1}$:	3351—3384	3332—3353

The assignment of these bands was done on the basis of the relatively high wavenumber differences of $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands, $\Delta\tilde{\nu} = 197—200\ \text{cm}^{-1}$ (*XX—XXI*), $\Delta\tilde{\nu} = 141—180\ \text{cm}^{-1}$ (*I—XIX*) as well as of the IR spectra of similar compounds [6]. The value ε of the $\nu(NH_2)$ and $\nu(NH)$ bands was found virtually not to alter with all the compounds studied in the concentration range $c \approx 10^{-2}—10^{-3}\ \text{mol dm}^{-3}$ in chloroform, this being as evidence that an intramolecular hydrogen bonding was involved. Similarly, the same situation was observed when the IR spectra of compound *I* were measured in tetrachloromethane in the range of concentrations $c \approx 10^{-3}—10^{-4}\ \text{mol dm}^{-3}$.

In the IR spectra of compounds *X*, *XI*, and *XIX* containing the alkylamino and dialkylamino groups, respectively, higher $\Delta\tilde{\nu}$ values ($\Delta\tilde{\nu} = 159\ \text{cm}^{-1}$, $169\ \text{cm}^{-1}$, and $172\ \text{cm}^{-1}$) are observed, which can be explained by the presence of the N—H···N intramolecular hydrogen bond



The highest $\Delta\tilde{\nu}$ values are observed with compounds having the P=O groups ($\Delta\tilde{\nu} = 197\ \text{cm}^{-1}$ and $200\ \text{cm}^{-1}$) pointing out that the P=O group forms stronger hydrogen bonds than the P=S group [7—10]. The ν(P=S) and the ν(P=O) bands

Table 1

Infrared and ultraviolet spectral data of substituted thiophosphoryl and phosphorylhydrazines

Compound	R^1	R^2	$\tilde{\nu}/\text{cm}^{-1}$				$\Delta\tilde{\nu}/\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\log(\varepsilon/(\text{m}^2\,\text{mol}^{-1}))$
			$\nu_{as}(NH_2)$	$\nu(NH)$	$\nu_s(NH_2)$	$\nu(P{=}S)$			
I	CH_3O	i-C_4H_9O	3419	3384	3264	644	155	210.5	1.86
II	C_2H_5O	CH_3O	3411	3361	3280	653	131	208.5	2.11
III	C_2H_5O	C_2H_5O	3416	3364	3281	643	135	208.5	2.05
IV	C_2H_5O	C_3H_7O	3421	3356	3281	661	140	209.5	1.79
V	C_2H_5O	i-C_3H_7O	3417	3366	3277	643	140	210.0	1.91
VI	C_2H_5O	i-C_4H_9O	3423	3364	3266	659	157	209.5	1.88
VII	C_2H_5O	C_2H_5	3400	3356	3259	643	141	213.5	2.21
VIII[a]	C_2H_5O	C_6H_5	3409	3353	3264	640	145	211.0	2.62
IX	C_2H_5O	$C_2H_5OCH_2CH_2O$	3421	3351	3291	644	133	210.0	1.87
X	C_2H_5O	i-C_3H_7NH	3416	3367	3257	661	159	211.0	2.38
XI	C_2H_5O	$(C_2H_5)_2N$	3412	3380	3243	701	169	209.5	2.50
XII	C_3H_7O	C_3H_7O	3410	3365	3261	648	149	211.0	2.10
XIII	i-C_4H_9O	i-C_4H_9O	3421	3361	3277	661	144	209.5	1.89
XIV	C_6H_5O	C_6H_5O	3352	3308	3162	642	190	224.5	1.91
XV	$C_2H_5OCH_2CH_2O$	CH_3O	3413	3358	3281	643	132	211.0	1.91
XVI	$CH{\equiv}CCH_2O$	C_2H_5O	3417	3356	3307	624	110	208.5	2.14
XVII	$CH{\equiv}CCH_2O$	i-C_3H_7O	3421	3356	3309	626	114	208.0	2.15
XVIII	$ClCH_2CH_2O$	C_3H_7O	3416	3356	3267	660	149	209.0	1.96
XIX	$(CH_3)_2N$	i-C_4H_9O	3417	3383	3245	706	172	211.0	1.55
XX[b]	C_3H_5O	C_2H_5O	3423	3332	3226	—	197	211.5	1.33
XXI[b]	C_4H_9O	C_4H_9O	3416	3353	3216	—	200	212.0	1.48

a) Measured in acetonitrile; *b*) $\nu(P{=}O)$, $\tilde{\nu}/\text{cm}^{-1}$: *XX* — 1229 and *XXI* — 1247.

Table 2

Characterization of the prepared thiophosphoryl- and phosphorylhydrazines

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%			$n(\lambda_D, 20\ °C)$ Yield/%
			N	S	P	
I	$C_5H_{15}N_2O_2PS$	198.22	14.20	16.25	15.71	1.5220
			14.24	16.28	15.14	87.3
IV	$C_5H_{15}N_2O_2PS$	198.22	13.74	16.42	15.52	1.4931
			14.13	16.18	15.63	96.8
V	$C_5H_{15}N_2O_2PS$	198.22	14.13	16.17	15.63	1.4935
			14.63	16.63	15.34	99.1
VI	$C_6H_{17}N_2O_2PS$	212.25	13.19	15.11	14.59	1.4920
			13.42	15.28	15.58	89.7
VII	$C_4H_{13}N_2OPS$	168.21	16.65	19.06	18.41	1.5350
			16.37	18.86	18.14	53.6
VIII	$C_8H_{13}N_2OPS$	216.19	12.95	14.82	14.33	1.5935
			12.58	14.88	13.78	90.4
IX	$C_6H_{17}N_2O_3PS$	228.26	11.66	13.34	12.89	1.4995
			12.27	14.04	13.57	79.4
X	$C_5H_{16}N_3OPS$	197.24	21.31	16.26	15.71	1.5122
			21.81	16.60	16.21	66.9
XI	$C_6H_{18}N_3OPS$	211.27	19.89	15.18	14.66	1.5102
			19.97	15.65	14.48	93.4
XII	$C_6H_{17}N_2O_2PS$	212.25	13.20	15.11	14.60	1.4940
			13.39	15.40	14.56	93.8
XIII	$C_8H_{21}N_2O_2PS$	240.26	11.66	13.34	12.85	1.4846
			11.77	13.23	12.94	96.7
XIV	$C_{12}H_{13}N_2O_2PS$	280.28	9.90	11.14	11.05	1.5240
			9.97	11.34	10.85	98.1
XV	$C_5H_{15}N_2O_3PS$	214.76	13.07	14.97	14.46	1.5134
			13.76	15.31	14.12	72.7
XVI	$C_5H_{11}N_2O_2PS$	194.22	14.42	16.51	15.95	1.5270
			13.92	16.98	15.61	85.9
XVII	$C_6H_{13}N_2O_2PS$	208.13	13.46	15.41	14.88	1.5160
			13.46	15.22	14.19	90.9
XVIII	$C_5H_{14}ClN_2O_2PS$	232.67	12.03	13.78	13.31	1.5238
			11.90	14.05	13.98	82.6
XIX	$C_6H_{18}N_3OPS$	211.27	19.89	15.17	14.66	1.4910
			19.47	15.31	14.39	96.5
XXI	$C_8H_{21}N_2O_3P$	224.23	12.49	—	13.81	1.4502
			12.39		13.46	99.7

of the prepared compounds are observed in the region of $\tilde{\nu}$ = 626—706 cm^{-1} and $\tilde{\nu}$ = 1229—1247 cm^{-1}, respectively.

In the UV spectra of the studied compounds (Table 2) relatively strong bands are observed in the region of λ = 208—224 nm (log (ε/(m^2 mol^{-1})) = 1.55—2.62 (*I—XIX*) and log (ε/(m^2 mol^{-1})) = 1.33 and 1.48 (*XX, XXI*).

Experimental

IR spectra of the compounds prepared were recorded with a Specord IR 71 instrument (Zeiss, Jena) in chloroform ($c \approx 10^{-2}$—10^{-3} mol dm^{-3}) and in tetrachloromethane ($c \approx 10^{-3}$—10^{-4} mol dm^{-3}). The wavenumber calibration was checked against the spectrum of polystyrene. UV spectra were recorded with a Unicam SP 8000 in methanol ($c = 2 \times 10^{-5}$—5.5×10^{-5} mol dm^{-3}).

Thiophosphorylhydrazines (I—XIX)

To hydrazine hydrate (0.3 mol) in water (10 cm^{-3}) dialkyl chlorothiophosphate (0.1 mol) was added with stirring at 35—40 °C and the reaction mixture was stirred for 1—3 h at 40 °C. The completion of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was cooled, water (100 cm^3) and chloroform (100 cm^3) were added. The chloroform layer was washed with water (3 × 100 cm^3), dried with sodium sulfate, chloroform, and unreacted starting compounds were distilled off under reduced pressure and the residue crystallized from cyclohexane.

O,O-Dialkylphosphorylhydrazines (XX and XXI)

To a mixture of tetrachloromethane (120 cm^3), dichloromethane (200 cm^3), anhydrous finely powdered potassium carbonate (41.4 g; 0.3 mol), and triethylbenzylammonium chloride (4 g; 17.5 mmol) a solution of hydrazine hydrate (12.5 g; 0.2 mol) was added dropwise with stirring at 20—25 °C. After addition of hydrazine hydrate, stirring was continued for 15 min and then dialkyl phosphonate (0.2 mol in 40 cm^3 of dichloromethane) was added. After addition the stirring was continued for 4 h at room temperature. Potassium carbonate was filtered off and washed with dichloromethane. The solvent was distilled off under reduced pressure and the residue crystallized from cyclohexane.

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