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Sorption Properties of Phosphorylated Indoles

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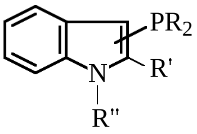
Abstract—Sorption properties of 1- and 3-substituted indoles containing a P(III) atom were estimated by gas chromatography. The sorption properties were shown to depend on the nature of substituents on the phosphorus atom.

It is known that the sorption properties of organophosphorus compounds are determined by their molecular structure. These properties primarily depend on the nature and steric arrangement of substituents on the phosphorus atom [1]. Gas-chromatographic separation of polar compounds on organophosphorus sorbents involves the donor–acceptor interaction of the analytes with the lone electron pair of P(III) [2].

The sorption properties of compounds **I**–**VIII** were evaluated by GLC using reference sorbates. The physicochemical and sorption characteristics of **I**–**VIII** are listed in Table 1.



I–VIII

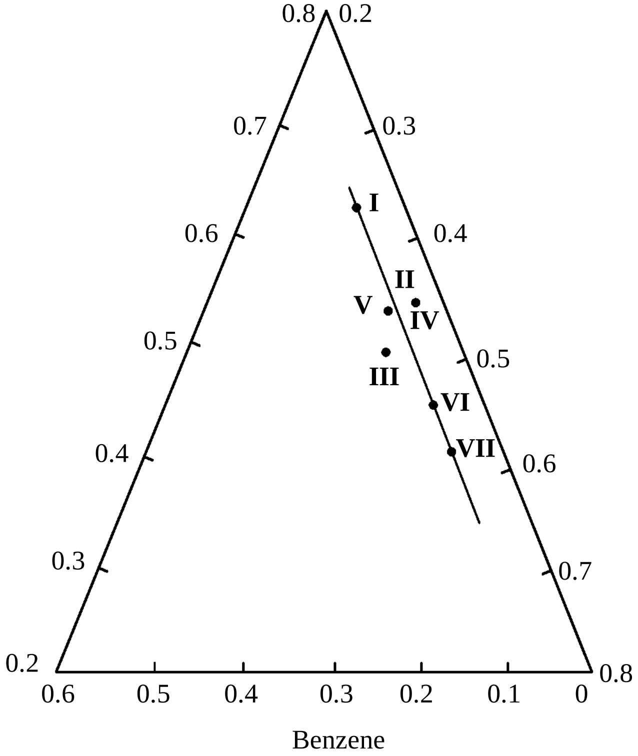
I–IV (C^3PR_2), **V–VIII** (NPR_2); R = OEt (**I, V**), OPr (**II, VI**), OPh (**III, VII**), NEt_2 (**IV, VIII**); R' = H (**I–III**, **V–VIII**), Me (**IV**); R" = H (**I–IV**), PR_2 (**V–VIII**).

Yields, constants, ^{31}P NMR spectra, and soprtion characteristics of phosphorylated indoles **I–VIII**

Comp. no.	Yield, %	bp, °C (*p*, mm)	n_D^{20}	d_4^{20}	MR_D		^{31}P NMR spectrum, δ_P, ppm
					found	calculated	
I	43	69–70 (1)	1.5002	1.0359	67.37	66.71	142
II	42	76–78 (0.9)	1.5010	1.0256	76.12	75.96	143
III	48	70–71[a]	–	–	–		152
IV	34	151–152 (0.6)	1.5620	1.0472	93.12	94.40	94
V	59	92–93 (0.6)	1.5420	1.1086	67.35	66.71	128
VI	50	103–104 (0.7)	1.5438	1.0975	76.29	75.96	128
VII	47	78–80 (0.07)	1.5440	1.0723	98.13	97.57	140
VIII	76	126–128 (0.5)	1.5603	1.0288	90.59	89.78	101

Comp. no.	GLC retention index			Found, %		Formula	Calculated, %	
	benzene	ethanol	nitromethane	N	P		N	P
I	7.32	8.40	9.12	6.10	12.94	$C_{12}H_{16}NO_2P$	5.90	13.08
II	7.16	8.11	9.01	5.35	11.59	$C_{14}H_{20}NO_2P$	5.28	11.70
III	7.63	8.68	9.60	4.48	9.45	$C_{20}H_{16}NO_2P$	4.20	9.31
IV	7.02	8.03	9.00	14.08	9.92	$C_{17}H_{28}N_3P$	13.75	10.14
V	6.18	7.15	8.60	5.38	13.20	$C_{12}H_{16}NO_2P$	5.90	13.08
VI	6.04	7.00	8.22	5.48	11.67	$C_{14}H_{20}NO_2P$	5.28	11.70
VII	6.48	7.71	8.92	4.32	9.47	$C_{20}H_{16}NO_2P$	4.20	9.31
VIII	6.32	7.50	8.10	14.93	10.35	$C_{16}H_{26}N_3P$	14.44	10.65

[a] Melting point.



Retention fractions for indole derivatives **I–VII**.

As follows from the table, substituents on the P(III) atom affect the sorption properties of compounds **I**–**VIII**. The retention indices increase with increasing alkoxyl chain length and decrese in going from alkoxyl to aroxyl substituents on phosphorus.

Obviously, both electron donors and electron acceptors can interact with two centers: phosphoryl group and/or nitrogen atom.

To assess the contributions in the sorption properties of different-in-nature intermolecular interactions, we constructed a tringlular graph [3] whose scales are fractions calculated from the retention times of benzene, ethanol, and niromethane (see figure).

It is readily seen from the figure that in the benzene–ethanol–nitromethane coordinate system the points corresponding to the compounds studied fall in the range of low retention fractions, and the contribution of dispersion interaction is small ($\leq$0.15 retention fractions). From corresponding characteristics of benzene we obtain the contribution of π-donor interaction, which varies from 0.19 for P(OEt)$_2$ to 0.25 retention fractions for PN(Et)$_2$.

In the ^{1}H NMR spectrum of compound **I**, protons of the ethoxy group give a triplet at δ 1.01 ppm (J_{HH} 5 Hz) and a quartet at δ 3.90 ppm (J_{HH} 5 Hz), protons of the benzene ring give a multiplet at δ 7.30–7.85 ppm, and the =C^{2}H proton gives a signal at δ 7.26 ppm.

In the ^{13}C NMR spectrum of compound **VIII**, the signals of the benzene ring carbons neigboring to the phosphorus atom are split by C–P coupling; therewith, δ_C varies insignificantly and depends on the distance between the coupled atoms, ppm: **I** 111.8 (C^7), **VIII** (C^7, J_{HC^7} 9 Hz), **I** 136.1 (C^2), and **VIII** 139.3 (C^2, J_{HC^2} 14 Hz).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Brucker WP-80 spectrometer at 80 and 20.1 MHz, respectively, internal reference TMS. The ^{31}P NMR spectra were obtained on Brucker WP-80 (32.4 MHz) and RYa-2303 (24 MHz) spectrometers, reference 85% H_3PO_4.

Gas chromatography was performed on an LKhM-8MD chromatograph with a thermal conductivity detector, using 2-m columns packed with phosphorylated indole derivatives on a Chromaton (15 wt%). The sorbtion properties of compounds **I**–**VIII** were evaluated by the Rohrschneider method [1]. The contributions into the sorption properties of the compounds were evaluated using a triangular coordinate system [3]. The fractions were calculated directly from the retention times of reference sorbates.

Diethyl (3-indolyl) phosphonite (I) [4], (3-indolyl) dipropyl phosphonite (II), (3-indolyl) diphenyl phosphonite (III), and (2-methyl-3-indolyl) tetraethylphosphonodiamidite (IV) were prepared from 0.05 mol of (3-indolyl)magnesium iodide and, respectively, diethyl phosphorochloridite, dipropyl phosphorochloridite, diphenyl phosphorochloridite, and diamidophosphorous chloride in absolute ether with vigorous stirring (0°C) under argon. The Grignard reagent was prepared from 0.05 mol of magnesium, 0.05 mol of methyl iodide, and 0.05 mol of indole (2-methylindole). The reaction mixture was decomposed with aqueous ammonium chloride and hydrochloric acid, which were preliminarily cooled to 0°C. The ethereal layer was separated, washed with a sodium hydrocarbonate solution, and dried with sodium sulfate. The ether was removed at reduced pressure. Compounds **I**, **II**, and **IV** were purified by distillation, and compound **III**, by reprecipitation from ethanol into water (pH 6).

Diethyl (1-indolyl)phosphite (V), dipropyl (1-indolyl)phosphite (VI), diphenyl (1-indolyl)phosphite (VII), and (1-indolyl) tetraethylphosphorodiamidite (VIII) [5] were prepared from 0.01 mol of indole and 0.01 mol of diethyl diethylphosphoramidite, dipropyl diethylphosphoramidite, diphenyl diethylphosphoramidite, and hexaethylphosphorous triamide, respectively, under dry argon at 135–140°C. The reaction products were purified by double distillation at atmospheric pressure.

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