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DIPOLE MOMENTS OF ORGANOPHOSPHORUS COMPOUNDS.

16. CONFORMATIONS OF TRIMETHYLSILYL GROUPS IN SOME PHOSPHITES, PHOSPHATES, AND PHOSPHONATES

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Studies of the isomerism arising from rotation around the P-X bond have been largely limited to compounds of three- or four-coordinated phosphorus with alkyl group substitution at the X atom [1-4]. It has been shown that conformations with R-X and $\mathrm{P}\overset{\downarrow}{=}\mathrm{Y}$ groups in gauche orientation are energetically preferred here [2-4].

The present work was a study of the geometrical structures of organophosphorus compounds containing the bulky, polar trimethylsilyl group $[(CH_3)_3SiO]_3P{=}Y$ with Y = UEP, the unpaired unshared electron pair (I), O (II), S (III), Se (IV); $[(CH_3)_3SiO]_2P(Y)C_6H_5$, Y = UEP (V), O (VI), S (VII), Se (VIII); $(CH_3)_3SiOP(Y)(OC_2H_5)_2$, Y = UEP (IX), O (X), S (XI), Se (XII).

Tris(trimethylsilyl) phosphate (II) has been studied earlier [5], using an additive scheme based on m(P → O) 1.2 D. We, however, calculated the dipole moments (DM) of compounds (I)-(XII) using a more exact value of the O-P bond polarity, namely 0.6 D [1].

Dipole moments and Kerr constants were measured for tris(trimethylsilyl) phosphate (II), thiophosphate (III), and selenophosphate (IV); using an additive scheme, the same parameters were calculated for conformers differing in the relative orientation of trimethylsilyl group and P=Y bond (Fig. 1).

The conformations with two $(CH_3)_3Si$ groups in trans (t) and gauche$_2$ (g_2) positions are destabilized by 1,3-parallel interaction. Since the gauche (g) and cis (c) forms are not separated by an energy barrier, it is impossible that they exist in equilibrium with one another. For this reason, consideration was limited to the following geometrical structures in the case of compounds with three nonregular substituents: ccc, tcc, $g_1g_2g_1$, tg_1g_1, tg_1g_2. Calculation of the DM's of the various conformers was carried out with the following values of the valence angles at the phosphorus atom: $\angle$O-P-O 104°, $\angle$O=P-O 115° [6]. Values of the DM for the P=O, P=S, and O-P bonds (2.95, 2.62, and 0.60, respectively) were taken from [1]. The $(CH_3)_3Si$-O group moment (1.10 D) was calculated from the measured DM of hexamethyldisiloxane (0.68 D), the Si-O-Si valence angle being assumed equal to 144° [7]. Comparison of the experimental and calculated values of the DM's of the various conformations of compounds (II)-(IV) (Table 1) showed the predominant conformation for (II) to be that with the phosphoryl and

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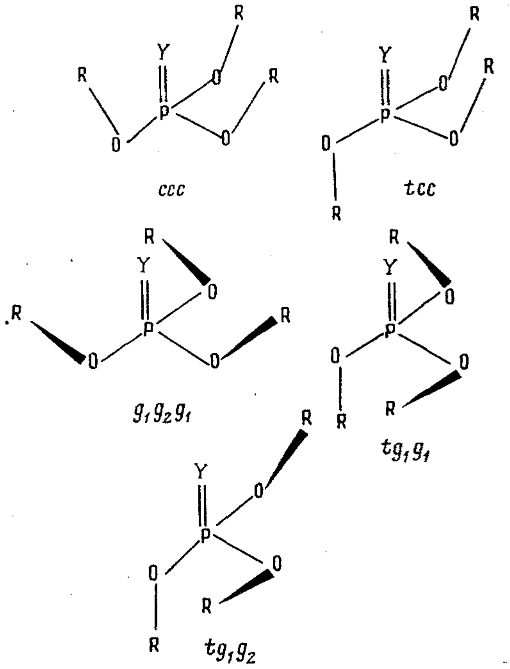

Fig. 1. Possible phosphate conformations [R=$(CH_3)_3Si$].

trimethylsilyl groups in cis orientation. Lacking knowledge of the P-O-Si valence angle in these compounds, the latter was varied from 120 to 144° in the DM calculation of the phosphate (II) (in analogy with the P-O-Si [7] and P-O-C [6] angles, where 130° is the mean). In any event, the calculated moment for the form with gauche-oriented $(CH_3)_3SiO$ group was considerably higher than the measured value. The calculations thus showed preferential cis orientation of the trimethylsilyl group with respect to the P=O bond.

For similar reasons, the thiophosphate (III) would be logically assumed to be a conformational equilibrium mixture of ccc and tcc forms.

An original method of calculating multiple bond moments has been developed in connection with the work of [1] on the DM's of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane 1-oxide and sulfide [8]. Since the analogous selenide is not known at the present time, other model compounds were used for calculating the P=Se bond moment [2, 9]. Values of the DM based on m(P=Se) 3.73 D [9] proved to be considerably higher than the measured DM. Analysis of the results obtained with the more trustworthy value, m(P=Se) 3 D [2], suggested that it is again the cis orientation of the trimethylsilyl group with respect to the P=Se bond which predominates.

Measured values of the Kerr constant were used to select forms sensitive to conformation changes. The following components of polarizability were used in calculating Kerr constants for the various conformations: for the O_3PO phosphate group, b_1 (along the axis of symmetry) = 4.16, $b_2 = b_3 = 2.84$ Å^3; for the thiophosphate group, $b_1 = 8.69$, $b_2 = b_3 = 4.92$ Å^3 [10]. For polarizability ellipsoid of the $(CH_3)_3SiO$ group; b_1 (along the Si-O bond) = 9.13, $b_2 = 8.65$, and $b_3 = 9.83$ Å^3, values determined in our earlier work [11]. Measured and calculated KC values are shown in Table 1. Combined treatment of the data on DM's and KC's for the phosphate (II) and the thiophosphate (III) through graphs similar to that of Fig. 2 definitely showed that it was here a matter of an equilibrium between conformers with preferential cis orientation of the trimethylsilyl group with respect to the P=Y bond.

The fact that passage from liquid to solid states did not lead to the disappearance of bands from the IR spectra of compounds (II)-(IV) was an indication, first, of the presence of essentially a single isomer in the liquid and dissolved states, and second, of identity of isomer spectra in the region from 400 to 3600 cm^{-1}. Let us now discuss this latter point in terms of the DM and KC data. The absorption spectra of (I)-(IV) showed the following bands for the $(CH_3)_3Si$ group: a doublet at $\sim$1255-1265 cm^{-1} ($SiCH_3$ deformation vibrations): 850 and 770 cm^{-1} (Si-C bond stretching vibrations); 1428, 1463, 1480, 2855, 2907, and 2967 cm^{-1} (CH_3 group deformation and stretching vibrations); for the Si-O-C fragment, 1030 and 1070 cm^{-1}. Bands primarily related to $P(-O-)_3$ fragment vibrations were also observed in the 650-800 cm^{-1} region of the spectrum. The bands at 1278 cm^{-1} (liquid) and 1270 cm^{-1} (solid) in the spec-

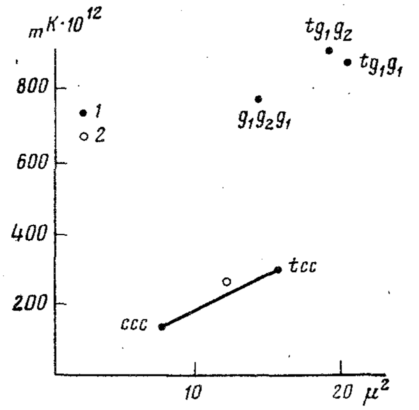

Fig. 2. Comparison of calculated (1) and measured (2) Kerr constants and second-power dipole moments of (III).

trum of (II) were assigned to $\nu_{P=O}$. It has been suggested in [12] that $\nu_{P=O}$ should be assigned to the 1254-1278 cm^{-1} doublet in the spectrum of (II), from which it would then follow that (II) is itself a mixture of two isomers, in the liquid state and in solution. Study of the spectra of (I)-(IV) showed that this assignment, and the conclusions based on it, are in error, the band at 1254 cm^{-1} undoubtedly arising from deformational vibrations in the Si-CH$_3$ group. The 647 cm^{-1} band in the spectrum of (III) was assigned to $\nu_{P=S}$.

Similar results came out of a study of the isomerism arising from rotation around the P=O bond in the phosphonates (VI)-(VIII). Dipole moments for these compounds were measured in benzene solution at 25°C. Dipole moments were also calculated for the six most probable conformations with cis, gauche, and trans orientation of the $(CH_3)_3SiO$ group relative to the P=Y bond (Table 2).

Calculations were carried out with the following values of the valence angles at the phosphorus atom: O-P-O = 104°, C-P=O, 115° [4]. The P-Ph group moment (1.18 D) was calculated from the measured DM for the triphenylphosphine [13]. It is clear from the calculations that the preferred form of the phosphonate (VI) is that in which the P=O and $OSi(CH_3)_3$ groups are in cc configuration. The measured values of the DM for the thiophosphonate (VII) and the selenophosphonate (VIII) were close to those calculated for the g_1g_1 conformation. It is, however, difficult to believe that the conformation would change so radically on passing from the phosphonate to the thio- and selenophosphonates. It would be more reasonable to assume that (VII) and (VIII) exist predominantly in structures with cis orientation of the P=Y and $(CH_3)_3SiO$ groups (cf. Table 2).

Thus, in compounds containing four-coordinated phosphorus, the trimethylsilyl group is preferentially cis-oriented with respect to the P=Y bond, differing in this respect from the alkyl radicals. Similar conclusions have been reached through study of $(CH_3)_3SiO$ group orientation in the 1,3,2-dioxaphospholanes [14].

Since the trimethylsilyl group preferentially enters into the cis position, and alkyl group preferentially into the gauche orientation with respect to the P=Y bond, it can be expected that the same would be true even if both groups are present in the molecule together. We have therefore studied the geometrical structures of O,O-diethyl O-trimethylsilyl phosphate (X), thiophosphate (XI), and selenophosphate (XII). Dipole moments for these compounds

TABLE 1. Experimental and Calculated Values of the DM and KC for the Phosphites (I) and (IX), and the Phosphates (II)-(IV)

Compound	Parameter	Conformation					Experiment
		ccc	tcc	$g_1g_2g_1$	tg_1g_1	tg_1g_2	
(I)	μ, D	0,66	1,02	1,89	2,44	2,11	1,86
(II)	μ, D	3,12	4,34	4,16	4,94	4,82	3,09 (CCl_4) 3,14 (C_6H_6)
(III)	$_mK\cdot10^{12}$	43	−24	506	413	432	−8
	μ, D	2,76	3,99	3,83	4,58	4,46	3,47 (CCl_4) 3,51 (C_6H_6)
(IV)	$_mK\cdot10^{12}$	144	299	779	895	920	261
	μ, D	3,14	4,37	4,18	4,96	4,86	3,65 (CCl_4) 3,73 (C_6H_6)
(IX)	μ, D	0,32	1,21	1,73	1,98	1,66	1,80

TABLE 2. Experimental and Calculated Values of the DM for the Phosphonite (V), and the Phosphonates (VI)-(VIII)

Compound	μ_{calc}, D					μ_{exp}, D
	cc	g_1g_1	g_1g_2	tg_1	tg_2	
(V)	1,23	1,36	1,71	2,34	2,47	1,57
(VI)	3,55	4,01	4,15	4,95	5,05	3,40
(VII)	3,26	3,70	3,86	4,67	4,75	3,65
(VIII)	3,64	4,08	4,23	5,06	5,15	3,97

were measured in C_6H_6 at 25°C, and calculated for the various possible conformers (Table 3). The value of the C_2H_5O group moment (1.10 D) was obtained for the measured DM for diethyl ether [13] and used in these calculations.

Comparison of the measured and calculated moments indicated that the phosphonates (X)-(XII) exist in forms with the trimethylsilyl group in cis orientation, and the two ethyl groups in gauche orientation, with respect to the P=Y bond.

The DM method was also used to study the structures of the phosphites (I) and (IX), and the phosphonate (V), three-coordinated phosphorus compounds containing trimethylsilyl groups. Measured values of the DM for these compounds, together with values calculated from the additive vector scheme, are shown in Tables 1 and 2. The O-P-O and C-P-O valence angles in the phosphites were assumed equal to 96.5 and 120°, just as in [6]. The C-P-O angle in the phosphonite (V) was assumed equal to 99°, in analogy with the C-P-C angle in trimethylphosphine [6]. Analysis of the data of Tables 1 and 2 indicated that the $(CH_3)_3SiO$ group in three-coordinated phosphorus compounds is gauche-oriented with respect to the unshared electron pair of the phosphorus atom, just as the alkoxy group.

EXPERIMENTAL

All operations were carried out in an atmosphere of dry argon. The ^{31}P NMR spectra were obtained with an NMR-KGU-4 system (10.2 MHz), using 85% H_3PO_4 as an internal standard. Compounds (I) and (V) were prepared by the methods of [15] and [16], reacting trimethylsilyldiethylamine with the requisite hydrophosphoryl derivative. The phosphite (IX) was synthesized by the procedure of [17], reacting sodium diethylphosphite with trimethylchlorosilane in benzene. Compounds (II) and (IV) were obtained by boiling an excess of trimethylchlorosilane with either H_3PO_4 or $PHP(O)(OH)_2$. The phosphate (X) was synthesized by reacting trimethylsilyldiethylamine with diethyl phosphate. Each of the S and Se compounds were obtained through interaction of equimolar quantities of sulfur (or selenium) with the three-coordinated phosphorus derivative. Each compound was purified by being shaken with sodium for several hours at 110°C and then subjected to vacuum distillation, the entire procedure being twice repeated. Purity was checked by gas—liquid chromatography on a Chrom-4 system.

The characteristic constants of the silyl esters are summarized in Table 4.

Dipole moments and Kerr constants were determined in CCl_4 and C_6H_6, working at 25°C.

The IR spectra were obtained with a UR-20 spectrometer (400-3600 cm^{-1}), following the method of [18] and working with solid samples prepared by cooling liquid films to —140°C.

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TABLE 3. Experimental and Calculated Values of the DM for the Phosphates (X)-(XII)

Compound	μ_{calc}, D					μ_{exp}, D
	$g_1g_2g_1$	tg_1g_1	tg_1g_2	cg_2g_1	cg_1g_1	
(X)	3,43	4,34	4,41	3,27	3,44	3,29
(XI)	3,40	3,99	4,06	3,03	3,12	3,23
(XII)	3,45	4,36	4,43	3,29	3,41	3,22

TABLE 4. Silyl Esters of Phosphorus Acids

Compound	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Found, %				Empirical formula	Calculated,				δ_P, ppm
				C	H	P	Si		C	H	P	Si	
(I)	79 (11)		1,4107										−116
(II)	77 (0,07)	0,9589	1,4092	34,10	8,30	9,88	26,79	$C_9H_{27}O_4PSi_3$	34,37	8,65	9,85	26,79	27
(III)	48 (0,06)	0,9715	1,4349	32,68	7,89	9,38	25,42	$C_9H_{27}O_3PSSi_3$	32,70	8,23	9,37	25,49	−32
(IV)	62 (0,06)	1,0937	1,4497	29,27	7,13	8,22	22,28	$C_9H_{27}O_3PSeSi_3$	28,64	7,21	8,21	22,32	−22
(V)	57 (0,07)		1,4762										−141
(VI)	77 (0,06)	1,0249	1,4703	47,96	7,92	10,62	19,25	$C_{12}H_{23}O_3PSi_2$	47,65	7,66	10,24	18,57	0
(VII)	76 (0,06)	1,0356	1,4991	45,30	7,30	9,76	17,64	$C_{12}H_{23}O_2PSSi_2$	45,25	7,28	9,72	17,63	−62
(VIII)	73 (0,06)	1,1733	1,5166	39,91	6,37	8,41	15,36	$C_{12}H_{23}O_2PSeSi_2$	39,44	6,34	8,46	15,37	−60
(IX)	57 (11)		1,4118										−126
(X)	95 (10)	1,0179	1,4083	37,19	8,57	13,17	11,88	$C_7H_{19}O_4PSi$	37,15	8,46	13,69	12,41	4
(XI)	52 (0,06)	1,0272	1,4433	35,01	7,80	12,15	10,96	$C_7H_{19}O_3PSSi$	34,69	7,90	12,78	11,59	−57
(XII)	56 (0,06)	1,2060	1,4630	30,24	6,76	10,79	9,75	$C_7H_{19}O_3PSeSi$	29,07	6,62	10,71	9,71	−55

CONCLUSIONS

1. A study has been made of the dipole moments, Kerr constants, and IR spectra of silicon-containing phosphites, phosphates, and phosphonates.

2. The silicon-containing phosphates and phosphonates exist as equilibrium mixtures of various conformers, the predominant form being that in which the P=O (S, Se) and $(CH_3)_3SiO$ groups are in cis orientation.

3. The trimethylsilyl group preferentially occupies a gauche position with respect to the unshared electron pair of the phosphorus atom in compounds containing phosphorus in three-coordination.

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