TWIST FORM IN EQUILIBRIUM OF STEREOISOMERS OF 5-PHENYL-2,4,6-TRIISOPROPYL-1,3,5-DIOXAPHOSPHORINANE AND ITS DERIVATIVES

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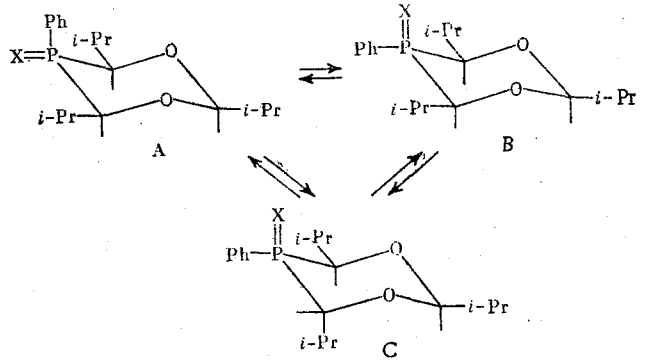
Previously it was shown that three stereoisomers are present in the equilibrium of the stereoisomers of 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (I), its oxide (II), and its sulfide (III) [1, 2]. The amount of stereoisomers with equivalent protons on the C atoms attached to phosphorus and an axial (A) and equatorial (B) orientation of the Ph, and also of the stereoisomer with nonequivalent protons on the C atoms attached to phosphorus (C) is respectively 22, 64, and 14%, 54, 46 and 0%, and 0, 52 and 48% for (I)-(III). From a comparison of the equilibria of (I) and 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane, where the stereoisomer with an axial (a) orientation of the Ph on the P atom predominates, the theory was expressed that a repelling interaction exists between the α-phenyl and an equatorial (e) i-Pr group at the C–P bond in (I) due to a flattening of the phosphorus-containing fragment of 1,3,5-dioxaphosphorinanes [1]. To verify this theory it was necessary to determine the conformation of the C isomers of compounds (I)-(III). A chair conformation for C contradicts the given theory, since in them such repulsion is possible at both positions of Ph.



X = unshared electron pair (UEP) (I); O (II); S (III)

The (II) stereoisomers were synthesized in the present paper and a study was made of the steric structure of the (II) and (III) stereoisomers employing the dipole moment (DM) and PMR spectroscopy methods.

The (II) stereoisomers were obtained by the oxidation of (I) with H_2O_2. To establish the relation between the (I) and (II) stereoisomers we took samples of (I) with a variable ratio of the stereoisomers [products of the kinetic and thermodynamic control of the reaction for the preparation of (I)]. The relation between the (I) and (III) stereoisomers was previously established in a similar manner [2]. The structure of the latter was determined from the PMR spectra, and the (I) stereoisomers with δ ^{31}P 38 and 62 ppm were assigned the chair conformation with e-isopropyl groups and respectively an α- and e-orientation of the Ph on the P atom (A and B). Only the nonequivalence of the protons on the C atoms attached to the P atom was established for the (I) stereoisomer with δ ^{31}P 41 ppm (C). The oxidation of (I), containing larger amounts of the A and B stereosiomers, gave oxides with mp 57° (δ ^{31}P –16 ppm in CH_3CN) and 215° (δ ^{31}P –12 ppm in CH_3CN). In addition, from (I), containing substantial amounts of the C stereoisomer, we isolated an oxide with mp 129°

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TABLE 1. Experimental and Calculated Dipole Moments of (II) and (III) Stereoisomers

Conformation	Orientation of substituents	(II) μ, D		(III) μ, D	
		μ_{calc}	μ_{expt} (mp)	μ_{calc}	μ_{exp} (mp)
Chair	P=X$_e$	2,94	3,19 (57°)	3,43	3,43 (93°)
	P=X$_a$	5,33	5,69 (215°)	5,76	5,75 (146°)
Twist	4,6 *a, a*	4,61[1]; 3,76[2] *		5,04[1]; 4,17[2]	
	4,6 *e, e*	4,01; 4,35		4,44; 4,79	
	4,6 *a, e*	4,20; 3,95	3,59 (129°)	4,64; 4,39	4,60 (124°)
	4,6 *e, a*	4,40; 4,15		4,84; 4,59	

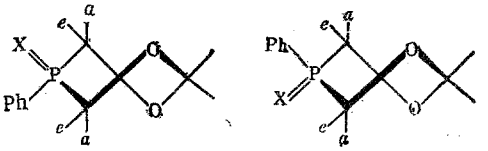
*1 and 2 = the DM of two twist forms, which differ in the position of the P=X bond relative to the remainder of the molecule, are given.

(δ ^{31}P −32 ppm in CH_3CN). The PMR spectra of the (II) stereoisomers (Fig. 1) proved to resemble the spectra of the (III) stereoisomers [2], which were obtained from the same samples. In the spectra of the stereoisomers with mp 57 and 215° the protons on the C atoms in positions 4 and 6 are equivalent, which confirms the chair conformation and the e-orientation of the i-Pr group on the given C atoms. According to the W rule [3], the zero value of the SSCC of the proton at C^2 with the nucleus of the P atom attests to an *a*-orientation of the proton and an e-orientation of the isopropyl. A comparison of the SSCC of the protons on the C atoms attached to the P atom, with the nucleus of the P atom having the similar SSCC values in the spectra of the stereoisomers of 5-oxo-5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane with a known structure [4], makes it possible to determine the orientation of the Ph. In the stereoisomer with mp 215° the Ph occupies an e-position, while in the stereoisomer with mp 57° it occupies an *a*-position. In the spectrum of the stereoisomer with mp 129° the protons on the C atoms attached to the P atom are nonequivalent. As a result, a genetic relation was established between stereoisomers (I) and (II), and (II) and (III).

The PMR spectra give adequate information regarding the steric structure of stereoisomers A and B of (II) and (III). However, they do not permit determining the conformation of the stereoisomer with nonequivalent protons on the C atoms attached to the P atom (C). This isomer can be assigned both the chair conformation, with one axial and the other an equatorial isopropyl group at C^4 and C^6, and the twist conformation. An analysis of the DM of the stereoisomers permits making a choice between these possibilities (Table 1).

The DM of the (II) and (III) stereoisomers were determined in CCl_4 [mp 215° (II) and 146° (III)] and in benzene [mp 57 and 129° (II), and 93 and 124° (III)] at 20°C. The values of the geometric parameters and bond polarities were taken from [4].

The data in Table 1 confirm the structure of the stereoisomers of (II) with mp 57 and 215°, and of (III) with mp 93 and 146°, as having the chair conformation with e-i-Pr groups and a different orientation of the Ph on the P atom. However, for the stereoisomers of (II) with mp 129°, and of (III) with mp 124°, the experimental DM does not agree with the calculated values for the chair conformation and can be explained by an equilibrium of the conformations in which the twist forms predominate. The conformal equilibrium of two chair forms which differ in the orientation of the Ph on the P atom is improbable, since in one of the conformations, which interchange via inversion, two *a*-i-Pr groups should be present. The boat conformation is energetically unfavorable due to the shielding at the C–P bond.



In the equilibrium of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane, its oxide, and its sulfide (IV)-(VI) are respectively 86 and 14%, 79 and 21%, and 92 and 8% of the stereoisomers present with an *a*- and an e-orientation of the Ph on the P atom and e-methyls [1]. A change in the position of the equilibrium when going from (IV)-(VI) to (I)-(III) was explained by the nonequivalence of the position of the *a*- and e-phenyl on the P atom relative to the e-substituents on the C^4 and C^6 atoms [1]. The appearance of the twist form in the equilibrium of (I)-(III) confirms the existence of a repelling interaction of the *a*-phenyl

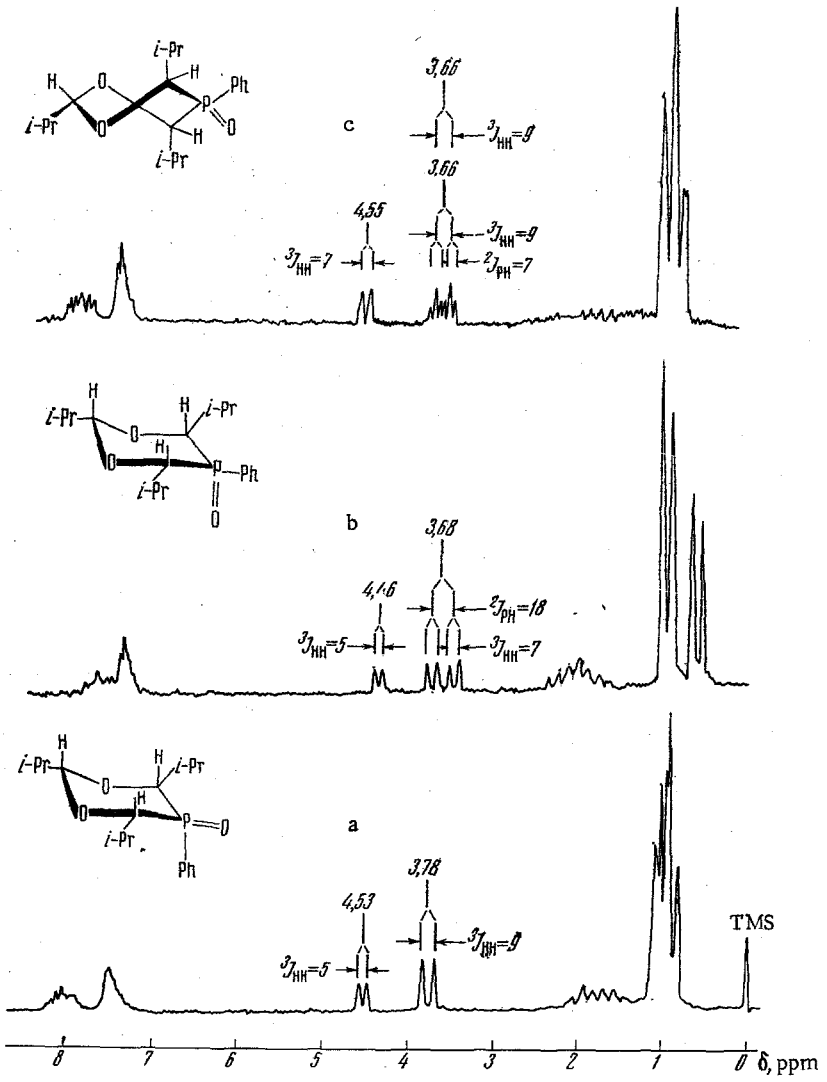


Fig. 1. PMR spectra of (II) stereoisomers in CCl_4: a) with mp 57°; b) with mp 215°; c) with mp 129°.

and e-isopropyl at the C–P bond. In (II) the syn-axial interactions of phenyl and the phosphoryl group becomes equalized and a larger amount of the conformer with an *a*-phenyl appears in the equilibrium. The thiophosphoryl group has greater steric requirements than the phosphoryl group. Since the existence of (III) in the conformation with an *a*-phenyl is difficult due to strain, together with the stereoisomer in the chair conformation with an e-phenyl on the P atom, the twist form appears in the equilibrium.

A predominance of the form with nonequivalent protons on the C atoms attached to the P atom was observed for the equilibrium of 5-benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane [5]. In harmony with our results it may be assumed that this is the twist form, caused by the interactions of the substituents on the P atom with the e-phenyl groups on the C atoms attached to the P atom in the chair conformation.

EXPERIMENTAL

The PMR spectra were recorded on a Varian T-60 spectrometer (60 MHz, 34.5°), using TMS as the internal standard. The ^{31}P NMR spectra were recorded on a KGU-4 NMR spectrometer (10.2 MHz), with noise decoupling from the protons at a frequency of 25.2 MHz. The samples represented 5 vol. % solutions in the indicated solvents.

The dipole moments were determined as described in [6]. The coefficients of the calculation equations were: $\alpha = 20.0084$ and $\gamma'' = 0.2559$, $\alpha = 4.4180$ and $\gamma'' = -0.0074$, $\alpha = 3.4968$ and $\gamma'' = 0.0010$, respectively, for the stereoisomers with mp 215, 129 and 57° (II), and $\alpha =$

7.1058 and $\gamma'' = 0.2410$, $\alpha = 19.6456$ and $\gamma'' = 0.4084$, $\alpha = 12.7756$ and $\gamma'' = 0.4245$ for the stereoisomers with mp 93, 146 and 124° (III).

5-Phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (I). To 17 g (0.15 mole) of phenylphosphine in an argon atmosphere were added 10 ml of MeOH, 50 ml (0.55 mole) of isobutyraldehyde, and 5 ml of conc. HCl. The mixture was left standing overnight. The next day the volatile components were removed in vacuo, and the residue was dissolved in 50 ml of C_6H_6 and washed first with 1 N KOH solution to pH 9-10, and then with water until neutral. The solvent was removed in vacuo, and the residue was distilled. The yield of (I) was 42 g (88%), bp 100-105° (0.1 mm), n_D^{18} 1.5189, δ ^{31}P 38; 41; 62 ppm. Found: P 10.26%. $C_{18}H_{29}O_2P$. Calculated: P 10.05%.

5-Phenyl-5-oxo-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (II). With stirring and cooling, a solution of 16.5 g of (I) in 50 ml of MeCN was oxidized with H_2O_2. The next day the volatile components were partially removed in vacuo. The obtained crystals were filtered, and the filtrate was diluted with 50 ml of C_6H_6 and refluxed using a Dean–Stark trap until all of the water was removed. The filtrate was evaporated in vacuo to leave a solid residue. The residue was combined with the previously obtained crystals and treated with petroleum ether. The insoluble portion, after washing with ether and a double recrystallization from MeCN, gave 4.3 g (25% yield) of the stereoisomer with mp 215°, δ ^{31}P –12 ppm (CH_3CN). Found: C 67.02; H 9.05; P 9.57%. The residue, after removal of the ether and a double recrystallization from MeOH, gave 2.8 g (16%) of the stereoisomer with mp 129°, δ ^{31}P –32 ppm (CH_3OH). Found: C 66.21; H 8.99; P 9.54%. The residue, after removal of the petroleum ether and vacuum distillation, gave 3.5 g (20%) of the stereoisomer with mp 57°, bp 120° (0.1 mm), δ ^{31}P –16 ppm (CH_3CN). Found: C 66.53; H 9.10; P 9.30%. $C_{18}H_{29}O_3P$. Calculated: C 66.62; H 9.02; P 9.55%.

5-Phenyl-5-thio-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (III). The (III) stereoisomers were obtained by the methods given in [1].

CONCLUSIONS

In the equilibrium of 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and its derivatives the stereoisomer with nonequivalent protons on the carbon atoms attached to phosphorus is found predominantly in the twist form.

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