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CONFORMATIONAL ANALYSIS OF 2-PHENYL-2-OXO-5,6-BENZO-1,3,2-DIOXAPHOSPHEPINE WITH DATA FROM VIBRATIONAL SPECTROSCOPY, DIPOLE MOMENTS, AND THE KERR EFFECT

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2-Phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepine exists in a melt and solutions in polar solvents as a three-component equilibrium of two chair forms (C) with axial and equatorial arrangement of the phenyl group and the twist-boat form (TB) with a pseudoequatorial position of the phenyl substituent, a-C $\rightleftarrows$ e-C $\rightleftarrows$ e-TB. The two-component equilibrium e-C $\rightleftarrows$ e-TB is observed in nonpolar solvents. The e-TB conformation occurs in the crystalline state. The dipole moment of the P=O groups is 3.5 D. The angle of rotation of the plane of the phenyl group with respect to the P=O bond in the e-TB conformation was 54 or 129°.

We have been conducting structural studies of 2-X-5,6-benzo-1,3,2-dioxaphosphepines by vibrational spectroscopy for the past ten years. A series of compounds with P^{III} and P^{IV} and such exocyclic substituents X as NR_2 (R = Me, Et), OMe, OPh, and Ph were studied [1-7]. In most cases, the compounds are conformationally inhomogeneous and are characterized by a three-component equilibrium of forms of the chair (C) and twist-boat (TB) family, and the chair conformations are energetically preferred to the TB form in all experimental conditions and are always stabilized in the crystalline state. The two-component equilibrium a-C $\rightleftarrows$ e-C was only found in 2-phenyl-2-thiono-5,6-benzo-1,3,2-dioxaphosphepine. In P^{IV} derivatives, the predominant orientation of the P=Y double bond (Y = O, S, Se) in the C form is a function of the nature of the exocyclic substituent at the P atom. For X = NR_2, Ph, the P=Y bond occupies an axial (a) position, and for X = OMe, OPh, it occupies an equatorial (e) position (the conformers are subsequently designated by the orientation of the P—X exocyclic

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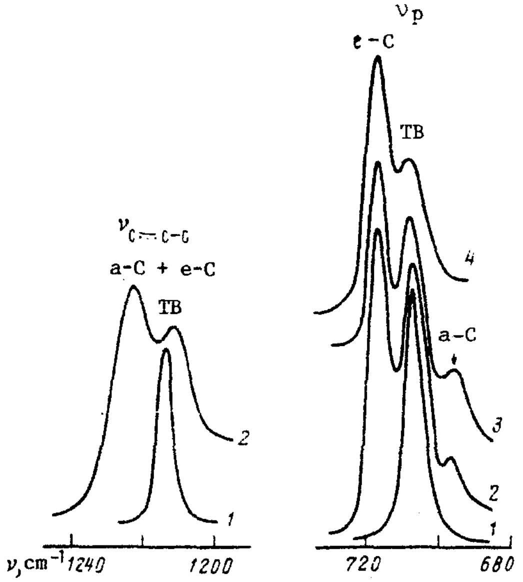


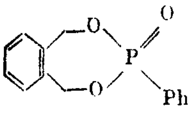
Fig. 1. Raman spectra of the molecule of (I): 1) crystals; 2) melt, 23°C; 3) solution in CH_3CN; 4) solution in C_6H_6.

TABLE 1. Populations of Conformers of Compound (I), %

Melt		Solution			ν, cm⁻¹	Assignment	Conformation
373 K	293 K	CH_3CN	CS_2	C_6H_6			
9	10	18		0	696	ν_P	a-C
51	42	39		35	705		T(TB)
40	48	43		65	715		e-C
47	41	35	31		1213	νC=C–C	T(TB)
53	59	65	69		1224		C

bond). In view of the above, it was interesting to find the system for which a nonchair conformer occurs in the crystalline state.

The present study concerns 2-phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepine (I). The vibrational spectra were obtained for (I)



(I)

in a wide range of temperatures (293-423 K), in different aggregate states, and in solutions with variation of the polarity of the medium. As should have been expected, the most intense bands characterizing the dioxaphosphepine ring are assigned to totally symmetric (pulsation) νPO_2 vibrations and νC=C–C stretching vibrations of the o-xylylene fragment. In the crystal, the 708 and 1213 cm⁻¹ bands belong to them, respectively. Additional bands of ν_P at 696, 715 cm⁻¹ and νC=C–C at 1224 cm⁻¹ appear in these regions of the spectrum when the sample melts (403 K). When the melting point decreases to 293 K (supercooled liquid), the relative intensity of the "new" bands at 715 and 1224 cm⁻¹ increases. A further decrease in the temperature causes crystallization of the substance, the spectrum is simplified, and the 708 and 1213 cm⁻¹ bands again remain. Variation of the polarity of the medium also causes significant redistribution in the relative intensities of the bands. In the νC=C–C 1213/1224 cm⁻¹ doublet, the intensity of the low-frequency component at 1213 cm⁻¹ decreases with a decrease in the polarity of the medium ($CH_3CN \rightarrow CS_2$). In the ν_P 696/708/715 cm⁻¹ triplet, changing from a polar (CH_3CN) to a nonpolar solvent (C_6H_6) is accompanied by the disappearance of the 695 cm⁻¹ band, a decrease in the intensity of the 708 cm⁻¹ band, and an increase

TABLE 2. Dipole Moments (μ, D) and Kerr Constants ($_{m}K \cdot 10^{12}$, esu) of Compound (I)

		a-C	*e*-C	T	a-TB[a]	*e*-TB[a]	a-TB[b]	*e*-TB[b]	Experimental
μ[c]		6,09/6,58	3,02/3,45	4,44/4,94	4,62/5,12	4,32/4.82	4,78/5,28	4,25/4,74	8,98
$_{m}K$	ω = 0°[d]	−2005/−2363	390/456	428/516	555/667	34/21	1092/1329	−419/−513	11
	ω = 90°	−611/−688	−189/−308	−695/−863	−655/−810	−1069/−1339	363/420	−1419/−1758	

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[a] According to preliminary data from x-ray structural analysis.

[b] According to calculations with the Dillon–Geise method.

[c] The values for $m_{P=O}$ = 3.0 D are given in the numerator and the values for $m_{P=O}$ = 3.5 D are given in the denominator.

[d] Angle of rotation around the P–C_{sp^2}(Ph) bond: ω = 0° when the plane of the phenyl group is parallel to the P=O bond.

in the 715 cm^{-1} band (Fig. 1). A complex conformational picture with the participation of at least three forms in the equilibrium is observed. The populations of each of the three forms in different experimental conditions were calculated from the relative intensities of the bands (Table 1).

The preceding study of 5,6-benzo-1,3,2-dioxaphosphepines revealed a number of characteristics in the vibrational spectra and correlated them with the structure of the conformers participating in the equilibrium. The doublet in the region of νC$\doteq$C—C at 1204-1225 cm^{-1} corresponds to the C $\rightleftarrows$ TB(T) equilibrium, and the low-frequency constituent is responsible for the TB(T) conformation, while the high-frequency constituent is responsible for the C conformation [1]; in the case of equilibrium of chair forms (a-C $\rightleftarrows$ e-C), which differ due to the orientation of the exocyclic substituents at the P atom, this vibration is not sensitive to such a transition and a single band corresponds to νC—C—C. The rule that the conformer with an equatorial P—Y bond (a-C) has a higher intrinsic frequency of νP=Y than the one with the axial bond (e-C) holds here.

The pulsation vibrations are sensitive to all of the conformational transitions noted above, and the ν_p frequencies obey a reverse rule for the a-C $\rightleftarrows$ e-C transition than for νP=Y. Guided by these considerations and knowing the proportions of the individual forms, it is possible to reliably interpret the observed spectral picture in the case of compound (I). First, it is clear from the populations measured in the different solvents that conformers with frequencies of ν_p 696 and 715 cm^{-1} maximally differ in polarity, and the 696 cm^{-1} band belongs to the more polar form, while the 715 cm^{-1} belongs to the less polar form. According to the calculated dipole moments (DM) reported below (Table 2), the a-C and e-C conformers exhibit the maximum difference in polarity. The DM of the T and TB forms are close and have an intermediate value. The ν_p 696 cm^{-1} band thus belongs to a-C and the ν_p 715 cm^{-1} band belongs to e-C. The single band of νC$\doteq$C—C at 1224 cm^{-1} corresponds to both of these forms; the ν_p 708 cm^{-1} and νC$\doteq$C—C 1213 cm^{-1} bands belong to the T(TB) conformer. The course of the temperature dependence of the melt shows (Table 1) that although it loses out energetically to the e-C form, this form is nevertheless stabilized in the crystal. Table 1 also suggests that the amounts of the T(TB) form and both C forms measured with the bands of different vibrations (ν_p and νC$\doteq$C—C) are close, which confirms the validity of the assignment.

Additional confirmation can be obtained from an examination of the IR spectra. Going from crystals to solutions is also accompanied by significant complication of the spectra. In particular, 701/718, 744/760 doublets and the 793/805/813 cm^{-1} triplet are observed in a solution of CH_3CN instead of the individual bands of the crystal, ν_p 698, ν_{as} OPO 758, and ν_{as} POC 815 cm^{-1}. However, the most pronounced changes take place in the region of νP=O. The single band of νP=O 1256 cm^{-1} (in petrolatum) is transformed into a 1250/1275 doublet and 1245/1265/1275 cm^{-1} triplet in solutions of CS_2 and CH_3CN. Addition of the complexing agent $SnCl_4$ to a solution of CS_2 shifts both bands to the low-frequency region, which indicates that these bands belong to νP=O. A decrease in the polarity of the medium significantly increases the intensity of the low-frequency band at 1250 cm^{-1} and the 1265 cm^{-1} band disappears, so that these bands were assigned to the e-C and a-C conformers, respectively, and the T(TB) form has a value of νP=O 1275 cm^{-1}.

It was not possible to determine which flexible form participates in the equilibrium, T or TB, with vibrational spectroscopy. An important conformational parameter in compounds with a P—Ph bond — rotation of the plane of the phenyl group around the P—$C_{sp}2$(Ph) bond — was also not established. To answer these questions, we studied compound (I) by the DM and Kerr effect methods. The theoretical DM and Kerr constants (KC) were calculated from the preliminary data from x-ray structural analysis of (I) using the Dillon—Geise method. The additive bond and group moments and anisotropies of polarizability were determined in analyzing the corresponding 1,3,2-dioxaphosphorinanes [8, 9]. In such systems, the moment of the P=O bond can assume values within the limits of 3-3.5 D [10], and for this reason, the theoretical DM and KC reported in Table 2 were calculated for these extreme values. In addition, rotation of the plane of the phenyl group around the P—$C_{sp}2$(Ph) bond was taken into consideration in calculating the KC. The study of the characteristics of this rotation showed that a rotamer with a perpendicular position of the phenyl plane and P=Y bond is realized in the a-C form in all of the 1,3,2-dioxaphosphorinanes with a P—Ph bond, and the plane is parallel to the P=Y bond in the e-C form [9]. The results were analyzed in consideration of these findings.

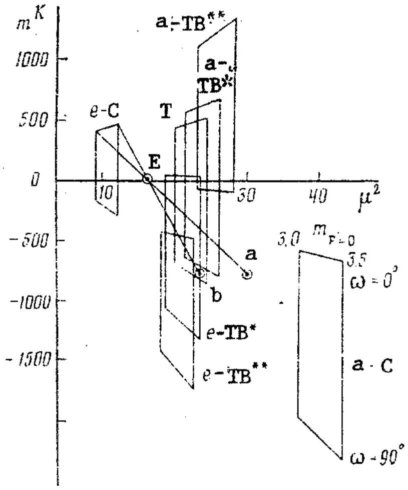

Fig. 2

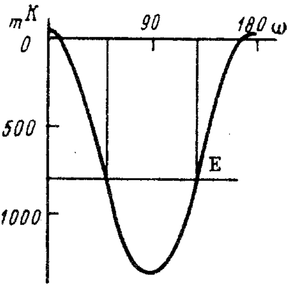

Fig. 3

Fig. 2. Graphic comparison of the DM–KC square of compound (I). The vertical segments correspond to the variation in the KC when the angle of rotation of the phenyl group (ω) changes from 0 to 90° for all designated forms; the sloping lines are the variations of the DM due to a change in $m_{P=O}$ = 3.0-3.5 D, as designated for the a-C conformation. E: experimental; points a and b: explanations in text. TB*: according to preliminary data from x-ray structural analysis, TB**: according to calculations of the Dillon–Geise method.

Fig. 3. Dependence of the KC of the e-TB* form (see Fig. 2) on the angle of rotation of the phenyl group (ω = 0°, where the plane of the phenyl is parallel to the P=O bond). E: value of $_{m}K$ found from the graph in Fig. 2.

The presence of a highly polar and highly anisotropic P=O group makes the graphic comparison of the square of the DM and KC informative (Fig. 2), since the regions on the graph corresponding to different conformers are far from each other. The graph was analyzed with respect to the two-component equilibrium e-C $\rightleftarrows$ T(TB) found in nonpolar solvents by vibrational spectroscopy. The position of the experimental point on the graph corresponds to this equilibrium and allows determining the DM of the P=O group. If point (a) corresponding to the flexible form for $m_{P=O}$ = 3.0 D is plotted with the known proportions of the forms [0.65 e-C, 0.35 T(TB)], it will be outside of the regions of the T and TB conformers, indicating a high value of $m_{P=O}$. On the contrary, for $m_{P=O}$ = 3.5 D, the position of point (b) corresponding to 35% of the flexible form indicates realization of the e-TB form, detected by x-ray diffraction. It is thus also possible to determine the angle of rotation of the phenyl group in this conformation. According to the graph of the dependence of the KC of the e-TB form on this angle (Fig. 3), angles of 54 or 129° correspond to the required value of $_{m}K = -800 \cdot 10^{-12}$ esu, which is close to the value detected by x-ray diffraction (30 and 150°).

Stabilization of the flexible TB form in the crystalline state was actually detected for the compound studied for the first time in the 5,6-benzo-1,3,2-dioxaphosphepine series. All of the previously studied 5,6-benzo-1,3,2-diheterophosphepines in the crystalline state had a chair conformation.

EXPERIMENTAL

The Raman spectra were made on a Bruker Dilor RTI-30 spectrometer. An ILA-120 Ar^+ laser (Karl Zeiss, Germany) (λ 4880 Å) was used as the light source. The spectra of the crystal and melt were made in capillaries 1.5 mm in diameter and the spectra of solutions were made in capillaries 5 mm in diameter. The radiating power of the laser and the slit width varied as a function of the problem solved. The IR spectra were made on a Specord IR-75 spectrophotometer with the standard method. The DM and KC were measured in CCl_4 at 25°C. The coefficients of the calculation equations and experimental values were: α = 12.3165, β = –5.8209, γ = 0.5784, δ = 0.4253; μ = 3.98 D, $_{m}K = 11 \cdot 10^{-12}$ esu.

2-Phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepine (I). A solution of 3 g of $PhP(O)Cl_2$ [11] in 10 ml of abs. CH_2Cl_2 was added by drops in 50 min to a mixed solution of 2.12 g of phthalyl alcohol and 3.1 g of NEt_3 in 20 ml of abs. CH_2Cl_2 while cooling to 0°C. The precipitated $NEt_3 \cdot HCl$ salt was filtered off, and the solution was washed with water acidified with HCl and then with Na_2CO_3 solution and water. After drying with anhydrous Na_2SO_4 and evaporation of the solvent, 3.67 g (92%) of white crystals was obtained. Recrystallization from benzene separated 2.8 g (70%) of pure product with mp 133-134°C. Found, %: C 64.55, H 5.01, P 12.01. $C_{14}H_{13}O_3P$. Calculated, %: C 64.62, H 5.03, P 11.90; M 260.22.

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BASICITY AND CONFORMATIONAL ANALYSIS OF CARBAMOYLMETHYLPHOSPHORYL COMPOUNDS

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547.1'118

The basicity in nitromethane of carbamoylmethylphosphoryl compounds (CMP), $RR'P(O)CHR'''C(O)NR_2''$, containing different substituents at the phosphorus or nitrogen atoms and in the methylene bridge and binary reactants $(CMP)_2X$, where $X = (CH_2)_5$ or p-$CH_2C_6H_4CH_2$, was investigated. The values of pK_a are linearly correlated with $\Sigma\sigma P$, the constant of the substituents at the phosphorus atom. Conformational analysis of CMP and tetraphenylmethylenediphosphine dioxides substituted in the methylene bridge showed that bulky substituents reduce the population of complexing conformations.

Diphenyl(carbamoylmethyl)phosphine oxides (CMP) have attracted attention as efficient extracting agents [1, 2], which requires studying their properties and particularly their basicity. We previously established the structure of the products of protonation of CMP with perchloric acid [3]. The basicity of CMP containing different substituents R, R' at

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