GEOMETRICAL STRUCTURES OF PHOSPHORUS-CONTAINING HETEROCYCLES

21. 2-ALKOXY- AND 2-PHENOXY-2-OXO-1,2-OXAPHOSPHORINANES

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Extensive study has shown that the conformations of the 2-R-2-oxo-1,3,2-dioxaphosphorinanes are determined by the exocyclic substituent at the P atom, the preferred forms being the chair conformation with equatorial P=0 bond for R=Cl, OMe, OPh, H, and Br, and a conformation with axial orientation of the phosphoryl group for R=Alk and NAlk₂ [1, 2]. It therefore seemed of interest to investigate the 1,3,2-oxazaphosphorinanes, 1,2-oxaphosphorinanes, and phosphorinanes, compounds in which the groups affecting the conformation (NAlk, $CH_2,...$) have been introduced into the ring directly. While the substituents at the ring N of the 2-oxo- and 2-thiono-1,3,2-oxazaphosphorinanes are either alkyl of phenyl groups, the 2-chloro, 2-methoxy, and 2-phenoxy derivatives have chair conformations with the single bond in equatorial orientation (differing in this respect from the 2-dialkylamino derivatives), and the relations applying to the 1,3,2-dioxaphosphorinanes carry over to the 1,3,2-oxazaphosphorinanes.

The present work was devoted to the 2-oxo-1,2-oxaphosphorinanes, compounds whose structures have been only imperfectly investigated. An analysis of PMR spectra [4-9] has indicated that the 3-methyl-, 5-methyl-, 6-methyl-, and 4,5-dimethyl-2-oxo-1,2-oxaphosphorinanes exist in chair conformations. These compounds are geometrical isomers, differing in the orientation of the exocyclic substituents at the P atom. From what is known concerning the structures of the 1,3,2-dioxaphosphorinanes, it can be supposed that the most stable of these isomers would be those with the P=0 group in equatorial orientation. Correlation of the P=0 bond absorption frequencies in the IR spectra has assigned the equatorial bond orientation to the 1250cm⁻¹ frequency, the axial bond orientation to the 1237-cm⁻¹ frequency, and the mixed chair conformations to the 1240-1245-cm⁻¹ frequency range [9].

We have undertaken a study of compounds which do not carry substituents in the acyclic portion of the molecule, measuring dipole moments (DM) and Kerr constants (KC), and drawing on the methods of IR spectroscopy



X=OMe (1), OEt (II), OC₆H₅ (III), OC₆H₄CH₅-p (IV), OC₆H₄Cl-p (V), OC₆H₄Br-p (VI)

The trans isomer of 2,4-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (VII), a compound existing in a rigid chair conformation with the 4-CH₃ groups and the P=0 bond in diequatorial orientation [10], was used as a model for calculating dipole moments and Kerr constants, the P-atom environment in its molecule being similar to that met in the compounds under study here.



Fig. 1. Internal rotation relative to the exocyclic P-O bond.

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Fig. 2. Graphical comparison of μ^2 for (III) and (V), (VI). The filled circle covers measured values, the open circles calculated values.

Fig. 3. Graphical comparison of μ^2 for (IV) and (V), (VI).



 $\mu = 6,36 \text{ D}$ [10]; $_mK = 346 \cdot 10^{-12}; \nu_{P=0} = 1270 \text{ cm}^{-1}$

The dipole moments of these cyclic phosphonates can be described in terms of the following bond DM's, calculated from measured values for compounds symmetrically substituted with respect to the P atom [10, 11]: $m_{O-P} = 0$, $m_{CH_3-P} = 0.86$ D, together with $m_{H-C} = 0.28$, and $m_{C-O} =$ 1.12 D, the latter obtained from measurements on the 1,3-dioxanes. The effective dipole moment of the phosphoryl group was calculated from these bond moments and the known conformation of (VII); the value obtained, 3.3 D, is consistent with the 3.81 D reported for the cis isomer [10], m_{P-O} changing little with passage into the axial orientation. Analysis of KC values for the 1,3,2-dioxaphosphorinanes having shown that it is the anisotropy of the polarizability of the P-O bond which alters most radically here [12], the calculation of the Kerr constant of (I) was carried out with the effective value $\gamma_{P-O} = -1.24$ Å³, the latter obtained by tensor decomposition of the molar KC for the model compound (VII) (with $\gamma_{P-O} =$ 0.81, $\gamma_{P-C} = 1.49$, $\gamma_{C-O} = 0.43$ Å³ [10, 11]).

Angles and bond lengths were taken from the x-ray studies on 2-oxo-1,3,2-dioxaphosphorinane [13] and 1-phenyl-1-oxo-phosphorinane [14], compounds which also exist in chair conformations. In view of the PMR data for the various alkyl derivatives [4-9], only chair conformations were considered in freating the 1,2-oxaphosphorinane derivatives.

Inhibition of internal rotation relative to the exocyclic P-O bond opens the possibility for the existence of trans (T), gauche' (G', relative to the P-O bond), cis (C), and gauche" (G", relative to the P-C bond) conformations (Fig. 1), thus increasing to eight the number of possible 1,2-oxaphosphorinane conformers.

> TABLE 1. Calculated and Experimental Dipole Moments for Compounds (I)-(VI), and the Kerr Constant for Compound (I)

Compound	P = 0 eq				$P = O_{ax}$				
	T	G'	G ″	c	T	G'	<i>G″</i>	c	μexp ^{, D}
(I) $_{m}K \cdot 10^{12} = 314$ (I) μ , D (II) (III) (IV) (V)	1091 6,59 6,33 6,68	259 4,82 4,87 4,80	544 5,08 5,08 5,08 5,08	352 4,31 4,46 4,25	-49 2,04 2,25 1,96	-89 3,23 3,18 3,26	-228 3,57 3,46 3,47	-208 4,03 3,86 4,10	4,46 4,40 4,76 4,66 5,11
(VI)	4,85	5,42	5,35	5,55	3,62	3,35	3,26	3,10	5,06

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Fig. 4. Graphical comparison of the Kerr constant and the second-power DM for compound (I).

Fig. 5. IR spectra of compound (IV) in the 800-1400-cm⁻¹ region: a) suspension in mineral oil; b) CCl₄ solution; c) acetonitrile solution.

Solution of this complex conformational problem requires either an increase in the number of isoconformational compounds involved in the study or an increase in the number of different types of physical measurements carried out on the available compounds. Since the Exner principle [15] indicates that the 2-phenoxy derivatives should be isoconformational with the p-substituted analogs (IV)-(VI), comparison was made of the second-power DM's of compounds (III)-(VI). Determination of the DM and KC of the methoxy derivative made it possible to carry out a graphical comparison of two physical properties of a single compound. Introduction of the Kerr effect of compounds (IV)-(VI) brings a new variable, namely the angle of benzene ring rotation, into the discussion. This angle can be estimated once the conformation of the molecule has been determined exactly. The IR data having shown that each of the compounds involved in the present work exists as an equilibrium mixture of two conformers in CCl4 solution, it was necessary to determine the angle of benzoyl ring rotation in each. Such determination could not be made on the basis of KC measurements alone.

TABLE 2.	Experimental	Characteristics	of	Compounds	(I) - ((VI)
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Compound	a	٧"	щD	δ 31P, ppm ●	$^{\nu}P = 0 \cdot cm^{-1} \dagger$
(I) (II) (III) (IV) (V) (V) (VI)	26,30 23,57 21,50 19,44 21,25 17,87	0,1508 0,0746 0,2933 0,3439 0,1407 0,3902	4,46 4,40 4,76 4,66 5,11 5,06	-34, -26 -22 -29 -16 (CCl ₄) -22 (CCl ₄) -20 (CCl ₄)	1263, 1280 1260, 1280 (film) 1265, 1280 1268, 1282 1270, 1290 1267, 1280

*Chemical shifts measured relative to an 85% H₃PO₄ solution. +In CCl₄ solution.

Calculated dipole moments for (I)-(VI), and the Kerr constant for (I), are given in Table 1, together with experimentally measured values of these parameters. Graphical comparison of the second-power DM's for (III)-(V), (VI), and (IV)-(V), (VI) is shown in Figs. 2 and 3. Compounds (V) and (VI) are considered together since their theoretical and experimental DM's are almost identical, $m_{C_6H_4-C1}$ and $m_{C_6H_4-Br}$ both being equal to 0.85 D according to calculations based on the measured dipole moments of chlorobenzene and bromobenzene. An analogous comparison of μ^2 and mK for compound (I) is shown in Fig. 4. Since the point covering the experimentally determined DM falls between the points for the two chair conformations in Figs. 2 and 3, we will first consider those aspects of the IR spectra which indicate that one has here to do with an instance of conformational equilibrium. The P=0 group absorption band appears as a strong flat peak in the spectra of each of the compounds in question. It has been shown [9] that a two-chair equilibrium does not give rise to doublet absorption, but rather to absorption at frequencies intermediate to those for axial and equatorial P=0group configurations in the $1240-1245-cm^{-1}$ region of the spectrum. We have analyzed the entire 800-1300-cm⁻¹ region of the spectrum, and carried out measurements in CCl₄ ($\varepsilon = 2.24$) and acetonitrile (ε = 38) solutions, and in the crystalline state. In most cases the absorption band had doublet form, with the band intensity varying with the dielectric constant of the solvent (Fig. 5), the indication being that one had to do with a conformational equilibrium in each system. The content of the second component of the equilibrium mixture is considerably higher in (I) than in (III)-(VI). The ³¹P NMR spectra showed a second peak with $\delta^{31}P$ equal to -34 ppm, the principal signal being at -26 ppm. Comparison of these values with the ^{31}P chemical shifts in the cis and trans isomers of (VII) (-28 and -23 ppm) suggested that the principal signal corresponds to an equatorial P=0 group orientation.

Study of Figs. 2 and 3 shows that the chair conformer with the P=O group in the equatorial position and the phenoxyl radical in gauche orientation must predominate in the conformational equilibrium (it is impossible to distinguish between the two gauche forms). The second component makes up no more than 20% of the equilibrium mixture and has axial P=O group orientation. It was not possible to determine the PhO group orientation in this conformer. One could only tentatively exclude the cis conformation from consideration here, since there is no obvious reason why the structure could not be realized even with the PhO group in the axial position.

The point covering the experimental values for the (I) parameters falls in the region for chair conformation with the P=O group in the equatorial position. The cis structure can be excluded from consideration here on the basis of the same spectral data that were used in establishing the existence of the conformational equilibrium. Just as with the phenoxyl derivatives, one is then led to the conclusion that the predominant form (up to 60%) has the chair conformation with the axial OCH₃ group in gauche orientation (**G**" or $G' \rightleftharpoons G"$). The second component of the equilibrium is a chair conformer with the equatorial OCH₃ group in gauche (G' or G" or G' $\rightleftharpoons G' \rightleftharpoons G"$) or trans orientation with respect to the P=O group. The fact that the DM's of (I) and (II) are identical is an indication that these conformations are quite similar.

The data obtained here suggest that there is a marked tendency for the $2-\infty -1, 2-\infty -1, 2-\infty -1, 2-\infty -1, 2-\infty -1, 2-\infty -1, 3, 2-0 + 0, 2-\infty -1, 3-\infty -$

EXPERIMENTAL

The dipole moment and Kerr constant of compound (I) were determined in CC14 solution, working at 20°C and following the methods of [11]. Values of the coefficients in the working equations are given in Table 2.

The synthesis of (II) has been described in [4]. Compound (I) was prepared in a similar manner; yield, 25%; bp 98-100°C (1 mm); n_D^{20} 1,4565. Found: C 39.93; H 7.31; P 20.63%. C₅H₁₁O₃P. Calculated: C 40.00; H 7.33; P 20.66%.

Compounds (III)-(VI) were synthesized from the phenyldiethylphosphite and 1,4-dibromobutane. The reaction mixture, with a slight excess of the phosphite, was heated in an Arbuzov flask, working under dry nitrogen with continuous agitation, for 4 h at 200-210°C, the C_2H_5Br distilling off as the reaction proceeded. The reaction product was subjected to threefold distillation. Yield of (III), 28%; bp 152-153°C (0.02 mm); np^{2°} 1.5041. Found: C 56.30; H 5.95; P 14.91%. C₆H₁₃O₃P. Calculated: C 56.60; H 6.13; P 14.62%. Yield of (IV), 35%; bp 152-153°C (0.02 mm), product solidified as a yellow powder, mp 71°C. Found: C 58.56; H 6.87; P 13.41%. C₁₁H₁₅O₃P. Calculated: C 58.40; H 6.63%; P 13.83%. Yield of (V), 40%; bp 145-147°C (0.04 mm); np^{2°} 1.5430. Found: C 48.82; H 4.71; P 12.78%. C₁₀H₁₂-O₃PCl. Calculated: C 48.68; H 4.86; P 12.57%. Yield of (VI), 34%; bp 165-170°C (0.02 mm), product solidified as a white powder; mp 63°C. Found: C 41.23; H 4.12; P 10.65%. C₁₀H₁₂-O₃PBr. Calculated: C 41.06; H 4.21; P 10.12%.

CONCLUSIONS

1. A determination has been made of the dipole moments of the 2-(p-X-phenoxy)-2-oxo-1,2-oxaphosphorinanes, and of the dipole moment and Kerr constant of 2-methoxy-2-oxo-1,2oxaphosphorinane.

2. These compounds exist as equilibrium mixtures of two chair conformations, the predominating form being that with an equatorial phosphoryl group and gauche-oriented alkoxy and phenoxy radicals.

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