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CONFORMATIONS OF CERTAIN

DIALKYLARYLPHOSPHINES AND THEIR OXIDES

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The energy of $p - \pi$ coupling in R₂EAr aromatic compounds containing an unshared electron pair (USP) is determined by two geometrical factors: 1) the valence angles at the hetero atom, which, in turn, are fixed by the unshared pair hybridization and the energy of pair interaction with the aromatic ring π system [1], and 2) the spatial orientation of the aryl ring.

In the course of a study of the dimethyl- and di(tert-butyl)-p-tolylphosphines [3], we have shown that both the first and the second of these factors are unfavorable for $p - \pi$ coupling in the dialkylarylphosphines, the situation here being different from that met with the aromatic amines. In fact the unshared pair of the phosphorous is coplanar with the benzoyl ring, and accordingly orthogonal to the π system of the latter, a situation in which the second-power cosine law predicts zero possibility of $p - \pi$ interaction.

The present paper will report the results of a study of the geometrical structures of dimethylphenylphosphine (I), diftert-butyl)phenylphosphine (II), dimethyl-p-cyanophenylphosphine (III), dimethyl-p-tolylphosphine

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Compound	Solvent	عد) <u>عد</u>	$\Delta B B_1 \Delta \omega_2$	μ, D
(l)	C ₆ H ₁₂	1,339	5,9	1,2
(Il)	C ₆ H ₁₂	0,906	6,2	1,5
(III)	Dioxane	14,374	706	4,4

TABLE 1. Experimentally Determined Dipole Moments and Double Refractions of the Dialkylaryphosphines

TABLE 2. Dipole Moments and Double Refractionsof Dialkylarylphosphine Oxides

Compound	Solvent	.∆ε Δω ₂	$\Delta n_D^2 \Delta \omega_2$	∆B B1702	μ. D	
(IV)	CCl ₄	14,997	0,628	259	4,30	
(V)	CCl ₄	27,730	0,485	241	4,85	
(V1)	Dioxane	15,347	0,357	127	4,60	

oxide (IV), di (tert-butyl)-p-tolylphosphine oxide (V), and dimethyl-p-cyanophenylphosphine oxide (VI) based on measurement of dipole moments (DM) and Kerr constants (KC).

The fact that the arylphosphines (I)-(III) readily oxidize in solution meant that the measured values of DM's and KC, s of these compounds were less accurate than those of the compounds (IV)-(VI). Dipole moments (Table 1) were determined from the concentrational variation of the solution dielectric constant $(\Delta \varepsilon / \Delta v_2)$, calculation being through a modified Higashi equation [4, 5]; the KC's were determined from the $\Delta \varepsilon / \Delta v_2$ values and the concentrational variation of the specific KC $(\Delta B / \Delta v_2)$. The equations derived in [6] were used in treating the data for (IV)-(VI).

Values of the parameters required for developing the relation between the molar KC and the angle of aryl group rotation with respect to the USP direction were obtained in the following manner. The CeH5P group moment (0.76 D) was determined from the experimentally measured DM for (I), following the method described in [3]. The moment of (III) was used to determine the polarity of the $PC_{gH_4}CN$ -p group. Calculations based on an additive vector scheme gave the value 3.91 D, while the difference between the moments of the $C_{gH_5}P$ and benzonitrile (4.04 D) groups was 3.28 D. The interaction moment of 0.63 D was directed toward the CN group, thus indicating a certain redistribution of the electron density of the PC_sH₅Cn-p system.* The calculated values of the KC's for the arylphosphines could be sensitive to the orientation of the molecular dipole moment. The KC for (IV) was therefore calculated by two methods, the one assuming the experimental DM (cf. Table 2) to be directed along the phosphoryl group (A) (a procedure justified by the fact that the radical group moments were essentially identical in value) and the other working from a DM based on the sum of moments of the corresponding phosphine [3] and the value m(P=O) = 2.98 D [7] (B). Since the results obtained from such calculations were consistent with the experimental data in both cases (Table 3), work on the other arylphosphine oxides was carried out by method (A). The ArCN group moment was set equal to the DM of benzonitrile for the calculations on (VI). Calculations on the components of the polarizability ellipsoid were based on bond and group parameters, some of which have been given earlier in [3]. Using the data on the benzonitrile molecular ellipsoid [8] with correction for the isotropic polarizability of the C - H bond, the following values were obtained for the C₈H₄CN group polarizability: (b = 0.65 Å³): b₁ = 15.51; b₂ = 10.95; b₃ = 7.50 Å³. Parameter values for the P=O bond were taken from [9].

Calculations were carried out for two positions of the benzene ring, one in which in the dihedral angle between the bisector of the $C_{sp3} - P - C_{sp3}$ angle and the plane of the phenyl ring is zero ($\varphi = 0$) and the other in which this angle is 90° ($\varphi = 90^{\circ}$). Observed and calculated values of the KC are shown in Table 3. Comparison indicates the value of the angle φ for the (I) and (II) conformations to be close to 0°. The fact that the KC of (III) was relatively insensitive to the angle of aryl rotation made it impossible to reach any decision concerning the conformation of this compound. The experimentally determined constant was higher than the

^{*}Decision as to whether this interaction proceeds through direct polar coupling or through competetive coupling from two acceptor groups would require additional experimental data on the DM's of various substituted arylphosphines.

Compound	Measured	Calculated			
		¢ — 0°	ę = 90°		
(1) (1) (1) (1) (1) (1) (1) (1) (1) (1)	1 2 132 30,0 44,4 24,9	3 6 96 33,4(A): 27,6(B) 35,3 24,2	4 8 90 73,8(А);50,2(В) 46,7 85,9		

TABLE 3. Experimental and Calculated Values of the Kerr Constant $(_{m}K \cdot 10^{11})$

calculated in this case. The nonadditivity of the KC exaltation indicated interaction between the phosphorous atoms and the CN group, the situation here being similar to that pointed out above in the case of the DM's. Generalizing the data of the present work and that already given in [3], it can be concluded that the spatial position of the aromatic ring in the dialkylarylphosphines is such as to eliminate the possibility of interaction between the unshared electron pair of the phosphorus and the ring π electrons. The data presently available do not permit a decision concerning the conformation of dimethyl-p-cyanophenylphosphine. In the four-coordinated analogs of the latter compound, the bisector of the CPC angle is also directed along the plane of the benzoyl ring.

EXPERIMENTAL

All operations with P(III) compounds were carried out in an atmosphere of argon. The procedures for determining the DM's and KC's have been shown earlier in [3].

<u>Dimethylphenylphosphine (I).</u> This compound was prepared from phenylchlorophosphine and CH₃MgI; bp 70-71°C (15 mm); mD^{20} 1.5650; d_4^{20} 0.9662; cf. [10].

Differt-butyl)phenylphosphine (II). To 16.7 g of differt-butyl)chlorophosphine [11] dissolved in 50 ml abs. ether at 20°C there was added a phenyllithium solution prepared by dissolving 2.3 g Li and 21.8 g C₆H₅Br in 250 ml ether. This mixture was boiled for 1 h, and 75 ml of a saturated NH₄Cl solution and 200 ml benzene then added to it. The organic layer was evaporated down to 100 ml and extracted with concentrated HCl (3×30 ml). The combined extract was then washed with 50 ml benzene, neutralized with a 40% KOH solution, and the precipitated oil extracted with benzene (2×100 ml). The combined extract was washed with water 50 ml water, and dried over Na₂SO₄. The solvent was evaporated off in vacuum and the residue distilled. The resulting mass was held at 90°C for 4 h and once more distilled. Yield of (II) 15.0 g (73%), bp 113-114°C (6 mm); np²⁰ 1.5350; d₄²⁰ 0.9333; found MR 74.15; calculated MR 73.49; cf. [12].

Dimethyl-p-carboxyphenylphosphine Oxide. A Grignard reagent was prepared by adding 21.6 g Mg and 154.0 g p-BrC₆H₄CH₃ to 700 ml ether; to this 72.5 g $(CH_3)_2P(O)Cl$ dissolved in 250 ml THF was added dropwise at 0-2°C. After boiling for 2 h, the mixture was broken down with a saturated NH₄Cl solution and then acidified with HCl (1:1). The aqueous solution was neutralized with a saturated Na₂CO₃ solution and extracted with CHCl₃ (5 × 50 ml). The combined extract was dried over Na₂SO₄, the solvent evaporated off in vacuum, and the residue distilled. The fraction boiling at 130-145°C (2 mm) was treated with 250 ml water, the insoluble residue (4.0 g) filtered off, and the filtrate extracted with heptane (2 × 20 ml). The aqueous layer was mixed with 250 ml pyridine and 248.0 g finely pulverized KMnO₄ added, the rate of addition being adjusted so as to maintain the mixture at the boiling point. After additional boiling for 5 h, the pyridine was driven off with water vapor, and the MnO₂ filtered off. The result was 43.0 g of a substance with 241-242.5°C mp. After recrystallization from alcohol—benzene solution the yield was 37.0 g (28%); mp 244.5-245°C, cf. [13].

<u>Dimethyl-p-carbamoylphenylphosphine Oxide.</u> A mixture of 10.3 g dimethyl-p-carboxyphenylphosphine and 12 ml SOCl₂ in 70 ml THF was boiled for 1.5 h and then allowed to evaporate. The residue was dissolved in 30 ml THF, and the resulting solution slowly poured into a continuously agitated concentrated NH₄OH solution. The precipitated crystals were filtered off and washed with alcohol. The result was 6.7 g of a substance with 280-283°C mp. Recrystallization from methanol solution gave a yield of 4.5 g (44%), mp 288-290°C. Found: C 54.7; H 6.2; P 15.5%. C₉H₁₂O₂P. Calculated: C 54.8; H 6.1; P 15.7%.

<u>Dimethyl-p-cyanophenylphosphine Oxide (III)</u>. To 3.9 g dimethyl-p-carbamoylphenylphosphine oxide 3 ml POCl₃ were added. This mixture was heated for 1 h at 60-70°C, dissolved in 20 ml water, made alkaline with dry NaOH, and extracted with CHCl₃ (5×10 ml). The combined extract was dried over Na₂SO₄, and the

solvent evaporated off in vacuum. The yield of (II) was 2.0 g (57%), mp 159-160.5°C (alcohol - benzene). Found: C 60.4; H 5.8; N 7.7; P 17.3%. $C_{3}H_{10}ONP$. Calculated: C 60.3; H 5.6; N 7.8; P 17.3%.

<u>Dimethyl-p-cyanophenylphosphine</u>. A solution containing 6.9 g dimethyl-p-cyanophenylphosphine oxide and 11 ml SiHC I₃ dissolved in 100 ml benzene was boiled for 2 h and then cooled; to it there was then added 9 ml SiHCl₃ and boiling continued for another hour. The resulting mixture was broken down with a 40% KOH solution, the organic layer separated off, washed with water, and dried over Na₂SO₄. The solvent was evaporated off in vacuum, and the residue distilled. The yield was 4.2 g (65%), bp 104°C (3 mm) (mp 36-37°C, thermometer in mass). Found: C 66.3; H 6.2; P 19.0%. C₉H₁₀NP. Calculated: C 66.4; H 6.2; P 19.0%. The syntheses of (IV) and (V) have been described in [13,14].

CONCLUSIONS

It is characteristic of the conformations of the dialkylphenylphosphines and their oxides that the bisector of the CPC angle lies in the plane of the benzoyl ring.

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