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DIPOLE MOMENTS AND STRUCTURE OF ORGANOPHOSPHINE AND ORGANOARSINE COMPOUNDS

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SUMMARY

The formal charge distributions in and the dipole moments of some organophosphines and arsines have been calculated, and the dipole moments of (p-chlorophenyl)dichlorophosphine (2.28 D) and (p-bromophenyl)dichlorophosphine (2.04 D) have been determined in benzene at 35° C. The differences between the observed and the calculated moments are explained in terms of d_π–p_π back-bonding and hyperconjugative effects in alkylhaloarsines. The mesomeric effects operating in the aromatic systems are evaluated by comparing the moments with those for the corresponding aliphatic systems. In unsaturated compounds the differences are attributed to mesomeric effects involving the expansion of arsenic valence shell.

INTRODUCTION

From the point of view of physical measurements in relation to structure, the organohalophosphines have not received as much attention as the analogous organohaloarsines[1–5]. This is especially the case with regard to dipole moment measurements[6].

The shortening of the As–X bond in $(CH_3)_nAsX_{3-n}$ (where X = halogen atom) below the sum of the covalent radii has been attributed to d_π–p_π back bonding, the strength of the π-bond increasing with the number of halogen atoms[7,8]. The observed shortening of the C–As bond in (β-chlorovinyl)arsinedichloride has been interpreted in terms of the conjugation of the non-bonded arsenic electrons with the olefinic double bond[9]. In order to evaluate the extent of the above effects, the moments of organophosphines and organoarsines have been theoretically calculated using the method developed by Smith *et al.*[10]. An analysis of the dipole moments of several aliphatic and aromatic phosphines and arsines should give an idea of the extent of mesomerism operating in these molecules. In this connection, the dipole moments of *para*-substituted phenyldichlorophosphines of the type X–C_6H_4–PCl_2 (where X = Cl or Br) have been measured in benzene at 35°.

EXPERIMENTAL

Materials

Benzene was purified as described in the literature[11] (p-chlorophenyl)- and (*p*-bromophenyl)dichlorophosphines were prepared by Friedel and Craft's method[12,13]. The fractions boiling at 133°/20 mmHg [(*p*-chlorophenyl)dichlorophosphine] and 76°/8 mmHg [(*p*-bromophenyl)dichlorophosphine] were collected.

TABLE 1

DIELECTRIC CONSTANT AND POLARIZATION DATA[a]

Compound	*(p-Chlorophenyl)-dichlorophosphine*	*(p-Bromophenyl)-dichlorophosphine*
Mole fraction ($f \times 10^{-5}$)	1.73–6.27	1.04–5.32
Dielectric constant	2.2637–2.2934	2.2608–2.2829
Density g/ml	0.86736–0.86399	0.86888–0.86410
Hedestrand's constants:		
(1) α	3.01	2.30
(2) β	0.87	1.30
Total polarization		
P_2^∞ (ml^3)	151.54	137.35
1.05 MR_D (ml^3)	49.10	55.28
Orientation Polarisation		
P_o (ml^3)	102.44	82.07
Electric moment (D)	2.28	2.04

[a] In benzene at 35±0.02°.

TABLE 2

PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION AND DIPOLE MOMENTS BY THE METHOD OF SMITH *et al.*[10,a]

Compound	β_{ab}	γ_{ab}	*Basic molecule*
H–C	0.13	0.000	
C–P	β_C^P 0.329 β_P^C 0.174	α_{C-P} −0.881	$(CH_3)_3P$
H–P	0.113	0.319	PH_3
C–C	β_C^C 0.430	α_{C-C} 0.000	
C–As	β_C^{As} 0.163 β_{As}^C 0.403	α_{C-As} −0.529	$(CH_3)_3As$
F–As	0.133	−1.738	AsF_3
Cl–As	0.304	−1.311	$AsCl_3$
Br–As	0.389	−1.115	$AsBr_3$
I–As	0.504	−0.678	AsI_3
Cl–C	0.710	−1.490	
C=C	1.700	0.000	
Cl–P	0.361	α_{C-C} −0.570	PCl_3

[a] All bond angles and distances were taken from the literature[18].

TABLE 3

FORMAL CHARGE DISTRIBUTION IN PHOSPHINES AND ARSINES

Molecule	C_1	C_2	C_3	C_4	C_5	H	H_1	H_2	H_3	H_4	H_5	P	As
$(CH_3)_3P$	0.346					0.051						−1.445	
$(C_2H_5)_3P$	0.309	0.0073				0.040	0.010					−1.472	
$(C_3H_7)_3P$	0.307	0.066	0.016			0.040	0.009	0.002				−1.474	
$(C_4H_9)_3P$	0.307	0.065	0.014	0.003		0.040	0.009	0.002	0.000_4			−1.471	
$(C_5H_{11})_3P$	0.307	0.065	0.014	0.003	0.001	0.040	0.009	0.002	0.000_4	0.000_1		−1.471	
PH_3											0.238	0.715	
CH_3PH_2	0.396					0.052					0.209	−0.970	
$(CH_3)_2PH$	0.371					0.048					0.182	−1.213	
$CH_3CH_2PH_2$	0.355	0.840				0.046	0.011				0.208	−0.981	
$(CH_3CH_2)_2PH$	0.331	0.078				0.043	0.009				0.179	−1.237	
$(CH_3)_3As$	0.214					0.028							−0.893
$(C_2H_5)_3As$	0.191	0.045				0.025	0.006						−0.911
$(C_3H_7)_3As$	0.189	0.040	0.010			0.025	0.010	0.001					−0.906
$(C_4H_9)_3As$	0.190	0.040	0.009	0.002		0.025	0.005	0.001	0.000_3				−0.912
AsF_3[a]													3.726
$AsCl_3$													2.058
$AsBr_3$													1.544
AsI_3													0.810

[a] $\varepsilon_F = -1.242$, $\varepsilon_{Cl} = -0.686$, $\varepsilon_{Br} = -0.515$, $\varepsilon_I = -0.270$.

(1). (p-Chlorophenyl)dichlorophosphine. Found: P, 11.68. Calcd.: P, 11.78%.
(2). (p-Bromophenyl)dichlorophosphine. Found: P, 14.50. Calcd.: P, 14.52%.

Measurement of dipole moment

The dielectric constant measurements were made with an a.c. mains-operated heterodyne beat apparatus, as described in the literature[14]. Densities of solutions were obtained using an Ostwald–Sprengel pyknometer with ground-in caps at both ends. The polarization of the solute at infinite dilution was obtained using the mean values of Hedestrand's constants α and β[15]. Electronic polarization of the solute was calculated by the addition of bond refractions[16,17]. 5% of the electronic polarization was taken as the value of the atomic polarization. The results are given in Table 1.

Calculation

The parameters used for calculating the formal charge distribution in the phosphines and in some arsines, and the formal charges are given in Tables 2, 3 and 4. The difference between the calculated and the observed values of moments are given in Table 5.

TABLE 4

CHARGE DISTRIBUTION IN HALOPHOSPHINES AND HALOARSINES

Compound	C_1	C_2	*H*	H_1	*P*	*As*	*F*	*Cl*	Cl_1	*Br*	*I*
CH_3AsF_2	0.491		0.064			2.206	−1.444				
$(CH_3)_2AsF$	0.352		0.046			0.669	−1.649				
CH_3AsCl_2	0.407		0.053			1.279		−0.293			
$(CH_3)_2AsCl$	0.321		0.042			0.321		−1.214			
CH_3AsBr_2	0.379		0.049			0.959				−0.743	
$(CH_3)_2AsBr$	0.309		0.040			0.185				−1.043	
CH_3AsI_2	0.332		0.043			0.446					−0.454
$(CH_3)_2AsI$	0.285		0.037			−0.077					−0.717
$(ClCH{=}CH)AsCl_2$	0.606	0.710	0.079	0.092		1.320		−0.910	−0.986		
$(ClCH{=}CH)_2AsCl$	0.369	0.087	0.048	0.011		1.266		−0.927			
$(ClCH{=}CH)_3As$	0.549	0.680	0.071	0.088		0.426		−1.182	−1.007		
$C_2H_5AsCl_2$	0.472	0.644	0.061	0.084		0.683			−1.033		
PCl_3					0.822				−0.274		
CH_3PCl_2	0.523		0.068		0.240				−0.484		
$(CH_3)_2PCl$	0.446		0.058		−0.493				−0.748		
$ClCH_2PCl_2$	1.036		0.135		0.342			−0.447	−0.754		
$BrCH_2PCl_2$	0.935		0.122		0.322			−0.454		0.0593	

DISCUSSION

Trivalent phosphorus compounds have been shown to have a pyramidal structure by X-ray studies[18]. The moments calculated for the (p-chlorophenyl)- and (p-bromophenyl)dichlorophosphines (using the bond moments P–Cl 0.64, C–Cl 1.55, C–Br 1.50, C–P 0.45 and H–C 0.4 D)[19] are 2.40 and 2.27 D respectively. These calculated values are in close agreement with the experimental values of 2.28 and 2.04 D respectively. The higher moment of the chloro compound compared with the bromo

TABLE 5

COMPARISON OF OBSERVED AND CALCULATED DIPOLE MOMENTS

Compound	$\mu_{obs.}$	$\mu_{calcd.}$	$\mu_{difference}$
1 $(CH_3)_3P$	1.19		
2 $(C_2H_5)_3P$	1.48[a]		+0.09
	1.35[b]	1.39	−0.05
3 $(C_3H_7)_3P$	1.48	1.45	+0.03
4 $(C_4H_9)_3P$	1.48	1.46	+0.02
5 $(C_5H_{11})_3P$	1.48	1.46	+0.02
6 PH_3	0.55		
7 CH_3PH_2	1.10	1.00	+0.10
8 $(CH_3)_2PH$	1.23	1.16	+0.07
9 $C_2H_5PH_2$	1.17	1.09	+0.08
10 $(C_2H_5)_2PH$	1.36	1.36	0.00
11 $(CH_3)PCl_2$		1.88	
12 $(CH_3)_2PCl$		2.37	
13 $ClCH_2PCl_2$		1.86	
14 $BrCH_2PCl_2$		1.73	
15 $(CH_3)_3As$	0.86		
16 $(C_2H_5)_3As$	1.05	1.15	−0.10
17 $(C_3H_7)_3As$	1.01	1.03	−0.02
18 $(C_4H_9)_3As$	0.93	1.03	−0.10
19 CH_3AsF_2[c]	2.88	3.76	−0.88
20 $(CH_3)_2AsF$	2.37	3.29	−0.82
21 CH_3AsCl_2	2.80	3.05	−0.25
22 $(CH_3)_2AsCl$	2.68	3.08	−0.40
23 CH_3AsBr_2	2.66	2.68	−0.02
24 $(CH_3)_2AsBr$	2.71	2.87	−0.16
25 CH_3AsI_2	2.30	1.95	+0.35
26 $(CH_3)_2AsI$	2.54	2.25	+0.29
27 $ClCH{=}CHAsCl_2$[d]	2.61	2.79	−0.18
	2.20	2.94	−0.74
28 $Cl(CH{=}CH)_2AsCl$	1.46	3.10	
		2.75	
29 $Cl(CH{=}CH)_3As$	0.39	0.95	−0.56
		2.13	

[a] Ref. 27. [b] Ref. 16. [c] Ref. 17. [d] Ref. 28.

TABLE 6

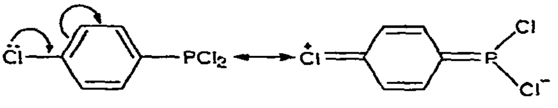
MESOMERIC MOMENTS IN THE SYSTEM X–C_6H_4–PCl_2 (X = Cl or Br) AND $(C_6H_5)_2AsCl$

Compound	*Experimental moment (D)*	*Calculated value for X–CH_2–PCl_2[a] (D)*	*Mesomeric moment (D)*
Cl–C_6H_4–PCl_2	2.28	1.86	+0.42
Br–C_6H_4–PCl_2	2.04	1.73	+0.31
$(C_6H_5)_2AsCl$	2.73[b]	3.08	−0.35

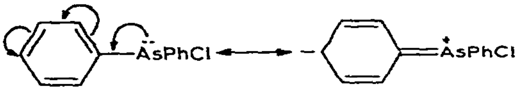
[a] Calculated using the method of Smith *et al.*[10]. [b] Value taken from ref. 29.

compound may be due to the higher electronegativity of chlorine compared to that of bromine.

The mesomeric moment operating in the system $X–C_6H_4PCl_2$, where $X=Cl$ or Br, is derived as the difference between the experimentally observed value for $X–C_6H_4–PCl_2$ and that calculated for $X–CH_2–PCl_2$ using the charge distribution scheme of Smith *et al.*[10]. The direction of mesomeric moment is explicable in terms of the contribution of structures such as:



whereas in diphenylarsine chloride the direction of the mesomeric moment is governed by contributions of structures such as:



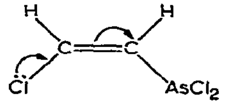
The close agreement between the observed and the calculated moments of trialkylphosphines and arsines (Table 5) shows that only inductive effects are present. Furthermore, the alkylphosphines have virtually identical dipole moments. This is also the case for the corresponding n-alkyl sulphides[19], and implies that the hydrocarbon chains tend (as a mean conformation) to be nearly perpendicular to the direction of the primary moment in the molecules.

The difference in moments between the experimentally observed[20] and the theoretically calculated ones (back moment) (Table 5) in dialkylhaloarsines increases in the order bromoarsines < chloroarsines < fluoroarsines. This trend is in accord with the order of the strength of the d_π–p_π "back bond" in many organometallic halides[7,8,21–23]. The strength of this "back bond" is greater the greater the electronegativity of the donor atom. That is, the back bonding involved in As–F linkage is larger than in As–Cl and As–Br bonds. This back bonding neutralizes the large positive charge on arsenic induced by the electronegative halogen atoms, by the overlap of the filled orbitals of fluorine with the empty 3*d* orbitals of arsenic, thereby imparting a certain amount of double bond character to the bonds. This is in line with the observed shortening of As-halogen bonds with respect to the calculated ones[7].

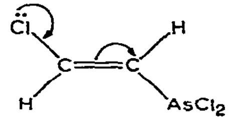
The increase in the back moment from bromo- to chloro-arsines in monoalkyldihaloarsines should be more than that from the bromo to chloro compounds in the corresponding dialkylmonohaloarsines since the back moment (or the shortening) of the metal to halogen bonds[7] increases with the number of halogen atoms on the metal. This is however not the case. This anomaly may be due to the fact that the bond angles and bond distances in monoalkyldihaloarsines are assumed to be the same as those in the corresponding dialkylmonohaloarsines. Although the differences in the moments are not in the expected order, the trend in the same series of haloarsines is in the expected order of decreasing back bonding from fluoro- to bromo-arsines.

In both dimethyliodoarsine and methyldiiodoarsine, the calculated moments are less than the observed moments. This indicates that in contrast to the situation in the other haloarsines, the mesomeric or the hyperconjugative effect of the methyl group outweighs the d_π–p_π back bonding. This conclusion is in agreement with the X-ray[24,25] and electron diffraction[7] studies on the iodoarsines. The bond lengths (As–I = 2.54 Å) agree well with those calculated from covalent radii (2.54 Å) thereby indicating that there is no double bond between arsenic and iodine.

For (β-chlorovinyl)dichloroarsine (Lewisite II *cis* form) mesomeric effects of the type:



cis



trans

account for an experimental value which is lower than that calculated (Table 5). The mesomeric effect in the *trans* isomer is higher than that in the *cis* isomer. This is in line with the UV studies of (β-chlorovinyl)dichloroarsine[26], which show the presence of conjugation of the non-bonded arsenic electrons with the olefinic double bond. Further, electron diffraction studies have shown the As–Cl distance in the *cis* and *trans* isomers of (β-chlorovinyl)dichloroarsine (Lewisites) to be normal (2.17 Å)[9], but the C–As distance (1.90 Å) is less than that (1.98 Å) found in $(CH_3)_3As$[27]. The observed decrease in the C–As distance may be the result of conjugation of the nonbonded arsenic electron with the olefinic double bond. The C–Cl distance (1.70 Å) in the Lewisites also appears to be less than the sum of the covalent radii (1.76 Å), but is approximately of the same order as those in chloroethylenes[28]. The value (1.46 D) observed[29] in (β, β′-dichlorodivinyl)arsine chloride seems to be very low compared with those calculated for the two isomers. There is no information about the nature or the isomeric composition of the sample used for measurements in both (β, β′-dichlorodivinyl)arsine and tris(β-chlorovinyl)arsine.

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