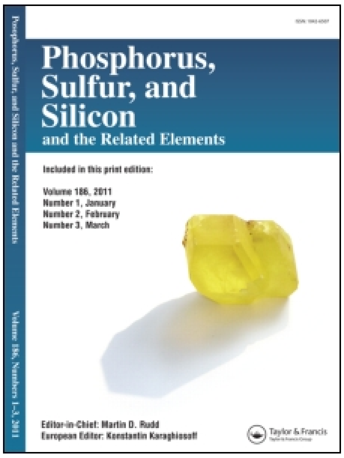

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DIPOLE MOMENTS OF SOME PHENYL AND CHLOROPHENYL PHOSPHORUS-HALOGEN COMPOUNDS

Chengrui Wang[a]; E. Bock[b]; J. Peeling[b]; A. F. Janzen[b]
[a] Department of Chemistry, Wuhan University, Wuhan, China [b] Department of Chemistry, University of Manitoba, Winnipeg, Canada

To cite this Article Wang, Chengrui , Bock, E. , Peeling, J. and Janzen, A. F.(1991) 'DIPOLE MOMENTS OF SOME PHENYL AND CHLOROPHENYL PHOSPHORUS-HALOGEN COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 1, 123 — 125

To link to this Article: DOI: 10.1080/10426509108038840

URL: http://dx.doi.org/10.1080/10426509108038840

Phosphorus, Sulfur, and Silicon, 1991, Vol. 57, pp. 123–125
Reprints available directly from the publisher
Photocopying permitted by license only

DIPOLE MOMENTS OF SOME PHENYL AND CHLOROPHENYL PHOSPHORUS-HALOGEN COMPOUNDS

CHENGRUI WANG
Department of Chemistry, Wuhan University, Wuhan, China 430072

and

E. BOCK, J. PEELING and A. F. JANZEN
Department of Chemistry, University of Manitoba, Winnipeg, Canada R3T 2N2

(Received December 8, 1989; in final form August 14, 1990)

The electric dipole moments of o-$ClC_6H_4PCl_2$ **1**, $C_6H_5PF_4$ **2**, o-$ClC_6H_4PF_4$ **3**, $C_6H_5P(O)F_2$ **4**, $C_6H_5P(O)HF$ **5**, $C_6H_5P(O)H(OH)$ **6**, and o-$ClC_6H_4P(O)Cl_2$ **7**, were determined in dilute benzene solution at 25°C. The phosphoryl bond moment P=O in compounds **4**, **5**, and **7** was estimated using simple bond-additivity calculations. The results obtained were 4.55D, 3.64D, and 5.52D for compounds **4**, **5**, and **7**, respectively. Dipole moments for compounds **2** and **3** were also calculated theoretically using INDO MO techniques. The calculated values differed from the experimental values by about 12%.

Key words: Molecular electric dipole moments; phenylphosphorus halogen compounds.

INTRODUCTION

The molecular electric dipole moment is an important molecular property which, in favourable circumstances, can provide information on molecular structure and conformation and on the electric charge distribution within the molecule. As part of an ongoing study of organophosphorus halogen compounds we determined the electric dipole moments of o-$ClC_6H_4PCl_2$ **1**, $C_6H_5PF_4$ **2**, o-$ClC_6H_4PF_4$ **3**, $C_6H_5P(O)F_2$ **4**, $C_6H_5P(O)HF$ **5**, $C_6H_5P(O)H(OH)$ **6**, and o-$ClC_6H_4P(O)Cl_2$ **7** molecules the dipole moments of which had not been reported in the literature heretofore.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 1.

The measured dipole moment values for compounds **4**, **5**, and **7** can be used to estimate the bond moment of the phosphoryl bond, P=O, in these molecules. The estimates can be accomplished by adopting the values of the P-phenyl, P-Cl, and P—F bond moments of Emsley and Hall[7] and the dipole moment of 1.58D for the chlorobenzene molecule[8] and by further assuming a vector-bond model for the

TABLE I

Dipole moments in benzene solution at 25°C

	Compound	ω_{2max}	$\alpha-\nu$	μ 10^{-30} Cm	μ D
1	o-$ClC_6H_4PCl_2$	0.016	4.4736	9.87	2.96
2	$C_6H_5PF_4$	0.012	9.8125	13.58	4.07
3	o-$ClC_6H_4PF_4$	0.011	8.3520	13.64	4.09
4	$C_6H_5P(O)F_2$	0.014	8.6904	12.01	3.60
5	$C_6H_5P(O)HF$	0.010	7.4898	10.51	3.15
6	$C_6H_5P(O)H(OH)$	0.018	3.1235	6.74	2.02
7	o-$ClC_6H_4P(O)Cl_2$	0.012	8.1712	13.84	4.15

ω_{2max} is the maximum mass fraction of solute in solution,

$$\alpha = \lim_{\omega_2 \to 0} \frac{d\varepsilon_{21}}{d\omega_2} \text{ and } \nu = \lim_{\omega_2 \to 0} \frac{dn^2_{21}}{d\omega_2}$$

where ε_{21} and n_{21} is the dielectric constant and refractive index of the solution, and μ the derived dipole moment in Coulomb meter and Debye units, respectively.

total molecular dipole moment and a tetrahedral structure for all three molecules. A straightforward calculation then yields for the P=O bond moment the values of 4.55D, 3.64D, and 5.52D for compounds **4**, **5**, and **7**, respectively. These values may be compared with the value derived by Cumper[9] for this bond moment of 2.88D and 2.95D in $R_3P{=}O$ and $(C_6H_5)_3P{=}O$ molecules, respectively. At first sight the large difference between our values and those of Cumper could be attributed to the presence of the halogen atoms in our molecules. However, due to the numerous simplifying assumptions that one is forced to make in such calculations the bond moment values obtained have only qualitative significance at best and do not warrant any further analysis.

We have also calculated theoretical values for the dipole moments of the pentacoordinated molecules $C_6H_5PF_4$ and o-$ClC_6H_4PF_4$, respectively, using the INDO MO method. It is our experience that the results of such calculations are usually in fair agreement with the experimentally determined values. Table 2 gives a comparison of the experimental and calculated values. It is seen that experimental values differ from the calculated values by some 12%. In view of the fact that the experimental values include the so-called solvent effect the agreement between the two sets of values is quite acceptable.

TABLE II

Comparison of experimental and INDO MO calculated dipole moments

	Compounds	μ (exp.) 10^{-30} Cm	μ (exp.) D	μ (calcd.) 10^{-30} Cm	μ (calcd.) D
2	$C_6H_5PF_4$	13.58	4.07	11.77	3.53
3	o-$ClC_6H_4PF_4$	13.64	4.09	15.14	4.54

EXPERIMENTAL

Materials. Fisher certified reagent "Spectroanalyzed" and "Chromatoquality" benzene was used as solvent. It was dried by repeated shaking with Linde molecular sieve 4A in a specially constructed glass column equipped with a fritted disk and a ground-glass joint which fitted into the corresponding joint on the dielectric constant cell. o-$ClC_6H_4PCl_2$ was obtained from Strem Chemicals Co. and was used without further purification. $C_6H_5PF_4$ was prepared after the method of Schmutzler[1] and the distilled fraction having a boiling point range 131.5–133.0°C was used. It was stored at 0°C prior to use. $C_6H_5P(O)F_2$ was prepared after the method of Schmutzler[2] and subsequently purified by distillation at 77°C/13 mm Hg. The $C_6H_5P(O)HF$ was prepared by slowly and carefully adding $C_6H_5PCl_2$, to 49% aqueous hydrogen fluoride solution in a Teflon bottle, followed by 10 minutes of stirring and distillation at 76–77°C/8 mm Hg. The $C_6H_5P(O)H(OH)$ was prepared according to the procedure of Buckler and Epstein[3] by dissolving phenylphosphine in ethanol at 0°C and the slow addition of 30% H_2O_2. The mixture was stirred for two hours at 0°C. Subsequent removal of solvent under reduced pressure gave a white solid which, after drying under vacuum for 24 hours, had a melting point of 73–74°C. o-$ClC_6H_4PF_4$ and o-$ClC_6H_4P(O)Cl_2$ were prepared by mixing o-$ClC_6H_4PCl_2$ with SbF_3 in a flask equipped with a reflux condenser. The mixture while stirred was slowly heated to 50°C. There ensued a vigorous exothermic reaction and the temperature of the reacting mixture was kept at or below 130°C for one hour. Subsequent distillation under reduced pressure yielded two products, viz., o-$ClC_6H_4PF_4$ collected at 23.0°C/0.1 mm Hg, and o-$ClC_6H_4P(O)Cl_2$ collected at 60–62°C/0.1 mm Hg.

Determination of Dipole Moments. The dielectric constants of a series of dilute (maximum concentration 2×10^{-2} mass fraction) benzene solutions of the different compounds were determined using a dipolemeter type DMO1, manufactured by the Wissenschaftliche-Technische Werkstätten GMBH (Germany). The instrument was calibrated as described by Bock and Dojack.[4] The refractive indices of the solutions were determined using an Abbe refractometer and a sodium-vapour light source. All measurements were carried out at 25°C. The molecular dipole moments were extracted from the raw data, i.e. the dielectric constants and refractive indices of the dilute solutions, after the method of Guggenheim as modified by Smith.[5] Procedures for calculating dipole moments μ from dilute solutions in nonpolar solvents have been discussed previously.[6]

ACKNOWLEDGEMENTS

The financial assistance of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1. R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).
2. R. Schmutzler, *J. Chem. Soc.*, 4551 (1964).
3. S. A. Buckler and M. Epstein. *Tetrahedron*, **18**, 1221 (1962).
4. E. Bock and E. F. Dojack, *Can. J. Chem.*, **45**, 1097 (1967).
5. J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950).
6. C. Wang, *Huaxue Tongbao*, **1**, 5 (1981).
7. J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper and Row Pub. Co., London, 1976, 1st ed., Chapt. 2, pp. 39–55.
8. A. L. McClellan, Tables of experimental dipole moments. W. H. Freeman and Co., San Francisco and London, 1963.
9. C. W. N. Cumper, *Tetrahedron*, **25**, 3131 (1969).