

DIPOLE MOMENTS AND VALENCE ANGLES IN
TRIARYLPHOSPHINES AND THEIR OXIDES

I.P.Romm, E.N.Guryanova, N.A.Rozanelskya, K.A.Kocheshkov

Karpov Institute of Physical Chemistry
107120 Moscow, USSR

(Received in UK 11 October 1976; accepted for publication 19 November 1976)

Measurements of dipole moments (DM) provide valuable information about the CXC valence angles (θ) in compounds of the type Ar_3X where X is a group V element (P, Sb, Bi) /1,2/. A considerable widening of the valence angles at P in tris(2,6-dimethyl) substituted species was first suggested using this approach /1/. Later, θ was X-ray determined to be $109,5^\circ$ in both trimesitylphosphine /3/ and tris(2,6-dimethylphenyl)phosphine /4/ (cf. 103° in triphenylphosphine /5/). The DM values are also important in connection with the problem of dipole moments of lone pairs (LP) on phosphorus and the problem of conjugation in aromatic phosphines.

Unfortunately, there is a considerable discrepancy in the reported values of DM. The value of 1.37 D for trimesitylphosphine in benzene solution obtained by Mislow et al. /6,7/ is very near to DM of triphenylphosphine (1.4-1.5 D) whereas according to our measurements /1,8/ in cyclohexane, this compound has DM of 0.98 D. As the phosphine DM values are of importance in connection with a number of principle problems of structure of these compounds, we have undertaken a thorough investigation of DM for a wider range of compounds. Both arylphosphines and their oxides have been studied in order to determine the effect of methyl substituents on the DM values and structures of respective compounds. Measurements of refractions and DM's were carried out in solutions at 25°C . The results appear in Table 1 where α , β and γ are slopes of ϵ , d and n_D^2 vs. C (mole fraction) lines, respectively, P_∞ is polarization at infinite dilution obtained by extrapolation according to Hedestrand, R_D is molar refraction, μ is dipole moment calculated from the equation $\mu = 0.22 \sqrt{P_\infty - R_D}$. For preparation of phosphines 2 to 4 see ref. /11/. Freshly prepared compounds only have been used.

The DM values for phosphine 1 reported earlier (/1/, solutions in benzene and cyclohexane) and obtained in this work (solution in hexane) agree well. With phosphine 2, the difference between the DM values obtained

Table 1

No.	Compound	s*	α	β	γ	P_{∞}	A_D	μ
1.	Triphenylphosphine	H	3.28	0.96		133.21	87.63	1.49
		CH						1.52
		B						1.53
2.	Trimesitylphosphine	H	3.09	1.30		156.38	135.41	1.01
		CH						0.98
		B	3.28	0.75		157.75	135.41	1.04
3.	Tridurylphosphine	CH	3.28	1.00	2.24	171.49	151.16	0.99
4.	Tris(2,6-dimethylphenyl)phosphine	CH						0.74
5.	Triphenylphosphine oxide	B	30.00	0.96	1.27	506.63	83.52	4.53
6.	Tri-p-tolylphosphine oxide	B	34.60	0.84		592.25	99.4**	4.88
7.	Trimesitylphosphine oxide	B	26.27	1.00	1.83	494.46	133.17	4.18

* Solvents: H - hexane, CH - cyclohexane, B - benzene.

** Calculated from additivity rule.

in various solvents (Table 1) is also insignificant. Hence the solvent effect by benzene is of little importance. The value of DM for tridurylphosphine (3) is practically the same as that for phosphine 2 and considerable below that for phosphine 1. As the contributions to DM from the methyl substituents compensate each other in 3 as well as in the mesityl radical, we expect compound 3 to have a structure similar to other 2,6-dimethyl derivatives with θ of about 110° , well above that value in 1. The results for phosphines 2 to 4 demonstrate that the 2,6-dimethyl substituents in the phenyl rings cause a considerable decrease in DM, mostly on account of an increase in θ .

Mislow et al. /7/ have criticized our value of 1.0 D for phosphine 2 /1/ and give DM of 1.37 D for the same compound. The discrepancy which arises from the difference in P_{∞} values (cf. 157 cm^3 /1/ and 178 cm^3 /7/) is worth a discussion. As mentioned, solvent effects can be ruled out. The DM values determined in our experiment are believed to be accurate to within 0.02 D. As a rule the results obtained with our technique agree well with the literature data. For instance, the data in table 1 for compounds 1 and 5 as well as those reported in /1/ for tri-o- and tri-p-tolylphosphine agree with the results obtained by other authors /10,11/. Neither there is any ground to doubt accuracy of the technique applied in /6,7/, the more so that the same DM value for 2 has been obtained by the classical Debye method /6/ and from dielectric losses measurements /7/. The good agreement of the lower

DM value for phosphine 2 (~ 1.0 D) and for compounds 3 and 4 (0.99 and 0.74 D respectively) argues in favour of our data. It should be noted that the value reported in /6,7/ leads to an unusually high value of about 2.5-3.0 D for the dipole moment of LP /7/ (according to other authors /12-14/, phosphorus LP have DM of 1.0 to 1.6 D).

Our DM value for phosphine oxide 5 agrees well with the literature data /10/. The DM for 6 predicted from the vector additivity rule gives a good fit to the experimental value which suggest that, as in the case of triphenylphosphine, the p-methyl substituents in the rings have little effect on the molecular structure. It is most interesting that the DM value for phosphine oxide 7 (4.18 D) is well below that for compound 5. This seems to imply a widening of the CPC angle in the mesityl derivative. The change of the CPC angle should cause a change in the phosphorus hybridization state and in the nature of the P-O bond. We have measured the IR spectra of the oxides in mesitylene solution. The P-O stretching frequencies in the spectra of trimesityl- and tris(2,6-dimethylphenyl)phosphine oxides have nearly the same value (1170 and 1174 cm^{-1} , respectively) which is lower than in the case of phosphine oxides 5 and 6 (1207 and 1200 cm^{-1} , respectively).

We thank Dr. A.I.Bokanov for valuable discussions.

References

1. I.P.Romm, E.N.Guryanova, K.A.Kocheshkov, Dokl. Akad. Nauk USSR, 212, 112 (1973). (Russ.)
2. I.P.Romm, V.I.Lodochnikova, O.P.Syutkina, E.N.Guryanova, E.M.Panov, Zh. strukt. khim., 16, 498 (1975); (Russ.) I.P.Romm, O.P.Syutkina, V.I.Lodochnikova, E.N.Guryanova, E.M.Panov, Zh. obshch. khim., in print. (Russ.)
3. J.F.Blount, C.A.Maryanoff, K.Mislow, Tetrahedron Lett., No. 11, 913 (1975).
4. A.N.Sobolev, L.A.Chetkina, I.P.Romm, E.N.Guryanova, Zh. strukt. khim., 17, 103 (1976). (Russ.)
5. J.J.Daly, J. Chem. Soc., 1964, 3799.
6. H.J.Halpern, K.Mislow, J. Am. Chem. Soc., 89, 5224 (1967).
7. M.P.Warchol, E.N.DiCarlo, C.A.Maryanoff, K.Mislow, Tetrahedron Lett., No. 11, 917 (1975).
8. I.P.Romm, N.A.Rozanelskaya, E.N.Guryanova, A.I.Bokanov, B.I.Stepanov, Zh. obshch. khim., 43, 1650 (1973). (Russ.)

9. B.I.Stepanov, E.W.Karpova, A.I.Bokanov, Zh. obshch. khim., 39, 1544 (1969); B.I.Stepanov, A.I.Bokanov, A.B.Kudryavtsev, Yu.G.Plyashkevich, Zh. obshch. khim., 44, 2358 (1974); A.I.Bokanov, N.A.Rozanel'skaya, B.I.Stepanov, Zh. obshch. khim., 44, 760 (1974). (Russ.)
10. C.W.N.Cumper, A.A.Foxton, J.Read, A.I.Vogel, J. Chem. Soc., 1964, 430.
11. H.Schindlbauer, Monatsch. Chem., 96, 1793 (1965).
12. J.P.Fayet, P.Mauret, J. chim. phys., 68, 156 (1971).
13. E.I.Matrosov, G.M.Petov, M.I.Kabachnik, Zh. strukt. khim., 15, 250 (1974). (Russ.)
14. B.D.Chernokalskii, A.S.Gelfond, Yu.G.Galyametdinov, F.Yu.Akhmadullina, Referaty dokladov XI Mendeleevskogo s"ezda po obshchei i prikladnoi khimii (Proceedings of the XIth Mendeleev Conference on General and Applied Chemistry), Nauka Press, Moskow (1975).