DIPOLE MOMENTS AND VALUE OF VALENCE ANGLE OF CAsC IN TRIARYLARSINES

I. P. Romm, O. P. Syutkina,
E. N. Gur'yanova, E. M. Panov,
and K. A. Kocheshkov

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As a continuation of studying compounds of type Ar_3X (X is a Group V element) by the method of dipole moments (DM) [1-3] we measured the DM of triphenyl-, tri-p-tolyl, tri-p-chlorophenyl-, and trimesitylarsine in benzene at 25°C. In Table 1 are given α, β, and γ, the slope tangents of lines ε—C, d—C, and $n_D{}^2$—C (C = mole fractions); P_∞ is the polarization at infinite dilution, obtained by the Hedestrand extrapolation; R_D is the molar refraction. The DM were calculated using the equation $\mu = 0.22\sqrt{P_\infty - 1.05\ R_D}$.

The insertion of substituents (CH_3, Cl) in the p position leads to a substantial change in the DM. The total contribution of the DM of the substituents (μ_1) can be calculated using the equation $\mu_1 = \mu_{\text{subt}}\sqrt{3 + 6\cos\theta}$, where the DM of the substituent (μ_{subt}) is equal to 0.37 D for CH_3 and 1.59 D for Cl, and θ is the value of the CAsC angle. The dipole moments of compounds (II) and (III) can be depicted by the vector sum μ_1 and the DM of triphenylarsine (1.14 D). The best agreement with experiment gives $\theta = 102°$ (1.63 and 0.97 D for (II) and (III), respectively). The value of the θ angle of triarylarsines (I)-(III), obtained from the DM data in solution, agrees exceedingly well with the value of this angle (102°) in tri-p-tolylarsine [8] and tris-(2, 5-xylyl)-arsine [9], which was found by the x-ray structure analysis method.

It is interesting that the DM of trimesitylarsine is smaller than that of triphenylarsine by 0.44 D. Since the insertion of three CH_3 groups in the 2, 4, 6 positions of the phenyl ring does not change the DM of the radical, and the rotation of the phenyl or mesityl group around the axis of the As—C bond cannot change the contribution of this group to the DM of the molecule, the observed difference in the DM of arsines (I) and (IV) is most probably related to the higher value of the CAsC angle in trimesitylarsine when compared with triphenylarsine. The insertion of CH_3 groups into the o-position of the phenyl rings of compounds of type $(C_6H_5)_3X$ leads to a substantial change in the structure and properties of the molecule. Thus, in trimesityl-, triduryl, and tris(2, 6-dimethylphenyl)phosphine the CPC angle is much greater (roughly 110° [1, 10, 11] than in triphenylphosphine (103°), which finds reflection in the DM values of the phosphines [1, 10].

Starting with the difference in the DM values of arsines (I) and (IV), it is impossible to estimate the value of CAsC in trimesityl- arsine, since the relation between the DM of the unshared electron pair of the As atom and the value of this angle is not known.

The work on determining the value of the CAsC valence angle of trimesitylarsine is being continued.

TABLE 1. Dipole Moments of R_3As (Benzene, 25°C)

Compound No.	R	α	β	γ	P_∞	R_D	μ*, D
(I)	Phenyl	3,45	1,17	1,39	119,4	88,3	1,14
(II)	p-Tolyl	5,33	1,12	1,34	163,0	103,4	1,62
(III)	P-Chlorophenyl	3,28	1,93	1,57	129,1	103,1	1,00
(IV)	Mesityl	2,29	1,26	1,84	151,4	134,7	0,70

*Data for (I): 1.07 [4]; 1.23 [5]; 1.36 [6]; for (II): 1.74 [7].

L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 468-470, February, 1977. Original article submitted July 27, 1976.

EXPERIMENTAL

The studied arsenic compounds were synthesized by the Grignard reaction in ether. The reaction mixture was decomposed with dilute HCl solution. After drying the ether solution the products were isolated in up to 80% yields. The melting points of triphenylarsine (60°, from alcohol), tri-p-tolylarsine (151°, from alcohol), and tri-p-chlorophenylarsine (107°, from alcohol) agree with the data given in [12-14]. $(p\text{-ClC}_6H_4)_3As$. Found: Cl 25.64%. $C_{18}H_{12}AsCl_3$. Calculated: Cl 26.00%. When preparing trimesitylarsine the reaction was run in an ether–tetrahydrofuran mixture. The product has mp 177° (from n-hexane, cf. [13]).

CONCLUSIONS

Based on measuring the dipole moments of triphenyl-, tri-p-tolyl-, tri-p-chlorophenyl-, and trimesitylarsine, the value of the CAsC valence angle was estimated for the first three compounds (102°). This angle should be substantially greater for trimesitylarsine.

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CHEMILUMINESCENCE IN REACTIONS OF ORGANIC PEROXIDES WITH BUTYLLITHIUM

A. A. Panasenko, V. S. Sultanova,
V. G. Kozlov, and V. P. Kazakov

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Chemiluminescence (CL) was observed in the reactions of Grignard reagents and alkali-metal organometallic compounds with oxygen [1, 2], and also of aromatic Grignard reagents with aromatic peroxides [3].

The results of studying a new luminescent reaction of the organic peroxides: benzoyl, lauryl, and tert-butyl peroxide with butyllithium in either toluene, heptane, or THF solution are reported in the present paper.

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