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EVIDENCE FOR THE CONTRIBUTION OF THE LONE PAIR TO THE MOLECULAR DIPOLE MOMENT OF TRIARYLPHOSPHINES

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We wish to report evidence that the overall dipole moment of triphenylphosphine and derivatives is dominated by the contribution of the partial moment of the lone pair on phosphorus.

Some years ago, the observation that the dipole moment (μ) of trimesitylphosphine (1), 1.37 D, is close to the range of moments (1.39 - 1.54 D) reported for triphenylphosphine (2) led us to the conclusion[1] that the C-P-C bond angles (θ) in the former should not deviate much from those in the latter. Our confident expectation that 1 should have bond angles near 103° was therefore rudely shattered by the discovery[2] that these angles in fact average 109.7°. The nature of the dilemma can be stated in the following terms. On the reasonable assumption that the previously calculated[1] group moment of phenyl, μ_R = 1.09 D, equals that of mesityl,[3] and given μ of 1 = 1.37 D, the calculated value of θ = 103.7° for 1 is significantly smaller than the observed 109.7° and is in fact indistinguishable from θ_{ave} of 2.[4] Alternatively, given a θ_{ave} of 1 = 109.7°, the calculated μ of 1, 1.08 D, is significantly smaller than the observed 1.37 D.

A careful reevaluation of the dipole moments of 1 and 2 by use of the microwave absorption method yielded values of 1.35 ± 0.03 D and 1.40 ± 0.03 D, respectively (benzene, 25°),[5] which are in good agreement with the μ of 1.44 D previously reported for 2 by Hassel, et al.,[6] using the same method, and with the previously reported[1] μ of 1, determined by the classical method.[7] We note that our value for μ of 1 is grossly different from the recently reported[8,9] values of 0.98 and 1.01 D, which were also determined by the classical method.[7] This voids the experimental basis for the conclusion,[8] based on the lower values, that the phosphorus pyramid in 1 has suffered an unusually large flattening ($\theta \approx 115°$), even though this conclusion accidentally accords, in a qualitative sense, with the results of the subsequent X-ray analysis.[2,10]

One is thus forced to the conclusion that the root of the difficulty lies in the failure of the earlier analysis[1] to take explicit account of the contribution of the lone pair to the overall moment. Such neglect is entirely justifiable as long as there are not significant changes in θ relative to 2, as is the case for tolylphosphines[1] but not, as we now know, for 1.

Within the framework of the equivalent (localized) orbital formalism, the lone pair of electrons may make a sizable and even dominant contribution to the overall molecular moment.[11] This contribution (μ_{LP}) is non-zero when the electrons occupy a hybrid (sp^n) orbital and vanishes when the electrons are symmetrically disposed about the nucleus in an unhybridized s or p orbital. On the assumption that interorbital angles do not differ substantially from internuclear angles, it is then possible to express μ_{LP} analytically as a function of θ.[12,13] For phosphines, $\mu_{LP} = 0$ at $\theta = 90°$ and $120°$, and achieves its maximum value (μ_{LP}^{max}) at $\theta = 101.5°$, corresponding to sp hybridization of the lone pair orbital. These considerations may now be applied to the case of 1 and 2.

The relationship between μ_{LP} and θ is given by eq. 1. The variation of the overall moment μ with θ is expressed by eq. 2. The second term of eq. 2 represents the vectorially summed contribution of the three aryl ligands, on the assumption of C_3 symmetry.

$$\mu_{LP} = 2\mu_{LP}^{max}\sqrt{-3\cos\theta\,(1 + 2\cos\theta)}/(1 - \cos\theta) \qquad \text{eq. 1}$$

$$\mu = \mu_{LP} - \mu_R\sqrt{3(1 + 2\cos\theta)} \qquad \text{eq. 2}$$

For 1 and 2, μ and θ are known quantities. If μ_R and μ_{LP}^{max} are taken to be the same for the two molecules,[14] the four equations lead to the following values for the four unknowns: $\mu_R = 1.18$ D, $\mu_{LP}^{max} = 2.93$ D, $\mu_{LP} = 2.52$ D for 1, and $\mu_{LP} = 2.92$ D for 2.[15]

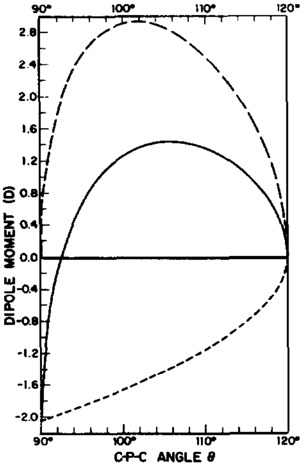

Figure 1. The calculated overall dipole moment, μ, of trimesityl- and triphenylphosphine (1 and 2) as a function of C-P-C bond angle, θ (solid curve). Variation of component partial moments with θ is given by the dashed curves:

μ_{LP}	long dashes
$\mu_R\sqrt{3}\,(1 + 2\cos\theta)$	short dashes

It is instructive to examine in further detail the variation of μ with θ given in eq. 2. As shown in Figure 1 (solid line), when $\theta = 90°$, $\mu = \sqrt{3}\mu_R = 2.04$ D. The negative sign signifies that the moment is directed toward the base of the phosphorus pyramid. As θ increases, the negative contribution from the ligands slowly decreases while at the same time the positive contribution from the μ_{LP} rapidly increases. Near $\theta = 92.5°$, the overall moment reverses direction toward the apex of the pyramid. This direction is maintained for all values of $\theta > 92.5°$. The contribution of the lone pair thus dominates the molecular moment of these and related triarylphosphines.

Figure 1 also reveals that as θ spreads from 101° to 110°, μ changes only slightly, from 1.32 D at 101°, by way of a maximum of 1.43 D at 105.5°, to 1.34 D at 110°. Over the same range of bond angles, the resultant of μ_R (second term of eq. 2) decreases from -1.61 to -1.15 D, while the vectorially opposite μ_{LP} simultaneously decreases from 2.93 to 2.49 D. It is this compensating effect which accounts for the observed insensitivity of μ to a large change in θ.

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References and Notes

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