

Steric Effects on the Ultraviolet Spectra of Monoarylphosphines

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The u.v. absorption spectra have been determined for a series of primary, secondary, and tertiary monoarylphosphines in which the aryl group varies through phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl, and mesityl, and the phosphorus substituents through H, Me, Et, Pr^t, and Bu^t. The spectra contain a charge-transfer band which is sensitive to steric effects. The spectra show that the amount of conjugation of the phosphorus lone-pair of electrons with the aryl ring is small and is reduced still further by steric crowding. The possible conformational changes induced by the steric effects are discussed.

THE u.v. spectra of arylphosphines have been studied by many workers and there has been a long debate on the interpretation of the spectra.¹ However, there has not been a detailed study of steric effects which alter the interaction of the phosphorus lone pair of electrons with the aryl ring. It was therefore of interest to study the effects of a systematic increase in steric crowding on the spectra of phenylphosphine and its analogues in the light of our success using this approach for the study of arene-thiols and aryl sulphides.²

RESULTS

The u.v. spectra of a series of primary, secondary, and tertiary phosphines in cyclohexane and 5% ethanol in water were determined. The group R was varied through H, Me, Et, and Pr^t, and included Bu^t for the secondary phosphine. The spectra of the phosphines in cyclohexane which are given in Table 1, contain four bands, an intense band (log ϵ 4.0–4.3) at 209 ± 2 nm, a slightly less intense band (log ϵ 3.8–4.1) at 219 ± 2 nm, a moderately intense band (log ϵ 3.3–3.7) in the central region from 237 to 255 nm, and a weak band (log ϵ 2.8–3.4) at 266 nm. The last band has a well resolved vibrational fine structure and the short wavelength band shows inflections.

A narrower range of tolyl and mesityl compounds were studied. The bands in their spectra, which are given in Table 2, show similar trends and the main effect of methylation of the ring is to shift the bands to longer wavelength.

An increase in the polarity of the solvent produces a small hypsochromic shift of 0–5 nm and a decrease in intensity

other bands showed less vibrational fine structure when the polarity of the medium was increased.

TABLE 2

$\lambda_{\max.}/\text{nm}$ (log ϵ) Values of the main bands in the u.v. spectra of tolyl- and mesityl-phosphines

Compound	217s (4.00)	227s (3.81)	237s (3.72)	272 * (2.86)
<i>o</i> -TolylPH ₂	217s (4.00)	227s (3.81)	237s (3.72)	272 * (2.86)
<i>o</i> -TolylPHBu ^t	216s (4.15)	225s (3.96)	253 (3.58)	272 * (3.40)
<i>o</i> -TolylPMe ₂	210s (4.20)	216s (4.11)	254 (3.68)	272 * (3.44)
<i>m</i> -TolylPH ₂	216s (4.15)		237s (3.70)	272 * (2.89)
<i>m</i> -Tolyl-PHBU ^t	216s (4.20)	227s (3.95)	252 (3.60)	272* (3.41)
<i>m</i> -TolylPMe ₂	210s (4.18)	216s (4.08)	253 (3.63)	272 * (3.40)
<i>p</i> -TolylPH ₂	209s (3.95)	225s (3.72)	235s (3.66)	272 * (2.46)
<i>p</i> -TolylPHBU ^t	213s (3.86)	225s (3.79)	247 (3.56)	272 * (3.18)
<i>p</i> -TolylPMe ₂	210s (4.00)	225s (3.76)	253 (3.56)	272 * (3.22)
MesitylPH ₂	205 (4.59)		237 (3.91)	275 * (2.99)
MesitylPMe ₂	206 (4.76)	230 (4.15)	265 (3.36)	275 * (3.32)

* Exhibit vibrational fine structure.

TABLE 3

$\lambda_{\max.}/\text{nm}$ (log ϵ) Values in the main bands in the u.v. spectra of tertiary phosphines in dilute hydrochloric acid

Compound	220 (3.96)	266 * (2.93)
PhP ⁺ Me ₂ H	220 (3.96)	266 * (2.93)
PhP ⁺ MeEtH	219 (3.93)	266 * (2.90)
PhP ⁺ Et ₂ H	218 (3.95)	266 * (2.91)
PhP ⁺ Pr ^t ₂ H	219 (3.98)	266 * (2.90)
<i>o</i> -TolylP ⁺ Me ₂ H	220 (3.92)	272 * (3.11)
<i>m</i> -TolylP ⁺ Me ₂ H	220 (3.90)	272 * (3.15)
<i>p</i> -TolylP ⁺ Me ₂ H	225 (4.11)	267 * (2.86)
MesitylP ⁺ Me ₂ H	206 (4.67)	235 (4.04)
		278 * (3.26)

* Exhibit vibrational fine structure.

TABLE 4

$\lambda_{\max.}/\text{nm}$ (log ϵ) Values of the main bands in the u.v. spectra of primary and secondary phosphines in concentrated hydrochloric acid

Compound	222 (4.00)	267 * (3.06)
PhP ⁺ H ₃	222 (4.00)	267 * (3.06)
PhP ⁺ MeH ₂	222 (3.97)	267 * (3.02)
PhP ⁺ EtH ₂	222 (4.00)	267 * (3.05)
PhP ⁺ Pr ^t H ₂	222 (4.02)	267 * (3.06)
PhP ⁺ Bu ^t H ₂	223 (4.02)	267 * (3.08)
<i>o</i> -TolylP ⁺ H ₃	225 (3.88)	275 * (3.18)
<i>m</i> -TolylP ⁺ H ₃	214 (3.85)	227 (3.81)
<i>p</i> -TolylP ⁺ H ₃	230 (3.94)	270 * (2.94)
MesitylP ⁺ H ₃	214 (4.28)	244 (4.00)
<i>o</i> -TolylP ⁺ Bu ^t H ₂	225 (3.91)	276 * (3.20)
<i>m</i> -TolylP ⁺ Bu ^t H ₂	227 (3.88)	274 * (3.19)
<i>p</i> -TolylP ⁺ Bu ^t H ₂	210 (3.73)	233 (4.03)
<i>p</i> -MeOC ₆ H ₄ P ⁺ H ₃	246 (4.22)	278 * (3.18)

* Exhibit vibrational fine structure.

TABLE 1

$\lambda_{\max.}/\text{nm}$ (log ϵ) Values of the main bands in the u.v. spectra of phenylphosphines in cyclohexane solution

Compound	208s (4.11)	220s (3.87)	237s (3.72)	266 * (2.75)
PhPH ₂	208s (4.11)	220s (3.87)	237s (3.72)	266 * (2.75)
PhPHMe	208s (4.11)	220s (3.91)	245 (3.73)	266 * (3.23)
PhPHEt	208s (4.11)	220s (3.83)	242 (3.70)	266 * (3.23)
PhPHPr ^t	209s (4.09)	220s (3.88)	243 (3.68)	266 * (3.21)
PhPHBu ^t	209s (4.04)	218s (3.92)	248 (3.58)	266 * (3.30)
PhPMe ₂	210s (4.11)	220s (3.88)	252 (3.70)	
PhPMeEt	208s (4.10)	220s (3.92)	253 (3.48)	266 * (3.36)
PhPEt ₂	208s (4.11)	219s (3.93)	255 (3.43)	266 * (3.36)
PhPPr ^t ₂	210s (4.03)	219s (3.86)	254 (3.28)	266 * (3.26)

* Exhibit vibrational fine structure.

mainly for the band in the central region. Primary, secondary, and tertiary phosphines were similarly affected. The

The spectra of the protonated phosphines which are given in Tables 3 and 4 contain only two bands.

DISCUSSION

As the bulk of the alkyl group is increased the central band shifts steadily to longer wavelength and decreases in intensity. As expected the effects are greater for the tertiary phosphines than the secondary phosphines. When the steric crowding involves a mesitylene group the shift and intensity reduction is large as soon as the PH_2 group is replaced by a PMe_2 group, showing that the main effect has a steric origin.

The positions and intensities of the central band are similar to those observed for the alkyl aryl sulphides.² The trends are characteristic of transitions involving charge-transfer states which have mixed with locally excited states.^{2,3}

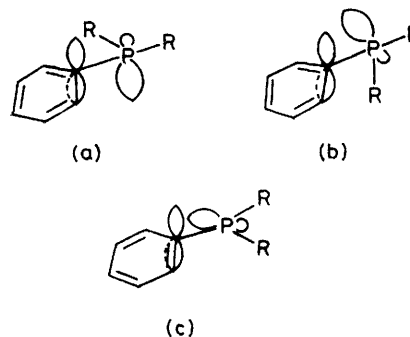
The locally excited benzenoid bands at short and long wavelengths in the spectra are little affected by changing the alkyl groups bound to the phosphorus atom. In this respect they resemble more closely the spectra of the benzyl sulphides which possess little ground state conjugation, and in both series the weak 1L_b band appears at 266 nm.^{2,4} The 1L_b is at short wavelength in the spectra of the secondary and tertiary aryl phosphines than in the spectra of the alkyl aryl sulphides and consequently it overlaps the central charge-transfer band which makes it impossible to carry out interference experiments for d orbital participation. However the bands are well separated in the spectra of the primary phosphines and indeed it has already been shown that there is d orbital participation.⁵ Our spectra confirm these conclusions. The involvement of d orbitals indicates that there is limited p_π overlap even for the primary phosphines and it seems probable that d orbital involvement will be greater and thus p_π overlap less for the secondary and tertiary phosphines.

The relatively small hypsochromic shifts produced by increasing the hydrogen-bonding properties of the solvent also supports a limited degree of conjugation because the basicity of the lone pair is greater in the phosphines than in the sulphides whose spectra show somewhat larger hypsochromic shifts.

The spectra of the phosphines in hydrochloric acid which are similar to the spectra of arylphosphonium compounds,⁶ contain an intense band near 220 nm and a weaker band near 270 nm. Although the removal of the charge-transfer state accounts for the disappearance of the central band it is not expected to alter greatly the locally excited states since the steric effects on the central band shows that the charge-transfer state lies above the locally excited state.³ Thus the effects of protonation upon the bands in the region below 225 nm appear to be due to changes in inductive and d orbital interactions.

There is a difference of opinion on the amount of stabilising energy due to p_π bonding in arylphosphines.^{7,8} The u.v. spectra show that the interaction of the aryl ring with the phosphorus lone-pair is quite limited in the

ground state. On the other hand it shows that it is not absent and that it is possible for steric effects to modify the interaction. These conclusions are in accordance with the photoelectron spectra.⁹ Studies of the Kerr



effect indicate that there is little population of conformation (a) in which both phosphorus substituents are on the same side of the aryl ring^{4,8} and there is also ample evidence that the phosphorus lone-pair has a high proportion of s character. Thus to allow for some alteration in the phosphorus-aryl interaction as required by the changes in the u.v. spectra there would need to be present both conformers (b) and (c). An increase in steric crowding about the phosphorus atom could also increase the $\widehat{\text{CPC}}$ bond angles with a resultant increase in the p character of the lone-pair. However, this appears to operate in the wrong direction for p_π overlap.

EXPERIMENTAL

U.v. spectra were recorded on a Perkin-Elmer 402 instrument using 5 mm silica cells. Commercial spectroscopic grades of solvents were used, purified further by distillation and purged with nitrogen for 30 min before use. The amount of stray light at short wavelength was checked as before.² The phosphines were weighed (5–50 mg) in nitrogen-filled volumetric flasks (5, 10, and 25 ml), the concentration chosen being suitable for direct estimation of the intensity of a particular band. The spectra of the protonated tertiary phosphines were determined in 5*N*-hydrochloric acid, and those of the primary and secondary in the concentrated acid. The phosphines were prepared by standard methods and isolated by distillation under reduced nitrogen atmosphere until pure by b.p. and n.m.r. examination.

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REFERENCES

- H. H. Jaffe, *J. Phys. Chem.*, 1954, **58**, 185; C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Canad. J. Chem.*, 1961, **39**, 171; B. I. Stephanov, A. I. Bokanov, and B. A. Korolev, *Teor i eksp. Khim.*, 1968, **4**, 171; O. A. Yakutina, G. V. Ravovski, B. V. Timokhin, and Y. L. Frolov, *Zhur. obschchi Khim.*, 1972, **42**, 1733; A. Goetz, *Tetrahedron Letters*, 1971, 1499.
- I. W. Jones and J. C. Tebby, *J.C.S. Perkin II*, 1979, 217.
- J. N. Murrell, *J. Chem. Soc.*, 1956, 3779; *Quart. Rev.*, 1961, **15**, 191; A. Mangini, A. Trombetti, and C. Zauli, *J. Chem. Soc.*, (B), 1967, 153.
- E. N. Tsvetkov and M. I. Kabachnik, *Russ. Chem. Rev.*, 1971, **40**, 97; J. W. Raksy, R. A. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1968, **90**, 5236; I. P. Romm, E. M. Sadykova, E. N. Gur'yanova, I. D. Kolli, and K. A. Kocheshkov, *Doklady Akad. Nauk. S.S.S.R.*, 1970, **195**, 372.

⁵ J. E. Bissey and H. Goldwhite, *Tetrahedron Letters*, 1966, 3247.

⁶ M. A. A. Beg and Samiuzzaman, *Tetrahedron*, 1968, **24**, 191.

⁷ E. N. Tsvetkov, *J. Gen. Chem. (U.S.S.R.)*, 1975, **45**, 489.

⁸ I. P. Romm and E. N. Gur'yanova, *J. Gen. Chem. (U.S.S.R.)*, 1976, **46**, 445.

⁹ W. Shafer and A. Schweig, *Angew. Chem. Internat. Edn.*, 1972, **11**, 836.