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d-ORBITAL PARTICIPATION IN ARYL PHOSPHINES -
A SUBSTITUENT INTERFERENCE EXPERIMENT.

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A particularly elegant method of testing whether there is conjugation between 3d orbitals on an atom of a third row element and an adjacent benzene ring is the substituent interference experiment, developed by Goodman, and recently applied to silicon (2) and sulfur (3) compounds. In essence the method consists of a comparison of the absorption intensities of the electronic spectra of related benzene derivatives in the 2600Å region. The compounds required are: a) a monosubstituted benzene bearing a moderately perturbing substituent (e.g. methyl or methoxyl); b) a monosubstituted benzene bearing a substituent with the element in question attached to the ring; the remaining bonds from the element are preferably to hydrogen, to minimize second-order effects; c) a para-disubstituted benzene bearing both the above substituents.

If there is withdrawal of electrons from the benzene ring into the 3d orbitals of the substituent then the intensity of the benzene analog transition in the para-disubstituted compound will be weaker than that in monosubstituted compound with the more intense transition. For example (see Table I) the band in p-methoxyphenylsilane is markedly less intense than that in anisole; the same applies to p-methylthiophenol and thiophenol. However in p-cresol (where the oxygen substituent has no available d-orbitals) the band is considerably more intense than that in toluene or phenol.

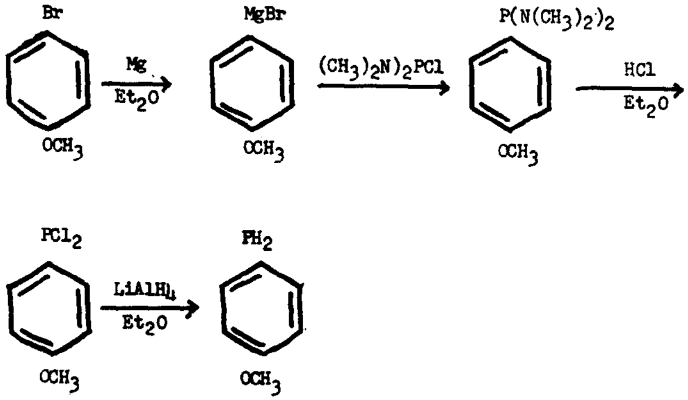
Table I Intensities of some 2600-Å benzene analog transitions

Compound	E_s*	(mμ)**	Ref.
p-$CH_3OC_6H_4SiH_3$	1075	281	(2)
$C_6H_5SiH_3$	243	271	(2)
$CH_3OC_6H_5$	1630	272	(2)
p-$CH_3C_6H_4SH$	300	275	(3)
C_6H_5SH	700	269	(3)
p-$CH_3C_6H_4OH$	1840	277	(3)
$CH_3C_6H_5$	205	268	(2)
C_6H_5OH	1320	269	(3)

* Smoothed molar extinction coefficient.

**Maximum of the 2600-Å benzene analog transition.

Because of our interest in the spectroscopic properties of phosphorus compounds, and because the result would allow a comparison of phosphorus with the other third row elements already studied, we have carried out a substituent interference experiment on aromatic compounds bearing a phosphorus substituent. As in the experiments with silicon, a methoxy group was chosen as the moderately perturbing substituent. Phenyl phosphine was prepared by the lithium aluminum hydride reduction of phenylphosphorus dichloride. The desired p-methoxyphenylphosphine was prepared by the route outlined below; the relative orientation of substituents was confirmed by the proton magnetic resonance spectrum of the compound which, in the aromatic region, showed an AA'MM' pattern, and by the infrared spectrum which had bands at 1033, 1074, 1105, and 1182 cm^{-1}, and a characteristic pattern in the 1650-2000 cm^{-1} region attributable to a p-disubstituted benzene (4)



The ultraviolet spectra of p-methoxyphenylphosphine, phenylphosphine, and anisole are shown in Figure 1. The marked decrease in intensity of the benzene analog transition in p-methoxyphenylphosphine as compared with anisole shows that the phosphine substituent is withdrawing electrons from the benzene ring into the 3d orbitals (or, much less probably, the 4p orbitals) of phosphorus.

A confirmation of this result lies in the data published by Schindlbauer for p-methylphenylphosphine (5). In this compound, also,

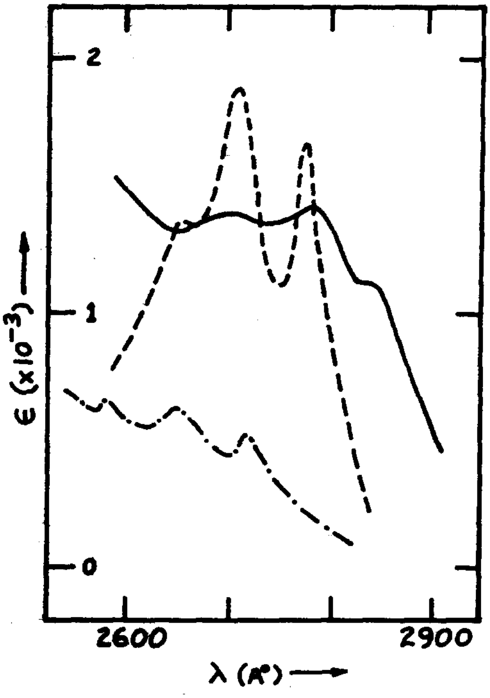


Figure 1. Ultraviolet Spectra of the Benzene Analog Transition of Anisole (— — — —), p-Methoxyphenylphosphine (————), and Phenylphosphine (—·—·—·—).

the expected decrease in intensity, as compared with phenylphosphine, is noted (see Table II).

Table II

Intensities of the 2600A benzene analog transition in some phosphorus compounds and non-phosphorus containing analogs

Compound	E_s	mμ	Ref.
$C_6H_5PH_2$	590	265	*
p-$CH_3OC_6H_4PH_2$	1400	276	*
$CH_3OC_6H_5$	1630	272	(2)
p-$CH_3C_6H_4PH_2$	355	264	(4)
$CH_3C_6H_5$	205	268	(2)

*Present work.

Thus the behavior of phosphorus parallels that of its neighbors in the periodic table, and it is clear that for these third row elements there is convincing evidence of conjugation of their 3 d orbitals with an adjacent unsaturated system. Further chemical and spectroscopic consequences of this observation are currently under investigation.

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