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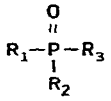
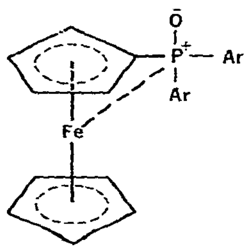
Electronic effects in ferrocenylphosphine oxides

Jaffé, in his extended investigations of the electronic spectra of aromatic phosphoryl compounds[1-3], recognized the absence of significant conjugation between the phenyl groups and the central phosphorus atom in triphenylphosphine oxide and related phenylphosphoryl compounds. Later, Griffin and collaborators[4], following a general prediction by Berlin and Butler[5], were able to show that such conjugation, or d_π–p_π bonding, in aromatic phosphine oxides may increase in importance with enhanced electron donor power of the aromatic substituents. Thus, appreciable d_π–p_π interaction was found by these workers in such phosphoryl compounds as tri-2-pyrrylphosphine oxide and tri-2-furylphosphine oxide, that is, in compounds with heteroaromatic ring systems of well established electron donor character relative to the phenyl ring[6]. Goetz and co-workers[7] arrived at similar findings in their investigation of certain phenylphosphine oxides substituted in *para* position. It would appear that the results of these workers simply reflect the small contributions received by the excited state from such polar structures as, for example, (Ia) in the case of triphenylphosphine oxide with its distinctly electronegative phenyl ligands, and, correspondingly, the large contributions received by the excited state from structures like (Ib) in the trifurylphosphine oxide case with its electron releasing heteroaromatic ligands.



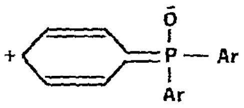
$$R_1-\underset{R_2}{\underset{|}{\overset{\overset{O}{\parallel}}{P}}}-R_3$$

II, $R_1 = R_2 = R_3 =$ ferrocenyl
III, $R_1 = R_2 =$ ferrocenyl
$R_3 =$ phenyl

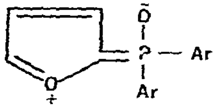


In connection with studies in this laboratory on interannular resonance effects in phosphoryl-bridged macromolecular ferrocene compounds, it was of interest to investigate the spectroscopic behavior of phosphine oxides bearing ferrocenyl substituents. Several such compounds, for example, triferrocenylphosphine oxide (II) and diferrocenylphenylphosphine oxide (III), had previously been synthesized by Sollott *et al*[8,9]. We expected the electron donor properties of the ferrocene group in these ferrocenylphosphoryl derivatives to result in similarly extensive d_π–p_π interaction between the phosphoryl and ferrocenyl groups as observed in the analogous cases involving pyrryl or furyl ligands[4]. Assuming a net stabilization of the excited state as a result of more significant contributions from polar forms of the type (Ic), such d_π–p_π interaction should manifest itself in bathochromic and, possibly, hyperchromic shifts of typical $V \leftarrow N$ bands and other conjugation-sensitive absorptions relative to the parent metallocene or derivatives comprising non-conjugated ferrocenyl groups.

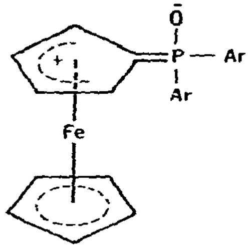
Table 1 contains a collection of essential absorption maxima, recorded in polar and non-polar solvents, of the two ferrocenylphosphine oxides (II) and (III), with corresponding data on diferrocenylphenylmethane[10,11] and ferrocene listed for comparison. The tabulation includes the two strongest bands of the spectrum due to allowed or essentially allowed transitions $(V \leftarrow N)$[12] in the 205-mμ and 255-mμ regions, and also comprises the two characteristic, low-intensity ligand-field[13] bands in the regions near 330 and 440 mμ.



Ia
(Ar = phenyl)



Ib
(Ar = 2-furyl)



Ic
(Ar = phenyl or
ferrocenyl)

TABLE 1

ULTRAVIOLET ABSORPTION MAXIMA

Compound	*Solvent*[a]	$\lambda_{max}(m\mu)$[b]							
Triferrocenylphosphine oxide(II)	EtOH	206	(114,000)	257	(11,800)	334	(580)	442	(450)
	$CHCl_3$	—	—	255	(14,500)	335	(600)	443	(430)
	C_6H_{12}	206	(118,000)	255	(12,400)	332	(530)	440	(460)
Diferrocenylphenylphosphine oxide(III)	EtOH	206	(79,000)	257	(8,300)	335	(590)	442	(300)
	$CHCl_3$	—	—	255	(11,000)	335	(680)	441	(300)
	C_6H_{12}	205	(89,000)	254	(9,600)	333	(460)	440	(330)
Diferrocenylphenylmethane	EtOH	204	(88,600)	254	(7,800)	327	(170)	442	(225)
	$CHCl_3$	—	—	253	(8,400)	328	(200)	442	(220)
	C_6H_{12}	206	(82,700)	254	(8,100)	327	(150)	441	(250)
Ferrocene	EtOH	202	(44,000)	245	(2,900)	325	(55)	440	(95)
	Iso-C_5H_{12}[c]	202.5	(51,400)	240	(3,500)	324	(58)	440	(107)

[a] EtOH = 95% ethanol; C_6H_{12} = cyclohexane; Iso-C_5H_{12} = isopentane. [b] Molar extinction coefficients, ε, in parentheses. Bands in 250-mμ and 330-mμ regions occasionally appearing as shoulders. [c] Values in isopentane taken from ref. 12.

The listed data show very small, if any, bathochromic and hyperchromic shifts relative to ferrocene or the practically non-conjugated model compound, diferrocenylphenylmethane. (Insignificant resonance effects in the latter compound, probably through hyperconjugation, are indicated by the minute shifts, with respect to ferrocene, of the maxima in the 255-mμ and 330-mμ regions and in the region, not tabulated here, near 270 mμ.) In fact, by plotting the absorption in a log ε *vs.* λ system on the basis of extinction coefficients calculated in all cases for a single ferrocene chromophore unit, one would obtain virtually coinciding curves for phosphine oxides (II) and (III), with these curves in turn very closely approaching the curves for ferrocene and diferrocenylphenylmethane in the range from about 200 to 280 mμ and in the vicinity of 440 mμ. The only difference to be noticed would be in the 330-mμ region, with (II) and (III) exhibiting small bathochromic shifts and a minor intensity enhancement relative to the non-conjugated compounds. These findings suggest little, if any, excited state stabilization through contributions from such structures as (Ic). The overall picture, contrasting the earlier expectation, rather shows a state of affairs comparable to that observed[1,2] for triphenylphosphine oxide, with each ferrocene chromophore in essence absorbing independently and only very weak d_π–p_π interaction existing between ligands and central atom.

To reconcile these spectroscopic findings with the well established[14–17,34] electron donor properties of the ferrocene group*, it would appear tempting to propose excited state contributions from structures involving participation of non-bonding (E_{2g}) iron d-electrons as exemplified schematically in (IV)**. Such d-electron participation in metallocene chemistry is well documented in cases involving protonation[20,21], hydrogen bonding[22], stabilization of α- and β-carbonium ions[23–25], etc. The interaction depicted by (IV), brought about by valence shell expansion of the central P atom, would enable the latter to accommodate the additional bond, this valence shell expansion being facilitated by the formal positive charge on phosphorus, resulting in contraction and, thus, enhanced utilization of phosphorus d-orbitals.

The coordinate covalent nature of the P–O bond, implied in structure (IV) and corroborated by the insensitivity of the maxima to solvent polarity reflected in the data of Table 1***, would seem to be in accord with the concept of predominant coordinate covalent (semipolar) P–O bonding advanced by Jensen[26], Gillis *et al.*[27], Wagner[28], and Baliah and Subbarayan[29] for phosphine oxides comprising ligands in a comparable electronegativity range. Other literature reports, however, conflicting with the coordinate covalent P–O bonding concept, ascribe predominant double-bond character [as implied in formulae (II) and (III)] to the phosphoryl group in the corresponding compounds[19,30–33]. For (II), a force constant calculation ($k = 8.58 \times 10^5$ dyne cm^{-1}) from the P–O stretching band at 1175 cm^{-1}, using Robinson's approach[31], indeed suggests a bond order of approximately 1.78, cor-

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* With the aid of the correlation of Bell *et al.*[18], neglecting steric effects[19], a phosphoryl absorption shift constant (a measure of Pauling's electronegativity) of 2.0, identical with that found by Bell *et al.*[18] for the methyl group, can be calculated for the ferrocene unit on the basis of the P–O stretching absorption (8.51 μ) in (II).

** The author is indebted to a referee for stressing the unlikelihood of ground-state interaction in (IV).

*** Increased dipole moments and, hence, net stabilization of the excited state in going from the non-polar cyclohexane to the polar ethanol solvent would be anticipated in the case of predominant contributions to the ground state from non-polar structures of the type $\geq$P=O.

responding to a P–O bond length of about 1.47 Å*. (For comparison, phosphorus–oxygen distances of 1.76 and 1.44 Å were established[31] for the limiting cases of pure P–O single bond and pure P=O double bond, respectively.) A reconciliation of these apparent bond order inconsistencies must await further experimental evidence, *e.g.*, from X-ray crystallographic studies, NMR, or dipole measurements.

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* The approximate character of these figures results from use of the infrared, rather than Raman, absorption in this calculation, believed to be justified on the basis of the findings of Bell's group[18]