

NMR Spectroscopy and Cyclic Voltammetry of N-Aryl-*P,P,P*-triphenylphospha- λ^5 -azenes. Substituent Effects and Correlation with Molecular Orbital Calculations

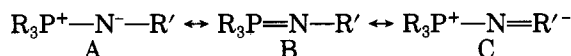
Martin Pomerantz,* Dennis S. Marynick,* Krishnan Rajeshwar,* Whe-Narn Chou,
Linda Throckmorton, Eric W. Tsai, Patty C. Y. Chen, and Terry Cain

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065

Received October 16, 1985

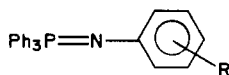
NMR chemical shifts and coupling constants, from ^{31}P , ^{15}N , and ^{13}C NMR spectroscopy, are reported for a series of *N*-aryl-*P,P,P*-triphenylphospha- λ^5 -azenes [$\text{RC}_6\text{H}_4\text{N}=\text{PPh}_3$; R = *p*-NO₂, *p*-CN, *m*-NO₂, *p*-CF₃, *p*-Cl, *p*-F, H, *p*-CH₃, *p*-OCH₃, and *p*-N(CH₃)₂]. The chemical shifts (^{31}P , ^{13}C , and ^{15}N) as well as the one bond P-C-1 coupling constant ($^1J_{\text{PC-1}}$) are shown to correlate well with the Hammett σ^- constants, while $^3J_{\text{PC-2}}$ correlates with σ_{R} . Correlation of ^{13}C chemical shifts with those of the corresponding anilines indicates that the Ph₃PN group is less electron donating than the NH₂ group. PRDDO molecular orbital calculations have been carried out and are shown to correlate well with and help explain the above observations in terms of inductive and resonance effects. Further, the observations and calculations suggest that $p\pi-\sigma^*$ PN bonding is competitive with $p\pi-d\pi$ PN bonding. Electrochemical studies are reported for this series of phospha- λ^5 -azenes, and it is shown that oxidation potentials obtained by cyclic voltammetry (CV) are directly related to the Hammett σ^+ constants and with the calculated (PRDDO) ionization potentials ($-E_{\text{HOMO}}$). The change in the energy of the lone pair orbital (HOMO) with substituent is discussed. All oxidations are irreversible except the *p*-OCH₃ compound (1i) which is partially reversible and the *p*-N(CH₃)₂ compound (1j) which is completely reversible on the CV time scale. The *m*- and *p*-NO₂ compounds (1a,c) are also shown to undergo reversible electrochemical reduction. Transport parameters have been obtained for several of these compounds from the electrochemical data.

The phospha- λ^5 -azene system is interesting in that one can write either a dipolar resonance form (A) or a multiple PN bonded resonance form which involves a $p\pi-d\pi$ double bond (B).^{1,2} Further, when the R' group is electron ac-



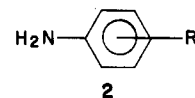
cepting by resonance, forms of the type C must also be included in the resonance hybrid. There are a number of ways that one can probe the electronic structure and the relative importance of resonance forms A-C in these systems.

We recently reported on the ^{31}P and ^{15}N NMR spectra of a limited series of *N*-aryltriphenylphospha- λ^5 -azenes (1a,e,g-j)³ and noted that, contrary to numerous suggestions in the literature,⁴⁻⁷ ^{31}P chemical shifts are not directly



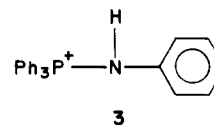
- 1a. R = *p*-NO₂
- 1b. R = *p*-CN
- 1c. R = *m*-NO₂
- 1d. R = *p*-CF₃
- 1e. R = *p*-Cl
- 1f. R = *p*-F
- 1g. R = H
- 1h. R = *p*-CH₃
- 1i. R = *p*-OCH₃
- 1j. R = *p*-N(CH₃)₂

related to $p\pi-d\pi$ bonding. This was accomplished by first demonstrating the similarity between the substituent induced ^{15}N chemical shifts of the phospha- λ^5 -azenes 1a,e,g-j and the anilines 2 with the same substituents. In these



latter compounds (2) resonance forms analogous to B ($p\pi-d\pi$ bonding) cannot be involved and so it was concluded that the substituent effect on $\delta_{^{15}\text{N}}$ in 1 is not due to contributions from form B. Further, the linear relationship between $\delta_{^{15}\text{N}}$ and $\delta_{^{31}\text{P}}$ for 1a,e,g-j suggested that the substituent effect on $\delta_{^{31}\text{P}}$ is likewise not due to contributions from resonance form B.

Although there are, as we noted,³ a few systematic studies of the ^{31}P NMR spectra of phospha- λ^5 -azenes 1a-j, there are precious few studies of the ^{13}C NMR spectra of these compounds.⁸ There are none involving substituent effects as in the series 1a-j although the ^{13}C spectrum of the parent (1g) has been reported,^{9,10} and very briefly discussed.¹⁰ By comparing the chemical shift ($\delta_{^{13}\text{C}}$) of the carbon para to the nitrogen in 1g with the corresponding $\delta_{^{13}\text{C}}$ in the protonated species, 3, it was concluded that there



is a very modest delocalization of negative charge into the *N*-phenyl ring in 1g.¹⁰ This conclusion is based on the often used premise that the charge density on an atom such as carbon can be probed by examining chemical shift changes relative to a standard, or within a related series. While this premise seems to be valid quite often, partic-

(1) Kwart, H.; King, K. G. "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur"; Springer-Verlag: Berlin, 1977.

(2) Hudson, R. F. "Structure and Mechanism in Organo-phosphorus Chemistry"; Academic Press: New York, 1965; Chapter 3.

(3) Pomerantz, M.; Ziemnicka, B. T.; Merchant, Z. M.; Chou, W.-N.; Perkins, W. B.; Bittner, S. *J. Org. Chem.* 1985, 50, 1757.

(4) Bödeker, J.; Köckritz, P.; Köppel, H.; Radeaglia, R. *J. Prakt. Chem.* 1980, 322, 735.

(5) Murphy, P. C.; Tebby, J. C. In "Phosphorus Chemistry—Proceedings of the 1981 International Conference"; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 171, p 573.

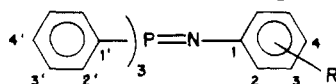
(6) Briggs, E. M.; Brown, G. W.; Cairns, P. M.; Jirincy, J.; Meidine, M. F. *Org. Magn. Reson.* 1980, 13, 306.

(7) Martin, G. J.; Sanchez, M.; Marre, M.-R. *Tetrahedron Lett.* 1983, 24, 4989.

(8) Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur* 1981, 9, 235.

(9) Fritz, H.; Weis, C. D. *J. Org. Chem.* 1978, 43, 4900.

(10) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* 1976, 41, 2716.

Table I. ^{31}P , ^{15}N , and ^{13}C NMR Chemical Shifts of Phospha- λ^5 -azenes 1a-j in CDCl_3 Solvent

compd	substituent	$\delta_{31\text{P}}^a$	$\delta_{15\text{N}}^{b,c}$	$\delta_{13\text{C}}^d$ for indicated C							
				4'	3'	2'	1'	1	2	3	4
1a	<i>p</i> -NO ₂	7.79 ^b	100.10	132.41	128.98	132.50	129.21	159.96	122.25	125.48	138.03
1b	<i>p</i> -CN	6.60		132.19	128.86	132.46	129.67	156.68	123.34	132.89	98.54 ^e
1c	<i>m</i> -NO ₂	6.28		132.11	128.83	132.50	129.88	152.74	117.15 ^k	148.97 ^m	111.94
1d	<i>p</i> -CF ₃	5.47		131.98	128.77	132.55	130.26	154.99	129.51 ⁱ	128.74 ⁿ	118.59 ^f
1e	<i>p</i> -Cl	4.59 ^b	77.59	131.80	128.66	132.54	130.65	149.87	124.38	128.42	122.04
1f	<i>p</i> -F	3.79		131.67	128.58	132.53	131.00	147.04	123.78	114.88	156.02
1g	H	3.73 ^b	77.66	131.63	128.56	132.61	130.98	150.91	123.43	128.57	117.39 ^e
1h	<i>p</i> -CH ₃	3.35 ^b	74.79	131.54	128.52	132.61	131.22	148.25	123.18	129.21	126.29 ^h
1i	<i>p</i> -OCH ₃	3.13 ^b	71.77	131.54	128.52	132.61	131.33	144.33	123.87	114.17	151.92 ⁱ
1j	<i>p</i> -N(CH ₃) ₂	2.61 ^b	70.07	131.47	128.48	132.65	131.41	142.10	123.81	115.22	143.64 ^j

^a In ppm downfield from external 85% H₃PO₄; extrapolated to infinite dilution. ^b From ref 3. ^c In ppm downfield from liquid NH₃. ^d In ppm downfield from internal (CH₃)₄Si; concentration: 50 mg/mL. ^e $\delta_{13\text{C}}$ for the CN group is 121.01. ^f $\delta_{13\text{C}}$ for the CF₃ group is 125.37. ^g These values are in good agreement with those previously reported in ref 9 and 10. ^h $\delta_{13\text{C}}$ for the CH₃ group is 20.52. ⁱ $\delta_{13\text{C}}$ for the OCH₃ group is 55.52. ^j $\delta_{13\text{C}}$ for the N(CH₃)₂ group is 42.08. ^k C2. ^l C6. ^m C3. ⁿ C5.

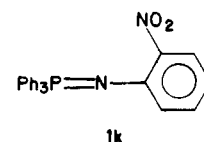
ularly when the structures being compared are very closely related, as in the case above,¹⁰ it must be remembered that chemical shifts are actually made up of a complex blending of numerous contributions.¹¹

Before discussing the results of our NMR and MO studies, we briefly summarize the current state of electrochemical information on phospha- λ^5 -azenes and some related species. In the Results and Discussion section we will describe our electrochemical studies and will also relate them to MO calculations.

The pertinent literature contains relatively few studies of the electrochemical behavior of organophosphorus compounds. An early study describes the evaluation of electrolytic reduction techniques for the preparation of subvalent organometallics from haloderivatives of diphenylphosphine.¹² Nitro derivatives of the type (NO₂-C₆H₄O)₃P=O subsequently were investigated by polarography, cyclic voltammetry, and coulometry.¹³ A mechanism involving an initial two-electron transfer followed by cleavage of the oxygen-carbon bond was proposed for these compounds.¹³ Another paper from the same group describes an electrochemical characterization of triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO).¹⁴ Initial one-electron transfer leading to formation of the anion radical was found to be accompanied by follow-up chemical reactions involving the solvent and this species. Anodic oxidation of TPP also has been described.¹⁵ In the presence of water, oxidation of TPP yields TPPO via a cation radical intermediate. Note that in all of the preceding studies as well as in what follows, nonaqueous solvents such as acetonitrile were employed; the rationale for this being simply that the potential for prolonging the lifetime of radical intermediates exists in these aprotic media.

The electrochemistry of phosphorus-nitrogen compounds is of particular interest because of the availability of two reaction sites for removal and addition of an elec-

tron, but very little has been done with these systems. Thus, polarographic and cyclic voltammetric reduction of some cyclic phosphazenes have been described,^{16,17} as has polarographic reduction, in dimethyl formamide (DMF), of 1a,c,g and the *o*-nitro derivative 1k.¹⁸ The parent



compound 1g has more recently been examined in acetonitrile by polarography, cyclic voltammetry and coulometry.¹⁹ Only the reduction behavior was probed in this study, however. Initial generation of the anion radical was found to be accompanied by follow-up hydrogen abstraction and electron transfer according to the classical Hoijtink scheme (cf. ref 20).

In this paper, we present further studies of the ^{31}P NMR spectra of a series of *N*-aryltriphenylphospha- λ^5 -azenes (1), particularly those not previously reported³ (1b-d,f) and on the ^{13}C NMR spectra of the entire series (1a-j). We will discuss the substituent effect on chemical shifts and coupling constants. Further we describe a cyclic voltammetry (CV) study of the oxidation and reduction of the series 1a-j in acetonitrile. We will focus on the primary oxidation step and correlation of the CV oxidation potentials corresponding to this step with the nature of the substituent.

In addition, we report an extensive series of molecular orbital calculations on 1a-j, using the partial retention of diatomic differential overlap (PRDDO) approximations.²¹ The PRDDO method is an efficient approximate molecular orbital technique which is designed to reproduce the corresponding ab initio calculation with the same basis set at a fraction of the computational expense. This approach

(11) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980; Chapter 2.

(12) Dessy, R. E.; Chivers, T.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

(13) Santhanam, K. S. V.; Wheeler, L. O.; Bard, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 3386.

(14) Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1118.

(15) Schiavon, G.; Zecchin, S.; Cogoni, G.; Bontampelli, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *48*, 925.

(16) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972; Chapter 3.

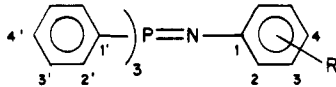
(17) Allcock, H. R.; Birdsall, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 7561; *Inorg. Chem.* **1971**, *10*, 2495.

(18) Pen'kovskii, V. V.; Egorov, Yu. P.; Shapoval, G. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1971**, *41*, 742.

(19) Pak, C. M.; Gulick, W. M., Jr. *J. Korean Chem. Soc.* **1974**, *18*, 341.

(20) (a) Hoijtink, G. J.; vanSchooten, J. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 1089. (b) Hoijtink, G. J.; vanSchooten, J.; deBoer, E.; Aulsberg, W. I. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 355.

(21) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.

Table II. NMR Coupling Constants (Hz) in Phospha- λ^5 -azenes 1a-j (CDCl₃ Solvent)^a


compd	substituent	¹ J _{PN} ^b	¹ J _{PC-1'}	² J _{PC-2'}	³ J _{PC-3'}	⁴ J _{PC-4'}	² J _{PC-1}	³ J _{PC-2}	⁴ J _{PC-3}	⁵ J _{PC-4}
1a	<i>p</i> -NO ₂	32.2	100.1	9.9	12.2	2.5	2.3	19.1	1.8	c
1b	<i>p</i> -CN		99.8	9.8	12.2	2.8	2.1	18.8	1.9	c
1c	<i>m</i> -NO ₂		99.9	9.7	12.1	2.9	1.9	18.4 ^e	2.0 ⁱ	c
								17.9 ^h	1.5 ^j	
1d	<i>p</i> -CF ₃		99.5	9.7	12.1	2.9	2.2	18.4	1.7	c,d
1e	<i>p</i> -Cl	32.7	99.2	9.6	11.9	2.8	2.3	17.5	0.9	1.0
1f	<i>p</i> -F		99.0	9.5	12.0	2.8	2.4	16.7	0.6	1.2 ^e
1g	H	32.9	99.0	9.6	11.9	2.9	2.6	17.5	1.4	0.6 ^f
1h	<i>p</i> -CH ₃	32.9	98.7	9.5	11.9	2.9	2.7	17.4	1.2	0.8
1i	<i>p</i> -OCH ₃	34.2	98.6	9.5	11.9	2.9	2.8	16.6	0.7	1.1
1j	<i>p</i> -N(CH ₃) ₂	34.7	98.4	9.5	11.9	2.8	3.0	16.7	0.6	0.7

^aAll values of J_{PC} are ± 0.1 Hz. ^bFrom ref 3. ^cToo small to measure. ^d¹³C-¹⁹F coupling constants (in Hz) are as follows: ¹J_{FC} (CF₃ group) = 270.3; ²J_{FC-4} = 32.2; ³J_{FC-3} = 3.7; ⁴J_{FC-2} too small to measure; ⁵J_{FC-1} = 1.1; all other couplings with F were too small to measure. ^e¹³C-F coupling constants (in Hz) are as follows: ¹J_{FC-4} = 234.8; ²J_{FC-3} = 21.7; ³J_{FC-2} = 7.4; ⁴J_{FC-1} = 2.4; all other couplings with F were too small to measure. ^fThese values are in reasonable agreement with those previously reported: Fritz, H.; Weis, C. D. *J. Org. Chem.* 1978, 43, 4900; Albricht, T. A.; Freeman W. J.; Schweizer, E. E. *J. Org. Chem.* 1976, 41, 2716. ^g³J_{PC-2}. ^h³J_{PC-6}. ⁱ⁴J_{PC-3}. ^j⁴J_{PC-5}.

should be especially useful here, since the systems under study are large (up to 179 basis functions for a minimum basis set calculation including d functions on phosphorus) and without symmetry. We present here correlations of calculated PRDDO eigenvalues with measured oxidation potentials for these systems, along with various correlations of overlap populations and Mulliken charges with NMR coupling constants and chemical shifts. The nature of the highest occupied molecular orbital (HOMO) and how substituents affect it are discussed.

Results and Discussion

NMR Spectroscopy. As pointed out previously, when examining ³¹P NMR spectra of phosphaazenes 1 it is necessary to extrapolate the ³¹P chemical shifts to infinite dilution because of the relatively large and nonsystematic effect of concentration on δ_{31P} .³ Table I shows these extrapolated ³¹P chemical shifts, the ¹⁵N chemical shifts,³ and the ¹³C chemical shifts in the series of phospha- λ^5 -azenes 1a-j. The carbon numbering scheme is as shown in the table. Table II shows the various NMR coupling constants for 1a-j, including ¹J_{PN}³ and the couplings of all the carbon atoms with the phosphorus atom. In addition, with fluorine-containing substituents, the carbon-fluorine coupling constants are given in the footnotes.

There are a fairly large number of linear correlations of the NMR parameters with Hammett σ constants²² and with other NMR parameters which are suggested by these data. Several of these are presented in Table III. Refer to paragraph at end of paper about supplementary material which shows a few representative plots. The table includes the parameters plotted, the slopes of the lines thus obtained and correlation coefficients. This is not an exhaustive compilation of plots, but rather a number of the more significant ones. Further, those presented in the table show either excellent or satisfactory correlations.²³ It is clear that the chemical shifts of the phosphorus, nitrogen, and the carbon atoms of the phenyl ring attached to the phosphorus, where differences are measurable, are linearly related to σ^- . For the substituted phenyl ring, C-1

Table III. Linear Relationships between NMR Parameters and Hammett σ Values

plot of					
Y	vs.	X	no. of points	slope	r ^e
δ_{31P}		$\sigma^{-a,b}$	10	2.87	0.987 ^f
δ_{15N}		σ^{-a}	6	16.70	0.974 ^e
δ_{13N}		δ_{31P}	6	5.74	0.986 ^e
$\delta_{13C-1'}$		$\sigma^{-a,b}$	10	-1.28	0.982 ^f
δ_{13C-1}		$\sigma^{-a,b}$	10	9.06	0.964
$\delta_{13C-3'}$		$\sigma^{-a,b}$	10	0.286	0.981
$\delta_{13C-4'}$		$\sigma^{-a,b}$	10	0.533	0.982 ^f
δ_{31P}		$\delta_{13C-1'}$	10	-2.25	0.997
$\delta_{13C-1'}$		¹ J _{PC-1'}	10	-1.36	0.982
¹ J _{PN}		σ_R^d	6	-2.48	0.965
¹ J _{PN}		σ_R^{+d}	6	-1.29	0.960
¹ J _{PC-1'}		$\sigma^{-a,b}$	10	0.970	0.982 ^{e,f}
³ J _{PC-2}		σ_R^{-d}	9	2.74	0.980

^aFrom ref 22. ^b σ^- values used for *p*-NO₂, *p*-CN, and *p*-CF₃. Since σ^- is the same as σ for other substituents, σ values were used for these. ^cFrom ref 3. ^dEhrenson, S.; Brownless, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* 1973, 10, 1. ^eWithout *m*-NO₂, which is somewhat off the line: slope = 0.927; $r = 0.994$. ^fSee paragraph at end of paper about supplementary material concerning these plots. ^gCorrelation coefficient.

is linearly related to σ^- , but there is no obvious relationship between the other carbon chemical shifts and any Hammett σ values. There does, however, seem to be a relationship between the ¹³C chemical shifts of the aryl substituted ring carbons in 1 and those of the corresponding anilines (2). Plots of δ_{C-1} , δ_{C-2} , δ_{C-3} , and δ_{C-4} against the carbon chemical shifts reported for the corresponding anilines^{24,25} give good to excellent correlations with interesting slopes. For C-1 the slope is 0.938 ($r = 0.986$), for C-2 the slope is 0.386 ($r = 0.982$; without C-2 for the *m*-nitro compound because of steric hindrance), for C-3 the slope is 0.988 ($r = 0.998$) and for C-4 the slope is 0.981 ($r = 0.998$). We feel these plots show that there is less delocalization of a nitrogen lone pair of electrons into the aryl ring in the phospha- λ^5 -azenes than in the anilines since all carbons are at least slightly deshielded relative to the

(22) Exner, O. In "Correlation Analysis in Chemistry: Recent Advances"; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10.

(23) The generally accepted convention is that for an excellent correlation r is between 0.99 and 1.00 and for a satisfactory correlation r is between 0.95 and 0.99. Shorter, J. "Correlation Analysis of Organic Reactivity, with Particular Reference to Multiple Regression"; Research Studies Press: Chichester, 1982.

(24) Bremser, W.; Ernst, L.; Franke, B.; Gerhards, R.; Hardt, A. "Carbon-13 NMR Spectral Data", 2nd ed.; Verlag Chemie: Weinheim, 1979.

(25) The C-13 NMR data, from ref 24, consists of the Sadtler spectra for compounds 1a,c-i all taken in CDCl₃ solvent and 1b taken in (C-D₃)₂SO from the Bruker spectra. Further *N,N*-diethyl-*p*-phenylenediamine was used (Sadtler spectrum—CDCl₃) instead of the *N,N*-dimethyl derivative (to compare with 1j) since the latter was not reported.

Table IV. Selected Properties of the Calculated PRDDO Wave Functions

compd	substituent	basis set ^a	HOMO ^b	LUMO ^b	Mulliken charges				overlap populations		
					C-1	N	P	C-1'	N-C-1	P-N	P-C-1'
1a	<i>p</i> -NO ₂	I	-0.2287	0.1924	0.166	-0.523	0.638	-0.0716	0.7532	1.1437	0.7931
1b	<i>p</i> -CN	I	-0.2204	0.1957	0.163	-0.521	0.637	-0.0719	0.7523	1.1440	0.7931
1c	<i>m</i> -NO ₂	I	-0.2242	0.1924	0.150	-0.523	0.635	-0.0718	0.7475	1.1481	0.7925
1d	<i>p</i> -CF ₃	I	-0.2157	0.2000	0.157	-0.530	0.635	-0.0706	0.7582	1.1503	0.7917
1f	<i>p</i> -F	I	-0.2022	0.2026	0.146	-0.523	0.631	-0.0715	0.7440	1.1532	0.7911
1g	H	I	-0.2015	0.2053	0.148	-0.521	0.631	-0.0718	0.7440	1.1533	0.7908
1h	<i>p</i> -CH ₃	I	-0.1979	0.2056	0.145	-0.523	0.630	-0.0713	0.7430	1.1550	0.7905
1i	<i>p</i> -OCH ₃	I	-0.1886	0.2046	0.136	-0.525	0.629	-0.0709	0.7408	1.1573	0.7902
1j	<i>p</i> -N(CH ₃) ₂	I	-0.1707	0.2078	0.129	-0.526	0.627	-0.0704	0.7379	1.1613	0.7894
1a	<i>p</i> -NO ₂	II	-0.1953	0.2040	0.145	-0.706	1.181	-0.146	0.7831	0.6823	0.6049
1b	<i>p</i> -CN	II	-0.1884	0.2077	0.143	-0.705	1.180	-0.146	0.7817	0.6814	0.6043
1c	<i>m</i> -NO ₂	II	-0.1904	0.2004	0.129	-0.709	1.179	-0.146	0.7752	0.6859	0.6028
1d	<i>p</i> -CF ₃	II	-0.1825	0.2121	0.137	-0.713	1.181	-0.145	0.7771	0.6860	0.6014
1f	<i>p</i> -F	II	-0.1705	0.2150	0.129	-0.712	1.179	-0.146	0.7710	0.6855	0.5995
1g	H	II	-0.1687	0.2177	0.128	-0.710	1.179	-0.146	0.7711	0.6844	0.5992
1h	<i>p</i> -CH ₃	II	-0.1660	0.2179	0.126	-0.713	1.179	-0.146	0.7701	0.6861	0.5986
1i	<i>p</i> -OCH ₃	II	-0.1595	0.2167	0.117	-0.715	1.178	-0.146	0.7675	0.6880	0.5974
1j	<i>p</i> -N(CH ₃) ₂	II	-0.1453	0.2201	0.110	-0.718	1.178	-0.145	0.7642	0.6902	0.5954

^aBasis set I has d orbitals on phosphorus, basis set II does not. ^bAtomic units.

anilines and C-1 and, particularly, C-2 are deshielded by several ppm. The effect should be most pronounced in the ortho and para positions (C-2 and C-4) and is indeed quite significant at position 2. The effect at position 4 is considerably attenuated because, for nine of the ten compounds, this is the site of the substituent and its effect overshadows the effect of the nitrogen para to it. Position 1 also shows a large effect since it is closest to the nitrogen.

PRDDO calculations show consistently greater delocalization of the nitrogen lone pair into the aryl ring for free aniline when compared to the parent compound **1g**, with the largest effects seen at the 1 and 4 positions. For instance, the PRDDO calculated populations for the nitrogen lone pair of aniline are 0.28e, 0.25e, 0.06e, and 0.46e for C-1, C-2, C-3, and C-4, respectively, while the corresponding values for **1g** are 0.19e, 0.21e, 0.04e, and 0.32e, qualitatively consistent with the relative chemical shifts observed. Clearly, the phosphazeno group is significantly less electron donating than an NH₂ group, and this effect can be easily traced to the partial positive charge on the phosphorus. Thus, the calculated Mulliken charge on phosphorus in **1g** is 0.63e, and a significant fraction (0.16e) of the HOMO is distributed to the phosphorus.

Although there are suggestions in the literature that the phosphazeno group is similar to an NH₂ group toward a phenyl ring,²⁶ this is the first suggestion that the phosphazeno group is indeed less electron donating than an NH₂ group.

The ¹³C chemical shift assignments were made by comparing with the parent system (**1g**),^{9,10} by applying the standard incremental shifts of monosubstituted benzenes,²⁷ by comparing with the corresponding anilines (**2**), and by noting the magnitude of the carbon-phosphorus coupling constants.

In addition to the linear correlations of ¹J_{PN} with σ_R and σ_R^+ previously noted,³ the other linear relationships involving coupling constants are ¹J_{PC-1'} with the chemical shift of the attached carbon atom, C-1', and also with σ^- and, surprisingly, of ³J_{PC-2} with the resonance parameter, σ_R^- .

Since the substituent effect on the carbon chemical shifts of the atoms in the phenyl rings bonded to the

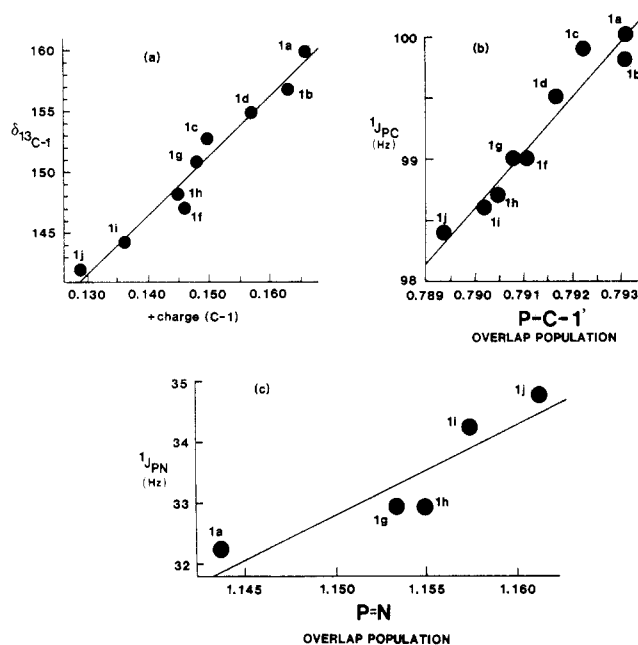


Figure 1. Representative plots of PRDDO parameters (with d orbitals on P) vs. NMR parameters: (a) + charge on C-1 vs. δ_{13C-1} ; (b) $J_{PC-1'}$ vs. P-C-1' overlap population; (c) J_{PN} vs. P-N overlap population (refer to text for slopes and correlation coefficients).

phosphorus atom, on the chemical shifts of the phosphorus and nitrogen atoms, and on the chemical shifts of the ipso carbon (C-1) in the substituted aryl ring are all directly related to σ^- and to one another, it is reasonable to assume that the major contribution to the chemical shift variation in these atoms is the electron density.

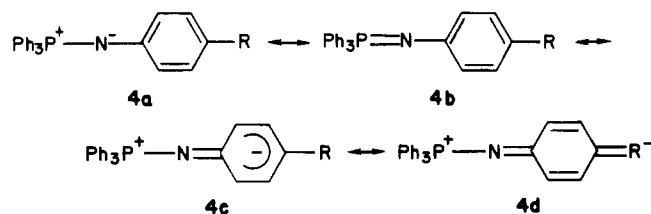
This idea is supported for the phosphorus by the PRDDO calculations, which show a good correlation ($r = 0.981$, slope = 470) between the phosphorus chemical shifts and the Mulliken charges as the substituent is varied. (Refer to Table IV for selected properties of the calculated PRDDO wave functions.) Further support comes from the calculated Mulliken charges of the carbons of the substituted phenyl ring which also show crude correlations with the observed chemical shifts. Unfortunately, with the exception of C-1, the calculated charges of the phenyl carbons bound to phosphorus show essentially no variation as a function of substituent. This is perhaps not unexpected, since such inductive effects are very long range (seven to ten bonds). Indeed, the chemical shift variations

(26) See, e.g.: Schuster, I. *Tetrahedron* 1977, 33, 1075. Yolles, S.; Woodland, J. H. R. *J. Organomet. Chem.* 1975, 93, 297.

(27) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; Chapter 5.

observed are in general much smaller for the phosphorus bound carbons than for the carbons in the phenyl ring bound to nitrogen. For C-1, a reasonable linear correlation ($r = 0.980$, slope = 483) between the Mulliken charge and chemical shift exists (see Figure 1a and Table IV).

The delocalization of the lone pair on nitrogen into the substituted aryl ring indicates significant changes in the contribution of resonance form **4c**, and more importantly **4d** with the very strongly electron-accepting substituents, R, relative to forms **4a** and **4b**. The importance of reso-



nance forms **4c** and **4d** can be seen in the PRDDO wavefunctions with an APS population analysis (see Computational Details section), which show an increase in the N-C-1 bond order from electron-donating to electron-withdrawing groups. For instance, when $R = N(CH_3)_2$ the N-C-1 bond order is 1.028, but for $R = NO_2$, the corresponding bond order is 1.061. The larger N-C-1 bond order for the electron-withdrawing NO_2 substituent is a direct manifestation of the enhanced importance of resonance forms **4c** and **4d**.

As pointed out with the nitrogen chemical shifts and the more limited set of phosphorus chemical shifts,³ we believe these NMR data cannot be used to determine changes in the extent of the contributions of the double bonded resonance form **4b**. All we are looking at is the greater or lesser contributions of **4c** and **4d** relative to **4a** and **4b**. As was pointed out above, the ^{13}C chemical shifts of C-1 in the phospha- λ^5 -azenes (**1**) are linearly related to the C-1 chemical shifts of the anilines,^{24,25} and this supports the idea that the differences in δ_{C-1} in the series **1** cannot be due to differences in contributions of resonance form **4b** since analogous forms cannot be written for the anilines **2**. A very similar argument was made when the ^{15}N chemical shifts of **1** were shown to be linearly related to those of **2**.³

The other type of NMR information obtainable from the spectra are coupling constants. We argued in a previous paper³ that since $^1J_{PN}$ changed with a substituent as a function of σ_R and σ_R^+ , this coupling constant was a measure of the $p\pi-d\pi$ bonding. The important additional observations that we are reporting here are, first, that $^1J_{PC-1'}$ varies linearly with σ^- and with both δ_{31P} and $\delta_{13C-1'}$ and that $^3J_{PC-2}$ varies linearly with σ_R^- . The slopes of the lines involving $^1J_{PC-1'}$ are opposite to the corresponding lines involving the PN coupling constants. Thus, as $^1J_{PN}$ increases, $^1J_{PC-1'}$ decreases and vice versa.

While there are several possible explanations for the variation of the one-bond coupling constants with substituent, it is significant that $^1J_{PN}$ and $^1J_{PC-1'}$ respond in opposite directions. One intriguing possibility is that the PN bonding is not solely $p\pi-d\pi$, but involves $p\pi-\sigma^*$ overlap. Thus, it is possible to have the lone pair on nitrogen interact with a σ^* , antibonding orbital, of the P-C-1' bond. This would undoubtedly change the s character of the P-C-1' bond and also the PN bond and would allow for changes in coupling constants due to s character and for the inverse relationship of the coupling constants, since 1J is directly related to, among other things, s-character. It is also clearly true that participation of σ^* orbitals will lengthen the P-C-1' bond and shorten the P-N bond. It

has been argued earlier²⁸ that as C-H bond lengths increase, the one-bond coupling constant $^1J_{CH}$ decreases. If this relationship can be extended to the phosphaazene systems, one would expect increased σ^* participation to result in a decrease in $^1J_{P-C-1'}$ and an increase in $^1J_{PN}$. σ^* overlap in the phospha- λ^5 -azene system has been suggested before on the basis of CNDO calculations.^{29a} In addition, both theoretical^{29b} and experimental^{29c} approaches have led to the suggestion that σ^* orbitals are important for π acceptance by phosphines in transition-metal compounds. While we do not feel our relatively small basis set PRDDO calculations are capable of unambiguously distinguishing between σ^* and d orbital effects, we offer the following observations. Just as $^1J_{PN}$ and $^1J_{PC-1'}$ shift in opposite directions as the substituent is varied, the PN and PC-1' overlap populations (Table IV) follow a similar trend. With d orbitals on phosphorus, reasonable linear correlations exist between the PN and PC-1' overlap populations ($r = 0.993$, slope = -0.221) between $^1J_{PC-1'}$ and the PC-1' overlap populations ($r = 0.978$, slope = 450, Figure 1b), and between $^1J_{PN}$ and the PN overlap population ($r = 0.900$, slope = 142, Figure 1c). The negative slope of the PN vs. PC-1' overlap population plot is consistent with the observed behavior of the coupling constants and is certainly suggestive of σ^* participation. Interestingly, these correlations hold reasonably well when the calculations are repeated without d orbitals on phosphorus. In fact, without d orbitals, the correlation of $^1J_{PN}$ with PN overlap population improves significantly, yielding a correlation coefficient of 0.967 and a slope of 325. With both basis sets, the dominant changes in PN overlap populations arise from π -type interactions. When d orbitals are present, the π interactions are mainly d-p, while without d orbitals the interactions are necessarily of the p-p type. As expected, the PN bonding increases substantially when d orbitals are present on P. The overlap population (Table IV) increases from 0.68 (without d) to 1.15 (with d). Similarly, the degrees of bonding increase from 1.21 to 1.95. Of course, it is well-known that d orbital effects are generally overestimated in small basis set calculations. Perhaps the most meaningful conclusion which can be reached from the population analyses is that in general the correlations between the coupling constants and overlap populations do not vanish when d orbitals are removed from the basis set and that even without d orbitals on P the PN bond order is significantly greater than one. These facts indicate that π bonding through σ^* orbitals is at least an energetically reasonable possibility and is likely to be competitive with d orbital participation.

The variation of $^3J_{PC-2}$ with the resonance parameter σ_R^- is interesting and seems to be consistent with other three-bond coupling constant observations. Thus, as the group R gets more electron attracting, $^3J_{PC-2}$ increases and this is in agreement with the observations that $^3J_{CH}$ and $^3J_{CC}$ both increase when an electronegative substituent is put on the end of these three-bond systems.³⁰ This is the first time, however, that a relationship with σ_R^- has been observed in systems such as these.

Electrochemical Oxidation. With the exception of **1j** and to an extent **1i** (see below), all the compounds undergo irreversible oxidation over the time scale of the

(28) Bartow, D. S.; Richardson, J. W. *J. Chem. Phys.* 1963, 42, 4018. Muller, N.; Pritchard, D. E. *J. Chem. Phys.* 1959, 31, 1471.

(29) (a) Gray, G. A.; Albright, T. A. *J. Am. Chem. Soc.* 1977, 99, 3243; 1976, 98, 3857. (b) Marynick, D. S. *J. Am. Chem. Soc.* 1984, 106, 4064. (c) Tossell, J. A.; Moore, J. H.; Giordano, J. C. *Inorg. Chem.* 1985, 24, 1100.

(30) Marshall, J. L. "Carbon-Carbon and Carbon-Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis"; Verlag Chemie: Deerfield Beach, FL 1983; Chapters 2 and 3.

Table V. CV Parameters for the Oxidation of 1a-j at a Scan Rate of 0.1 V/s^{a,b}

compd	substituent	E_{pa} , ^c V	compd	substituent	E_{pa} , ^c V
1a	<i>p</i> -NO ₂	0.844	1f	<i>p</i> -F	0.480
1b	<i>p</i> -CN	0.741	1g	H	0.465
1c	<i>m</i> -NO ₂	0.752	1h	<i>p</i> -CH ₃	0.371
1d	<i>p</i> -CF ₃	0.740	1i	<i>p</i> -OCH ₃	0.210
1e	<i>p</i> -Cl	0.512	1j	<i>p</i> -N(CH ₃) ₂	-0.195 ^d

^a Electrolyte composition: CH₃CN/0.1 M tetrabutylammonium perchlorate (TBAP)/5 mM concentration of 1a-j; Pt working electrode. ^b Vs. Ag/AgNO₃ reference. ^c E_p = CV peak potential. Here and in what follows, the subscripts a and c denote anodic and cathodic, respectively. ^d First wave only, see Table VI.

CV experiment. Table V shows the CV parameters for the oxidation of 1a-j at a potential scan rate of 0.1 V/s. See paragraph at end of paper about supplementary material which shows typical behavior for selected compounds. In the case of 1i, partial reversibility is evident; the peak current ratio, i_{pc}/i_{pa} approaches unity for scan rates in the neighborhood of 10 V/s. For the other compounds (excluding 1j), no cathodic wave was found on the return scan up to at least this limit. Comparison of the CV anodic peak amplitudes with a standard compound (e.g., ferrocene) reveals an *n* value close to unity once the differences in diffusion coefficients of these compounds (see below) are taken into account. The above diagnostic features for all the compounds (except 1j) are consistent with a rapid chemical reaction subsequent to the initial electron transfer (i.e., an "EC" mechanism). These mechanistic aspects will be the subject of a future publication.

Returning to the primary oxidation step, the behavior of 1j stands in stark contrast to the other compounds discussed above. Table VI presents relevant CV parameters for this compound for the oxidation branch of the CV scan on Pt (completely analogous behavior was evident on C). Note the well-behaved, successive one-electron transfers (again confirmed by comparative examination with ferrocene) to yield the cation radical and dication, respectively. An intense purple coloration emanated from the electrode surface during the CV scan. Both sets of anodic waves are electrochemically reversible as indicated by the CV parameters listed in Table VI for 1i. The behavior of 1j is strikingly reminiscent of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine and is consistent with the *p*-NMe₂ functionality present in the aryl ring system of 1j.³¹

The stability of the cation radical is directly correlatable with the ease of oxidation of 1g and its derivatives. The compound 1j is the most readily oxidized member of this family ($E_{pa} = -0.195$ V). The next easily oxidized member, 1i ($E_{pa} = 0.210$ V), shows a partially reversible anodic wave (see above). Further lowering of charge density on the substituted aryl ring system and the N reaction site (see below) leads to rapid dismutation of the radical cation; a behavior exemplified by all the other compounds in this series.

We have examined the systematic shift in the CV peak potentials for the primary oxidation wave for this series of phosphazenes 1a-j via plots of E_{pa} vs. σ^+ .³² Thus, a plot of this type using E_{pa} obtained at 0.1 V/s vs. σ^+ ²² provides a straight line of slope 0.398 and an excellent correlation coefficient of 0.997 (see paragraph at end of paper about supplementary material which shows this plot).

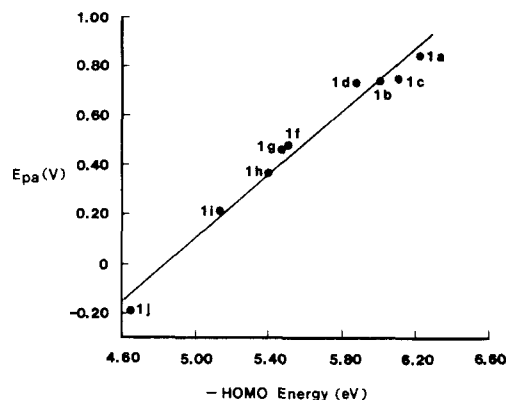


Figure 2. Correlation of E_{pa} vs. the Koopmans' theorem ionization potential, $-E_{HOMO}$, for 1a-1j (1e was excluded for reasons outlined in the text).

When the polarographic half-wave potentials, $E_{1/2}$ reported for anilines 2 in aqueous buffered media,³³ are plotted against E_{pa} for the phosphazenes with the same substituents (1a,c,e,g-i) an excellent straight line ($r = 0.999$; slope = 0.845) is obtained (see paragraph at end of paper about supplementary material which shows this plot). We take this trend as evidence that the site of electron abstraction in the phosphazenes 1 is the lone pair on nitrogen which is delocalized into the aromatic ring. It is also pertinent to note that E_{pa} for TPP is +0.830 V at 0.1 V/s in CH₃CN/0.1 M NaClO₄.¹⁵ This value is much more positive than for anilines or for 1g (+0.465 V). These slopes can be easily rationalized by differential solvation effects in the two vastly different solvent systems that are being compared.

Additional evidence concerning the nature of the molecular orbital involved in the primary oxidation step comes from the PRDDO calculations. Figure 2 shows a plot of E_{pa} vs. the Koopmans' theorem ionization potential (the negative of the eigenvalue of the highest occupied molecular orbital, $-E_{HOMO}$). The strong correlation found here ($r = 0.988$ slope = 0.644) suggests that the substituent effects observed in the electrochemical studies are due to electronic effects in the ground state and not to differential solvation or other solution phase phenomena. Similar PRDDO correlations have been reported on much smaller organic systems (substituted bicyclo[1.1.0]butanes).³⁴ A detailed analysis of the PRDDO wavefunctions utilizing Mulliken and APS population analyses suggests the following observations. As noted in the discussion of NMR chemical shifts, all HOMO's (which roughly correspond to the nitrogen lone pair orbital) are very delocalized. Electron populations on the nitrogen bound to phosphorus range from 0.82e (NO₂) to 0.45e [N(CH₃)₂]. The substituent effects are best divided into three groups: π accepting (NO₂ and CN), π donating (N(CH₃)₂, OCH₃, and to a lesser extent F), and groups with σ effects only (H, CH₃, and CF₃). The π -accepting groups lower the energy of the HOMO via stabilization of the resonance structures of the type 4c and 4d which increase the N-C bond order slightly and result in a more localized HOMO than in the parent system. In effect, the HOMO is tied up in a partial N=C double bond. In contrast, the π -donating groups destabilize the HOMO, resulting in a lower oxidation potential. This effect can be traced to the mixing of the lone pair orbitals on the nitrogen bound to phosphorus and the

(31) Adams, R. N. "Electrochemistry at Solid Electrodes"; Dekker: New York, 1969.

(32) Zuman, P. "Substituent Effects in Organic Polarography"; Plenum: New York, 1967.

(33) Suatoni, J. C.; Snyder, R. E.; Clark, R. O. *Anal. Chem.* 1961, 33, 1894.

(34) Gassman, P.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* 1979, 101, 5793.

Table VI. CV Parameters for Oxidation of 1j^{a,b}

scan rate, V/s	first wave				second wave			
	E_{pa} , V	E_{pc} , V	ΔE_p , ^c V	i_{pc}/i_{pa} ^{c,d}	E_{pa} , V	E_{pc} , V	ΔE_p , ^c V	i_{pc}/i_{pa} ^{c,d}
0.02	-0.207	-0.270	0.063	1.04	0.265	0.202	0.065	1.12
0.05	-0.205	-0.272	0.067	1.23	0.267	0.199	0.068	1.18
0.10	-0.202	-0.275	0.073	1.27	0.269	0.197	0.072	1.21
0.20	-0.200	-0.278	0.078	1.28	0.272	0.195	0.077	1.23

^a Electrolyte composition: CH₃CN/0.1 M TBAP/5 mM 1j; Pt working electrode. ^b See paragraph at end of paper about supplementary material showing the CV traces. ^c $\Delta E_p = E_{pa} - E_{pc}$; i_p = peak current. ^d Ratio corrected for current at switching potential: Nicholson, R. S. *Anal. Chem.* 1966, 38, 1406.

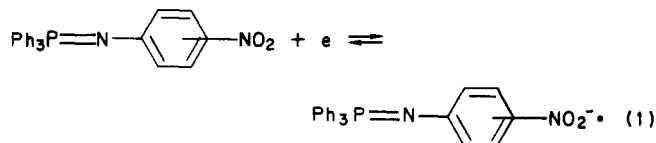
Table VII. CV Parameters for Reduction of 1a and 1c^a

scan rate, V/s	compd 1a				compd 1c			
	E_{pc} , V	E_{pa} , V	ΔE_p , V	i_{pa}/i_{pc} ^b	E_{pc} , V	E_{pa} , V	ΔE_p , V	i_{pa}/i_{pc} ^b
0.02	-1.728	-1.660	0.068	0.95	-1.601	-1.535	0.066	0.99
0.05	-1.730	-1.658	0.072	0.96	-1.603	-1.532	0.071	0.99
0.10	-1.732	-1.655	0.077	0.97	-1.606	-1.529	0.077	0.98
0.20	-1.734	-1.652	0.082	0.99	-1.610	-1.528	0.081	0.97

^a Electrolyte composition: CH₃CN/0.1 M TBAP/5 mM of compound; C working electrode. ^b Ratio corrected for current at switching potential: Nicholson, R. S. *Anal. Chem.* 1966, 38, 1406.

π -type orbital on the substituent. In each case, the substituent orbital is at a slightly lower energy than the nitrogen lone pair. For instance, for the parent compound 1g the nitrogen lone pair orbital is at $E = -0.205$ au, while for unsubstituted *N,N*-dimethylaniline the substituent lone pair lies at $E = -0.228$ au. Mixing of these two orbitals in the compound 1j stabilizes the dimethylamino lone pair ($E = -0.2594$ au) and destabilizes the lone pair on the nitrogen bound to phosphorus ($E = -0.1709$ au). Of course, both orbitals are highly delocalized, and identifying the HOMO as a nitrogen lone pair is at best a simplification. The remaining substituents, for which significant π effects are not expected, affect the energy of the HOMO through an inductive mechanism. This is indicated by the total APS charge on the carbon bound to nitrogen, which increases from 0.126e for the CH₃-substituted compound to 0.143e for the CF₃ species. Similar trends are seen in the Mulliken charges.

Electrochemical Reduction. With the exception of the nitro derivatives 1a and 1c, the compounds are resistant to reduction up to -2.5 V. This observation is consistent with that of previous authors¹⁹ who report an E_{pc} value of -3.03 V at 0.12 V/s in acetonitrile for 1g on a Hg-coated Pt electrode. See paragraph at end of paper about supplementary material containing typical reduction for 1a and 1c on C. Corresponding CV parameters for these compounds are assembled in Table VIII. The reduction is less reversible on the Pt surface as shown by consistently larger ΔE_p values. The CV behavior may be represented by eq 1. The anion radical presumably un-



dergoes hydrogen abstraction, further electron-transfer finally leading to the amine derivative.^{18,35} Previous authors have studied the reduction of 1a and 1c polarographically on a Hg pool electrode in DMF.¹⁸ Unfortunately, the reduction potentials quoted by these authors are not directly comparable with our values because of their choice of Hg as a pseudoreference. However, these authors applied the Tomés criterion³⁶ for the primary re-

Table VIII. Diffusion Coefficients from CV^a for Selected Compounds

compd	CV slope ^b 10 ⁻⁴ A/(V/s) ^{1/2}	D , 10 ⁻⁵ cm ² /s
ferrocene	16.46	3.90 (2.40) ^c
1j	9.01 (7.97) ^d	1.17 (0.91) ^d
1a	9.64	1.34
1c	10.20	1.50

^a CV scans from C working electrode. ^b Cf. eq 2. Values averaged from at least three replicate sets. ^c Value for comparison obtained in CH₃CN/0.2 M LiClO₄; Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* 1960, 82, 5811. ^d Values in parentheses are for the cation radical of 1j obtained from the second anodic wave.

duction wave for 1a and 1c. Electrochemical reversibility was observed; a finding consistent with our data in Table VII.

Transport Parameters from Electrochemical Data. For reversible electrochemical processes, the CV peak current, i_p , is given by eq 2. Here k is the Randles-Sevcik constant equal to 2.69×10^5 (cf. ref 36), and the other

$$i_p = kn^{3/2}AD^{1/2}C^*v^{1/2} \quad (2)$$

terms have their usual electrochemical identity, namely, n = number of electrons involved in the electrochemical reaction, A = electrode area, D = diffusion coefficient of electroactive species of bulk concentration, C^* and v = potential scan rate. Thus, D may be computed from the slope of i_p vs. $v^{1/2}$ plots. The CV slopes thus measured on C electrodes and the corresponding D values are assembled in Table VIII for 1a,c,j. The value for the reference compound, ferrocene, is also shown for comparison. Note that the D values for the phospho- λ^5 -azenes are roughly one-third that for ferrocene in keeping with the larger size of these molecules.

Summary

We have presented NMR chemical shift and coupling constant data, from ³¹P, ¹⁵N, and ¹³C NMR spectroscopy, of a series of *N*-aryltriphenylphospha- λ^5 -azenes (1a-j). We have correlated these parameters with appropriate Hammett substituent constants and with the corresponding NMR parameters of the substituted anilines 2. Using these observations and the results of PRDDO molecular orbital calculations, we have discussed the changes of chemical

shifts and coupling constants in terms of inductive and resonance (electron density) effects and have suggested that $p\pi-\sigma^*$ PN bonding should be competitive with $p\pi-d\pi$ PN bonding. Electrochemical studies are reported, and we show that oxidation potentials, obtained by cyclic voltammetry, for **1a-j**, are directly correlated with the Hammett σ^+ constants and with the calculated (PRDDO) ionization potentials ($-E_{\text{HOMO}}$).

Experimental Section

All the phospho- λ^5 -azenes (**1a-j**) are known compounds and were made by either the Staudinger reaction using the appropriate azide and triphenylphosphine (compounds **1a-i**)³⁷⁻³⁹ or by the method of Horner,^{39,40} using dibromotriphenylphosphorane and the appropriate aniline (compound **1j**). The properties matched those reported. The NMR spectra were obtained on a Nicolet NT-200 wide-bore spectrometer with a 4.7-T superconducting solenoid. ³¹P spectra were taken at 80.99 MHz by using an external 85% H₃PO₄ standard, CDCl₃ solvent, and 12-mm tubes. Concentrations of 300 mg/3 mL, 200 mg/3 mL, 100 mg/3 mL, and 30 mg/3 mL were employed. The chemical shifts reported were obtained by extrapolation of the observed shifts to infinite dilution. Two-level broad-band proton decoupling was employed with a pulse angle of approximately 90° and a post acquisition delay of 1 s. The data were collected using 32 K data points and a total sweep width of 3610 Hz and were processed without exponential multiplication. ¹³C NMR spectra were taken at 50.31 MHz using CDCl₃ solvent, (CH₃)₄Si as internal standard and concentrations of 150 mg/3 mL in 12 mm tubes. Two level broad band proton decoupling was employed with a pulse angle of approximately 36° and a post acquisition delay of 10 s. The data were collected using 32 K data points and a total sweep width of 11,100 Hz, and were processed by zero filling to 64K data points. No exponential line broadening was employed. The variable temperature probe was maintained at 25 °C for all measurements.

Cyclic voltammetry was performed in dry acetonitrile obtained by distillation of HPLC-grade solvent (Fisher Scientific) from P₂O₅. Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals) was used as supporting electrolyte (0.1 M). Three-electrode cell geometry with positive feedback IR compensation was used in all cases; all measurements pertain to ambient temperature.

An EG&G (Princeton Applied Research) electrochemistry system assembled from Model 173 and 175 modules was used in conjunction with an IBM Instruments Inc. or a Bioanalytical Systems Inc. electrochemical cell. The working electrode was either Pt or C and had a nominal geometric area of 0.20 cm²; the reference electrode was Ag/0.1 M Ag⁺ in acetonitrile. All potentials herein were quoted with respect to this reference. Pretreatment of the working electrode surfaces prior to use followed usual procedures.⁴⁰ Frequent monitoring of the cyclic voltammogram peak shape and peak separation potential, ΔE_p for the ferrocene/ferricenium ion redox couple (which was used as a "calibrant"), provided a convenient means of assessing the efficacy of these pretreatment procedures. Fast scan (>0.5 V/s) cyclic voltammograms were recorded on a Tektronix Model 5441 storage oscilloscope.

The electrochemical behavior of each compound (see above) was probed in the usual manner by scanning first positive from

the rest potential (usually 0 V) to +1.0 V and then in the negative-going direction to ca. -2.5 V.

Computational Details. The geometry of the parent complex **1** was derived from the experimental X-ray diffraction work on N-(*p*-bromophenyl)triphenylphospho- λ^5 -azene,⁴² with all C-H distances idealized to 1.085 Å. A C-F distance of 1.378 was employed for the fluoro derivative. The geometries of the other substituents were taken from known derivatives or smaller model compounds as follows: CN (benzotrile),⁴³ CH₃ (toluene),⁴³ CF₃ (toluene and CF₄),⁴³ N(CH₃)₂,⁴⁴ OCH₃ (an average of five representative compounds), and NO₂ (nitrobenzene).⁴⁵ All calculations employed a minimum basis set of Slater orbitals with standard exponents.⁴⁶ For each molecule, calculations were done with and without a set of d orbitals (exponent = 1.70) on the phosphorus. Standard Mulliken⁴⁷ and Armstrong, Perkins, and Stewart (APS)⁴⁸ population analyses were performed on all wave functions. Dipole moments were also calculated for **1g** and **1a** for which experimental values are known. Our calculated results and experimental values (in parentheses) are 4.70 D (4.85 D)⁴⁹ for **1g** and 8.90 D (9.14-9.89 D)⁴⁹ for **1a**. These calculations include d orbitals in the phosphorus basis set. Without d orbitals on phosphorus, the calculated values are 5.83 and 6.87 D, respectively. The excellent agreement found here for the calculations including d orbitals on phosphorus strongly suggest that our calculated charge distributions are reasonable, and form a suitable basis for the study of the bonding, NMR substituent effects, and electrochemical correlations discussed in this paper. For this reason, most of the results discussed here refer to the calculations including d orbitals. Calculations are reported for all substituents studied experimentally, except the chloro derivative, which is omitted due to computational difficulties.⁵⁰ A summary of selected properties calculated from the PRDDO wave functions is presented in Table IV.

Acknowledgment. We thank the Robert A. Welch Foundation [Grants Y-684 (M.P.) and Y-743 (D.S.M.)], the Organized Research Fund of UTA, and the National Science Foundation (Grant PMR 8108132) for financial support.

Registry No. **1a**, 14562-02-8; **1b**, 74395-06-5; **1c**, 14796-86-2; **1d**, 13406-22-9; **1e**, 31641-65-3; **1f**, 18523-51-8; **1g**, 2325-27-1; **1h**, 2327-67-5; **1i**, 14796-89-5; **1j**, 77116-68-8.

Supplementary Material Available: Representative plots of NMR parameters vs. σ^+ , oxidation branch of cyclic voltammetry scans, oxidation branch of CV for **1j**, plot of CV peak potential vs. σ^+ , plot of CV peak vs. polarographic $E_{1/2}$ values for anilines, and reduction branch of CV for **1a** and **1c** (6 pages). Ordering information is given on any current masthead page.

(42) Hewlin, M. J. *C. J. Chem. Soc. B* **1971**, 942.

(43) Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; Kennard, O.; Wheatley, P. J.; Whiffen, D. H. "Tables of Interatomic Distances and Configurations in Molecules and Ions"; Chemical Society: London, 1958; Spec. Publ.—Chem. Soc. No. 11.

(44) Davis, R. E.; Schueler, V. J., private communication.

(45) Trotter, J. *Acta Crystallogr.* **1959**, *12*, 881.

(46) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1972**, *52*, 2769.

(47) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428.

(48) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

(49) Lutsikii, A. E.; Samarai, L. I.; Kochergina, L. A.; Shepel, A. V.; Shevchenko, Z. A.; Derkach, G. I.; Kozlov, E. S.; Drach, B. J. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 1973. Goetz, H.; Probst, D. *Justus Liebigs Ann. Chem.* **1968**, *715*, 1.

(50) Proper evaluation of many of the substituent effects due to Cl seem to require d orbitals on both P and Cl, but the current version of PRDDO allows d orbitals on one center only.

(37) Staudinger, H.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861.

(38) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(39) Wiegräbe, W.; Bock, H. *Chem. Ber.* **1968**, *101*, 1414.

(40) Horner, L.; Oediger, H. *Justus Liebigs Ann. Chem.* **1959**, *627*, 142.

(41) Adams, R. N., in ref 31, Chapter 7, p 187.