Characteristic peaks in ^1H NMR: **10**, 2.46 (s); **9**, 1.44 (s), 11.84 (s, 2 OH belonging to **10** and **9**) in the case of **5a** or 9.42 (s, 3 OH belonging to **10**, **9** and PhOH) in the case of **5b**; **11a**, 3.87 (d, $^3J_{HP}$ = 12.0); **12**, 3.83 (d, $^3J_{HP}$ = 12.0)

Characteristic peaks in ^{13}C NMR: **9**, 89.6, 23.8, 23.6; **10**, 197.7, 161.9, 26.1; **11a**, 89.8; 55.5 (d, $^2J_{CP}$ = 6.0); **12**, 54.5 (d, $^2J_{CP}$ = 5.3).

Acknowledgment. We thank the C.N.R.S. for financial support (U.A. 473).

Substituent Effects on the ^{31}P, ^{15}N, and ^{13}C NMR Spectra of *N*-(Arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes and on the ^{15}N and ^{13}C NMR Spectra of the Corresponding Arenesulfonamides

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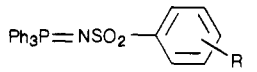
Received July 28, 1986

As part of our ongoing program in the synthesis and study of phospha-λ⁵-azenes,[2-5] we have examined, and report on, the ^{31}P, ^{15}N, and ^{13}C NMR spectra of a series of *N*-(arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **1**.



RC6H4N=PPh3

1a, R = *p*-NO_2
b, R = *m*-NO_2
c, R = *p*-CN
d, R = *p*-CO_2CH_3
e, R = *p*-Br
f, R = *p*-Cl
g, R = *p*-F
h, R = H
i, R = *p*-CH_3
j, R = *p*-OCH_3
k, R = *p*-NH_2

2a, R = *p*-NO_2
b, R = *p*-CN
c, R = *m*-NO_2
d, R = *p*-CF_3
e, R = *p*-Cl
f, R = *p*-F
g, R = H
h, R = *p*-CH_3
i, R = *p*-OCH_3
j, R = *p*-$N(CH_3)_2$

This work stems from our study of a series of *N*-aryl-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **2**[2,3] where we examined the ^{31}P, ^{13}C, and ^{15}N NMR spectra, oxidation, and reduction by cyclic voltammetry (CV) and carried out PRDDO molecular orbital calculations. The observations were, in general, explained by inductive and resonance effects and were aided and reinforced by the calculations. The observed correlations between experimentally measured parameters and Hammett substituent constants were explained by contributions of resonance forms A, B, and C to the resonance hybrid, and it was suggested that the

$$\underset{A}{Ph_3P^+N^-Ar} \leftrightarrow \underset{B}{Ph_3P^+N{=}Ar^-} \leftrightarrow \underset{C}{Ph_3P{=}NAr}$$

double bond in form C was not necessarily completely of the pπ-dπ type but could also involve overlap of a nitrogen electron pair with a σ* orbital of the P–C(Ar) bond.[2,3] The present work was undertaken to see if this explanation is equally applicable to the substituent effects shown by the series of *N*-(arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes **1**.

Our initial expectation was that since the SO_2 group insulates the nitrogen lone pair from direct resonance interaction with the ring but does allow for ready transmission of inductive effects, the dependence of the majority of NMR parameters, particularly chemical shifts, would be on the Hammett σ_p and σ_m substituent constants and not on σ^- as had been observed with the series **2**. In addition, we thought that the dependence of $^1J_{PN}$ on σ_R or σ_R^+ which was observed with **2** would not be observed in this case, but a solid prediction here is difficult to make.

In this paper we report on the ^{31}P, ^{15}N, and ^{13}C NMR spectra of the sulfonylphospha-λ⁵-azenes **1**, including both chemical shifts and coupling constants and the correlation of these parameters with Hammett substituent constants.

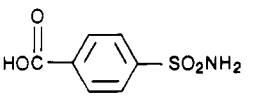
Results and Discussion

Syntheses. The phospha-λ⁵-azenes **1a–k** were synthesized by our previously described procedure[4] using the corresponding arenesulfonamides **3**, triphenylphosphine, and diethyl azodicarboxylate (eq 1). All sulfonamides **3**

$$\underset{3}{RC_6H_4SO_2NH_2} + Ph_3P + C_2H_5O_2CN{=}NCO_2C_2H_5 \xrightarrow{THF} RC_6H_4SO_2N{=}PPh_3 + C_2H_5O_2CNHNHCO_2C_2H_5 \quad (1)$$

a, R = *p*-NO_2
b, R = *m*-NO_2
c, R = *p*-CN
d, R = *p*-CO_2CH_3
e, R = *p*-Br
f, R = *p*-Cl
g, R = *p*-F
h, R = H
i, R = *p*-CH_3
j, R = *p*-OCH_3
k, R = *p*-NH_2

were either from commercial sources or were prepared in the standard way from the corresponding sulfonyl chlorides. **3d** was prepared by esterification (CH_2N_2) of sulfonamide **4** and **3c** was made by diazotization of sulfanilamide followed by a Sandmeyer reaction using $NiCl_2$ and NaCN.[6] Table I lists some of the properties of those *N*-sulfonylphospha-λ⁵-azenes not reported in ref 4 and that have not been prepared previously. It should also be pointed out that the melting point of **1k** reported previously[4] is incorrect and the correct value is 196–198 °C.



4

In order to obtain ^{15}N NMR spectra, a series of ^{15}N-labeled compounds (67% ^{15}N) was prepared (**1a***, **e***, **f***, **g***, **h***, **i***, **j***, **k***). These were made from the labeled sulfonamides that had been synthesized, in turn, from the corresponding sulfonyl chlorides and $^{15}NH_3$. Table I also lists these labeled compounds along with some properties.

p-$RC_6H_4SO_2{}^{15}N{=}PPh_3$

1a*, R = NO_2
1e*, R = Br
1f*, R = Cl
1g*, R = F
1h*, R = H
1i*, R = CH_3
1j*, R = OCH_3
1k*, R = NH_2

NMR Spectroscopy. In Table II are listed the ^{31}P, ^{15}N, and ^{13}C chemical shifts for the series of *N*-(arylsulfonyl)-phospha-λ⁵-azenes **1a–k**. As was done previously,[2,3] the

(1) On leave from the Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland.
(2) Pomerantz, M.; Marynick, D. S.; Rajeshwar, K.; Chou, W.-N.; Throckmorton, L.; Tsai, E. N.; Chen, P. C. Y.; Cain, T. *J. Org. Chem.* **1986**, *51*, 1223.
(3) Pomerantz, M.; Ziemnicka, B. T.; Merchant, Z. M.; Chou, W.-N.; Perkins, W. B.; Bittner, S. *J. Org. Chem.* **1985**, *50*, 1757.
(4) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712.
(5) Bittner, S.; Assaf, Y.; Pomerantz, M. *J. Org. Chem.* **1982**, *47*, 99.
(6) Andrews, C. H.; King, H.; Walker, J. *Proc. R. Soc. London, Ser. B* **1946**, *B133*, 20.

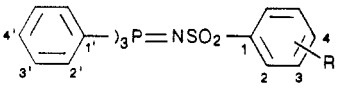
0022-3263/87/1952-0159$01.50/0

Table I. Some Properties of *N*-(Arylsulfonyl)phospha-λ^5-azenes 1 and ^{15}N-Labeled Derivatives 1*[a]

compd	R	mp, °C	yield, %	recryst solvent	IR (cm^{-1}; KBr)
1a*	*p*-NO_2	233–234	73	$CHCl_3$	
1c	*p*-CN	188–189	23	MeOH	2230 (CN); 1274 (SO_2); 1150 (PN); 810 (SN)
1d	*p*-CO_2CH_3	151.5–153	66	MeOH	1725 (CO); 1277 (SO_2); 1140 (PN); 800 (SN)
1e (1e*)	*p*-Br	215–218	85 (84)	$CHCl_3$	1265 (SO_2); 1150 (PN); 798 (SN)
1f*	*p*-Cl	216–218	84	$CHCl_3$	
1g (1g*)	*p*-F	170–172	74 (74)	$CHCl_3$	1265 (SO_2); 1150 (PN); 800 (SN)
1h*	H	157–159	58	dioxane–H_2O	
1i*	*p*-CH_3	188–191	84	MeOH	
1j (1j*)	*p*-OCH_3	152–153	80 (79)	MeOH	1250 (SO_2); 1140 (PN); 805 (SN)
1k	*p*-NH_2	196–198[b]	79	$CHCl_3$–MeOH	

[a] Values in parentheses refer to ^{15}N-labeled compounds (1*). [b] The melting point of **1k** was incorrectly reported in ref 4. This is the correct value.

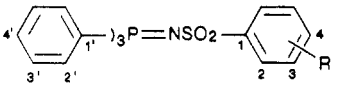
Table II. ^{31}P, ^{15}N, and ^{13}C NMR Chemical Shifts of *N*-(Arylsulfonyl)phospha-λ^5-azenes 1a–k in $CDCl_3$ Solvent



compd	substit	$\delta_{^{31}P}$[a] (ppm)	$\delta_{^{15}N}$[b] (ppm)	$\delta_{^{13}C}$ (ppm)[c] 4′	3′	2′	1′	1	2	3	4
1a (1a*)	*p*-NO_2	16.66	96.93	133.17	128.91	133.01	126.53	151.66	126.94	123.39	148.52
1b	*m*-NO_2	16.59		133.15	128.90	132.98	126.40	147.82	121.10[d] 131.70[e]	147.51[f] 129.32[g]	124.80
1c	*p*-CN	16.46		133.12	128.87	132.98	126.53	150.03	126.42	131.97	113.77[d]
1d	*p*-CO_2CH_3	15.91		132.96	128.79	133.04	126.82	149.97	125.75	129.41	131.48[e]
1e (1e*)	*p*-Br	15.49	95.99	132.92	128.78	133.04	126.87	145.14	127.43	131.12	124.68
1f (1f*)	*p*-Cl	15.55	95.98	132.91	128.77	133.04	126.90	144.66	127.23	128.14	136.28
1g (1g*)	*p*-F	15.36	95.78	132.90	128.76	133.03	126.92	142.26	128.12	114.88	163.54
1h (1h*)	H	15.29	95.22	132.78	128.70	133.06	127.13	146.05	125.66	128.00	130.21
1i (1i*)	*p*-CH_3	14.97[j]	95.45	132.71	128.66	133.09	127.30	143.40	125.67	128.56	140.42[k,l]
1j (1j*)	*p*-OCH_3	14.74	95.70	132.73	128.68	133.08	127.26	138.58	127.52	113.10	160.95[m]
1k (1k*)	*p*-NH_2	14.28	95.66	132.64	128.64	133.12	127.48	135.86	127.40	113.54	148.49

[a] In ppm downfield from external 85% H_3PO_4; extrapolated to infinite dilution. [b] In ppm downfield from NH_3(l). Obtained using an external $K^{15}NO_3$ solution in H_2O which had been standardized against neat CH_3NO_2. Shifts were calculated using $\delta(NH_3) = \delta(CH_3NO_2) + 380.23$. Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectorscopy*; Wiley: New York, 1979; Chapter 3. [c] Downfield from internal $(CH_3)_4Si$; concentration: 50 mg/mL. [d] C-2. [e] C-6. [f] C-3. [g] C-5. [h] $\delta_{^{13}C}$ for the CN group is 118.00. [i] $\delta_{^{13}C}$ for the CO group is 166.18 and for the OCH_3 is 52.31. [j] This is in good agreement with the value reported (δ = 14.6). Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1976**, *41*, 2716. [k] The carbon chemical shifts agree with those reported. Fritz, H.; Weis, C. D. *J. Org. Chem.* **1978**, *43*, 4900. [l] $\delta_{^{13}C}$ for the CH_3 group is 21.29. [m] $\delta_{^{13}C}$ for the OCH_3 group is 55.37.

Table III. NMR Coupling Constants in *N*-(Arylsulfonyl)phospha-λ^5-azenes 1a–k ($CDCl_3$ Solvent; All Values Given in Hz)[a]



compd	substit	$^1J_{PN}$[b]	$^1J_{PC-1'}$	$^2J_{PC-2'}$	$^3J_{PC-3'}$	$^4J_{PC-4'}$	$^3J_{PC-1}$	other
1a (1a*)	*p*-NO_2	34.4	104.3	10.9	13.0	ca. 3.1[c]	2.3	$^2J_{NC-1}$ = 6.3; $^2J_{NC-1'}$ = 3.0
1b	*m*-NO_2		104.2	10.8	13.0	3.0	2.1	
1c	*p*-CN		104.3	10.8	13.0	ca. 2.9[c]	2.3	
1d	*p*-CO_2CH_3		104.3	10.7	13.0	ca. 3.3[c]	2.2	
1e (1e*)	*p*-Br	34.8	104.3	10.7	13.0	2.9	2.3	$^2J_{NC-1}$ = 5.9; $^2J_{NC-1'}$ = 3.0
1f (1f*)	*p*-Cl	34.8	104.2	10.7	12.9	ca. 2.4[c]	2.4	$^2J_{NC-1}$ = 5.9; $^2J_{NC-1'}$ = 3.0
1g (1g*)	*p*-F	34.9	104.2	10.6	12.9	ca. 2.7[c]	2.4	$^2J_{NC-1}$ = 6.0; $^2J_{NC-1'}$ = 3.1; $^1J_{FC-4}$ = 250.4; $^2J_{FC-3}$ = 22.2; $^3J_{FC-2}$ = 8.9; $^4J_{FC-1}$ = 3.1
1h (1h*)	H	34.9	104.3	10.7	12.9	2.9	2.4	$^2J_{NC-1}$ = 5.8; $^2J_{NC-1'}$ = 3.1
1i (1i*)	*p*-CH_3	35.0	104.3	10.8	13.0	3.0	2.7[d]	$^2J_{NC-1}$ = 5.9; $^2J_{NC-1'}$ = 3.1
1j (1j*)	*p*-OCH_3	35.2	104.2	10.7	12.9	3.0	2.6	$^2J_{NC-1}$ = 5.8; $^2J_{NC-1'}$ = 3.1
1k (1k*)	*p*-NH_2	35.4	104.1	10.7	12.9	3.0	2.5	$^2J_{NC-1}$ = 5.7; $^2J_{NC-1'}$ = 3.1

[a] ±0.1 Hz except where one peak of the doublet is under another.[c] [b] Obtained from the ^{31}P spectrum. [c] One of the peaks of the doublet was under a larger peak of another ^{13}C resonance. [d] The P–C coupling constants are in good agreement with those reported. Fritz, H.; Weis, C. D. *J. Org. Chem.* **1978**, *43*, 4900.

^{31}P chemical shifts were extrapolated to infinite dilution, although in this case the slopes of the plots of concentration vs. $\delta_{^{31}P}$ are considerably less than in the case of the *N*-aryltriphenylphospha-λ^5-azenes **2**.[2,3] The carbon numbering scheme is shown in the table. Table III shows the various coupling constants.

There are a number of linear correlations of the NMR parameters with Hammett σ constants[7] and with other NMR parameters that are suggested by the data. These are presented in Table IV.

In this case, with the *N*-(arylsulfonyl)phospha-λ^5-azenes **1**, the correlation of the ^{31}P and ^{13}C chemical shifts, where

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

Table IV. Linear Relationships between NMR Parameters and Hammett σ Constants

plots of X vs. Y		no. of points	slope	correltn coeff (r)
		For the Series 1		
$\delta_{^{31}P}$	$\sigma_{p(m)}$[a]	11	1.74	0.994
$\delta_{^{13}C-1'}$	$\sigma_{p(m)}$[a]	11	−0.768	0.975
$\delta_{^{13}C-3'}$	$\sigma_{p(m)}$[a]	11	0.208	0.969
$\delta_{^{13}C-4'}$	$\sigma_{p(m)}$[a]	11	0.406	0.978
$^1J_{PN}$	σ_p[a]	8	−0.712	0.991
$^1J_{PN}$	$\delta_{^{31}P}$	8	−0.420	0.989
		For the Series 1 vs. 3		
1	3			
$\delta_{^{13}C-1}$	$\delta_{^{13}C-1}$	11	0.854	0.984
$\delta_{^{13}C-2}$	$\delta_{^{13}C-2}$	11	0.885	0.998
$\delta_{^{13}C-3}$	$\delta_{^{13}C-3}$	11	0.995	0.998
$\delta_{^{13}C-4}$	$\delta_{^{13}C-4}$	11	1.000	0.999

[a] The σ values were taken from ref 7.

there are significant substituent effects, is best with σ_p and σ_m, rather than with σ^- as was the case with the *N*-aryl-phospha-λ^5-azene series 1. This is reasonable since, as pointed out above, the SO_2 group no longer allows direct conjugative pπ-type interaction of the nitrogen lone pair with the substituent R. Transmission of the electronic effects through the SO_2 group causes the dependency on $\sigma_{p(m)}$. A comparison of the slopes of the plots of $\delta_{^{31}P}$, $\delta_{^{13}C-1'}$, $\delta_{^{13}C-3'}$, and $\delta_{^{13}C-4'}$, vs. $\sigma_{p(m)}$ with the similar plots of the *N*-aryltriphenyl-λ^5-phosphazenes 1 (using σ^-) shows the electronic effect to be attenuated only by about 24–40%, a rather modest amount.

The ^{15}N chemical shifts in this series of compounds, 1, are seen to change in a most interesting way. They do not behave as the other chemical shifts and cannot be correlated acceptably with any σ nor the Taft dual substituent parameter equation.[8] This, at first glance, may seem strange since we are comparing chemical shifts in a related series of compounds; but, as is well-known, ^{15}N chemical shifts are a complicated combination of diamagnetic and paramagnetic terms.[9] These include not only electron density but also such things as the electronic excitation energy, electrons in nonspherically symmetric orbitals, and the multiple bonding to the nitrogen. Although the same arguments apply to the phosphorus chemical shifts, $\delta_{^{31}P}$ does seem to follow electron density. The difference between the two atoms is the lone electron pairs on nitrogen which must have substantial effect on the paramagnetic shielding term. Indeed, in the case of the *N*-aryl-phospha-λ^5-azenes 2 the resonance effect in donating and withdrawing electron density to and from the nitrogen was substantial and the ^{15}N chemical shift range of about 30 ppm[3] was mainly a reflection of electron density changes. In the case of the *N*-(arylsulfonyl)phospha-λ^5-azenes 1 the very substantially reduced interaction of the nitrogen electron pair with the substituent R results in the electron density effect being much smaller and now more comparable in magnitude to the other effects.

Thus, while the ^{15}N chemical shift is not directly related to electron density the ^{31}P and ^{13}C shifts are.

That the C_1–C_4 ^{13}C chemical shifts behave as expected for disubstituted benzenes,[10] and in particular substituted sulfonamides, is shown by the good to excellent plots (Table IV) of the various ^{13}C chemical shifts of the phospha-λ^5-azenes 1 against the corresponding shifts of the substituted sulfonamides 3 (Table V). Further, the Taft DSP treatment, using σ_I and σ_R^0 for C-1 in 1, gives ρ_I = 4.43 and ρ_R = 20.38 with f = 0.058.[10]

None of the P–C coupling constants show a dependence on substituents, indicating that either the factors which determine J, namely, the Fermi contact, orbital, and spin-dipolar terms, do not change within the series or they change in such a way that the changes mutually cancel. This latter explanation would seem to be less likely. Further, the observation that $^1J_{PC}$ varies with substituent in the N-aryl series, 2, but not in the *N*-arylsulfonyl series, 1, would appear to be related to the fact that the nitrogen lone pair in 2 is delocalized into the aryl ring while it is not in 1. The dependence of $^1J_{PN}$ on the resonance constants, σ_R and σ_R^+, in 1 but on $\sigma_{p(m)}$ in 2 also implies that electron delocalization of the nitrogen lone pair into the aryl ring is important in 2 and only the inductive interaction of the entire arylsulfonyl system is important in 1 in influencing the PN coupling constant.

This is completely consistent with the previous suggestion[2,3] that overlap of a nitrogen lone pair can be with a PC σ^* orbital in addition to a phosphorus d orbital. If one assumes that the double-bond character of the PN bond is essentially constant in the series 1, since no electron density is removed from or donated to the nitrogen by the substituent R, then the extent of d and more importantly σ^* participation would be constant, resulting in no change in $^1J_{PC}$. Contrast that with the situation in the series 2 where direct resonance interaction causes changes in the PN double-bond character and ultimately changes in the one bond PC coupling constant.[2]

This explanation then requires that the PN coupling constant changes in 1 are due to one or more of the factors other than changes in multiple bonding. One of several possibilities is that with increasing electron-withdrawing ability of the NSO_2Ar group the PN bond becomes richer in p character, giving rise to a lower coupling constant.

In order to see if the lack of correlation of the ^{15}N chemical shifts was unique to the phosphazene system, 1, or was observable in other similar systems, we examined the ^{15}N NMR spectra of the parent, ^{15}N-labeled, arenesulfonamides, **3a***, **e***, **f***, **g***, **h***, **i***, **j***, **k*** (67% ^{15}N), and these are shown in Table V. It should be noted that the spectra were run in Me_2SO rather than $CDCl_3$ because of solubility problems and that our chemical shifts agree very well with those for **3h** and **3k** reported by Roberts,[11] after conversion to the NH_3(l) scale (see footnote d in Table V).

Although there is a very rough trend of greater shielding with more electron-withdrawing groups, there is no direct correlation with any σ or with the ^{15}N chemical shifts of the sulfonylphospha-λ^5-azenes, 1. Indeed, the fact that the NO_2 sulfonamide **3a** has a more shielded nitrogen than the NH_2 sulfonamide **3k** strongly emphasizes the lack of correlation of ^{15}N chemical shift with charge density and that other factors are coming into play. These other factors, mentioned above, are generally more important for atoms with nonbonding electron pairs.[9]

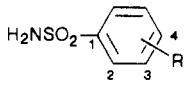
Work on these and related phospha-λ^5-azenes is continuing.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 599B

(8) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.
(9) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979; Chapter 1.
(10) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429.
(11) Schuster, I. I.; Doss, S. H.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 4693.

Table V. ^{15}N and ^{13}C Chemical Shifts of Arenesulfonamides ($RC_6H_4SO_2NH_2$; 3) in Me_2SO Solvent



compd	substit	δ_{15N} (ppm)[a,b]	δ_{13C} (ppm)[c] for indicated C			
			1	2	3	4
3a (3a*)	*p*-NO_2	94.54	150.38	128.21	125.41	150.17
3b	*m*-NO_2		146.33	121.45[e]	148.31[g]	127.25[k]
				132.53[f]	131.79[h]	
3c	*p*-CN		148.70	127.32	134.01	115.29[i]
3d	*p*-CO_2CH_3		148.30	126.91	130.71	133.24[j]
3e (3e*)	*p*-Br	94.65	144.30	128.67	132.93	126.38
3f (3f*)	*p*-Cl	94.72	143.74	128.46	129.87	137.52[k]
3g (3g*)	*p*-F	95.01	141.28	129.39	116.75	164.56[l]
3h (3h*)	H	94.50[d]	144.92	126.45	129.78	132.79[k]
3i (3i*)	*p*-CH_3	94.75	142.76	126.49	130.14	142.22[k,m]
3j (3j*)	*p*-OCH_3	95.47	136.94	128.56	114.83	162.51[n]
3k (3k*)	*p*-NH_2	96.27[d]	130.81	128.33	113.48	152.70[k]

[a] Concentration = 100 mg/0.7 mL Me_2SO. [b] In ppm downfield from NH_3(l). Obtained by first using a 5-mm concentric tube containing $K^{15}NO_3$ in H_2O, which had been standardized against neat CH_3NO_2, in a 12-mm tube containing $CDCl_3$, and then replacing the inner tube with one containing the labeled sulfonamides and measuring the chemical shift difference. The shifts were calculated using $\delta(NH_3) = \delta(CH_3NO_2) + 380.23$. Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectorscopy*; Wiley: New York, 1979; Chapter 3. [c] In ppm downfield from external Me_4Si in $CDCl_3$. Samples were contained in 5-mm tubes in Me_2SO and these were put inside a concentric tube containing $CDCl_3$ and Me_4Si. Concentration: 150 mg in 0.6 mL except for **3a** and **3d** which were 50 mg/0.6 mL and **3e** which was 100 mg/0.6 mL. [d] These values are in good agreement with those reported (Schuster, I. I.; Doss, S. H.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 4693), 279.7 and 278.1 upfield from external 1 M $H^{15}NO_3/D_2O$ for **3h** and **3k**, respectively, and converted to the NH_3(l) scale, 94.3 and 95.9, respectively, using the conversion factor of −6.2 ppm for the HNO_3 relative to neat CH_3NO_2 (Martin, G. J.; Martin, M. L.; Gouesnard, J.-P. *^{15}N-NMR Spectroscopy*; Springer-Verlag: Berlin, 1981; Chapter 4) and 380.23 ppm to convert to the NH_3(l) scale.[b] [e] C-2. [f] C-6. [g] C-3. [h] C-5. [i] δ_{13C} for the CN is 118.66. [j] δ_{13C} for the CO is 166.09 and for the CH_3 is 53.36. [k] The δ_{13C} values are in reasonable agreement with those reported. Bremser, W.; Ernst, L.; Franke, B.; Gerhards, R.; Hardt, A. *Carbon-13 NMR Spectral Data*, 2nd ed.; Verlag Chemie: Weinheim, 1979. For **3b**: *Sadtler Standard C-13 NMR* Spectra No. 5281. For **3h** and **3i**: Birchall, J. D.; Glidewell, C. *J. Chem. Soc. Dalton Trans.* **1978**, 604. For **3k**: Chang, C.-J.; Floss, H. G.; Peck, G. E. *J. Med. Chem.* **1975**, *18*, 505. [l] $^1J_{CF}$ = 250.1, $^2J_{CF}$ = 22.5, $^3J_{CF}$ = 9.3, and $^4J_{CF}$ = 3.2 Hz. [m] δ_{13C} for the CH_3 is 21.77. [n] δ_{13C} for the OCH_3 is 56.39.

spectrometer using KBr pellets. NMR spectra were recorded by using $CDCl_3$ solvent and 12-mm tubes on a Nicolet NT-200 WB spectrometer with a 4.7 T superconducting solenoid, at 200.07 MHz for ^1H, 80.99 MHz for ^{31}P, 50.31 MHz for ^{13}C, and 20.28 MHz for ^{15}N. The ^{31}P spectra were recorded by using external (concentric 5-mm tube) 85% H_3PO_4 standard, with concentrations of 100 mg/3 mL, 65 mg/3 mL, and 30 mg/3 mL and the reported chemical shifts were extrapolated 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 16K data points, zero-filled to 32K, and processed without exponential line broadening. The sweep width was 3610 Hz. The ^{13}C spectra were obtained by using $(CH_3)_4Si$ internal standard and a concentration of 150 mg/3 mL. Two-level broad-band proton decoupling was employed, a pulse angle of about 23°, and a post acquisition delay of 10 s. The data were collected using 32K data points and a total sweep width of 11 100 Hz and was processed by zero-filling to 64K data points. No exponential line broadening was employed. The exception was in obtaining the ^{13}C spectra of the sulfonamides **3** where 150 mg was dissolved in 0.6 mL of Me_2SO in a 5-mm tube and this was put into a concentric 12-mm tube containing $CDCl_3$ for lock and $(CH_3)_4Si$ as external standard. For **3a** and **3d** 50 mg in 0.6 mL of Me_2SO and for **3e** 100 mg in 0.6 mL of Me_2SO were used. In all these cases the spectra were obtained and treated the same as for the phosphazenes **1** except that the sweep widths were different. For **3a–c, e, h–k** the total sweep width was 10 kHz, for **3d** and **3g** it was 14.1 kHz, and for **3f** it was 12 kHz. The ^{15}N spectra were obtained by using gated broad band proton decoupling (decoupler on during acquisition), a pulse angle of about 23° and a post acquisition delay of 6 s. For the phosphazenes **1*** an external standard (concentric 5-mm tube) of a solution of $K^{15}NO_3$ in H_2O that had been standardized against neat CH_3NO_2 was used and chemical shifts relative to NH_3(l) were calculated by using $\delta(NH_3) = \delta(CH_3NO_2) + 380.23$.[12] The data were collected using 32K data points and a total sweep width of 14 kHz and was processed by zero-filling to 64K data points. No exponential line broadening was employed. For **1k*** the concentration was 120 mg/3 mL of $CDCl_3$ while for **1a*,e*–j*** the concentration was 200 mg/3 mL of $CDCl_3$. For the sulfonamides **3a*,e*–k*** a different procedure was employed. A 5-mm tube containing 100 mg of the sample in 0.7 mL of Me_2SO was used and contained within a concentric external 12-mm tube containing $CDCl_3$. The internal 5 mm tube was replaced by the standard $K^{15}NO_3/H_2O$ sample (5-mm tube) and the chemical shift difference was obtained and then related to NH_3(l) as described above. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. THF (tetrahydrofuran) was distilled from $LiAlH_4$ before use and the preparation of the phospha-λ^5-azenes was carried out under dry argon.

***p*-Carbomethoxybenzenesulfonamide (3d).** *p*-Carboxybenzenesulfonamide (10.7 g; 0.053 mol) was esterified with the diazomethane prepared from 5.6 g of *N*-methyl-*N*-nitrosourea (0.054 mol) in ether.[13] The product was recrystallized from acetone to give 2.75 g (38%) of off-white solid, mp 174–178 °C (lit.[14] mp 177 °C, 175–180 °C).

***p*-Cyanobenzenesulfonamide (3c)** was prepared by the method of Andrews et al.[16] (**3k**; 20.0 g; 0.116 mol) was diazotized ($NaNO_2$/HCl) and then treated with KCN (37.9 g; 0.582 mol) and $NiCl_2$ (27.6 g; 0.213 mol). The resulting solid was filtered with suction, washed with acetone, and recrystallized from water (Norit). The yield of **3c** was 10.7 g, 51%, mp 163–165 °C (lit.[15] mp 165–166 °C).

Preparation of the *N*-(Arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ^5-azenes 1. The procedure, using triphenylphosphine, the sulfonamide, and diethyl azodicarboxylate (1:1:1 ratio/THF solvent/0 °C), reported previously[4] was employed. The sulfonylphosphazenes usually precipitated and were recrystallized by

(12) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979; Chapter 3.

(13) Arndt, F. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. II, p 165.

(14) Manousek, O.; Exner, O.; Zuman, P. *Collect. Czech. Chem. Commun.* **1968**, *33*, 4000. Isozaki, M. *Repts. Govt. Chem. Ind. Res. Inst. Tokyo* **1950**, *45*, 295; *Chem. Abstr.* **1952**, *46*, 4269e.

(15) Taken on a Varian T-60, 60 MHZ spectrometer.

(16) Ott, D. G. *Synthesis with Stable Isotopes of Carbon, Nitrogen and Oxygen*; Wiley: New York, 1981; pp. 201–202.

using the indicated solvents (Table I and ref 4).

***N*-[(*p*-Cyanophenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (1c)**: ^{1}H NMR ($CDCl_3$): δ 7.3–7.8 (m, Ar *H*). Anal. Calcd for $C_{25}H_{19}N_2O_2PS$: C, 67.70; H, 4.55; N, 6.32. Found: C, 67.77; H, 4.38; N, 6.07.

***N*-[(*p*-Carbomethoxyphenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (1d)**: ^{1}H NMR ($CDCl_3$)[15] δ 3.90 (s, 3 H, OCH_3), 7.3–7.9 (m, 19 H, Ar *H*). Anal. Calcd for $C_{26}H_{22}NO_4PS$: C, 65.67; H, 4.66; N, 2.94. Found: C, 65.32; H, 4.60; N, 2.75.

***N*-[(*p*-Bromophenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (1e)**: ^{1}H NMR ($CDCl_3$) δ 7.2–7.9 (m, Ar *H*). Anal. Calcd for $C_{24}H_{19}BrNO_2PS$: C, 58.08; H, 3.86; N, 2.82. Found: C, 58.25; H, 3.91; N, 2.82.

***N*-[(*p*-Fluorophenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (1g)**: ^{1}H NMR ($CDCl_3$) 6.85 (t, 2 H, Ar *H*), 7.3–7.9 (m, 17 H, Ar *H*). Anal. Calcd for $C_{24}H_{19}FNO_2PS$: C, 66.20; H, 4.40; N, 3.21. Found: C, 66.52; H, 4.72; N, 3.14.

***N*-[(*p*-Methoxyphenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (1j)**: ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3 H, OCH_3), 6.67 (d, 2 H, Ar *H*), 7.3–7.9 (m, 17 H, Ar *H*). Anal. Calcd for $C_{25}H_{22}NO_3PS$: C, 67.10; H, 4.95; N, 3.13. Found: C, 67.23; H, 4.97; N, 3.08.

General Procedure for the Preparation of ^{15}N-Labeled Sulfonamides 3a*,e*–k*. The procedure was similar to that given in the literature for a substituted naphthalenesulfonamide.[16] A mixture of ammonium sulfate–$^{15}N_2$ (67.3% ^{15}N; 9 mmol), the benzenesulfonyl chloride (18 mmol), and K_2CO_3 (72 mmol) in acetonitrile (100 mL) was cooled in an ice bath. Water (72 mL) was then added, the flask was stoppered, and the mixture was stirred magnetically at room temperature overnight. The organic layer was separated, the solvent was removed under vacuum, and the residue was recrystallized from water or ethanol–water. All melting points agreed with those reported for the unlabeled material.

^{15}N-Labeled *N*-(Arylsulfonyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azenes 1a*,e*–k*. The procedure for **1a*,e*–g*,i*–k***, using the appropriate ^{15}N-labeled sulfonamides, was the same for the unlabeled compounds.[4] **1h*** was made from the ^{15}N-labeled sulfonamide **3h*** and triphenylphosphine dibromide as described for the unlabeled compound by Horner.[17] The properties of the labeled phosphazenes **1a*,e*–k*** are presented in Table I.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant Y-684), the Organized Research Fund of The University of Texas at Arlington, and the National Science Foundation (Grant PMR 8108132) for financial support.

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

Resonance and Solvent Effects on Absorption Spectra. 6. Substituent Solvation Effects on Nitrogen-15 Chemical Shifts of Para-Substituted Anilines and Para-Substituted 2-Nitroanilines[1]

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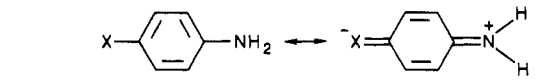
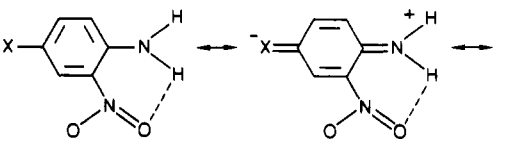
Received July 28, 1986

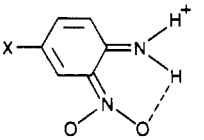
Our earlier studies[1,3] of substituent effects on the ^{15}N chemical shifts (δ(^{15}N)) and on the UV/vis spectra absorption maxima for para-substituted anilines **1** and para-substituted 2-nitroanilines **2** showed important distinctions arising from the fact that ground-state charge distributions are predominant for the ^{15}N shifts whereas excited-state charge distributions are predominant for the UV/vis spectral shifts. In the present work, more extensive determinations have been made of substituent ^{15}N chemical shifts (δ(^{15}N)) in both series **1** and series **2** in the strong hydrogen-bond-acceptor dipolar solvent, dimethyl sulfoxide (Me_2SO). Our objective has been to learn whether substituent solvation assisted resonance (SSAR) effects[3-5] contribute significantly to the NMR shift measurements in either or both of these series of neutral compounds.



1



2



SSAR effects of certain conjugated π-electron-acceptor (+R) substituents have been found to give significant enhancements in acidities in Me_2SO of phenols, anilines, toluenes, and other acids.[4-6] The magnitudes of these acidity enhancements increase with increasing π-electron donation to the conjugated substituent from the deprotonation center of the anionic forms. Solvation by Me_2SO of the NH's of both series **1** and series **2** is expected to impart some anionic character, but the present study is directed toward ascertaining whether this is sufficient to permit the observation of SSAR effects on the δ(^{15}N) values of neutral solutes. An affirmative answer has been obtained.

"Nonsolvated" para substituents, X, are either non-hydrogen-bond-donor π-electron donors (–R) or π acceptors (+R) with weakly enhanced charges at individual electronegative atoms, e.g., SC_6H_5, CF_3, SCF_3, and SF_5. Both subsets of substituents are well-represented in our data.

Results and Discussion

For non-SSAR substituents, the ^{15}N shifts are well-correlated by the following equations:

$$\delta(^{15}N)\ (1;\ \text{non-SSAR}) = (10.7 \pm 0.6)\sigma_F + (29.9 \pm 0.9)\sigma_R - 52.9 \pm 0.2 \quad n = 7,\ r = 0.997,\ SD = 0.3 \qquad (1)$$

$$\delta(^{15}N)\ (2;\ \text{non-SSAR}) = (11.8 \pm 1.0)\sigma_F + (22.4 \pm 1.4)\sigma_R - 34.7 \pm 0.4 \quad n = 7,\ r = 0.995,\ SD = 0.5 \qquad (2)$$

(1) Part 5: Yokoyama, T.; Tabuchi, H.; Taft, R. W.; Kamlet, M. J., submitted for publication in *J. Magn. Reson.*

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(3) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Spectrochim. Acta, Part A* **1984**, *40A*, 669.

(4) Mishima, M.; McIver, R. T., Jr.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717 and reference given therein.

(5) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.*, in press.

(6) Taft, R. W.; Bordwell, F. G., to be submitted.

0022-3263/87/1952-0163$01.50/0