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

N-[(p-Cyanophenyl)sulfonyl]-P,P,P-triphenylphospha-λ^5-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-λ^5-azene (1d): ^{1}H NMR ($CDCl_3$)[15] δ 3.90 (s, 3 H, OC*H*$_3$), 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-λ^5-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-λ^5-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-λ^5-azene (1j): ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3 H, OC*H*$_3$), 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-λ^5-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.

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[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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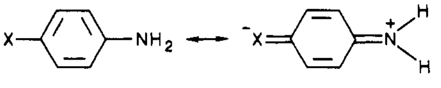
Our earlier studies[1,3] of substituent effects on the ^{15}N chemical shifts ($\delta(^{15}N)$) and on the UV/vis spectra absorption maxima for para-substituted anilines **1** and para-substituted 2-nitroanilines **2** showed important distinctions arising from the fact that ground-state charge distributions 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 ($\delta(^{15}N)$) 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.



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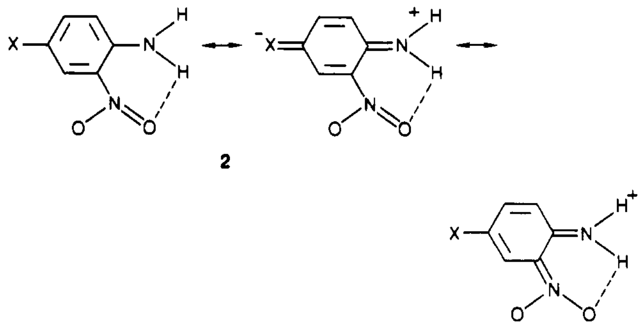

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SSAR effects of certain conjugated π-electron-acceptor (+R) substituents have been found to give significant enhancements in acidities in Me_2SO of phenols, anilines, toluenes, and other acids.[4-6] The magnitudes of these acidity enhancements increase 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 $\delta(^{15}N)$ 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:

$$\delta(^{15}N)\ (1;\ \text{non-SSAR}) = (10.7 \pm 0.6)\sigma_F + (29.9 \pm 0.9)\sigma_R - 52.9 \pm 0.2$$

$$n = 7,\ r = 0.997,\ SD = 0.3 \qquad (1)$$

$$\delta(^{15}N)\ (2;\ \text{non-SSAR}) = (11.8 \pm 1.0)\sigma_F + (22.4 \pm 1.4)\sigma_R - 34.7 \pm 0.4$$

$$n = 7,\ r = 0.995,\ SD = 0.5 \qquad (2)$$

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

[2] (a) Toyama University. (b) University of California; presently, Department of Chemistry, Kyushu University 33, Fukuoka, 812 Japan. (c) Naval Surface Weapons Center. (d) University of California.

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

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0022-3263/87/1952-0163$01.50/0 © 1987 American Chemical Society

Table I. ^{15}N **NMR Spectral Data** ($\delta(^{15}N)$ **Values (ppm)) of 4-Substituted Anilines (1) and 4-Substituted 2-Nitroanilines (2) and Corresponding Substituent Parameters**

substituent	$-\delta(^{15}N)$ (1)[a]	$-\delta(^{15}N)$ (2)[a]	σ_F[b]	σ_R[b]	$\Delta\sigma_R$[c]	σ_I[d]	σ_R^-[d]	σ_p^-[e]
OCH_3	58.4	37.4	0.25	−0.27	0.00[f]	0.27	−0.45	−0.13
CH_3	55.2	36.7	0.00	−0.08	0.00[f]	−0.04	−0.11	−0.12
F	55.8	35.8	0.44	−0.25	0.00[f]	0.50	−0.45	0.15
Cl	52.9	32.7	0.45	−0.17	0.00[f]	0.46	−0.23	0.26
H	53.0	34.6	0.00	0.00	0.00[f]	0.00	0.00	0.00
CO_2CH_3	41.9	25.4	0.24	0.16	0.08	0.30	0.34	0.74
$CO_2C_2H_5$	42.3	25.9	0.24	0.16	0.08	0.30	0.34	0.74
$COCH_3$	41.0	24.7	0.26	0.17	0.10	0.28	0.47	0.82
CF_3	45.7	27.7	0.44	0.07	0.00[f]	0.45	0.17	0.56
SCF_3	45.2	27.0	0.48	0.10	0.00[f]	0.42	0.14	0.63
CN	39.8	23.4	0.60	0.10	0.07	0.56	0.33	0.99
SO_2CH_3	41.2	24.2	0.59	0.12	0.02	0.59	0.38	1.05
NO_2	33.5	18.8	0.65	0.18	0.18	0.65	0.46	1.23
SO_2CF_3	31.4		0.84	0.21	0.09			

[a] Chemical shift values upfield from $HCONH_2$ as external reference in 1.7 M Me_2SO-d_6 solution. [b] From ref 5. [c] From ref 6. [d] From Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1. [e] From ref 9. [f] Non-SSAR substituent.

For both series 1 and series 2, the correlation coefficient between the independent variables σ_F and σ_R is 0.071. The field/inductive effect substituent parameters, σ_F, and the resonance effect substituent parameters, σ_R, are those applicable to gas-phase proton-transfer equilibria.[5,7] Table I gives values for these parameters as well as the ^{15}N chemical shift values obtained for both series 1 and 2 ($-\delta(^{15}N)$ values are upfield from $HCONH_2$, an external reference for 1.7 M Me_2SO-d_6 solutions).

If the SSAR substituents are included with the non-SSAR substituents, equations of the form of eq 1 and 2 poorly describe the ^{15}N shift results,[8] as do other conventional substituent parameter correlations such as those given in Table I.[8] For the same 13 substituents in both series, the correlation equations are

$$\delta(^{15}N)\ (\text{series 1}) = (13.7 \pm 2.5)\sigma_F + (39.2 \pm 3.3)\sigma_R - 52.3 \pm 1.0$$

$$r = 0.977,\ \text{SD} = 1.8 \qquad (3)$$

$$\delta(^{15}N)\ (\text{series 2}) = (12.5 \pm 1.7)\sigma_F + (28.8 \pm 2.2)\sigma_R - 33.9 \pm 0.7$$

$$r = 0.983,\ \text{SD} = 1.2 \qquad (4)$$

It will be noted that the SD's for eq 3 and 4 are unacceptably high compared to those for eq 1 and 2. On the other hand, all 13 substituents common to the data for both series 1 and series 2 (Table I) are fitted (eq 6 and 7) with essentially the same excellent correlation coefficients as for eq 1 and 2 utilizing the following equation, which has been shown to satisfactorily incorporate SSAR effects:[5,6]

$$\delta(^{15}N) = A_0 + \sigma_F\rho_F + \sigma_R\rho_R + \Delta\sigma_R\rho_s \qquad (5)$$

where (as in eq 1 and 2) A_0 is the shift for the unsubstituted derivative, σ_F and σ_R are gas phase field/inductive and resonance effect parameters,[5] and $\Delta\sigma_R$ is a parameter for the SSAR effect of an appropriate π-electron-acceptor substituent.[6] These parameters, which are based upon the horizontal deviations shown in Figure 1 of ref 4, have recently been found to apply (with use of eq 5) with generality and excellent precision to many appropriate acidities and reaction rates in both Me_2SO and hydroxylic solvents.[6] Values of σ_F, σ_R, $\Delta\sigma_R$ are given in Table I.

For valid evaluation by eq 5, the three kinds of substituent parameters (σ_F, σ_R, and $\Delta\sigma_R$) must be mutually noncolinear to a very significant degree. For the correlations by eq 6 and 7, this essential condition is met by the correlation coefficients beteen the independent variables: r (σ_F vs. σ_R) = 0.441, r (σ_F vs. $\Delta\sigma_R$) = 0.503, r (σ_R vs. $\Delta\sigma_R$) = 0.609.

The σ_R parameter is believed to be directly proportional to the total π electronic charge that is delocalized to the substituent as a whole. This is only one of the factors that determine the substituent SSAR effect.[4-6] Equally important is the intensity of the charge that is localized at an electronegative atom of the substituent so that it is solvent accessible. Thus, for example, the $\Delta\sigma_R$ value (Table I) for SO_2CF_3 (0.09) is less than that for NO_2 (0.18) because the negative charges at oxygen are smaller for the former (due to the effect of CF_3) relative to the latter, despite the fact that more charge is delocalized into SO_2CF_3 (σ_R = 0.21) than into NO_2 (σ_R = 0.18). For this reason, with appropriate choice of π-electron-acceptor substituents, the correlation coefficient between $\Delta\sigma_R$ and corresponding σ_R values can be kept below a value of 0.65 for a data set, and useful estimates of the terms in eq 5 can be obtained. The present two data sets (for the same 13 substituents; cf. Table I) give

$$\delta(^{15}N)\ (\text{series 1}) = (11.8 \pm 0.9)\sigma_F + (31.1 \pm 1.5)\sigma_R + (37.4 \pm 4.3)\Delta\sigma_R - 53.0 \pm 0.4$$

$$n = 13,\ r = 0.998,\ \text{SD} = 0.7 \qquad (6)$$

$$\delta(^{15}N)\ (\text{series 2}) = (11.3 \pm 0.7)\sigma_F + (23.6 \pm 1.1)\sigma_R + (23.5 \pm 3.1)\Delta\sigma_R - 34.4 \pm 0.3$$

$$n = 13,\ r = 0.998,\ \text{SD} = 0.5 \qquad (7)$$

Both the standard deviations and correlation coefficients for eq 6 and 7 are very good, considering that ranges of ^{15}N shift of ca. 25 and 19 ppm, respectively, are involved. Although the shift measurements are precise to less than 0.1 ppm, the relatively large 1.7 M concentrations that are necessary make it likely that concentration effects on the shifts as large as 0.5 ppm may be involved.

It is significant that essentially the same correlation coefficient (0.997 ± 0.02) applies for eq 1, 2, 6, and 7 and that the standard deviations for these equations are 2 to 3 times smaller than those for eq 3 and 4. Also, the intercepts in these equations are equal to the experimental value for the unsubstituted member within the errors of estimates. Further, it is to be noted that within the errors of the estimates, the ρ_F values (dependence upon σ_F) are

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(7) Hehre, W. J.; Pau, C.-F.; Headley, A. D.; Taft, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 1711.

(8) Single-parameter correlations using σ_p^- values from ref 9 give the following: for series 1, r = 0.972, SD = 1.8; for series 2, r = 0.984, SD = 0.8. Using σ_I,σ_R^- dual parameters (cf. Table I) gives the following: for series 1, r = 0.987, SD = 1.4; for series 2, r = 0.990, SD = 0.9.

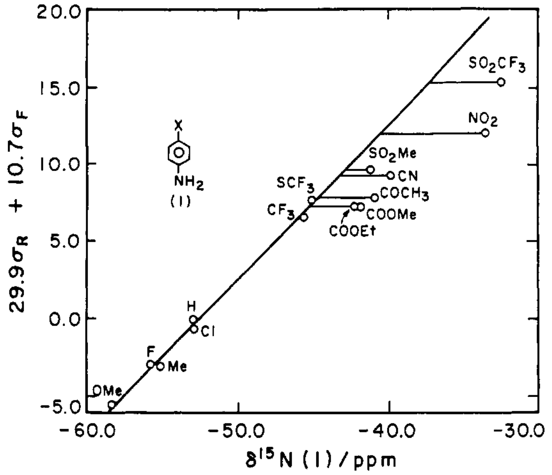
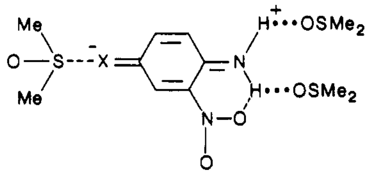


Figure 1. ^{15}N substituent chemical shifts for para-substituted anilines plotted vs. corresponding values estimated for substituents with no solvated substituent assisted resonance effects. Horizontal deviations show the estimated SSAR effects. Ordinate: $29.9\sigma_R + 10.7\sigma_F$ (cf. eq 1). Abscissa: $\delta(^{15}N)$ for series 1 (ppm).

the same for eq 1, 2, 6, and 7. Likewise, the ρ_R values (dependence upon σ_R) are the same within the errors of the estimates for eq 1 as for eq 6 and for eq 2 as for eq 7. Finally, it is important to note that the value of ρ_s (the dependence on $\Delta\sigma_R$) is larger (37.4 ± 4.3 compared to 23.5 ± 3.1) for the para-substituted anilines (series 1) than for series 2, and a similar relationship holds for the ρ_R values. These smaller responses for series 2 are due to the diminished π-electron delocalization to the π-electron-acceptor substituents, which results from the electron withdrawal by the 2-NO_2 group.

In the rates of nucleophilic aromatic substitution reactions, the "activating" 2-NO_2 substituent withdraws sufficient charge in the reaction transition states that little or no substituent SSAR effects are observed.[10] On the other hand, without "activation" by 2-NO_2, the rates are quite significantly increased by substituent SSAR effects.[10,11] In the present case, the appearance of significant SSAR effects on the ^{15}N shifts for series 2 can be accounted for by the enhancement in NH_2 acidities due to the 2-NO_2 group. This enhanced acidity increases hydrogen bonding between the NH_2 group and the Me_2SO medium. With increased hydrogen-bond-donor ability, the NH_2 delocalizes more π electronic charge,[12] thus partly offsetting the loss from the presence of the NO_2 group. The retention of the SSAR effects for the strongly conjugated π-acceptor (SSAR) substituents is expressed by the following kind of resonance form:[13]



In series 1, the ^{15}N shift due to the p-SO_2CF_3 substituent was also determined (31.4). If this data point is included in series 1, the 14 substituents give the following correlation equation:

$$\delta(^{15}N) = (12.6 \pm 0.9)\sigma_F + (31.5 \pm 1.6)\sigma_R - (37.2 \pm 4.7)\sigma_R - 53.2 \pm 0.04$$

$$r = 0.998, \mathrm{SD} = 0.7 \qquad (8)$$

Eq 8 does not differ from the corresponding eq 7 in any term, well within the errors of the estimates.

The presence of SSAR effects in the ^{15}N shifts of para-substituted anilines in Me_2SO solutions is illustrated by the horizontal lines of deviation in Figure 1. In this figure, the observed values of $\delta(^{15}N)$ are plotted vs. the corresponding values estimated for non-SSAR substituents by eq 1. Similar results apply for series 2 data. It may be concluded that SSAR effects are quite general and are applicable to physical as well as chemical properties of appropriate systems.

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Registry No. 1 (X = OCH_3), 104-94-9; 1 (X = CH_3), 106-49-0; 1 (X = F), 371-40-4; 1 (X = Cl), 106-47-8; 1 (X = H), 62-53-3; 1 (X = CO_2CH_3), 619-45-4; 1 (X = $CO_2C_2H_5$), 94-09-7; 1 (X = $COCH_3$), 619-55-6; 1 (X = CF_3), 455-14-1; 1 (X = SCF_3), 372-16-7; 1 (X = CN), 873-74-5; 1 (X = SO_2CH_3), 5470-49-5; 1 (X = NO_2), 100-01-6; 1 (X = SO_2CF_3), 473-27-8; 2 (X = OCH_3), 96-96-8; 2 (X = CH_3), 89-62-3; 2 (X = F), 364-78-3; 2 (X = Cl), 89-63-4; 2 (X = H), 88-74-4; 2 (X = CO_2CH_3), 3987-92-6; 2 (X = $CO_2C_2H_5$), 76918-64-4; 2 (X = $COCH_3$), 1432-42-4; 2 (X = CF_3), 400-98-6; 2 (X = SCF_3), 404-74-0; 2 (X = CN), 6393-40-4; 2 (X = SO_2CH_3), 21731-56-6; 2 (X = NO_2), 97-02-9.

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(12) Bromilow, J.; Brownlee, R. T. C.; Lopéz, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

(13) Cf. also: Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1982**, *47*, 1734.

Diphenylmethylsilyl Ether (DPMS): A Protecting Group for Alcohols

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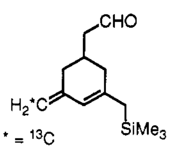
During an investigation on the stereochemical course of allylmetal–aldehyde condensations[2] we undertook the synthesis of the pentadienylsilane **1**.[3] Our experience in the synthesis of the related allylsilane **2** suggested that a *tert*-butyldimethylsilyl (TBDMS) protected alcohol should serve as an appropriate aldehyde precursor. Unfortunately all attempts to remove the TBDMS gorup in **3** completely destroyed the sensitive pentadienylsilane moiety. We therefore chose to develop a new protecting group which would satisfy the immediate requirements of



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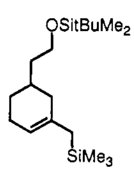

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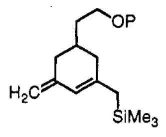

3 P=TBDMS
4 P=DPMS

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[1] (a) Fellow of the Alfred P. Sloan Foundation (1985-1987), NSF Presidential Young Investigator (1985-1990). (b) Undergraduate Research Participant. (c) Taken in part from the Ph.D. Thesis of E. J. Weber, University of Illinois, Urbana, 1985.

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