methylsilyl)oxy]propionitrile (83% yield). Its spectral properties were in complete agreement with those previously reported by West.[10] MS *m/e* 142 (M − 15, 62.1), 101 (96.8), 98 (100), 73 (89.7).

Reaction of Isobutylene Oxide with Trimethylsilyl Cyanide. In a two-necked 2-mL round-bottomed flask equipped with reflux condenser, was placed a mixture of 10 μL of diethylaluminum chloride solution and 0.116 g (1.17 mmol, 155 μL) of trimethylsilyl cyanide. To this was added 0.89 g (1.23 mmol) of isobutylene oxide over a period of 45 min. The mixture was then stirred for 48 h at room temperature. GLC analysis of this mixture revealed the formation of 3-methyl-3-[(trimethylsilyl)-oxy]butyronitrile (52% yield). A similar reaction with aluminum chloride as catalyst gave the same product (20%). 3-Methyl-3-[(trimethylsilyl)oxy]butylronitrile had the following spectral properties: ^{1}H NMR δ 0.193 (s, 9 H), 1.430 (s, 6 H), 2.482 (s, 2 H); ^{13}C (B) NMR δ 3.215 (q), 30.103 (q), 34.592 (t), 71.899 (s), 117.400 (s); IR 2251 (C≡N), 1260 (SiCH$_3$), 1050 cm^{-1} (SiO).[11]

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research Grant No. 80-0006.

Registry No. Trimethylsilyl cyanide, 7677-24-9; 3,3-dimethyloxetane, 6921-35-3; 3,3-dimethyl-4-[(trimethylsilyl)oxy]butyronitrile, 81956-58-3; 2-methyloxetane, 2167-39-7; 4-methyl-4-[(trimethylsilyl)oxy]butyronitrile, 66408-81-9; oxetane, 503-30-0; 4-[(trimethylsilyl)oxy]butyronitrile, 72049-81-1; propylene oxide, 75-56-9; 3-methyl-3-[(trimethylsilyl)oxy]propionitrile, 31649-95-3; isobutylene oxide, 558-30-5; 3-methyl-3-[(trimethylsilyl)oxy]butyronitrile, 14904-41-7; 2,2-dimethyl-3-[(trimethylsilyl)oxy]propionitrile, 42202-45-9.

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Nitrogen-15 Nuclear Magnetic Resonance Studies of Benzenediazonium Ions. Effects of Solvent, Substituent, Anion, and 18-Crown-6[†1a]

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Effects of solvent change on the ^{15}N resonance positions for *p*-*n*-butylbenzenediazonium tetrafluoroborate are small. In contrast, the influence of substituents on the ^{15}N chemical shifts for para-substituted benzenediazonium tetrafluoroborates in acetonitrile are relatively large. For the *p*-*n*-butylbenzenediazonium cation in dichloromethane, replacement of the tetrafluoroborate anion by chloride produces small downfield shifts of the ^{15}N resonance positions for both nitrogens. Complexation of benzenediazonium tetrafluoroborates by 18-crown-6 in *N*,*N*-dimethylformamide induces relatively large changes in the ^{15}N chemical shifts. Attempts to detect crown ether complexation of other species with diazonium-like termini by ^{15}N NMR were unsuccessful.

A variety of spectroscopic methods[2] have been employed to assess the influence of aromatic ring substituents, solvents, anions, and specific complexing agents such as crown ethers[3] upon the structure and bonding of benzenediazonium ions. Infrared and ultraviolet spectral studies have recently been augmented by investigations which utilize ^{1}H and ^{13}C NMR.[4-7] Although it is a technique which could potentially provide much additional information, ^{15}N NMR spectroscopy has rarely been applied to the study of aromatic diazonium salts. Only ^{15}N chemical shifts of five benzenediazonium tetrafluoroborates solubilized[8] by 1.2–1.8 equiv of 18-crown-6 in CDCl$_3$ have been reported.[9]

Experimental difficulties encountered in making natural-abundance ^{15}N NMR measurements for uncomplexed benzenediazonium salts include problems of diazonium salt solubility in most organic solvents and of stability during the long pulse delays and numerous transients which are required. However, we have overcome these difficulties and report here the effects of solvent, substituent, and anion on the ^{15}N chemical shifts for N1 and N2 of uncomplexed benzenediazonium salts as well as the changes in these chemical shifts when 18-crown-6 is present.

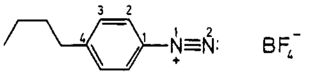
Results and Discussion

Table I. Effect of Solvent on the ^{15}N and ^{13}C NMR Chemical Shifts of 1[a]

	chemical shift, δ				
solvent	N1[b]	N2[b]	C1[c]	C4[c]	B[d]
dichloromethane	143.8	58.1	110.1	160.4	43
nitromethane	143.6	58.8	110.4	160.9	59
acetonitrile	143.5	58.8	111.2	160.6	103
acetone	144.0	59.7	111.9	159.8	123
1,4-dioxane	144.4	59.9	112.2	159.5	128
N,*N*-dimethylformamide	143.7	60.3	112.0	161.0	166

[a] Corrected for diamagnetic susceptibility of solvent.[10] (The largest correction, for nitromethane, was 1.4 ppm upfield.) [b] Upfield from external 1 M H^{15}NO$_3$ in D$_2$O. [c] Downfield from external Me$_4$Si. [d] Lewis basicity parameter.[11]

The solubility of benzenediazonium salts in organic solvents may be significantly enhanced by the attachment of lipophilic groups at the para position.[3,5,7] Natural-abundance ^{15}N NMR spectra of *p*-*n*-butylbenzenediazonium tetrafluoroborate (1) were measured in six organic



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[†] Contribution No. 6379 from the Gates and Crellin Laboratories.

(1) (a) Supported by the National Science Foundation. (b) IBM Graduate Fellow, 1979–1980.

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Table II. Effect of Solvent on the ^{15}N NMR Chemical Shifts of Benzonitrile[a]

solvent	$\delta^{15}N$[b]	AN[c]
1,4-dioxane	117.2	10.8
acetone	117.8	12.5
N,N-dimethylformamide	118.5	16.0
acetonitrile	119.3	18.9
dichloromethane	119.9	20.4
nitromethane	121.2	20.5
methanol	121.8	41.3

[a] Corrected for diamagnetic susceptibility of solvent.[10] [b] Upfield from external 1 M $H^{15}NO_3$ in D_2O. [c] Acceptor number.[14]

solvents. The ^{15}N chemical shifts for N1 and N2 as well as the ^{13}C chemical shifts for C1 and C4 are recorded in Table I. Assignment of the ^{15}N resonance lines is based upon the labeling studies conducted in earlier work.[9] In general, the effects of solvent changes are not large. This agrees with the report[12] of only small NN stretching frequency changes for benzenediazonium chlorides with solvent variation.

Although the range of chemical shifts is small, a qualitative correlation is found between the chemical shifts for N2 and C1 of **1** and an empirical measure of solvent Lewis basicity, *B*.[11] The terminal nitrogen shifts upfield and C1 shifts downfield with increasing basicity of the solvent. These correlations indicate some type of Lewis acid-base interaction between the diazonium cation and the solvent. The upfield shift of N2 with increasing solvent basicity may arise from diamagnetic shielding of the terminal nitrogen through complexation with solvent molecules.[13] The concomitant downfield shift of C1 is then a reasonable consequence of a reduced resonance interaction of C1 with the diazonium group because of partial transfer of the positive charge to solvent.[9] Neither the smaller N1 and C4 chemical shift changes for **1** nor the NN stretching frequency variations for benzenediazonium chlorides[12] correlate with solvent basicity.

Table III. ^{15}N NMR Chemical Shifts of Para-Substituent Benzenediazonium Tetrafluoroborates in Acetonitrile[a]

substituent	concn, M	chemical shift, δ N1	chemical shift, δ N2
MeO	0.8	140.5	51.9
n-butyl	0.5	142.4	57.6
H	1.1	143.6	60.1
HO_2C	0.5	144.6	59.6
O_2N	0.3	146.1	59.4

[a] Upfield from external 1 M $H^{15}NO_3$ in D_2O.

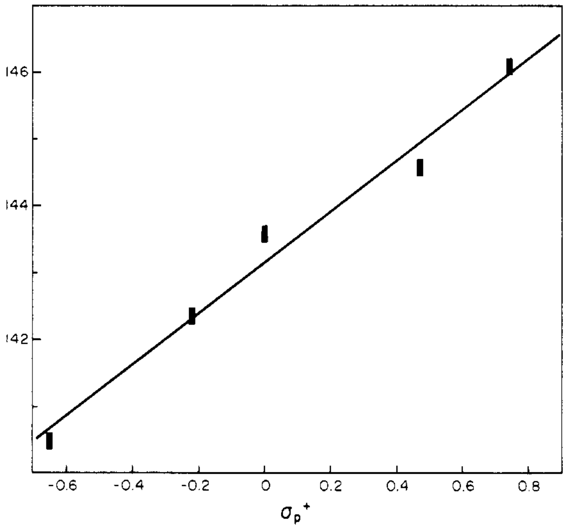
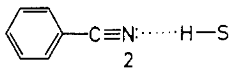


Figure 1. Plot of ^{15}N chemical shifts of N1 in para-substituted benzenediazonium tetrafluoroborates vs σ^+: slope 3.83, intercept 143.2 ppm, correlation coefficient 0.979.

Even though benzonitrile is isoelectronic with the benzenediazonium ion, ^{15}N NMR measurements reveal the interactions of the two species with solvents to be quite different. Thus, the chemical shift of N2 in **1** correlates with solvent basicity, whereas the ^{15}N chemical shift for benzonitrile exhibits a qualitative correlation (Table II) with AN, the solvent acceptor number, which is an empirical measure of Lewis acidity.[14] Olah and Kiovsky[15] report that protonation of acetonitrile shifts the ^{15}N resonance upfield by 102 ppm. Therefore, the upfield ^{15}N chemical shifts observed for benzonitrile in the more acidic solvents are consistent with hydrogen-bond formation between the cyano nitrogen lone pair of electrons and the solvent, as depicted in **2**.



2

Infrared studies of aryldiazonium salts in acetone have shown that variations of the counterion may affect the NN stretching frequency.[16] The change in stretching frequency observed in going from tetrafluoroborate to chloride is about 5 cm^{-1}. Even larger effects have been noted for other anions.[17] To probe the influence of anion variation upon the ^{15}N NMR chemical shifts for a benzenediazonium ion in an organic solvent, we replaced the tetrafluoroborate anion in a 1.2 M solution of **1** in dichloromethane by chloride.[18] This substitution causes small downfield shifts of both the N1 (1.4 ppm) and N2 (0.8 ppm) resonances, consistent with an enhanced level of covalent bonding between the benzenediazonium cation and anion for the chloride counterion.[19]

In contrast to the rather small changes in the ^{15}N chemical shifts for N1 and N2 of free benzenediazonium ions caused by variation of the solvent and anion, the

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(19) For instance the ^{15}N chemical shifts for the azo nitrogens of 1-phenyl-3,3-dimethyltriazine, PhN=NNMe$_2$ (Axenrod, R.; Mangiaracina, P.; Pregosin, P. S. *Helv. Chim. Acta* **1976**, *59*, 1655-1660) are significantly downfield from the ^{15}N resonances observed for benzenediazonium cations.

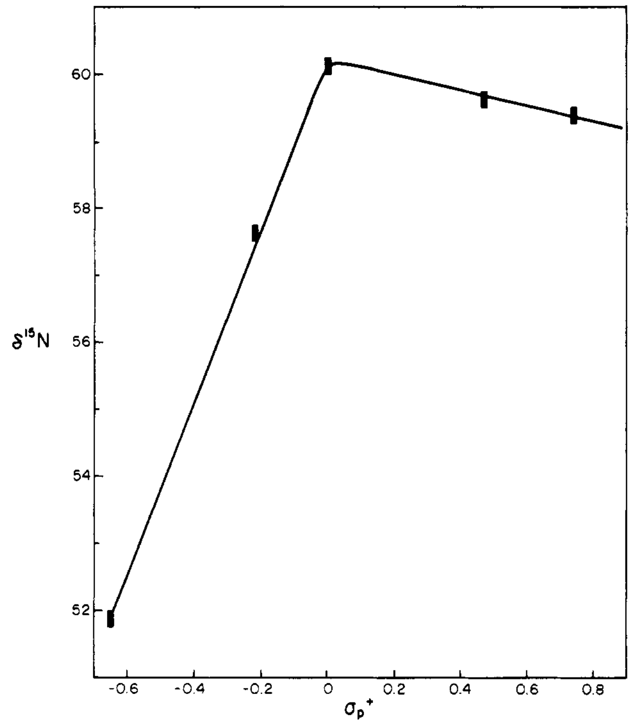
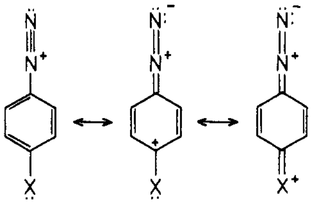


Figure 2. Plot of ^{15}N chemical shifts of N2 in para-substituted benzenediazonium tetrafluoroborates vs. σ^+.

influence of para substituents is substantial. Data for five benzenediazonium tetrafluoroborates was obtained in acetonitrile and is recorded in Table III.

With electron-donating substituents, the N1 resonance shifts downfield as expected for an increase in the diazo character (**3b,c**) of the resonance hybrid.[9,20] The N1



3a 3b 3c

chemical shifts correlate well with σ_p^{+}[21] (Figure 1). Similar correlations with σ^+ have been reported for the half-wave potential of the one-electron reductions of substituted benzenediazonium salts,[22] and for both the frequency and logarithm of the intensity of the NN stretching vibrations of aryldiazonium salts in solution.[16] A general relationship between the electron-donating or -withdrawing properties of ring substituents and ^{13}C NMR chemical shifts of substituted benzenediazonium tetrafluoroborates or hexafluorophosphates in SO_2 has also been noted.[4]

Curiously, the N2 chemical shift does not correlate with either σ_p^+ or σ_p (Figure 2). The N2 resonance for benzenediazonium salts with electron-donating substituents shift uniformly downfield with increased electron-donating power, as expected for an increase in diazo character of the resonance hybrid.[20] The ^{15}N NMR chemical shifts for N2 of these diazonium ions are somewhat more sensitive to substituent changes than those for N1. This indicates substantial positive charge on the terminal nitrogen in agreement with molecular orbital calculations (STO-3G-HF) of electron populations for the gas-phase benzenediazonium ion.[23] The N2 resonances for benzenediazonium salts with electron-attracting para substituents fall on a line of opposite (but much smaller) slope relative to that for the electron-donating substituents. This situation is not easily reconciled within the framework of resonance structures **3a–c**. A possible explanation is that when the para substituent is not electron donating, resonance structures **3b** and **3c** are so unimportant that any increases in electron-withdrawing power act primarily to enhance the positive charge on N2 (resulting in a downfield shift[13]) instead of influencing the contributions of **3b** and **3c** to the resonance hybrid.

Table IV. Effect of Adding 1 Equivalent of 18-Crown-6 on the ^{15}N NMR Chemical Shifts of Benzenediazonium Tetrafluoroborate in Dimethylformamide

para substituent	$\Delta\delta N1^a$	$\Delta\delta N2^a$
MeO	−4.5	1.5
n-butyl	−4.5	2.3
H	−5.7	3.2

[a] A positive number indicates a downfield shift in the presence of 18-crown-6.

Comparison of the data in Table III with the ^{15}N NMR chemical shifts for para-substituted benzenediazonium tetrafluoroborates solubilized by 18-crown-6 in $CDCl_3$[9,24] reveals a greater sensitivity of both the N1 and N2 resonances to substituent effects for the uncomplexed benzenediazonium ions in acetonitrile. Because solvent changes are small for **1**, complexation by the crown ether appears to be responsible for the diminished sensitivity of the N1 and N2 resonances to the effect of para-substituent variation.

To investigate more fully the influence of crown ether complexation upon the ^{15}N resonances of aryldiazonium ions, we determined ^{15}N chemical shifts for three benzenediazonium tetrafluoroborates in the presence and absence of 1 equiv of 18-crown-6 (Table IV). Dimethylformamide rather than acetonitrile was used as the solvent because of the strong interactions of the latter with 18-crown-6.[25] Unfortunately, the ^{15}N NMR spectrum of *p*-nitrobenzenediazonium tetrafluoroborate in dimethylformamide could not be obtained because the decomposition of this salt was too rapid.

^{13}C NMR[5,7] and IR[5] spectral evidence strongly suggest that interactions of crown ether with N1 increases the contribution of the diazonium form **3a** to the resonance hybrid.[3] The concomitant decrease in delocalization of the positive charge onto the ring is similarly evident in the chemistry of complexed aryldiazonium salts.[26] The data in Table IV show that addition of 18-crown-6 produces a substantial upfield shift and a smaller downfield shift of the N1 and N2 resonances, respectively, for all three benzenediazonium ions. The upfield shift for the N1 resonance is consistent with a decrease in the contribution of diazo forms **3b** and **3c** to the resonance hybrid for the crown ether complexed salts.[26] The smaller downfield shift of the N2 resonance is most likely a consequence of in-

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[20] Relative to *p*-methoxybenzenediazonium tetrafluoroborate in dimethylformamide, the N1 and N2 resonances of diazoquinone in dimethyl sulfoxide are downfield by approximately 28 and 52 ppm, respectively.

[21] Values for σ_p^+ are taken from: Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337.

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[24] ^{13}C NMR measurements[5,7] demonstrate that most of the benzenediazonium salt will exist in the crown ether complexed form under these conditions.

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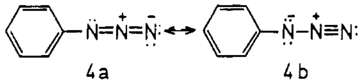
creased positive charge on N2, which also suggests increased diazonium character. These conclusions accord with recent CNDO/2 calculations for free and ether-complexed benzenediazonium ion by Bartsch and Čársky[27] which suggest that on complexation the positive charge density on N1 is increased.

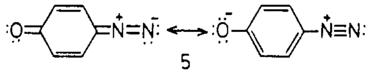
Izatt and co-workers[28] have studied the complexation of benzenediazonium cations with 18-crown-6 in methanol by calorimetric titration. The extent of complexation was found to be highest for the *p*-nitro substituent which was an order of magnitude greater than that for *p*-methoxy. Therefore, the smaller influence of 1 molar equiv of 18-crown-6 on the N1 and N2 resonances for benzenediazonium ions bearing more electron-donating para substituents (Table IV) may arise from a lesser proportion of the aryldiazonium salt being converted into the crown ether complexed form.[29]

Several unsuccessful attempts were made to detect crown ether complexation of other species by ^{15}N NMR spectroscopy. Spectroscopic[30] and chemical studies[31] of phenyl azide indicate that resonance structure **4b** makes



4a 4b

an important contribution to the azido group. The possibility that the diazonium-like terminus of organic azides might be complexed by 18-crown-6 was negated by ^{15}N NMR measurements. Thus, the azide ^{15}N NMR chemical shifts for a 2.4 M solution of phenyl azide in chloroform were unaffected by the addition of 1 equiv of 18-crown-6. Similarly, addition of up to 5 equiv of 18-crown-6 to a 0.1 M solution of ^{15}N-labeled *p*-toluenesulfonyl azide in dimethyl sulfoxide did not change the ^{15}N chemical shifts. Also, no ^{15}N resonance changes were observed on addition of 1 equiv of 18-crown-6 to a 1.4 M solution of diazoquinone tetrahydrate (**5**) in dimethyl sulfoxide.



5

Addition of 1 equiv of 18-crown-6 to a 1.9 M solution of benzonitrile (isoelectronic with the benzenediazonium ion) in cyclohexane induced a 1.1-ppm upfield shift of the ^{15}N resonance. However, the same change was produced by the addition of 1 equiv of 1,4-dioxane which indicates a solvent effect rather than a specific interaction.

Experimental Section

Spectra. The ^{15}N NMR spectra were measured at 18.25 MHz with a Bruker WH-180 spectrometer by using 15–25 mL samples in 25-mm sample tubes. Lock and reference signals were provided by a concentric 5-mm tube containing a 1 M solution of 95% $H^{15}NO_3$ in D_2O. All spectra were proton coupled and obtained at ambient probe temperature. The accumulation of 1000–4000 transients (20-μs pulse, 10-s repetition rate) gave reasonable signal/noise ratios. The solvent effects for ^{15}N shifts were determined with 1.2–1.6 M solutions of 1 and 1.9 M solutions of benzonitrile. Substituent effects for aryldiazonium tetrafluoroborates were obtained for 0.3–1.0 M solutions of the salts. The influence of 18-crown-6 was determined by using 0.5–1.5 M solutions of benzenediazonium tetrafluoroborates.

Materials. Commercially available spectrophotometric grade dichloromethane, nitromethane, acetonitrile, acetone, chloroform, and cyclohexane were used in this study. The other solvents and benzonitrile used were reagent grade materials. The 18-crown-6 was purchased from Aldrich Chemical Co. and used without purification.

The aryldiazonium fluoroborates were synthesized by standard techniques.[32] The *p*-*n*-butylbenzenediazonium fluoroborate was purified by several recrystallizations from dichloromethane/diethyl ether. The other salts were recrystallized from acetonitrile/ether.

A dichloromethane solution of *p*-*n*-butylbenzenediazonium chloride was prepared by treating the fluoroborate in dichloromethane with 1 equiv of tetramethylammonium chloride.[18] The solution was filtered and its spectrum taken immediately.

A mixture of 1-, 2-, and 3-^{15}N-labeled *p*-toluenesulfonyl azides was prepared as described previously.[33] Phenyl azide was synthesized by using the method of Lindsay and Allen.[34] *p*-Diazoquinone was obtained from *p*-hydroxybenzenediazonium chloride[35] by the procedure of Puza and Doetschman.[36]

Registry No. 1, 72302-28-4; 1 chloride, 41888-25-9; benzonitrile, 100-47-0; *p*-methoxybenzenediazonium tetrafluoroborate, 459-64-3; benzenediazonium tetrafluoroborate, 369-57-3; *p*-carboxybenzenediazonium tetrafluoroborate, 456-25-7; *p*-nitrobenzenediazonium tetrafluoroborate, 456-27-9.

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