J. Org. Chem. 1981, 46, 2153-2159 2153

Crown Cation Complex Effects. 12.[1] Dissolution and Complexation of Arenediazonium Cations in Nonpolar Media. An Assessment of Solvent Effects and Reactivity by Infrared and Nuclear Magnetic Resonance Spectroscopy

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Received October 10, 1980

A number of arenediazonium salts (largely tetrafluoroborates) have been surveyed to determine their solubility properties and the influence of crown ethers and quaternary ammonium salts thereupon. Analysis has been by a variety of spectral techniques including IR and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. These studies reveal that solvation of the diazo linkage is not the major factor in determining solubility and that a variety of cosolvents may be used in addition to polyethers to achieve solubility. The data further suggest that solubility is influenced by local dielectric effects and that yield enhancements in a number of arenediazonium salt reactions conducted in nonpolar solutions may result from suppression of side reactions with traditional aqueous and alcoholic cosolvents rather than by anion activation or specific complexation.

Since the original observation that arenediazonium tetrafluoroborates are solubilized[3] and stabilized[4,5] by crown ethers in nonpolar solutions, the nature of the stabilization has been of considerable interest. This stabilization operates in solution[4,6] and in the solid phase[7,8] and has even been observed as a remote substituent effect.[9] Bartsch and co-workers have correlated the extent of stabilization with a large number of crown ethers[10] and have conducted ESCA experiments aimed at delineating the interactions.[11] Izatt et al. have determined thermodynamic parameters for the interaction.[12] More recently, it has been shown that glymes as well as crowns afford solubilization,[13] and we have generalized this to carboxylates, quaternary salts, and small amounts of dipolar aprotic solvents.[1]

Table I. Solubility of p-X-$C_6H_4N_2^+BF_4^-$ in $CHCl_3$ or $CDCl_3$[a]

compd	X	solubility, mg/mL
1	Cl	*b*
2	CH_3	*b*
3	CH_3CH_2	6.1
4	CH_3CH_2O	*c*
5	$(CH_3)_2CH$	1.6
6	$CH_3CH_2CH_2CH_2$	*d*
7	$(CH_3)_3C$	23
8	$CH_3CH_2CH_2CH_2O$	*d*

[a] Alcohol-free chloroform or deuteriochloroform was used, as appropriate. [b] Solubility in these cases was below the limit detectable by proton NMR spectroscopy (single sweep). [c] Solubility was below the limit detectable by UV analysis (see text). [d] Freely soluble.

Most of the studies which have been conducted on arenediazonium tetrafluoroborates and hexafluorophosphates have focused on the stabilization of the diazonium compound to thermal, photochemical, or nucleophilic assault. Much of the recent work, however, has been directed at using these stable, safe, and easy to purify compounds in synthetic applications.[14] A detailed understanding of the solution interactions between the arenediazonium cations and solvents,[15] crowns,[10] and other salts and nucleophiles[16] seemed desirable in order to maximize the useful transformations of these species rather than restricting their reactivity. We felt that analysis of arenediazonium ion solutions by IR and proton, fluorine, and carbon NMR would afford a useful and more detailed picture than is currently available of diazonium salt solvation by various solvents and complexing agents and, by inference, reactivity. We report the results of those studies here.

Results and Discussion

The first observation of diazonium ion solubilization by a crown ether was necessarily made on an otherwise insoluble salt in a poorly solvating solvent.[3] It is known from earlier work that arenediazonium salts are generally insoluble in nonpolar solutions but soluble in such polar media as acetone, acetonitrile, DMF, and methanol. Note that these species are not generally soluble in water: they precipitate from this solvent in the most common preparation.[17] Certain highly lipophilic salts such as (n-decyloxy)benzenediazonium[18] and 4-*tert*-butylbenzenedi-

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(1) Paper 11: Rosenberg, D. E.; Beadle, J. R.; Korzeniowski, S. H.; Gokel, G. W. *Tetrahedron Lett.* **1980**, 4141.

(2) (a) E. I. du Pont de Nemours & Co., Inc., Wilimington, DE. (b) Deceased Oct 31, 1978.

(3) Gokel, G. W.; Cram D. J. *J. Chem. Soc., Chem. Commun.* **1973**, 481.

(4) Bartsch, R. A.; Chen, H.; Haddock, N. F.; Juri, P. N. *J. Am. Chem. Soc.* **1976**, *98*, 6753.

(5) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W., Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564.

(6) Sheppard, W. A.; Gokel, G. W.; Webster, O. W.; Betterton, K.; Timberlake, J. W. *J. Org. Chem.* **1979**, *44*, 1717

(7) Haymore, B. L., Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541.

(8) Bartsch, R. A.; Haddock, N. F.; McCann, D. W. *Tetrahedron Lett.* **1977**, 3779.

(9) Gokel, G. W.; Korzeniowksi, S. H.; Blum, L. *Tetrahedron Lett.* **1977**, 1633.

(10) Bartsch, R. A.; Juri, P. N. *J. Org. Chem.* **1980**, *45*, 1011.

(11) Bohman, O.; Ahlberg, P.; Nyholm, R.; Martensson, N.; Sigbahn, K.; Bartsch, R. A. *J. Chem. Res.* (*S*) **1979**, 292.

(12) Izatt, R. M.; Lamb, J. O.; Rossiter, B. E.; Izatt, N. I.; Christensen, J. J.; Haymore, B. L.; *J. Chem. Soc., Chem. Commun.* **1978**, 386.

(13) (a) Bartsch, R. A.; Juri, P. N.; *Tetrahedron Lett.* **1979**, 407. (b) Bartsch, R. A.; Juri, P. N.; Mills, M. A. *Ibid.* **1979**, 2944. (c) Bartsch, R. A.; Yang, I. W. *Ibid.* **1979**, 2503.

(14) Korzeniowski, S. H.; Blum, L.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 1871.

(15) Ishida, K.; Kobori, N.; Kobayashi, M.; Minato, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 285.

(16) Korzeniowski, S. H.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 1637.

(17) Roe, A. *Org. React.* **1949**, *5*, 193.

(18) (a) Bradley, W.; Thompson, J. D. *Chimia* **1961**, *15*, 147. (b) Bradley, W.; Thompson, J. D. *Nature* (*London*) **1965**, *178*, 1069.

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azonium tetrafluoroborates[19] are soluble in certain nonpolar solutions, but relatively little is known about the former, and 4-*tert*-butylaniline has become commercially available only in recent months.[20] Moreover, 4-*tert*-butylbenzenediazonium tetrafluoroborate is quite soluble in CH_2Cl_2 or $ClCH_2CH_2Cl$ but much less so in $CHCl_3$ (or $CDCl_3$, see Table I). We therefore initiated these studies with a search for a stable, readily prepared, or available arenediazonium salt which could be used for spectral studies, especially NMR.

Solubility of Arenediazonium Salts. The halo-, nitro-, and methylbenzenediazonium tetrafluoroborates and hexafluorophosphates are easy to prepare from readily available precursors[21,22] but are, alas, nearly insoluble in $CHCl_3$, CH_2Cl_2, etc. in the absence of a solubilizing agent. We undertook the preparation of 4-ethyl- (**3**), 4-isopropyl- (**5**), 4-*n*-butyl- (**6**), and 4-*n*-butoxybenzenediazonium (**8**) tetrafluoroborates in the hope of finding one which would be stable yet freely soluble in nonpolar media and therefore suitable for general study. The solubilities in $CHCl_3$ of several arenediazonium tetrafluoroborate salts are shown in Table I. Certain of the simple salts like 4-chloro (**1**) and 4-methyl (**2**) were already known to be less soluble than the ability of ^1H NMR could detect (one scan, CW),[3] and these compounds did not appear sufficiently promising to attempt to assess the solubility by UV analysis. Certain other of the compounds were freely soluble in $CHCl_3$, and it did not seem necessary to quantitate the solubility of these. The solubilities of the intermediate compounds were determined by UV analysis of saturated solutions. 18-Crown-6-complexed **1** and soluble **6** exhibited UV extinction coefficients (at 280 nm) of 15 240 and 10 000, respectively. By use of the average (12 623) of these values, the very slight solubility of the intermediate compounds could be determined with modest accuracy. These solubilities were double checked by covering a known quantity of salt with a known volume of solvent, stirring, filtering, and then evaporating. The solubility (by weight) of the dissolved salt agreed well (±5%) with the values determined by other methods.

It appears from the data in Table I that the 4-*n*-butyl (**6**) and 4-*n*-butoxy (**8**) compounds are the most soluble of the arenediazonium salts listed. The latter is much more stable than the former, making it preferable for spectral studies to the other compounds listed in the table. Moreover, either **6** or **8** is far more soluble in $CHCl_3$ than the most commonly used choice, 4-*tert*-butyl (**7**). Compound **8** exhibits good stability, it is easy to prepare, and its ^1H NMR spectrum is simple even at 60 MHz. From the information noted in Table I, it is clear that **8** happens to possess just the right balance of lipophilicity and crystallinity so that it can exhibit both stability and solubility. The *n*-butyl compound **6** is also quite soluble in nonpolar solutions but decomposes on storage even when kept cold and protected from the light and atmosphere.

A survey of the data shown in Table II suggests that the stretching frequency observed for an arenediazonium cation will lie in the range 2283 ± 11 cm^{-1} irrespective of solvent, as long as there is no unusual or highly polar substitution pattern (see Figure 1A). The electronegatively substituted 3,4,5-trichlorobenzenediazonium tetrafluoroborate absorbs at 2301 cm^{-1}, and the 4-methoxy compound absorbs at 2247 cm^{-1}.[23] It is interesting to note that the N≡N stretch of 4-(diethylamino)benzenediazonium tetrafluoroborate (Nujol mull) is reported to absorb at 2247 cm^{-1} and the related, but much more sterically compressed, 2,4,6-trichloro salt is reported to absorb at 2267 cm^{-1}.[24]

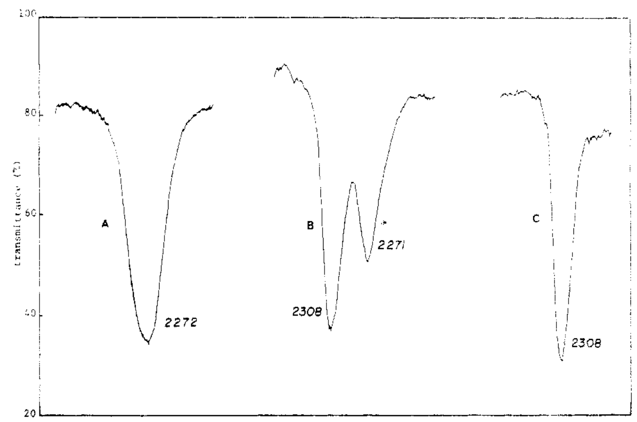

Figure 1. 4-*tert*-Butylbenzenediazonium tetrafluoroborate (**7**) in $CHCl_3$ solution: (a) in the absence of 18-crown-6 (**9**); (b) in the presence of 1 equiv of **9**; (c) in the presence of 5 equiv of **9**. Line positions are in wavenumbers.

When a complex of 18-crown-6 and an arenediazonium salt is formed as a solid and then mulled with Nujol,[4,7,25] a single absorption is observed, generally between 2300 and 2325 cm^{-1}. The single, new absorption band indicates that the crown remains complexed and is interacting with the diazo linkage imparting to it more triple bond character. Bartsch[26] has advanced such an argument to account for ^{13}C NMR chemical shift differences which we reported in preliminary fashion.[25]

A more interesting picture emerges when the diazonium salts are solubilized by crowns or other agents. In the presence of 1 equiv of 18-crown-6 polyether (**9**), two peaks are usually observed in the IR spectrum, one at or near the original position, and a new peak in the 2300–2325-cm^{-1} range identified above as the crown-complexed band (see Figure 1B). When 4 equiv more of **9** (total 5 equiv) is added, none of the noncomplexed salt is observed (see Figure 1C) except in one case (see below). The infrared spectra of 4-*tert*-butylbenzenediazonium tetrafluoroborate (**7**) in the absence of **9** and in the presence of 1 and 5 equiv of **9** are shown in Figure 1A–C, respectively. Since the mulled samples of complex show a single complexed line and no noncomplexed material, it seems reasonable to assume that Nujol or hydrocarbon media are not strong enough solvators of the diazonium compound to permit egress from the crown's solvating hole. That two peaks are observed when a full 1 molar equiv of **9** is present (see Table II) suggests that the solvent competes with the crown even when the diazonium salt is insoluble in its absence. As we will show later, the polarity of the crown per se is probably also playing a solvating role. We note that in all of these studies except those involving the 4-*n*-butoxy compound (**8**), when 5 equiv of crown (**9**) is present, full complexation is observed (i.e., only a single

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[19] Swain, C. G.; Rogers, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 799.

[20] The Aldrich Chemical catalog lists 4-*tert*-butylaniline, although it has not, to our knowledge, been previously available from this or any other domestic source.

[21] Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572.

[22] Rutherford, K. G.; Redmond, W. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 133.

[23] Aroney, M.; Le Fevre, R. J. W.; Werner, R. L. *J. Chem. Soc.* **1955**, 276.

[24] Whetsel, K. B.; Hawkins, G. F.; Johnson, F. E. *J. Am. Chem. Soc.* **1956**, *78*, 3360.

[25] Korzeniowski, S. H.; Petcavich, R. J.; Coleman, M. M.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 2647.

[26] Bartsch, R. A. In: Izatt, R. M.; Christensen, J. J. "Progress in Macrocyclic Chemistry"; Wiley: New York, 1981; in press. We thank Professor Bartsch for providing us with a copy of this manuscript in advance of publication.

Table II. IR Spectra of Arenediazonium Compounds

compd[o]	substituent	$\nu_{N\equiv N}$, cm^{-1}	crown[a] (equiv)	other[a] (equiv)	solvent	notes
11	H	2295			mull	
11[o]	H	2285			mull	
12	4-F	2292			mull	
1	4-Cl	2287			mull	
1	4-Cl	2322	9 (1)		mull	*b*
1	4-Cl	2270		$Me_4N^+Cl^-$ (1)	$CHCl_3$	*c*
1	4-Cl	2273		$Me_4N^+Cl^-$ (2)	$CHCl_3$	*c*
1	4-Cl	2272		BTEAC (1)	$CHCl_3$	*c*
1	4-Cl	2280, 2314	9 (1)		$CHCl_3$	*c, d*
1	4-Cl	2314	9 (5)		$CHCl_3$	*c*
13	3,4-Cl_2	2283			mull	
14	3,4,5-Cl_3	2301			mull	
15	4-Br	2286			mull	
15	4-Br	2321	9 (1)		mull	*b*
16	4-I	2278			mull	
2	4-CH_3	2286			mull	
3	4-CH_3CH_2	2281			mull	
3	4-CH_3CH_2	2275			CH_2Cl_2	
3	4-CH_3CH_2	2270, 2309	9 (1)		CH_2Cl_2	*c, e*
3	4-CH_3CH_2	2310	9 (5)		CH_2Cl_2	*c*
3	4-CH_3CH_2	2270			$CHCl_3$	
3	4-CH_3CH_2	2268	10 (1)		$CHCl_3$	*f*
3	4-CH_3CH_2	2271, 2307	9 (1)		$CHCl_3$	*c, g*
3	4-CH_3CH_2	2306	9 (5)		$CHCl_3$	*c*
3	4-CH_3CH_2	2264		BTEAC (1)	$CHCl_3$	*c*
3	4-CH_3CH_2	2260		BTEAC (5)	$CHCl_3$	*c*
3	4-CH_3CH_2	2272	10 (1)	NaCl (1)	$CHCl_3$	*h*
3	4-CH_3CH_2	2258		$Me_4N^+Cl^-$ (1)	$CHCl_3$	*c*
7	4-*t*-C_4H_9	2277			mull	
7	4-*t*-C_4H_9	2306	9 (1)		mull	*b*
7	4-*t*-C_4H_9	2272			$CHCl_3$	
7	4-*t*-C_4H_9	2271, 2308	9 (1)		$CHCl_3$	*c, i*
7	4-*t*-C_4H_9	2308	9 (5)		$CHCl_3$	*c, i*
7	4-*t*-C_4H_9	2270			CH_2Cl_2	*c, j*
7	4-*t*-C_4H_9	2272, 2309	9 (1)		CH_2Cl_2	*c, k*
7	4-*t*-C_4H_9	2309	9 (5)		CH_2Cl_2	*c, l*
17	4-MeO	2247			mull	
8	4-*n*-BuO	2245			$CHCl_3$	
8	4-*n*-BuO	2245, 2294	9 (1)		$CHCl_3$	*c, m*
8	4-*n*-BuO	2250, 2295	9 (5)		$CHCl_3$	*c, n*

[a] All values in parentheses below are approximate peak heights relative to baseline. [b] The preformed, solid, 1:1 complex was used. [c] The two solids were stirred with solvent until solution occurred. [d] The peak intensities were approximately 2280 (1):2314 (2.39). [e] The peak intensities were approximately 2270 (1):2309 (1.49). [f] Crown **10** was added to a solution of **3**. [g] The peak intensities were approximately 2271 (1):2307 (1.19). [h] The three solids were stirred together until solution occurred. [i] The peak intensities were approximately 2271 (1):2308 (1.36). [j] The 2270-cm^{-1} band was quite broad; the same absorption was sharp in chloroform. [k] The peak intensities were approximately 2272 (1):2309 (1.30). [l] The crown-complexed band was quite sharp. [m] The peak intensities were approximately 2245 (1):2294 (1). [n] The peak intensities were approximately 2245 (1):2294 (2.33). The 2245-cm^{-1} band appeared as a weak shoulder. [o] The anion with compound **11** in the second entry in the table was PF_6. BF_4 was used in all other cases.

absorption is detected). In the case of highly lipophilic **8**, almost, but not quite, complete complexation is observed when 5 equiv of **9** is added. It is interesting that **8** is not fully complexed even when 7 equiv of **9** is present (see Table II). Generally 5 equiv of **9** is sufficient to fully complex the diazonium cation. Full complexation of the 4-*tert*-butyl compound **7** by 5 equiv of **9** is observed even in the more polar solvent dichloromethane. In our preliminary report,[25] two bands were reported for the latter case, a fact which is unaccountable and unquestionably in error. Typical spectra (of crown complexed **3**) are shown in Figure 1.

Quaternary Ion and Polar Solvent Assisted Solubilization of Arenediazonium Cations. It now seems clear that nonspecific as well as the remarkable crown–complex interaction can lead to dissolution of otherwise insoluble arenediazonium compounds. Although 15-crown-5 is neither sufficiently large nor sufficiently polar to induce solubilization, certain glymes and glycols are.[13] Since the crowns exhibited a significant deactivating effect on the diazonium salts,[4,5] we sought an alternative solubilization method. We found that quaternary ammonium salts solubilized otherwise insoluble $ArN_2^+BF_4^-$ compounds. We termed this solubilization "gegenion metathesis"[16] and presumed it to be due to anion exchange with concomitant formation of the more soluble diazonium chlorides. The presumed reaction is shown in eq 1. It

$$ArN_2^+BF_4^- + Me_4N^+Cl^- \rightleftharpoons ArN_2^+Cl^- + Me_4N^+BF_4^- \quad (1)$$

was thought that precipitation of the complex cation–complex anion pair was responsible, at least in part, for driving the diazonium chloride into solution. It was also suspected that an equilibrium of the type shown in eq 2

$$ArN_2^+Cl^- \rightleftharpoons ArN{=}NCl \quad (2)$$

might also be influential. If the covalent azochloride structure was present, it could certainly help explain the enhanced solubility. This notion could never be reconciled with the IR spectrum which showed clearly that the strongest absorption was due to a triple rather than double bond.[25] In fact, the data in Table II suggest that it is really a local dielectric effect rather than formation of azochloride, which is important. Instead of the appearance of double bond absorption at a lower wavenumber, a slight

Table III. Solubilization of 4-Chlorobenzenediazonium Tetrafluoroborate (1) in Dichloromethane with Polar Solvents or Complexes[a]

solvent (additive) in CH_2Cl_2 (v/v)	solubility of 1, mg/mL	solvent (additive) in CH_2Cl_2 (v/v)	solubility of 1, mg/mL
pure CH_2Cl_2	<0.5	10% MeCN	3.7
5% CH_3CH_2OH	1.3	5% Me_2NCHO	3.2
5% $CH_3OCH_2CH_2OH$	1.5	10% Me_2NCHO	8.4
10% $CH_3OCH_2CH_2OH$	3.4	5% $CH_3O(CH_2CH_2O)_7H$[b]	14.2
5% MeCN	1.4	5% 18-crown-6	41.6

[a] A weighed amount of solid 1 was stirred vigorously in contact with a small amount of the specified solvent mixture. Additional solvent mixture was added dropwise at ambient temperature until complete homogeneity was apparent. Solubility was determined from the total volume. [b] Structure approximate. The product is sold by Aldrich with a stated molecular weight of 350. The above compound has a molecular weight of 340.

Table IV. NMR Spectra of Benzenediazonium Compounds

subst	amt 9, equiv	shift[a]						solvent	mode[a]	notes
		ipso	ortho	meta	para	C-1	C-2			
4-Br	0	*b*	8.50	8.07	*b*	*c*	*c*	$CDCl_3$	H	*d*
4-Et	1	112.96	131.09	130.74	158.48	26.56	14.07	$CDCl_3$	C	
4-Et	5	113.44	130.28	129.87	157.21	28.92	13.64	$CDCl_3$	C	
4-*t*-Bu	0	*b*	8.51, 8.60	7.75, 7.84	*b*	*b*	1.34	$CDCl_3$	H	*e*
4-*t*-Bu	0	*b*	8.60	8.04	*b*	*b*	1.37	Me_2SO-d_6	H	*f*
4-*t*-Bu	0	110.19	132.43	128.87	167.33	36.66	30.08	CH_2Cl_2	C	
4-*t*-Bu	0.1	110.67	132.24	128.83	166.93	36.49	30.10	CH_2Cl_2	C	
4-*t*-Bu	1.0	113.58	130.29	128.43	164.54	36.19	30.14	CH_2Cl_2	C	
4-*t*-Bu	5.0	113.64	129.64	128.27	164.10	35.95	29.97	CH_2Cl_2	C	
4-*n*-Bu	0	110.39	132.47	131.25	159.10	36.42	32.23	$CDCl_3$	C	C3, 22.14; C4, 13.56
4-*n*-Bu	1	113.19	130.63	129.87	156.23	35.62	31.78	$CDCl_3$	C	C3, 21.65; C4, 13.14
4-*n*-Bu	5	112.61	129.97	129.16	155.16	34.73	31.02	$CDCl_3$	C	C3, 20.87; C4, 12.42[g]
4-*n*-BuO	0	*b*	8.43, 8.27	7.13, 6.97	*b*	4.10	1.80	$CDCl_3$	H	J = 9.6 Hz;[h] C3, 1.37; C4, 0.97
4-*n*-BuO	1	*b*	8.47, 8.33	7.33, 7.17	*b*	4.20	1.83	$CDCl_3$	H	J = 9 Hz;[h] C3, 1.37; C4, 1.03
4-*n*-BuO	5	*b*	8.47, 8.30	7.40, 7.27	*b*	4.20	1.83	$CDCl_3$	H	J = 9 Hz;[h] C3, 1.37; C4, 1.03
4-*n*-BuO	0	101.26	135.64	117.50	168.87	70.13	30.43	$CDCl_3$	C	C3, 18.77; C4, 13.48
4-*n*-BuO	1	104.49	133.40	116.80	167.05	*i*	30.00	$CDCl_3$	C	C3, 18.30; C4, 13.05
4-*n*-BuO	5	104.68	132.14	116.05	165.76	*i*	29.15	$CDCl_3$	C	C3, 17.38; C4, 12.19

[a] All chemical shifts in parts per million (δ) downfield from internal Me_4Si. [b] No proton attached to this carbon. [c] No such position in this molecule. [d] Spectrum recorded in the presence of 1 equiv of 9, which appeared at 3.64 ppm. [e] J = 5.4 Hz. [f] Data from ref 26 and 27. [g] The slight upfield shift observed when an additional 4 equiv of 9 is added is reproducible. [h] Coupling constants measured by hand and are approximate. [i] A large peak due to the presence of 9 obscures this absorption.

strengthening of the triple bond is observed. It is curious that when 15-crown-5-complexed NaCl is also present in a $CDCl_3$ solution of 3, no effect on the N≡N stretching frequency is apparent. This suggests that both the tetraalkylammonium cation and the chloride anion influence the solvation and solubilization of the arenediazonium cation.

If small dielectric effects can exert such strong solvating influences, it seems reasonable to assume that addition of a small amount of almost any polar solvent would also facilitate solubilization. We have already reported[1] that small amounts of acetonitrile added to benzene facilitate the phase-transfer Gomberg–Bachmann (ptGB) reaction. An examination of the data presented in Table III shows clearly that numerous substances can be used to induce solubilization of these materials although crowns and glymes are especially useful in this respect.

An interesting confirmation of the dielectric effect is that less than 1 equiv of quaternary ammonium salt is required to induce solubilization of 1. In fact, 1.76 mmol of 1 dissolved in 5 mL of CH_2Cl_2 when only 0.44 mmol (0.25 equiv) of benzyltriethylammonium chloride (BTEAC) was added. The interaction can be readily detected by IR spectroscopy (see Table II).

Nuclear Magnetic Resonance Analysis. In keeping with our general understanding of crown–arenediazonium ion complexation, we anticipated that arenediazonium compounds which are soluble in halocarbon solutions would show an association with crown when 1 equiv of the latter was present, but not until a large excess of crown was added would the maximal effect be realized. An examination of the data presented in Table IV confirms this notion. Included in Table IV are data from our preliminary report,[25] now augmented by data for readily accessible

Table V. ^{19}F NMR Chemical Shifts for Fluorine Substituted Benzenediazonium Compounds

salt	anion	solvent	δ with no crown	δ with crown	Δδ	notes
4-F	PF_6	CH_3CN	83.37	88.44	5.07	32
	BF_4	CH_3CN	83.97	88.00	4.03	
	PF_4	Me_2CO	85.25	89.78	4.53	
	BF_4	Me_2CO	85.99	89.98	3.94	
	PF_6	CH_3OH	84.71			
	BF_4	CH_3OH	84.88	88.65	3.77	
	PF_6	H_2O	83.02			
	BF_4	H_2O	83.12	83.18	0.06	
	PF_6, Cl	$CHCl_3$	84.39	87.74	3.35	*a*
	BF_4, Cl	$CHCl_3$	84.44	86.75	2.31	*a*
	BF_4, Cl	$CHCl_3$	82.46	86.67	4.21	*b*
3-F	PF_6	CH_3CN	103.69	104.30	0.61	
	BF_4	CH_3CN	104.01	104.38	0.37	
	PF_6	Me_2CO	104.79	104.79	0.00	
	BF_4	Me_2CO	105.15	105.10	−0.05	
	PF_6	CH_3OH	104.25			
	BF_4	CH_3OH	104.26	104.62	0.36	
	PF_6	H_2O	103.50			
	BF_4	H_2O	103.61	103.54	−0.07	
	PF_6, Cl	$CHCl_3$	103.30	103.63	0.33	*a*
	BF_4, Cl	$CHCl_3$	103.49	103.75	0.24	*a*
2-F	BF_4	H_2O	101.93	101.90	−0.03	
	BF_4, Cl	$CHCl_3$	102.00	105.20	3.20	*a*

[a] Prepared by gegenion metathesis[16] using 4 equiv of BTEAC. [b] Prepared by gegenion metathesis[16] using 2 equiv of $Me_4N^+Cl^-$.

and highly soluble 4-*n*-butoxybenzenediazonium tetrafluoroborate (8).

The trends seem quite clear and consistent. When the salt is soluble in a nonpolar solvent, addition of the first equivalent of crown results in the largest incremental effect on the carbon chemical shifts. This is so for the ipso and para carbons. Although a carbon bearing a positively charged substituent might be expected to appear at very low field, the positive charge in this case is part of a highly shielding triple bond system. When the crown ether is present and presumably interacting with the positive charge, any possibility of resonance dispersal into the ortho and para positions of the aromatic ring is reduced, and the triple bond becomes more localized. The net result of this would presumably be an upfield shift of the 2- and 4-carbons and a downfield shift (more localized charge) on the ipso carbon. Additional evidence for this notion is found in the IR spectra. The arenediazonium salts show increased N≡N stretching frequencies (stronger bond, more triple bond character) when complexed by crown ethers.

Our studies of the proton spectra of these solutions have proved less rewarding. In chloroform solution, we have observed only minor differences in the chemical shifts of either ortho or meta protons in the presence and absence of crown ethers. We have attributed this to the rapid exchange of diazonium salts with the crown and to the small magnitude of the chemical shifts. Bartsch and coworkers have observed a chemical shift difference for the ortho hydrogens of **7** of about +0.07 ppm when these spectra were recorded in Me_2SO-d_6 solution in the presence of 1 equiv of **9**.[26,27]

Additional interesting information on the crown ether–diazonium ion interaction could presumably be gleaned from analysis of the ^{15}N NMR spectra. Unfortunately, all of the ^{15}N NMR spectra thus far reported for these species have been in the presence of crown ether on otherwise insoluble salts, precluding any comparisons.[26]

Solvation and the Remote Substituent Effect. Our original motivation for studying arenediazonium cations in nonpolar solution was as a means of overcoming the numerous synthetic problems associated with these compounds when transformations are attempted in aqueous or other polar solutions. We have, in fact, achieved some success in this endeavor.[1,9,14,16,29,30] We were further convinced by the reports of crown-enhanced stabilization that the reactivity of arenediazonium ions could be influenced by working in nonpolar solutions. We now believe most of our success in the latter area relates primarily to our ability to reduce side reactions rather than to enhance inherent reactivity.

The point is admirably demonstrated in our phase-transfer modification of the Gomberg–Bachmann unsymmetrical biaryl synthesis.[1,14] In the classical approach,[31] the diazonium compound is reacted in a heterogenous mixture of arene and water or a related polar substance. The yield of product depends on the relationship between the partition coefficient and reaction rate. In our system, no second liquid phase is present to complicate the reaction between the diazonium salt and arene. Biaryls are therefore produced in quite satisfactory yields.

If one presumes that there is very strong solvation of the positive nitrogen in polar solvents, shifting solvation from it to the ring (lipophilic–lipophilic interactions) should have enhanced the reactivity. A physical manifestation of any major change from specific to nonspecific solvation should have been observed in the ^{19}F chemical shifts of 2-, 3-, and 4-fluorobenzenediazonium salts in various solvents in the presence and absence of complexing crown ether. The data accumulated on this question are presented in Tables V and VI.

Note first that σ_P as calculated[32] from the ^{19}F NMR data remains similar throughout a range of solvents, suggesting

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(27) Bartsch, R. A.; 179th National Meeting of the American Chemical Society, Houston, TX, Mar 1980; Abstract ORGN 33.

(28) Duthaler, R. O.; Förster, H. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4974.

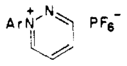
(29) Korzeniowski, S. H.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 3519.

(30) Ahern, M. F.; Gokel, G. W. *J. Chem. Soc., Chem. Commun.* **1979**, 1019.

(31) Bachmann, W. E.; Hoffman, R. H. *Org. React.* **1944**, *2*, 224. Dermer, O. C.; Edmison, M. T. *Chem. Rev.* **1957**, *57*, 77.

(32) Weigert, F. J.; Sheppard, W. A. *J. Org. Chem.* **1976**, *41*, 4006.

Table VI. Calculations of σ Parameters[a]

compd ($Ar = C_6H_4F$)	solvent	$\int_H^m$	$\int_H^p$	$\int_m^p$	σ_I	σ_R	σ_p
$ArN_2^+PF_6^-$	CH_3CN	−10.03	−30.35	−20.32	+1.50	+0.69	2.19
	CH_3CN/18C6	−9.41	−25.27	−15.86	+1.40	+0.54	1.94
	acetone	−8.91	−28.45	−19.54	+1.34	+0.66	2.00
	acetone/18C6	−8.90	−23.91	−15.01	+1.34	+0.51	1.85
	$CHCl_3$/18C6	−9.39	−24.76	−15.37	+1.41	+0.52	1.93
	CH_3OH	−9.43	−28.97	−19.54	+1.41	+0.66	2.07
	H_2O	−10.18	−30.66	−20.48	+1.52	+0.69	2.21
$ArN_2^+BF_4^-$	$CHCl_3$/18C6	−9.23	−24.57	−15.34	+1.38	+0.52	1.90
$ArN_2^+Cl^-$	$CHCl_3$/BTEAC	−9.91	−28.96	−19.05	+1.48	+0.65	2.13
	$CHCl_3$/BTEAC/18C6	−9.64	−26.64	−17.00	+1.44	+0.58	2.02
	CH_3CN	−4.18	−5.82	−1.64	+0.67	+0.06	0.73
	CH_3CN/18C6	−4.17	−5.80	−1.63	+0.67	+0.06	0.73

[a] Calculated by the method of Taft with $\int_H^m = -7.10\sigma_I + 0.60$ and $\int_m^p = -29.5\sigma_R$.

that the nitrogen–nitrogen link does not seem to enjoy highly specific solvation in polar media. Clearly, there is a substantial interaction between the crown and diazonium ion in all of the solvents, but the chemical shift difference is comparable in all of them. It should be noted that the crown–diazonium ion interaction has been measured calorimetrically and falls in the range $\Delta H = -10$ to -14 kcal/mol.[12] One of the most significant pieces of information is found in a comparison of 2-fluoro-substituted benzenediazonium salts with the corresponding 3- and 4-substituted compounds. If there were a strong, nitrogen-specific solvation, the *o*-fluorine chemical shift should be affected more than either the *m*- or *p*-fluorines.[32] An examination of the data in Table VI shows that this is not the case. Coupled with the virtual constancy of σ_P, it seems clear that the arenediazonium compounds do not exhibit the highly specific nitrogen solvation one might have expected in solvents of varying polarity.

The effect of crown ether solvation on the diazonium ion is obviously favorable, despite the entropic cost. The association is small, although clearly manifested on compounds which are soluble in the absence of crown. An important role played by the crown ether in solubilizing such compounds may be in breaking down the crystal lattice, or simply increasing the overall polarity of the medium. In fact, our technique of gegenion metathesis may well be an example of the latter phenomenon.

It seems likely to us that in those cases where gegenion exchange occurred readily and quantitatively, the aryldiazonium chlorides were produced in nonpolar solutions. We presume that their solubility reflects a diminished lattice energy for the chlorides compared to the tetrafluoroborates, although melting points for the former are unavailable to confirm this hypothesis. When addition of a quaternary ammonium salt to a diazonium ion suspension yields the arenediazonium cation, this probably results from local solvent dielectric effects. As evidence for the latter, we have added small amounts of polar solvents which should be capable only of nonspecific interactions with the diazonium salt and found that solubilization can be achieved by a variety of substances, roughly in accordance with their dielectric and solvating powers (see above and Table III).

Some general observations which can be made concerning the data in Tables V and VI are noted as follows. First, a crown effect was observed in all solvents but water. This is not unexpected since water is the most polar of the solvents examined, and if there is a nitrogen-specific solvation, it should be observed in this case. A further indication of this results from a consideration of the anion effect[33] (see Table V). On comparison of PF_6^- and BF_4^-, the former is generally thought to be more diffuse and therefore more charge dilute. Hexafluorophosphate should be more dissociated than tetrafluoroborate and provide less solvation to the diazonium salt. Addition of crown ether to solutions containing the PF_6^- anion should therefore result in larger chemical shift differences between complexed and noncomplexed species. This is so because when PF_6^- is the anion, crown solvation is likely to substitute largely for solvent whereas with BF_4^- it probably alters the orientation of BF_4^- with relation to the cation more significantly. Direct evidence on these questions may be available from a detailed study of the ^{14}N or ^{15}N NMR spectra of these species. We hope to complete such studies in the future.

Conclusion and Summary

There are several important conclusions which can be drawn from the data reported here. First, and purely pragmatic, is that 4-*n*-butoxybenzenediazonium tetrafluoroborate is stable and quite soluble in a variety of nonpolar solvents and therefore of considerable utility in assessing solution interactions between arenediazonium ions and other species in nonpolar solutions. This salt should be of use in future work involving either ^{14}N or ^{15}N NMR spectroscopy.

Second, there is considerable evidence of a significant crown–arenediazonium ion interaction, but outside of apparent N_α—C and N≡N bond stabilization, and some remote substituent interactions, it does not exhibit a significant electronic effect on these molecules. It further appears that much of the recently explored synthetic utility of these substances derives from enhanced solubility in nonpolar solvents and a diminution of side reactions and other competetive processes. As in a number of other cases we have reported,[34] the crown effect is most pronounced in media of low polarity and inherently low solvating power for ions, and this effect declines with increasing solvent polarity.

Finally, it appears that the modifications of the gegenion metathesis process represent an alternative method for crown solubilization and therefore utility in synthesis. Moreover, it seems likely that many of the reactions which have been conducted by using crown ethers as phase-transfer catalysts can be done with open-chained polyethers, quaternary ammonium salts, or added dipolar

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(33) Juri, P. N.; Bartsch, R. A. *J. Org. Chem.* **1980**, *45*, 2028.

(34) (a) DiBiase, S. A.; Gokel, G. W. *J. Org. Chem.* **1978**, *43*, 447. (b) DiBiase, S. A.; Lipisko, B. A.; Haag, A.; Wolak, R.; Gokel, G. W. *Ibid.* **1979**, *44*, 4640. (c) DiBiase, S. A., Wolak, R., Dishong, D. M.; Gokel, G. W. *Ibid.* **1980**, *45*, 3630.

aprotic solvents instead, since complexation per se of the nitrogen–nitrogen linkage is probably not crucial to the reaction's success.

Experimental Section

Melting points were determined on either a Thomas-Hoover or a Meltemp capillary device and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 225 in the indicated medium with a resolution of ± 1.5 cm^{-1}. Routine NMR spectra were recorded on a Varian Associates EM-360, and high-field ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian XL-100 using a MONA multinuclear probe and 5-mm-o.d. tubes. Samples were as concentrated as possible or to 15 wt %, whichever was greater. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. Carbon spectra were recorded in $CDCl_3$ (unless otherwise specified), and the solvent provided the deuterium lock signal. Fluorine spectra are reported relative to internal fluorotrichloromethane (F-11) which also provided the lock signal. Ultraviolet data were recorded on a Perkin-Elmer 552 spectrophotometer.

Solvents used in this study were AR grade from various commercial suppliers and were used without further purification unless otherwise specified. Dichloromethane was Baker HPLC Reagent grade, and AR grade $CHCl_3$ was washed with concentrated H_2SO_4 and water, dried over Na_2SO_4, and distilled prior to use. 15-Crown-5 (**10**), 18-crown-6 (**9**), and $Me_4N^+Cl^-$ were obtained from the Aldrich Chemical Co., and $PhCH_2NEt_3{}^+Cl^-$ was prepared as previously described.[35] $MeO(CH_2CH_2O)_nH$ was obtained from Aldrich which specified an average molecular weight of 350.

Arenediazonium Salts. The arenediazonium tetrafluoroborates used in these studies were generally prepared by the method of Roe.[17] The melting points of compounds **2** and **11** agreed well with the literature values.[36] The three fluorine-substituted salts, 2-F (**22**), 3-F (**20**), and 4-F (**12**) were found to have the following melting points: 163–164, 154.5–156, and 161–161.5 °C, respectively. The first and last of these were found to have somewhat higher values than those previously reported[37] (159 and 154.4 °C, respectively), and **20** is a new compound. Compounds **1**, **15**, and **17** had melting points which also agreed well with the literature values.[38] Compound **7** was prepared as described by Swain.[19]

4-Ethylbenzenediazonium Tetrafluoroborate (3). 4-Ethylaniline was diazotized in the presence of 48% tetrafluoroboric acid at 0 °C. Compound **3** was obtained in 70% yield as a white solid, mp 78.5–79.5 °C. A second sample of **3** was obtained in only 46% yield and had a melting point of 84–88 °C. Anal. Calcd for $C_8H_9N_2BF_4$: N, 12.73. Found: N, 13.1.

4-Ethoxybenzenediazonium Tetrafluoroborate (4). *p*-Phenetidine was diazotized as above, and **4** was obtained (68%) as a white solid, mp 74–75 °C. The literature value is 103 °C dec. When we determined the melting point, we noted complete melting as specified above, and the melt remained colorless. If heating was continued, bubbling began, and a color change occurred at 103–105 °C. Anal. Calcd for $C_8H_9N_2OBF_4$: N, 11.86. Found: N, 12.15.

4-Isopropylbenzenediazonium Tetrafluoroborate (5). *p*-Cumidine was diazotized as above, and **5** was obtained (90%) as a white solid, mp 108–110 °C dec. Anal. Calcd for $C_9H_{11}N_2BF_4$: N, 11.97. Found: N, 12.40.

4-*n*-Butylbenzenediazonium Tetrafluoroborate (6). *p-n*-Butylaniline was diazotized as above and **6** was obtained (93%) as a colorless liquid which darkened on being allowed to stand even when protected from the atmosphere and light. Combustion analysis was not attempted on this sample, but IR, ^{1}H NMR, and ^{13}C NMR data all supported the structural assignment.

4-*n*-Butoxybenzenediazonium Tetrafluoroborate (8). *p-n*-Butoxyaniline was diazotized as above and **8** was obtained (51%) as a white solid, mp 47–48 °C. Anal. Calcd for $C_{10}H_{13}N_2OBF_4$: N, 10.61. Found: N, 11.00.

3,4-Dichlorobenzenediazonium Tetrafluoroborate (13). 3,4-Dichloroaniline was diazotized as above, and **13** was obtained (55%) as a white solid, mp 129.5–131.5 °C. Anal. Calcd for $C_6H_3N_2BCl_2F_4$: N, 10.73. Found: N, 10.70.

3,4,5-Trichlorobenzenediazonium Tetrafluoroborate (14). 3,4,5-Trichloroaniline was diazotized as above, and **14** was obtained (40%) as a white solid, mp 200–203 °C. Anal. Calcd for $C_6H_2N_2BCl_3F_4$: N, 9.48. Found, N, 9.75.

4-Iodobenzenediazonium Tetrafluoroborate (16). 4-Iodoaniline was diazotized as above, and **16** was obtained (82%) as a white solid, mp 123–124 °C. Anal. Calcd for $C_6H_4N_2BF_4I$: N, 8.81%. Found: N, 9.14%.

Determination of Diazonium Salt Solubilities. Solubilities were determined approximately by UV analysis (see text) or by titration. In the latter case, solvent was added dropwise from a 10 mL buret to a 25 mL erlenmeyer flask containing a weighed portion of diazonium salt and a magnetic stirring bar. Addition was continued until a homogeneous solution was apparent and then stirring was stopped long enough to determine if full solution had occurred. For example, **1** (253 mg) required 17.80 mL of 5% $MeO(CH_2CH_2O)_nH$ in MeCN to dissolve it (solubility: 14.2 mg/mL). Much less of a 5% 18-crown-6 in MeCN solution (6.35 mL) was required to dissolve **1** (264 mg).

4-Chlorobenzenediazonium Tetrafluoroborate (1)–18-Crown-6 (9) Complex. A solution of **1** (0.11 g, 0.5 mmol), **9** (0.13 g, 0.5 mmol), and $CHCl_3$ (alcohol free, 2 mL) was prepared at 0 °C. The solvent was removed in vacuo and Et_2O added until the oil clouded. The mixture was cooled gradually to −20 °C and filtered to obtain the **1**–**9** complex as a white solid, mp 115–116.5 °C.

Acknowledgment. We thank D. E. Rosenberg and E. R. Wonchoba for technical assistance and the NIH for a grant (GM 26990) which supported this work.

Registry No. **1**, 673-41-6; **2**, 459-44-9; **3**, 52436-73-4; **4**, 3108-14-3; **5**, 403-48-5; **6**, 72302-28-4; **7**, 52436-75-6; **8**, 76832-54-7; **9**, 17455-13-9; **10**, 33100-27-5; **11**·BF_4^-, 369-57-3; **11**·PF_6^-, 369-58-4; **12**·BF_4^-, 459-45-0; **12**·Cl^-, 20893-71-4; **12**·PF_6^-, 53260-51-8; **13**, 405-02-7; **14**, 2106-38-9; **15**·BF_4^-, 673-40-5; **16**, 1514-50-7; **17**·BF_4^-, 459-64-3; **20**·BF_4^-, 1996-38-9; **20**·Cl^-, 20893-73-6; **20**·PF_6^-, 57103-74-9; **22**·BF_4^-, 446-46-8; **22**·Cl^-, 53559-92-5; 4-ethylaniline, 589-16-2; *p*-phenetidine, 156-43-4; *p*-cumidine, 99-88-7; *p-n*-butylaniline, 104-13-2; *p-n*-butoxyaniline, 4344-55-2; 3,4-dichloroaniline, 95-76-1; 3,4,5-trichloroaniline, 634-91-3; 4-iodoaniline, 540-37-4; 4-chlorobenzenediazonium tetrafluoroborate 18-crown-6 complex, 74317-29-6; 1-(3-fluorophenyl)pyridazinium PF_6^-, 76832-56-9; 1-(4-fluorophenyl)pyridazinium PF_6^-, 76832-58-1.

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[35] Durst, H. D.; Gokel, G. W. "Experimental Organic Chemistry"; McGraw-Hill: New York, 1980; p 331.

[36] Roe, A.; Graham, J. R. *J. Am. Chem. Soc.* **1952**, *74*, 6297.

[37] Schiemann, G.; Pillarsky, R. *Chem. Ber.* **1929**, *62*, 3035.

[38] Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *J. Org. Chem.* **1977**, *42*, 643 and references therein.