

CROWN-CATION COMPLEX EFFECTS. VII.
SPECTRAL STUDIES OF ARYLDIAZONIUM IONS IN NONPOLAR SOLUTIONS

Stephen H. Korzeniowski,[†] Robert J. Petcavich,
Michael M. Coleman and George W. Gokel^{†*}
Departments of Chemistry and Material Science
The Pennsylvania State University
University Park, PA 16802 USA

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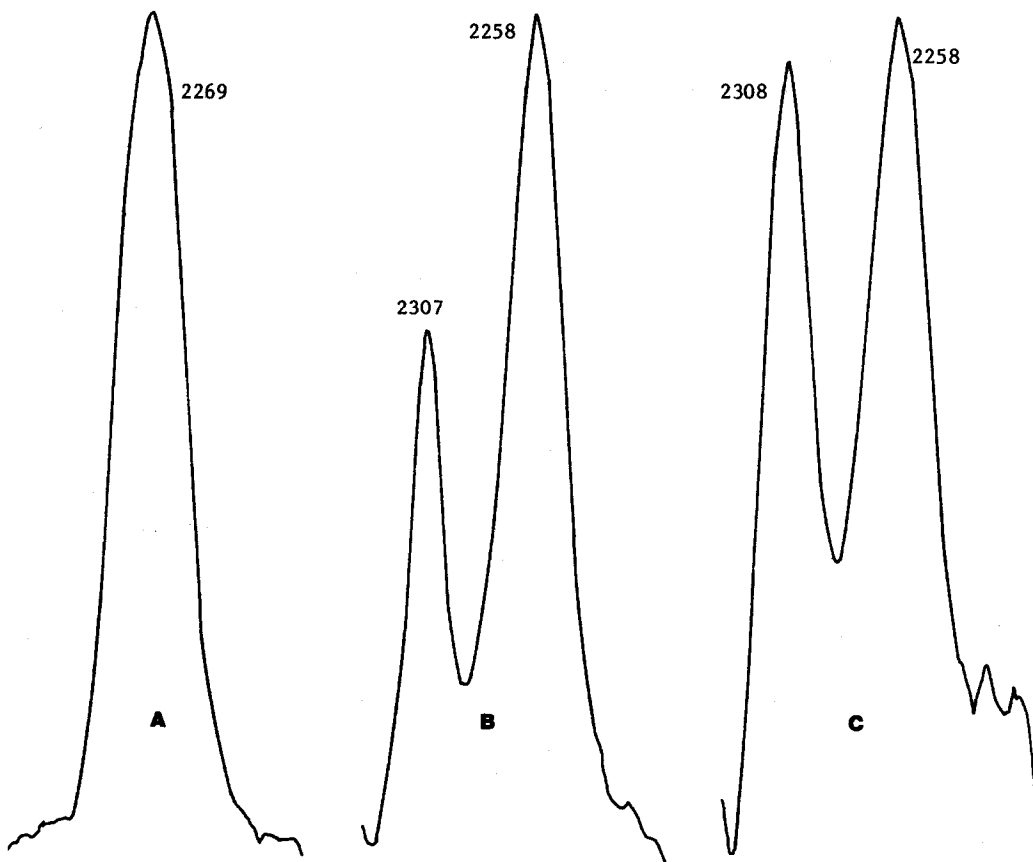
The solubility of aryldiazonium chlorides in nonpolar solvents like dichloromethane and chloroform is not a widely recognized property and the question of whether the compound is predominantly ionic (diazonium ion) or covalent (diazochloride) in such media is an interesting one. No solution spectrum of an aryldiazonium chloride is reported in the literature¹ and to our knowledge, no ¹³C-nmr spectrum has been reported for any aryldiazonium salt² complexed by a crown ether.

Nonpolar solutions of aryldiazonium chlorides can readily be prepared by metathetical gegenion exchange between stable aryldiazonium tetrafluoroborates and ammonium chlorides as we have previously reported.³ By this method, a 0.1 M solution of 4-chlorobenzenediazonium chloride (1) in chloroform was obtained and its Fourier transform infrared (FT-IR) spectrum recorded (KBr cells) at 20°C. An intense absorption at 2273 cm⁻¹ (attributed to $\nu_{N=N}$) indicates that the predominant species in solution is the ionic chloride. Rather than attempt to determine the spectrum of an isolated sample of unstable 1, we compared with it 4-chlorobenzenediazonium tetrafluoroborate (2) which exhibited $\nu_{N=N}$ band at 2297 cm⁻¹ when mullied with Nujol. The diazonium absorption was observed at 2322 cm⁻¹ when the preformed complex⁴ between 2 and 18-crown-6 (3) was examined as a mull. The solution spectrum (chloroform) of 2 in the presence of equimolar 3 showed a single band at 2266 cm⁻¹, a result which probably reflects the insolubility of 2 in the absence of 3. Similarly, $\nu_{N=N}$ for 4-bromobenzenediazonium tetrafluoroborate (4) alone (mull), as the 1:1 complex⁵ with 3 (mull) and in the presence of equimolar 3 (chloroform solution) were 2295 cm⁻¹, 2321 cm⁻¹ and 2269 cm⁻¹, respectively. These results seem consistent with reports of solid 1:1 complexes

between aryldiazonium salts and macrocyclic polyethers.^{6,7}

Inasmuch as most aryldiazonium tetrafluoroborates are insoluble in non-polar media in the absence of 3, the observation of a single $\nu_{\text{N}\equiv\text{N}}$ band in the presence of 3 could reflect "solvent forcing" (the cation selectively and uniquely solvated by the macrocyclic ligand). We therefore examined both the infrared and ^{13}C -nmr of chlorocarbon soluble^{6,8} 4-t-butylbenzenediazonium tetrafluoroborate (5)⁹ in order to ascertain what is the intrinsic affinity of the cation for the macrocyclic ligand. In the absence of any crown ether, a solution of 5 in dichloromethane (0.67 M in diazonium ion) exhibited the $\nu_{\text{N}\equiv\text{N}}$ band at 2269 cm^{-1} .¹⁰ Upon addition of 3 (1 eq.), two absorption bands were observed at 2307 cm^{-1} (complexed) and 2258 cm^{-1} (non-complexed). The relative intensities were 1.0:1.4 respectively. In the presence of 5 eq. of 3, the two absorptions appeared at 2308 cm^{-1} and 2258 cm^{-1} but their relative intensities were almost equal (see Figure 1). As anticipated, the presence of 12-crown-4 (whose cavity is too small to ac-

Figure 1: FT-IR Spectra of 5 in Dichloromethane Solution at 35°C. A: 5 in the absence of 3; B: 5 in the presence of 1 eq. 3; and C: 5 in the presence of 5 eq. 3 (values in cm^{-1}).



comodate the $-N=N$ group) neither altered the position of the 2269 cm^{-1} band nor was any new band observed in the $2350\text{-}2250\text{ cm}^{-1}$ region.

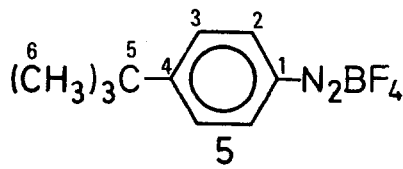
Due to the previously reported negative entropy effect,¹¹ it was also anticipated that lowering the temperature would enhance complexation and accordingly, the intensity of the 2308 cm^{-1} band. The effects of temperature and crown ether on the 2308 cm^{-1} and 2258 cm^{-1} band intensities are shown in table I.

TABLE I. Complexation of 4-t-Butylbenzenediazonium Tetrafluoroborate (5) by 18-Crown-6 (3) in Dichloromethane Solution

Temperature ($^{\circ}\text{C}$)	Peak Intensities ($2308\text{ cm}^{-1}/2258\text{ cm}^{-1}$) in the Presence of 18-Crown-6 (<u>3</u>)	
	1 eq. of <u>3</u>	5 eq. of <u>3</u>
35	0.69	0.96
5	0.81	1.08
-15	0.75	1.15
-35	0.77	1.33

In the presence of 3 (1 eq.) complexation seems to be favored by a decrease in temperature with the greatest change in peak ratios observed at the lowest temperature in the presence of the largest amount of 3. This result is consistent with our earlier observation that para-nucleophilic aromatic substitution is completely inhibited at 4°C in the presence of excess 3.¹² Similar results were observed in 1,2-dichloroethane solution.

The complexation phenomenon (between 3 and 5) in dichloromethane was also detected by ^{13}C -nmr (see table II). The largest change in chemical shifts were observed at C-1 and C-4: in the absence and presence of 1.0 equivalents of 3, $\Delta\delta \approx 3\text{ ppm}$. The chemical shift of C-2, but not C-3, is also affected by the presence of 3.



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TABLE II. ^{13}C -nmr Chemical Shifts of 5 in Dichloromethane Solution

Eq. <u>3</u> Added	C-1	C-2	C-3	C-4	C-5	C-6
0	110.19	132.43	128.87	167.33	36.66	30.08
0.1	110.67	132.24	128.83	166.93	36.49	30.10
1.0	113.58	130.29	128.43	164.54	36.19	30.14
5.0	113.64	129.64	128.27	164.10	35.95	29.97

Notes and References

[†]Department of Chemistry

- To our knowledge, all previously reported infrared data related to this work has been obtained on mullied samples of aryldiazonium cations paired with complex anions: M. Aroney, R.J.W. deFevre and R.L. Werner, *J. Chem. Soc.*, 276 (1955); R.H. Nuttall, E.R. Roberts and D.W.A. Sharp, *Spectrochimica Acta*, 17, 947 (1961). The two studies involving chloride anion were carried out in the solid state: K.B. Whetsel, G.F. Hawkins and F.E. Johnson, *J. Amer. Chem. Soc.*, 78, 3360 (1956); L.A. Kazitayna, O.A. Reutov and Z.F. Buchkovskii, *Chem. Abstr.*, 54, 23798b (1960).
- G.A. Olah and J.L. Grant, *J. Amer. Chem. Soc.*, 97, 1546 (1975).
- S.H. Korzeniowski and G.W. Gokel, *Tetrahedron Lett.*, 1977 (in press).
- The mp of the preformed 1:1 complex between 2 and 3 is 115-116.5°C.
- The mp of the preformed 1:1 complex between 3 and 4 is 121-122.5°C.
- R.A. Bartsch, H. Chen, N.F. Haddock and P.N. Juri, *J. Amer. Chem. Soc.*, 98, 6753 (1976).
- B.A. Haymore, J.A. Ibers and D.W. Meek, *Inorg. Chem.*, 14, 541 (1975).
- C.G. Swain and R.J. Rogers, *J. Amer. Chem. Soc.*, 97, 799 (1975).
- Twice recrystallized 5 [mp 98.5-99.5°C (dec.)] was prepared in 29% overall yield from t-butylbenzene by the standard method.⁸
- The 1:1 solid complex preformed from 3 and 5 exhibited the N≡N stretching band at 2306 cm^{-1} and 5 alone absorbed at 2277 cm^{-1} (both mulls).⁶ Swain and Rogers reported 2270 cm^{-1} for 5 (KBr).⁸
- G.W. Gokel and D.J. Cram, *J.C.S. Chem. Commun.*, 482 (1973).
- G.W. Gokel, S.H. Korzeniowski and L. Blum, *Tetrahedron Lett.*, 1977 (in press).