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Onium Ions. XIII.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Benzenediazonium Ions Indicating Ambident Character

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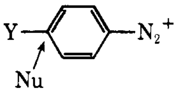
Received November 6, 1974

Abstract: Carbon-13 nuclear magnetic resonance spectroscopic study of a series of benzenediazonium fluoroborate or hexafluorophosphate salts in sulfur dioxide solution at −30° was carried out. Data reflecting charge delocalization show the ambident nature of benzenediazonium ions. The Spiesecke–Schneider relationship is maintained when considering σ_p for $-N_2^+$ and the para cmr shift of the benzenediazonium ion.

One aspect of benzenediazonium ions which has received relatively little attention in the literature is nucleophilic aromatic substitution of the aromatic ring at ring positions other than that originally containing the $-N_2^+$ substituent. Several review articles[2] on diazonium ion chemistry have provided examples of substitution (**1** and **2**) of nucleofugal leaving groups (Y) such as nitro, hydroxide, or halides in the ortho or para positions to the diazonium group. We have recently reported[1] nucleophilic dediazoniation reactions of arenediazonium ions where substitution took place at positions other than the ipso position originally carrying the $-N_2^+$ group. These reactions indicate the ambident nature of benzenediazonium ions.



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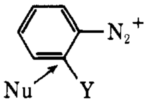

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Nu = NO_2, OH, halogens

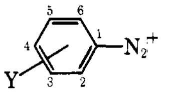
It was considered of interest to study directly the ambident nature of benzenediazonium ions by cmr spectroscopy, a method well suited for such structural studies. In addition, a near-linear relationship between carbon-13 chemical shifts and Hammett σ_p parameters for a series of substituted benzenes has been reported.[3] We have, therefore, considered it of interest to extend this relationship to include $-N_2^+$, a substituent representing an outer limit of electron-withdrawing power, in the series of monosubstituted benzenes.

Results and Discussion

Previous experimental studies indicate that the diazonium group, as an aromatic ring substituent, is approximately twice as electronegative as the nitro group.[4] This behavior is in accordance with proton nmr studies.[5] A more sensitive method to study the structure and charge distribution of benzenediazonium ions is carbon-13 nmr since carbon-13 chemical shifts of phenyl ring carbons in substituted benzenes can be used to monitor changes in charge distribution at those carbons. The assignment of resonances was made by the now familiar procedures of Grant and coworkers.[6,7] In addition to showing the trend of charge delocalization, aryl carbon shieldings of substituted benzenediazonium ions show approximate additivity.[8] To assure correct assignments, "off-resonance" proton-decoupling experiments were also carried out. Table I summarizes carbon-13 chemical-shift parameters of substituted benzenediazonium salts studied as the stable tetrafluoroborate or hexafluorophosphate salts in SO_2 solution, generally at −30°.

As can be seen from Table I, there is a marked upfield shift of the C-1 (ipso) carbons bearing the $-N_2^+$ substituent

Table I. Carbon-13 Chemical Shifts of Benzenediazonium Salts[a]

	C-1	C-2	C-3	C-4	C-5	C-6	$-CF_3$	$-CH_3$
H	115.8	134.5	134,2	144.5	134,2	134.5		
4-Cl[b]	113.2	134.3	132.7	149.5	132.7	134.3		
4-Br	114.8	137.8	135.7	140.8	135.7	137.8		
2-F[c]	102.4	161.8	119,4	146.4	128.2	133.1		
4-F[c]	108.6	136.4	121.6	170.1	121,6	136.4		
$2-CH_3$	113.0	145.2	133,5	142.3	132,5	133.4		18.1
$4-CH_3$	109.1	133.0	133.8	157.1	133.8	133,0		22.7
$2,4-(CH_3)_2$	108.6	145.1	133.9	156.7	130.6	132.2		17.9, 22.5
$2-OCH_3$	99,4	164.0	114.8	155.5	123.7	131,7		58.6
$4-OCH_3$	105.0	135.9	118,3	170.6	118.3	135.8		57.4
$2-CF_3$	110,7	131.4	131,0	143.5	136.2	135.9	*d*	
$4-CF_3$	118.1	133.4	129.3	141.0	129.3	133,4	*d*	
$2-NO_2$	108.2	155.6	129,2	144.1	137.8	137.3		
$4-NO_2$[e]	123.0	135.8	127.3	154.6	127.3	135.8		

[a] Carbon-13 chemical shifts of benzenediazonium fluoroborates or fluorophosphates are reported in parts per million from external TMS (capillary). Recorded in SO_2 at −30°. [b] Recorded in CH_3CN. [c] Due to $^{13}C-^{19}F$ coupling, C-2 appears as a doublet at 167.3 and 156.3; C-4 appears as a doublet at 175.5 and 164.7, average values are reported. [d] Due to $^{13}C-^{19}F$ coupling, C-2 appears as a quartet at 136.2, . . ., 129.7, 128.3; $2-CF_3$ appears as a quartet at 137.1, 126.2, 115.3, 104,5; C-4 appears as a quartet at 143,3, 142,0, 140.5, 139.2; $4-CF_3$ appears as a quartet at 138.5, 127.6, 116.7, 105.8, average values are reported, [e] Recorded in DMSO-d_6.

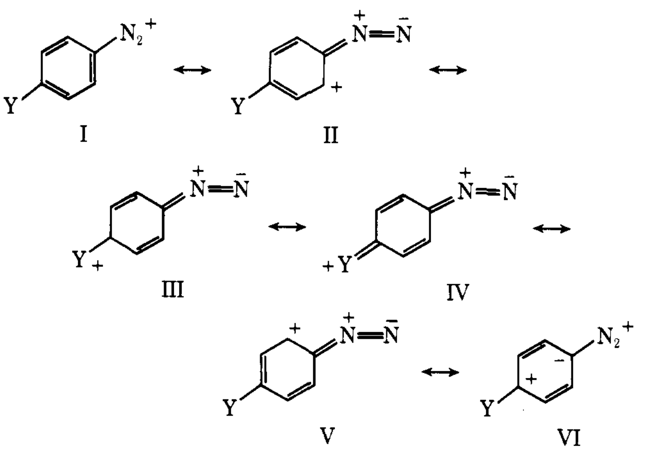
indicating significant shielding. This effect is enhanced when a substituent (Y) on the ring is electron releasing. Concomitantly, there is a marked downfield shift of those carbons bearing a substituent, indicating the electron-deficient nature of those carbons relative to benzene. Largest downfield shifts were observed for carbon atoms of benzenediazonium ions bearing a substituent which could best accommodate positive charge. In addition to the inductive effects of these substituents, one should thus consider the quinoidal-type resonance structures (IV) (*vide infra*) as significant contributors to the overall resonance form. Downfield shifts (relative to benzene) of 41.4 ppm for 4-fluorobenzenediazonium ion, 35.3 ppm for 2-methoxybenzenediazonium ion, and 41.9 ppm for 4-methoxybenzenediazonium ion are striking examples of this substituent effect.

Fluorine-substituted benzenediazonium ions show anticipated one-bond coupling such as in the case of 2-fluorobenzenediazonium ion (J_{CF} = 276.8 Hz), as well as long range (two- and three-bond) coupling of C-1 (J_{CF} = 12.6 Hz), C-3 (J_{CF} = 15 Hz), C-4 (J_{CF} = 9.6 Hz), C-5 (J_{CF} = 2 Hz), and C-6 (J_{CF} = 3.9 Hz) for the same ion. For the symmetrical 4-fluorobenzenediazonium ion, $^{19}F-^{13}C$ coupling constants observed are C-4 (J_{CF} = 271.8 Hz), C-2 (J_{CF} = 12.8 Hz), and C-3 (J_{CF} = 24.8 Hz).

One-bond and long-range $^{19}F-^{13}C$ coupling was observed for the 2-trifluoromethylbenzenediazonium ion. The $2-CF_3$ carbon showed the largest coupling with J_{CF} = 273.9 Hz. Carbon-2 of this ion appeared as a quartet with J_{CF} = 36 Hz. $^{19}F-^{13}C$ coupling was observed for 4-trifluoromethylbenzenediazonium ion with J_{CF} = 274.1 Hz for the $4-CF_3$ substituent. C-4 of this ion appears as a quartet with J_{CF} = 34.4 Hz. C-3 appears as a quartet with J_{CF} = 4.1 Hz. The observation of $^{19}F-^{13}C$ coupling was utilized in peak assignments of the aromatic carbons, J_{CF} values decreasing with distance from the fluorine substituent.

The relationship between cmr chemical shifts and electron density in mono- and disubstituted aromatic systems has been extensively discussed.[9,10] In monosubstituted aromatics, a good correlation of para carbon shifts with Hammett σ substituent constants and electron densities obtained from molecular-orbital calculations has been achieved.[11-15] Lewis and Johnson determined the Hammett constants (σ_p = 1.9; σ_m = 1.7) for the diazonium group in the ionization of benzoic and phenylacetic acids. A σ_p = 3 was obtained for *p*-hydroxy and *p*-aminobenzenediazonium ions; results which indicate that the diazonium group ($-N_2^+$) is the most powerful electron-withdrawing group known.[16,17] It was suggested that in addition to the inductive effect, an extremely strong resonance effect is operative and is most important at the para position. In fact, when we plot the σ_p substituent constant for $-N_2^+$ against the para carbon shift ($\delta^{13}C$ 144.5 ppm) of the benzenediazonium ion, the Spiesecke–Schneider relationship is maintained. Levy has shown a relationship between para carbon-13 chemical shifts and total charge densities.[18] Olah and Forsyth calculated a positive charge density of 0.060 [CNDO/2] for C-4 of the benzenediazonium ion, results which maintain the linear relationship originally demonstrated by Levy.[19]

On the basis of carbon-13 chemical shifts for benzenediazonium salts studied, it can be concluded that canonical structures I–VI are significant resonance contributors. Cmr data thus provide direct experimental proof for the ambident nature of benzenediazonium ions.



Experimental Section

Materials. All benzenediazonium ions were prepared according to procedures summarized by Roe.[20] Generally, 0.1 mol of the aniline derivative is dissolved in 0.5 mol of 50% aqueous HBF_4 and cooled to ice-bath temperature. The solution is stirred continuously by an overhead stirrer. Sodium nitrite (0.2 mol) in water is slowly added until the solid arenediazonium fluoroborate or hexafluorophosphate salt precipitates from solution. The stable salts were collected and purified in the usual manner. The 4-chloro-, 4-bromo-, and 4-nitrobenzenediazonium salts are products available from Ozark-Mahoning Co.

Nmr Spectroscopy. Pmr spectra were obtained on a Varian Associates Model A-56/60-A spectrometer equipped with a variable-temperature probe.

Cmr spectra were obtained on a Varian Associates XL-100 spectrometer equipped with a broad-band decoupler, and variable temperature probe. The instrument operates at 25.2 MHz for carbon-13 and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000-5000 pulses, each of width 20-35 μsec, needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the fluorine-19 external sample of fluorobenzene. Chemical shifts were measured from the carbon-13 signal of 5% carbon-13 enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

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Electron Spin Resonance Study of Heterocycles. V. Quinolyl Radicals[1]

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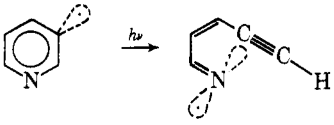
Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591. *Received August 23, 1974*

Abstract: 2-, 3-, and 4-quinolyl and 4-isoquinolyl radicals were generated in argon matrices, and their esr spectra were examined. All are found to be σ radicals, and the observed coupling constants are in good agreement with those calculated by INDO molecular orbital theory. Unlike pyridyl radicals, they are stable against uv irradiation.

Pyridyl radicals (2-, 3-, and 4-) generated in argon matrices have been all found to undergo a ring-rupture rearrangement when irradiated with uv light,[2] *e.g.*



(1)

We report here the results of matrix-isolation esr studies of 2-, 3-, and 4-quinolyl and 4-isoquinolyl radicals. All of these radicals were found to be σ radicals as in the case of pyridyls. However, unlike pyridyl radicals, they were proved to be stable against uv irradiation. The stability is attributed to the increased aromaticity of the quinolyl systems. The resolved hyperfine structures of these radicals were readily identified with those of the corresponding protons of pyridyl radicals.[2] It indicates little effect of the fused benzene ring upon the nature of the semifilled orbitals of the quinolyl and isoquinolyl radicals.

Experimental Section

Detailed descriptions of the apparatus and the method which would permit generation of molecular anions within a rare gas matrix at ~4°K and the esr investigation of the resulting anions have been presented previously.[3] In the present series of experiments, desired quinolyl radicals were generated by photolysis of the anions of quinolyl chlorides (or bromides) produced by this technique.

Argon matrices were prepared in which quinolyl halides (electron acceptors) were trapped together with Na atoms (electron donors), the composition being roughly 1000:10:1 for argon atoms, the halide molecules, and the Na atoms, respectively. Irradiation of these matrices with "red light" ($\lambda > 5800$ Å) resulted in the disappearance of the esr signals due to Na atoms, and the appearance of a broad singlet signal ($\Delta H_{\text{peak-to-peak}} \simeq 20$ G) at the position corresponding to $g = 2.00$. In each case, the photoinduced broad singlet was assigned to the anions of the quinolyl halide. Subsequent irradiation of the matrix with more energetic "yellow light" ($\lambda > 5000$ Å) caused the conversion of the singlet into a spectrum consisting of several hyperfine components symmetrically spaced about the position of $g = 2.00$. The final spectrum was readily recognized as that of the quinolyl (or isoquinolyl) radicals resulting from the cleavage of the C–Cl (or C–Br) bond. Let QX denote the quinolyl halide. The photoinduced reaction sequence described above can then be summarized as follows:

$$\begin{tikzcd}
\mathrm{QX} + \mathrm{Na} \arrow[r, "h\nu", "\lambda > 5800\ \text{Å}"'] & (\mathrm{QX})^{-} + \mathrm{Na}^{+} \arrow[d, "h\nu", "\lambda > 5000\ \text{Å}"'] \\
 & \mathrm{Q}\cdot + \mathrm{X}^{-}\cdot
\end{tikzcd} \qquad (2)$$

Quinolyl halides (2-chloroquinoline, 2-chloro-4-methylquinoline, 3-bromoquinoline, 4-chloroquinoline, and 4-bromoisoquinoline) were obtained from Aldrich Chemical Co. and were used as received. An Oriel xenon-mercury high-pressure arc lamp (1 kW) equipped with appropriate sharp cut-off filters was used for the irradiation of the matrices. All the esr spectra were obtained while