A Computational (DFT, MP2) and GIAO NMR Study of Substituent Effects in Benzenediazonium Mono- and Dications

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^{15}N and ^{13}C NMR chemical shifts were computed by GIAO-DFT and GIAO-MP2 for a series of *p*-substituted benzenediazonium mono- and dications in order to probe the electronic effects of the substituents on the diazonium moiety. Optimized geometries and N/N vibrational frequencies were also considered for comparison. The GIAO-DFT derived ^{15}N chemical shifts correlate more closely with the experimental values as compared to GIAO-MP2. Energy minimizations at the B3LYP/6-311+G(2d,p), M062X-6-311+G(2d,p), MP2/6-311+G(2d,p), G2(MP2), and CBS-Q levels were carried out. Relative dication stability order

$HCO^+ > HOMe^+ > HN(Me)_2^+ > HOH^+ > HCN^+ > HNO_2^+$ was derived from isodesmic proton transfer reactions. The N_β-protonated dications were less stable than the corresponding *p*-R$^+$ dications. Among the regioisomeric N_β-protonated dications (with R = –F, –Cl, and –CN), those with the R group in the *para* position were preferred. For the regioisomeric, ring-protonated benzenium-diazonium dications, the *meta*-protonated dications were more favored (by DFT and MP2). Influence of the counterion and solvent on the computed ^{15}N NMR chemical shifts in PhN$_2^+$ X$^-$ were also assessed.

Introduction

Aromatic diazonium compounds constitute an extremely valuable class of onium salts that serve as precursors to a wide range of organic intermediates employed in the pharmaceutical and dyestuffs industry.[1] Arenediazonium salts have also become increasing important in organometallic chemistry, with the Matsuda–Heck coupling reaction as a noteworthy example.[2,3] Despite the fact that the mechanistic aspects of diazotization and dediazoniation in arenediazonium salts have been extensively studied over the years,[1] structural/mechanistic studies focusing on the nature of bonding in ArN$_2^+$ have not been extensive.

The ambident character, importance of the canonical mesomeric forms, in PhN$_2^+$ was demonstrated by Olah and Grant[4] via a ^{13}C NMR study with a relatively large set of isomeric (*ortho* and *para*) substituents, but the available data on ^{15}N NMR have remained limited, and have not been expanded much beyond those reported by Roberts et al.,[5,6] who also studied solvent effect on the ^{15}N and ^{13}C NMR chemical shifts in *p*-*t*BuPhN$_2^+$ BF$_4^-$ and found rela-

tively small changes.[6] The N$_\alpha$ shifts gave good correlation with σ_p+ substituent constants, but N$_\beta$ did not correlate with either σ_p+ or σ_p. Replacing BF$_4$ for Cl as counterion led to small downfield shifts for both nitrogens, and complexation to 18-crown-6 led to upfield shifts for N$_\alpha$ and small downfield shifts for N$_\beta$.[6]

Based on potential energy surface analysis at various levels, Glaser and Horan[7] studied the nature of bonding in parent benzenediazonium cation and suggested a synergistic model involving σ-dative (from N$_2$ to Ph) and π-back dative (from Ph to N$_2$) interactions, in which most of the positive charge is carried by the phenyl group. They suggested that electron density distribution in PhN$_2^+$ is better represented by this model than the classical Lewis–Kekulé structures. In the context of the same study, the N chemical shifts for PhN$_2^+$ were computed using the IGLO method. Whereas correspondence with the experimental values was poor with IGLO (DZ), good correspondence was observed with IGLO (basis II).

Protonation of the *para* substituent provides the opportunity to understand the importance of mesomeric and inductive effects on the Ar–N–N linkage. The first example of a protosolvated diazonium-oxonium dication was reported by Laali and Olah in 1985,[8] by protonation of *p*-methoxybenzenediazonium tetrafluoroborate in superacidic media. Study of the ^{15}N$_\beta$-labeled counterpart showed an ca. 8 ppm upfield shift, consistent with strongly electron-withdrawing nature of oxonium substituent in the resulting dication, reflecting diminishing diazo character. A proton-coupled ^{15}N NMR spectrum ruled out an *N*-protonated dication.

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Table 1. GIAO-DFT and GIAO-MP2 NMR spectroscopic data and reported experimental values for *p*-substituted PhN_2^+.

p-Substituent	B3LYP (M062X) NMR[a]			MP2 NMR[a]			Experimental NMR[b]		
	N_α	N_β	C_{ipso}	N_α	N_β	C_{ipso}	N_α	N_β	C_{ipso}
H	230.3 (195.4)	338.5 (320.6)	105.2 (116.3)	305.0	298.5	98.4	223.8	316.8	115.2
$N(CH_3)_2$	247.2 (198.8)	381.5 (356.6)	85.7 (89.3)						
OH	234.7 (194.2)	355.2 (333.2)	93.9 (101.3)	315.8	297.7	87.6	227.2	323.2	102.1
OCH_3	237.2 (195.2)	359.4 (336.0)	92.2 (99.8)	316.7	294.6	86.0	225.5	320.8	103.1
CH_3	232.9	345.5	100.1	309.1	296.9	94.8	224.6	317.1	113.3
F	230.0	344.7	99.8	305.8	298.4	92.8			
CF_3	228.3	337.2	107.4						
HC=O	229.8 (195.2)	340.0 (321.8)	107.8 (119.3)	303.8	300.6	99.9			
CN	229.2 (194.1)	342.7 (323.4)	106.2 (149.8)	302.9	301.4	98.6			
NO_2	227.9 (194.1)	338.9 (321.9)	109.8 (121.6)	301.2	302.6	99.5	221.8	316.9	121.8
N_2^+	215.0	338.0	127.5						

[a] Corrected values (see computational methods). [b] From ref.[5].

To the best of our knowledge no other experimental or theoretical study of diazonium dications have since been reported with the goal to gauge substituent effects over a wider set, and to examine relative energies and variations in the ^{15}N chemical shifts. The present work examines these topics by applying computational quantum-chemical methods.

Results and Discussion

GIAO NMR Study of Substituent Effect in Benzenediazonium Monocations

Focusing first on the monocations, a set of *para* substituents ranging from strongly electron-donating to strongly electron-withdrawing were computed by GIAO NMR (^{15}N and ^{13}C) at the DFT and MP2 levels of theory. The results are summarized in Table 1 along with the reported experimental values (from ref.[5]). It can be noted that overall GIAO-DFT performs better in reproducing the experimental values relative to GIAO-MP2, which greatly overestimates the $^{15}N_\alpha$ shifts. The discussion therefore focuses mainly on the GIAO-DFT data. In comparing B3LYP with M062X (reported in parentheses), the former does better in reproducing the $^{15}N_\alpha$ shifts, whereas the latter provides closer correspondence with $^{15}N_\beta$ and with C(*ipso*) chemical shifts. With electron-donating *para* substituents, the N_β and to a lesser extent N_α are downfield shifted, in the decreasing order $Me_2N > OMe > OH > Me$. This is accompanied by shielding at the *ipso* carbon. In concert with the early experimental ^{15}N data,[5] this trend correlates with relative electron-donating ability of the substituents (as in Figure 1), reflecting diminished diazo character with decreasing electron-donating ability of the *para* substituent.

The same general trend in substituent effect is observed considering the computed N/N vibrational frequencies in the monocations (Table 2), with gradual shifts to higher fre-
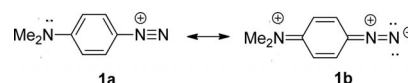

Figure 1. Contributing resonance structures.

quency by moving from strongly donating *p*-R groups to strongly electron-withdrawing. The same insight could also be gained considering the computed bond lengths in the optimized structures (see Table 3), showing longer C–N_α and R–C bonds and shorter N_α–N_β bonds, in going from strongly donating to strongly withdrawing substituents.
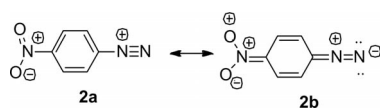
Table 2. Computed (and experimental) N/N vibrational frequencies for *p*-substituted PhN_2^+.

p-Substituent	Exp. ν_{NN} cation	B3LYP/6-311+G(2d,p)	
		ν_{NN} cation	ν_{NN} dication
$N(CH_3)_2$		2250	2361
OH		2291	2373
OCH_3	2252	2283	2367
HC=O		2326	2374
CN		2320	2373
NO_2	2308	2336	2376

Changes in the computed GIAO-DFT shifts for electron-withdrawing substituents appear less straightforward (Table 1). The net effect for *p*-F and *p*-Me are similar and this may reflect a balance of pπ back-bonding and inductive withdrawal effects for F. Strong electron-withdrawing effect of *p*-CF_3 is manifested in deshielding at C_{ipso} and shielding at –N_2^+, along with a noticeably longer C–N_α bond in the optimized structure. Similar effects are noted for *p*-CN and *p*-COH. Comparing *p*-NO_2 with R = H, C_{ipso} is deshielded, N_α is upfield shifted but N_β has hardly changed. The same trend is observed by comparing the experimental ^{15}N shifts, and was also noted previously by Roberts et al.[5] who suggested minor contribution by resonance structures like **2b** in Figure 2.

Table 3. Critical bond lengths for the mono- and dications from optimized geometries.

| p-Substituent | B3LYP/6-311+G(2d,p) | | | | | |
| | Monocations | | | Dications | | |
	N_α–N_β [Å]	C–N_α [Å]	C–R [Å]	N_α–N_β [Å]	C–N_α [Å]	C–RH⁺ [Å]
N(CH₃)₂	1.112	1.349	1.339	1.099	1.400	1.483
OH	1.107	1.364	1.326	1.098	1.408	1.476
OCH₃	1.108	1.361	1.316	1.098	1.404	1.446
F	1.104	1.374	1.317			
CF₃	1.102	1.385	1.522			
HC=O	1.102	1.383	1.507	1.098	1.414	1.439
CN	1.102	1.382	1.428	1.100	1.411	1.429
NO₂	1.101	1.387	1.497	1.098	1.413	1.457
N₂⁺	1.097	1.414	1.414			

Table 4. Solvent and counterion effect on computed NMR shifts.[a]

| Environment for PhN₂⁺ | B3LYP NMR | | | MP2 NMR | | |
	N_α	N_β	C_{ipso}	N_α	N_β	C_{ipso}
Gas phase	230.3	338.5	105.2	302.0	298.5	98.4
Gas phase-BF₄⁻	229.4	334.3	116.7	299.2	301.4	109.5
Gas phase-FSO₃⁻	239.4	342.2	119.3	–	–	–
CHCl₃	232.8	336.4	109.3	305.6	297.1	102.2
CHCl₃/BF₄⁻	229.4	334.3	116.7	304.1	301.6	109.2
CHCl₃/FSO₃⁻	239.4	342.2	117.9	–	–	–
CH₃CN	233.4	334.7	110.6	305.7	296.2	103.9
CH₃CN/BF₄⁻	234.9	334.1	115.8	305.5	301.4	109.7
CH₃CN/FSO₃⁻	239.4	342.2	117.9	–	–	–

[a] Corrected values (see computational methods).

Figure 2. Mesomeric forms in the p-nitrobenzenediazonium cation.

The most deshielded C_{ipso} is observed in the case of p-N₂⁺, also showing the longest C–N_α bond length within the set.

Collectively, the NMR spectroscopic data, –N₂⁺ vibrational frequencies, and variations in critical bond lengths in the optimized structures in substituted ArN₂⁺ underscore the interplay of diazonium-diazo mesomeric character as a function of the substituents.

Solvent and Counterion Effects in PhN₂⁺ X⁻

Focusing on counterion and solvent effects, GIAO-DFT data were computed for PhN₂⁺ with BF₄⁻ and FSO₃⁻ in the gas phase as well as in CHCl₃ and MeCN as representative solvents (Table 4). For the gas phase studies, association with BF₄⁻ leads to shielding at –N₂⁺ and deshielding at C_{ipso}. With FSO₃⁻ as counterion, deshielding at –N₂⁺ and at C_{ipso} is observed. These changes imply increased diazo character with the more inert/less nucleophilic counterion. Solvent effect on the ¹⁵N shifts are relatively small in both solvents. Counter ion effects determined in solvent (by PCM) are similar to those found in the gas phase.

Benzenediazonium Dications

Geometry optimizations were performed by B3LYP/6-311+G(2d,p), M062X/6-311+G(2d,p) and MP2/6-311+G(2d,p), and in selected cases by G2(MP2) and CBS-Q on the dications formed by protonation of the para-substituents (with R = NMe₂, OMe, OH, CN, HCO, and NO₂). The computed ΔE_r and ΔG_r values lead to relative electronic stability order HN⁺Me₂ > CN⁺H > HCOH⁺ > HNO₂⁺ > HOMe⁺ > HOH⁺, irrespective of the basis set and the method (Table 5). The relative dication stability order HCO⁺ > HOMe⁺ > HN(Me)₂⁺ > HOH⁺ > HCN⁺ > HNO₂⁺ was derived via isodesmic proton transfer reactions with H₃O⁺ or NH₄⁺ (see Table 5). These isodesmic reactions represent an estimation of relative proton affinities for O- and N-protonation, respectively. The results appear encouraging toward generation and direct NMR study of other arenediazonium dications, in an effort to expand the earlier reported work.[8]

In selected cases, diazonium dications resulting from N_β-protonation of PhN₂⁺ as well as their regioisomeric fluoro-, chloro-, and cyano-substituted derivatives were computed by B3LYP/6-311+G(2d,p) and by MP2/6-311+G(2d,p). Formation of N_β-protonated dications are significantly less favorable as compared to the p-R⁺ dications. Moreover, among the isomeric N_β-protonated dications (with R = F, Cl and CN) the para isomers are more favored (Table 6).

For the N_β-protonated dications, relative dication stability order p-Cl > p-F > p-CN was derived from isodesmic proton transfer reactions (with NH₄⁺/NH₃) (Table 6). Col-

Table 5. Computed ΔE_r and ΔG_r values at various levels of theory.

| p-Substituent | Protonation of the para substituent [kcal/mol][a] | | | | | | | |
| | B3LYP/6-311+G(2d,p) | | M062X/6-311+G(2d,p) | | MP2/6-311+G(2d,p) | | G2(MP2) | CBS-Q |
	ΔE_r	ΔG_r	ΔE_r	ΔG_r	ΔE_r	ΔG_r	ΔG_r	ΔG_r
N(CH₃)₂	–127.7 (83.5)	–118.8	–129.4	–121.3				
OH	–83.8 (86.9)	–77.8	–85.1	–78.7	–86.4	–80.2	–81.7	–71.1
OCH₃	–96.0 (74.8)	–90.0	–96.5	–89.8	–98.0	–92.0		
HC=O	–118.6 (52.1)	–110.3	–116.8	–108.6	–114.9	–106.5	–110.3	–115.4
CN	–119.4 (91.8)	–112.8	–117.5	–110.8	–116.5	–109.7	–114.1	–116.2
NO₂	–111.8 (99.4)	–104.1	–111.6	–104.0	–107.9	–100.4		

[a] p-Substituent-protonated dication minus p-PhN₂⁺. In parenthesis, p-substituent-protonated dication minus p-PhN₂⁺ computed via isodesmic proton transfer reactions with H₃O⁺ or NH₄⁺ as applicable.

Table 6. Computed ΔE_r values for N_β protonation.

| Substituent | ΔE_r for protonation on N_β [kcal/mol][a] | |
	B3LYP/6-311+G(2d,p)	MP2/6-311+G(2d,p)
H	−38.0 (173.2)	−20.5
p-Cl	−48.4 (162.8)	−30.1
o-Cl	−42.0 (169.2)	−23.6
m-Cl	−37.8 (173.4)	−19.3
p-F	−40.6 (170.6)	−23.9
o-F	−36.6 (174.6)	−19.5
m-F	−33.0 (178.2)	−15.7
p-CN	−36.8 (174.4)	−16.5
o-CN	−33.6 (177.6)	−16.3
m-CN	−30.0 (181.2)	−12.6

[a] N_β-Protonated structure (dication) minus diazonium cation. In parenthesis, N_β-protonated dication minus parent diazonium cation (isodesmic reactions with NH_4^+/NH_3).

lectively, the data reflect relative p-π back bonding ability of the p-R substituent, represented by extended resonance structures shown in Figure 3.
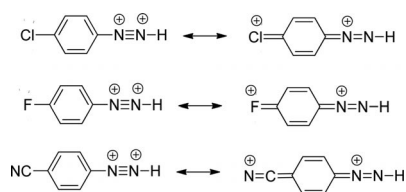
Figure 3. Extended resonance structures in N-protonated dications.

It is known that PhN_2^+ is susceptible to electrophilic attack at the *meta* position,[7] consistent with the powerful deactivating effect of $–N_2^+$. This is borne out computationally in the context of the present study (Table 7). Comparison of the ΔE_r values for *ortho*-, *meta*-, *para*- and *ipso*-protonation shows that the dication arising from *meta* protonation has the lowest energy.

Table 7. Computed ΔE_r values for benzenium-diazonium dications.

| Method | ΔE_r for ring protonation [kcal/mol][a] | | | | |
	N_β	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
B3LYP/6-311+G(2d,p)	−38.0	−52.2	−64.0	−67.2	−61.0
MP2/6-311+G(2d,p)	−20.5	−47.0	−57.1	−58.4	−55.0

[a] Protonated structure (dication) minus diazonium cation.

GIAO NMR Studies of Benzenediazonium Dications

Benzenediazonium dications bearing p-R$^+$ substituents were studied by GIAO-DFT to examine the changes in their ^{15}N and ^{13}C NMR shifts (Table 8). The observed trends were compared with critical bond length data from the optimized geometries (see Table 3). Consistent with "umpolung" reactivity, protonation of p-NMe$_2$, p-OH, and p-OMe switches them from strongly electron-donating to highly withdrawing (as in Figure 4). This causes notable ^{15}N upfield shifts and concomitant downfield shifts of C_{ipso}, implying strongly diminishes diazo character of the diazonium moiety, which is also reflected in longer C–N$_\alpha$ and C–R$^+$ bonds (see Table 3).

Table 8. GIAO-DFT NMR spectroscopic data for the p-RH$^+$ dications.[a]

| p-Substituent | B3LYP NMR | | | M062X NMR | | |
	N_α	N_β	C_{ipso}	N_α	N_β	C_{ipso}
N(CH$_3$)$_2$	218.8	336.6	116.4	188.5	324.5	128.2
OH	216.2	336.3	121.2	187.3	326.4	132.9
OCH$_3$	217.5	336.5	118.4	187.9	325.5	130.4
HC=O	217.7	336.6	129.9	189.4	326.8	142.4
CN	217.3	336.8	125.5	188.8	327.0	137.7
NO$_2$	216.3	337.8	128.3	187.8	328.4	139.7

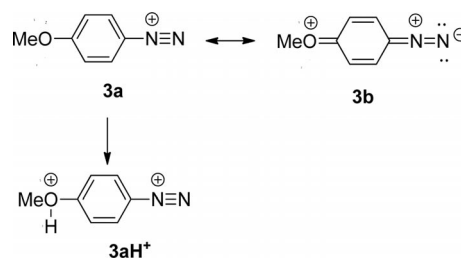[a] Corrected values (see computational methods).

Figure 4. Charge delocalization in the monocation and dication.

Remarkably, the GIAO-DFT shifts for the diazonium moiety and C_{ipso} are very similar, irrespective of the nature of the cationic substituent, suggesting that electronic communication between $–N_2^+$ and the p-R is practically switched off, when the *para* substituent is protonated. The finding that computed $\Delta\delta^{13}C$ values (dication minus monocation) are rather small, implies that the resulting dications have limited benzenium ion character.

It can be surmised that the p-R protonated dications represent examples of "extreme" diazonium ion character in PhN_2^+, which is induced via the cationic *para* substituents. Given their favorable relative energy data, it should be possible to extend the earlier study[8] by direct NMR studies in superacid media. Experimental work along these lines have been initiated in this laboratory.

Computational Methods

Calculations were performed with the Gaussian 03 package of programs.[9] Structures were fully optimized by density functional theory (DFT) with the B3LYP[10] functional and the 6-311+G(2d,p) basis set. All computed geometries were verified to be minima by harmonic vibrational frequency calculations (no imaginary frequencies). Second-order Møller–Plesset (MP2) perturbation theory[11] optimizations at the MP2/6-311+G(2d,p) level were also carried out, and the accurate composite models G2(MP2)[12] and CBS-Q[13] were applied for geometry optimizations on selected compounds. DFT geometry optimizations at the M062X[14]/6-311+G(2d,p) level were performed with the Gaussian 09 suite of programs.[15] NMR chemical shifts were calculated by the GIAO (gauge independent atomic orbitals)[16] method at the B3LYP/6-311+G(2d,p) and MP2/6-311+G(2d,p) levels, and in selected cases at the GIAO-M062X/6-311+G(2d,p) level. The ^{13}C and ^{15}N NMR chemical shifts were referenced to TMS and NH$_3$ respectively (GIAO magnetic shielding tensors were 182.5 ppm for ^{13}C and 31.9 ppm for ^1H in TMS, and 258.4 ppm for ^{15}N in NH$_3$; these values are related to the GIAO isotropic magnetic suscep-

tibility). The computed ^{15}N shift for $MeNO_2$ at the GIAO-B3LYP/6-311+G(2d,p), GIAO-M062X/6-311+G(2d,p), and GIAO-MP2/6-311+G(2d,p) levels were 411.6, 453.1, and 310.4 ppm, respectively. Considering the experimental shift of 380.5 ppm for $MeNO_2$, appropriate corrections were applied to the computed ^{15}N shifts by substracting 31 and 72.6 ppm from the calculated GIAO-B3LYP/6-311+G(2d,p) and GIAO-M062X/6-311+G(2d,p) values, respectively, and by adding 70 ppm to the calculated GIAO-MP2/6-311+G(2d,p) values. Solvation effects in CH_3Cl and CH_3CN were estimated by geometry optimizations with the polarized continuum model (PCM).[17]

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