

Charge Distribution Differences in Benzenium and Nitrobenzenium Ions Based on ^{13}C Nuclear Magnetic Resonance Studies and Their Relevance to the Isomer Distribution in Electrophilic Aromatic Substitutions¹

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Abstract: Several stable benzenium and nitrobenzenium ions were prepared in solution by protonation and nitration of hexasubstituted benzenes. Carbon-13 and fluorine-19 nmr spectra of the two types of ions indicate significant differences in the pattern of charge distribution. The charge distribution differences are discussed in relation to observed differences in isomer ratios and to the potential importance in interpretation of substituent effects in electrophilic aromatic substitution.

The existence of arenium ions or σ complexes, considered to be intermediates in electrophilic aromatic substitution reactions, has been established in many studies by direct observation of the species as stable ions.³ Most investigations have dealt with σ complexes resulting from the alkylation or protonation of aromatic systems. Recently, the direct observation of long-lived σ complexes in the nitration⁴ and chlorination^{4a} of hexa- and pentasubstituted benzenes was reported. We now report an investigation of the electronic differences between nitrobenzenium ions and benzenium ions formed in protonation.

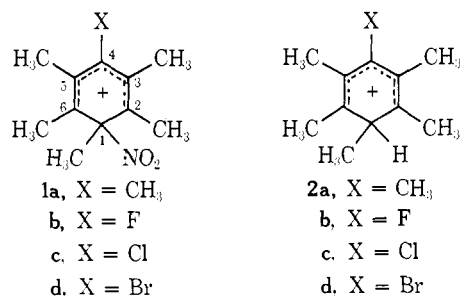
The observation of significant differences in electron distributions in the σ complexes produced by various electrophiles could have important consequences regarding the interpretation of kinetic substituent effect data and isomer ratios in electrophilic aromatic substitution. The distribution of charge in ion-like transition states has been shown to be of importance in determining the balance between resonance and field-inductive effects of substituents,⁵ as well as the sensitivity to substituent influence, when the balance of contributing effects is constant.⁶ Thus, if charge distributions differ in σ complexes, then electrophilic reactions for which σ complex formation is rate-determining could display different responses to substituent influences, even in the case that bond formation (*i.e.*, progress along the reaction coordinate) is equal for the different reactions.

Benzenium ions have been investigated by a variety

of physical methods, including vapor pressure and conductivity measurements, X-ray crystallography, uv and ir spectroscopy, and ^1H , ^{19}F , and ^{13}C nmr spectroscopy. Perhaps the best tool for determining details of the electron distribution in these ions is ^{13}C nmr spectroscopy⁷⁻¹⁰ because of the close relationship of cmr chemical shifts to electron density.¹¹ Accordingly, we have measured cmr chemical shifts of the σ complexes resulting from the nitration and protonation of a series of hexasubstituted benzenes. Previous cmr studies of benzenium ions provide a basis for comparison.⁷⁻¹⁰

Results

Nitrobenzenium ions 1a-d were prepared by the addition of a solution of hexamethylbenzene or 1-halo-2,3,4,5,6-pentamethylbenzene in SO_2 to a vigorously stirred solution of $\text{NO}_2^+\text{BF}_4^-$ - FSO_3H - SO_2 at -78° . Tables I and II summarize the ^{13}C and ^1H nmr data for these ions, measured at -80° . Peak assignments were made on the basis of peak positions and intensities in analogy with previous studies and by observations of ^1H - ^1H , ^{13}C - ^1H , and ^{19}F - ^{13}C coupling.



The nmr data are consistent with the formation of ions **1a-d**. The cmr chemical shift at the site of nitra-

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Table I. Carbon-13 Shieldings of Nitrobenzenium and Benzenium Ions^a

Ion	C ₄	C _{3,5}	C _{2,6}	C ₁ , methylene	CH ₃ -C _{3,5}	CH ₃ -C _{2,6}	CH ₃ -C ₁	CH ₃ -C ₄
1a	205.8	142.5	181.4	98.7	15.2	20.4	23.7	27.0
1b	192.2	133.1	191.9	98.4	10.1	21.0	24.2	
	(<i>J</i> _{CF} = 331.1) ^b	(<i>J</i> _{CF} = 17.3)	(<i>J</i> _{CF} = 26.3)		(<i>J</i> _{CF} = 3.2)			
1c	197.7	142.7	184.3	99.4	16.3	21.6	24.3	
1d	200.5	145.5	181.5	99.9	19.5	21.7	24.5	
2a	191.9	139.5	193.8	57.7	14.5	23.3	20.5	23.3
2a^c	191.8	139.5	193.6	57.5	14.8	23.5	20.6	23.5
2b	187.0	129.7	202.3	57.1	9.4	23.2	20.2	
	(<i>J</i> _{CF} = 313.3) ^b	(<i>J</i> _{CF} = 17.1)	(<i>J</i> _{CF} = 23.1)		(<i>J</i> _{CF} = 4.7)			
2c	185.9 ^d	139.7	196.8	58.7	15.6	24.1	21.1	
Mes ^e	196.0	135.0	196.0	53.3				

^a $\delta(^{13}\text{C})$, ppm from TMS. ^b ^{13}C - ^{19}F coupling constants in Hz. ^c SO_2 used as solvent instead of SO_2ClF . ^d Assignment tentative, due to similar peaks from other isomers. ^e 2,4,6-Trimethylbenzenium ion from protonation of mesitylene; see ref 8.

Table II. Pmr Parameters^a for Nitrobenzenium and Benzenium Ions

Ion	CH ₃ -C ₄	CH ₃ -C _{3,5}	CH ₃ -C _{2,6}	CH ₃ -C ₁	H-C ₁
1a	2.97	2.32	2.50	1.95	
1b		2.24	2.57	2.02	
1c		2.48	2.62	2.07	
2a	3.04	2.58	2.88	1.87, d	4.30, b
				(<i>J</i> _{CH} = 7)	
2b		2.34	2.74	1.77, d	4.30, b
				(<i>J</i> _{CH} = 8)	

^a Chemical shifts in ppm from external TMS at 60 MHz. Coupling constants in Hz, d, doublet; b, broad.

tion, C₁, shows a pronounced upfield shift from that of the ring carbons in hexamethylbenzene ($\delta(^{13}\text{C})$ 132.3),¹² indicative of a change in hybridization from aromatic sp² to aliphatic sp³ at C₁. The nitro group is expected to have a deshielding effect,¹³ so the change in cmr shift at C₁ upon nitration ($\Delta\delta(^{13}\text{C}) \sim 33$) is not as great as upon protonation (*vide infra*). Cmr shifts for the ortho and para carbons, C_{2,4,6}, are substantially downfield from normal arene chemical shifts, indicating deshielding by lowering of the electron density at those positions in going to the arenium ions. The cmr shifts for C_{3,5} indicate little positive-charge development at the meta positions upon formation of the ions. The pmr spectrum of **1a** has been reported previously.⁴ Ions **1b** and **1c** have pmr spectra consisting of three singlets with peak area ratios of 2:2:1, corresponding to the *o*-CH₃, *m*-CH₃, and C₁ CH₃ groups.

The nmr spectra indicated that ions **1a**-**c** were formed exclusive of any other isomeric products.¹⁴ Nitration of 1-bromo-2,3,4,5,6-pentamethylbenzene gave a mixture of three isomeric ions in roughly equal proportions, judging by cmr peak intensities. The three ions were **1d** and the benzenium ions from nitration ortho and meta to the bromine substituent. All three isomers exhibited the same cmr shift at the site of nitration. The proper number of peaks were present to account for all the sp² hybridized carbons. Peak assignments in

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(14) The observed isomers are apparently the products at equilibrium. The nmr spectra of the reported benzenium and nitrobenzenium ions show completely reversible, temperature-dependent behavior consistent with rapid, intramolecular 1,2-shifts. When a fluorine substituent is present, no temperature dependence is observed in the nmr spectra up to -20°, presumably because the σ complex is highly stabilized by the electron-donating resonance effect of the fluorine.

the cmr spectrum could be made for **1d**, because the symmetry of the ion meant that peak intensities for nuclei in the ortho and meta positions were roughly twice as great as those for the unsymmetrical ions present in about the same amount. Specific assignments could not be made for the other peaks, except for those corresponding to carbon atoms substituted by the bromine substituent, which were upfield of similar carbons substituted by methyl groups.

Benzenium ions **2a**-**d** were formed by the addition of the appropriate hexasubstituted benzene to a rapidly stirred solution of HF-SbF₅ (1:1 molar) in SO₂ClF at -78°. Tables I and II summarize the nmr data for these ions, measured at -80°. The pmr spectrum of **2a** has been reported previously.¹⁵ Because the cmr data for nitrobenzenium ions were obtained from SO₂ solutions, the cmr spectrum of **2a** was determined from solutions in both SO₂ and SO₂ClF; no significant solvent effect was observed.

The cmr data are characteristic of benzenium ions. The cmr chemical shift for C₁ in ions **2a**-**c** is about 75 ppm upfield from the ring carbon shift in hexamethylbenzene, demonstrating the transformation from sp² to sp³ hybridization upon formation of the ion. The C₁ shift is similar to the cmr shift for the carbon at the site of protonation in other arenium ions;⁷⁻¹⁰ the previously determined cmr parameters for the 2,4,6-trimethylbenzenium ion (mesitylenium ion) are given in Table I for comparison.⁸ The C_{2,4,6} chemical shifts show the expected deshielding resulting from positive charge development ortho and para to the protonation site, while C_{3,5} chemical shifts are little different from those in neutral arenes.

The pmr data for ions **2a** and **2b** are also consistent with the formation of benzenium ions. The methyl group at C₁ in each of the ions occurs as a doublet due to coupling with the methine proton at C₁. The methine protons in **2a** and **2b** appear downfield from the methyl protons at a chemical shift typical of protonated polyalkylbenzenes.^{15d} Pmr chemical shifts could not be determined for ions **2c** and **2d** because of the presence of other isomers; however, peaks indicating protonation were present at δ 4.2-4.6 in the pmr spectra of the HF-SbF₅-SO₂ClF solutions of 1-chloro- and 1-bromo-2,3,4,5,6-pentamethylbenzene.

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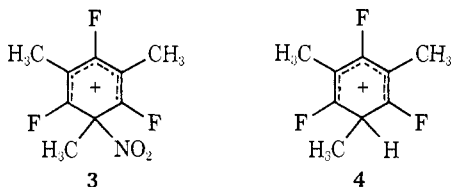
Ions **2a** and **2b** were formed free of other isomeric products. Protonation of 1-chloro-2,3,4,5,6-pentamethylbenzene gave a mixture of isomeric ions, which consisted of about 50% **2c** and about 25% each of the ions resulting from protonation ortho and meta to the chlorine substituent. The cmr spectrum of the ion mixture showed three separate peaks for the C₁ carbons (in a range of 1.4 ppm), with the peak for C₁ in **2c** at roughly twice the height of the other two. The proper number of peaks were present to account for all the ring carbons in the three isomers, but definite assignments could not be made except for ion **2c**. Protonation of 1-bromo-2,3,4,5,6-pentamethylbenzene also gave a mixture of ions. Cmr shieldings could not be determined for ion **2d** or the other isomeric ions, because no one ion dominated to the extent that absorbances could be assigned on the basis of relative intensities. In addition, a few peaks were present in the cmr spectrum, which could not be attributed to ions from protonation at the 2, 3, and 4 positions, thus indicating the presence of another product or products in minor amounts.

Discussion

The ¹³C nmr spectra of benzenium and nitrobenzenium ions show distinct differences between the two types of σ complexes. C₄ in the nitrobenzenium ions is consistently deshielded relative to C₄ in the benzenium ions, while C₂ and C₆ are consistently shielded in nitrobenzenium ions relative to benzenium ions. A small difference in chemical shifts is also seen for C₃ and C₅, with ions **1a-c** showing less shielding than ions **2a-c** at those positions. In both types of ions, C_{2,4,6} are considerably deshielded relative to the meta positions, C_{3,5}.

The same pattern of shielding differences is exhibited by the methyl carbons in ions **1a** and **2a**. The methyl group attached at C₄ is deshielded, and the C_{2,6} methyls are shielded in **1a** compared with **2a**. In addition, methyl carbons at C_{3,5} are slightly deshielded in **1a** relative to **2a**.

The pattern of deshielding at the para positions and shielding at the ortho positions in nitrobenzenium ions compared with benzenium ions is reinforced by examining the ¹⁹F chemical shifts in ions **3** and **4**, which we have previously reported. Nitration of trifluoromesitylene gave ion **3** with chemical shifts of ϕ -16.20 for the *p*-F and ϕ 42.97 for the two *o*-F.⁴ Protonation gave ion **4** with chemical shifts of ϕ 1.8 for the *p*-F and ϕ 35.8 for the two *o*-F.¹⁶ The *p*-F is deshielded, and the *o*-F's are shielded in the nitration σ complex relative to the protonation σ complex.



The observed shielding differences indicate a dissimilar distribution of electron density in the cationic pentadienyl π system of the nitrobenzenium and ben-

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zenium ions. This interpretation is based on the assumption that differences in the ¹³C chemical shifts of similarly substituted sp² hybridized carbons primarily reflect differences in electron densities associated with the carbon atoms. The total change in chemical shifts for the five carbons in the cationic π system relative to five carbons of the precursor hexamethylbenzene is very nearly the same for ion **1a** ($\Delta\delta(^{13}\text{C}) = 192.1$) and ion **2a** ($\Delta\delta(^{13}\text{C}) = 197.0$). This similarity in total shifts relative to the precursor suggests that the same amount of positive charge has been introduced into the π system in both ions. In both types of ions, most of the positive charge is located at the ortho and para positions. However, in nitrobenzenium ions, relative to benzenium ions, the electron distribution is apparently polarized toward the nitro group, resulting in a gain in electron density and more shielding at the ortho positions and a loss of electron density and deshielding at the para position and, to a lesser extent, at the meta positions. The same interpretation can be made on the basis of the less direct evidence of the methyl carbon shieldings in **1a** and **2a** and the fluorine shieldings in **3** and **4**.

The chemical significance of a difference in the charge-distribution pattern is evident from the observations of isomeric benzenium and nitrobenzenium ions. If the charge distribution patterns were identical in both types of σ complexes, then the two reactions should give the same proportion of isomers at equilibrium for each substrate, according to a theoretical substituent-effect model in which the field-inductive and resonance effects of substituents are predictable on the basis of the charge-distribution pattern.^{5e} More charge is delocalized to the para position in a nitrobenzenium ion than in a benzenium ion; hence a substituent at the para position should have a greater effect on the stability of the charged system in a nitrobenzenium ion than in a benzenium ion. This expectation is borne out by our experiments, in which nitration of 1-chloro-2,3,4,5,6-pentamethylbenzene gave the single isomeric ion, **1c**, while the protonation product mixture consisted of three isomeric ions. The electron-donating resonance effect of the para-Cl substituent is clearly more important in the nitrobenzenium ion. Both nitration and protonation gave mixtures of isomeric ions when the substrate was 1-bromo-2,3,4,5,6-pentamethylbenzene, but unfortunately the proportions of the isomers could not be determined in the protonation-product mixture.

The charge-distribution pattern is expected to be a contributing factor in determining kinetic substituent effects in electrophilic aromatic substitution reactions for which σ complex formation is the rate-determining step. Nitration and other substitutions involving strongly electrophilic reagents can proceed through initial π -complex-like transition states of highest energy,¹⁷ followed by σ complex formation giving separate ionic intermediates for each isomer in which the charge distribution differs significantly from the simple benzenium ion. For instance, the ¹⁹F chemical shifts of the σ complex formed in the chlorination of trifluoromesitylene suggest that the electron distribution may be even more polarized than in the nitrobenzenium ions, since the *p*-F is deshielded and the *o*-F's are shielded relative to the corresponding fluorines in ion **3**.⁴ We have previously demonstrated the dependence of isomer ratios in elec-

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trophilic substitution reactions on the position nature of the transition states;¹⁷ the present work indicates the potential importance of the electron-distribution pattern within the σ complex type of transition state.

Experimental Section

Materials. Pentamethylbenzene and hexamethylbenzene were commercially available in high purity and were used without further purification. 1-Chloro-2,3,4,5,6-pentamethylbenzene was prepared by chlorination of pentamethylbenzene in nitromethane at 0°, using chlorine catalyzed with ZnCl₂, mp 154.5° (lit.¹⁸ mp 155°). 1-Bromo-2,3,4,5,6-pentamethylbenzene was prepared by bromination of pentamethylbenzene with bromine in acetic acid at 25°, mp 161.2° (lit.¹⁹ mp 160–162°). 1-Fluoro-2,3,4,5,6-pentamethylbenzene was prepared from 2,3,4,5,6-pentamethylaniline by the Schieman reaction, mp 72.5° (lit.²⁰ mp 59°). The pentamethylaniline was obtained by reduction of 1-nitro-2,3,4,5,6-pentamethyl-

benzene prepared by nitration of pentamethylbenzene with the nitrating agent described by Olah and Lin.²¹

Nitronium tetrafluoroborate was prepared according to the procedure of Olah and Kuhn²² or the modified procedure introduced by Kuhn.²³ Antimony pentafluoride was triply distilled before preparation of the (1:1 *M*) HF-SbF₅ solution. Fluorosulfuric acid was doubly distilled before use.

Nmr Study of Ions. The benzenium and nitrobenzenium ions were prepared as described in the text and then were transferred by precooled pipets, or by direct pouring, to precooled nmr tubes. Proton spectra were obtained with a Varian Associates Model A56/60 spectrometer equipped with a variable-temperature probe. External TMS (capillary tube) was used as reference. Carbon-13 spectra were obtained on a Varian Associates Model XL-100 spectrometer, using ¹³C-enriched TMS (capillary tube) as reference.

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Dynamical Study of Mechanistic Details in Organic Reactions. I. A Two-Step Study of Isomerizations of Cyclopropane-Type Molecules

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Abstract: A brief explanation is presented for the results of experimental and theoretical investigations of geometrical and optical isomerizations of substituted cyclopropanes. In particular, the results of *ab initio* quantum mechanical calculations of the potential-energy surfaces for these reactions (notably in geometries of the transition states and suitability of static reaction paths) have shown the important fact that the reactions proceed roughly in sequence: ring opening, rotation of the terminal groups in the diradical species, and ring closure. In connection with these results, a preliminary dynamical study of the mechanism has been carried out in which the coupled rotations of the two terminal methylene groups on the trimethylene diradical and then the symmetric ring closure (or ring opening) of trimethylene (or cyclopropane) to cyclopropane (or trimethylene) are studied separately. The rotation surface is rather flat. Consequently, the possible trajectories are quite diverse, and only a few of them follow the previously proposed static-reaction paths. On the contrary, for ring closure the surface is very steep and the actual trajectories appear to deviate only slightly from the static path. The influence of different substituents on the trajectories is briefly investigated.

The theoretical investigation of a chemical reaction is essentially a two-step study. The first step is *static*. It consists in computing the potential energy of the reaction system as a function of the different geometrical parameters. Hence, some information on the reaction mechanism can be obtained, such as (i) the *minimum-energy path* to go from reactants to products and consequently the shape of the *reaction coordinate*; (ii) the difference between the calculated energies for the reactants and for the system at the *transition state*, which is compared to the *activation energy* of the reaction as a first approximation. In recent years, the growth of scientific computers as well as the realization of fast programs for quantum mechanical calculations has made the extensive investigation of potential-energy

surfaces possible, for many organic reactions involving rather complex molecules.

The second step is of a *dynamical* nature. It consists in obtaining dynamical trajectories on the potential surface. Classical mechanics is supposed to describe correctly the atomic motion. In certain cases, such a study, at the end, allows the obtaining of the rate constant of the reaction. This was done for the first time by Karplus, Porter, and Sharma for the exchange reaction $H + H_2 \rightarrow H_2 + H$.² In other respects, the dynamical study brings new information on the mechanism of the reaction. Thus, Polanyi and Wong³ studied the relative influence of initial translational

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