Aromatic Hydrogen Isotope Effects in Reactions of Benzenediazonium Salts

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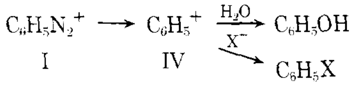
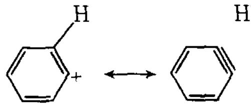
Abstract: Kinetic secondary deuterium isotope effects, k_H/k_D, are 1.22 ± 0.01 for each ortho position, 1.08 ± 0.01 for each meta position, and 1.02 for the para position in dediazoniations of benzenediazonium fluoborate in aqueous H_2SO_4, CH_3CO_2H, or CH_2Cl_2 solutions at 25°. These ortho effects are the largest secondary aromatic hydrogen isotope effects yet observed, are comparable in magnitude to those observed for β deuterium in tertiary aliphatic ester solvolyses, and strongly indicate rate-determining formation of phenyl cation. A vibrational analysis of benzenediazonium ion indicates that the isotope effect cannot arise solely from relief of strain on the ortho hydrogens but may result from diminishing of the force constants of all the vibrations of the C–H bonds in the ortho, meta, and para positions by 10, 4, and 1%, respectively. This is attributed to substantial hyperconjugative delocalization of positive charge onto ortho and meta hydrogens in the transition state. The slightly lower isotope effect of 1.48 ± 0.02 for 3,5-dimethylbenzenediazonium-*2,4,6-d*$_3$ *vs.* 1.52 ± 0.02 for benzenediazonium-*2,4,6-d*$_3$ confirms that hyperconjugation rather than relief of strain is the source of the kinetic isotope effect. Molecular orbital calculations by the INDO method predict the ground state of phenyl cation to be a singlet, essentially linear at C_1, with positive charge partially distributed throughout the molecule, especially at the ortho hydrogens.

In the preceding paper,[3] we presented evidence that the mechanism of reactions of benzenediazonium ion (I) in solution in the absence of strong bases, reducing agents, or light is slow decomposition to form singlet cation IV which then reacts rapidly with the solvent or other nucleophiles present.



$$\underset{\text{I}}{C_6H_5N_2^+} \longrightarrow \underset{\text{IV}}{C_6H_5^+} \begin{array}{l} \xrightarrow{H_2O} C_6H_5OH \\ \xrightarrow{X^-} C_6H_5X \end{array}$$

Delocalization of the positive charge of IV or its immediately preceding transition state I* into the ring is not possible since the vacant orbital lies in the plane of the ring. The only means of stabilization available, therefore, is hyperconjugation with the ortho hydrogens and to lesser extents with the meta and para hydrogens.[5] Since hyperconjugation should strongly stabilize such an otherwise localized carbonium ion, large secondary deuterium isotope effects would be expected if the ortho hydrogens were replaced with deuterium. Investigations by Lewis and Boozer demonstrated that β-deuterium isotope effects k_H/k_D of 1.1–1.3 are observed in SN1 solvolyses.[6a] The kinetic isotope effect is highly dependent on conformation, with maximum values arising when the angle between the vacant orbital being produced and the C–H bond is 0 or 180° [6b] and values near zero or slightly inverse when the angle is 90°.[6c] In the *cis-2-d*-cyclopentyl tosylate system (k_H/k_D = 1.20),[6b] the angle begins near 0° but changes to ~60° in the carbonium ion. The solvolysis of I is the first example of a system where the dihedral angle remains at 0° throughout formation of the carbonium ion. A near-maximum isotope effect of 1.2–1.3 would be expected.



Results and Discussion

Ring-Hydrogen Isotope Effects. Table I gives rate constants and isotope effects for dediazoniation of variously deuterated forms of I. They are all consistent with constant isotope effects (k_H/k_D) of 1.22 ± 0.01 for each ortho hydrogen atom, 1.08 ± 0.01 for each meta hydrogen, and 1.02 ± 0.01 for the para hydrogen. For example, the observed k_H/k_D for I-*2,4,6-d*$_3$ is 1.52 ± 0.03, in agreement with $(1.22)^2(1.02) = 1.52$; the observed 1.19 ± 0.02 for I-*3,5-d*$_2$ agrees with $(1.08)^2 = 1.17$; and the observed 1.74 ± 0.05 for I-*2,3,4,5,6-d*$_5$ agrees with $(1.22)^2(1.08)^2(1.02) = 1.77$. The 31 kinetic runs in aqueous H_2SO_4 are listed in chronological order. The constancy of the isotope effects even into the nonaqueous solvents is a further indication that the same mechanism is acting in methylene chloride or acetic acid as in water.

The 1.22 value for the isotope effect per ortho deuterium is comparable to the largest values per β deuterium observed in SN1 solvolyses.[6] It is larger than the 1.10 per β-D observed in solvolyses of *tert*-butyl chloride,[7a,c] where hyperconjugation is hindered by free rotation of the methyl groups,[8] and considerably above the 1.07 per β-D observed for solvolysis of α-phenyl-β-d_3 ethyl chloride,[7b] because that gives a benzyl-type cation already stabilized by distribution of the positive charge by conventional resonance. The isotope effect in the meta position (1.08 per D) is smaller than that in the ortho position but still comparable to those in the *tert*-butyl chloride and α-phenylethyl chloride solvolyses. The isotope effect in the para position is small, just barely larger than the experimental error. These isotope effects offer strong support for the phenyl cationic nature of the solvolytic transition-state structure and against any triplet-type structure with the charge resident in the π cloud. As will be shown in the next section, k_H/k_D values no greater than 1.01–1.02 would be expected if the force constants of the C–H bonds were not altered significantly in the transition state I*, either by hyperconjugation or by relief of strain.

The Origin of the Ring-Hydrogen Isotope Effects. Several factors may be considered to affect the frequencies of vibrations involving the ring hydrogens and hence to affect the kinetic isotope effect: (1) hyperconjugative stabilization of the positive charge in I* which results in decreased stretching and bending C–H force constants; (2) nonbonded interactions between the N_2 group and the ring protons, which would be decreased in I* relative to I, especially those associated with the in-plane bending vibration of the ortho hydrogens; (3) decoupling of the ring C–H vibrations with those of the C–N vibrations as the C–N bond is being broken.

In order to estimate the importance of these various ef-

Table I. Ring-Hydrogen Isotope Effects in Dediazoniation of Benzenediazonium Fluoborate at 25°

Solvent	Deuteration	$10^4[ArN_2^+]$, M	10^5k_1, sec^{-1}	k_H/k_D
0.10 M H_2SO_4	None	7.37	4.61 ± 0.04	
0.10 M H_2SO_4	*2,4,6-*d_3	2.23	3.07 ± 0.06	1.50
1.0 M H_2SO_4	None	8.14	4.42 ± 0.02	
1.0 M H_2SO_4	*2,4,6-*d_3	9.20	2.92 ± 0.01	1.51
1.0 M H_2SO_4	None	8.41	4.16 ± 0.01	
1.0 M H_2SO_4	*4-d*	9.02	4.05 ± 0.01	1.03
1.0 M H_2SO_4	*2,4,6-*d_3	8.53	2.70 ± 0.01	1.54
0.86 M H_2SO_4[b]	None	8.10	4.29 ± 0.01	
0.86 M H_2SO_4[b]	*2,3,4,5,6-*d_5	7.93	2.39 ± 0.03	1.79
0.86 M H_2SO_4[b]	None	8.26	4.41 ± 0.01	
0.86 M H_2SO_4[b]	*2,4,6-*d_3	8.02	2.91 ± 0.02	1.52
0.86 M H_2SO_4[b]	None	7.93	4.21 ± 0.01	
0.86 M H_2SO_4[b]	*3,5-*d_2	8.12	3.55 ± 0.01	1.19
0.86 M H_2SO_4[b,c]	None	8.32	4.79 ± 0.01	
0.86 M H_2SO_4[b,c,d]	*4-d*	8.30	4.57 ± 0.07	1.05
0.86 M H_2SO_4[b]	None	8.22	4.37 ± 0.04	
0.86 M H_2SO_4[b]	*3,5-*d_2	8.19	3.71 ± 0.03	1.18
0.86 M H_2SO_4[b]	None	7.79	4.32 ± 0.03	
0.86 M H_2SO_4[b]	*2-d*	8.21	3.57 ± 0.01	1.21
0.86 M H_2SO_4[b]	None	8.36	4.48 ± 0.02	
0.86 M H_2SO_4[b]	*2-d*	8.01	3.64 ± 0.03	1.23
0.86 M H_2SO_4[b]	None	7.98	4.40 ± 0.02	
0.86 M H_2SO_4[b,e]	*4-d*	7.95	4.32 ± 0.02	1.02
0.86 M H_2SO_4[b]	None	8.21	4.33 ± 0.02	
0.86 M H_2SO_4[b]	*4-d*	8.26	4.25 ± 0.02	1.02
0.86 M H_2SO_4[b]	None	7.99	4.39 ± 0.01	
0.86 M H_2SO_4[b]	*2,3,4,5,6-*d_5	8.31	2.65 ± 0.02	1.66
0.86 M H_2SO_4[b]	*2,3,4,5,6-*d_5	7.97	2.49 ± 0.02	1.76
0.86 M H_2SO_4[b]	None	7.89	4.45 ± 0.02	
0.86 M H_2SO_4[b]	*2,4,6-*d_3	8.01	2.97 ± 0.07	1.50
0.86 M H_2SO_4[b]	*2,4,6-*d_3	8.23	2.87 ± 0.02	1.55
CH_2Cl_2[a]	None	4.31	2.24 ± 0.03	
CH_2Cl_2[a]	*2,4,6-*d_3	4.99	1.42 ± 0.01	1.58
CH_3CO_2H	None	6.86	2.21 ± 0.01	
CH_3CO_2H	*4-d*	6.72	2.17 ± 0.01	1.02
CH_3CO_2H	*2,4,6-*d_3	8.09	1.44 ± 0.01	1.53

[a] At 25.24°. [b] Reference 2b. [c] At 25.10°. [d] Open-system preparation. [e] Closed-system preparation.

fects, vibrational analyses of I and IV were performed by the Wilson FG method.[9] The computer program was a version of the Wolfsberg-Schachtschneider program,[10] obtained from W. H. Saunders, Jr.,[11] and was modified by use of the DGIVEN program (QCEP67.3) for matrix diagonalization and by adaptation for use on the IBM 360 Model 65 computer. A 13-atom model of C_{2v} symmetry was employed having a valence-bond force field including all normal modes of the molecule. The geometry of the ring was taken to be that of benzene. The N-N bond length was taken to be 1.11 Å, and the C-N bond length was taken to be 1.42 Å[12] in the ground state and 1.42 or 1.74 Å in the transition state.

Valence-bond force constants for the vibrations of the aromatic ring were derived from those of benzene.[13] The force constants for the vibrations involving the nitrogen atoms were approximated from literature values[9] or were adjusted to approximately fit observed spectra of I. For ground-state calculations, the force field was either diagonal or contained the interaction force constants calculated for benzene.[13] For transition-state models, the force constants of all vibrations involving the C-N bond were varied proportionately. The reaction coordinate was generated by inclusion of appropriate interaction force constants between the C-N and N-N stretching vibrations and/or between the C-N and 1,2-C-C or 1,6-C-C stretching vibrations such that the reaction coordinate frequency was between 0 and $50i$ cm^{-1}.

For models having diagonal force fields in the ground state in which the force constants for vibrations involving hydrogens are not varied from ground-state values, the calculated isotope effects are less than 1.01 per D for the ortho position and less than 1.004 per D for meta and para positions. Inclusion of interaction force constants of the magnitude calculated for benzene[13] gives similar results. Previous calculations[10b] for substitution reactions using simple force fields and no force constant changes at hydrogen also gave kinetic isotope effects generally less than 1.005 per D for positions β to the reaction center and somewhat less for more remote positions.

Thus these calculations clearly indicate that the large observed ring deuterium isotope effects can be accounted for only by changes in force constants at those atoms. To account for the observed ortho deuterium isotope effect by reduction of only the force constant of the in-plane wagging motion of the ortho C-H bonds, its value in the transition state must be about half of its ground-state value. Such a large required decrease seems to rule out relief of nonbonded interactions between the ortho hydrogens and the departing nitrogen as the sole explanation for the observed isotope effect. The complexity of the model and the great uncertainty in the nature of both ground-state and transition-state force fields rule out quantitative analysis of the observed isotope effects. Nevertheless, the observed kinetic isotope effects can be reproduced by reduction of all force constants for vibrations involving the ortho, meta, and para hydrogens by 10, 4, and 1%, respectively. Such changes in force constants are in qualitative accord with the predictions of molecular orbital calculations (see below) that the positive charge in IV is partially delocalized onto the ring hydrogens, especially those in the ortho position. Thus the isotope effect can be attributed to substantial hyperconjugative stabilization in the transition state I* immediately preceding IV.

An experimental distinction between hyperconjugation and relief of nonbonded interactions as the origin of the isotope effect can be made by introduction of methyl substitu-

Table II. Ring-Hydrogen Isotope Effects in Dediazoniation of 3,5-Dimethylbenzenediazonium Salt in 4.00 M H_2SO_4 at 25°

Deuteration	$10^3[ArN_2^+]$, M	10^4k_1, sec^{-1}	k_H/k_D
None	2.00	4.40 ± 0.03	
None	2.00	4.38 ± 0.03	
None	1.00	4.23 ± 0.05	
2,4,6-d_3	1.00	2.82 ± 0.04	1.50
None	1.00	4.33 ± 0.07	
2,4,6-d_3	1.00	2.97 ± 0.11	1.46

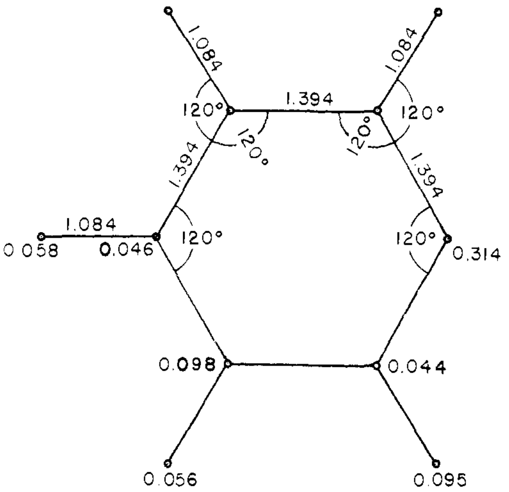


Figure 1. Charges on various atoms of a singlet phenyl cation having the same bond angles and bond lengths as benzene, as calculated by the INDO molecular orbital method.

ents into the meta positions of I. If nonbonded (steric) interactions were important, the buttressing by meta-methyl substituents should increase the ortho-hydrogen kinetic isotope effect. Alternatively, if hyperconjugation in I* were the dominant effect, the introduction of methyl groups might actually decrease the isotope effect since electron donation from the methyl groups should slightly lessen the need for and therefore the magnitude of hyperconjugation in I*. The observation (Table II) that meta-methyl substitution decreases the kinetic isotope effect slightly (1.48 ± 0.02 *vs.* 1.52 ± 0.02 for the hydrogen analog) excludes the nonbonded or steric explanation and implies that the origin of the isotope effect is lowering of ortho C-H bond force constants by hyperconjugation.

MO Calculations for Phenyl Cation. Molecular orbital calculations by Extended Hückel[14] and INDO methods[15,16] indicate the ground state of phenyl cation to be a singlet with substantial delocalization of the positive charge throughout the molecule, especially onto the ortho hydrogens. The theoretical structure of minimum energy calculated by the INDO method[16] has substantially shortened C1-C2 and C1-C6 bonds and an essentially linear bond at C1, in accord with calculations for analogous vinyl cations. The calculated in-plane bending force constant for ortho C-H bonds is 65% of that for meta C-H bonds.[16] These calculations thus predict that the formation of IV should be accompanied by a substantial decrease in force constants at the ortho C-H bonds, in accord with the large kinetic isotope effects observed for the ortho hydrogens.

Our semiempirical self-consistent-field molecular orbital calculations by the INDO method utilized a computer program, obtained from K. Morokuma, similar to program QCEP141, giving energies agreeing with that program generally within the truncation error. The criteria for convergence were agreement within 10^{-4} for electron densities and agreement within 10^{-5} hartrees for electronic energy between successive iterations. Calculations by this method for benzene give a C-C bond length of 1.387 Å, in agreement with the observed value of 1.394 Å; reduction in symmetry to D_{3h} results in an increase in energy. Results of calculations for phenyl cation having the same bond lengths and bond angles as benzene are shown in Figure 1. The positive charge is mostly in the in-plane orbital of C1, with net charges primarily at C1 (0.314), C3 and C5 (0.098), and H2 and H6 (0.095). The π-bond orders vary little from that of benzene (0.660-0.671). The highest occupied orbital is a σ orbital composed primarily of the C-H bonds at positions 2, 3, 5, and 6 and possessing two nodal planes.

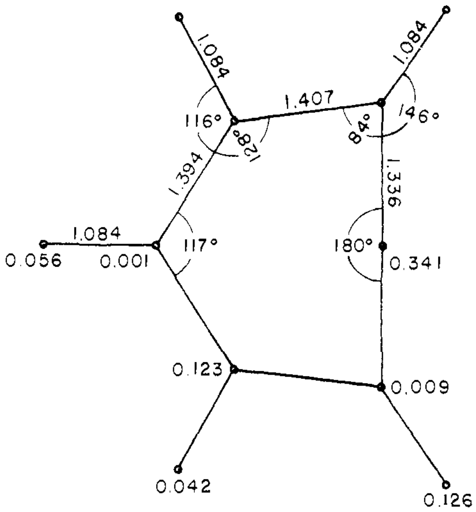


Figure 2. Charges on various atoms of the best structure for singlet phenyl cation, as calculated by the INDO molecular orbital method.

The energy of phenyl cation was minimized by systematic variation of all geometric parameters, subject to maintenance of C_{2v} symmetry and constant C-H bond length. After five iterations, the structure had converged to within 0.001 Å for bond lengths and 0.5° for bond angles to give the structure shown in Figure 2. The resultant stabilization in energy caused by geometric changes is 94 kcal mol^{-1} (4.05 eV), which is substantially larger than the stabilization observed in the optimization of the structure of benzyne (41 kcal mol^{-1}). The energy of the triplet state of this structure is 146 kcal mol^{-1} above that of the singlet, which indicates that the ground state is a singlet, in accord with the experimental observations.[3]

The molecular orbitals for the structure shown in Figure 2 are generally similar to those for the structure in Figure 1, except that the energies of the two highest occupied π orbitals are reversed in order. The π-bond order varies from 0.636 for the C2-C3 and C5-C6 bonds to 0.671 for the C1-C2 bonds to 0.676 for the C3-C4 and C4-C5 bonds. The positive charge is localized to a greater extent on C1, C3, C5, H2, and H6 atoms than in the structure of Figure 1. The most remarkable feature about this structure is the essentially linear bond at C1, which is accompanied by a substantial shortening of the C1-C2 and C1-C6 bonds. In general, INDO calculations have proved quite satisfactory for predicting bond angles in stable molecules[17] and have given satisfactory bond lengths except perhaps for atoms with unshared pairs of electrons. However, INDO calculations have not been adequately tested for charged molecules. Nevertheless, these calculations provide a reasonable indication of delocalization of the charge onto the ortho hydrogens, in accord with the large kinetic isotope effect associated with this position.

Experimental Section

For benzenediazonium (I) fluoborate and solvents, *cf.* ref 3.

Aniline-*2,4,6,N,N-d*$_5$.[18] $C_6H_5NH_3Cl$, Eastman pure, 6.0 g (0.046 mol) in 30 ml of D_2O was refluxed 24 hr under N_2. The D_2O was distilled at 20 mm until the solid residue was dry. The procedure was repeated twice with fresh 20-ml portions of 99.7% D_2O (General Dynamics). Then the solution was neutralized with anhydrous Na_2CO_3 and extracted with three 15-ml portions of ether (Et_2O). The Et_2O was distilled, 0.1 g of Zn powder added, and the aniline was distilled, yield 3.0 g (70%): bp 181–183°; λ_{max} (EtOH) 235 nm (ϵ 8400), 285.5 (1500); nmr (20% in CCl_4) s at δ 6.75; ir ν_{max} (CCl_4) 3340 cm^{-1} (N–H stretch), 3060 (C–H stretch), 2600, 2540, 2490, 2440 (N–D stretch), 2360 (C–D stretch), 1850 (weak), 1600, 1480, 1310, 1290, 1260, 1240, 1080, 960, 920, 849, 838, 680, and 550 cm^{-1}. Analysis by glc on a 6-ft 5% silicone XE-60 Chromosorb W S60-80 column at 120° and 20 psi of He showed no volatile impurities except 1–2% Et_2O.

I-*2,4,6-d*$_3$ BF_4^-. Aniline-*2,4,6,N,N-d*$_5$, 2.0 g (0.02 mol), in 12 ml of 48% HBF_4 was diazotized with 1.5 g (0.022 mol) of $NaNO_2$. The salt was recrystallized once from 5% HBF_4 and twice from $(CH_3)_2CO$–$HCCl_3$, mp 119–121° dec; ν_{max} (KBr) 3050 cm^{-1} (C–H stretch), 2295 (N–N stretch), 2270 (C–D stretch); nmr s at δ_{TMS} (20% in CH_3CN) 8.04. The purity as determined by coupling with C_6H_5OH was 100 ± 1%. Fluorobenzene-*2,4,6-d*$_3$ isolated from its decomposition was examined by mass spectroscopy. At a plate voltage of 40 V, only three peaks at *m/e* 98, 99, and 100 appear. After correction for the 6.6% natural abundance of ^{13}C, 0.8% d_2, 98.6% d_3, and 0.6% d_4 were calculated from relative intensities of the three peaks.

Aniline-*4-d*. Anhydrous Et_2O was passed through a 50-cm column of Dow 812 desiccant resin (K salt of sulfonated styrene–divinylbenzene copolymer) immediately before use. Freshly distilled *p*-bromotoluene, 42.75 g (0.25 mol, bp 182°), in 200 ml of dry Et_2O was added in small portions with stirring to 50 ml of dry Et_2O and 6.0 g (0.25 mol) of Mg strips. Stirring was continued for 1 hr longer; then 30 ml of 50% D_2SO_4 in D_2O was added in small portions and the mixture stirred for 1 hr, during which all solid dissolved. H_2O, 100 ml, was added in small portions and the aqueous layer extracted with three 10-ml portions of Et_2O and discarded. The combined Et_2O layers were dried over Drierite and distilled through a 60-cm column packed with glass helices, total yield of toluene-*4-d*, 21.5 g (93%), bp 105–110°. Complete ir and nmr data were given in ref 2a and 2b; nmr showed the CH_3 at δ 1.63 and the ring at δ 6.53 with areas 3.00/4.20, indicating 0.80 ± 0.05 D.

Toluene-*4-d* (9.3 g, 0.10 mol), $KMnO_4$ (40 g, 0.25 mol), reagent KOH (13.0 g, 0.23 mol), and water (500 ml) were refluxed for 5 hr in a 1-l. three-necked flask fitted with a mechanical stirrer. When no more oily droplets remained, the solution was cooled and the precipitate of MnO_2 dissolved by addition of reagent Na_2SO_3. Benzoic-*4-d* acid was obtained on acidification with H_2SO_4, 7.0 g (57%), mp 118–119°; in its ir spectrum, peaks for benzoic acid at 1460, 1075, 710, and 685 cm^{-1} were missing, and new peaks appeared at 880, 715, 700, and 615 cm^{-1}.

Benzoic-*4-d* acid (7.0 g, 0.057 mol) and $SOCl_2$ (35 ml of Eastman pure) were refluxed 30 min. The solution was poured slowly into 120 ml of 15 *M* aqueous NH_3 at 0°. The solution was filtered, then extracted with Et_2O. Acidification of the NH_3 solution and extraction with Et_2O yielded 1.0 g of benzoic-*4-d* acid. The former extracts gave 3.5 g (51%) of benzamide-*4-d*, mp 125°: ir ν_{max} (KBr) d 1425, 1400 cm^{-1} *vs.* s 1400 cm^{-1} for benzamide, no peak at 920 cm^{-1}, but new peaks at 872, 705, and 614 cm^{-1}.

Benzamide-*4-d* (3.0 g, 0.025 mol) was dissolved in a solution of KOH (4.3 g, 0.78 mol) and Br_2 (4.50 g, 0.028 mol) in 40 ml of H_2O at 0°. Additional KOH (5.6 g, 0.10 mol) was added, and the solution was heated at 75° for 45 min, cooled, and extracted with Et_2O. The Et_2O solution was dried over Drierite and distilled from 0.1 g of Zn powder. After all the Et_2O had distilled, the aniline distilled at 20 mm, yield 1.6 g (72%). Analysis of aniline-*4-d* by glc on a 5% XE-60 on Chromosorb W S60-80 column at 120° and 20 psi of He showed 1–2% Et_2O as the major impurity. Ir ν_{max} (10% in CCl_4) new peaks (not in aniline) at 2305 and 2280 cm^{-1} (C–D stretch), 1445, 840, and 600 cm^{-1}; nmr δ_{TMS} (20% in CCl_4) br 6.2, br 6.75, s 3.15, ratio of aromatic peaks/NH_2 group was 4.1:2.0; uv λ_{max} (EtOH) 235 nm (ϵ 8500), 286.5 (1600), same as aniline.

I-*4-d* BF_4^-. Aniline-*4-d* (0.75 g, 0.008 mol) was dissolved in 5.5 ml of 48% HBF_4 and diazotized by dropwise addition of 0.60 g (0.0087 mol) of $NaNO_2$ in 2.0 ml of H_2O. The salt was recrystallized from 5% HBF_4 and twice from $(CH_3)_2CO$–$CHCl_3$, yield 0.150 g (10%), mp 119° dec; ir similar to that of I BF_4^- except for new peaks at 870 and 610 cm^{-1}. The mass spectrum of fluorobenzene produced by pyrolysis showed 16.5% d_0, 83.1% d_1, 0.4% d_2, and less than 0.2% d_3 or higher.

I-*4-d* BF_4^- and the other diazonium salts studied in 0.86 *M* H_2SO_4 were prepared by two modifications of literature procedures[19] for replacing Li by D. The first procedure used an open system under a N_2 atmosphere, in a 100-ml three-necked round-bottomed flask fitted with a reflux condenser with $CaCl_2$ drying tube, a N_2 inlet through a no-air rubber stopper, and an equalizing dropping funnel containing the bromoaniline in Et_2O. *n*-Butyllithium was stirred by a magnetic stirring bar and cooled during the addition of the bromoaniline. The second procedure used a closed evacuated 50-ml centrifuge tube fitted with a no-air rubber stopper and magnetic stirring bar. A 10-ml syringe was used to introduce the *n*-butyllithium and bromoaniline solutions.

In the open-system procedure, 8.0 g (47 mol) of *p*-$BrC_6H_4NH_2$ [recrystallized from EtOH, dried 2 hr at 40° (1 mm), mp 66°] in 10 ml of anhydrous Et_2O was added dropwise through the dropping funnel to 70 ml (170 mmol) of *n*-C_4H_9Li in hexane. During addition, the solution was kept at −20° with constant stirring. The bright yellow precipitate of the aryllithium compound first appeared after 15–40 min, and stirring was continued at 25° for 2 hr more. The precipitate was washed thrice with dry Et_2O, which was then withdrawn through the no-air stopper by hypodermic syringe. Deuteration was effected with 5.0 ml (270 mmol) of D_2O, added dropwise through the no-air stopper. The mixture was refluxed for 1 hr. The LiOH was filtered and washed several times with Et_2O, and the washings and filtrate were distilled through a Vigreux column. The main fraction of aniline-*4,N,N-d*$_3$ (6.23 g, 78%), bp 175–178°, was immediately diazotized as above. Recrystallization and drying yielded 5.43 g (44%), mp 118–120° dec. The mass spectrum of fluorobenzene produced by pyrolysis showed 37.2% d_0, 62.8% d_1, and 0.0% d_2.

Anal. Calcd for $C_6H_4DN_2BF_4$: C, 37.38; H, 3.15; N, 14.52. Found: C, 37.12; H, 3.02; N, 14.22.

A second sample was prepared by the closed, evacuated system. To 20 ml (48 mmol) of *n*-C_4H_9Li in hexane was added 2.0 g (12 mmol) of vacuum-dried *p*-$BrC_6H_4NH_2$ dissolved in dry Et_2O. The yellow precipitate was washed thrice with Et_2O with interspersed centrifuging and allowed to react with 3.0 ml (162 mmol) of D_2O. The deuterated I BF_4^- was then prepared as above, yield 1.48 g (37%), mp 119–121° dec. The mass spectrum of fluorobenzene from pyrolysis showed 17.5% d_0, 82.0% d_1, and 0.5% d_2.

Anal. Calcd for $C_6H_4DN_2BF_4$: C, 37.38; H, 3.15; N, 14.52. Found: C, 37.33; H, 3.23; N, 14.62.

I-*2-d*$_1$ BF_4^-. The open-system procedure was used. *o*-$BrC_6H_4NH_2$ [recrystallized from EtOH, dried 2 hr at 25° (1 mm), mp 32°], 1.00 g (5.9 mmol), in 8 ml of dry Et_2O was added dropwise to 13 ml (31 mmol) of *n*-C_4H_9Li solution at 0° in a 50-ml three-necked flask. The precipitate was washed with Et_2O and hydrolyzed with 1.0 ml (54 mmol) of D_2O. The *o*-$DC_6H_4ND_2$ was worked up as above and immediately diazotized to yield 0.53 g (27%) of white needles, mp 119.5–121° dec. The mass spectrum of fluorobenzene produced by pyrolysis showed 12.3% d_0, 84.0% d_1, and 3.7% d_2.

Anal. Calcd for $C_6H_4DN_2BF_4$: C, 37.38; H, 3.15; H, 14.52. Found: C, 37.20; H, 3.28; N, 14.44.

I-*2,3,4,5,6-d*$_5$ BF_4^-. The preparation was based on the Pt-catalyzed exchange of aromatic compounds with D_2O.[20] D_2 gas, prepared from dilute D_2SO_4 and Zn in D_2O with reagent $CuSO_4$ as catalyst, was bubbled through a mixture of 350 mg of PtO_2 in 3.5 ml of D_2O until all the oxide had been converted to Pt black (D_2). A mixture of 4.00 g (40 mmol) of aniline-*2,4,6,N,N-d*$_5$, 22.00 g (1.1 mol) of D_2O, and 350 mg of the Pt was shaken in a sealed, evacuated tube at 130° for 72 hr. The tube was cooled and opened, and 10 ml of Et_2O was added. The mixture was centrifuged to remove Pt, and two 3-ml portions of Et_2O were used to wash the Pt. The combined Et_2O was extracted with two 5-ml portions of dilute NaOH to remove traces of C_6H_5OH, dried, and distilled through a Vigreux column to give 2.76 g (69%) of aniline-*2,3,4,5,6,N,N-d*$_7$, bp 174–179°. Nmr showed that 75% was aniline-*2,3,4,5,6,N,N-d*$_7$ and 25% aniline-*2,4,6,N,N-d*$_5$. The same procedure was therefore repeated with 1.76 g (18 mmol) of the d_7–d_5 mixture, 10.0 g (0.5

mol) of D_2O, and 0.20 g of the Pt catalyst: bp 180–183°, yield 1.32 g (75%), with an nmr now showing less than 10% of d_5. This aniline-d_7 (1.00 g, 0.01 mol) was diazotized by the previous procedure to yield 0.520 g (26%), mp 118.5–120° dec. The mass spectrum of fluorobenzene from pyrolysis showed 0.0% d_0, d_1, and d_2, 3.5% d_3, 9.4% d_4, and 87.1% d_5.

Anal. Calcd for $C_6D_5N_2BF_4$: C, 36.61; N, 14.22. Found: C, 36.63; N, 14.31.

I-*3,5-d*$_2$ BF$_4^-$. Aniline-d_7, 1.23 g (0.0132 mol), was added to 1.5 g (0.015 mol) of 37% HCl, and the resulting HCl salt was equilibrated with three 70-ml portions of distilled water, isolated, and purified as described for aniline-*2,4,6*-d_3 above to yield 0.892 g (72%): bp 179–182°; nmr singlets δ_{TMS} (20% in CC_4) at 3.2 (2.05, NH), 5.9 (1.1, CH), and 6.8 (1.9, CH). Diazotization of 0.75 g yielded 0.63 g (42%), mp 119–121°, ir 890 cm^{-1} but no peaks from 880 to 700 cm^{-1}. The mass spectrum of fluorobenzene from pyrolysis showed 0.0% d_0, 4.1% d_1, 95.9% d_2, and 0.0% d_3.

Anal. Calcd for $C_6H_3D_2N_2BF_4$: C, 37.12; H, 3.64; N, 14.42. Found: C, 37.37; H, 3.74; N, 14.28.

3,5-Dimethylbenzenediazonium Salts. 3,5-Dimethylaniline, Eastman pure, was distilled from Zn dust, bp 221–222°. Glc on a 4-ft Apiezon L column at 210° showed only a single peak. 3,5-Dimethylaniline, 3.0 g (0.25 mol), was stirred with 5 ml of 1 *M* HCl. The HCl salt was collected, dried, and equilibrated with two successive portions of D_2O as described for aniline-*2,4,6*-d_3. Nmr on the HCl salt in D_2O showed signals for CH_3 at $\delta \sim 2.0$ and the ring at ~ 7.2 in a ratio of 2.00 to 0.02 (99% exchange). The solution after the second equilibration with D_2O was decolorized with charcoal and stored in a sealed flask. A small portion was converted to the free amine, ν_{max} 3440, 3350, 3215, 2940, 2245 (C–D stretch), 1620, 1580, 1455, 1400, 1322, 1065, 954, and 770 cm^{-1}, but no aromatic CH absorption at 3030, 1170, 825, or 685 cm^{-1}.

To study the decomposition of the 3,5-dimethylbenzenediazonium salts, 3,5-dimethylaniline, 62 mg (5×10^{-4} mol), was dissolved in 4 ml of 1 *M* HCl at 0° and diazotized by dropwise addition of a solution of 90 mg (6×10^{-4} mol) of $NaNO_2$ in 1 ml of water. Addition of $NaNO_2$ was stopped when a permanent blue color on KI-starch test paper was obtained. Excess $NaNO_2$ was destroyed by adding 50 mg of urea; excess must be removed to avoid undesirable side reactions producing colored by-products. The deuterated diazonium salt was prepared simultaneously by the same procedure except that 320 mg of a 20% solution of the deuterated amine hydrochloride in D_2O was used instead of the free amine. Each of the diazonium solutions was poured into 495 ml of 4.0 *M* H_2SO_4 previously equilibrated at 25° and shaken rapidly. The decompositions were conducted in stoppered 1-cm cells at 25.1 ± 0.1° in the water-jacketed cell block of a Zeiss PMQ II spectrophotometer. After 5 min, absorbance (*A*) was measured every 2 min for 2 hr (3-4 half-lives), then after 24 hr. *A* dropped from an initial value of 1.3 to 0.01–0.03. Thus no significant amount of colored side products was formed. The uv spectrum of the final solution was identical with that of a 10^{-3} *M* solution of 3,5-dimethylphenol in 4.0 *M* H_2SO_4, ν_{max} 272 nm (ϵ 1130), 278 (1100).

References and Notes

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(5) The interaction responsible for weakening the aromatic hydrogen force constants in IV may include and may even result predominantly from overlap of the inner lobe of the vacant sp^2 atomic orbital on C_1 inside the ring with the small inner lobes of the H-binding sp^2 orbitals of the other carbons, but overlaps outside the ring may also be important.

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