

Experiments and Calculations for Determination of the Stabilities of Benzyl, Benzhydryl, and Fluorenyl Carbocations: Antiaromaticity Revisited

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Abstract: The following pK_R values for the formation of benzyl, benzhydryl, and fluorenyl carbocations in 50:50 (v:v) trifluoroethanol/water at $I = 0.50$ (NaClO_4) were determined as $pK_R = -\log(k_{\text{HOH}}[\text{H}_2\text{O}]/k_{\text{H}})$, where k_{H} is the second-order rate constant for acid-catalyzed reaction of the alcohol to form the carbocation and k_{HOH} is the second-order rate constant for capture of the carbocation by water: (R^+ , pK_R); PhCH_2^+ , ≤ -20 ; $\text{PhC}(\text{Me})^+$, -15.4 ; $\text{PhC}(\text{Me})_2^+$, -12.3 ; Ph_2CH^+ , -11.7 ; $\text{Ph}_2\text{C}(\text{Me})^+$, -9.3 ; 9-fluorenyl carbocation (9-Fl^+), -15.9 ; 9-methyl-9-fluorenyl carbocation (9-Me-9-Fl^+), -11.1 . The pK_R for Ph_2CH^+ is in fair agreement with the value estimated using acidity functions,^{1a} but the pK_R for 9-Me-9-Fl^+ is ca. 4 units more positive than that from the acidity function method,^{1a} so that the difference in the acidity of benzhydryl and fluorenyl carbocations is smaller than estimated in earlier work. The 12 π -electron cyclic fluorenyl system in 9-Fl^+ and 9-Me-9-Fl^+ causes only 5.7 kcal/mol and 2.4 kcal/mol, respectively, destabilization of the corresponding acyclic carbocations Ph_2CH^+ and $\text{Ph}_2\text{C}(\text{Me})^+$. The pK_R values show that "antiaromatic" destabilization of the 9-fluorenyl carbocations must be small. Ab initio calculations of the structures and energies of 9-Fl^+ and Ph_2CH^+ and of the corresponding alcohols at the 3-21G//3-21G and 6-31G**//3-21G levels indicate that Ph_2CH^+ is ca. 8–10 kcal/mol more stable than 9-Fl^+ , which is in good agreement with the stability difference calculated from the pK_R data. This indicates that electronic factors play the major role in determining the relative energies of these carbocations. Force field calculations were performed to estimate the contribution of van der Waals and ring strains to the difference in the pK_R values for Ph_2CH^+ and 9-Fl^+ . Assuming hypothetical structures for Ph_2CH^+ and 9-Fl^+ which are free of van der Waals and ring strains, it is then estimated that there is an 8–11 kcal/mol decrease in π -electron stabilization on moving from Ph_2CH^+ (C_{2v}) and 9-FlOH to 9-Fl^+ and Ph_2CHOH . It is concluded that 9-fluorenyl carbocations are not antiaromatic. The difference in the energy of the 9-fluorenyl and benzhydryl carbanions relative to the alcohols was calculated to be -13.2 kcal/mol at the 6-31G**//3-21G level. This difference is attributed to the difference in the energies of the HOMOs for the two carbanions.

Introduction

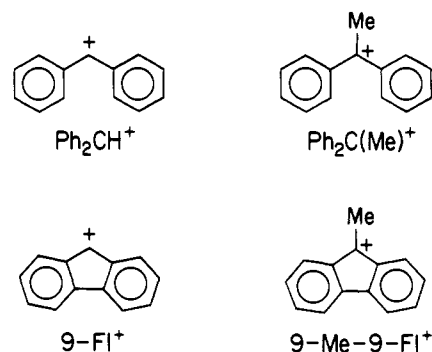
The results of early studies on the reactions of 9-fluorenyl derivatives¹⁻³ emphasized the relatively low chemical reactivity of these compounds and the instability of the putative 12 π -electron 9-fluorenyl carbocation (9-Fl^+ , Chart I) intermediate of a stepwise solvolysis reaction.^{4a} More recent studies of the products formed from photolysis of 9-fluorenyl derivatives were consistent with the generation of such carbocation reaction intermediates.⁵ This led finally to the direct observation of 9-Fl^+ ^{6,7} and 9-Me-9-Fl^+ (Chart I)⁷ as transient intermediates generated by laser flash photolysis of the corresponding alcohols.^{6,7} These results suggested to us that 9-Fl^+ and 9-Me-9-Fl^+ should also be accessible for study as intermediates of $\text{D}_N + \text{A}_N$ (S_N1)⁸ solvolysis reactions.

We report here the results of studies on the mechanism for solvolysis and other nucleophilic substitution reactions of 9-fluorenyl and 9-methyl-9-fluorenyl derivatives. These studies confirm our prediction that these reactions proceed through carbocation intermediates.

We have also measured the relative thermodynamic stability of 9-fluorenyl, benzhydryl, and benzyl carbocations as the pK_R values for their reactions with water. These were determined by a kinetic method as $pK_R = -\log(k_{\text{HOH}}[\text{H}_2\text{O}]/k_{\text{H}})$, where k_{H} is the second-order rate constant for the hydrogen-ion-catalyzed reaction of the alcohol to form the carbocation and k_{HOH} is the second-order rate constant for capture of the carbocation by water.^{9,10}

The values of pK_R for the formation of 9-Fl^+ and 9-Me-9-Fl^+ in 50:50 (v:v) trifluoroethanol/water are considerably less negative than those for formation of the simple benzyl carbocation (PhCH_2^+), and they are surprisingly similar to the pK_R values for the benzhydryl (Ph_2CH^+) and the α -methylbenzhydryl carbocations ($\text{Ph}_2\text{C}(\text{Me})^+$), respectively. These results show that, relative to simple alkyl carbocations or the benzyl carbocation, 9-Fl^+ and 9-Me-9-Fl^+ are highly stabilized by the polycyclic array

Chart I



of 12 π -electrons, and they have prompted us to question the proposed antiaromatic nature of 9-Fl^+ and 9-Me-9-Fl^+ .^{4a} This proposal is supported by the general rule that systems with $4n$ π -electrons are antiaromatic and intrinsically unstable⁴ and by

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the observations that 9-fluorenyl derivatives are less reactive than the corresponding benzhydryl derivatives in solvolysis reactions² and that the pK_R for the 9-phenyl-9-fluorenyl carbocation is 4 units more negative than that for the trityl carbocation.¹

The theoretical basis for the claim of antiaromaticity for 9-Fl⁺ has not been subject to scrutiny by the most modern computational methods. We report the results of ab initio calculations, performed at the 6-31G*//3-21G level, of the stabilities of the fluorenyl and benzhydryl carbocations relative to the respective alcohols. The calculations are in good agreement with the experimental data, and they also show that the atomic charges, bond lengths, and energies of the π -molecular orbitals are similar for the fluorenyl and benzhydryl carbocations. These data strongly support the conclusion that there is no antiaromatic destabilization of the 9-fluorenyl carbocation by the polycyclic array of 12 π -electrons.

Experimental Section

Materials. Benzhydryl, α -methylbenzhydryl, benzyl, and cumyl alcohols, benzhydryl chloride, 9-fluorenyl, 9-fluorenone, 9-bromofluorene, methylmagnesium iodide, 3,5-dinitrobenzoyl chloride, triethylamine, 4-(dimethylamino)pyridine, *p*-toluenesulfonic acid, sodium methoxide, dry ethyl ether, and 2,2,2-trifluoroethanol were from Aldrich. Acetic anhydride was from Baker. Sodium azide and mercaptoethanol were from Fluka. HPLC grade methanol was from Fisher. Benzhydryl alcohol and 9-bromofluorene were recrystallized from hexanes, and α -methylbenzhydryl alcohol was recrystallized from heptane. All other chemicals were reagent grade and were used without further purification. Water for the kinetic studies was distilled and then passed through a Milli-Q purification system. Silica gel was Merck kieselgel 60 (70–230 mesh).

Synthesis. ¹H NMR spectra at 200 MHz and ¹³C NMR spectra at 50 MHz were recorded on a Varian Gemini spectrometer.

9-Methyl-9-fluorenyl. A Grignard reaction of MeMgI (25 mL of a 3 M solution in ethyl ether, 75 mmol) with 9-fluorenone (10.5 g, 58 mmol) was carried out in dry ethyl ether at 0 °C under argon. Recrystallization of the crude product from toluene gave the alcohol as prisms: mp 174 °C (lit.¹¹ mp 172–174 °C); ¹H NMR δ 7.7–7.25 (8 H, m, Ar), 2.0 (1 H, s, OH), 1.71 (3 H, s, CH₃).

9-Methyl-9-fluorenyl 3,5-Dinitrobenzoate. 9-Methyl-9-fluorenyl (1 g, 5 mmol), 3,5-dinitrobenzoyl chloride (1.8 g, 8 mmol), triethylamine (0.98 mL, 7 mmol), and 4-(dimethylamino)pyridine (125 mg, 1 mmol) were dissolved in dichloromethane (60 mL), and the mixture was stirred at room temperature under argon for 4 h. The solvent was evaporated, and the residue was dissolved in ethyl ether (150 mL). The ethereal solution was washed with 0.1 M HCl (3 \times 100 mL), saturated NaHCO₃ (2 \times 100 mL), and brine (100 mL), dried with MgSO₄, and evaporated to give a yellow solid (1.8 g). A sample of this material (350 mg) was purified by column chromatography on silica gel, eluting with 3:97 ethyl acetate/chloroform. There was some decomposition on the column to give dibenzofulvene, which eluted as a fluorescent band before the dinitrobenzoate ester. The ester was obtained as a yellow gum (250 mg) (this compound slowly decomposes to give dibenzofulvene upon standing or in chloroform solution at room temperature): ¹H NMR δ 9.16 (1 H, t, *J* = 2 Hz, Ar(NO₂)₂), 9.06 (2 H, d, *J* = 2 Hz, Ar(NO₂)₂), 7.75–7.26 (8 H, m, Ar), 2.04 (3 H, s, CH₃).

α -Methylbenzhydryl Acetate. α -Methylbenzhydryl alcohol (3 g, 15 mmol), acetic anhydride (4.6 g, 45 mmol), triethylamine (6.3 mL, 45 mmol), and 4-(dimethylamino)pyridine (350 mg, 3 mmol) were dissolved in dichloromethane (75 mL) and heated under reflux for 90 h. The solution was washed with 0.1 M HCl (3 \times 100 mL), 0.1 M NaOH (3 \times 100 mL), and brine (100 mL), dried with MgSO₄, and evaporated to give a yellow oil (2.8 g). This was triturated with hexane to give the acetate as white crystals (110 mg): IR (CDCl₃) 1735 cm⁻¹ (C=O); ¹H NMR δ 7.35–7.20 (10 H, m, Ar), 2.20 (3 H, s, COCH₃), 2.12 (3 H, s, CH₃); ¹³C NMR δ 169.1 (C=O), 145.5, 128.0, 127.0, 125.7 (Ar), 84.5 (C), 26.9 (COCH₃), 22.4 (CH₃); MS *m/z*, found M⁺ 240.1148, C₁₆H₁₆O₂ requires 240.1150.

9-Methyl-9-fluorenyl, α -Methylbenzhydryl, and Cumyl Methyl Ethers. The corresponding alcohols were reacted in HPLC grade methanol at room temperature with *p*-toluenesulfonic acid as a catalyst. The progress of the reactions was followed by HPLC, and the reactions were quenched with solid sodium acetate after the disappearance of 50–80% of the starting alcohols but before the formation of substantial amounts of alkene elimination products. Purification by column chromatography on silica gel gave the methyl ethers in 50–60% yield. α -Methylbenzhydryl and cumyl methyl ethers were oils. 9-Methyl-9-fluorenyl methyl ether

was obtained as a white solid: mp 31 °C.

9-Fluorenyl Methyl Ether. 9-Bromofluorene (1.32 g, 5.4 mmol) was suspended in methanol (50 mL), and sodium methoxide (700 mg, 13 mmol) was added. The mixture was heated under reflux for 18 h. The solvent was evaporated, the solid residue extracted with ethyl ether (50 mL), and the ethereal solution dried with MgSO₄. Purification by column chromatography on silica gel gave the methyl ether as an oil: MS *m/z*, found 196.0887, C₁₄H₁₂O requires 196.0888.

General Procedures. Unless stated otherwise, the kinetic and product studies were at 25 °C in 50:50 (v:v) trifluoroethanol/water or 5:45:50 (v:v:v) methanol/trifluoroethanol/water at *I* = 0.50 (NaClO₄). Reactions were initiated by making a 100-fold to 200-fold dilution of a solution of the substrate in acetonitrile into 2–4 mL of the reaction mixture. Aqueous solutions containing NaN₃ were adjusted to pH 6–7 with concentrated HClO₄ before use.

HPLC Analyses. Unless otherwise stated, the products were cleanly separated by HPLC as described previously^{10,12} and were detected by the UV absorbance at the following wavelengths: benzyl, 257 nm; cumyl, 258 nm; benzhydryl, 259 nm; α -methylbenzhydryl, 259 nm; 9-fluorenyl, 270 nm; 9-methyl-9-fluorenyl, 274 nm. These wavelengths are λ_{max} for the corresponding alcohols.

In all cases where the progress of the reaction was monitored by HPLC, the peak areas were normalized to a constant injection volume by using 3-(4-methoxyphenyl)-1-propanol (0.2–1 mM) as an internal standard. PhC(Me)₂OH was used as an internal standard in the determination of the initial velocity for its reaction in 50:50 (v:v) trifluoroethanol/water.

The products of solvolysis and nucleophilic substitution reactions were identified as described previously.^{10,12} The alkene products of elimination reactions were identified by showing that their retention times were identical with those for authentic samples. The extinction coefficients of the alcohols and the corresponding trifluoroethyl ethers and azide adducts were shown to be identical using methods described in previous work.^{10,12} Relative extinction coefficients of $\epsilon_{olefin}/\epsilon_{ROH}$ = 34 at 258 nm for α -methylstyrene and PhC(Me)₂OH and $\epsilon_{olefin}/\epsilon_{ROH}$ = 22 at 259 nm for α -phenylstyrene and Ph₂C(Me)OH were determined by UV spectroscopy. Relative extinction coefficients of $\epsilon_{ROH}/\epsilon_{RSEtOH}$ = 1.62 at 274 nm for 9-Me-9-FIOH and the corresponding mercaptoethanol S-adduct were determined by comparison of the increase in the peak area for the thiol adduct with the decrease in the peak area for the alcohol upon reaction of the latter in aqueous 0.10 M HClO₄ containing 1% mercaptoethanol.

The ratios of product yields were determined periodically over several half-lives of the reactions in order to show that the products were stable to the reaction conditions.

Product Studies. Reactions of Ph₂CHCl (2 mM) at 22 \pm 2 °C in a volume of 3 mL were initiated by injection of 30 μ L of substrate in acetonitrile with vortexing to ensure rapid mixing, and the products were immediately analyzed by HPLC. Product studies for the reactions of α -methylbenzhydryl acetate, 9-methyl-9-fluorenyl 3,5-dinitrobenzoate,

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and 9-bromofluorene were carried out on the same reaction solutions as for the kinetic studies.

Constant ratios of product yields from the acid-catalyzed reactions of 9-fluorenyl methyl ether (0.5 mM, $[\text{HClO}_4] = 0.50 \text{ M}$), 9-methyl-9-fluorenyl methyl ether (0.1 mM, $[\text{HClO}_4] = 1.6 \text{ mM}$), α -methylbenzhydryl methyl ether (5 mM, $[\text{HClO}_4] = 1 \text{ mM}$), and cumyl methyl ether (10 mM, $[\text{HClO}_4] = 0.01 \text{ M}$) were observed over the first 30%, 20%, 35%, and 20% of the reaction, respectively.

Constant ratios of product yields from the acid-catalyzed reaction of 9-fluorenyl (0.5 mM, $[\text{HClO}_4] = 0.50 \text{ M}$) in 5:45:50 (v:v:v) methanol/trifluoroethanol/water were determined during the first 10% of the reaction.

The acid-catalyzed reaction of 9-methyl-9-fluorenyl methyl ether (0.04 mM, $[\text{HClO}_4] = 0.10 \text{ M}$) with 1% mercaptoethanol in water ($I = 1.00$, NaClO_4) gave 9-Me-9-FIOH and a second product that was assigned as the mercaptoethanol S-adduct because the reactivity of a thiol¹⁰ is much greater than that of an alkyl alcohol.^{25b} The initial yield of the mercaptoethanol S-adduct was determined by extrapolation to zero time of its yield determined during the disappearance of 40% of the methyl ether. The extrapolation is short, and the yield of the S-adduct extrapolated to zero time (17.3%) differs only slightly from the earliest observed yield (18.3%).

Calculation of Product Yields and Rate Constant Ratios. Fractional yields of substitution or elimination products were calculated as the ratio of the HPLC peak area for the product divided by the sum of the peak areas for all products, with correction, where necessary, of peak areas for differences in the extinction coefficients of the various products. The area of the α -phenylstyrene peak, which forms as a product of the acid-catalyzed reaction of α -methylbenzhydryl methyl ether, was corrected for the small ($\sim 0.1\%$) amount of alkene that was present as an impurity in the substrate.

Product rate constant ratios for reaction of substrates with water and trifluoroethanol were calculated using eq 1, where A_{ROH} and A_{ROTFE} are

$$k_{\text{HOH}}/k_{\text{TFE}} = (A_{\text{ROH}}/A_{\text{ROTFE}})([\text{TFE}]/[\text{H}_2\text{O}]) \quad (1)$$

the peak areas for the alcohol and the trifluoroethyl ether (which have identical extinction coefficients at the wavelength of analysis), respectively.

The product rate constant ratios $k_{\text{az}}/k_{\text{s}}$ (M^{-1}) for reaction of 9-methyl-9-fluorenyl 3,5-dinitrobenzoate and 9-bromofluorene were calculated using eq 2, where A_{RN_3} and A_{ROS} are the peak areas for the azide

$$k_{\text{az}}/k_{\text{s}} (\text{M}^{-1}) = (A_{\text{RN}_3}/A_{\text{ROS}})(1/[\text{N}_3^-]) \quad (2)$$

and total solvent adducts (which have identical extinction coefficients at the wavelength of analysis), respectively. The values of $k_{\text{az}}/k_{\text{s}}$ determined at five values of $[\text{N}_3^-]$ agreed to within $\pm 10\%$.

For reactions of benzhydryl chloride and α -methylbenzhydryl acetate, the azide adducts and trifluoroethyl ethers coeluted from the HPLC column. Therefore, values of $k_{\text{az}}/k_{\text{s}}$ (M^{-1}) were determined from the ratio of the intercept and slope of a double reciprocal plot according to eq 3, with five values of $[\text{N}_3^-]$, where A is the combined peak area for

$$1/(A - A_0) = 1/(A_{\text{max}} - A_0)\{1 + (k_{\text{s}}/k_{\text{az}})(1/[\text{N}_3^-])\} \quad (3)$$

the azide and trifluoroethanol adducts at a given $[\text{N}_3^-]$, A_0 is the area of this peak at $[\text{N}_3^-] = 0$, and A_{max} is the area of this peak for quantitative conversion of substrate to the azide adduct.

Kinetic Methods. Rate constants for the reactions of α -methylbenzhydryl acetate (1 mM) were determined by following the disappearance of the substrate by HPLC with peak detection at 259 nm. The reactions of 9-methyl-9-fluorenyl 3,5-dinitrobenzoate and 9-bromofluorene (0.1 mM) were followed spectrophotometrically by monitoring the increase in absorbance at 307 and 273 nm, respectively. First-order rate constants k_{obsd} were obtained from the slopes of semilogarithmic plots of reaction progress against time, which were linear over at least 3 half-lives of the reactions. The values of k_{obsd} were reproducible to within $\pm 5\%$. The second-order rate constant for the reaction of N_3^- with 9-bromofluorene was obtained from the slope of a plot of k_{obsd} against $[\text{N}_3^-]$, using five values of $[\text{N}_3^-]$.

The perchloric acid-catalyzed reactions of PhCH_2OH (20 mM), $\text{PhC}(\text{Me})_2\text{OH}$ (20 mM), Ph_2CHOH (10 mM), 9-FIOH (0.5 mM), and 9-Me-9-FIOH (1 mM) were monitored by following the formation of the corresponding trifluoroethyl ethers by HPLC under initial velocity con-

ditions. Aliquots (100 μL) were withdrawn at various times and were immediately neutralized with 100 μL of 3 M NaOAc and analyzed by HPLC. The reactions were followed during the reaction of 3–4% of the substrate. This was shown to correspond to $\leq 10\%$ of the approach of the reaction to equilibrium. Similarly, the reaction of $\text{Ph}_2\text{C}(\text{Me})\text{OH}$ (10 mM) was monitored by following the initial velocity of formation of α -phenylstyrene (up to 1%, which corresponds to $\ll 10\%$ of that formed at equilibrium). The reaction of 9-Me-9-FIOH (0.1 mM) in water containing 1% mercaptoethanol was monitored by following the initial velocity of the effectively irreversible formation of the mercaptoethanol S-adduct over the first 5% of the reaction.

Apparent pseudo-first-order rate constants k_{app} were determined from the slopes of plots of the peak areas for the products, A , against time according to eq 4, where A_0 is the area of the substrate (alcohol) peak

$$k_{\text{app}} = \{(dA/dt)/A_0\}(\epsilon_{\text{s}}/\epsilon_{\text{p}}) \quad (4)$$

determined at zero time and $\epsilon_{\text{s}}/\epsilon_{\text{p}}$ is the ratio of the extinction coefficients of the starting alcohol and the product at the wavelength used for detection. Apparent second-order rate constants k_{H} were obtained as the slopes of plots of k_{app} against $[\text{H}^+]$. True second-order rate constants for the formation of the carbocations from the corresponding alcohols, k_{H} , were obtained by correction of k_{H} for regeneration of the alcohol from reaction of the carbocation with water, according to Scheme I and eq 5,

$$k_{\text{H}} = k_{\text{H}}(1/f_{\text{p}}) \quad (5)$$

where f_{p} is the fraction of carbocation intermediate that is converted to the reaction product. This fraction was determined from the product yields observed for a reaction which generates the carbocation from a second substrate with a leaving group other than OH/H^+ .

Studies of 9-Methyl-9-fluorenyl in Sulfuric Acid. Sulfuric acid solutions were prepared by mixing a known weight of concentrated sulfuric acid with a known weight of water. Solutions of 9-Me-9-FIOH in acetic acid were prepared by injecting 25 μL of a solution of 9-Me-9-FIOH in acetic acid into 2.5 mL of sulfuric acid solution to give a final substrate concentration of 0.025 mM. The absorbance at 487 nm^{1a} was determined within 5 s after mixing. The species present in 58% (by weight) sulfuric acid were analyzed by neutralization of the sulfuric acid followed by HPLC analysis as follows. To 5 mL of 58% (by weight) sulfuric acid was added 50 μL of a solution of 9-methyl-9-fluorenyl in acetic acid, to give a final substrate concentration of 0.1 mM. After $< 30 \text{ s}$ this solution was added either to 50 mL of ice-cold 2 M sodium acetate followed by extraction with ether or to an ice-cold suspension of 8 g of sodium methoxide in 50 mL of methanol followed by the addition of a further 50 mL of methanol and filtration. After evaporation of the solvents, the residues were dissolved in methanol/water and the products were analyzed by HPLC with peak detection at 274 nm.

Ab Initio Calculations. In most cases, initial examinations of the potential energy surfaces of the benzyl, 9-fluorenyl, and benzhydryl alcohols and carbocations were performed at the STO-3G¹³ level employing the GAUSSIAN 86¹⁴ program or with the semiempirical AM1¹⁵ Hamiltonian using MOPAC 4.0.¹⁶ These calculations were performed on an IBM 4381/23. Some species were also examined by force field calculations with the MM2¹⁷ force field employed by MACROMODEL¹⁸ or with the MMX¹⁹ force field available in PCMODEL.²⁰ The former program was used on a VAX 6000 and the latter on an IBM PS/2 Model 50Z.

Final calculations were performed with the GAUSSIAN 88²¹ program on the Cray Y-MP8/864 at the Ohio Supercomputer Center. All geometry optimizations were performed by restricted Hartree-Fock calculations with the split-valence 3-21G basis set.²² All geometrical parameters were fully optimized at the minimum energy structures, and rotational potentials about certain bonds were evaluated by geometry optimizations at fixed dihedral angles. Full use was made of symmetry to decrease integral storage requirements and CPU time for the Hartree-Fock calculations, but calculations were also performed without symmetry restrictions on PhCH_2OH , 9-FIOH, 9-Fl⁺, and Ph_2CH^+ to determine if lower energy structures could be located. Single-point calculations with the polarization basis set 6-31G*²³ were also performed on each minimum energy structure located with the 3-21G basis set. Single-point calculations on the optimized 3-21G structures for the carbanions 9-Fl⁻ and Ph_2CH^- were also performed with the diffuse function augmented 6-31+G basis set.²⁴

Results

Experiments. Unless stated otherwise, all rate constants and product data are for reaction in 50:50 (v:v) trifluoroethanol/water at 25 °C and $I = 0.50$ (NaClO_4).

First-order rate constants k_{solv} for the solvolysis reactions of α -methylbenzhydryl acetate, 9-methyl-9-fluorenyl 3,5-dinitro-

(25) (a) A rate constant of $k_{\text{solv}} = 1.6 \text{ s}^{-1}$ was estimated for solvolysis of Ph_2CHCl in 50:50 (v:v) trifluoroethanol/water from $k_{\text{obsd}} = 7.27 \times 10^{-5} \text{ s}^{-1}$ in 80% acetone in water [Rappoport, Z.; Ta-Shma, R. *J. Am. Chem. Soc.* 1983, 105, 6082–6095] and a rate constant ratio of 22 000 for the solvolyses of 4-methoxybenzyl chloride in 50:50 (v:v) trifluoroethanol/water and in 80:20 (v:v) acetone/water (ref 30b). (b) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* 1984, 106, 1373–1383.

Table I. Product Rate Constant Ratios k_{az}/k_s (M^{-1}), k_{HOH}/k_{TFe} , and k_p/k_s for Reaction of Benzyl, Benzhydryl, and 9-Fluorenyl Carbocations Generated from R-X in 50:50 (v:v) Trifluoroethanol/Water^a

R	X	k_{az}/k_s (M^{-1}) ^b	k_{HOH}/k_{TFe} ^c	k_p/k_s ^c
PhC(Me) ₂	OMe/H ⁺ ^d		1.3 ^e	0.004 ^e
Ph ₂ CH	Cl	18	1.7	
Ph ₂ C(Me)	OAc	74	5.5	0.055
	OMe/H ⁺ ^f		5.0 ^g	0.015 ^g
9-Fl	Br		0.9	
	OMe/H ⁺ ^h		0.7 ⁱ	
9-Me-9-Fl	DNB	6.5	0.90	≤0.04
	OMe/H ⁺ ^j		0.8 ^k	<0.01 ^k

^a At 25 °C and $I = 0.50$ (NaClO₄). Rate constants are defined in Schemes I and II. ^b Determined by HPLC product analysis at five values of [N₃⁻]. ^c Dimensionless ratio of rate constants, determined by HPLC product analysis. ^d [HClO₄] = 0.01 M. ^e Determined during disappearance of 20% of substrate. ^f [HClO₄] = 1 mM. ^g Determined during disappearance of 35% of substrate. ^h [HClO₄] = 0.50 M. ⁱ Determined during disappearance of 30% of substrate. ^j [HClO₄] = 1.6 mM. ^k Determined during disappearance of 20% of substrate.

benzoate, and 9-bromofluorene were determined to be $1.0 \times 10^{-4} s^{-1}$, $1.6 \times 10^{-3} s^{-1}$, and $4.8 \times 10^{-4} s^{-1}$, respectively. The values of k_{obsd} for reaction of the first two compounds were independent of [N₃⁻] in the range 0–0.50 M, but the reaction of azide ion with 9-bromofluorene was found to be bimolecular with $k_N = 1.7 \times 10^{-2} M^{-1} s^{-1}$. The effect of azide ion on the rate of reaction of benzhydryl chloride was not determined because the half-lives of these reactions were too short to measure by our methods;^{25a} however, evidence will be presented in the Discussion that this compound reacts with nucleophiles by a D_N + A_N (S_N1)⁸ mechanism.

Table I gives the rate constant ratios k_{az}/k_s (M^{-1}), determined from product analysis, for reactions in which the azide adduct is formed by partitioning of a carbocation intermediate. A rate constant ratio of $k_{az}/k_s = 36 M^{-1}$ was determined by product analysis for the reaction of 9-bromofluorene, which is in excellent agreement with $k_N/k_{solv} = 35 M^{-1}$ from the kinetic studies.

Table I gives dimensionless product rate constant ratios k_{HOH}/k_{TFe} determined for solvolysis of benzhydryl chloride, α -methylbenzhydryl acetate, 9-bromofluorene, and 9-methyl-9-fluorenyl 3,5-dinitrobenzoate and for the perchloric acid-catalyzed reactions of cumyl, α -methylbenzhydryl, 9-fluorenyl, and 9-methyl-9-fluorenyl methyl ethers. The substrates with an α -methyl group also underwent elimination to yield small amounts of the corresponding alkenes, and rate constant ratios k_p/k_s (Table I) for their elimination and solvolysis reactions were calculated from the ratios of the yields of the alkene and solvent adducts. Rate constant ratios $k_{MeOH}/k_{TFe} = 6.6$ for the uncatalyzed reaction of 9-bromofluorene and $k_{MeOH}/k_{TFe} = 6.2$ for the perchloric acid-catalyzed reaction of 9-fluorenyl were determined in 5:45:50 methanol/trifluoroethanol/water at $I = 0.50$ (NaClO₄).

Table II gives second-order rate constants k_H ($M^{-1} s^{-1}$) for the perchloric acid-catalyzed cleavage of benzyl, benzhydryl, and fluorenyl alcohols to give the corresponding carbocations (Scheme I). These were determined by following the initial velocity of formation of (i) the corresponding trifluoroethyl ethers from PhC(Me)₂OH, Ph₂CHOH, 9-FIOH, and 9-Me-9-FIOH in 50:50 (v:v) trifluoroethanol/water, (ii) α -phenylstyrene from Ph₂C(Me)OH in 50:50 (v:v) trifluoroethanol/water, or (iii) the mercaptoethanol S-adduct from the reaction of 9-Me-9-FIOH in 1% mercaptoethanol in water. There was no detectable formation of the trifluoroethyl ether from the reaction of PhCH₂OH in 0.50 M HClO₄ for 107 days, and the value of k_H (Table II) is an upper limit based on the smallest HPLC peak area for this product that could have been detected in this experiment.

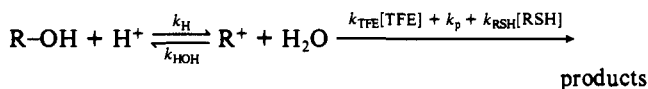
In all cases, k_H in Table II was calculated by correction of the observed rate constants for the fraction of substrate ionization that fails to give product [(1 - f_p), eq 5] due to regeneration of the alcohol by the k_{HOH} step (Scheme I). The fraction of substrate ionization that gives solvolysis product (f_p , eq 5) was calculated from the partitioning ratios k_{HOH}/k_{TFe} and k_p/k_s (Table I) de-

Table II. Rate Constants for Acid-Catalyzed Formation of Benzyl, Benzhydryl, and 9-Fluorenyl Carbocations from the Respective Alcohols in 50:50 (v:v) Trifluoroethanol/Water (Scheme I)^a

R ⁺	range of [H ⁺] (M)	k_H ($M^{-1} s^{-1}$) ^b
PhCH ₂ ⁺		≤2 × 10 ^{-9c}
PhCH(Me) ⁺ ^d		3 × 10 ⁻⁵
PhC(Me) ₂ ⁺	0.005–0.025	7.3 × 10 ⁻³
Ph ₂ CH ⁺	0.05–0.25	4.9 × 10 ⁻⁴
Ph ₂ C(Me) ⁺	0.01–0.05	2.7 × 10 ^{-2e}
9-Fl ⁺	0.125–0.50	1.3 × 10 ^{-6f}
9-Me-9-Fl ⁺	0.01–0.05	4.8 × 10 ⁻³
	(0.02–0.10)	(2.3 × 10 ⁻³) ^g

^a At 25 °C and $I = 0.50$ (NaClO₄). ^b Second-order rate constant for perchloric acid-catalyzed formation of the carbocation from the alcohol determined by following the initial velocity of formation of the trifluoroethyl ether at five values of [H⁺], unless otherwise noted. ^c Upper limit at [HClO₄] = 0.50 M, see text. ^d Data from ref 10. ^e Determined by following the initial velocity of formation of α -phenylstyrene at five values of [H⁺]. ^f Determined using three values of [H⁺]. ^g In aqueous solution containing 1% mercaptoethanol at 25 °C and $I = 1.00$ (NaClO₄) and determined by following the initial velocity of formation of the mercaptoethanol S-adduct at five values of [H⁺].

termined for the solvolyses of benzhydryl chloride and 9-methyl-9-fluorenyl 3,5-dinitrobenzoate or the acid-catalyzed reactions of cumyl, α -methylbenzhydryl, and 9-fluorenyl methyl ethers or from $k_{RSH}/k_{HOH}[HOH] = 0.21 M^{-1}$ for the acid-catalyzed reaction of 9-methyl-9-fluorenyl methyl ether in 1% mercaptoethanol in water.

Scheme I

This analysis assumes that the product-determining steps in the stepwise reactions of R-OH/H⁺ and R-X or R-OMe/H⁺ involve capture of common liberated carbocation intermediates. This is valid for the reactions of the benzhydryl, α -methylbenzhydryl, and 9-methyl-9-fluorenyl derivatives because, for these, diffusional separation of the ion or ion-molecule pair (R⁺·X⁻ or R⁺·MeOH) to give the free carbocations ($k_d \approx 1.6 \times 10^{10} s^{-1}$)^{25b} is much faster than the capture of these intermediates by solvent (k_s , Table III). However, the rate constants for diffusional separation of ion-molecule pairs of the cumyl and 9-fluorenyl carbocations are similar to k_s for carbocation capture by solvent (Table III) so that, for these, some product should be formed by direct capture of the ion-molecule intermediate. The ion-molecule intermediate of the reaction of R-OH/H⁺ (R⁺·H₂O) will react to regenerate R-OH faster than that of the reaction of R-OMe/H⁺ (R⁺·MeOH) because there is an additional molecule of water present in the solvation shell of the former species. Therefore, the rate constant ratios k_{HOH}/k_{TFe} for partitioning of the ion-molecule intermediate of the reaction of R-OMe/H⁺ (R⁺·MeOH) that were used to calculate f_p for the reaction of R-OH/H⁺ to form R-OTFE (eq 5) may overestimate the fractional yield of R-OTFE from the intermediate of this reaction (R⁺·H₂O). This would lead to a very small (<20%) underestimate of the values of k_H (eq 5) for PhC(Me)₂OH and 9-FIOH.^{26a}

The dissolution of 9-Me-9-FIOH in sulfuric acid resulted in an increase in absorbance at 487 nm. The absorbance change reached one-half the maximum value in 86% (by weight) sulfuric

(26) (a) Studies by Grunwald et al. of the acid-catalyzed racemization of 1-phenylethanol in ¹⁸O-labeled water suggest that there are 6–8 molecules of water in the solvation shell of the 1-phenylethyl carbocation intermediate: Grunwald, E.; Heller, A.; Klein, F. S. *J. Chem. Soc.* 1957, 2604–2613. If there were on average four reactive molecules of water, one of trifluoroethanol, and one of the leaving group in the solvation shell of the 9-fluorenyl carbocation, then the ratio of f_p values for [9-Fl⁺·HOH] and [9-Fl⁺·MeOH] generated from 9-FIOH/H⁺ and 9-FIOMe/H⁺, respectively, would be equal to 1.2 for a value of $k_{HOH}/k_{TFe} = 0.7$ (Table I). This ratio would decrease for larger numbers of solvent molecules in the solvation shell. (b) More O'Ferrall, R. A.; Slac, S. *J. Chem. Soc. B* 1970, 260–268. Neuenschwander, M.; Vögeli, R.; Fahrni, H.-P.; Lehmann, H.; Ruder, J.-P. *Helv. Chim. Acta* 1977, 60, 1073–1086.

Table III. Rate and Equilibrium Constants and pK_R Values for the Formation and Rate Constants for the Reaction of Benzyl, Benzhydryl, and 9-Fluorenyl Carbocations in 50:50 (v:v) Trifluoroethanol/Water^a

R^+	k_s (s ⁻¹) ^b	k_H (M ⁻¹ s ⁻¹) ^c	k_{HOH} (M ⁻¹ s ⁻¹) ^d	$K_{eq} = k_H/k_{HOH}$	pK_R^e
PhCH ₂ ⁺		$\leq 2 \times 10^{-9}$ ^f	$\geq 1 \times 10^{10}$ ^g	$\leq 2 \times 10^{-19}$	≤ -20
PhCH(Me) ⁺ ^h	1×10^{11}	3×10^{-5}	3×10^9	1×10^{-14}	-15.4
PhC(Me) ₂ ⁺	1.7×10^{10} ⁱ	7.3×10^{-3}	5×10^8	1.5×10^{-11}	-12.3
Ph ₂ CH ⁺	2.8×10^8	4.9×10^{-4}	9×10^6	5.4×10^{-11}	-11.7
Ph ₂ C(Me) ⁺	6.8×10^7	2.7×10^{-2}	2×10^6	1.4×10^{-8}	-9.3
9-Fl ⁺	1.4×10^{10} ^j	1.3×10^{-6}	4×10^8	3.3×10^{-15}	-15.9
9-Me-9-Fl ⁺	7.7×10^8	4.8×10^{-3}	2×10^7	2.4×10^{-10}	-11.1
		$(2.3 \times 10^{-3})^k$	$(3 \times 10^7)^l$	$(7.7 \times 10^{-11})^k$	$(-11.9)^{k,m}$

^a At 25 °C and $I = 0.50$ (NaClO₄). ^b Calculated from k_{az}/k_s (M⁻¹) with $k_{az} = 5 \times 10^9$ M⁻¹ s⁻¹ for the diffusion-limited reaction of N₃⁻ with benzylic carbocations, unless noted otherwise. ^c Data from Table II. ^d Second-order rate constant for reaction of the carbocation with water calculated from values of k_s and k_{HOH}/k_{TFE} (Table I) and eq 6, with [H₂O] = 27.8 and [TFE] = 6.85 M, see text. ^e Log ($K_{eq}/27.8$). The uncertainty in the pK_R values is estimated to be ± 0.2 unit based upon the uncertainties in the values of k_H ($\pm 20\%$) and k_{HOH} ($\pm 20\%$). ^f Upper limit, see text. ^g Lower limit, see text. ^h Data from ref 10. ⁱ Interpolated from data in ref 37, see text. ^j Estimated value, see text. ^k In aqueous solution containing 1% mercaptoethanol at 25 °C and $I = 1.00$ (NaClO₄). ^l Extrapolated from value of k_s in 50:50 (v:v) TFE/H₂O. ^m Log ($K_{eq}/55.6$).

acid for which $H_R = -15.7$.^{1a} These results are in fair agreement with work by Deno et al.,^{1a} who reported that solutions of concentrated sulfuric acid which initially contain 9-Me-9-FlOH undergo a spectral change with an apparent pK_R of -16.6.

The UV spectrum of a solution of 9-Me-9-FlOH in 58% (by weight) sulfuric acid does not correspond to that of either 9-Me-9-FlOH or dibenzofulvene,^{26b} which might form from dehydration of the alcohol. The species present within 30 s of dissolution of 9-Me-9-FlOH (0.1 mM) in 58% (by weight) sulfuric acid were analyzed by neutralization of the acid with sodium methoxide in methanol or with aqueous sodium acetate, followed by product analysis by HPLC with peak detection at 274 nm, which is λ_{max} for 9-Me-9-FlOH (see Experimental Section). The quench into NaOMe/MeOH resulted in a complex mixture, consisting of dibenzofulvene (ca. 12% of the total peak area) along with another four major and three minor peaks, but there was no detectable recovery (<2%) of 9-Me-9-FlOH. The quench into NaOAc/H₂O resulted in a slightly different mixture, consisting of dibenzofulvene (ca. 9% of the total peak area) and 9-Me-9-FlOH (ca. 2% of the total peak area) along with another three major and three minor peaks, five of which corresponded to those obtained from the quench into NaOMe/MeOH.

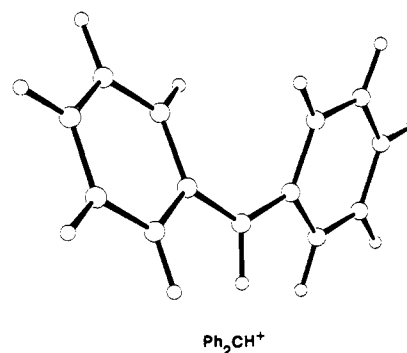
Calculations. The minimum energy structure of PhCH₂⁺ was assumed to have C_{2v} symmetry, but no initial assumptions concerning the structures of 9-Fl⁺ and Ph₂CH⁺ were made. The energy surfaces of 9-Fl⁺ and Ph₂CH⁺ were initially examined with the semiempirical AM1 Hamiltonian and with ab initio calculations at the STO-3G level. Minimum energy conformations were refined at the 3-21G level, and the potential energies associated with rotations about the Ph-C⁺ bonds of Ph₂CH⁺ were also evaluated at the 3-21G level. Single-point calculations at the 6-31G*/3-21G level were performed on all three carbocations. The results of these calculations are summarized in Table IV.

Geometries of all optimized structures located at the 3-21G level are presented in the supplementary material. The minimum energy structure for 9-Fl⁺ has planar C_{2v} symmetry, but slight distortions to structures of C_s symmetry can be accomplished at little cost in energy. For example, the puckered structure in which C-9 is twisted 5° out of the plane of the phenyl rings is only 0.16 kcal above the C_{2v} structure at the 3-21G level. Ph₂CH⁺ has considerably more potential for structural variation, but only two enantiomeric minima of C₂ symmetry were located. In these structures, the phenyl rings are rotated about the Ph-C⁺ bonds by $\pm 18.59^\circ$ with respect to the H-C⁺ bond (Figure 1). A similar propeller-like structure is well-documented for triarylmethyl carbocations.²⁷ The planar C_{2v} structure of Ph₂CH⁺ is the transition state for interconversion of the two enantiomeric C₂ structures and lies 2.0 kcal/mol above them at the 3-21G level and 1.2 kcal/mol above them at the 6-31G*/3-21G level. The C_{2v} structure is at an energy minimum if C_s symmetry is maintained during the phenyl group rotations. Relative energies of the various conformers of Ph₂CH⁺ are summarized in Figure 2.

Table IV. Ab Initio Energies of Optimized Benzyl, 9-Fluorenyl, and Benzhydryl Systems^a

species	point group	energy (hartrees) ^b	
		3-21G//3-21G	6-31G*/3-21G
PhCH ₂ OH	C _s	-342.669 485	-344.582 466
PhCH ₂ ⁺	C _{2v}	-267.380 452	-268.886 641
9-FlOH	C _s	-569.786 577	-572.980 152
9-Fl ⁺	C _{2v}	-494.506 067	-497.297 340
9-Fl ⁻	C _{2v}	-494.743 981	-497.523 583
			(-497.376 028) ^c
Ph ₂ CHOH	C ₁	-570.943 496	-574.131 059
Ph ₂ CH ⁺	C ₂	-495.676 365	-498.464 238
Ph ₂ CH ⁺	C _{2v}	-495.673 182	-498.462 387
Ph ₂ CH ⁻	C ₂	-495.873 510	-498.653 506
			(-498.507 965) ^c

^a All structures were fully optimized by standard RHF procedures within the constraints of the indicated point groups at the 3-21G level. Calculations with no symmetry restraints indicate that all structures, except the C_{2v} structure of Ph₂CH⁺, are global minima. See text for details. ^b 1 Hartree = 627.51 kcal/mol. ^c Energy obtained at the 6-31+G//3-21G level.

**Figure 1.** Minimum energy structure of Ph₂CH⁺ calculated at the 3-21G level. The structure has C₂ symmetry with both phenyl groups rotated 18.59° out of the plane defined by the central sp² carbon.

No stable minima of C₁ symmetry were located. All of these structures collapsed to one of the C₂ enantiomers if complete relaxation of geometry was allowed.

Figure 2 shows that the van der Waals and bending energies of Ph₂CH⁺, estimated by MMX calculations, decrease significantly as the two phenyl rings are rotated out of the plane while C₂ symmetry is maintained. The bond lengths and atomic charges at the 3-21G level for all three carbocations are summarized in Figure 3.²⁸

The energy surfaces of 9-FlOH and Ph₂CHOH were examined by MM2 calculations prior to commencement of the ab initio calculations. Two unique minimum energy conformations were located for both alcohols with the MM2 force field after elimi-

(27) Gomes de Mesquita, A. H.; MacGillavry, C. H.; Eriks, H. *Acta Crystallogr.* 1965, 18, 437-443.

(28) In Figure 3, charges on hydrogens are summed into the carbons to which they are bonded.

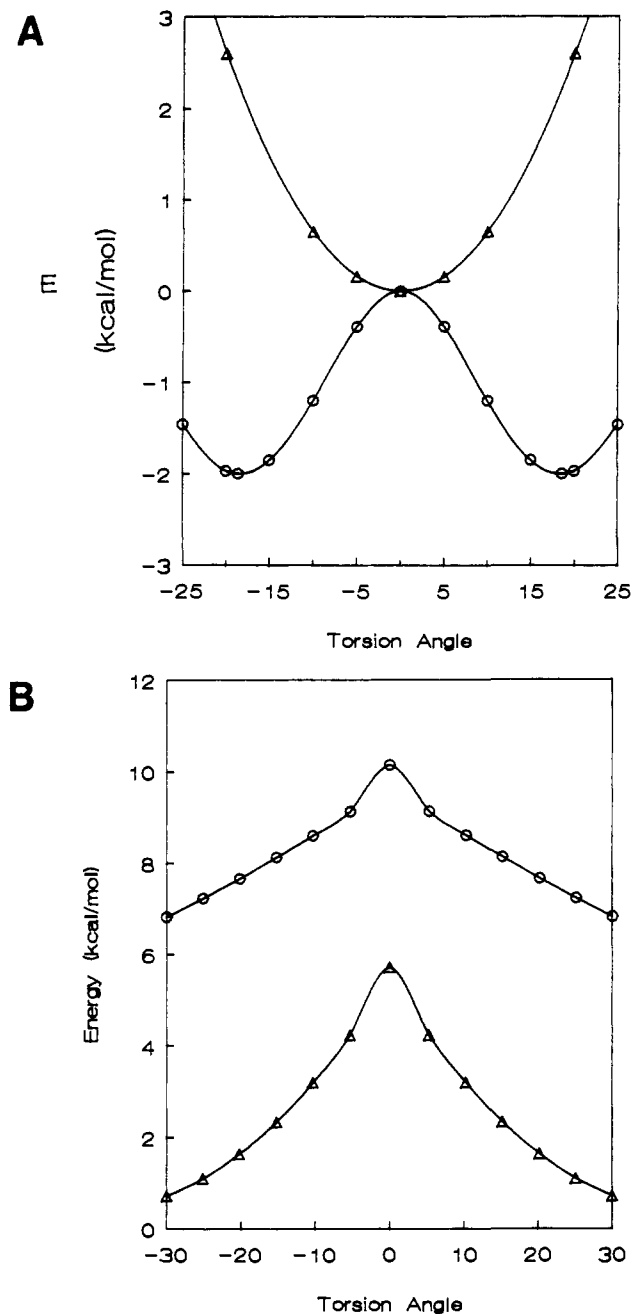


Figure 2. (A) Relative energies of C_2 (O) and C_s (Δ) conformations of Ph_2CH^+ determined by restricted Hartree-Fock calculations at the 3-21G level. The planar C_{2v} structure was arbitrarily assigned an energy of 0 kcal/mol. The torsion angle is defined by the rotation of the phenyl rings out of the plane defined by the central sp^2 carbon. (B) van der Waals (O) and bending (Δ) strain energies estimated by MMX force field calculations for C_2 conformations of Ph_2CH^+ as a function of the torsion angle.

nation of enantiomeric conformers. These were used as starting points for ab initio minimizations. In 9-FIOH the only significant conformational degree of freedom is rotation about the C-O bond. The minimum energy structure at the 3-21G level has C_s symmetry and an H-C-O-H dihedral angle of 180° (Figure 4). The only other stable conformations are enantiomers which have an H-C-O-H dihedral angle of $\pm 68.6^\circ$. These structures are 5.0 kcal/mol less stable than the C_s conformer. There is considerably more rotational freedom in Ph_2CHOH , but the 3-21G calculations found only two unique minima within 1.3 kcal/mol of each other. The lower energy conformer, which has an H-C-O-H dihedral angle of 64.87° , is shown in Figure 4. The 3-21G calculations for both alcohols were done at a number of different fixed H-C-O-H dihedral angles so that it is unlikely that any lower energy

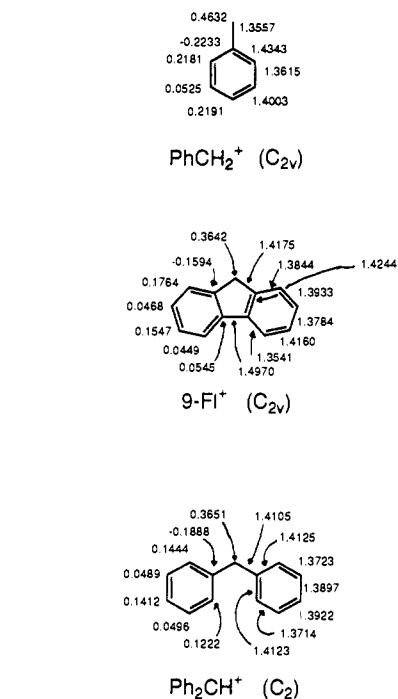


Figure 3. Bond lengths (right side, Å) and atomic charges (left side) calculated at the 3-21G level for PhCH_2^+ , 9-FI $^+$, and Ph_2CH^+ . Charges on hydrogens are summed into the carbons to which they are bonded.

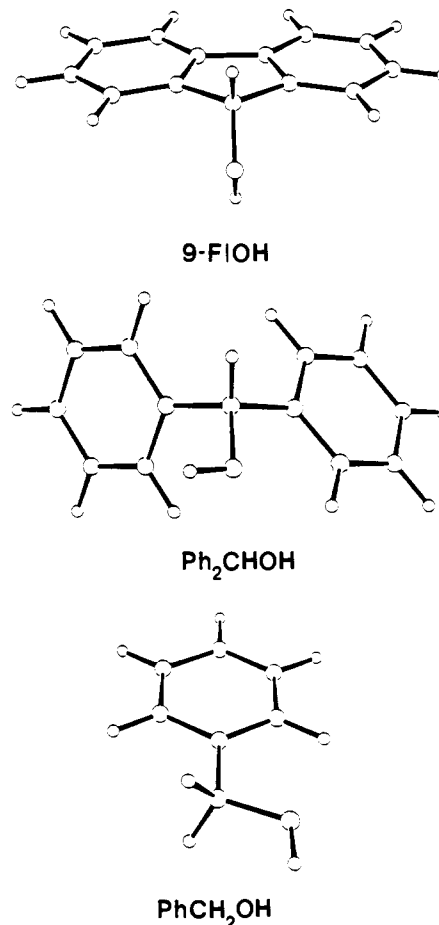
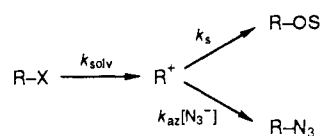


Figure 4. Minimum energy structures for 9-FIOH, Ph_2CHOH , and PhCH_2OH calculated at the 3-21G level.

conformations were missed. The potential energy surface of PhCH_2OH was examined by STO-3G and 3-21G calculations. The lowest energy conformer has C_s symmetry with the C-O bond lying in the plane of the aromatic ring (Figure 4). Single-point

Scheme II



calculations for all three alcohols were also done at the 6-31G**/3-21G level (Table IV).

The structures of the carbanions 9-FI⁻ and Ph₂CH⁻ were optimized at the 3-21G level, and single-point calculations were performed at both the 6-31G**/3-21G level and the 6-31+G**/3-21G level. The latter calculations were performed because the diffuse function augmented basis sets usually perform better for anions than do other basis sets.²⁹ In these calculations, Ph₂CH⁻ retains the enantiomeric C₂ minima found for Ph₂CH⁺, but the phenyl rings are rotated out of the pseudoplane of the molecule by only ±10.72°, rather than 18.59° found for the carbocation. The energies of these two species are collected in Table IV, along with the results for the other species.

Discussion

Reaction Mechanisms. In 50:50 (v:v) trifluoroethanol/water, the reactions of α-methylbenzhydryl acetate and 9-methyl-9-fluorenyl 3,5-dinitrobenzoate are zeroth-order in [N₃⁻] in the range 0–0.50 M but give ≥75% yields of the respective azide adducts at [N₃⁻] = 0.50 M. This shows that these substrates react by a D_N + A_N (S_N1)⁸ mechanism through carbocation intermediates that are trapped by azide ion (Scheme II).

We were unable to determine the kinetic order for the fast reaction of azide ion with benzhydryl chloride. However, a chloride common ion rate depression has been reported for this substrate,^{30a} which shows that the reaction proceeds through a free carbocation intermediate. The capture of this intermediate by azide ion is the only detectable pathway for formation of the azide adduct. A concurrent bimolecular substitution reaction of azide ion is not important because this reaction would cause the product rate constant ratio k_{az}/k_s (M⁻¹) to increase with increasing concentrations of azide ion,^{30b} but no such increase is observed.

The bimolecular reaction of azide ion with 9-bromofluorene probably proceeds by a concerted mechanism that is enforced by the insignificant lifetime of the 9-fluorenyl carbocation in the presence of azide ion.³¹ The rate constant ratio $k_{\text{N}}/k_s = 35 \text{ M}^{-1}$ for the second-order reaction of azide ion and the solvolysis reaction of 9-FIBr in 50:50 (v:v) trifluoroethanol/water falls between $k_{\text{N}}/k_{\text{solv}} = 1.8 \text{ M}^{-1}$ for the reaction of 1-phenylethyl bromide in the same solvent³² and the extremely large ratio observed for reactions of cyclopentadienyl iodide and bromide.³³ The latter compounds are highly resistant to solvolysis¹⁻³ but undergo rapid bimolecular substitution reactions with halide ions.³³ The enhanced reactivity of cyclopentadienyl and 9-fluorenyl derivatives in bimolecular substitution by anionic nucleophiles is consistent with stabilization of the transition states for these reactions by delocalization of negative charge into the ring systems, which is favored by the stability of the resulting cyclic (4n + 2) π-electron systems.³³

(29) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612.

(30) (a) Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *J. Chem. Soc., Chem. Commun.* **1966**, 122–123. (b) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1990**, *111*, 9507–9512.

(31) $1/k_{\text{nuc}} \approx 10^{-17} \text{ s}$ for collapse of [N₃⁻-9-FI⁺-Cl⁻] to give 9-FIN₃ was estimated from $k_s = 1.4 \times 10^{10} \text{ s}^{-1}$ (Table III), $k_{\text{az}}/k_s = 10^8 \text{ M}^{-1}$ for partitioning of the trianisylmethyl carbocation between azide ion and solvent [Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544], $K_{\text{az}} = 0.3 \text{ M}^{-1}$ for formation of a cation–anion pair from free ions,^{25b} and $k_{\text{nuc}} = k_{\text{az}}/K_{\text{az}}$. This is much shorter than the time for a single bond vibration ($\sim 10^{-13} \text{ s}$), which shows that there is no chemical barrier to collapse of the triple ion complex and that this species is probably a transition state, not an intermediate.

(32) Estimated by interpolation of a linear Hammett plot of log ($k_{\text{N}}/k_{\text{solv}}$) for the reactions of ring-substituted 1-phenylethyl bromides that bear electron-withdrawing substituents: Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1383–1396.

(33) Breslow, R.; Canary, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3950–3952.

This is similar to the stabilization of the transition state for nucleophilic substitution α to a carbonyl group by delocalization of the negative charge from the nucleophile onto the carbonyl oxygen.³⁴

The good nucleophile azide ion provides no assistance to the formation of benzhydryl, α-methylbenzhydryl, and 9-methyl-9-fluorenyl carbocations from neutral derivatives. Therefore, the acid-catalyzed substitution reactions of the very weak nucleophile trifluoroethanol with benzhydryl, α-methylbenzhydryl, and 9-methyl-9-fluorenyl alcohols should also proceed without nucleophilic assistance through the liberated carbocation intermediates (Scheme I).³⁵ Although a bimolecular substitution reaction is observed between azide ion and 9-bromofluorene, the following observations provide evidence that the acid-catalyzed reaction of trifluoroethanol with 9-fluorenyl alcohol also proceeds by the concurrent stepwise reaction mechanism shown in Scheme I.

(1) The product rate constant ratios $k_{\text{MeOH}}/k_{\text{TfE}} = 6.2$ for the acid-catalyzed reaction of 9-FIOH and $k_{\text{MeOH}}/k_{\text{TfE}} = 6.6$ for the reaction of 9-FIBr are identical within the experimental error of ±10%. Constant rate constant ratios for different leaving groups are consistent with partitioning of a common 9-FI⁺ intermediate between reaction with methanol and trifluoroethanol. Furthermore, the values of $k_{\text{MeOH}}/k_{\text{TfE}}$ for these reactions are very similar to those determined for carbocations whose reactivities (k_s) toward 50:50 (v:v) trifluoroethanol/water are close to that estimated for 9-FI⁺ (Table III).³⁶

(2) 9-Fluorenyl is 3600-fold less reactive in acid than is 9-methyl-9-fluorenyl (Table II). By comparison, benzhydryl alcohol is only 50-fold less reactive in acid than is α-methylbenzhydryl alcohol. The extremely low reactivity of 9-fluorenyl shows that it is unlikely that the transition state for the acid-catalyzed nucleophilic substitution reaction is stabilized by nucleophilic solvent assistance.

Rate and Equilibrium Constants. There is good evidence that the reaction of azide ion with ring-substituted benzyl^{10,12,30b} and benzhydryl³⁸ carbocations is diffusion-limited. The reaction of azide ion with 9-FI⁺ and 9-Me-9-FI⁺ is also expected to be diffusion-limited, because these carbocations are at least as unstable as the corresponding benzhydryl and α-methylbenzhydryl carbocations. The diffusion-limited reaction of azide ion ($k_{\text{az}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)³⁹ serves as a “clock” for the reaction of these carbocations with 50:50 (v:v) trifluoroethanol/water (k_s , Table III) and allows for the calculation of k_s from the product rate constant ratios k_{az}/k_s (M⁻¹) (Table I).

The reported⁷ value of $k_s = 2.5 \times 10^9 \text{ s}^{-1}$ for capture of 9-Me-9-FI⁺ in 10:90 methanol/water, generated as an intermediate of laser flash photolysis of 9-Me-9-FIOH, is in good agreement with $k_s = 8 \times 10^8 \text{ s}^{-1}$ for capture of this carbocation in 50:50 (v:v) trifluoroethanol/water (Table III) when the 3-fold difference in the reactivities of the two solvents toward carbocations is taken into account.⁴⁰ There is fair agreement between $k_s = 2.8 \times 10^8 \text{ s}^{-1}$ for capture of the benzhydryl carbocation in 50:50 (v:v) trifluoroethanol/water (Table III) and the approximate value of $k_s \approx 9 \times 10^8 \text{ s}^{-1}$ reported for capture of Ph₂CH⁺ generated by laser

(34) Bartlett, P. D.; Trachtenberg, E. N. *J. Am. Chem. Soc.* **1958**, *80*, 5808–5812. Kost, D.; Aviram, K. *J. Am. Chem. Soc.* **1986**, *108*, 2006–2013.

(35) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821–4828.

(36) The value of $k_{\text{MeOH}}/k_{\text{TfE}}$ for 9-FI⁺ lies between $k_{\text{MeOH}}/k_{\text{TfE}} = 7.0$ for reaction of 4-MeArCH(Me)⁺ (for which $k_s = 6 \times 10^8 \text{ s}^{-1}$)^{25b} and $k_{\text{MeOH}}/k_{\text{TfE}} = 5.3$ for reaction of 3-MeOArC(Me)₂⁺ (for which $k_s = 2 \times 10^{10} \text{ s}^{-1}$).³⁷ The estimated reactivity of 9-FI⁺ ($k_s = 1.4 \times 10^{10} \text{ s}^{-1}$, Table III) falls between the reactivities of these two carbocations.

(37) Richard, J. P.; Amyes, T. L.; Vontor, T. *J. Am. Chem. Soc.* **1991**, *113*, 5871–5873.

(38) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913–6914. McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. A.; Steenken, S. *Ibid.* **1991**, *113*, 1009–1014.

(39) Diffusion-limited rate constants of (4–7) × 10⁹ M⁻¹ s⁻¹ have been measured directly for the reaction of azide ion with benzylic carbocations in water or predominantly aqueous solutions.³⁸ Therefore, the estimated error in the rate constants k_s and k_{HOH} reported in this work is ±20%.

(40) There is a 3-fold difference in the reactivity of 10:90 (v:v) methanol/water ($k_s = 1.4 \times 10^8 \text{ s}^{-1}$) and 50:50 (v:v) trifluoroethanol/water ($k_s = 5 \times 10^7 \text{ s}^{-1}$) toward the 1-(4-methoxyphenyl)ethyl carbocation.¹⁰

flash photolysis of 4-cyanophenyl benzhydryl ether in 33% acetonitrile in water.³⁸ The agreement between the values of k_s given in Table III and k_s for capture of carbocations generated by laser flash photolysis is consistent with the formation of common carbocation intermediates in the flash photolytic and nucleophilic substitution reactions.

The value of k_s for capture of $\text{PhC}(\text{Me})_2^+$ (Table III) was obtained by interpolation of a linear Hammett plot of $\log k_s$ values for the reaction of a series of ring-substituted cumyl carbocations.³⁷ The value of $k_s = 1.4 \times 10^{10} \text{ s}^{-1}$ for 9-Fl⁺ (Table III) was calculated from $k_s = 8 \times 10^8 \text{ s}^{-1}$ for the capture of 9-Me-9-Fl⁺ (Table III) with the assumption that 9-Fl⁺ and 9-Me-9-Fl⁺ show the same difference (17-fold) in reactivity in 50:50 (v:v) trifluoroethanol/water as was previously reported in 90:10 trifluoroethanol/water.⁷ The value estimated for k_s in Table III is slightly smaller than $k_s = 2.3 \times 10^{10} \text{ s}^{-1}$ in 90:10 trifluoroethanol/water for the reaction of 9-Fl⁺ generated as an intermediate of laser flash photolysis of 9-FIOH.

Second-order rate constants k_{HOH} ($\text{M}^{-1} \text{ s}^{-1}$, Scheme I and Table III) for the reaction of benzyl, benzhydryl, and fluorenyl carbocations with water were calculated from the values of k_s (s^{-1}) and $k_{\text{HOH}}/k_{\text{TFE}}$ (Table I) using eq 6. The value of k_{HOH} for PhCH_2^+

$$k_s = k_{\text{HOH}}[\text{H}_2\text{O}] + k_{\text{TFE}}[\text{TFE}] \quad (6)$$

is a lower limit calculated from $k_s \geq 4 \times 10^{11} \text{ s}^{-1}$ for PhCH_2^+ ^{30b} and $k_{\text{HOH}}/k_{\text{TFE}} = 1.05$ for the reaction of benzyl tosylate.⁴¹ Equilibrium constants $K_{\text{eq}} = k_{\text{H}}/k_{\text{HOH}}$ for the formation of benzyl, benzhydryl, and fluorenyl carbocations from the corresponding alcohols (Scheme I) are listed in Table III, along with the values of $\text{p}K_{\text{R}} = \log(K_{\text{eq}}/[\text{H}_2\text{O}])$. The $\text{p}K_{\text{R}}$ values for $\text{PhC}(\text{Me})_2^+$ and 9-Fl⁺ may be up to 0.1 unit *too negative* if the values of k_{H} for the respective alcohols have been underestimated by 20% (see Results).

A change in solvent from 50:50 (v:v) trifluoroethanol/water to pure water leads to a -0.8 unit change in the $\text{p}K_{\text{R}}$ for 9-Me-9-Fl⁺ (Table III). Using -0.8 as a correction for the solvent effect on the $\text{p}K_{\text{R}}$ for Ph_2CH^+ gives $\text{p}K_{\text{R}} = -12.5$ for this carbocation in water, which lies between the values of -13.3^{1a} and -11.8⁴² that were determined by the acidity function method using respectively H_{R} acidity values determined for the ionization of substituted triarylmethyl alcohols^{1a} and H^{R} acidity values determined for the ionization of benzhydryl alcohols.⁴² We conclude that the acidity function method gives reliable ionization constants in water not only for triarylmethyl carbocations⁹ but also for the more unstable diarylmethyl carbocations.

The acidity of 9-Me-9-Fl⁺ in water determined by our kinetic method ($\text{p}K_{\text{R}} = -11.9$, Table III) is significantly lower than the earlier estimate of $\text{p}K_{\text{R}} = -16.6$ from the acidity function method.^{1a} However, the spectral change that is observed in concentrated solutions of sulfuric acid cannot correspond to the conversion of 9-Me-9-FIOH to 9-Me-9-Fl⁺ because in 58% (by weight) sulfuric acid, which is well below the percent acid where a spectral change is observed, there is no detectable 9-Me-9-FIOH, but rather a complex mixture of products is formed, one of which was identified as the dehydration product dibenzofulvene. Alkenes such as α -phenylstyrene are more stable than their water adducts in concentrated H_2SO_4 because of the small activity coefficient for water in these solvents.⁴³ This suggests that in concentrated H_2SO_4 9-Me-9-FIOH is first converted to dibenzofulvene and that this compound, which is known to be unstable,^{26b} then reacts to form several other products. In any event, the failure to detect 9-Me-9-FIOH in concentrated H_2SO_4 shows that the previously published value^{1a} of $\text{p}K_{\text{R}} = -16.6$ for 9-Me-9-Fl⁺ must be incorrect.

The $\text{p}K_{\text{R}}$ values for the carbocations listed in Table III have also been estimated from the oxidation potential of the corresponding radicals in acetonitrile using the appropriate thermodynamic cycle to relate this reaction to the addition of the solvent

Table V. Thermodynamic Results for Eqs 7 and 8

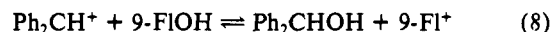
eq	$\Delta H_{\text{el}}^{\text{a}}$ (kcal/mol)		ΔG^{b} (kcal/mol)
	3-21G//3-21G	6-31G*//3-21G	
7	-5.4	-8.2	≤ -5.6
8	+8.4	+10.0	+5.7

^a Obtained from the ab initio energies of Table IV. ^b Calculated from the $\text{p}K_{\text{R}}$ data of Table III at 298 K.

water to a carbocation³ and by making the assumptions that the differences in oxidation potential of the various radicals are the same in water as in acetonitrile and that the difference in free energy between an alcohol and the corresponding hydrocarbon is independent of structure.^{44a} The assumptions are shown to be valid by the good agreement ($\pm 0.5 \text{ p}K_{\text{R}}$ unit for Ph_2CH^+ , $\text{Ph}_2\text{C}(\text{Me})^+$, and 9-Fl⁺) between the resulting estimated $\text{p}K_{\text{R}}$ values and the data in Table III, after correcting this data for a change in solvent from 50:50 (v:v) trifluoroethanol/water to water.^{44b}

The $\text{p}K_{\text{R}}$ data in Table III show that the 12 π -electron array of the fluorene ring system is effective at stabilizing a positive charge nominally located at C-9. Comparisons between 9-Fl⁺ and $\text{PhCH}(\text{Me})^+$ or 9-Me-9-Fl⁺ and $\text{PhC}(\text{Me})_2^+$ show that the fluorene ring system is about as effective at stabilizing a positive charge as is the combination of a phenyl and methyl group. The fluorene system is somewhat less stabilizing than two phenyl groups, but the differences in the stabilities of 9-Fl⁺ and Ph_2CH^+ (5.7 kcal/mol) and of 9-Me-9-Fl⁺ and $\text{Ph}_2\text{C}(\text{Me})^+$ (2.4 kcal/mol) are not large.

Calculations. The ab initio calculations provide insight into the reasons for the differences in the stabilities of PhCH_2^+ , 9-Fl⁺, and Ph_2CH^+ relative to the respective alcohols. The ab initio energies from Table IV and the $\text{p}K_{\text{R}}$ data from Table III can be used to calculate ΔH_{el} (the electronic contribution to ΔH) and ΔG , respectively, for the reactions of eqs 7 and 8. The results



of these calculations are shown in Table V. The value of $\Delta H_{\text{el}} = 10.0 \text{ kcal/mol}$ calculated in this work for eq 8 is very close to the value of 10.1 kcal/mol from MINDO/3 calculations for hydride ion transfer from fluorene to Ph_2CH^+ to form Ph_2CH_2 and 9-Fl⁺.^{45a}

ΔH_{el} contains no vibrational or rotational contributions or zero-point energy corrections. These would be expected to cancel, in part, for the equilibria of eq 7 and 8. The calculation of ΔH_{el} also does not consider corrections for the population of higher energy conformers or enantiomeric conformations. These are important only for Ph_2CHOH and Ph_2CH^+ . The effects of enantiomeric conformations of the lowest energy conformers of Ph_2CHOH and Ph_2CH^+ on the energetics of eq 8 will cancel. A conformation of Ph_2CHOH that is 1.3 kcal/mol above the ground state was located at the 3-21G level (see Results). At 298 K, that conformation will represent ca. 10% of the population of Ph_2CHOH . Corrections for the existence of this conformation would change the values of ΔH_{el} for eq 8 in Table V by ca. 0.1 kcal/mol.

The agreement between the values for ΔH_{el} and ΔG is quite remarkable, given the large number of factors either not considered in the calculation of ΔH_{el} or which might cause ΔG for a solution reaction to differ from ΔH_{el} for a gas-phase reaction. This indicates that the energies of these three carbocations relative to the respective alcohols are dominated by ΔH_{el} and that other contributions to ΔG for eqs 7 and 8, such as ΔS and the change in the free energy of solvation, are probably small.

(44) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132-137. (b) The $\text{p}K_{\text{R}}$ values from ref 44a are estimated for a reaction in water. The value of -0.8 determined for 9-Me-9-Fl⁺ is used to correct the $\text{p}K_{\text{R}}$ values in Table III for a change in solvent.

(45) (a) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Westermann, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 4485-4491. (b) Feng, J.; Leszczyński, J.; Weiner, B.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 4648-4655.

(41) Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1241-1246.

(42) Mindl, J.; Večera, M. *Collect. Czech. Chem. Commun.* **1971**, *36*, 3621-3632.

(43) Deno, N. C.; Groves, P. T.; Saines, G. *J. Am. Chem. Soc.* **1959**, *81*, 5790-5795.

It is clear from the results of Table V that the electronic energy of 9-FI⁺ produces no large antiaromatic destabilization of this species. The bond lengths and atomic charges for 9-FI⁺ are close to the respective bonds lengths and atomic charges for Ph₂CH⁺ (Figure 3). These results are in agreement with an earlier ¹H and ¹³C NMR study of Ph₂CH(Me)⁺ and 9-Me-9-FI⁺, which found no evidence for antiaromatic character in the latter carbocation.^{45a}

There is good evidence for antiaromatic destabilization of systems such as the cyclopentadienyl carbocation which are open-shell triplets in their symmetrical *D_{5h}* structures. These species undergo Jahn–Teller distortion to structures of lower symmetry to remove the π -orbital degeneracy responsible for the triplet electronic state of the *D_{5h}* structure.^{45b} The available p*K_R* data for the cyclopentadienyl carbocation indicate that this species is ca. 27 kcal/mol less stable than the allyl carbocation relative to the respective alcohols at 25 °C.³

The *C_{2v}* structure of 9-FI⁺ produces no π -orbital degeneracy, so this carbocation is not subject to Jahn–Teller distortions. There is a small difference between the energies of 9-FI⁺ and Ph₂CH⁺ relative to the respective alcohols. However, this difference is best attributed to specific structural features of the individual alcohols and carbocations as discussed in the following sections and not to the more general phenomenon of antiaromaticity.

Steric Effects. Ab initio calculations indicate that the planar *C_{2v}* structure of Ph₂CH⁺ is not the most stable conformation of this species. Rotation of the phenyl rings out of the plane defined by the cationic sp² carbon relieves steric strain and causes a decrease in the π -stabilization of the carbocation which we estimate by the following calculations.

(a) The nonplanar *C₂* structure of minimum energy for this carbocation, from ab initio calculations, has ca. 2.5 kcal/mol less van der Waals strain and ca. 3.5 kcal/mol less bending strain than does the fully planar *C_{2v}* structure (MMX force field calculations, Figure 2), but there is no significant difference (ca. 0.5 kcal/mol) in the sums of the bending and van der Waals strains in Ph₂CHOH and Ph₂CH⁺ (*C₂*).

(b) The observed difference in the energy of the strained, planar *C_{2v}* structure for Ph₂CH⁺ and the twisted *C₂* structure of minimum energy is 1–2 kcal/mol (Figure 2A).

(c) The additional π -stabilization present in the fully planar carbocation compared with the *C₂* structure of minimum energy is estimated from the difference in the energy of the *C₂* structure for Ph₂CH⁺ and a hypothetical planar carbocation which is free of the 6.0 kcal/mol van der Waals and bending strains. This is equal to the difference in energies for the *C_{2v}* and *C₂* structures (1–2 kcal/mol, Figure 2A) minus the excess strain energy for the *C_{2v}* structure (6 kcal/mol, Figure 2B), i.e., –(4–5) kcal/mol.

Significant bond angle strain is introduced into 9-FI⁺ by its structure, which forces five sp² carbons into a planar ring. The MMX calculations indicate that there is 4 kcal/mol more bending strain in 9-FI⁺ than in 9-FIOH, so that a hypothetical 9-FI⁺ which is free of excess van der Waals and bending strains would be ca. 4 kcal/mol more stable than calculated by the ab initio procedure.

These data allow for a crude estimate of (ΔH_{el})_{cor} for the interconversion of planar Ph₂CH⁺ and 9-FI⁺, where the carbocations are given hypothetical structures that are free of van der Waals and bending strains. (ΔH_{el})_{cor} is equal to ΔH_{el} obtained from ab initio calculations (8–10 kcal/mol, eq 8) plus a 4–5 kcal/mol correction for the additional resonance stabilization of strain-free planar Ph₂CH⁺ minus a 4 kcal/mol correction for the additional strain energy of 9-FI⁺ that is not present in 9-FIOH. These corrections approximately cancel so that (ΔH_{el})_{cor} is ca. 8–11 kcal/mol, which is about equal to ΔH_{el} obtained from the ab initio calculations (Table V).

We recognize the limitations of these calculations, which include the failure to include σ -bonding factors not related to bending strain and the use of generalized MMX force field parameters for the cationic carbons of Ph₂CH⁺ and 9-FI⁺. However, such errors in these calculations should not affect the conclusion that the difference in the π -stabilization energies of 9-FI⁺ and Ph₂CH⁺ is relatively small.

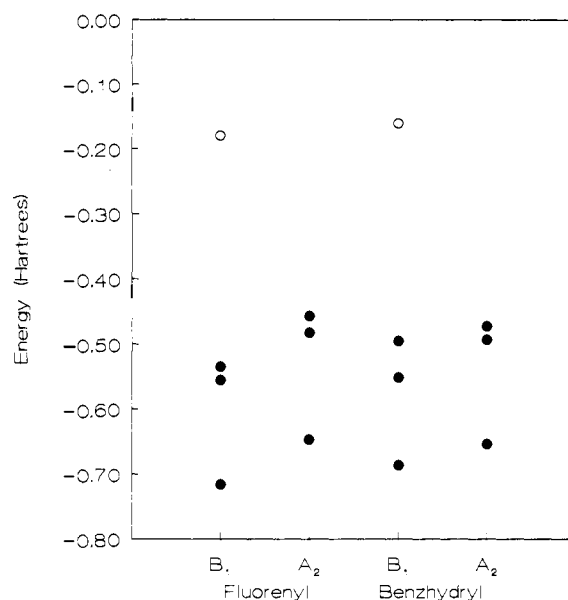


Figure 5. Energies of the π -molecular orbitals of 9-FI⁺ and Ph₂CH⁺ (*C_{2v}*) at the 6-31G*/3-21G level. Filled circles (●) are doubly occupied orbitals, and open circles (○) are the LUMOs of the two carbocations. Orbital symmetries are indicated on the x-axis.

Electronic Effects. The value of (ΔH_{el})_{cor} = 8–11 kcal/mol is consistent with a decrease in π -electron stabilization on moving from Ph₂CH⁺ (*C_{2v}*) and 9-FIOH to 9-FI⁺ and Ph₂CHOH. However, an examination of the π -stabilization energies for the reactants and products in eq 8 fails to provide any evidence that this change is due to antiaromatic destabilization of 9-FI⁺.

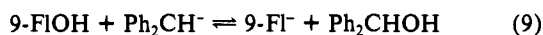
Figure 5 shows the orbital energies of the seven lowest lying π -orbitals of Ph₂CH⁺ (*C_{2v}*) and 9-FI⁺ at the 6-31G*/3-21G level. These orbitals have either *B₁* or *A₂* symmetry (the two carbocations lie in the *yz* plane in this discussion). The *A₂* orbitals are anti-symmetric with respect to reflection through σ_v , while the *B₁* orbitals are symmetric. In planar Ph₂CH⁺, the filled *B₁* orbitals are lower in energy than similar *A₂* orbitals because the *B₁* orbitals are stabilized by interaction between the two aromatic π -systems through the p_x orbital on the central carbon. The *A₂* orbitals must have a node at that carbon. In 9-FI⁺, the interactions across the C4a–C4b bond further stabilize the *B₁* orbitals and destabilize the *A₂* orbitals relative to their energies in Ph₂CH⁺. The sum of the 12 one-electron (orbital) energies for the 12 π -electrons of 9-FI⁺ is 50.4 kcal/mol more negative than that for Ph₂CH⁺ (*C_{2v}*) at the 6-31G*/3-21G level. That is, the additional C4a–C4b bond at 9-FI⁺ compared to Ph₂CH⁺ causes a significant increase in the π -stabilization energies for the so-called antiaromatic carbocation.⁴⁶

If formation of 9-FI⁺ is favored by 50.4 kcal/mol due to the greater π -stabilization for this carbocation than for planar Ph₂CH⁺, then the calculated value (ΔH_{el})_{cor} = 8–11 kcal/mol requires that the π -stabilization energy of 9-FIOH should be ca. 58–61 kcal/mol greater than that of Ph₂CHOH. The difference in π -stabilization of these alcohols cannot be determined from the calculations summarized in Table IV because it is not possible to identify pure π -type orbitals for these species, due to symmetry-allowed mixing of π - and σ -orbitals. Crude calculations suggest that the additional C4a–C4b bond in 9-FIOH leads to significant π -stabilization of 9-FIOH relative to Ph₂CHOH. For instance, at the 6-31G*/3-21G level, the difference between the sums of the one-electron energies of the 12 π -electrons in two molecules

(46) The sum of the 12 π -electron orbital energies of the individual cations is not equal to the π -electron energy, because it counts twice each of the two-electron interaction energies between the π -electrons. However, 9-FI⁺ and Ph₂CH⁺ (*C_{2v}*) have similar size and shape so that the sums of the π -electron orbital energies for the two cations will overestimate the π -electron energies to the same extent. These errors will cancel in the difference between the two sums, which is roughly equal to the difference in π -stabilization energies for the two carbocations.

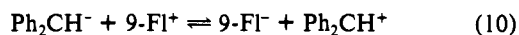
of benzene and of the 12 π -electrons of biphenyl (D_{2h}) is -29.3 kcal/mol.⁴⁷ The magnitude of this difference is substantially smaller than 58–61 kcal/mol. This suggests that there are additional π -stabilization factors present in the alcohols which are not duplicated in this crude model or that there is a significant error in our estimate of $(\Delta H_{el})_{cor}$. In any event, these calculations do not provide any evidence for π -destabilization of 9-F1⁺ compared to Ph₂CH⁺ relative to the corresponding alcohols.

9-Fluorenyl Carbanions. These calculations also provide an explanation for the relatively high stability of 9-fluorenyl carbanions. The difference in the carbon acidities of diphenylmethane and fluorene, measured in a number of solvents, is $\Delta pK_a \approx 10$,⁴⁸ which corresponds to a stabilization of 9-F1⁻ compared with Ph₂CH⁻ of 13.6 kcal/mol, relative to the corresponding hydrocarbons at 298 K. The data in Table IV do not allow a comparison with the hydrocarbons, but ΔH_{el} for eq 9 has been calculated to



be -17.2 kcal/mol at the 3-21G level and -13.2 kcal/mol at the 6-31G**//3-21G level.

The difference in the stabilities of Ph₂CH⁻ and 9-F1⁻ is due primarily to the difference in the energies of the LUMOs of Ph₂CH⁺ and 9-F1⁺ (Figure 5) which, upon the addition of two π -electrons, become the HOMOs of Ph₂CH⁻ and 9-F1⁻, respectively. The two electrons enter an orbital of B_1 symmetry which is stabilized for 9-F1⁻ compared with Ph₂CH⁻ by the interaction across, the C4a–C4b bond. At the 6-31G**//3-21G level, the LUMO of 9-F1⁺ is at 0.01965 hartree (12.3 kcal/mol) lower energy than the LUMO of the C_{2v} structure for Ph₂CH⁺, or at 0.02060 hartree (12.9 kcal/mol) lower energy than the LUMO of the minimum energy C_2 structure of Ph₂CH⁺. The value of ΔH_{el} for the transfer of two electrons from Ph₂CH⁺ to 9-F1⁺ (eq 10) is equal to (2)(-12.9 kcal/mol) = -25.8 kcal/mol, if it is



assumed that the two-electron interaction energies at the HOMOs of 9-F1⁻ and Ph₂CH⁻ are identical. This assumption is probably correct, because it gives a value of ΔH_{el} for eq 10 which is in good

(47) The difference between the sums of the one-electron energies for electrons in orbitals of A_1 and B_2 symmetry for diphenylmethane and fluorene, both restricted to C_{2v} symmetry, is -25.2 kcal/mol at the 6-31G**//3-21G level. This is not very different from the results for the more crude model of two benzene molecules and biphenyl.

(48) Streitwieser, A., Jr.; Bors, D. A.; Kaufman, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1394–1395.

agreement with $\Delta H_{el} = -23.2$ kcal/mol (at the 6-31G**//3-21G level) calculated from $\Delta H_{el} = -13.2$ kcal/mol for eq 9 minus $\Delta H_{el} = 10.0$ kcal/mol for eq 8.

Are 9-Fluorenyl Carbocations Antiaromatic? Aromaticity and antiaromaticity refer, respectively, to the stabilization of a cyclic $(4n + 2)$ π array of electrons due to a specific bonding interaction and the destabilization of a cyclic $4n$ π array of electrons due to an antibonding interaction.^{4a} 9-F1⁺ and 9-R-9-F1⁺ have been concluded to be antiaromatic, based on the observation that these carbocations are more unstable than the corresponding benzhydryl carbocations.⁴⁻⁷ However, this conclusion is both misleading and incorrect.

The description of 9-F1⁺ as antiaromatic is misleading because it implies an exceptionally unstable carbocation, and this is not supported by the data in Table III. The pK_R value for the reaction of 9-F1⁺ is considerably less negative than that for reaction of the resonance-stabilized benzyl carbocation, and the small difference in the values of pK_R for 9-F1⁺ and Ph₂CH⁺ indicates that the latter cation is only slightly more stable relative to the respective alcohols.

It is incorrect to attribute the small difference in stability between 9-F1⁺ and Ph₂CH⁺ to antiaromaticity because this implies significant π -destabilization of 9-F1⁺ compared to Ph₂CH⁺, and there is *no evidence* that this is true. A number of other factors also contribute to the sign and the magnitude of ΔG for eq 8, including the difference in the π -stabilization energies for 9-FIOH and Ph₂CHOH and changes in van der Waals and bending strains on moving from reactants to products. We were unable to identify which of these factors is responsible for the small difference in the stabilities of 9-F1⁺ and Ph₂CH⁺. However, the calculations show that the observed difference in the stability for these carbocations actually opposes the difference in the π -stabilization energies, which are substantially greater for 9-F1⁺ than for Ph₂CH⁺. We suggest, therefore, that 9-F1⁺ no longer be referred to as antiaromatic.

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Supplementary Material Available: Listings of minimum energy geometries obtained by 3-21G//3-21G optimizations of PhCH₂OH, 9-FIOH, Ph₂CHOH, PhCH₂⁺, 9-F1⁺, Ph₂CH⁺, 9-F1⁻, and Ph₂CH⁻ (8 pages). Ordering information is given on any current masthead page.