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Hyperaromatic Stabilization of Arenium Ions: Cyclohexa- and Cycloheptadienyl Cations—Experimental and Calculated Stabilities and Ring Currents

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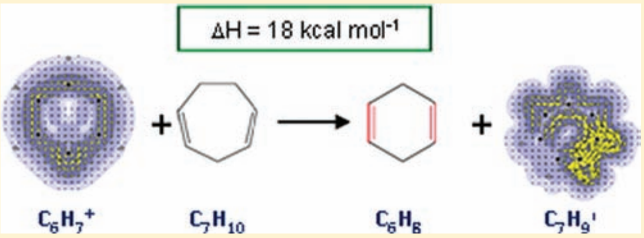
S *Supporting Information*



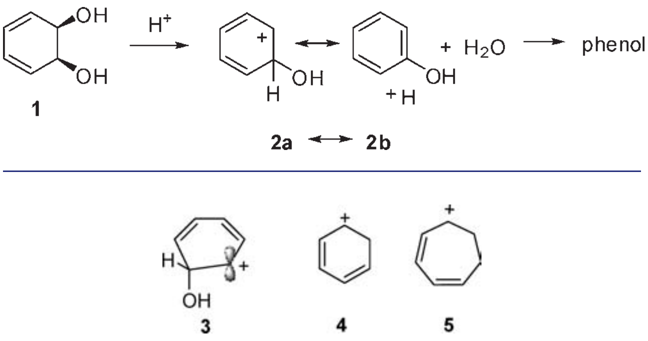
ABSTRACT: Measurements of pK_R show that the cycloheptadienyl cation is less stable than the cyclohexadienyl (benzenium) cation by 18 kcal mol^{-1}. This difference is ascribed here to "hyperaromaticity" of the latter. For the cycloheptadienyl cation a value of K_R = [ROH][H$^+$]/[R$^+$] is assigned by combining a rate constant for reaction of the cation with water based on the azide clock with a rate constant for the acid-catalyzed formation of the cation accompanying equilibration of cycloheptadienol with its trifluoroethyl ether in TFE—water mixtures. Comparison of pK_R = −16.1 with pK_R = −2.6 for the cyclohexadienyl cation yields the difference in stabilities of the two ions. Interpretation of this difference in terms of hyperconjugative aromaticity is supported by the effect of benzannelation in reducing pK_R for the benzenium ion: from −2.6 down to −3.5 for the 1*H*-naphthalenium and −6.0 for the 9*H*-anthracenium ions, respectively. MP2/6-311+G** and G3MP2 calculations of hydride ion affinities of benzenium ions show an order of stabilities for substituents at the methylene group consistent with their hyperconjugative abilities, i.e., $(H_3Si)_2$ > cyclopropyl > H_2 > Me_2> $(HO)_2$ > F_2. Calculations of ring currents show a similar ordering. No conventional ring current is seen for the cycloheptadienyl cation, whereas currents in the F_2-substituted benzenium ion are consistent with antiaromaticity. Arenium ions where the methylene group is substituted with a single OH group show characteristic energy differences between conformations, with C−H or C−OH bonds respectively occupying or constrained to axial positions favorable to hyperconjugation. The differences were found to be 8.8, 6.3, 2.4, and 0.4 kcal mol^{-1} for benzenium, naphthalenium, phenanthrenium, and cyclohexenyl cations, respectively.

INTRODUCTION

Two previous papers[1,2] have explored evidence for hyperconjugative aromaticity of arenium ions based on (a) measurements of high *cis*/*trans* reactivity ratios for acid-catalyzed formation of the hydroxy-substituted ions from arene dihydrodiols and (b) the dependence of these values on the expected aromaticity of the ions, i.e., benzenium >1,2-naphthalenium > 9,10-phenanthrenium.[3] Reaction of benzene *cis*-1,2-dihydrodiol **1** to form a hyperconjugatively stabilized 2-hydroxybenzenium ion **2** as the first and rate-determining step of its acid-catalyzed dehydration to phenol is illustrated in Scheme 1. It was proposed that the favorable effect of hyperconjugation is enhanced by the aromatic character of the no-bond structure **2b**, which contributes to resonance stabilization of the ion.

The slower reactions of the *trans* compared with *cis* isomers of the arenedihydrodiols was suggested to arise from formation of the arenium ion intermediate in an unfavorable conformation **3** in which OH rather than H occupies an axial position that is optimal for hyperconjugation. The advantage of an aromatic resonance structure is then offset by the siting of a positive charge on an oxygen rather than a hydrogen atom.

Scheme 1



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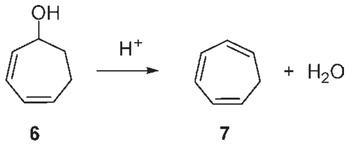
Scheme 2



In the second paper,[2] *cis/trans* reactivity ratios for 2-HO groups were compared with those of other 2-substituents in the acid-catalyzed dehydration of 1,2-dihydro-1-naphthols. With the exception of groups subject to neighboring group participation in their *trans* configuration, an order H < Me < Bu^t < Ph < NH_3^+ < HO ~ MeO was established, which is consistent with a reasonable expectation of relative capacities for σ-interaction with a positively charged center. It was also shown that while a *cis*-β-hydroxyl group caused a nearly constant rate reduction of ~10^3-fold for a carbocation-forming reaction, consistent with the influence of an inductive effect, the effect of a *trans*-β-hydroxyl substituent was highly sensitive to the "aromatic" stability of the arenium ion intermediate, with a maximum rate reduction of 10^7-fold for formation of a β-hydroxybenzenium ion, consistent with an additional contribution from loss of hyperconjugative stabilization of the cation.

In the present paper the stability of the benzenium ion (cyclohexadienyl cation) **4** is compared with that of the cycloheptadienyl cation **5**, using equilibrium measurements of ease of formation from the corresponding alcohol (K_R). In the absence of hyperconjugative aromatic stabilization, the difference in stability should reflect uncanceled ring strain effects between cycloheptadienol and the cation **5**. Although it is difficult to predict exact magnitudes for ring strain effects, a sufficiently large difference may be taken as indicative of stabilization of the cyclohexadienyl cation not available to its seven-membered counterpart, for which a no-bond resonance structure contributing to hyperconjugation does not contain an aromatic ring.

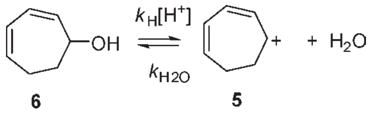
In addition, high-level calculations of the stabilization have been undertaken to ensure that arguments based on a simple valence-bond representation of resonance and hyperconjugation have a firm foundation. The computations assess both energies and magnetic ring currents.

Finally, a review of the literature identifies other possible examples of aromatic hyperconjugation. The evidence comes from spectroscopic properties (IR and NMR) and effects of benzannelation on the stabilities of arenium ions. It also comes from reactivities of aromatic molecules toward electrophilic aromatic substitution and from comparisons of acid-catalyzed dehydration of arene hydrates (or *cis*-dihydrodiols) and ring-opening of arene oxides. It is argued that the breadth and importance of the influence of this type of aromaticity justifies the designation "hyperaromatic" for the stabilization of arenium ions.

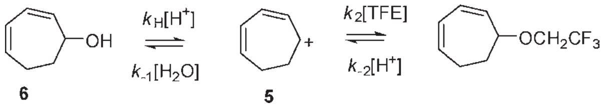
■ RESULTS

Experimental Results. A rate constant for acid-catalyzed dehydration of 1-hydroxy-2,4-cycloheptadiene (2,4-cycloheptadienol **6**, Scheme 2) to form cycloheptatriene **7** in aqueous solution was determined spectrophotometrically as 6.8×10^{-6} M^{-1} s^{-1} (see Experimental Section, Table S1, and Figure S1). For this reaction, unlike that of arene dihydrodiols,[1−3] the rate-determining step is not formation of a carbocation intermediate but deprotonation of the cation to form the cycloheptatriene product.

Scheme 3



Scheme 4



Determination of a rate constant for carbocation formation is nevertheless required to evaluate an equilibrium constant for carbocation formation $K_R = [ROH][H^+]/[R^+]$, where R^+ is the 2,4-cycloheptadienyl cation **5**, ROH is the 2,4-cycloheptadienol **6**, and a value for K_R may be deduced from the ratio of rate constants for formation and reaction of the carbocation with water, i.e., $K_R = k_{H_2O}/k_H$ in Scheme 3.

In these circumstances, Richard and Jencks have shown that a rate constant for carbocation formation may be deduced from measurements of a rate constant for equilibration of the alcohol and trifluoroethyl ether in solvent mixtures of water and trifluoroethanol (TFE) (Scheme 4).[4] As reaction of the carbocation with water or TFE is much faster than loss of a proton to form cycloheptatriene, the latter reaction can be neglected on the time scale of the equilibration.

The approach to equilibrium may be monitored by HPLC. Tables S2 and S3 list HPLC peak intensities for cycloheptadienol and its trifluoroethyl ether as a function of time, for 0.1 and 1.0 M $HClO_4$ in aqueous mixtures containing 30, 50, and 70% TFE (plus 10% of acetonitrile). From these measurements rate constants k_{obs} and equilibrium constants K_{eq} for equilibration of the alcohol and ether may be determined. Expressions for k_{obs} and K_{eq} in terms of the microscopic rate constants in Scheme 4 are shown in eqs 1 and 2. These equations contain three unknowns, the rate constants k_H and k_{-2}, which represent acid-catalyzed conversion of cycloheptadienol and its trifluoroethyl ether, respectively, to the carbocation intermediate, and the ratio of rates for reaction of the carbocation with H_2O and TFE, $k_{-1}[H_2O]/k_2[TFE]$, denoted x.

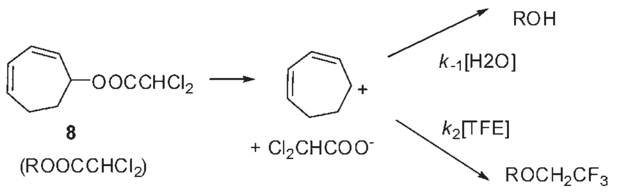
$$k_{obs} = \frac{k_H}{(1 + x)} + \frac{xk_{-2}}{(1 + x)} \qquad (1)$$

where $$x = \frac{k_{-1}[H_2O]}{k_2[TFE]}$$

$$K_{eq} = \frac{k_H k_2[TFE]}{k_{-1}k_{-2}[H_2O]} \qquad (2)$$

Experimentally, the value of K_{eq} was taken as the ratio of concentrations of alcohol **6** and ether when the equilibration reaction was complete. For both kinetic and equilibrium measurements it was supposed that the extinction coefficients of the alcohol and trifluoroethyl ether were equal. A value of x was

Scheme 5



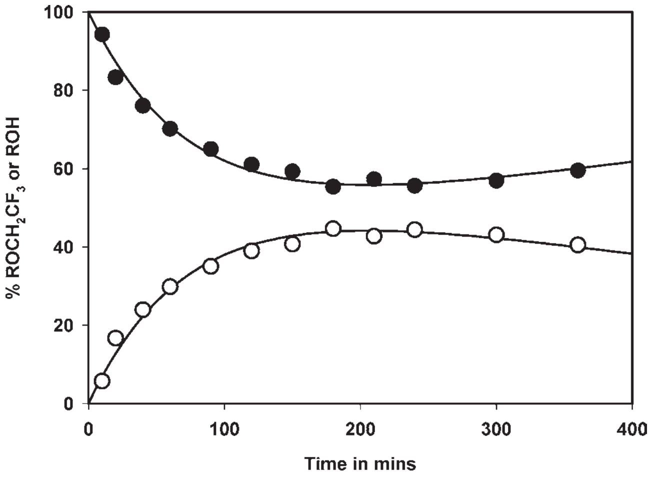


Figure 1. Plots of % cycloheptadienol (ROH, ●) and its trifluoromethyl ether ($ROCH_2CF_3$, ○) versus time for equilibration in 70% TFE:30% H_2O (v/v) with 0.1 M $HClO_4$ at 25 °C.

determined by generating the carbocation in TFE−H_2O mixtures of the same composition as used for the kinetic and equilibrium measurements. Partitioning between the two solvent components gave x as the ratio of alcohol and trifluoroethyl ether products formed (eq 3). As shown in Scheme 5, the dichloroacetate ester of the cycloheptadienol **8** was used as a precursor to generate the carbocation. This substrate was chosen because it has a convenient half-life (~100 s, $k = (7.4 \pm 0.55) \times 10^{-3}\ s^{-1}$) for solvolysis in water. The solvolysis was monitored by HPLC (Table S4).

$$x = \frac{k_{-1}[H_2O]}{k_2[TFE]} = \frac{[ROH]}{[ROCH_2CF_3]} \tag{3}$$

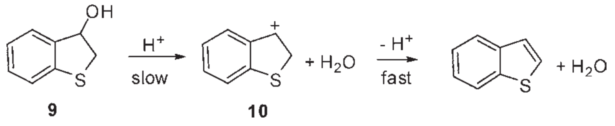
Plots of percentages of cycloheptadienol and its trifluoroethyl ether as a function of time during their equilibration in 70% TFE and 30% water in the presence of 0.1 M $HClO_4$ are shown in Figure 1. As can be seen, instead of reaching constant fractions of dienol and ether as the reaction approaches equilibrium, at longer times the mixture contains decreasing percentages of ether. This is attributed to evaporation and was corrected for as described in the Experimental Section to give the satisfactory fit of calculated to experimental measurements shown in the figure. Values of K_{eq} were based not on measurements of dienol and ether at 0.1 M $HClO_4$ but on a ratio of concentrations at 1 M acid, at which (acid) concentration the reaction was much faster than at 0.1 M and the limiting ratio of dienol to ether remained constant on the time scale of the experiment (Table S3). For the kinetic measurements in 50% and 30% TFE, greater scatter of the HPLC measurements than in Figure 1 was observed, and the precision of the derived values of k_{obs} is probably not better than 50%. As will be seen, this level of precision is nevertheless satisfactory for the purpose of the analysis.

Table 1. Rate and Equilibrium Constants from Kinetic and Product Analyses of Equilibration of Cycloheptadienol and Its Trifluoromethyl Ether in TFE−H_2O Mixtures (v/v) and 0.1 M H^+ at 25 °C

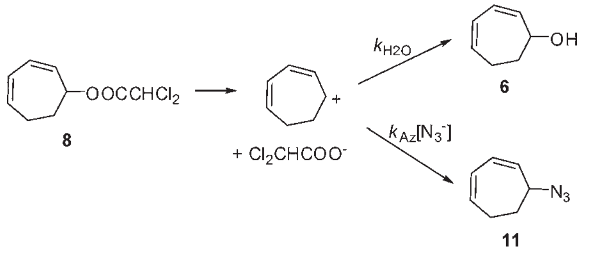
% TFE[a]	x[b]	10^4k_{obs} (s^{-1})	K_{eq}	10^3k_H ($M^{-1}\ s^{-1}$)	10^4k_{-2} ($M^{-1}\ s^{-1}$)	log k/k_o[c]
30	27.6	7.2	0.195	3.3	6.1	−0.02
50	12.6	6.0	0.56	2.9	4.2	0.23
70	6.05	22.2	1.31	8.9	11.2	0.66

[a] Reaction solutions also contain 10% acetonitrile. [b] [ROH]/[ROTFE] from ratio of products for solvolysis of dichloroacetoxycycloheptadienol **8**. [c] Log of ratio of rate constants for dehydration of benzothiophene hydrate **9** in TFE−H_2O (k) and water (k_o).[5]

Scheme 6



Scheme 7



Combination of x with k_{obs} and K_{eq} gave the values of k_H and k_{-2} shown in Table 1. However, it should be noted that these measurements refer to TFE−H_2O mixtures. To extrapolate a value for water, log k_H was plotted against values of log k/k_o for the dehydration of benzothiophene hydrate **9**, where k and k_o are rate constants for its reaction in a TFE−H_2O mixture and H_2O, respectively.[5] As shown in Scheme 6, formation of the carbocation **10** is rate-determining for this dehydration reaction, which is judged to be a suitable model for representing solvent effects on the analogous carbocation formation from cycloheptadienol.

The three-point plot of log k_H for cycloheptadienol **6** against log k/k_o for benzothiophene hydrate is shown in Figure S2. The straight line through the points is drawn with slope 1.0 as observed for a number of comparable reactions.[5] The extrapolated value of k_H in water is $(2.6 \pm 1.0) \times 10^{-3}\ M^{-1}\ s^{-1}$. The scatter evident in this plot is tolerable because an error as large as 2-fold in k_H affects a derived value of pK_R for the cycloheptadienyl cation by only 0.3 log unit. As indicated below, the measurement for water is corroborated by a value for 50% aqueous TFE−H_2O mixture requiring no extrapolation.

To obtain K_R for the cycloheptadienyl cation, k_H must be combined with a rate constant k_{H_2O} for reaction of the ion with

Table 2. Products from Solvolysis of 2,4-Cycloheptadienyl Dichoroacetate 8 in Aqueous Solution at 25 °C in the Presence of Sodium Azide

$[NaN_3]$ (M)	% dienol	% azide	[azide]/[dienol]
0.00	100	0.00	0.0
0.10	88.1	11.9	0.14
0.20	77.7	22.3	0.29
0.40	60.9	39.1	0.64
0.60	55.9	44.1	0.79
0.80	41.9	58.2	1.39

water (Scheme 3). A value of k_{H_2O} can be obtained from the azide clock[4,6] by trapping the carbocation formed from solvolysis of the cycloheptadienyl dichloroacetate **8** by reaction with azide ion in competition with water as shown in Scheme 7. Product proportions were determined by HPLC. The cycloheptadienyl azide **11** was not isolated, but the HPLC peak was identified from its retention time relative to the alcohol, based on the fact that its rate of formation was the same as that of other products, and by the dependence of the final peak intensity on the concentration of azide ions.

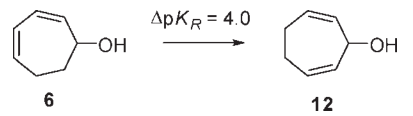
Product ratios of cycloheptadienyl azide (RN_3) to cycloheptadienol (ROH) for different concentrations of azide ion are shown in Table 2 and plotted against $[N_3^-]$ in Figure S3, to give a straight line with slope 1.58. The relationship between product ratio and $[N_3^-]$ based on Scheme 7 is given by eq 4, so that the slope of the plot corresponds to the ratio of rate constants for reaction of the cycloheptadienyl cation with azide ions and water, k_{Az}/k_{H_2O}. With the usual assumption for a carbocation of this stability,[6] that the reaction with azide ions is diffusion controlled with rate constant $k_{Az} = 5.0 \times 10^9\ M^{-1}\ s^{-1}$, we obtain from the slope of the plot $k_{H_2O} = (3.2 \pm 0.3) \times 10^9\ s^{-1}$. Combining k_{H_2O} with $k_H = 2.6 \times 10^{-3}\ M^{-1}\ s^{-1}$ gives $K_R = 1.23 \times 10^{12}$ and $pK_R = -12.1$.

$$[RN_3]/[ROH] = k_{Az}[N_3^-]/k_{H_2O} \qquad (4)$$

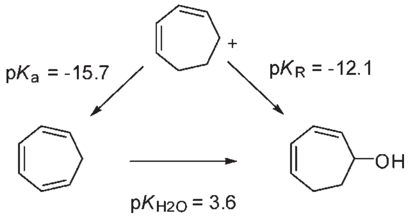
A value of k_{H_2O} was also determined for a 1:1 TFE−H_2O mixture (v/v). Product percentages of azide (RN_3), alcohol (ROH), and trifluoroethyl ether ($ROCH_2CF_3$) are listed in Table S5, and $[RN_3]/[ROH]$ is plotted against concentration of azide ions in Figure S4 to give a straight line of slope $k_{Az}/k_{H_2O} = 3.7 \pm 0.1$, from which $k_{H_2O} = 1.5 \times 10^9$. Combination with $k_H = 2.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ (from Table 1) gives $pK_R = -11.7$. As found previously for carbocation-forming reactions,[5] values in water and in the TFE−H_2O mixture show rather small differences. This directly determined value thus reinforces the value extrapolated (with greater uncertainty) for water. The rate constant for formation of the trifluoroethyl ether from the cycloheptadienyl cation is 1.2×10^8, which on combination with $k_{-2} = 4.2 \times 10^{-4}$ from Scheme 4 gives $pK = -11.5$ in 1:1 TFE−H_2O, where $K = [ROCH_2CF_3][H^+]/[R^+]$.

A value of pK_R was also required for the isomeric 2,6-cycloheptadienol **12** (Scheme 8). This was estimated by supposing that the difference in free energy of formation of the parent hydrocarbons, 1,3- and 1,4-cycloheptadiene, corresponds to the difference in their heats of hydrogenation[7,8] to form cycloheptane, $\Delta\Delta H = 6.0$ kcal mol^{-1}. Assuming that the free energies of transfer of the two hydrocarbons to aqueous solution are the same, a correction of 0.5 kcal mol^{-1} from the estimated difference between substitution of an OH group in 1,3- and 1,4-cyclohexadiene[9] leads to a difference in values of pK_R at 25 °C of 5.5/1.36 = 4.0 and $pK_R = -16.1$ for 2,6-cycloheptadienol.[10]

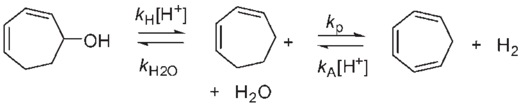
Scheme 8



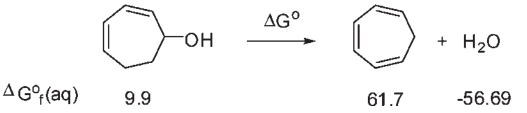
Scheme 9



Scheme 10



We also wished to estimate the equilibrium constant for dehydration of the cycloheptadienols to form cycloheptatriene (eq 5). Guthrie has reported a free energy of formation $\Delta G°_f$(aq) for cycloheptatriene,[11] and $\Delta G°$ for the equilibria can be found if $\Delta G°_f$(aq) for the cycloheptadienols is known. A value of $\Delta G°_f$(g) for 1,3-cycloheptadiene has been reported,[12] and the required $\Delta G°_f$(aq) can be derived if ΔG_t, the free energy of transfer to aqueous solution, and the increment in free energy for replacement of H by OH can be estimated. The derivation of corresponding values for 1,3- and 1,4-cyclohexadienes has been described,[9] and Table S6 summarizes data for saturated and unsaturated seven-membered rings. Assuming that the effect of OH substitution in the 1,3-cycloheptadiene is the same as for 1,3-cyclohexadiene (−39.7 kcal mol^{-1}),[9] one obtains a value of $\Delta G°_f$(aq) which may be combined with values for cycloheptatriene and water in eq 6 to give $\Delta G° = -4.9$ kcal mol^{-1} and $pK_{H_2O} = -4.9/1.36 = -3.6$ at 25 °C, where $K_{H_2O} = 2.5 \times 10^{-4}$ refers to the reverse *hydration* reaction. The dehydration is correspondingly favorable, with equilibrium constant $1/K_{H_2O} = 4000$.



(5)

This equilibrium constant may be combined with $pK_R = -12.1$ to derive a $pK_a = -15.7$ for deprotonation of 1,3-cycloheptadienyl cation to cycloheptatriene based on the cycle in Scheme 9. Arrows in the cycle indicate the directions of reaction to which equilibrium constants refer.

The availability of a pK_a for the 1,3-cycloheptadienyl cation leads to a complete evaluation of rate constants for the dehydration reaction based on the relationships in Scheme 10, in which

k_A and k_p are rate constants respectively for protonation of cycloheptatriene by H_3O^+ and deprotonation of the 1,3-cycloheptadienyl cation in water. The measured rate and equilibrium constants for acid-catalyzed dehydration of the cycloheptadienol, k_{de} and $1/K_{H_2O}$, can be expressed in terms of the microscopic rate constants in Scheme 10 as shown in eqs 6 and 7.

$$k_{de} = \frac{k_H k_p}{k_{H_2O} + k_p} = \frac{k_H}{1 + k_{H_2O}/k_p} \quad (6)$$

$$K_{H_2O} = \frac{k_{H_2O} k_A}{k_H k_p} \quad (7)$$

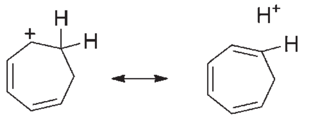
Combining the values of $k_{de} = 6.8 \times 10^{-6}$ M^{-1} s^{-1}, $K_{H_2O} = 2.5 \times 10^{-4}$, and $k_H = 2.6 \times 10^{-3}$ M^{-1} s^{-1} leads to $k_A = 1.70 \times 10^{-9}$ M^{-1} s^{-1} and $k_p/k_{H_2O} = 2.6 \times 10^{-3}$. The consistency of this analysis is confirmed by the finding that the derived value of k_p/k_{H_2O} shows a good fit to a correlation of $\log k_p/k_{H_2O}$ with pK_{H_2O} for a wide range of carbocations.[13] As expected for formation of a nonaromatic alkene, the low value of k_p/k_{H_2O} implies that the deprotonation step is strongly rate-determining in the dehydration reaction. From the previously determined value of $k_{H_2O} = 3.0 \times 10^9$ s^{-1} from the azide trapping measurements, we obtain $k_p = 7.9 \times 10^6$ s^{-1}. This value shows a satisfactory fit to a plot of $\log k_p$ against pK_a for other carbocations.[13]

Computational Results. The measured difference in values of pK_R for cyclohexa- and cycloheptadienyl cations was compared with a calculated difference in hydride ion affinities (ΔHIA) of the ions in the gas phase. G3MP2 calculations gave HIA values of −215.1 and −223.3 kcal mol^{-1} for the six- and seven-membered ring cations, respectively. This corresponds to a difference of 8.2 kcal mol^{-1} compared with the experimental value based on ΔpK_R in aqueous solution of 13 kcal mol^{-1}.

The discrepancy between calculated and experimental values is perhaps not so large as to deserve comment. However, a comparison of 2-cyclohexenyl and 2-cycloheptenyl cations gave HIA values of −229 and −226.8 kcal mol^{-1}, respectively. This suggests that 2 kcal mol^{-1} of the reduced difference in stability of the seven- relative to the six-membered ring in the gas phase might be attributed to the larger size of the ion. Correction for this implies a value of ΔHIA closer to 10.4 kcal mol^{-1} for comparison with the solution value. Little or no contribution is expected from the difference of alcohol from hydrocarbon reference molecules for pK_R and ΔHIA.[9]

A formal, if unlikely, possibility is that hyperconjugation in the cycloheptadienyl cation benefits from a no-bond resonance structure which includes, if not an aromatic structure, at least the *homo*aromatic structure of cycloheptatriene[14] (Chart 1). Greater electron delocalization in the gas phase could then lead to a smaller difference in stability from the cyclohexadienyl cation than in solution. In principle, the existence of such stabilization might be taken to imply "homohyperaromatic" character for the cycloheptadienyl cation! Alternatively, the ion might be viewed as an antiaromatic bis-homocyclopentadienyl structure,[15] but this would imply a less rather than more stable structure. The symmetry of the ion is C_2, and the calculations show a nonplanar pentadienyl cation fragment and no unusual bond distances. Details of the geometry are provided in the Supporting Information.

Chart 1



In addition to calculations for the parent cyclohexadienyl cation, hydride ion affinities were estimated for a series of 6-substituted cations, including OH and other substituents of differing hyperconjugating ability, namely CH_3, SiH_3, F, Cl, SH, NH_2, PH_2, and spirocyclopropyl. HIA values for both mono- and disubstituted ions are shown in Table 3. The calculations were made at the G3MP2 level and gave values which correlated well with HIAs calculated at the MP2/6-311+G** level ($HIA_{MP2} = 1.082 HIA_{G3} + 29.62$, $r^2 = 0.998$, $n = 18$).

The geometries of the ions in Table 3 were also calculated at the MP2/6-311+G** level. The calculations showed that the pentadienyl segments of the ions are very nearly planar. For the 6-hydroxycyclohexadienyl ion, the 1,2,3,4 = 2,3,4,5 dihedral angle is 4.4°, while the cross-ring 1,2,4,5 dihedral is 0.4°. However, the tetrahedral carbon at the 6-position is 10.5° out of the plane and allows substituents to occupy either a pseudoaxial or a pseudoequatorial position.

In the table, the axial substituent is indicated by bold letters, and the final two columns of the table provide dihedral angles with respect to the plane of the ring. For the disubstituted cations the dihedral angles are equal. Where more than one conformation is identified, HIA is reported for the more stable. An exception is made for SH where two structures are reported, one in which the SH is pseudoaxial and one in which it is symmetrically bridged between adjacent carbon atoms.

The hydride ion affinities are also shown as ΔHIA values relative to the cyclohexadienyl cation. Positive values of ΔHIA imply a stabilizing effect of the substituent and negative values destabilization. Also shown are average carbon−carbon bond lengths within the cyclohexadienyl ring. Of interest here is the variation in bond lengths indicated by the average deviation from the averaged length. Thus electron delocalization leading to aromaticity (as a consequence of hyperconjugation) might be expected to lead to equalization of bond lengths around the ring. The differences between substituents are not large, but as discussed below, the smallest variation (0.013 Å) and largest (0.052 Å) are associated with the strongest and weakest hyperconjugating substituents, SiH_3 and F, respectively (with 0.010 Å for spirocyclopropyl).

Details of energies of carbocations and neutral compounds used for the computation of hydride ion affinities shown in Table 3 or referred to elsewhere in the paper are listed in Table S7. Geometric coordinates for the cations and the compounds are listed in Table S8.

Magnetic Ring Currents. A defining characteristic of aromatic molecules is the existence of a ring current induced by application of a perpendicular external magnetic field. Experimentally, this is manifested in measurable magnetic response quantities such as NMR chemical shifts and magnetic susceptibility. These second-order quantities can be evaluated by appropriate integration over the current density distribution, which is a function that shows the current vector per inducing field at each point in space and, most importantly for interpretation, corresponds to the organic chemist's qualitative idea of a

Table 3. Calculated Hydride Ion Affinities (HIA, G3MP2)[a] and Selected Geometric Features (MP2/6-311+G) for 6-Substituted Cyclohexadienyl Cations: 6-X,6-Y-$C_6H_5^+$; ΔHIA Values Calculated as HIA(6-X,6-Y-$C_6H_5^+$) − HIA($C_6H_7^+$)**

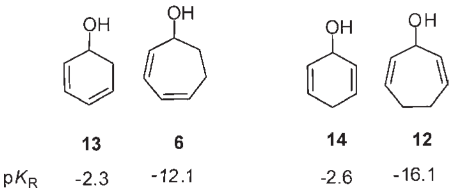
	G3MP2[b]				
X, Y	HIA	ΔHIA	average ring bond lengths, Å	ω_X,[c] deg	ω_H,[d] deg
H, H[e]	−215.1[e]	0	1.419 ± 0.032	54.6	54.6
CH_3, **H**	−214.7	0.4	1.416 ± 0.032	48.9	64.0
CH_3, CH_3	−214.6	0.5	1.419 ± 0.032	58.3	NA
spirocyclopropyl[f]	−195.6	19.5	1.405 ± 0.010	29.2	NA
NH_2, **H**	−218.8	−3.7	1.415 ± 0.024	20.1	98.7
OH, **H**	−225.2	−10.0	1.417 ± 0.027	21.8	91.7
OH, OH	−236.4	−21.3	1.432 ± 0.052	57.9	NA
F, **H**	−233.3	−18.2	1.419 ± 0.033	24.6	89.9
F, F	−251.5	−36.4	1.433 ± 0.052	58.8	NA
SiH_3, H	−196.6	18.5	1.409 ± 0.013	83.5	17.8
SiH_3, SiH_3	−193.0	22.1	1.411 ± 0.016	55.6	NA
PH_2, H	−207.7	7.4	1.412 ± 0.018	83.8	23.3
SH, H[g]	−221.8	−6.7	1.415 ± 0.016	74.3	39.2
Cl, **H**	−230.9	−15.9	1.420 ± 0.032	31.4	82.4

[a] In kcal/mol. The experimental value for the enthalpy of the hydride ion, H = 333.1 kcal/mol, is used. Pseudoaxial substituents for the monosubstituted σ complexes are indicated in bold. [b] G3MP2 enthalpies are at 298 K. [c] The dihedral angle defined by substituent X, C6, C1, and the hydrogen attached to C1. [d] The dihedral angle defined by the hydrogen attached to C6, C6, C1, and the hydrogen attached to C1. [e] The experimental value is −215.9 kcal/mol, calculated from data available in Bartmess, J. E. In *NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, June, 2005; http://webbook.nist.gov. [f] The phenonium cation: spiro[2.5]octa-4,6-dienyl$^+$. [g] The thio-substituted ion also has a more stable, symmetrically bridged, C_s structure, d(C−S) = 1.948 Å. The endo form is more stable than the exo form by 0.4 kcal/mol, and more stable than the unbridged form by 2.7 kcal/mol

ring current. Circulations around rings can be visualized directly, and their diatropic (anticlockwise in our convention) or paratropic (clockwise) direction can be used to diagnose aromaticity or antiaromaticity. The quantities that can be calculated from the full current density function include nucleus-independent chemical shifts (NICS) of which the most sophisticated variant is NICS$(0)_{\pi zz}$, which is computed at the center of a molecule and extracts the out-of-plane tensor component of the isotropic NICS and includes contributions only from π orbitals.[16] NICS$(0)_{\pi zz}$ values are reported in this paper for a number of potentially hyperaromatic molecules.[17]

The technical question of how to calculate and map[18] the current density with ab initio wave functions has been solved by using "distributed origin" methods developed by Bader and others.[19] In this paper, the continuous transformation of origin of current density diamagnetic zero (CTOCD-DZ) method (known more informatively as the "ipsocentric" method) is used to display maps of current density evaluated at 1 bohr above the plane of the potentially aromatic ring. The key to the ipsocentric approach is that current density at any point is computed with that point as the origin. This has the effect of enabling modest basis sets to deliver results of a quality that would require huge numbers of basis functions in other approaches. The arrows in the maps indicate the strength and direction of the induced current, and direct inspection reveals concerted global ring-current circulations, if any are present. In delocalized π-monocycles, the current density is dominated by contributions of HOMO π-orbitals, and the ring current may be characterized numerically in terms of the maximum magnitude of current density per unit inducing magnetic field. This gives a standard unit for estimation of ring currents in aromatic systems. For benzene, for example, the value of this "j_{max}" quantity is 0.079 au when calculated at the level of theory used in this paper for computation of ring currents of arenium ions (cf. Discussion below).

Chart 2

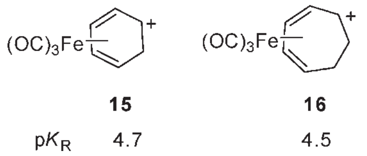


■ DISCUSSION

Cycloheptadienyl Ion. The experiments described above confirm that, as measured by pK_R, the stability of the cycloheptadienyl cation is indeed much less than that of the cyclohexadienyl cation (benzenium) ion, a result which is corroborated by G3MP2 calculations for the gas phase. Comparison between the ions is complicated, however, by the fact that, although the ions correspond to single structures, their pK_R values measure stability relative to isomeric alcohols. The carbocations are characterized by at least two values of pK_R, therefore. The relevant values are shown under the structures of their respective alcohols in Chart 2.

Values of pK_R for the first pair of structures come from direct experimental measurements,[13] while those for the second are inferred from the relative stabilities of their isomeric alcohols.[8,9] In both cases, the implied difference in stabilities of the two ions is large. For the first pair (**13** and **6**), the measured values of −2.3 and −12.1 imply a difference of nearly 10^{10}-fold in equilibrium constant or 13 kcal mol^{-1} in free energy. For the second pair (**14** and **12**), the values of pK_R are −2.6 and −16.1, and the difference is more than 13 powers of 10, or 18 kcal mol^{-1}. These differences are certainly consistent with the operation of "hyperconjugative

Chart 3



aromaticity" as a stabilizing influence for the benzenium ion which is absent for the cycloheptadienyl cation.[20]

Two questions arise. First, could the differences represent instability of the cycloheptadienyl cation arising from ring strain rather than stabilization of the benzenium ion? And second, which of the two comparisons of pK_R values is the more appropriate, that for the 2,4-dienols (**13** and **6**) or that for the 2,5- and 2,6-dienols (**14** and **12**)?

It seems unlikely that the cycloheptadienyl cation is subject to substantially greater strain than its dienol reactant. Although cycloheptane has a strain energy of 6 kcal mol^{-1} relative to a formally strainless cyclohexane,[21] Turner's studies of heats of hydrogenation of cycloheptene, 1,3- and 1,4-cycloheptadienes, and cycloheptatriene offer little evidence that the conjugation in the latter molecules is impaired.[7] Thus, the 1,3-diene is more stable than the 1,4-diene by 6 kcal mol^{-1}, whereas cycloheptatriene shows appreciable stabilization by homoconjugation.[14] Consistently, G3 computations show a 5.1 kcal mol^{-1} difference between the 2,4- and 2,6-cycloheptadienols. Greater strain for the 1,4-cycloheptadiene may supplement resonance stabilization of the 1,3-isomer as a contribution to this difference in energies, but the importance of resonance is confirmed by computations and experimental measurements which favor a C_s structure with planar double bonds as the most stable conformation of the 1,3-isomer.[22] Although a role for ring strain cannot be excluded, it seems unlikely that this could amount to more than 2−3 kcal mol^{-1}.

More significant indeed is that the difference in energy of 1,3- and 1,4-cyclohexadienes is only 0.3 kcal mol^{-1} (0.1 kcal mol^{-1} by G3 computation), compared with the 6 kcal mol^{-1} for the cycloheptadienes.[7,8] This is consistent with the known distortion of the 1,3-cyclohexadiene from a planar structure which limits stabilization arising from conjugation of the double bonds.[21] In answer to the second question, therefore, it is clear that the first comparison in Chart 1 is distorted by a lack of conjugation between the π-bonds in the case of 2,4-cyclohexadienol, which partially compensates for the greater stability of the cyclohexadienyl cation. The comparison which more directly reflects the relative stabilities of the two cations is thus almost certainly that shown for the second pair of structures, for which the π-bonds are unconjugated. This indeed is confirmed by the similar heats of hydrogenation of 1,4-cyclohexadiene and 1,4-cycloheptadiene to form the saturated hydrocarbon, namely 53.9 compared with 55.9 kcal mol^{-1} (in acetic acid at 25 °C).[7,8]

If the pK_R values for the carbocations reacting to form 2,5- and 2,6-dienols (**14** and **12**) are taken as a guide, the implied stabilization of the cyclohexadienyl cation attributable to hyperconjugation is 18 kcal mol^{-1}. This value may indeed be moderated by a contribution from strain energy for the cycloheptadienyl cation. However, it is hard to imagine that the increase in strain between dienol and cation is greater for the seven- than the six-membered ring. Qualitatively the evidence offered by this comparison is consistent with the conclusion reached by Sieber, Schleyer, and Gauss from their MP2 computational study that the "aromatic" stabilization energy of the benzenium ion[20] is close to half that for benzene itself, estimated as 30−36 kcal mol^{-1}.[23]

Chart 4

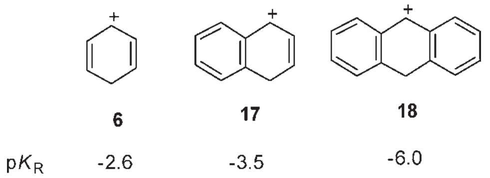
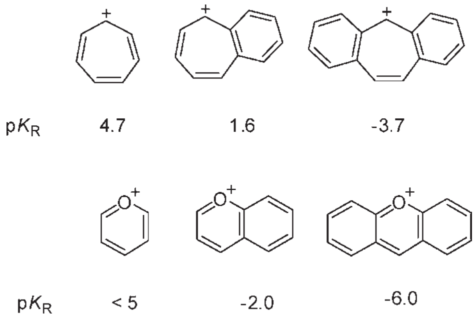


Chart 5



A further, and less obvious, comparison may be made with the pK_R values for the cyclohexadienyl and cycloheptadienyl cations coordinated by an iron tricarbonyl group (**15** and **16**, Chart 3). Following coordination, the difference in stabilities of the parent ions is lost, and the coordinated ions are found to have practically the same values of pK_R, i.e., 4.6 and 4.4.[24,25] This is certainly consistent with, if it does not require, loss of aromaticity through coordination of $Fe(CO)_3$. Computations indeed confirm a loss of aromaticity for coordination of $Fe(CO)_3$ to benzene or the tropylium ion.[25] If strain in the cations is unaffected by coordination, the similar pK_R values for the coordinated ions supports assignment of the difference in stabilities of the parent ions to aromaticity of the benzenium ion.

Benzannelation. Further evidence of aromatic stabilization of the benzenium ion comes from the effect of benzannelation. Solvolysis measurements indicate that normally benzylic cations are more stable than allylic cations.[26,27] One might have expected therefore that the cyclohexadienyl cation would be stabilized by benzannelation. That this is not the case is indicated by the comparison below of values of pK_R = −2.6, −3.5, and −6.0, respectively, for the benzenium (**6**), 1-naphthalenium (**17**), and 9-anthracenium (**18**) ions in Chart 4.[13,28]

This behavior is characteristic of aromatic ions, as is illustrated in Chart 5 for benzannelation of the tropylium ion[29,30] and pyrilium ion.[31,32] Olah has measured ^{13}C chemical shifts of 178.1, 180.9, and 183.4 ppm at the formal charge centers of the benzenium, 1*H*-naphthalenium, and 9*H*-anthracenium ions shown in Chart 4. He notes that if these represent relative magnitudes of charge, benzannelation is associated with localization rather than delocalization of charge.[33] This is consistent with a significant influence of hyperconjugation on delocalization. From an IR study of the same ions,[34] Koptyug's group observed an increase in stretching frequencies and C−H force constants for the CH_2 group on going from the benzenium to 1*H*-naphthalenium to 9*H*-anthracenium.[35] In an article summarizing the extensive work of Koptyug's group, Shubin and Borodkin note that Koptyug concluded that, while protonation led to loss of aromaticity of the neutral molecule, "some compensation effect was borne by hyperconjugation of the ring CH_2 fragment with the electron-deficient part of the arenium ion".[36]

It is more difficult to find examples of benzannelation of nonaromatic ions for comparison. However, as shown in Chart 6, an approximate $pK_R = -8.7$ for the dibenzocycloheptadienyl cation **19** may be inferred from equilibrium measurements in aqueous trifluoroacetic acid,[37] which indicates that the phenyl groups confer substantial stabilization relative to the parent cycloheptadienyl cation, with $pK_R = -16.1$. With respect to ^{13}C chemical shifts, Olah has shown from measurements for methyl-substituted and dibenzo cyclooctadienyl dications (**20**) that, in the absence of aromatic hyperconjugation, and in contrast to the ions of Chart 5, benzannelation leads to delocalization rather than localization of charge.[38]

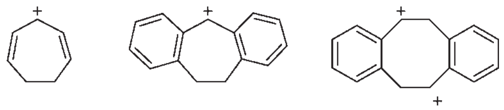
Arene Oxides. The combination of aromaticity and the striking difference in hyperconjugative capacity of C−H and C−O bonds offers a plausible explanation for an anomalous pattern of reactivity of arene oxides toward acid-catalyzed ring-opening. This is apparent from comparisons between the reactivity of epoxides and of alcohols yielding a common carbocation intermediate save for the presence of a β-hydroxy group in the case of formation from the epoxide. As illustrated in Scheme 11 for styrene oxide **21**[39] and α-phenethyl alcohol **22**,[40] for which rate constants of 27 and $3.0 \times 10^{-6}\ M^{-1}\ s^{-1}$ respectively at 25 °C in aqueous solution are shown, the epoxide is characteristically 10^6-10^7 times more reactive than the alcohol. This provides a remarkable contrast to benzene oxide **23** and the corresponding alcohol, benzene hydrate **24**, for which the reactivity of the alcohol is significantly *greater* than that of the epoxide (for which the rate constant was measured at the higher temperature of 30 °C).[41]

A clue to the origin of this behavior is provided by the dependence of the ratio of rate constants for arene oxides and corresponding alcohols (arene hydrates) upon the stability of the aromatic molecule from which they are derived.[26] As shown in Chart 7, this is reminiscent of the similar dependence of ratios of rate constants for carbocation-forming reactions of *cis*- and *trans*-dihydrodiols.[1] In the chart, the arrows indicate the direction of ring-opening for unsymmetrical oxides. The temperatures of measurement were 30 and 25 °C respectively for the arene oxides and alcohols (and epoxide of dihydronaphthalene).

One explanation offered for this behavior is that arene oxides are stabilized by homoconjugation.[26] This possibility was investigated by thermochemical measurements and computations for benzene oxide and naphthalene oxide by Thibblin, who concluded that stabilization of benzene oxide could account for a fraction of the reactivity difference but that there must be another factor involved.[42] This is consistent with a recent assessment that the stabilization of norcaradiene[43] is smaller than that of cycloheptatriene and probably does not represent a contribution from homoaromaticity.[14]

What that factor might be is suggested by Sayer's proposal that the epoxide ring opens initially to a conformation in which the OH group is close to pseudoaxial with respect to the carbocation center, as in **25**.[44] Formation of such a conformation would prevent stabilization of the carbocation by "aromatic" hyperconjugation of a C−H bond, which of course would be possible in the initially formed conformation from reactions of the alcohols. As expected, the difference from the "normal" reactivity ratio for hyperconjugatively nonaromatic cations (such as the tetralyl cation **26**) is maximized when the aromaticity of the cation formed from the alcohol (hydrate) is greatest, as in the case of benzene oxide and benzene hydrate. Strictly speaking, the results do not require that **25** exists in a conformational energy

Chart 6



Scheme 11

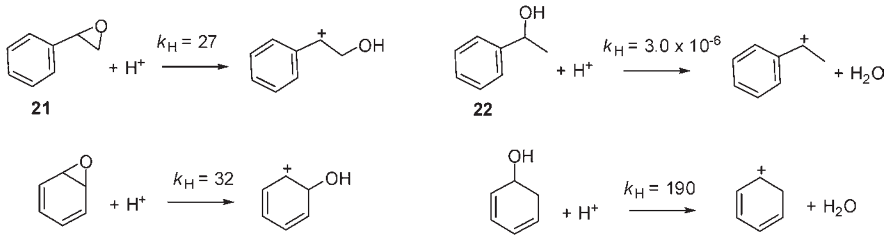
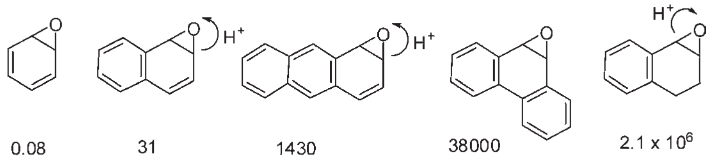
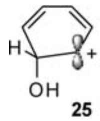


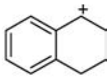
Chart 7



minimum, only that its instability is reflected in the transition state for reactions of the arene oxides.



25



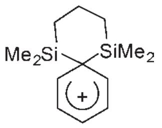
26

Electrophilic Aromatic Substitution. Protonated aromatic molecules such as the benzenium ion correspond to the simplest of Wheland intermediates of electrophilic aromatic substitution, and specifically aromatic hydrogen isotope exchange.[45] In principle, structure **25** corresponds to a Wheland intermediate formed from attack of HO^+ on a benzene ring in an electrophilic hydroxylation reaction.

There can be little doubt that hyperconjugation facilitates electrophilic aromatic substitution. However, most substitutions involve displacement of or by a proton, and in those cases one may suppose that the intermediates are consistently stabilized by C−H hyperconjugation. Where the influence of hyperconjugation most obviously appears is in the displacement of leaving groups which are more strongly hyperconjugating than hydrogen, namely silicon, germanium, tin, and lead. These were studied in the 1960s by Eaborn and co-workers,[45−47] who found indeed that proto-desilylation and corresponding displacements of other group 14 elements by acids occur with exceptional ease. Thus, trimethylsilyl benzene is 10^4 times as reactive as benzene itself despite the protonation step being rate-determining.[46] Moreover, relative reactivities of $ArMR_3$ with $HClO_4$ in ethanol are $1.0{:}36{:}3.5 \times 10^5{:}2 \times 10^8$ for M = Si, Ge, Sn, and Pb, respectively, an order opposite to that of decreasing bond strength. However, while the importance of hyperconjugation in stabilizing the Wheland intermediates was recognized at the time,[45,46,48] there was no reference to its aromatic character or to the papers by Mulliken[49,50] in which this was discussed.

X-ray Structures of Wheland Intermediates. Apart from measurements of their stabilities and of NMR and IR spectra, crystal structures of benzenium ions have been determined by X-ray crystallography and might have been expected to yield direct evidence of hyperconjugation. The earliest studies were of hexa or heptamethyl benzenium ions, and these have been further intensively investigated by Koptyug's group[36] and by Hubig and Kochi[51] for structures corresponding to attack of different electrophiles on methyl-substituted benzenes. More recently, with the choice of a sufficiently non-nucleophilic carborane anion, Reed succeeded in isolating and determining structures for the parent benzenium ions with attachment of electrophilic groups H^+, CH_3^+, Cl^+, Br^+, Et_3Si^+, and Ag^+.[52]

Of interest are electrophiles showing angles between the bond to the electrophile and the plane of the ring larger than normal for a tetrahedral carbon. It has been suggested that variations in this angle might represent a continuity of structures and bonding between σ- and π-complexes. However, in the case of Et_3Si^+, for which the angle is particularly large, there can be little doubt of the σ-character of the complex. Muller has determined a crystal structure of the disilylated benzenium ion **27** and demonstrated the presence of bond length alternations characteristic of a σ complex as well as tell-tale ^1H and ^{13}C NMR spectra. His results are supported by MP2 and B3LYP calculations for both **27** and the parent benzenium ion.[53] Moreover, $\text{NICS}(1)_{zz}$ values would place **27**, with a value of −26.0, much closer to benzene (−29.6) than to a benzenium ion (−14.6). Muller comments that these observations suggest that the disilyl cation **27** is intermediate in character between the aromatic benzene on the one hand and classical (*sic*) arenium ions such as the benzenium ion on the other.

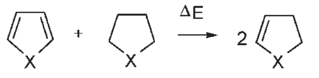


27

Aromatic Hyperconjugation. Muller's characterization of the benzenium ion as a classical structure is symptomatic of a reluctance to take up Mulliken's suggestion that hyperconjugation may be particularly pronounced as a consequence of extra stabilization arising from its aromatic character.[49,50] Two reasons for this have been (a) that until recently there has been a lack of unambiguous experimental support for the concept and (b) that in 1953 calculations were not sufficiently accurate to establish the magnitude of the effect. Moreover, in the late 1950s and 1960s, hyperconjugation was subjected to an extended and unfavorable critique by Dewar.[54,55]

Nevertheless, the wide scope of σ-bond interactions was early indicated by the pronounced negative hyperconjugation of fluorine atoms[56] and further illustrated by the σ-delocalization of silicon and other Group 14 elements.[57] In the 1990s, improvement in the effectiveness of computations allowed better assessment of the magnitude of C−H and C−C hyperconjugation. In 1993, Sieber, Schleyer, and Gauss reported calculations for the phenonium ion and benzenium ions, supporting enhanced hyperconjugative interaction with the cyclopropane and methylene group conferring aromatic stabilization on the ions.[20] Olah[58] and Suraya Prakesh[59] queried the aromatic character of this delocalization, but it is confirmed in principle by Muller's results for disilylbenzenium ions[53] and the experimental work and calculations of the present papers.[1−3]

Thus, despite its long antecedents,[20,48−50] there has been little recognition of or effort to develop a concept of hyperconjugative aromaticity. As an exception, Nyulaszi and Schleyer have reported calculations for cyclopentadienes indicating hyperconjugative delocalization when the methylene group is substituted with electropositive elements SiH_3, GeH_3, or SnH_3 or a cyclopropane ring and found stabilization energies of up to 10 kcal mol^{-1} based on the isodesmic reaction shown in eq 9.[60] Although Stanger[61] has criticized Schleyer's analysis, we found it convincing. Of interest in connection with the present paper is an inference that electronegative substituents Cl and F are destabilizing, suggesting an antiaromatic character for interactions with bonds to these atoms.[60]



(9)

X (ΔE, kcal/mol) = CH_2 (0), CMe_2 (0.9), C◁ (3.7), $C(SiH_3)_2$ (9.9), $C(GeH_3)_2$ (9.3), $C(SnH_3)_2$ (13.8), CCl_2 (-5.1), CF_2 (-9.5)

Computational Analysis: Stabilization Energies. A key feature in the interpretation of hyperconjugative stabilization of arenium ions presented so far is the contribution of a strongly stabilizing aromatic structure within a simple valence no-bond resonance representation of the hyperconjugation (**2a** ↔ **2b**) shown in Scheme 1. However, such a description can hardly be sustained without the support of a more rigorous assessment of the magnitudes of the stabilization energies involved. A series of G3MP2 or MP2/6-311+G** calculations have been undertaken therefore, (a) to assess relative stabilizations arising from different substituents at the methylene group of a benzenium ion, especially H and OH, (b) to determine the dependence of any stabilization on the stereochemical relationship between hyperconjugating group and charge center, and (c) to evaluate the magnitude of the stabilization as a function of the aromaticity of the arenium ion (especially benzenium compared with naphthalenium and phenanthrenium).

The importance of hyperconjugative interactions of differently substituted methylene groups (point a, above) was explored through calculations at the G3MP2 level of relative hydride ion affinities (ΔHIA, eq 10) of the doubly substituted ions **28**. In addition to $CX_2 = CH_2$ and $C(OH)_2$ in **28**, calculations were carried out for $C(SiH_3)_2$, CMe_2, and CF_2, and with CH_2 replaced by cyclopropyl to provide a comparison with a wider range of potentially hyperconjugating groups than studied experimentally. The effects are summarized under eq 10 as stabilization energies of CX_2 relative to CH_2 (ΔHIA) and are abstracted from the more comprehensive Table 3. It can be seen that the order found, i.e. SiH_3 > cyclopropyl > Me ~ H > HO > F, is a reasonable one for hyperconjugative stabilization of a positive charge. The slightly more favorable hyperconjugation of CH_3 than H contrasts with normal behavior in solution and may represent the greater importance of polarizability (size) for the ions in the gas phase. The CF_2 and $C(OH)_2$ groups are quite strongly destabilizing relative to CH_2. It is not clear if this represents weaker "favorable" hyperconjugation than CH_2 or, as Nyulaszi and Schleyer's results for substituted cyclopentadienes suggest,[70] a manifestation of antiaromatic character for the ions.

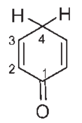
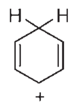
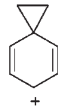
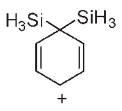
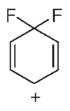
28

(10)

X	SiH_3	▷	CH_3	H	OH	F
ΔHIA (kcal mol^{-1})	22.1	19.5	0.5	0	-21.3	-36.4

With respect to aromatic (or antiaromatic) character of arenium ions some indication might be sought in changes in geometry. Thus, Olah and Suraya Prakesh have suggested that stabilization of the benzenium ion or phenonium ion arises from delocalization within the cyclopentadienyl cation fragment of the ions and does not extend importantly to hyperconjugative interactions with the CH_2 or cyclopropyl group.[58,59] In principle, this might be assessed from comparisons of crystal structures. However, Muller has shown that for silicon-substituted benzenium ions there is good agreement between crystallographically determined geometries and those from MP2 or B3LYP calculations for the gas phase.[53] Moreover, the consistency of the calculations lends itself to identification of systematic trends. In Table 4, variations in the length of the σ-bonds to the methylene group (C3−C4) and π-bonds of the formal cyclohexadienyl cation (C2−C3 and C1−C2) are compared for the different substituents X. For a reference structure exhibiting little delocalization, we have followed Sieber, Schleyer, and Gauss in choosing cyclohexa-2,5-dienone.[20] More substituents are included in Table 3, in which variations in average bond lengths within the cyclohexadienyl ring are listed as a concise indication of the degree of equalization of bond lengths.

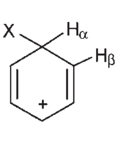
Table 4. Bond Lengths of Methylene-Substituted Benzenium Ions Computed at the MP2/6-311+G Level**

Bond					
$C_3{-}C_4$	1.479	1.467	1.420	1.435	1.511
$C_2{-}C_3$	1.350	1.379	1.390	1.393	1.365
$C_1{-}C_2$	1.497	1.412	1.405	1.404	1.423

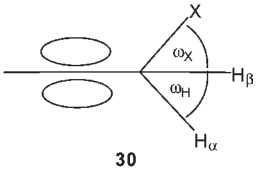
The main conclusion to be drawn from the geometries is that the C3−C4 bond length shows a small but significant variation with changes in substituent. While this is not unambiguous evidence of hyperconjugative delocalization, it is apparent that it is associated with a tendency to equalization of all three C−C bond lengths consistent with aromatic character, especially for the most strongly interacting substituents, silyl and cyclopropyl. This contrasts with fluorine substituents for which bond alternation is accentuated rather than reduced. The degree of equalization of bond lengths can be expressed, e.g., by Julg[53,62] or HOMA[63] parameters but is apparent from inspection of the bond lengths themselves and, in principle (in the case of CF_2 and presumably $C(OH)_2$), can be associated with antiaromaticity as well as aromaticity. However, it should also be noted that available evidence suggests that "aromatic" delocalization of electrons is not greatly impaired by disparities in bond lengths.[64]

The stereochemical dependence of this conjugative interaction, i.e., point b above, was examined by looking at a benzenium ion with a singly substituted methylene group. For the di-X-substituted ions the methylene group (CX_2) is close to tetrahedral, and the C−X bonds are symmetrically located above and below the plane of the ring. For the benzenium ion with a single OH substituent, the preferred conformation places the C−H bond in a pseudoaxial location with respect to the charge center, while the OH group adopts a pseudoequatorial position.

In Table 3, geometries at the methylene group for a series of substituents X are compared. These are expressed in terms of the dihedral angles ω_X and ω_H between the C−X or C−H bond of the methylene group and a β-sp_2 C−H bond of the benzenium ion (**29**) as in **30**. It can be seen that whether C−X or C−H bonds adopt a pseudoaxial position depends on the relative hyperconjugating ability of the X and H substituents. The pseudoaxial dihedral angles range from 82 to 99° and the pseudoequatorial from 20 to 31°. Only for the CH_3 group, which in the gas-phase calculations has a hyperconjugating capacity very similar to that of hydrogen, are intermediate values of dihedral angles, $\omega_H = 64°$ and $\omega_{Me} = 49°$, observed. A fuller characterization of these geometries is shown in Table S7.



29



30

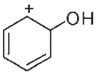
That neighboring group interactions are encompassed by the calculations is shown by an SH substituent for which, in addition to the hyperconjugating structure, a structure of similar energy in which the sulfur atom symmetrically bridges α- and β-carbon atoms is identified. For OH, the bridged ion, protonated benzene oxide, is significantly less stable than the unbridged β-hydroxy cyclohexadienyl cation. A difference between unbridged SH and OH monosubstituted ions is that the OH occupies a pseudoequatorial position relative to a pseudoaxial hydrogen atom while the SH occupies a pseudoaxial position, with hydrogen pseudoequatorial. The pseudoaxial orientation of the C−S bond might seem surprising insofar as the substituted ion is *less* stable than the parent cyclohexadienyl cation. Presumably this is because, although C−S hyperconjugation is more favorable than C−H, the stabilizing effect is overridden by an unfavorable inductive effect. In Table 3 it is noticeable that all the second-row elements except chlorine occupy pseudoaxial positions. Indeed, a crystal structure of ipso-protonated chlorobenzene shows even chlorine in a pseudoaxial position.[52]

For the gas-phase calculations, the structures of monosubstituted cyclohexadienyl cations shown in Table 3 correspond to stable conformations. Generally they represent a single minimum energy structure. This may differ from the situation in solution where the difference in reactivities of *cis*- and *trans*-arene dihydrodiols[1] or 2-substituted dihydro-1-naphthols[2] found experimentally suggests formation of distinct conformers of carbocations with β-C−H and β-C−X bonds respectively in pseudoaxial positions. A difference in energy between conformations in the gas phase nevertheless may be calculated by constraining the dihedral angle ω_X (in **30**) to a reasonable value for the less stable conformer. Thus in the case of an HO-substituted benzenium ion, if the dihedral angle ω_{OH} is increased to 80°, the energy of the ion increases by 8.8 kcal mol^{-1}. This may be taken as a guide to the difference in energies of two "stable" conformations existing in solution or, alternatively, of different transition states for carbocation formation originating respectively from *cis*- and *trans*-dihydrodiol precursors.

At this point we return to the question of whether the unfavorable influence of OH reflects more importantly absence of activation by C−H or "positive" deactivation by C−OH (over and above the expected influence of an inductive effect).[1] So far it has been supposed that the presence or absence of C−H hyperconjugation controls reactivity. However, Nyulaszi and Schleyer's demonstration of antiaromaticity for cyclopentadienes with electronegative substituents raises the possibility that formation of a carbocation with C−OH in a pseudoaxial position may be intrinsically unfavorable, and that this factor may be more important in determining the difference in reactivities between *cis*- and *trans*-dihydrodiols than stabilization of the *cis* isomer by C−H hyperconjugation (eq 9).

Evidence on this point is conflicting. The correlation of rates of reaction of *cis* 2-OH or 2-OMe substituents by a Taft relationship in the acid-catalyzed dehydration of 2-substituted 1,2-dihydro-1-naphthols described in a previous paper[2] suggests that the influence of these (*cis*) substituents on the stability of the parent naphthalenium ion is mainly inductive. This implies that stabilization of the parent naphthalenium ion by hyperconjugative resonance is substantially retained in the β-HO substituted ion, provided that a β-C−H bond occupies a pseudoaxial position. On the other hand, NICS calculations for benzenium ions with the methylene group substituted by OH or a halogen (and C−H occupying a pseudoaxial position) imply that by this criterion there is no ring current associated with these ions. Thus, NICS$(0)_{\pi zz}$ calculations for $C_6H_6OH^+$ (+7.8 ppm) and $C_6H_6F^+$ (−0.4 ppm) reveal no special (hyper)aromaticity compared to the benzenium ion (−18.0 ppm). The value for the latter ion is approximately half that for benzene (−35.9 ppm). In contrast, the disubstituted $C_6H_5(SiH_2)_2{}^+$ (−27.9 ppm) and $C_6H_5F_2{}^+$ (12.1 ppm) show enhanced "hyperaromaticity" and "hyperantiaromatcity" (as in Nyulaszi and Schleyer's cyclopentadiene analogues).[17,60]

Table 5. Dihedral Angles and Energy Differences between Conformations for β-Hydroxy Arenium Ions[a]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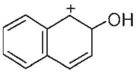
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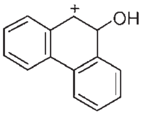
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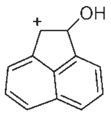
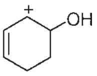

34


35

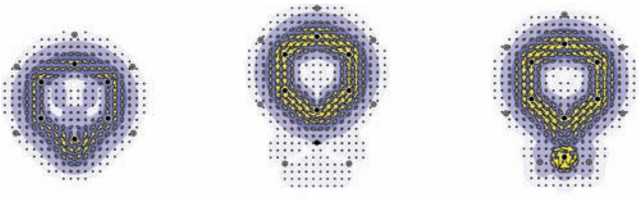
	31	32	33	34	35
dihedral angle ω_{OH} for stable conformer (deg)	22	37	29	53	27
constrained dihedral angle ω_{OH} (deg)	80	80	80	55[b]	82[b]
ΔE (kcal mol^{-1})	8.8	6.0	4.3	0.8	0.8

[a] Calculated at MP2/6-311+G** for cyclohexadienyl and cyclohexenyl cations and at MP2/6-31G* for the larger ions. [b] Stable but higher energy conformer.

A further important feature of the experimental results is the dependence of the *cis*/*trans* rate ratio for reaction of arenedihydrodiols on the extent of hyperconjugative aromatic stabilization of the arenium ion intermediate formed from them (point c above). This too could be tested by calculation, by comparing the difference in energies of stable and constrained conformations of arenium ions bearing a β-hydroxy group for benzenium (**31**), naphthalenium (**32**), and phenanthrenium (**33**) ions and for the nonaromatic acenaphthenium (**34**) and cyclohexenyl (**35**) cations shown in Table 5. The comparison represents a progression from the potentially strongly aromatic ring of the benzenium ion to the two nonaromatic rings, with intermediate degrees of aromaticity for the rings formally bearing the positive charge of the naphthalenium and phenanthrenium ions. This too is expressed as a difference in energies between stable conformations and conformations in which the C−OH rather than the C−H bond is constrained to be axial. The differences (ΔE) are listed in Table 5 under the relevant structures together with the constrained dihedral angle ω_{OH} between the C_β−OH and $C_\alpha{}^+$−H bonds for the arenium ions. For the "nonaromatic" cations **34** and **35**, both conformations are accessible and no constraint was necessary. Because of the size of the phenanthrenium, naphthalenium, and acenaphthenium ions, the calculations for these ions are at a lower level (MP2-6-31G*) than the G3MP2 calculations which have been cited hitherto. Further details are provided in Table S8.

Computational Analysis: Ring Currents. Further insight into the aromaticity of arenium ions is provided by an evaluation of ring currents.[18] A "current-density map" based on the distributed-gauge ("ipsocentric") method CTOCD-DZ[19,65] at the RHF/6-31G** level of theory, calculated at $1a_o$ above the median plane using the SYSMO and GAMESS packages[66,67] for the structure optimized at the B3LYP/6-31G** level with GAUSSIAN 09,[68] has been obtained for the benzenium ion and is shown in Chart 8 (**36**). The map shows the summed contribution of all occupied orbitals of π symmetry, which in

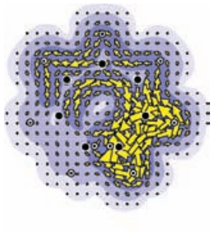
Chart 8



$C_6H_7^+$ **36** $C_6H_5(SiH_3)_2^+$ **37** $C_6H_5(CH_2)_2^+$ **38**

qualitative terms should capture all the contributions from the conventional π system of the ring, plus any contribution that may arise from the antisymmetric combination of CH bonds of the methylene group. There is a clear indication of a global ring current passing above and below all carbon centers, including that of the CH_2 group, which is thus consistent with aromatic character deriving from hyperconjugative participation of these hydrogens. The π current in **36** is roughly half as strong as in benzene in the 1 bohr plotting plane; the maximum magnitude of current density per unit inducing field is 0.046 au, compared to 0.079 au for benzene calculated at the same level of theory. If the CH_2 group is replaced by $C(SiH_3)_2$, or by a spirocyclopropyl ring, calculations at the same level of theory show that the ring current persists, and indeed becomes stronger, as indicated by the respective maps (**37** and **38**).

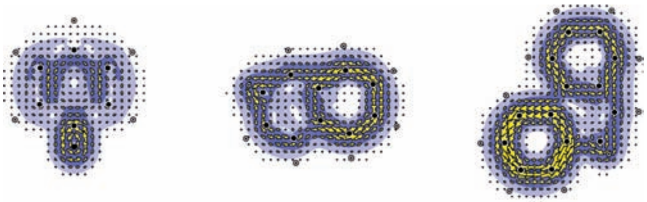
In contrast to structures **36**−**38**, for the cycloheptadienyl cation **39** there is no evidence of an appreciable π ring current of the conventional type. Structure **39** is nonplanar, and π-orbital symmetries are therefore approximate; the map also contains some distracting large local currents where the plotting plane intersects CC/CH σ bonds, but the significant feature of the map is what is missing, i.e., a global circulation concentrated on the carbon centers of the seven-membered ring. This negative result is of interest insofar as this ion is potentially homoaromatic (or perhaps more properly "homohyperaromatic"!) in analogy with cycloheptatriene. The lack of current is consistent with the large energy difference between the cyclohexadienyl and 2,4-cycloheptadienyl cations that is implied by the pK_R values for the two cations (ΔpK_R = 13.5), as discussed above.



$C_7H_9^+$ **39**

Of particular interest is the result for the benzenium ion in which the methylene group is replaced by CF_2 (**40**, Chart 9). It can be seen that the ring current is lost and that the behavior here is consistent with antiaromatic character for this ion, and presumably also for the corresponding ion in which the fluorine atoms are replaced by OH groups. Finally, structures **41** and **42** indicate that the hyperconjugative ring current persists in the magnetic maps for naphthalenium and phenanthrenium cations, where the maps correspond to perturbed versions of the maps for the parent hydrocarbons. The uniform global perimeter circulation of naphthalene, for example, gains a short-circuiting cross current in the less symmetrical environment of the $C_{10}H_9^+$ cation, where the conventional aromatic ring current in the unsubstituted benzene ring (diminished by <10% from the value for benzene itself) is appreciably stronger than the hyperaromatic current in the protonated ring. A fuller account of currents and their orbital analysis for Wheland intermediate systems is in preparation.

Chart 9



$C_6H_5F_2^+$ **40** 1-naphthalenium **41** 9-phenanthrenium **42**

SUMMARY

In conclusion, comparison of pK_R values for cyclohexadienyl (benzenium) and cycloheptadienyl cations reinforces evidence from the difference in reactivity of *cis*- and *trans*-benzenedihydrodiols toward acid that the arenium ions they give rise to are "hyperaromatic", with stabilization energies as large as 18 kcal mol^{-1}. Further evidence is provided by the structure dependence of relative reactivities of arene oxides and arene hydrates, reactivity patterns in electrophilic aromatic substitution (especially ipso displacement of Group 14-substituted benzenes by protons), and the effect of benzannelation on the stability of the benzenium ion. The behavior is most simply interpreted as arising from the contribution of an aromatic no-bond resonance structure within a valence bond representation of hyperconjugative stabilization of the ions. The interpretation is endorsed by G3 calculations of ion stabilities and by current density maps pointing to cyclic delocalization of cyclohexadienyl π electrons with involvement of electrons from the CH bonds of a methylene group. The term "hyperaromaticity" is suggested as an extension of the term "hyperconjugation",[69] in analogy with homoconjugation and homoaromaticity.[1,70]

EXPERIMENTAL SECTION

Analytical Methods and Synthesis. NMR spectra were measured on a Varian 300 MHz spectrometer. UV−vis spectra were measured with a Cary 50 spectrophotometer which was also used to monitor acid-catalyzed dehydration of cycloheptadienol to cycloheptatriene. HPLC measurements were made with a Waters 600 HPLC system equipped with dual-wavelength absorbance detection and a HiChrom-5 (4.6 × 250 mm) C-18 reverse-phase column. Cycloheptadienol was prepared from the epoxide of cycloheptatriene and was treated with dichloroacetyl chloride to furnish the dichloroacetate ester as described below.

Cycloheptadiene-1,2-oxide. To an ice-cold solution of *m*-chloroperbenzoic acid (0.38 g, 5.1 mmol) in dichloromethane (20 mL) was added 1,3-cycloheptadiene (0.50 g, 5.3 mmol) over 10 min. The mixture was stirred overnight at room temperature and the precipitated *m*-chlorobenzoic acid removed by filtration. The filtrate was poured into ice-cold saturated aqueous sodium bicarbonate (20 mL) and quickly extracted with chloroform (25 mL). The organic layer was separated and washed with 5% sodium thiosulfate solution (20 mL) followed by saturated sodium bicarbonate (20 mL) and water (20 mL). Drying over sodium sulfate, filtration, and removal of the solvent under reduced pressure gave 1,3-cycloheptadiene 1,2-oxide (0.32 g, 56%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (t, 2H, J = 4.5 Hz), 3.43 (s, 2H), 5.76–5.93 (m, 4H).[71]

2,4-Cycloheptadienol (6)[72]. To a stirred solution of 1,3-cycloheptadiene-1,2-oxide (0.32 g, 2.9 mmol) in anhydrous diethyl ether (10 mL) was added 3 mL (4.8 mmol) of 1.6 M methyllithium in hexane. The resulting mixture was allowed to warm to room temperature, and unreacted methyllithium was hydrolyzed with 5% aqueous sodium hydroxide (5 mL). The aqueous layer was separated and extracted with 3 × 10 mL of diethyl ether. The combined organic solutions were washed with saturated aqueous sodium chloride (10 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (70:30 cyclohexane:ethyl acetate) to give 2,4-cycloheptadienol (0.30 g, 94%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (m, 1H), 2.08 (m, 1H), 2.32 (m, 2H), 4.43 (s, 1H), 5.80–6.00 (m, 4H).

1-Dichloroacetoxy-2,4-cycloheptadiene (8). To a stirred ice-cold solution of 2,4-cycloheptadienol **6** (0.10 g 0.92 mmol) in anhydrous dichloromethane (5 mL) was added 0.1 mL of anhydrous pyridine (1.26 mmol). The resulting mixture was allowed to come to room temperature and stirred for 2 h. The reaction was quenched by the addition of 5 mL of saturated sodium bicarbonate solution, and the organic layer was separated and washed with water (3 × 10 mL) and saturated sodium chloride solution (10 mL). The solution was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (70:30 cyclohexane:ethyl acetate) to give 1-dichloroacetoxy-2,4-cycloheptadiene (0.10 g, 49%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86–2.02 (m, 1H), 2.11–2.26 (m, 1H), 2.39 (dd, J = 11.5, 5.5 Hz, 2H), 5.59 (s, 1H), 5.82 (ddd, J = 16.3, 11.6, 5.8 Hz, 2H), 5.95 (s, 1H), 6.01 (ddd, J = 15.5, 11.5, 6.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.1, 30.2, 64.5, 76.1, 124.3, 127.8, 128.7, 136.1, 163.7; m/z (ES) 95.1 $[M{-}OCOCHCl_2{+}H^+]^+$.

Kinetic Measurements and Product Analyses. Acid-catalyzed dehydration of 2,4-cycloheptadienol was monitored by UV–vis spectrophotometry at 240 nm in the concentration range 2.0–6.0 M $HClO_4$. Reactions were initiated by injection of 20 μL of a 1.8×10^{-2} M solution of substrate in acetonitrile into 2 mL of acid in a cuvette thermostatted at 25 °C. Measured first-order rate constants determined at different acid concentrations are shown in Table S1. Logs of second-order rate constants were plotted against the acidity parameter X_o, and a value for dilute aqueous solution was extrapolated at $X_o = 0$ (Figure S1).[73]

Equilibration of 2,4-cycloheptadienol with its trifluoroethyl ether in aqueous trifluoroethanol containing 30, 50, and 70% (v:v) TFE in the presence of $HClO_4$ was monitored by HPLC. Typically 50 μL of a 10^{-2} M solution of cycloheptadienol was injected into 500 μL of TFE–H_2O, 0.1 M in $HClO_4$. Samples of 25 μL were quenched at various times in three drops of saturated sodium bicarbonate solution, followed by addition of 200 μL of acetonitrile to minimize broadening of HPLC peaks. The analysis involved isocratic elution of samples with a 70:30 (v/v) acetonitrile–water mixture at a flow rate of 1 mL/min.

In the course of the reaction, it was noticeable that, as expected, the concentration of the trifluoroethyl ether at first increased. However, instead of reaching a constant value, at long reaction times it began to decrease (Figure 1). As there was no sign of reaction to form a new product, the most plausible explanation seemed to be that the ether is sufficiently volatile to be lost through evaporation. The behavior was confirmed insofar as if the reaction was carried out at a substantially higher concentration of acid (1 M $HClO_4$ instead of 0.1 M), so that it was complete in a much shorter time, a larger amount of the trifluoromethyl ether was obtained than in the slower reactions.

The reactions at 1 M $HClO_4$ were too fast for the determination of reliable rate constants. Kinetic analyses were carried out therefore using the equilibrium concentration of trifluoroethyl ether obtained at the higher acid concentration to evaluate rate constants from measurements at 0.1 M $HClO_4$. To correct for the loss of ether at longer reaction times, the percentages of trifluoromethyl measured as a function of time (t) were fitted to the modified first-order kinetic expression $a(1 - ct)(1 - e^{-kt})$, where a is the limiting percentage of ether at 1 M $HClO_4$ and $1 - ct$ is a correction term based on the supposition that loss through evaporation increases linearly with the concentration of trifluoroethyl ether and the time of reaction. The value of c was chosen to give a best fit of calculated to experimental data.

The quality of fit for the measurements in 70% TFE–30% water is shown in Figure 1. The fit here is substantially better than for measurements at 50% and 30% TFE, for which the reaction was significantly slower and the extent of loss of trifluoroethyl ether correspondingly greater. This is apparent from the poor quality of the plot of log k at the three solvent compositions against values of log k/k_{H_2O} for the dehydration of benzothiophene (Figure S2). However, uncertainty in the extrapolated rate constant has a relatively mild effect on derived rate and equilibrium constants. Thus omission of the point for 30% TFE modifies the value in water from 2.6 to 1.7×10^{-3} M^{-1} s^{-1} and pK_R for 2,4-cycloheptadienol from −12.1 to −12.25.

Rate constants for solvolysis of the dichloroacetate ester of cycloheptadienol in water were also determined by HPLC. The reaction was initiated by injection of 50 μL of a stock solution in acetonitrile (10^{-2} M) into 2 mL of water. Samples of 25 μL were withdrawn every few minutes and quenched in 250 μL of MeCN, in which the dichloroacetate ester showed no further reaction in 24 h. The HPLC analysis was performed with the detector set at a wavelength of 250 nm using a solvent mixture of 30:70 (v:v) aqueous acetonitrile.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Reactions of cycloheptadienol and its dichloroacetate ester in water and aqueous TFE (Tables S1–S5); free energies of formation of seven-membered ring hydrocarbons (Table S6); plots of kinetic data and products from solvolysis of cycloheptadienyl dichloroacetate in azide buffers (Figures S1–S4); computational data (Tables S7 and S8); NMR spectra; and complete ref 68. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Lawlor, D. A.; Kudavalli, J. S.; MacCormac, A. C.; Coyne, D. A.; Boyd, D. R.; More O'Ferrall, R. A. *J. Am. Chem. Soc.* **2011**, *133*, DOI: 10.1021/ja207160z (preceding paper in this issue).

(2) Kudavalli, J. S.; Coyne, D.; More O'Ferrall, R. A. *J. Org. Chem.* **2011**submitted.

(3) A preliminary report of this work has appeared: Kudavalli, K. J.; Boyd, D. R.; Coyne, D.; Keeffe, J. R.; Lawlor, D. A.; MacCormac, A. C.; More O'Ferrall, R. A.; Rao, S. N.; Sharma, N. D. *Org. Lett.* **2010**, *12*, 5550–5553.

(4) Richard, J. P.; Rothenburg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361–1372.

(5) Fujio, M.; Keeffe, J. R.; More O'Ferrall, R. A.; O'Donoghue, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 9982–9992.

(6) McClelland, R. A. *Tetrahedron* **1996**, *52*, 6823–6858.

(7) Turner, R. B.; Mallon, M.; Doering, W. Von E.; Roth, W. R.; Scroder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605–8610.

(8) Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189–228.

(9) Dey, J.; O'Donoghue, A. C.; More O'Ferrall, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 8561–8574.

(10) The previously reported value of −11.8 in ref 3 is in error.

(11) Guthrie, J. P. *Can. J. Chem.* **1992**, *70*, 1042–1054.

(12) Frenkel, M.; Kabo, G. J.; Marsh, K. N.; Rogonov, G. N.; Wilhoit, R. C. *Thermodynamics of Compounds in the Gas State*, Vols. I and II; Thermodynamics Research Center: College Station, TX, 1994.

(13) Lawlor, D. A.; More O'Ferrall, R. A.; Rao, S. N. *J. Am. Chem. Soc.* **2008**, *130*, 17997–18007.

(14) Chen, Z.; Jiao, H.; Wu, J. I.; Herges, R.; Zhang, S. B.; Schleyer, P. v. R. *J. Phys. Chem. A* **2008**, *112*, 10586–10594.

(15) We thank a referee for pointing this out.

(16) (a) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863–866. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842–3888.

(17) Schleyer, P. v. R.; Wu, J. Unpublished results.

(18) Steiner, E.; Fowler, P. W. *J. Chem. Soc., Chem. Commun.* **2001**, 2220–2221.

(19) (a) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223–231. (b) Coriani, S.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Theor. Chim. Acta* **1994**, *89*, 181–192. (c) Steiner, E.; Fowler, P. W. *J. Phys. Chem.* **2001**, *105*, 9553–9562.

(20) Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987–6988.

(21) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS monograph 177; American Chemical Society: Washington, DC, 1982.

(22) Nevins, N.; Stewart, E. L.; Allinger, N. L.; Bowen, P. J. *J. Phys. Chem.* **1994**, *98*, 2056–2061.

(23) Schleyer, P. v. R.; Puhlhofer, F. *Org. Lett.* **2002**, *4*, 2873–2876.

(24) Galvin, M.; Guthrie, P. J.; McDonnell, C. M.; More O'Ferrall, R. A.; Pelet, S. *J. Am. Chem. Soc.* **2009**, *131*, 34–35.

(25) Guthrie, J. P.; O'Connor, C.; McDonnell, C. M.; More O'Ferrall, R. A., to be published.

(26) Rao, S. N.; More O'Ferrall, R. A.; Kelly, S. C.; Boyd, D. R.; Agarwal, R. *J. Am. Chem. Soc.* **1993**, *115*, 5458–5465.

(27) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw Hill: New York, 1962.

(28) MacCormac, A. C.; McDonnell, C. M.; More O'Ferrall, R. A.; O'Donoghue, A. C.; Rao, S. N. *J. Am. Chem. Soc.* **2002**, *124*, 8575–8583.

(29) Doering, W. Von E.; *J. Am. Chem. Soc.* **1954**, *76*, 3203–3206.

(30) Berti, G. *J. Org. Chem.* **1957**, *22*, 230.

(31) Bunting, J. W. *Adv. Phys. Org. Chem.* **1979**, *25*, 1–82.

(32) Canalini, G.; Degani, I.; Fochi, R.; Spunta, G. *Ann. Chim. (Rome)* **1967**, *57*, 1045.

(33) Olah, G. A.; Staral, J. S.; Ascensio, G.; Liang, G.; Forsyth, D. A.; Mateescus, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299–6308.

(34) Koptyug, V. A.; Korobeinicheva, I. K.; Andreeva, T. P.; Bushmelev, V. A. *J. General Chem. USSR* **1968**, *38*, 1920.

(35) Sycheva, I. M.; Shchegoleva, L. N.; Mitasov, M.; Derendyaev, B. G. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.* **1981**, *12*, 143.

(36) Shubin, V. G.; Borodkin, G. I. In *Carbocation Chemistry*; Olah, G. A., Surya Prakash, G. K., Eds.; Wiley: Hoboken, NJ, 2004; pp 125−158.

(37) Ceccon, A.; Gambaro, A.; Romanin, A.; Venzo, A. *Angew. Chem., Int. Ed.* **1983**, *22*, 559–560.

(38) Olah, G. A.; Staral, J. S.; Liang, G.; Paquette, L. A.; Melega, W. P.; Carmody, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3349–3355.

(39) Ross, A. M.; Pohl, T. M.; Piazza, K.; Thomas, M.; Fox, B.; Whalen, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1658–1665.

(40) Boyd, D. R.; McMordie, R. A. S.; Sharma, N. D.; More O'Ferrall, R. A.; Kelly, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 7822–7823 and references cited therein.

(41) Kasparek, G. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 198–202.

(42) (a) Jia, Z. S.; Brandt, P.; Thibblin, A. *J. Am. Chem. Soc.* **2001**, *123*, 10147–10152. (b) Brandt, P.; Jia, Z. S.; Thibblin, A. *J. Org. Chem.* **2002**, *67*, 7676–7682.

(43) Roth, W. R.; Klarner, F.-G.; Siepert, G.; Lennartz, H.-W. *Chem. Ber.* **1992**, *127*, 217–224.

(44) Nashed, N. T.; Bax, A.; Loncharich, R. J.; Sayer, J. M.; Jerina, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 1711–1722.

(45) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: Chichester, 1990.

(46) Eaborn, C.; Pande, K. C. *J. Chem. Soc.* **1960**, 1566–1571.

(47) Eaborn, C.; Emokpae, T. A.; Sidorov, V. I.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1454–1459.

(48) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49–70.

(49) Pickett, L. W.; Muller, N.; Mulliken, R. S. *J. Chem. Phys.* **1953**, *31*, 1400–1401.

(50) Muller, N.; Pickett, L. W.; Mulliken, R. S. *J. Am. Chem. Soc.* **1954**, *76*, 4770–4778.

(51) Hubig, S. M.; Kochi, J. *J. Org. Chem.* **2000**, *65*, 6807–6818.

(52) Reed, C. A.; Kim, K.-C.; Stoyanaov, E. S.; Tasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796–1804.

(53) Panisch, R.; Bolte, M.; Muller, T. *Organometallics* **2007**, *26*, 3524–3529.

(54) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166–178.

(55) Dewar, M. J. S. *Hyperconjugation*; Ronald Press: NewYork, 1962.

(56) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

(57) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183–190.

(58) Olah, G. A.; Head, N. J.; Rasul, G.; Surya Prakash, G. K. *J. Am. Chem. Soc.* **1995**, *117*, 875–882.

(59) Suraya Prakesh, G. K. In *Carbocation Chemistry*; Olah, G. A., Surya Prakash, G. K., Eds.; Wiley: Hoboken, NJ, 2004; Chapter 4.

(60) Nyulaszi, L. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872–6875.

(61) Stanger, A. *Chem.—Eur. J.* **2006**, *12*, 2745–2751.

(62) Julg, A.; Francois, P. *Theor. Chim. Acta* **1967**, *8*, 249–259.

(63) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236–1244.

(64) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikemma Hommes, W. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318. (b) Keeffe, J. R., cited by Bernsconi, C. F.; Wenzel, P. J.; Ragains, M. L. *J. Am. Chem. Soc.* 2008, *130*, 4934–4944.

(65) Steiner, E.; Fowler, P. W.; Jenneskens, L. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 362–366.

(66) Lazzeretti, P.; Zanasi, R. University of Modena, Italy, 1980. Extra mapping and orbital contribution routines by Steiner, E.; Fowler, P. W.; Havenith, R. W. A.; Soncini, A. Interface to GAMESS, Havenith, R. W. A.

(67) Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. *Mol. Phys.* **2005**, *103*, 719–747.

(68) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.

(69) Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41–56.

(70) Winstein, S. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III.

(71) Crandall, J. K.; Banks, D. B.; Colyer, R. A.; Watkins, R. J.; Arrington, J. P. *J. Org. Chem.* **1968**, *33*, 423–425.

(72) Rigby, J. H.; Bazin, B.; Meyer, J. H.; Mhammadi, F. *Org. Lett.* **2002**, *4*, 799–801.

(73) (a) Bagno, A.; Scorrano, G.; More O'Ferrall, R. A. *Rev. Chem. Intermed.* **1987**, *7*, 313–352. (b) Cox, R. A. *Adv. Phys. Org. Chem.* **2000**, *34*, 1–66.