Gas Phase Deprotonation of Benzhydryl Cations: Carbene Basicity, Multiplicity, and Rearrangements

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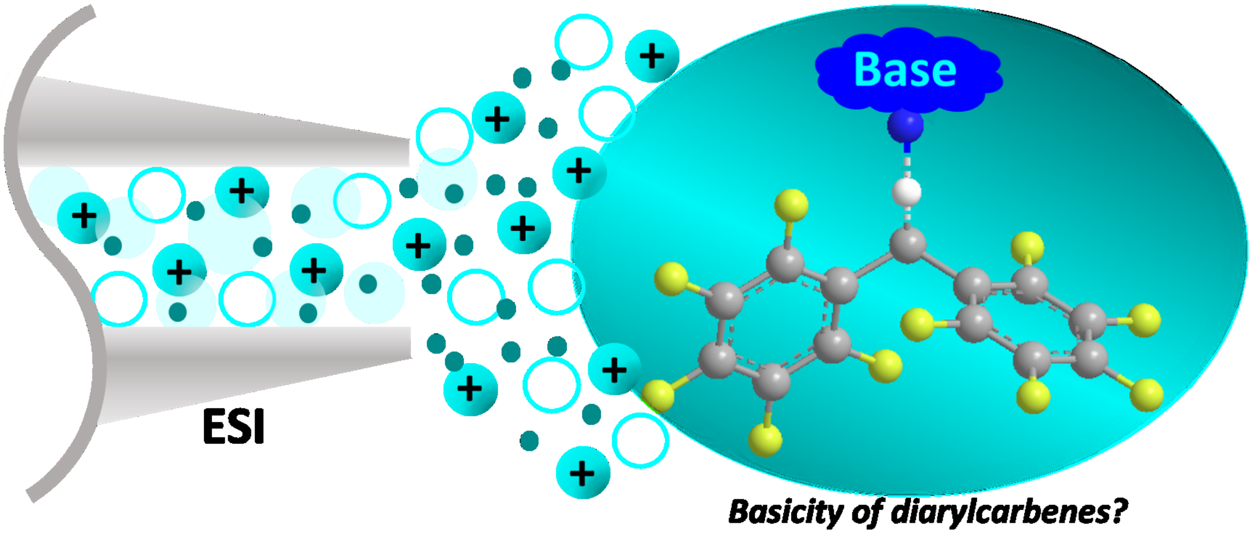
TOC graphic



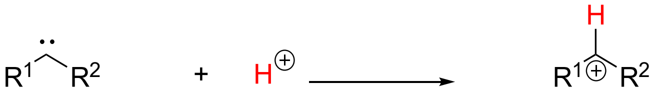
Abstract.

Many fundamental properties of carbenes, particularly basicity, remain poorly understood. Herein, an experimental and computational examination of the deprotonation of a series of benzhydryl cations has been undertaken. These studies represent the first attempt at providing experimental values for diarylcarbene basicities. Pathways to deprotonation, including whether the singlet or triplet carbene is formed, are probed. Because diarylcarbenes are expected to be among the strongest organic bases known, assessing the energetics of protonation of these species is of fundamental importance for a wide range of chemical processes.

Introduction.

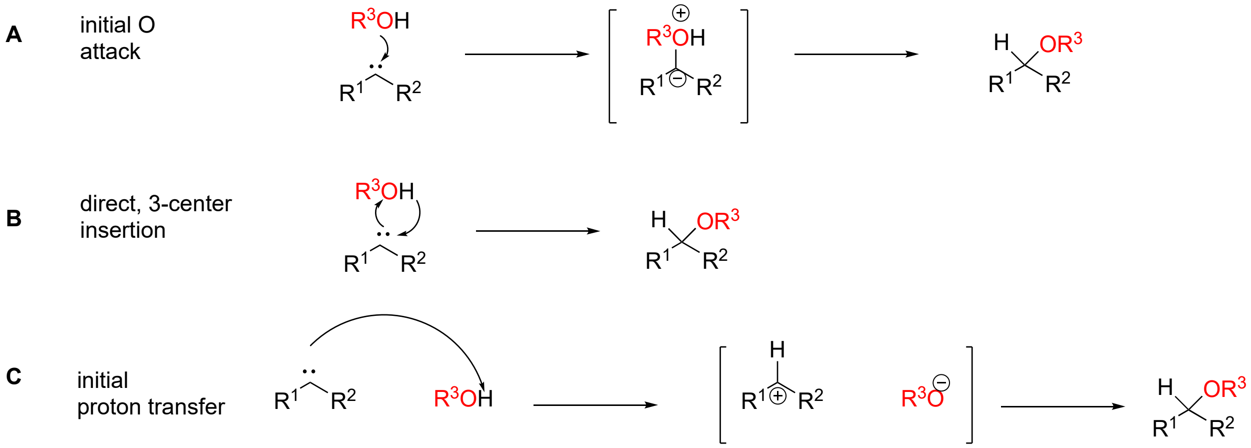
Carbenes are molecules with the formula CXY, where the carbon atom is divalent and features two nonbonding electrons. They are key species in many organic reactions, serve as ligands for organometallic catalysts, and function as effective catalysts in their own right.[1-4]

Despite the many applications of carbenes, fundamental properties remain unknown. A key example is the energetics of the protonation of carbenes. It is known that this process should yield the corresponding cation (Scheme 1); however, for many years, there was only indirect evidence to support this.[5,6] Many of the known experimental carbene proton affinities (PAs) are for *N*-heterocyclic carbenes, while those for the traditional acyclic reactive carbenes are rarer.[5,7-22]



Scheme 1. Protonation of carbene to yield the corresponding cation.

Another key reaction of carbenes, the insertion of singlet carbenes into O-H bonds, has various possible mechanisms (Scheme 2). In the case of diarylcarbenes, the mechanism for O-H insertion is known to proceed via a proton transfer mechanism, with the diaryl (benzhydryl) carbocation as an intermediate.[6,23-27] Despite this well-established mechanism, the energetics of the protonation are not fully understood, since fundamental properties, such as the experimental proton affinities of carbenes, are unknown.[7] New insights into the energetics of these processes are therefore essential and of major importance for assessing the heats of formation of the corresponding carbenes.[5,7,11,13-16,18] The lack of experimental proton affinities for diarylcarbenes is especially remarkable since they are among the strongest organic bases.[5]



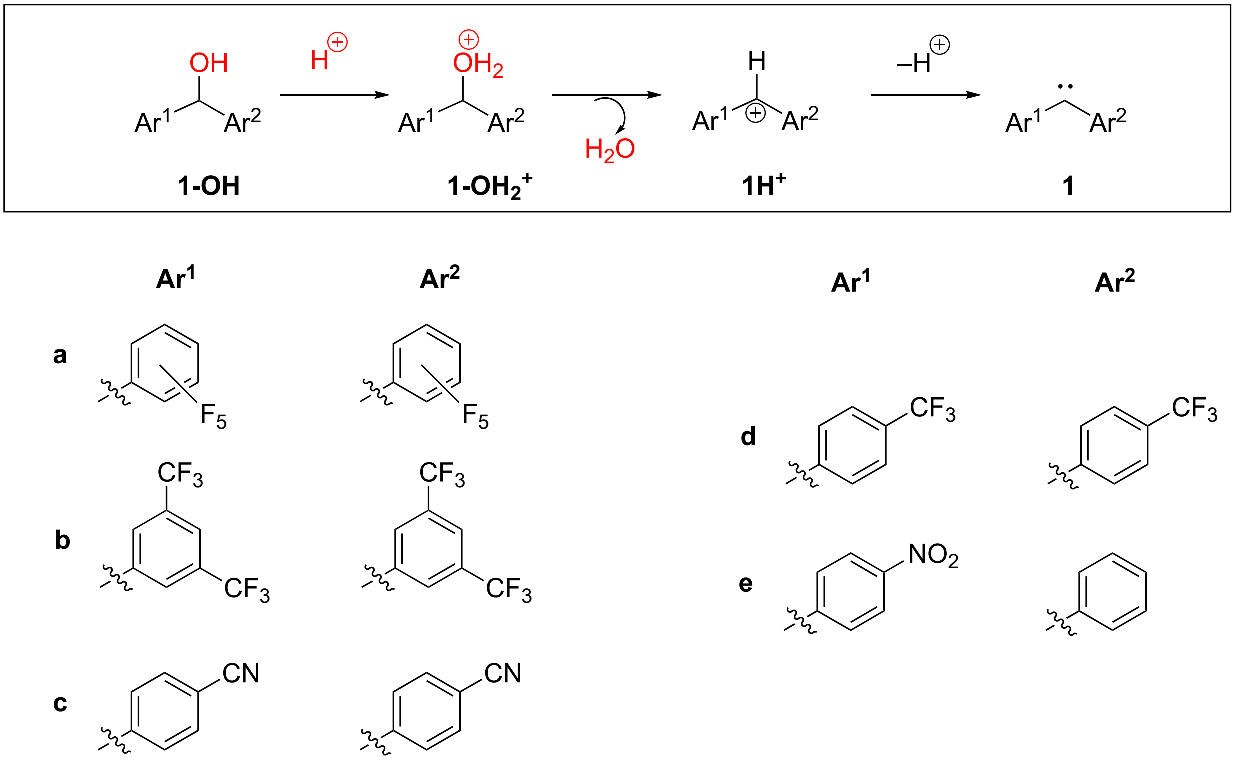
Scheme 2. Three pathways for O-H insertion.

Herein, for the first time, the gas phase acidity of a series of benzhydryl cations is examined, as a step toward obtaining the corresponding diarylcarbene basicities.

Results and Discussion.

Experimental acidity of benzhydryl cations.

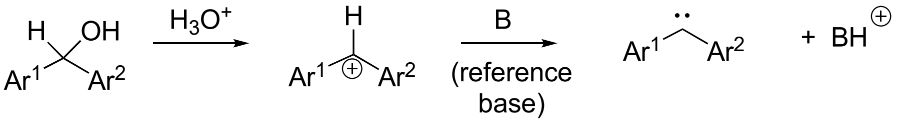
Five protonated carbenes were examined (**1aH⁺-1eH⁺**, Scheme 3). These benzhydryl cations feature different substituents at the phenyl rings directly attached to the carbene center.



Scheme 3. Compounds studied.

These acidities have not heretofore been measured; deprotonation of these benzhydryl cations should reflect the basicity of the corresponding diarylcarbene **1** (Scheme 3). Therefore, our main goal was to generate the benzhydryl cations and measure the gas phase deprotonation energy. To do this, we used a bracketing method in our mass spectrometers, described in detail in the Experimental section.

i. Fourier Transform mass spectrometric experiments. Initially we conducted these experiments in a Fourier Transform ion cyclotron resonance mass spectrometer (FTMS). Vaporization of the benzhydryl alcohol (**1-OH**) followed by reaction with hydronium ions (generated from electron ionization of water, see Experimental section for details) yields a *m/z* ratio corresponding to the benzhydryl cation **1H$^+$** (Scheme 4). Reference bases with known proton affinities (PAs) are then allowed to react with **1H**$^+$, and the presence (or absence) of proton transfer, as indicated by the formation of **BH**$^+$, allows one to ascertain the acidity of **1H**$^+$ (Scheme 4).

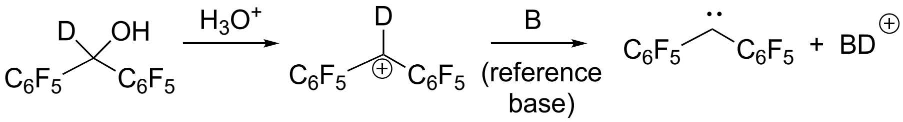


1-OH **1H**$^+$ **1**

Scheme 4. Acidity bracketing experiment in FTMS.

We first examined the perfluoro derivative **1aH**$^+$. We found that reference bases *N,N'*-dimethylcyclohexylamine (PA = 235.1 kcal/mol), TMEDA (*N,N,N',N'*-tetramethyl-1,2-ethanediamine, PA = 242.1) and TMPDA (*N,N,N',N'*-tetramethyl-1,3-propanediamine, PA = 247.4 kcal/mol) all become protonated in the presence of **1aH**$^+$. Although the acidity of benzhydryl cations has not been measured before, calculations have been conducted on the parent diphenylcarbene PA, yielding a value of 275 kcal/mol (for the singlet carbene, MP2/DZ//HF/DZ).[28] We note that this is a calculation at a level of theory that is probably not enough to properly describe the energetics of the carbene, and we also know that perfluorophenyl substitution is sure to lower the PA, but still, the presence of **BH**$^+$ when *N,N'*-dimethylcyclohexylamine is used as the reference base, (implying a PA for **1a** under 235 kcal/mol) seemed rather surprising. We thus entertained the possibility that the protonated reference base signal **BH**$^+$ was not arising from **1aH**$^+$, but from some other proton source.

To ensure that we are not seeing deprotonation of **1aH**$^+$ to form **BH**$^+$, we synthesized the corresponding alcohol of the deutero derivative, **1aD-OH**, and allowed it to react with hydronium in the FTMS to generate deuterated **1aD**$^+$ (Scheme 5). We then allowed the deuterated perfluoro diarylcarbene **1aD**$^+$ to react with both *N,N'*-dimethylcyclohexylamine (PA = 235.1 kcal/mol) and TMPDA (PA = 247.4 kcal/mol), respectively. We see *no deuteron* transfer to either of these reference bases, indicating the acidity of **1aD**$^+$ is above 247.4 kcal/mol. Figure 1 shows the mass spectra for the reaction of **1aD**$^+$ with *N,N'*-dimethylcyclohexylamine. We still see the protonation of the reference base at *m/z* 128 (whose provenance is unknown to us), but the *m/z* signal corresponding to **BD**$^+$ (*m/z* 129) does not appear. We next allowed **1aD**$^+$ to react with DBU (PA = 250.5 kcal/mol); for this reaction, we do see deuteron transfer to form **BD**$^+$, indicating that DBU is basic enough to de-deuterate **1aD**$^+$. This places the acidity of **1aD**$^+$ between TMPDA (PA = 247.4 kcal/mol) and DBU (PA = 250.5 kcal/mol).



1aD-OH **1aD**$^+$ **1a**

B = N,N'-dimethylcyclohexylamine, TMPDA - no reaction
B = DBU - reaction occurs

Scheme 5. Acidity bracketing with deuterated substrate.

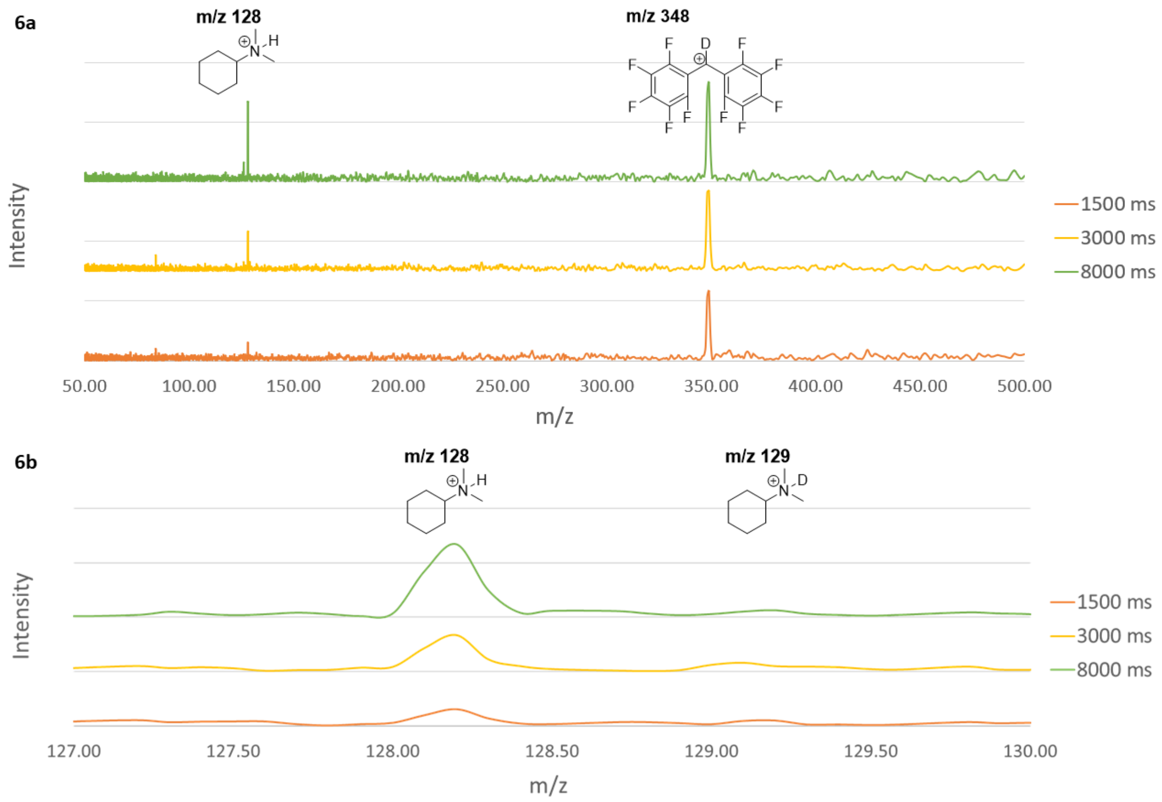


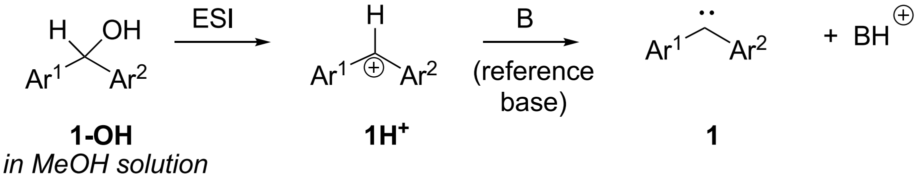
Figure 1. (a) Spectrum showing reaction of *N,N′*-dimethylcyclohexylamine with **1a-D$^+$**. (b) Enlarged spectrum showing lack of deuterated *N,N′*-dimethylcyclohexylamine.

Volatility issues precluded the use of reference bases with PAs higher than DBU. However, the results with the deuterated **1aD$^+$** do show that the proton transfer we observed, to form **BH$^+$**, in our initial reactions of **1aH$^+$** with reference bases *N,N′*-dimethylcyclohexylamine and TMPDA, did not result from deprotonation of the **1aH$^+$**.

The provenance of the reference base protonation is unknown. We considered the possibility that stray electrons might generate the radical cation of the reference base **B** to form **B$^{+\bullet}$**. This radical cation could serve as the acid/proton donor. To exclude this possibility, double resonance experiments with **1aH$^+$** and *N,N′*-dimethylcyclohexylamine ("**B**") were conducted. We irradiated the *m/z* ratio corresponding to the radical cation of

N,N′-dimethylcyclohexylamine (**B$^{+\bullet}$**, *m/z* 127) to ascertain the effect, if any, on the protonated *N,N′*-dimethylcyclohexylamine signal (**BH$^+$**). We find that irradiation of the signal at *m/z* 127 does not affect the protonated base signal, indicating that the protonated reference base does not arise from the radical cation. We are still unsure from whence the **BH$^+$** signal arises, but our studies do indicate that neither the **1aH$^+$** nor **B$^{+\bullet}$** appear to be the sources.

ii. Quadrupole ion trap experiments. The constant presence of proton transfer, regardless of whether the reference base is actually deprotonating the reactant benzhydryl cation, complicates the bracketing of the benzhydryl cation acidities in the FTMS. We thus turned to an alternate instrument, a quadrupole ion trap that we have modified to allow for bracketing experiments.[22] The benzhydryl cations **1H$^+$** are generated from electrospray ionization (ESI) of a solution containing the corresponding alcohol (Scheme 6, details in Experimental section). The **1H$^+$** cations are then allowed to react with reference bases and the absence or presence of proton transfer is ascertained. We again started with the perfluoro derivative **1a** (Table 1).



Scheme 6. Generation of benzhydryl cations via electrospray ionization.

We find that TMEDA (PA = 242.1 kcal/mol), 1-pyrrolidino-1-cyclopentene (PA = 243.6 kcal/mol) and TMPDA (PA = 247.4 kcal/mol) are all unable to deprotonate **1aH$^+$** (Table 1). However, DBN (PA = 248.2 kcal/mol) and DBU (PA = 250.5 kcal/mol) both deprotonate **1aH$^+$**. We therefore bracket the acidity of the perfluorobenzhydryl cation derivative **1aH$^+$** to be 248 ± 3 kcal/mol. *We also note that this result is consistent with the bracketing of **1aD$^+$** in the FTMS described above*.

For the tetra-trifluoromethyl derivative **1b**, DBN (PA = 248.2 kcal/mol) and weaker bases cannot deprotonate **1bH$^+$**; however, DBU (PA = 250.5 kcal/mol) and MTBD (PA = 254.0) do deprotonate **1bH$^+$** (Table 1). We thus bracket the acidity of **1bH$^+$** to be 249 ± 3 kcal/mol.

For the 4,4'-dicyano derivative **1c**, TMPDA (PA = 247.4 kcal/mol) and DBU (PA = 250.5 kcal/mol) are unable to deprotonate **1cH$^+$**; however, MTBD (PA = 254.0 kcal/mol) does, placing the acidity of **1cH$^+$** at 252 ± 4 kcal/mol (Table 1).

tBuP$_1$(dma) (PA = 260.6 kcal/mol) is able to deprotonate both the 4,4'-di-trifluoromethyl and 4-nitro benzhydryl cations, while HP$_1$(dma) (PA = 257.4) is unable to do so, placing the acidity of both **1dH$^+$** and **1eH$^+$** at 259 ± 4 kcal/mol (Table 1).

Table 1. Summary of results for acidity bracketing of benzhydryl cations **1aH$^+$-1eH$^+$**.

Reference base[a,b]	*PA (kcal/mol)*[c]	*Proton transfer to reference base*[d]				
		1aH$^+$	**1bH$^+$**	**1cH$^+$**	**1dH$^+$**	**1eH$^+$**
N,N,N',N'-tetramethylethylenediamine	242.1	–	–			
1-(cyclopent-1-en-1yl)pyrrolidine	243.6	–				
N,N,N',N'-tetramethyl-1,3-propanediamine	247.4	–	–	–		
DBN	248.2	+	–	–		
DBU	250.5	+	+	–		
MTBD	254.0		+	+	–	–
HP$_1$(dma)	257.4			+	–	–
tBuP$_1$(dma)	260.6			+	+	+
tOctP$_1$(dma)	262.0			+	+	+
BEMP	263.8				+	+

[a] References [8,29,30]; [b] DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; MTBD = 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; HP$_1$(dma) = Imino-tris(dimethylamino)phosphorane; tBuP$_1$(dma) = *tert*-Butylimino-tris(dimethylamino)phosphorane; tOctP$_1$(dma) = *tert*-Octylimino-tris(dimethylamino)phosphorane; BEMP = 2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine. [c] Reference base PAs typically have an error of ±2 kcal/mol. [d] The "+" symbol indicates the occurrence and the "–" symbol indicates the absence of proton transfer.

A summary of our experimental data is shown in Table 2. At present, we are unable to experimentally ascertain the acidity values for benzhydryl cations with ΔH_{acid} values much higher than **1eH$^+$** due to the low volatility of reference bases, though future plans include instrument modifications that would allow us to explore less acidic benzhydryl cations.

Table 2. Experimental ΔH_{acid} for benzhydryl cations **$1H^+$**.

Benzhydryl cation	Experimental ΔH for deprotonation (kcal/mol)
$1aH^+$	248 ± 3
$1bH^+$	249 ± 3
$1cH^+$	252 ± 4
$1dH^+$	259 ± 4
$1eH^+$	259 ± 4

These data represent the first time that the acidity of these benzhydryl cations have been measured. Next, we investigated the chemistry taking place when we deprotonate these benzhydryl cations.

iii. Structures and pathways. Diphenylcarbene (**DPC**), the parent carbene for **1a** - **1e**, is known to have a triplet ground state.[4,31] Carbenes **1a** - **1e** are therefore likely to have triplet ground states as well, since electron withdrawing groups should increase the singlet-triplet gap (ΔE_{S-T}).[32-35] In agreement, the calculated values for the singlet-triplet gap, ΔE_{S-T}, are larger for **1a** - **1e** than for **DPC** (Table 3). For calculating the energetics of reactive carbenes, single point calculations at the CCSD(T) level of theory on structures that have been optimized using a less expensive computational method (typically DFT) are the usual choice.[36] Here, the ΔE_{S-T} values calculated at the CCSD(T)/cc-pvdz//B3LYP-D3/def2-tzvp level of theory are shown in Table 3. Due to the size of the largest carbene, **1b**, the ΔE_{S-T} could only be calculated at the DLPNO-CCSD(T)/cc-pvdz//B3LYP-D3/def2-tzvp level of theory. DLPNO-CCSD(T) has been previously shown as a reliable alternative to CCSD(T) for calculating the ΔE_{S-T} of a series of arylcarbenes, including the parent carbene **DPC**.[37]

Table 3. Singlet-triplet gap, $\Delta E_{S\text{-}T}$, calculated for **1a** - **1e**.

Diarylcarbene	Substituent	$\Delta E_{S\text{-}T}$ (kcal/mol)[a]
1a	perfluoro	4.9
1b	3,3’,5,5’-tetra-CF_3	3.7[b]
1c	4,4’-di-CN	5.2
1d	4,4’-di-CF_3	4.8
1e	4-NO_2	4.6
DPC	parent diphenylcarbene	3.3

[a] Calculations were conducted at the CCSD(T)/cc-pvdz//B3LYP-D3/def2-tzvp level of theory; [b] The DLPNO-CCSD(T)/cc-pvdz//B3LYP-D3/def2-tzvp level of theory was used for **1b** (see text).

In order to provide further insight into the deprotonation of these species, the enthalpies of deprotonation were calculated at the CBS-QB3 level of theory. Since these are demanding calculations for large systems, we focused on the two smallest species in this study, **1c** and **1e**. First, we checked whether this method is able to reproduce the $\Delta E_{S\text{-}T}$ obtained in the CCSD(T) calculations to assess if with CBS-QB3 we can also properly describe the complex electronic structure of these species. The calculated $\Delta E_{S\text{-}T}$ values for **1c** and **1e** with the CBS-QB3 method are 4.8 kcal/mol and 3.9 kcal/mol, respectively. These values compare favorably to those calculated using CCSD(T) (5.2 kcal/mol and 4.6 kcal/mol respectively). Also, while the CBS-QB3 $\Delta E_{S\text{-}T}$ values are somewhat lower than those with CCSD(T) (less than 1 kcal/mol difference), they are consistent with experimental results in that carbenes with electron-withdrawing groups, like **1c** and **1e**, have larger singlet-triplet gaps than the parent **DPC** (the $\Delta E_{S\text{-}T}$ value with CBS-QB3 is 2.3 kcal/mol).

In Table 4, we summarize the calculated and experimental ΔH$_{acid}$ values for the protonated carbenes **1cH⁺** and **1eH⁺**. For these diarylcarbenes, the experimental enthalpy of deprotonation correlates best to the calculated enthalpy of deprotonation to the singlet carbene. We do know, from other studies of proton transfer in the gas phase, that spin-forbidden proton transfer is possible.[10,38-42] Tian and Kass showed that the methyl cation is deprotonated to yield the more stable triplet carbene, in bracketing experiments in the gas phase.[10] Triplets are more stable for diarylcarbenes **1a-1e**, so it is possible that we could also see spin-forbidden proton transfer to yield these triplet ground states, but our calculations imply otherwise, for **1c** and **1e**.[43]

Table 4. Experimental and calculated ΔH$_{acid}$ values for benzhydryl cations **1cH⁺** and **1eH⁺** (in kcal/mol)

Benzhydryl cation	Calculated ΔH for deprotonation, to singlet[a]	Calculated ΔH for deprotonation, to triplet[a]	Experimental ΔH for deprotonation
4,4'-di-CN (**1cH⁺**)	250.3	245.5	252 ± 4
4-NO$_2$ (**1eH⁺**)	257.8	253.9	259 ± 4

[a] Calculated values at the CBS/QB3 level of theory

***iiia. Benzhydryl cation versus tropylium*.** We also used computational approaches to probe other mechanistic aspects of this experiment. For these calculations that do not involve carbenes, we used B3LYP/6-31+G(d) since in our experience, this level of theory yields acidities and relative enthalpies that are consistent with gas-phase measurements.[21,22,44-47]

We considered the possibility that the initial cation formed is not the benzhydryl, but rather, the tropylium, or cycloheptatrienyl, cation (Figure 2). Calculations of the relative stabilities of the benzhydryl cation and tropylium structures are shown in Table 5.

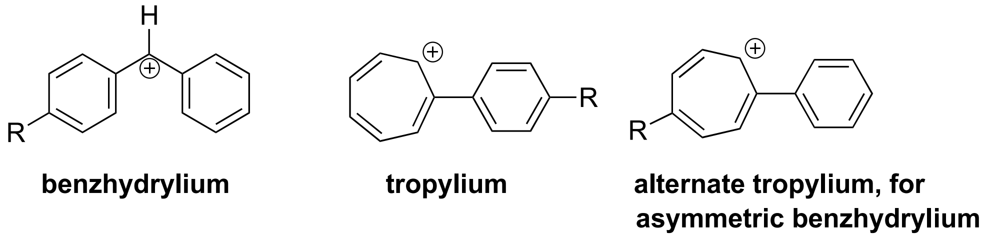

benzhydrylium **tropylium** **alternate tropylium, for asymmetric benzhydrylium**

Figure 2. Structures of benzhydryl cation and tropylium ions.

Table 5. Relative stabilities of benzhydryl cation and tropylium structures for protonated diarylcarbenes.[a,b]

Protonated substituted diarylcarbene	Relative enthalpy of benzhydryl cation structure	Relative enthalpy of tropylium structure,	Relative enthalpy of alternate tropylium structure, if relevant
1aH⁺	0.0	+0.7	
1bH⁺	0.0	+7.9	
1cH⁺	0.0	+6.8	
1dH⁺	0.0	+5.3	
1eH⁺	0.0	+5.7	+7.5

[a] All values are in kcal/mol. [b] Calculations at B3LYP/6-31+G(d).

For all these cations, the benzhydryl cation appears to be more stable than the tropylium, though for **1aH⁺**, the difference is small (the tropylium is less stable by only 0.7 kcal/mol). For **1bH⁺**, **1cH⁺**, **1dH⁺**, and **1eH⁺**, the tropylium is less stable than the benzhydryl cation by more than 5 kcal/mol. Therefore, if dehydration of the protonated benzhydryl alcohol precursor **1-OH** yields the most stable cation, we are likely to produce the benzhydryl cation (as shown in Scheme 3).

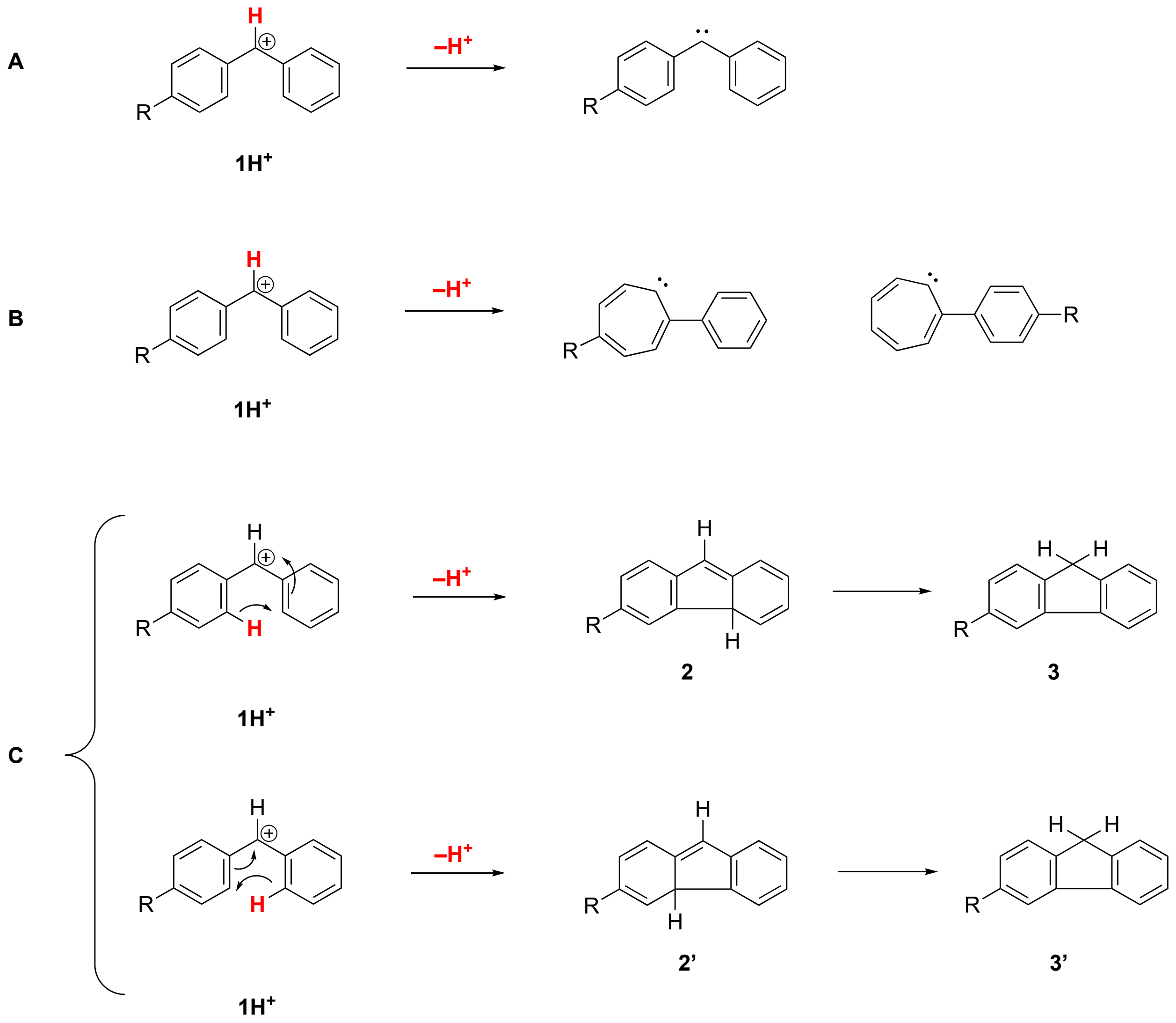
In terms of rearrangement, evidence indicates that the barrier for benzyl cation conversion to tropylium is prohibitively high in the gas phase. Calculations by Dewar estimated a barrier of 32.7 kcal/mol, using MINDO/3.[48] Hoppilliard conducted calculations on a dihydroxy benzyl cation derivative and reported rearrangement barriers as "very high in energy."[49] Through experimental gas phase studies, Kebarle concluded that rearrangement of the ground state benzyl cation to tropylium does not occur in the gas phase.[50-52]

We also believe we most likely have the benzhydryl cation structure because the cations are generated from solution via electrospray. Mayr's work with benzhydryl cation electrophilicity established that the solution-phase ions are *not* tropylium ions.[3] In our work, the benzhydrols **1-OH** are dissolved in methanol, with a small amount of acid (see Experimental section), then electrosprayed into the mass spectrometer. Electrospray ionization is widely accepted as a gentle method which captures the ions that already exist in solution.[53] Thus, there is a high probability that the cations generated in solution and electrosprayed are, as in Mayr's studies, benzhydryl cations.

iiib. Pathways after deprotonation. We also need to consider pathways that may occur after deprotonation of the benzhydryl cation, since rearrangements are possible. Pathways for the deprotonation of **1H$^+$** are shown in Scheme 7. We show a general "asymmetric" benzhydryl cation with substitution "R" on just one ring, as this has the most possible pathways. Pathway A is simple deprotonation to yield the diarylcarbene, singlet or triplet. Pathway B involves ring expansion; expansion into the substituted and non-substituted ring are options. Pathway C generates a fluorene; again with this substrate, there are two possibilities since the parent cation is substituted asymmetrically (via **2** to form **3** and via **2'** to form **3'**, Scheme 7). Fluorene has been seen as a rearrangement product of diarylcarbene in the high-intensity excimer laser photolysis of diaryldiazomethane, although it is not observed in the conventional UV lamp photolysis of diaryldiazomethane.[54,55] Wentrup and co-workers hypothesize that any rearrangement from diphenylcarbene to fluorene occurs via hot or more likely higher excited states; our mass spectrometric methods are designed to be under thermally equilibrated conditions, so formation of fluorene should be less likely.[56]

Pathway B involves carbenes; as noted earlier in the manuscript, calculating the enthalpies of reaction for these singlet and triplet paths are computationally prohibitively demanding. The barrier for rearrangement of diphenylcarbene to the ring-expanded phenylcycloheptatetraene was recently calculated by Régimbald-Krnel and Wentrup at B3LYP/6-311+G**//B3LYP/6-31G* to be 19.3 kcal/mol.[56] Substitution by electron-withdrawing groups would most probably lower this barrier, based on studies of phenylcarbene rearrangement.[57-64] If the barrier is indeed less than 20 kcal/mol, then we cannot discount Path B, since formation of the initial ion-molecule complexes between a charged and neutral reactant (in our case, the protonated carbene and reference base) is generally estimated to be about 20 kcal/mol exothermic.[65]

However, we did calculate Pathway C (Scheme 7) for **1bH$^+$** through **1eH$^+$** (Table 6) at the 6-31+G(d) level of theory. The perfluorobenzhydryl cation **1aH$^+$** is not included, as it is unable to form fluorene due to the lack of a proton beta to the cationic site.



Scheme 7. Deprotonation pathways.

Table 6. Enthalpies for the fluorene path. [a,b,c]

Benzhydryl cation	ΔH from benzhydryl cation to **2**	ΔH from benzhydryl cation to fluorene **3**	experimental acidity, ΔH
1bH$^+$	210.8	186.6	249 ± 3
1cH$^+$	212.0	178.0	252 ± 4
1dH$^+$	213.8	180.4	259 ± 4
1eH$^+$	216.9/218.7	184.0/184.0	259 ± 4

[a] All values are in kcal/mol. [b] Calculations at the B3LYP/6-31+G(d) level of theory. [c] ΔH at 298 K. For **1eH$^+$**, the two values represent **2/2'** and **3/3'** enthalpies.

Interestingly, the enthalpy to form fluorene from the benzhydryl cations is much lower than our experimental values of deprotonation. For example, we measure the proton affinity of **1bH$^+$** to be 249 ± 3 kcal/mol. The computed ΔH to form, say, **2** from **1bH$^+$** (Scheme 7) is 210.8 kcal/mol (Table 6). If the formation of **2** were taking place, then we would find that all reference bases **B** with PAs of about 211 or higher would produce signal corresponding to protonated reference base, **BH$^+$**. Instead, we find that only reference bases with PAs above DBN (PA = 248.2 kcal/mol) effect reaction. Table 7 shows our experimental results versus that expected if path C were taking place. We are thus reasonably certain that the fluorene path is not at play under our experimental conditions.

Table 7. Hypothetical bracketing table if reaction between reference base and **1bH⁺** followed path C (Scheme 7).

Reference base[a,b]	*PA (kcal/mol)*[c]	*Proton transfer to reference base*	
		experimentally observed for **1bH⁺**	hypothetical, if **1bH⁺** formed **2** and/or **3**
N,N,N',N'-tetramethylethylenediamine	242.1	–	+
N,N,N',N'-tetramethyl-1,3-propanediamine	247.4	–	+
DBN	248.2	–	+
DBU	250.5	+	+
MTBD	254.0	+	+

[a]Reference [29]; [b]DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; MTBD = 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. [c]Reference base PAs typically have an error of ±2 kcal/mol. [d]The "+" symbol indicates the occurrence and the "–" symbol indicates the absence of proton transfer.

Conclusions.

For the first time, the experimental gas phase acidities of a series of benzhydryl cations were measured. There is a dearth of thermochemical data for carbenes, and these measurements represent a first attempt to ascertain values that correspond to carbene basicity for the diarylcarbene family. Our studies indicate that the benzhydryl cation structure is the most stable and most likely structure generated experimentally. We also determined that reaction with reference bases follows a deprotonation path that is unlikely to involve fluorenes. Quantum chemical calculations suggest that we are measuring deprotonation of the benzhydryl cations to form the corresponding singlet carbenes, for **1c** and **1e**. This study represents an important step toward understanding the energetics of some of the strongest organic bases known, the diarylcarbenes.

Experimental.

All of the carbene precursors (the benzhydryl alcohols) were commercially available, except for the deuterated substrate described herein, which was synthesized following literature procedure.[66]

The bracketing method was used to measure the gas phase acidity of the benzhydryl cations. For the FTMS experiments (manuscript section i), a Fourier transform ion cyclotron resonance mass spectrometer with dual cell setup (described previously) was used.[67-71] The magnetic field is 3.3 T; the baseline pressure is 1 x 10^{-9} Torr. The solid benzhydrol carbene precursors were introduced into the cell via a heatable solids probe, while liquid reference acids bases were introduced via a system of heatable batch inlets. Water was pulsed into the cell, and ionized by an electron beam (typically 8 eV (for HO^-), 20 eV (for H_3O^+), 6 μA (for H_3O^+), 9 μA (for HO^-), 0.5 s) to generate hydronium ions. Protonated carbene ions were generated by reaction of the benzhydrol with the hydronium ions. The protonated carbene ions were then selected, and transferred from one cubic cell to another via a 2-mm hole in the middle trapping plate. Transferred ions were cooled with pulsed argon gas that allowed the pressure to rise to 10^{-5} Torr. Reaction with reference bases was then tracked. Experiments were conducted at ambient temperature. The typical protocol for bracketing experiments has been described previously.[44,46,67,68,71] The occurrence of proton transfer is regarded as evidence that the reaction is exothermic (denoted as “+” in the tables). Bracketing experiments are run under pseudo-first-order conditions with the neutral reactant in excess, relative to the reactant ions. Reading the pressure of the neutral compounds from the ion gauges is not always accurate; therefore, we “back out” the neutral substrate pressure from fast control reactions (described previously).[45,46,67,72-74]

We also conducted bracketing experiments in a house-modified quadrupole ion trap (manuscript section ii) mass spectrometer (previously described).[22] To generate the protonated carbene ions via electrospray ionization (ESI), the corresponding benzhydrols were dissolved in methanol. To facilitate ionization, we added 1 μL of a 0.1 *M* HBF_4 solution and 1 μL of 0.1 *M* CF_3SO_3H solution to a 10 mL aliquot of the benzhydrol-methanol solution. Final concentrations of these solutions were ~2 x 10^{-4} *M*. A flow rate of 30 μL/min was used for the electrospray ionization. ESI should vaporize only those ions that already exist in solution; we thus trap and isolate the desired protonated benzhydryl cation reactant.[53]

The capillary temperature was 190°C. Neutral reference bases were added with the helium gas flow. The protonated carbene ions were allowed to react with neutral reference bases for 0.03-10,000 ms. The occurrence of proton transfer was regarded as evidence that the reaction was exothermic ("+" in Table); otherwise the reaction was regarded as endothermic ("–" in Table). The typical electrospray needle voltage was ~1.80 kV. A total of 10 scans were averaged.

Computational Details

The $\Delta E_{S\text{-}T}$ values were calculated employing several methods and levels of theory. The DLPNO-CCSD(T) method implemented in the ORCA program system was used[75] with the TightPNO criteria. Within the DLPNO calculations, the Dunning correlation consistent basis sets cc-pVDZ was used.[75] The DFT calculations were carried out using the Gaussian09 program.[76] The geometries used for the single point calculations were optimized at the B3LYP-D3/def2-tzvp level of theory.[76,77] CCSD(T) single points calculations were performed using the Molpro software.[78] For carbenes **1c** and **1e**, and

CBS-QB3 enthalpies were calculated using Gaussian 09 software packages.[79,80] For calculations at B3LYP/6-31+G(d)), Gaussian 09 was used.[77,81-84] The geometries were fully optimized and frequencies were calculated; no scaling factor was applied. The optimized structures had no negative frequencies. The temperature for the enthalpy calculations was set to 298 K.

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SUPPORTING INFORMATION AVAILABLE

Cartesian coordinates for all calculated species are available.

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