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Excited state carbon acids. Photodeprotonation and photoreduction of suberenes by amines

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Abstract

The excited singlet state carbon acidity of the benzylic position of 5H-dibenzo[a,d]cycloheptene (suberene) (**2**) and several derivatives has been studied in the presence of a variety of amine bases using steady-state and time-resolved fluorescence studies and the measurement of quantum yields of proton (deuteron) exchange. The purpose of the present work is to study the effect of substituents at the 5-(benzylic)position on the excited state carbon acidity of **2** as well as the possibility of base catalysis of deprotonation. Primary kinetic isotope effects for deprotonation were measured by fluorescence quenching of **2** using EtOH and ethanolamine as bases along with the deuterated derivative, 5,5-dideuteriodibenzo[a,d]cycloheptene (**3**) and were 2.7 ± 0.4 and 1.4 ± 0.2, respectively. The magnitudes of these isotope effects suggest that the transition state for C–H bond ionization is early and moves closer to the reactant when a stronger base is used. The deprotonation rate is enhanced by primary amine bases, with rates approaching the diffusion controlled limit (in CH_3CN), demonstrating that C–H depronation rates can be very fast in S_1. A Brønsted β coefficient of 0.07 ± 0.02 determined for general base catalysis of the excited state deprotonation of **2** by a series of primary amines is consistent with this conclusion. Product studies show that tertiary and secondary amines facilitate photoreduction of **2** rather than photodeprotonation. Substitution of the 5-position of compound **2** with methyl or phenyl groups substantially reduced the kinetic acidity and a stereoelectronic effect for deprotonation is proposed to account for this decrease in reactivity.

Keywords: Excited state carbon acids; Photoreduction; Proton transfer

1. Introduction

Deprotonation of C–H bonds in the ground state (S_0) by a suitable base, to generate the corresponding carbanion, is a fundamental reaction in organic chemistry [1]. The corresponding deprotonation of potential carbon acids in S_1 has received much less attention although most hydrocarbons with benzylic protons have been predicted to be much stronger carbon acids in S_1 (by as much as 30 pK_a units), as indicated by Förster cycle calculations [2]. For example the dibenzylic protons of fluorene (**1**) have been predicted to have $pK(S_1) \approx -9$, compared with its relative modest ground state acidity ($pK(S_0) = 23$) [2]. This predicted enhancement in acidity on going from S_0 to S_1 for benzylic hydrocarbons by far exceeds the enhancement in acidity observed for phenols, which typically have $\Delta pK \approx 7$–9 [2]. However, unlike the situation for phenols, the predicted enhanced acidity of benzylic hydrocarbons has not been observed for **1** and other fluorenes [2b,c]. Since the deprotonation rates of carbon acids (in S_0) are known to be inherently slow [1d,3] due to the lack of hydrogen bonding between the solvent and C–H bond, and to the geometrical and solvation changes required for this process, it is not surprising that short S_1 lifetimes might preclude observing carbon acid ionization.

We reported that both 5H-dibenzo[a,d]cycloheptene (suberene) (**2**) and an isomer, 5H-dibenzo[a,c]cycloheptene (**4**), exhibit enhanced carbon acidity (at the 5-position) on excitation in the presence of water acting as base (in CH_3CN) (Eq. (1)) [4,5]. Thus photolysis in the presence of D_2O resulted in a facile exchange of the dibenzylic protons. The estimated $pK_a(S_1)$ of these compounds [4] was ≈ -1, making them vastly more acidic than in the ground state ($pK(S_0) \approx 35$). Indeed, these suberene isomers were the first examples of excited state carbon acids to be documented in the literature. The excited state carbon acid behavior of the azulenium cation has been reported by Grellmann et al. [6] in which neutral azulene is the product. Since a carbanion is not formed in this carbon acid deprotonation, it does fit into the definition of a carbon acid in the traditional sense.

In the present study the effect of amine bases on the rate of C–H deprotonation in S_1 for **2** is examined. The correlation

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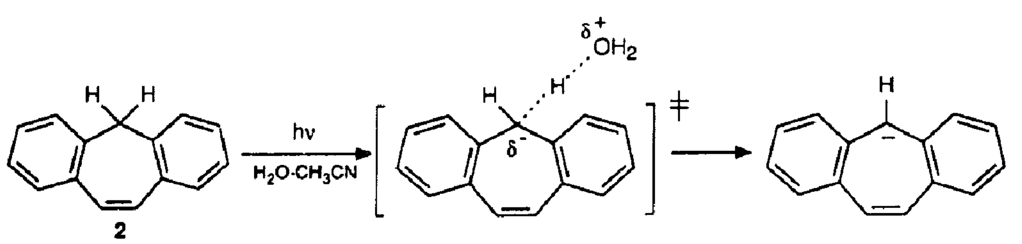


(1)

observed between base strength and the rate of deprotonation should provide new insights concerning the transition state of this reaction. In addition, two derivatives of **2** substituted at the 5-(benzylic) position are studied to determine the effect of substitution at the site of exchange on the excited state carbon acid behaviour of this system.

2. Experimental details

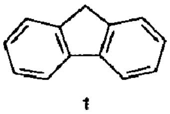
2.1. General

^{1}H NMR analyses were performed on Perkin-Elmer R32, Bruker WM250 or AM360 spectrometers in $CDCl_3$. ^{13}C NMR were acquired on either the WM250 or AM360 instrument. Mass spectra and GC/MS were performed on either a Kratos Concept H (EI) or Finnigan 3300 instrument using chemical ionization (CI/methane). GC analyses were carried out on a Varian 3700 gas chromatograph using an SE-54 capillary column and a Hewlett-Packard 3390A integrator. UV spectra were obtained on either a Unicam SP8-400 or Cary 5 instrument. Preparative photolyses were carried out in a Rayonet RPR 100 photochemical reactor using 254 or 300 nm lamps. Reaction mixtures for these photolyses were contained in 100 or 200 ml quartz tubes.

2.2. Materials

Anhydrous CH_3CN required for fluorescence quenching studies was dried over CaH_2 at reflux and used immediately. The amines bases Et_3N (BDH), piperidine (BDH), ethanolamine (EA) (Aldrich), n-propylamine (PA) (Aldrich), 2-methoxyethylamine (Aldrich), 2-aminoethylnitrile (Lancaster) and 2,2,2-trifluoroethylamine (Aldrich) were obtained commercially and used as received after passing purity checks (GC, ^{1}H NMR). Preparative thin layer chromatography (TLC) was carried out on 20×20 cm silica gel GF Uniplates (Analtech).

Preparation of **2** and **3** involving the reduction of the corresponding ketone with $LiAlH_4$ or $LiAlD_4$ has already been reported by us [4]. The substituted derivatives **5–8** were prepared by reaction of either **9** or **10** with the appropriate organometallic reagent (MeMgBr or PhLi). Intermediates **9** and **10** were made via standard reaction of the corresponding dibenzosuberenols with $SOCl_2$. The dibenzosuberenols were made via simple $LiAlH_4$ ($LiAlD_4$) reduction of **11** in THF or diethyl ether.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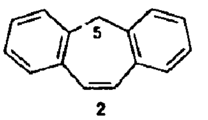

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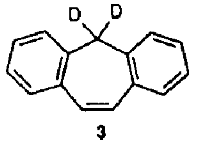

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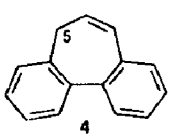

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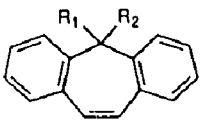


	R_1	R_2
5	H	CH_3
6	D	CH_3
7	H	Ph
8	D	Ph
9	H	Cl
10	D	Cl

2.2.1. 5-Methyl-5H-dibenzo[a,d]cycloheptene (5-methylsuberene) (5)

The compound was recrystallized from 95% EtOH as colourless cystals, mp = 58–59 °C, ^{1}H NMR (250 MHz), more abundant conformer: δ 1.42 (dd, J = 7.2, 0.8 Hz, 3H, CH_3), 4.24 (q, J = 7.2 Hz, 1H, CH), 7.00 (s, 2H, vinyl); less abundant conformer: δ 1.96 (d, J = 7.3 Hz, 3H, CH_3), 3.57 (q, J = 7.3 Hz, 1H, CH), 7.21 (s, 2H, vinyl); for both conformers: δ 7.1–7.6 (m, 8H, arom.); ^{13}C NMR δ 15.4, 17.3 (CH_3), 38.0, 49.3 (CH), 123.1, 125.3, 126.2, 127.6, 128.3, 128.8, 129.9, 130.8, 131.4, 133.9, 135.3, 141.7, 142.6; MS (CI) (m/z) 207 (M+1), 235 (M+29), 247 (M+41); HRMS, calc. for $C_{16}H_{14}$ 206.1096, obs. 206.1093; UV-Vis (CH_3CN) λ_{max} (ϵ): 211 nm (25600), 220 nm (sh 20700), 288 nm (12200).

2.2.2. 5-Methyl-5D-dibenzo[a,d]cycloheptene (5-methyl-5-deuterosuberene) (6)

^{1}H NMR (360 MHz), more abundant conformer: δ 1.31 (s, 3H, CH_3), 6.91 (s, 2H, vinyl); less abundant conformer: δ 1.86 (s, 3H, CH_3), 7.12 (s, 2H, vinyl); for both conformers: δ 7.1–7.4 (m, 8H, arom.); MS (CI) (m/z) 208 (M+1), 236 (M+29), 248 (M+41).

2.2.3. 5-Phenyl-5H-dibenzo[a,d]cycloheptene (5-phenylsuberene) (7)

The compound was recrystallized from 95% EtOH as colourless crystals, mp = 143–144 °C, ^{1}H NMR (90 MHz), δ 5.38 (s, 1H, CH), 6.6–7.5 (m, 15H, arom. and vinyl); MS (CI) (m/z) 269 (M+1), 297 (M+29), 309 (M+41); HRMS, calc. for $C_{21}H_{16}$, 268.1252, obs. 268.1234; UV-Vis (CH_3CN) λ_{max} (ϵ) 205 nm (sh, 38900), 292 (12100).

2.2.4. 5-Phenyl-5D-dibenzo[a,d]cycloheptene (5-phenyl-5-deuterosuberene) (8)

^{1}H NMR (250 MHz), δ 6.6–6.7 (m, 2H, arom.), 6.75 (s, 2H, vinyl), 7.0–7.1 (m, 3H, arom.), 7.3–7.5 (m, 8H, arom.); MS (CI) (*m/z*) 270 (M+1), 298 (M+29), 310 (M+41); ^{13}C NMR, δ 57.1 (t, 19 Hz, C-D), 125.8, 126.7, 127.1, 127.2, 128.5, 129.8, 130.3, 130.8, 134.7, 140.3, 141.8

2.3. Product studies

Samples (30–100 mg) were dissolved in 30–200 ml solvent or solvent mixture and placed in a quartz tube (100 or 200 ml) cooled with a cold finger (running tap water) and continuously purged with a stream of argon via a long needle syringe needle. Length of photolysis varied from 5 min to several hours depending on the efficiency of the photochemical reaction. All photolyses were repeated in the absence of light as a check whether any thermal reactions took place. None were observed. Representative photolyses are decribed below.

2.3.1. Photolysis of 6 and 8 in 50% 5 M NaOH/EtOH

Photolysis of **6** (50 mg) for 2 h (254 nm) gave $<5\%$ yield of **5**; ^{1}H NMR (90 MHz) 3.52, 4.18 (growth of the methine proton quartets of **5**). Photolysis of **8** using the same conditions did not result in any changes in the ^{1}H NMR spectrum.

2.3.2. Photolysis of 2 and 3 in the presence of Et_3N

Photolysis of **2** (100 mg) in 0.01 M Et_3N/CH_3CN for 30 min with 254 or 300 nm lamps resulted in the formation of **17** as the major product (21%) and several minor products. The major product was isolated by preparative TLC, ^{1}H NMR (90 MHz) δ 3.12 (s, 4H, $2CH_2$), 4.08 (s, 2H, CH_2), 7.0–7.3 (m, 8H, arom.); MS (CI) (*m/z*) 195 (M+1), 223 (M+29), 235 (M+41). Photolysis of **3** gave the corresponding dideutero product, viz., 5,5-dideutero-**17**.

2.3.3. Photolysis of 5 in the presence of Et_3N

Photolysis of **5** (50 mg) in 0.01 M Et_3N/CH_3CN for 5 min (254 nm) gave the corresponding photoreduction product, 5-methyl-5H-dibenzo[a,d]cycloheptane (5-methylsuberane) (9%) and several Et_3N adducts (8%) as indicated by GC/MS. The major product produced (5-methylsuberane) was isolated by prep. TLC, ^{1}H NMR (90 MHz) δ 1.70 (d, J=7 Hz, 3H, CH_3), 3.19 (s, 4H, $2CH_2$), 4.42 (q, J=7 Hz, 1H, CH), 7.0–7.3 (m, 8H, arom.); MS (CI) *m/z*: 209 (M+1), 237 (M+29), 249 (M+41).

2.3.4. Photolysis of 7 in the presence of Et_3N

Photolysis of **7** (50 mg) in 0.01 M Et_3N/CH_3CN for 10 min (254 nm) gave the corresponding photoreduction product, 5-phenyl-5H-dibenzo[a,d]cycloheptane (5-phenylsuberane) (17%), at least four Et_3N adducts (11%), and other minor products as indicated by GC/MS. No attempts were made to carry prep. TLC to isolate 5-phenylsuberane due to the complexity of the product mixture.

2.3.5. Photolysis of 3 in the presence of piperidine

Photolysis of **3** (100 mg) in 0.5 M piperidine/CH_3CN for 30 min (254 nm) gave **2a** (10%) and 5,5-dideutero-17 (10%) (^{1}H NMR), in addition to several minor products which were not identified.

2.3.6. Photolysis of 3 in the presence of ethanolamine (EA) and n-propylamine (PA)

Photolysis of **3** (50 mg) in 0.01 M EA/CH_3CN (254 nm) for 30 min resulted in the growth of proton resonances in the ^{1}H NMR at δ 3.77 and 3.79 ppm due to **2a** (34%) and **2** (5%), respectively. Repetition of the photolysis in 0.10 EA/CH_3CN for 5 min also resulted in the growth of signals at δ 3.77 and 3.79 ppm due to **2a** (21%) and **2** (2%). Photolysis of 3 (55 mg) in 0.01 M PA/CH_3CN (300 nm) for 30 min resulted in formation of **2a** (40%) and **2** (6%).

2.3.7. Photolysis of 6 in the presence of ethanolamine (EA) and n-propylamine (PA)

Photolysis of **6** (50 mg) in 0.10 M EA/CH_3CN (254 nm) for 1 h resulted in the formation of **5** (15%) (^{1}H NMR (360 MHz) δ 1.36 and 1.91 (singlets from **6** overlapping doublets from **5**), 3.52 and 4.18 (quartets due to CH of **5**)). Repetition of the photolysis in 0.50 M EA/CH_3CN resulted in 42% yield of **5** according to GC/MS. Irradiation of **6** (100 mg) in 0.50 M PA/CH_3CN for 1 h (254 nm) gave **5** (50%), 5-methyl-5-deuterosuberane (photoreduction product) (3%) and two adducts (6%).

2.3.8. Photolysis of 8 in the presence of ethanolamine (EA) and n-propylamine (PA)

Photolysis of **8** (100 mg) in 0.50 M EA/CH_3CN (254 nm) for 1 h resulted in a trace yield of **7** ($<2\%$), as indicated by a growth of a minor signal at δ 5.32 (s, 1H, CH of **7**). Photolysis in 0.50 M PA/CH_3CN gave **7** ($<2\%$), 5-phenyl-5-deuterosuberane (photoreduction product) (5%) and one major Et_3N adduct (5%), the latter two being identified by GC/MS only.

2.4. Quantum yields

The quantum yields for deuterium exchange were measured in a Rayonet RPR 100 photochemical reactor with 254 nm lamps, using the photochemical exchange reaction of **3** in 50% H_2O/CH_3CN as the secondary actinometer ($\Phi = 0.035 \pm 0.006$) [4]. Solutions were photolyzed for predetermined times as to give 5–20% conversion. The percent deuterium loss was measured using ^{1}H NMR (360 MHz). The light intensity of the Rayonet reactor (254 lamps) was measured to be 1.57×10^{-4} einsteins min^{-1} and varied within 10–15%.

2.5. Steady-state and time-resolved fluorescence lifetime measurements

Steady state fluorescence measurements were carried out on a Perkin-Elmer MPF 66 spectrophotometer (uncorrected mode) at ambient temperature. Each sample ($\approx 10^{-6}$ M) was prepared in 3.0 ml quartz cuvettes and purged with argon for 10 min prior to each measurement. The fluorescence lifetimes (τ) were measured on a Photon Technology International (PTI) LS-1 instrument using a hydrogen flash lamp as the excitation source and single photon counting. Decays were analyzed by software supplied by PTI and were all first order.

3. Results and discussion

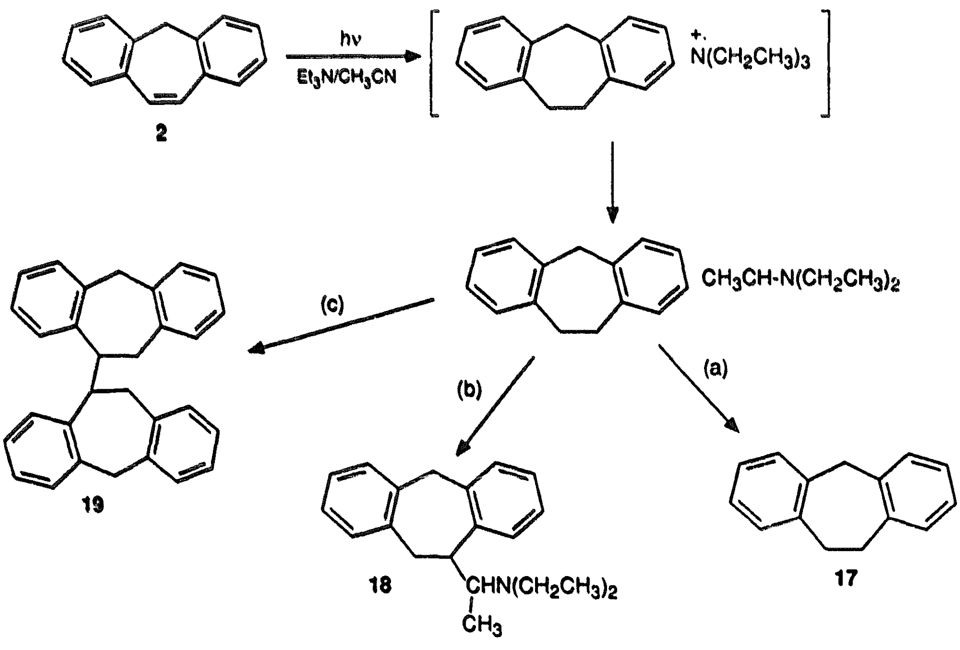
3.1. Substrates

Suberenes **2** and **3** were available from a previous study [4]. Derivatives **5–8** (overall yield >80%) were prepared by the reaction of CH_3MgBr or PhLi with the corresponding chloride **9** or **10**, which in turn was prepared via initial $LiAlH_4$ ($LiAlD_4$) reduction of dibenzosuberenone (**11**) (Aldrich), followed by treatment with $SOCl_2$. All compounds were shown to be >98% by GC and ^{1}H NMR prior to the study.

Suberenyl (5H-dibenzo[a,d]cycloheptenyl) and related systems are known to prefer a conformation in which the seven-membered cycloheptatriene ring adopts a boat conformation [7]. Substitution at the 5-position will result in the possibility of observing (by ^{1}H NMR) two major conformations in which the 5-substituent is either pseudo axial or pseudo equatorial (**12a** or **12b**, respectively), assuming that the interconversion (which requires flipping of the boat conformation) rate is not very fast. At ambient temperature (20–30 °C), the ^{1}H NMR of **5** showed two sets of signals for the methyl (at δ 1.42 and 1.96, as doublets, J = 7.2 Hz), methine (quartet) and vinyl (singlet) protons in the ratio of 3:2. It is known that bulkier substituents prefer the pseudo axial position in suberenyl systems [7]. We assign the more dominant set of these signals (with methyl at δ 1.42) to the conformation with methyl group (δ 1.96) pseudo axial (**12a**). This is also consistent with the fact that an equatorial methyl group should be more deshielded than an axial methyl since the former is closer to the periphery of the two benzene rings. Attempts to collapse the two methyl signals by raising the temperature up to 50 °C were unsuccessful indicating that the barrier to ring flipping is relatively high for this system. As expected, two methyl signals at δ 1.30 and 1.87 (appearing as singlets since coupling to deuterium was not resolvable) in a 3:2 ratio was also observed for the deuterated analog **6**. Only one methine signal (δ 5.38) was observable for **7**. This is consistent with the expectation that the larger phenyl group would have a much greater preference to be at the pseudo axial position. The ^{13}C NMR of **8** showed a single methine carbon at δ 57.1 (t, J = 19 Hz) which is also consistent with only one conformation.

3.2. Proton/deterium exchange studies in aqueous CH_3CN

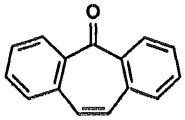
The excited state carbon acidity of suberene derivatives **5** and **7** was investigated initially in aqueous CH_3CN solution. Irradiation of **5** or **7** in 50% D_2O/CH_3CN for 2.5 h (Rayonet RPR 100 photochemical reactor; 254 nm lamps; argon purged; at ≈ 17 °C) did not result in any observable proton exchange according to both ^{1}H NMR and MS. The substrates



Scheme 1.

could be recovered unchanged. Under identical conditions, photolysis of **2** (or **3**) gave significant and readily observable deuterium (protium) incorporation at the 5-position [4]. As further evidence of lack of reactivity of these systems, photolysis of the deuterated derivatives **6** or **8** in 50% 5 M NaOH/EtOH for 2 h resulted in < 5% deuterium exchange according to the ^{1}H NMR of the reaction mixture.

The lack of reactivity observed for these suberene derivatives was initially surprising. However, it seems reasonable that the explanation lies in the conformations available for these substrates. In a study of the photosolvolysis of suberane derivatives **13–16**, whose available conformations can also be represented by structures **12a** and **12b** (with the slight modification that a CH_2CH_2 unit replaces the alkene bridge), Budac et al. [8] showed that a stereoelectronic effect governed the reactivity of these substrates: those substrates (**14–16**) that failed to react via photosolvolysis – which requires initial C–OH bond heterolysis – all had the hydroxyl group at the pseudo equatorial position as the predominant conformer. Thus cleavage of the C–OH bond would not result in any significant overlap of the developing π orbital with the π orbitals of the two benzene rings. A similar stereoelectronic requirement for carbanion formation would also be expected for suberene derivatives **5** and **7**, in addition to any other substituent effect which might also be introduced by substitution at the 5-position. Thus the complete lack of reactivity in **7** can be readily explained since the proton at the 5-position is at the pseudo equatorial position. Abstraction of this proton would result in an incipient carbanion that would not receive any stabilization from conjugation to the π system of the benzene rings. Suberene **5** exists as a mixture of two conformers **12a** and **12b** (ratio 3:2). Although the unreactive conformer **12a** dominates, the complete lack of observable reactivity in aqueous solution for this substrate indicates that the methyl group probably also imparts inhibitory steric and inductive (electron donating) effects which reduces its reactivity to the extent that it is not observable in aqueous solution.



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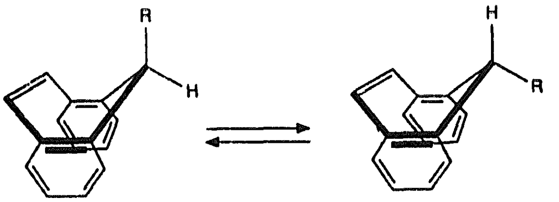
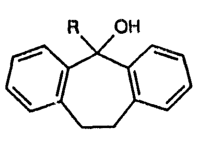


12a **12b**



13 R = H
14 R = CH_3
15 R = $CH(CH_3)_2$
16 R = Ph

3.3. *Exchange and product studies in the presence of amines*

In all previous studies of excited state carbon acid behavior, water was used as the deprotonation base [4,5,9]. These studies also showed that aqueous media were more effective in promoting these reactions over solvents such as MeOH and EtOH, and that solutions of high pH had only a modest effect in increasing the efficiency of the exchange. The latter observation is consistent with the fact that water is sufficiently basic to deprotonate the benzylic protons of these compounds and that in bulk water, added bases such as hydroxide ion (up to pH 14) do not compete significantly with water. However, a stronger base than water in a non-aqueous but polar solvent might be expected to enhance the efficiency of the excited state carbon acid behavior since the hydroxide ion is highly solvated thereby reducing its kinetic basicity. Such a finding would open up a new avenue for studying these excited state proton transfer reactions. We chose to investigate the use of amines (in CH_3CN) since many were readily available with known $pK_{BH}{}^+$ values.

Photolysis of **2** in 0.01 M Et_3N/CH_3CN (0.5 h) resulted in the formation of the photoreduction product suberane (**17**, 20%) and several minor products (5%), according to ^{1}H NMR and GC analysis of the reaction mixture (Scheme 1). Photolysis of **3** as above did not result in any observable deuterium exchange at the benzylic position of substrate (only the photoreduction product 5,5-dideutero-**17** was observed) indicating that benzylic proton exchange is not involved in the reaction of **2** with Et_3N. The photoreduction of **2** by Et_3N in CH_3CN is expected based on the extensive studies of Lewis and coworkers [10] on the reaction of photoexcited trans-stilbene with ground state amines. In polar solvents such as CH_3CN, electron transfer from the amine to photoexcited stilbene generates the radical anion of stilbene which subsequently gives rise to the observed products. This mechanism is illustrated in Scheme 1 for the reaction of **2** with Et_3N. The initial step involves electron transfer from ground state Et_3N to **2** in S_1 resulting in a radical ion pair. Transfer of a proton from a carbon α to the nitrogen of the amine then occurs to form a radical pair which can either (a) disproportionate to give reduced product **17**; (b) combine to give adduct **18**; or (c) diffuse apart to yield dimer **19**. The major product observed after photolysis of **2** in the presence of Et_3N was **17** indicating that disproportionation is the preferred route for this system. No attempts were made to fully characterize **18** and **19** and other minor products expected in this reaction. Photolysis of suberene **5** and **7** under the same conditions as used for **2** also resulted predominantly in the reduction of the vinyl bond of these compounds.

Comparison of photoreduction product yields for **2**, **5** and **7** indicated that the latter two compounds are ≈ 3–5 fold more reactive on photolysis in the presence of Et_3N. This could arise due to a competing excited state carbon acid dissociation for **2**, that is, Et_3N may react as a base and abstract a proton from the 5-position, to generate an ion pair, which would result in no net chemistry. Evidence that proton exchange can occur in competition with photoreduction was obtained by employing a secondary amine in the photolysis. Thus photolysis of **3** in 0.5 M piperidine/CH_3CN (0.5 h) gave both exchange of deuterium in **3** and photoreduction of the vinyl bond in about equal ($\approx 10\%$) yield, in addition to minor products.

Primary amines have significantly higher ionization potentials than secondary and tertiary amines (e.g., n-propylamine (8.78 eV) > piperidine (8.04 eV) > Et_3N (7.82 eV) [11]). Thus, n-propylamine should be considerably less willing to undergo electron transfer reaction than the latter two amines. This has been demonstrated in various photochemical studies involving the use of amines as electron donors and as bases [12,13]. As primary amines, we chose to study n-propylamine (PA) and ethanolamine (EA), the latter being a stable and readily available reagent.

Photolysis of **3** in 0.01 M EA/CH_3CN (same conditions as noted for above photolyses involving piperidine and Et_3N) for 30 min resulted in 44% exchange of deuterium (to give **2a** and **2**) according to a ^1H NMR of the product mixture (Fig. 1). No reduction products were observed. Use of higher concentrations of EA (up to 0.10 M) resulted in an increase in the amount of deuterium loss for the same length of irradiation time (Fig. 1). For comparison, photolysis of **3** in 0.01 M H_2O/CH_3CN under otherwise identical conditions resulted in no observable exchange or any other reaction. That the amine portion of EA was responsible for the enhanced exchange of **3** was confirmed by photolyses in 0.01 M EtOH/CH_3CN and 0.01 M PA/CH_3CN. No deuterium exchange was observed in the former reaction whereas the latter reaction gave similar results as was observed for EA.

At this point, it occurred to us that perhaps amine bases could effect the photochemical exchange of a variety of excited state hydrocarbons and not retricted only to suberenes. However, photolysis of either 9,9-deuteriofluorene and α,α-dideuterodiphenyl methane in 0.1 M EA/CH_3CN (1 h) failed to give any exchange. Thus, although primary amine bases are much more effective than H_2O or EtOH in promoting excited state carbon acid behavior, the suberene system is still a necessary structural feature. We have already presented our rationale for the need of this system for efficient carbanion photogeneration in previous articles [4,5,14].

We next turned our attention to **5** and **7** since photolysis of these compounds in D_2O/CH_3CN gave no deuterium incorporation. It would be of interest to see if exchange is enhanced in the presence of EA and PA, as was observed for **2** (**3**). Irradiation of the deuterated 5-methyl derivative **6** in 0.10 M EA/CH_3CN (1 h) resulted in $\approx 15\%$ exchange. Photolysis in 0.50 M EA/CH_3CN resulted in 42% exchange. In both cases, no reduction or other products were observed. Photolysis of **6** in 0.5 M PA/CH_3CN also resulted in extensive exchange of deuterium (50% by MS) but in this case some photoreduction (3%) product was observed, as well as several minor addition products (by GC). The low yields observed for the electron transfer products indicate that PA

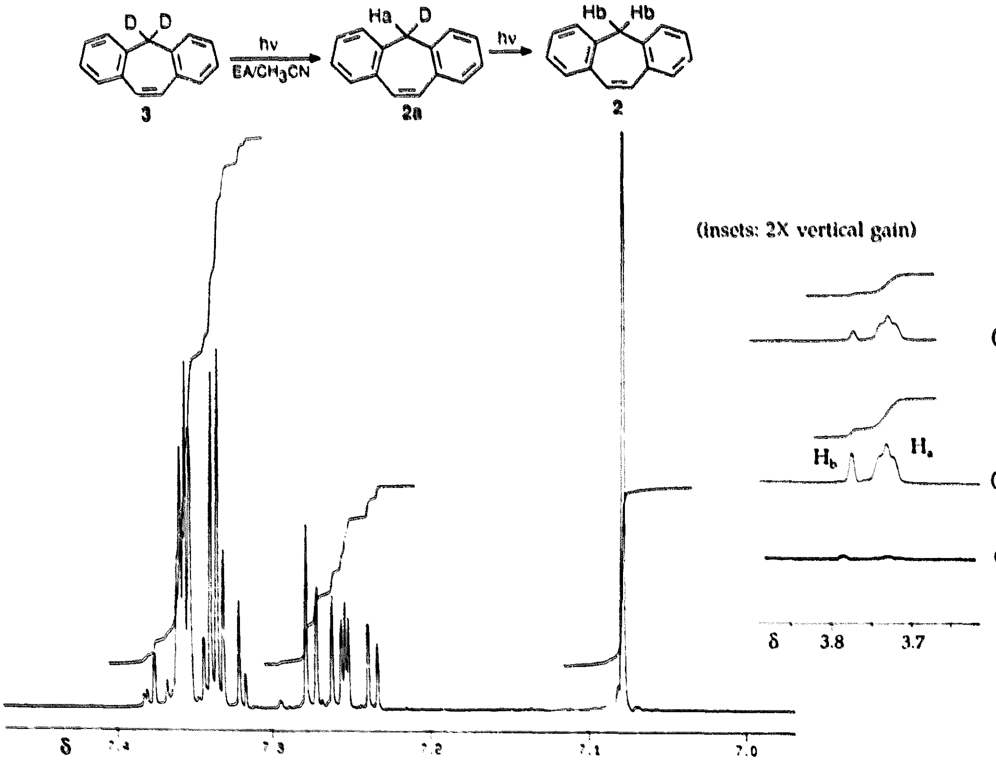


Fig. 1. ^1H NMR (360 MHz) spectra showing incorporation of protium at the dibenzylic position (δ 3.77 (t), monohydrogen; 3.79 (s), dihydrogen) on photolysis of 5,5-dideuterosuberene (**3**) in EA/CH_3CN. (a) before photolysis ($<2\%$ residual hydrogen). (b) photolysis for 30 min in 0.01 M EA/CH_3CN ($\approx 44\%$ exchange). (c) photolysis for 5 min in 0.10 M EA/CH_3CN ($\approx 25\%$ exchange). In all runs, the vinyl and aromatic protons are unchanged.

functions primarily as a base. The complete lack of the electron transfer (photoreduction) pathway for EA is consistent with an ionization potential which should be slightly higher than for PA due to the inductive withdrawing effect of the hydroxyl group [15]. Photolysis of the deuterated 5-phenyl derivative **8** in 0.5 M EA/CH_3CN or 0.5 M PA/CH_3CN for 1 h resulted in only a trace of deuterium exchange (< 2% according to ^1H NMR). The photoreduction product (≈ 5%) as observed only with the use of PA.

The use of a stronger base in EA and PA (compared with water) resulted in observable carbon acid behavior in **5** implying that the methyl group does have an intrinsic retarding effect on carbon acid ionization, even when the conformation is stereoelectronically suitable for C–H abstraction. However, because **7** (**8**) exists completely in a conformation which is stereoelectronically unfavourable for C–H abstraction, even the use of EA and PA failed to result in exchange. An alternative explanation for the lack of reactivity of **7** (**8**) which may be raised at this point is that it has an intrinsically much shorter lifetime due to a more efficient internal conversion due to rotation of the phenyl group. As will be shown in section 3.5, this explanation can be ruled out since all of **3**, **5** and **7** have singlet lifetimes in the range 2–5 ns (in an inert solvent), which cannot account for the complete lack of reactivity in **7**. The finding that primary amine bases can catalyze the exchange of **5** (**6**) whereas the hydroxide ion was not effective in aqueous solution can be explained by noting: (i) the hydroxide ion is strongly solvated in water, thereby reducing its kinetic basicity (note that the substrates are short-lived) and (ii) the internal return may be very high using the hydroxide ion, thereby reducing the observable amount of exchange.

3.4. *Quantum yields for exchange*

For a more quantitative comparison in the efficiency of proton exchange observed for suberenes studied in this work using EA or water as the base, quantum yields of exchange (Φ) were measured (Rayonet RPR 100 reactor; 254 nm lamps; 360 MHz ^1H NMR for analysis) using the value for **3** in 50% H_2O/CH_3CN ($\Phi = 0.035 \pm 0.006$) [4] as the secondary actinometer (Table 1). It is clear that EA is vastly more superior compared with H_2O in promoting exchange, which is consistent with their relative basicities. The quantum yield for the exchange of **3** in 0.10 M EA/CH_3CN is already more than two times higher than in 50% H_2O/CH_3CN. Although we have not made accurate measurements of Φ at high EA concentrations, quantum yields are in excess of 0.1. Thus the use of EA and other primary amines provide a means for significantly increasing the quantum efficiency for excited state carbon acid dissociation.

Table 1
Quantum yields for exchange (Φ) for **3**, **6** and **8** in EA/CH_3CN

Compound	Base/solvent	Φ [a]
3	50% H_2O/CH_3CN	0.035 ± 0.006 [b]
3	0.01 M EA/CH_3CN	0.024 ± 0.006
3	0.10 M EA/CH_3CN	0.08 ± 0.02
6	0.10 M EA/CH_3CN	0.004 ± 0.001 [c]
8	0.10 M EA/CH_3CN	0.000 [c]

[a] Quantum yields were measured by 360 MHz ^1H NMR (Rayonet RPR 100 reactor, 254 nm lamps) using the reaction of 3 in 50% H_2O/CH_3CN as a secondary actinometric standard, $\Phi = 0.035 \pm 0.006$, first entry [4].

[b] From Ref. [4].

[c] For these systems, $\Phi = 0.000$ in 50% H_2O/CH_3CN.

3.5. *Steady-state and time-resolved fluorescence measurements*

In previous studies of excited state carbon acids of suberenes [4,5], fluorescence studies provided the means for measuring the rates of C–H bond ionization. We found [4,5] that fluorescence quenching by water was directly associated with excited state carbon acid behavior and that the rate of quenching (k_q) was equatable to the rate of C–H bond ionization (k_H) in S_1. The observation of higher quantum efficiency for exchange with the use of primary amine bases should therefore be corroborated by fluorescence quenching studies.

The fluorescence excitation and emission spectra (λ_{ex} = 280 nm) of **2**, **5** and **7** in 100% CH_3CN are shown in Fig. 2. The excitation spectra are all similar and resemble the structureless S_0 S_1 absorption band for these compounds, which are essentially identical. Their fluorescence emission spectra differ to a higher degree. They all span the same wavelength range (320–500 nm) with emission of **7** showing better defined vibrational structure (ring stretching modes), and **2** and **7** displaying a larger Stokes shift. A more structured emission compared with the excitation spectrum coupled with a large Stokes shift are often associated with a fluorescent excited state that is more rigid and planar than the equilibrium ground state [16–18]. Qualitatively, one can argue that both **2** and **7** attain an excited state geometry that is more planar (enhanced conjugation with the alkene moiety bridging the two benzene rings) than is possible with **5**. This is consistent with the fact that a substantial fraction (≈ 40%) of **5** has the methyl group at the pseudo equatorial position which would make planarization of the ring system prohibitive (hence reduced Stokes shift). It is not apparent at this time why **7**, which has its phenyl group oriented exclusively at the pseudo axial position, has a more pronounced fine structure in its emission although its Stokes shift is the same as for **2**. The detailed photophysical properties of these compounds remain a topic for additional studies.

Fluorescence quantum yields (Φ_f) of **5** and **7** were measured in 100% CH_3CN using the known value for **2** as the secondary fluorescence standard ($\Phi_f = 0.86 \pm 0.05$, [4]) (Table 2). Fluorescence lifetimes of **5** and **7** (in 100% CH_3CN) were measured by single photon counting with all decays being good first order (Table 2). The large Φ_f of **2**, **5** and **7** (in 100% CH_3CN) is consistent with what is known for other locked stilbenes, many of which have Φ_f close to

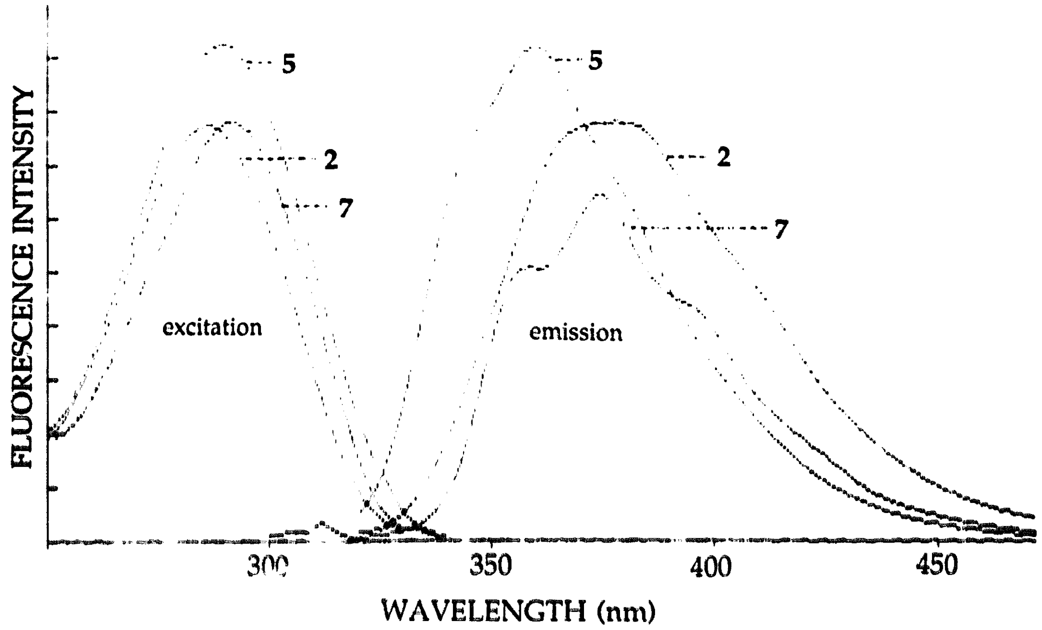


Fig. 2. Fluorescence excitation and emission spectra for **2**, **5** and **7** in 100% CH_3CN (λ_{ex} = 280 nm, slits 5 × 5 nm).

unity [19]. The lower Φ_f value and shorter lifetime for **7** are consistent with an additional internal conversion pathway available for this compound, which is most likely associated with the rotation of the phenyl group. However, the complete lack of reactivity observed for **7** cannot be completely accounted for by its shorter lifetime, which is only 30% shorter than **5**.

Fluorescence quenching rate constants (k_q) of **2**, **3**, **5** and **7** by various bases in CH_3CN were obtained by fitting the quenching data obtained by steady-state fluorescence measurements into the Stern-Volmer equation. Shown in Figs. 3 and 4 are representative steady-state fluorescence quenching date for **2** and **5** using EA as the base. In all cases, good linear Stern-Volmer plots were obtained. The value of k_q was then calculated by using the lifetime of the appropriate substrate measured in the absence of quencher (Table 3). As demonstrated for **2**–**4** in previous studies [4,5], fluorescence quenching by added bases to CH_3CN solution is directly associated with carbon acid deprotonation at the 5-position. Thus, the k_q values (Table 3) are equatable to k_H, the bimolecular deprotonation rate by the base. Several k_q's were also measured using lifetime data and these gave identical values with those obtained from the steady-state measurements showing that the quenching phenomenon is a dynamic process.

Table 2
Fluorescence quantum yields (Φ_f) and lifetimes (τ) for **2**, **5** and **7** in 100% CH_3CN [a]

Compound	Φ_f [b]	τ [c] (ns)
2	0.89 ± 0.10 [d]	5.08 ± 0.08 [d]
3	–	4.72 ± 0.08 [d]
5	0.98 ± 0.10	2.91 ± 0.06
7	0.57 ± 0.05	2.03 ± 0.06

[a] CH_3CN was dried by refluxing over CaH_2.
[b] Measured using **2** as the secondary fluorescence standard.
[c] Measured using single photon counting (PTI LS 1 instrument; H_2 lamp) with good first order decays ($\chi^2 < 1.3$).
[d] Data from Ref. [4].

A primary kinetic isotope effect for the quenching of **2** and **3** by H_2O as base consistent with C–H bond dissociation was reported in previous work, (($k_H/k_D)_q$ = 2.8 ± 0.4) [4]. With EtOH as base a similar kinetic isotope effect was obtained (2.7 ± 0.4). However, the quenching rates involving EtOH are larger than for water (Table 3). The quenching rate is further enhanced (for **2**) on going to THF. The relative rates of quenching observed for H_2O, EtOH and THF are expected since the quenching studies were carried out in low concentration of base (in CH_3CN) and hence should reflect the relative basicity of these bases in the gas phase (ethers > alcohols > water), which is opposite to the trend in bulk solvent (water > alcohols > ethers) [20]. Gas phase conditions are approximated in dilute CH_3CN, where there is no significant hydrogen bonding. Indeed, the fluorescence quenching experiment described here can be used as a probe for the relative basicity of the compounds in aprotic solvents which reflect reflective gas phase basicities.

Proton (deuterium) exchange studies involving **2** and related systems in the presence of amines indicated that primary amines efficiently catalyze the excited state carbon acid ionization of these systems. In comparison, tertiary and secondary amines promote photoreduction via initial electron transfer. The results for fluorescence quenching of **2** and related systems by amines should offer revealing information (Table 3). The magnitude of k_q for fluorescence quenching of **2**, **5** and **7** by Et_3N as a quencher are all close to the diffusion

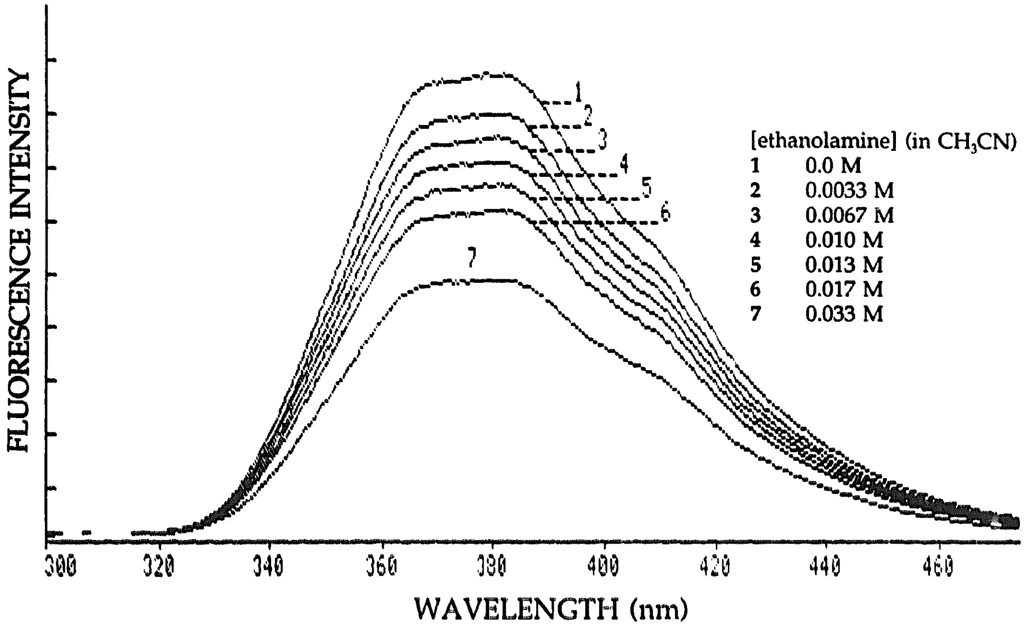


Fig. 3. Fluorescence quenching of 2 by ethanolamine (EA) in CH$_3$CN (λ_{ex} = 280 nm).

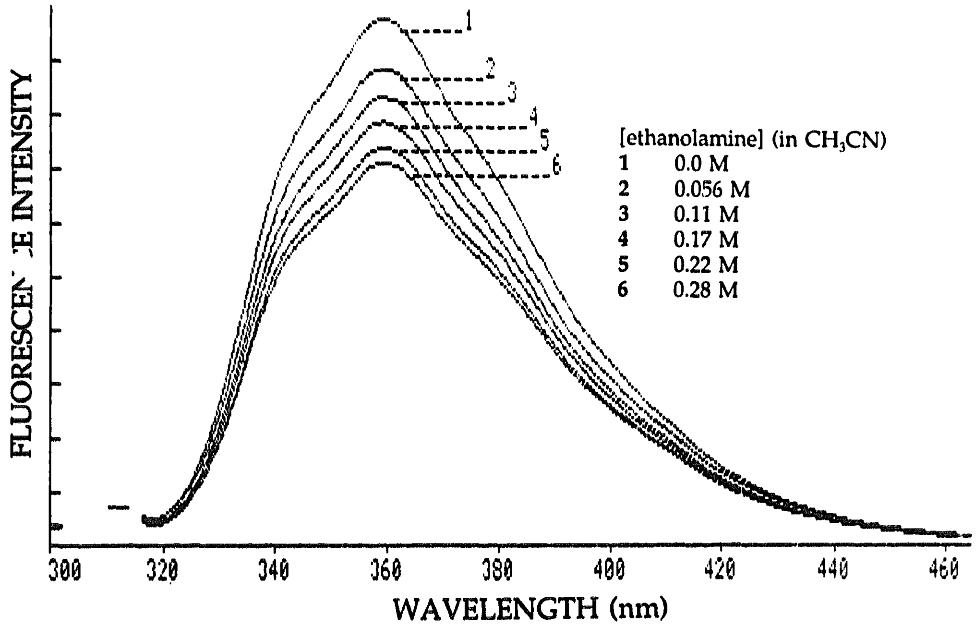


Fig. 4. Fluorescence quenching of 5 by ethanolamine (EA) in CH$_3$CN (λ_{ex} = 280 nm).

limit in CH$_3$CN, which is 1.9×10^{10} M^{-1}s^{-1} at 25 °C [21]. Lewis et al. [13,22] observed similar k_q values for the electron transfer quenching of styrenes and arenecarbonitriles by Et$_3$N. Thus, the k_q values for Et$_3$N measured in this work supports a photoreduction mechanism involving an initial electron transfer from Et$_3$N to **2**, **5** and **7**.

Values of k_q measured for **2** and **3** using primary amines are much faster than for H$_2$O, EtOH or THF but do not approach the diffusion limit in CH$_3$CN as closely as with Et$_3$N. Comparison of quenching rates for **2**, **5** and **7** by primary amines EA and PA with the observed exchange efficiencies suggests that these bases quench exclusively via deprotonation.

The primary isotope effect for the quenching for **2** and **3** using EA as quencher was $(k_H/k_D)_q = 1.4 \pm 0.2$, which is smaller than the value measured using H$_2$O as the base. This smaller isotope effect is consistent with a transition state for proton removal that was earlier (closer to the reactant) compared with when H$_2$O was used as the base. This is expected since the deprotonation of an acid will be more exothermic when a stronger base is used. An approximate position for the transition state for proton removal may be obtained by a

Table 3
Rates of fluorescence quenching (k_q) in CH_3CN for suberene derivatives as determined by Stem-Volmer analysis [a]

Compound	Base (quencher)	k_q ($M^{-1} s^{-1}$), 10^9
2	H_2O	0.17 ± 0.01 [b]
	EtOH	0.86 ± 0.04
	THF	2.1 ± 0.1
	PA	8.3 ± 0.2
	EA	6.4 ± 0.2
	$CH_3OCH_2CH_2NH_2$	6.7 ± 0.2
	$NCCH_2CH_2NH_2$	5.1 ± 0.2
	$CF_3CH_2CH_2NH_2$	3.5 ± 0.2
	Et_3N	9.2 ± 0.2
3	H_2O	0.061 [b]
	EtOH	0.32 ± 0.02
	EA	4.7 ± 0.2
5	H_2O	– [c]
	EA	0.47 ± 0.05
	PA	0.56 ± 0.05
	Et_3N	10.9 ± 0.2
7	H_2O	– [c]
	EA	0.17 ± 0.05
	PA	0.19 ± 0.05
	Et_3N	9.4 ± 0.2

[a] Quenching rate constants (at 22 ± 2 °C) were obtained by fitting the data with the Stern-Volmer equation (all linear plots) and calculating the rate of quenching (k_q) using the lifetime of the appropriate compound measured in 100% CH_3CN.

[b] From Ref. [4].

[c] No observable fluorescence quenching.

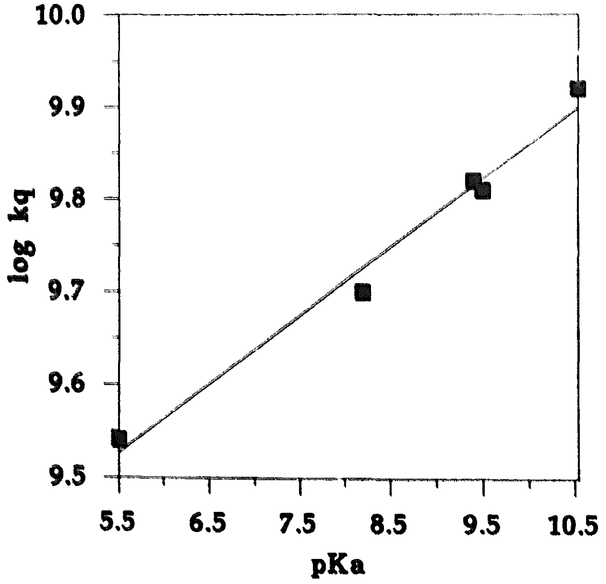


Fig. 5. Brønsted catalysis plot of log k_q vs. pK_{BH}^+ of primary amines for **2** in CH_3CN.

Brønsted plot. Although exact pK_{BH}^+ values for primary amines are not all well established in CH_3CN, they should retain their relative basicity. A reasonably linear Brønsted plot using pK_{BH}^+ values for the amines in water is shown in Fig. 5 with a slope (β) of 0.07 ± 0.02. This low value of β is indicative of an early transition state for proton transfer and hence insensitivity to base strength.

4. Summary and conclusions

This study has shown that the deprotonation of excited state carbon acids is subject to general base catalysis by primary amines. The Brønsted catalysis law ($\beta = 0.07$) appears to be applicable in describing the phenomenon. Secondary and tertiary amines react predominatly via electron transfer, resulting in photoreduction and addition products. With the exception of secondary and tertiary amines, fluorescence quenching rate constants of **2** by added bases reflect the relative basicity of the bases in the gas phase. Additional studies delineating this effect may provide a simple fluorescence technique for measuring the relative basicity of simple bases in the gas phase, by a solution technique. Deprotonation of the C–H bond at the 5-position of suberene (**2**) is stereoelectronically controlled, requiring the proton to be in the pseudo axial position for maximal overlap of the incipient carbanion with the π system of the two benzene rings.

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