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Excited state proton transfer to and from carbon: studies of enhanced excited state basicity of biphenyl derivatives and carbon acidity of dibenzosuberenes

Deepak Shukla, Matthew Lukeman,
Yijian Shi, Peter Wan*

Department of Chemistry, University of Victoria, Box 3065, Victoria, BC, Canada V8W 3V6

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Abstract

Excited state proton transfer (ESPT) to and from carbon atoms of organic molecules are rare chemical events and only a handful of examples are known. In this work, we report additional examples of excited (singlet) state carbon acids (proton transfer from carbon to solvent water) displayed by several dibenzosuberene derivatives, the first system in which excited state carbon acid behavior was explicitly demonstrated. Substituent effects, quantum yields for exchange, and rate constants for quenching by water (acting as the base for the ESPT) are reported. For examples of ESPT to carbon, we report the photoprotonation in water and acid of two simple biphenyl derivatives. Unlike what is observed in ground state protonation, protonation of the excited state occurs exclusively on the ring not containing the activating substituent (hydroxy or methoxy), as demonstrated by deuterium incorporation experiments. Laser flash photolysis (LFP) data are consistent with formation of transient cyclohexadienyl cations obtained via protonation of the benzene ring. These results are consistent with the substantial charge transfer inherent in excited state biphenyls, making the ring not containing the electron donating activating substituent the more basic site.

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Keywords: Excited state proton transfer; Carbon acid; Carbon base; Photoprotonation; Deuterium exchange

1. Introduction

The acid–base behavior of excited states of organic molecules is a subject of continuing interest and span several areas of photochemistry and chemical physics, ranging from very fast dynamic and fundamental studies of excited state intramolecular proton transfer (ESIPT) [1] to organic photochemical reactions initiated by a change in acidity/basicity of the molecule on photoexcitation [2]. The vast majority of ESIPT systems involve proton transfer between two heteroatoms, either directly or via a solvent bridge [1]. Examples of ESIPT between oxygen and carbon are now known although the number of systems is still very limited [3].

This paper is concerned with new examples of excited state proton transfer (ESPT) from a carbon atom to solvent (excited state carbon acids) and from the solvent (water) to a carbon atom (of an aromatic ring; photoprotonation). Proton transfer to and from carbon is of fundamental interest in organic chemistry. Such processes are generally considered to be slow in the ground state due to a variety of factors including the fact that C–H bond is not strongly polarized and the lack of significant hydrogen bonding interactions to and from carbon atoms. Any excited state version of these reactions must be intrinsically fast in order to compete with fluorescence decay and other deactivational processes. What makes them fast in the excited state is of fundamental interest in photochemistry.

The first examples of excited state carbon acids were discovered in our laboratory, initially for the compound dibenzosuberene (**1**) (also known as suberene) [4]. Photolysis of this compound in D_2O–CH_3CN resulted in moderately efficient ($\Phi = 0.030$) exclusive exchange of the methylene 5-position, to give mono-deuterated **1**-5D, presumably via the ion pair **2** (Eq. (1)):

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* Corresponding author. Tel.: +1-250-721-8976;
fax: +1-250-721-7147.
E-mail address: pwan@uvic.ca (P. Wan).

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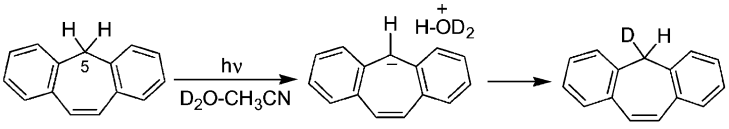
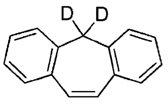


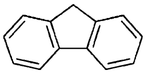
1 **2** **1**-*5D* (1)

Continued photolysis eventually gave the fully deuterated derivative **1**-5D_2. Related compounds such as fluorene (**3**) and diphenylmethane (**4**) failed to react suggesting that the driving force for deprotonation is due to the formation of an incipient 8π (4*n*) formally ground state "antiaromatic" carbanion (in the central cycloheptatrienyl ring system of **2**), which is apparently very favorably formed on the excited state surface [4c]. The estimated excited state pK_a of **1** is about −1 or less [4b]. Since this first discovery we have reported a number of related ring systems that also behave as excited state carbon acid, all of which are isoelectronic to the dibenzosuberene system [5]. However, no studies of the effect of ring substitution of **1** (apart from simple substitution at the reactive 5-position [5e]) and other structural modifications on excited state carbon acidity has been carried out to date. Such a study would be worthwhile to further substantiate the formation of a carbanion on the excited state surface as ring substituents are known to substantially affect the efficiency of formation of charged intermediates. In this work, we report the results of a study of the excited state carbon acidity of dibenzosuberene derivatives **5**–**9**. Compounds **5**–**8** probe the effect on excited state acidity by simple electron donating and withdrawing substituents whereas **9** was designed to probe the effect on reactivity by benzannelating the remaining alkene moiety of the central ring system. Our selection of substrates for study was limited by the difficulty in making substituted suberenes, which is in general not trivial.

ESPT to aromatic carbon atoms by aqueous acid is well documented although the number of examples is limited [2,6]. Many aromatic compounds are anticipated to become more basic at the aromatic carbon framework on photoexcitation, but the increase in basicity is in most cases insufficient for proton transfer from neutral water and hence the lack of examples of such systems. More recently, we have shown that alkoxy- and hydroxy-substituted biphenyls have enhanced charge transfer character, facilitating photosolvolysis (and photodehydroxylation) and photoprotonation at the ring not containing the substituent [3c,7]. It appears that in selected biphenyl systems, there is sufficient charge transfer character to facilitate protonation of the ring system in neutral or mild acid. We now report the full details of the photoprotonation of two simple biphenyl systems **10** and **11** (initially reported in preliminary form [7a]) to explore ESPT from solvent water to the ring carbon of these compounds, to complement the above study on proton transfer from carbon.



1-*5D*$_2$



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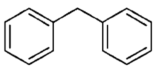

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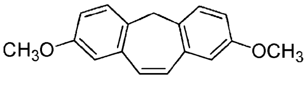

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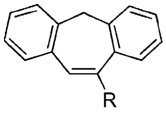
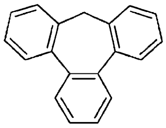


6 R = OCH_3
7 R = CN
8 R = Br



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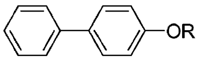


10 R = H
11 R = CH_3

2. Experimental details

2.1. General

^{1}H NMR spectra were recorded on either a Bruker AC 300 (300 MHz) or AM 360 (360 MHz) instrument in $CDCl_3$ or acetone-d_6. GC/MS and mass spectra were determined on either a Finnegan 3300 (CI) or a Kratos Concept 1H (FAB and HRMS). UV spectra were recorded on a Perkin-Elmer Lambda 4B or a Pye-Unicam 800 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 283 instrument. Melting points were determined on a Reichart 7905 melting point apparatus (uncorrected). Preparative thin layer chromatography (Prep TLC) was carried out using 1000 μm silica gel plates from Analtech. pH measurements were taken using a Corning 140 pH meter.

2.2. Materials

Ethanolamine, 1-methyl-2-pyrrolidinone, $Fe_2(CO)_9$, 4-hydroxybiphenyl (**10**) and 4-methoxybiphenyl (**11**), 9,10-dibromodibenzosuberone (**16**), furan, and 3-methylanisole were purchased from Aldrich and used as received after purity checks by UV and/or NMR. CH_3CN and THF were standard reagent grade and dried over CaH_2 or Na, respectively, and distilled prior to use. The D_2O used for solvent isotope studies, preparatory photolysis and NMR spectroscopy was 99.9% D (MSD Isotopes). Standard buffer solutions (Fisher Scientific), were used for product quantum yield experiments and fluorescence spectrophotometry work. Solvents for fluorescence studies were of the highest available purity and checked for spurious emission before use.

2.2.1. 3-Bromomethyl-4-bromoanisole (**12**)

A mixture of 3-methylanisole (15 g, 123 mmol) and *N*-bromosuccinimide (13.3 g, 76 mmol) in 50 ml CCl_4 was stirred under reflux for 24 h. The mixture was cooled, filtered and CCl_4 was removed to yield crude 4-bromo-3-methylanisole as a red oil which was taken to the next step without further purification (yield 23 g, 93%). Treatment of this compound (20 g, 99.50 mmol) with *N*-bromosuccinimide (20 g, 115 mmol) and benzoyl peroxide (0.20 g) in refluxing CCl_4 (ca. 20 h), yielded crude **12** as a reddish brown solid. Recrystallization from boiling petroleum ether (30–60 °C) yielded pure **12** as yellow needle shaped crystals (yield 15 g, 54%); m.p. 91 °C (literature [8] m.p. 91–92 °C); ^{1}H NMR (90 MHz, $CDCl_3$), δ (ppm): 7.5–6.6 (m, 3H, aromatic), 4.52 (s, 2H, Ar–CH_2–), 3.74 (s, 3H, –OCH_3).

2.2.2. 2,8-Dimethoxysuberone (**14**)

Compound **12** (14 g, 50 mmol) was dissolved in dry THF (325 ml) and hexane (100 ml, dry) in a 1 l two necked flask and was cooled to −100 °C (CO_2–Et_2O slurry). *n*-BuLi (50 mmol) was added at such a rate that the temperature of the reaction mixture did not rise above −99 °C. After 1 h at −100 °C, a stream of CO_2 gas was bubbled through the reaction mixture for 1.5 h at −100 to −80 °C. After this, the cooling bath was removed and the temperature was allowed to rise to 25 °C (approximately 2 h). A stream of argon was bubbled through the reaction mixture for ∼1.5 h to remove excess CO_2. The reaction mixture was again cooled to −100 °C and *n*-BuLi (30 mmol, 30% excess) was added at such a rate that the temperature never exceeded −98 °C. The reaction mixture was stirred for 30 min at −100 °C, then allowed to warm to 25 °C, and stirred for 6 h at 25 °C. The reaction was quenched by pouring into 5% HCl solution and the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 150 ml). The combined organic layers were washed with 5% NaOH solution and dried over anhydrous $MgSO_4$. Removal of CH_2Cl_2 yielded 2.0 g of the crude product which upon recrystallization from CH_2Cl_2/MeOH (1:1) afforded slightly yellow needle like crystals of **14** (yield 1.3 g, ∼10% from **12**); m.p. 121 °C (literature [9] m.p. 119–121 °C); ^{1}H NMR ($CDCl_3$), δ (ppm): 3.12 (s, 4H, –CH_2CH_2–), 3.85 (s, 6H, –OCH_3), 6.60–8.20 (m, 6H, aromatic).

2.2.3. 2,8-Dimethoxysuberenone (**15**)

A mixture of **14** (1.3 g, 4.8 mmol), *N*-bromosuccinimide (0.87 g, 5.0 mmol) and benzoyl peroxide (0.1 g) in CCl_4 (50 ml) were stirred with reflux for 36 h. The reaction mixture was cooled to room temperature and filtered through a sintered funnel and washed with water (2 × 100 ml). The organic layer was dried over anhydrous $MgSO_4$ and the CCl_4 evaporated to afford 1 g of the crude material which was analyzed to be a mixture of 10,11-dibromo-2,8-dimethoxydibenzosuberone and 10,10′-dibromo-2,8-dimethoxydibenzosuberenone by NMR. The mixture was separable by competitive recrystallization from 95% EtOH/H_2O (1:1). The dibromo compound crystallized out first as long yellow crystals and was filtered out. On further cooling of the filtrate white crystals of 10,10′-dibromo-2,8-dimethoxydibenzosuberone came out of the solution.

The combined dibromo compounds (0.4 g) were dissolved in 15 ml of 2,4,6-trimethylpyridine (collidine) and refluxed for 24 h. The reaction mixture was cooled in an ice bath and quenched with an excess of 20% HCl and extracted with CH_2Cl_2 (2 × 100 ml). The combined CH_2Cl_2 layers were washed with water (2 × 50 ml), dried over anhydrous $MgSO_4$ and removed to yield 0.25 g (∼20%) of **15**; m.p. 119–121 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.75 (s, 6H, –OCH_3), 6.90 (s, 2H, –CH=CH–), 6.8–7.25 (m, 6H, aromatic); IR (KBr, cm^{-1}), ν: 1690 (strong, C=O stretching), 1645 (medium, vinylic C=C stretching), 1600 and 1460 (medium, aromatic C=C stretching); mass spectrum (EI) (*m*/*z*): 266 (M^+).

2.2.4. 2,8-Dimethoxysuberene (**5**) and **5**-5D_2

$AlCl_3$ (0.35 g, 2.6 mmol) was slowly added under an inert atmosphere to a stirred suspension of $LiAlH_4$ (0.047 g, 1.3 mmol) in diethyl ether (200 ml; dry) at −4 °C. The mixture was allowed to stir for additional 10 min at 0 °C and then **15** (0.2 g, 0.7 mmol) was introduced. The reaction mixture was allowed to attain room temperature and refluxed for 4 h. At the end of reflux the reaction was cooled in an ice bath and carefully quenched by addition of water (∼75 ml), followed by the addition of a sufficient amount of 10% HCl to dissolve the suspension. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and CH_2Cl_2 removed to yield 0.18 g (∼50%) of the crude product. Recrystallization from 50% EtOH/H_2O afforded 0.17 g of pure **5** as a white crystalline solid; m.p. 185–187 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.75 (s, 6H, –OCH_3), 3.60 (s, 2H, $ArCH_2Ar$), 6.90 (s, 2H, –CH=CH–), 6.8–7.25 (m, 6H, aromatic); mass spectrum (EI) (*m*/*z*): 252 (M^+); HRMS 252.3153 (calc. 252.3154).

Treatment of **15** with $LiAlD_4$/$AlCl_3$ in dry THF afforded **5**-5D_2; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.75 (s, 6H, –OCH_3), 6.90 (s, 2H, –CH=CH–), 6.80–7.25 (m, 6H, aromatic); mass spectrum (EI) (*m*/*z*): 254 (M^+).

2.2.5. 10-Bromodibenzo[a,e]cyclohepten-5-one (**17**)

trans-10,11-Dibromodibenzo[a,e]cyclohepten-5-one (**16**) (5 g, 13.6 mmol; Aldrich) was dissolved in a 3 M methanolic KOH (22.3 g KOH in 125 ml CH_3OH) and refluxed with stirring for 1 h to give a yellow colored solution. The hot reaction mixture was filtered through a sintered funnel (to remove the precipitated KBr) and the filtrate cooled in an ice bath for 2 h to afford crude material which was recrystallized from warm hexanes to yield pure **17** as pale yellow crystalline solid (yield 80%); m.p. 116–117 °C (literature [10] m.p. 117 °C); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.8 (s, ArCH=CBr–), 7.0–7.7 (m, 8H, aromatic); mass spectrum (CI) (*m*/*z*): 286 $(M^+ + 1)$.

2.2.6. *10-Methoxydibenzo[a,e]cyclohepten-5-one (**18**)*

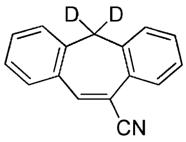
A solution of **17** in a methanolic solution of KOH (3 M, 250 ml) was refluxed with stirring for 16 h. After reflux the reaction mixture was allowed to stand at 0 °C for 24 h which afforded yellow crystals of pure **18**; m.p. 132 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.9 (s, 3H, $–OCH_3$), 6.4 (s, 1H, –CH=C–), 7.4–8.2 (m, 8H, aromatic); mass spectrum (CI) (*m*/*z*): 237 $(M^+ + 1)$.

2.2.7. *10-Methoxysuberene (**6**) and **6**-5D$_2$*

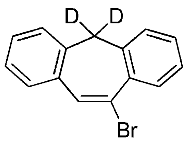
Reduction of **18** with $LiAlH_4/AlCl_3$ in dry THF, in a manner described earlier, yielded **6** which was purified by recrystallization from hexanes to afford pure **6** as a white crystalline solid; m.p. 146 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.9 (s, 3H, $–OCH_3$), 3.7 (s, 2H, $ArCH_2Ar$), 6.3 (s, 1H, –CH=C–), 7.2–7.8 (m, 8H, aromatic); mass spectrum (CI) (*m*/*z*): 223 $(M^+ + 1)$. Reduction of **18** with $LiAlD_4/AlCl_3$ in dry THF, in a usual manner, yielded **6**-5D$_2$, ^{1}H NMR ($CDCl_3$), δ (ppm): 3.9 (s, 3H, $–OCH_3$), 6.3 (s, 1H, –CH=CR–), 7.2–7.8 (m, 8H, aromatic); mass spectrum (CI) (*m*/*z*): 225 $(M^+ + 1)$.

2.2.8. *10-Bromosuberene (**8**) and **8**-5D$_2$*

Reduction of 10-bromosuberone (**17**) with $LiAlH_4/AlCl_3$ in dry THF afforded **8** which was purified by column chromatography (silica gel, hexanes) and recrystallized from 95% EtOH to afford a white crystalline solid; m.p. 62 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.70 (s, 2H, $ArCH_2Ar$), 7.10–7.35 (m, 7H, aromatic), 7.65 (s, 1H, –CH=CBr–), 7.70–7.85 (m, 1H, ArH next to Br); mass spectrum (EI) (*m*/*z*): 271 (M^+); (CI) (*m*/*z*): 272 $(M^+ + 1)$. Reduction with $LiAlD_4/AlCl_3$ afforded **8**-5D$_2$, ^{1}H NMR ($CDCl_3$), δ (ppm): 7.10–7.35 (m, 7H, aromatic), 7.65 (s, 1H, –CH=CBr–), 7.70–7.80 (m, 1H, ArH closest to Br); mass spectrum (CI) (*m*/*z*): 274 $(M^+ + 1)$.



7-*5D$_2$*



8-*5D$_2$*

2.2.9. *10-Cyanosuberene (**7**) and **7**-5D$_2$*

A mixture of **8** (0.2 mmol) and CuCN (0.4 g, 6 mmol) were dissolved in 1-methyl-2-pyrrolidinone (100 ml) and refluxed for 36 h at 180 °C. The reaction mixture was cooled to 100 °C and poured into a 1:1 NH_3/H_2O solution (300 ml) and stirred at room temperature for 12 h. The solution was then filtered through a Celite pad, and the filtrate was extracted with CH_2Cl_2 (3×100 ml). The combined organic layers were dried over $MgSO_4$ and evaporated to yield a yellow oil. The oil was dissolved in 1:2 Et_2O/H_2O (500 ml) mixture and stirred overnight at room temperature. The ether layer was separated, dried and removed to yield the crude material which on purification by column chromatography (silica gel, CH_2Cl_2) afforded pure **7** as a white solid; m.p. 97–99 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 3.80 (s, 2H, $ArCH_2Ar$), 7.10–7.75 (m, 8H, aromatic), 7.80 (s, 1H, –CH=C–); IR (KBr, cm^{-1}), ν: 2220 (medium, CN stretching), 1606 (strong, vinyl C=C stretching), 1480 (medium, aromatic C=C stretching); mass spectrum (CI) (*m*/*z*): 218 $(M^+ + 1)$; HRMS 217.2723 (calc. 217.2724). Treatment of **8**-5D$_2$ as above afforded **7**-5D$_2$, ^{1}H NMR ($CDCl_3$), δ (ppm): 7.10–7.75 (m, 8H, aromatic), 7.80 (s, –CH=C–); mass spectrum (CI) (*m*/*z*): 220 $(M^+ + 1)$.

2.2.10. *10,13-Epoxy-10,13-dihydrotribenzo[a,c,e]-cyclohepten-5-one (**19**)*

To a stirred mixture of **17** (3.8 g, 13.3 mmol) and potassium *t*-butoxide (3 g, 13.3 mmol) in THF (150 ml, dry) at 0 °C, freshly distilled furan (50 ml) was added under an inert atmosphere. The reaction mixture immediately turned to a brick-red color. The reaction was allowed to stir at room temperature for additional 18 h after which it was poured over an ice cold solution of 10% HCl. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 75 ml). The combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was removed to yield a yellow colored solid. The crude material was recrystallized from petroleum ether (40–60 °C) to yield **19** as yellow colored prisms (yield 2.86 g, 79%); m.p. 205–206 °C (literature [10] m.p. 203–207 °C); ^{1}H NMR ($CDCl_3$), δ (ppm): 6.0 (s, 2H, –CH=CH–), 7.35 (s, 2H, –CH–O–CH–), 7.42–8.25 (m, 8H, aromatic); mass spectrum (CI) (*m*/*z*): 273 $(M^+ + 1)$.

2.2.11. *Tribenzosuberone (tribenzo[a,c,e]cyclohepten-5-one) (**20**)*

To a stirred solution of **19** (1.5 g, 5.86 mmol) in benzene (70 ml), $Fe_2(CO)_9$ (9.0 mmol) was added and the mixture was refluxed for 4 h. The reaction was cooled and filtered through a Celite pad. The filtrate was washed with brine solution (2 × 50 ml), dried over $MgSO_4$ and benzene was evaporated to yield a pale yellow solid which on recrystallization from hexanes afforded **20** as a yellow crystalline solid; m.p. 175–176 °C (literature [10] m.p. 176.5–177.5 °C); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.32–7.80 (m, 12H, aromatic); mass spectrum (CI) (*m*/*z*): 257 $(M^+ + 1)$; (EI) (*m*/*z*): 228 (M^+).

2.2.12. *Tribenzosuberene (**9**) and **9**-5D$_2$*

Using the above procedure for reduction using $LiAlH_4/AlCl_3$, reduction of **20** afforded crude **9** which on recrystallization from EtOH gave pure **9** as a white crystalline solid; m.p. 107–108 °C (literature [11] m.p. 105–115 °C); ^{1}H NMR ($CDCl_3$), δ (ppm): 3.65 (s, 2H, $ArCH_2Ar$), 7.1–7.8 (m, 12H, aromatic); mass spectrum (CI) (*m*/*z*): 243 $(M^+ + 1)$; (EI) (*m*/*z*): 242 (M^+). Reduction using $LiAlD_4$ gave **9**-5D$_2$, ^{1}H NMR ($CDCl_3$), δ (ppm): 7.1–7.8 (m, 12H, aromatic); mass spectrum (CI) (*m*/*z*): 245 $(M^+ + 1)$; (EI) (*m*/*z*): 244 (M^+).

2.3. Deuterium exchange studies

All preparative photolysis were carried out in a Rayonet RPR 100 photochemical reactor equipped with 254 or 300 nm lamps. The solutions were contained in quartz tubes (∼100–200 ml) which were cooled to ≤15 °C with tap water by means of a cold finger. All solutions were purged with argon (via a stainless steel needle) for 5 min prior to and during irradiation. General work-up following photolysis involved extraction with CH_2Cl_2, followed by drying of the organic layer and evaporation of the solvent under reduced pressure. Photolysis products were analyzed directly or after purification by preparative TLC, by GC/MS and ^1H NMR. In all cases, control experiments (“in the dark”) were conducted to determine any contribution of thermal reaction.

2.4. Quantum yields

Quantum yields of deuterium (protium) incorporation from solvent to the suberenes were measured using an optical bench (200 W Hg lamp) for photolysis at 280 nm and GC/MS for analysis. Potassium ferrioxalate actinometry was employed for measurement of light intensity. In general, a 3.0 ml solution (10^{-3} substrate) in the appropriate solvent was irradiated in a quartz cuvette with stirring/purging with a stream or argon. Conversions were kept below 15% in all runs. After photolysis, the solution was transferred to a test tube, saturated with NaCl and extracted with CH_2Cl_2. The photolysate was then analyzed by GC/MS and deuterium (protium) enrichment calculated after correcting for natural abundance ^{13}C.

2.5. Fluorescence measurements

Steady-state fluorescence measurements were carried out on either a Perkin-Elmer MPF-66 or Photon Technology International (PTI) A-1010 Quanta-Master luminescence spectrometer. For systematic fluorescence quenching studies, a series of substrate solutions in CH_3CN (dry) with varying concentrations of H_2O were prepared in Suprasil quartz cuvettes. A set of three samples was prepared at each concentration of H_2O. The fluorescence intensity was measured for each and an average of three values was taken. These values of fluorescence intensities over the range of H_2O concentration were then used in Stern–Volmer analysis. Fluorescence quantum yields (Φ_f) of all suberene derivatives (except for **9** (**9**-$5D_2$)) were measured relative to the known fluorescence quantum yield for suberene (**1**) [4b]. The standard used for **9** (**9**-$5D_2$) was diphenyl ether due to better spectral overlap of emission bands.

Fluorescence lifetimes were measured using a PTI LS-1 instrument with a H_2 lamp as excitation source. The lifetimes (τ) were calculated by mathematical deconvolution using software supplied by PTI, of the lamp profile from the sample decay function. The value of χ^2, the fitting parameter, was taken as a measure of agreement between the calculated line and experimental data. The weighted residuals and autocorrelation functions were also utilized in judging the quality of the calculated curve. All systems studied in this work exhibited good single exponential decay kinetics unless otherwise indicated.

2.6. Laser flash photolysis (LFP)

All transient spectra and kinetic measurements were recorded using nanosecond LFP with excitation by a Spectra Physics YAG laser (Model GCR-12, 266 nm excitation). Samples of OD ≈ 0.3 at the excitation wavelength were prepared and irradiated in quartz cells. Flow cells were used for spectra in order to eliminate complications from long-lived intermediates and static cells were used for the quenching studies. Flow cell solutions were purged continuously with either O_2 or N_2, while static cells were purged for a minimum of 10 min prior to irradiation.

3. Results and discussion

3.1. Synthesis of suberenes

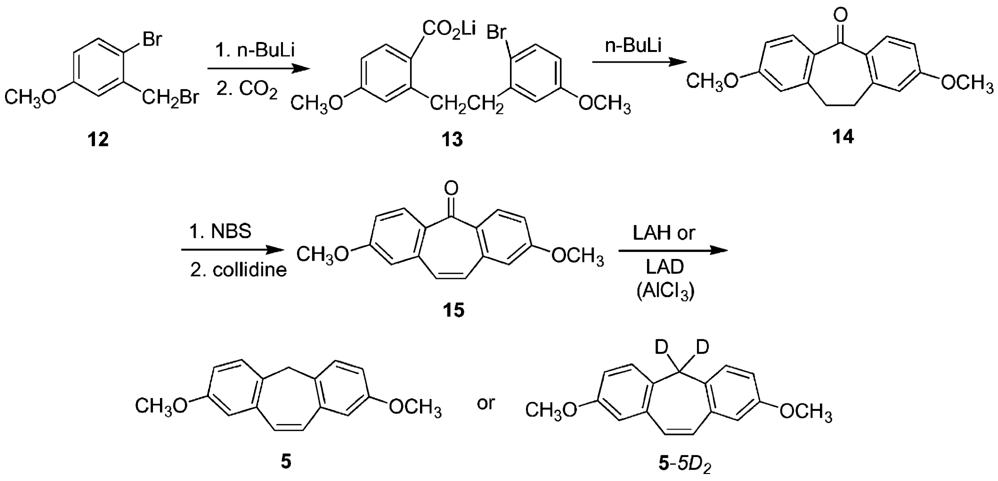
2,8-Dimethoxysuberene (**5**) and its dideutero compound **5**-$5D_2$ were synthesized according to the method outlined in Scheme 1. Ketone **14** was synthesized following reported procedures [9], via the Parham cyclization of the lithium salt of the carboxylic acid (**13**) generated in situ by the treatment of **12** with 1 equiv. of *n*-BuLi followed by the addition CO_2. Bromination of **14** with NBS followed by debromination with collidine gave **15**, which was reduced with either LAH or LAD (with $AlCl_3$), to give **5** and **5**-$5D_2$, respectively.

10-Methoxysuberene (**6**) was synthesized according to the method outlined in Scheme 2. Treatment of commercially available *trans*-9,10-dibromodibenzosuberone (**16**) in refluxing 3 M KOH/MeOH for 1 h gave >90% yield of mono-debrominated ketone **17**. Subsequent additional reflux (3 h) resulted in the formation of **18** as a yellow crystalline solid. Reduction of **18** with LAH/LAD gave the desired **6** or **6**-$5D_2$. 10-Bromosuberene (**8**) was readily prepared by LAH reduction of **17**. Similarly, **8**-$5D_2$ was also prepared from **17** using LAD. 10-Cyanosuberene (**7**) and **7**-$5D_2$ were prepared by reaction of **8** or **8**-$5D_2$ with CuCN in refluxing 1-methyl-2-pyrrolidone.

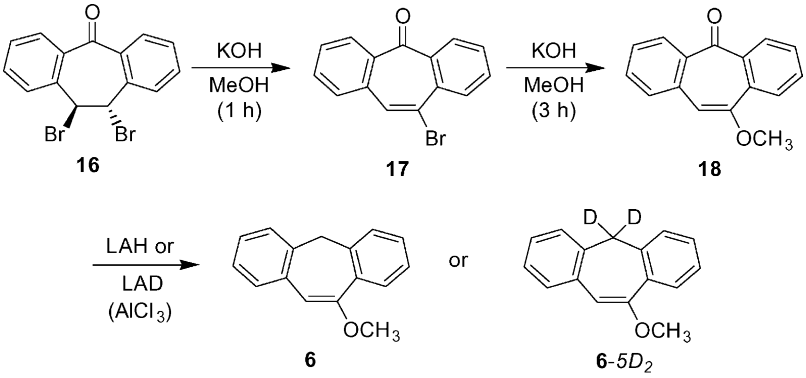
Tribenzosuberene (**9**) and its dideutero analog **9**-$5D_2$ were synthesized according to the method outline in Scheme 3. Treatment of ketone **17** with potassium *t*-butoxide in the presence of furan afforded the adduct **19**. Subsequent deoxygenation with $Fe_2(CO)_9$ yield tribenzosuberenone (**20**). Reduction with LAH/LAD as above gave the desired compounds **9** or **9**-$5D_2$.

3.2. Deuterium exchange studies

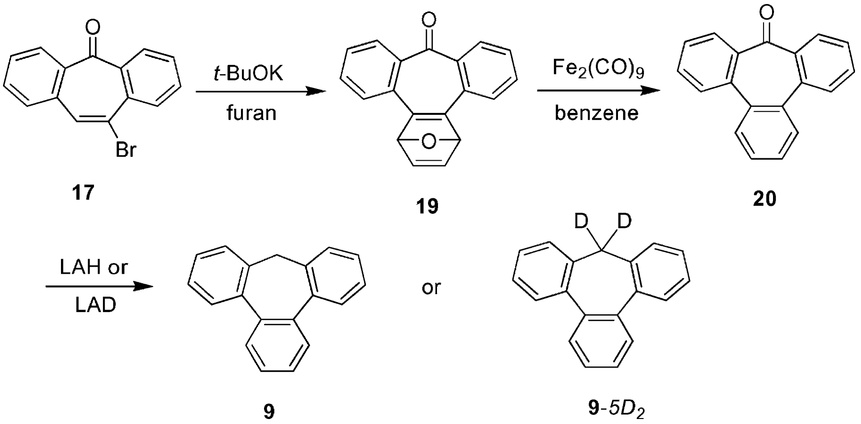
Photolysis of all of **5**–**7** in 1:1 (v/v) D_2O–CH_3CN (5–120 min) resulted in mono (major) and dideuterium (minor)



Scheme 1.

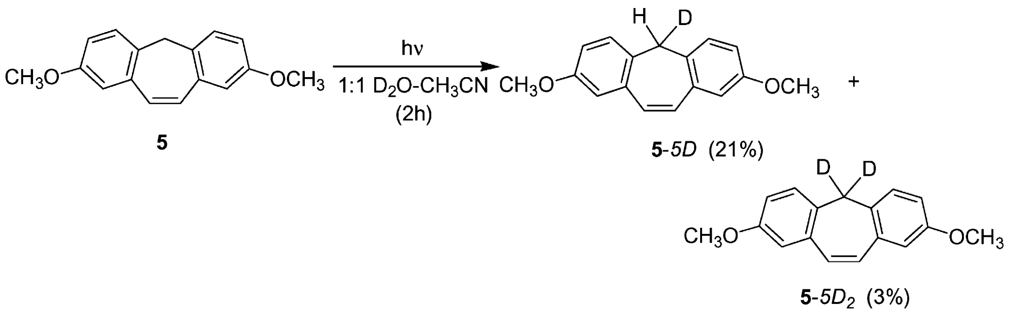


Scheme 2.



Scheme 3.

incorporation at the 5-position of these compounds, as shown in Eq. (2) for **5**:



5

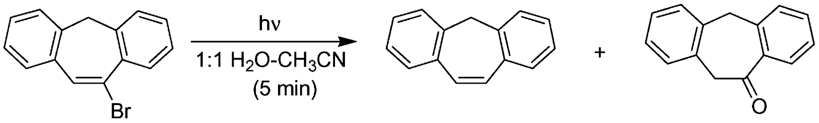
5-*5D* (21%)

5-*5D*$_2$ (3%)

(2)

No exchange was observed in the dark. The photoexchange can be followed conveniently by NMR. For example, for **5**, a new unresolved triplet at δ 3.58 (coupling to deuterium not resolvable) appears on photolysis, at a slightly higher field to the original methylene signal at δ 3.58 (which is now reduced in intensity). The aromatic and vinyl signals remain unchanged during the photolysis, even at high conversion, consistent with the lack of deuterium incorporation at these positions. Photolysis of the corresponding dideutero analogs **5**-5D$_2$, **6**-5D$_2$ and **7**-5D$_2$ in 1:1 H_2O–CH_3CN resulted in *protium* incorporation, to give the corresponding monodeuterated products and **5**–**7**. The advantage of these runs is that both mono and diprotium incorporation can be monitored by NMR. This is illustrated in Fig. 1 which shows that **5**-5D$_2$ can be converted to high yields (>50%) of **5**-5D and **5** after several hours of photolysis, as followed by NMR. Moreover, it is clear from the plot that the exchange is sequential, that is, the deuterium is exchanged off one at a time. Photolysis runs of **6** (or **6**-5D$_2$) could not be taken to high conversion due to residual *thermal* hydrolysis of the vinyl methoxy ether group, which gave the ketone.

The photochemistry of suberene **8** (or **8**-5D$_2$) in 1:1 D_2O–CH_3CN (1:1 H_2O–CH_3CN) was dominated by photoreduction, to give **1**, and photohydrolysis, to give **21** (Eq. (3)):



8

1 (12%)

21 (15%)

(3)

No deuterium (or protium) incorporation was observable. The failure of **8** to undergo excited state carbon acid deprotonation is understandable considering the expected facile

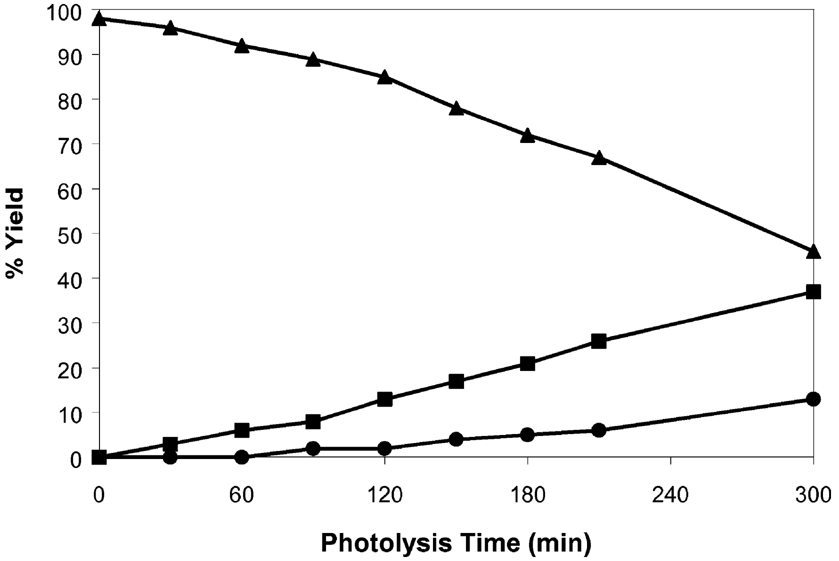


Fig. 1. Plot of extent of protium incorporation on photolysis of **5**-5D$_2$ in 1:1 H_2O–CH_3CN, as monitored by NMR: circles, **5**; squares, **5**-5D; triangles, **5**-5D$_2$.

debromination of the vinyl–Br bond, either homolytically (to give **1**, after reduction by the solvent), and heterolytically (to give **21**, via the vinyl cation). No reaction was observed in the absence of photolysis. Suberene **8** was not studied further.

Photolysis of tribenzosuberene (**9**) in 1:1 $D_2O–CH_3CN$ (or **9**-$5D_2$ in 1:1 $H_2O–CH_3CN$) did not result in detectable deuterium (protium) incorporation, even on extended photolysis, and the substrate was recovered unchanged. Notwithstanding other explanations, it would appear that benzannelation of the vinyl moiety significantly affects (reduces) the excited state carbon acidity of the compound. Subsequent photolysis of **9** in 1 M NaOD/EtOD (60 min) did result in the formation of **9**-5D (15%) and **9**-$5D_2$ (3%). Photolysis in neat EtOD gave no exchange. Further experiments using a basic medium for exchange studies were carried out with **9**-$5D_2$ using ethanolamine in CH_3CN. For example, photolysis of **9**-$5D_2$ in 0.5 M ethanolamine in CH_3CN (60 min) gave **9**-5D (26%) and **9**-$5D_2$ (7%). Use of higher concentrations of ethanolamine resulted in higher yields of exchange products. No exchange was observed without photolysis. Base catalysis of exchange observed in this system is further evidence for a mechanism of exchange involving C–H bond dissociation (carbon acid).

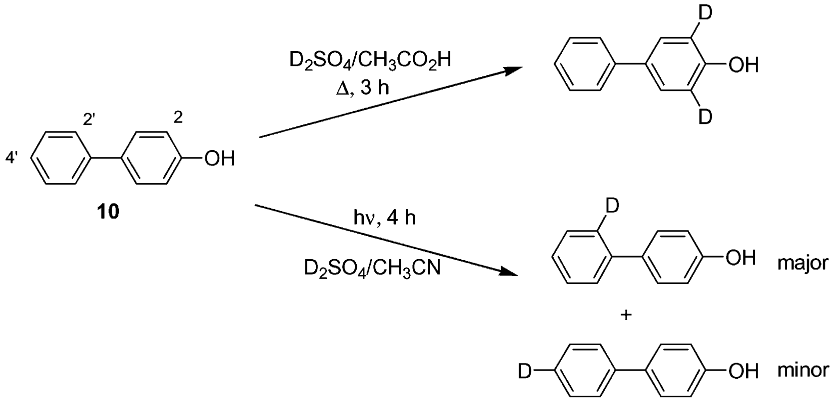
Quantum yields of deuterium (or protium) incorporation (Φ_{ex}) for the suberenes were measured using GC/MS for analysis and potassium ferrioxalate actinometry to monitor light intensity, on an optical bench photolysis set-up. The results for selected runs are shown in Table 1. It is clear that values measured for Φ_{ex} are not hugely different from those initially reported for the parent suberene (**1**) suggesting that the effects of substituents/structure is not large, discounting any large differences in reactive excited state lifetimes (*vide infra*). An exception might be argued for **9** (**9**-$5D_2$) where exchange was not observable in H_2O (D_2O). Although the quantum yields measured are all below 0.1, it should be pointed out that the methylene position for which exchange is being followed has two identical hydrogens (deuteriums). Since exchange can only occur sequentially, by deprotonating one proton, 50% exchange of this position should be regarded as equating to a quantum efficiency of unity. Therefore, realistically, the measured quantum yields reported in Table 1 should be multiplied by a factor of 2 to obtain the true measure for quantum efficiency for exchanging one proton (deuterium) at the 5-position of these compounds. Moreover, as shown in prior work [4b], a significant proportion (>90%) of deprotonated protons undergo "internal return" without exchange at all. Thus the intrinsic reactivity of these systems is much higher than suggested by their measured Φ_{ex} (vide infra).

Table 1
Quantum yields (Φ_{ex}) for deuterium (protium) incorporation for **5**–**7** and **9** (**5**-$5D_2$, **6**-$5D_2$, **7**-$5D_2$ and **9**-$5D_2$)

Compound	Φ_{ex}[a]		
	100% CD_3CN	7:3 $D_2O–CH_3CN$	1:1 $D_2O–CH_3CN$
1[b]	0.000	0.029	0.030
1-$5D_2$[b]	0.000[c]	0.045[c]	0.035[c]
5	0.000	0.0079	0.0071
5-$5D_2$	0.000[c]	0.011[c]	0.0076[c]
6	0.000	>0.01[d]	>0.01[d]
6-$5D_2$	0.000[c]	≈0.03[c,d]	
7	0.000	0.035	
7-$5D_2$	0.000[c]	0.046[c]	
9	0.000	0.000	0.000
9-$5D_2$	0.0086[e], 0.016[f]	0.000[c]	0.000[c]

[a] Errors about ±10% of quoted value.
[b] Data from Ref. [4b] for comparison purposes.
[c] In 100% CH_3CN, 7:3 $H_2O–CH_3CN$, or 1:1 $H_2O–CH_3CN$.
[d] Estimated as quantum yield not reliably measurable due to competing thermal hydrolysis.
[e] In 1 M ethanolamine/CH_3CN.
[f] In 2 M ethanolamine/CH_3CN.

The regioselectivity with respect to carbon acidity of suberenes **5**–**9** is not an issue as only the 5-position (methylene) is reactive. However, it is an issue with respect to proton transfer (photoprotonation) to carbon for biphenyls **10** and **11**. The regioselectivity of thermal proton transfer was studied by refluxing 4-hydroxybiphenyl (**10**) (5 mg) in 2:1 (v/v) 20% (w/w) $D_2SO_4–CH_3COOH$ (30 ml) for 3 h, which gave exclusive deuterium incorporation at the 2-position (*ortho* to phenol OH) (Eq. (4)):



(4)

The δ 6.93 signal (corresponding to H2) nearly disappeared after reflux, while the δ 7.49 peak (corresponding to H3) was converted from a doublet to a singlet with integration corresponding to two protons. No deuterium incorporation was observed at lower temperatures (<55 °C, 24 h). Deuterium incorporation observed solely at this position indicates that while the hydroxy substituent activates the position *ortho* to it, no activation is felt in the ring appended at the *para* position; that is, there is minimal charge transfer to the unsubstituted ring in the ground state.

Photolysis of **10** in 3:7 15% D_2SO_4–CH_3CN for 4 h resulted in deuterium incorporation exclusively at the 2′ and 4′-positions (71 and 18%, respectively) on the ring not bearing the substituent (Eq. (4)). The deuterium incorporation can be followed by ^1H NMR (360 MHz), although this method of analysis cannot differentiate between mono or dideuteration of the equivalent 2′-positions. Following photolysis, the doublet centered at δ 7.52 assigned to the two equivalent 2′-protons and the doublet of doublets centered at δ 7.29 assigned to the 4′-proton were both reduced in intensity. While the area of the doublet of doublets at δ 7.39 assigned to the 3′-protons was *not* reduced in intensity following photolysis, this peak was partially converted to a broad doublet, which is consistent with deuterium incorporation at an adjacent position. Peaks corresponding to protons on the ring bearing the OH group were not changed upon photolysis. Photolysis under neutral conditions (D_2O–CH_3CN, 6 h) led only to deuterium incorporation at the 4′-position. The peak area for the proton at this position indicated about 15% exchange, while the areas of all other peaks were unchanged. In the region corresponding to protons at the 3′-position (δ 7.39), a broad doublet corresponding to the deuterated substrate was observed to have grown in, consistent with deuteration at the 4′-position. No deuterium incorporation was evident when dark conditions are employed. The pH dependent regioselectivity for photoprotonation of **10** suggests that different reactive species are present in the two media. It is known [12] that the excited singlet state pK_a of **10** is ∼2, indicating that upon excitation, deprotonation to form the corresponding phenolate **22** (see Section 3.4) should be efficient in neutral (or basic) aqueous solution. It is assumed then that protonation of excited state of **22** is responsible for the observed deuterium incorporation at the 4′-position under neutral conditions. In the D_2SO_4 solution used for photolysis in acid, the medium is too acidic to allow for efficient deprotonation (pH < 1), and therefore it is **10**∗ that is being protonated by solvent.

4-Methoxybiphenyl (**11**) was chosen for study to complement the results obtained for **10**. While both **11** and **10** feature related activating substituents, **11** cannot deprotonate to form a phenolate upon excitation. Upon irradiation in 3:7 15% D_2SO_4–CH_3CN for 2 h, ^1H NMR analysis indicated deuterium incorporation exclusively at the 2′-position (40%), with no observable exchange occurring at the 4-position (although a small amount of residual exchange cannot be completely ruled out by NMR). This reactivity is consistent with that observed for **10** under acidic conditions. Upon irradiation in neutral conditions (3:7 D_2O–CH_3CN), no deuterium incorporation was observed at any position, even on extended photolysis (8 h). The lack of exchange under these conditions further corroborates the assertion that the deuterium exchange observed for **10** in neutral media arises from protonation of the phenolate.

3.3. Fluorescence quenching and lifetime measurements

Efficient fluorescence quenching by H_2O (in CH_3CN) has been shown to be a good indicator of excited state carbon acid dissociation for suberenes [4b]. Indeed, we have argued that the water quenching rate constants (k_q) are a measure (if not a direct measure) of the deprotonation rate in S_1 [4b]. The fluorescence emissions of **5**–**7** were quenched by added water (in CH_3CN) with varying efficiencies (Fig. 2). The fluorescence of **9** was not affected by added water. These observations are consistent with their observed reactivity with respect to carbon acidity in water; that is, compound **9** was not reactive in water. Of those that exhibited quenching by water, Stern–Volmer plots of quenching were linear, and provided quenching rate constants (Fig. 3) for both dihydro and dideutero compounds. These rate constants and other fluorescence parameters are reported in Table 2. The observed primary isotope effect for fluorescence quenching of dihydro vs. dideutro compound is entirely consistent with the quenching pathway involving heterolytic cleavage of the benzylic C–H bond (deprotonation) via S_1. It seems reasonable then that k_q^H are a direct measure of reactivity with respect to excited state carbon acidity. Thus, substitution by two electron donating methoxy groups (in **5**) clearly retards the deprotonation rate (by an order of magnitude), whereas substitution of one methoxy group at the vinyl 10-position had almost no effect. In contrast, substitution at the 10-position with an electron withdrawing group (cyano) enhances the reactivity marginally.

If the mechanism of deuterium incorporation for **10** and **11** is protonation of S_1 by H_3O^+ (D_3O^+), an increase in the concentration of acid should lead to an increase in the overall rate for deactivation of S_1. Fluorescence measurements (steady-state and time resolved) were performed to probe this effect. Compound **11** was chosen for steady-state experiments, as competing fluorescence from the phenolate would not complicate the analysis. Samples were prepared in 1:9 (v/v) CH_3CN–H_2O(H_2SO_4) such that the $[H^+]$ of the aqueous portion spanned the range of neutral (pH = 7) to $[H^+] = 2.3$ M. The strong fluorescence intensity ($\lambda_{max} = 328$ nm) decreased smoothly as the concentration of acid was increased (Fig. 4). Stern–Volmer analysis of the fluorescence quenching gave a linear plot with $k_q = 8.6 \times 10^7\ M^{-1}\,s^{-1}$. Fluorescence lifetime measurements performed for **11** also showed significant quenching by acid, as the fluorescence lifetime for **11** in water ($\tau_f = 6.5$ ns) was reduced to 1.3 ns in 10% H_2SO_4. Fluorescence lifetime measurements for **10** gave similar results as those observed for **11**. The above fluorescence data are consistent with a mechanism involving reaction of S_1 via protonation by H_3O^+.

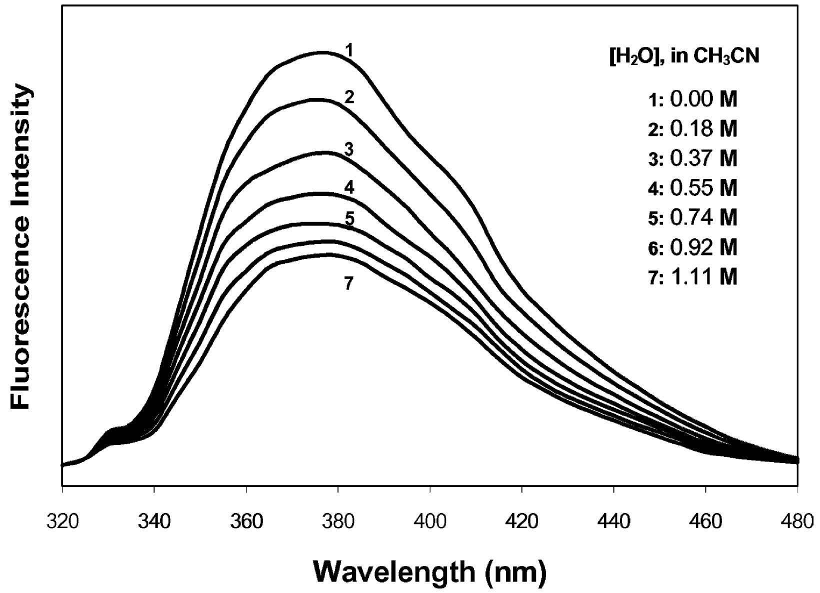
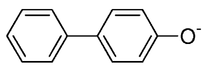


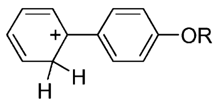
Fig. 2. Quenching of fluorescence emission of **6** by H_2O in CH_3CN ($\lambda_{ex} = 300$ nm).

3.4. Nanosecond LFP

LFP experiments were carried out only for the biphenyls **10** and **11** since the proposed carbanion intermediate **2** from C–H ionization of suberene (**1**) has not been detected by nanosecond LFP. This is not unexpected as **2** is known to be antiaromatic (in S_0) [4] and would be protonated by water (or its counterion H_3O^+) at very fast rates. The above results for **10** and **11** would indicate that these compounds are protonated efficiently in S_1 to give the corresponding phenyl-substituted cyclohexadienyl cations **23** or **24** in aqueous medium. It is known [13] that such intermediates are expected to very short-lived in aqueous medium, as deprotonation by water is fast. Previous studies [13] indicate that a variety of cyclohexadienyl cations are, however, much longer lived in $(CF_3)_2CH_2OH$ (HFP) and hence are readily detectable by nanosecond LFP. Thus HFP was chosen as the solvent for LFP studies of **10** and **11**.



22



23 R = H
24 R = CH_3

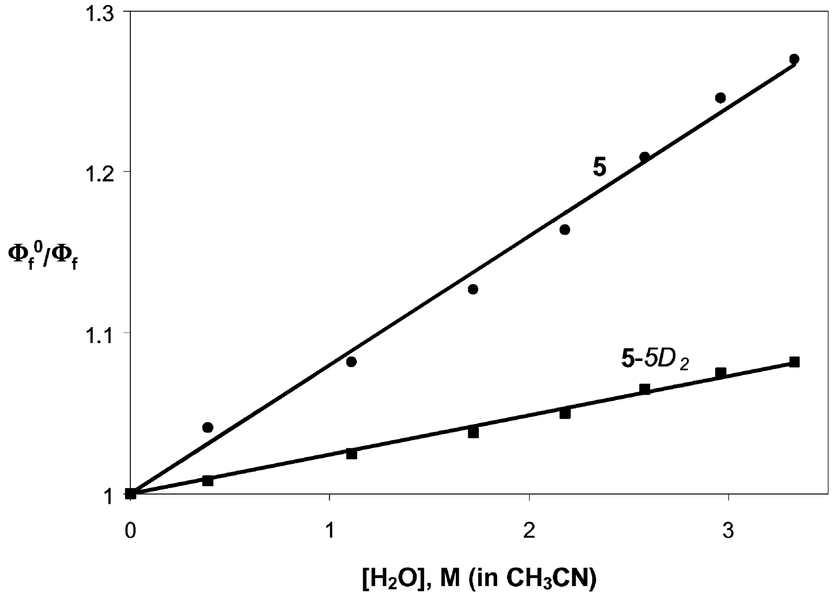


Fig. 3. Linear Stern–Volmer plots of fluorescence quenching by H_2O (in CH_3CN) for **5** and **5**-$5D_2$, providing the isotope effect for quenching, $k_q^H/k_q^D = 3.0$, for this compound.

Table 2
Photophysical and kinetic parameters for suberenes **1**, **5**–**7**, and **9**

Compound	Φ_f[a]	λ_{max} (nm)[b]	τ[c]	k_q^H ($\times 10^{-8}$ M^{-1} s^{-1})[d]	k_q^D ($\times 10^{-8}$ M^{-1} s^{-1})[e]	k_H/k_D[f]
1[g]	0.86	385	5.0	1.68	0.61	2.75
5	0.47	410	5.1	0.15	0.051	3.0
6	0.0051	390	3.6	1.8	0.72	2.5
7	0.0048	385	4.4	2.0	0.83	2.75
9	0.18[h]	325	3.2	–[i]	–[i]	–[i]

[a] Fluorescence quantum yield in neat CH_3CN measured relative to suberene **1** ($\Phi_f = 0.86$ [4b]).

[b] λ_{max} of fluorescence emission band.

[c] Fluorescence lifetime in neat CH_3CN measured by single photon counting.

[d] Stern–Volmer quenching rate constant (by water in CH_3CN) for dihydro compound.

[e] Stern–Volmer quenching rate constant (by water in CH_3CN) for dideutero compound.

[f] Primary isotope effect for fluorescence quenching of dihydro vs. dideutro compound by water.

[g] Data from Ref. [4b] for comparison purposes.

[h] Fluorescence quantum yield measured relative to diphenyl ether ($\Phi_f = 0.03$ [14]).

[i] Fluorescence quenching by added water not observed. Fluorescence quenching was observed by added ethanolamine in CH_3CN, with $k_q = 3.5 \times 10^8$ M^{-1} s^{-1} (for **9**) and $k_q = 2.1 \times 10^8$ M^{-1} s^{-1} (for **9**-5D_2), consistent with exchange being observed in this solvent system.

LFP of **10** is expected to give cyclohexadienyl cation **23**. Excitation of **10** (266 nm, N_2 purged) in HFP gave a transient absorption spectrum with two bands corresponding to two distinct species (Fig. 5). The transient absorption at 370 nm is short-lived component ($k_d = 1.2 \times 10^5$ s^{-1}) and is quenched completely by oxygen. This species is most likely the triplet state of **10**, although radical species generated from two photon absorptions cannot be excluded. The longer wavelength band ($\lambda_{max} = 510$ nm, $k_d = 4.3 \times 10^4$ s^{-1}) is not affected by oxygen, but is completely quenched by the addition of a small amount of water. This transient is assigned to the cyclohexadienyl cation **23** on the basis of its long wavelength absorption (due to the extended conjugation), its sensitivity to water, and its insensitivity to oxygen. LFP of **11** was expected to give a transient similar in nature to that observed for **10**, both in terms of chemical sensitivity, and absorption wavelength. Indeed, LFP of **11** in HFP did generate a spectrum similar to that observed for **10** containing two bands. The shorter wavelength band ($\lambda_{max} = 370$ nm, $k_d = 1.1 \times 10^6$ s^{-1}) was quenchable by oxygen ($k_d = 4.5 \times 10^6$ s^{-1} under O_2). On similar reasoning as for **10**, this transient is assigned to the triplet state of **11**. A longer wavelength band was also observed with $\lambda_{max} = 520$ nm and $k_d = 1.7 \times 10^6$ s^{-1}. This transient was not affected by oxygen, but was completely quenched by the addition of ~10% water. On the basis of the wavelength range of absorption and observed chemical sensitivity, this band is assigned to the cyclohexadienyl cation **24**. This transient decays at a rate of ~50-fold faster than the analogous transient observed for **10**, an effect likely due to the decreased donating ability of the methoxy substituent as compared with hydroxy substituent ($\sigma_p^+(OH) = -0.92$ and $\sigma_p^+(OCH_3) = -0.78$ [15]).

3.5. *Structure and reactivity for ESPT to and from carbon*

With respect to excited state carbon acidity of the suberenes, the efficiency of deprotonation, as measured by

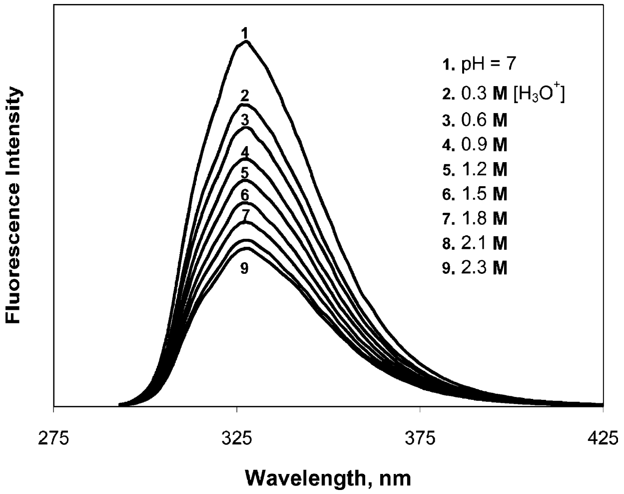


Fig. 4. Quenching of fluorescence emission of **11** by acid in aqueous solution ($\lambda_{ex} = 285$ nm).

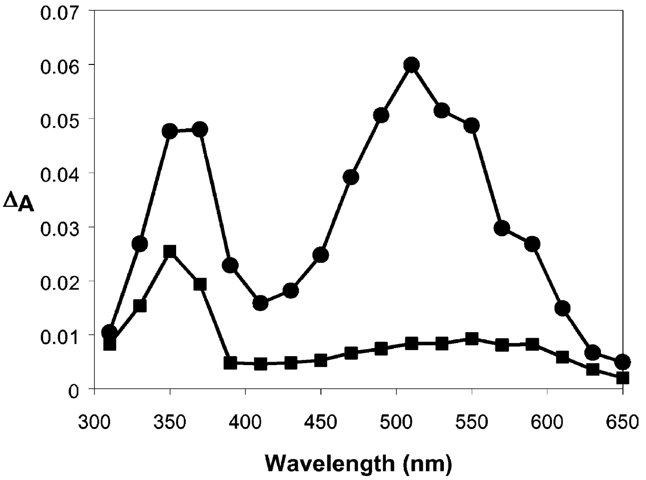


Fig. 5. LFP spectra observed for **10** in HFP.

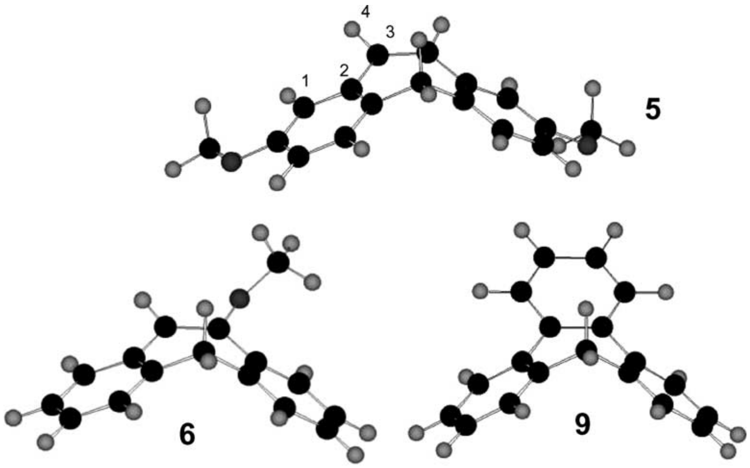


Fig. 6. Minimized ground state geometries (Chem3D, AM1) for suberenes **5**, **6** and **9**. The dihedral angles as defined by atoms 1–4 (a measure of the overlap between the π system of the benzene ring and the alkene moiety) are 31°, 33.5° (average value as there are two such angles for this compound) and 43° for **5**, **6** and **9**, respectively.

rates of fluorescence quenching by water, differ by more than an order of magnitude, with the cyano derivative **7** being the most reactive. Moreover, the tribenzo derivative **9** was completely unreactive in water, and showed exchange only in the presence of added base (ethanolamine). The primary isotope effects observed for fluorescence quenching are entirely consistent with water (or ethanolamine) acting as the deprotonating base (of the methylene position) in these systems. The rate constants are well below the diffusion control limit, which is not surprising considering the intrinsic slow rates for such reactions (in the ground state). There is certainly plenty of room to improve the rate of reaction, perhaps with derivatives with multiple electron withdrawing groups.

As a possible explanation of the observed relative reactivity of the suberene systems, the minimized ground state structures (Chem3D, AM1) of **5**, **6** and **9** were calculated and shown in Fig. 6. These compounds all adopt a “butterfly” geometry, with the internal cycloheptatrienyl ring adopting a “boat-like” conformation. Although not readily obvious, **9** is the most distorted from planarity (internal ring is more boat-like) of the three compounds. A quantitative measure of the distortion from planarity of these systems is the dihedral angle defined by atoms 1–4 (Fig. 6). This dihedral angle also measures the degree of overlap between the π system of benzene ring and the alkene (the larger the angle, the lesser the π overlap). The Chem3D calculations gave dihedral angles of 31°, 33.5° (average value as there are two such angles for this compound) and 43° for **5**, **6** and **9**, respectively. Although it is not known what geometry the excited singlet state will adopt, it seems reasonable to assume that the some degree of planarization is required on the excited state surface before carbon acid deprotonation from the methylene position can occur. This is due to the requirement of overlap of the internal cycloheptatrienyl ring system on deprotonation, to generate a cyclically conjugated 8π (4*n*) carbanion. Otherwise, there would be no obvious driving force for reaction. Based on these considerations, the tribenzo derivative **9** would be expected to be least reactive, due to the greatest distortion from planarity, and this was indeed observed. Of course, the effect of benzannelation is not explicitly taken into account in this simple model of reactivity.

Our results for the biphenyls indicate that the charge transfer character inherent in many biaryls can be utilized for carbon protonation of the more basic ring system, and as a method for photogenerating interesting cyclohexadienyl cations that cannot be readily generated thermally. Again, as in the suberene systems, the intrinsic reactivity, as measured by fluorescence quenching, is not high for carbon protonation of these compounds, so there is much room for improvement. It would be desirable, for example, to devise compounds that can be readily photoprotonated by water (hence acting as strong “photobases”). Work in this and related areas are continuing in our laboratory.

Acknowledgements

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