phenylazo)phenol) to −22 eu (**2** and 4-hydroxy-4′-nitrostilbene). This has a dramatic effect on the temperature dependence of K_{assoc}. at −17 °C **2** and the nitrostilbene have K_{assoc} of 25 900 M^{-1}; at −22 °C **2** and the nitrophenylazophenol have K_{assoc} in excess of 44 000.

(5) As was the case with **1** the **2**–pNP complex could be isolated. Its single-crystal X-ray (two views) is shown below together with a vertical view of **1**–pNP. The complexes are qualitatively the same; the guest pNP is docked within the cavity and tied down by a single hydrogen bond to the pyridine. There is however one striking difference between the complexes. In **1**–pNP the pyridine is held rigidly pointing into the cavity, while in **2**–pNP the pyridine parallels the cavity walls, forming a near ideal hydrogen bond with the projecting phenolic hydroxyl. We suggest that it is the *flexibility* of **2**, its ability to undergo *minor* conformational changes to accommodate the guest, that inter alia accounts for the remarkably stable nature of **2**-phenol complexes.[9] An excess of rigidity is perhaps not for the best.

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Enhanced Formation of $8\pi(4n)$ Conjugated Cyclic Carbanions in the Excited State: First Example of Photochemical C–H Bond Heterolysis in Photoexcited Suberene

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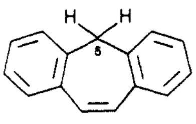
The formation of carbanions via ionization of carbon acids is well-known in the ground state.[1] Förster cycle[2] calculations of a number of hydrocarbons and their conjugate bases show that the benzylic protons of these compounds become vastly more acidic in the excited singlet state, by as many as 30 orders of magnitude. However, to our knowledge, there are no known examples of C–H bond heterolysis in the excited state, although Förster cycle calculations indicate that hydrocarbons such as fluorene ($pK_a(S_1) \approx -9$)[2] should ionize readily in the singlet excited state, in neutral or even acidic medium, and therefore should be expected to undergo rapid exchange of the acidic proton with solvent protons (or deuterons). Tolbert[2a] noted that experimental verification of the increased thermodynamic acidity of these hydrocarbons in the excited state has not been available because of the inherent slow rate of proton transfer from carbon, which does not compete favorably with other deactivational processes available for excited states. We report here the first example of photochemical C–H bond ionization, in which 5*H*-dibenzo[*a*,*d*]cycloheptene (**1**) (suberene) on photolysis in D_2O/CH_3CN undergoes rapid proton exchange at the benzylic 5-position (for deuterium). Additionally, the proposed carbanion intermediate is an $8\pi(4n)$ system (in the internal cyclic array), which has antiaromatic character in the ground state, but its formation is greatly enhanced in the excited state, compared to the corresponding carbanions derived from fluorene (**2**, 6π internal cyclic array) and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (suberane) (**3**, nonconjugated internal array) systems, which do not undergo observable benzylic proton exchange on excitation.



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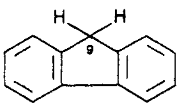

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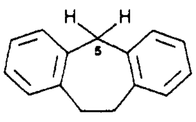

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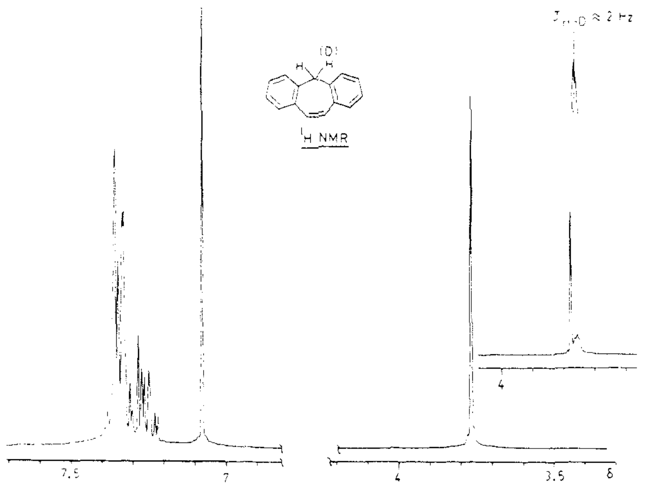
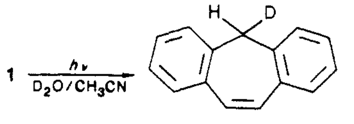


Figure 1. Proton (250 MHz) NMR of suberene (**1**) before and after photolysis. The upper insert is the spectrum of the photolyzed sample showing decrease in intensity of the methylene singlet of **1** at δ 3.78 and formation of the methylene proton of **4** at δ 3.76 as a 1:1:1 triplet ($J_{H-D} \approx 2$ Hz). The region δ 7–7.4 remains unchanged in the photolyzed sample.



(1)

4

We recently reported[3] that the suberenyl carbanion[4] is formed much more efficiently than similar dibenzannelated carbanions, including the fluorenyl anion, via photodecarboxylation of the corresponding carboxylic acids. Cycloheptatrienyl anions in the ground state have been shown to be antiaromatic or at least greatly destabilized compared to similar systems lacking the 8π conjugated cyclic array.[5] We made the hypothesis[3] that in the excited singlet state, ground-state antiaromatic carbanions are stabilized compared to ground-state aromatic carbanions or related nonconjugated cyclic systems. As an additional test of this hypothesis, suberene (**1**) should have a much greater propensity to undergo benzylic C–H bond heterolysis than fluorene (**2**) or suberane (**3**). Photolysis of 10^{-3} M solution of **1** in 50% D_2O/CH_3CN (v/v) at 254 nm in a Rayonet reactor for 30–60 min resulted in ≈40% conversion to α-deuteriosuberene (**4**) (eq 1). Photodecomposition of **1** was insignificant. No deuterium incorporation was observed when an identical solution was kept in the dark. The quantum yield for formation of **4** is ca. 0.03, which is low but substantial for such a process. The structure of **4** was confirmed by its mass spectrum and more definitively by both ^1H (250 MHz) and ^{13}C NMR. As shown in Figure 1, the product mixture after photolysis in D_2O/CH_3CN of a sample of pure **1** consists of two methylene signals: a sharp singlet at δ 3.78 due to **1** and a 1:1:1 triplet ($J_{H-D} \approx 2$ Hz) at δ 3.75 due to **4**. Integration of these two methylene signals gave a yield of 40–50% of **4**, after taking into account that **4** has only one observable proton per molecule. The aromatic and

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† NSERC Canada University Research Fellow, 1984–1989.

[1] (a) Buncel, E. *Carbanions: Mechanistic and Isotopic Aspects*; Elsevier: Amsterdam, 1975. (b) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965. (c) *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part A.

[2] (a) Tolbert, L. M. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1987; Part C. (b) Vander Donckt, E.; Nasielski, J.; Thiry, P. *J. Chem. Soc., Chem. Commun.* **1969**, 1249. (c) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

[3] McAuley, I.; Krogh, E.; Wan, P. *J. Am. Chem. Soc.* **1988**, *110*, 600.

[4] Also known as suberenide or 5*H*-dibenzo[*a*,*d*]cycloheptenide anion.

[5] (a) Tolbert, L. M.; Ali, M. Z. *J. Org. Chem.* **1982**, *47*, 4793. (b) Staley, S. W.; Ordeval, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 3384. (c) Staley, S. W.; Ordeval, A. W. *Ibid.* **1974**, *96*, 1618. (d) Dauben, H. J., Jr.; Rifi, M. R. *Ibid.* **1963**, *85*, 3041. (e) Doering, W. v. E.; Gaspar, P. P. *Ibid.* **1963**, *85*, 3043. (f) Breslow, R.; Chang, H. W. *Ibid.* **1965**, *87*, 2200. (g) Breslow R.; Chu, W. *Ibid.* **1973**, *95*, 411. (h) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

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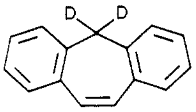
vinylic regions (δ 7–7.4) of the ^{1}H NMR spectrum remain essentially unchanged, indicating no observable deuterium incorporation into other positions of the compound. The ^{13}C NMR spectrum (^{1}H decoupled) shows carbon 5 of **1** at δ 41.6 and the same carbon of **4** at δ 41.26, as a 1:1:1 triplet ($J_{C-H} \approx 20$ Hz). Again, no changes are observed in the other carbon signals, indicating that deuterium incorporation is exclusively at the 5-position of **1**. Extended photolysis of **1** does result in formation of ≈5–10% yield of α,α'-dideuteriosuberene (**5**), as indicated by mass spectrometry.



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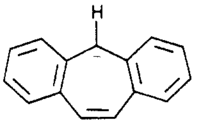

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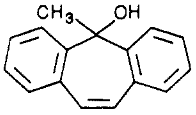

7

Although a radical mechanism resulting in incorporation of deuterium from solvent D_2O is unlikely, we have ruled this out by showing that deuterium is not incorporated when **1** is photolyzed in pure CD_3CN. Additionally, when pure **5**[6] is photolyzed in H_2O/CH_3CN, facile formation of **4** and subsequently **1** is observed, as shown by both ^{1}H and ^{13}C NMR. Again no exchange is observed when **5** is photolyzed in pure CH_3CN.

Photolysis of **2** and **3** under similar conditions as described above for **1** resulted in no observable deuterium incorporation in recovered substrates, consistent with the absence of a simple radical mechanism, since such a mechanism should not show such a drastic selectivity in reactivity. In the ground state, **2** undergoes deuterium incorporation at the 9-position with a half-life of about 10 h in refluxing D_2O/CH_3CN (pD ≈ 12), unlike **1** and **3**, which do not undergo exchange under these and more forcing conditions. These observations are consistent with their known ground-state pK_a's, with fluorene (**2**) being the most acidic (p$K_a \approx 23$)[1] and **1** and **3** much less acidic (p$K_a \geq 32$).[1,7] The observed facile photoexchange of **1** suggests that it becomes vastly more acidic kinetically than **2** and **3** in the excited state, implying that there is inherent stability associated with an $8\pi(4n)$ conjugated cyclic carbanion in S_1.

Steady-state fluorescence studies show that water is a very efficient quencher of S_1 of **1** but not the corresponding singlet states of **2** and **3**. For example, on going from pure CH_3CN to 80% H_2O/CH_3CN, the fluorescence quantum yield of **1** decreases by over an order of magnitude. Furthermore, the fluorescence lifetime of **1** also decreases, from 4.6 ns (pure CH_3CN) to 0.13 ns (80% H_2O/CH_3CN). On the other hand, the lifetime of **2** stays unchanged at ca. 6 ns in the different solvents. *It is therefore reasonable to assume that water is acting as the deprotonating base for photoexcited* **1**, *resulting in formation of transient suberenyl carbanion* **6**. Consistent with this proposal are the observations that neither the fluorescence intensity or fluorescence lifetime of **7** are changed significantly on going from pure CH_3CN to aqueous CH_3CN, since this suberene derivative has no benzylic protons. These results rule out a lifetime effect in explaining the observed reactivity differences in photoionization of the benzylic C–H bonds of **1–3**.

In summary, we have discovered a way to promote photochemical C–H bond heterolysis, viz., by choosing a compound which on ionization of the C–H bond gives formally a ground-state antiaromatic carbanion. This opens up a way for studying carbon acids in the excited state, a previously inaccessible area experimentally. In addition, the results of this and a previous study[3] suggest that $8\pi(4n)$ conjugated cyclic carbanions have aromatic[8] character in S_1.[9]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for an operating grant and a postgraduate scholarship to E.K. Additional support was provided by the University of Victoria. Single-photon fluorescence lifetime measurements and analyses were carried out at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Research Program of the Division of Research Resources of NIH (RR00886) and by the University of Texas at Austin.

Registry No. 1, 256-81-5; **4**, 114185-93-2.

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(6) A sample of pure **5** was made by $LiAlD_4/AlCl_3$ reduction of dibenzosuberenone in diethyl ether.

(7) The pK_a of **1** has not been measured to our knowledge, but other cycloheptatriene derivatives have pK_a's in the 31–38 range,[5] which show they are much weaker acids than cyclopentadiene derivatives. On the other hand, they are not much less acidic than simple diphenylmethanes (p$K_a \approx 30$–35)[1] but are antiaromatic nevertheless (by NMR studies).[5a,b] It is informative to compare the calculated p$K_a(S_1)$'s for suberene (**1**) and fluorene (**2**) by using the Förster cycle. A p$K_a(S_1)$ value of −8.5 for **2** was reported by Vander Donckt and co-workers.[2b,c] Our calculations give a p$K_a(S_1)$ of −4 for **2**. For **1**, the difficulty in calculating its p$K_a(S_1)$ is in estimating the ground-state pK_a as well as the $E_{0,0}$ value for the anion (which is expected to have antiaromatic character). We have generated the suberenyl anion in THF with *n*-BuLi. The anion has a deep red-brown color, with a long wavelength $\lambda_{max} = 800$ nm! Our best estimate of $E_{0,0}$ is ≈ 34 kcal mol^{-1}. By using a p$K_a(S_0)$ of 32 for **1**, we calculate a p$K_a(S_1) = -7$ for suberene (**1**). It is clear from these calculated results that *both* **1** and **2** are expected to be vastly more acidic in S_1 than in S_0; the Förster cycle method does not predict that **1** should be vastly more acidic than **2** in S_1 as experimentally observed (at least kinetically).

(8) We use Breslow's[5h] working definition of aromaticity and antiaromaticity, based on relative stabilization or destabilization associated with cyclic π-systems, compared to reference compounds. As excited states are short-lived, it would not be fair, for example, to use an NMR criterion for aromaticity of excited states.

(9) We[10] have recently carried out Pariser–Parr–Pople π-SCF calculations of the above and related monocyclic systems which show that many ground-state antiaromatic systems become pseudoaromatic in the first excited singlet state, as indicated by more delocalized charge distributions in S_1. Jug and co-workers[11] have recently suggested such a possibility by using SINDO1 calculations on several monocyclic systems.

(10) Chak, B.; Dingle, T.; Wan, P., unpublished results.

(11) Padma Malar, E. J.; Jug, K. *Tetrahedron* **1986**, *42*, 417.

π-Facial Selectivity: Heteroatom Directed Syn/Anti Stereoselection in Diels–Alder Cycloadditions of Plane-Nonsymmetric Cyclopentadienes†

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The synthetic utility of the Diels–Alder reaction is enhanced due to the regiospecificity and stereocontrol (endo/exo) engendered by favorable orbital interactions.[1] There is considerable current interest in the diastereoselectivity exerted by an adjacent heteroatom-substituted center on these cycloadditions, although the factors responsible for the observed facial stereoselection are still not fully understood.[2-4] It is clear that an allylic heteroatom can

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† Dedicated to Professor Z. Valenta on the occasion of his 60th birthday.

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(1) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 876. (b) Desimoni, G.; Tacconi, G.; Bario, A.; Pollini, G. P. *Natural Product Syntheses through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, DC, 1984; Chapter 5. (c) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Chapter 7. (d) Gleiter, R.; Bohm, M. C. *Pure Appl. Chem.* **1983**, *55*, 237.

(2) (a) Gree, R.; Kessabi, J.; Mosset, P.; Martelli, J.; Carrie, R. *Tetrahedron Lett.* **1984**, *25*, 3697. (b) Franck, R. W.; Argade, S.; Subramaniam, C. S.; Frechet, D. M. *Tetrahedron Lett.* **1985**, *26*, 3187. (c) Franck, R. W.; John, T. V. *J. Org. Chem.* **1983**, *48*, 3269. (d) Koizumi, T.; Hakamada, I.; Yoshii, E. *Tetrahedron Lett.* **1984**, *25*, 87. (e) Takayama, H.; Hayashi, K.; Koizumi, T. *Tetrahedron Lett.* **1986**, *27*, 5509. (f) Schmidlin, T.; Gamboni, R.; Strazewski, P.; Tamm, C. *Helv. Chim. Acta* **1983**, *66*, 1796. (g) Kahn, S. D.; Hehre, W. J. *Tetrahedron Lett.* **1986**, *27*, 6041. (h) Koizumi, T.; Arai, Y.; Takayama, H.; Kuriyama, K.; Shiro, M. *Tetrahedron Lett.* **1987**, *28*, 3689. (i) McDougal, P. G.; Rico, J. G.; Van Derveer, D. *J. Org. Chem.* **1986**, *51*, 4492. (j) Grabley, S.; Kluge, H.; Hoppe, H.-U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 664.

0002-7863/88/1510-4074$01.50/0