1-hydroxy-2-isopropyl-10-(methoxycarbonyl)-1,2,3,4,4a,4b,5,6,7,8,8a,10a-dedecahydrophenanthrene (**1a**). Marine organisms frequently produce different phenanthrene-based diterpenes[10] from those in terrestrial microorganisms or plants.[11] Chatancin provides a new class of diterpenes and biosynthetic interests.

Chatancin (**1a**) inhibited PAF-induced platelet aggregation (IC_{50} 2.2 μM) and the binding of PAF to its receptors (IC_{50} 0.32 μM), but had no effect (>300 μM) on adenosine diphosphate induced, arachidonic acid induced, and collagen-induced platelet aggregation. Thus chatancin is a new type of specific PAF antagonist initially isolated from marine sources. The hemiketal or ether moiety accounts for its activity, because **3** and **4** had no activity. The details will be reported elsewhere in due course.

Acknowledgment. We thank Dr. T. Higa, a professor of Ryukyu University, for collection of the soft coral, and Mr. Y. Furukawa and Misses Y. Kuboniwa, T. Shimoji, and E. Yorikane of our laboratories for their technical assistance.

Supplementary Material Available: Experimental procedures and the data of X-ray analysis (9 pages). Ordering information is given on any current masthead page.

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Dimethyl Sulfoxide Phase C–H Bond Dissociation Energies for Phenalene and Benzanthrene

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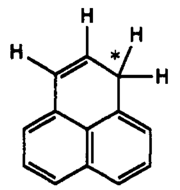
Summary: Comparisons of fluorene, phenalene, and benzanthrene sp^3C-H homolytic bond dissociation energy data, data collected with the aid of a cycle that utilizes acid-base and redox data collected in dimethyl sulfoxide solution, indicate that the sp^3C-H bonds in phenalene and benzanthrene are about 18 and 16 kcal/mol weaker (in a homolytic sense) than the sp^3C-H bond in fluorene.

Phenalene (**1**) and fluorene (**2**) are isomeric aromatic hydrocarbons that have long fascinated organic chemists.[1] The planarity, symmetry, and stability displayed by the anionic, radical, and cationic derivatives of phenalene[2,3] and fluorene[4] have prompted many investigations of their chemistry.[5] Much of the interest in phenalene results from its presence,[6] and the presence of the phenalenyl radical,[7] in liquids derived from fossil fuels. Since most of the chemical reactions associated with the combustion and conversion of fossil fuels are thought to involve free radicals, it is surprising that there are no experimental bond dissociation energies (BDEs) for the indicated bond in phenalene.[8] In this paper, with the aid of dimethyl sulfoxide (DMSO) phase acidity[9] and redox data, we report DMSO-phase C–H BDEs for phenalene (**1**), fluorene (**2**), and benzanthrene (**3**), an analogue of phenalene.



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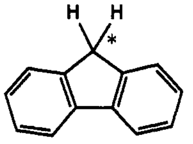

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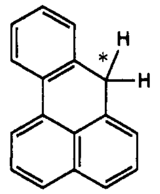

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Table I. Dimethyl Sulfoxide Phase Acidity Constants (pK_a's) for Phenalene (1), Fluorene (2), and Benzanthrene (3), Second Harmonic Alternating Current Voltammetry Crossing Potentials ($E_{1/2}$, in Volts, vs NHE) for the Oxidations of Carbanions Derived from 1–3,[14] and ΔpK_a and ΔBDE Values for 1 and 3, Relative to 2 (kcal/mol)

acid	pK_a	$E_{1/2}$	ΔpK_a, kcal/mol	ΔBDE[15]
phenalene (1)[16]	18.2[17]	−0.73	−6.0	−18
fluorene (2)[18]	22.6[9]	−0.21[19]	(0)	(0)
benzanthrene (3)[16]	20.2[20]	−0.74	−3.3	−16

Estimates of *relative* DMSO-phase BDEs for acids H–A have been obtained via eq 1, where pK_a(H–A) is the

$$\Delta \text{BDE(H–A)} = 1.37\ pK_a(\text{H–A}) + 23.06E_{1/2}(\text{A}^-) \quad (1)$$

DMSO-phase equilibrium acidity constant for organic acid H–A, and $E_{1/2}$ (A^-) is the DMSO-phase reversible oxidation potential for the conjugate base, A^- derived from H–A.[10] Equation 1 has been shown to yield DMSO,[11] and aqueous phase[12] BDE data that agree with gas-phase values, when a constant of about 56 kcal/mol is added to its right side.[13]

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[14] Electrochemistry conditions: DMSO solvent; 0.1 M $Et_4N^+BF_4^-$ electrolyte; Pt working and Ag/AgI reference electrodes (ferrocene/ferrocenium = +0.875 V as internal standard, values corrected to NHE by subtracting 0.125 V). SHACV: 20/110° ϕ shift, ac amplitude = 25 mV, and frequency = 50 Hz. CV: 0.1 V/s sweep rate.

[15] The uncertainties in the absolute and ΔBDE data in Table I are estimated to be ±3 and ±1 kcal/mol, respectively.[11,12]

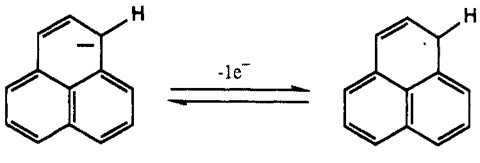
[16] Syntheses of phenalene (1) and benzanthrene (3): Boudjouk, P.; Johnson, P. D. *J. Org. Chem.* **1978**, *43*, 3979–3980. Melting point, thin-layer chromatography, and NMR data for these species were used to ensure sample purity, and were consistent with literature values.

0022-3263/90/1955-5805$02.50/0

The acidity and redox data necessary to estimate C–H homolytic bond strengths for phenalene (**1**) and benzanthrene (**3**), relative to fluorene (**2**), are shown in Table I.

Consider the acidity data first. Inspection of Table I reveals that DMSO-phase pK_a's for phenalene and benzanthrene are 18.2 and 20.2, respectively.[21] Therefore, for the phenalene framework, replacement of the two vinylic hydrogens in **1** with a fused benzene ring (as in **3**) strengthens the indicated bond (in a DMSO-phase heterolytic sense) by 3.4 kcal/mol.[17,22] The data also indicate that, in DMSO, phenalene is 4.9 pK units more acidic than fluorene (**2**), and, interestingly, only 0.3 pK units more acidic than 1,3-cyclopentadiene (pK_a = 18.0[9]).[17]

The redox data listed in Table I were collected with the aid of second harmonic alternating current voltammetry, a technique that yields "crossing potentials", a parameter similar in interpretation to half-wave potentials for reversible redox couples, for the redox process under consideration.[23] At cyclic voltammetry sweep rates of 0.1 V/s, the oxidation of the phenalenide anion (**4** in eq 2), forming the phenalenyl radical (**5**), is reversible, while the oxidations of the benzanthrenide and fluorenide anions are irreversible. Therefore, on the time scale of the CV experiments, the planar phenalenyl radical is persistent,[24] while the planar benzanthrenyl and fluorenyl radicals are not. It is also of interest to note that, in DMSO solution, the phenalenide anion, compared to the fluorenide anion, is 6.7 kcal/mol *less* basic, yet 12.0 kcal/mol *easier* to oxidize.



+ 1e$^-$ (2)

4 **5**

ΔBDE data for phenalene, fluorene, and benzanthrene are also found in Table I. These data reveal that replacement of the two vinylic hydrogens in **1** with a fused benzene ring (as in **3**) strengthens the indicated bond (in a DMSO-phase homolytic sense) by ca. 2 kcal/mol, an effect comparable in magnitude to that observed in the gas phase for propene and toluene (C–H BDEs = 86 and 88 kcal/mol, respectively).[25] More significantly, the indicated C–H bond in phenalene is about 18 kcal/mol weaker than the indicated C–H bond in its isomeric analogue, fluorene. Using the 56 kcal/mol constant in eq 1[11] yields an estimate of 64 kcal/mol for the sp^3 C–H bond in phenalene.[26] Previous estimates of the C–H BDE for phenalene have ranged from 48 to 73 kcal/mol.[8] Our value for the C–H BDE for phenalene is within these estimates and is indicative of one of the weakest C–H bonds present in any closed-shell neutral hydrocarbon.[27] The weakness of the sp^3 C–H bond in phenalene seems reasonable in light of the presence of the phenalenyl radical in liquids derived from fossil fuels. However, the small difference in the C–H BDEs for benzanthrene and phenalene does not seem sufficient to fully account for the observed difference in the *kinetic* stabilities of the radicals derived from these species. We are currently examining this issue.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Illinois Department of Energy and Natural Resources, for support of this work.

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(17) The pK_a for phenalene was measured vs 9-phenylfluorene and 9-(*p*-tolyl)fluorene.[9] The phenalene pK_a *per hydrogen* is ca 0.5 pK_a units less than the value in Table I, because there are six equivalent sites at which the phenalenide anion can be protonated. The *per hydrogen* pK_a has been inserted into eq 1, and is used when *comparing* acidities of species in Table I. We thank an editor for this suggestion.

(18) A commercially available (Aldrich) sample of fluorene (**2**) was thrice recrystallized (from ethanol) to a constant melting point.

(19) Arnett et al.[5] obtained a SHACV value of –0.25 V for the fluorenide oxidation in sulfolane/3-methylsulfolane.

(20) The pK_a for benzanthrene was measure vs 9-benzylfluorene and 2-naphthylacetonitrile.[9]

(21) Streitwieser et al.[2] have measured cyclohexylamine-phase pK_a values of 18.5 and 21.4 for **1** and **3**.

(22) Replacement of two vinylic hyrogens in cyclopentadiene (pK_a = 18.0) with a fused benzene ring [forming indene (pK_a = 20.1)] results in a similar 2.9 kcal/mol strengthening (in a heterolytic sense) of the appropriate sp^3 C–H bond.[9]

(23) The $E_{1/2}$ value for the reversible CV oxidation of the phenalenide anion is equal to the SHACV crossing potential shown in Table I.

(24) Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463–1467.

(25) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(26) (a) Kebarle et al.[26b] have estimated that the gas phase sp^3 C–H homolytic BDE for fluorene is 80 ± 5 kcal/mol. The ΔBDE data in Table I therefore suggest that the BDE for phenalene is ca. 62 kcal/mol. (b) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 3399–3406.

(27) (a) The gas phase C–H BDE for isotoluene has been determined to be 65±3 kcal/mol.[27b] (b) Bartmess, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 335–337.

Dimethyl Sulfoxide Phase NH Equilibrium Acidities for Urazole and Substituted Urazoles: For Urazole and 1-Substituted Urazoles, Which Proton Is More Acidic?

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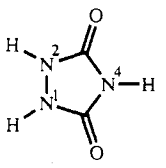
Summary: Determinations of the dimethyl sulfoxide (DMSO) phase pK_a's for urazole (pK_a = 13.1) and various (methylated and phenylated) mono- and disubstituted urazoles indicate that replacement of hydrogen with methyl and/or phenyl acidifies the urazole moiety, indicate that the acidifying effects of these substituents are additive, and suggest that the protons bound to the N-1 and N-4 atoms in urazole are of comparable thermodynamic acidity.

We have undertaken a systematic study of the dimethyl sulfoxide (DMSO) phase pK_a's for urazole[1] (**1**) and several substituted urazoles. Examination of the structure[2] of **1** reveals two varieties of protons: the protons bonded to



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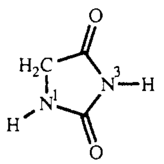

2

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(1) The IUPAC name for urazole is 1,2,4-triazolidine-3,5-dione.

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