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Note

A proton and carbon NMR spectroscopic study of 5-substituted acenaphthenes

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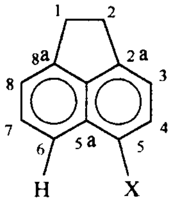
ABSTRACT: The proton and carbon NMR spectra of eight 5-substituted acenaphthenes were obtained. The ^{13}C chemical shifts of C-6 and C-2a of these compounds were compared with those of carbons located at structurally similar positions in 1-substituted naphthalenes (viz. C-8 and C-4). The ^{13}C chemical shifts of C-2a were also analysed using the dual substituent parameter (DSP) equation. The results revealed (i) diminished steric interactions between the 5-substituent and the adjacent *peri*-carbon (C-6) and (ii) an enhanced transmission of both polar and resonance effects to the carbon *para* (C-2a) to the variable substituent, X, in acenaphthenes relative to the corresponding carbons (C-4) in 1-substituted naphthalenes. The higher ρ_I and ρ_R values observed for C-2a of acenaphthenes suggest higher polarizability in this system than in naphthalenes. AM1 calculations of charge also showed enhanced substituent effects in the case of most of the substituents in the acenaphthene system. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^1H NMR; ^{13}C NMR; acenaphthenes, naphthalenes; AM1 calculations

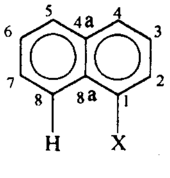
INTRODUCTION

Our recent papers[1,2] on ^1H, ^{13}C and ^{17}O NMR spectral studies of 4,1-disubstituted naphthalenes revealed an enhanced transmission of substituent effects to C-1 and side-chains from the variable substituent at C-4 relative to that found in *para*-disubstituted benzenes. The acenaphthene molecule can be considered as a naphthalene derivative with a distorted carbon framework since the dimethylene bridge across a pair of proximate *peri*-positions brings these two *peri*-carbons spatially closer.

This results in the concomitant widening of C5—C5a—C6 bond angle[3] involving the other two *peri*-positions. This could alter the steric and polar interactions in series 1 relative to series 2 and hence could influence the transmission of substituent effects. This prompted us to perform an NMR spectral study of 5-substituted acenaphthenes (series 1) and the results are reported in this paper.



Series 1



Series 2

EXPERIMENTAL

Compounds

5-Nitroacenaphthene[4] (m.p. 101–102 °C; lit.[4] 101.5–102.5 °C), acenaphthene-5-carboxylic acid[5] (m.p. 219–221 °C; lit.[5] 220–221 °C), 5-bromoacenaphthene[6] (m.p. 51–52 °C; lit.[6] 52 °C), 5-chloroacenaphthene[7] (m.p. 69–70 °C; lit.[7] 70–70.5 °C) and 5-cyanoacenaphthene[5] (m.p. 110 °C; lit.[5] 110–111 °C) were prepared by literature methods.[4–7] 5-Acetylacenaphthene (m.p. 59–61 °C) was prepared by the Friedel–Crafts acylation of acenaphthene. Methyl 5-acenaphthoate (m.p. 54–55 °C) was obtained by the esterification of acenaphthene-5-carboxylic acid. 5-Ethylacenaphthene (m.p. 39–40 °C) was prepared by the Wolff–Kishner reduction of 5-acetylacenaphthene. Methyl 5-acenaphthoate and 5-acetyl- and 5-ethylacenaphthene afforded satisfactory C,H analyses.

NMR measurements

The ^1H NMR spectra of the 5-substituted acenaphthenes were measured at 300 MHz (Varian VXR-300) for approximately 0.03 M solutions in $CDCl_3$ with TMS as internal reference. Broad-band and off-resonance decoupled ^{13}C NMR spectra were obtained at 75 MHz in $CDCl_3$ with TMS as internal reference. A pulse angle of 37.5° (5 s) and a repetition time of 3.72 s were used in the same instrument for approximately 0.5 M solutions in $CDCl_3$. The accuracy of the ^1H chemical shifts is considered to be 0.02 ppm and that of ^{13}C chemical shifts to be 0.05 ppm. H,C-COSY experiments were also

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Table 1. ^{1}H chemical shifts of 5-substituted acenaphthenes

	δ (ppm)						
Substituent	H-3	H-4	H-6	H-7	H-8	—CH_2—	Others
C_2H_5	[a]	[a]	7.65	7.39	[a]	3.26	2.98, 1.32
H	7.27	7.43	7.58	7.43	7.27	3.41	7.58 (H-5)
Cl	7.15	7.45	7.82	7.52	7.31	3.35	—
Br	7.12	7.65	7.76	7.54	7.32	3.40	—
$COCH_3$	7.28	8.06	8.72	7.60	7.35	3.40	2.73
$COOCH_3$	7.15	8.20	8.60	7.50	7.25	3.20	3.93
NO_2	7.27	8.46	8.53	7.65	7.43	3.45	—
CN	7.19	7.71	7.75	7.54	7.31	3.33	—

[a] Multiplet centered at 7.18 ppm.

obtained using the standard Varian software (HETCOR) with a spectral width of 1000 Hz in the ^{1}H direction and 4500 Hz in the ^{13}C direction.

The MOPAC-6.0 package furnished by QCPE[8] was used to calculate atom electron densities. It puts into effect the semi-empirical Hamiltonians AM1 and PM3. The calculations are of the RHF[9] self-consistent field type. All optimizations, with a view to obtaining energy minima with respect to nuclear coordinates, were performed by the simultaneous relaxation of all the geometric parameters employing the standard BFGS[10] method. In all cases the criterion for the completion of calculations were a scalar gradient of 0.01.

RESULTS AND DISCUSSION

Assignments of ^{1}H and ^{13}C chemical shifts

The ^{1}H NMR spectrum of unsubstituted acenaphthene has a singlet at 3.41 ppm readily assignable to the methylene protons. The triplet at 7.43 ppm was assigned to H-4,7 on the basis of multiplicity. The doublet appearing downfield at 7.58 ppm was assigned to H-5,6 in view of the known deshielding at *peri*-positions and the other doublet at 7.27 ppm was assigned to H-3,8.

The aromatic protons of all the 5-substituted acenaphthenes, except 5-ethylacenaphthene, afford first-order spectra. In all these compounds, H-6 appears far downfield as a result of the proximity of this proton to the 5-substituent leading to van der Waals deshielding and/or anisotropic effects. ^{1}H chemical shifts of all the 5-substituted acenaphthenes were assigned on the basis of the above considerations and the data are listed in Table 1.

The assignments of proton-bearing carbons were made from the proton-noise decoupled and off-resonance decoupled ^{13}C NMR spectra and H,C-COSY two-dimensional NMR spectra (Table 2). The quaternary carbon signals were assigned on the basis of substituent effect considerations. The ^{13}C shifts for unsubstituted acenaphthene assigned in the present study agree well with the literature assignments based on selective proton decoupling.[11,12] The two methylenic carbon chemical shifts were not distinguished since they hardly differ.

A comparison of the SCS values of the *peri*-carbons (C-6) in 5-substituted acenaphthenes (series 1) and C-8 in 1-substituted naphthalenes (series 2) was made (Table 3) with a view to assessing the influence of changes in the naphthalene framework in acenaphthene on the shieldings of the proximate *peri*-carbons (C-6). The data in Table 3 reveal less negative SCS values for C-6 of acenaphthenes than for naphthalenes, suggesting that the 5-substituent and C-6 have diminished steric interactions in the former. The SCS values of C-2a of series 1

Table 2. ^{13}C chemical shifts of 5-substituted acenaphthenes

	δ (ppm)											
Substituent	C-3	C-4	C-5	C-6	C-7	C-8	C-2a	C-5a	C-8a	C-8b	C-1,2	Others
C_2H_5	118.88	126.72	128.57	119.01[a]	126.18	119.15[a]	143.71	136.06	146.35	139.48	30.52, 30.26	26.10, 15.23
H[b]	119.04	127.66	122.13	122.13	127.66	119.04	145.84	131.54	145.84	139.19	30.21, 30.21	—
Cl	119.33	127.23	126.68	119.24	128.66	120.00	146.03	[c]	144.99	140.11	30.64, 29.75	—
Br	119.89	130.72	116.63	121.57	128.90	120.02	146.08	[c]	145.70	140.09	30.51, 29.79	—
$COCH_3$	117.90	132.82	129.7	122.36	130.27	120.19	152.97	130.15	145.87	139.48	30.56, 30.31	199.99, 28.44
$COOCH_3$	118.23	132.99	130.07	121.84	129.69	119.80	152.81	133.40	146.09	139.39	30.28, 30.20	167.71, 51.66
NO_2	117.74	127.54	139.82	119.81	131.81	121.19	155.75	[c]	146.52	[c]	30.46, 30.49	—
CN	118.57	134.26	104.27	119.70	130.15	120.82	152.46	130.53	146.58	138.28	30.65, 30.07	117.90

[a] May require reversal of assignments.

[b] Lit.:[11,12] C-3,8, 118.9; C-4,7, 127.5; C-5,6, 122.0; C-2a,8a, 145.6; C-5a, 131.4; C-8b, 139.0; C-1,2, 30.2.

[c] Signals not seen owing to fortuitous overlap.

Table 3. SCS values of C-6 of 5-substituted acenaphthenes and C-8 of 1-substituted naphthalenes[a]

Substituent	SCS (ppm) C-6 (acenaphthenes)	C-8 (naphthalenes)
NH_2	−4.72[a]	−6.15[a]
CH_2CH_3	−3.13	−4.14[b]
H	0.00	0.00
Cl	−2.89	−3.50[c]
Br	−0.56	−1.00[b]
$COCH_3$	0.23	−2.05[b]
$COOCH_3$	−0.29	−1.84[b]
CN	−2.43	−3.12[b]
NO_2	−2.32	−4.90[b]

[a] In acetone-d_6, taken from Ref. 13.
[b] From Refs 14–17.
[c] From Ref. 18.

and C-4 of series 2 (carbons *para* to the variable substituent) are listed in Table 4 to facilitate comparison. The data clearly reveal that the chemical shift of C-2a in series 1 is influenced to a larger extent than C-4 of series 2 by the variable substituent. This is also evident from the value of the slope, 1.36 ($r = 0.993$), obtained in the Lynch plot of chemical shifts of C-2a of acenaphthenes *vs.* the chemical shifts of C-4 of 1-X-naphthalenes.

Table 4. SCS values of C-2a of 5-X-acenaphthenes and C-4 of 1-X-naphthalenes

X	C-2a (series 1)	C-4 (series 2)
NH_2	−12.12[a]	−10.79[a]
Et	−2.13	−1.48[b]
H	0	0
Cl	0.19	−0.80[c]
Br	0.24	−0.01[b]
COMe	7.13	4.92[b]
COOMe	6.97	5.37[b]
CN	6.62	5.23[b]
NO_2	9.91	6.60[b]

[a–c] See Table 3.

Table 6. Charge, Φ_X, and variation in charge, $(\Delta\Phi)_X$, at C-2a of 5-X-acenaphthenes and C-4 of 1-X-naphthalenes by AM1 calculations

X	C-2a (series 1) Charge, Φ_X	$(\Delta\Phi)_X$ [a]	C-4 (series 2) Charge, Φ	$(\Delta\Phi)_X$ [a]
NH_2	−0.109	−0.046	−0.187	−0.069
OMe	−0.098	−0.035	−0.153	−0.035
Et	−0.069	−0.006	−0.123	−0.005
H	−0.063	0	−0.118	0
Cl	−0.060	0.003	−0.116	0.002
Br	−0.047	0.016	−0.103	0.015
COMe	−0.028	0.035	−0.098	0.020
COOMe	−0.023	0.040	−0.082	0.036
CN	−0.035	0.028	−0.091	0.027
NO_2	−0.010	0.053	−0.072	0.046

[a] $(\Delta\Phi)_X = \Phi_X - \Phi_H$.

Correlations employing dual substituent parameter equation

The DSP analysis of the chemical shifts of C-2a of series 1 using σ_I and σ_R values reported by Bromilow *et al.*[19] affords ρ_I and ρ_R values of larger magnitude than those of the C-4 of series 2 (Table 5), revealing that both the inductive and resonance effects are transmitted from the variable substituent, X, to C-2a to a larger extent in series 1 than in series 2. This enhanced transmission in series 1 could probably be ascribed to a decrease in the steric interaction between the 5-substituent and the *peri*-position which could lead to an enhanced coplanarity of the substituents. Although the larger SCS values of substituents such as NO_2, COMe, COOMe and NH_2 could be accounted for by the above explanation, the larger SCS values observed for substituents such as CN, Br and Cl suggest the additional involvement of other factors.

Probably the structural deformation inherent in acenaphthenes relative to naphthalenes enhances the polarizability of the acenaphthene system. The enhanced influence of the substituents at C-2a of acenaphthenes is also supported by the AM1 calculations of charge at C-2a of acenaphthenes and C-4 of naphthalenes. The charge and the substituent-induced variation in the charge, $(\Delta\Phi)_X$, computed by AM1 calculations and

Table 5. Results of DSP correlations of C-2a of 5-substituted acenaphthenes and C-4 of 1-substituted naphthalenes

Series	Atom	ρ_I	ρ_R	R	λ[a]	n	Ref.
5-X-acenaphthenes	C-2a	8.13	26.18	0.994	3.22	8[b]	This work
1-X-naphthalenes	C-4	4.00	21.2	0.994	—	13	14,15

[a] $\lambda = \rho_R/\rho_I$.
[b] Amino group excluded from the correlations as the data pertain to measurement in a different solvent.

listed in Table 6, show that for most of the substituents the $(\Delta\Phi)_X$ values for C-2a of acenaphthenes are higher than those for C-4 of corresponding 1-substituted naphthalenes.

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