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Synthesis and carbon-13 NMR study of some methanesulfonyloxy and trifluoroacetoxy derivatives of naphthalene

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Abstract—Several mono- and di-methanesulfonyloxy (mesyloxy) and trifluoroacetoxy derivatives of naphthalene were prepared and their C-13 NMR recorded. The C-13 NMR spectra were analysed and the complete assignment of aromatic carbon chemical shifts reported. The substituent induced chemical shifts of naphthalene due to mesyloxy and trifluoroacetoxy groups were derived and compared with that of the hydroxy substituent. Carbon chemical shifts of disubstituted naphthalenes were calculated by simple additivity of substituent induced chemical shifts. The experimental chemical shifts were compared with the calculated shifts and deviations discussed in terms of steric and electronic effects of the substituents.

INTRODUCTION

The carbon chemical shifts primarily reflect the electronic charges at the particular carbon. The distribution of charges can be influenced by many factors, such as mesomeric, π-inductive, steric or direct electric field effects and anisotropy effects of the substituent. Polycyclic aromatics, specially naphthalenes, are particularly well suited for the study of substituent induced chemical shifts (SCS), as these compounds contain both proximate (*ipso*, *ortho* and *peri*) and distant carbons. To the best of our knowledge, substituent effects of strong electron withdrawing groups such as methanesulfonyloxy (mesyloxy) and trifluoroacetoxy groups on the naphthalene system have not been studied before. In this work, we have synthesized a series of mono- and di-mesyloxy and trifluoroacetoxy derivatives of naphthalenes, and studied their C-13 NMR. The synthesis of the bis(trifluoroacetoxy)naphthalenes and most of the dimesyloxynaphthalenes studied here, is reported for the first time. From the electronic point of view there is strong possibility of oxygen lone pair donation into the naphthalene ring by resonance. This contribution, however, would be reduced owing to the presence of strong electron withdrawing mesyl and trifluoroacetyl groups. C-13 NMR provides a unique method of studying the electronic changes at the carbons.

There have been many carbon-13 NMR studies of naphthalene derivatives [1]. It has been observed that substituent induced chemical shifts obtained from mono-substituted naphthalenes can be used to predict the shifts in the disubstituted naphthalenes with the use of simple additivity rules [2–6]. Deviation from additivity rule occurs when there is some interaction between the two substituents. This deviation has been explained in terms of steric as well as electronic effects [7]. In this paper we attempt to verify the additivity rule for the mesyloxy and trifluoroacetoxy substituents.

The literature survey indicates that carbon-13 NMR of some dihydroxy naphthalenes have not been reported. We have recorded the C-13 NMR of four such dihydroxynaphthalenes and report their chemical shifts, and the calculated shifts using the additivity rule. The compounds investigated in this work are shown in Table 1.

EXPERIMENTAL

All melting points are uncorrected. I.r. spectra were recorded on a Perkin–Elmer instrument model 237B and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed on a Carlo–Erba Elemental Analyser 1106. Trifluoroacetic anhydride was prepared as described in the literature [8]. 1,3-, 1,4-, 1,5-, 1,8-, 2,3- and 2,7-dihydroxynaphthalene were purchased from Fluka. 1- and 2-naphthyl mesylate [9] and trifluoroacetates [10] were prepared by literature methods.

Preparation of dimesyloxy derivatives of naphthalene: a general procedure

To a mixture of 2,7-dihydroxynaphthalene (480 mg, 3 mmole) in pyridine (2 ml) was added methanesulfonyl chloride (1.14 g, 10 mmole) dropwise at 0°C under nitrogen. The reaction mixture was stirred at room temp for 4 h. The resulting brown mixture was transferred to a separatory funnel CH_2Cl_2 (30 ml). The organic layer was washed with H_2O (20 ml), 5% HCl (2 × 30 ml), and brine (20 ml). The brown organic layer was dried ($MgSO_4$) and decolourised with activated charcoal. After removal of the solvent the residual white solid was crystallized to give 1,7-dimesyloxynaphthalene (**10**), as white crystals (576 mg, 58%), m.p. 116–117°C (CH_2Cl_2–Et_2O). Found: C, 45.26; H, 3.61; S, 20.50%. Anal. calcd for $C_{12}H_{12}O_6S_2$: C, 45.58; H, 3.82; S, 20.27; ν_{max} (KBr) 3006, 2916, 2746, 1606, 1506, 1456, 1406, 1361, 1331, 1181, 1166, 1146, 1036, 986, 946, 856, 826 cm^{-1}.

1,3-*Dimesyloxynaphthalene* (**7**), white crystals (25%), m.p. 131–132°C (CH_2Cl_2–Et_2O). Found: C, 44.87; H, 3.73; S, 20.39; ν_{max} (KBr) 3034, 2936, 1636, 1600, 1578, 1510, 1368, 1348, 1330, 1180, 1160, 1050, 990, 970, 868, 810, 759 cm^{-1}.

1,4 *Dimesyloxynaphthalene* (**8**), oil (45%).

1,5 *Dimesyloxynaphthalene* (**9**), white crystals (20%); m.p. 210–211°C (CH_2Cl_2–Et_2O). Found: C, 45.26; H, 3.69; S,

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Table 1. Compounds studied

Compound	Position of substituents* C-1	C-2	C-3	C-4	C-5	C-7	C-8
1	OH		OH				
2	OH			OH			
3	OH					OH	
4	OH						OH
5	OMs						
6		OMs					
7	OMs		OMs				
8	OMs			OMs			
9	OMs				OMs		
10	OMs					OMs	
11	OMs						OMs
12		OMs	OMs				
13		OMs				OMs	
14	OTFA						
15		OTFA					
16	OTFA		OTFA				
17	OTFA				OTFA		
18	OTFA					OTFA	
19	OTFA						OTFA
20		OTFA	OTFA				
21		OTFA				OTFA	

*OMs ≡ O–SO_2Me; OTFA ≡ O–CO–CF_3.

20.07; ν_{max} (KBr) 3004, 2936, 1600, 1400, 1331, 1236, 1176, 1161, 924, 906, 806 cm^{-1}.

1,7 *Dimesyloxynaphthalene* (**10**), white crystals (58%), m.p. 117–118°C (CH_2Cl–Et_2O). Found: C, 45.26; H, 3.67; S, 20.32.

1,8 *Dimesyloxynaphthalene* (**11**), white crystals (55%); m.p. 116–117°C (CH_2Cl_2–Et_2O). Found: C, 44.60; H, 3.61; S, 20.50; ν_{max} (KBr) 3006, 2910, 2756, 1606, 1574, 1406, 1371, 1346, 1336, 1246, 1186, 1171, 1026, 978 cm^{-1}.

2,3 *Dimesyloxynaphthalene* (**12**), colourless needles (67%), m.p. 157–158°C (CH_2Cl_2–Et_2O). Lit. [9] m.p. 157.5–158.5°C. Found: C, 45.31; H, 3.65; S, 20.28; ν_{max} (KBr) 3018, 1395, 1370, 1355, 1245, 1180, 1075, 975, 930, 905, 896, 880, 826, 770, 760 cm^{-1}.

2,7-*Dimesyloxynaphthalene* (**13**), colourless plates (70%), m.p. 109–110°C (CH_2Cl_2–Et_2O). Lit. [9] m.p. 109–110°C. Found: C, 45.61; H, 3.71; S, 20.01; ν_{max} (KBr) 3011, 2931, 1631, 1581, 1511, 1361, 1341, 1246, 1211, 1181, 1132, 966, 911, 876, 861 cm^{-1}.

Preparation of difluoroacetyl derivatives of dihydroxynaphthalenes: a general procedure

To a mixture of 2,3-dihydroxynaphthalene (205 mg, 1.28 mmole) in Et_2O (1 ml) in a pear-shaped flask was added trifluoroacetic anhydride (2.10 g, 10 mmole). The flask was stoppered immediately and the reaction mixture was allowed to stand at room temp for 48 h. Trifluoroacetic acid and excess trifluoroacetic anhydride were then removed by passing a stream of dry nitrogen through the reaction mixture. The residual solid was dissolved in dry hexane and a stream of dry N_2 was passed through it to remove the hexane and any remaining trifluoroacetic acid. The residue was then crystallized from hexane to give 2,3-bis(trifluoroacetyloxy)naphthalene (**20**) as colourless plates (280 mg, 80%), m.p. 70–71°C. Anal. calcd for $C_{14}H_6O_4F_6$: C, 47.74; H, 1.72. Found: C, 47.97; H, 2.40; ν_{max} (KBr) 1800, 1400, 1340, 1225, 1170, 1145, 1130, 1100, 905, 770 cm^{-1}.

1,3-*Bis(trifluoroacetoxy)naphthalene* (**16**), white crystals (81%), m.p. 35–36°C (hexane). Found: C, 47.07; H, 2.62; ν_{max} (KBr) 1800, 1400, 1350, 1235, 1170, 905, 750 cm^{-1}.

1,5-*Bis(trifluoroacetoxy)naphthalene* (**17**), colourless needles (84%), m.p. 80–81°C (hexane). Found: C, 46.96; H, 2.57; ν_{max} (KBr) 1795, 1395, 1350, 1235, 1210, 1140, 780 cm^{-1}.

1,7-*Bis(trifluoroacetoxy)naphthalene* (**18**), colourless needles (73%), m.p. 44–45°C (hexane). Found: C, 47.22; H, 2.44; ν_{max} (KBr) 1785, 1595, 1390, 1345, 1225, 1210, 1140, 780 cm^{-1}.

1,8-*Bis(trifluoroacetoxy)naphthalene* (**19**). The reaction mixture was taken up in hexane and filtered off any insoluble compound to give **19** as yellow oil (77%); ν_{max} (neat) 1788, 1608, 1580, 1413, 1360, 878, 823, 763 cm^{-1}.

2,7-*Bis(trifluoroacetoxy)naphthalene* (**21**), colourless needles (83%); m.p. 57–58°C (hexane).

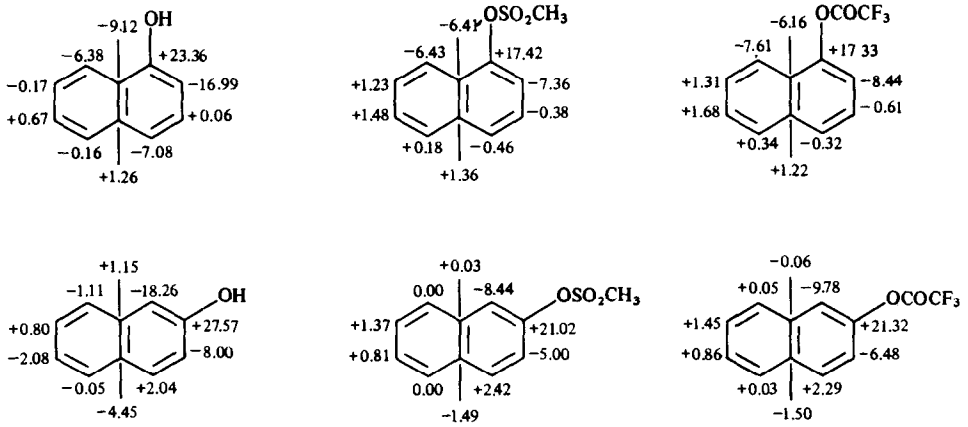
The carbon-13 NMR spectra were recorded on a Varian XL-200 NMR spectrometer, operating in the Fourier transform mode, with a digital resolution of 0.31 Hz at 50.3 MHz. The compounds were studied as 10 mole % solution in $CDCl_3$ or acetone-d_6 with TMS as internal standard. The spectra were obtained in the usual way with wide band proton decoupling or with single frequency off-resonance decoupling (SFORD) for the assignment of certain signals.

Spectral analysis

Assignment of C-13 NMR resonances of compounds **1–4** was achieved using known substituent induced chemical shifts for the hydroxyl group [3] and additivity rules. Mesyl derivatives of α-naphthol (**5**) and β-naphthol (**6**) showed ten and nine signals in the aromatic region respectively. The signal at 127.87 ppm in **6** is very strong indicating accidental degeneracy of two carbon resonances. The signals were assigned using SFORD spectra, known substituent effects, and comparing with lower number of signals observed for the mesyl derivatives of symmetrical diols. C-13 NMR signals of the dimesyl derivatives of diols, **7–13**, were assigned using SFORD spectra and substituent induced shifts for the mesyloxy group obtained from **5** and **6**. The C-13 NMR signals of the trifluoroacetyloxy compounds, **14–21**, were also assigned on the same basis as the mesyloxy derivatives. The assignment of the aromatic carbons for the compounds **1–21** is shown in Table 2. Substituent induced shifts for mesyloxy and trifluoroacetyloxy groups are shown in Scheme 1. Hydroxy group substituent induced shifts [3] are also shown in Scheme 1 for comparison.

Table 2. Carbon-13 NMR chemical shifts (ppm) for some substituted naphthalenes

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Solvent
1	155.27	101.61	156.71	101.61	126.71	127.38	122.37	122.92	121.12	136.86	Acetone-d_6
2	146.79	108.55	108.55	146.79	122.85	125.66	125.66	122.85	126.77	126.77	Acetone-d_6
3	152.65	108.99	123.78	119.87	129.98	119.22	155.37	104.65	127.18	130.73	Acetone-d_6
4	154.94	109.43	127.60	120.22	120.22	127.60	109.43	154.94	115.83	138.05	Acetone-d_6
5	145.29	118.42	125.40	127.41	128.05	127.26	127.01	121.44	127.11	134.88	$CDCl_3$
6	119.43	146.80	120.78	130.29	127.87	126.59	127.15	127.87	133.55	132.03	$CDCl_3$
7	145.34	114.19	145.84	119.04	128.11	128.38	127.82	121.75	125.89	134.18	$CDCl_3$
8	143.71	118.06	118.06	143.71	122.01	128.29	128.29	122.01	128.29	128.29	$CDCl_3$
9	145.16	119.56	126.80	121.03	145.16	119.56	126.80	121.03	128.67	128.67	$CDCl_3$
10	144.82	119.90	126.18	127.46	130.47	122.23	147.71	113.95	127.18	133.28	$CDCl_3$
11	142.62	121.80	128.08	126.48	126.48	128.08	121.80	142.62	120.55	136.98	$CDCl_3$
12	122.27	138.98	138.98	122.27	127.83	127.71	127.71	127.83	131.76	131.76	$CDCl_3$
13	119.38	147.64	121.59	130.24	130.24	121.59	147.64	119.38	133.90	130.49	$CDCl_3$
14	145.24	117.34	125.17	127.55	128.21	127.46	127.09	120.26	127.36	134.74	$CDCl_3$
15	118.09	147.10	119.30	130.16	127.90	126.64	127.23	127.92	133.46	132.02	$CDCl_3$
16	147.49	113.62	147.45	119.57	130.10	130.39	129.84	122.45	126.15	135.84	$CDCl_3$
17	145.10	118.69	126.83	120.00	145.10	118.69	126.83	120.00	127.04	127.04	$CDCl_3$
18	144.80	118.64	126.04	127.33	130.57	120.78	147.98	111.31	125.88	133.14	$CDCl_3$
19	144.33	109.74	127.56	121.87	121.87	127.56	109.74	144.33	121.39	133.98	$CDCl_3$
20	120.80	137.74	137.74	120.80	127.73	131.52	131.52	127.73	131.55	131.55	$CDCl_3$
21	118.21	147.98	120.25	130.25	130.25	120.25	147.98	118.21	133.79	130.55	$CDCl_3$



Scheme 1. Substituent induced chemical shifts (SCS) in $CDCl_3$ solution. SCS defined as δ (naphthalene derivative) $-$ δ(naphthalene).

RESULTS AND DISCUSSION

The dimesyloxynaphthalenes were prepared in moderate yields while excellent yields were obtained for trifluoroacetoxynaphthalenes. The trifluoroacetates are known to be extremely sensitive to hydrolysis [10]. To avoid contact with water, a convenient experimental procedure is developed (see Experimental). However, we were unable to trifluoroacetylate the 1,4-dihydroxynaphthalene. During work-up procedure the reaction mixture decomposes quickly into black materials.

It can be seen that mesyloxy and trifluoroacetoxy substituent effects are similar but differ much from that of the hydroxy (Scheme 1). There is a reduction in the oxygen lone pair donation to the naphthalene ring in mesyloxy and trifluoroacetoxy compounds, as these groups tend to hold the oxygen lone pair within itself by resonance. There is thus competition for the oxygen lone pair between the naphthalene ring and the mesyl (or trifluoroacetyl) group.

It is well known in naphthols that the mesomeric effect dominates the inductive effect. Hence, in naphthols, shielding of carbons is observed in five conjugated positions of the ring, as shown by the five canonical structures possible from the classical resonance theory. The C-8 position in α-naphthol is shielded, even though the canonical structures do not show negative charge on this carbon. This shielding of C-8 in all α-substituted naphthalenes is believed to be due to the γ-gauche interaction [11] of the oxygen atom. This

arises due to the polarization of the C–H bond caused by the steric interaction of the substituent in the α position. However, this polarization may also be attributed to direct electric field effects [1].

The shielding of carbons is observed to be always greater in the substituted ring (ring A) than in the other ring. This is due to the contribution of resonance structures with negative charge in ring A being more, as these structures leave the aromaticity undisturbed in ring B. Direct electric field effects along with steric factor may also contribute to the shielding of C-2 position in 1-substituted naphthalene as demonstrated

Table 3. Differences from the additivity rule for disubstituted naphthalenes (ppm)

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
	a	26.75	−24.90	30.20	−26.91	−1.81	0.87	−4.15	−5.60	−13.24	2.50
1	b	27.04	−25.09	29.95	−27.46	−1.91	0.66	−4.15	−5.78	−13.59	2.92
	c	−0.29	0.19	0.25	0.55	0.16	0.21	0.00	0.18	0.35	−0.42
	a	18.27	−17.96	−17.96	18.27	−5.67	−0.90	−0.90	−5.67	−7.59	−7.59
2	b	16.66	−17.28	−17.28	16.66	−5.99	−0.97	−0.97	−5.99	−7.16	−7.16
	c	1.61	−0.68	−0.68	1.61	0.32	0.07	0.07	0.32	−0.43	−0.43
	a	24.13	−17.52	−2.73	−8.65	1.46	−7.29	28.86	−23.87	−7.18	−3.63
3	b	23.74	−17.31	−2.47	−8.83	1.33	−7.12	28.29	−24.41	−7.02	−3.65
	c	0.39	−0.21	−0.26	0.18	0.13	−0.17	0.57	0.54	−0.16	0.02
	a	26.42	−17.08	1.09	−8.30	−8.30	1.09	−17.08	26.42	−18.53	3.69
4	b	19.71	−18.94	0.75	−9.05	−9.05	0.75	−18.94	19.71	−17.10	2.78
	c	6.71	1.86	0.34	0.75	0.75	0.34	1.86	6.71	−1.43	0.91
	a	17.47	−11.59	20.06	−8.83	0.24	2.60	2.04	−6.12	−7.63	0.66
7	b	19.84	−12.36	20.64	−8.90	0.18	2.85	2.04	−6.43	−7.90	1.39
	c	−2.37	0.77	−0.58	−0.07	0.06	−0.25	0.00	0.31	0.27	−0.73
	a	15.84	−7.72	−7.72	15.84	−5.86	2.51	2.51	−5.86	−5.23	−5.23
8	b	16.96	−7.74	−7.74	16.96	−6.43	2.71	−2.71	−6.43	−5.05	−5.05
	c	−1.12	0.02	0.02	−1.12	0.57	−0.20	−0.20	0.57	−0.18	−0.18
	a	17.29	−6.22	1.02	−6.84	17.29	−6.22	1.02	−6.84	−4.85	−4.85
9	b	17.60	−5.88	0.85	−6.89	17.60	−5.88	0.85	−6.89	−5.05	−5.05
	c	−0.31	−0.34	0.17	0.05	−0.31	−0.34	0.17	0.05	0.20	0.20
	a	16.95	−5.88	0.40	−0.41	2.60	−3.55	21.93	−13.92	−6.34	−0.24
10	b	17.42	−5.99	0.43	−0.46	2.62	−3.52	22.25	−14.87	−6.38	−0.13
	c	−0.47	0.11	−0.03	0.05	−0.02	−0.03	−0.32	0.95	0.04	−0.11
	a	14.75	−4.07	2.30	−1.39	−1.39	2.30	−4.07	14.75	−12.97	3.46
11	b	10.99	−7.74	2.71	−0.28	−0.28	2.71	−7.74	10.99	−12.82	2.72
	c	3.76	3.67	−0.41	−1.11	−1.11	−0.41	3.67	3.76	−0.15	0.74
	a	−5.60	13.20	13.20	−5.60	−0.16	1.93	1.93	−0.16	−1.76	−1.76
12	b	−6.02	16.02	16.02	−6.02	0.00	2.18	2.18	0.00	−1.46	−1.46
	c	0.42	−2.82	−2.82	0.42	−0.16	−0.25	−0.25	−0.16	−0.30	−0.30
	a	−8.49	21.86	−4.19	2.37	2.37	−4.19	21.86	−8.49	0.38	−3.03
13	b	−8.44	22.39	−4.19	2.42	2.42	−4.19	22.39	−8.44	0.06	−2.98
	c	−0.05	−0.53	0.00	−0.05	−0.05	0.00	−0.53	−0.05	0.32	−0.05
	a	19.42	−12.15	21.67	−8.30	2.23	4.61	4.06	−5.42	−7.37	2.32
16	b	19.62	−14.92	22.63	−10.10	0.39	3.13	2.17	−7.59	−7.66	1.16
	c	−0.20	2.77	−0.96	1.80	1.84	1.48	1.89	2.17	0.29	1.16
	a	17.23	−7.09	1.05	−7.87	17.23	−7.09	1.05	−7.87	−6.48	−6.48
17	b	17.67	−6.76	0.70	−7.93	17.67	−6.76	0.70	−7.93	−4.93	−4.94
	c	−0.44	−0.33	0.35	0.06	−0.44	−0.33	0.35	0.06	−1.54	−1.54
	a	16.93	−7.14	0.26	−0.54	2.70	−5.00	22.20	−16.56	−7.64	−0.38
18	b	17.38	−7.00	0.25	−0.29	2.63	−4.80	22.63	−17.39	−6.22	−0.28
	c	0.45	−0.14	0.01	−0.25	0.07	−0.20	−0.43	0.83	−1.42	−0.10
	a	16.46	−16.04	1.78	−6.00	−6.00	1.78	−16.04	16.46	−12.13	0.46
19	b	9.72	−7.13	1.07	0.02	0.02	1.07	−7.13	9.72	−12.32	2.44
	c	6.74	−8.91	0.71	−6.02	−6.02	0.71	−8.91	6.74	0.19	−1.98
	a	−7.07	11.96	11.96	−7.07	−1.95	3.68	3.68	1.95	−1.97	−1.97
20	b	−7.49	14.84	14.84	−7.49	0.08	2.31	2.31	0.08	−1.56	−1.56
	c	0.42	2.88	2.88	0.42	1.87	1.67	1.67	1.87	−0.41	−0.41
	a	−9.66	22.20	−5.53	2.38	2.38	−5.53	22.20	−9.66	0.27	−2.97
21	b	−9.73	22.77	−5.62	2.32	2.32	−5.62	22.77	−9.73	−0.12	−3.00
	c	0.07	−0.57	0.09	0.06	0.06	0.09	−0.57	0.07	0.39	0.03

a: experimental shift/naphthalene.
b: calculated shift from additivity/naphthalene.
c: $\Delta\delta = a - b$.

by the high field shift of C-2 carbon in 1-nitronaphthalene [7]. Deshielding of carbons in ring B is observed in mesyloxy and trifluoroacetoxy naphthalenes, indicating that the conjugation of oxygen lone pair by mesomerism is non-existent in the quinonoid positions in ring B. The deshielding is attributed to the inductive effect of the substituents. It has been shown [12] in naphthalenes and related systems, that electrostatic field induced π polarization is the dominant, if not exclusive, long-range mechanism transmitting the influence of inductive substituent effects. As expected, this effect is greater in trifluoroacetoxy derivatives than in the corresponding mesyloxy derivatives.

The validity of an additivity rule for carbon chemical shifts in naphthalenes has been examined. Important differences have been shown [7] to exist in the case of compounds where the substituents are sterically crowded or substituents *para* to one another. Table 3 shows the experimental chemical shifts relative to naphthalene in row a, calculated chemical shifts relative to naphthalene using additivity rule in row b and also any deviation from additivity rule given by equation 1 in row c:

$$\Delta\delta = \delta \text{ (expt)} - \delta \text{ (calcd)}. \quad (1)$$

A positive value for this difference $\Delta\delta$, signifies that the carbon is shifted lower field than that predicted from the additivity rule.

For the dihydroxynaphthalenes, the additivity rule is obeyed very well as shown by the low $\Delta\delta$ values, except for the C-1/C-8 positions in **4** which is displaced to lower field ($\Delta\delta > 0$). Steric crowding in the *peri* positions has been invoked to explain deviations in 1,8 disubstituted naphthalenes. However, the steric factor seems small in **4**. It is the removal of the γ-gauche interaction, by the removal of the hydrogen attached to carbons in these compounds that lead to the deviation. In fact the calculated difference is almost equal to the shielding of C-8 in the α-naphthol due to γ-gauche effect.

Dimesyloxy derivatives **7**–**13** strictly follow the additivity rule, except for 1,8 disubstituted derivative **11**. Steric interaction between the two *peri* substituents in **11** probably caused down field shifts of C-2/C-7. Whatever little mesomeric interaction of oxygen lone pair at C-2/C-7 is completely removed by the steric crowding of the two bulky mesyloxy groups, presumably rotating the oxygen lone pair away from conjugation with the aromatic ring. The fact that *para* disubstituted compound **8** follows the additivity rule also indicates that the mesyloxy group does not affect the resonance process [13]. Strangely, no deviation from additivity is observed for 2,3 mesyloxy naphthalene **12**, indicating less steric interaction between the groups *ortho* to each other, compared to *peri* interaction in 1,8-dimesyloxynaphthalene. So it seems that in **12** the conformation of the mono-substituted derivative is retained.

The bis(trifluoroacetoxy) derivatives follow the additivity rule except for **19** and **20** which show *peri* and *ortho* interactions respectively. Deshielding by 6.7 ppm of the *ipso* carbons (C-1/C-8) in **19** follows the pattern shown by the corresponding dihydroxy and dimesyloxy compounds, where the removal of γ-gauche interaction leads to the shifting of the *ipso* carbons down field. However, the appreciable shielding observed for the *ortho* and *para* carbons of **19** is puzzling. This may be explained if we invoke the introduction of mesomerism by which the oxygen lone pair is transmitted to *ortho* and *para* carbons, increasing shielding. This will be settled by a study of electrophilic substitution rates in these systems.

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