Reference Data

Substituent effects on ¹³C and ¹H chemical shifts in 2-isopropyl- and 2,6-diisopropylnaphthalene and their oxidation products

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ABSTRACT: ¹³C and ¹H spectral assignments were made for three 2-substituted- and six 2,6-disubstituted naphthalenes with isopropyl, 2-hydroxy-2-methylethyl and 2-hydroperoxy-2-methylethyl substituents by the use of proton–proton decoupling, 2D H,H-COSY and 2D-C,H-COSY techniques. The downhill simplex method was used for calculations of the best set of ¹³C and ¹H incremental shifts. An excellent additivity of substituent effects was found for both, the ¹³C and ¹H spectra of 2,6-disubstituted naphthalenes. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ¹³C NMR; ¹H NMR; naphthalene derivatives; substituent effects; incremental shift calculation; downhill simplex method

INTRODUCTION

2-Isopropylnaphthalene (1), 2,6-diisopropylnaphthalene (2) and their oxidation products (2-hydroxy-2-methylethyl and 2-hydroperoxy-2-methylethyl derivatives) are compounds of great interest for modern chemical technology. The oxidation of 2-isopropylnaphthalene and 2,6-diisopropylnaphthalene with oxygen in the liquid phase to the corresponding hydroperoxides 3, 6 and 8 is a key step



Compound	Х	Y
1	CHMe ₂	Н
2	CMe ₂ OH	Н
3	CMe ₂ OOH	Н
4	CHMe ₂	$CHMe_2$
5	CMe ₂ OH	$CHMe_2$
6	CMe ₂ OOH	$CHMe_2$
7	CMe_2OH	CMe ₂ OH
8	CMe ₂ OOH	CMe ₂ OOH
9	CMe ₂ OOH	CMe ₂ OH

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in new, environmentally safe syntheses of 2-naphthol,¹ 2-hydroxy-6-isopropylnaphthalene² and 2,6-dihydroxynaphthalene,³ which are important compounds for the production of dyes, agrochemicals, drugs, liquid-crystal materials and heat-resistant polymers. Alcohols **2**, **5**, **7** and **9** are by-products formed in the course of the oxidation of **1** or **4** by decomposition of the creresponding hydroperoxides, **7** also being a promising starting material for liquid-crystal chemistry.

Among the aforementioned compounds, only 2-isopropylnaphthalene is a relatively common compound, complete ¹³C and ¹H spectral assignments of which were made by Ernst and Schulz.⁴ Compounds **6** and **8** we have isolated for the first time only recently in our investigations on the oxidation of 2-isopropyl- and 2,6-diisopropylnaphthalene.⁵

The hitherto unknown compounds **5** and **9** are described for the first time in this paper. Taking into account the great practical importance of 2-isopropyl- and 2,6-diisopropylnaphthalene and their oxidation products, and also their possible derivatives, we report here their ¹³C and ¹H spectral assignments and the incremental shifts of the isopropyl, 2-hydroxy-2-methylethyl and 2-hydroperoxy-2-methylethyl substituents at position 2 of the naphthalene ring.

RESULTS AND DISCUSSION

Assignments of the ¹H and ¹³C NMR spectra were made by the use of proton–proton decoupling, 2D H,H-COSY and 2D C,H-COSY techniques (Tables 1 & 2). In the case of three very close signals of C-3, C-6 and C-7 in the ¹³C NMR spectrum of 2-isopropylnaphthalene (1) we applied the reliable assignments given by Ernst and Schulz based on the 2D INADEQUATE experiment.⁴

The downhill simplex method⁶ was used to calculate 30 ¹³C and 21 ¹H incremental shifts for the naphthalene ring. The algorithm based on this method proved to be effective in finding the set of incremental shifts which ensures the best fit of the experimental and the calculated chemical shifts (Tables 3 and 4). In general, the method consists in the multi-dimensional minimization of the function

$$F(Z_{j,k}) = \sum_{i} \sum_{j} (\delta_{i,j}^{e} - \delta_{i,j}^{c})^{2}$$

where $Z_{j,k}$ is the incremental shift brought about by the *k*-substituent to position *j* of the naphtahalene ring, $\delta_{i,j}^{e}$ is the experimental chemical shift for position *j* of the compound *i* and $\delta_{i,j}^{e}$ is the corresponding chemical shift calculated according to the equation

$$\delta_{i,j}^{\rm c} = \delta_j^{\rm n} + \sum Z_{j,k}$$

where δ_{i}^{n} is the chemical shift for position *j* of the naphthalene ring.

The standard deviations of the calculated values of the ${}^{13}C$ and ${}^{1}H$ chemical shifts in relation to the experimental data amount to 0.035 and 0.006 ppm, respectively. The ${}^{13}C$ and ${}^{1}H$ incremental shifts for the isopropyl group obtained based on the NMR spectra of 2-isopropylnaphthalene and three of its 2,6-derivatives are in good or even very good agreement with the values given by Ernst and Schulz,⁴ which were calculated for 2-isopropylnaphthalene only.

The results obtained demonstrate both an excellent additivity of effects of the substituents in 2,6-disubstituted naphthalene derivatives and the adequacy of the downhill simplex method for calculations of the incremental shifts.

EXPERIMENTAL

Spectra

NMR experiments were carried out on a Varian Unity INOVA-300 spectrometer operating at 300 or 75.5 MHz (for ¹H and ¹³C, respectively) using dilute solutions of the investigated compounds in $CDCl_3$ (10 mmol ml⁻¹) or saturated solutions of lower concentration in the case of poorly soluble compounds **7**, **8** and **9**. NMR spectra were referenced

Reference Data

Compound		Chemical shifts of naphthalene ring carbons											Х		Y	
No.		1	2	3	4	5	6	7	8	4a	8a	deviation ^a	С	Me	С	Me
1	Found	124.08	146.20	125.67	127.86	127.57	125.04	125.79	127.59	132.14	133.69		34.21	23.93		
	Calc.	124.08	146.30	125.74	127.82	127.57	125.03	125.77	127.58	132.07	133.65	0.049				
2	Found	122.35	146.41	123.52	127.84	127.43	125.66	126.01	128.10	132.24	133.12		72.62	31.62		
	Calc.	122.38	146.44	123.51	127.91	127.48	125.74	126.06	128.14	132.29	133.16	0.050				
3	Found	124.38	141.97	123.55	128.39	127.52	126.11 ^b	126.07 ^b	128.14	132.68	133.20		84.09	26.05		
	Calc.	124.41	141.97	123.62	128.41	127.54	126.18	126.16	128.17	132.71	133.22	0.048				
4	Found	123.78	145.53	125.70	127.52	123.78	145.53	125.70	127.52	132.26	132.26		34.18	23.98	34.18	23.98
	Calc.	123.77	145.51	125.69	127.52	123.77	145.51	125.69	127.52	132.26	132.26	0.012				
5	Found	122.06	145.67	123.47	127.61	123.68	146.25	125.97	128.06	132.47	131.74		72.66	31.66	34.18	23.94
	Calc.	122.07	145.65	123.46	127.61	123.68	146.22	125.98	128.08	132.48	131.77	0.018				
6	Found	124.11	141.10	123.52	128.09	123.73	146.69	126.14	128.09	132.88	131.79		84.09	26.04	34.20	23.92
	Calc.	124.10	141.18	123.57	128.11	123.74	146.66	126.08	128.11	132.90	131.83	0.040				
7	Found	122.00	146.38	123.76	128.20	122.00	146.38	123.76	128.20	132.01	132.01		72.71	31.72	72.71	31.72
	Calc.	121.98	146.36	123.75	128.17	121.98	146.36	123.75	128.17	131.99	131.99	0.019				
8	Found	124.07 ^c	142.37	124.00 ^c	128.71	124.07 ^d	142.37	124.00 ^d	128.71	132.49	132.49		84.12	26.08	84.12	26.08
	Calc.	124.07	142.33	123.97	128.70	124.07	142.33	123.97	128.70	132.47	132.47	0.025				
9	Found	124.03 ^e	141.90	123.93 ^e	128.68	122.05	146.78	123.82 ^e	128.22	132.43	132.06		84.11	26.09	72.74	31.72
	Calc.	124.01	141.89	123.87	128.67	122.04	146.80	123.85	128.20	132.41	132.05	0.026				

Table 1. Experimental and calculated ¹³C NMR chemical shifts (ppm) of 2-substituted and 2,6-disubstituted naphthalenes

^a The standard deviation for all compounds amounts to 0.035.

b,c,d,e The reverse assignment cannot be excluded.

Table 2. Experimental and calculated ¹H NMR chemical shifts (ppm) of 2-substituted and 2,6-disubstituted naphthalenes

	C	Chemical sl	hifts of naj	Standard	$X = CMe_2A^b$		$Y = CMe_2B^c$					
	1	3	4	5	6	7	8	deviation ^a	A ^b	Me	Bc	Me
Found	7.62	7.38	7.77	7.80	7.39	7.43	7.79		3.06	1.33		
Calc.	7.623	7.375	7.761	7.788	7.390	7.425	7.777	0.0080				
Found	7.90	7.57	7.79	7.79	7.43	7.43	7.80		2.10	1.63		
Calc.	7.896	7.570	7.788	7.793	7.431	7.438	7.803	0.0038				
Found	7.85	7.59	7.84	7.80	7.45	7.45	7.82		7.33	1.67		
Calc.	7.846	7.594	7.836	7.803	7.446	7.447	7.816	0.0037				
Found	7.58	7.34	7.71	7.58		7.34	7.71		3.03	1.31	3.03	1.31
Calc.	7.592	7.350	7.718	7.592		7.350	7.718	0.0101				
Found	7.87	7.55	7.75	7.61		7.37	7.75		2.03	1.64	3.05	1.33
Calc.	7.865	7.546	7.745	7.597		7.363	7.745	0.0072				
Found	7.82	7.58	7.79	7.62		7.38	7.76		7.46	1.67	3.05	1.32
Calc.	7.814	7.570	7.792	7.607		7.372	7.757	0.0080				
Found	7.87	7.56	7.77	7.87		7.56	7.77		1.81	1.62	1.81	1.62
Calc.	7.870	7.559	7.772	7.870		7.559	7.772	0.0013				
Found	7.83	7.59	7.83	7.83		7.59	7.83		7.27	1.65	7.27	1.65
Calc.	7.830	7.592	7.831	7.830		7.592	7.831	0.0013				
Found	7.81	7.58 ^d	7.82	7.87		7.56 ^d	7.78		7.35	1.65	1.85	1.62
Calc.	7.820	7.582	7.819	7.880		7.568	7.784	0.0069				
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^a The standard deviation for all compounds amounts to 0.006.

 b A = H, OH or OOH.

 $^{\circ}$ B = H, OH or OOH.

^d The reverse assignment cannot be excluded.

Table 3. Substituent effects on ¹³C chemical shifts in 2-substituted and 2,6-disubstituted naphthalenes

		Incremental shift ^a										
Substituent	1	2	3	4	5	6	7	8	4a	8a		
CHMe ₂ ^b CMe ₂ OH CMe ₂ OOH	-3.80 -5.50 -3.47	20.48 20.62 16.15	-0.08 -2.31 -2.20	-0.06 0.03 0.53	$-0.31 \\ -0.40 \\ -0.34$	$-0.79 \\ -0.08 \\ 0.36$	$-0.05 \\ 0.24 \\ 0.34$	-0.30 0.26 0.29	-1.39 -1.17 -0.75	$0.19 \\ -0.30 \\ -0.24$		

^a Relative to naphthalene: $\delta_1 = 127.88$, $\delta_2 = 125.82$, $\delta_{4a} = 133.46$. ^b The incremental shifts for the isopropyl group quoted by Ernst and Schulz⁴ are -3.79, 20.47, -0.09, -0.04, -0.32, -0.77, -0.02, -0.30, -1.35 and 0.22, respectively.

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Table 4. Substituent effects on ¹H chemical shifts in 2-substituted and 2,6-disubstituted naphthalenes

	Calculated incremental shift ^a											
Substituent	1	3	4	5	6	7	8					
CHMe ₂ ^b CMe ₂ OH CMe ₂ OOH	-0.197 0.076 0.027	-0.075 0.120 0.143	-0.059 -0.031 0.016	$-0.030 \\ -0.027 \\ -0.017$	$-0.059 \\ -0.018 \\ -0.006$	$-0.023 \\ -0.013 \\ -0.002$	-0.042 -0.018 -0004					

^a Relative to naphthalene: $\delta_1 = 7.82, \ \delta_2 = 7.45$.

^b The incremental shifts for the isopropyl group quoted by Ernst and Schulz⁴ are -0.20, -0.09, -0.07, -0.05, -0.07, -0.04 and 0.06, respectively.

to TMS. In the C,H-COSY experiments the relaxation delay was 1 s and the polarization and refocusing delays were 3.57 and 2.38 ms, respectively.

Materials

2,6-Diisopropylnaphthalene (4) (>99%, m.p. $68.8 \,^{\circ}$ C, lit.⁷ m.p. $69-70 \,^{\circ}$ C) and technical-grade 2-isopropylnaphthalene 1 (about 90%) were obtained from Rütgers Kureha Solvents (Duisburg, Germany). The technical-grade 2-isopropylnaphthalene was recrystallized a few times from methanol¹ at $-5 \,^{\circ}$ C to give the high-purity product (99%).

The preparation of 2-(2-hydroperoxy-2-methylethyl)-6-(2-methylethyl)naphthalene (6) and 2,6-di(2-hydroperoxy-2-methylethyl)naphthalene (8) was described in a previous paper.⁵

2-(2-Hydroxy-2-methylethyl)naphthalene (**2**) and 2-(2-hydroperoxy-2-methylethyl)naphthalene (**3**) were prepared according to the procedures given by Fieser and Chang⁸ and Kirichenko *et al.*,⁹ respectively. 2-(2-Hydroxy-2-methylethyl)-6-(2-methylethyl)naphthalene (**5**) was

2-(2-Hydroxy-2-methylethyl)-6-(2-methylethyl)naphthalene (5) was prepared by reduction of 2-(2-hydroperoxy-2-methylethyl)-6-(2-methylethyl)naphthalene **6** with Na₂SO₃. To a stirred solution of **6** (15 g, 61.4 mmol) in EtOH (120 ml) a solution of Na₂SO₃ (15.5 g, 123 mmol) in water (105 ml) was added dropwise at 40 °C during 1 h, the mixture was stirred at the same temperature for 2 h and water (105 ml) was added. The mixture was cooled to 5 °C and the crystalline product was filtered and washed with water (3 × 50 ml) to give the crude alcohol **5** (12.8 g, 92%). A sample of the crude product was recrystallized three times from hexane to give chromatographically pure **5**, m.p. 78–79 °C. Elemental analysis: calculated for C₁₆H₂₀O, C 84.16, H 8.83; found, C 84.56, H 9.16%. 2,6-Di(2-hydroxy-2-methylethyl)naphthalene (7) was prepared following the procedure described above for 5, starting from dihydroperoxide 8 (15 g, 54.3 mmol). The crude dialcohol 7 (11.55 g, 87%) was obtained. A sample of the crude product was recrystallized from EtOH–water (4:1, v/v) to give pure 7, m.p. 156–158 °C, lit.⁷ m.p. 156–159 °C.

2-(Hydroperoxy-2-methyl)-6-(2-hydroxy-2-methylethyl)naphthalene (9) was obtained by the catalytic oxidation of alcohol **5** in an alkaline water emulsion. To a thermostated glass reactor with a magnetic stirrer, connected with an oxygen container, alcohol **5** (9 g, 39.4 mmol), an aqueous solution of NaOH (9 ml, 0.3%), CuCN (0.0018 g) and palmitic acid (0.0082 g) were added. The oxidation was carried out with vigorous stirring at atmospheric pressure of oxygen at 90 °C for 27 h. The reaction mixture was extracted with toluene (18 ml), the organic layer was separated and left in a refrigerator at 5 °C for 48 h and the precipitated crystals were filtered. The crude hydroperoxide **9** (5,37 g), containing 86.5% of the product contaminated with dialcohol **7**, was recrystallized four times from toluene–propan-2-ol (10:1, v/v) to give the product of satisfactory purity (99%), m.p. 124–126.5 °C. Elemental analysis: calculated for C₁₆H₂₀O₃, C 73.82, H 7.74; found, C 73.86, H 7.76; O_{active}: calculated 6.15; found, 6.08%.

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