427. 3,7-*Dialkylnaphthalene*-1-*sulphonic Acids. Preparation, Properties, and Nuclear Magnetic Resonance Studies*

By D. C. F. GARBUTT, K. G. R. PACHLER, and J. R. PARRISH

Dialkylnaphthalenes in which both alkyl groups were n-hexyl, n-octyl, branched-chain octyl, n-decyl, or n-dodecyl have been prepared and shown to be the 2,6-isomers. From these the 3,7-dialkylnaphthalene-1-sulphonic acids have been made and characterised. Nuclear magnetic resonance data for these compounds and naphthalenesulphonic acids are reported. The substituent effects on the chemical shifts of the aromatic protons are derived and discussed.

THE commercial " dinonylnaphthalenesulphonic acid " has been used in studies of micelle formation in non-polar solvents,[1] and as a liquid cation-exchanger in studies of complex ions.[2] The substance is reported to be a mixture of isomers, and its equivalent weight may differ from the theoretical value.[3] We have prepared five pure 3,7-dialkylnaphthalene-1-sulphonic acids in order to study their behaviour as liquid ion-exchangers.

The straight-chain dialkynaphthalenes were made by acylation of the 2-alkylnaphthalenes and reduction of the ketones. The required 2-alkylnaphthalenes are well known,[4] and 2,6-dihexylnaphthalene has been reported previously.[5] Since the di-n-octyl, di-n-decyl, and di-n-dodecyl derivatives were made by the same method as the di-n-hexylnaphthalene, they were expected to be the 2,6-isomers too. This is supported by their ultraviolet spectra which are characteristic of 2,6-dialkylnaphthalenes and different from those of the 2,7-dialkylnaphthalenes.[6]

The branched-chain dioctylnaphthalene has been prepared before[7] by direct low-temperature alkylation of naphthalene with 1,1,3,3-tetramethylbutyl chloride. A β,β′-configuration was assigned to it on the basis of an *X*-ray crystallographic study. In this laboratory the same compound was obtained by low-temperature alkylation of naphthalene in nitrobenzene with 1,1,3,3-tetramethylbutyl bromide, but 1,1,3,3-tetramethylbutyl chloride under the same conditions gave a mixture of 2,6- and 2,7-di-t-butylnaphthalene. Its ultraviolet spectrum shows this dioctylnaphthalene to be 2,6-di-(1,1,3,3-tetramethylbutyl)naphthalene.

These 2,6-dialkylnaphthalenes were monosulphonated with chlorosulphonic acid at low temperature. Under these conditions 2,6-di-t-butylnaphthalene has been shown to give 3,7-di-t-butylnaphthalene-1-sulphonic acid,[8] and our compounds were expected to have the same structure. However, while this work was in progress the synthesis of 2,6-dioctyl- and 2,6-didodecylnaphthalene-1-sulphonic acid was reported.[9] These compounds were apparently made by the same method as we used, and the sulphonic group was assigned to the 1-position on the basis of their nuclear magnetic resonance spectra, which were not published. Insufficient data on these sulphonic acids are available for a comparison to be made with our sulphonic acids which were characterised by the preparation of their *S*-benzylisothiouronium salts and their *p*-toluidine salts. Our compounds have been proved to be 3,7-dialkylnaphthalene-1-sulphonic acids (2,6-dialkylnaphthalene-4-sulphonic acids) by the detailed nuclear magnetic resonance studies reported below.

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[1] S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, 1955, **10**, 139; 1957, **12**, 465.

[2] J. M. White, P. Tang, and N. C. Li, *J. Inorg. Nuclear Chem.*, 1960, **14**, 255.

[3] F. M. Fowkes, *J. Phys. Chem.*, 1962, **66**, 1843.

[4] J. P. Wibaut, K. Van Nes, and J. Stofberg, *Rec. Trav. chim.*, 1954, **73**, 501.

[5] B. Bannister and B. B. Elsner, *J.*, 1951, 1061.

[6] R. A. Friedel and M. Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

[7] D. N. Andreev and A. D. Petrov, *Zhur. priklad. Khim.*, 1948, **21**, 134.

[8] M. Menard, L. Mitchell, J. Komlossy, A. Wrigley, and F. L. Chubb, *Canad. J. Chem.*, 1961, **39**, 729.

[9] I. J. Heilweil, *J. Colloid Sci.*, 1964, **19**, 105.

Physical Properties

The water solubilities and emulsion clearing times (see Experimental section) for the sulphonic acid derivatives of the straight-chain dialkylnaphthalenes are collected in Table 1. Solutions of the sulphonic acids in xylene were used for the partition experiments.

Although 3,7-dihexylnaphthalene-1-sulphonic acid has a relatively high solubility in water and in the aqueous phase during partition, and it tends to increase the stability of the emulsion formed, the other compounds should be very suitable as liquid ion-exchangers. The relatively high absolute solubility of 3,7-dioctylnaphthalene-1-sulphonic acid is counteracted by the fact that it does not enter the aqueous phase to an appreciable extent during partition.

Table 1

Compound R-naphthalene-1-sulphonic acid	Water solubility (p.p.m.)	Emulsion clearing time (sec.)					Concentration in aqueous phase (p.p.m.)				
		pH 12·2	pH 10·4	pH 9·1	pH 7·6	pH 1·3	pH 12·2	pH 10·4	pH 9·1	pH 7·6	pH 1·3
R = 3,7-di-n-hexyl ...	>100	120	—	—	—	300	60	—	—	—	15
R = 3,7-di-n-octyl ...	100	105	90	100	90	90	1	2	1	<1	1
R = 3,7-di-n-decyl ...	13	60	75	75	90	150	5	7	3	4	2
R = 3,7-di-n-dodecyl	4	45	60	50	60	45	2	3	1	<1	2

Comparative figures for the branched-chain derivative could not be obtained owing to its very low solubility both as the free acid and the sodium salt in either aromatic or aliphatic hydrocarbons. Its absolute solubility in water was greater than 100 p.p.m. The solubilities of even the straight chain sulphonic acid derivatives in aliphatic solvents were remarkably low (<5%) when compared to the apparently high solubility [2] (at least 48% in heptane) of the commercial " dinonylnaphthalene sulphonic acid."

Nuclear Magnetic Resonance Studies

Naphthalene.—The spectrum of naphthalene in deuterochloroform (5 mole %) was recorded as a reference, and analysed on an A_2B_2 basis,[10] yielding the following parameters: $J_{1,2} = 8{\cdot}3$ c./sec.; $J_{1,3} = 1{\cdot}3$ c./sec.; $J_{2,3} - J_{1,4} = 6{\cdot}2$ c./sec.; $\tau_1 = 2{\cdot}20$; $\tau_2 = 2{\cdot}56$.

Wells [11] has shown that the coupling constant $J_{2,3}$ in dinitronaphthalene derivatives is 7·2 to 7·8 c./sec., and the analysis of naphthalene-1-sulphonic acid and naphthalene-1,5-disulphonic acid yielded $J_{2,3} = 7{\cdot}3$ c./sec. These coupling constants vary comparatively little with substitution. Thus the assumption that $J_{1,4} = 0$ c./sec.[10] does not seem to be justified. The coupling constant $J_{1,4}$ will more probably be near 1 c./sec.

The resonances of the low-field moiety (α-protons) of the naphthalene spectrum were considerably broadened, indicating inter-ring couplings ($J_{1,5}$ and $J_{4,8}$, respectively). This broadening of α-protons appeared to be a general feature of all spectra and has been utilised in the assignment of resonances. Such a long-range coupling $J_{4,8}$ of 0·8—0·9 c./sec. has been found in a 100 Mc./sec. nuclear magnetic resonance study of quinoline and its mononitro-derivatives.[12]

2,6-Dialkylnaphthalenes and their Sulphonic Acid Derivatives.—Table 2 summarises the nuclear magnetic resonance data for these compounds. The τ values for the aliphatic protons are included for completeness. Sulphonation of these compounds destroyed their symmetry leading to a doubling of some of their resonances, or a broadening if the separation was not great enough to be resolved.

The aromatic protons of dialkylnaphthalenes showed typical three-spin patterns and

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[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, " High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, pp. 147—149.

[11] P. R. Wells, *J.*, 1963, 1967.

[12] P. J. Black and M. L. Hefferman, *Austral. J. Chem.*, 1964, **17**, 558.

were analysed as ABX systems on the assumption that the *para-* and inter-ring couplings were negligible. The spectra of the monosulphonic acids were more complicated. The two protons of the sulphonated ring were shifted far towards lower field. They exhibited a characteristic *meta*-coupling of approximately 1·5 c./sec., proving that the sulphonic group had entered the 4-position. The three-spin system of the protons of the other ring was not much changed as compared to the spectrum of the corresponding dialkylnaphthalene.

To clarify the assignment of the two *meta*-coupled protons of the sulphonated ring we measured the spectra of the commercially available sodium salts of naphthalene-1,5- and naphthalene-2,7-disulphonic acids. Naphthalene-1,5-disulphonic acid showed a well separated ABC spectrum which was analysed by means of an IBM 704 electronic computer. In the three-spin spectrum of the napthalene-2,7-disulphonic acid, two of the protons happened to have almost equal chemical shifts. Thus the parameters derived are not as accurate. The results for both compounds appear in Table 3.

TABLE 2

		Chemical shifts of aromatic protons						Chemical shifts of aliphatic protons		
No.	Compound	τ_1	τ_3	τ_4	τ_5	τ_7	τ_8	Ar–CH_2–	–CH_2–	–CH_3
1	Naphthalene	2·20	2·56	$=\tau_1$	$=\tau_1$	$=\tau_3$	$=\tau_1$	—	—	—
2	2,6-Dihexylnaphthalene	2·47	2·74	2·31	$=\tau_1$	$=\tau_3$	$=\tau_4$	7·27 t; $J = 7·2$	8·2—8·8 *c*	9·12
3	2,6-Dioctylnaphthalene	2·46	2·72	2·35	$=\tau_1$	$=\tau_3$	$=\tau_4$	7·27 t; $J = 7·3$	8·2—8·8 *c*	9·13
4	2,6-Didecylnaphthalene	2·46	2·74	2·35	$=\tau_1$	$=\tau_3$	$=\tau_4$	7·27 t; $J = 7·1$	8·2—8·8 *c*	9·12
5	2,6-Didodecylnaphthalene	2·47	2·74	2·35	$=\tau_1$	$=\tau_3$	$=\tau_4$	7·27 t; $J = 6·9$	8·2—8·8 *c*	9·12
6	2,6-Di-t-butylnaphthalene	2·27	2·48	2·25	$=\tau_1$	$=\tau_3$	$=\tau_4$	—	—	8·59
7	2,6-Di-(1,1,3,3-tetramethyl-butyl)-naphthalene	2·29	2·49	2·29	$=\tau_1$	$=\tau_3$	$=\tau_4$	—	8·17	9·26 (3,3,4) 8·55 (1,1)
			τ_2			τ_6				
8	3,7-Dioctylnaphthalene-1-sulphonic acid	—	1·93	1·60	2·27	2·65	2·29	7·32 b, t; $J \sim 6·6$	8·2—8·8 *c*	9·15 9·20
9	3,7-Didecylnaphthalene-1-sulphonic acid	—	1·99	1·59	2·27	2·61	2·23	7·16, 7·28	8·2—8·8 *c*	9·09
10	3,7-Di-t-butylnaphthalene-1-sulphonic acid	—	1·80	1·46	*a*	*a*	*a*	—	—	8·78, 8·82
11	3,7-Di-(1,1,3,3-tetramethylbutyl)-naphthalene-1-sulphonic acid	—	1·69	1·40	2·18	2·43	2·13	—	8·17—8·21	9·29 9·36 (3,3,4) 8·55 8·58 (1,1)

a, Not resolved due to low concentration; *b*, broad; *c*, complex pattern; t, triplet.

TABLE 3

	Chemical shifts				
Compound	τ_1	τ_2	τ_3	τ_4	Coupling constants (c./sec.)
Naphthalene-1,5-disulphonic acid	--	1·66	2·15	1·02	$J_{2,3} = 7·3$; $J_{2,4} = 1·0$; $J_{3,4} = 8·7$
Naphthalene-2,7-disulphonic acid	1·53	—	2·00	2·02	$J_{1,3} = 1·5$; $J_{1,4} \sim 0$; $J_{3,4} = 8·6$

TABLE 4

Coupling constants

	Coupling constant (c./sec.)			Coupling constant (c./sec.)		
Compound No.*	$J_{1,3}$ (= $J_{5,7}$)	$J_{3,4}$ (= $J_{7,8}$)	Compound No.*	$J_{2,4}$	$J_{5,6}$	$J_{6,8}$
2	1·5	8·1	8	1·6	8·9	~1·5
3	1·8	8·6	9	1·6	8·6	1·7
4	1·5	8·4	11	~1·3	8·7	1·6
5	1·6	8·3				
6	1·7	8·7				
7	1·5	8·8				

* As listed in Table 2.

In naphthalene-1,5-disulphonic acid the proton in position 3 was identified by its two large *ortho*-couplings. It is clear from the results on naphthalene,[10,11] on dinitronaphthalenes,[11] and from the values in Table 4, that the α,β-coupling is always approximately 8·5 c./sec. and greater than the β,β-coupling, and that these couplings do not change appreciably with substituents. Thus we have assigned the low field proton to the 4-position. The assignment of the resonances in naphthalene-2,7-disulphonic acid is obvious from the magnitude of the splittings. In both compounds the hydrogen in position 4 exhibited further line-broadening attributed to inter-ring couplings ($J_{4,8}$).

Although a quantitative comparison of the nuclear magnetic resonance results for the sodium salts of the sulphonic acids in deuterium oxide solutions, with those obtained from chloroform solutions of dialkylnaphthalenesulphonic acids, is not possible, a qualitative idea of the substituent effect of the sulphonic acid group on the chemical shifts of the aromatic protons may be gained. The chemical shifts relative to the τ values of the 1- and 2-protons of naphthalene are given in the Figure.

The effect of the sulphonic acid group on the proton in the *peri*-position is small (—0·15 p.p.m.) as seen from the τ value of the proton in position 4 of the sodium salt of naphthalene-1-sulphonic acid ($\tau_4 = 1{\cdot}17$). Thus the substitution of a sulphonic acid group into the naphthalene ring shifts the nuclear magnetic resonances of the *o*- and *p*-protons appreciably to lower field, affecting the *p*-proton most. The shift of *m*-protons and the *peri*-effect are of less significance.

We have therefore assigned those resonances of the 3,7-dialkylnaphthalene-1-sulphonic acids at lowest field to the proton in position 4. The assignment is supported by the fact that these resonances show the characteristic line-broadening mentioned above.

Coupling constants.—The coupling constants observed agree well with those reported by other authors on similar systems (naphthalene,[10] mononitronaphthalenes,[11] and quinoline derivatives [12]). The α,β interactions are always found to be slightly larger than β,β interactions. It is known from *X*-ray analyses that the C_1–C_2 bond distance is considerably shorter than the C_2–C_3 distance (1·365 Å as compared to 1·404 Å). This is thought to be due to the increased double bond character of the C_1–C_2 bond.[13a] The nuclear magnetic resonance results may be explained on this basis.

Chemical shifts.—The chemical shifts of the aromatic protons of 2,6-dialkylnaphthalenes show in general a small high-field shift compared to naphthalene. A significant difference is observed for naphthalene derivatives with straight-chain and branched-chain substituents. The average relative shifts for each group are given in the Figure.

Zweig and his co-workers [14] have shown that for methoxybenzenes the chemical shifts of aromatic protons are linearly related to the π-electron density of the corresponding carbon atom obtained from Hückel molecular orbital calculations. The electron-releasing effect of an alkyl group attached to an aromatic ring is well known. Hence in the dialkylnaphthalenes an increased π-electron density resulting in a high-field shift of the proton resonances would be expected, but the observed high-field shift of branched-chain alkyl substituents is negligibly small. Since the inductive effect of these groups is greater than that of straight-chain alkyl groups, the observed high-field shift in naphthalene derivatives with straight-chain alkyl substituents must be attributed to hyperconjugation.

The average values for the effects of the introduction of a sulphonic group on the chemical shifts of the aromatic protons in dialkylnaphthalenes (straight- or branched-chain) are given in the Figure.

The detailed studies of nitronaphthalenes [11] and mononitroquinolines [12] have shown that in the interpretation of chemical shifts, inductive effects, electric field effects,[15] and magnetic anisotropy effects have to be considered as well as changes in π-electron density

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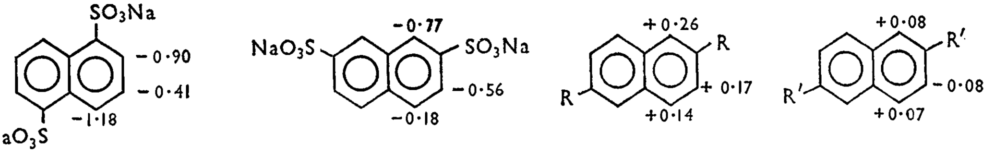
[13] R. T. Morrison and R. N. Boyd, " Organic Chemistry," Allyn and Baker, Boston, 1960, (*a*) p. 805, (*b*) p. 812.

[14] A. Zweig, J. E. Lehnsen, J. E. Lancaster, and M. T. Neglia, *J. Amer. Chem. Soc.*, 1963, **85**, 3940.

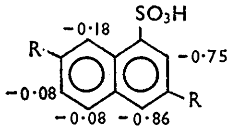
[15] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

due to mesomeric effects. The sulphonic acid group is a strongly electronegative, electron-withdrawing substituent, and the general low field shift of all protons (see Figure) indicates an overall decrease of the π-electron density of the naphthalene ring system. The pronounced low-field shift of the protons in positions 2 and 4 is interpreted as a decrease in π-electron density due to the mesomeric effect. It is well understood, by comparison of resonance structures and resonance energies, that the mesomeric effect only influences the ring to which the substituent is attached.[13b] It is, however, noteworthy that the chemical shift of the 4-proton is more affected than that of the 2-proton. To what extent the other two effects mentioned above influence the chemical shifts of these protons, and whether these effects are responsible for the relatively great low field shift of the proton in position 8, is difficult to assess.

Effect of Substituents on the chemical shifts of naphthalene protons



(Relative to naphthalene; R = straight-chain alkyl; R′ = branched-chain alkyl)



(Relative to alkyl naphthalenes; R = straight- and branched-chain alkyl)

Experimental

The nuclear magnetic resonance spectra of naphthalene, dialkylnaphthalene derivatives and their monosulphonic acids were recorded for dilute solutions ($\leqslant 5$ mole%) in deuterochloroform on a Varian A-60 spectrometer operating at 60 Mc./sec. (sample temperature 38°c), with tetramethylsilane as internal reference. The spectra of the sodium salts of the naphthalenesulphonic acids were determined for dilute solutions in deuterium oxide (100 mg./0·5 ml.) with sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal reference. The τ-values reported are estimated to be accurate to $\pm 0{\cdot}01$ p.p.m., and coupling constants to $\pm 0{\cdot}2$ c./sec.

6-Acyl-2-alkylnaphthalenes.—A solution of 2-alkylnaphthalene (0·2 mol.) and acid chloride (0·2 mol.) in nitrobenzene (150 ml.) was stirred and cooled to −5° while powdered aluminium chloride (0·23 mol.) was added in portions over a period of 60 to 100 min. The stirrer was replaced by a capillary bubbler and the reaction vessel was evacuated. After all the hydrogen chloride had been evolved the complex was decomposed with crushed ice. The organic layer was separated and washed with 2N-hydrochloric acid. The nitrobenzene was removed by steam distillation and the crystalline residue purified by recrystallisation from a suitable solvent. The following 6-acyl-2-alkylnaphthalenes were prepared by the above method:

6-Hexanoyl-2-hexylnaphthalene, 53% yield, m. p. 54—55° (lit.,[5] 55°).

6-Octanoyl-2-octylnaphthalene, 49% yield, m. p. 57° (methanol) (Found: C, 85·3; H, 10·7. $C_{26}H_{38}O$ requires C, 85·3; H, 10·4%); *2,4-dinitrophenylhydrazone*, m. p. 121·5—122° (ethanol) (Found: C, 70·6; H, 7·8; N, 10·3. $C_{32}H_{42}N_4O_4$ requires C, 70·4; H, 7·7; N, 10·3%).

6-Decanoyl-2-decylnaphthalene, 45% yield, m. p. 67·5—68° (ethancl) (Found: C, 85·5; H, 10·9. $C_{30}H_{46}O$ requires C, 85·3; H, 10·9%); *2,4-dinitrophenylhydrazone*, m. p. 120° (ethanol) (Found: C, 72·0; H, 8·6; N, 9·0. $C_{36}H_{50}N_4O_4$ requires C, 71·8; H, 8·3; N, 9·3%).

6-Dodecanoyl-2-dodecylnaphthalene, 47% yield, m. p. 76·5—77·5° (ethyl acetate) (Found: C, 85·6; H, 11·4. $C_{34}H_{54}O$ requires C, 85·4; H, 11·3%); *2,4-dinitrophenylhydrazone*, m. p. 119—119·5° (ethyl acetate) (Found: C, 72·9; H, 8·8; N, 8·4. $C_{40}H_{58}N_4O_4$ requires C, 73·0; H, 8·8; N, 8·5%).

2,6-*Dialkylnaphthalenes.*—(*a*) By the Huang-Minlon reduction procedure used by Bannister and Elsner [5] the following were obtained from the corresponding 6-acyl-2-alkylnaphthalenes:

2,6-Dihexylnaphthalene, m. p. 36—37° (ethanol at 0°) lit.,[5] 36·5—37°), $\lambda_{\text{max.}}$ 324 (ε 1300), 316·5 (ε 600), 309 (ε 1000), 303 (ε 600), 274 (ε 6100), and 230 mμ (ε 172,000) (in cyclohexane).

2,6-*Dioctylnaphthalene*, 55% yield, m. p. 43—44° (ethanol) (Found: C, 88·4; H, 11·3. $C_{26}H_{40}$ requires C, 88·6; H, 11·4%), $\lambda_{\text{max.}}$ 324 (ε 1500), 316·5 (ε 700), 309 (ε 1100), 303 (ε 1000), 274 (ε 6800), and 230 mμ (ε 169,000) (in cyclohexane).

(*b*) The Huang-Minlon reduction procedure of Asinger *et al.*[16] was modified as follows: after the reduction, all unchanged hydrazone and the azine that had formed, were converted back into the ketone without separation from the hydrocarbon, by heating on a steam-bath with 1 : 1 hydrochloric acid. The mixture was then reduced a second time and the hydrocarbon separated on silica gel by eluting with hexane. The following were prepared by this method from the corresponding 6-acyl-2-alkylnaphthalenes:

2,6-*Didecylnaphthalene*, 50% yield, m. p. 47—48° (ethanol) (Found: C, 88·3; H, 11·9. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%); $\lambda_{\text{max.}}$ 324 (ε 1300), 316·5 (ε 600), 309 (ε 900), 303 (ε 500), 274 (ε 6100), and 230 mμ (ε 167,000) (in cyclohexane).

2,6-*Didodecylnaphthalene*, 47% yield, m. p. 57—58° (ethanol) (Found: C, 87·8; H, 12·1. $C_{34}H_{56}$ requires C, 87·9; H, 12·1%); $\lambda_{\text{max.}}$ 324 (ε 1300), 316·5 (ε 600), 309 (ε 1000), 303 (ε 900), 274 (ε 5900), and 230 mμ (ε 151,000) (in cyclohexane).

2,6-*Di*-(1,1,3,3-*tetramethylbutyl*)*naphthalene.*—A solution of naphthalene (10·6 g.) in nitrobenzene (50 ml.) was cooled to −5° and with constant stirring was treated first with powdered aluminium chloride (1 g.) and then dropwise with 1,1,3,3-tetramethylbutyl bromide (32 g.) in nitrobenzene (30 ml.) over a period of 35 min. The reaction mixture was stirred at −5° for a further 25 min., a capillary bubbler fitted and the reaction vessel was evacuated for a further 60 min. Ice was added and the organic layer washed with water. The nitrobenzene was removed by steam distillation, leaving a crystalline mass (11 g.). Repeated recrystallisation from methanol yielded 2,6-di-(1,1,3,3-tetramethylbutyl)naphthalene (3·25 g.), m. p. 126°; $\lambda_{\text{max.}}$ 323 (ε 600), 316 (ε 300), 308 (ε 500), inflexion 302 (ε 400), 272 (ε 5300), and 232 mμ (ε 135,000) (in cyclohexane).

2,6-*Di-t-butylnaphthalene.*—Naphthalene (50 g.) in nitrobenzene (300 ml.) was cooled to 0° and was treated with stirring first with powdered aluminium chloride (10 g.) followed by 1,1,3,3-tetramethylbutyl chloride (116 g.) dropwise over a period of 2 hr. Stirring at 0° was continued for a further 2 hr. Ice was added and the organic layer washed with water. The nitrobenzene was removed by steam-distillation leaving an oil (100 g.). Thin-layer chromatography with hexane on silica gel showed the product to be a mixture of 2,6- and 2,7-di-t-butylnaphthalene, identical to a sample prepared according to Crawford and Glesmann.[17] No 2,6-di-(1,1,3,3-tetramethylbutyl)naphthalene was observed. A sample of 2,6-di-t-butylnaphthalene, m. p. 147—148°, was isolated from the mixture by crystallisation from methanol.

3,7-*Dialkylnaphthalene*-1-*sulphonic Acids.*—2,6-Dialkylnaphthalene (2 g.) in 1,2-dichloroethane (20 ml.) was cooled in ice and, with stirring, was treated dropwise with chlorosulphonic acid (1·1 mol.). The mixture was left to stand at 0° for 2 hr. The solvent was removed under vacuum and the oily residue treated with a few drops of water. The mass crystallised and was recrystallised from 1,2-dichloroethane. The following sulphonic acids were prepared by this method:

3,7-*Dihexylnaphthalene*-1-*sulphonic acid* (*monohydrate*), m. p. 67—68° (Found: C, 67·2; H, 8·9. $C_{22}H_{32}O_3S,H_2O$ requires C, 67·0; H, 8·6%); $\lambda_{\text{max.}}$ 327 (ε 2400), 318·5 (ε 1200), 312·5 (ε 1900), 280 (ε 6000), and 232 mμ (ε 80,200) (in ethanol); S-*benzylisothiouronium salt*, m. p. 178° (methanol–water) (Found: C, 66·3; H, 8·0; S, 12·1. $C_{30}H_{42}N_2O_3S_2$ requires C, 66·4; H, 7·8; S, 11·8%); p-*toluidine salt*, m. p. 222—223° (decomp.) (ethanol–water) (Found: C, 72·2; H, 8·5; S, 6·9. $C_{29}H_{41}NO_3S$ requires C, 72·1; H, 8·5; S, 6·6%).

3,7-*Dioctylnaphthalene*-1-*sulphonic acid* (*monohydrate*), m. p. 79—80° (Found: C, 69·5; H, 9·3; S, 7·3. $C_{26}H_{40}O_3S,H_2O$ requires C, 69·3; H, 9·3; S, 7·1%); $\lambda_{\text{max.}}$ 327 (ε 2200), 318 (ε 1200), 312·5 (ε 1800), 280 (ε 5800), and 232 mμ (ε 78,500) (in ethanol); S-*benzylisothiouronium salt*, m. p. 152—153° (methanol–water) (Found: C, 68·3; H, 8·6; S, 10·8. $C_{34}H_{50}N_2O_3S_2$ requires C, 68·2; H, 8·4; S, 10·7%); p-*toluidine salt*, m. p. 212—213° (decomp.) (ethanol–water) (Found: C, 73·6; H, 9·2; S, 6·1. $C_{33}H_{49}NO_3S$ requires C, 73·5; H, 9·1; S, 5·9%).

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3,7-*Didecylnaphthalene*-1-*sulphonic acid*, m. p. 115—116° (dried in vacuum at 100°) (Found: C, 73·6; H, 10·0; S, 6·6. $C_{30}H_{48}O_3S$ requires C, 73·8; H, 9·8; S, 6·6%); $\lambda_{max.}$ 327 (ε 2300) 318 (ε 1200), 312·5 (ε 1800), 280 (ε 6000), and 232 mμ (ε 81,700) (in ethanol); S-*benzylisothiouronium salt*, m. p. 132—133° (methanol–water) (Found: C, 69·6; H, 8·9; S, 10·0. $C_{38}H_{58}N_2O_3S_2$ requires C, 69·7; H, 8·9; S, 9·8%); p-*toluidine salt*, m. p. 194—195° (decomp). (ethanol–water) (Found: C, 74·7; H, 9·6; S, 5·7. $C_{37}H_{57}NO_3S$ requires C, 74·6; H, 9·6; S, 5·4%).

3,7-*Didodecylnaphthalene*-1-*sulphonic acid*, m. p. 117—118° (dried in vacuum at 100°) (Found: C, 75·1; H, 10·2; S, 6·0. $C_{34}H_{56}O_3S$ requires C, 75·0; H, 10·3; S, 5·9%); $\lambda_{max.}$ 327 (ε 2400), 318 (ε 1300), 312·5 (ε 1900), 280 (ε 6300), and 232 mμ (ε 86,500) (in ethanol); S-*benzylisothiouronium salt*, m. p. 132—133° (methanol–water) (Found: C, 70·9; H, 9·3; S, 8·9. $C_{42}H_{66}N_2O_3S_2$ requires C, 71·0; H, 9·3; S, 9·0%); p-*toluidine salt*, m. p. 182—183° (decomp.) (ethanol–water) (Found: C, 75·7; H, 10·0; S, 5·1. $C_{41}H_{65}NO_3S$ requires C, 75·6; H, 10·0; S, 4·9%).

3,7-*Di*-(1,1,3,3-*tetramethylbutyl*)*naphthalene*-1-*sulphonic acid*, m. p. 155—156° (dried in vacuum at 100°) (Found: S, 7·5. $C_{26}H_{40}O_3S$ requires S, 7·4%); $\lambda_{max.}$ 326 (ε 1400), inflexion 318 (ε 900), 311·5 (ε 1300), 279 (ε 5200), and 233 mμ (ε 73,400) (in ethanol); S-*benzylisothiouronium salt*, m. p. 223—224° (ethanol–water) (Found: C, 67·9; H, 8·7; S, 10·6. $C_{34}H_{50}N_2O_3S_2$ requires C, 68·2; H, 8·4; S, 10·7%); p-*toluidine salt*, m. p. 226° (decomp.) (ethanol–water) (Found: C, 73·2; H, 9·5; S, 6·1. $C_{33}H_{49}NO_3S$ requires C, 73·5; H, 9·1; S, 5·9%).

3,7-Di-t-butylnaphthalene-1-sulphonic acid (monohydrate), m. p. 159—160° (lit.,[8] m. p. 158°).

Physical Properties.—Solubilities of the sulphonic acids in water were determined spectroscopically using the ultraviolet absorption band at 232 mμ for concentrations less than 10 p.p.m., and the band at 280 mμ for concentrations greater than 10 p.p.m.

A 5% solution of each of the sulphonic acids in xylene was prepared. Each of these solutions was equilibrated as outlined below with the following solutions: 0·1N-sodium hydroxide at pH 12·1; 0·1N-sodium chloride at pH 10·4, 9·1, and 7·6; 0·1N-hydrochloric acid at pH 1·3.

The organic solution (10 ml.) in a 100-ml. cylindrical, graduated, separating funnel was treated with the aqueous solution (50 ml.). The separating funnel was stoppered and laid horizontally in a reciprocating box shaker. It was shaken for 10 min., removed and immediately clamped upright for the emulsion to separate. The time taken for complete separation of the two phases was recorded. The organic layer was completely clear. The aqueous layer, which was slightly cloudy due to small amounts of entrained material, was left to stand overnight for complete clarification. A sample of the aqueous layer was removed and its pH measured. The optical density of the aqueous layer was then determined using as a blank a sample of the same aqueous solution treated in the same manner with pure xylene.

NATIONAL CHEMICAL RESEARCH LABORATORY,
COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, P.O. BOX 395,
PRETORIA, SOUTH AFRICA.

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