Aromatic Sulphonation. Part 68.[1] Sulphonation of the Ten Dimethylnaphthalenes and 2-Methylnaphthalene: Isomer Distribution and Correlations with Molecular Orbital Theory †

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The isomer distribution for the mono- and di-sulphonation of 2-methylnaphthalene (2-MN) and all ten dimethylnaphthalenes (DMNs) with SO_3 in nitromethane as solvent have been determined at 0 and/or 12 °C. From the substitution pattern it is evident that steric factors play a more important role in the sulphonation than in most other electrophilic substitutions. In the disulphonations the substitution of the second sulpho-group occurs in part in the same ring as the first one. This may infer that the directing effect of the first (pyro)sulphonic acid group is relatively small. The positional order of substitution for the monosulphonation of a given substrate is in excellent agreement with that predicted by the localization energies, calculated by a simple Huckel m.o. treatment, utilizing the inductive model for the methyl substituent, provided that allowance is made for steric factors.

ELECTROPHILIC substitution of aromatic hydrocarbons † has been of interest to organic chemists for many decades. Extensive studies on the mechanistic aspects of nitration,[2] halogenation,[3] and sulphonation [4,5] have been performed. The recent discovery of *ipso*-attack aroused a renewed interest in this field.[2,3,6] Although most of the research studies have been restricted to benzene derivatives, some data are available for the alkyl substituted naphthalenes. Bromination with molecular bromine [7] and nitration with nitric acid in acetic anhydride [8] of the dimethylnaphthalenes (DMNs) have been reported and the additivity principle has been tested. A quantitative study of the cationic phenylation of symmetrical DMNs appeared recently.[9] The two methylnaphthalenes (MNs) and some DMNs have been iodinated with iodine–periodic acid.[10] Attempts have been made to correlate various appropriate m.o. parameters with the partial rate factors for bromination [7] and protium–deuterium exchange [11,12] and with the isomer distribution for chloromethylation of the DMNs.[11] Protonation with super acids of some DMNs has also been reported.[13]

Both because of the dearth of appropriate data on polycyclic aromatic compounds and as a continuation of our sulphonation studies [5b,14] it was thought of interest to sulphonate the MNs and DMNs. Recently we have reported the results of naphthalene [15] and 1-MN.[4] Now we report an extensive study on the isomer distributions of the aprotic sulphonation of 2-MN and the ten DMNs with SO_3 in nitromethane as solvent and on the correlation of the substitution pattern with the localization energies. On the sulphonation of these hydrocarbons only a very limited amount of information has appeared in the literature.

The sulphonation of 2-MN with sulphuric acid has been studied extensively.[16] Reaction with chlorosulphonic acid in nitrobenzene results in the formation of 2-methylnaphthalene-8-sulphonic acid,[17] whereas with chlorosulphonic acid in CCl_4 some of the 1-isomer is also formed.[18]

† For reasons of convenience, the aromatic ring positions of the sulphonic acids have been numbered as for the parent hydrocarbons.

Sulphonation with concentrated sulphuric acid of 1,2-, 1,6-, and 1,7-DMN [19] results in the formation of the 4-sulphonic acids. 2,3-DMN with sulphuric acid in CCl_4 at 40 °C results in the formation of the 5-sulphonic acid,[20] whereas at elevated temperatures without solvent the 6-sulphonic acid is formed.[21] As to the sulphonation of 2,6-DMN in 98% H_2SO_4 both the 1-sulphonic acid [22] and the 4-isomer [23] are reported as the main products. At 150 °C these products isomerize to the 3-sulphonic acid.[22,24] In 98% H_2SO_4 at 40 °C 2,7-DMN sulphonates mainly at the 3-position.[22]

2,6-Dialkylnaphthalenes (alkyl $\geqslant C_4H_9$) with chlorosulphonic acid yield the 4-sulphonic acids.[25,26] Sulphonation of 2,6-di-t-butylnaphthalene with two equivalents of chlorosulphonic acid leads to the formation of 2,6-di-t-butylnaphthalene-4,8-disulphonic acid;[27] the same product is obtained on starting with 2,7-di-t-butylnaphthalene.

RESULTS

The ten DMNs and 2-MN were monosulphonated with 1 equivalent of SO_3 in nitromethane at 0 and/or 12 °C, whereas the disulphonation of the DMNs was effected with 3 equivalents of SO_3 at 12 °C. The sulphonation products, obtained as sulphonates in D_2O, were assigned on the basis of ^1H n.m.r. spectroscopic results which are listed in Table 1.

The isomer distributions of the mono- and di-sulphonations of 2-MN and the ten DMNs are listed in Table 2, together with those for 1-MN reported previously.[4] Some of the disulphonations were still incomplete at the reaction temperature of 12 °C, *e.g.* the disulphonate mixtures obtained from 2,6-DMN still contained 13% 1- and 6% 4-sulphonic acid and that of 2,3-DMN 11% of the 5-sulphonic acid. At 0 °C nearly all disulphonations were incomplete. The temperature change from 0 to 12 °C had a marked influence on the isomer distributions for the monosulphonations of the β,β-DMNs, whereas those for *e.g.* 1,2-, 1,3-, 1,5-DMN were the same within 3% for the two temperatures. The isomer distributions of this aprotic sulphonation proved to be independent of the reaction time, illustrating that the isomer distributions are kinetically controlled.

The calculated values of the cation localization energies of naphthalene and its mono- and di-methyl derivatives, obtained by simple Hückel m.o. calculations using the

TABLE 1

^{1}H N.m.r. data of the mono- and di-methylnaphthalenesulphonates in D_2O

Naphthalene substituents	Position of SO_3^-	CH_3	CH_3	Ring position (δ) 1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H
2-Me	1	3.03				7.5(m) [a]	7.5(m) [a]	7.5(m) [a]	7.5(m) [a]	7.5(m) [a]	9.25(d,br)
	4	2.41		7.5(m) [a]		8.23(s,d)		8.95(d,br)	7.5(m) [a]	7.5(m) [a]	7.5(m) [a]
	5	2.36		7.5(m) [a]		7.5(m) [a]	8.85(d)		8.36(d,d)	7.5(m) [a]	7.5(m) [a]
	6	2.21		7.15(s,br)		7.04(d,br)	7.65(m) [a]	8.51(s,d)		8.08(d,d)	7.65(m) [a]
	8	2.68		8.75(s,br)		7.27(d,d)	7.69(d)	7.77(d,d)	7.50(t)	8.40(d,d)	
1,2-Me_2	4	2.19(1)	2.32(2) [b]			8.10(s)		8.91(d)	7.80(t)	7.57(t)	7.87(d)
	4,6	2.11	2.38 [c]			8.14 or 8.17(s)		9.42(s,d)		8.15(d,d)	8.01(d)
	4,7	2.43	2.38 [c]			8.14 or 8.17(s)		9.12(d)	8.35(d,d)		8.73(s,d)
1,3-Me_2	4	2.22(1)	2.89(3)		6.91(s)			9.21(d)	7.74(t,d)	7.39(t,d)	7.67(d)
	5	2.27(1)	2.54(3)		6.89(s)		8.55(s,br)		8.33(d,d)	7.6(m) [a]	7.6(m) [a]
	7	2.44(1)	2.08(3)		6.70(s)		7.6(m) [a]	7.6(m) [a]	8.02(d,d)		8.60(s,d)
	4,6	2.52(1)	2.94(3)		7.04(s)			9.80(s,d)		8.75(d,d)	8.60(m) [a]
	4,7	2.52(1)	2.94(3)		7.08(s)			9.38(d)	8.30(d,d)		8.63(s,d)
	5,7	2.53(1)	2.62(3)		7.06(s)		8.51(s,br)		8.81(s,d)		8.77(s,d)
1,4-Me_2	2	3.10(1)	2.45(4)			8.05(s)		7.40(m) [a]	7.25(m) [a]	7.25(m) [a]	7.88(m) [a]
	6	2.28(1)	2.54(4)		6.70(s)	6.70(s)		8.59(s,d)		8.10(m) [a]	7.80(m) [a]
	2,6	3.20(1)	2.82(4)			8.07(m) [a]		8.53(s,d)		8.07(m) [a]	8.07(m) [a]
	2,7	3.23(1)	2.72(4)			8.07(s)		8.02(d)	8.14(d,d)		8.78(s,d)
1,5-Me_2	2	3.10(1)	2.63 [c]			8.16(d)	7.67(d)		7.14(m) [a]	7.14(m) [a]	7.77(d,br)
	3	2.58	2.36 [c]		7.88(s,d)		8.46(s,br)		7.14(m) [a]	7.14(m) [a]	7.40(d,d)
	2,7	3.22(1)	2.63(5)			8.17(d)	7.66(d)		7.82(s,br)		8.55(s,br)
	2,6	3.09(1)	3.09(5)			8.14(d)	7.92(d)		8.14(d)	7.92(d)	
1,6-Me_2	4	2.42(1)	2.69(6)		7.20(d)	8.17(d)		8.70(s,br)		7.27(d,d)	7.65(d)
	2,4	3.20(1)	2.69(6)			8.95(s)		8.63(s,br)		7.29(d,d)	7.97(d)
	4,7	2.60(1)	3.20(6)		7.36(d)	8.34(d)		8.91(s,br)			8.76(s,br)
1,7-Me_2	4	2.38(7)	2.33(1)		7.15(d)	8.10(d)		8.80(d)	7.55(d,d)		7.56(s,d)
	2,4	3.17(1)	2.47(7)			8.87(s)		8.70(d)	7.57(d,d)		7.79(s,br)
	4,6	2.38(1)	3.06(7)		7.31(d)	8.18(d)		9.51(s)			8.19(s,br)
1,8-Me_2	4	2.70(1)	2.65(8)		7.26(d)	8.21(d)		8.93(d,br)	7.69(t)	7.34(d,br)	
	4,7	2.72(1)	3.25(8)		7.30(d)	8.22(d)		8.98(d)	8.49(d)		
	2,4	3.28(1)	2.75(8)			9.01(s)		8.81(d,d)	7.69(t)	7.32(m) [a]	
2,3-Me_2	1	2.28(2)	2.90(3)				7.38(s)	9.21(d)	7.60(m) [a]	7.60(m) [a]	7.60(m) [a]
	5	2.22(2)	2.51(3)	7.30(s)			8.61(s)		8.29(d,d)	7.50(t)	7.67(d)
	6	2.07(2)	2.07(3)	7.12(s)			7.37(s)	8.35(s)		7.98(d,d)	7.67(d)
	5,7	2.14(2)	2.46(3)	7.55(s)			8.58(s)		8.70(s,d)		8.58(s,d)
	1,5	2.85(2)	2.66(3)				8.92(s)		8.54(m)	7.87(t)	9.45(d,d)
	1,6	2.85(2)	2.20(3)				7.64(s)	8.43(s,d)		8.20(d,d)	9.35(d)
	1,7	2.95(2)	2.24(3)				7.35(s)	7.80(d)	8.06(d,d)		9.82(s)
2,6-Me_2	1	3.02(2)	2.43(6)			7.25(d)	7.4(m) [a]	7.4(m) [a]		7.4(m) [a]	9.05(d)
	4	2.47(2)	2.70(6)	7.45(s,br)		8.17(s,d)		8.64(s,br)		7.34(d,d)	7.53(d)
	4,8	2.81(2)	2.81(6)	8.95(s,br)		8.41(s,d)		8.95(s,br)		8.41(s,d)	
	1,5	3.03(2)	3.03(6)			7.71(d)	9.26(d)			7.71(d)	9.26(d)
	4,7	2.37(2)	3.19(6)	7.6(m) [a]		8.22(s,d)		8.83(s)			8.66(s)
2,7-Me_2	1	2.98(2)	2.66(7)			7.15(m) [a]	7.52(d)	7.52(d)	7.22(d,d)		8.94(s,br)
	3	2.91(2)	2.24(7)	7.19(s) [d]			8.53(s)	7.62(d)	7.05(m) [a]		6.93(s) [d]
	4	2.41(2)	2.38(7)	7.05(s,br)		8.11(s,d)		8.73(d)	7.15(m) [a]		7.57(s)
	1,6	2.94(2)	3.19(7)			7.19(d)	7.88(d)	8.65(s)			9.14(s)
	1,5	3.08(2)	2.83(7)			7.76(d)	9.02(d)		8.37(s,d)		9.23(s,br)
	3,5	3.02(2)	2.45(7)	7.42(s)			9.48(s)		8.13(s,d)		7.28(s,br)
	3,6	2.94(2)	2.94(7)	7.54(s)			8.72(s)	8.72(s)			7.54(s)

[a] Centre of unresolved multiplet. [b] The assignment of the methyl signals may be the reverse. [c] The assignment of the methyl signals to the isomers is unknown, except for δ 3.10 of 1,5-DMN-2-sulphonate. [d] The assignment of these protons may be the reverse.

inductive model for the methyl substituent with $\delta\alpha_r = -0.3$, are reported in Table 3.

DISCUSSION

Monosulphonation.—Sulphonation of 1,2-, 1,3-, 1,6-, 1,7-, and 1,8-DMN occurs predominantly at the 4-position. This is in accord with other well known electrophilic substitutions, such as bromination with molecular bromine [7] and chloromethylation,[11] except for 1,7-DMN which was not reported. The 4-position is substituted in the nitration of 1,2- and 1,3-DMN,[8] and in the succinoylation of 1,6- and 1,7-DMN.[28] The bromination of 1,6-DMN [8] was stated to occur equally fast at the 4- and 5-position, in contradiction to earlier reports.[29] The lower degree of 4-sulphonation of 1,3-DMN as compared with 1,2-, 1,6-, 1,7-, and 1,8-DMN is thought to be caused by steric hindrance, since the 4-position is known to be very reactive towards bromination,[7] nitration,[8,30] and protonation.[13] On acetylation [31] and succinoylation [32] of 1,3-DMN the 7-substituted product is formed.

Sulphonation of 1,8-DMN occurs exclusively at the 4-position. This is remarkable because the data for other electrophilic substitutions are diverse. For example, nitration with nitric acid in acetic anhydride is reported to occur exclusively at the 2-position, whereas with acetic acid as solvent 79% of the 4-nitro-derivative is found.[8] Protium–deuterium exchange indicates the 2- and 4-position to be of equal reactivity,[12] but later

protio-detritiation showed the 4-position to be more reactive.[33] Bromination with molecular bromine occurs almost exclusively at the 4-position,[7,34] whereas with hydrobromous acid in acetic acid 30% of the 2-bromo-derivative is found.[34] Upon sulphonation of 1,5-DMN the 2- and 3-sulphonic acids are formed in equal amounts. From studies on protonation with super acids [13] and on protium–deuterium exchange [12] it appears that the 4-position is the most reactive towards electrophiles.

Sulphonation of 1,4-DMN results in the formation of 87% 2- and 13% 6-sulphonic acid. It was established that in nitration the nitronium ion adds initially to the *ipso*-position, with the eventual formation of 1-methyl-4-nitromethylnaphthalene.[36] The bromination of 1,4-DMN is reported to exhibit the same kinetics as 1,5-DMN, and yields again substantial amounts of (structurally not assigned) acetoxy-products.[35] Protonation of 1,4-DMN with ' magic ' acid is reported to occur at the 2-position

TABLE 2

Isomer distributions of the mono- and di-sulphonations of the two MNs and the ten DMNs

Naphthalene substituents	Temp. (°C)	Isomer distribution (%) [a] Monosulphonation					Disulphonation [b]			
Rel 1-Me	0 and 12	4 (95)					2,4 (53)	4,6 (5)	4,7 (42)	
2-Me	0	1 (8)	4 (15)	5 (15)	6 (14)	8 (49)				
1,2-Me_2	0 and 12	4 (98)					4,6 (51)	4,7 (49)		
1,3-Me_2	0 and 12	4 (80)	5 (12)	7 (8)			4,6 (3)	4,7 (81)	5,7 (16)	
1,4-Me_2	0 and 12	2 (87)	6 (13)				2,6 (6)	2,7 (92)		
1,5-Me_2	0 and 12	2 (50)	3 (50)				2,6 (7)	2,7 (88)		
1,6-Me_2	12	4 (97)					2,4 (91)	4,7 (9)		
1,7-Me_2	0	4 (98)					2,4 (80)	4,6 (14)		
1,8-Me_2	0	4 (95)					1,4 (20)	4,7 (80)		
2,3-Me_2	0	1 (7)	5 (70)	6 (21)			1,5 (13)	1,6 (25)	1,7 (8)	5,7 (54) [c]
	12	1 (7)	5 (64)	6 (29)						
2,6-Me_2	0	1 (22)	4 (74)				1,5 (13)	4,7 (10)	4,8 (77) [d]	
	12	1 (22)	4 (74)							
2,7-	0	1 (40)	3 (38)	4 (22)			1,5 (33)	1,6 (47)	3,5 (12)	3,6 (8)
	12	1 (47)	3 (34)	4 (19)						

[a] The first datum gives the position(s) of the sulphonate substituents; the datum between brackets the relative yield in %. [b] The reaction temperature for the disulphonation is 12 °C. [c] The reaction mixture still contained 11% of the 5-sulphonic acid. [d] The reaction mixture still contained 6% 1- and 13% 4-sulphonic acid.

TABLE 3

Localization energies of naphthalene and its methyl derivatives

Naphthalene substituents	Ring position 1	2	3	4	5	6	7	8
	2.2985	2.4796						
1-Me	2.2985	2.3289	2.4813	2.1926	2.2708	2.4802	2.4408	2.3007
2-Me	2.1838	2.4796	2.4314	2.2999	2.2991	2.4414	2.4797	2.2702
1,2-Me_2	2.1838	2.3289	2.4428	2.1833	2.2673	2.4363	2.4385	2.2653
1,3-Me_2	2.2999	2.2922	2.4813	2.0904	2.2433	2.4803	2.4042	2.3018
1,4-Me_2	2.1926	2.3195			2.2675	2.4363		
1,5-Me_2	2.2708	2.3276	2.4407	2.1930				
1,6-Me_2	2.2991	2.2985	2.4814	2.1687	2.1614	2.4802	2.3976	2.3025
1,7-Me_2	2.2702	2.3274	2.4409	2.1906	2.2705	2.4351	2.4408	2.1833
1,8-Me_2	2.3007	2.2964	2.4828	2.1695				
2,3-Me_2	2.1928	2.4314			2.2796	2.4482		
2,6-Me_2	2.1815	2.4414	2.4314	2.2695				
2,7-Me_2	2.1610	2.4797	2.3959	2.3004				

Chloromethylation [11] yields the 4-substituted product. Upon nitration,[8] bromination,[7] and phenylation [9] all three isomers are formed, except the 3-nitro-derivative, but in different amounts. From the kinetics of the bromination it is evident that the proton removal from the σ-complex for 4-substitution is the rate-limiting step, indicating steric hindrance for this step.[35] This may also be concluded from the relative high yield of the additionally formed (structurally not assigned) acetoxy-compounds (40%).[35] The steric factor may explain the absence of the 4-sulphonic acid among the products. The relatively large amount of the 3-isomer may then be explained in terms of a 1,2-sulpho-shift in the initially formed σ-complex for 4-substitution (however see later).

followed by a 1,2-hydrogen shift and a 1,2-methyl shift to an equilibrium state.[13] However there is a total lack of confirmational evidence. Protium–deuterium exchange,[12] phenylation,[9] and chloromethylation [11] indicate the 2-position to be more reactive than the 5- and 6-position of the unsubstituted ring. Benzoylation gave mainly the 2-benzoyl derivative and acetylation led to mixtures of the 2- and 6-acetyl derivatives.[37]

Sulphonation of 2-MN with SO_3 in nitromethane occurs for 48% at the 8-position; the 4-, 5-, and 6-sulphonic acids are formed in equal amounts (*ca.* 14%). The low yield of the 1-sulphonic acid (8%) illustrates steric hindrance for the sulphonation, since the 1-position is, relatively, much more reactive towards protonation,[13]

nitration,[38] bromination,[7] and chloromethylation.[11,39] In the Friedel–Crafts acetylation all seven possible isomers are formed, and the isomer distribution depends on the experimental conditions.[40]

The three β,β-DMNs all sulphonate at all the unsubstituted positions, except for the 3-position with 2,6-DMN. Protonation with ' magic ' acid [6,13] and bromination [7] occur exclusively at the 1-position which is the position also mainly substituted upon nitration (73—82%).[8] Substitution at the 1-position is further predominant for succinoylation of 2,6- [41] and 2,7-DMN.[42] Apparently steric hindrance is important in the sulphonation process. This is demonstrated by the low degree of 1-substitution in the sulphonation of 2,3-DMN. The same observation was made for the acetylation and benzoylation of 2,3-DMN.[43]

The formation of 38% of the 3-sulphonic acid in the sulphonation of 2,7-DMN is interesting in view of the lack of 3-substitution with 2-MN and 2,6-DMN. The protium–deuterium exchange data for 2,6- and 2,7-DMN show a similar order of reactivity as for sulphonation, *viz.* for 2,6-DMN 1 > 4 > 3 and for 2,7-DMN 1 > 3 > 4.[12] A similar behaviour is observed for the Friedel–Crafts acylations which favour substitution at the 1-position, except for the acetylation of 2,6-DMN [31,44] and the acetylation of 2,7-DMN [45] both in solvents containing a nitro-group.[45] The former results in the predominant formation of the 4-acetyl derivative and the latter gives the 1- and 3-isomers in equal amounts.

Disulphonation.—The disulphonation of 1,2-DMN results in the formation of the 4,6- and 4,7-disulphonic acids, in equal amounts.

Upon treatment of 1,3-DMN with 3 equivalents of SO_3 in nitromethane the 4,7-disubstituted product is formed predominantly. In addition 16% of 1,3-DMN-5,7-$(SO_3H)_2$, containing two sulphonic acid groups in the *same* ring, is formed. This product results mainly from the 5-sulphonic acid.

Substitution of a second sulphonic acid group in the sulpho-containing ring is found to be the main process in the sulphonation of 1,6-DMN (91%) and 1,7-DMN (80%). This (unexpected) type of substitution also operates for 20% with 1,8-DMN, for which the main product is the 1,8-DMN-4,7-disulphonic acid (80%). Upon disulphonation of 2,3-DMN a substantial amount of the 5,7-disubstituted product is formed (54%). The formation of considerable amounts of these ' *meta* '-disulphonic acids is remarkable, since it is commonly accepted that electron-withdrawing substituents deactivate the ring to which they are attached more strongly than the other one; in this case substitution would be expected to take place at the most reactive position of the other ring.[46] In this respect it is further of interest that a substantial amount of the 2,4-disulphonic acid is formed upon sulphonation of 1-MN-4-SO_3H both in 95.0% H_2SO_4 (30%) and with SO_3 in nitromethane (53%),[4] and that reaction of acenaphthene-5-sulphonic acid in 95.2% H_2SO_4 leads to the formation of 28% of the 3,5-disulphonic acid.[47] In contrast, the nitration of 4-nitro-1,8-DMN [48] and 5-nitro-2,3-DMN [49] did not lead to substitution in the nitro-group-containing ring.

The disulphonation of 1,4- and 1,5-DMN results, mainly, in the formation of the 1,4- and 1,5-DMN-2,7-disulphonic acid respectively. The high selectivity in these sulphonation processes is thought to originate in the directive power of the (pyro)sulphonic acid group, possibly through 1,2-sulpho-shifts.

On disulphonation of 2,3-DMN four disulphonic acids are obtained of which the 5,7-isomer predominates. Dinitration of 2,3-DMN with nitric acid in acetic anhydride afforded the 1,4-, 1,5-, and 1,8-dinitro-derivatives in roughly equal amounts.[49] Diacetylation yielded 25% of the 1,5- and 1,6-disubstituted products in a ratio of 4 : 1.[43]

Upon disulphonation (81%) of 2,6-DMN the main product is the 4,8-disulphonic acid (77%) beside the 1,5- and 4,7-isomers, which are formed in 13 and 10% respectively. Diacetylation also afforded mainly the 4,8- and 1,5-disubstituted products.[44]

Four disulphonic acids are formed upon reaction of 2,7-DMN with 3 equivalents of SO_3 in nitromethane, the 1,5- and 1,6-isomers being the main products. In contrast, the diacetylation of 2,7-DMN yields the 1,3- and 1,5-isomers in equal amounts.[50]

Steric Hindrance towards α-Substitution.—Comparison of our sulphonation results with other electrophilic substitutions indicates that sulphonation at an α-position of the naphthalene skeleton is subject to steric hindrance. This was confirmed by the observation of a primary kinetic isotope effect, $k_H/k_D = 1.9$,[51] for the sulphonation at the 1-position of naphthalene. Apparently there is steric repulsion from the *peri*-hydrogen on formation of the sulphonic acid from the preceding σ-complex. The primary kinetic isotope effect for the aprotic sulphonation of naphthalene illustrates a reduction in the α-substitution as result of the rate-limiting character of the proton-removal step. The reduction in α-substitution is very pronounced if an adjacent β-methyl group is present, as in for example 2-MN and 2,3-DMN. If on formation of an α-sulphonic acid from the preceding σ-complex steric hindrance is encountered from the *peri*-hydrogen, then it is to be expected that introduction of a sulphonic acid group *peri* to an α-methyl or an α-sulpho-group will be impossible; this is, in fact, observed (Table 2).

Correlation with Molecular Orbital Theory.—There have been several attempts to correlate the various electrophilic substitutions with m.o. parameters.[52] For the dimethylnaphthalenes this was performed for chloromethylation,[11] bromination,[7] and protium–deuterium exchange.[12] Dallinga, Smit, and Mackor reported that the partial rate factors for protium–deuterium exchange in symmetrically substituted DMNs correlate with the relative change in electron density within the molecule induced by the two methyl groups,[12] using a simple Hückel m.o. treatment with the inductive model for the methyl substituent with $\delta\alpha_r = -0.3$. The rate constants for bromination by molecular bromine proved to

correlate best with a transition-state model.[7] The chloromethylation and Mackor's hydrogen-exchange rate data [12] could be excellently correlated with localization and superdelocalization energies calculated by the ω-technique.[11,53]

A comparison of the substitution pattern for the mono-sulphonation of the mono- and di-methylnaphthalenes with various parameters obtained by simple Hückel m.o. calculations, using the inductive model for the methyl substituent with $\delta\alpha_r = -0.3$, shows that the best correlation is found with the localization energies (Table 3). This is evident from the data for 1-MN and 1,2-, 1,3-, and 1,8-DMN which predict that the 4-position will be the most reactive one as is, in fact, observed.

Although for 1,6-DMN the lowest localization energies are those for the 4- and 5-positions, the values of which are roughly equal, sulphonation takes place, in fact, only at the 4-position. Both positions are, however, brominated with molecular bromine almost equally rapidly.[7] Apparently steric reasons diminish the degree of α-substitution adjacent to the 6-methyl group (*cf.* also section steric hindrance). This interpretation is substantiated by the sulphonation behaviour of 2-MN and 2,3-, 2,6-, and 2,7-DMN, since the localization energies predict the 1-position to be the most reactive which contrasts with that actually observed. The same holds for the sulphonation of 1,4-, 1,5-, and 1,7-DMN, all of which according to the localization energy criterion should have the α-position *peri* to a methyl substituent as the most reactive one, but at which, in fact, no sulphonation takes place.

Since steric repulsion plays a major role in the sulphonation of the methylnaphthalenes, we shall now elaborate on the observed isomer ratio in relation to the localization-energy differences due regard being given to steric hindrance. With naphthalene the β : α ratio for sulphonation (*viz.* 0.14 at 0 °C) is relatively large in comparison with most other substitutions mainly as a result of steric hindrance towards α-substitution. As an approximation the high β : α ratio may be directly correlated with the difference in the localization energies, $\Delta L_{\beta,\alpha}(=L_\beta - L_\alpha) = 0.1811$. On the basis of directly correlating the observed β : α ratios with the localization-energy differences some apparent anomalies can be rationalized, as will now be discussed.

TABLE 4

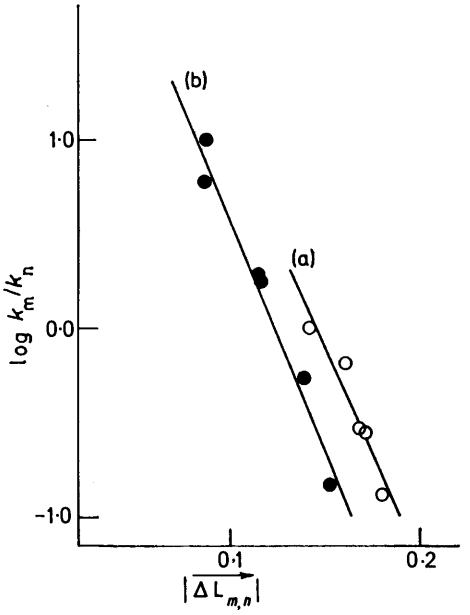
Selected β- to α-sulphonation ratios with the corresponding differences in localization energies of naphthalene and some methyl derivatives.[a,b]

Naphthalene substituents	(β : α) substitution positions	ratio	$\Delta L_{\beta,\alpha}$
	2 : 1	0.14	0.1811
2-Me	6 : 8	0.29	0.1712
2,3-Me_2	6 : 5	0.30	0.1686
1,3-Me_2	7 : 5	0.67	0.1609
2-Me	6 : 4	0.93	0.1415
2-Me	6 : 5	1.00	0.1423

[a] Compared are only the sterically 'unhindered' α- and β-positions of the naphthalene skeleton, *i.e.* those without an adjacent methyl group. [b] The compounds are listed in the order of increasing β : α substitution ratio.

In Table 4 the β : α ratios for sulphonation of the methylnaphthalenes are listed for 'unhindered' positions, *i.e.* positions which are sterically comparable with those of naphthalene. Actually [see Figure (a)] there is a linear correlation between $\log(k_\beta/k_\alpha)$ and $\Delta L_{\beta,\alpha}$ (slope −0.0451, intercept 0.145, cc 0.957). For positions with no adjacent methyl groups, the ratio of β- to α-substitution increases with decreasing $\Delta L_{\beta,\alpha}(=L_\beta - L_\alpha)$. Considering the steric hindrance for the sulphonation at the α-positions without adjacent methyls (see earlier), the linear correlation between $\log(k_\beta/k_\alpha)$ and $\Delta L_{\beta,\alpha}$ infers that this steric effect must be constant.

The degree of β-substitution is relatively decreased by the presence of an adjacent β-methyl substituent,



Plots of (*a*) $\log(k_\beta/k_\alpha)$ *vs.* $\Delta L_{\beta,\alpha}$ (see Table 4), and (*b*) $\log(k_\alpha/k_{\alpha'})$ *vs.* $\Delta L_{\alpha',\alpha}$ (see Table 5)

apparently as result of steric repulsion between the methyl and the incoming sulphonic acid group. There is, in fact, no substitution at the indicated position with 2-MN,* 1,6-, 1,7-, and 2,6-DMN for which $\Delta L_{3,4} = 0.1315$, $\Delta L_{7,4} = 0.2289$, $\Delta L_{6,4} = 0.2445$, and $\Delta L_{3,4} = 0.1619$ respectively. However with 2,7-DMN there is 39% of 3-sulphonation with a 3 : 4 substitution ratio of 1.8, $\Delta L_{3,4}$ being 0.0954.

Further, the degree of β-substitution decreases even more if the methyl group is present at an adjacent α-position. This is the result of enhanced steric hindrance due to the relatively short C_α–C_β bond length [for naphthalene C(1)–C(2): 1.361 Å *vs.* C(2)–C(3): 1.421 Å].[54] In fact there is no 2-sulphonation with 1-MN [4] and 1,6-, 1,7-, and 1,8-DMN, with $\Delta L_{2,4}$ equal to 0.1363, 0.1298, 0.1368, and 0.1269 respectively.

* Because of the limit of detection of the 3-sulphonic acid (*ca.* 3%) the 3 : 4 substitution ratio for sulphonation of 2-MN can be maximal 0.2.

Also the degree of α-substitution diminishes as a result of an adjacent β- or *peri*-methyl group. The relevant data of the methylnaphthalenes, possessing a β-methyl substituent, are presented in Table 5. The relatively

TABLE 5

Selected α- : α′-sulphonation ratios with the corresponding differences in localization energies of some methyl substituted naphthalenes [a,b]

Naphthalene substituents	(α : α′) substitution positions	ratio	$\Delta L_{\alpha',\alpha}$
2,3-Me_2	5 : 1	10.00	0.0868
2-Me	8 : 1	6.125	0.0864
2,6-Me_2	4 : 1	3.36	0.0880
2-Me	4 : 1	1.875	0.1161
2-Me	5 : 1	1.75	0.1153
2,7-Me_2	4 : 1	0.55	0.1394
1,3-Me_2	5 : 4	0.15	0.1528

[a] Compared are the α-positions with an adjacent (α′) and those without an adjacent β-methyl group (α) of the naphthalene skeleton. [b] The compounds are listed in the order of decreasing α : α′ substitution ratio.

unhindered α-positions (α) are compared with the α-positions having an adjacent β-methyl group (α′). The plot of $\log(k_\alpha/k_{\alpha'})$ *versus* $\Delta L_{\alpha',\alpha}$ [Figure (b)] is linear (slope −0.0414, intercept 0.122, cc 0.966). The lack of sulphonation at the 5-position with 1,6-DMN can now be understood considering that $\Delta L_{5,4} = 0.0073$. With 2,3-DMN the observed high ratio of 5- to 1-sulphonic acid (10) is, in part, due to a reduction in the degree of 1-substitution as result of the buttressing effect [4,55] caused by the two adjacent methyl groups at C(2) and C(3).

Sulphonation at an α-position *peri* to a methyl group does not occur with the MNs and DMNs; it is prevented for steric reasons. Thus, although the delocalization energies indicate the 8-position of 1,7-DMN to be the most reactive one, only the 4-sulphonic acid is formed exclusively, $\Delta L_{4,8}$ being 0.0073. Similarly with 1,4- and 1,5-DMN the reactive positions for electrophilic substitution are the unsubstituted α-positions, but in the sulphodeprotonation of each substrate only the two possible β-isomers are formed.

Selectivity.—From the previous section it is obvious that the substitution for sulphonation with SO_3 in nitromethane as solvent exhibits a high selectivity and that it strictly follows the reactivity order determined by the localization energies, provided that steric factors are taken into account. The high selectivity of the sulphonating reagent is also illustrated by the substitution pattern for sterically equivalent α-positions. This is evident from the exclusive 4-sulphonation (and thus the absence of 5-substitution) with 1-MN and 1,2- and 1,7-DMN for which $\Delta L_{5,4}$ is 0.1363, 0.0840, and 0.0799 respectively. The high selectivity of the sulphonating reagent is also apparent with 2-MN, which gives 48% of 8-substitution * and equal amounts (14%) of the 4- and 5-sulphonic acids ($\Delta L_{4,8} \approx \Delta L_{5,8} \approx 0.0293$).

* It can be argued that the 8-sulphonation is suppressed by a buttressing effect, caused by the *peri*-hydrogen and its adjacent methyl group at the 2-position. Such a view is in accordance with the correlation line of Figure (b). The same argument holds for the 4-substitution of 2,6-DMN where the effect is even more pronounced.

Isomerization.—The differences in localization energies $\Delta L_{6,2}$ for 1,4-DMN (0.1168) and $\Delta L_{3,2}$ for 1,5-DMN (0.1131) are nearly equal. The associated isomer ratios for sulphonation are, however, completely different, *viz.* 6.4 for the 2 : 6 ratio of the former and 1.0 for the 2 : 3 ratio of the latter one. This may indicate that the substitution process of 1,4- and 1,5-DMN is complicated by an isomerization process, *viz.* a 1,2-sulpho-shift in the respective σ-complexes. A direct comparison with the other substrates is impossible in view of the absence of β-sulphonation adjacent to an α-methyl group. However, information can be obtained from the 6 : 1 substitution ratio of 2-MN (1.75) for which $\Delta L_{6,1} = 0.2576$. From the Figure (a) it follows that the β : α substitution ratio is equal to 1 for $\Delta L_{\beta,\alpha} = 0.1449$. The same should apply if both the α- and β-position experience the same additional steric hindrance towards substitution. Thus changing the methyl group from the 1-position, as in (I) which gives some 2-sulphonation, to the 2-position as in (II) now with the same degree of 1-sulphonation

(I) (II)

should be accompanied with $\Delta L_{I,II} = 0.1449$, provided that the *peri*-buttressing effect of (I) may be neglected. The substitution ratio of an ' unhindered ' β-position over a β-position adjacent to an α-methyl group of 1.75 (see 2-MN) may now be correlated with a difference in localization energies of 0.1127 (0.2576 − 0.1449). The 3 : 2 sulphonic acid ratio 1.0 observed for 1,5-DMN with $\Delta L_{3,2} = 0.1131$ is in agreement with the former calculated values. These data seem to render the isomerization of the σ-complex at the 4-position highly improbable. Despite the fact that the 4-position of 1,5-DMN is the most reactive one, as is apparent from $\Delta L_{3,4} = 0.2477$ and $\Delta L_{2,4} = 0.1346$; attack at this position by SO_3 does not lead to sulphonic acid products.

Thus only the sulphonation of 1,4-DMN may be subject to isomerization reaction(s). The localization energies of 1,4-DMN predict the *ipso*-position to be the most reactive one towards electrophiles, as is, in fact, observed for nitration [36] and protonation.[6] In view of both the high reactivity of the 1-position and the possible 1,2-sulpho-shift in 1,4-DMN it may well be that the 2-sulphonic acid results (in part) from the *ipso*-σ-complex ($\Delta L_{2,1} = 0.1269$). It is hard to say whether the 6-substitution results from direct sulphonation or from initial formation of the σ-complex at the 5-position and a subsequent 1,2-sulpho-shift ($\Delta L_{6,5} = 0.1688$).

Disulphonation.—There are no suitable m.o. parameters for the sulphonic acid group available, and this renders a comparison of the disulphonic acid isomer ratio of the MNs and DMNs with, for example, the localization energies as yet impossible. A few remarks may, however, be made.

First, substantial amounts of disulphonic acids are formed in which the two sulpho-groups are contained in one and the same ring in a 1,3-orientation (see Table 2). This observation infers that the first (pyro)sulphonic acid group either deactivates both rings almost equally strongly, or that its deactivating power is only small.

Second, it can be questioned whether the deactivation of the (pyro)sulphonic acid group is mesomeric and/or inductive in character.[56,*] That it is not strongly mesomeric in character may be concluded from the behaviour of 1,6- and 1,7-DMN, which both yield mainly the 2,4-disulphonic acid. Apparently the sulphonation does not discriminate between the β-positions of the non-sulpho-group-containing ring. The non-discriminating behaviour is also observed with 1,2-, 2,3-, 2,6-, and 2,7-DMN. Disulphonation of 1,3-DMN, however, yields 80% of the 4,7-disubstituted product.

From the results it can be concluded that the disulphonation roughly follows the reactivity order, as predicted by the localization energies calculated for the unsubstituted DMNs with due obeyance of steric factors. This may infer that the deactivating effect of the (pyro)-sulphonic acid substituent with these compounds is relatively small.

In sharp contrast is the observation that the 2,7-disulphonic acid is the main product upon sulphonation of 1,4- and 1,5-DMN. The disubstitution of 1,5-DMN is especially illustrative, since the 2- and 3-monosulphonic acids are formed in equal amounts. However, the possibility of isomerizations through 1,2-sulpho-shifts from the preceding σ-complex upon disulphonation of these substrates cannot be excluded (*cf.* the discussion for the monosubstitution of 1,4-DMN).

Although there is confirmational evidence for the 'small' directing effect of the (pyro)sulphonic acid group in the isomer distribution of *meta*-substituted benzenesulphonic acids,[58,59] it is evident from our data that the extent to which this effect operates requires further study.

EXPERIMENTAL

Materials.—2-MN and the DMNs were commercially obtained ultra-grade products, and used without further purification.

Sulphonation Procedure.—To the desired MN or DMN (2 mmol) in nitromethane (7 ml) was added at 0 or 12 °C with stirring under dry nitrogen during 10 min a solution of SO_3 (1.7 or 6 mmol) in nitromethane (7 ml). After additional stirring for 45 min the reaction mixture was quenched with D_2O (3 ml) and the resulting suspension slowly heated in order to hydrolyse any (solid) sulphonic anhydride(s). After cooling the D_2O layer was separated, washed with methylene chloride, and bubbled through with nitrogen. The resulting solution was subjected to ^1H n.m.r. analysis.

^1H N.m.r. Analysis.—The structural assignments of the products were based on ^1H n.m.r. analysis with use of the double and triple resonance technique. The compositions of the reaction mixtures were determined by multicomponent ^1H n.m.r. analysis.[60] In some cases larger amounts of the sulphonation reagent and substrate were employed and H_2O instead of D_2O used to isolate the potassium sulphonates after neutralization. Repeated crystallization was then applied in order to enrich certain isomer(s) to facilitate the ^1H n.m.r. assignment and/or analysis.

The ^1H n.m.r. data are given in Table 1. The assignments were based on substituent shielding parameters, signal area ratios, and coupling constants. The spectra were recorded with Varian HA 100 and XL 100 spectrometers, using tetramethylsilane as external standard.

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* Recently it was established that the SO_3^- substituent exhibits a significant $-M$ effect in addition to the combined inductive and direct field effect.[57]

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