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AROMATIC SULPHONATION—80[1]
SULPHUR TRIOXIDE SULPHONATION OF SOME TRI- AND TETRA-METHYLNAPHTHALENES

HANS J. A. LAMBRECHTS and HANS CERFONTAIN*
Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

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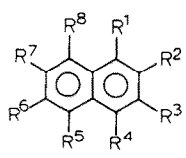
Abstract—1,2,3-Trimethylnaphthalene (1,2,3-Me_3N), 1,4,5-Me_3N, 1,6,7-Me_3N, 1,2,3,4-Me_4N, 1,4,5,8-Me_4N and 1,4,6,7-Me_4N have been sulphonated with SO_3 in nitromethane and the isomer distributions of the mono- and di-sulphonic acid mixtures, obtained by reaction with 1 equivalent of SO_3 at 0° and 3 equivalents of SO_3 at 12° respectively, are reported. The sulphodeprotonation isomer distribution follows the reactivity order predicted by the localization energies, provided that steric factors are taken into account, i.e. that sulphodeprotonations *peri* to a methyl and sulpho group do not occur. Disulphonation of 1,4,5-Me_3N and 1,4,5,8-Me_4N leads predominantly to the 3,6- and 2,7-disulphonic acid respectively, i.e. the "non-crossed" disulphonic acids.

Electrophilic aromatic substitution is an important area in the field of organic chemistry, and extensive reviews on the mechanistic aspects of nitration,[2] halogenation,[3] and sulphonation[4] are available. Recently we reported on the sulphonation of the ten dimethylnaphthalenes (Me_2N's) and showed[5] that the isomer distributions for the mono-sulphonation are in excellent agreement with those predicted by the localization energies, calculated by simple Hückel MO treatment, provided that steric factors were taken into account. Both because of the lack of appropriate data on the Me_3N's and Me_4N's and as an extension of our naphthalene sulphonation studies,[5,6] we have investigated the sulphonation of the compounds **1a–f**. No literature information is available on the sulphonation of **1a–f**.



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	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
a	Me	Me	Me	H	H	H	H	H
b	Me	H	H	Me	Me	H	H	H
c	Me	H	H	H	H	Me	Me	H
d	Me	Me	Me	Me	H	H	H	H
e	Me	H	H	Me	Me	H	H	Me
f	Me	H	H	Me	H	Me	Me	H

Compound sheet

RESULTS

The hydrocarbons **1a–f** have been sulphonated in nitromethane with both 1 equivalent at 0° and 3 equivalents of SO_3 at 12° to effect the mono- and di-substitution respectively. The assignments of the resulting sulpho products, obtained as sulphonic acids in D_2O, were based on the ^1H NMR data listed in Table 1. The isomer distributions for the mono- and disulphonation are listed in Table 2.

The cation localization energies of the polymethylnaphthalenes **1a–f**, calculated by the simple Hückel MO treatment using the inductive model for the methyl substitutent with $\delta\alpha_r = -0.3$, are collected in Table 3.

DISCUSSION

Monosulphonation

The monosulphonation of 1,2,3-Me_3N (**1a**) occurs predominantly at the 4-position (62%) and further with equal rate at the 5- and 7-positions. Also on bromination[7] and nitration[7] the 4-position is the most reactive one, and with chloromethylation[7] the 4-substituted product was the only one isolated in a yield of 86%. The monosulphonation of 1,4,5-Me_3N (**1b**) proceeds mostly at the 3-position (58%) and further with equal rate at the 2- and the 6-position. With 1,6,7-Me_3N (**1c**) exclusively the 4-sulphonic acid is formed, whereas on chloromethylation both the 4- and 5-substituted products are reported.[7]

Sulphonation of 1,2,3,4-Me_4N (**1d**) leads to the exclusive formation of the 6-substituted product, just like the Friedel–Crafts acetylation, benzoylation, and succinoylation.[8,a] Apparently the sulphonation and the acylation at the 5-position is prevented as result of steric hindrance by the *peri*-methyl group, as was also observed for the sulphonation of various Me_2N's.[5] Introduction of a sulphonic acid group at such an α-position would lead to a *peri*-strain which will be very much greater than that of the *peri* methyl–methyl interaction of 1,8-Me_2N which is reported to be 25 kJ/mol.[10] 1,4,5,8-Me_4N (**1e**) under monosulphonation conditions yields 92% of the 2-sulphonic acid, and already 6% of the 2,7-disulphonic acid.

[a]The predicted reactivity ratio for the 5- and 6-positions of **1d**, as calculated on the basis of the relative rates of protiodetritiation of the tritium substituted 1- and 2-methylnaphthalenes is, however, 99.6:0.4.[9]

Table 1. ^{1}H NMR chemical shifts (ppm) of the tri- and tetra-methylnaphthalenesulphonic acids in D_2O

Hydrocarbon	Position of SO_3^-	CH_3	CH_3	CH_3	CH_3	2-H	3-H	4-H	5-H	6-H	7-H	8-H
1,2,3-Me_3N	4	2.33(1)[a]	2.44(2)[a]	2.97(3)					9.27(d,d)	7.73[b]	7.73[b]	8.00[b]
	5	2.27[c]	2.24[c]	2.64(3)				8.60(s)		8.35(d,d)	7.73[b]	8.00[b]
	7	2.42[c]	2.24[c]	2.09(3)				7.20(br s)	7.73[b]	8.00[b]		8.60(d,d)
	4,6	2.28(1)	2.00(2)	2.89(3)					9.83(s)		8.75(d,d)	8.71(d)
	4,7	2.30(1)	1.98(2)	2.85(3)					9.39(d)	8.21(d)		8.21(s)
	5,7	2.48(1)	1.83(2)	2.08(3)				8.02(s)		8.46(br s)		8.02(s)
1,4,5-Me_3N	2	3.00(1)	2.60(4)[a]	2.41(5)[a]			7.88(s)			6.75(m)[b]	6.97(m)[b]	7.72(m)[b]
	3	2.65(1)[a]	3.15(4)	2.46(5)[a]		8.02(s)				6.91(m)[b]	7.06(t)	7.38(d)
	6	2.55(1)[a]	2.35(4)[a]	3.17(5)		6.70(br s)[a]	6.72(br s)[a]				8.15(d)	7.72(m)[b]
	2,6	3.02(1)[a]	2.89(4)	3.11(5)[a]								
	2,7	3.22(1)	2.72(4)	2.62(5)			7.94(s)			7.63(s)		8.62(s)
	3,6	2.62(1)	3.22(4)	3.26(5)		8.02(s)					8.21(d)	7.63(d)
1,6,7-Me_3N	4	2.60(1)[a]	2.60(6)[a]	2.41(7)[a]		7.31(d)	8.15(d)		8.67(s)			7.68(s)
	2,4	3.26(1)	2.55(6)	2.24(7)			8.90(s)		8.60(s)			7.86(s)
1,2,3,4-Me_4N	6	2.28(1)	2.01(2)[a]	1.96(3)[a]	2.10(4)				8.50(s)		7.94(d,d)	7.80(d)
1,4,5,8-Me_4N	2	3.12(1)	2.72(4)[a]	2.68(5)[a]	2.55(8)[a]		7.94(s)			6.76(d)[a]	6.84(d)[a]	
	2,6	3.04(1)	2.79(4)	3.04(5)	2.79(8)		7.96(s)				7.96(s)	
	2,7	3.13(1)	2.48(4)	2.48(5)	3.13(8)		7.85(s)			7.85(s)		
1,4,6,7-Me_4N	2	3.10(1)	2.53(4)	2.25(6)[a]	2.28(7)[a]		7.93(s)		7.34(s)			7.71(s)

[a] The assignment of these signals may be the reverse.

[b] Present in unresolved multiplet, centred at the given chemical shift.

[c] The assignment of these methyl signals to the 5- and 7-isomers in unknown.

Table 2. Isomer distribution of the mono- and di-sulphonic acids formed by sulphonation with SO_3 in nitromethane at 0 and 12°C respectively

Substrate	Isomer Distribution (%)[a] Monosulphonation			Disulphonation		
1,2,3-Me_3N	4(62)	5(19)	7(19)	4,6(23)	4,7(54)	5,7(23)
1,4,5-Me_3N	2(20)	3(58)	6(20)[b]	3,6(70)	2,7(24)	2,6(6)
1,6,7-Me_3N	4(100)[c]			2,4(100)		
1,2,3,4-Me_4N	6(100)[d]					
1,4,5,8-Me_4N	2(100)[e]			2,6(7)	2,7(93)	
1,4,6,7-Me_4N	2(100)[f]					
1,2,3-Me_3N-4-SO_3H	4,6(37)	4,7(63)				
1,2,3-Me_3N-5-SO_3H	5,7(100)					
1,2,3-Me_3N-7-SO_3H	5,7(21)	4,7(79)				
1,4,5-Me_3N-2-SO_3H	2,7(100)					
1,4,5-Me_3N-3-SO_3H	3,6(100)					
1,4,5-Me_3N-6-SO_3H	2,6(37)	3,6(63)				
1,6,7-Me_3N-4-SO_3H	2,4(100)					
1,4,5,8-Me_4N-2-SO_3H	2,6(7)	2,7(93)				

[a] The first datum gives the position(s) of the sulphonate substituent(s) and the one between brackets the yield in %.
[b] The reaction mixture contained ≃3% of the 3,6-disulphonic acid.
[c] The reaction mixture contained 96% of the 4- and 2% of the 2,4-di--sulphonic acid.
[d] Also with 3 equivalents of SO_3 only the 6-sulphonic acid was obtained.
[e] The reaction mixture contained in addition ≃ 6% of the 2,7-disulphonic acid.
[f] Also with 3 equivalents of SO_3 only the 2-sulphonic acid was formed.

Table 3. Localization energies of the tri- and tetra-methylnaphthalenes

Naphthalene substituents	Ring position 1	2	3	4	5	6	7	8
1,2,3-Me_3	1.8949	1.9815	2.1525	2.0935	2.2435	2.4364	2.4037	2.2685
1,4,5-Me_3	1.8751	2.3192	2.2851	1.9029	1.9877	2.2903	2.4371	2.1652
1,6,7-Me_3	1.9904	2.2982	2.4409	2.1693	2.1700	2.1441	2.1033	2.1927
1,2,3,4-Me_4	1.7836	1.9868			2.2327	2.3917		
1,4,5,8-Me_4	1.8730	2.2798						
1,4,6,7-Me_4	1.8744	2.2862			2.1650	2.1041		

Disulphonation

Disulphonation of **1a** yields mainly the 4,7-disulphonic acid (54%), besides equal amounts of the 4,6- and 5,7-isomers, that of **1b** gives predominantly the 3,6-disulphonic acid (70%) as well as the 2,6- and 2,7-isomer, whereas **1c** yields exclusively the 2,4-disulphonic acid. It is interesting that the second sulpho group enters with **1a** in part (23%) and with **1c** exclusively into the same ring as the first one. The relative amounts of these "meta-disulpho" isomers correlate extremely well with those obtained on disulphonation of 1,3-, 1,6- and 1,7-Me_2N.[5]

Under conditions for disulphonation, **1d** and **1f** only yield the 6- and 2-sulphonic acid respectively, illustrating that sulphodeprotonation at a β-position adjacent to a β-sulpho group does not occur. Disulphonation of **1e** yields predominantly the 2,7-disulphonic acid[b] with some of the 2,6-isomer.

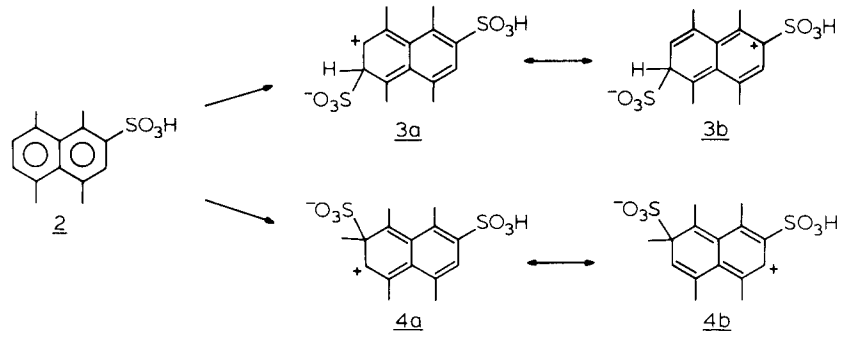
There is a strong preference for the formation of the "noncrossed" over the "crossed" disulphonic acid with **1b** and **1e**, which was also observed with 1,4-Me_2N and 1,5-Me_2N.[5,c] This preference may be explained in terms of the difference in energy content of the σ-complexes leading as intermediates from the monosulphonic acid, e.g. **2**, to the "non-crossed" and "crossed" disulphonic acid (Scheme 1). The stabilizing contribution to the respective σ-complex will be far less for **3b** than **4b** in view of the strong electron withdrawing effect of the sulpho group,[12] rendering the σ-complex leading to the "non-crossed" disulphonic acid more stable than that leading to the "crossed" one.

Correlation with Molecular Orbital Theory

The most reactive positions, as predicted by the localization energies, are the *ipso* (with the *ipso* α- more reactive than the *ipso* β-positions), followed by the unsubstituted α-positions (Table 3). However, products

[b] The 250 MHz ^{13}C NMR spectrum (D_2O) shows eight signals (at 143.2, 141.6, 139.3, 136.9, 136.7, 130.0, 27.4 and 24.3 ppm), illustrating that the carbon atoms 9 and 10 have different chemical shifts. This infers that the "non-crossed" isomer with C_s symmetry is formed.

[c] Also on disulphonation of 1,2,3,6,7,8-hexahydropyrene predominantly the "non-crossed" 4,10-disulphonic acid is formed.[11]



Scheme 1

that would result from sulphodemethylation and sulphodeprotonation *peri* to a methyl or a sulphonic acid group were never found for the SO_3 sulphonation in the benzene[13] and naphthalene[5,6b] series.[d,e]

Previously we reported that the logarithms of the sulphonation ratios for α- and β-positions without an adjacent methyl group ($\log k_\beta/k_\alpha$) and between an α'-position (i.e. with an adjacent β-methyl group) and an α-position devoid of such a group ($\log k_\alpha/k_{\alpha'}$) vary linearly with the differences of the localization energies $\Delta L_{\beta,\alpha}$ and $\Delta L_{\alpha',\alpha}$ respectively. For **1a** the isomer ratio for the positions 4:5:6:7, calculated on the basis of these correlations, is $70:17 < 1:13$ which is in good agreement with the observed one (Table 1). With **1b** sulphonation takes place at the 3-position, i.e. the most reactive one after the *ipso*-positions and the positions *peri* to Me and SO_3H. For **1c** $\Delta L_{3,4} = 0.2716$ and $\Delta L_{5,4} = 0.0007$ (Table 2). Thus[5] $\log(k_3/k_4) \ll -2$ or $(k_4/k_3) \gg 100$ and $\log(k_4/k_5) \gg 2$ or $(k_4/k_5) \gg 100$, and in fact with **1c** exclusively 4-substitution is observed.

Considering the restrictions for *ipso*- and *peri*-substitution (see before), sulphonation of the presently studied Me_4N's has to take place at the most reactive β-position(s), as is in fact observed.

Sulphonation of the monosulphonic acids of the Me_3N's and Me_4N's roughly follows the same reactivity order as predicted by the localization energies of the unsubstituted parent hydrocarbons, although the number of available positions, in view of the restrictions for *peri*- and *ipso*-substitution, is rather limited with these highly substituted naphthalenes.

Ipso-*attack and a subsequent* 1,2-*sulpho shift*

We have previously indicated that the 1,4-DMN-2-sulphonic acid might (in part) be formed from 1,4-DMN via another route than direct sulphodeprotonation, viz. by *ipso*-attack followed by a 1,2-sulpho shift in the *ipso*-σ-complex, and eventual removal of the carbon bonded proton from the resulting 2-σ-complex.[5] With **1b**, **1e** and **1f**, which substrates are structurally related to 1,4-DMN, such an alternative route is even more likely, as the $\Delta L_{2,1}$'s for 1,4-DMN, **1e** and **1f** are 0.1269,[5] 0.4068 and 0.4118 respectively and $\Delta L_{3,4}$ for **1b** is 0.3822. We have however no direct evidence in favour of this additional sulphonation route for these hydrocarbons.

It is of interest to note (i) that Fischer and Leonard[16] obtained *ipso*-nitration-adducts of several 1,4,5,8-tetraalkylnaphthalenes, and (ii) that Hart and Murray[17] proposed that the electrophilic oxidation of **1d** with peroxytrifluoroacetic acid proceeds by initial addition of the electrophile to the methyl substituted 1- and 2-positions, i.e. by *ipso*-attack.

EXPERIMENTAL

Materials. 1,2,3-Me_3N,[8] 1,4,5-Me_3N,[18] and 1,4,5,8-Me_4N[18] were prepared by known procedures. 1,6,7-Me_3N (Aldrich) was obtained commercially and used without further purification.

Sulphonation procedure, analysis and determination of the isomer distribution ratios. To a solution of the desired TMN (2 mmol) in nitromethane (7 ml) was added dropwise with stirring under dry nitrogen a solution of SO_3 (2 or 6 mmol) in nitromethane (7 ml) within 15 min. The reaction mixture was kept at 0° when using 1 equivalent of SO_3 (2 mmol) and at 12° when using 3 equivalents of SO_3 (6 mmol). With **1a** and **1b** the reaction mixtures are initially homogeneous and remain so during the sulphonation. With **1c–f** the mixtures are initially homogeneous, but after some time a precipitate of (part of) the resulting sulphonic anhydride(s) is formed. After an additional stirring for 15 min the reaction mixture was quenched with D_2O (3 ml) and slowly heated to ≈50° to hydrolyse any (precipitated) sulphonic anhydride(s). After cooling the two resulting layers were separated; the D_2O layer was washed with methylene chloride, freshly distilled from calcium chloride. Nitrogen was bubbled through the solution to remove the CH_2Cl_2 and the ^1H and ^{13}C NMR spectra of the resulting D_2O solution were recorded using Varian HA 100 and XL 100 spectrometers, and a Bruker WM 250 spectrometer respectively. The ^1H chemical shifts are relative to neat tetramethylsilane (capillary) as external reference and the ^{13}C chemical shifts are relative to sodium 4,4-dimethyl-4-silapentanoate as internal reference.

The isomer distribution ratios were determined by ^1H NMR multicomponent analysis.[19]

For the various monosulphonic acids as substrates, the sulphonation isomer ratios have been calculated from the compositions of the mono- and di-sulphonic acid mixtures, as described for 1,2,3-Me_3N as a typical example. 1,2,3-Me_3N-5-sulphonic acid only yields the 5,7-disulphonic acid. The additional 4% of this isomer in the disulphonic acid mixture then originates from the 7-SO_3H and the additional 15% of the 7-SO_3H forms the 4,7-$(SO_3H)_2$. The remaining 39% of the 4,7-$(SO_3H)_2$ thus originates from the 4-SO_3H which apparently yields (62-39) = 23% of the 4,6-$(SO_3H)_2$. The latter value agrees with the actually observed value of 23%. The sulphonation isomer ratios thus obtained were converted up to a total yield of 100%, as no other products than the disulphonic acids were found to be present.

[d] Sulphodeprotonation *peri* to a methyl group and sulphodemethylation were both observed in the SO_3-dioxan sulphonation of 2,7-dimethyl-1,6-methano[10]annulene[14] for which the $\alpha:\beta$ reactivity ratio is very much greater than that of naphthalene.[6a]

[e] The sulphonation of the methylanthracenes with SO_3 leads *only* to sulpho products resulting from initial *ipso*-attack (*viz.* sultones) in the case of 1,3-di- and 1,4,9-tri-methylanthracene.[1,15]

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