Aromatic Sulphonation. Part 70.[1] The Sulphuric Acid Sulphonation of α,ω-Diphenylalkanes, Biphenylene, Fluorene, 9,10-Dihydrophenanthrene, 10,11-Dihydro-5*H*-benzo[*a*,*d*]cycloheptene, and Triptycene

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The sulphonic acid isomer distribution for the sulphonation of α,ω-diphenylalkanes, biphenylene (2a), fluorene (2b), 9,10-dihydrophenanthrene (2c), 10,11-dihydro-5*H*-benzo[*a*,*d*]cycloheptene (2e), and triptycene (3) with concentrated aqueous and with fuming sulphuric acid at 25 °C has been determined by multicomponent ^{1}H-n.m.r. analysis. With $Ph[CH_2]_nPh$ in 95.4% H_2SO_4 the degree of *ortho*-substitution increases with increasing length of the alkylidene chain to reach for $n \geqslant 4$ the same limiting value as observed for the 1-phenylalkanes ($Ph[CH_2]_nMe$) with $n \geqslant 3$. Further sulphonation of the α,ω-bis(sulphophenyl)alkanes yields the *o,o',p,p'*-tetrasulphonic acids.

Sulphonation of (2a) and biphenylene-1-sulphonic acid in 98.4% H_2SO_4 yields the 2,6- and 1,6-(or 1,7-)disulphonic acid respectively.

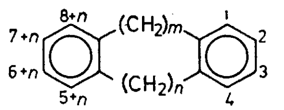
The sulphonation of (2b), (2c), and (2e) in 95.3—98.3% H_2SO_4 leads to a mixture of disulphonic acids, that of (3) to a mixture of trisulphonic acids, all containing one sulpho-group per phenylene. The isomer distribution for the monosulphonation of (2b) has been estimated from the disulphonic acid isomer composition. For (2c), (2e), and (3) the substitution ratio per phenylene has been estimated.

The isomer distributions of the tri- and of the tetra-sulphonic acid mixtures obtained from (2b), and of the tetrasulphonic acid mixture formed from (2e) have also been determined.

THE sulphonation of aromatic hydrocarbons has been the subject of numerous studies and reviews have appeared up till 1971.[2] Since that time we have reported extensively on the sulphonation of alkylated benzenes.[3] In one of the studies on the monoalkylbenzenes [3b] which dealt with the dependence of the *ortho*-substitution on both the size and the branching of the alkyl group, evidence was obtained for conformational control of the *ortho*-sulphonation. We considered it worthwhile to extend that study and we therefore now report on the sulphonation of α,ω-diphenylalkanes (1), polyhydrodibenzocycloalkanes (2), and triptycene (3). On the sulphonation of biphenyl [*i.e.* (1) with $n = 0$] we reported very recently.[3e]

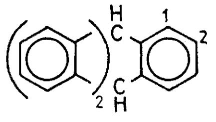
$Ph—(CH_2)_n—Ph$

(1)



(2)

a: *m*=*n*=0
b: *m*=1; *n*=0
c: *m*=2; *n*=0
d: *m*=*n*=1
e: *m*=2; *n*=1



(3)

RESULTS AND DISCUSSION

α,ω-*Diphenylalkanes*.—The sulphonation of α,ω-diphenylalkanes (1) in 95.4% H_2SO_4 at 25.0 °C leads to the formation of bis(sulphophenyl)alkanes. The content of *ortho*-sulphonic acid groups under conditions of homogeneous sulphonation was obtained as described before.[2d] The results are presented in Table 1. The Σ*ortho*/Σ(*ortho* + *meta* + *para*) ratio increases with increasing length of the polymethylene chain to reach eventually a limiting value which is the same as that observed for alkylbenzenes with a long linear side-chain (Figure). Up to $n = 4$ the *ortho*-content still appears to be lower than that of the corresponding 1-phenylalkane.

TABLE 1

Sulphonation of α,ω-diphenylalkanes in 95.4% H_2SO_4 at 25.0 °C

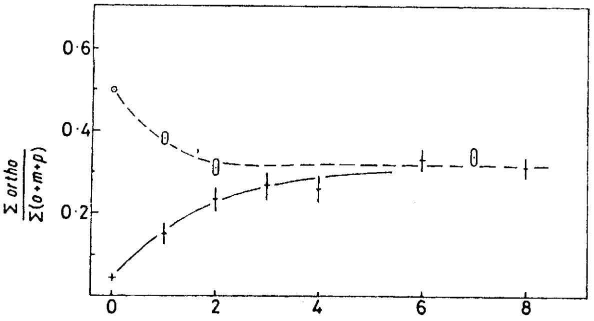
Substrate	Addendum	$\frac{\Sigma\ ortho}{\Sigma(o+m+p)}$ [a,b]	Ref.
PhPh		0.044 ± 0.002	3*e*
$PhCH_2Ph$		0.15 ± 0.02	3*d*
$Ph(CH_2)_2Ph$		0.23 ± 0.03	
$Ph(CH_2)_2Me$		0.31 ± 0.02	3*d*
$Ph(CH_2)_3Ph$		0.27 ± 0.03	
$PhCH_2CHMeCH_2Ph$		0.26 ± 0.03 (0.27 ± 0.01)	
$PhCH_2CHMe_2$		0.266 ± 0.01	3*d*
$Ph(CH_2)_4Ph$		0.26 ± 0.03	
	5 vol.% CF_3CO_2H	0.23 ± 0.02	
	30 vol.% CF_3CO_2H	0.12 ± 0.01	
$Ph(CH_2)_6Ph$		0.33 ± 0.03	
$Ph(CH_2)_8Ph$		0.31 ± 0.03	
$Ph(CH_2)_7Me$		0.34 ± 0.02	3*d*

[a] Σ *ortho*/Σ(*o* + *m* + *p*) ≡ (2 *o,o'* + *o,m'* + *o,p'*)/(2 *p,p'* + 2 *m,p'* + 2 *m,m'* + 2 *o,p'* + 2 *o,m'* + 2 *o,o'*). [b] The datum between brackets was determined from the aromatic hydrogen pattern (see Experimental section).

The degree of *ortho*-substitution of 2-methyl-1,3-diphenylpropane is the same as that of both 1,3-diphenylpropane and isobutylbenzene within experimental error.

As exemplified with 1,4-diphenylbutane the *ortho*-sulphonic acid content decreases on addition of trifluoroacetic acid to the sulphuric acid medium. This behaviour of addenda on the degree of *ortho*-substitution is general and has been studied in detail with toluene.[3a]

The α,ω-bis(sulphophenyl)alkanes in 95.4% H_2SO_4 were further sulphonated by addition of sulphur trioxide. The ^{1}H-n.m.r. spectra of the resulting 104% H_2SO_4 solutions eventually all exhibited an aromatic ABX pattern. The ratio of the area of the aromatic and aliphatic signals further revealed the presence of only three aromatic hydrogens per phenyl ring. The spectra were therefore assigned to the *o,o',p,p'*-tetrasulphonic acids.



Degree of *ortho*-substitution in the sulphonation of $Ph(CH_2)_nX$; X = Ph (+ —— +), X = Me (⊙ —— ⊙)

Polyhydrodibenzocycloalkanes (2).—A compilation of the isomer distribution for the mono- or di-sulphonation of some of the polyhydrodibenzocycloalkanes (as subsequently reported for the individual hydrocarbons in this section) is given in Table 2.

TABLE 2

Isomer distribution for the sulphonation of some polyhydrodibenzocycloalkanes (2) and triptycene (3) in concentrated aqueous sulphuric acid at 25 °C

Substrate	% H_2SO_4	Type of sulphonation	Substitution ratio (%)				Remarks
			1-	2-	3-	4-	
(2a)	89.9	mono	$\leqslant 1$	$\geqslant 99$			*a*
(2b)	98.3	mono	3 ± 1	73 ± 5	5 ± 2	19 ± 3	*a*
(2c)	98.3	di	16 ± 3	53 ± 3	30 ± 3	$\leqslant 2$	*b*
(2e)	95.3	di	13 ± 2	12 ± 3	51 ± 4	24 ± 3	*b*
(3)	98.3	tri	9 ± 2	91 ± 2			*b*

[a] Estimated from the disulphonic acid isomer composition. [b] Substitution ratio per phenylene

Biphenylene (2a).—The sulphonation of (2a) in 89.9% H_2SO_4 at 25 °C for 30 days leads to the formation of a disulphonic acid which is either the 2,6- or the 2,7-isomer. The dinitrobiphenylene obtained on nitration of (2a) with nitric acid in 72% H_2SO_4 was assigned unambigiously to be the 2,6-isomer;[4] it is highly likely, therefore, that in the sulphonation also the 2,6-isomer is formed.

Sulphonation of potassium biphenylene-1-sulphonate in 95.0% H_2SO_4 for 30 days at 25 °C leads to β-sulphonation of the nonsubstituted phenylene ring. The further sulphonation of the biphenylene-2,6- and -1,6- or 1,7-disulphonic acid in fuming sulphuric acid failed.

Fluorene (2b).—The disulphonic acid mixture obtained in the sulphonation of (2b) in 98.3% H_2SO_4 at 25 °C contained 1 ± 1% 1,5-, 3 ± 1% 1,7-, 30 ± 4% 2,5-,* 4 ± 2% 2,6-, 56 ± 4% 2,7-, and 6 ± 2% 3,5-disulphonic acid. Nitration of (2b) with fuming nitric acid in acetic acid gives similarly 2,5- and 2,7-dinitrofluorene as the main products.[5]

The monosulphonic acid isomer distribution could not be determined directly because of the very low solubility of fluorene itself which strongly reduces the effective rate of its conversion into the monosulphonic acids. It was estimated from the composition of the disulphonic acid mixture to be 3 ± 1% 1-, 73 ± 5% 2-, 5 ± 2% 3-, and 19 ± 3% 4-substitution. This isomer distribution compares with a ratio of 0% 1-, 69% 2-, 2% 3-, and 29% 4-substitution in the HNO_3–Ac_2O nitration,[6] and partial rate factors for protiodetritiation of the 1—4 position of 21, 16 800, 124, and 5 500 respectively [7] which reactions encounter at least at position 4 a much lower degree of steric hindrance than the sulphonation.

The isomer distribution of the trisulphonic acids resulting on further sulphonation of the disulphonic acid reaction mixture in 104% H_2SO_4 at 25 °C was determined to be 6 ± 2% 1,3,7-, 3 ± 1% 1,5,7-, 4 ± 2% 1,3,5-, 6 ± 2% 2,4,6-, and 81 ± 3% 2,4,7-trisulphonic acid.

The isomer distribution of the tetrasulphonic acids eventually resulting on further sulphonation of the disulphonic acid mixture in 105% H_2SO_4 at 25 °C was found to be 19 ± 3% 1,3,5,7- and 81 ± 3% 2,4,5,7-tetrasulphonic acid. The sulphonation of fluorene thus eventually leads to a mixture of 1,3,5,7- and 2,4,5,7-tetrasulphonic acid. It proceeds in stages, of which each step is much slower than the preceding one. The various sulphonation steps are shown in the Scheme, the main routes are indicated by solid lines, the minor ones by dotted lines.

9,10-*Dihydrophenanthrene* (2c).—On sulphonation of (2c) in 98.3% H_2SO_4 at 25 °C a mixture of disulphonic acids was formed, containing one sulpho-group per phenyl ring. The spectra of the sulphuric acid solution only allowed the determination of the substitution ratio for the available positions per phenylene ring; these were found to be 16 ± 3% 1-, 53 ± 3% 2-, and 30 ± 3% 3-substitution. The degree of 4-substitution is below the limits of ^{1}H-n.m.r. detection which is 2%.

From the sulphonation mixture of (2c) in 98.3% H_2SO_4 the dipotassium 2,6-disulphonate has been isolated as the main product. As a result of the low degree of 1-substitution, the amount of the 1,8-disulphonic acid will be negligibly small ($\leqslant$3%).

Efforts to further sulphonate the disulphonic acid mixture in 104% H_2SO_4 at 25 °C for 24 h, and also in 98.4% H_2SO_4 at 80 °C for 10 days failed as a result of oxidation.

Considering that the sulphonation encounters stronger steric hindrance than nitration and chlorination the isomer distribution for the monosulphonation is com-

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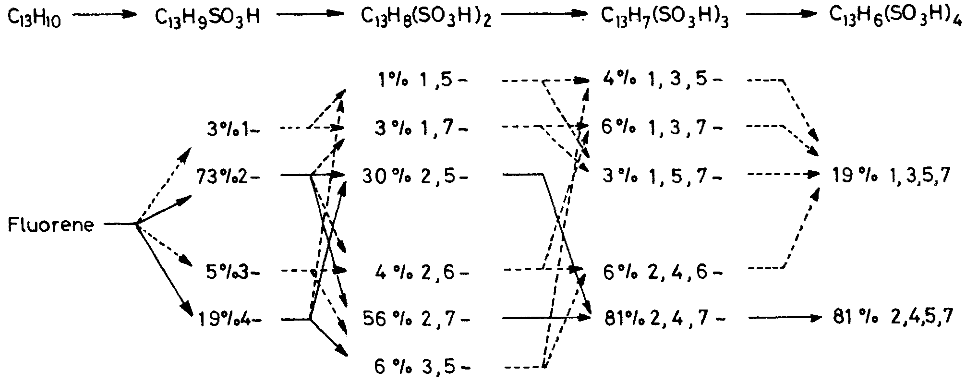
* From the reaction mixture obtained from fluorene in 98% H_2SO_4 at 25 °C the dipotassium 2,5-disulphonate has been isolated.

parable with those for HNO_3–Ac_2O nitration (the yield of the isolated 2- and 4-nitro-derivatives being 64 and 4% respectively 8)), chlorination (the partial rate factors for the positions 1—4 being 500, 26 000, 1 150, and 9 000 respectively 9)) and protiodetritiation (the partial rate factors being 100, 2 840, 189, and 1 970 respectively 7)).

The f_4/f_2 value for the sulphonation of (2c) is <0.04 which agrees with the partial rate factor ratio of 0.03 for the equivalent positions in biphenyl.[3e] It is smaller than that of fluorene (<0.04 *vs.* 0.26, *cf.* Table 2). This difference may be explained in terms of a lower degree of steric hindrance for the 4-substitution of fluorene compared with that of 9,10-dihydrophenanthrene.

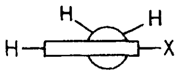
9,10-*Dihydroanthracene* (2d).—Reaction of (2d) with 98.3% H_2SO_4 led to its oxidation, as was apparent from the evolution of SO_2 and the darkening of the reaction mixture (the sulphuric acid-catalysed conversion of 9,10-dihydroanthracene into anthracene was reported previously 10)). Also reaction of (2d) with 6 equivalents of SO_3 in CCl_3F at 0 °C failed to give sulphonation, but instead afforded the oxidation product anthracene.



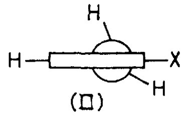
SCHEME

10,11-*Dihydro*-5H-*dibenzo*[*a,d*]*cycloheptene* (2e).—Sulphonation of (2e) in 95.3% H_2SO_4 at 25 °C led to a mixture of disulphonic acids containing one sulpho-group per phenylene. The ratio of sulphonation of the four available positions per phenylene was estimated as 13 ± 2% 1-, 12 ± 3% 2-, 51 ± 4% 3-, and 24 ± 3% 4-substitution. The content of the 4,6-disulphonic acid was 4 ± 2%. Further sulphonation of the disulphonic acid reaction mixture in 104% H_2SO_4 at 25 °C led to a mixture of 41 ± 3% 1,3,6,8-, 45 ± 3% 1,3,7,9-, 10 ± 2% 2,3,6,8-, and 4 ± 2% 2,4,6,8-tetrasulphonic acid.

In the sulphonation of (2e) the degree of substitution is much smaller *para* to the CH_2 than to the CH_2CH_2 group. Using the σ^+ constants reported by Taylor,[7] the reaction constant for the sulphonation by the $H_2S_2O_7$ mechanism $\rho = -5.7$,[2b] and the reported f_o/f_p ratios,[2d] the partial rate factors for the sulphonation of the 2-, 3-, and 4-positions of diphenylmethane were calculated to be 1.9, 2.2, and 21 respectively and those of 1,2-diphenylethane 3.8, 3.1, and 30 respectively. Application of the additivity principle leads to an expected isomer distribution for (2e) of 6% 1-, 45% 2-, 45% 3-, and 4% 4-substitution. The much lower degree of 2-substitution observed may be explained in terms of a lower degree of hyperconjugative stabilization of the transition state for the 2-substitution of (2e), as compared with that for the 3-substitution of (2e) and with that for the 4-substitution of diphenylmethane, probably as a result of a different conformation of the CH_2 between the two phenyls as compared with the CH_2 of the ethylene bridge relative to its adjacent phenyl of (2e). A Stewart molecular model does show that the conformation of the CH_2 between the two phenyls is as in (Ia), whereas the conformation of the benzylic hydrogens of the ethylene bridge is shown in (IIa) with the two methylenes of the C_2H_4 bridge in an eclipsed position. Supporting evidence for the conformational explanation comes further from the differences in chemical shift between the benzylic hydrogens of mono-*ortho*- and non-*ortho*-disulphonic acids, $\Delta\delta_{\alpha\text{-H}}$, the value of which is related to the conformation of the benzylic methylenes.[3b] For the disulphonic acids of (2e) $\Delta\delta_{\alpha\text{-H}} = 22$ Hz for the methylene between the two phenyls, whereas it is 36 Hz for the benzylic hydrogens of the ethylene bridge. The former value is coincidentally equal to that of the CH_2 of the fluorene-1, *x*-disulphonic acids ($x = 5$ or 7) which, according to a molecular model, has conformation (IIIb). The value of 36 Hz is ascribed to conformation (IIb). It is higher than the value of 26 Hz observed for the 4,*y*-disulphonic acids ($y = 7$ or 8) of (2c), for which a molecular model indicates conformation (IVb). This indicates some type of buttressing as results of strain, similar to that observed



(I)



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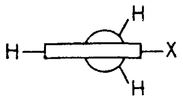

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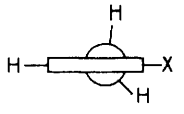

(IV)

a;X=H
b;X=SO3H

in a comparison of neopentylbenzene- and toluene-*o*-sulphonic acid.[3b]

Triptycene (3).—Sulphonation of (3) in 98.3% H_2SO_4 at 25 °C led to a mixture of trisulphonic acids containing one sulpho-group per phenylene. The ratio of sulphonation of the two different positions per phenylene was found to be 9 ± 2% 1- and 91 ± 2% 2-substitution. The very low reactivity of the α- as compared with the β-position was also observed in nitration [11] and protiodetritiation [12] and is related to the fact that triptycene has a strained ring fused to the aromatic ring in which the bond angles are less than the normal values.[12]

For 1,*x*,*y*-triptycenetrisulphonic acid ($x = 2$ or 3; $y = 2$ or 3) $\Delta\delta_{\alpha\text{-H}}$ (see before) = 63 Hz, a value which is similar to those observed for *e.g.* *o*-isopropylbenzene- and *o*,*p*′,*p*″-triphenylmethanetri-sulphonic acid. Given the fixed conformation of the methine H to the adjacent 1-sulpho-group of the triptycenetrisulphonic acid, this similarity further substantiates the previously proposed [3b] interpretation of the variation of the $\Delta\delta_{\alpha\text{-H}}$ in terms of conformational differences.

EXPERIMENTAL

Materials.—1,4-Diphenylbutane and 1,6-diphenylhexane were obtained from 1,4-diphenylbuta-1,3-diene and 1,6-diphenylhexa-1,3,5-triene (both from Frinton) respectively by hydrogenation at atmospheric pressure in anhydrous ethanol using PtO_2 as a catalyst.[13] 1,3-Diphenylpropane and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene were obtained by Wolff–Kishner reduction of dibenzyl ketone (Frinton) and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (Aldrich) respectively.[14] 1,1-Dibenzylethene was obtained by conversion of 1,1-dibenzylethanol (obtained from the Grignard compound of methyl bromide and dibenzyl ketone [15]) with $POCl_3$ in pyridine into 2-methyl-1,3-diphenylpropene,[16] and subsequent hydrogenation.[13] Biphenylene was synthesized from anthranilic acid.[17] 1,2-Diphenylethane, fluorene, 9,10-dihydrophenanthrene, 9,10-dihydroanthracene, and triptycene were commercial products. Potassium biphenylene-1-sulphonate was obtained as follows. A solution of butyl-lithium [from 1-bromobutane (90 g) and lithium (11.4 g) in 500 ml anhydrous ether [18]] was added to a solution of biphenylene (8.1 g) in ether (50 ml), and the reaction kept for 4 days in the dark.[19] To the resulting deep red ethereal solution of 1-lithiobiphenylene [19] was added slowly with stirring trimethylchlorosilane (84 ml) which led to vigorous reaction and precipitation of LiCl. The reaction mixture was then set aside overnight, refluxed for 1 h, and then hydrolysed by slowly adding 10% aqueous ammonium chloride. The ethereal layer was separated and dried and the ether removed by distillation; the residual crude 1-(trimethylsilyl)-biphenylene was purified by repeated distillation; yield 5.0 g (42%), b.p. 60—64 °C/2.5 mmHg. I.r. ν($CHCl_3$)/cm^{-1}: 3 030 (m, arom C–H), 2 950—2 850 (s, aliph. C–H), 1 230 (s), 870—840 (s, Si–C); ^{1}H-n.m.r. δ(CCl_4): 7.50 (m, 7 H, arom H), 1.10 [s, 9 H, $Si(CH_3)_3$].

To 1-(trimethylsilyl)biphenylene (5 g) in anhydrous carbon tetrachloride (25 ml) at 0 °C was added with stirring during 10 min sulphur trioxide (2 g).[20] The resulting mixture was refluxed for 15 min and the solvent subsequently removed by rotary evaporation. To the crude trimethylsilyl ester of biphenylene-1-sulphonic acid was then added a solution of potassium hydroxide (1.35 g) in water (10 ml). After the mixture had been stirred for 1 h the excess of water was distilled off and the residual crude potassium biphenylene-1-sulphonate recrystallized three times from aqueous ethanol (10% v/v water); yield 2.0 g (31%); i.r. ν(KBr)/cm^{-1}: 1 220—1 170 (vs, $-SO_3^-$), 1 040 (m), 670 (m), and 640 (m); ^{1}H-n.m.r. δ(D_2O): 7.38—7.01 (m) (Found: C, 53.2; H, 2.5; K, 14.5; S, 11.9. Calc. for $C_{12}H_7KO_3S$: C, 53.3; H, 2.6; K, 14.5; S, 11.9).

Sulphonation Procedures.—The sulphonation of aromatic hydrocarbons in concentrated aqueous sulphuric acid, as well as the consecutive sulphonation of the resulting disulphonic acid mixture by addition of sulphur trioxide to yield a fuming sulphuric acid solution, has been described earlier.[21]

Isolation of Potassium Sulphonate Salts.—After the sulphonation of the aromatic hydrocarbon (1.0—1.5 g) with an excess of sulphuric acid (10 ml) at 25 °C for 24 h any residual hydrocarbon was filtered off, the filtrate made alkaline with concentrated aqueous potassium hydroxide to pH 10, the solution filtered again, the water removed by rotary evaporation, and the residue fractionally crystallized, or extracted with dry ethanol and then recrystallized.

^{1}H-*N.m.r. Sulphonic Acid Isomer Analysis.*—The composition of the sulphonic acid mixtures has been determined by multicomponent ^{1}H-n.m.r. analysis [22] from the spectra obtained with a Varian HA 100 spectrometer (using neat tetramethylsilane as an external standard), directly from the sulphuric acid sulphonation mixture (the fuming sulphuric acid solutions were, in general, first diluted to *ca.* 99% H_2SO_4 to improve the spectral resolution), as will be described for the individual substrates below.

With the exception of biphenylene, the number of sulpho-groups introduced was determined from the area ratio of the aromatic and aliphatic hydrogens. In accordance with the strong deactivating effect of the sulphonic acid group,[23] the spectra always showed that the difference in the number of sulpho-groups per phenyl was either zero, or one (as with fluorene-2,4,7-trisulphonic acid). This was concluded amongst others from the absence of a simultaneous presence of the low-field aromatic singlet of the hydrogen, which is in between two *meta*-orientated sulpho-groups and the high-field aromatic absorption of a non-sulphonated phenyl(ene).

α,ω-Diphenylalkanes.—The degree of *ortho*-substitution of these hydrocarbons was determined from the ratio of the areas of the low-field benzylic absorption * (of the *o*-sulphobenzylic moiety) and the total benzylic absorption. For 1,1-dibenzylethane, the degree of *ortho*-substitution was also determined from the aromatic hydrogen pattern. This analysis is based on the general observation that the H-3 absorption of an alkylbenzene-2-sulphonic acid is shifted downfield relative to the H-3 and H-5 of the corresponding 4-sulphonic acid [24] (*cf.* ref. 3*b*) which shift in the present case amounts to 0.16 p.p.m.

Biphenylene.—The ^{1}H-n.m.r. spectrum of the sulphonation mixture of (2a) in 89.9% H_2SO_4 at 25 °C obtained after 30 days exhibits a singlet (7.50, nH) and an AB absorption (δ 7.20 and 7.92, $J = 7$ Hz, 2nH) which may be explained in terms of the presence of the 2,6- or the 2,7-disulphonic acid. The ^{1}H-n.m.r. spectrum of the sulphonation mixture of potassium biphenylene-1-sulphonate in

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* The benzylic hydrogens of $HO_3SC_6H_4(CH_2)_nC_6H_4SO_3H$ which are *ortho* to a sulpho-group are at a somewhat lower field than those which are *meta* or *para* to such a group: 0.22, 0.22, 0.26, 0.25, and 0.26 p.p.m. for $n = 2$, 3, 4, 6, and 8, and 0.30 for 1,1-dibenzylethane.

95.0% H_2SO_4 after 30 days exhibits an absorption pattern δ 7.38 (t, J = 7 Hz, 1 H, H-3), 7.41 [d, J = 7 Hz, 1 H, H-8 (or H-5)], 7.61 (d, J = 7 Hz, 2 H, H-2 + H-4), and 7.64 [s, 1 H, H-5 (or H-8)] which may be explained in terms of the presence of the 1,6-(or the 1,7-)isomer.

Fluorene.—The ^{1}H-n.m.r. spectrum of the disulphonic acid reaction mixture of (2b) in 98.3% H_2SO_4 showed a strong broadened methylene singlet at δ 4.28 and a very weak one at 4.50. The weak singlet was assigned to the methylene hydrogens of the disulphonic acids in which one sulpho-group is *ortho* to the methylene group, *i.e.* the 1,5-, 1,6-, and 1,7-isomer and the strong singlet to the acids in which there is no sulpho-group *ortho* to the CH_2 group. The absence of any methylene absorption in between 4.55 and 5.50 illustrated the absence of the 1,8-isomer. As to the aromatic hydrogens, the singlet at 9.31 was assigned to H-4 of the 3,5-disulphonic acid and the doublet at 9.00 (J = 8.5 Hz) to H-4 of the 1,5- and 2,5-isomers. The remaining aromatic absorption is very much larger than that due to the other hydrogens of the 1,5-, 1,6-, 1,7-, 2,5-, and 3,5-disulphonic acids, and is ascribed to the hydrogens of the 2,6-, 2,7-, and 4,5-isomers, of which the 2,7-isomer is the main sulphonation product at 85 °C.[25] From the area ratio of the specific absorptions it was calculated that the reaction mixture contained 4 ± 2% (1,5- + 1,6- + 1,7-), 30 ± 4% 2,5-, 60 ± 4% (2,6- + 2,7- + 4,5-), and 6 ± 2% 3,5-disulphonic acid.

A Stewart molecular model study revealed that the introduction of a sulpho-group at position 5 of fluorene-4-sulphonic acid is sterically very strongly hindered and thus retarded. This is already apparent from the sulphonation of the non-planar biphenyl-2-sulphonic acid, which does not give any 2′-substitution.[23b] The content of the fluorene-4,5-disulphonic acid was, therefore, taken to be negligibly small. The data for the 2,5- and 3,5-isomer illustrate that sulphonation proceeds preferentially *para* to the other phenyl rather than *para* to the methylene. Accordingly, the content of the 2,6-isomer will be much smaller than that of the 2,7-isomer and that of the 1,6-isomer will be negligibly small. Thus the main products are the 2,7- and the 2,5-isomer with the content of the former being much greater than that of the latter. Accordingly it was assumed that the amount of 1,7- is (3 ± 1) times that of the 1,5-isomer.

Further fluorene-2,4,6-trisulphonic acid is formed from both the 2,6- and the 3,5-disulphonic acid. The latter disulphonic acid yields in addition the 1,3,5-trisulphonic acid which is almost exclusively formed in this way and not from the 1,5-disulphonic acid which will yield predominantly the 1,5,7-trisulphonic acid.[*] Thus the content of 2,6-disulphonic acid is equal to 4 ± 2% [=6 − (6 − 4)] and thus that of the 2,7-isomer 56 ± 4%. The disulphonic acid mixture thus contains 1 ± 1% 1,5-, 3 ± 1% 1,7-, 30 ± 4% 2,5-, 4 ± 2% 2,6-, 56 ± 4% 2,7-, and 6 ± 2% 3,5-disulphonic acid.

The monosulphonic acid isomer distribution of fluorene was estimated from the composition of the disulphonic acid mixture as follows. The content of the 1-sulphonic acid (which yields the 1,5- and 1,7-isomer) will be *ca.* 3% and that of the 3-sulphonic acid (yielding the 2,6- and 3,5-isomer) *ca.* 5%. The mole fractions of the fluorene-2- and -4-sulphonic acid (x and y) were obtained from the contents of the 2,5- and 2,7-isomer, assuming the ratio of 2- and 4-substitution of fluorene ($x : y$) to be the same as that of the 7- and 5-substitution of both the 2- and 4-sulphonic acid. Thus $[2,5\text{-}(SO_3H)_2]/[2,7\text{-}(SO_3H)_2] = 2y/x$ and since $x + y = 0.92$ it follows that the degree of 2- and 4-substitution are 73 and 19% respectively.

The ^{1}H-n.m.r. spectrum of the mixture obtained upon further sulphonation of the fluorenedisulphonic acid mixture in 104% H_2SO_4 at 25 °C for 4 days, showed the presence of a mixture of trisulphonic acids. It exhibited a low-field doublet at δ 9.97 (J = 1 Hz), assigned to H-4 of the 1,3,5- and H-5 of the 2,4,6-isomer, a weak methylene absorption at 5.14, assigned to the 1,3,5-, 1,3,6-, 1,3,7-, and 1,5,7-isomers, and a strong methylene absorption at 4.77 (br,s) due to the 2,4,6- and 2,4,7-isomers. The absence of any significant absorption between δ 5.14 and 6.0 illustrated the absence of the 1,3,8-isomer. From the area ratio of these specific absorptions, it was calculated that the mixture contained 10% (1,3,5- + 2,4,6-) and 13% (1,3,5- + 1,3,6- + 1,3,7- + 1,5,7-) in addition to the 2,4,5- and 2,4,7-trisulphonic acid. Based on the strongly dominating *meta*-directing effect of the sulpho-substituent [23,26] and the absence of the 1,6-isomer in the disulphonic acid mixture, the amount of the 1,3,6-isomer was taken to be negligibly small. Further, the content of the 2,4,5-trisulphonic acid was neglected in view of the strong steric hindrance towards the sulphonation of the 2,4-disulphonic acid at position 4 (see before). Fluorene-2,4,5,7-tetrasulphonic acid (see later) thus only results from the 2,4,7-trisulphonic acid, the content of which is accordingly also (see later) 81 ± 3%. Further, fluorene-1,5-disulphonic acid yields almost completely, and the 1,7-isomer predominantly, the 1,5,7-trisulphonic acid. The content of that isomer is thus 3 ± 1% and that of the 1,3,7-isomer accordingly 6 ± 2%. Thus, the trisulphonic acid isomer distribution was calculated to be 6 ± 2% 1,3,7-, 3 ± 1% 1,5,7-, 4 ± 2 (=10 + 13 + 81 − 100)% 1,3,5-, 6 ± 2% 2,4,6-, and 81 ± 3% 2,4,7-isomer.

The ^{1}H-n.m.r. spectrum of the reaction mixture of the further sulphonation of the fluorenedisulphonic acid mixture in 105% H_2SO_4 for 30 days showed the presence of a tetrasulphonic acid mixture. It exhibited a weak singlet at 9.97, a singlet shoulder at 9.20, and a weak broadened singlet at 5.18, assigned respectively to H-4, H-2, and the methylene hydrogens of 1,3,5,7-tetrasulphonic acid; further, a strong singlet at 9.15 and a broadened singlet at 4.99 were assigned to the aromatic and methylene hydrogens of the 2,4,5,7-isomer. The content of the 1,3,5,7- and 2,4,5,7-isomer, as calculated from the aromatic singlets, is 19 ± 3 and 81 ± 3%, respectively.

From the reaction mixtures of fluorene in 104 and 98% H_2SO_4 at 25 °C the potassium salts of fluorene-2,4,7-tri- and -2,5-di-sulphonate have been isolated respectively; ^{1}H-n.m.r. δ(D_2O): 2,4,7-trisulphonate 9.17 (d, J = 8.5 Hz, 1 H, H-5), 8.71 (d, J = 1.5 Hz, 1 H, H-3), 8.47 (d, J = 1.5 Hz, 1 H, H-1), 8.37 (d, J = 2 Hz, 1 H, H-8), 8.19 (dd, J = 2 + 8.5 Hz, 1 H, H-6), 4.43 (s, 2 H, $-CH_2-$); 2,5-disulphonate 9.21 (d, J = 8.5 Hz, 1 H, H-4), 8.18—8.42 (m, 3 H, H_3-1,3,6), 7.46—7.70 (m, 2 H, H_2-7,8), and 3.94 (s, 2 H, $-CH_2-$).[†]

9,10-*Dihydrophenanthrene.*—The substitution ratio per phenyl was determined as follows. The ^{1}H-n.m.r. spectrum of the disulphonic acid reaction mixture in 98% H_2SO_4 exhibited a strong broadened singlet at 3.38 and a very much weaker one at 3.64. The latter is assigned to the

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[*] The relative contents of the 2,5- and 3,5-disulphonic acid illustrate that the sulphonation proceeds predominantly *para* to the other phenyl, rather than *para* to the methylene.

[†] The assignments of H-3 and H-4 of the 2,5-disulphonate were made by comparison with the assignments of H-6 and H-5 of the 2,4,7-trisulphonate.

benzylic hydrogens which have a sulpho-group in the *ortho*-position, the former to the benzylic hydrogens with a sulpho-group in the *meta*- and *para*-positions. As to the aromatic hydrogens the doublets at 8.74 ($J = 1.5$ Hz) and 7.98 ($J = 8.5$ Hz) were assigned to H-4 and H-1 of the 3-substituted phenyl ring. The remaining aromatic absorption is much larger than that due to the hydrogens of the 1- and 3-substituted phenyl ring products, and is assigned to the 2-substituted phenyl ring products. The absence of any absorption at lower field than 8.74 infers the absence of a 4-substituted product (*cf.* the absorption of H-4 of fluorene-1,5- and -2,5-disulphonic acid at 9.00, and of H-4 of fluorene-3,5-disulphonic acid at 9.31).

From the sulphonation mixture of (2c) in 98.3% H_2SO_4 at 25 °C a dipotassium disulphonate has been isolated as the main product; this, on the basis of its ^{1}H-n.m.r. D_2O spectrum, is identified as the 2,6-isomers: 8.47 (d, $J = 1.8$ Hz, 1 H, H-5), AB [8.06 (d, $J = 1.8$ Hz) + 7.66, $J_{AB} = 8$ Hz, 2 H, H_2-7,8], 8.00—8.12 (m, 3 H, H_3-1,3,4), and 3.01 (s, 4 H, $-CH_2-CH_2-$). The unlikely possibility that the isolated precipitate consists of a mixture of the 2,6-isomer and equal amounts of the 2,7- and the 3,6-isomer, however, cannot be excluded.

10,11-*Dihydro*-5H-*dibenzo*[a,d]*cycloheptene*.—The substitution ratio per phenyl ring was determined as follows. The ^{1}H-n.m.r. spectrum of the disulphonic acid reaction mixture in 95.3% H_2SO_4 exhibited a strong broadened singlet at δ 4.63, a weaker one at 4.95 and a very weak one at 5.27. The last one is assigned to the C(5)H_2 of the disulphonic acid (which has two sulpho-groups *ortho* to that group), and the second and the first to the C(5)H_2 of the disulphonic acids which have respectively one and no sulpho-group *ortho* to the C(5)H_2. The spectrum further showed a weak broadened singlet at 3.97 and a strong one at 3.61. These absorptions are assigned to the CH_2 of the ethylene bridge which, respectively, do have and which do not have a sulpho-group in *ortho*-position. It then follows for the area (A) ratios:

$$\%\text{4-substitution} = 100\,(A_{4.95} + 2A_{5.27})/(A_{4.63} + A_{4.95} + A_{5.27})$$

$$\%\text{1-substitution} = 100\,A_{3.97}/(A_{3.61} + A_{3.97})$$

$$\%\text{4,6-}(SO_3H)_2 = 100\,A_{5.27}/(A_{4.63} + A_{4.95} + A_{5.27})$$

The ^{1}H-n.m.r. spectrum of the tetrasulphonic acid reaction mixture obtained on further sulphonation of the disulphonic acid mixture in 104% H_2SO_4 exhibited two broadened singlets at δ 5.07 and 5.33, and a much weaker one at 5.64. The last is assigned to the C(5)H_2 of the 2,4,6,8-tetrasulphonic acid (resulting from the sulphonation of the 2,6-, 2,8-, and 4,6-disulphonic acids), the second to the C(5)H_2 of the 1,3,6,8- and 2,3,6,8-tetrasulphonic acid (the latter resulting from the 2,6-disulphonic acid,* the former from the 1,8-, 2,7-, and 3,6-disulphonic acid), and the first to the C(5)H_2 of 1,3,7,9-tetrasulphonic acid (resulting from 1,7-, 1,9-, and 3,7-disulphonic acid). The spectrum further showed a broadened singlet at δ 4.28 overlapping in part with a broad absorption down to 3.7. The singlet is assigned to the CH_2 of the ethylene bridge with an *ortho*-sulpho-group; the broad absorption comprises the CH_2 of the ethylene bridge which have no *ortho*-sulpho-group.

The aromatic part of the spectrum consisted of (i) two strong doublets (each with $J \simeq 1$ Hz) of equal intensity at δ 8.96 and 8.70, assigned to both the H_2-2,8 and H_2-4,6 of the 1,3,7,9-isomer and the H-2 and H-4 of the 1,3,6,8-isomer, respectively, (ii) two weaker doublets ($J \simeq 1$ Hz) of equal intensity at δ 8.90 and 8.61, assigned both to the H-7 and H-9 of the 1,3,6,8-isomer and the H_2-3,7 and H_2-1,9 of the 2,4,6,8-isomer respectively, and (iii) two weak singlets at 8.46 and 8.48, assigned respectively to H-1 and H-4 of the 2,3,6,8-isomer (in fuming sulphuric acid, these hydrogens absorb at 8.36 and 8.34 as a result of conversion of the 2,3-disulphonic acid moiety into the intramolecular anhydride †). The tetrasulphonic acid isomer distribution was calculated from the area ratios using the following equations:

$$\%1,3,7,9\text{-}(SO_3H)_4 = 100\,A_{5.07}/(A_{5.07} + A_{5.33} + A_{5.64})$$

$$\%2,4,6,8\text{-}(SO_3H)_4 = 100\,A_{5.64}/(A_{5.07} + A_{5.33} + A_{5.64})$$

$$\%2,3,6,8\text{-}(SO_3H)_4 = 200\,(A_{8.46} + A_{8.48})/A_{\text{arom}}$$

$$\%1,3,6,8\text{-}(SO_3H)_4 + 2 \times \%\,1,3,7,9\text{-}(SO_3H)_4 = 2A_{8.96}/A_{\text{arom}} = 2A_{8.70}/A_{\text{arom}}$$

to be 41 ± 3% 1,3,6,8-, 45 ± 3% 1,3,7,9-, 10 ± 2% 2,3,6,8-, and 4 ± 2% 2,4,6,8-isomer. The degree of 2- and 3-substitution of the hydrocarbon (2e) was calculated from the tetrasulphonic isomer distribution and the degree of 1- and 4-substitution as follows. The 1,3- + 7,9-disulphobenzo-moieties of the tetrasulphonic acid originate from the 1-, 3-, 7-, and 9-sulphobenzo-moieties of the disulphonic acids, and similarly the 2,4- and 6,8-disulphobenzo-moieties from the 2-, 4-, 6-, and 8-sulphobenzo-ones. Accordingly,

$$\%\text{1-} + \%\text{3-substitution} = \tfrac{1}{2}(\%1,3,6,8\text{-}) + \%1,3,7,9\text{-}(SO_3H)_4$$

$$\%\text{2-} + \%\text{4-substitution} = \tfrac{1}{2}(\%1,3,6,8\text{-}) + \%2,3,6,8\text{-} + \%2,4,6,8\text{-}(SO_3H)_4$$

from which it was calculated that the degree of 2- and 3-substitution is 12 ± 3 and 51 ± 4%, respectively.

Triptycene.—The ^{1}H-n.m.r. spectrum of the trisulphonic acid reaction mixture of triptycene [δ($CDCl_3$): 7.83—7.72 (m, 6 H, α-H's), 7.53—7.31 (m, 6 H, β-H's), and 5.37 (s, 2 H, methine H's)] in 98% H_2SO_4 exhibited a weak triplet ($J = 8$ Hz) at δ 7.66 and a singlet of about equal intensity at 6.98 which were assigned respectively to the H-3 and the methine H adjacent to the sulpho-group of a 1-sulphonated phenylene group.

It further showed a singlet (8.50), an AB (8.19 and 8.08, $J = 9$ Hz), and a singlet at 6.35 in an area ratio of *ca.* 3 : 6 : 2 which were assigned respectively to H-1, H_2-3,4, and the methine H's of a 2-substituted phenylene group. The degree of 1- and 2-substitution per phenylene was determined from the area ratio of the aromatic triplet at 7.66 and the total aromatic hydrogen absorption, and from the area ratio of the singlet at 8.50 and the total aromatic absorption, to be 10 ± 2 and 90 ± 2% respectively. It was further determined from the area ratio of the methine hydrogen absorptions at 6.98 and 6.35 as follows. Consider the mole

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* The sulphonation of the 2,6-disulphonic acid is thought to lead to a mixture of the 2,3,6,8- and 2,4,6,8-tetrasulphonic acid, since (i) the sulphonation *meta* to the sulpho-group at position 2, *i.e.* at position 4, will encounter strong steric hindrance from the sulpho-group at position 6, and (ii) the sulphonation of *meta*-alkylbenzenesulphonic acids in oleum yields in part 5-alkylbenzene-1,2-disulphonic anhydrides.[27]

† In concentrated sulphuric acid the chemical shifts of H_2-3,6 are 0.11 p.p.m. greater for benzene-1,2-disulphonic acid than for the corresponding intramolecular anhydride.[26]

fraction of $1,1',q''$-, $1,4',q''$-, and $1,p',q''$-trisulphonic acid ($p = 2,3$ and $q = 2,3$) to be negligibly small, k and l respectively. Then the mole fraction of the $2,2',r''$-isomer ($r = 2,3$) will be $1 - k - l$. For the area ratio it then follows: $A_{6.98}/A_{6.35} = (2k + l)/[l + 2(1 - k - l)]$. Taking the ratio of 1- to 2-substitution to be the same for the sulphonation of the first and second phenylene,[3d] it follows that $k = \frac{1}{2}l^2$. From this equation and the observed area ratio, it was calculated that $k = 0.020$ and $l = 0.20$. Accordingly the degree of 1-substitution per phenylene is $(2/3 \times 0.020 + 1/3 \times 0.20) \times 100 = 8 \pm 2\%$ and that of 2-substitution $(1/3 \times 0.020 + 2/3 \times 0.20 + 1 \times 0.78) \times 100 = 92 \pm 2\%$, which values agree with those obtained in other ways.

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