2.861 Å (bifurcated). This result further substantiates the hypothesis that the threshold temperature for desolvation is related to the crystal packing.

Glucuronamide hydrate also dehydrates anisotropically in a manner similar to the hydrates discussed in the previous paper. Glucuronamide hydrate crystallizes in needles, and analysis of the crystal packing shows that the water molecules of crystallization are arranged in tunnels parallel to the needle axis as shown in Figure 3. Cutting crystals of glucuronamide hydrate perpendicular to the needle axis and activation of the cut end with powdered anhydrous compound shortened the incubation period for dehydration and produced a clear front advance. This behavior is entirely consistent with the crystal packing which shows water tunnels parallel to the needle axis and with previous studies on the anistropic desolvation of crystal hydrates.[1]

The clear front advancement shown in Figure 4 allowed the measurement of the rate of front advance at 60, 65, and 70 °C. The rate of front advance followed zero-order kinetics, and rate constants at these temperatures gave an activation energy of 37.2 kcal/mol. This favorably compares with the published value of 38.6 kcal/mol which was determined by application of the Avrami-Erofeev equation to weight loss data.[2]

It is clear from Table II that bond lengths of equivalent bonds in glucuronamide hydrate are quite different. In addition, these bond lengths show much more variation than the corresponding bond lengths in anhydrous glucuronamide.[5] In anhydrous glucuronamide the C-C bond lengths vary vrom 1.508 to 1.541 Å, and the C-O single bond lengths vary from 1.394 to 1.431 Å. In glucuronamide hydrate, the C-C bond lengths vary from 1.362 to 1.632 Å, and the C-O bond lengths vary from 1.293 to 1.552 Å. The bond angles in glucuronamide hydrate also show much more variation than those in anhydrous glucuronamide. In glucuronamide hydrate, the tetrahedral bond angles vary from 100.1° to 116.4°, while in anhydrous glucuronamide these angles vary from 107.0° to 113.3°.

The variation in equivalent bond lengths and angles of glucuronamide hydrate and the differences between the bond lengths of glucuronamide hydrate and glucuronamide indicate that the real standard deviations in bond lengths and angles are much larger than those obtained from the least-squares refinement. Attempts to find crystals which refined to give more consistent bond lengths and angles failed because of the poor quality of the crystals. In addition, the large peaks in the final difference map could not be interpreted in terms of disorder. Thus, the variations in bond lengths and angles are probably the result of the poor quality of the crystals. However, the low R factor and reasonable crystal packing and intermolecular distances leave little doubt that the structure is approximately correct.

In conclusion, the data for glucuronamide are completely consistent with the hypothesis that the water tunnel area and hydrogen bonding are the main factors which control the threshold temperature for dehydration.

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Registry No. Glucuronamide hydrate, 83232-07-9.

Supplementary Material Available: temperature factors; Table II, bond lengths and angles; Table III, intermolecular contacts and hydrogen bonds (6 pages). Ordering information is given on any current masthead page.

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On the Sulfonation Positional Reactivity Order of Arenesulfonic Acids[1]

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Available isomer distributions of the sulfonation (sulfodeprotonation) of the arenemonosulfonic acids and some of their methyl, *tert*-butyl, and phenyl derivatives have been compiled. The observed positional reactivity orders for the sulfonic acids of the aromatic hydrocarbons have been analyzed in terms of three factors, viz., (i) the differences in the localization energies of the positions under scrutiny of the corresponding aromatic hydrocarbon, containing all the substituents except the sulfo group, (ii) the (electronic) directing effect of the sulfonic acid substituent, and (iii) the difference in steric hindrance for the introduction of the (second) sulfonic acid group. It appears that each of these three factors is decisive for the positional reactivity order if the two other factors are nondiscriminating.

Some time ago it was reported that the positional reactivity order for sulfonation of monosulfonic acids of a given dimethylnaphthalene (DMN) roughly follows the reactivity order, as predicted by the localization energies (L) calculated for the various positions of the unsubstituted DMN with due observance of steric factors.[2] On the basis of this argument it would be expected that the main product of the disulfonation of 1,8-dimethylphenanthrene would be the 2,7-disulfonic acid, L_2 and L_3 being 2.3628

(1) Aromatic Sulfonation. 83. For part 82, see H. Cerfontain, A. Koeberg-Telder, K. Laali, and H. J. A. Lambrechts, accepted for publication in *J. Org. Chem.*

(2) K. Lammertsma and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 673 (1979).

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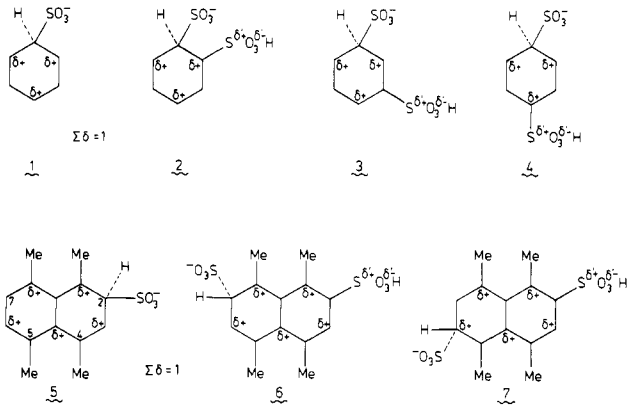
Chart I



and 2.4411, respectively. However, in fact, the main isomer formed (in 70% yield) is the 2,6-disulfonic acid.[1] The predominant formation of this nonsymmetrical disulfonic acid was tentatively ascribed[1] to the dominance of the substituent effect of the first sulfonic acid substituent in governing the relative stabilities of the σ complexes for the introduction of the second sulfo group.

In order to obtain more information on the above-described controversy, we have now compiled isomer distribution data for the sulfonation of arenesulfonic acids available in the literature. In addition, isomer distribution data are given which we have calculated from reported compositions of mono- and disulfonic acid mixtures resulting from the respective mono- and disulfonation of a given arene by the method exemplified before for 1,2,3-trimethylnaphthalene-5-sulfonic acid.[3] The data are all in Table I. The data are compared with (i) the differences in localization energies for the appropriate positions of the corresponding aromatic hydrocarbon, containing all the substituents except the sulfonic acid group, (ii) the directing (electronic) effect of the sulfonic acid substituent, and (iii) the relative factor of steric retardation, all for the positions under scrutiny. The strong decrease in rate of electrophilic substitution of a given position of an arene by a sulfonic acid substituent is due to the destabilization of the σ complex by that substituent due mainly to electric repulsion between the carbon ring positions which carry part of the positive charge of the σ-complex arenium ion moiety and the positively charged sulfur of the sulfonic acid substituent (see Chart I).[4] This repulsive charge interaction and thus the destabilization of the σ complex will be substantially greater when the sulfonic acid substituent is at a position which in the absence of the sulfo substituent would carry part of the positive charge of the σ-complex arenium ion moiety than when it is adjacent to such a position. Thus the energies of the σ complexes for the hydrocarbon systems benzene and 1,4,5,8-tetramethylnaphthalene increase in the order $1 < 3 < 2 \simeq 4$ and $5 < 6 < 7$, respectively. As to the sulfonation of benzenesulfonic acid, the ortho and para positions are more deactivated than the meta position. Similarly, for 1,4,5,8-tetramethylnaphthalene-2-sulfonic acid, the 6-position is more deactivated than the 7-position.[3]

The steric requirements of a sulfonic acid group are very substantial and in aromatic substitution roughly comparable in magnitude to those of a *tert*-butyl group.[6] In planar arenes no sulfonation was ever observed peri to a methyl or sulfonic acid substituent[1-3] or of a "cavity" hydrogen of phenanthrene (4- and 5-H) and perylene (1-, 6-, 7-, and 12-H).[1,7] The steric hindrance for substitution ortho to a sulfonic acid group is very large, but not prohibitive. In fact, it is, as expected, larger than that for substitution ortho to a methyl, $\Delta S_6^{\ddagger} - \Delta S_4^{\ddagger}$ for the sulfonation of toluene-3-sulfonic acid in 104.0% H_2SO_4 being 11.5 ± 1.0 cal mol^{-1} K^{-1}.[8]

There is some steric hindrance for the introduction of a sulfo group peri to hydrogen, as appears from the small, but significant, kinetic isotope effect of hydrogen for sulfonation of the 1-position of naphthalene (at 0 °C $k_H/k_D = 1.8 \pm 0.1$[9]). The degree of the steric hindrance is, however, small, as appears from the difference in activation entropy for substitution of naphthalene at the 1- and 2-position (for 75.5% H_2SO_4 $\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}$ is only -2.6 ± 2 cal mol^{-1} K^{-1}[10] and for SO_3 in nitromethane -0.5 ± 1.1 cal mol^{-1} K^{-1}[11]).

There is a significant larger steric hindrance for sulfonation ortho to methyl. For the sulfonation of toluene in 90–99.5% H_2SO_4 $\Delta S_o^{\ddagger} - \Delta S_p^{\ddagger} = -4.9 \pm 0.4$ cal mol^{-1} K^{-1},[12] and for the sulfonation of *p*- and *o*-toluenesulfonic acid in 99.5% H_2SO_4 $\Delta S_{o\text{-Me}}^{\ddagger} - \Delta S_{p\text{-Me}}^{\ddagger} = -9 \pm 4$ cal mol^{-1} K^{-1}.[10] The steric hindrance for sulfonation ortho to methyl will be enhanced if that methyl is buttressed by an *o*-methyl and more so by an *o*-sulfo group or a *peri*-methyl. Finally, substitution between two methyl substituents in a meta orientation will be more difficult than expected on the basis of additivity of the steric effects of the two methyls. Further, in the naphthalene series the steric hindrance is greater for the sulfonation of a β-position ortho to an α- than to a β-methyl.[2]

The order of steric hindrance listed in Table I is based on the generalizations outlined just above. The peri positions which encounter only *peri*-H steric hindrance are italic, and the positions which do not encounter steric hindrance are boldface.

Benzene Series. For benzenesulfonic acid and its methyl derivatives the observed reactivity order is as predicted on the basis of ΔL and the SO_3H substituent effect, provided one considers, if necessary, the effect of steric hindrance.

Biphenyl Series. For the three biphenylsulfonic acids most striking is the very low degree of ortho sulfonation. For the 3- and 4-sulfonic acid this is due to the steric compression between the incoming sulfo group and the sulfophenyl and the concomitant loss of interphenyl conjugative stabilization on forming the 2′-sulfonic acid from the preceding σ complex. With biphenyl-2-sulfonic acid, the degree of inter-ring conjugation is small, due to the steric repulsion between the sulfo and phenyl substituents. The relay of the substituent effect of the SO_3H group to the other phenyl ring will thus be less with biphenyl-2-

(3) H. J. A. Lambrechts and H. Cerfontain, *Tetrahedron*, **38**, 1667 (1982).
(4) Sulfur is electropositive toward oxygen.[5]
(5) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960, p 88–90.
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(10) H. Cerfontain and A. Telder, *Recl. Trav. Chim. Pays-Bas*, **86**, 527 (1967).
(11) For the sulfonation of naphthalene with SO_3 in nitromethane the 1 isomer/2 isomer distribution at −20, 0, and 25 °C is 88.9: 11.1, 88.0:12.0, and 84.8:15.2, respectively, corresponding with $\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger} = -1.2 \pm 0.3$ kcal mol^{-1} and $\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger} = -0.5 \pm 1.1$ cal mol^{-1} K^{-1}. K. Lammertsma and H. Cerfontain, unpublished results.
(12) C. W. F. Kort and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **87**, 24 (1968).

Table I. Sulfonation of Arenesulfonic Acids: Kinetically Controlled Disulfonic Acid Isomer Distributions and Predicted and Observed Positional Reactivity Orders

no.	arenesulfonic acid (=ArH)[a]	reagent[b]	temp, °C	positions			isomer distribution of $ArSO_3H$, %			$L_p - L_q$[c]	$L_q - L_r$[c]	reactivity order: predicted on the basis of steric hindrance[d]	reactivity order: predicted on the basis of ΔL	reactivity order: predicted on the basis of subst eff S[a]	reactivity order: obsd[e]
				p	q	r	p	q	r						
							Alternant Arenes								
							Benzene Series[f]								
1	1-S	104 A	25	2	3	4	<0.5	48.6	2.8	0.0000	0.0000	2 < 3 = 4	2 = 3 = 4	2 = 4 < 3	2 << 3 > 4
2	1-Me-2-S	99.6 A	25	4	5		99	<1		−0.0995		4 = 5	4 > 5	4 > 5	4 >> 5
3	-3-S	103 A	25	4	5	6	35	50	14.5	−0.0995	0.1077	4 < 6 < 5	4 > 5 < 6	4 < 5 > 6	4 ≃ 5 > 6
4	-4-S	104 A	25	2	3		50	<0.4	50	−0.0995		2 > 3	2 > 3	2 > 3	2 >> 3
5	1,2-Me_2-3-S	103 A	25	4	5	6	<1	99	<1	0.0000	−0.0028	4 < 6 < 5	4 = 5 ≃ 6	4 < 5 > 6	4 << 5 >> 6
6	-4-S	103 A	25	5	6		<1	99		−0.0028		5 < 6	5 ≃ 6	5 < 6	5 << 6
7	1,3-Me_2-2-S	104 A	25	4	5	6	50	<0.3	50	0.1970		4 < 5	4 > 5	4 > 5	4 >> 5
8	-4-S	104 A	25	5	6		<1	99		0.1970		5 < 6	5 < 6	5 < 6	5 << 6
9	-5-S	104 A	25	2	4	6	72.8	13.6	13.6	−0.0018		2 > 4	2 ≃ 4	2 = 4	2 > 4
10	1,4-Me_2-2-S	104 A	25	3	5	6	<0.5	6.9	93	0.0000	0.0000	3 < 6 < 5	3 = 5 = 6	3 = 5 < 6	3 < 5 < 6
11	1,2,3-Me_3-4-S	104 A	25	5	6		<0.4	100		0.0819		5 < 6	5 < 6	5 < 6	5 << 6
12	1,2,4-Me_3-5-S	104 A	25	3	6		100	0.4		−0.0866		3 > 6	3 > 6	3 > 6	3 >> 6
							Biphenyl Series[g]								
13	2-S	97 A	25	2′	3′	4′	<3	26	45	−0.1442	0.0970	2′ < 3′ = 4′	2′ > 3′ < 4′	2′ < 3′ > 4′	2′ < 3′ ≃ 4′
14	3-S	97 A	25	2′	3′	4′	0.0	0.5	99	−0.1442	0.0970	2′ < 3′ = 4′	2′ > 3′ < 4′	2′ = 3′ = 4′	2′ < 3′ << 4′
15	4-S	97 A	25	2′	3′	4′	0.3	0.9	97.4	−0.1442	0.0970	2′ < 3′ = 4′	2′ > 3′ < 4′	2′ < 3′ > 4′	2′ < 3′ << 4′
16	2,2′-methano-4-S	98 A	25	3′	4′	5′	<1	78	1			3′ < 4′ = 5′		3′ > 4′ < 5′	3′ << 4′ >> 5′
				4′	6′		78	20				4′ > 6′		4′ = 6′	4′ > 6′
17	2,2′-methano-6-S	98 A	25	4′	5′	6′	80	20				4′ = 5′ > 6′		4′ < 5′ > 6′	4′ > 5′ >> 6′
18	2,2′-ethano-4-S	98 A	25	3′	4′	5′	≃30	≃10	≃60			3′ < 4′ = 5′		3′ > 4′ < 5′	3′ > 4′ < 5′
19	3,5-Ph_2-4′-S	98 A	25	4	4″			>98				4 << 4″			4 << 4″
				2″	3″	4″			>98	−0.1442[h]	0.0970[h]	2″ < 3″ = 4″	2″ > 3″ < 4″		(2″ + 3″) << 4″
20	3,5-Ph_2-4′,4″-S_2	98 A	25	4	4‴			>98				4 << 4‴			4 << 4‴
				2‴	3‴	4‴			>98	−0.1442[h]	0.0970[h]	2‴ < 3‴ = 4‴	2‴ > 3‴ < 4‴		(2‴ + 3‴) << 4‴
							Naphthalene Series[i]								
21	1-S	104 A	57	3	4	5	<15	<3	75	0.1811	0.0000	3 > 4 = 5	3 < 4 = 5	3 > 4 < 5	3 ≃ 4 << 5
22		98.5 A	25				<2	<2	58						3 ≃ 4 << 5
21		104 A	57	5	6	7	75	10	15–0	−0.1811	0.0000	5 < 6 = 7	5 > 6 = 7	5 = 7 < 6	5 > 6 ≃ 7
22		98.5 A	25				58	32	10						5 > 6 > 7
23	2-S	99 A	57	4	5	6	<21	67	1	0.0000	−0.1811	4 = 5 < 6	4 = 5 > 6	4 < 5 > 6	4 < 5 >> 6
24		98.5 A	25				4	74	<2						4 < 5 >> 6
23		99 A	57	5	7	8	67	11	21–0	−0.1811	0.1811	5 = 8 < 7	5 > 7 < 8	5 = 7 > 8	5 > 7 ≃ 8
24		98.5 A	25				74	3	18						5 > 7 < 8
25		104 A	20				78		22						5 >> 7 < 8
26	1-Me-4-S	95 A	25	2	6	7	30	10	60	−0.1613	0.0394	2 < 6 = 7	2 > 6 > 7	2 ≃ 6 < 7	2 > 6 < 7
27		B	12				53	5	42						2 > 6 < 7
28	1,2-Me_2-4-S	B	12	6	7		51	49		−0.0022		6 = 7	6 ≃ 7	6 < 7	6 ≃ 7
29	1,3-Me_2-4-S	B	12	6	7		4	96		0.0761		6 = 7	6 < 7	6 < 7	6 < 7
30	-5-S	B	12	2	7		<2	>98		0.1120		2 < 7	2 < 7	2 > 7	2 << 7
31	-7-S	B	12	4	5		≃50	≃50		−0.1529		4 < 5	4 > 5	4 > 5	4 ≃ 5
32	1,4-Me_2-2-S	B	12	6	7		5	95		0.0000		6 = 7	6 = 7	6 < 7	6 < 7
33	-6-S	B	12	2	3		25	75		0.0000		2 = 3	2 = 3	2 < 3	2 < 3
34	1,5-Me_2-2-S	B	12	6	7		14	86		−0.1131		6 < 7	6 > 7	6 < 7	6 < 7
35	-3-S	B	12	6	7		⩾90	⩽10		−0.1131		6 < 7	6 > 7	6 > 7	6 > 7

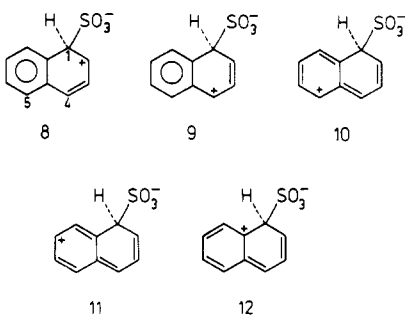
36	1,6-Me_2-4-S	B	12	2	7		91	7		−0.0991		2 < 7	2 > 7	2 < 7	2 > 7
37	1,7-Me_2-4-S	B	12	2	6		80	14		−0.1134		2 ≃ 6	2 > 6	2 ≃ 6	2 > 6
38	1,8-Me_2-4-S	B	12	2	6	7	20	<1	80	−0.1864	0.1864	2 = 7 < **6**	2 > 6 < 7	2 ≃ 6 < 7	2 >> 6 << 7
39	1,8-ethano-2-S	95 A	25	4	5	7	6	66	28	0.0000	−0.1269	*4* = *5* > 7	4 = 5 > 7	4 < 5 = 7	4 < 5 > 7
40	-4-S	95 A	25	2	7		25	75		0.0000		2 = 7	2 = 7	2 < 7	2 < 7
41	2,3-Me_2-5-S	B	12	1	7		≃20	≃80		−0.2554		1 < **7**	1 > 7	1 ≃ 7	1 < 7
42	2,6-Me_2-1-S	B	12	5	7		99	<2		−0.2499		5 < 7	5 > 7	5 = 7	5 >> 7
43	-4-S	B	12	7	8		11	89		0.1619		7 < *8*	7 < 8	7 > 8	7 < 8
44	2,7-Me_2-1-S	B	12	5	6		≃40	≃60		−0.0955		*5* > 6	5 > 6	5 < 6	5 ≃ 6
45	1,2,3-Me_3-4-S	B	12	6	7		37	63		0.0327		**6** = **7**	6 < 7	6 < 7	6 < 7
46	-7-S	B	12	4	5		79	21		−0.1500		4 < *5*	4 > 5	4 > 5	4 > 5
47	1,4,5-Me_3-3-S	B	12	6	7		98	≤2		−0.1468		6 < **7**	6 > 7	6 > 7	6 >> 7
48	-6-S	B	12	2	3		37	63		0.0587		2 > 3	2 < 3	2 < 3	2 ≃ 3
49	1,4,5,8-Me_4-2-S	B	12	6	7		7	93		0.0000		6 = 7	6 = 7	6 < 7	6 < 7
50	1,8:4,5-dipropano-2-S	B	12	6	7		11	89		0.0000		6 = 7	6 = 7	6 < 7	6 < 7
								1,6-Methano[10]annulene Series[j]							
51	2-S	C	12	4	5	7	<5	<5	>90	<<0.0[k]	0.0000	4 > *5* = *7*	4 < 5 = 7	4 > 5 < 7	(4 + 5) < 7
								Biphenylene Series[l]							
52	2-S	B	0	6	7	8	65	35	<5	0.0000	−0.0563	**6** = **7** = **8**	6 = 7 > 8	6 > 7 < 8	6 > 7 > 8
								Anthracene Series[m]							
53	1-S	96 A	170	5	8					0.0000		*5* = *8*	5 = 8	5 < 8	5 > 8
54	2-S	67–75 A	143	6	7					0.0000		6 = 7	6 = 7	6 < 7	6 < 7
55	9,10-Ph_2-2-S	D	110	6	7		35	45		0.0000		**6** = **7**	6 = 7	6 < 7	6 ≃ 7
								Phenanthrene Series[n]							
56	1,8-Me_2-2-S	B	0	6	7		≃70	≃30		0.0783		**6** > 7	6 < 7	6 > 7	6 > 7
57	-3-S	B	0	6	7		≃30	≃70		0.0783		**6** > 7	6 < 7	6 < 7	6 < 7
58	4,5-ethano-1-S	B	0	6	8		30	70		−0.1100		6 < *8*	6 > 8	6 = 8	6 < 8
59	9,10-Me_2-3-S	B	0	6	7		98	≤2		−0.0859		**6** = **7**	6 > 7	6 < 7	6 > 7
60	2,4,5,7-Me_4-1-S	B	0	6	8	9	<15	70	30–15	0.2568	−0.1488	6 < 8 < *9*	6 < 8 > 9	6 = 8 ≃ 9	6 < 8 > 9
61	3,4,5,6-Me_4-1-S	B	0	7	8	9	≃3	90	6	0.2157	−0.0366	7 < *8* = *9*	7 < 8 > 9	7 > 8 ≃ 9	7 << 8 > 9
								Pyrene Series[o]							
62	1-S	B	0	3	4	5	55	<3	<3	−0.0829	0.0000	*3* = *4* = *5*	3 > 4 = 5	3 ≃ 4 > 5	3 > 4 ≃ 5
				3	6	8	55	18	23	0.0000	0.0000	*3* = *6* = *8*	3 = 6 = 8	3 > 6 = 8	3 > 6 ≃ 8
63	1-Me-6-S	B	0	2	3	8	<3	14	83	0.2337	0.0455	2 < *3* = *8*	2 < 3 < 8	2 > 3 < 8	2 < 3 < 8
64	-8-S	B	0	2	3	6	2	<2	96	0.2337	0.0453	2 < *3* = *6*	2 < 3 < 6	2 > 3 < 6	2 ≃ 3 << 6
								Perylene Series[o,p]							
65	3-S	B	0	5	9	10	1.5		96	0.3705	0.0000	5 > *9* = *10*	5 < 9 = 10	5 ≃ 9 > 10	5 << (9 + 10)
				(8 + 11)	9	10	3		96	0.3705	0.0000	8 = 11 > *9* = *10*	8 = 11 < 9 = 10	8 = 11 > 9 > 10	(8 + 11) << (9 + 10)
								Nonalternant Arenes							
								Azulene Series[q]							
66	1-S	B	0	2	3	5		>98		0.4376	−0.4164	2 < *3* ≃ 5	2 < 3 > 5	2 < 3 > 5	2 << 3 >> 5
67		C	15					>98							2 << 3 >> 5
68	4,6,8-Me_3-1-S	C	15	2	3	5		>98		0.4376[r]	−0.4164[r]	2 ≃ *3* < 5	2 < 3 > 5	2 < 3 > 5	2 << 3 >> 5
69	1,3-*t*-Bu_2-5-S	C	15	7	8		>98			−0.2004[r]		7 > 8	7 > 8	7 > 8	7 >> 8
								Fluoranthene Series[s]							
70	3-S	98 A	7	7	8	9			*t*	−0.0636	0.0000	**7** = **8** = **9**	7 > 8 = 9	7 > 8 < 9	8 < 9[t]

[a] For reasons of convenience, the aromatic ring position of the mono- and disulfonic acids have been numbered as for the parent hydrocarbons; S stands for SO_3H. [b] A stands for % H_2SO_4, B for SO_3 in nitromethane, C for SO_3 in dioxane, and D for 102% H_2SO_4 in $MeCO_2H/(MeCO)_2O$. [c] The ΔL data were calculated: for the benzene series from K. Lammertsma, C. J. Verlaan, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2,* 719 (1978); for the naphthalene series from K. Lammertsma and H. Cerfontain, *ibid.*, 673 (1979), and H. J. A. Lambrechts and H. Cerfontain, *Tetrahedron,* **38**, 1667 (1982); for the phenanthrene series from H. Cerfontain, A. Koeberg-Telder, K. Laali, and H. J. A. Lambrechts,

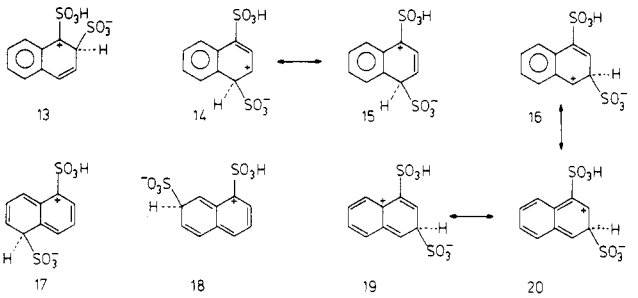
Footnotes for Table I (*Continued*)

accepted for publication in *J. Org. Chem.*; for the pyrene series from H. Cerfontain, K. Laali, and H. J. A. Lambrechts, *ibid.*, in preparation; for the biphenyls, biphenylene, perylene, azulene, and fluoranthene from C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations", Pergamon Press, Elmsford, NY, 1965. For the methyl derivatives of the arenes, the localization energies L were calculated with the simple Hückelmolecular orbital treatment by using the inductive model for the methyl substituent with $\delta\alpha_r = -0.3$. [d] The positions which encounter steric hindrance due to a *peri*-H interaction are italic, and positions for which the substitution is not retarded by steric hindrance are boldface. [e] The symbols $>>$, $>$, $\simeq$, $<$, and $<<$ stand for $\aleph > 30$, $30 > \aleph > 1.7$, $1.7 > \aleph > 0.6$, $0.6 > \aleph > 0.03$, and $\aleph < 0.03$, respectively. [f] A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, **26**, 1953 (1970); A. Koeberg-Telder and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 633 (1973). [g] T. A. Kortekaas, H. Cerfontain, and J. M. Gall, *ibid.*, 445 (1978); T. A. Kortekaas and H. Cerfontain, *ibid.*, 224 (1979); Z. R. H. Schaasberg-Nienhuis, H. Cerfontain, and T. A. Kortekaas, *ibid.*, 844 (1979). [h] The data for biphenyl have been used. [i] Numbers 21 and 23: A. A. Spryskov, and B. I. Karavaev, *Zh. Obshch. Khim.*, **23**, 1712 (1953); *Chem. Abstr.* **48**, 13667 (1954). Numbers 22 and 24: P. de Wit and H. Cerfontain, to be submitted for publication. Number 25: H. E. Fierz-David and C. Richter, *Helv. Chim. Acta*, **28**, 257 (1945). Number 34: H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J. Chem. Soc. Perkin Trans. 2*, 989 (1974). The other substrates are from K. Lammertsma, C. J. Verlaan, and H. Cerfontain, *ibid.*, 719 (1978), K. Lammertsma and H. Cerfontain, *ibid.* 673 (1979), and H. J. A. Lambrechts and H. Cerfontain, *Tetrahedron*, **32**, 1667 (1982). [j] K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.*, **100**, 8244 (1978). [k] See text. [l] H. Cerfontain, K. Laali, and H. J. A. Lambrechts, *Recl. Trav. Chim. Pays-Bas* **F 101**, 313 (1982). [m] M. Battegay and P. Brandt, *Bull. Soc. Chim. Fr.*, **31**, 910 (1922); **33**, 1667 (1923); see ref 27; A. Etienne, J. C. Lepeley, and R. Heymes, *Bull. Soc. Chim. Fr.*, **59**, 835 (1949). [n] H. Cerfontain, A. Koeberg-Telder, K. Laali, and H. J. A. Lambrechts, accepted for publication in *J. Org. Chem.* [o] H. Cerfontain, K. Laali, and H. J. A. Lambrechts, accepted for publication in *Recl. Trav. Chim. Pays-Bas.* [p] C. Marschalk, *Bull. Soc. Chim. Fr.*, **41**, 74 (1927). [q] P. de Wit, H. J. A. Lambrechts, and H. Cerfontain, to be submitted for publication. [r] The L values refer to nonsubstituted azulene. [s] T. Holbro and N. Campbell, *J. Chem. Soc.*, 2652 (1957); N. Campbell and N. H. Heir, *ibid.*, 1233 (1955). [t] The main isolated product is the 3,9-disulfonic acid.

Chart II



Scheme I



sulfonic acid than with the 3- and 4-sulfonic acids.[13] Further, it should be realized that the ΔL values of Table I refer to planar biphenyl, whereas the actual interphenyl angle in (both heptane and CCl_4) solution and in the gas phase is 23°[15] and 40°,[16,17] respectively. Given these considerations, one can conclude that the observed reactivity orders are in line with those based on the ΔL's, the directing effect of the sulfonic acid substituent, and the steric effects.

The difference in the partial rate factor ratio for the 4′- and 5′-positions of 2,2′-methano- (78:1) and 2,2′-ethanobiphenyl-4-sulfonic acid ($\simeq$1:6) is remarkable. The large difference is ascribed to the difference in the interphenyl angles (which are 0° and 20°,[18,19] respectively) and the difference in hyperconjugative stabilization of the σ complex for 5′-substitution. Thus, the conjugative stabilization of the σ complex for 4′-substitution will be less with the ethano than with the methano derivative, and the hyperconjugative stabilization of the σ complex for 5′-substitution will be greater for the ethano than for the methano derivative.

Naphthalene Series. With naphthalene-1- and -2-sulfonic acids the degree of sulfonation in the ring which carries the sulfo substituent is very small.[20,21] This may be explained in terms of the mesomeric structures describing the σ complexes for substitution of each of the

(13) The presumed lower degree of inter-ring conjugation is substantiated by the 10 times smaller rate of sulfonation of the biphenyl-2- than the -4-sulfonic acid in 93–98% H_2SO_4 at 25 °C.[14]

(14) T. A. Kortekaas, H. Cerfontain, and J. M. Gall, *J. Chem. Soc., Perkin Trans. 2*, 445 (1978).

(15) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340, 1357 (1959); **33**, 109 (1960).

(16) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949).

(17) I. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1974 (1944).

(18) G. H. Beavan, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.* **854** (1952).

(19) K. E. Howlett, *J. Chem. Soc.*, 1249 (1955).

(20) H. E. Fierz-David and C. Richter, *Helv. Chim. Acta*, **28**, 257 (1945).

(21) Sulfonation in 98.5% H_2SO_4 at 25.0 °C of naphthalene-1-sulfonic acid yields 58% 1,5-, 32% 1,6-, and 10% 1,7-disulfonic acid and of naphthalene-2-sulfonic acid yields 4% 1,3-, 74% 1,6-, 18% 1,7-, and 4% 2,6- and 2,7-disulfonic acid: P. de Wit and H. Cerfontain, unpublished results.

naphthalenesulfonic acids at the various positions. As exemplified for the sulfonation of naphthalene at the 1-position, these structures are of two types, viz., benzenoid (8 and 9) and quinoid (10–12, Chart II), of which the latter are higher in energy and thus far less contributing than the former.

The σ complex for the sulfonation of naphthalene-1-sulfonic acid at the 2-position is relatively high in energy in view of the repulsion between the positive charges on the mutually adjacent C^1 and the sulfonic acid S in the sole benzenoid mesomeric structure (13; see Scheme I). For the substitution at the 4-position, the repulsive charge interaction between the adjacent C^1 and S in the σ complex will be less, since there are now two benzenoid mesomeric structures (14 and 15). Accordingly, the positive charge at C^1 will be less in the σ complex for sulfonation at the 4- than at the 2-position. In the sole benzenoid mesomeric structure for substitution at C^3 (16) there is no repulsive interaction of positive charges on the adjacent C^1 and S. Thus, as to the sulfonic acid substituent effect, the positional reactivity order for sulfonation in the same ring as the 1-SO_3H substituent is $2 < 4 < 3$. For the other ring, sulfonation at the 5- and 7-positions proceeds via σ complexes which are (in view of the only weakly contributing high-energy quinoid mesomeric structures 17 and 18, respectively) of higher energy than the σ complexes leading to the 6- and 8-sulfonation. Thus the positional reactivity order as result of the directing effect of 1-SO_3H substituent is $5 \simeq 7 < 6 \simeq 8$. As to the relative rate of sulfonation of 3- and 7-positions, the energy is relatively very high for two of the five quinoid mesomeric structures (19 and 20) of the former σ complex and for one of the five quinoid mesomeric structures (18) of the latter. The energy is higher for 18 than for 19 and 20. In view of the relative contributions of these structures to the respective σ complexes, the rate of sulfonation at the 3- and 7-positions will not be very much different. Accordingly, the 1-SO_3H substituent of naphthalene leads to a positional reactivity order for sulfonation of $2 < 4 < 3 \simeq 5 \simeq 7 < 6 \simeq 8$. By similar reasoning the 2-SO_3H substituent of naphthalene will lead to a positional reactivity order of $1 < 3 \simeq 4 \simeq 6 = 8 < 5 = 7$. These orders have been listed in the next to the last column of Table I for both the naphthalene and the 1,6-methano[10]annulene series.

For the two naphthalenesulfonic acids proper, the more recent data of de Wit and Cerfontain (no. 22 and 24) are preferred over those of Spryskov and Karavaev (no. 21 and 23) in view of the method of analysis (^1H NMR vs. derivatization). The observed reactivity orders for the naphthalenesulfonic acids and their methyl derivatives are in general as predicted on the basis of ΔL, the SO_3H substituent effect, and the steric factors. For the somewhat deviating behavior of substrate no. 28 see the Discussion.

1,6-Methano[10]annulene Series. Sulfonation of 1,6-methano[10]annulene-2-sulfonic acid yields almost exclusively the 2,7-disulfonic acid. This agrees with the very strong preference for protonation of the parent hydrocarbon at the 2- over the 3-position[22,23] and the high 2:3 partial rate factor ratio for the protiodetritiation of 11,11-difluoro-1,6-methano[10]annulene,[24] which observations infer that $\Delta L_{2,3} \ll 0$.

Biphenylene Series. The observed positional reactivity order of the 2-sulfonic acid is in agreement with the predictions by ΔL and the SO_3H substituent effect, the steric hindrance for all the positions but the 3-position being absent.

Anthracene Series. The reported (apparently kinetically controlled) formation of a mixture of 1,5- and 1,8-anthracenedisulfonic acid on sulfonation of anthracene-1-sulfonic acid with 96% H_2SO_4 at 150–180 °C[25] was severely questioned by Suter[26] in view of the reported thermodynamically controlled formation of a mixture of anthracene-2-sulfonic acid and anthracene-2,6- and 2,7-disulfonic acid on reaction of anthracene with 67–75% H_2SO_4 at 140–145 °C.[27]

With 9,10-diphenylanthracene-2-sulfonic acid the α-positions are not accessible for sulfonation for steric reasons (9-phenylanthracene is not sulfonated at the 1- and 8-positions but only at the 4-, 5-, and 10-positions[28]). The

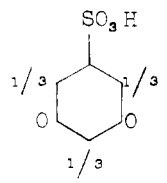
Table II. Directing Effect of the Sulfonic Acid Substituent in the Sulfonation of Arenesulfonic Acids: Reactivity Orders of Positions of Which Both the L's (of the Parent Arene) and the Steric Factors Are the Same

		reactivity order	
no.	arenesulfonic acid[a]	predicted by subst eff S[a]	obsd
1	benzene-1-S	3 > 4	3 > 4
10	*p*-xylene-2-S	5 < 6	5 < 6
22	naphthalene-1-S	4 < 5	4 << 5
		6 > 7	6 > 7
22	naphthalene-2-S	4 < 5	4 < 5
24, 25		5 > 8	5 > 8
32	1,4-dimethylnaphthalene-2-S	6 < 7	6 < 7
33	-6-S	2 < 3	2 < 3
38	1,8-dimethylnaphthalene-4-S	2 < 7	2 < 7
39	1,8-ethanonaphthalene-2-S	4 < 5	4 < 5
40	-4-S	2 < 7	2 < 7
49	1,4,5,8-tetramethylnaphthalene-2-S	6 < 7	6 < 7
50	1,8:4,5-dipropanonaphthalene-2-S	6 < 7	6 < 7
51	1,6-methano[10]annulene-2-S	5 < 7	5 << 7
52	biphenylene-2-S	6 > 7	6 > 7
53	anthracene-1-S	5 < 8	5 > 8[b]
54	-2-S	6 < 7	6 < 7
55	9,10-diphenylanthracene-2-S	6 < 7	6 < 7
62	pyrene-1-S	3 > 6	3 > 6
		3 > 8	3 > 8
65	perylene-3-S	9 > 10	9 ? 10
70	fluoranthene-3-S	8 < 9	8 < 9

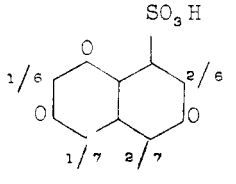
[a] S stands for SO_3H. [b] The structure of the products has been questioned (see text).

(22) P. Warner and S. Winstein, *J. Am. Chem. Soc.*, **91**, 7785 (1969).
(23) K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.*, **102**, 3257, 4528 (1980).
(24) R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 1287 (1975).
(25) M. Battegay and P. Brandt, *Bull. Soc. Chim. Fr.* **31**, 910 (1922); **23**, 1667 (1923).
(26) C. M. Suter, "The Organic Chemistry of Sulfur", Wiley, New York, 1944, p 301.
(27) Soc. St. Denis, German Patents 73961 and 76280; Friedländer, **3**, 196, and **4**, 270, respectively, cited in ref 26.
(28) H. Cerfontain, A. Koeberg-Telder, C. Ris, and C. Schenk, *J. Chem. Soc., Perkin Trans. 2*, 966 (1975).
(29) As an alternative, it could be explained in terms of a difference in the rotamer population of the 1-methyl group of 1,2-dimethylnaphthalene compared with 1-methylnaphthalene and toluene,[30,31] due to the *peri*-H and the gear-wheel type of *o*-methyl hydrogen interaction (the C^1–C^2 bond length of napthalene is relative small[32]). Accordingly, the hyperconjugative stabilization effect of the 1-methyl of 1,2-dimethylnaphthalene would be different, whereas the Hückel MO calculation presumed the "inductive" parameter $\delta\alpha$, for this methyl to be equal to those of other methyls, viz., −0.3.[2,33] The change in the methyl hyperconjugative stabilization of 1,2-dimethylnaphthalene would manifest itself in the NMR chemical shifts. This is, however, contrary to the actual observation, as the observed and the by-factor-analysis-calculated ^{13}C chemical shifts of 1,2-dimethylnaphthalene are equal (cf. Table VI of ref 30), rendering this alternative explanation improbable.
(30) D. K. Dalling, K. H. Landner, D. M. Grant, and W. R. Woolfenden, *J. Am. Chem. Soc.*, **99**, 7142 (1977).

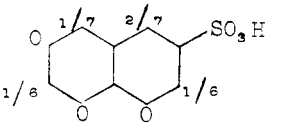
Chart III. Fractions of Mesomeric Structures of the σ Complexes which are Destabilized by the Positive Charge on the Sulfur of the SO_3H Substituent and the Derived Reactivity Orders



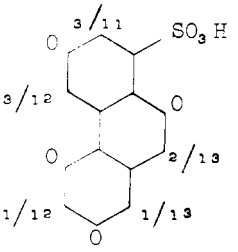
2=4<3



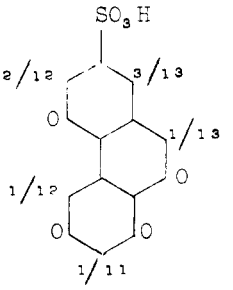
2<4<7<5<3=6=8



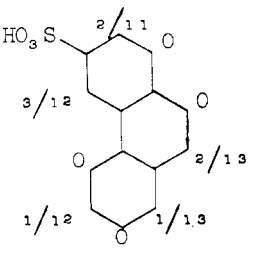
1<3=6<8<4=5=7



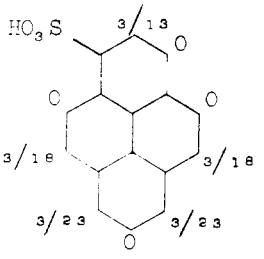
2<4<9<6<8
8<3=5=7=10



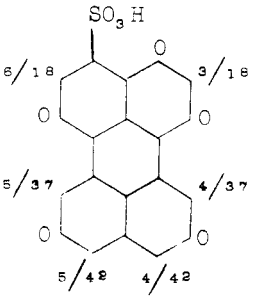
1<3<7<5<10
10<4=6=8=9



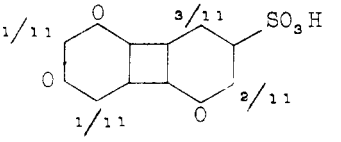
4<2<9<6<8
8<1=5=7=10



2<5=9<6=8
8<3=4=7=10



2<5<12<10<7<9
9<1=4=6=8=11



1<3<5=7<6=8

Table III. Effect of ΔL (Parent Arene) in the Sulfonation of Arenesulfonic Acids: Reactivity Orders of Positions for Which Both the Effect of the Sulfonic Substituent and the Steric Factor Are the Same

		reactivity order	
		predicted	
no.	arenesulfonic acid[a]	by ΔL	obsd
14	biphenyl-3-S	3′ < 4′	3′ < 4′
22	naphthalene-1-S[b]	5 > 7	5 > 7
24	naphthalene-2-S[b]	5 > 7	5 > 7
26, 27	1-methylnaphthalene-4-S[b]	2 > 6	2 > 6
37	1,7-dimethylnaphthalene-4-S	2 > 6	2 > 6
42	2,6-dimethylnaphthalene-1-S	5 > 7	5 > 7
61	3,4,5,6-tetramethyl-phenanthrene-1-S	8 > 9	8 > 9
65	perylene-3-S	5 < 9	5 < 9

[a] S stands for SO_3H. [b] There is a small difference in the steric factor, but it is opposed to the L factor.

observed positional reactivity orders with the exception of the first one (no. 53) are in agreement with the SO_3H substituent effect.

Table IV. Effect of Steric Hindrance in the Sulfonation of Arenesulfonic Acids: Reactivity Orders of Positions for Which Both the L's (of the Parent Arene) and the Effect of the Sulfonic Acid Substituent Are the Same

		reactivity order	
		predicted by steric	
no.	arenesulfonic acid[a]	hindrance	obsd
1	benzene-S	2 < 4	2 < 4
9	1,3-dimethylbenzene-5-S	2 > 4	2 > 4
10	1,4-dimethylbenzene-2-S	3 < 5	3 < 5

[a] S stands for SO_3H.

Phenanthrene Series. The observed positional reactivity orders of the monosulfonic acids are in agreement with the predictions on the basis of ΔL, the SO_3H substituent effect, and the steric factors.

Pyrene Series. The listed positional reactivity orders, predicted by the SO_3H substituent, are based on the same type of reasoning as outlined for the naphthalene series. The observed reactivity order can be explained on the basis of the positional orders predicted by ΔL, the SO_3H substituent effect, and the steric factors.

Perylene Series. The sulfonation of the 3-sulfonic acid yields mainly the 3,9- and 3,10-disulfonic acids. On the basis of the directing effect of the SO_3H substituent, it can

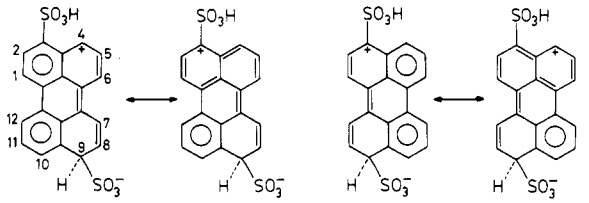
(31) D. A. Forsyth, P. Lucas, and R. M. Burk, *J. Am. Chem. Soc.*, **104**, 240 (1982).
(32) W. C. Herndon, *J. Am. Chem. Soc.*, **96**, 7605 (1974).
(33) K. Lammertsma, C. J. Verlaan, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 719 (1978).

Table V. Reactivity Orders for Positions with Opposing Factors as to the Sulfonic Acid Substituent and the Localization Energies, but with the Same Steric Hindrance[a]

		reactivity order			
		predicted by			
no.	arenesulfonic acid[b]	ΔL[a]	subst eff S[b]	obsd	$\lvert\Delta L\rvert$
28	1,2-dimethylnaphthalene-4-S	6 > 7	6 < 7	6 ≃ 7	0.0022
53	biphenylene-2-S	7 > 8	7 < 8	7 > 8	0.0563
60	9,10-dimethylphenanthrene-3-S	6 > 7	6 < 7	6 < 7	0.0859
44	2,7-dimethylnaphthalene-1-S[c]	5 > 6	5 < 6	5 < 6	0.0955
18	biphenyl-2-S	3′ < 4′	3′ > 4′	3′ < 4′	0.0970
20	biphenyl-4-S	3′ < 4′	3′ > 4′	3′ < 4′	0.0970
36	1,6-dimethylnaphthalene-4-S	2 > 7	2 < 7	2 > 7	0.0991
65	perylene-3-S	(8 + 11) < (9 + 10)	8 = 11 > 9 > 10	(8 + 11) << (9 + 10)	0.3701

[a] The substrates are listed in the order of increasing ΔL. [b] S stands for SO_3H. [c] There is a small difference in the steric factor, but it is opposed to the observed reactivity order.

be argued that the degree of substitution is greater for the 9- than the 10-position, viz., by considering the mesomeric structures **21–24**. The energy of these structures will



21 **22** **23** **24**

decrease in the order **22** > **24** ≫ **23** > **21** in view of (i) the more quinoid character of **22** and **24** as compared with the biphenyl-like structures **21** and **23** and (ii) the electric repulsion between the positive charges of the SO_3H sulfur and the carbon to which it is bound in **22** and **23**. Thus the SO_3H substituent effect predicts the positional reactivity order to be 9 > 10.

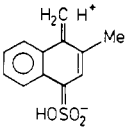
Azulene Series. With the sulfonation of the sulfonic acids of this nonalternant arene, the observed extreme positional reactivity orders are determined by the large differences in the localization energies of the parent arene. The directing effect of the SO_3H substituent (which predicts the same order) is relatively small.

Fluoranthene Series. To explain the predominant formation of the 3,9- over the 3,8-disulfonic acid in the sulfonation of fluoranthene-3-sulfonic acid, one can set up an argument very similar to that advanced to explain the reactivity order 9 > 10 in the sulfonation of perylene-3-sulfonic acid. The ΔL criterion would, however, predict the 3,7-disulfonic acid to be the main isomer.

Discussion

The positional reactivity order in the sulfonation of an arenesulfonic acid is governed by three factors, viz.: the delocalization energies of the positions under comparison of the corresponding aromatic hydrocarbon, the electronic effect of the sulfonic acid substituent, and steric factors. For positions which have the same ΔL and the same steric hindrance, the electronic sulfonic acid substituent effect[34] is decisive (Table II). Similarly, ΔL is decisive for positions for which the effect of the sulfonic acid substituent and the steric effect are the same (Table III), and the steric factor is determinative if each of the two other factors is the same (Table IV).

In the absence of a difference in steric factors the positional reactivity of positions for which the localization energies of the parent arene are the same is governed by the sulfonic acid substituent. However, the directing effect of the sulfonic acid group is overruled by the ΔL factor when $|\Delta L|$ is large (> 0.1, Table V). The behavior of 1,2-dimethylnaphthalene-4-sulfonic acid (no. 28) is remarkable. Although $\Delta L_{6,7}$ is only very small (–0.0022), the substitution pattern is not determined solely by the sulfonic acid substituent effect, as the degree of 6- and 7-substitution is about equal. This may be explained in terms of hyperconjugation between the 1-methyl and 4-sulfo groups in the arenesulfonic acid, as shown in **25**.



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Accordingly, (i) the directing power of the sulfonic acid substituent will be less than in other naphthalenesulfonic acids, and (ii) the directing effect of the 1-methyl will be less than that of the 2-methyl. Both these effects will lead to an increase in the 6:7 substitution ratio, as is in fact observed.[29]

Opposing factors of ΔL, of the SO_3H substituent effect, and of steric hindrance are observed for a large number of arenesulfonic acids (see Table I), viz.: no. 3 (positions 5, 6), 26 (2, 6 and 6, 7), 28 (6, 7), 30 (2, 7), 31 (4, 5), 34 (6, 7) 35 (6, 7), 36 (2, 7), 38 (2, 6 and 6, 7), 41 (1, 7), 43 (7, 8), 44 (5, 6), 56 (6, 7), 58 (6, 8), 61 (7, 8), and 63 (2, 3).

Conclusion

In the absence of a satisfactory simple model for the calculations of the reactivity order for the electrophilic substitution of sulfonic acid substituted aromatic hydrocarbons, it appears that the present model which considers the separated factors of the localization energies of the parent aromatic hydrocarbon, including all the alkyl and phenyl substituents except the sulfonic acid group, and the directing electronic effect of the SO_3H substituent

(34) It was suggested by one of the referees that the destabilization of the positive charge by the substituent sulfonic acid group could be obtained more simply by counting the fraction of mesomeric structures[35] of the various σ complexes which are destabilized by the positive charge on the sulfur of the sulfonic acid substituent. Isolating the effect of only the sulfonic acid group for the nonalkylated alternant arenesulfonic acids give the reactivity orders collected in Chart III. These reactivity orders differ only slightly in some cases from those advanced in the present paper and used as prediction in Table I (last column but one). The method of counting the fraction of mesomeric structures presumes the equivalence of the various mesomeric structures in describing a given σ complex. This is not in accordance, however, with the valence bond MO approximation.[36]

(35) Cf. W. C. Herndon, *Tetrahedron*, **29**, 3 (1973); *J. Am. Chem. Soc.*, **95**, 2404 (1973); **96**, 7605 (1974); **98**, 887 (1976); W. C. Herndon and M. L. Ellzey, Jr., *ibid.*, **96**, 6631 (1974).

(36) C. A. Coulson, "Valence", 2nd ed., Oxford University Press, London, 1961, Chapter IX.

explains satisfactorily the observed positional reactivity orders, provided that allowance is made for the differences in the steric factors.

It further appears that the substituent effect satisfactorily predicts the reactivity order of positions for which the L's of the parent arene are the same, provided that the steric effects are the same.

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Carbon-13 Nuclear Magnetic Resonance Chemical Shifts and the Twist Conformations of 1,3-Dioxanes. Geminal Substitution at the 4-Position: A Guaranty for the Chair Form?[1a]

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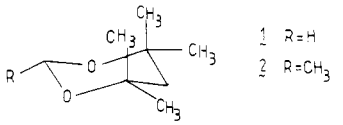
In contrast to earlier reports, the ^{13}C NMR chemical shifts for a set of 2,2,4,4-tetramethyl-substituted 1,3-dioxanes together with the derived substituent effects show that a pseudoaxial substituent in the 2,5- or 1,4-twist form is so greatly disfavored that these derivatives rather exist in the 2,4-diaxially substituted chair form. Those derivatives with syn-axial methyl groups at the 2- and 4-positions but without a geminal substitution at both of them seem, however, to greatly prefer either a 2,5- or 1,4-twist form. In the shift increment parametrization the new δ-syn-axial 2a,4a ($\alpha_a\gamma_a$) increments have large positive values at C(2) and C(4) which almost cancel out the negative γ_a effects. Their influences at C(5) and C(6) are small, however.

On the basis of the ^{13}C NMR chemical shifts[1b] and the ^1H vicinal coupling constants[2] it has been concluded that 2,4-syn-diaxially methyl-substituted 1,3-dioxane rings always escape into twist conformations. On assumption of the additivity of conformational energies, the above postulate also found some support in thermochemical studies,[3] e.g., in that of 2,2,4,4,6-pentamethyl-1,3-dioxane.[3c] On the other hand, Burkert's molecular mechanics calculations[4a] speak for the conclusion that all 2,2,4,4-tetramethyl-substituted 1,3-dioxanes greatly prefer the chair conformation.

In a recent paper[5] we reported the ^{13}C NMR spectra of methyl-substituted 1,3-dioxanes and used the data for 1,3-dioxane itself and 44 methyl derivatives known to exist in chair conformations to calculate the values of different substituent effects on the ^{13}C chemical shifts of the ring carbon atoms. In the same context[5] it was pointed out that 4,4,6,6-tetramethyl-substituted 1,3-dioxanes with the possible exception of the *cis*-2,4,4,5,6,6-hexamethyl derivative exist predominantly in the chair conformation. This observation is also in agreement with the enthalpies of formation[3d,h] of **1** and **2**. As to the conformation-holding influence of the geminal substitution at position 4 (and/or



at position 2), some controversy between Burkert's calculations[4a] and our ^{13}C NMR results[5] still exists. In order to get a consistent insight into the chair–twist equilibria of 1,3-dioxanes with all the available data,[1-6] we prepared *trans*-2,4,4,6-tetramethyl- (**3**) and *trans*-2,2,4,5,5,6-hexamethyl-1,3-dioxane (**6**) and a set of 2,2,4,4-tetramethyl-substituted 1,3-dioxanes (**7**, **10–12**), and their ^{13}C NMR spectra were recorded. The ^{13}C chemical shifts of **4**, **5**, **8**, and **9** were available from our earlier work.[5] The aim of the present study is to establish with the necessary shift data to what extent the simultaneous geminal substitution at C(2) and C(4) is a guaranty for the chair form and to establish how strong a conformation-holding group is a single geminal substituent in the case of 2,4-syn-diaxially methyl-substituted 1,3-dioxanes.

Experimental Section

Compound **3** was prepared with the method of Eliel and Nader.[7] Compounds **6**, **7**, and **10–12** were prepared conventionally from 2,2-dimethoxypropane and a suitable diol.[1b,2,8]

The ^{13}C spectra were recorded on a JEOL FX-60 FT NMR spectrometer operating at 15.03 MHz with 8K data points. Samples were prepared in 10-mm-o.d. tubes as 10% v/v solutions in $CDCl_3$ with 2% Me_4Si as a reference. The deuterium of the solvent provided the lock signal, and the probe temperature was kept at 298 ± 1 K. The ^{13}C chemical shifts of compounds **7–12** are collected in Table I, those of compounds **4–6** in Table II and

(1) (a) This report is also part 2 in "^{13}C Chemical Shifts: Sensitive Detectors in Structure Determination" (for part 1 see ref 5) and part 5 in "^{13}C NMR Studies of Saturated Heterocycles" (for part 4 see ref 5). (b) Kellie, G. M.; Riddell, F. G. *J. Chem. Soc. B.* **1971**, 1030.

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