



## Structural Features of Linear Alkylbenzene Sulfonates as Observed in $^{13}\text{C}$ Magnetic Resonance Spectra

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### ABSTRACT

Fourier-transform  $^{13}\text{C}\{^1\text{H}\}$  nuclear magnetic resonance spectroscopy of the internally substituted phenylhexadecanes and their *para*-sulfonates has been done as a part of a general study of alkylaryl sulfonates thought to be of significance in complex surfactants, such as the petroleum sulfonates and various synthetic products. The systematics of structural variations and their effects on observed chemical shifts of specific carbon atoms is detailed with the aim of developing rapid, nondestructive methods of analysis of complex mixtures of both hydrocarbons and hydrocarbon sulfonates. Advantages and restrictions of the  $^{13}\text{C}$  spectrometric method are illustrated in the case of a mixture of alkylbenzene sodium sulfonates typical of a synthetic surfactant.

### INTRODUCTION

A variety of monoisomeric linear alkylbenzene sulfonates has been synthesized (1) for the purpose of determining their ability to promote very low interfacial tensions between hydrocarbons and water. The interest in such systems is generated, at least in part, by their applications to tertiary oil recovery processes (2,3). In that context, extensive studies have been done involving complex commercial surfactants and crude oils or hydrocarbon mixtures (4-7). As such investigations do not reveal clearly the possible relationships among structural features of surfactant components and details of the observed interfacial tension behavior (8,9), a need was felt to correlate results with those obtained using single, pure surfactants and well-defined oils (1,10,11). That requires, on the one hand, a reasonable knowledge of the principal composition of a variety of commercial surfactants and, on the other, assurance of the identity, and purity, of selected monoisomeric species characteristically present in the complex mixtures.

High resolution proton magnetic resonance spectroscopy has been used to some extent in the characterization of simple surfactant mixtures (12), but is more generally applicable to relatively pure substances, with relation to proof of structure or sample purity (13,14). In general, compounds of high molecular weight yield broad, poorly resolved lines in proton spectra, and the relatively narrow range of resonance positions, or chemical shifts, does not permit selective recognition of nuclei in closely similar structural situations. In  $^{13}\text{C}$  spectra of comparable compounds and mixtures, the spectral lines are usually narrower and the range of chemical shifts is more than an order of magnitude greater (15,16).

In preliminary investigations of several commercial surfactants, we have clearly identified spectral components and patterns characteristic of linear alkyl groups and substituted aromatic systems (17,18), largely benzenoid in some cases, which suggest that in those instances the total

carbon content is dominated by relatively simple alkylbenzene sulfonates. As average equivalent weights of those substances were of the order of 300-500, we have undertaken to correlate the observed spectra of alkylbenzene sulfonates with a range of structural variations possible in such molecules, but not ordinarily encountered in less complex compounds. The work reported here is primarily concerned with the internally substituted phenylhexadecanes and their sodium sulfonates. A mixture of closely related species, representative of a synthetic surfactant, was analyzed and the results compared with the reported composition of the mixture.

### EXPERIMENTAL PROCEDURES

The synthesis of linear alkylbenzenes and their corresponding sodium sulfonate derivatives was reported previously (1). Spectroscopically pure hydrocarbons were obtained by repeated fractionation under reduced pressure, treatment with concentrated sulfuric acid (98%), adsorption and elution from a silica gel column, and then vacuum distillation at  $\pm 1$  C. The alkylbenzene sodium sulfonates were purified by solvent extraction followed by partition between water, isopropyl alcohol, and pentane solvents.

Analytical investigation (acid-base titration) and spectroscopic analysis (mass spectrometry, infrared, and proton nuclear magnetic resonance) showed the purified hydrocarbons and the sulfonates to be of high purity and having monoisomeric structures.

Infrared spectra were obtained with a Beckmann IR 9 spectrophotometer. Neat liquid samples of the hydrocarbons suspended between 1.5 in. diameter sodium chloride plates were used. The sulfonates were dissolved in carbon tetrachloride, and the IR spectra were obtained using 0.1 mm cavity sodium chloride cells. A potassium bromide pellet containing 0.5% n-hexadecylbenzene sodium sulfonate was used due to the insolubility of this sulfonate in carbon tetrachloride.

The masses of molecular ions of the phenylalkanes were determined with a Dupont Instruments mass spectrometer model No. 21,491. The measurements were carried out using 70 eV at 250 C.

Proton nuclear magnetic resonance (PMR) spectra were obtained with a Varian HA-100 spectrometer in the CW mode with a field sweep time of 1000 sec, a sweep width of 1000 Hz, and an  $H_1$  field of 0.2 milligauss. The field was locked to internal tetramethylsilane (TMS) in deuteriochloroform solutions at the ambient temperature, ca. 28 C. Chemical shifts are reported in ppm downfield from TMS ( $\delta$  scale).

Proton-decoupled  $^{13}\text{C}$  Fourier-transform (CMR) spectra were taken at ambient temperature, ca. 32 C, and 22.615 MHz, with a Bruker WH-90 spectrometer, using the deuterium resonance of solvent deuteriochloroform as a lock signal. Chemical shift values were calculated relative to internal TMS at low concentrations in the sample solutions or to

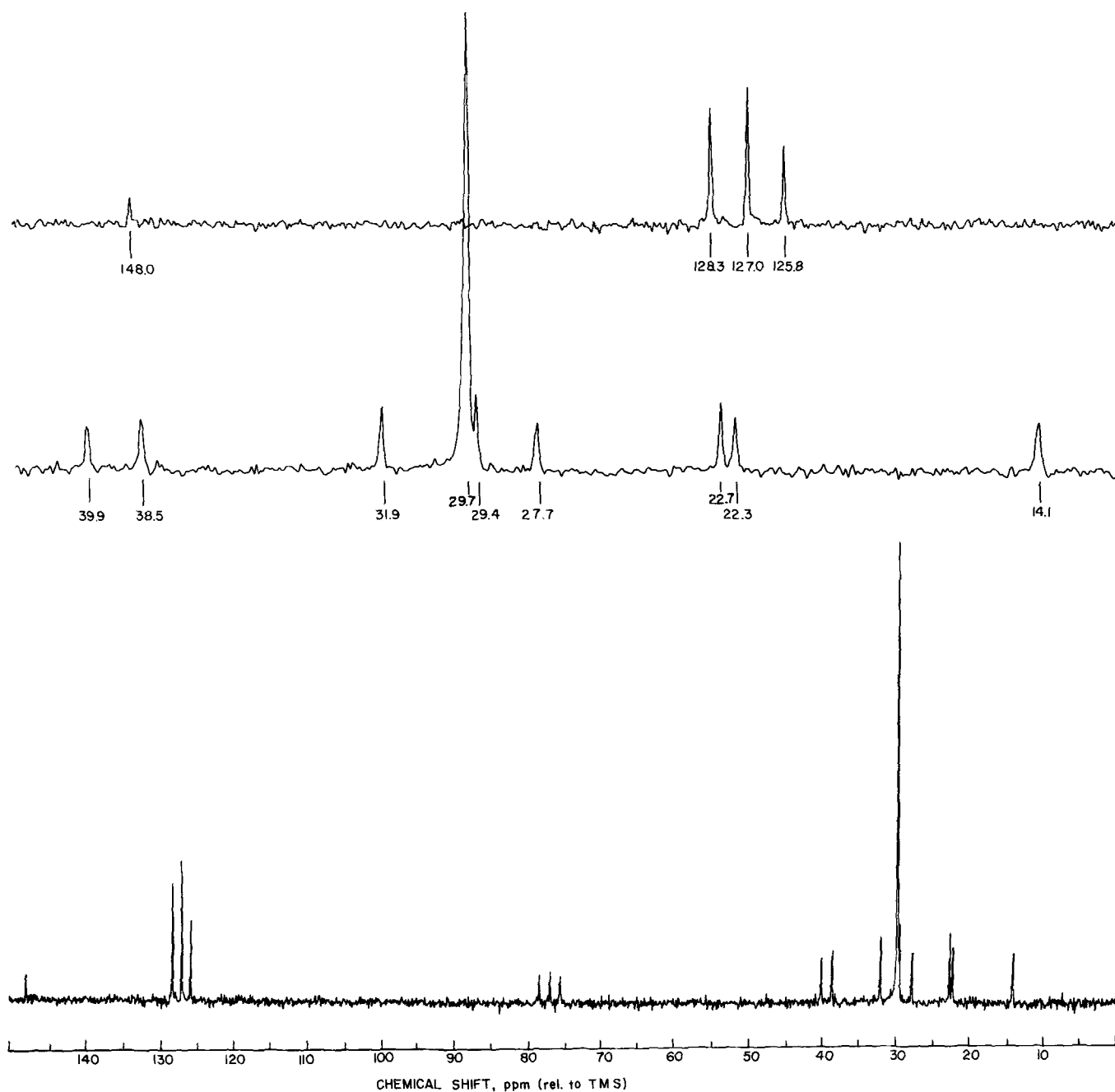


FIG. 1. Proton-decoupled Fourier-transform  $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-phenylhexadecane (10% by weight in deuteriochloroform). Lower: full spectrum. Middle: expansion of the alkyl region. Upper: expansion of the aryl region.

the locking frequency where TMS could not be conveniently added to the solutions. Free induction decays of radiofrequency pulses producing an  $18^\circ$  tip angle for  $^{13}\text{C}$  were accumulated as 8192 data points in the time domain when observing a 6024-Hz region spanning the desired spectral range. Data acquisition time was 0.7 sec, and no additional delay between pulses was introduced. Thus, signal averaging over 5000 pulses could be accomplished in about 1 hr. The  $18^\circ$  tip angle was found to give satisfactory results for both alkyl and aryl  $^{13}\text{C}$  signals with respect to saturation effects and adequate signal-to-noise ratios. All spectra were obtained with natural abundance  $^{13}\text{C}$  (1.1 atom %).

Spectroscopic samples were ordinarily prepared by dissolving appropriate weights of surfactants or hydrocarbons in deuteriochloroform, as received from the suppliers. In most cases, those samples contained a small amount of water, which was not removed. Several preparations were

carefully dried with molecular sieves or were vacuum-dessicated prior to solution. In those spectra, line positions and integrated intensities were found to be the same as for wet samples, although in some instances observed line widths were different.

## RESULTS

The synthetic scheme for the preparation of alkylbenzene sodium sulfonates was followed by infrared absorption spectra for the appearance and disappearance of the characteristic absorptions of the functional groups involved (carbonyl, hydroxyl, and sulfonate). The infrared spectra of the phenylalkanes prepared were identical with those previously published by the American Petroleum Institute (19) and Gray et al. (20) for linear alkylbenzenes and internally substituted phenyldodecane, respectively.

The synthesized alkylbenzene sulfonates possessed the

TABLE I  
Chemical Shifts in the Phenylhexadecanes

Alkyl carbon	1-phenyl	2-phenyl	3-phenyl	4-phenyl	5-phenyl	6-phenyl	7-phenyl	8-phenyl
16	14.1	14.1	14.1	14.0	14.0	14.0	14.0	14.1
15	22.7	22.7	22.7	22.6	22.7	22.6	22.6	22.8
14	31.9	31.9	31.9	31.9	31.9	31.9	31.9	32.1
13	29.4	29.4	29.4	29.3	29.3	29.3	29.3	29.5
12	29.7	29.7	29.7	29.7	29.6	29.6	29.6	29.7
11	29.7	29.7	29.7	29.7	29.6	29.6	29.6	29.9
10	29.7	29.7	29.7	29.7	29.6	29.6	29.7	27.8
9	29.7	29.7	29.7	29.7	29.6	29.6	27.6	37.2
8	29.7	29.7	29.7	29.7	29.6	29.6	36.9	*46.3
7	29.7	29.7	29.7	29.7	27.6	36.9	*46.0	37.2
6	29.7	29.7	29.7	27.6	36.9	*46.0	36.9	27.8
5	29.7	29.7	27.6	36.9	*46.0	36.9	27.6	29.9
4	29.7	27.7	36.5	*45.8	36.7	27.2	29.4	29.5
3	31.5	38.5	*47.9	39.2	29.6	31.9	31.9	32.1
2	29.4	*39.9	29.7	20.7	22.8	22.6	22.6	22.8
1	*36.0	22.3	12.2	14.0	13.9	14.0	14.0	14.1
Aryl carbon								
o (2)	128.4	127.0	127.8	127.9	127.7	127.7	127.7	127.8
m (3)	128.3	128.2	128.2	128.2	128.1	128.2	128.2	128.3
p (4)	125.6	125.8	125.7	125.7	125.7	125.7	125.7	125.8
b (1)	143.0	148.0	146.0	146.5	146.5	146.5	146.5	146.4

expected characteristic strong, broad doublet sulfonate absorption in the 1250-1170  $\text{cm}^{-1}$  region (3). Three strong single absorption bands at 1130, 1040, and 1010  $\text{cm}^{-1}$  were also observed. *n*-Hexadecylbenzene sodium sulfonate showed a doublet at 840-815  $\text{cm}^{-1}$  indicating *para* substituent absorption. The other internally substituted alkylbenzene sulfonates exhibited a single distinctive *para*-absorption at 830  $\text{cm}^{-1}$ . This may be attributed to the phenyl group attached to a bridged carbon atom bearing two alkyl groups. The absence of any absorption bands at 750 or 800  $\text{cm}^{-1}$ , the characteristic absorption of the *ortho* or the *meta* isomer respectively, indicates that the prepared sulfonates possessed essentially monoisomeric structures.

The purified phenylalkanes showed molecular ions corresponding to their molecular weights. The mass spectra indicated the high purity of the hydrocarbon since no molecular ions or fragmentation patterns corresponding to the starting materials or intermediate products were detected.

The isomeric hexadecylbenzene sulfonates, in which the sulfonated phenyl group is attached at various positions on the normal aliphatic hydrocarbon chain, were examined by both PMR and CMR. In all cases, the spectroscopic evidence indicated greater than 95% *para* sulfonation on the benzene ring. Proton spectra of both sulfonates (sodium salts) and parent hydrocarbons, obtained with 10 wt % chloroform solutions, were consistent with the assigned structures with respect to both peak positions and relative intensities, and significant line broadening was observed in the former for all protons on or near the benzene sulfonate group. In those spectra a broad line appeared near the middle of the spectrum, at 3.3 ppm, which was attributed to trapped water in what was presumed to be a micelle with the alkyl chains of the amphiphyle oriented outward in the chloroform solvent (oil external). No comparable peak was observed in the hydrocarbon solutions. Dilution of the sulfonate samples with wet deuteriochloroform caused the presumed water proton peak to narrow and move upfield to the position characteristic of molecularly dispersed water in chloroform. Doublets at 6.87 and 7.73 ppm, and a total absence of other peaks except for a small residual signal attributable to residual  $\text{CHCl}_3$ , in the aromatic spectral region confirmed that sulfonation was exclusively *para* to the alkyl group. The peak corresponding to the  $\alpha$ -carbon of the side chain was very broad, as would be expected in an aggregated structure.

A representative  $^{13}\text{C}$ -NMR (CMR) spectrum for 2-phenylhexadecane is shown in Figure 1. It was obtained with approximately 3000 transients in a period of about 40 min from a 10 wt % solution in deuteriochloroform. Other details are given in the experimental section. In Figure 1 a 4000 Hz region of the spectrum, containing all observed lines, is displayed. The alkyl region, to the right, is from 0 to 50 ppm, relative to TMS. The deuterated chloroform triplet (resulting from coupling of natural abundance  $^{13}\text{C}$  with  $^2\text{H}$ , nuclear spin 1, in  $\text{CDCl}_3$ ) is observed near the center of the spectrum, between 75 and 80 ppm, and the aryl carbon spectrum, to the left. Peak assignments are listed in Table I. More detailed views of the alkyl and aryl regions of the spectrum on expanded scales are shown in the upper part of Figure 1. The spectrum of 4-(1-heptylnonyl)benzene sodium sulfonate is shown in Figure 2. As in the proton spectra, several of the carbon lines are broadened in a pattern consistent with the formation of micelles by the sulfonate. The sulfonate spectrum was obtained with no special precautions, and the solutions contained a small but undetermined amount of water. In dried samples, the lines are even broader, in essentially the same sequential pattern.

Purity of the several isomeric alkylbenzene sulfonates was indicated by the spectral patterns observed. That is, the numbers of lines and relative intensities are consistent in each case with the expected products. Assignments of specific lines to individual carbon atoms is based primarily on comparisons with frequencies observed for a variety of alkanes and substituted benzenes (15), although specific, precise parameters resulting from regression analysis of the data obtained here are slightly different from those reported for pure alkanes and one-to-six carbon alkylbenzenes. However, general trends and relative differences are substantially the same. For these data, using the calculated parameters, fits are much closer than those obtained for a broader range of molecular species and solution conditions. Here, we are concerned primarily with hydrocarbons in the molecular weight region around 300 daltons, and sulfonates, around 400 daltons, all in deuteriochloroform solution at a concentration of ca. 10 wt %, a rather well-defined and restricted set of conditions. Parameters obtained in the regression analysis are given in Table III, according to the equation for the chemical shift,  $\delta_i^1$ , for carbon *i*, as affected

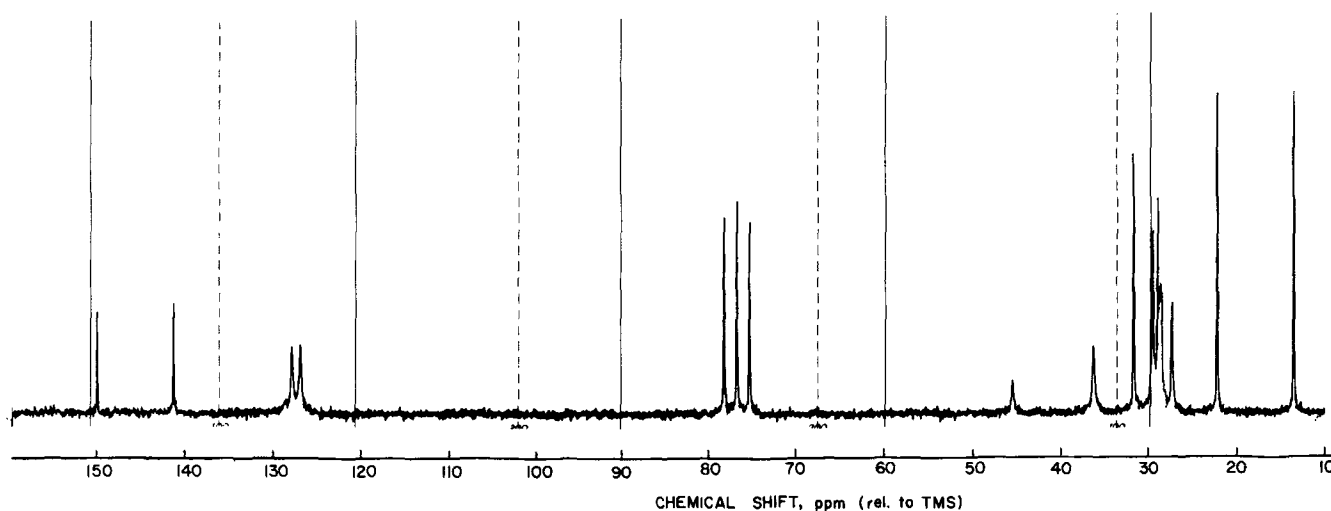


FIG. 2. Proton-decoupled Fourier-transform  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 4-(1-heptylonyl)benzene sodium sulfonate (10% by weight in deuteriochloroform).

TABLE II

Chemical Shifts in the Hexadecylbenzene Sodium Sulfonates

Alkyl carbon <sup>a</sup>	(1-propyltridecyl)	(1-butylododecyl)	(1-pentylundecyl)	(1-hexyldecyl)	(1-heptylonyl)
16	14.0	14.0	14.0	14.0	14.1
15	22.6	22.6	22.6	22.6	22.7
14	31.9	31.9	31.9	31.9	32.0
13	29.3	29.4	29.4	29.3	29.3
12	29.7	29.7	29.7	29.6	29.5
11	29.7	29.7	29.7	29.7	29.9
10	29.7	29.7	29.8	29.7	27.7
9	29.7	29.7	29.8	27.5	36.6
8	29.7	29.7	27.7	36.5	*46.0
7	29.7	27.7	36.5	*45.9	36.6
6	27.7	36.7	*45.9	36.5	27.7
5	36.9	*45.7	36.5	27.5	29.9
4	*45.9	36.2	27.2	29.3	29.5
3	39.1	29.7	31.9	31.7	32.0
2	20.7	22.6	22.6	22.6	22.7
1	14.0	14.0	14.0	14.0	14.1
Aryl carbon					
o (3)	127.3	127.5	127.4	127.3	127.6
m (2)	126.4	126.5	126.4	126.4	126.5
(SO <sub>3</sub> <sup>-</sup> ) (1)	140.6	140.0	140.5	140.4	140.6
b (4)	149.2	149.6	149.5	149.4	149.6

<sup>a</sup>Retains numbering of the corresponding hydrocarbon.

by  $n_{ij}$  carbons at the  $j$ th position relative to  $i$  (17).

$$\delta_c^i = B + \sum_j A_j n_{ij} \quad (I)$$

Effects of the phenyl group, treated as a single entity, refer to attachment at a secondary carbon in an alkane (values for primary carbon attachment in parentheses). In those cases,  $A_{\phi\alpha}$  is for the carbon to which the phenyl group is bonded,  $A_{\phi\beta}$ , to the carbon first removed, and  $A_{\phi\gamma}$ , to that second removed. No effects were observed beyond that in a linear chain. There is some evidence that branching at the carbon atoms  $\beta$  or  $\gamma$  to the phenyl group does not give satisfactory results with this highly simplified treatment. In other cases, it appears to be satisfactory for a wide range of alkylbenzenes.

The effects attributable to *para* sulfonation are similarly handled as a perturbation on the parent hydrocarbon. Thus, in the aryl group, the *ortho* carbon (*meta* to the principal alkyl group) is shifted -1.8 ppm, the *meta* carbon, -0.3 ppm, and the *para* carbon, or alkyl-bridgehead, +3.0 ppm. The sulfonated carbon atom is shifted +14.7 ppm. All values refer to the sodium salt in chloroform solutions. In that

connection, the 1-phenyl, 2-phenyl, and 3-phenyl isomers of the hexadecane series were insoluble, and spectra with reasonable signal-to-noise ratios were not observed at the saturation limit. As noted previously (see Experimental), spectra of other sulfonates gave evidence of micelle formation in that line broadening, diminishing to the methyl termini of the alkyl side chains, was significant in the sodium sulfonate-chloroform but not in the corresponding hydrocarbon-chloroform solutions. Formation of the 15-crown-5-etherate of the  $\text{Na}^+$  ion sharpened the spectra, but resulted in pronounced shifts of aryl carbon atoms. Those effects are being investigated further and will be reported on elsewhere.

Shift assignments for the group of isomeric hydrocarbons and for five of the sulfonates are given in Tables I and II. Table II retains the alkyl carbon designations of the parent hydrocarbons. Alkylbenzene sulfonates having a total normal chain length range of 12 to 18 carbons gave closely comparable results, predictable on the basis of the parameters in Table III and the noted effects of *para* sulfonation. The additive character of the parameters is clearly evident in the "stick figure" spectra presented in Figure 3. There the spectrum of hexadecane (A) is compared with

TABLE III  
Chemical Shift Parameters

Parameter	ppm	Parameter	ppm
B	-1.5	$A_{\phi\alpha}$	16.5(21.9)
$A_{\alpha}$	8.6	$A_{\phi\beta}$	7.2(8.8)
$A_{\beta}$	9.2	$A_{\phi\gamma}$	-2.0(-2.0)
$A_{\gamma}$	-2.5		
$A_{\delta}$	0.3		

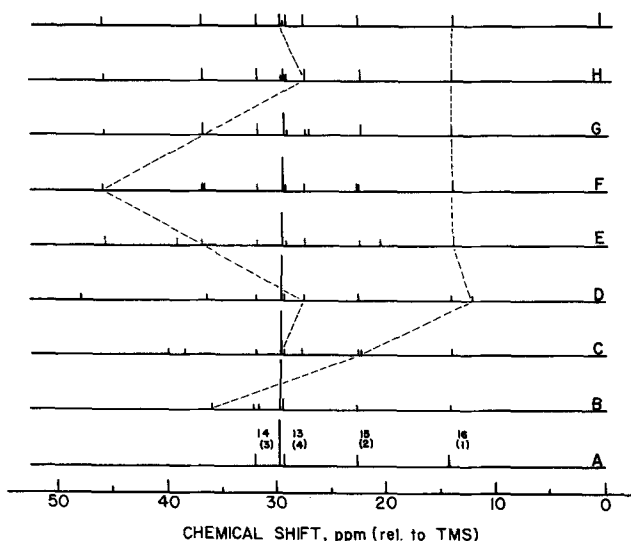


FIG. 3. "Stick figure" spectra of the phenylhexadecanes and hexadecane (A). Spectra B through I are for the 1-phenyl to 8-phenylhexadecanes, respectively. Numbers above spectrum A refer to carbon numbers in the alkyl chains. Line positions of C-1 and C-5 are connected by the dashed lines.

the internally substituted phenyl derivatives. In each, carbon atoms toward the termini of the long side chains, C-11 to C-16, maintain fixed spectral positions, as indicated. C-1, at the short chain termini, is degenerate with C-16 for the 8-phenyl to 4-phenyl derivatives, but the combination of phenyl and end effects causes its signal to move, first upfield, then downfield, as the phenyl group is moved to the end of the chain. Initial spectral positions in the parent alkane are, from right to left in 3A: C-1,16; C-2,15; C-4,13; C-5,13; C-3,14. C-5 is the point of attachment in 5-phenylhexadecane (spectrum F), but the C-5 absorption line shifts as shown in Figure 3 in higher and lower isomers,

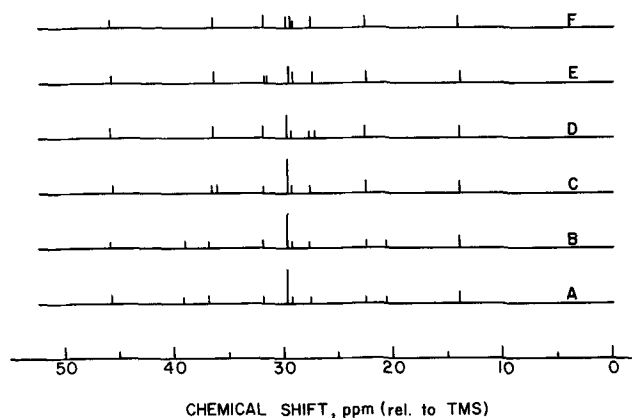


FIG. 4. "Stick figure" spectra of the hexadecylbenzene sodium sulfonates and 4-phenylhexadecane (A). Spectra B through F are for the sulfonates corresponding to 4-phenyl through 8-phenylhexadecane, respectively.

as the point of attachment moves to other carbon atoms in the chain. In Figure 4, the spectrum of 4-phenylhexadecane (A) is compared with its sodium sulfonate (B) and it is apparent that the effect of *para* sulfonation is essentially negligible in the alkyl portion of the molecule. Other sulfonates are represented by the stick figures in 4C through 4F.

#### ANALYSIS OF A MIXTURE

A synthetic surfactant comprising singly substituted alkylbenzene sulfonates with side chains in the range C<sub>11</sub>-C<sub>14</sub> was obtained from Universal Oil Products (our number UOP-1). The analysis provided with the sample indicated essentially no normal side chains, but a range of isomers corresponding to attachment of the phenyl group at all other positions in the alkyl chains. Thus, the mixture contained molecules branched only at the point of attachment to the benzene ring, each having two alkyl chains, one short and one long, or two of equal length, on the tertiary carbon at the bridgehead. Relative abundances of possible chains in the mixture, C<sub>1</sub> to C<sub>12</sub>, exclusive of the tertiary carbon, are listed in Table IV, column 3, as calculated from the UOP analytical data. As the data were provided for each isomer at each overall alkyl chain length, those abundances are sums of a number of items and the possible error is difficult to estimate, but is probably of the order of 10% (relative).

A spectrum of the mixture is shown in Figure 5, with an

TABLE IV

Analysis of Relative Abundances of Side Chains  
in a C<sub>11</sub>-C<sub>14</sub>benzene Sodium Sulfonate Mixture

Chain length <sup>a</sup>	% Of total from <sup>13</sup> C peak integrals	% Of total from reported analytical data
C <sub>1</sub>	7.9 <sup>b</sup> , 8.0 <sup>c</sup>	6.7
C <sub>2</sub>	7.5 <sup>b</sup> , 7.5 <sup>c</sup>	7.2
C <sub>3</sub>	7.3 <sup>b</sup>	8.5
C <sub>4</sub>	12.1 <sup>d</sup>	9.9
C <sub>5</sub> -C <sub>12</sub>	65.2 <sup>e</sup>	65.9
Mean	C5.9	C5.8

<sup>a</sup>Exclusive of the tertiary carbon, e.g., 4-(1-butylheptyl)benzene sodium sulfonate contains one C<sub>4</sub> and one C<sub>6</sub> chain.

<sup>b</sup>From integrals of the peaks representing aryl bridgehead carbon atoms. C<sub>3</sub> abundance is least accurate because of the necessary peak resolution.

<sup>c</sup>From integrals of the methyl group peaks.

<sup>d</sup>From integrals of peak envelopes 22.6-22.8 and 27.2-27.8 ppm, by difference.

<sup>e</sup>From integrals of peak envelopes 29.3-29.7 and 22.6-22.8 ppm, by difference.

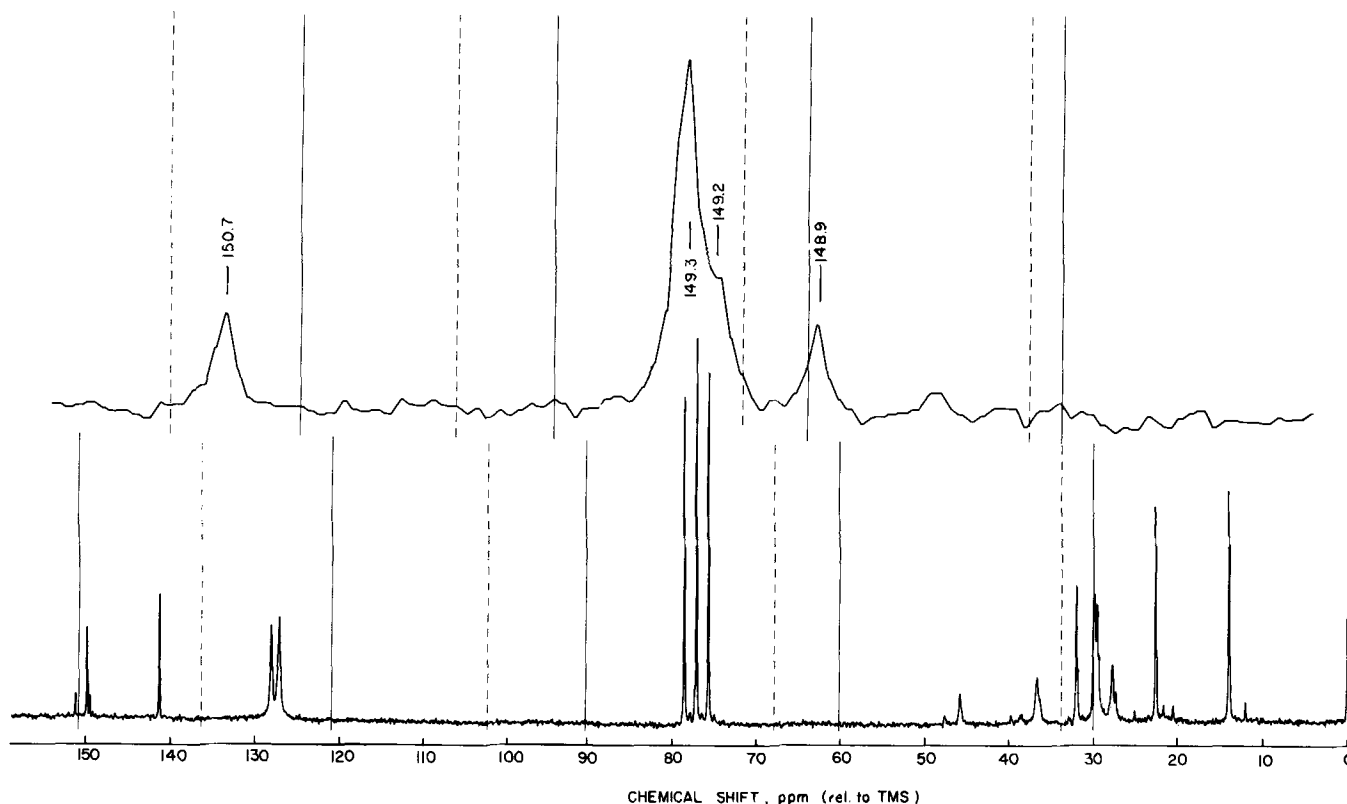


FIG. 5. Proton-decoupled Fourier-transform  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of UOP-1. a. Full spectrum. b. Expansion of the aryl bridgehead carbon region, in which full scale corresponds to 3.8 ppm.

expansion of the bridgehead carbon region (phenyl C-4). Noteworthy features in the latter are the separate peaks corresponding to the 2-phenyl and 3-phenyl isomers, having  $\text{C}_1$  and  $\text{C}_2$  short chains, and the poorly resolved shoulder for the 4-phenyl isomer, with a  $\text{C}_3$  short chain. The principal peak in that region contains contributions from 5-phenyl to 7-phenyl isomers. The alkyl portion of the complete spectrum contains minor peaks attributable to various short chains:  $\text{C}_1$  at 22.3 ppm;  $\text{C}_2$ , 12.2 ppm;  $\text{C}_3$ , 20.7 ppm; all of which are sharp and well separated. Similar characteristic peaks at 39.2 ( $\text{C}_3$ ), 38.5 ( $\text{C}_1$ ), and 39.9 ( $\text{C}_1$ ) are too broad and weak to provide accurate integrals. Relative abundances (peak integrals) of the four bridgehead carbon peaks and of the three methyl peaks were calculated from the spectral data to provide the values in column 2, Table IV, for  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$ . The value listed there for  $\text{C}_4$  was obtained by difference in the peak integrals for the 22.6-22.8 ppm and 27.2-27.8 ppm spectral regions. The former contains contributions from  $\text{C}_4$ - $\text{C}_{12}$  chains and the latter, from  $\text{C}_5$ - $\text{C}_{12}$  chains. We estimate errors of 7-10% on the  $\text{C}_1$ - $\text{C}_3$  values and 10-15% for  $\text{C}_4$ . Mean chain lengths for all species were calculated from the respective analytical data and appear to agree to well within the experimental error estimates. In the spectral analysis the intensity of the peak envelope at 29.3-29.7 ppm was compared with that at 22.6-22.8 ppm, which represents a single carbon atom (second from the chain terminus) in each chain longer than  $\text{C}_4$ , and corrected for the accidental degeneracies occurring in  $\text{C}_2$  and  $\text{C}_4$  short chains. The former contains resonances for carbon atoms more than three removed from either end of the alkyl group or the point of phenyl attachment and provides a measure of mean chain length. It should be noted that in our calculations the peaks from methyl and methylene carbons were treated separately, as the relaxation of the former contains a contribution from spin-rotational interactions, so that the nuclear Overhauser enhancements (21) are not the same. For the several mobile

methylene carbons the enhancements should be comparable. There is essentially no enhancement for the quaternary aryl bridgehead carbons and their relaxation behaviors have been observed to be closely similar, so that those comparisons depend only on the accuracy of integration.

## DISCUSSION

For this group of compounds the shift parameters are really little more than a concise way of presenting a related group of data and allowing an easy method of predicting line positions for similar compounds. For example, the two  $\beta$ -carbons in 4-(1-heptylnonyl)benzene sodium sulfonate are expected to be at the same resonance position:

$$\delta = -1.5 + 2(8.6) + 2(9.2) + 2(-2.5) + 0.3 + 7.2 = 36.6 \text{ ppm} \quad (11)$$

as observed. Thus, for any normal hydrocarbon chain having a phenyl group attached at a given position, these parameters should give reliable predictions.

In the phenyl group of the hydrocarbon, the o, m, p, and b (bridgehead) carbons are at 127.7, 128.2, 125.7, and 146.5 ppm in the cases where the shortest side chain is four carbons long, or more. One then expects for the sulfonate that the corresponding positions will be found at, or near, 127.4, 126.4, 140.4, and 149.5 ppm.

Proton decoupling results in the enhancement of absorption signals for  $^{13}\text{C}$  to which protons are directly attached to a maximum of three through the nuclear Overhauser effect (NOE) (21). In these cases, only the quaternary carbons at the alkyl bridgehead and the point of sulfonation do not have such attached protons. Examination of the spectra presented in Figures 2 and 5 are illustrative. It will be noted that those less intense lines are also not broadened as much as others in, or close to, the benzene ring. If the broadening is indeed attributable to decreased rate of molecular motion resulting from micellar aggregation, those  $^{13}\text{C}$

nuclei which are predominantly relaxed by dipolar interaction with the spins of attached protons are expected to be most affected by the decreased rate of motion with respect to the applied field, as compared with those relaxed by other mechanisms, such as random encounters with solvent or neighboring molecules.

Estimated line positions were calculated for the linear alkanes and one-to-six carbon alkylbenzenes reported previously (17), as well as other straight chain derivatives measured in this laboratory, using the parameters in Table III. The mean standard deviation was 0.5 ppm for the comparison of calculated and observed shifts. For the higher molecular weight compounds, all in 10 wt % deuteriochloroform solution, the standard deviation was ca. 0.2 ppm. However, it should be emphasized that additional branching of the side chains, especially near the phenyl group, or further substitution on the benzene ring require that additional parameters be introduced to accommodate conformational effects and restrictions.

As one purpose of these investigations is to provide a basis for analysis of complex mixtures which may contain one or more of these related species, it is interesting to compare the results of a CMR spectrometric examination of a relatively simple mixture of similar molecular species with those of other methods of analysis, in this instance, presumably chromatography and mass spectrometric measurements. Data were provided to us for the sample designated UOP-1 as percentages of the several internally substituted isomers of alkylbenzene sodium sulfonates having side chains from C<sub>11</sub> to C<sub>14</sub>. The CMR results do not provide that kind of molecular detail, but do permit interpretation in terms of relative numbers of short chains on tertiary carbons bridged to the aryl group, and of mean chain lengths of longer chains, by integration of selected peaks characteristic of specific carbon atoms in the alkyl chains.

That example is admittedly a simple and straightforward case, but one which is of considerable interest in connection with investigation of alkylation and sulfonation processes under varying conditions, or with distribution studies in oil-water systems. Given additional detailed information on the chemical shift patterns of other groups of alkylaryl sulfonates, similar characterizations for mixtures of those compounds should be done easily and nondestructively. For more complex mixtures involving many classes of compounds, it may be possible only to identify the classes themselves, with qualitative estimates of relative abundances. However, as such information is often difficult to obtain by other methods, CMR can make valuable contributions to the investigation of those mixtures.

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