^{33}S NMR Spectroscopy. 2. Substituent Effects on ^{33}S Chemical Shifts and Nuclear Quadrupole Coupling Constants in 3- and 4-Substituted Benzenesulfonates. Correlation between Chemical Shifts and Nuclear Quadrupole Coupling Constants†

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Substituent effects on ^{33}S NMR parameters in 3-$XC_6H_4SO_3Na$ (X = NO_2, NH_3^+, CF_3, SO_3^-, OH, H, CH_3, NH_2, and O^-) have been studied. The results obtained confirm that ^{33}S chemical shifts and line widths depend upon the electronic properties of substituents present on the aromatic ring. The trends observed are consistent with the behavior found for previously reported 4-substituted benzenesulfonates, whose list has been now enlarged to include ionic substituents (O^-, NH_3^+, $NH(CH_3)_2^+$, SO_3^-). Dual substituent parameter analysis of ^{33}S nuclear quadrupole coupling constants using charged and uncharged substituents has been performed. A linear relationship between ^{33}S chemical shifts and nuclear quadrupole coupling constants demonstrates that in 3- and 4-substituted benzenesulfonates substituents affect ^{33}S NMR parameters in the same way, probably by expansion or contraction of p valence shell electrons around the sulfur nucleus. ^{17}O NMR data suggest that sulfur d orbitals are little effective in transmitting substituent effects.

Introduction

In a previous work,[1] we have reported that the ^{33}S NMR parameters of 4-$XC_6H_4SO_3Na$ depend upon electronic properties of substituents present on the aromatic ring. In particular, it was found that line widths (LW) and nuclear quadrupole coupling constants (χ) increase with the electron-releasing or -withdrawing properties of substituents. Furthermore, chemical shifts (δ) show the occurrence of a reverse substituent effect (SE).[2]

The interpretation of experimental data led to systematic correlations between ^{33}S δ, χ, and the electronic properties of substituents. Indeed, substituent chemical shift effects ($\Delta\delta$) and χ values were correlated with the Hammett−Taft inductive and mesomeric substituent constants, σ_I and σ_R, by the dual substituent parameter (DSP) equation[3]

$$\Delta\delta\ (\chi) = \rho_I\ \sigma_I + \rho_R\sigma_R$$

where ρ_I and ρ_R are the transmission coefficient of inductive and resonance effects.

DSP analysis revealed that both inductive and resonance effects are important in determining δ and χ values, with the inductive contribution predominating over the resonance counterpart (i.e., $|\rho_I| > |\rho_R|$).

It was not possible to determine the normal or reverse character of SE on χ, because of the uncertainty in the signs of the χ values as calculated from LW values. Anyway, the DSP analysis gave a good fit only assuming a change in the signs of the χ values on going from electron-withdrawing to electron-releasing groups and, hence, an inversion of the component of the electric field gradient (EFG) tensor at the sulfur atom along the C(1)−S axis.

Table 1. ^{33}S Chemical Shifts (δ)[a] and Line Widths (LW in Hz) in 3-$XC_6H_4SO_3Na$ and 4-$XC_6H_4SO_3Na$ Considered in This Work (σ_I and σ_R Are the Hammett-Taft Substituent Constants Used in DSP Analysis)

X	δ	LW	σ_I	σ_R
3-NO_2	−15.9	100	0.65	0.13
3-NH_3^+	−15.1	37	0.60	−0.18
3-CF_3[b]	−14.2	19.5	0.40	0.00
3-SO_3^-	−13.9	22	0.29	0.06
H	−11.4	8.8	0.00	0.00
3-CH_3[b]	−10.9	18.8	0.01	−0.18
3-OH	−12.3	15	0.33	−0.70
3-NH_2	−11.1	19	0.08	−0.74
3-O^-	−9.5	70	−0.26	−0.55
4-$NH(CH_3)_2^+$	−15.3	55	0.70	−0.14
4-NH_3^+	−14.3	22	0.60	−0.18
4-SO_3^-	−13.8	19	0.29	0.06
4-O^-	−8.1	140	−0.26	−0.55

[a] Values referred to Na_2SO_4 1 M in H_2O. [b] Values taken from ref 5.

All these results suggested that in 4-substituted benzenesulfonates SE on ^{33}S δ and χ have the same origin and could be ascribed to variations in the electron density on sulfur.

In the present work, investigations of SE on the ^{33}S NMR parameters of 4-substituted benzenesulfonates have been completed, introducing ionic substituents (namely O^-, NH_3^+, SO_3^-, and $NH(CH_3)_2^+$). Moreover, results regarding SE on δ and χ of 3-substituted benzenesulfonates are reported.

Results and Discussion

The ^{33}S δ and LW values in 3- and 4-substituted benzenesulfonates considered are reported in Table 1. In 3-substituted benzenesulfonates, too, ^{33}S NMR parameters depend on the electronic properties of substituents

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on the aromatic ring, showing the same behavior already found for the para series.[1]

Chemical Shifts. A reverse SE on δ is also evident in 3-substituted benzenesulfonates. Indeed, the DSP analysis of $\Delta\delta$ gives the following results:

$$\rho_I = -6.21 \qquad \rho_R = -1.58$$
$$SD = 0.29 \qquad f = 0.11$$

The meaning of the DSP analysis and the relative importance of mesomeric and inductive terms have been discussed in detail for 4-substituted compounds.[1] The results obtained for the 3-substituted benzenesulfonates allow us to verify the arguments previously presented.

In the 4-substituted benzenesulfonates the DSP analysis, now including ionic substituents, confirms the results previously obtained.[1,4]

$$\rho_I = -5.91 \qquad \rho_R = -3.31$$
$$SD = 0.19 \qquad f = 0.07$$

Within the limits of experimental error, the inductive effect is almost the same in both series of compounds ($(\rho_I)_{meta}/(\rho_I)_{para} = 1.05$). As expected, in the meta series the mesomeric coefficient decreases to about one-half with respect to the para series ($(\rho_R)_{meta}/(\rho_R)_{para} = 0.48$).

Line Widths and Nuclear Quadrupole Coupling Constants. It had been demonstrated that the ^{33}S nuclear relaxation in 4-substituted benzenesulfonates is dominated by the quadrupolar mechanism, at least at a magnetic field in the range 4.7−9.4 T.[1] This has been also verified at 11.7 T both for 3- and for 4-substituted benzenesulfonates; therefore, eq 1 can be used to obtain χ values[5]

$$LW = 1/\pi T_1 = 1/\pi T_2 \qquad (1)$$
$$1/T_1 = 3.948\chi^2(1 + \epsilon^2/3)\tau_q$$

where $\epsilon = (q_{yy} - q_{xx})/q_{zz}$ is the asymmetry parameter of the EFG tensor at the sulfur nucleus, q_{xx}, q_{yy}, and q_{zz} are the components of the EFG tensor, and τ_q is the correlation time describing the motional modulation of the interaction between the ^{33}S quadrupole moment and the EFG.

Furthermore, in all the benzenesulfonates examined in this work, ^{33}S LW depends on different electron-withdrawing or -releasing abilities of substituents, which should mainly affect q_{zz}. Indeed, the influence of ϵ on LW should be near to zero, because of the symmetry of the electronic distribution around the ^{33}S nucleus in the $-SO_3^-$ moiety.

For each molecule the τ_q has been taken as the correlation time of the sphere having a radius equal to the half of the largest interatomic distance, which was obtained from standard bond lengths and angles. τ_q values have been calculated as previously described[1] (Table 2). The reliability of the calculated τ_q values has been checked in 3-$SO_3^-C_6H_4SO_3Na$ and 3-$NH_3^+C_6H_4SO_3$-Na by measuring ^{13}C spin−lattice relaxation times and the experimental τ_c values obtained for C(4) and C(6) ($\tau_c = 28 \times 10^{-12}$ s in 3-$SO_3^-C_6H_4SO_3Na$ and $\tau_c = 24 \times 10^{-12}$ s in 3-$NH_3 + C_6H_4SO_3Na$) are in a reasonable agreement with the calculated τ_q values. The uncertainty on τ_q values may be accepted because χ depends on the square root of τ_q. In any case, the results reported below permit the verification a posteriori of the reliability of calculated τ_q values.

Table 2. τ_q (10^{-12} s) and ^{33}S χ Absolute Values (MHz) in 3-$XC_6H_4SO_3Na$ and 4-$XC_6H_4SO_3Na$ Considered in This Work (I and II are the Sets of Signs Assigned to Perform DSP Analysis and Linear Correlation between δ and χ)

X	τ_q	$\lvert\chi\rvert$	set I	set II
3-NO_2	31	1.5_9	+	−
3-NH_3^+	26	1.0_3	+	−
3-CF_3	30	0.6_8	+	−
3-SO_3^-	35	0.6_7	+	−
H	16	0.5_8	−	+
3-CH_3	27	0.7_0	−	+
3-OH	25	0.6_4	−	+
3-NH_2	26	0.7_2	−	+
3-O^-	23	1.5_3	−	+
4-$NH(CH_3)_2^+$	24	1.3_3	+	−
4-NH_3^+	21	0.8_7	+	−
4-SO_3^-	24	0.7_5	+	−
4-O^-	21	2.2_9	−	+

The ^{33}S χ absolute values (Table 2) have been calculated from the observed LW values (Table 1) reduced by 2 Hz to account for the effect of water solvation on the ^{33}S relaxation rate.[6]

For 3-substituted benzenesulfonates the results of the DSP analysis are

$$\rho_I = \pm 2.62 \qquad \rho_R = \pm 1.16$$
$$SD = 0.20 \qquad f = 0.19$$

The DSP of χ values in the complete 4-substituted series gives almost the same results obtained without considering charged substituents:

$$\rho_I = \pm 2.91 \qquad \rho_R = \pm 1.71$$
$$SD = 0.17 \qquad f = 0.14$$

Also in 3-substituted benzenesulfonates the EFG undergoes inversion on going from electron-withdrawing to electron−releasing substituents.

Although it is not possible to ascertain the normal or reverse character of SE, because of the uncertainty in the χ signs, it is clear that the inductive effect dominates over the resonance effect both in 3- and 4-substituted benzenesulfonates. However, the results reported below (eq 2) demonstrate that SE has the same character in both 3- and 4-substituted benzenesulfonates.

The χ values in benzenesulfonates with ionic substituents in the meta and para positions fit well with data relative to uncharged substituents, thus showing that there is no detectable effect on χ which could be attributed to the distortion of the core electron symmetry by the electric charge on the molecule.[7]

Correlation between Chemical Shifts and Nuclear Quadrupole Coupling Constants. A good linear correlation can be found between the ^{33}S δ and χ values in 3- and 4-substituted benzenesulfonates:

$$\delta = \pm 2.01\chi - 12.66 \qquad (2)$$
$$SD = 0.31 \quad \text{corr coeff} = 0.993$$

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This proves experimentally that the SE operates in the same way both on the ^{33}S δ and on the χ.

Further insight can be gained by examining the theoretical relationships that correlate χ and screening constant, σ, to electron density.

It is well-known that Saika and Slichter[8] have approximated Ramsey's equation[9] as

$$\sigma = \sigma_d + \sigma_p \tag{3}$$

where σ_d and σ_p are, respectively, the diamagnetic and paramagnetic contributions to the screening constant for the observed atom. According to Jameson and Gutowsky,[10] the paramagnetic term for ^{33}S is

$$\sigma_p = (e^2h^2/6\pi^2m^2c^2)\Delta E^{-1}[\langle r^{-3}\rangle_{3p}P_u + \langle r^{-3}\rangle_{3d}D_u] \tag{4}$$

χ values are also dependent on $\langle r^{-3}\rangle$ and on electron distribution around the nucleus:[11]

$$\chi = (1 - \gamma_\infty)(e^2Q/h)[(4/5)\langle r^{-3}\rangle_{3p}P'_u + (4/7)\langle r^{-3}\rangle_{3d}D'_u] \tag{5}$$

In these equations m and e denote the electron mass and charge, respectively, ΔE is an average electronic excitation energy, $\langle r^{-3}\rangle$ is the expected value of the inverse cube of the mean radius of 3p and 3d orbitals, P_u, P'_u, and D_u, D'_u are functions of p and d orbitals populations, respectively, but have different expressions for δ and χ, and γ_∞ is the Sternheimer antishielding factor.

In 3- and 4-substituted benzenesulfonates SE on d electron contribution in eqs 4 and 5 should be negligible with respect to p electrons because of the significantly lower density of d orbitals into the region close to the nucleus.[12] This is confirmed by the ^{17}O NMR spectra. Indeed the ^{17}O δ range in 3- and 4-substituted benzenesulfonates (1 ppm)[13] is small if compared to benzaldehydes (67 ppm), benzoates (14 ppm), and nitrobenzenes (37.1 ppm),[14] and ^{17}O χ values are nearly constant (about 4.3 MHz). Since sulfur d electrons could be involved only in bonding with oxygen atoms, the approximately constant values of ^{17}O NMR parameters suggest that any d electron contribution to the S−O bond is little affected by the electronic properties of the substituents present on the aromatic ring.

Neglecting d electrons in eqs 4 and 5 one obtains:

$$\sigma = \sigma_d + K' \frac{P_u}{P'_u}\Delta E^{-1}\chi(1 - \gamma_\infty)^{-1}$$

or

$$\delta = \delta_d + K' \frac{P_u}{P'_u}\Delta E^{-1}\chi(1 - \gamma_\infty)^{-1} \tag{6}$$

Comparing eqs 2 and 6, it is evident that the intercept in eq 2 represents the value of the diamagnetic contribution to ^{33}S δ in 3- and 4-substituted benzenesulfonates ($\delta_d = -12.66$, value referred to a solution of Na_2SO_4 1 M in H_2O) and, as expected, all the δ variations observed should be ascribed to the paramagnetic term.

The existence of a linear relationship between δ and χ implies that the terms P_u/P'_u, ΔE, and γ_∞, are nearly constant in the compounds examined.

The calculation of the population terms P_u[10,15] and P'_u[16] shows that the ratio P_u/P'_u is a constant only for small variations of sulfur 3p orbital populations.

As far as ΔE is concerned, it can be concluded that the excitation energies of all the compounds examined are almost equal and the presence of substituents with different electronic properties on the aromatic ring does not induce a significant variation in the degree of mixing of electronic ground and excited states.

Along the same line, γ_∞ is not significantly influenced by the electronic properties of substituents on the aromatic ring.

In conclusion, variations in ^{33}S δ and χ seem to be mainly controlled by the magnitude of the term $\langle r^{-3}\rangle_{3p}$. On the other hand, the role of d orbitals is difficult to evaluate only on the basis of ^{33}S NMR data. A deeper knowledge of the behavior of ^{17}O NMR parameters, particularly χ, could give an important contribution in ascertaining the role of (d−p)π polarization in the $-SO_3^-$ moiety.

Experimental Section

In this work ^{33}S NMR spectra were recorded at 11.7 T using a 10 mm broadband probe head. ^{17}O NMR spectra were recorded by a selective 15 mm probe head. Spectra of both nuclei were recorded under proton-noise decoupling (Waltz sequence). Typical recording parameters were as follows: spectral width 1500 Hz for ^{33}S and 45 000 Hz for ^{17}O spectra, 90° observing pulse, $T = 22 \pm 1$ °C; acquisition times and number of transients were optimized on each sample in order to obtain spectra with good digital resolution and signal-to-noise ratio.

Further experimental details have been reported elsewhere.[1]

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