^{13}C-NMR SPECTRA OF BENZENESULPHONYL DERIVATIVES

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^{13}C-NMR chemical shifts and ^1J(CH) and ^3J(CH) coupling constants have been determined for a series of $C_6H_5SO_2X$ derivatives (X = Cl, C_6H_5, ONa, OCH_3, OC_2H_5, OC_6H_5, NH_2, $NHNH_2$, $N(CH_2)_5$, NHC_6H_5) in hexadeuteriodimethyl sulphoxide solutions, and the substituent shift values of benzene nucleus have been calculated for the individual SO_2X groups. These groups, carrying partial positive charge at the sulphur atom, have electron-acceptor effects on the benzene nucleus, and increasing electron-donor character of the substituent X is connected with a proportional increase of mesomeric acceptor influence on the benzene nucleus and with increase in absolute values of ^1J(CH).

So far relatively little attention has been paid to ^{13}C-NMR spectra of aromatic compounds containing sulphone group or a sulphonyl group derivative. Authors of the published papers (benzenesulphonic acid in aqueous sulphuric acid[1]; sodium benzenesulphonate and benzenehexasulphonic acid in heavy water[2]; sodium 4-toluenesulphonate in heavy water[3]; sodium 5-sulphosalicylate and disodium 3,5-disulphosalicylate in heavy water[4]; amides, anilides and piperidide of benzenesulphonic acid in hexadeuteriodimethyl sulphoxide[5]; anilides of benzenesulphonic acid in hexadeuterioacetone[6]; 2-arylsulphonylamido-2-thiono-5-methyl-1,3,2-dioxaphospholanes[7]) have not yet treated systematically the influence of sulphonyl groups on ^{13}C-NMR spectra of aromatic compounds. Hence also the available table of empirical substituent parameters for calculation of carbon chemical shifts in benzene derivatives[8] lack the data of substituents derived from sulphonyl group.

The aim of this study of benzenesulphonyl derivatives type $C_6H_5SO_2X$ was to supply the missing data and contribute to understanding of influence of the SO_2X groups on ^{13}C-NMR spectra of aromatic compounds.

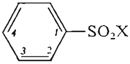
EXPERIMENTAL

The studied substances were available commercially in sufficient purity or were prepared according to known procedures[9].

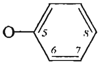
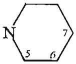
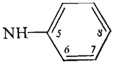
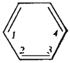
The ^{13}C-NMR spectra were recorded on a FT-spectrometer JNM FX-100 (JEOL) with digital quadrature detection at 25·05 MHz. The samples measured were 0·5—0·75M solutions of the substances in hexadeuteriodimethyl sulphoxide placed in 10 mm test tubes. The measurement was carried out at 30°C with internal deuterium lock, external standard tetramethylsilane

TABLE I

Carbon-13 Chemical Shifts (±0·05 ppm) for the Compounds of Type



in Hexadeuteriodimethyl Sulphoxide (ppm)

X	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$
Cl	146·75	125·69	128·37	129·69	—	—	—	—
ONa[a]	147·42	125·74	128·03	129·10	—	—	—	—
OCH_3	134·56	127·78	129·88	134·47	58·43 (CH_3)	—	—	—
OCH_2CH_3	135·73	127·59	129·93	134·36	69·05 (CH_2)	15·89 (CH_3)	—	—
	134·51	128·37	129·93	135·14	149·18	122·19	130·22	127·69
NH_2	144·18	125·79	129·15	132·03	—	—	—	—
NH_2[b]	145·5	130·2[c]	127·0[c]	133·1	—	—	—	—
$NHNH_2$	138·31	127·78	129·25	132·85	—	—	—	—
	135·73	127·54	129·49	133·20	48·05	26·12	24·32	—
$N(CH_2)_5$[b]	137·1	130·6[c]	128·7[c]	134·2	—	—	—	—
	139·58	126·80	129·30	133·05	137·72	120·24	129·30	124·33
NHC_6H_5[b]	141·0	130·4[c]	128·0[c]	134·1	—	—	—	—
NHC_6H_5[d]	140·6	127·6	129·5	133·3	138·4	121·5	129·7	125·2
	141·23	127·30	129·93	133·88	—	—	—	—

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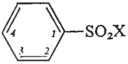
[a] Ref.[2], in D_2O, the ^{13}C chemical shifts: 58·85, 61·68, 62·12, 64·43 referred to dioxane; [b] ref.[5], in hexadeuteriodimethyl sulphoxide; [c] ref.[5], the shifts for $C_{(2)}$ and $C_{(3)}$ can be opposite; [d] ref.[6], in hexadeuterioacetone.

and combined accumulation in time and frequency domain. The apparatus parameters during determination of chemical shifts: spectral width 5000 Hz, 8 k memory, pulse width 7 μs (90° pulse ~25 μs), pulse repetition time 3 s, complete noise decoupling. The apparatus parameters during determination of coupling constants: spectral width 1000 Hz or less, 8 k memory, pulse width 20 μs, repetition time 10 s, gated decoupling beside acquisition time. The chemical shifts determined with respect to external tetramethylsilane were recalculated to the internal standard ($\delta = 0{\cdot}00$) by subtraction of a correction 1·20 ppm determined by measurement of pure hexadeuteriodimethyl sulphoxide ($\delta = 39{\cdot}60$) with external tetramethylsilane.

Assignment of the signals: in case of the compounds having one benzene ring and in that of diphenylsulphone the signals of $C_{(1)}$ and $C_{(4)}$ carbon atoms were unambiguously assigned on the basis of comparison of the proton-decoupled and proton-coupled spectra. The signal of the $C_{(2)}$ carbon atoms was differentiated from that of $C_{(3)}$ by selective decoupling of *ortho*-protons. The signals of carbon atoms in spectra of benzenesulphonanilide and phenyl benzenesulphonate were assigned by comparison with reference spectra of 4′-nitro and 4′-amino derivatives of the both compounds and with the chemical shift values calculated from the measured signal shifts of these derivatives by means of the published[8] substitution parameters. The found values were verified by comparison with literature data for benzenesulphonanilides[6]. The signals of the carbon atoms at *meta*-positions of the two benzene rings of phenyl benzenesulphonate were differentiated by means of the below-mentioned regularities in values of the $^1J(CH)$ coupling constants.

TABLE II

Carbon—13 Substitution Chemical Shifts in the Compounds of Type



$\Delta\delta$ (ppm) with respect to benzene in hexadeuteriodimethyl sulphoxide ($\delta = 128{\cdot}42$); positive value denotes a downfield shift

X	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
Cl	18·33	—2·73	—0·05	1·27
ONa	19·00	—2·68	—0·39	0·68
OCH_3	6·14	—0·64	1·46	6·05
OCH_2CH_3	7·31	—0·83	1·51	5·94
OC_6H_5	6·09	—0·05	1·51	6·72
NH_2	15·76	—2·63	0·73	3·61
$NHNH_2$	9·89	—0·64	0·83	4·43
$N(CH_2)_5$	7·31	—0·88	1·07	4·78
NHC_6H_5	11·16	—1·62	0·88	4·63
C_6H_5	12·81	—0·92	1·51	5·46

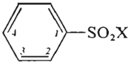
RESULTS AND DISCUSSION

The values of ^{13}C-chemical shifts and corresponding substituent shifts (deviations from the chemical shift of benzene) of the measured compounds $C_6H_5SO_2X$ are given in Tables I and II. Values of the coupling constants $^1J(CH)$ and $^3J(CH)$ are given in Table III. The $^1J(CH)$ values of all the compounds show the known[10] regularity, *viz* $^1J(C_{2,6}H) > {}^1J(C_{3,5}H) > {}^1J(C_4H)$. Absolute values of both these constants and the difference $^1J(C_{2,6}H) - {}^1J(C_4H)$ show parallel increase with increase of the chemical shifts $C_{(4)}$.

Judging from values of the chemical shifts, sulphonyl group has electron-acceptor effect (partial positive charge at the sulphur atom) on benzene ring in the whole studied set of derivatives, because all the substituent shifts are positive for $C_{(1)}$ and $C_{(4)}$, being negative for $C_{(2)}$. The acceptor effect of sulphonyl group (which, according to the tables of empirical substituent shifts, can be placed between nitro and carbonyl groups), however, depends strongly on properties of the substituent X. There is a parallel between a marked decrease in chemical shifts of $C_{(1)}$ (within the range 13·2 ppm) and a distinct increase in $C_{(4)}$, $C_{(2)}$ and $C_{(3)}$ (within the ranges 6·0, 3·7 and 1·9

TABLE III

The Coupling Constants J(CH) (Hz) for the Compounds of Type



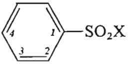
X	^1J(CH)[a]			^3J(CH)	
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1)}$[b]	$C_{(4)}$[b]
Cl	163·3	162·1	161·1	7·5	7·6
ONa	162·7	161·5	160·6	6·9	7·5
OCH_3	166·7	165·5	164·1	7·6	7·0
OC_2H_5	166·0	165·3	164·1	8·1	7·4
OC_6H_5	167·7[c]	166·7[c]	164·2	7·3	6·7
NH_2	165·3	163·2	162·6	8·5	7·7
$NHNH_2$	166·5	164·7	162·7	7·8	7·4
$N(CH_2)_5$	166·0	164·6	163·1	7·1	7·1
NHC_6H_5	166·9[c]	164·6[c]	163·5	6·7	7·0
C_6H_5	165·5	165·3	163·3	8·0	8·2

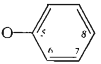
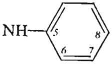
[a] ±0·3 Hz; [b] ±0·5 Hz; [c] ±0·5 Hz due to partial overlapping of the signals.

ppm, respectively). According to the present experience these trends correspond to lowering of inductive and increase of mesomeric acceptor effects of the substituent. Thus the effect of SO_2X is changed from a predominantly inductive one for X = Cl (comparable with *e.g.* $\overset{(+)}{N}(CH_3)_3$ (ref.[11])) to a predominantly mesomeric one for X = OC_2H_5 (comparable with *e.g.* COCl (ref.[8])). Correlation of this change in effects of SO_2X groups with properties of the substituents X showed that the mesomeric acceptor effect of the SO_2X group on the benzene ring connected with SO_2 increases roughly proportionally with increasing overall donor capacity of the substituent. Effect of ONa substituent in the SO_3Na group does not contradict this regularity. In hexadeuteriodimethyl sulphoxide this salt exists as an ion pair, and the $O^{(-)}$ anionic group has a strongly lowered donor effect. In aqueous solution sodium benzenesulphonate is completely dissociated, and values of substituent shifts correspond to the mentioned regularity: $C_{(1)}$ 13·9; $C_{(2)}$ 3·0; $C_{(3)}$ 0·6; $C_{(4)}$ 3·2. Simultaneous and comparable withdrawal of electrons by mesomeric effects from the benzenesulphonyl as well as from the ring of substituent X is connected unequivocally with values

TABLE IV

Changes in ^{13}C Chemical Shifts of Phenyl and Substituents X. Due to Their Bond with Sulphonyl Group as Compared with Benzenesulphonyl Chloride, Parent Alcohols, Phenols and Aniline; Positive Value Denotes a Downfield Shift



C	X OCH_3[a]	 OC_2H_5[b,c]	 	 
1	—12·2	—11·0	—13·2	—7·2
2	2·1	1·9	2·7	1·1
3	1·5	1·6	1·6	0·9
4	4·8	4·7	5·5	3·4
5	—	—	— 6·1	—8·7
6	—	—	6·5	5·1
7	—	—	0·4	0·0
9	—	—	6·6	5·7

[a] For OCH_3 9·4; [b] for OCH_2 12·1; [c] for CH_3 —1·7.

of changes of chemical shifts of carbon atoms of these rings caused by their linkage to sulphonyl group as compared with benzenesulphonyl chloride and the parent group of the substituent X, respectively (simultaneous increase of chemical shifts in *ortho* and *para* positions and their lowering at *ipso* position, Table IV). The inner reason of the acceptor effect of sulphonyl group lies in strongly polarized S—O bonds the length of which corresponds to partial double bond (0·143 nm in $CH_3SO_2CH_3$, SO_2 and SO_3) (ref.[12]). Thus the oxygen atoms can withdraw electrons from the double bond to give polar structures. Even though sulphonyl group with its substituents cannot assume the configuration of plane triangle similar to that of NO_2 and $CO_2^{(-)}$ groups (which is favourable for mesomeric shifts), it can, in some cases (*e.g.* SO_2Cl), exert a predominantly inductive effect on the benzene ring, and, in other cases (*e.g.* diphenylsulphone, phenyl benzenesulphonate), it produces a predominantly mesomeric effect on the both benzene rings. For better understanding of these changes in mechanism of the acceptor action of the sulphonyl group derivatives it is, therefore, necessary to presume also changes in geometry of these compounds and, hence, in the type of hybridization of the sulphur atomic orbitals enabling symmetrical mesomeric shifts between the substituents and the both oxygen atoms through the sulphur atom. This presumption is supported by published[12] structural data concerning bis(4-bromophenyl)sulphone and 2-(3-aminobenzenesulphonylamido)-5-bromopyrimidine. In these compounds the S—O bonds are longer (0·154 and 0·150 nm, respectively) and agree with the S—OH bond length in sulphuric acid; the OSO angle is opened to 131°, and the CSC (CSN) angle is 100°; the S—C bond length (0·184 nm) is, however, similar to that in dimethyl sulphone and corresponds to a single bond.

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