EFFECTS OF MEDIUM AND SUBSTITUENTS ON DISSOCIATION OF 4,4′-DISUBSTITUTED BIS(BENZENESULFON)IMIDES

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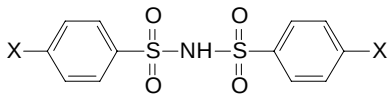
Ten 4,4′-disubstituted bis(arenesulfon)imides of the general formula $XC_6H_4SO_2NHSO_2C_6H_4X$ have been synthesized and their structures confirmed by their ^{1}H NMR spectra. Elemental analyses are presented for the compounds not yet described. The dissociation constants of these model substances have been measured potentiometrically in pyridine, dimethylformamide, methanol, ethanol, propylene carbonate, acetone, acetonitrile, 1,2-dichloroethane and tetramethylene sulfone. The pK_{HA} values obtained have been correlated with three sets of the Hammett substituent constants and the results have been used to discuss the solvent and substituent effects on the dissociation of the compounds studied. Sulfonimides with electron-acceptor substituents behave as rather strong acids in some solvents (pyridine, dimethylformamide, methanol and ethanol), whereas normal substituent dependences are found in other solvents. The experimental data have also been interpreted with the help of the statistical methods based on latent variables. From the calculations it follows that only the first principal component, which correlates well with the substituent constant sets adopted, is statistically significant in describing the substituent effect on the acid-base process studied.
Key words: Sulfonamides; Dissociation; Substituent; Solvent; Chemometrics.

Hammett[1] used substituted benzoic acids and their dissociation in water as the basic model and model process, respectively, for studies of substituent effects in the benzene nucleus. It is, of course, possible to observe effects of substituents and media also on other types of substrates and in other media. The present paper, which continues a series of papers dealing with dissociation of sulfonamides of various kinds[2–7], is focused on the dissociation of 4,4′-disubstituted bis(arenesulfon)imides **1**.



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Generally, the compounds having two sulfonyl groups and one hydrogen attached to a nitrogen atom will behave as relatively strong acids since sulfonyl group is a powerful electron acceptor. Obviously, the substituent effects will be transmitted from the benzene nucleus through sulfonyl group in a similar way as in monosubstituted ben-

zenesulfonamides[2–4]. The combined effects of the two substituents should result (particularly in aprotic media) in a strong influence upon the stability of particles present in the equilibrium mixture. The substitution at *para* position was chosen for the reason of more complex influence of substituent at this position as compared with that at the non-alternating *meta* position[8].

Using the Beilstein XFIRE data base we found that there are 39 compounds of this kind with *para–para*-disubstitution described in literature (the literature search was performed for the following substituents: hydrogen, halogen, alkyl, alkoxy, alkylcarbonyl, amino, nitro, and alkylcarbonylamino). No complex study dealing with dissociation of the said compounds has been found in literature. Dauphin et al.[9] focused their attention only on the pK_{HA} values of unsubstituted (1.45), dimethyl (1.70) and diamino (2.89) derivatives in water; the same value for the diamino derivative was also found by other authors[10]. Although Dauphin's paper[9] presents a calculation of parameters of the Hammett relation, the number of experimental points is evidently insufficient. Other literature data about the substrates studied by us involve the ^{1}H NMR spectra of diamino, dimethyl, dibromo and unsubstituted derivatives[11], ^{13}C NMR spectra of dimethyl and dichloro derivatives[12], IR spectra of the parent substance and its dimethyl derivative[13], mass spectrum of the unsubstituted parent substance[14], and a study of antibacterial activity of the diamino derivative (sulfanilimide)[15].

The chief aim of the present work is to discuss the combined substituent effects from both nuclei of the model substrates on the stability of the conjugated bases and on solvation of the conjugated bases by solvents of various types. When formulating the problem we anticipated that the simultaneous action of both substituents can decide whether the substance will behave as a weak or a strong acid.

EXPERIMENTAL

Measurements

The ^{1}H NMR spectra of the model compounds prepared were measured with a Bruker AMX 360 apparatus using 5% solutions of the substances in $(CD_3)_2SO$ and referring the chemical shifts to the solvent signal. The pK_{HA} values of the A- and B-type imides studied were determined in methanol (MeOH), ethanol (EtOH), acetonitrile (AN), dimethylformamide (DMF), pyridine (Py), acetone (Ac), propylene carbonate (PC), 1,2-dichloroethane (DCE), and tetramethylene sulfone (TMS) by means of potentiometric titration using an automatic titrator Radiometer RTS-622 or Radiometer Titrilab 3 with the same electrode arrangement and titration agent as in our previous works[2–7]. The solvents used were purified by standard methods.

Synthesis of *p*-Substituted Bis(arenesulfon)imides

Except for the diamino derivative, the bis(arenesulfon)imides were obtained by the reaction of the corresponding benzenesulfonamide with a slight excess of benzenesulfonyl chloride in alkaline medium[16]. The benzenesulfonamides were obtained by reacting the benzenesulfonyl chlorides with excess ammonia[2]. The benzenesulfonyl chlorides were obtained by direct chlorosulfonation of benzene

derivatives[2] or by the Sandmeyer reaction of the respective benzenediazonium chlorides with cuprous chloride in glacial acetic acid saturated with silver oxide[2,17]. The starting benzene and aniline derivatives were commercial samples except for fluorobenzene which was prepared from benzenediazonium salt[18]. The preparation of bis(aminobenzenesulfon)imide started from acetanilide which was transformed into 4-acetylaminobenzenesulfonyl chloride[19] and then (by the above-described method) into bis(acetylaminobenzenesulfon)imide which was reacted with concentrated NaOH solution[20] to give the required amino derivative. Table I presents the melting points, reaction temperatures and yields of the bis(arenesulfon)imides, yields of the preparation of the arenesulfonyl chlorides and arenesulfonamides, and elemental analyses of the methoxy and acetyl derivatives.

RESULTS AND DISCUSSION

The ^{1}H NMR chemical shifts of all the model substituted bis(arenesulfon)imides prepared are presented in Table II. The chemical shifts of the acidic proton are not included because they mostly formed very broad signals. A paper by DeChristoper[11] gives the shifts of the parent compound and its methyl, nitro, and bromo derivatives which agree well with our values. However, the paper[11] only gives a single value for the whole multiplet of aromatic section of the molecules. The values of dissociation constants of the model substrates in the individual solvents are given in Table III in the form of the average value $\overline{pK}_{HA}$ (together with the respective standard deviations). When discussing the results one must realize the difficult comparison of pH in the individual nonaqueous media which follows from the fact that no absolute scale has been defined so far. The solvents were chosen so as to cover the main solvent types most frequently used for titrations.

For orientation let us give the pK_{HA} values of the standards used in the solvents studied by us (the following survey of solvents gives in succession the name of solvent, pK_{HA} of benzoic acid, and pK_{HA} of picric acid with the corresponding references): amphiprotic solvents (methanol – 9.41, 3.67, refs[23,24]; ethanol – 10.25, 4.10, refs[25,26]), dipolar aprotic protophobic solvents (acetonitrile – 20.70, 11.00, refs[27,28]; acetone – 18.20, 9.20, refs[29,30]; tetramethylene sulfone – 26.30, 17.40, refs[30,31]; propylene carbonate – 19.70, 9.30, ref.[31]), dipolar aprotic protophilic solvents (dimethylformamide – 12.27, 3.65, refs[27,32]; pyridine – 9.80, 3.50, refs[33,34]), and inert solvents (1,2-dichloroethane – 20.00, 13.70, ref.[35]). The substituents were selected so as to cover the whole spectrum of substituent σ constants. They can be classified as substituents without any distinct mesomeric effects (CH_3, H, Cl, Br), those with positive mesomeric effects (NH_2, OCH_3, $NHCOCH_3$, F), and those with negative mesomeric effects ($COCH_3$, NO_2).

The experimental results obtained were treated by several mathematical statistical methods. The treatment by simple linear regression involved all the experimental points obtained (each experiment was repeated three or four times). The methods working with latent variables – the principal component analysis (PCA)[36], conjugated deviation analysis (CDA)[37], and projection of latent structures (PLS)[38] – adopted the average

TABLE I

Melting points, reaction temperatures, yields of syntheses of bis(arenesulfon)imides of general formula (p-X-$C_6H_4SO_2)_2NH$, preparation methods and yields of starting substituted benzenesulfonyl chlorides, yields of syntheses of substituted benzenesulfonamides, elemental analyses of methoxy and acetyl derivatives

X	M.p. of imide, °C		Reaction temperature, °C chloride+amide	Yield of imide %	Method of preparation of chlorides	Yields of chlorides %	Yields of amides %
	found	(ref.)					
H	155–156	157–158 (16)	50–55	53	–	–	88
F	178–179	182–183 (16)	55–60	60	chlorosulfonation	28	40
Cl	206–208	207–208 (16)	65–70	41	chlorosulfonation	80	80
Br	226–228	232–233 (16)	75–80	69	chlorosulfonation	94	74
NO_2	241–242	240–241 (21)	55–60	39	diazotation	78	100
NH_2	264–266	260–261 (20)	–	36[a]	–	–	–
CH_3	170–172	171–172 (16)	70–75	62	–	–	–
CH_3O[b]	165–167	–	65–70	44	chlorosulfonation	34	50
CH_3CO[c]	216–218	–	50–55	35	diazotation	60	81
CH_3CONH	282–284	282–284 (22)	35–40	46	chlorosulfonation	97	88

[a] The yield of alkaline hydrolysis of the acetyl derivative. [b] Elemental analysis (calculated/found): $C_{14}H_{15}NO_6S_2$ (357.12, C – 47.06/47.24, H – 4.23/4.46, N – 3.92/3.81, S – 17.96/18.01%). [c] Elemental analysis (calculated/found): $C_{16}H_{15}NO_6S_2$ (381.14, C – 50.42/50.56, H – 3.98/4.16, N – 3.68/3.71, S – 16.83/16.82%).

values $\overline{pK}_{HA}$. The calculation by the method of simple linear regression according to the classical Hammett equation ($pK_{HA} = pK^0 - \rho\sigma$, adapted from ref.[1]) was carried out separately for all the media studied using three sets of substituent constants, viz. σ_P (the universal constants according to Exner[39]), σ_{P6} and σ_{F6} (the constants designed for applications to nonaqueous media[40]). In all the media, the statistical characteristics of the results obtained with σ_P were the worst ones, the results of calculations using the other two sets of substituent constants being of comparable quality. This difference is due to the fact that the σ_{P6} and σ_{F6} constants were determined by a statistical calculation using the data for dissociation of benzoic acids in organic solvents whereas the σ_P constants are rather restricted to processes in aqueous media. Table IV presents the regression parameters and statistical characteristics of the Hammett relation using the σ_{F6} constant set. With propylene carbonate, acetone, acetonitrile, and tetramethylene sulfone solvents the correlation coefficients are above 0.997 when using the constants for organic solvents. The lower value observed with 1,2-dichloroethane (0.992) can be caused by specific effects of this solvent or lower precision of measurements in inert media. The distinctly worse values of statistical characteristics in pyridine, dimethylformamide, methanol, and ethanol are caused by the lower value of slope ρ and, in addition to it – for dimethylformamide and pyridine – by the considerable remoteness of the pK_{HA} values for the amino derivative. The small slope value is probably due to the fact that the bis(benzenesulfon)imides studied behave as rather strong acids in methanol, ethanol, pyridine and dimethylformamide (except just for the amino derivative in Py and DMF). The different behaviour of these acids in both groups of solvents also confirms

TABLE II
^{1}H NMR spectra of 4,4′-disubstituted bis(arenesulfon)imides

X	^{1}H NMR, δ, ppm
NH_2	4.5 s (H-7, **H**$_2$O and (ArSO$_2$)$_2$N**H**); 6.64 m, 4 H (H-3,5); 7.45 m, 4 H (H-2,6)
OCH_3	3.86 s, 6 H (H-7); 7.00 m, 4 H (H-3,5); 7.63 m, 4 H (H-2,6);
CH_3	2.39 s, 6 H (H-7); 7.28 d, 4 H (H-3,5); 7.61 d, 4 H (H-2,6)
$NHCOCH_3$	2.12 s, 6 H (H-7 (NHCOC**H**$_3$)); 7.63 m, 8 H, 2 × 2 AA′ BB′ (H-2,6 and H-3,5); 10.26 m, 2 H (H-7 (N**H**COCH$_3$))
H	7.48 m, 4 H (H-3,5); 7.52 m, 2 H (H-7); 7.74 m, 4 H (H-2,6)
F	7.23 m, 4 H (H-3,5); 7.71 m, 4 H (H-2,6)
Cl	7.49 m, 4 H (H-3,5); 7.68 m, 4 H (H-2,6)
Br	7.61 m, 8 H, 2 × 2 AA′ BB′ (H-2,6 and H-3,5)
$COCH_3$	2.64 s, 6 H (H-7); 7.79 m, 4 H (H-2,6); 7.97 m, 4 H (H-3,5)
NO_2	7.94 m, 4 H (H-2,6); 8.28 m, 4 H (H-3,5)

the value of the $2\rho_{BS}/\rho$ ratio (ρ_{BS} is the value of reaction constant for substituted benzenesulfonamides[2–4]). If neglecting the different solvation of the two substrate types (benzenesulfonamides and bis(benzenesulfon)imides), one should expect the value 1 for this ratio. Values close to 1 are found in Table IV for solvents with high-quality Hammett correlations (Ac, AN, TMS, DCE), whereas, on the other hand, the values of the fraction are much higher (as high as 18.72 in the case of pyridine) for solvents with low correlation coefficients. The fraction confirms that the two types of substrates behave differently in these solvents. Logically, the effect of substituents on stabilization of conjugated base is much lower for strong acids (i.e. the value of reaction constant is lower too) than for weaker acids. The value of fraction for the solvents in which imides

TABLE III

Average values of pK_{HA} (and their standard deviations $s(pK_{HA})$) of model substrates in individual solvents: Py pyridine, DMF dimethylformamide, MeOH methanol, EtOH ethanol, PC propylene carbonate (2-oxo-5-methyl-1,3-dioxolane), Ac acetone, AN acetonitrile, DCE 1,2-dichloroethane, TMS tetramethylene sulfone (1,1-dioxotetrahydrothiophene, tetrahydrothiophene 1,1-dioxide)

X	$\overline{pK}_{HA}/s(\overline{pK}_{HA})$								
	Py	DMF	MeOH	EtOH	PC	Ac	AN	DCE	TMS
NH_2	4.27 (0.14)	6.44 (0.05)	–	–	12.73 (0.10)	–	14.27 (0.10)	–	20.79 (0.06)
OCH_3	3.63 (0.06)	4.26 (0.05)	4.33 (0.04)	4.82 (0.04)	10.59 (0.06)	11.59 (0.02)	12.52 (0.04)	14.61 (0.04)	18.78 (0.10)
CH_3	3.61 (0.10)	3.87 (0.04)	4.12 (0.02)	4.84 (0.11)	10.22 (0.04)	11.19 (0.03)	12.03 (0.08)	14.35 (0.05)	18.45 (0.03)
$NHCOCH_3$	3.65 (0.10)	4.10 (0.08)	–	–	–	–	11.98 (0.10)	–	18.33 (0.10)
H	3.56 (0.02)	3.66 (0.05)	3.78 (0.03)	4.45 (0.05)	9.54 (0.10)	10.63 (0.02)	11.44 (0.05)	13.95 (0.09)	18.12 (0.07)
F	–	3.44 (0.05)	3.49 (0.01)	4.23 (0.05)	8.93 (0.07)	9.82 (0.07)	10.76 (0.07)	13.40 (0.07)	16.96 (0.11)
Cl	3.45 (0.06)	3.46 (0.12)	3.24 (0.01)	4.09 (0.05)	8.30 (0.01)	9.38 (0.02)	10.25 (0.05)	13.16 (0.14)	16.64 (0.05)
Br	3.45 (0.05)	3.46 (0.07)	3.37 (0.04)	4.14 (0.04)	8.33 (0.05)	9.43 (0.04)	10.33 (0.03)	13.16 (0.15)	16.80 (0.07)
$COCH_3$	3.48 (0.07)	3.35 (0.05)	3.40 (0.05)	3.63 (0.04)	7.93 (0.08)	9.13 (0.03)	9.84 (0.06)	12.67 (0.09)	16.27 (0.06)
NO_2	3.47 (0.03)	3.31 (0.05)	3.02 (0.03)	3.92 (0.13)	6.31 (0.03)	7.71 (0.03)	8.16 (0.04)	11.79 (0.07)	14.54 (0.13)

behave as weak acids indicates that e.g. DCE destabilizes bis(benzenesulfon)imide anion more than benzenesulfonamide anion etc. The effect of medium on pK^0 values can be discussed but roughly because of the limitations connected with non-existence of a universal pH scale for all media. With regard to the fact that similar standardization was used for the measurements in all the solvents, it is possible to carry out such a discussion. The sequence of pK^0 values in the individual media agrees well with that of pK_{HA} values of the standard picric acid in these solvents. It somewhat differs from that in the earlier published works dealing with the dissociation of benzenesulfonamides[2–4], benzoic acids[29,41,42], and *N*-phenylsulfonylbenzamides[5].

For benzenesulfonamides the lowest pK^0 value was observed in Py, and it increased in the order: MeOH, EtOH, DMF, Ac, AN, DCE, and TMS. In the case of benzoic acids the respective sequence was: MeOH, Py, EtOH, DMF, Ac, DCE, AN, TMS; for *N*-phenylsulfonylbenzamides: Py, MeOH, DMF, AN; for bis(arenesulfon)imides: Py, DMF, MeOH, EtOH, PC, Ac, AN, DCE, TMS. Generally, the presence of two SO_2 groups adjacent to the reaction centre has two effects. One, the distinct electron-acceptor effect stabilizes the negative charge of conjugated base by extensive delocalization; two, the distinct steric effect (similar to that of nitro group in picric acid) prevents

TABLE IV
Regression parameters and statistical characteristics of the Hammett dependence ($pK_{HA} = pK^0 - \rho\sigma_{F6}$) for individual solvents

Solvent	$pK^0(s_{pK})$	$\rho(s_\rho)$	$s(r)$	n	$2\rho_{BS}/\rho$[a]
MeOH	3.86 (0.03)	1.41 (0.10)	0.162 (0.932)	32	[b]
EtOH	4.48 (0.05)	1.20 (0.15)	0.216 (0.855)	24	2.41
AN	11.47 (0.02)	4.45 (0.05)	0.082 (0.998)	33	0.94
Ac	10.61 (0.02)	4.08 (0.06)	0.099 (0.997)	32	1.09
TMS	17.90 (0.02)	4.46 (0.06)	0.130 (0.997)	36	0.99
PC	9.60 (0.01)	4.55 (0.04)	0.076 (0.999)	33	[c]
DMF	4.08 (0.09)	2.10 (0.25)	0.486 (0.851)	30	1.93
DMF[d]	3.77 (0.04)	1.01 (0.12)	0.180 (0.851)	27	4.02
Py	3.66 (0.03)	0.54 (0.08)	0.162 (0.797)	27	7.62
Py[d]	3.57 (0.02)	0.22 (0.05)	0.075 (0.678)	24	18.72
DCE	13.93 (0.02)	2.93 (0.07)	0.110 (0.992)	31	1.19

[a] The ρ_{BS} value gives the reaction constant for substituted benzenesulfonamides[2–4]. [b] The ρ_{BS} value 0.52 for methanol[2] is uncertain, so the $(2\rho_{BS}/\rho)$ ratio was not given. [c] The dissociation of benzenesulfonamide was not measured in propylene carbonate. [d] The calculation without the pK_{HA} values for the amino derivative.

establishing of the homoconjugation equilibrium. Hence, the imides studied by us show similar behaviour to that of picric acid, which explains the good correlation of the pK^0 values measured in the individual solvents with the pK_{HA} values of picric acid. In the case of the substrates studied we can presume that the dissociation equilibrium will be strongly affected by the solvent ability of stabilization of the proton. This ability is highest in Py and DMF, which belong among dipolar aprotic protophilic solvents: the lowest values of pK^0 dissociation constants are observed in these solvents. Amphiprotic methanol and ethanol can solvate well both the conjugated base and the proton. That is why they have a similar effect on pK^0 as have Py and DMF. The solvents PC, Ac, AN and TMS belong among dipolar aprotic protophobic solvents which solvate the proton very poorly, and since they solvate the conjugated base poorly too, the equilibrium is shifted in favour of the undissociated form: the pK_{HA} values of the acids measured increase. In the inert DCE solvent the stabilization of both the proton and the conjugated base is probably very low.

For the analysis of substituent effects by the method using the latent variables we created a matrix of average values $\overline{pK}_{HA}$. The rows and columns of the matrix corresponded to the substituents and solvents, respectively (the solvents in which imides behave as mild acids: PC, Ac, AN, DCE, TMS). The matrix of 10×5 magnitude was filled to 90% and was treated by the principal component analysis (PCA)[36] and conjugated deviation analysis (CDA)[37]. According to statistical criteria we found the first principal latent variable to be statistically significant in both types of calculations, interpreting 99.78% of variability in both the cases (score vector in standardized form NH_2 – 1.00, OCH_3 – 0.69, CH_3 – 0.62, $NHCOCH_3$ – 0.61, H – 0.53, F – 0.40, Cl – 0.32, Br – 0.33, $COCH_3$ – 0.25, NO_2 – 0.00). The second principal component described only 0.11% of variability and was statistically insignificant. The first principal component from the PCA calculations was correlated with the vector of σ_{F6} substituent constants. The correlation coefficient of this regression has the value of 0.999. The values of loading vectors (PC – 3.45, AN – 3.61, TMS – 3.61, Ac – 4.50, DCE – 4.50) are very close to each other and indicate a lower difference of Ac and DCE on one hand and that of the other solvents on the other hand. This distribution can be caused by e.g. a different magnitude of reaction constant. The calculations by the method of projection of latent structures (PLS) using the pK_{HA} values of the substrates studied by us for the matrix of dependent variables and analogous values of a series of benzoic acids[29] or, as the case may be, benzenesulfonamides[2–4] for the matrix of independent variables showed the same structure of both matrices and brought no new results.

In conclusion we would like to stress the risk connected with the application of the Hammett correlations to such series of substituted derivatives which, from the point of view of their acidity, lie at the border between strong and weak acids. This border is different in different solvents and can lie at a relative high pH value in some solvents. As it follows from the present study the situation can be similar to that of the change in

reaction mechanism connected with a change in substituent which is manifested by a break in the Hammett dependence.

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