

**EFFECTS OF SUBSTITUENTS AND MEDIUM  
ON ACIDITY OF  $\alpha,\alpha$ -BIS(BUTYLSULFONYL)TOLUENES**

Miroslav LUDWIG, Jan PETRZILEK, Jiri KULHANEK and Oldrich PYTELA

*Department of Organic Chemistry,**University of Chemical Technology, 532 10 Pardubice, The Czech Republic*

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Seven substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes and three 2-aryl-1,1,3,3-tetraoxo-1,3-dithiolanes have been prepared and their  $^1\text{H}$  NMR, IR, and MS spectra measured. The  $\text{p}K_{\text{HA}}$  values of the substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes have been determined by potentiometric titration in dimethyl sulfoxide, dimethylformamide, and 80% (v/v) mixture of dimethyl sulfoxide and water. The results are interpreted by the Yukawa-Tsuno relationship (parameter  $r = 0.43 - 0.49$ ) and classified in relation to analogous *N*- and *O*-acids by the methods with latent variables (the method of conjugated deviations).

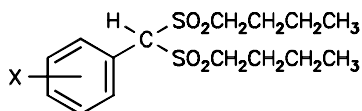
From the point of view of substituent effects, benzyl cation represents an important model of *C*-acids. Direct acidity measurements of substituted toluenes were carried out in gas phase<sup>1,2</sup> and in dimethyl sulfoxide<sup>3,4</sup>. Quantum-chemical calculations<sup>5</sup> proved that a study of substituent effects upon the dissociation of toluene in gas phase can adopt aniline and phenol as models. As expected the dominant effect is the stabilization of conjugated base, the sensitivity to substituents being increased in the order: aniline, phenol, toluene. A more logic order of sensitivity was found in the correlations of changes of equilibrium Gibbs energies in gas phase<sup>6</sup> and dimethyl sulfoxide<sup>7</sup> with the substituent constants  $\sigma_{\text{F}}$  and  $\sigma_{\text{R}}$  where the sensitivity increases in the order: phenol, aniline, toluene. A comparative study of substituent effects on the dissociation of toluenes and anilines in dimethyl sulfoxide<sup>3</sup> showed a roughly double sensitivity of toluene ( $\rho \approx 12$ ) as compared with that of aniline ( $\rho \approx 5.67$ ). According to Taft and Topsom<sup>7</sup> the transition from gas phase to polar aprotic solvent (DMSO) is connected with an additional substituent effect due to solvation, this effect being increased with decreasing acidity of the weak acid. The behaviour of benzyl anion in protic solvents has not been extrapolated.

The acidity of weak acids is increased by attaching strong electron acceptor groups to the atom carrying the acidic proton, on the other hand the same effect decreases the sensitivity, which can be documented e.g. by the toluene or aniline series<sup>8,9</sup>. A suitable electron-acceptor substituent is the  $\text{SO}_2\text{R}$  group, which possesses a distinct  $-M$  effect

(due to the large electronegativity difference between sulfur and oxygen) and, at the same time, is relatively inert chemically. The evidence of acidifying properties of sulfonyl group is given in literature<sup>10-15</sup>. Some authors<sup>10,11,14</sup> ascribe the acidity increase not to the mesomeric effect but to a manifestation of *d* orbitals of sulfur, whereas others<sup>16,17</sup> take a skeptical view of this interpretation. The behaviour of benzyl anion with attached sulfonyl groups was studied experimentally using substituted  $\alpha,\alpha$ -bis(benzylsulfonyl)toluenes in the medium of 80% aqueous dimethyl sulfoxide<sup>18</sup>. The substituent effects were interpreted by means of the  $\sigma_p^-$  constant, and the reaction constant had the value  $\rho = 2.53$ . As compared with toluene in dimethyl sulfoxide ( $\rho \approx 12$ ) the sensitivity decrease is considerable, being caused by both the presence of benzylsulfonyl groups and the change of medium.

Acidity measurements of *C*-acids are complicated by the rate of splitting off of the proton from carbon, hence it is possible to determine both the kinetic and the equilibrium (thermodynamic) acidities<sup>19</sup>. The papers<sup>20-22</sup> report the ionization of trisubstituted methanes  $\text{HC}(\text{X})(\text{SO}_2\text{R})_2$  and  $\text{HC}(\text{X})(\text{CN})_2$  indicating the diffusion-controlled deprotonation. If X = aryl, then the deprotonation rate is reduced, and this effect must be taken into account in experimental measurements of thermodynamic acidities.

The aim of our work was to synthesize new *C*-acids and study the effects of medium and substituents upon the acidity ( $\text{p}K_{\text{HA}}$ ) of these model substrates. For the model compounds we chose the substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes (*I*) and 2-phenyl-1,1,3,3-tetraoxo-1,3-dithiolanes (*II*). These compounds have not been studied yet except for the syntheses of the parent  $\alpha,\alpha$ -bis(butylsulfonyl)toluene (*Ia*, refs<sup>23,24</sup>) and dithiolanes<sup>24</sup>. The present paper continues our investigation of acidity of various series of substituted weak *N*- and *O*-acids in various media<sup>9,25-28</sup>.



*Ia*, X = H

*Ib*, X = 4-F

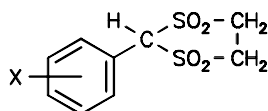
*Ic*, X = 4-Cl

*Id*, X = 3-Cl

*Ie*, X = 4-CF<sub>3</sub>

*If*, X = 3-NO<sub>2</sub>

*Ig*, X = 4-NO<sub>2</sub>



*IIa*, X = H

*IIb*, X = Cl

*IIc*, X = NO<sub>2</sub>

## EXPERIMENTAL

The  $^1\text{H}$  NMR spectra of solutions of model compounds in deuteriochloroform with hexamethyldisiloxane as the internal reference were measured with a JEOL FX-100 or Bruker AM-400 apparatus. The mass spectra were measured with a Kratos MS 25RSA apparatus. The sample was introduced by the GC/MS technique or (in the case of sulfones) direct inlet. The IR spectra were measured with a Perkin-Elmer PE 684 spectrophotometer using the KBr technique. The potentiometric acidity measurements of model compounds in dimethylformamide, dimethyl sulfoxide, and 80% (v/v) aqueous dimethyl sulfoxide were carried out on an automatic titrator Radiometer RTS-622 using the same procedure, electrodes, and titrant as those in ref.<sup>25</sup>.

The substituted benzaldehydes were synthesized by known ways<sup>29,30</sup>. 3-Nitrobenzaldehyde was obtained by the nitration of unsubstituted benzaldehyde, the other benzaldehydes were synthesized from the corresponding benzyl bromides by the Sommelet reaction with urotropin (0.1 mol benzyl bromide, 0.11 mol urotropin, 100 ml chloroform, reflux 1 h). 4-Chlorobenzaldehyde was a commercial sample.

### Synthesis of 2-Aryl-1,3-dithiolanes<sup>31</sup>

Dry hydrogen chloride was bubbled through an equimolar mixture of the respective substituted benzaldehyde and 1,2-ethanedithiol at ca 60 °C 2 h. Then water was distilled off under reduced pressure, and the product was recrystallized from ethyl acetate. In this way obtained were the parent 2-phenyl-1,3-dithiolane (yield 73%, m.p. 24 – 26 °C; ref.<sup>24</sup> gives m.p. 29 °C), 2-(4-chlorophenyl)-1,3-dithiolane (yield 80%, m.p. 58 – 59 °C; ref.<sup>24</sup> gives m.p. 62 °C), and 2-(4-nitrophenyl)-1,3-dithiolane (yield 72%, m.p. 77 – 78 °C; ref.<sup>24</sup> gives m.p. 79 °C).

### Synthesis of 2-Aryl-1,1,3,3-tetraoxo-1,3-dithiolanes II

*Method A:* A solution of 2-aryl-1,3-dithiolane (0.1 mol) in acetic acid (500 ml) was heated to boiling and 30% hydrogen peroxide (60 ml, 0.53 mol) was added thereto during 10 min. The reaction mixture was evaporated and the dry residue was washed with saturated solution of sodium hydrogen carbonate.

*Method B:* A solution of 2-aryl-1,3-dithiolane (0.1 mol) in acetic acid (500 ml) was treated with 30% hydrogen peroxide (60 ml, 0.53 mol), and the reaction mixture was evaporated until dry.

*Method C:* The respective dithiolane (0.1 mol) was dissolved in ethanol (900 ml), and 2% aqueous solution of sodium tungstate (100 ml) was added followed by 30% hydrogen peroxide (30 ml, 0.26 mol). The mixture was heated to 80 °C, and another 30 ml peroxide was added. After filtration with charcoal, concentration, and cooling, the crystalline products were collected by suction.

*Method D:* A saturated solution of potassium permanganate was added into a solution of dithiolane (0.1 mol) in acetic acid (250 ml) with stirring until permanent violet colour. The reaction mixture was filtered and the filtrate was evaporated until dry.

*Method E:* A solution of dithiolane (0.1 mol) in ethyl acetate (300 ml) was vigorously stirred, and a solution of  $\text{KMnO}_4$  (41.2 g, 0.26 mol) in water (1 000 ml) and a solution of sulfuric acid (12.8 g, 0.13 mol) in water (200 ml) were added simultaneously during 2 h. The product was isolated as sub C.

The 2-aryl-1,1,3,3-tetraoxo-1,3-dithiolanes II were then washed with saturated solution of sodium hydrogencarbonate and recrystallized from ethanol. The yields and products of the oxidation reactions are given in Table I. The melting points of known substances do not agree with the literature data, but the spectral analyses confirmed the structure of the compounds prepared. The IR spectra contain strong signals due to  $\text{SO}_2$  group (1 350 and 1 150  $\text{cm}^{-1}$ ). The mass spectra show a weak molecular peak and fragments  $M - 155$  ( $M - \text{SO}_2\text{C}_2\text{H}_4 + \text{H}$ , 100%),  $M = 64$  ( $\text{SO}_2$ , ca 40%).

Synthesis of Substituted  $\alpha,\alpha$ -Bis(butylthio)toluenes

The respective benzaldehyde (0.1 mol) and butanethiol (0.2 mol) were dissolved in benzene (300 ml), and a little amount of 4-toluenesulfonic acid was added. In the course of reaction, water was removed by azeotropic distillation 4 h. The mixture was filtered with charcoal, and the filtrate was evaporated to give an oily residue. The structure and purity of the prepared compounds were checked by elemental analyses and GC/MS method. The mass spectra of  $\alpha,\alpha$ -bis(butylthio)toluenes show the following peaks:  $M^+$  (weak),  $M - 89$  ( $M - SC_4H_9$ , 100%),  $M - 146$  ( $M - SC_4H_9 - C_4H_9 - H$ , ca 40%).

Synthesis of Substituted  $\alpha,\alpha$ -Bis(butylsulfonyl)toluenes I

*Method A:* A solution of substituted  $\alpha,\alpha$ -bis(butylthio)toluene (0.1 mol) in 50% aqueous acetic acid (500 ml) was cooled with intensive stirring and solid potassium permanganate was added until permanent violet colour. After several days' standing, the precipitated product was collected by suction, washed with water, extracted with ethanol in a Soxhlet apparatus, and 90% of solvent was evaporated from the extract.

*Method B:* The respective  $\alpha,\alpha$ -bis(butylthio)toluene (0.1 mol) was dissolved in ethanol (900 ml), and 2% aqueous solution of sodium tungstate (100 ml) was added. To the suspension formed, 30% hydrogen peroxide (30 ml, 0.26 mol) was slowly added, whereafter the mixture was heated to 80 °C and another 30 ml peroxide was slowly added. After filtration with charcoal, concentration, and cooling the crystalline products were collected by suction.

The obtained products were recrystallized from ethanol (compound *Ig* from a mixture of acetic acid and heptane). The reaction conditions, yields, melting points, and results of elemental analyses

TABLE I  
Reaction conditions, melting points and yields in syntheses of compounds II

Compound	Method	Reaction medium	Reaction temp., °C	M.p., °C	Yield %
<i>Ila</i>	A	AcOH	116	212 – 213 <sup>a</sup>	3
<i>Ila</i>	D	AcOH–H <sub>2</sub> O	25 – 40	<sup>b</sup>	0
<i>Ilb</i>	A	AcOH	116	<sup>b</sup>	0
<i>Ilb</i>	B	AcOH	25 – 40	<sup>b</sup>	0
<i>Ilb</i>	C	EtOH–H <sub>2</sub> O	80 – 85	178 – 180 <sup>c</sup>	12
<i>Ilb</i>	D	AcOH–H <sub>2</sub> O	25 – 40	<sup>b</sup>	0
<i>Ilb</i>	E	benzene	25 – 40	<sup>d</sup>	0
<i>Ilc</i>	A	AcOH	116	<sup>b</sup>	0
<i>Ilc</i>	B	AcOH	25 – 40	<sup>b</sup>	0
<i>Ilc</i>	C	EtOH–H <sub>2</sub> O	80 – 85	135 – 140	7
<i>Ilc</i>	D	AcOH–H <sub>2</sub> O	25 – 40	<sup>b</sup>	0
<i>Ilc</i>	E	benzene	25 – 40	<sup>d</sup>	0

<sup>a</sup> Ref.<sup>32</sup> gives m.p. 118 °C; <sup>b</sup> only the corresponding 4-substituted benzoic acid was isolated; <sup>c</sup> ref.<sup>32</sup> gives m.p. 218 °C; <sup>d</sup> the starting thiole was isolated.

are given in Table II. The infrared spectra of all the products contained two strong bands corresponding to sulfonyl group (1 360 – 1 320  $\text{cm}^{-1}$ , 1 150 – 1 130  $\text{cm}^{-1}$ ), the bands of C–H bond vibration of butyl group (2 960 – 2 860  $\text{cm}^{-1}$ ), and signals of substituted aromatic ring. The mass spectra showed the following fragments:  $M^+$  (10 – 47%),  $M - 121$  ( $M - \text{SO}_2\text{C}_4\text{H}_9$ , ca 50%),  $M - 241$  ( $M - \text{SO}_2\text{C}_4\text{H}_9 - \text{SO}_2\text{C}_4\text{H}_9 + \text{H}$ , 70 – 100%),  $M - 241 + 16$  ( $M - 241 + \text{O}$ , 20 – 60%). The  $^1\text{H}$  NMR spectra showed four to five aromatic signals ( $\delta \approx 8.4 - 7.5$ ) and signals of aliphatic protons of butylsulfonyl group ( $\delta \approx 3.4 - 0.75$ ). All the spectra contain a signal of acidic proton at  $\delta = 5.3$ .

### Treatment of Results

The results were treated with the help of our own mathematical-statistical programmes using a personal computer PC/AT.

## RESULTS AND DISCUSSION

The syntheses of 2-aryl-1,1,3,3-tetraoxo-1,3-dithiolanes and  $\alpha,\alpha$ -bis(butylsulfonyl)-toluenes were carried out in similar ways. From the standpoint of reaction products, the synthesis and oxidation of  $\alpha,\alpha$ -bis(butylthio)toluenes were studied in more detail. The analysis of mixture after the reaction of benzaldehydes with 1-butanethiol showed beside the required  $\alpha,\alpha$ -bis(butylthio)toluenes also the starting materials,  $\alpha$ -butylthio- $\alpha$ -hydroxytoluenes, dibutyl disulfide, and  $\alpha$ -butylthiotoluene. The oxidation of  $\alpha,\alpha$ -bis(butylthio)toluenes with potassium permanganate in aqueous ethanol can provide the non-overoxidized products. However, the products are not easily isolated, and therefore we also adopted the oxidation with hydrogen peroxide catalyzed by sodium tungstate in aqueous ethanol. This procedure gives comparable yields, and the isolation of products is easier than that in the oxidation with potassium permanganate.

The average values of  $\text{p}K_{\text{HA}}$  of the substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes *I* in dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 80% (v/v) aqueous dimethyl sulfoxide (DMSO-W) are given in Table III.

For the interpretation of dissociation constants from Table III we adopted the Yukawa-Tsuno equation and the correlations obtained were good except for dimethylformamide ( $R_{\text{DMF}} = 0.987$ ,  $R_{\text{DMSO}} = 0.993$ ,  $R_{\text{DMSO-W}} = 0.996$ ), the residual standard deviations ( $s_{\text{DMF}} = 0.253$ ,  $s_{\text{DMSO}} = 0.156$ ,  $s_{\text{DMSO-W}} = 0.131$ ) being comparable with the experimental accuracy. The reaction constants found ( $\rho_{\text{DMF}} = 3.49$ ,  $\rho_{\text{DMSO}} = 2.92$ ,  $\rho_{\text{DMSO-W}} = 3.15$ ) correspond to the cognate  $\alpha,\alpha$ -bis(benzylsulfonyl)toluenes<sup>18</sup> ( $\rho = 2.53$ ). The greater  $\rho$  value in dimethylformamide as compared with that in dimethyl sulfoxide agrees with the results obtained for other weak acids (e.g. *N*-arylbenzenesulfonamides<sup>9</sup>  $\rho_{\text{DMF}} = 3.69$ ,  $\rho_{\text{DMSO}} = 3.28$ ), the reason is probably in the lower basicity and polarity of dimethylformamide<sup>33,34</sup>. The change of the reaction constant on going from dimethyl sulfoxide to aqueous dimethyl sulfoxide is very small and, in addition – in contrast to the expectation – opposite, although the difference is not statistically significant. According to the value of reaction constant  $\rho_{\text{DMSO}}$  the delocalization of the electron pair is greater in the model studied than in the nitrogen analogue – *N*-phenyl-

TABLE II  
Reaction conditions and physical data in syntheses of compounds I

Compound	Method	Reaction		M.p., °C (Yield, %)	Formula (M.w.)	Calculated/Found			
		medium	temp., °C			% C	% H	% S	% F, Cl or N
<i>Ia</i>	A	AcOH-H <sub>2</sub> O	25 - 40	93.5 - 94 <sup>a</sup> (8)	C <sub>15</sub> H <sub>24</sub> O <sub>4</sub> S <sub>2</sub> (332.5)	54.19	7.28	19.28	—
<i>Ib</i>	B	EtOH-H <sub>2</sub> O	80 - 85	85 - 87 (15)	C <sub>15</sub> H <sub>23</sub> FO <sub>4</sub> S <sub>2</sub> (350.5)	54.39	7.42	18.84	5.42
<i>Ic</i>	A	AcOH-H <sub>2</sub> O	25 - 40	81 - 82 (32)	C <sub>15</sub> H <sub>23</sub> ClO <sub>4</sub> S <sub>2</sub> (366.9)	49.11	6.32	17.48	9.66
<i>Id</i>	B	EtOH-H <sub>2</sub> O	80 - 85	67 - 69 (9)	C <sub>15</sub> H <sub>23</sub> ClO <sub>4</sub> S <sub>2</sub> (366.9)	49.11	6.32	17.48	9.66
<i>Ie</i>	B	EtOH-H <sub>2</sub> O	80 - 85	95 - 98 (7)	C <sub>16</sub> H <sub>23</sub> F <sub>3</sub> O <sub>4</sub> S <sub>2</sub> (400.5)	49.21	6.39	17.32	9.79
<i>If</i>	A	AcOH-H <sub>2</sub> O	25 - 40	107 - 108 (23)	C <sub>15</sub> H <sub>23</sub> NO <sub>6</sub> S <sub>2</sub> (377.5)	47.99	5.79	16.01	14.23
<i>Ig</i>	A	AcOH-H <sub>2</sub> O	25 - 40	121 - 122 (5)	C <sub>15</sub> H <sub>23</sub> NO <sub>6</sub> S <sub>2</sub> (377.5)	48.11	5.85	15.88	14.24
						47.42	6.14	16.99	3.71
						47.48	6.18	16.92	3.75
						47.42	6.14	16.99	3.71
						47.43	6.15	16.88	3.98

<sup>a</sup> Ref.<sup>23</sup> gives 92 °C.

benzenesulfonamide<sup>9</sup> ( $\rho = 3.28$ ) or the phenol used for comparison<sup>5,35</sup> ( $\rho_{\text{DMSO}} = 3.97$ ). The conclusions about electron delocalization are also confirmed by the value of the parameter  $r$  in the Yukawa–Tsuno equation ( $r_{\text{DMF}} = 0.48$ ,  $r_{\text{DMSO}} = 0.49$ ,  $r_{\text{DMSO-W}} = 0.43$ ). The values found for the parameter  $r$  indicate an about half extent of direct stabilization of reaction centre as compared with phenols and anilines, being approximately identical with those of  $N$ -arylbenzenesulfonamides<sup>9</sup> ( $r_{\text{DMF}} = 0.39$ ,  $r_{\text{DMSO}} = 0.42$ ).

A summary of behaviour of substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes as compared with substituted toluenes<sup>1,2,6,7</sup>, anilines (deprotonation<sup>8</sup>, protonation<sup>36</sup>), phenols<sup>35,37</sup>, and other suitable compounds such as  $N$ -arylbenzenesulfonamides<sup>9</sup>, diphenylamines (deprotonation<sup>8</sup>, protonation<sup>38</sup>), and triazenes<sup>39</sup> are given in Table IV. The data of Table IV were obtained by treating the set described (substituents: H, 3-CH<sub>3</sub>, 3-NO<sub>2</sub>, 3-OCH<sub>3</sub>, 3-Cl, 4-CH<sub>3</sub>, 4-CF<sub>3</sub>, 4-CN, 4-NO<sub>2</sub>, 4-OCH<sub>3</sub>, 4-F, 4-Cl, 4-Br) by the method of conjugated deviations<sup>40</sup>. The first latent variable interprets 98.9% of variability of set, which indicates its high homogeneity and, hence, mutual similarity in behaviour during substitution of the models compared. The results in Table IV show that the sensitivity to substitution increases with decreasing electronegativity of the atom from which the proton is split off. This expected relation remains maintained also when going from gas phase into an aprotic solvent (dimethyl sulfoxide) and, probably, into a protic one, too. The transition from gas phase into solvent is connected with a distinct lowering of sensitivity to substituents, this lowering being greater with phenol than with aniline. If these proportions are also valid for toluene, the value of reaction constant in dimethyl sulfoxide could be expected about 13.5 and in water about 13, i.e. an obvious reduction of the effect of medium upon the dissociation of  $C$ -acids. This conclusion is in accordance with the small change in reaction constant on going from dimethyl sulfoxide to

TABLE III

Average values of  $\text{p}K_{\text{HA}}$  and standard deviations  $s$  (from four measurements) of substituted  $\alpha,\alpha$ -bis(butylsulfonyl)toluenes  $I$  in DMF, DMSO, and DMSO-W at 25 °C

Compound	$\text{p}K_{\text{HA}} (s)$					
	DMF		DMSO		DMSO-W	
<i>Ia</i>	16.05	(0.05)	14.04	(0.12)	13.10	(0.03)
<i>Ib</i>	15.80	(0.03)	13.84	(0.03)	12.62	(0.03)
<i>Ic</i>	15.13	(0.09)	13.27	(0.05)	12.24	(0.06)
<i>Id</i>	14.65	(0.05)	12.88	(0.05)	11.73	(0.05)
<i>Ie</i>	14.39	(0.04)	12.52	(0.02)	11.31	(0.09)
<i>If</i>	13.59	(0.04)	12.00	(0.02)	10.76	(0.03)
<i>Ig</i>	12.36	(0.06)	10.97	(0.05)	9.80	(0.00)

80% aqueous dimethyl sulfoxide with the models studied by us. The presence of strong acceptor groups (e.g.  $\text{SO}_2$ ) on the atom carrying the acidic hydrogen results in a distinct reduction of sensitivity (to about one half with aniline, and obviously even more with toluene, see Table IV), which indicates a significant delocalization of electron pair of conjugated base into these groups. The substituents further connected to the electron-acceptor group are probably less important (butyl is identical with benzyl) unless they are able of participation in the conjugation (aryltoluenesulfonamides, difenylamines, triazenes). The transmission coefficient of  $\text{SO}_2$  group is about 0.45 (ref.<sup>41</sup>), which agrees with the results of Table IV. The sensitivity to substituents of dissociation of conjugated acids of weak bases is markedly lower than that of the weak bases themselves (diphenylamine, Table IV). Hence the magnitude of reaction constant is connected with the electron density and the extent of delocalization of electrons from the chemical neighbourhood of the atom carrying the acidic proton. The connection with electron density at this atom is indicated by the order obtained by the method of conjugated deviations from a set of chemical shifts of the atoms immediately attached to a substituted aromatic nucleus (toluene<sup>42</sup>, styrene<sup>43,44</sup>, phenylacetylene<sup>45</sup>, aniline<sup>46</sup>, anisol<sup>47</sup>, selenoanisol<sup>48</sup>, fluorobenzene<sup>49</sup>) and logarithm of dissociation constants of selected models (aniline<sup>3</sup>, phenol<sup>33</sup>, *N*-arylbenzenesulfonamide<sup>9</sup>,  $\alpha,\alpha$ -bis(butylsulfonyl)-toluene in dimethyl sulfoxide). The relative order given by the magnitude of regression coefficient value in the first latent variable is as follows:  $\delta^{13}\text{C CH}_3$  (0.000) <  $\delta^{13}\text{C C}\equiv$  (0.244) <  $\log K$  (phenol) (0.705) <  $\log K$  (*N*-arylbenzenesulfonamide) (0.711) <

TABLE IV

Regression coefficients<sup>a</sup> (R.c.) of dependence of  $\log K_a$  (or  $\Delta G$ ) of model compounds in gas phase (g) and in solutions upon the first latent variable obtained by CDA method

Medium	C-acids	R.c.	N-acids	R.c.	O-acids	R.c.
(g)	$\text{CH}_3\text{C}_6\text{H}_4\text{X}$	17.02	$\text{NH}_2\text{C}_6\text{H}_4\text{X}$	13.67	$\text{HOC}_6\text{H}_4\text{X}$	12.61
DMSO			$\text{NH}_2\text{C}_6\text{H}_4\text{X}$	5.54	$\text{HOC}_6\text{H}_4\text{X}$	3.02
W					$\text{HOC}_6\text{H}_4\text{X}$	2.23
DMSO	$(\text{C}_4\text{H}_9\text{SO}_2)_2\text{CHC}_6\text{H}_4\text{X}$	1.84	$\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_6\text{H}_4\text{X}$	2.18		
DMSO-W	$(\text{C}_4\text{H}_9\text{SO}_2)_2\text{CHC}_6\text{H}_4\text{X}$	1.94				
80% (v/v)	$(\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2)_2\text{CHC}_6\text{H}_4\text{X}$	1.95				
W			$\text{NH}_3^+-\text{C}_6\text{H}_4\text{X}$	2.27		
W			$\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{X}$	3.77		
W			$\text{C}_6\text{H}_5\text{NH}_2^+-\text{C}_6\text{H}_4\text{X}$	2.04		
DMSO-			$\text{C}_6\text{H}_5\text{N}=\text{NNHC}_6\text{H}_4\text{X}$	1.19		
EtOH 20%						

<sup>a</sup> Recalculated with respect to the value  $\rho$  (phenol, water, 25 °C) = 2.23.



$\log K$  ( $\alpha,\alpha$ -bis(butylsulfonyl)toluene) (0.726) <  $\delta$   $^{77}\text{Se}$  (0.780) <  $\delta$   $^{17}\text{OCH}_3$  (0.791) <  $\log K$  (aniline) (0.797) <  $\delta$   $^{19}\text{F}$  (0.916) <  $\delta$   $^{13}\text{C}=\text{C}$  (0.971) <  $\delta$   $^{15}\text{N}$  (1.000). As it is obvious from the given order the greatest changes in the character of interaction of substituents and the atom investigated are at a carbon atom where the splitting off of the proton is accompanied by a considerable extent of rehybridization; the role of the electronegativity connected with the hybridization cannot be neglected either. The character of the interaction between substituent and reaction centre in the models studied is comparable with that in anisole or phenol.

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