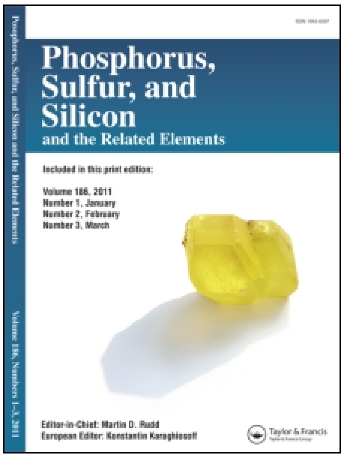

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Benzenethiols: pK a Values Measured in Solutions Against Quantum Chemically Computed Gaseous-Phase Proton Affinities

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BENZENETHIOLS: pK_a VALUES MEASURED IN SOLUTIONS AGAINST QUANTUM CHEMICALLY COMPUTED GASEOUS-PHASE PROTON AFFINITIES

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By the PM3 method, standard entropies, heats, and free energies of formation have been computed for 27 benzenethiols and anions formed at their heterolytic dissociation. The enthalpies and free energies of proton affinity (PA) for the benzenethiolate anions have been calculated. It has been found that the benzenethiols' pK_a quantities measured by different authors in water-acetone, water-ethanol, and methanol media correlate linearly with the PA values. The dependences established allow one to a priori *predict the protolytic properties of the benzenethiol series compounds.*

Keywords: Benzenethiols; pK_a; proton affinity; quantum chemical evaluation; quantitative structure–property relationships

Among the proton–donor groups, sulphohydryl-one occupies a significant place. In particular, it enters the composition of the molecule of 8-mercaptoquinoline-one of the more important analytical reagent, which forms with metal cations intra-complex compounds that are poorly soluble in water, but readily soluble in organic solvents.[1] Protolytic properties of mercapto compounds are responsible for their chemical behavior to a marked extent. For instance, in the case of substituted 8-mercaptoquinolines, thiosalicylic acid, and some other compounds, the sulphohydryl proton mobility influences the intramolecular hydrogen bonds strength, tautomerism, analytical, and other characteristics of

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substances.[1,2] In particular, nucleophilicity of thiolate anions depend on their basicity.[3,4]

Model compounds for studying the acid-base properties of different aromatic and heteroaromatic thiols could be benzenethiols.

Benzenethiol (mercaptobenzene, phenylmercaptane, phenylthiol, thiophenol) and its derivatives are significant also in their own right. Those have found a wide utility in the synthesis of drugs, pesticides, dyes, polymers, inhibitors of radical reactions, stabilizers, and other additions to synthetic rubbers.[5]

The benzenethiols reactivity in different chemical reactions depends on acid-base properties of the above thiols.[3,4]

The present work is aimed at quantum chemical evaluation of the benzenethiols proton affinities (PA) in comparison with the pK_a values measured in water-acetone, water-ethanol, methanol solutions, along with establishing quantitative relationships pK_a versus PA.

For rather simplified obtaining predictive quantitative relations, the semiempirical quantum chemical methods would be reasonable to use.

Earlier, for the series of inorganic and organic compounds belonging to different classes, we have established a correctness of the most important thermodynamic and molecular characteristics reproduction by the MNDO, AM1, and PM3 methods,[6–23] as well as of electronegativity, inductive, and mesomeric parameters of atomic groups.[24,25] Among the mentioned methods, PM3 seems to provide satisfactory results in obtaining the heats of formation for nitro derivatives[6,26] and dimethylsulphone.[8] There are NO_2- and SO_2-groups containing species among the subjects of our investigation.

That is the reason for selecting the PM3 method[26] for the purposes of this work.

COMPUTATIONAL METHODS

The computations were performed within the restricted Hartree-Fock formalism[27] using the software from the MOPAC package[27,28] with the complete geometry optimization (Broyden-Fletcher-Goldfarb-Shanno function minimizer)[29] involving Thiel's fast minimization algorithm.[30] The preliminary optimization was realized by the molecular mechanics method (the MMX procedure)[31] with the software of the PCMODEL complex.[31] In quantum chemical computations, the condition of the gradient norm not exceeding 0.02 kcal/(mol·Å) was preset. In some cases, the sufficient decrease in gradient norm was achieved by means of abandonment of the Thiel's fast minimization routine (the keyword "NOTHIEL" of the MOPAC package was applied), or under optimization with the Davidon-Fletcher-Powell method (keyword "DFP"),[27] or using combined approaches involving the keywords NOTHIEL and DFP.

In calculating the rotational contributions to thermodynamic functions the symmetry number was taken as unity.

The regression analysis was performed with the confidence level of 0.95 taking into account the student coefficient.

RESULTS AND DISCUSSION

The ΔG_f values were calculated from the relationship:

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

where the standard entropies of formation ΔS_f were calculated by the formula:

$$\Delta S_f = S - \Sigma S_i,$$

in which S_i are the entropies of the elements constituting molecule in their standard states[32,33] in view of hydrogen, nitrogen, oxygen, fluorine, rhombic sulphur, chlorine, bromine, iodine being the two-atomic molecules; $T = 298.15$ K.

Table I summarizes the computed quantities of thermodynamic properties for the benzenethiol series compounds, for which the pK_a values have been measured in various media by different authors.[34–37]

The computed thermodynamic quantities for benzenethiol (Table I) are in conformity with the experimental ones: $\Delta H_f = 26.66$,[38] 26.86 kcal/mol,[39] $S = 80.51$ cal/(mol·K),[38] $\Delta G_f = 35.28$ kcal/mol.[38] The aforesaid is valid also in respect to the experimental[40] and theoretical values (correlating linearly to each other with the correlation coefficient of 0.9736) of the dipole moments of benzenethiol, 2-carboxymethyl-, 4-chloro-, 4-bromo-, 4-iodobenzenethiols molecules (Table II). That lends support to the validity of the quantum chemical computations carried out.

For the anions (A^-) formed on benzenethiols (AH) dissociation, we have computed the proton affinity (Table III) represented by enthalpy[41–44] and free energy of reactions of proton detachment in gaseous phase $AH \rightarrow A^- + H^+$:

$$\Delta\Delta H_f = \Delta H_f(A^-) + \Delta H_f(H^+) - \Delta H_f(AH),$$

$$\Delta\Delta G_f = \Delta G_f(A^-) + \Delta G_f(H^+) - \Delta G_f(AH),$$

TABLE I Thermodynamic Properties of the Compounds XC_6H_4SH and $XC_6H_4S^-$

Compound	X	ΔH_f, kcal/mol	S, cal/(mol·K)	ΔG_f, kcal/mol
	XC_6H_4SH			
Benzenethiol	H	27.67	78.31	38.14
2-Methylbenzenethiol	2-CH_3	20.37	85.94	35.94
3-Methylbenzenethiol	3-CH_3	18.32	87.80	35.39
4-Methylbenzenethiol	4-CH_3	18.25	86.00	33.81
3-Acetylbenzenethiol	3-$COCH_3$	−13.66	99.45	5.60
4-Acetylbenzenethiol	4-$COCH_3$	−13.78	98.64	5.72
2-Mercaptobenzoic acid	2-COOH	−56.89	90.94	−37.50
4-Mercaptobenzoic acid	4-COOH	−61.70	93.09	−42.95
3-Mercaptomethylbenzoate	3-$COOCH_3$	−53.44	102.83	−27.88
4-Mercaptomethylbenzoate	4-$COOCH_3$	−53.49	101.67	−27.59
4-Aminobenzenethiol	4-NH_2	25.36	85.04	42.97
4-Acetylamidobenzenethiol	4-CH_3CONH	−15.16	104.44	14.09
3-Nitrobenzenethiol	3-NO_2	19.74	91.90	40.61
4-Nitrobenzenethiol	4-NO_2	19.27	91.25	40.33
4-Hydroxybenzenethiol	4-OH	−17.44	83.52	−3.54
3-Methoxybenzenethiol	3-OCH_3	−10.29	91.08	11.06
4-Methoxybenzenethiol	4-OCH_3	−10.37	92.01	10.71
3-Methylsulphobenzenethiol	3-CH_3SO_2	−35.27	104.37	−9.44
4-Methylsulphobenzenethiol	4-CH_3SO_2	−36.78	104.44	−10.97
4-Fluorobenzenethiol	4-F	−15.65	82.60	−6.22
3-Chlorobenzenethiol	3-Cl	21.16	85.53	30.44
4-Chlorobenzenethiol	4-Cl	21.10	84.81	30.59
2,4-Dichlorobenzenethiol*	2,4-xx-Cl	16.56	91.27	8.87
3-Bromobenznethiol	3-Br	35.54	87.68	41.66
4-Bromobenzenethiol	4-Br	35.62	87.73	41.72
3-Iodobenzenethiol	3-I	49.22	88.90	53.68
4-Iodobenzenethiol	4-I	49.25	89.21	53.62
	$XC_6H_4S^-$			
Benzenethiolate	H	−2.00	76.49	2.03
2-Methylbenzenethiolate	2-CH_3	−9.49	85.06	1.72
3-Methylbenzenethiolate	3-CH_3	−11.07	86.72	−0.38
4-Methylbenzenethiolate	4-CH_3	−11.25	85.76	−0.27
3-Acetylbenzenethiol	3-$COCH_3$	−49.18	96.75	−33.76
4-Acetylbenzenethiol	4-$COCH_3$	−50.54	96.03	−34.91
2-Mercaptobenzoic acid	2-COOH	−105.71	88.10	−90.12
4-Mercaptobenzoic acid	4-COOH	−100.78	91.18	−86.11
3-Mercaptomethylbenzoate	3-$COOCH_3$	−88.02	101.67	−66.77
4-Mercaptomethylbenzoate	4-$COOCH_3$	−91.68	98.85	−69.59
4-Aminobenzenethiolate	4-NH_2	−3.58	83.74	9.76
4-Acetylamidobenzenethiolate	4-CH_3CONH	−46.70	102.83	−21.62
3-Nitrobenzenethiolate	3-NO_2	−22.62	90.14	−5.88
4-Nitrobenzenethiolate	4-NO_2	−28.57	89.71	−11.70

(Continued on next page)

TABLE I Thermodynamic Properties of the Compounds XC_6H_4SH and $XC_6H_4S^-$ *(Continued)*

Compound	X	ΔH_f, kcal/mol	S, cal/(mol·K)	ΔG_f, kcal/mol
	XC_6H_4SH			
4-Hydroxybenzenethiolate	4-OH	−47.10	82.56	−35.57
3-Methoxybenzenethiolate	3-OCH_3	−40.37	90.74	−23.57
4-Methoxybenzenethiolate	4-OCH_3	−40.80	91.99	−24.37
3-Methylsulphobenzenethiolate	3-CH_3SO_2	−74.31	102.66	−52.62
4-Methylsulphobenzenethiolate	4-CH_3SO_2	−80.38	103.100	−58.83
4-Fluorobenzenethiolate	4-F	−49.74	80.62	−44.37
3-Chlorobenzenethiolate	3-Cl	−12.44	83.54	−7.22
4-Chlorobenzenethiolate	4-Cl	−12.70	83.58	−7.50
2,4-Dichlorobenzenethiolate**	2,4-di-Cl**	−19.80	90.63	−13.40
3-Bromobenznethiolate	3-Br	0.68	86.30	2.55
4-Bromobenzenethiolate	4-Br	0.64	86.67	2.44
3-Iodobenzenethiolate	3-I	14.67	87.12	15.02
4-Iodobenzenethiolate	4-I	14.72	87.49	14.91

*2,4-$X_2C_6H_3SH$, where X = Cl.

**2,4-$X_2C_6H_3S^-$, where X = Cl.

therewith ΔH_f (H^+) = 367.163 kcal/mol,[32,33,42,43] ΔG_f (H^+) = 362.570 kcal/mol.[42,43]

We have established that the pK_a values for benzenethiols in water-acetone,[34] water-ethanol[35,36] media and in methanol[37] correlate linearly with the gaseous-phase proton affinity (Table IV; **m** is the number of considered points, **r** is the correlation coefficient). An example of pK_a *vs* $\Delta\Delta G_f$ dependence has been presented in Figure 1.

That points to the about constant contribution of medium to the protolytic properties of all series of compounds outlined in Dmuchnovsky et al.,[34] Schwarzenbach and Rudin,[35] Bordwell and Andersen,[36] and David and Hallam.[37]

TABLE II Measured by the Second Debye Method in Benzene at 20°C[40] and PM3-Computed Dipole Moments of the Benzenethiols Molecules

Molecule	μ_{exper}, D	μ_{theor}, D
Benzenethiol	1.33	1.58
2-Mercaptomethylbenzoate	2.47*	2.86
4-Chlorobenzenethiol	1.16	1.17
4-Bromobenzenethiol	1.14	1.18
4-Iodobenzenethiol	1.4	1.21

*at 25°C.

TABLE III Enthalpies ($\Delta\Delta H_f$), Free energies ($\Delta\Delta G_f$) of the Benzenethiolate Anions $XC_6H_4S^-$ Proton Affinity Computed by the PM3 Method and the Benzenethiols XC_6H_4SH pK_a Values Measured in Solutions

XC_6H_4SH	X	$\Delta\Delta H_f$, kcal/mol	$\Delta\Delta G_f$, kcal/mol	pK_a	Conditions of pK_a determination*	Ref.
Benzenethiol	H	337.49	326.46	8.6	1	34
				7.78	2	35
				9.32	3	35
				7.76	4	36
				8.3	5	37
2-Methylbenzenethiol	2-CH_3	337.31	328.34	9.2	1	34
3-Methylbenzenethiol	3-CH_3	337.77	326.80	8.9	1	34
				7.99	2	35
				9.56	3	35
				7.96	4	36
4-Methylbenzenethiol	4-CH_3	337.66	328.49	9.3	1	34
				8.07	2	35
				9.70	3	35
				8.03	4	36
				8.4	5	37
3-Acetylbenzenethiol	3-$COCH_3$	331.65	323.21	6.93	2	35
				8.35	3	35
4-Acetylbenzenethiol	4-$COCH_3$	330.40	321.94	5.93	2	35
				7.28	3	35
2-Mercaptobenzoic acid	2-COOH	318.33	309.95	5.02	2	35
				6.18	3	35
4-Mercaptobenzoic acid	4-COOH	328.09	319.41	5.56	2	35
				7.28	3	35
3-Mercaptomethylbenzoate	3-$COOCH_3$	332.58	323.68	6.98	2	35
				8.40	3	35
4-Mercaptomethylbenzoate	4-$COOCH_3$	328.97	320.57	6.17	2	35
				7.50	3	35
4-Aminobenzenethiol	4-NH_2	338.22	329.37	9.7	5	37
4-Acetylamidobenzenethiol	4-CH_3CONH	335.62	326.86	8.6	1	34
3-Nitrobenzenethiol	3-NO_2	324.81	316.09	5.90	4	36
4-Nitrobenzenethiol	4-NO_2	319.33	310.54	4.99	2	35
				6.42	3	35
				5.11	4	36
				5.8	5	37
4-Hydroxybenzenethiol	4-OH	337.50	330.54	8.33	2	35
				10.02	3	35
				8.30	4	36
3-Methoxybenzenethiol	3-OCH_3	337.09	327.94	7.54	2	35
				9.20	3	35
				7.45	4	36
4-Methoxybenzenethiol	4-OCH_3	336.73	327.49	8.08	2	35
				9.76	3	35
				7.99	4	36
				8.8	5	37
3-Methylsulphobenzenethiol	3-CH_3SO_2	328.12	319.39	5.88	4	36
4-Methylsulphobenzenethiol	4-CH_3SO_2	323.55	314.71	5.57	4	36
4-Fluorobenzenethiol	4-F	333.08	324.42	8.1	1	34

(Continued on next page)

TABLE III Enthalpies ($\Delta\Delta H_f$), Free energies ($\Delta\Delta G_f$) of the Benzenethiolate Anions $XC_6H_4S^-$ Proton Affinity Computed by the PM3 Method and the Benzenethiols XC_6H_4SH pK_a Values Measured in Solutions *(Continued)*

XC_6H_4SH	X	$\Delta\Delta H_f$, kcal/mol	$\Delta\Delta G_f$, kcal/mol	pK_a	Conditions of pK_a determination*	Ref.
3-Chlorobenzenethiol	3-Cl	333.57	324.92	6.85	2	35
				8.17	3	35
				6.74	4	36
4-Chlorobenzenethiol	4-Cl	333.36	324.48	7.8	1	34
				7.06	2	35
				8.45	3	35
				6.96	4	36
				7.3	5	37
2,4-Dichlorobenzenethiol**	2,4-xx-Cl	330.80	321.75	7.2	5	37
3-Bromobenzenethiol	3-Br	332.30	323.46	6.90	2	35
				8.22	3	35
				6.77	4	36
4-Bromobenzenethiol	4-Br	332.18	323.29	7.00	2	35
				8.37	3	35
				6.99	4	36
3-Iodobenzenethiol	3-I	332.62	323.91	6.85	2	35
				8.08	3	35
				6.82	4	36
4-Iodobenzenethiol	4-I	332.63	323.86	6.99	2	35
				8.32	3	35
				6.94	4	36

*1 Determined by potentiometric titration in water-acetone mixture (1:3 by volume) at 27°C

2 Determined by potentiometric titration in 48.9 vol. % aqueous ethanol at 20–22°C

3 Determined by potentiometric titration in 95 vol. % aqueous ethanol at 20–22°C

4 Determined by spectrophotometric technique in 48 vol. % aqueous ethanol at 25°C

5 Determined by potentiometric titration in methanol

**$2,4\text{-}X_2C_6H_3SH$, where X = Cl

A measure of influence of constant medium component on benzenethiols basicity can be presented as: 1) deviation of **b** value in Table IV from a theoretical slope of dependence pK_a *vs* $\Delta\Delta G_f$ equal to $(\ln 10 \cdot RT)^{-1} = 0.7330$ mol/kcal and being referred to gaseous phase; 2) absolute **a** value (equal to zero for gaseous phase).[14,17]

As for the pK_a versus PA correlations for the pK_a values measured in methanol, confidence limits for the **a** and **b** coefficients are disproportionate with respect to the absolute **a** and **b** values.

Excluding from consideration the results of quantum chemical computations and experiment, for 4-aminobenzenethiol (**I**) in methanol solution leads to the increase in correlation coefficient **r** and the narrowing of confidence limits about the slope **b** and about the intercept **a**.

Deviation of the data for the compound **I** from the trend line could be due to its molecule's structural peculiarities responsible for the

TABLE IV Correlations of the Benzenethiols pK_a Values with the Benzenethiolate Anions Proton Affinities (PA)

Conditions of pK_a determination*	PA	Set of substituents X	**m**	**a**	**b**, mol/kcal	**r**
1	$\Delta\Delta H_f$	H, 2-CH_3, 3-CH_3, 4-CH_3, 4-CH_3CONH, 4-F, 4-Cl, 4-Br	8	−71.84 ± 33.50	0.2395 ± 0.0998	0.9234
1	$\Delta\Delta G_f$	H, 2-CH_3, 3-CH_3, 4-CH_3, 4-CH_3CONH, 4-F, 4-Cl, 4-Br	8	−93.70 ± 21.74	0.3134 ± 0.0667	0.9787
2	$\Delta\Delta H_f$	H, 3-CH_3, 4-CH_3, 3-$COCH_3$, 4-$COCH_3$, 2-COOH, 4-COOH, 3-$COOCH_3$, 4-$COOCH_3$, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	19	−49.22 ± 9.89	0.1690 ± 0.0298	0.9453
2	$\Delta\Delta G_f$	H, 3-CH_3, 4-CH_3, 3-$COCH_3$, 4-$COCH_3$, 2-COOH, 4-COOH, 3-$COOCH_3$, 4-$COOCH_3$, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	19	−49.45 ± 10.73	0.1743 ± 0.0332	0.9368
3	$\Delta\Delta H_f$	H, 3-CH_3, 4-CH_3, 3-$COCH_3$, 4-$COCH_3$, 2-COOH, 4-COOH, 3-$COOCH_3$, 4-$COOCH_3$, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	19	−53.05 ± 11.14	0.1849 ± 0.0335	0.9423

(Continued on next page)

TABLE IV Correlations of the Benzenethiols pK_a Values with the Benzenethiolate Anions Proton Affinities (PA) *(Continued)*

Conditions of pK_a determination*	PA	Set of substituents X	**m**	**a**	**b**, mol/kcal	**r**
3	$\Delta\Delta G_f$	H, 3-CH_3, 4-CH_3, 3-$COCH_3$, 4-$COCH_3$, 2-COOH, 4-COOH, 3-$COOCH_3$, 4-$COOCH_3$, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	19	−53.28 ± 12.08	0.1907 ± 0.0374	0.9335
4	$\Delta\Delta H_f$	H, 3-CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-CH_3SO_2, 4-CH_3SO_2, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	16	−47.10 ± 8.81	0.1627 ± 0.0265	0.9619
4	$\Delta\Delta G_f$	H, 3-CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-CH_3SO_2, 4-CH_3SO_2, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I	16	−46.87 ± 9.48	0.1665 ± 0.0293	0.9558
5**	$\Delta\Delta H_f$	H, 4-CH_3, 4-NH_2, 4-NO_2, 4-OCH_3, 4-Cl, 2,4-dichloro	7	−49.06 ± 30.23	0.1709 ± 0.0907	0.9080
5**	$\Delta\Delta G_f$	H, 4-CH_3, 4-NH_2, 4-NO_2, 4-OCH_3, 4-Cl, 2,4-dichloro	7	−50.30 ± 28.91	0.1797 ± 0.0892	0.9180
5***	$\Delta\Delta H_f$	H, 4-CH_3, 4-NO_2, 4-OCH_3, 4-Cl, 2,4-dichloro	6	−42.03 ± 21.90	0.1493 ± 0.0659	0.9531
5***	$\Delta\Delta G_f$	H, 4-CH_3, 4-NO_2, 4-OCH_3, 4-Cl, 2,4-dichloro	6	−43.03 ± 23.81	0.1567 ± 0.0737	0.9472

*Designated in Table III.

**Correlation series involves the PA and pK_a values for all the compounds, for which the pK_a values in methanol have been measured.

***Data for the species **I** (X = NH_2) are excluded.

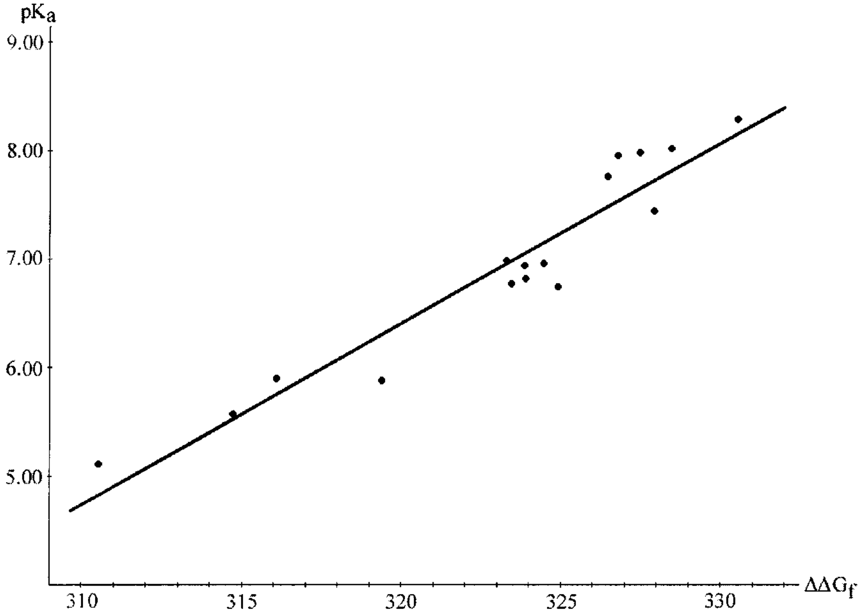

FIGURE 1 Dependence of benzenethiols XC_6H_4SH pK$_a$ values determined by spectrophotometric technique in 48 vol.% aqueous ethanol at 25°C (36) versus $\Delta\Delta G_f$ (kcal/mol). X = H, 3-CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-CH_3SO_2, 4-CH_3SO_2, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I. Correlation coefficient r = 0.9558.

differentiating contribution to interaction with a solvent. Among all the molecules of compounds for which the pK$_a$ values in methanol medium have been determined, the system **I** solely contains a strongly polarized bond of hydrogen-heteroatom apart from the H-S bond. That is why one can believe that the lesser reliability of linear relationships of pK$_a$ versus PA in the presence of PA and pK$_a$ values for 4-aminobenzenethiol **I** compared to the correlation series in the absence of these data is related to the additional possibility of hydrogen bonds formation by the protons of primary amino group of the above thiol with donor oxygen atom of methanol.

Provided that the data for the substance **I** are excluded from the correlation series, PA are related linearly also to the values of B comprising a slope of linear relationships of the $\Delta\nu/\nu$ ratios for stretching vibrations of S-H bond against the analogous $\Delta\nu/\nu$ ratios for stretchning vibrations of N-H bond in pyrrole.[37] Here ν is the frequency of the corresponding stretching vibration, and $\Delta\nu/\nu$ is the relative shift of frequency caused by a solvent: $\Delta\nu/\nu = [\nu(\text{in } CCl_4) - \nu(\text{in another solvent})]/\nu(\text{in } CCl_4)$.[37]

According to David and Hallam,[37] the quantity B characterizes the intrinsic acidity of sulphohydryl proton in molecule with no allowance for a solvent effect. The B values for benzenethiol, 4-methyl-, 4-amino-, 4-nitro-, 4-methoxy-, 4-chloro-, 2,4-dichlorobenzenethiols are equal to 2.30, 2.09, 3.65, 1.10, 2.27, 1.91, 1.78 respectively.[37]

Presented below are the quantitative relationships of B versus PA for the series of the compounds mentioned, excluding **I**:

$$\mathrm{B} = \mathbf{c} + \mathbf{d} \cdot \Delta\Delta \mathrm{H_f},$$

$$\mathbf{c} = -18.71 \pm 5.80, \quad \mathbf{d} = 0.06201 \pm 0.01744, \quad \mathbf{r} = 0.9801;$$

$$\mathrm{B} = \mathbf{e} + \mathbf{f} \cdot \Delta\Delta \mathrm{G_f},$$

$$\mathbf{e} = -18.87 \pm 8.17, \quad \mathbf{f} = 0.06429 \pm 0.02529, \quad \mathbf{r} = 0.9621.$$

Obviously the B value is not actually independent on a solvent, the more so as the results of computations and experiments for the given compound **I** deviate from the linear relationships, both pK$_a$ versus PA and B versus PA.

For some of the equalities pK$_a$ versus PA and B versus PA obtained (apart from the aforesaid for the pK$_a$ values of benzenethiol series involving the compound **I**, in methanol), relatively high (though satisfactory for regression analysis) are confidence limits about the slope and about the intercept, which in some cases (water-acetone and methanol media) is connected partially with a limited number of points (from 6 to 8). That does not decrease a predictive ability of the relationships stated. For the corresponding evaluations, of importance is a center of statistical distribution. Many authors publish coefficients in regression equations without data on error, which often exceeds absolute values of the coefficients. Especially as one could hardly expect the narrow confidence limits, pK$_a$ values in polar media in which solvation interactions take place are compared to gaseous-phase reactivity indexes ($\Delta\Delta \mathrm{H_f}$, $\Delta\Delta \mathrm{G_f}$). Even great **r** values are remarkable here.

In some cases the first digit of confidence limits coincides with the first significant digit of regression coefficients. Following the rules of rounding figures in a literal sense would result in rough estimates. Therefore, following the commonly accepted experience we give for the coefficients **a**, **b** and confidence limits the equal number of digit places, but not the significant figures.[13]

An argument in support of presenting "extra" significant digits consisits in the fact that the coefficients in the regression equations are intermediate on estimating the pK$_a$ and B values. Rounding off is reasonable for final results.[13]

CONCLUSION

Using the quantitative relationships found in this article, one could predict the pK_a and B values of the benzenethiols of given structure.

A priori evaluation of the said parameters by quantum chemical methods is important for molecular design of compounds with given properties, may serve as a base for expert decision on reasonability of synthesis that is sometimes labor- and time-consuming, requiring complicated device, rigid conditions, expensive, and toxic chemicals.

The collection of experimental data on acid-base properties and vibrational spectra of benzenethiols in combination with the results of PA values computations will favor the enhancement of reliability of the corresponding quantitative relationships.

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