DISSOCIATION OF NAPHTHOIC ACIDS IN NON-AQUEOUS MEDIA. COMPARISON OF BENZENE AND NAPHTHALENE SKELETONS

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Seven monosubstituted 1-naphthoic acids were synthesized by new or modified procedures, and their dissociation constants were measured potentiometrically at 25 °C in methanol, acetonitrile, dimethylformamide, and pyridine. Dissociation constants of these along with thirteen substituted 1-naphthoic acids and twenty-five substituted 2-naphthoic acids previously studied were measured at 25 °C in ethanol and dimethyl sulfoxide. The pK_{HA} values of 3- and 4-substituted 1-naphthoic acids were treated by simple linear regression and principal component analysis, and the results were used for comparison of model compounds and of corresponding 3- and 4-substituted benzoic acids with the aim of comparison of benzene and naphthalene skeletons. It has been found, the 3 and 4 positions of the 1-naphthyl system can roughly be compared with the *meta* and *para* positions of benzene, respectively.

Key words: Naphthoic acids; Benzoic acids; Dissociation; Ionization constants; Substituent effects; Solvent effects; Chemometrics.

The history of description of substituent effects in naphthalene derivatives starts from the Hammett equation. At first, the properties of naphthalene derivatives were related to the corresponding benzene derivatives with the presumption that the way of transmission of substituent effects is identical or very similar in both systems[1]. Later on, the reaction constants ρ describing the benzene series were used to calculate various position-dependent constants σ, σ_{ij}, σ_n or σ^N for the naphthalene skeleton[2–9]. The presumptions from which the definition of the said constants started, *i.e.*, the equality of reaction constants ρ for benzene and naphthalene derivatives[7,10], however, proved to be not quite justified. In spite of that, the reactivity of naphthalene derivatives continued to be compared with that of their benzene analogues, which is documented by several selected papers from the area of study of carboxylic acids[1,4,5,7,10–13]. Such a comparison can also be based on studies of acid-base properties of naphthoic and benzoic acids in non-

aqueous media. Our previous paper[14] gave dissociation constants of 38 substituted naphthoic acids in four organic solvents, and the data obtained were used to examine the substituent effects on dissociation of model compounds in non-aqueous media using the Hammett equation.

The present paper tries to extend the scope of both the series of compounds investigated and the number of non-aqueous media used in dissociation of naphthoic acids, and deals with a comparison of acid-base properties of 3- and 4-substituted 1-naphthoic acids and 3- and 4-substituted benzoic acids with the emphasis on finding the differences between effects of the naphthalene and benzene skeletons.

EXPERIMENTAL

The model compounds, except for those given below, were prepared by usual procedures. Their structure was verified by ^{1}H and ^{13}C NMR spectra measured with a Bruker AMX 360 apparatus. The dissociation constants (pK_{HA}) of twenty 3-, 4-, 5-, and 8-substituted 1-naphthoic acids and twenty-five 4-, 5-, 6-, 7-, and 8-substituted 2-naphthoic acids were determined at 25 °C by the method of potentiometric titration using an automatic apparatus TITRALAB 3 (Radiometer), the experimental arrangement and electrodes used being the same as those in our previous papers[14–17]. The solvents used were purified in standard ways.

3-Amino-1-naphthoic Acid

3-Amino-1-naphthoic acid was prepared according to ref.[18] except for the step leading to 3-nitronaphthalene-1-carbonitrile. Thus, naphthalen-1-amine (61.3 g, 0.428 mol) was acetylated and brominated to give 4-bromonaphthalene-1-acetamide (101.7 g, 0.385 mol), which was transformed into 4-cyanonaphthalene-1-acetamide (60 g, 0.285 mol). The latter compound was nitrated and hydrolyzed to give 4-amino-3-nitronaphthalene-1-carbonitrile (27.3 g, 0.128 mol), which was then diazotized. The diazonium salt was added during 30 min at –5 °C into a suspension of hypophosphorous acid prepared by adding dropwise a solution of $NaH_2PO_2 \cdot H_2O$ (66.7 g) in water (150 ml) into a mixture of concentrated sulfuric acid (41 ml) and water (41 ml) at –5 °C. The reaction mixture was left to stand 3 days in cold place. Then the separated solid was collected by filtration, washed, dried, and recrystallized from ethanol with charcoal. 3-Nitronaphthalene-1-carbonitrile was prepared in 30% yield (7.5 g), m.p. 184–189 °C (ref.[18] m.p. 183 °C). The nitrile was hydrolyzed to 3-nitro-1-naphthoic acid (5 g, 0.023 mol), which was then hydrogenated in methanol with palladium as a catalyst to give 3-amino-1-naphthoic acid (3.2 g, 0.017 mol).

3-Chloro-1-naphthoic Acid

First, 3-nitronaphthalene-1-carbonitrile was reduced to 3-aminonaphthalene-1-carbonitrile according to ref.[19]. This aminonitrile was also prepared, in a comparable yield, by the following procedure. A mixture of $FeSO_4 \cdot 7H_2O$ (35.5 g) and water (43 ml) was heated to boiling with intensive stirring and treated with a suspension of 3-nitronaphthalene-1-carbonitrile (3 g, 0.015 mol) in concentrated aqueous ammonia (20 ml) added dropwise within 10 min. Then concentrated aqueous ammonia was added until the mixture was alka-

line (pH 12), and the boiling was continued for another 15 min. After cooling, the mixture was filtered, the filter cake was dried and extracted with diethyl ether. After distilling off the ether, the crude product was recrystallized from ethanol with charcoal. In this way, we prepared 0.8 g of 3-aminonaphthalene-1-carbonitrile (31%) with m.p. 118–122 °C (ref.[8] m.p. 116–117 °C). The product was transformed into 3-chloronaphthalene-1-carbonitrile and then to 3-chloro-1-naphthoic acid[20].

4-Nitro-1-naphthoic Acid

4-Nitronaphthalen-1-amine was transformed into 4-nitronaphthalene-1-carbonitrile by the Sandmeyer reaction[21]. Then, 4-nitronaphthalene-1-carbonitrile (2 g, 0.010 mol) was heated with concentrated sulfuric acid (10 ml), glacial acetic acid (10 ml), and water (10 ml) at 120 °C for a period of 4 h, whereupon the reaction mixture was poured onto crushed ice (*ca* 50 g), and the separated solid was collected by filtration and dissolved in 5% aqueous sodium carbonate solution (70 ml). After clarification, the solution was acidified with hydrochloric acid to pH 1, the separated solid was collected by filtration, and recrystallized from methanol with charcoal. The 4-nitro-1-naphthoic acid thus prepared (0.8 g, 37%) had m.p. 225–227 °C (ref.[10] m.p. 221–223 °C).

4-Methyl-1-naphthoic Acid

A mixture of naphthalene-1-carbaldehyde (47.5 ml, 0.350 mol), ethane-1,2-diol (350 ml), 80% hydrazine hydrate (35 ml), and NaOH (46.7 g) was heated on a boiling water bath for 30 min and then refluxed for 3 h. After cooling, the mixture was treated with water (300 ml) and extracted twice with diethyl ether (200 ml). After distilling off the ether, the crude product was distilled in vacuum to give 26.7 g (54%) of 1-methylnaphthalene, b.p. 106–109 °C/1.5 kPa (ref.[22] b.p. 111 °C/1.6 kPa). 1-Methylnaphthalene was then acetylated to give 1-acetyl-4-methylnaphthalene[23].

A mixture of NaOH (4.8 g), water (60 ml), and crushed ice (60 g) was treated with bromine (2.4 ml). After the bromine was dissolved, the mixture was treated with 1-acetyl-4-methylnaphthalene (3.3 g, 0.018 mol) added at 50 °C, and the reaction mixture was refluxed for 1 h. After cooling, the solution was washed with diethyl ether (100 ml) and acidified with hydrochloric acid to pH 1. The unreacted hypobromite was removed by addition of $Na_2S_2O_5$. The separated solid was reprecipitated from a 5% aqueous sodium carbonate solution by addition of hydrochloric acid, and recrystallized from 70% aqueous ethanol with charcoal to give 0.7 g (21%) of 4-methyl-1-naphthoic acid, m.p. 168–176 °C (ref.[24] m.p. 176–177 °C).

5-Methoxy-1-naphthoic Acid

1-Nitronaphthalene was brominated[25] to give 1-bromo-5-nitronaphthalene, which was then reduced to 5-bromonaphthalen-1-amine[26]. A mixture of the latter (15 g, 0.068 mol), CuCN (6.4 g), and pyridine (5.8 ml) was heated at 190 °C for 1.5 h. The hot reaction mixture was transferred into dilute aqueous ammonia (200 ml), the solid was crushed and the suspension was left to stand overnight. Then the solid was collected by filtration, washed with dilute aqueous ammonia and water, and recrystallized from 50% aqueous ethanol. The yield was 5.7 g (50%) of 5-aminonaphthalene-1-carbonitrile, m.p. 129–135 °C (ref.[27] m.p. 141.5–145 °C).

A comparable yield of 5-aminonaphthalene-1-carbonitrile was also obtained by the procedure according to ref.[27].

5-Aminonaphthalene-1-carbonitrile was transformed into 5-hydroxynaphthalene-1-carbonitrile, which was then hydrolyzed to 5-hydroxy-1-naphthoic acid, and subsequently methylated to 5-methoxy-1-naphthoic acid[28].

RESULTS AND DISCUSSION

Tables I and II summarize the dissociation constants of monosubstituted 1- and 2-naphthoic acids in the form of $\overline{pK}_{HA}$ (along with the standard deviations) found in the individual solvents. The series of so far published non-aqueous media selected for this study – methanol (MeOH), acetonitrile (AN), *N*,*N*-dimethylformamide (DMF), and pyridine (Py) – was extended by amphiprotic ethanol (EtOH) and dipolar aprotic protophilic dimethyl sulfoxide (DMSO).

The pK_{HA} values obtained (each measurement was repeated three times) were treated by linear regression. The dissociation constants were correlated using the Hammett equation with the substituent constants $\sigma_{m,p}$ (ref.[29]) found for the benzene derivatives. The average dissociation constants $\overline{pK}_{HA}$ were analyzed by the method of projection to latent structures[30] (PLS).

A mere comparison of acidity of both naphthoic acids and benzoic acid in the media studied clearly shows an acidifying effect of the naphthalene skeleton as compared with that of the benzene ring. The respective values of dissociation constant ($\overline{pK}_{HA}$) of 1-naphthoic acid, 2-naphthoic acid, and benzoic acid are: in MeOH 8.92, 9.39, and 9.41; in DMF 12.00, 12.11, and 12.27; in Py 9.49, 9.74, and 9.81; in AN 20.13, 20.30, and 20.70; in EtOH 9.87, 10.15, and 10.25; in DMSO 10.63, 10.85, and 11.00 (the values for benzoic acid were taken from refs[31–34]). The order of acidity observed in individual solvents is identical with that found in other solvents, *e.g.*, in water[35,36] 3.69, 4.16, and 4.20; in 50% aqueous ethanol[10,24] 5.54, 5.66, and 5.74, respectively. The larger acidifying effect of the naphthalene skeleton as compared with benzene is probably due to better stabilization of the conjugate base by a more extensive delocalization of its negative charge in the naphthalene ring compared with the benzene ring.

The higher acidity of 1-naphthoic acid as compared with that of the 2-isomer is probably due to lowered coplanarity of carboxylic group and aromatic ring as a consequence of the effect of *peri* hydrogen substituent and thus lowered mutual conjugation[1,35,37,38]. No such effect can operate in the case of 2-naphthoic acid.

For the purpose of comparison of different effects of the naphthalene and benzene rings on the dissociation of the respective carboxylic acid, we

made use of a comparison of the series of 3- and 4-substituted 1-naphthoic acids (NA) with the series of 3- and 4-substituted benzoic acids (BA). If the 3- and 4-substituted 1-naphthoic acids are considered "pseudometa" and "pseudopara", respectively, it is possible to use a simple linear regression and correlate the pK_{HA} values measured for these acids by the Hammett relation, just in analogy to the common correlation of 3- and 4-substituted benzoic acids. For this correlation, we used $\sigma_{m,p}$ constants, although their

TABLE I
The average dissociation constants ($\overline{pK}_{HA}$) and their standard deviations (*s*) of substituted 1-naphthoic acids in various solvents at 25 °C

X	MeOH	DMF	Py	AN	EtOH	DMSO
H	8.98(0.02)[a]	12.00(0.02)[a]	9.49(0.06)[a]	20.13(0.01)[a]	9.87(0.02)	10.63(0.04)
3-NH_2	9.16(0.01)	12.47(0.01)	9.80(0.01)	20.63(0.05)	10.10(0.02)	11.29(0.02)
3-Cl	8.42(0.04)	10.98(0.04)	8.72(0.02)	19.67(0.01)	9.22(0.02)	9.85(0.09)
3-Br	8.50(0.01)	10.95(0.04)	8.63(0.01)	19.61(0.02)	9.29(0.02)	9.82(0.07)
3-NO_2	8.06(0.01)[a]	10.35(0.05)[a]	8.14(0.02)[a]	19.17(0.02)[a]	8.76(0.04)	9.22(0.01)
4-NH_2	10.33(0.02)	13.82(0.03)	10.90(0.04)	21.65(0.01)	11.32(0.03)	12.05(0.04)
4-OCH_3	9.58(0.01)[a]	12.58(0.05)[a]	10.15(0.05)[a]	20.97(0.06)[a]	10.52(0.01)	11.22(0.03)
4-CH_3	9.17(0.03)	12.17(0.01)	9.76(0.02)	20.57(0.01)	10.06(0.02)	10.95(0.02)
4-Cl	8.66(0.04)[a]	11.31(0.03)[a]	8.89(0.02)[a]	19.95(0.06)[a]	9.42(0.03)	9.97(0.01)
4-Br	8.68(0.02)[a]	11.28(0.04)[a]	8.88(0.03)[a]	19.91(0.00)[a]	9.35(0.01)	9.97(0.08)
4-CN	7.86(0.03)[a]	10.46(0.02)[a]	8.07(0.04)[a]	19.14(0.02)[a]	8.55(0.01)	9.14(0.06)
4-NO_2	7.75(0.06)	10.09(0.04)	7.88(0.01)	18.88(0.01)	8.47(0.03)	8.95(0.03)
5-NH_2	9.13(0.01)[a]	12.60(0.02)[a]	9.97(0.03)[a]	20.36(0.08)[a]	10.12(0.03)	11.34(0.06)
5-OCH_3	9.00(0.02)	12.06(0.02)	9.60(0.04)	20.14(0.02)	9.93(0.03)	10.66(0.03)
5-Cl	8.62(0.02)[a]	11.31(0.03)[a]	8.98(0.04)[a]	19.73(0.07)[a]	9.39(0.01)	10.11(0.04)
5-Br	8.58(0.03)[a]	11.19(0.07)[a]	8.96(0.08)[a]	19.80(0.12)[a]	9.37(0.02)	10.02(0.04)
5-CN	8.29(0.01)[a]	10.96(0.02)[a]	8.90(0.01)[a]	19.32(0.02)[a]	9.08(0.02)	9.69(0.03)
5-NO_2	8.32(0.04)[a]	10.86(0.07)[a]	8.55(0.06)[a]	19.24(0.08)[a]	9.09(0.03)	9.68(0.01)
8-Cl	8.38(0.02)[a]	11.93(0.06)[a]	9.40(0.04)[a]	19.70(0.06)[a]	9.37(0.03)	10.62(0.05)
8-NO_2	8.55(0.05)[a]	10.86(0.07)[a]	9.23(0.03)[a]	19.58(0.07)[a]	9.53(0.03)	10.24(0.03)

[a] Ref.[14]

TABLE II

The average dissociation constants ($\overline{pK}_{HA}$) and their standard deviations (*s*) of substituted 2-naphthoic acids in various solvents at 25 °C

X	MeOH[a]	DMF[a]	Py[a]	AN[a]	EtOH	DMSO
H	9.36(0.03)	12.11(0.05)	9.74(0.04)	20.30(0.05)	10.15(0.02)	10.85(0.03)
4-CH_3	9.39(0.03)	12.26(0.05)	9.89(0.04)	20.52(0.02)	10.26(0.02)	11.00(0.03)
4-Cl	8.87(0.04)	11.24(0.02)	8.98(0.07)	19.73(0.05)	9.61(0.03)	10.00(0.04)
4-Br	8.85(0.03)	11.20(0.04)	8.98(0.07)	19.76(0.03)	9.56(0.01)	10.04(0.05)
5-Br	9.03(0.02)	11.66(0.06)	9.29(0.04)	20.20(0.05)	9.73(0.02)	10.42(0.01)
5-NO_2	8.82(0.03)	11.40(0.03)	8.98(0.06)	19.94(0.10)	9.48(0.04)	10.23(0.01)
6-OCH_3	9.54(0.00)	12.47(0.01)	9.95(0.04)	20.77(0.01)	10.39(0.03)	11.11(0.05)
6-CH_3	9.44(0.02)	12.31(0.03)	9.87(0.04)	20.78(0.04)	10.28(0.01)	11.02(0.03)
6-Cl	9.13(0.02)	11.99(0.05)	9.39(0.05)	20.36(0.05)	9.90(0.03)	10.68(0.05)
6-Br	9.13(0.04)	11.87(0.00)	9.39(0.05)	20.48(0.01)	9.91(0.02)	10.64(0.04)
6-CN	8.77(0.05)	11.49(0.04)	8.99(0.07)	19.79(0.05)	9.49(0.04)	10.17(0.02)
6-NO_2	8.73(0.01)	11.37(0.04)	8.86(0.07)	19.91(0.06)	9.42(0.03)	10.13(0.04)
7-NH_2	9.59(0.05)	12.79(0.04)	10.32(0.02)	20.60(0.06)	10.56(0.02)	11.42(0.03)
7-OCH_3	9.39(0.03)	12.28(0.07)	9.78(0.03)	20.46(0.10)	10.24(0.04)	10.98(0.01)
7-CH_3	9.41(0.02)	12.27(0.02)	9.74(0.02)	20.50(0.07)	10.25(0.01)	10.98(0.01)
7-Cl	9.10(0.01)	11.89(0.05)	9.43(0.07)	20.18(0.04)	9.83(0.01)	10.56(0.02)
7-Br	9.10(0.01)	11.85(0.05)	9.33(0.05)	20.02(0.12)	9.81(0.03)	10.57(0.05)
7-CN	8.88(0.04)	11.52(0.03)	9.06(0.07)	19.76(0.04)	9.51(0.02)	10.32(0.04)
7-NO_2	8.79(0.02)	11.46(0.05)	8.97(0.06)	19.45(0.14)	9.37(0.04)	10.18(0.02)
8-OCH_3	9.49(0.02)	12.41(0.03)	9.70(0.05)	20.47(0.09)	10.44(0.01)	10.84(0.03)
8-CH_3	9.32(0.05)	12.15(0.06)	9.63(0.06)	20.46(0.02)	10.18(0.01)	10.91(0.04)
8-Cl	9.11(0.02)	11.72(0.02)	9.33(0.04)	20.32(0.10)	9.93(0.02)	10.34(0.02)
8-Br	9.07(0.03)	11.76(0.05)	9.23(0.04)	20.32(0.06)	9.95(0.01)	10.36(0.03)
8-CN	8.86(0.02)	11.39(0.07)	8.98(0.06)	20.05(0.15)	9.64(0.01)	10.07(0.02)
8-NO_2	8.85(0.02)	11.33(0.05)	8.99(0.02)	20.01(0.06)	9.63(0.01)	10.11(0.06)

[a] Ref.[14]

application to the naphthalene derivatives description is not fully legitimate. The results of this correlation are presented in Table III.

If we compare the values of dissociation constants of individual analogous acids, then almost in all the cases, we can observe higher acidity of the 3- and 4-substituted 1-naphthoic acids as compared with the corresponding benzoic acids[39–41], which is probably caused by the above-mentioned better stabilization of the conjugate base through a more extensive aromatic system. This acidifying effect of the naphthalene skeleton can be quantified by means of the relation $\Delta pK^0_{HA} = pK^0_{HA}(NA) - pK^0_{HA}(BA)$. The ΔpK^0_{HA} exhibit the following values in the individual solvents (given in parentheses): –0.29 (MeOH), –0.31 (DMF), –0.25 (Py), –0.17 (AN), –0.26 (EtOH), –0.35 (DMSO). Hence the increase in delocalization of the negative charge in conjugate

TABLE III
Parameters of linear regressions of pK_{HA} *vs* $\sigma_{m,p}$ of 3- and 4-substituted 1-naphthoic acids, and 3- and 4-substituted benzoic acids in various solvents

Solvent	1-Naphthoic acids (NA)			*n*	Benzoic acids (BA)		$\rho_{NA}/\rho_{BA}(s)$
	$pK^0(s)$	$\rho(s)$	$s(R)$		$pK^0(s)$	$\rho(s)$	
MeOH	9.10	1.71	0.120	36	9.39	1.47	1.16
	(0.02)	(0.05)	(0.986)		(0.08)[a]	(0.02)[a]	(0.04)
DMF	12.02	2.52	0.192	36	12.33	2.27	1.11
	(0.04)	(0.08)	(0.984)		(0.12)[a]	(0.01)[a]	(0.04)
Py	9.52	2.14	0.113	36	9.77	2.18	0.98
	(0.02)	(0.05)	(0.992)		(0.06)[b]	(0.15)[b]	(0.07)
AN	20.40	1.90	0.117	36	20.57	2.05	0.93
	(0.02)	(0.05)	(0.989)		(0.19)[a]	(0.01)[a]	(0.02)
EtOH	9.95	1.94	0.133	36	10.21	1.66	1.17
	(0.02)	(0.05)	(0.987)		(0.10)[a]	(0.01)[a]	(0.03)
DMSO	10.68	2.24	0.171	36	11.03	2.49	0.90
	(0.03)	(0.07)	(0.984)		(0.04)[c]	(0.09)[c]	(0.04)

[a] Ref.[39] [b] Calculated from the published data[40] (s = 0.160, R = 0.980, n = 11). [c] Calculated from the published data[41] (s = 0.145, R = 0.988, n = 21).

bases due to extension of aromatic system when going from benzene to naphthalene is roughly comparable in all the media used.

The order of reaction constants ρ for 1-naphthoic acids (increasing in the series: MeOH, AN, EtOH, Py, DMSO, DMF) is roughly comparable with that of benzoic acids (increasing in the series: MeOH, EtOH, AN, Py, DMF, DMSO). Hence, in both the series compared, lower ρ values are found in amphiprotic MeOH and EtOH and in dipolar aprotic protophobic AN. These solvents solvate well the conjugate base, and thus decrease the effect of substituent on its stabilization. On the other hand, higher ρ values are found with dipolar aprotic protophilic solvents Py, DMSO, and DMF, which, despite their good proton-solvation ability, provide a worse stabilization for the conjugate base and thus increase the importance of substituent effects.

Another interesting fact is the way in which solvation changes with extending the aromatic system. If we compare the ratios of reaction constants, ρ(NA)/ρ(BA), in Table III, we can see a particular improvement in solvation of conjugate bases of 1-naphthoic acids – as compared with conjugated bases of benzoic acids – in DMSO and AN, where these ratios are below unity. Dimethyl sulfoxide solvates the carboxylate group worse than the other solvents do; hence, the extension of the aromatic skeleton on going from benzene to naphthalene brings about a lowering of the reaction constant in this solvent. The influence of acetonitrile seems to be similar. The opposite is true for EtOH and MeOH, and also DMF, for which the values of ratios are above unity. In these solvents, the conjugate bases of benzoic acids are solvated better. In pyridine, the degrees of solvation of 1-naphthoic acids and benzoic acids appear to be comparable.

In order to compare the behaviour in both the series of compounds, we also used the PLS method. The matrix of independent variables $\boldsymbol{X}$ was formed by the $\overline{pK_{HA}}$ values of benzoic acids containing the same substituents as the 1-naphthoic acids measured in the same solvents. The dimensions of $\boldsymbol{X}$ matrix were 12 rows (substrates) and 6 columns (solvents) and were filled to 90% (the missing values were those of $\overline{pK_{HA}}$ of 3-amino derivative in MeOH, DMF, Py, AN, and EtOH, and those of 4-amino and 4-cyano derivatives in Py). The matrix of dependent variables, $\boldsymbol{Y}$, had the same dimensions and contained the $\overline{pK_{HA}}$ values of corresponding 1-naphthoic acids. The first latent variable explained 99.04% of variability of the matrix of benzoic acids ($\boldsymbol{X}$), while the extent of the explained variability by this first latent variable in the matrix of 1-naphthoic acids ($\boldsymbol{Y}$) was 99.32%. The second latent variable turned out to be statistically insignificant on the basis of *F*-test. The result of calculation indicates a very close latent structure of

the data sets and documents a large degree of similarity in the acid-base behaviour of 3- and 4-substituted 1-naphthoic acids and 3- and 4-substituted benzoic acids.

CONCLUSIONS

The dissociation constants of naphthoic acids in non-aqueous media make an extensive set of experimental values for study of substituent effects in naphthalene, and hence they were utilized for comparison of effects of the benzene and naphthalene skeletons. It was found that 3- and 4-substituted 1-naphthoic acids are more acidic than their benzene analogues, which is probably due to a more extensive delocalization of negative charge in the conjugate base of naphthoic acid. It was also found that the acid-base behaviour of the acids compared does not significantly differ from each other, and so the naphthalene 3α and 4α positions can roughly be compared with the benzene *meta* and *para* positions, respectively. Clearly, this fact is due to the impossibility of direct conjugation between the substituent and the reaction centre.

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