

REVERSAL DIPOLAR SUBSTITUENT'S EFFECTS IN THE IONIZATION ESTERIFICATION OF 8-SUBSTITUTED 1- PHENYLNAPHTHALENE -2- CARBOCYLIC ACIDS ⁺

دراسة التأثير العكسي للانتقال القطبي للمجاميع المعوضة في تفاعلات التأين والاسترة
للاحماض الكربوكسيلية (٨-المعوض -١ - فنيل نفتالين -٢ - حامض كربوكسيلي)

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Abstract:

The pka values of a series of 8-substituted – 1-phenylnaphthalene-2-carboxylic acids have been measured in 80% (v/v) 2- methoxyethanol- water at 25°C. In the ionization reaction reversed substituent polar effects were found. The results for the Esterification reaction show similar, but reduced, substituent effects.

المستخلص:

قيست قيم ثابت التأين للاحماض الكربوكسيلية (٨- المعوض - فنيل نفتالين -٢ - حامض كربوكسيلي) في محلول ٢- نيثوكسي ايثانول- ماء (٨٠% حجما) عند ٢٥ ° م وبينت النتائج التأثير العكسي للانتقال القطبي للمجاميع المعوضة في تفاعلات التأين والاسترة للاحماض الكربوكسيلية.

Introduction:

From previous work on inductive and electrostatic- field effect models, a field – effect model appears to give the more satisfactory description of the substituent polar effect. A reversal of the normal polar effect has been detected in some of theses systems and such behavior has been accounted for in terms of the angular dependence of the polar effect. Thus, either the normal or the reverse of the normal substituent polar effect would be expected on the basis of the geometrical disposition of the substituent with regard to the reaction centre. Recent studies have shown that reversed dipolar substituent's effects occur in the ionization of 8-(0- substitutedphenyl) – naphthoic acids. In this study, the reactivities of the 8- substituted- 1-Phenylnaphthalene -2-carboxylicacids (Figure 1) in their ionization, their reaction with diazodipheni methane in 2- methoxy ethanol have studied.

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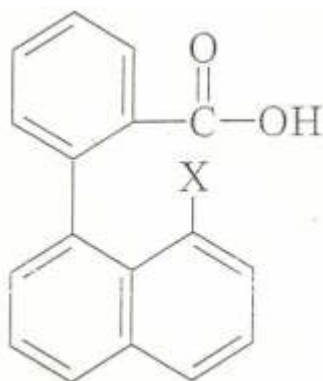


Figure 1: Stereochemical Situation

Experimental:

Materials:

The preparation of methyl-0- iodobenzoate, 8-methyl-1-bromo naphthalene has been described previously [1-10].

1-phenyl naphthalene -2- carboxylic acid: - Methyl 0- iodobenzoate (5 gm, 0.019 mole) and 1-iodonaphthalene (3gm, 0.02 mole) were stirred together at 150 °C while bronze (6gm) was added in small portions at 10 min, intervals, and the reaction was held at 170 °C for further 5 hours. Extraction of the cooled product with benzene followed by evaporation gave a brown solid, which was chromatographed on an alumina column, using analar benzene as the eluant. The solvent wased pressure and the crude ester, which was not, purified further, was then hydrolysed by the method of cooke and Harris [11].

A solution of alcoholic potassium hydroxide was prepared by dissolving hydroxide (15 gm) in 95% aqueous ethanol (950 ml) by refluxing for 10 min. to this alkaline solution was added the ester slowly. The mixture was refluxed for 15 min. the alcohol was distilled off, and the residue was heated in an oil bath at 130-140°C for a further 10 min.

The reaction mixture was dissolved in water: (100 ml) extracted with diethyl ether the aqueous solution was immered in an ice-bath and stirred while a 36% hydrochloride acid solution was added until the solution was strongly acid to litmus.

The precipitate was washed with water and recrystallised from aqueous ethanol to give colorless crystals, which had m.p. 160-162°C (lit [12] 159.5-161 °C) yield 3 gm., 63% of theory. The physical constants, elemental and listed in tables 1, 2 and 3.

8- Substituted – 1- Phenylnaphthalene -2- carboxylic acids (Br, Cl, CH₃). These acids were prepared by the method indicated above for 1-phenyl- naphthalene -2- caboxylic acid. The physical constants, elemental analysis and spectroscopic properties of these compounds are listed in tables 1, 2 and 3.

Table 1: Physical constant of the 8-Substituted-1- Phenylnaphthalene-2- carboxylic acids.

Substituent	Yield	m.p (c)			Recrystallisation solvent
		Found	Lit.	Ref.	
-H	63	160-162			Ethanol
-Cl	56	142-144			Ethanol

-Br	44	151-153			Ethanol
-CH ₃	70	166-167			Ethanol-benzene

Table 2: Elemental analysis of 8-substituted 1-phenylnaphthalene -2- carboxylic acids.

Substituent	Calculated			Found		
	C	H	Others	C	H	Others
-H	82.3	4.9		82.5	4.92	
-Cl	72.2	3.39	12.5(Cl)	72.1	4.1	12.4(Cl)
-Br	62.4	3.39	24.4(Br)	62.5	3.38	24.1(Br)
-CH ₃	82.4	5.4		82.8	5.6	

Table 3: Infra-red spectroscopic properties of 8-substituted-1- Phenylnaphthalene-2- carboxylic acids^(a).

Substituent	Acid carbonyl frequency ν_{\max} (cm ⁻¹)
-H	1714
-Cl	1705
-Br	1704
-CH ₃	1720

a: Spectra obtained in nujol mull.

Measurements:

Pka Values are determined at 25°C by potentiometric method. The rate coefficients for diazodiphenylmethan (DDM) reaction were determined at 30 °C, in the same way described by Bowden et al.[13] using equal acid (DDM) concentration(0.006M).

Results and Discussion:

The pka values were measured in 80% (v/v) 2-methoxyethanol-water at 25°C (table 4). The results in table (4) indicate that all the dipolar electron with drawing and normally acid strengthening substituents are acid-weakening in this case. This effect appears to rise from the stereochemical situation of substituents in the 8- substituted-1- Phenylnaphthalene-2- carboxylic acids system (Figure 1). In this system, the end of the substituted dipole embedded in the molecule has no longer a favorable position for transmission and is effectively opposed by the other end of the dipole. Thus, the normal effect of the dipole will be reversed as can be seen from the results in table (4), the halogens substituent's have a reversal of normal effect and are acid weakening. The methyl group has normal substituent effect.

Table 4: pka Value of 8-substituted-1- Phenylnaphthalene-2- carboxylic acids in 80% (v/v) 2-methoxyethanol-water at 25°C.

Substituent	pka	$\Delta pka \neq$
-H	6.22 (6.24) ^a	0.0
-Cl	6.63	0.41
-Br	6.65	0.43
-CH ₃	6.67	0.45

$\neq \Delta pka = pka(\text{substituted}) - pka(\text{H})$

a: From reference 6.

Esterification with DDM:

Table (5) shows the rate coefficient for the esterification with DDM of -8-substituted -1-phenylnaphthalene -2-carboxylic acids in 2-methoxyethanol at 30°C. This reaction has been used widely in the study of polar substituent effects. The rate determining step is the transfer of a proton from the acid to ddm. The general trend of the result is that is that expected on the basis of their pka value.

Table 5: Rate coefficient for the Esterification acids with (DDM) in 2-methoxyethanol at 30°C.

Substituent	K ₂ (min ⁻¹ . m ⁻¹)	LogK ₂
-H	2.20(2.14) ^a	0.34
-Cl	1.98	0.29
-Br	1.94	0.28
-CH ₃	1.89	0.27

a: From reference 6.

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