TRANSMISSION OF POLAR SUBSTITUENT EFFECTS IN 4`-SUBSTITUTED DIPHENYLACETYLENE-4-CARBOXYLIC ACIDS

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Abstract:

A series of 4'-substituteddiphenylacetylene-4-carboxylic acids' alkaline hydrolysis rate coefficients were measured in 70%(v/v) dimethyl sulfoxide- water at 30.0 C.   Using a solution of 80% (w/w) 2-methoxyethanol - water at 25.0 C, the pKa values of 4'-substituted diphenylacetylene-4-carboxylic acids have been determined. Esterification rate constants of corresponding acids with diazodiphenylmethane have been measured at 300C. For the transmission of dipolar ireversible dipolar substituent effects were seen for 4'-substituted diphenylacetylene-4-carboxylic acids. it was normal substituent effects are observed from 4`-substituted diphenylacetylene-4-carboxylic acids .Therefor it is conceivable to explain clearly the polar of substituent effect of the transmission via path of direct field of electrostatic in this system according to the results shown in tables 8,10 and 12.

Keywords: *Polar Substituent,4`-Substituted Diphenylacetylene -4-Carboxylic Acids .*

Introduction:

Many investigations have been carried out to attempt an analysis of the way in which the transmission of polar effects varies with molecular structure [1-11]. A large number of these have been concerned with the inductive and direct field methods of transmission.

In a number of model systems [3-8], the normal dipolar substituent effects were reversed, suggesting that field effects play a significant role in transmitting substituent effects. This information can now be used diagnostically to probe the conformation of an appropriate model based on our current knowledge of substituent effects.
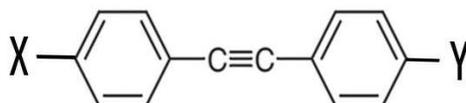
Diphenylacetylene is one such system(1)
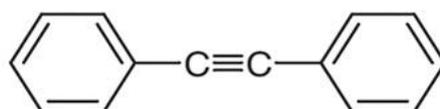
(1)

Diphenylacetylene (1) is a linear and coplanar [12,13].

However, as demonstrated in system (2) below, the relatively remote seat of the substitution from the reaction center should render the occurrence of direct primary or secondary steric effects and direct electrostatic field effects negligible or nonexistent.

(2)

To clarify, normal substituent effects would be anticipated if the substituent were X and the reactive site were Y.

For this research, a new system containing 4'-substituted diphenylacetylene -4-carboxylic acid has been created. To evaluate the acids' reactivity, their pka values and rates of esterification with diazodiphenylmethane (DDM) were determined.

EXPERIMENTAL

Materials:

The preparation of methyl 4-Iodobenzoate, 4`- substituted diphenylacetylene and cuprous phenylacetylide used in this work has been described [14].

Diphenylacetylene -4- carboxylic acid:-

This compound was prepared by the method of Castro et al. [15].

In a flash with a flat bottom (250 ml) and a magnetic mercury stirrer, bar of nitrogen is introduced. Cuprous phenylacetylide (1.9 g) and dry pyridine (75 ml) were added to a mercury-trap-equipped reflux condenser. Methyl 4-iodobenzoate (3 g.) was added during the nitrogen flush after the flash had been purged with nitrogen while being stirred. The contents were cooked for 8 hours in an oil bath at 120 °C with stirring. When the cuprous phenylacetylide was added, a yellow slurry was generated, which slowly dissolved to provide a yellow solution after warming. As the reaction grew stronger. When the reaction was finished, the color of the solution changed to a clear crimson liquid. The solution was cooled, diluted with water (200 mL), and extracted with ether three times.

After washing with dilute HCL and water, the ether extracts were dried on MgSO4. The dried extracts were condensed to yield 1.8g of crude 4-carboxymethyldiphenylacetylene (m. p. 63-65oc), which formed a pale brown crystalline after recrystallisation from petroleum ether (60-80 °C) / benzene. Tables 1.2 and 3 show the physical constants, elemental analyses, and spectroscopic properties.

The ester was saponified with 1.5N KOH at reflux for 45 min. The basic solution was extracted with ether. The aqueous phase was acidified by adding concentrated hydrochloric acid slowly and with vigrous stirring. After then, the solution was cooled down. It was filtered out, washed with cold water, and dried and recrystallized from chloroform/petroleum ether to give (0.93g.) of white needles for diphenylacetylene -4-carboxylic acid The physical constants, elemental analysis and spectroscopic properties are given in tables 4,5 and 6. **4`-substituted** diphenylacetylene-4-carboxylic acids $(NO_2,CL.OCH_3)$ were synthesised by the reaction of the cuprous4-substitutedphenylacetylides with methyl p-iodobenzoate. The procedures were the same as indicated for diphenylacetylene -4-carboxylic acid. The physical constants, elemental analysis and spectroscopic properties are given in tables 4,5 and 6.

Table 1

Physical constants of the methyl 4`-substituted diphenylacetylene-4-carboxylate.

Substituent	Yield (%)	m. p.(°C)	Recrystallisation solvent
H	66	66-69	Petroleum ether (60-80°) /benzene
			= =
CL	64	85-87	= =
NO2	78	101-103	= =
OCH$_3$	89	95-97	

Table 2.

Elemental analysis of methyl 4`-substituted. diphenylacetylene-4-carboxylate.

Substituent	Percentage composition %			
	Calculated		Found	
	C	H	C	H
H	81.3	5.1	81.4	5.2
CL	68.3	3.9	68.2	3.8
NO2	71.0	4.1	71.1	3.9
OCH$_3$	76.7	5.3	76.8	5.2

Table 3.

Infra-red spectroscopic properties of methyl 4`-substituted. diphenylacetylene-4-carboxylate.

Substituent	Ester carbonyl frequency	Triple bond frequency
H	1718	2212
CL	1722	2226
NO2	1716	2224
OCH$_3$	1720	2216

a- Spectra obtained in nujol mull

b- γ max (cm^{-1})

Table 4

Physical constants of the methyl 4`-substituted diphenylacetylene-4-carboxylic acids.

Substituent	Yield (%)	m. p.(^{0}C)			Recrystallisation Solvent
		Found	lit.	ref.	
H	55	220-223	221-222	16	chloroform/ether
CL	61	226-228	-		chloroform/Petroleum ether
NO2	87	315-317	-		chloroform/Petroleum ether
OCH$_3$	73	255-257	-		chloroform/Petroleum ether

Table 5.

Elemental analysis of methyl 4`-substituted diphenylacetylene-4-carboxylic acids.

Substituent	Percentage composition %			
	Calculated		Found	
	C	H	C	H
H	80.8	4.80	81.0	4.70
CL	70.0	3.77	69.8	3.80
NO2	67.3	3.63	67.2	3.65
OCH_3	75.9	5.12	76.1	5.2

Table 6.

Infra-red spectroscopic properties of 4`-substituted diphenylacetylene-4-carboxylic acids .

Substituent	Acid carbonyl frequency γ max(cm^{-1})	Triple bond frequency
H	1715	2206
Cl	1700	2192
No_2	1689	2190
OCH_3	1725	2198

c- . Spectra obtained in nujol mull

d- γ max (cm^{-1})

Measurements were determined pka as described by Bowden et al. [17,18], The pka values and rate coefficients of DDM esterification were determined at a wavelength of 525 nm,

The alkaline hydrolysis coefficients of the esters were determined using the method reported by Bowden et al. [19]. The concentrations of substrate hydroxide anion were 2x10-3 and 4x10-2 M, respectively. The reactions were monitored at the maximum difference between substrate and product, 310-390 nm.

RESULTS AND DISCUSSION

Pka ÷

The pka values were measured in 80% (v/v) 2-methoxyethanol-water at 25 °C (see table7). The result in table (7) indicate that all the dipolar electron-withdrawing, electron-donating groups are operating normally. The Hammett correlation for and the 4-substituted diphenyacetylene- 4-carboxylic acids shows a reasonably linear relation between the pka values and both σ and σ^n values, as shown in table (7) and (8) as is well as Figure 1. Thus, the ρvalue and using σ . for this system is about 0.43 and the ρ_o for benzoic acids for the same reaction an conditions is 1.69 [20]. Therefore the transmissive efficiency this system the ρ / ρ_o equals about 0.254. This transmissive fact can be calculated from the "inductive" transmission coefficient tabulated by Bowden [1] as 0.132. The value observed in this is

somewhat greater than would be estimated on the basis apparent inductive" transmission factors. This increase would expected on the basis of field effect transmission through space.

Esterification with DDM : Table (9) shows the rate coefficient for the esterification with DDM of 4`substituted diphenyl etylene-4-carboxylic acids in 2-methoxyethanol at 30.0 ^{o}C.

The effects of polar substituents have been extensively studied using this reaction [22].Proton transfer from the acid to DDM is the rate-limiting phase. Aplot of the logarithms of the rate coefficients against the values of the acids gives a linear relationship (see figure Hammette correlations have been obtained for the esterification of the 4-substituted diphenylacetylene -4-carboxylic acids both **σ** and **σ** ^{n} has shown in table 10.

The correlation using σwas very good and the correlation using σ^n was satisfactory and ρ was found to be 0.625 (see Figure3) ρ_o for the reference reaction of benzoic acids with DDM in the same solvent is 1.188 [23]. The transmissive efficiency. ρ / ρ_o be about 0.526 for can this system for the DDM reaction.

This is greater than that found for the ionisation reaction and that calculated on the basis of the "Inductive" transmission coefficients (see earlier) No simple explanation of this particular results especially as the result for the alkaline hydrolysis reaction (see later) ionisation reaction.

Table 7.

Pka values of 4`-substituted diphenylacetylene -4-carboxylic acids in 80% (v/v) 2-methoxyethanol. -water at 25 °C.

substituent	Pka	Δpka	σ	σ^n
NO2	6.12	-0.32	0.78	0.78
CL	6.36	-0.08	0.24	0.23
H	6.44	-0.0	0.0	0.0
OCH$_3$	6.56	-0.11	-0.11	-0.27

-The pka values are, reproducible to within ±0.02 unit Δpka = pka (substituted acid) -pka (unsubstituted acid)

* From ref. 21 .

Table 8.

Hammett correlation for the pka values of 4`-substituted diphenylacetylene-4-carboxylic acids in 80% (v/v) 2-methoxyethanol-water at 25 °C.

Substituent Constant	Reaction constant ρ	logkσ	r*	*n
σ	0.429	6.575	0.991	4
σ^n	0.475	6.30	0.985	4

r*is the correlation coefficient.

*n is the number of substituents studied.

Table 9.

Rate coefficients for the esterification of 4`-substituted diphenylacetylene-4-carboxylic acids with DDM in 2-methoxyethanol,at 30 °C together withσ and σ^n.

Substituent	k(min^{-1} M^{-1})	Logk$_2$	σ	σ^n
NO2	1.738	+0.240	0.78	0.78
CL	0.832	-0.080	0.23	0.24
H	0.574	-0.241	0.0	0.0
OCH3	0.407	-0.390	-0.27	-0.11

a- Rate coefficients can be reproduced to within ±3% from at least two independent measurements.

Table 10.

Hammett correlation for the logk$_2$ for the DDM esterification reaction of 4`-substituted diphenylacetylene-4-carboxylic acids . 2-methoxyethanol- at 30 °C.

Substituent Constant	ρ	logkσ	r*	*n
σ	0.625	0.59	0.989	4
σ^n	0.733	0.51	0. 899	4

*See table 8.

Alkaline Hydrolysis :-

In table(11) the rate coefficients for the alkaline hydrolysis of the methyl 4 - substituted diphenylace tylene-4-carboxylates in 70% (v/v) DMSO-water at 30 ºc are shown.

A plot of the logarithms of the rate coefficients against the pka values of the corresponding acids and logarithms of K$_2$ for the DDM esterification of the relevant acids are shown in figures 4 and 5 these give satisfactory linear relations and confirm that the simple polar factors are in control of reactivity in all three reactions. Hammett correlations for the effect of the 4`-substituents using both **σ** and **σⁿ**are shown in table(12). The correlation with **σ** is good and with **σⁿ** "is satisfactory and ρ was found to be 0.533 (see figure 6). A reference

ρ_o value for the alkaline hydrolysis of p-substituted ethyl benzoates at 30.0°C in 65% (v/v) DMSO water is available [24], being equal to 2.40. Thus ρ / ρ_o for the alkaline hydrolysis of the system under study here can be calculated to be about 0.22 . This value is in reasonable agreement with that of the ionisation reaction.

Table 11.

Rate coefficients k_2 for the alkaline hydrolysis of the methyl 4`-substituted diphenylacetylene-4-carboxylate in 70% DMSO- water at 2-methoxyethanol at 30 ^{0}C , together with σ and $\sigma^{n..}$

substituent	$K_2(min^{-1} M^{-1})$	$Logk_2$	σ	σ^n
NO_2	22.5	1.352	0.78	0.78
Cl	11.5	1.061	0.23	0.24
H	8.59	0.934	0.0	0.0
OCH_3	6.46	0.812	-0.27	-0.11

a- The measurements are the mean values of at least two determinition and the rate coefficients are reproducible to within ±3%.

Table 12.

Hammett correlation for the $logk_2$ of the methyl 4`-substituted diphenylacetylene-4-carboxylate in 70%(v/v) DMSO- water at 30 °C

Substituent Constant	ρ	$logk\sigma$	r^*	n^*
σ	0.533	0.73	0.998	4
σ^n	0.559	0.70	0. 975	4

*see table 8.

Conclusions:-

The evidence, including carbonyl stretching frequencies of esters, demonstrates that the system (2) exhibits normal substituent effects.

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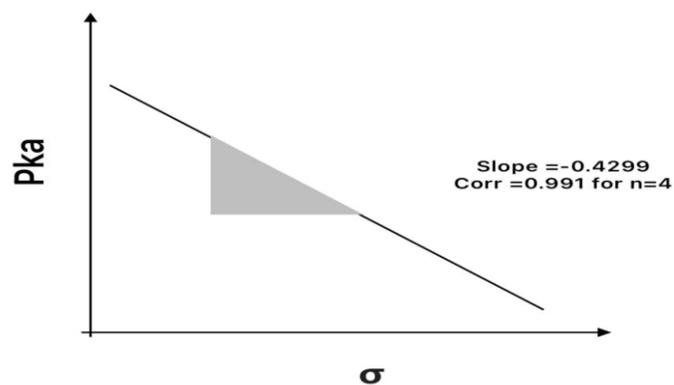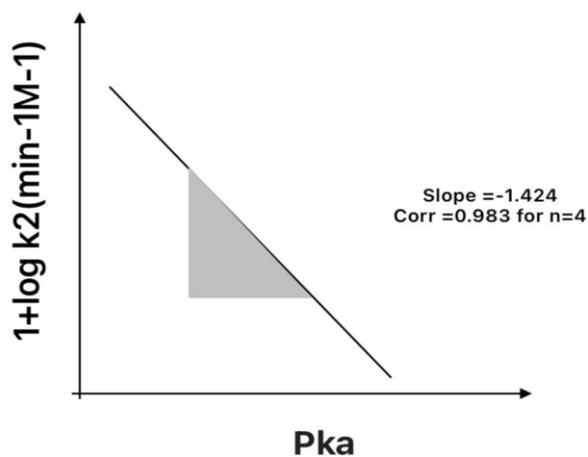
Appendices :

Slope =-0.4299
Corr =0.991 for n=4

Figure 1: Relationship between pka values of the 4`-substitured diphenylacetylene 4- carboxylic acids in 80% 2-methoxyethanol at 25° and σ

Slope =-1.424
Corr =0.983 for n=4

Figur 2: Relation between pka values in 80% 2-methoxyethanol- water at 25° and log K_2 for reaction with DDM in 2-methoxyethanol at 30° for 4`- substituted diphenylacetylene-4- Carboxylic acids
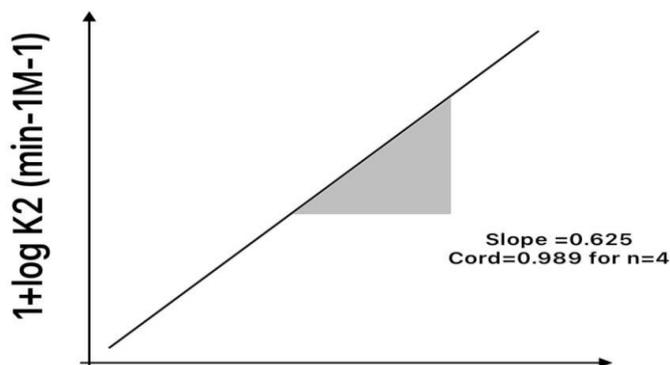
Figure 3: Relationship between log K2 for the reaction of 4`- substituted diphenylacetylene-4-substituted ` Carbo-xylic acids with DDM in 2-methoxyethanol at 30°c and their substitunt Constants, σ
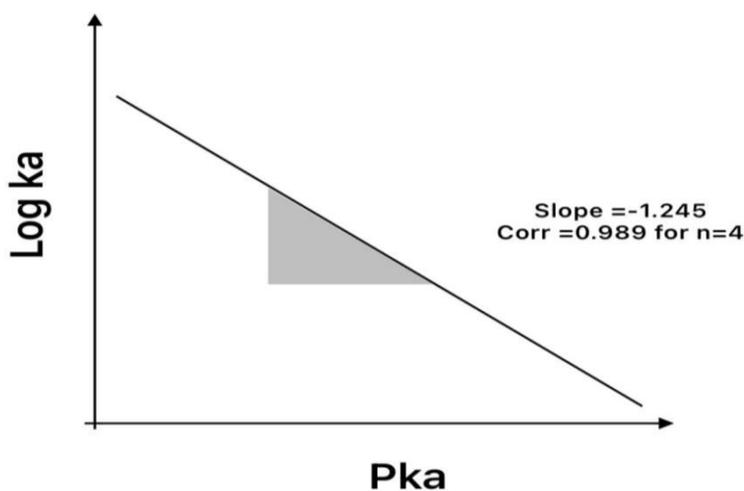
Figure. 4: Relationship between the pka values of 4`- substituted diphenylacetylene -4- carbo-xylic acids in 80% (v/v) 2-methoxyethanol and their log K2 of ester hydrolysis.
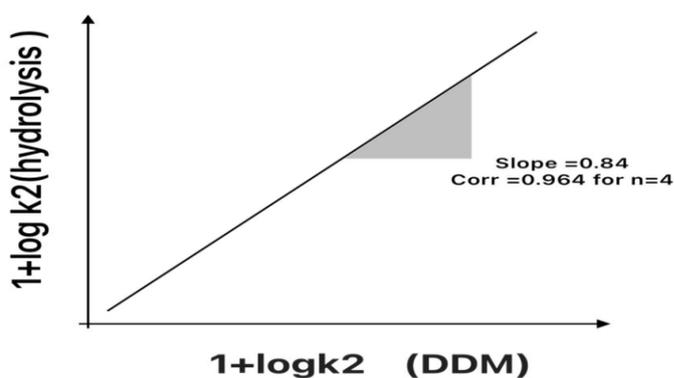
Figure 5: Relationship between log K2 of methyl 4 `-substituted diphenylacetylene-4-carboxylate of hydrolysis and esterification of their acids with DDM at 30 ᵒC
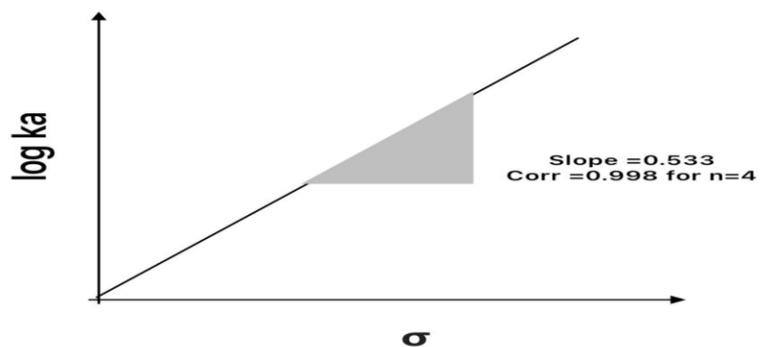
Figure 6: Relationship between log K2 for alkaline hydrolysis in 70% DMSO- water at 30ºc for methyl 4` - substituted diphenyl- acetylene- 4 carboxylat and substituents constant σ