



Review article

Can Non-bonded Pair of Electrons of Sp³ Nitrogen with Two Single σ -Bonds on Either Side Still Transmit Substituent Electronic Effects to the Reaction Site? Reversal of Attenuation Effect by Sp³ Nitrogen—A Chemical Education Perspective



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KEYWORDS

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Attenuation effect

Sp³ nitrogen

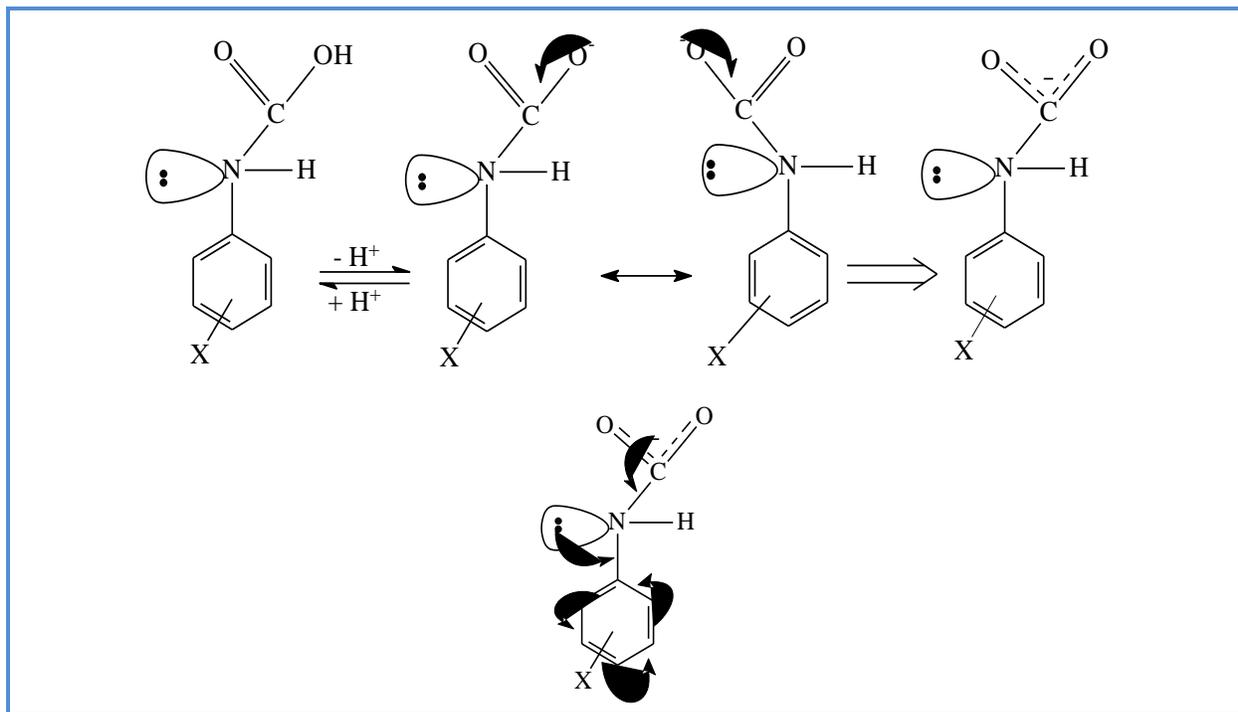
Carbamic acids

ABSTRACT

Dependence of reactivity of organic molecules on substituents was a well-established phenomenon in terms of Hammett and Taft equations in physical-organic chemistry. The well-known Hammett and Taft linear free energy relationships were extensively used in elucidating the organic reaction mechanisms. The exponential depletion of Hammett reaction constant (ρ), as a function of distance in terms of increasing the number of sp³ carbon atoms (-CH₂-) between the reaction center and the substituent, is understood from our laboratory experiments. But, introduction of sp² carbon atoms (-CH=CH-) between the reaction center and the substituent enhances the Hammett reaction constant (ρ). In the present work, we have tried and observed the same and even little more effective transmission of substituent effect through sp³ nitrogen (-NH-). However, the presence of a sp³ carbon by the side of sp³ nitrogen (-NH-CH₂-) depletes the substituent effect in the usual manner in *N*-phenyl glycines. Probable explanations were presented in support of our observation. In the present work, the observations were manifested in terms of Taft ρ^* values instead of Hammett ρ value as the pK_a values of only 4-nitrophenylcarbamic acid and carbamic acids and the Taft σ^* values of 4-nitrophenyl and H are available from literature.

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Graphical Abstract



Introduction

The term “attenuation” in general implies that it is the depletion of some property either physical or chemical with time, distance and medium. For instance, in physics attenuation is the continuous depletion of change of intensity of any property through a medium *i.e.*, sunglasses can attenuate the light intensity, lead (Pb) attenuates the intensity of X-rays and light and sound can be attenuated in water and air. In most of the cases, attenuation is an exponential property with the length of the medium. In spectroscopy, this refers to the putative “Beer-Lambert law”. In chemistry of particular interest, it is the diminution of electronic effects in a molecule during the course of a reaction. The electronic effects are mainly associated with the substituents. A detailed study of the attenuation effect in aromatic [1, 2] and aliphatic systems [3] is a major breakthrough from our laboratory which was reported earlier by A. Williams [4]. The substituent effects from the benzene moiety could be effectively spread to the reaction center through resonance from *para*-substituents and through inductive effect from *meta*-substituents. The spreading is more predominant if the conjugated π -electron system is present between the reaction center and the substituent and due to its polarization. This will diminish more rapidly upon introducing methylene groups between the ionizable proton and the ring carbon atom if the study involves the acid dissociation equilibriums. In addition, this is known

as attenuation through methylene group [1] and extensively narrated by Williams [4]. The present study is the extension to the attenuation effect through methylene group with the introduction of different sp^3 hybridized atom *viz.* nitrogen (-NH-) other than carbon between the reaction center and the substituent.

Experimental

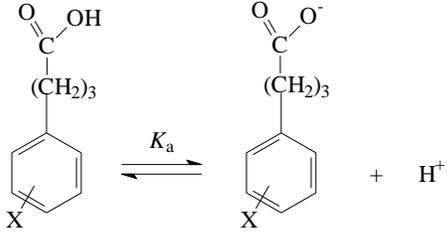
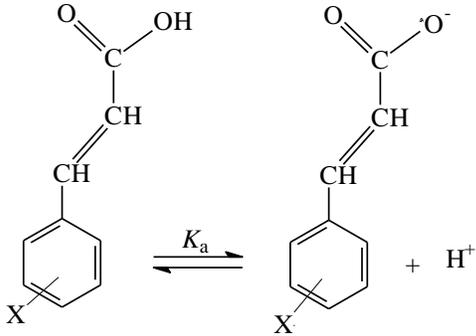
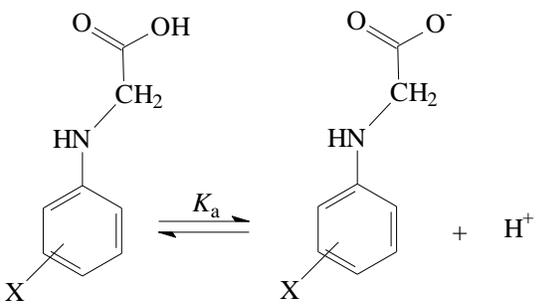
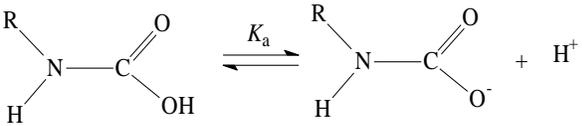
Methods

All calculations and curve fittings were done by Kaleida Graph software version 4.1 supplied by Synergy Software INC., Reading, PA, USA. All chemical structures were drawn using "Chemdraw" software.

Discussion

First, let us consider the acid dissociation equilibriums of different oxygen acids in aqueous solution with increasing length of carbon chain between the ionizable proton and the aromatic ring carbon (eqns. 2-6). In equation 1, the equilibrium is for carbon acid *viz.* for the dissociation of substituted benzenes. In this sense, hydrogen at *para*-position to the substituent is supposed to deprotonate. The Hammett ρ value of 5.42 is obtained for the equilibrium 1 from the attenuation effect of benzoic acids with increasing number of methylene groups between the ionizable proton and the ring carbon [1]. It is an interpolated value from the plot of Hammett ρ versus the number of methylene groups between the ionizable proton and the ring carbon. The rest of the Hammett ρ values for the equilibriums 2-7 are obtained from the plots of pK_a versus Hammett σ . Originally, these ρ values are negative. But, they were taken as positive as the Hammett ρ values which are usually obtained from the plots of $\log K$ versus Hammett σ . In the present work, the observations were manifested in terms of Taft ρ^* values instead of Hammett ρ value as the pK_a values of only 4-nitrophenylcarbamic acid and carbamic acids and the Taft σ^* values of 4-nitrophenyl and H are available from literature. The Taft reaction constant ρ^* values are obtained from the slopes of the plots of pK_a versus Taft σ^* values [5] for all the substituents for the equations 1-9. Taft σ^* values are from the reference 5.

<p style="text-align: center;">benzenes</p>	<p style="text-align: center;">Hammett $\rho = 5.42$ Taft $\rho^* = 7.61$</p>	(1)
<p style="text-align: center;">phenols</p>	<p style="text-align: center;">Hammett $\rho = 2.21$ Taft $\rho^* = 3.58$</p>	(2)
<p style="text-align: center;">Benzoic acids</p>	<p style="text-align: center;">Hammett $\rho = 1.00$ Taft $\rho^* = 1.45$</p>	(3)
<p style="text-align: center;">Phenylacetic acids</p>	<p style="text-align: center;">Hammett $\rho = 0.49$ Taft $\rho^* = 0.69$</p>	(4)
<p style="text-align: center;">Phenylpropionic acids</p>	<p style="text-align: center;">Hammett $\rho = 0.21$ Taft $\rho^* = 0.31$</p>	(5)

 <p style="text-align: center;">Phenylbutyric acids</p>	<p>Hammett $\rho = 0.12$ Taft $\rho^* = 0.18$</p>	(6)
 <p style="text-align: center;">Cinnamic acids</p>	<p>Hammett $\rho = 0.47$ Taft $\rho^* = 1.94$</p>	(7)
 <p style="text-align: center;">N-(4-substituted phenyl)-glycines</p>	<p>Taft $\rho^* = 0.46$</p>	(8)
 <p style="text-align: center;">R = H and 4-Nitrophenyl Carbamic acids</p>	<p>Taft $\rho^* = 2.46$</p>	(9)

The data for the equilibriums 1-9 are summarized in Table 1 given at the end. The data of Taft ρ^* and number of atoms between ionizable proton and the ring carbon atom obeyed the eqn. 10:

$$y = m1 + (m2)^{(m3-m0)} \quad (10)$$

Where y is Taft ρ^* and m_0 is the number of atoms, m_1 , m_2 and m_3 are some arbitrary constants. Equation 10 is modified for the present work which was the original version of Williams equation $y = (2.4)^{(2-m_0)}$ used in our earlier work¹. A plot of Taft ρ^* (y) versus the number atoms (m_0) is shown in Figure 1.

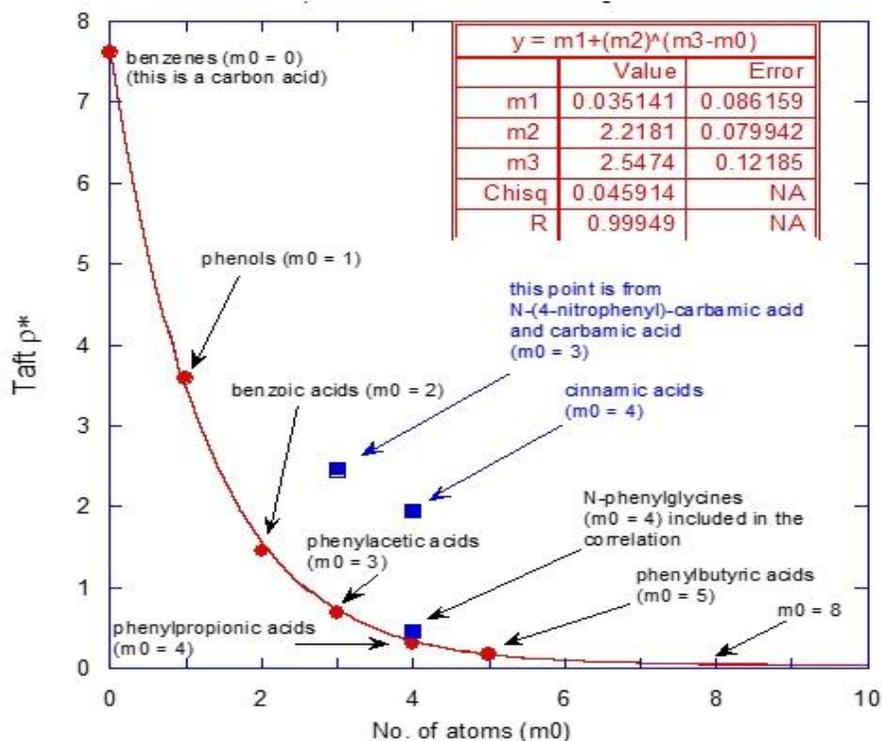
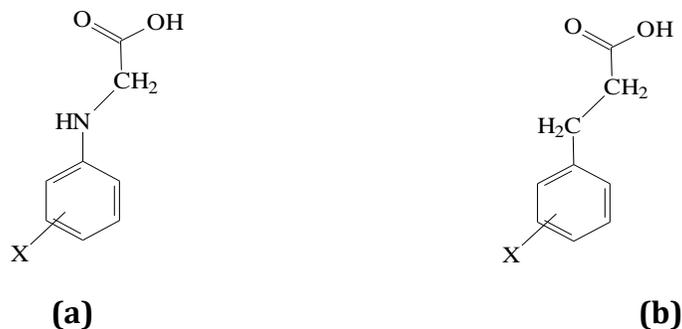


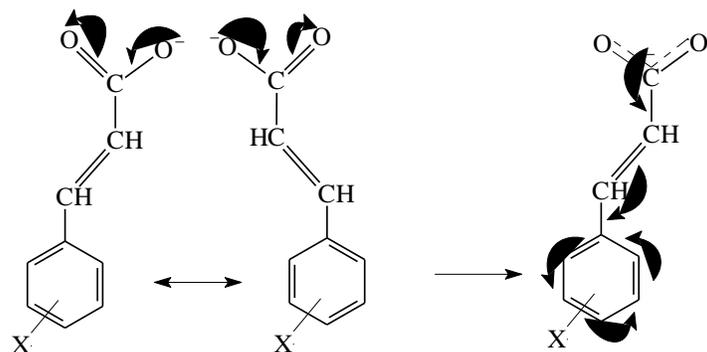
Figure 1. Plot of Taft ρ^* versus number of atoms (m_0) between ionisable proton and the benzene ring carbon atom

It is obvious from the Figure 1 that the Taft reaction constant ρ^* exponentially depletes as a function of number of atoms (m_0). After $m_0=8$, there is virtually no substituent effect on the dissociation equilibriums of these carboxylic acids and the exact Taft ρ^* value at this point is only 0.04 (computed from the plot) which is close to zero. It is surprising to see the point for *N*-phenyl glycines (**A** in Scheme 1) ($m_0=4$, the point in bottom blue square) is just same as that for phenyl propionic acids (**B** in Scheme 1) again with $m_0=4$.



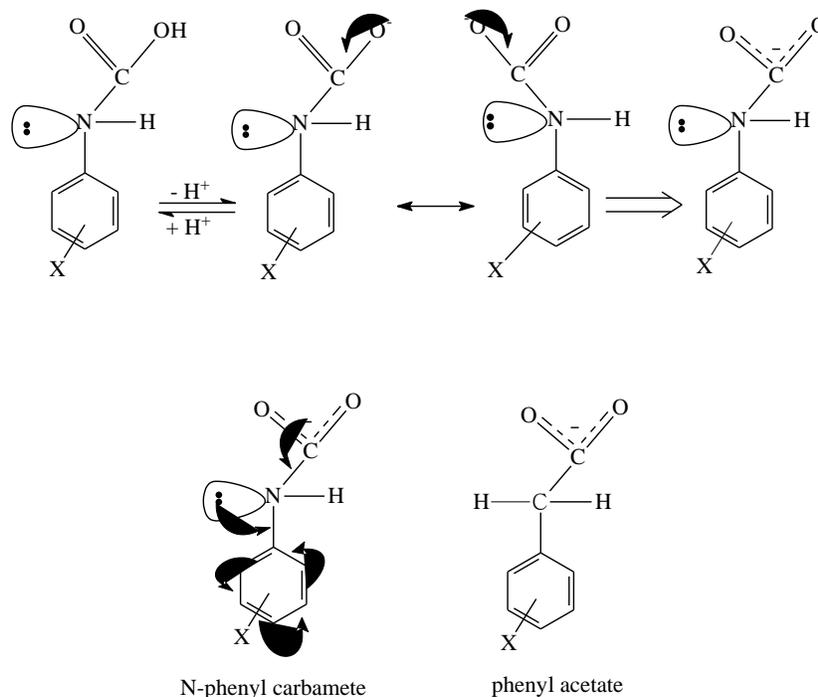
Scheme 1. (a) *N*-phenyl glycine (b) phenyl propionic acid

Whether it is carbon or nitrogen, and as long as they are in sp^3 hybridization, they behave in the same manner. However, cinnamic acids with $m=4$ has higher Taft ρ^* value of 1.94 (middle blue square in the Figure 1) in which the substituent effect is higher than either in **A** or **B** of the Scheme 1. This is explained due to the presence of the more polarizable and delocalizable π -electrons in cinnamic acid which can transmit substituent electronic effects more effectively to the reaction center as shown in Scheme 2.



Scheme 2. transmission of substituent electronic effects in cinnamic acid

It is to be noted that the nitrogen in **A**, in Scheme 1, is not adjacent to the carboxyl group. Otherwise, the situation would have been different with even higher Taft ρ^* value of 2.46 (top blue square in the Figure 1) for carbamic acids which is reflected in large difference in Taft ρ^* values of phenyl acetic acids and carbamic acids with $m=3$ as shown in Scheme 3. The non-bonded lone pair of electrons on nitrogen is only responsible in transmitting the electronic effects from substituent to the reaction site and vice versa. This is not possible in phenyl acetic acids as the reaction site is separated from the substituent by a sp^3 carbon, which is a σ -electron insulator. Hence a higher value of Taft ρ^* value of 2.46 is observed for carbamic acids compared to that for phenyl acetic acids is only 0.69 with same $m=3$.



Scheme 3. : transimtion of substituent electronic effects in N-Phenyl carbamate

In Scheme 3, there is a scope for the formation of zwitterion of *N*-phenyl carbamic acid by protonation of nitrogen. Such zwitterion formation is ruled out based on two facts [6] (i) the lifetime of such zwitterions was estimated to be in the range of 10^{-10} to 10^{-8} sec *i.e.*, 0.01 ns to 10 ns and (ii) the pK_a for nitrogen protonation of carbamates to form the zwitterionic species was estimated to be about -4. Hence, the *N*-phenyl carbamate in Scheme 3 is the sole species that exists in the solution.

Conflict of Interest

We have no conflicts of interest to disclose.

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