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Cyclopentadiene is not Aromatic and not Planar Like Benzene: Yet Deprotonation (pKa) from its Lone sp^3 Carbon Obeys Linear Free Energy Relationships (LFER)

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Abstract

Cyclopentadiene (CP) and its seven Cyano substituted derivatives obeyed Linear Free Energy Relationship (LFER) with an excellent correlation for pK_as of deprotonation equilibrium from the lone sp^3 carbon with Hammett σ_m values for the substituents at 2 and 3 positions, Taft σ values for 1 and 4 positions of CP; for disubstituted derivatives at 1or 4 and 2 or 3 positions we applied the sum of Taft σ* and Hammett σ_m values respectively. Deprotonation is facilitated by electron withdrawing capacity of the Cyano group with a positive Hammett-Taft reaction constant (ρ_{HT}; HT stands for Hammett-Taft) of 2.75. To the best of our knowledge, we are the first ones to apply the summation of Hammett and Taft σ*. Further, we determined the pK_a of the deprotonation equilibrium of unknown 1,4-dicyanoCP using the Hammett-Taft plot; the pK_a of this compound in question was also determined theoretically.*

Keywords: Cyclopentadiene, LFER, Hammett Equation, Taft Equation, DFT and pK_a

1. Introduction

We have recently reported the application of LFER to the deprotonation equilibriums of N(1)-H acidities of five membered nitrogen heterocycles as a small review and isoxazolium cations as a small note; several references were cited in both the publications [1,2]. In these studies, a lucid and clear identification of substituents has arrived in terms of their *ortho, meta* and *para* positions using a visual comparison with benzene [2]. Recently the study on substituent effects was reported by Yongge Qiu in the Diels-Alder reaction of CP and maleic anhydride [3]. He used Hammett σ_p substituent constants for both 1- and 2- substituted CPs without giving any justification. In the present work, though cyclopentadiene is not aromatic and not planar like benzene, a successful application of LFER was observed. Suitable explanations are given.

2. Methods

Linear correlation was done using the KaleidaGraph software, Version 4.1, Reading, PA, USA. The chemical structures are drawn using ChemDraw software. The pK_a values of all cyclopentadiene and its cyano substituted derivatives used in this work are from reference [4]. Gaussian 09 program [5] was used for all quantum mechanical calculations [5]. The pK_a values were determined using SMD_{sSAS} (scaled solvent-accessible surface) model and the geometries were optimized at the M06-2X [6] /6-31+(d,p) level like Lian et. al [7]. The nonspecific form of equation 1 of Scheme 1 is given by Equation 2 [7]:

$$AH(aq) \xrightarrow{\Delta G^{*}aq} A^{-}(aq) + H^{+}(aq) \qquad (2)$$

The pK_a of molecule AH is calculated according to Eqn 3:

$$pK_a = \Delta G^*_{aq}/2.303RT \quad (3)$$

The free energy in the 1 M standard state, $\Delta G^*_{aq,,}$ was calculated directly from the aqueous Gibbs free energies of the acid and conjugate base using Eqn 4:

$$\Delta G^*_{aq} = G^*_{aq}(A^-) + G^*_{aq}(H^+) - G^*_{aq}(AH) \quad (4)$$

The gas-phase standard phase correction term, $G^{o\rightarrow *}$ for both acid and conjugate base, cancel in this equation. The standard state aqueous free energy of proton, $G^*_{aq}(H^+)$, was calculated using Eqn. 5:

$$G^*_{aq}(H^+) = G^o_g(H^+) + \Delta G^*_{aq,solv}(H^+) + \Delta G^{o\rightarrow *} \quad (5)$$

In the above equation $G^o_g(H^+)$ = –6.29 kcal mol^{-1} and the experimentally measured hydration free energy $\Delta G^*_{aq,solv}(H^+)$ = –265.9 kcal mol^{-1} was taken from the literature [8-13]. $\Delta G^{o\rightarrow *}$ is the gas-phase standard correction and is used to convert from 1 atm ideal gas standard state to 1 M standard state, where superscripts ^{o} and * indicate 1 atm and 1 M standard states, respectively: $\Delta G^{o\rightarrow *}$ = RT ln 24.26 = 1.89 kcal mol^{-1} at 298 K [12]. The estimation of the value of $G^o_g(H^+)$ = –6.29 kcal mol^{-1} is from reference [8].

3. Discussion

Table 1 is the pK_a data of CPs. Figures 1 and 2 are the Hammett-Taft plots of pK_a versus σ_{HT} (here HT stands for Hammett-Taft). The dissociation equilibrium of cyclopentadiene is shown in scheme 1. As shown in our earlier publication [2] using visual comparison, the 2 and 3 positions are assumed to be *meta* to the deprotonation site from the lone sp^3 carbon of cyclopentadiene [2]. Positions 1 and 4 are assumed to be *ortho* to the deprotonation site. Accordingly, the substituent constants are summed up using Hammett and Taft substituent constants; these are clearly shown in column 3 (bold), Table 1.

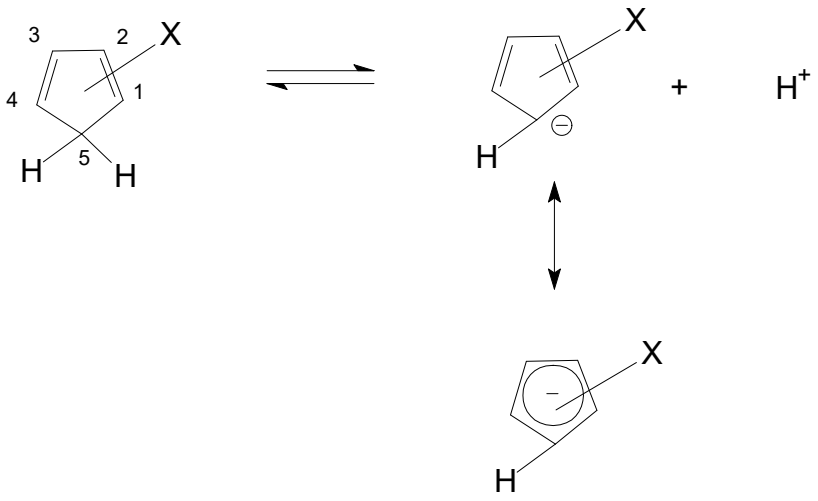
With the assumption described in the preceding paragraph, LFER plots are drawn; pK_a versus σ_{HT} are shown in figures 1 and 2. The loci of the plots are with negative sign. But they are to be understood as positive values as log K_a would have been plotted against HT. The LFER positive reaction constant (ρ_{HT}) indicates that the electron withdrawing CN substituents makes the cyclopentadiene more and more acidic.

A striking question we may anticipate from the readers is that Hammett equation originated from the study of ionization of *meta* and *para* substituted benzoic acids which are typically aromatic. And Taft equation originated from the study of acid and base catalyzed hydrolysis of ethyl acetates and then correcting the σ* values by a factor of 2.48 [14-17]. The factor 2.48 is the mean Hammett value of acid and base catalyzed hydrolysis of *meta* and *para* substituted methyl and ethyl benzoates and again which are typically aromatic. The substituent effects are transmitted efficiently to the reaction site through the delocalized π-electron cloud in the benzene ring. And they successfully follow LFER. The present study deals with the ionization of CP to give cyclopentadienyl anion. CP is not aromatic and not planar like benzene. It has no uninterrupted cloud of π-electrons. Yet, its deprotonation equilibrium is obeying LFER. The conjugate acid, CP, has a pK_a of 15 and is abnormally strongly acidic hydrocarbon by a driving force of aromatization to yield stable and planar cyclopentadienyl anion. It has an uninterrupted cloud of π-electrons which can transmit substituent effect to the ionization site from the substituent in the five membered CP ring. Figure 1 is the LFER plot wherein we have taken Taft σ* values for 1, 4 positions and Hammett σ_m values for 2 and 3 positions. Though the correlation coefficient is little poor (R = 0.9314) the trend is unmistakable. A replot of figure 1 is given in figure 2 without the point for 1,2,3-cyanoCP. The correlation is excellent with a correlation coefficient (R) of 0.9891 close to unity. At this juncture of research, we are not able to explain the deviation of the point of 1,2,3-cyanoCP. Though the CP is not aromatic the explanation for this is that the cyclopentadienyl anion is a planar, cyclic, regular-pentagonal ion; it has 6 π-electrons ($4n + 2$, where $n = 1$), which satisfies Hückel's rule of aromaticity. Therefore, cyclopentadiene aromatic anion with delocalized π electrons is more stable. The structure shown in scheme 1 with a circle inside the 5 membered pentagon is a resultant of five resonance structures in which each carbon atom carries about 1/5th of the total negative charge. Even the sodium and potassium salts of cyclopentadienyl anion, sodium/potassium CPs are known to be stable salts [18,19]. The fact that figure 2 conforms to Hammett's LFER, it does reflect that 1,2 and 3,4 are *ortho* and *meta* positions respectively.

There was a very detailed report about the thermodynamics of ionization of cyano carbon acids [20]. It was concluded in that study that the overall negative entropy is a favorable result for the ionization of cyano carbon acids. Therefore, though we have not performed any thermodynamic study in the present work, there is no reason for not assuming that the transition state for the deprotonation process may look more like the product type than the reactant type as shown in figure 3. Hence, the developing partial negative charge on the lone sp^3 carbon of the transition state makes the reactant approach planarity and aromaticity making the species transmit substituent effects efficiently. Therefore, the deprotonation process of CP conforms to LFER with a major contribution of the substituent effects from the product like transition state.

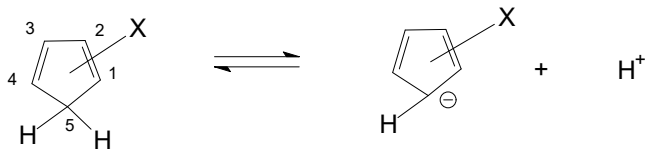
Figure 2 enabled us to determine the pK_a of unknown compound 1,4-diCyanoCP. To the best of our knowledge the pK_a of this compound is not reported in the literature. By taking Taft σ* value as 3.3 + 3.3 = 6.6 and substituting this value in the straight-line equation of Figure 2 i.e., y =13.003 -2.7541x, we get the pK_a of 1,4-diCynoCP as -5.18. Theoretical determination 1,4-diCyanoCP turned out to be -4.52. We have determined pK_a's of all the compounds by adopting SMD_{sSAS} model [7]. Since we did not get the pK_a anywhere close to -5.17 (pK_a of 1,4-diCP) at M06-2X/6-31+G(d,p) level [7] the geometry of 1,4-diCP was optimized at M06-2X/6-311++G(d,p) level. This level has a third layer of valence functions composed of uncontracted primitive set and good for final accurate measurements of energies (though

computationally more expensive); hence we have used this basis set. We have determined pK_a's of all the compounds used by adopting SMD_{sSAS} model [7]. The crucial α value for the SMD_{sSAS} model and their corresponding free energies are given in Table 2. The fact that we are getting almost the same value (pK_a of 1,4-diCynoCP) by both graphical LFER and theoretical method, it does reflect that our theoretical determination of pK_a value is correct and bolster our visualization of 1,2 position as *ortho* to the deprotonation site.



(1)

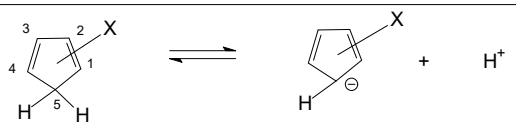
Scheme 1



Sl. No.	X	σ_{HT} (Hammett + Taft)	pK_a
1	H	**0.00**	15.0
2	2-CN	**0.56**	9.78
3	1,3-diCN	3.3+0.56 = **3.86**	2.52
4	1,2-diCN	3.3+0.56 = **3.86**	1.11
5	1,4-diCN	3.3 + 3.3 = **6.6**	-5.18*
6	1,2,4-triCN	3.3+0.56+3.3 = **7.16**	-6.00
7	1,3,4-triCN-2-CH_3	3.3+0.56+3.3+(-0.07) = **7.09**	-5.70
8	1,2,3,4-tetraCN	3.3+0.56+0.56+3.30 = **7.72**	-9.00

This value is not experimental value but obtained by substituting σ i.e., 3.3+3.3= 6.6 in straight line equation of Figure 2.

Table 1: pK_a Data of Cyclopentadienes



Sl. No:	Neutral Compound X	SMD_{sSAS} α	G in kcal/mol	Anion of the neutral Compound X^-	SMD_{sSAS} α	G in kcal/mol	ΔG in kcal/mol	pK_a by SMD_{sSAS} method	pK_a from Table 1
1	H	0.485	-121705.6983	$(H)^-$	0.485	-121414.2584	21.13987	15.4	15.0
2	2-CN	0.458	-179582.3808	$(2\text{-CN})^-$	0.456	-179298.7081	13.37267	9.76	9.78
3	1,3-diCN	0.990	-237438.9049	$(1,3\text{-diCN})^-$	0.990	-237165.2835	3.321375	2.42	2.52
4	1,4-diCN	0.500	-237498.0555	$(1,4\text{-diCN})^-$	0.500	-237234.2464	-6.49084	-4.52*	-5.18**
5	1,2-diCN	0.482	-237452.8172	$(1,2\text{-diCN})^-$	0.482	-237180.9515	1.56563	1.14	1.11
6	1,2,4-triCN	0.505	-295320.8759	$(1,2,4\text{-triCN})^-$	0.505	-295058.7748	-8.1989	-5.98	-6.00
7	1,3,4-triCN-2-CH_3	0.660	-295314.4008	$(1,3,4\text{-triCN-2-CH}_3)^-$	0.660	-295051.6245	-7.52371	-5.49	-5.70
8	1,2,3,4-tetraCN	0.475	-353192.8315	$(1,2,3,4\text{-tetraCN})^-$	0.475	-352935.2095	-12.678	-9.25	-9.00

*The geometry of this structure was optimized at M06-2X/6-311++G(d,p) level since we did not get the pK_a anywhere close to -5.17 at M06-2X/6-31+G(d,p) level [7].

**This value is not experimental value but obtained by substituting σ* i.e., 3.3+3.3= 6.6 in straight equation of Figure 2 (as already mentioned in the legend of Table 1).

Table 2: Theoretical pKa Data of Cyclopentadienes Determined by SMDsSAS Model. The Geometries of all the Structures were Optimized at M06-2X/6-31+G(d,p) level [6]

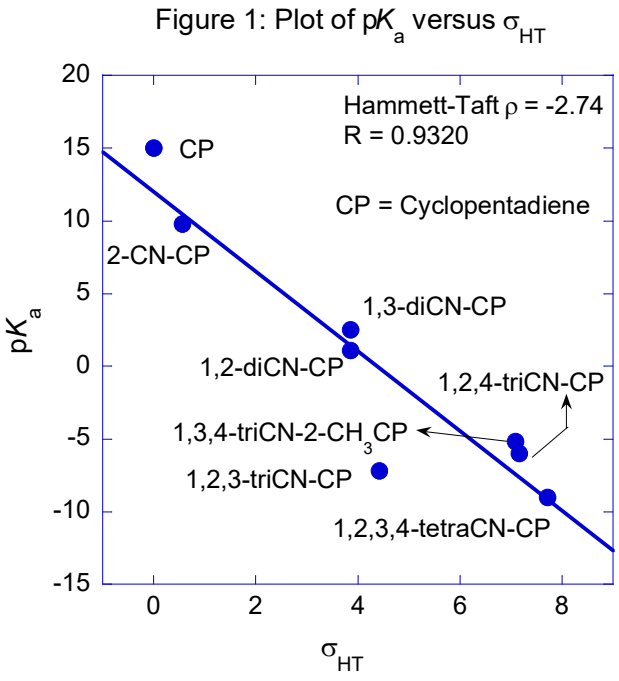


Figure 1: Plot of pK_a Versus σ_{HT}

Figure 2: Plot of pK_a versus σ_{HT}

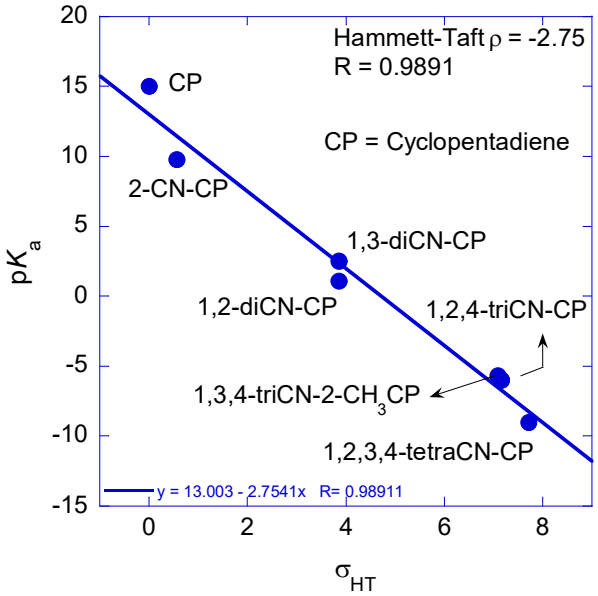


Figure 2: Plot of pKa Versus σ_{HT}

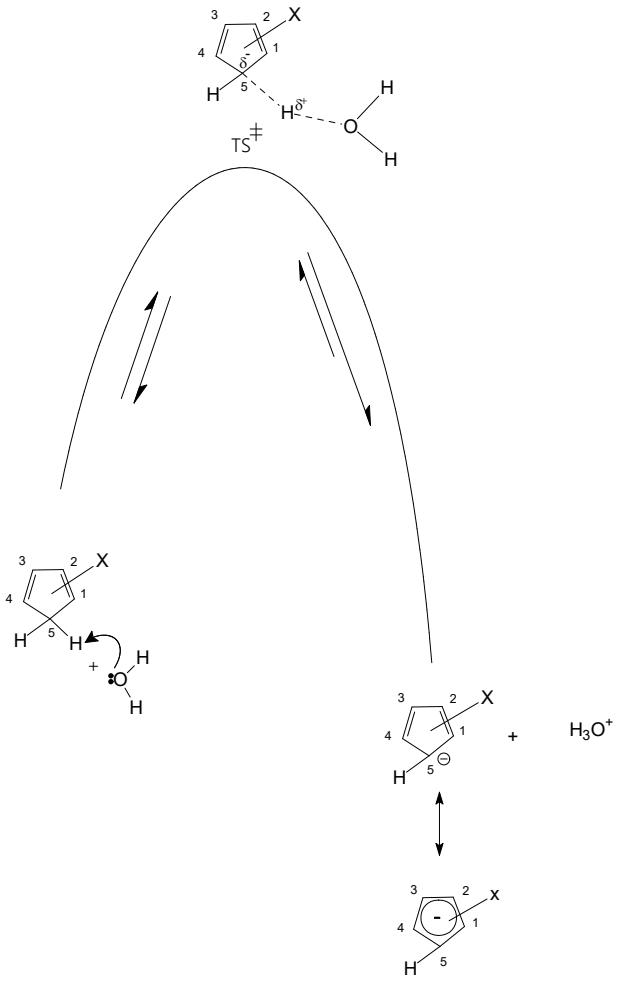


Figure 3

4. Conclusion

CP is non-aromatic, but its deprotonation conforms to LFER. The primary plausible reason for this is that the TS resembles the aromatic product that is its corresponding anion. The fact that we are getting pK_a value for 1,4-dicynoCP (which is not reported in the literature) determined by both theoretical (-4.52) and by Hammett-Taft LFER (-5.18) plot almost the same, it does reflect the value is reasonably correct; Thus, a pertinent and important inference from the preceding statement is that this also bolsters our visualization of 1, 4 position in Cyclopentadiene correspond to *ortho* relative to deprotonation site. The good linearity of Hammett-Taft plot (Figure 2) clearly reflects that 1,4 and 2,3 correspond to *ortho* and *meta* positions respectively. What is not comprehensible is that Yongge Qiu [3] in his article has taken para position in Cyclopentadiene and had used Hammett σ_p substituent constants; the discussion in our earlier article [1] and the findings in our present article clearly reflect that para position does not exist [1,3].

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Conflict of interest statement

The authors declare no conflicts of interest.

Availability of data and material

The supplementary file consists of all the required computational input and output files.

Authors Statement of contributions

All the authors make equal contribution.

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