

Is Hammett Correlation of Dipole Moments of *mono*-Substituted Benzenes Helpful to Distinguish *o,p*-Directing Groups from *m*-Directing Groups in an Aromatic Electrophilic Substitution? A Chemical Education Perspective

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Received November 21, 2021; Revised December 24, 2021; Accepted January 03, 2022

Abstract In chemistry literature it is so far achieved to distinguish *o,p*-directing groups from *m*-directing groups purely on the basis of only relative yields of *ortho*, *para* and *meta* electrophilic substituted products in the benzene ring and it is also based on their ability to disturb the pi-electron density at the carbons. It is for the first time in chemistry literature using dipole moment data a linear free energy relationship (LFER), Hammett equation is used to distinguish *o,p*-directing groups from *m*-directing groups. This could be achieved by constructing Hammett plots with dipole moments versus Hammett σ_{para} substituent constants for electron donating groups and Hammett σ_{meta} substituent constants for electron withdrawing groups. Good straight lines are obtained with correlation coefficients close to 0.9 with certainly an unmistakable trend.

Keywords: hammett equation, dipole moments, *o,p*-Directing groups, *m*-Directing groups

Cite This Article: R. Sanjeev, D. A. Padmavathi, and V. Jagannadham, "Is Hammett Correlation of Dipole Moments of *mono*-Substituted Benzenes Helpful to Distinguish *o,p*-Directing Groups from *m*-Directing Groups in an Aromatic Electrophilic Substitution? A Chemical Education Perspective." *World Journal of Chemical Education*, vol. 10, no. 1 (2022): 20-22. doi: 10.12691/wjce-10-1-3.

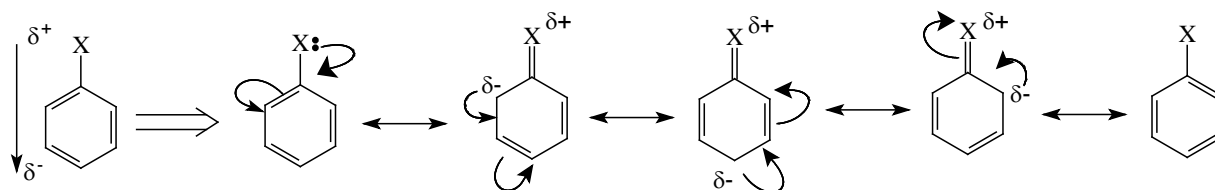
1. Introduction

It is a common practice in a physical-organic chemistry classroom to explain the trends of *o,p*-directing groups and *m*-directing groups purely based on the product yields of *ortho*, *para* and *meta* electrophilic substituted products in the benzene ring and on the stability of the Wheland intermediates or sigma-complexes or arenium ions [1]. It can also be explained how the substituent changes the electron density at C2, C3, C4. Though Hammett equation is a versatile tool [2] to predict organic reaction mechanisms, no attempt has been made to distinguish *o,p*-directing groups from *m*-directing groups applying a

linear free energy relationship (LFER) to dipole moment data of mono substituted benzene derivatives except a few reports on the application of Hammett equation to dipole moments [3,4,5]. It is for the first time an attempt is made in this direction.

2. Methods

All the linear correlations were done using the KaleidaGraph software version 4.1, Reading, PA, USA. The chemical structures are drawn using chemdraw. The dipole moments (in Coulomb meter) and Hammett substituent constants are from the references [6,7] and [8] respectively.

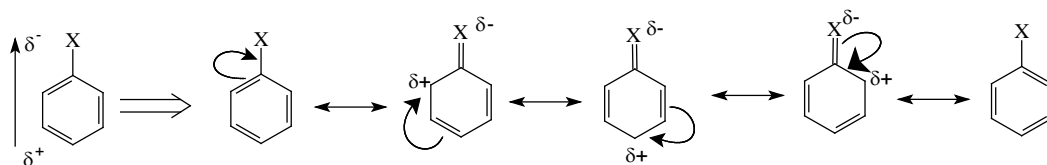


Scheme 1.

3. Discussion

Dipole moment arises in any molecule in which there will be a polarization of charges between two atoms in a molecule. It involves separation of negative and positive charges within the molecule. The bond dipole moment is a vector quantity. As the present work deals with mono substituted benzene derivatives the schematic representation of emergence of the dipole moment due to charge separation is seen in scheme 1. If the substituent X is an electron donating group, the resonance structures are as shown in scheme 1. Eventually two *ortho* carbons and the *para* carbon become partially negatively charged and X becomes partially positively charged. Hence there will be a dipole moment in the molecule.

If the substituent X is an electron withdrawing group, the resonance structures are as shown in scheme 2. Eventually two *ortho* carbons and the *para* carbon become partially positively charged and X becomes partially negatively charged. Hence there will be a dipole moment in the molecule with an opposite vector to that shown in scheme 1. Hence relatively the two *meta* carbons are less positive than the *ortho* and *para* carbons or in other words



Scheme 2.

Table 1. Dipole moments (DM/Coulomb meter) and Hammett substituent constants of mono-substituted benzenes (XC_6H_5)

| Sl. No. | X | σ_p ed | DM | σ_m ewd | DM |
|---------|---|---------------|------|----------------|------|
| 1 | H | 0.00 | 0.00 | | |
| 2 | S ⁻ | -1.21 | 10.7 | | |
| 3 | N(C ₂ H ₅)(n-C ₃ H ₇) | -0.95 | 6.14 | | |
| 4 | N(CH ₃) ₂ | -0.83 | 5.17 | | |
| 5 | N(C ₂ H ₅) ₂ | -0.72 | 6.10 | | |
| 6 | NH(CH ₃) | -0.84 | 5.60 | | |
| 7 | NH ₂ | -0.66 | 5.20 | | |
| 8 | NH ₂ NH | -0.55 | 5.57 | | |
| 9 | NH(C ₆ H ₅) | -0.56 | 3.40 | | |
| 10 | OH | -0.37 | 5.37 | | |
| 11 | t-Bu | -0.20 | 2.77 | | |
| 12 | i-pro | -0.15 | 2.64 | | |
| 13 | C ₂ H ₅ | -0.15 | 1.20 | | |
| 14 | CH ₃ | -0.17 | 1.20 | | |
| 15 | CH ₂ =CH- | -0.04 | 0.41 | | |
| 16 | CH ₃ O | -0.27 | 4.00 | | |
| 17 | SiH ₃ | | | 0.05 | 2.82 |
| 18 | SH | | | 0.25 | 4.10 |
| 19 | CF ₃ | | | 0.43 | 9.54 |
| 20 | CCl ₃ | | | 0.47 | 6.77 |
| 21 | COCl | | | 0.51 | 10.5 |
| 22 | CN | | | 0.56 | 10.7 |
| 23 | F | | | 0.34 | 5.33 |
| 24 | Br | | | 0.39 | 5.00 |
| 25 | Cl | | | 0.37 | 5.20 |
| 26 | I | | | 0.35 | 4.17 |
| 27 | CHO | | | 0.36 | 5.37 |
| 28 | COOCH ₃ | | | 0.32 | 6.20 |
| 29 | COCH ₃ | | | 0.38 | 10.1 |
| 30 | COC ₆ H ₅ | | | 0.34 | 9.00 |
| 31 | NO ₂ | | | 0.71 | 13.3 |
| 32 | SO ₂ Cl | | | 1.20 | 15.0 |
| 33 | CH=C- | | | 0.21 | 2.20 |

ed = electron donating, ewd = electron withdrawing.

they are more negative.

Hence one can expect an aromatic electrophilic substitution at *para* position when X is electron donating neglecting the small fraction of *ortho*-product due to steric reasons and at *meta* position when X is electron withdrawing (scheme 1 and scheme 2). The most common electron donating groups are RCH₂-, R-, RO-, -NH₂, RNH- and most common electron withdrawing groups are -NO₂, -SO₂Cl, -COR, -COOR, -CX₃, -CHX₂, -CH₂X (X is halogen) -CHO. Therefore, an electrophilic substitution will be taking place at *para* position to the substituent in mono-substituted benzenes with electron donating substituents and at *meta* position to the substituent with electron withdrawing substituents. Table 1 is the data of dipole moments of mono-substituted benzene derivatives with Hammett σ substituent constants.

Hammett plot is shown in Figure 1 with dipole moments versus Hammett σ_{para} substituent constants for electron donating groups (locus A) and Hammett σ_{meta} substituent constants for electron withdrawing groups (locus B). Two distinct good straight lines are obtained with correlation coefficients close to 0.9 is certainly an unmistakable trend.

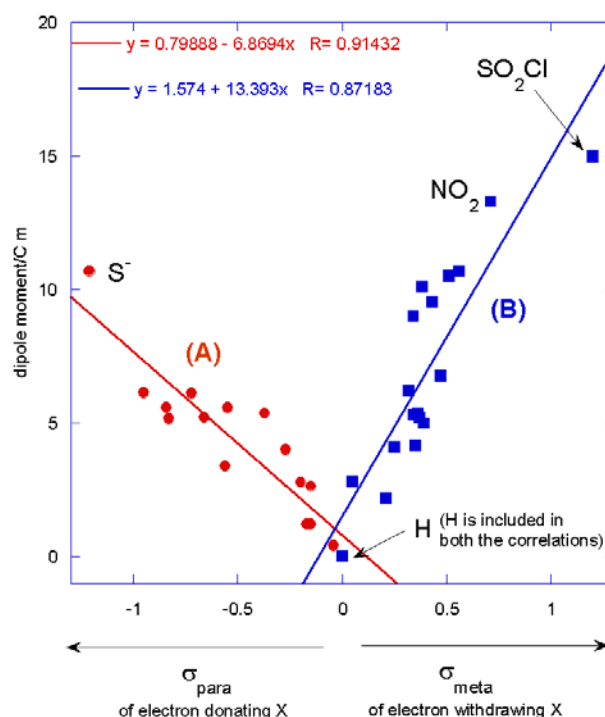


Figure 1. Plot of Dipole Moments of XC_6H_5 versus σ_{para} (for electron donating X) and σ_{meta} (for electron withdrawing X)

4. Conclusions

The influence of *o,p*-directing groups and *m*-directing groups in an aromatic electrophilic substitution are

distinguished with the help of Hammett equation applied to the dipole moment data of mono-substituted benzene derivatives.

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