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

R. Sanjeev¹, D. A. Padmavathi², V. Jagannadham²,*

¹Department of Chemistry, Geethanjali College of Engineering and Technology, Cheeryal-501301, Telangana, India
²Department of Chemistry, Osmania University, Hyderabad-500007, India
*Corresponding author: jagannadham1950@yahoo.com

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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 σpara substituent constants for electron donating groups and Hammett σmeta 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

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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 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, -CHX3 (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 σpara substituent constants for electron donating groups (locus A) and Hammett σmeta 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 XC6H5 versus σpara (for electron donating X) and σmeta (for electron withdrawing X)

4. Conclusions

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

Table 1. Dipole moments (DM/Coulomb meter) and Hammett substituent constants of mono-substituted benzenes (XC6H5)

| Sl. No. | X           | σed | DM  | σewd | DM  |
|--------|-------------|-----|-----|------|-----|
| 1      | H           | 0.00| 0.00|      |     |
| 2      | S           | -1.21| 10.7|      |     |
| 3      | N(C2H5)(α-C2H5) | -0.95| 6.14|      |     |
| 4      | N(CH3)2     | -0.83| 5.17|      |     |
| 5      | N(C2H5)2    | -0.72| 6.10|      |     |
| 6      | NH2CH3      | -0.64| 5.60|      |     |
| 7      | NH2        | -0.66| 5.20|      |     |
| 8      | NH2NH       | -0.55| 5.57|      |     |
| 9      | NH2(C2H5)   | -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     | CH3         | -0.15| 1.20|      |     |
| 14     | CH2         | -0.17| 1.20|      |     |
| 15     | CH2-CH-     | -0.04| 0.41|      |     |
| 16     | CH2O        | -0.27| 4.00|      |     |
| 17     | SiH3        | 0.05| 2.82|      |     |
| 18     | SH          | 0.25| 4.10|      |     |
| 19     | CF3         | 0.43| 9.54|      |     |
| 20     | CCl3        | 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     | COOCH3      | 0.32| 6.20|      |     |
| 29     | COCH3       | 0.38| 10.1|      |     |
| 30     | COC2H5      | 0.34| 9.00|      |     |
| 31     | NO2         | 0.71| 13.3|      |     |
| 32     | SO2Cl       | 1.20| 15.0|      |     |
| 33     | CH3C=      | 0.21| 2.20|      |     |

ed = electron donating, ewd = electron withdrawing.
distinguished with the help of Hammett equation applied to the dipole moment data of mono-substituted benzene derivatives.

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