A Comparative Study of Electric Dipole Moments of Some Monosubstituted Benzenes, Naphthalenes, Fluorenes, Biphenyls, Fluoranthenes & Pyrenes

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The electric dipole moments of monosubstituted benzenes, naphthalenes, fluorenes, biphenyls, fluoranthenes and pyrenes are compared. The mesomeric moments due to the conjugation of the substituents with the aromatic moieties have been evaluated and the conjugative abilities of the aromatic radicals have been rationalized.

Materials and Methods*

3-Nitrofluoranthene, 3-fluorofluoranthene, 3-iodofluoranthene, 3-methoxyfluoranthene, 3-benzyfluoranthene were prepared as described in the literature.

3-Aminofluoranthene was prepared in quantitative yield by the reduction of 3-nitrofluoranthene by hydrazine hydrate and Raney-nickel in ethanol-benzene. The m.p. agreed with the reported one.

3-Bromofluoranthene was prepared by the Sandmeyer reaction of 3-aminofluoranthene and recrystallized from ethanol; m.p. 106-7°. von Braun and Manz obtained this compound by direct bromination and by subsequent separation from the 8-isomer. They reported the m.p. 102-3°.

3-Cyanofluoranthene was prepared from 3-iodofluoranthene by refluxing with powdered cuprous cyanide and two drops of pyridine in dimethylformamide. It was recrystallized from ethanol; m.p. agreed with the literature value.

3-Chlorofluoranthene was prepared by the Sandmeyer reaction of 3-aminofluoranthene and recrystallized from ethanol; m.p. 96-97°.

3-Acetylfluoranthene was prepared by the acetylation of fluoranthene using Ac2O in the presence of anhydrous ZnCl2. The separation of 3-acetyfluoranthene from 8-acetyfluoranthene and its purification were done as reported in the literature. Relatively very high yield was obtained compared to the known procedure.

Benzene (AR) was purified by partial freezing, dried over sodium wire and distilled over phosphorus pentoxide.

The dielectric constants, densities and refractive indices were measured in benzene solution at 30° and the dipole moments were calculated as described in a previous paper.

Results and Discussion

The dipole moment values used for the discussion are taken from the literature except those of fluoranthenes which are reported for the first time. The polarization data of fluoranthenes are given in Table 1. The dipole moment values of some monosubstituted aromatics are given in Table 2.

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<table>
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<th>Substituent</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Pd (ml)</th>
<th>Red (ml)</th>
<th>µ (D)</th>
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<td>0-361</td>
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<td>74-8</td>
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<td>72-8</td>
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<td>84-3</td>
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<td>0-573</td>
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<td>0-759</td>
<td>180-6</td>
<td>83-8</td>
<td>2-20</td>
</tr>
</tbody>
</table>

*The experimental work was carried out when the author was in the Department of Chemistry, Annamalai University, Annamalainagar.
their moments are not the same in all the cases. The existing difference should then be attributed to the various effects arising out of the differences in the molecular structure. Comparing the moments of cyano, nitro, methoxy, amino dimethyl-amino derivatives of pyrene, naphthalene and fluoranthene we find that the conjugative interaction between the ring and the substituent decreases in the following order: (1) pyrene > (3) fluoranthene > (1) naphthalene > benzene. Halogeno substituents behave in a unique manner particularly in the case of fluoranthene system. All the halogenofluoranthenes have low dipole moment values compared to the halogeno derivatives of other hydrocarbons. This could not be readily rationalized.

When the substituent is in the 1-position of naphthalene or in an analogous position in other hydrocarbons, the peri-methine interaction is significant and should be taken into account in a comparative study of the type undertaken presently. Due to this steric effect (peri-methine interaction) the dipole moment is different from anticipated. In Table 3 the dipole moments of some aromatic amines are given which very well substantiate this view. The moment of dimethylaniline (1-60 D) is slightly higher than aniline (1-53 D). However the moment of N,N-dimethyl-o-toluidine (0-96 D) is apparently less than the moment of o-toluidine (1-59 D), presumably due to the steric inhibition of resonance. A similar inhibition of mesomeric effect is also observable in the case of 1-dimethylaminonaphthalene and 1-dimethylaminopyrene22.

When the substituent is in the 2-position of naphthalene the peri-methine interaction is absent. Thus 2-naphthyl, 2-fluorenyl and 4-biphenyl derivatives have higher moments than those of the corresponding benzene derivatives. The moments of monosubstituted fluorenes and biphensyls are nearly same in almost all the cases. This is indeed expected. 2-Nitrofluorene has the highest moment of all known monosubstituted aromatics.
the primary dipoles in these analogous series of compounds.

The calculation of the mesomeric moments of angular substituents is not straightforward. It requires a knowledge of the magnitudes and direction of the moments of the corresponding aromatic and aliphatic compounds relative to a common coordinate. Smith adopted a satisfactory procedure to calculate the mesomeric moments for dimethyl aniline and aniline. The same procedure was followed to evaluate the mesomeric moments of the other aromatic amines.

The mesomeric moment of the acetyl derivative of an aromatic hydrocarbon may be calculated as follows: The moment of acetone is resolved along one of the C-CH₃ axes and the axis perpendicular to it (see Fig. 1).

Acetone has a moment of 2·50 D (ref. 28). The angle CCO is taken as 120° (ref. 29). Since the moment of acetone is directed at an angle of 120° (along the C-O axis) to C-CH₃ bonds the components of the moment of acetone along and right angles to one of the C-CH₃ bonds are 1·25 and 2·17 D, respectively. Assuming the latter to be equal to the moment perpendicular to the C-Ph axis, we find that the moment acting along the C-Ph axis is 1·92 D. The mesomeric moment of acetonaphene is thus 1·92 – 1·25 = 0·67 D.

A similar approach can be made for the calculation of the mesomeric moments of the methoxy and formyl derivatives. The moment of dimethyl ether is 1·25 D (ref. 28). The valence angle COC may be taken as 112° (ref. 29). In acetaldehyde the observed moment (2·51 D) is assumed to lie between the C-H and C-O bonds of the formyl group, at an angle of 14° from the C-O bond.

In Table 4 the \( \mu_m \) values calculated for various compounds are presented. These mesomeric moments are not really the absolute mesomeric moments as they include contributions from induction and from changes in the state of hybridization of carbon orbital. The separate contributions from various effects are difficult to assess. Nevertheless, these may be taken to represent the net effect of the various forces operating in the molecule. Positive and negative signs are assigned to the moments (a positive sign indicates that the substituent is at the positive end of the dipole) and the mesomeric moments are presented in Table 4. These are invariably positive for electron-releasing groups and negative for electron-attracting groups. The former groups have large positive mesomeric moments, while the latter have small negative moments.

From an analysis of the data given in Table 4 the following conclusions can be reached: The mesomeric order for electron-attracting group is \(-NO_2 > -COCH_3 > -CHO > -CN\). The mesomeric order of the halogens is in agreement with the conclusion reached from other studies particularly the \( ^{13}C \) NMR spectral analysis of the monosubstituted benzenes.

It is also possible to arrange the various hydrocarbons in the decreasing order of their conjugating abilities. Pyrene (1) naphthalene (1) and fluoranthene (3) may be considered together because the steric environments of the substituents are identical in all the cases. The order seems to be the same as derived from the simple comparison of the dipole moments. This order, however, reflects the greater

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**Table 4 — Mesomeric Moments of Various Monosubstituted Aromatics**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Benzene (1)</th>
<th>Naphthalene (1)</th>
<th>Pyrene (1)</th>
<th>Fluoranthene (3)</th>
<th>Fluorene (2)</th>
<th>Biphenyl (4)</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>1·05</td>
<td>1·06</td>
<td>1·08</td>
<td>1·01</td>
<td>1·01</td>
<td>1·01</td>
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<tr>
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<td>0·99</td>
<td>1·01</td>
<td>1·24</td>
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<td>0·93</td>
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<tr>
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<td>0·83</td>
<td>0·79</td>
<td>1·01</td>
<td>0·75</td>
<td>0·77</td>
</tr>
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<td>I</td>
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<td>0·76</td>
<td>0·73</td>
<td>1·00</td>
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<tr>
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<td>1·97</td>
<td>1·77</td>
</tr>
<tr>
<td>N(CH₃)₂</td>
<td>1·69</td>
<td>0·97</td>
<td>1·36</td>
<td>—</td>
<td>2·24</td>
<td>2·16</td>
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</table>

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Notes: The calculations were made using dehydrohalogenation analysis of the monosubstituted benzenes.
polarizability of carbon-1 of pyrene compared to carbon-1 of naphthalene. The order is in agreement with the order of the reactive indices calculated and predicted for these positions. The fact that the 1-pyrenyl and 3-fluoranthyl derivatives have higher mesomeric moments even though the substituents are subjected to peri-methine interaction indicates that these positions have greater conjugative ability than the benzene carbon atom. The other hydrocarbons namely fluorene, biphenyl and naphthalene follow the order in which they are given.

References