# *Molecular Orbital Theory of Reactivity in Non-Alternant Hydrocarbons*

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In the past decades there have been proposed not a few theoretical indexes for explaining chemical reactivity of a conjugated system. These are such as π-electron density[1], self-polarizability[2], free valence[3], localization energy[4], Dewar's approximate localization energy[5], frontier electron density[6], superdelocalizability[7], and so forth[8,9]. These quantities were derived from entirely different physical grounds. Nevertheless, predictions of the position of chemical attack by these quantities agreed well with known experimental results. This remarkable fact has attracted the attention of theoretical chemists, and several authors have attempted to interrelate these quantities[3,5,10-12]. The mathematical relations underlying these quantities in alternant hydrocarbons and hetero-alternant molecules have been clarified by the present authors[13] and Baba[14]. That is, as far as some conditions are satisfied, theoretical indexes in static, localization, and frontier electron methods were found to be entirely parallel. If this were so, good coincidence between the indexes and experiments does not always mean that each one of these indexes is the true reflection of the process of reaction. Rather, a possibility might exist that some of them are not qualified as the " good " index in the most general sense and the coincidence of such quantities with experimental facts may due mainly to the existing mathematical relations.

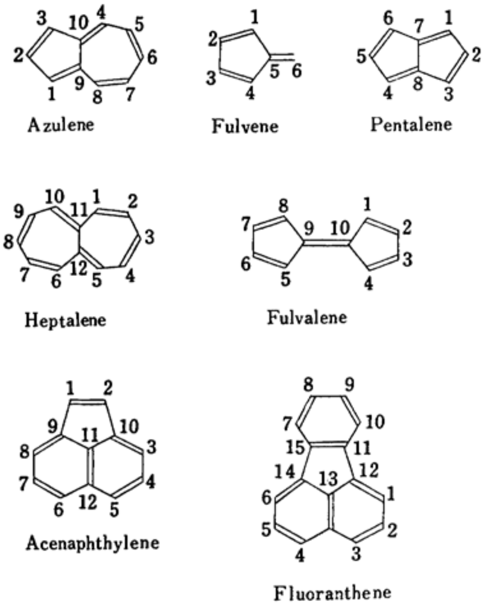

Fig. 1. Structure and numbering of non-alternant hydrocarbons.

In this connection we should compare the theoretical prediction of an index with experimental data with regard to the compounds in which no such mathematical interrelation as found in alternant hydrocarbons exists. This will serve as testing the availability of theories and finding out the theory closest to the true mechanism of reaction. For this purpose the most suitable material may be non-alternant hydrocarbons in which less intimate relations than in alternant molecules are expected between these theoretical indexes.

In the present paper frontier electron density and superdelocalizability for several non-alternant hydrocarbons were calculated. The structure and numbering of these hydrocarbons are shown in Fig. 1. The calculated values of frontier electron density and superdelocalizability were compared with known experimental results, together with other theoretical indexes.

## Results and Discussion

Theoretical indexes of non-alternant hydrocarbons were compared with experiments for three cases of reactions, that is, for electrophilic, radical and nucleophilic reactions, respectively.

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**Reaction with an Electrophilic Reagent.**—In Table I, the values of localization energy, frontier electron density and superdelocalizability for an electrophilic attack and the value of $\pi$-electron density were listed and compared with known experimental results. The values corresponding to the predicted position of attack are specified by italic letters. Experiments were once carried out for azulene, acenaphthylene and fluoranthene. As is seen in Table I, all indexes predict the same position as the most reactive for azulene and for acenaphthylene in accordance with experiments[15,16]. For fluoranthene, however, the situation is different. That is, the experiments showed that the bromination reaction occurred at two positions giving 3, 8-dibromofluoranthene[17,18]. The prediction of frontier

TABLE I. LOCALIZATION ENERGY ($L_r^{(E)}$), FRONTIER ELECTRON DENSITY ($f_r^{(E)}$), AND SUPERDELOCALIZABILITY ($S_r^{(E)}$) FOR ELECTROPHILIC ATTACK AND $\pi$-ELECTRON DENSITY ($Q_r$) IN COMPARISON WITH EXPERIMENTS

| Compounds (Experimental position of attack) | Position | $f_r^{(E)}$ | $S_r^{(E)}$ | $L_r^{(E)}$ | $Q_r$ |
|---|---|---|---|---|---|
| Azulene | 1 | *0.590* | *1.760* | *1.352* | *1.173* |
| (1) | 2 | 0.000 | 1.017 | 1.728 | 1.047 |
| | 4 | 0.051 | 0.706 | 1.808 | 0.855 |
| | 5 | 0.225 | 1.035 | 1.659 | 0.986 |
| | 6 | 0.000 | 0.680 | 1.959 | 0.870 |
| | 9 | 0.134 | 0.951 | — | 1.027 |
| Fulvene | 1 | *0.724* | *1.850* | *2.002* | *1.092* |
| | 2 | 0.276 | 1.399 | 2.238 | 1.073 |
| | 5 | 0.000 | 0.894 | 2.994 | 1.047 |
| | 6 | 0.000 | 0.675 | 2.230 | 0.623 |
| Pentalene | 1 | 0.029 | 0.467 | 2.380 | 0.815 |
| | 2 | *0.526* | *1.365* | *2.027* | *1.173* |
| | 7 | 0.416 | 1.241 | — | 1.198 |
| Heptalene | 1 | *0.333* | *0.816*a) | *1.660* | *1.125* |
| | 2 | 0.000 | 0.000 | 2.032 | 0.882 |
| | 3 | *0.333* | *0.816* | 1.715 | 1.119 |
| | 11 | 0.000 | 0.000 | — | 0.867 |
| Fulvalene | 1 | *0.361* | *1.351* | *1.987* | *1.097* |
| | 2 | 0.138 | 0.966 | 2.236 | 0.976 |
| | 9 | 0.000 | 0.569 | — | 0.853 |
| Acenaphthylene | 1 | *0.529* | *1.564* | *2.124* | *1.066* |
| (1) | 3 | 0.089 | 0.922 | 2.525 | 0.909 |
| | 4 | 0.005 | 1.026 | 2.513 | 1.008 |
| | 5 | 0.119 | 1.032 | 2.417 | 0.926 |
| | 10 | 0.069 | 1.041 | — | 1.044 |
| | 11 | 0.356 | 1.355 | — | 1.095 |
| | 12 | 0.021 | 0.819 | — | 0.998 |
| Fluoranthene | 1 | 0.083 | 0.779 | 1.77 | 0.947 |
| (3 and 8) | 2 | 0.057 | 0.820 | 1.82 | *1.005* |
| | 3 | *0.185* | *1.289* | *1.67* | 0.958 |
| | 7 | 0.150 | 1.078 | *1.71* | 0.997 |
| | 8 | *0.152* | *1.105* | 1.76 | *1.008* |

a) Calculated according to the formula of Eq. 27 of Ref. 7.

TABLE II. FRONTIER ELECTRON DENSITY ($f_r^{(R)}$), SUPERDELOCALIZABILITY ($S_r^{(R)}$) AND LOCALIZATION ENERGY ($L_r^{(R)}$) FOR RADICAL ATTACK AND FREE VALENCE IN COMPARISON WITH EXPERIMENTS

| Compounds (Experimental position of attack) | Position | $f_r^{(R)}$ | $S_r^{(R)}$ | Free valence | $L_r^{(R)}$ |
|---|---|---|---|---|---|
| Azulene | 1 | *0.299* | *1.186* | 0.480 | 1.721 |
| (1) | 2 | 0.100 | 0.962 | 0.420 | 1.728 |
| | 4 | 0.246 | 1.132 | *0.482* | *1.520* |
| | 5 | 0.123 | 0.986 | 0.429 | 1.655 |
| | 6 | 0.261 | 1.105 | 0.454 | 1.620 |
| | 9 | 0.161 | 0.901 | 0.149 | 2.710 |
| Fulvene | 1 | 0.485 | 1.378 | 0.505 | 2.002 |
| | 2 | 0.216 | 1.091 | 0.434 | 2.238 |
| | 5 | 0.036 | 0.746 | 0.075 | 2.994 |
| | 6 | *0.562* | *1.688* | *0.623* | *1.612* |
| Pentalene | 1 | *0.264* | *0.364*a) | *0.558* | *1.959* |
| | 2 | 0.263 | 0.363 | 0.432 | 2.027 |
| | 7 | 0.208 | 0.322 | 0.153 | 2.828 |
| Heptalene | 1 | *0.183* | *0.303*a) | *0.524* | *1.926* |
| | 2 | 0.166 | 0.288 | 0.441 | 2.032 |
| | 3 | 0.167 | 0.289 | 0.494 | 2.026 |
| | 11 | 0.137 | 0.262 | 0.158 | 2.817 |
| Fulvalene | 1 | *0.242* | *1.593*b) | *0.510* | *1.676* |
| | 2 | 0.180 | 1.402 | 0.498 | 1.848 |
| | 9 | 0.156 | 1.823 | 0.243 | — |
| Acenaphthylene | 1 | *0.368* | *1.564* | 0.37 | *2.124* |
| (1 and 2) | 3 | 0.195 | 1.046 | 0.41 | 2.262 |
| | 4 | 0.017 | 0.873 | 0.38 | 2.513 |
| | 5 | 0.238 | 1.112 | *0.48* | 2.193 |
| | 10 | 0.088 | 0.853 | 0.02 | — |
| | 11 | 0.088 | 0.947 | 0.11 | — |
| | 12 | 0.011 | 0.717 | 0.14 | — |
| Fluoranthene | 1 | 0.124 | 0.904 | 0.454 | 1.61 |
| | 2 | 0.069 | 0.798 | 0.398 | 1.82 |
| | 3 | *0.284* | *1.139* | *0.470* | *1.54* |
| | 7 | 0.136 | 1.066 | 0.438 | 1.71 |
| | 8 | 0.086 | 0.929 | 0.409 | 1.76 |

a) Calculated according to the modified formula of Eq. 27 of Ref. 7.

b) Calculated according to the formula of Eq. IV—4 of Ref. 7 (the constant term, $|\lambda_f|$ was omitted).

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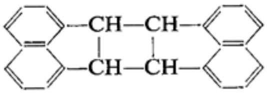
electron theory agreed well with this fact because the values of frontier electron density and superdelocalizability at 3 and 8 positions are larger than the other positions. On the other hand, the total $\pi$-electron density method (the static method) predict 8 and 2 positions as the most susceptible to an electophilic attack, and localization method 3 and 7 positions. Other compounds such as fulvene, pentalene, heptalene and fulvalene have never been synthesized and accordingly no available experimental data have hitherto been obtained. The prediction of all indexes agreed entirely with each other in these compounds.

**Reaction for a Radical Reagent.**—In Table II, localization energy, frontier electron density and superdelocalizability for radical attack and the values of free valence were shown in comparison with known experimental data. For azulene the experiments showed that radical reagents attack position 1[19]. As is clearly seen in Table II, the values of frontier electron density and superdelocalizability explain the experimental fact well, whereas other indexes such as free valence and localization energy predict that position 4 will be the most reactive. Some doubts have been pointed out in connection with the reliability of the free valence as a chemical reactivity index[5,20]. Not a few cases appeared in which this index failed to explain the experiments; for example, in phenanthrene and 2-pentene[21]. On the other hand, localization energy has proved to be a good index in the case of alternant hydrocarbons. It may be of theoretical interest to observe in non-alternant hydrocarbons the inability of localization energy to explain the experimental results of, for example, the electrophilic reaction of fluoranthene and radical attack of azulene stated above.

Acenaphthylene has been found to make a colorless dimer, and it has been suggested that the mechanism of formation is not a simple "collisional" one, but depends on the existence of van der Waals complexes and Crawford and Coulson considered that the formation of these complexes is probably facilitated by the presence of a high free valence at the reacting carbon atoms. They calculated the free valence in this molecule and found that the values of 5, 6 positions are larger than that of 1, 2 positions[20]. On the other hand, experiments showed that the dimer has the following structure indicating that the 1, 2 positions have greater reactivity than 5, 6 positions[20,22].



Hence, the free valence, as is stated by Crawford and Coulson[20], is not a sufficient guide to reactivity. Frontier electron method and localization method both predict that the 1, 2 positions will be more reactive than 5, 6 positions. This result coincides with the experiment although there may remain some questions as to the applicability of the reactivity indexes to such a dimer-forming reaction.

TABLE III. FRONTIER ELECTRON DENSITY ($f_r^{(N)}$), SUPERDELOCALIZABILITY ($S_r^{(N)}$) AND LOCALIZATION ENERGY ($L_r^{(N)}$) FOR NUCLEOPHILIC ATTACK AND $\pi$-ELECTRON DENSITY ($Q_r$)

| Compounds | Position | $f_r^{(N)}$ | $S_r^{(N)}$ | $L_r^{(N)}$ | $Q_r$ |
|---|---|---|---|---|---|
| Azulene | 1 | 0.008 | 0.613 | 2.090 | 1.173 |
| | 2 | 0.199 | 0.907 | 1.728 | 1.047 |
| | 4 | 0.442 | *1.559* | *1.231* | *0.855* |
| | 5 | 0.021 | 0.937 | 1.655 | 0.986 |
| | 6 | *0.522* | 1.530 | 1.280 | 0.870 |
| | 9 | 0.169 | 0.851 | — | 1.027 |
| Fulvene | 1 | 0.246 | 0.906 | 2.002 | 1.092 |
| | 2 | 0.156 | 0.783 | 2.238 | 1.073 |
| | 5 | 0.073 | 0.597 | 2.994 | 1.047 |
| | *6* | *1.124* | *2.701* | *0.984* | *0.623* |
| Pentalene | 1 | *0.500* | *1.000*[a] | *1.531* | *0.815* |
| | 2 | 0.000 | 0.000 | 2.027 | 1.173 |
| | 7 | 0.000 | 0.000 | — | 1.198 |
| Heptalene | 1 | 0.032 | 0.529 | 2.193 | 1.125 |
| | 2 | *0.332* | *1.401* | *2.032* | *0.882* |
| | 3 | 0.000 | 0.401 | 2.357 | 1.119 |
| | 11 | 0.271 | 1.252 | — | 0.867 |
| Fulvalene | 1 | 0.123 | 1.835[b] | *1.365* | 1.097 |
| | 2 | *0.221* | *1.837* | 1.452 | *0.976* |
| | 9 | 0.312 | 1.797 | — | 0.853 |
| Acenaphthylene | 1 | 0.208 | 0.861 | 2.124 | 1.066 |
| | 3 | 0.301 | 1.170 | 1.999 | *0.909* |
| | 4 | 0.029 | 0.719 | 2.513 | 1.008 |
| | 5 | *0.356* | *1.191* | *1.969* | 0.926 |
| | 10 | 0.106 | 0.664 | — | 1.044 |
| | 11 | 0.000 | 0.539 | — | 1.095 |
| | 12 | 0.000 | 0.616 | — | 0.998 |
| Fluoranthene | 1 | 0.243 | 1.028 | 1.46 | *0.947* |
| | 2 | 0.045 | 0.776 | 1.82 | 1.005 |
| | 3 | *0.326* | *1.197* | *1.41* | 0.958 |
| | 7 | 0.031 | 1.054 | 1.71 | 0.997 |
| | 8 | 0.079 | 0.793 | 1.76 | 1.008 |

a) See the first footnote of Table I.

b) Calculated according to the formula of Eq. IV—2 of Ref. 7 (the constant term, $2\lambda_{m+1}$, was omitted).

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For other compounds such as fulvene, pentalene, heptalene, fulvalene and fluoranthene there are no available data. The prediction of the most reactive position of these molecules by theoretical indexes agreed entirely with each other.

**Reaction for a Nucleophilic Reagent.**—Braun and Manz heated fluoranthene and CuCN for 6 hr. at 260°C and got 3-CN derivative[23]. The nature of this reaction has not been determined. The reaction may be nucleophilic or otherwise radical in nature. Provided that the reaction proceeds in radical mechanism the theories agree with the experiment because free valence, localization energy, frontier electron density and superdelocalizability all predict position 3 as the most reactive, as is seen in Table II. On the other hand if the reagent attacks the substrate molecule as a nucleophilic reagent, the $\pi$-electron density method fails to predict the correct position as is shown in Table III, whereas the localization and frontier electron methods both succeed also in this case.

For other molecules no experiment seems to have been carried out and all indexes predict the same position as the most reactive center except for acenaphthylene and fulvalene. Some experimental information may be looked for in relation to acenaphthylene; position 5 is predicted by the localization method and the frontier electron method, and position 3 by $\pi$-electron density method. In the case of fulvalene, disagreement of predictions by the localization method and the static method has been pointed out by Brown[12] in connection with the "chemical non-crossing rule"; that is, the former predict position 1, whereas the latter, position 2. The frontier electron density and the superdelocalizability predict position 2 as the most reactive center toward nucleophilic reagents in agreement with the static method.

As was stated above, the static method fails to explain the experimental results of fluoranthene with regard to the electrophilic attack and the radical reaction of azulene and acenaphthylene. The localization method also could not correctly predict the position of attack in the case of electrophilic reaction of fluoranthene and radical reaction of azulene. On the other hand, the predictions by the frontier electron method were entirely consistent with experiments for all molecules so far tested.

Since no ambiguous parameter has been used in the calculations stated above, such a comparison of availability of various theoretical indexes may be of significance in the sense that it may be able to afford us a clue to search for the "true" feature of substitution process in conjugated molecules.

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