

Evaluation of reaction site prediction in 3-ring PAHs according to calculation level

Byung-Dae Lee[†]

*Department of Health Management, Uiduk University, Gyeongju, 38004, Korea
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Abstract : The radical reaction position was calculated by varying the calculation level for ACEL and ANT, which are detected with the highest frequency and concentration in PAHs pollution sites. The results of each calculation level were compared and evaluated with the existing literature. HF, B3LYP, B3LYP-D, and MP2 were used as the method for each level used for calculation. Except for HF, the MK charge by B3LYP, B3LYP-D, and MP2 was consistent with the experimental results. It was found that the dispersion effect was negligible in the calculation of ACEL and ANT because the calculation results by the B3LYP and B3LYP-D methods were the same. In particular, it was found that the MK charge calculation result by MP2 agrees well with the product/PAH ratio obtained as a result of the experiment. Considering the calculation cost, it would be preferable to use B3LYP to predict the radical reaction site of ACEL and ANT. However, considering the product/PAH ratio, it takes more time to calculate, but it is judged that it is better to use the MP2.

Keywords : Reaction sites, calculation level, radical reaction, 3-ring PAHs.

1. Introduction

PAHs (Polycyclic Aromatic Hydrocarbons) are anthropogenically or naturally released into the environment by incinerators, coal mining processes, and volcanic activity [1-2]. According to the US Environmental Protection Agency, PAHs are composed of 16 substances. PAHs released into the environment temporarily stay in the atmosphere and eventually accumulate in soil or river/reservoir sediment [3-4]. When examining the PAHs

concentration at the contaminated site, 3-ring PAHs were detected with the highest concentration [5-6]. The reason is that 3-ring PAHs have a lighter molecular weight than other PAHs and are easily produced in incinerators. PAHs have properties such as carcinogenicity, reproductive toxicity, recalcitrance, and persistence and have adverse effects on the human body [7-9]. To date, various methods have been proposed as a treatment methods for PAHs. Incineration, chemical oxidation treatment, physical recovery, natural attenuation, etc., have been proposed and are in the stage of practical use. In the case of Korea, a chemical treatment method that can minimize environmental

[†]Corresponding author
(E-mail: bdlee@uu.ac.kr)

disputes (eg, Nimby phenomenon) can be suggested as an alternative because the land area is small [10–12]. Advantages of the chemical treatment method include a simple treatment process, high PAHs removal efficiency, controllable amount of oxidizing agent according to PAHs contamination level, and high safety of treatment facilities as the reaction occurs at room temperature and pressure. In addition, the treatment cost is low, the treatment time is very fast, and if the target removal efficiency is not reached after treatment, it can be treated again; therefore high-level skill is not required to operate the treatment facility. Chemical treatment can be combined with methods such as biological, UV, or ultrasonic treatment. As a disadvantage, most chemical treatment methods are carried out in the liquid phase, thus in the case of treatment containing organic matter, the amount of oxidizing agent may be increased. When PAHs are strongly adsorbed to the medium (eg, soil, fly ash, etc.), the removal efficiency can be lowered. Prediction of the various intermediates and final products generated during the chemical treatment of highly toxic PAHs is very important. Various theoretical calculation methods have reported many examples of predicting the final product [13–16]. Most methods predict intermediate or final products by calculating transition states and charges using the DFT (Density Functional Theory) method. In the DFT method, various methods exist depending on the HF (Hartree-Fock) ratio, and there are also various versions of the MP method. The main purpose of this study is to suggest the optimal method for predicting the final product during the chemical treatment of PAHs, among many calculation methods.

2. Calculation Methods

The radical reaction results of acenaphthylene (ACEL) and anthracene (ANT) used in this

study were obtained by referring to the existing literature [17]. The structures of ACEL and ANT were optimized at the HF, Lee-Yang-Parr exchange correlation functional (B3LYP), Lee-Yang-Parr exchange correlation functional with dispersion (B3LYP-D), and Møller-Plesset perturbation theory (MP2) level. The basis set used in all calculations is 6-31G(d,p). To predict the radical reaction position of ACEL and ANT, the plane figures of all the molecules in this study were drawn, and the three-dimensional features of these figures were confirmed with the Gauss View program [18]. With this Gauss View program, the Gaussian input files were created to run the Gaussian-09W program [19]. Meanwhile, to find out whether carbon in the benzene ring showed a high minus charge, the atomic charge distributions were calculated using the MK (Merz-Kollman/Singh) [20] methods with these optimized structures of molecules.

3. Results and Discussion

3.1. Chemical properties of ACEL, ANT, and final products

The molecular structures of ACEL and ANT, the subjects of this study, are shown in Fig. 1, and the physicochemical properties are shown in Table 1. As can be seen from Fig. 1, both ACEL and ANT molecules exhibit a planar structure and have a symmetrical structure around the central longitudinal axis of the molecule. Examining the physical and chemical properties, it was found that both materials did not volatilize well due to their high boiling point and low vapor pressure. Also, due to the high K_{ow} , it is expected that bioaccumulation in the environment will be high.

Table 2 shows the results of literature research on the chemically treated final products of ACEL and ANT. In the case of ACEL, a final product in which oxygen is bonded to the upper carbocyclic ring by OH radical attack has been reported. In the case

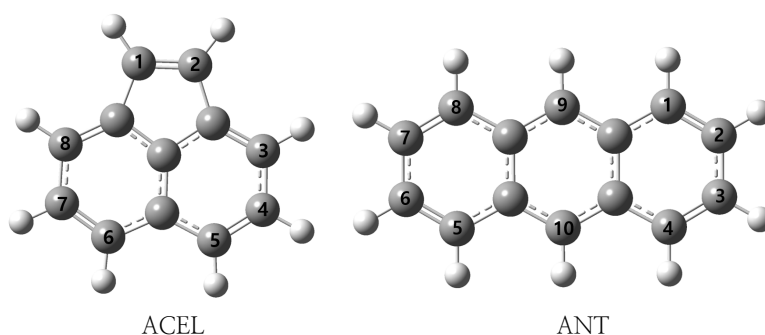


Fig. 1. Structure of ACEL and ANT.

Table 1. Chemical properties of ACEL and ANT [17]

PAH	Molecular weight	Boiling point (°C)	Log K_{ow}^*	Vapor pressure at 25°C (mmHg)
ACEL	152.2	280	4.05	4.80×10^{-3}
ANT	178.2	400	4.45	1.95×10^{-4}

*: n-octanol/water partition coefficient

Table 2. OH radical products of ACEL and ANT [17]

PAH	Reaction product	Product/PAH
ACE	1,8-naphthalic anhydride	<0.1
ANT	9,10-anthracenedione	0.71

of ANT, an final product in which oxygen is bound up and down the benzene ring located in the middle of the molecule has been reported.

3.2. MK charge according to the calculation level

According to the author's previous study, it was found that MK or CHelpG was more accurate than mulliken or NPA when calculating the atomic charge for intramolecular

reaction site analysis [15]. Therefore, only the MK charge was calculated in this study. Recently, many papers have been reported on the properties of various molecules using the Gaussian program [19–20]. In this study, MK charge values were calculated using HF (i.e., not considering electron correlation), B3LYP (including B3LYP–D considering dispersion effect), and MP2 (i.e., considering electron correlation). The results are shown in Tables 3 and 4. As shown in Table 3, in the case of

Table 3. Calculated atomic charge distributions of ACEL *

Position	Calculation methods	HF	B3LYP	B3LYP-D	MP2
1		-0.264	-0.230	-0.230	-0.269
2		-0.274	-0.234	-0.234	-0.276
3		-0.285	-0.219	-0.219	-0.228
4		-0.125	-0.111	-0.111	-0.188
5		-0.296	-0.218	-0.218	-0.217
6		-0.307	-0.223	-0.224	-0.229
7		-0.115	-0.109	-0.108	-0.179
8		-0.276	-0.211	-0.212	-0.219

*MK charges in electron.

ACEL, the charge values due to HF were -0.264 and -0.275 at carbon 1 and 2, and -0.296 and -0.307 at carbon 5 and 6, respectively, appeared higher. The higher the charge value, the easier the electrophilic reaction occurs. These results did not match the experimental results of the literature at all. The reason is considered to be that HF does not consider electron correlation. In the results of using the B3LYP method, the charge values were -0.230 and -0.234 at carbon 1 and 2, showing the highest charge values, and it was in good agreement with the experimental results. Unlike the HF, the reason why the DFT agrees well with the experimental results is because it uses the density function squared by the wave function instead of the wave function of electrons. However, the carbon 6 also showed a high charge value of -0.223. It was found that the charge calculation result by B3LYP-D, considering dispersion was almost the same as that of B3LYP. Therefore, it can be seen that the dispersion effect does not need to be considered in the charge calculation of ACEL. In the results of using the MP2, the charge values at carbon 1 and 2 were -0.269 and -0.276, which was very high than the charge values at other positions, which was in good agreement with the experimental results.

In the case of ANT, it was found that the

charge value at the carbon 9 and 10 position showed a very large value compared to other reaction positions regardless of the difference in the calculation method (i.e., HF, B3LYP, B3LYP-D, and MP2). From these results, it can be seen that in the case of ANT, all of the above four calculation methods agree well with the experimental results. However, the difference between the charge value at position 9 and 10 and the value at other positions appear in the order of MP2 > B3LYP = B3LYP-D >> HF thus the prediction of the final product by MP2 is considered to be the most accurate. The reason that the prediction of final products by MP2 agrees well with the experimental results in ACEL and ANT is thought to be because electron correlation is considered. In addition, considering the product/PAH ratio in Table 2, it can be seen that ANT is higher than ACEL. This means that it is easier for radicals to combine oxygen at position 9 and 10 of ANT than at other positions. It can be seen that the charge values in carbon 9 and 10 by MP2 are much higher than in other positions. This indicates that the experimental results (i.e., product/PAH ratio) are well explained by MP2 results. When the calculation time is expressed as a relative ratio, the order of HF < B3LYP < B3LYP-D < MP2 is shown.

Table 4. Calculated atomic charge distributions of ANT*

Position	Calculation methods	HF	B3LYP	B3LYP-D	MP2
1		-0.262	-0.223	-0.223	-0.269
2		-0.127	-0.106	-0.106	-0.125
3		-0.127	-0.115	-0.115	-0.137
4		-0.262	-0.216	-0.216	-0.260
5		-0.267	-0.207	-0.207	-0.252
6		-0.120	-0.123	-0.123	-0.143
7		-0.120	-0.096	-0.096	-0.114
8		-0.267	-0.229	-0.229	-0.281
9		-0.352	-0.449	-0.449	-0.555
10		-0.352	-0.434	-0.434	-0.534

*MK charges in electron.

4. Conclusions

In this study, the following results were obtained by comparing with the reported experimental results by performing various levels of calculations for ACEL and ANT, which are the 3-ring PAHs with the highest concentration at the PAHs contamination site.

1. Except for HF, the MK charge by B3LYP, B3LYP-D, and MP2 were all consistent with the experimental results.
2. The MK charge values of B3LYP-D and B3LYP were almost the same, indicating that dispersion effects were negligible in ACEL and ANT calculations.
3. It was found that the MK charge calculation result by MP2 agrees well with the product/PAH ratio result obtained as a result of the experiment.
4. In terms of the calculation cost, it would be preferable to use B3LYP to predict the radical reaction positions of ACEL and ANT. Considering the product/PAH ratio, it takes more time to calculate, but it is thought that using MP2 can get better

results.

Based on these results, it is expected that the B3LYP or MP2/MP4 method can be applied to the prediction of radical reaction products and decomposition pathways for 5-ring PAHs with high molecular weight and strong toxicity.

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