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Theoretical Study of Acenaphthylene and its Derivatives

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ABSTRACT

Polycyclic Aromatic Hydrocarbon (PAH) plays an important role in the formation of combustion-generated particles such as soot, and their presence in atmosphere aerosols has been widely shown. The formation of five -membered rings, detected in combustion effluent, is of great interest due to their genotoxic activity.

The present study reports an investigation of the electronic structure of Acenaphthylene by use of different chemical models .We also made a comparison between different chemical models.

Dnoor-acceptor disubstituted, enthalpy, entropy and rotation and transition division function at Zero point energy will be compared too.

The isotropic and anisotropic tensor of the Acenaphthylene structure were calculated with different chemical models HF/6-31G*, HF/6-31+G*, HF/6-31++G**, BLYP/6-31 G*, BLYP/6-31+G*, BLYP/6-31++G**, B3LYP/6-31G*, B3LYP/6-31+G* and B3LYP/6-31++G**, as well.

Keywords: PAH; Acenaphthylene; Electronic structure; Chemical models.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) containing unsaturated five membered rings externally fused to six-membered ring perimeters (CP-PAHs) are important in several contexts [1]. CP-PAHs have been identified as ubiquitous combustion effluents, and several representatives have been shown to possess considerable genotoxic activities [2].

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in natural environment.

They arise mainly from incomplete combustion of fossil fuels, automobile emissions, oil cracking, and natural resources such as forest fires and volcanoes. Geochemical processes yield PAHs when natural organic matter (NOM) is exposed to high pressure and temperature.

These compounds can be source pollutants (e.g. oil spill) or non point source (e.g. atmospheric deposition) and are among the most widespread organic pollutants. Anthropogenic practices, such as industrial processing, petroleum spills, and in complete combustion of fuel, also contribute to high levels of PAHs in the environment [3-7]. (PAHs) with external cyclopenta-fused five membered rings, such as the cyclopenta – fused naphthalene (Acenaphthylen) derivatives, belong to the class of nonalternant polycyclic aromatic hydrocarbons and may exhibit unusual (Photo) physical properties. Several qualitative models, e.g. Plat's ring perimeter model [8] Clar's model [9] and Randics conjugated circuits model [10-11]

Have either been or are frequently used for the rationalization of the properties and the reactivity of PAHs.

THEORETICAL METHOD:

We follow the approach used in our earlier study [12] of neutral PAHs in which we computed the harmonic frequencies using the density functional theory (DFT) approach. We

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use the B3LYP hybrid functional [13], which includes some rigorous Hartree-Fock exchange as well as a gradient correction for both exchange [14] and correlation [15]. The calculations were carried out using the Gaussian 98 system of programs [16]. The Becke-3 parameter density functional with the Lee-Yang-Parr correlation functional (B3LYP) [17, 18] was used in conjunction with 6-31G*, 6-31+G, 6-31++G** basis sets. Analytic harmonic frequencies at the same level of approximation were used to characterize the nature of the structures under study and to evaluate Zero-point energy correction (ZPE). In this study, we apply the HF, BLYP and B3LYP methods.

RSULTS AND DISCUSSION

1. Acenaphthylene and its derivative structures

In this study, we apply the HF, BLYP and B3LYP methods. The compounds considered for this study are calculated by B3LYP methods. The compounds considered for this study are shown in Figure 1.

2. The study of thermodynamic properties

A comparison of rotation and transition division function at zero point energy showed that calculated vibratory division function with Zero energy at 6-31 G* basis set, has maximum values using the data in table 1.

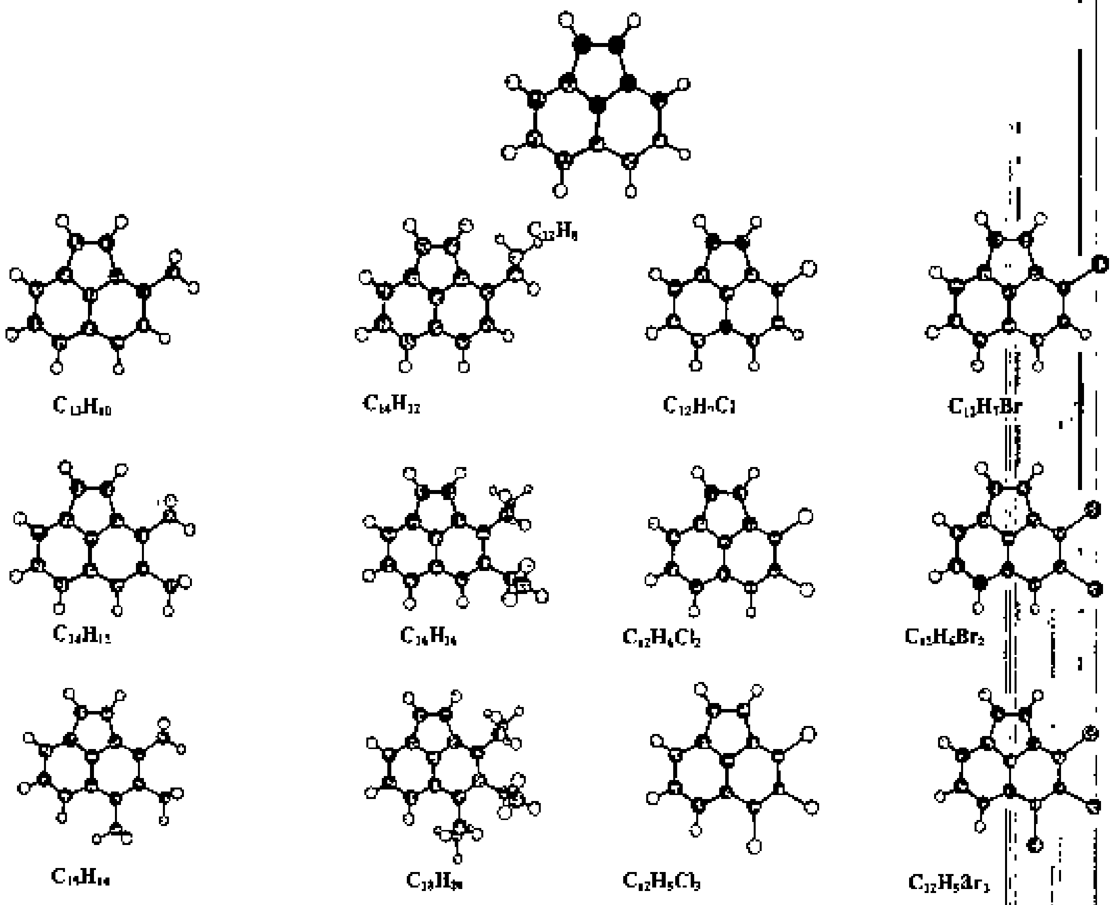

Fig.1.The geometric structure of Acenaphthylea and its derivatives.

Table 1. Optimized parameters at theoretical level of relative thermal enthalpy (ΔH) , thermal entropy (ΔS) and Gibbs free-energy (ΔG) at $25^{\circ}C$

Structure	method	Basis set	ΔS	$^{\Delta H}/_{\Delta G}$	$^{T}/_{R}$	$^{V}/_{E}$
	HF	6-31++g*	84.221	0.1789/0.1388	40.968/29.907	13.347/0.00
$C_{11}H_8$	BLYP	6-31g*	86.961	0.1637/0.1224	40.968/29.981	16.013/0.00
	B3LYP	6-31g**	86.094	0.1682/0.1273	40.968/29.938	15.188/0.00
	HF	6-31++g*	91.111	0.1699/0.126	41.568/31.138	18.404/0.00
$C_{22}H_7Cl$	BLYP	6-31g*	94.325	0.1556/0.110	41.568/31.220	21.537/0.00
	B3LYP	6-31g**	93.259	0.1599/0.1155	41.568/31.177	20.517/0.00
	HF	6-31++g*	92.794	0.1700/0.1268	42.201/31.875	18.719/0.00
$C_{12}H_7Br$	BLYP	6-31g*	96.901	0.1554/0.1094	42.201/31.957	31.957/0.00
	B3LYP	6-31g**	95.803	0.1597/0.1142	42.201/31.909	21.693/0.00
	HF	6-31++g*	92.797	0.2099/0.1658	41.230/30.563	21.0030/0.00
$C_{13}H_{10}$	BLYP	6-31g*	97.401	0.1924/0.1461	41.230/30.630	30.635/0.00
	B3LYP	6-31g**	95.831	0.1975/0.1519	41.230/30.592	24.008/0.00
	HF	6-31++g*	99.355	0.2417/0.1946	41.472/31.205	26.746/0.00
$C_{14}H_{12}$	BLYP	6-31g*	102.827	0.2218/0.1730	41.472/31.299	30.084/0.00
	B3LYP	6-31g**	101.901	0.2276/0.1792	41.472/31.271	29.100/0.00
	HF	6-31++g*	97.599	0.1609/0.1146	42.068/32.142	26.722/0.00
$C_{12}H_6Cl_2$	BLYP	6-31g*	101.386	0.1473/0.0991	42.068/32.199	25.895/0.00
	B3LYP	6-31g**	100.115	0.1514/0.1038	42.068/32.152	27.118/0.00
	HF	6-31++g*	101.158	0.1634/0.1155	43.070/33.322	24.765/0.00
$C_{12}H_6Br_2$	BLYP	6-31g*	106.414	0.147/0.0964	43.070/33.399	29.945/0.00
	B3LYP	6-31g**	105.079	0.151/0.1013	43.070/33.350	28.659/0.00
	HF	6-31++g*	101.286	0.2411/0.1944	41.472/31.161	25654/0.00
$C_{14}H_{12}$	BLYP	6-31g*	107.979	0.2212/0.1728	41.472/31.231	29.276/0.00
	B3LYP	6-31g**	105.807	0.2268/0.1789	41.472/31.188	28.147/0.00

Table 1. Continued...

$C_{16}H_{16}$	HF	6-31++g*	110.571	0.3050/0.2525	41.903/32.280	36.387/0.00
	BLYP	6-31g*	115.197	0.2783/0.2285	41.903/32.348	40.946/0.00
	B3LYP	6-31g**	114.871	0.2802/0.2254	41.903/32.303	30.574/0.00
$C_{12}H_5Cl_3$	BLYP	6-31g*	108.234	0.1391/0.0875	42.496/32.940	32.797/0.00
	B3LYP	6-31g**	106.672	0.1431/0.0923	42.496/32.891	31.375/0.00
$C_{12}H_5Br_3$	BLYP	6-31g*	115.559	0.1389/0.0837	43.743/34.432	37.384/0.00
	B3LYP	6-31g**	113.981	0.1426/0.0884	43.743/34.381	35.585/0.00
$C_{15}H_{14}$	BLYP	6-31g*	111.033	0.2502/0.1975	41.695/31.702	37.635/0.00
	B3LYP	6-31g**	110.063	0.2564/0.2041	41.695/31.659	36.709/0.00
$C_{18}H_{20}$	BLYP	6-31g*	128.644	0.3386/0.2775	42.280/33.028	53.336/0.00
	B3LYP	6-31g**	127.331	0.3496/0.2864	42.280/32.982	52.069/0.00

E=electronic	T= translational
R= rotational	V= vibrational

These values are more in electron acceptor substitutions especially in bromine (Br) than in electron donor substitutions.

Enthalpy (ΔH) and Gibbs free-energy (ΔG) at 6-31++G* basis set have maximum values. These changes are more for electron donor substitutions (methyl and ethyl) than electron acceptor substitutions (bromine and chlorine).

By studying of entropy for all of substitutions, it will be clear that 6-31G* basis set has most values among other basis sets and entropy in electron donor substitutions is more than electron acceptor substitutions (table 1).

3. Comparison of isotropic and anisotropic diagrams based on atomic number

A comparison of isotropic and anisotropic values showed that most values of isotropic are related to atoms of (Br) and (Cl) both of which are electron acceptor and least values of isotropic are related to methyl and ethyl (See figures 2,3).

CONCLUSION

Electronegative groups have more isotropic and anisotropic values. The more the atomic number of electronegative group, (the atom will be bigger) the more are changes.

The amount of entropy and enthalpy for electron donor substitutions like methyl and ethyl are more than of those for electronegative substitutions like Bromine and Chlorine.

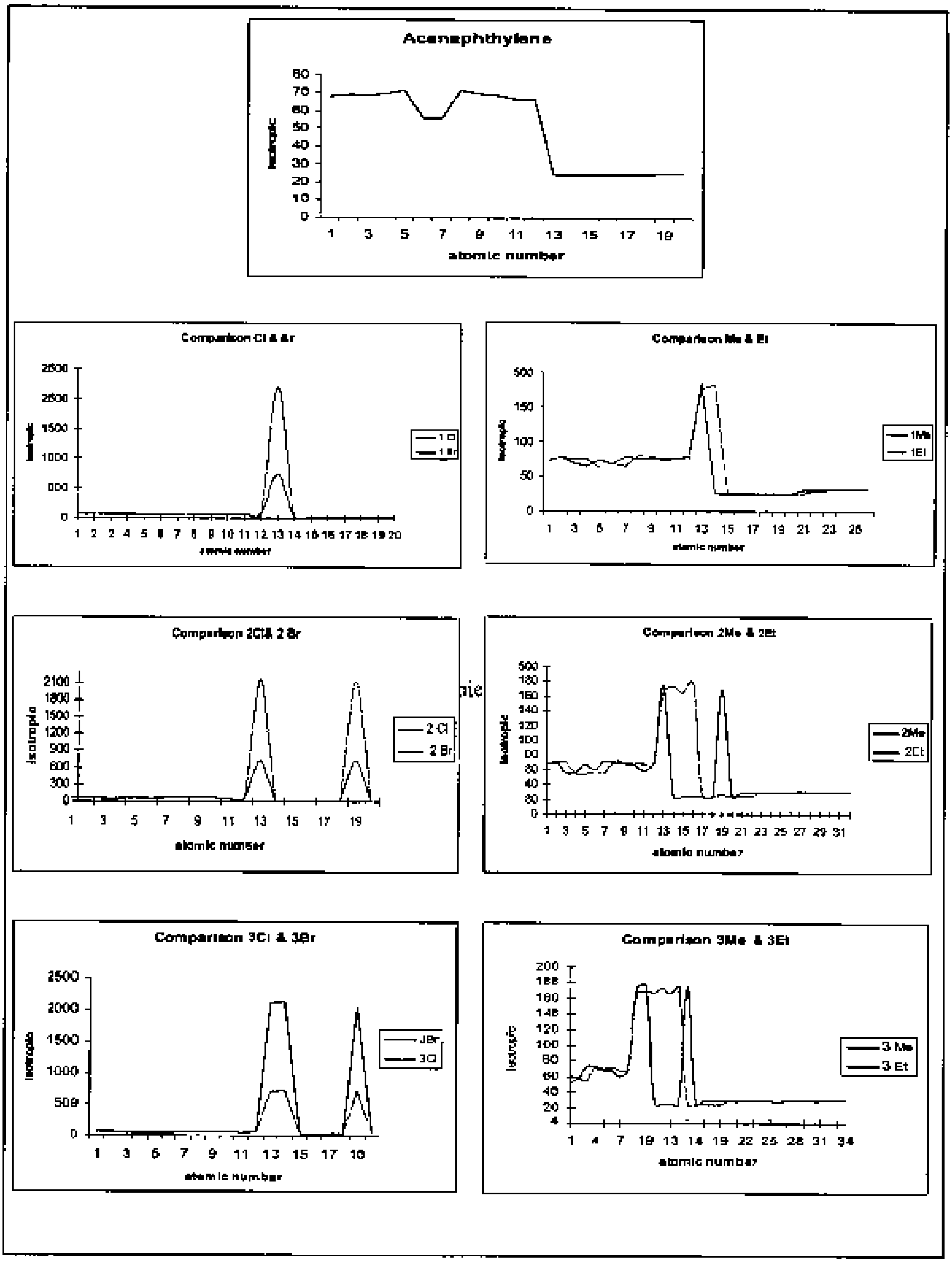

Fig.2. Comparison between Isotropic Shielding for Acenaphthylene and its derivatives

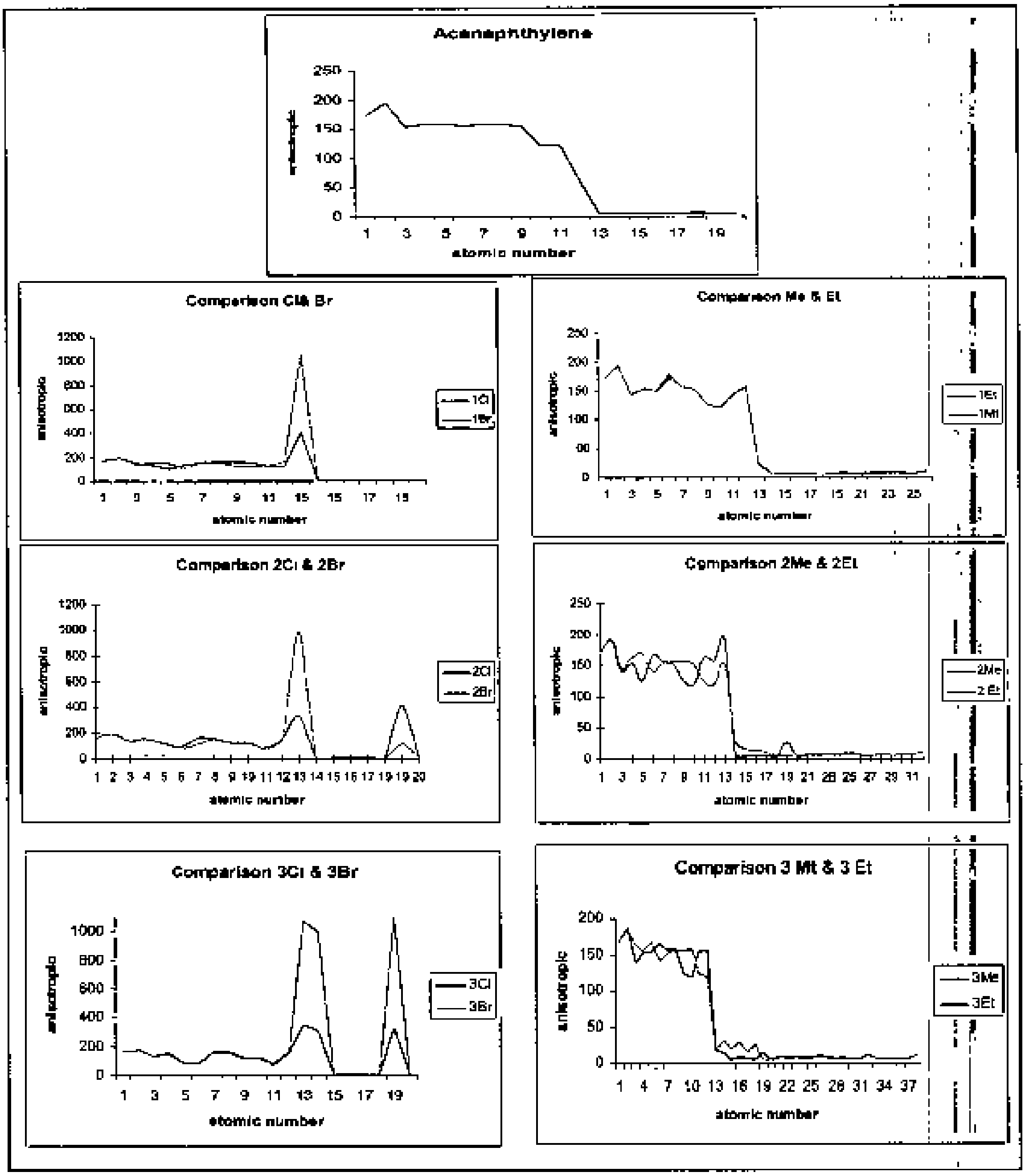

Fig.3.Comparison between Anisotropic Shielding for Acenaphthylene and its derivatives

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