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An Ab initio Investigation of Pyrene Electronic Structure

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds consisting of more than two benzene rings fused in a linear, angular, or clustered arrangement and do not contain hetero atoms or carry subsistent. PAHs originate from various sources. They are primarily formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, or tobacco. The present study reports an investigation of the electronic structure of Pyrene by use of different model chemistries. We also made a comparison between different model chemistries. Linear relationship between the energy and Z-matrix of the structure were found. The energy diagrams vs. the number of primitive Gaussian wave functions and vs. distance matrix shows the energy variations in model chemistries HF/6-31G*, HF/6-31++G**, MP2/6-31G, MP2/6-31++G**, BLYP/6-31G, BLYP/6-31++G**, B3LYP/6-31G and B3LYP6-31++G**, as well. High symmetry of the Pyrene molecules makes four regions in the study of the NMR shielding tensors. The isotropic and anisotropic tensors of the Pyrene structure, calculated with different model chemistries, too. The results show that only the C and D part of the Pyrene structure are affected by the magnetic field.

Keywords: Pyrene; Shielding tensor; Model chemistry; Electronic structure

INTRODUCTION

Since human civilization relies so heavily on combustion, polycyclic aromatic hydrocarbons (PAHs) are inevitably linked to our energy production. In this sense, PAH molecules can be considered as marker molecules as their abundance can be directly proportional to combustion processes in the region and therefore directly related to air quality. Different types of combustion yield different distributions of PAHs.

Thus, those produced from coal burning are different than those produced by motor-fuel combustion, which differ from those produced by forest fires. Some PAHs molecules are contained in crude oil, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. The fate of PAHs in soils and sediments is related to their solubility bioavailability, biodegradability and sorption/desorption mechanisms.

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Geochemical processes yield PAHs when natural organic matter (NOM) is exposed to high pressure and temperature. These compounds can be point source pollutants (e.g. oil spill) or non-point source (e.g. atmospheric deposition) and are one of the most widespread organic pollutants .Anthropogenic practices, such as industrial processing, petroleum spills, and incomplete combustion of fuel, also contribute to high levels of PAHs in the environment. [1-4].

Pyrene is a polycyclic aromatic hydrocarbon (PAH) consisting of four fused benzene rings, resulting in a large, flat aromatic system. Pyrene forms during incomplete combustion of organic materials. Animal studies have shown Pyrene is toxic to the kidneys and the liver. Pyrene has a wide spread of applications, from making pharmaceuticals, and plastics to be a valuable molecular probe for fluorescence spectroscopy or a probe to determine solvent environments.

(PAHs) with external cyclopenta-fused five-membered rings, such as the cyclopenta-fused Pyrene derivatives, belong to the class of non alternant polycyclic aromatic hydrocarbons and may exhibit unusual (photo) physical properties [5,6]. Several qualitative models, e. g. Plat's ring perimeter model [5] Clar's model [6] and Randic's conjugated circuits model [7-9[have either been or are frequently used for the rationalization of the properties and the reactivity of PAHs.

According to Platt's ring perimeter model [5] the aromatic hydrocarbon should be divided into two parts: a perimeter and an inner core. The perimeter should be considered as an n-annulene, while the inner core represents only a perturbation. The properties of the hydrocarbon are then interpreted as those of the n-annulene, using the Huckel (4n + 2) rules. Another view offers Clar's model (6) of aromatic hydrocarbons. In this model aromaticity is regarded as a local property. The Kekule resonance structure with the largest number of aromatic sextets, i.e. benzene-like moieties is preferred. The other rings in the PAH are less aromatic and are chemically more reactive.

THEORETICAL METHOD

The electronic structure of Pyrene as a highly symmetric molecule was the subject of the present study. Because of this symmetry, isotropic and anisotropic shielding values of this molecule divide it to four parts (A through D, See Fig.1) and then calculations performed with different model chemistries (See Table1). Gaussian 98 software package [10] is used to perform Hartree-Fock (HF), Density-Functional Theory (BLYP and B3LYP methods), Post Hartree-Fock (MP2 method) and the study of electronic charges distribution by Mulliken population method. The relation between primitive Gaussians with energy of the structure, Z-matrix and density matrix of the structures investigated, too. Isotropic and anisotropic NMR shielding tensors calculated for the interested structures with different model chemistries by using the continuous Set of the Gauge Independent Atomic Orbital (GIAO) method [11-14]. Because of the variable effects of solvent interactions, all the calculations were performed in gas phase which result the intrinsic properties of the structures.

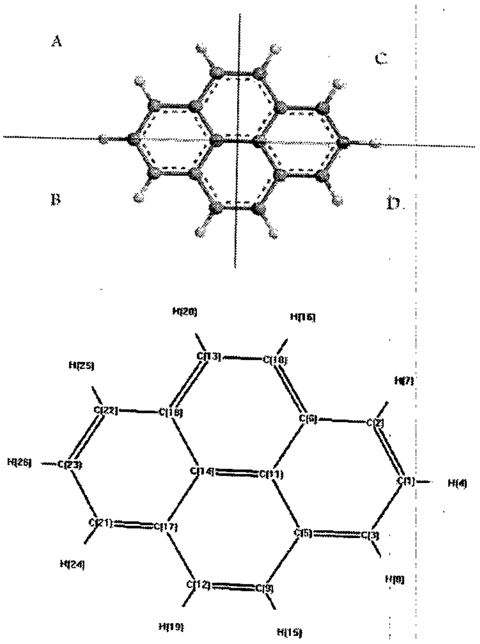

Fig.1. Pyrene is highly symmetric molecule (above), the optimized structure of Pyrene (below).

RSULTS AND DISCUSSION

1. Pyrene Structure

The Pyrene structure energy vs. its z-matrix was studied with different HF, DF (Density Functional) and MP2 methods (Table1). There is a high correlation coefficient (R2) for all four methods which indicates a totally optimized structure (Fig.2).

Table 1. Different Model Chemistries applied in the Structures

Applied model chemistries for Pyres Structure	
Hartree – Fock Models	Perturbation Method
1 HF/6-31G*	7 MP2/6-31G
2 HF/6-31G**	8 MP2/6-31G*
3 HF/6-31G*	9 MP2/6-31+G
4 HF/6-31++G	10 MP2/6-31++G
5 HF/6-31G*	11 MP2/6-31++G*
6 HF/6-31++G**	12 MP2/6-31++G**
Density Functional Methods	
13 BLYP/6-31G	19 B3LYP/6-31G
14 BLYP /6-31G*	20 B3LYP /6-31G*
15 BLYP /6-31+G	21 B3LYP /6-31+G
16 BLYP /6-31++G	22 B3LYP /6-31++G
17 BLYP /6-31++G*	23 B3LYP /6-31++G*
18 BLYP /6-31++G**	24 B3LYP /6-31++G**
Applied model chemistries for four devided Structure	
A Structure	B Structure
1 HF/6-31G	1 HF/6-31+G*
2 HF/6-31++G*	2 HF/6-31++G**
3 BLYP/6-31+G	3 BLYP/6-31++G
4 B3LYP/6-31G	4 B3LYP/6-31G*
5 B3LYP/6-31++G*	5 B3LYP/6-31++G**
6 MP2/6-31+G	
C Structure	D Structure
1 HF/6-31+G	1 HF/6-31++G
2 BLYP/6-31G	2 BLYP/6-31G*
3 BLYP/6-31++G*	3 BLYP/6-31++G**
4 B3LYP/6-31+G	4 B3LYP/6-31++G

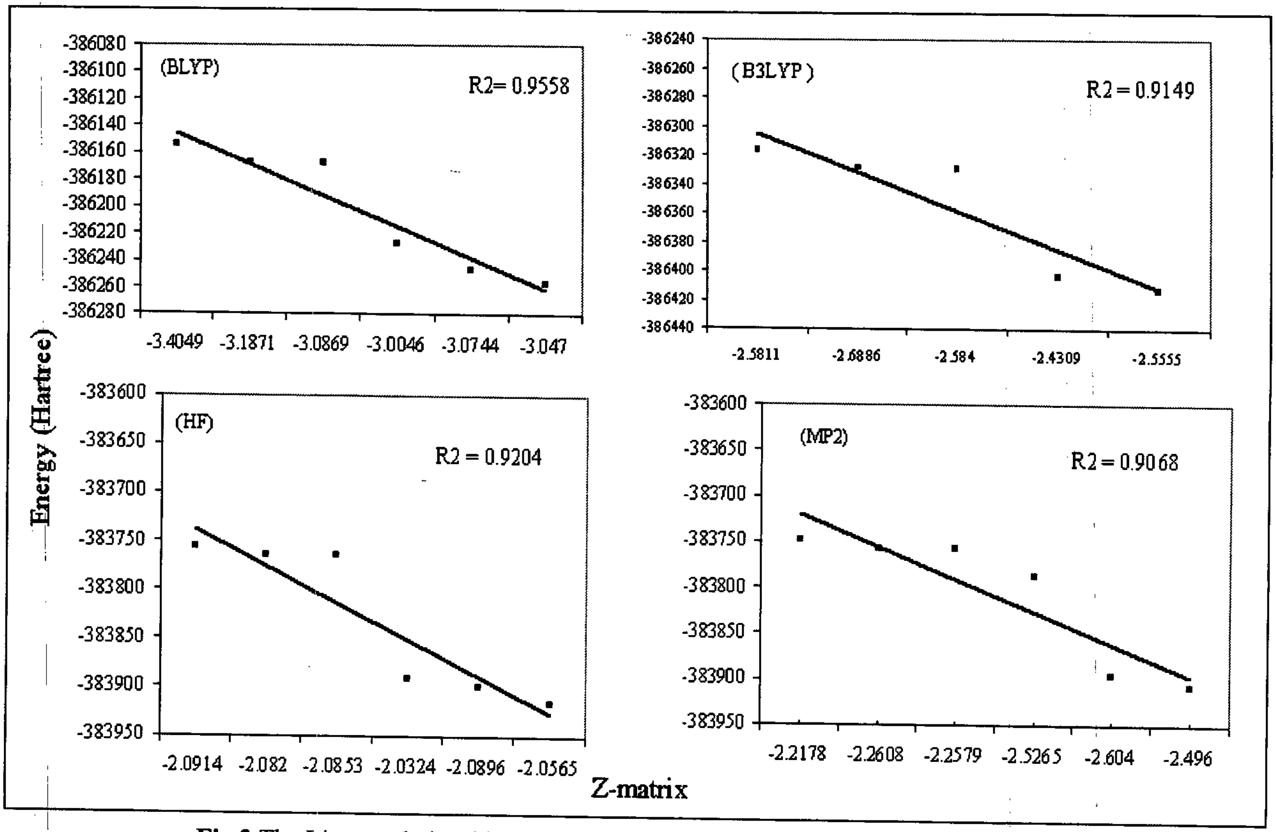

Fig.2. The Linear relationship between energy and Z-Matrix in different methods.

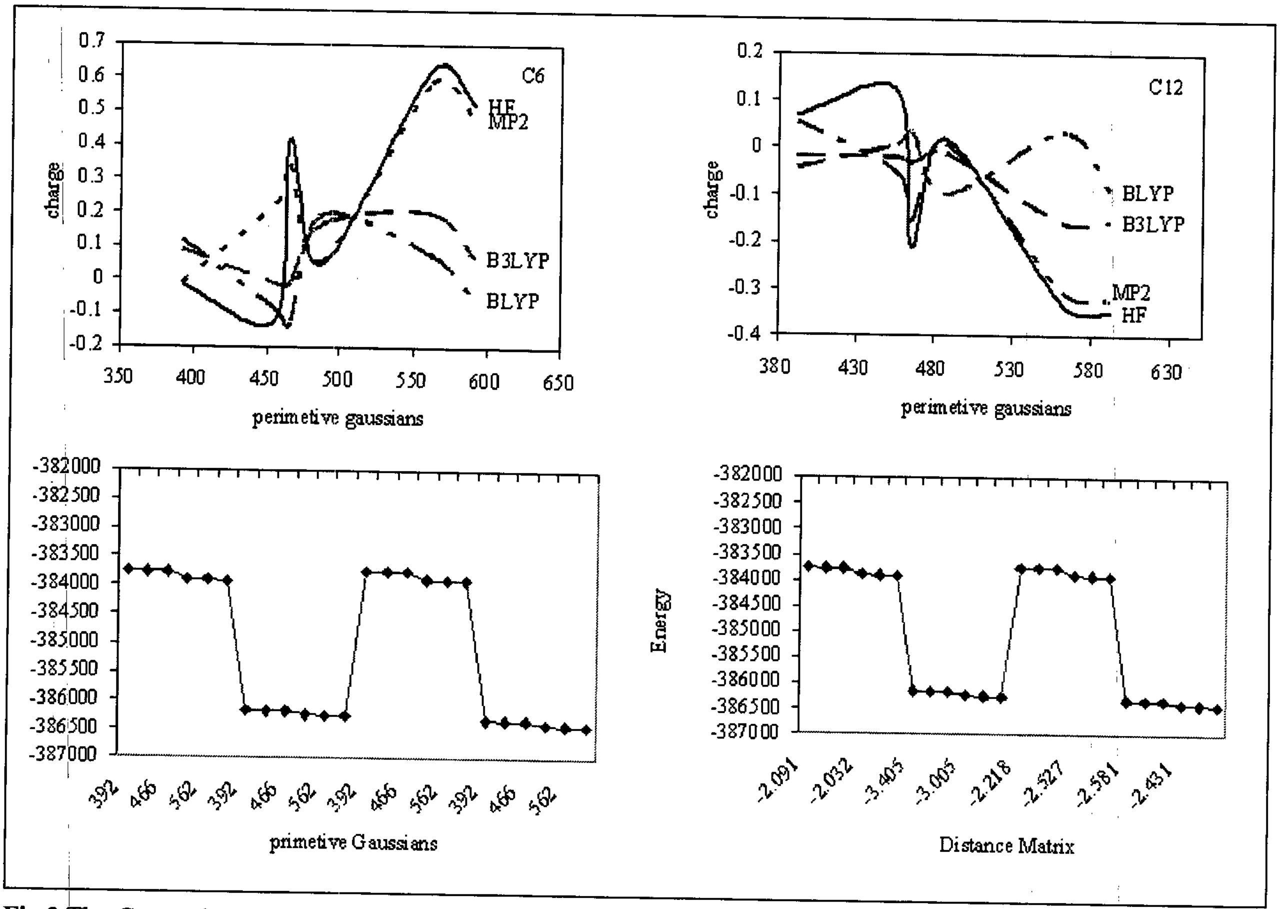

Fig.3. The Comparison between HF energy, primitive Gaussians and distance matrix, Charge distribution for C6 and C12 atoms in Pyrene.

1.1. The study of Atomic Charges

Models numbered 1, 6,7,12,13,18,19 and 24 are the best choices for calculations investigation of atomic charge changes of C6 atom vs. the primitive Gaussians shows an agreement between HF, MP2 and between DF methods together. In all of the methods there are some fluctuations but these are shown much stronger in HF and MP2 methods (see Fig.3).

In the case of C1 atom there is a complete agreement between all the methods, they show a highly positive charge center (except the Hydrogen types) on C1 atom (in the range of +0.124 to +0.268 in different methods) with using the 6-31++G basis set. This result, suggests that a nucleophilic or a free radical would more likely attack at this site.

The study of atomic charges in C12 atom indicates that the HF, MP2 and B3LYP methods are in consistency together, too (Fig.3) .

They all show a highly negative center (-0.217,-0.155 and -0.03, respectively)on the carbon atom with using the 6-31++G basis set (see Fig.4) .

2. Pyrene is divided to four structures A, B, C and D

As said before, high symmetry of the Pyrene molecules makes four regions (Fig.1) in the study of the NMR shielding tensors. The isotropic and anisotropic tensors of theses structures calculated with different model chemistries which can be found in Table1.

2.1 Structure A

In the case of Structure A, MP2/6-31+G has the lowest isotropic value of carbon atoms number 1and 6 while other carbon atoms (number2, 10 and 11), in other models, are not much affected by the magnetic field. This pattern can be seen exactly in the anisotropic form, too. Structure A includes hydrogens numbered 4, 7 and 16. There is no changes in isotropic and anisotropic form of the H7 and H16, but in both of isotropic and anisotropic diagrams H4 shows a great positive difference from changing model from B3LYP/6-31++G* to MP2/6-31+G. This difference is much higher in the anisotropic form (≅47.5 in the case of isotropic and 207.6 in the case of anisotropic) (See Figs. 5, 6).

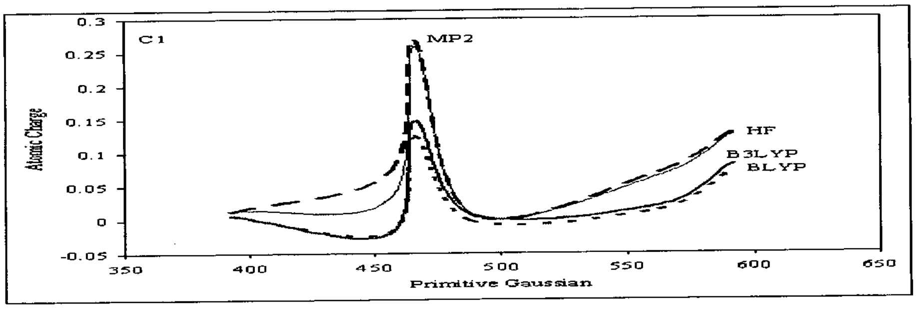

Fig.4. Calculated atomic Charges for C1 atom vs. Primitive Gaussian by different methods.

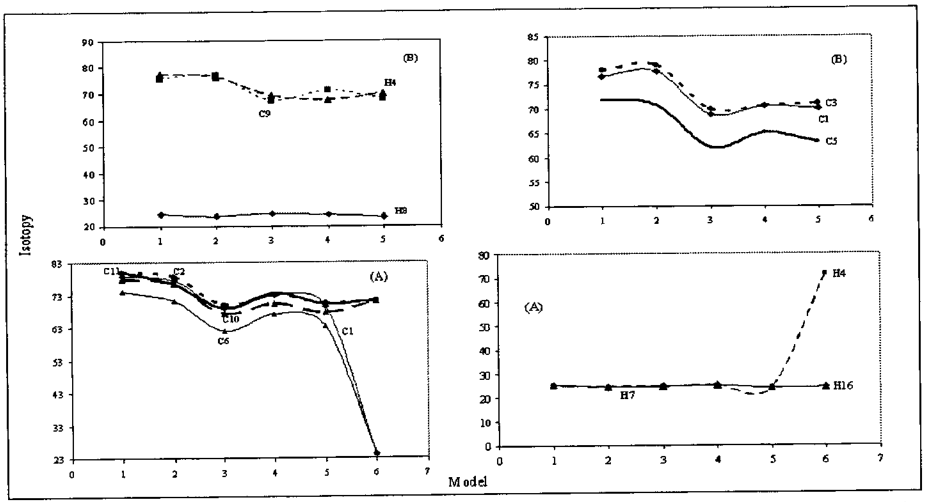

Fig.5. NMR Isotropic Shielding for A and B structures with different Model Chemistries.

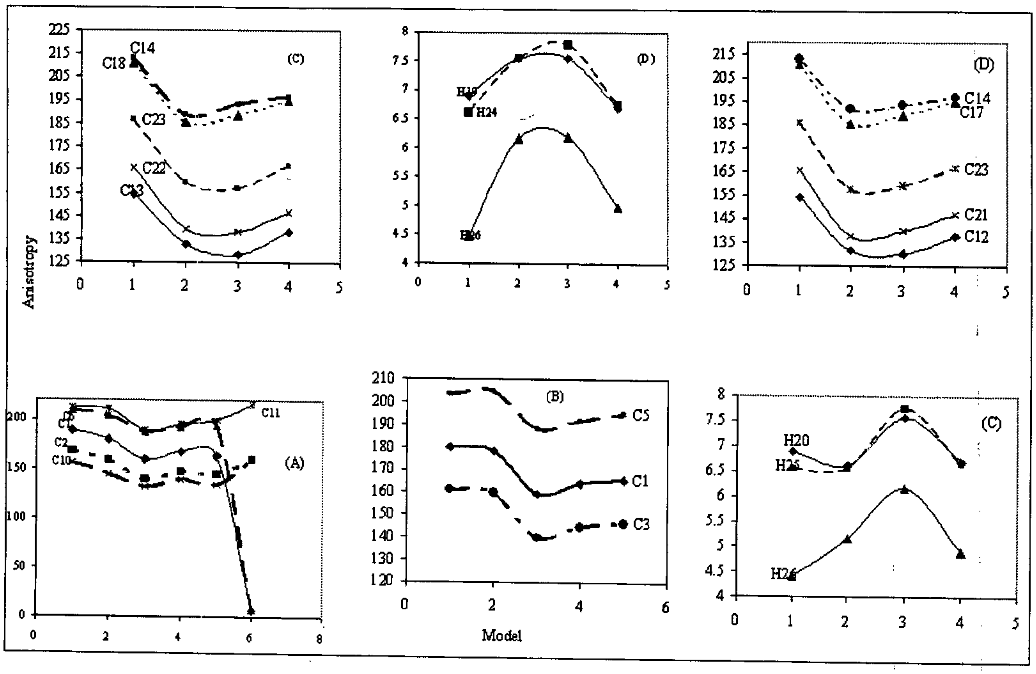

Fig.6. NMR Anisotropic Shielding for different structures with different Model Chemistries.

2.2 Structure B

The B structure includes C1, C3, C5 and C9, H4 and H8. Isotropic diagram indicates that all the carbon atoms, except C9, show a decreasing pattern in different models. H8 has a fixed value, so its isotropic value is nit model dependent and H4 has some fluctuations. The atoms have the same treat in an anisotropic magnetic field, too (See Figs. 5,6).

2.3 Structure C

Carbon atoms numbered 13,14,18,22 and 23 together with hydrogen atoms numbered 20, 25 and 26 are calculated in the frame of structure C. All the carbon atoms have an increasing treat both in isotropic and anisotropic field. There is an interesting point about the Hydrogens of this structure by the BLYP/6-31++G* model, these Hydrogens are strongly affected in the magnetic field and they have an exactly inverse treat in isotropic and anisotropic fields (See Figs. 6, 7).

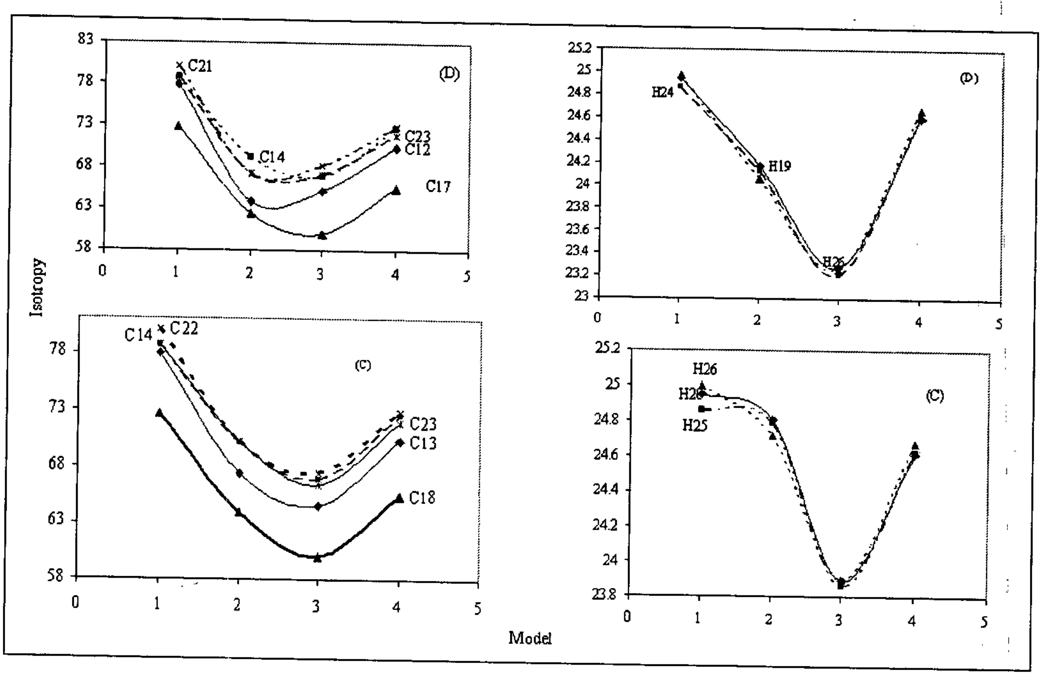

Fig.7. Isotropic Shielding for C and D structures with different Model Chemistries.

2.4 Structure D

Structure D includes C12, C14, C17, C21 and C23 and hydrogen atoms numbered 19, 24 and 26. In both isotropic and anisotropic forms, carbons have the lowest value by BLYP/6-31++G** model. This pattern can be seen for Hydrogens in isotropic field, too.

But in the case of anisotropic diagram of Hydrogens, BLYP/6-31++G** model shows the highest value (See Figs. 6, 7). These results show that only the C and D part of the Pyrene structure are affected by the magnetic field.

CONCLUSION

Pyrene electronic structure was studied by use of different model chemistries.Comparisons between different model chemistries were made, too. Linear relationship between the energy and Z-matrix of the structure were found, as well. The energy diagrams vs. the number of primitive Gaussian wave functions and vs. distance matrix shows the energy variations in model chemistries The results showed that only the C and D part of the Pyrene structure are affected by the magnetic field. The 6-31++G basis set suggested that Carbon atom in Pyrene structure named C1 can be a site for nucleophilic or a free radical attack because of its high positive charge.

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