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Extended Hückel Calculations on Some Norbornenyl-Fused Aromatic Compounds

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Some norbornenyl-fused aromatic systems are both planer and bridge molecules and their molecular properties can be calculated by various methods. In this study, some molecular properties of these molecules were determined theoretically, by using extended Hückel molecular orbital (EHMO or EHT) method and cycloaddition reactions of some norbornenyl-fused aromatic systems have been explained from EHMO data.

Key Words: Extended Hückel molecular orbital theory (EHMO), Norbornenyl-fused aromatic systems, Adduct, *bis*-Adduct.

INTRODUCTION

Quantum mechanical applications of theoretical calculations on the properties of atoms and molecules have been developed since 1930. Extended Hückel molecular orbital (EHMO) theory is one of these applications and it is the simplest molecular orbital theory of π-conjugated molecular systems. Theoretical calculations give us useful information about molecular structure, reactivity and reaction mechanisms. Possible reactions of molecules can be predetermined with the data such as atomic net charge, gross atomic orbital population, orientation and value of AO coefficients, *etc*. EHMO theory uses the following approximations: π-electron approximation; LCAO representation of the π-molecular orbitals; neglect of electron-electron and nuclear-nuclear repulsions (in fact, the assumption that these can be ignored). The diagonal elements of the effective Hamiltonian, coulombic integrals and the off-diagonal elements, resonance integrals, (accounted for only directly bonded atoms) are chosen as empirical parameters, all overlap integrals being neglected[1-3].

Norbornenyl-fused aromatic systems such as compounds 1-4 and next homologue in this series have recently claimed a special interest because of π-facial stereoselectivity. Benzonorbornadiene (**1**) and related compounds are of great scientific interest because of their unusual geometry and high reactivity. For example, these compounds exhibit in the photochemical di-π-methane rearrangement[4,5]. Therefore, functionalizations of these compounds are important. Some norbornenyl-fused aromatic systems show π-facial stereoselectivity for this

reason their synthesis and reactions became significant. Since these compounds behave diene or dienephile in the reactions of their π-bonds for preparing their derivatives, their reactions have became very important.

In this study, we investigated extended molecular orbital calculation of reaction of benzonorbornadiene (**1**), 2,3-norbornadienonapthalene (**2**), 2,3-norbornadienoanthracene (**3**) and 2,3-norbornadienonapthantracene (**4**). The properties of some mono adduct and *bis*-adduct norbornenyl-fused aromatic ring compounds have been investigated by extended Hückel molecular orbital (EHMO) method or EHT (Figs. 1-4).

EXPERIMENTAL

In this study, DATA GENERAL MV 4000 computer has been used. Computer package program is ICON 8 written in Fortran 77. The Source program has 290 KB file length. In this program input data are atomic coordinates of atoms in the molecule. For the calculations of Hamiltonian matrix in the program -13.6 eV for hydrogen atom s-coulomb potentials, -21.4 eV and -11.4 eV for carbon atom s-coulomb and p-coulomb potentials has been used, respectively. Exponent of wave functions at overlap matrix calculation have been chosen for hydrogen and carbon atoms 1.30 and 1.65, respectively. Adjustable parameter (K) has been taken as 1.75 at all calculations.

General procedure: The data as distance matrix, wave function, atomic net charge, overlap matrix, energy matrix have been calculated by EHMO. All the output data fiil voluminous pages[6]. Therefore, summary data have been given to Tables 1-6.
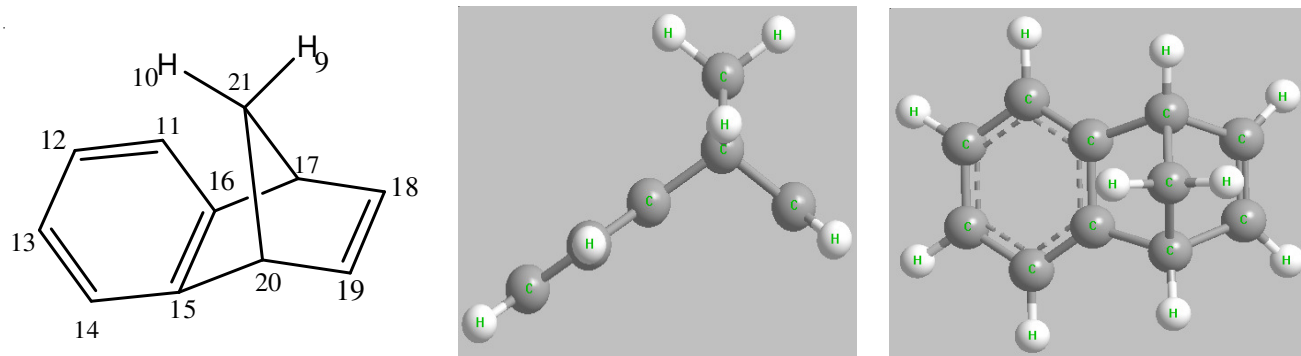
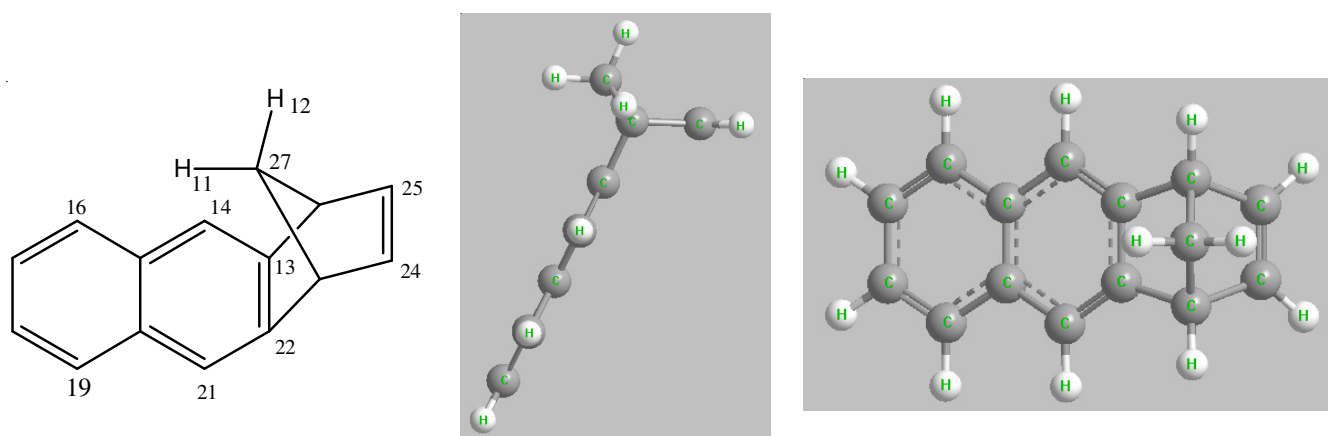Fig. 1. Computer generated drawing of the optimized structures for compound **1**

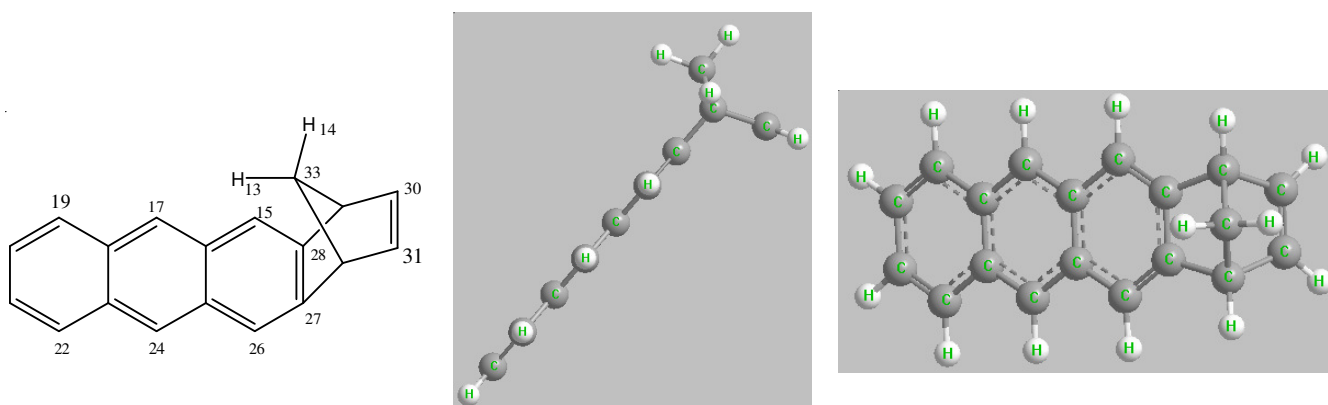Fig. 2. Computer generated drawing of the optimized structures for compound **2**

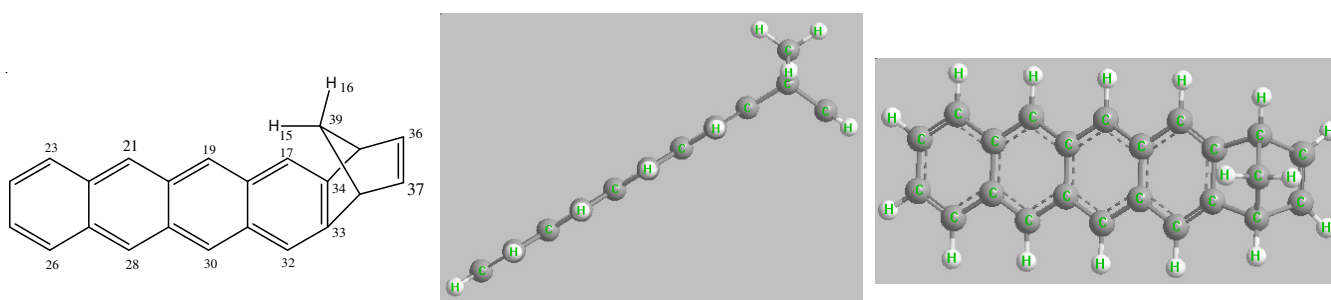Fig. 3. Computer generated drawing of the optimized structures for compound **3**

Fig. 4. Computer generated drawing of the optimized structures for compound **4**

TABLE-1
ATOMIC NET CHARGES, HOMO AND LUMO REDUCED
CHARGES OF BENZONORBORNADIENE (1) ATOMS

Atoms	Atomic net charges	HOMO reduced charges	LUMO reduced charges
H$_9$	0.04090	0.1680	0.0000
H$_{10}$	0.06139	0.0850	0.0000
C$_{11}$	-0.43474	0.3442	0.0124
C$_{12}$	-0.18216	0.1217	0.4517
C$_{13}$	-0.18216	0.1217	0.4517
C$_{14}$	-0.43474	0.3442	0.0124
C$_{15}$	0.39421	0.0470	0.3248
C$_{16}$	0.39421	0.0470	0.3248
C$_{17}$	-0.28741	0.2564	0.0653
C$_{18}$	-0.07530	**0.0574**	**0.1285**
C$_{19}$	-0.07530	**0.0574**	**0.1285**
C$_{20}$	-0.28741	0.2564	0.0653
C$_{21}$	0.78728	0.0842	0.0252

TABLE-2
ATOMIC NET CHARGES, HOMO AND LUMO REDUCED
CHARGES OF 2,3-NORBORNADIENONAPHTHALENE (2) ATOMS

Atoms	Atomic net charges	HOMO reduced charges	LUMO reduced charges
H$_{11}$	0.10417	0.0377	0.0798
H$_{12}$	0.09571	0.1169	0.0848
C$_{13}$	0.38521	0.0670	0.0878
C$_{14}$	-0.43628	**0.2885**	**0.0154**
C$_{15}$	0.05003	0.0074	0.1459
C$_{16}$	-0.24528	0.1752	0.3995
C$_{17}$	-0.14366	0.0839	0.0903
C$_{18}$	-0.14366	0.0839	0.0903
C$_{19}$	-0.24528	0.1752	0.3995
C$_{20}$	0.05003	0.0074	0.1459
C$_{21}$	-0.43628	**0.2885**	**0.0154**
C$_{22}$	0.38521	0.0670	0.0878
C$_{23}$	-0.20949	0.1918	0.1364
C$_{24}$	-0.07510	0.0835	0.0027
C$_{25}$	-0.07510	0.0835	0.0027
C$_{26}$	-0.20949	0.1918	0.1364
C$_{27}$	0.82035	0.0448	0.0731

TABLE-3
ATOMIC NET CHARGES, HOMO AND LUMO REDUCED
CHARGES OF 2,3-NORBORNADIENOANTHRACENE (3) ATOMS

Atoms	Atomic net charges	HOMO reduced charges	LUMO reduced charges
H$_{13}$	0.12557	0.0152	0.0630
H$_{14}$	0.13759	0.0758	0.0922
C$_{15}$	-0.34988	0.1881	0.1170
C$_{16}$	0.05702	0.0049	0.1407
C$_{17}$	-0.35528	**0.2407**	0.0797
C$_{18}$	0.03672	0.0155	0.0207
C$_{19}$	-0.17886	0.1214	0.2654
C$_{20}$	-0.12023	0.0686	0.0805
C$_{21}$	-0.12023	0.0686	0.0805
C$_{22}$	-0.17886	0.1214	0.2654
C$_{23}$	0.03672	0.0155	0.0207
C$_{24}$	-0.35528	**0.2407**	0.0797
C$_{25}$	-0.05702	0.0049	0.1407
C$_{26}$	-0.34988	0.1881	0.1170
C$_{27}$	0.38411	0.0764	0.0325
C$_{28}$	0.38411	0.0764	0.0325
C$_{29}$	0.14837	0.1368	0.1399
C$_{30}$	-0.06423	**0.0873**	**0.0140**
C$_{31}$	-0.06423	**0.0873**	**0.0140**
C$_{32}$	-0.14837	0.1368	0.1399
C$_{33}$	0.84050	0.0253	0.0584

TABLE-4
ATOMIC NET CHARGES, HOMO AND LUMO REDUCED
CHARGES OF 2,3-NORBORNADIENONAPHTH-
ANTHRACENE (4) ATOMS

Atoms	Atomic net charges	HOMO reduced charges	LUMO reduced charges
H$_{15}$	0.13542	0.0052	0.0459
H$_{16}$	0.16628	0.0474	0.0900
C$_{17}$	-0.27688	0.1105	0.1786
C$_{18}$	0.04718	0.0190	0.0694
C$_{19}$	-0.33856	**0.2134**	**0.0008**
C$_{20}$	0.05271	0.0001	0.0786
C$_{21}$	-0.30148	**0.2063**	**0.1441**
C$_{22}$	0.03521	0.0210	0.0008
C$_{23}$	-0.14214	0.0902	0.1772
C$_{24}$	-0.10423	0.0580	0.0657
C$_{25}$	-0.10423	0.0580	0.0657
C$_{26}$	-0.14214	0.0902	0.1772
C$_{27}$	0.03521	0.0210	0.0008
C$_{28}$	-0.30148	**0.2063**	**0.1441**
C$_{29}$	0.05271	0.0001	0.0786
C$_{30}$	-0.33856	**0.2134**	**0.0008**
C$_{31}$	0.04718	0.0190	0.0694
C$_{32}$	-0.27688	0.1105	0.1786
C$_{33}$	0.39351	0.0718	0.0248
C$_{34}$	0.39351	0.0718	0.0248
C$_{35}$	-0.10350	0.0951	0.1373
C$_{36}$	-0.04799	0.0792	0.0288
C$_{37}$	-0.04799	0.0792	0.0288
C$_{38}$	-0.10350	0.0951	0.1373
C$_{39}$	0.85134	0.0155	0.0458

TABLE-5
MOLECULAR ORBITAL ENERGY LEVELS OF SOME
NORBORNENYL-FUSED AROMATIC SYSTEMS

| Compd. No.	HOMO energy level (eV)	HOMO energy level (eV)	Total energy (eV)
1	-9.19857	-7.79892	-936.98230
2	-9.63815	-8.00845	-1255.02741
3	-9.91319	-8.72410	-1572.60004
4	-10.11184	-9.15437	-1889.97601

TABLE-6
EHT DATA OF TERMINAL CARBON ATOMS IN
INVESTIGATED COMPOUNDS

| S. No.	Compd.	Atomic net charges	Reduced charge at HOMO and LUMO	AOs coefficient at HOMO and LUMO	
1	C$_{18,19}$	-0.07530	**0.0574** **0.1285**	A 0.1845 B 0.1845	**-0.2479** **0.2479**
2	C$_{24,25}$	-0.07510	0.0835 0.0027	A -0.0422 B -0.0422	-0.1673 0.1673
3	C$_{30,31}$	-0.06423	**0.0873** **0.0140**	A 0.2193 B -0.2190	**0.0933** **-0.0933**
4	C$_{36,37}$	-0.04799	0.0792 0.0288	A -0.2064 B -0.2064	-0.1310 0.1310

RESULTS AND DISCUSSION

In this study, we have interpreted the results by investigating their adduct reactions with extented Hückel molecular orbital calculation of norbornenyl-fused aromatic compounds **1-4** (**Scheme-I**).

When solution of benzonorbornadiene (**1**) and tetrabromoxylene are treated in anhydrous dimethylformamide and
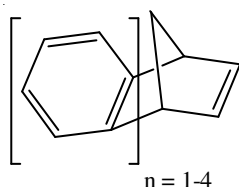
**Scheme-I:** Some norbornenyl-fused aromatic compounds

sodium iodine, mono-adduct is took place (**Scheme-II**)[7]. Reaction of mono-adduct has been occured on C_{18} and C_{19} in place of C_{11} and C_{14} carbons. In EHMO calculation values of **1**, the atomic net charges and LUMO reduced charges of C_{11}, C_{14}, C_{18}, C_{19} are found as - 0.43474, -0.070530 and 0.0124, 0.1285, respectively (Table-1). These values have proved that benzonorbornadiene behaves as a dienophile in a Diels-Alder cycloaddition reaction taking place from these centers (C_{18} and C_{19}).
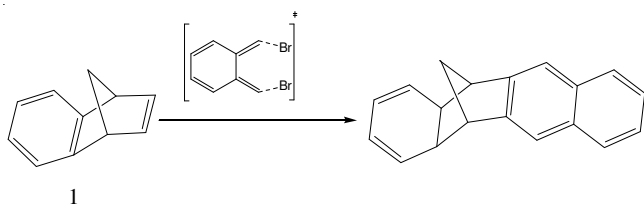
Scheme-II: Diels-Alder reactions of **1** with intermediate of tetrabromo-xylene

On the other hand, reaction of cyclopentadiene with benzonorbornadiene (**1**) in a sealed tube at 160 ºC led the formation of two cycloadduct in the ratio of 1:12[8]. These reactions are a Diels-alder addition reaction. The properties of carbon atoms on bicyclic part of benzonorbornadiene have been investigated. The values of Mulliken populations have been seen rather great when atomic net charges are calculated. It is understood that terminal π-bond in this compound behaves as an isolated π-bond. This π-bond acts as dienophile at Diels-Alder addition reaction. This is obvious that if we look at coefficients and orientations of atomic orbitals of lowest unoccupied molecular orbital (LUMO). This conclusion is also supported by the values of 2px AO coefficients at highest occupied molecular orbital (HOMO) of the π-bond (Table-1). Net atomic charge values of hydrogen atoms of methano bridge (H_{10}-C_{21}-H_9) are great, therefore, from a C_{18}-C_{19} carbon atom p-bond of dienophile attack is down. Consequently, the amount of *trans*-adduct is seen much more.

The naphthacene moiety in **4** has been proved to be a very reactive diene component in Diels-Alder cycloaddition reaction. For example, it reacted with maleic anhydride (boiling xylene) within 0.5 h to yield a white crystalline solid as *syn/anti* mixtures in 88 % yield[9]. *Syn* and *anti* products have been synthesized as a result of Diels-Alder cycloaddition reaction on the second and thrid rings in the napthantracene moiety in **4** (**Scheme-III**)[9]. The properties of carbon atoms at aromatic parts of 2,3-norbornadienonapthantracene have been investigated. The calculation of HOMO reduced charge on C_{19}, C_{30} and C_{21}, C_{28} in **4** were found to be as 0.2134 and 0.2063, respectively (Table-4). These values proved that the aromatic ring in **4** behaved as a diene resulting in the formation of cycloaddition products from these centers.
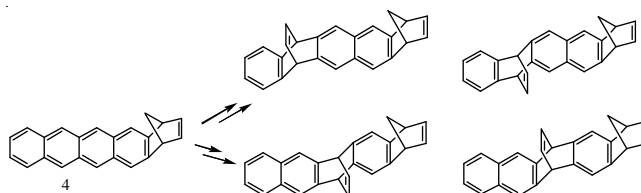
Scheme-III: Diels-Alder reactions of **4** with maleic anhydride

In addition, a π-facial stereoselectivity of 2,3-norbornadionoantracene (**3**) was observed in the experimental results. *Syn* and *anti* yields have been synthesized with reaction of dimethyl acetylenedicarboxylate and 2,3-norbornadienoanthracene (**3**) (**Scheme-IV**)[10]. The properties of carbon atoms at aromatic moiety of **3** have been investigated by means of EHMO calculation method. The distribution of π-electrons in **3** were theoretically studied. The value of HOMO reduced charges on C_{17} and C_{24} in **3** were found to be as 0.2407 (Table-3). These values have proved that the aromatic moiety behaves as a dien resulting in the cycloaddition products and the result of cycloaddition reaction has explained that it is took place in these centers (C_{17} and C_{24}).
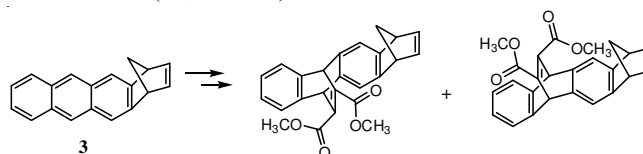
Scheme-IV: Diels-Alder reactions of **3** with dimethyl acetyenedicarboxylate

The reaction of benzonorbornadiene with iron carbonyls has been investigated[11]. Adduct yields and distribution have been chaning by depending on catalysis. It has observed a dimerization on $Fe(CO)_x(olefin)_y$ complex by behaving like an olefinic terminal double bond of norbornadiene. Values of AOs and reduced charge density at LUMO are ± 0.2479 and 0.1285, respectively. These results can be explained easly by back-bonding with iron (Table-6).

Conclusion

Some norbornenyl-fused aromatic compounds are rather large molecules for EHMO. These calculations have been carried out 5 to 10 min when we used the computer. The information which supported adduct reaction of norbornenyl-fused aromatic compounds, (EHMO), are seen from Table 1-6.

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