Theoretical study on monosubstituted fulvenes contain Cl ,S, P, and Si elements. Part A

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Abstract

MINDO/3-FORCES calculations have been done after complete optimization of geometry on X-monosubstituted fulvlene molecules , where X is Cl ,SH, PH_2, and SiH_3 . It was found that all these substituents are stabilizing . Also, all the substituents, in general, increase the dipole moment .Geometric parameters, heats of formation, orbital energies, electron densities of atoms are reported for all of these molecules.
Keywords:-MINDO/3-FORCES version 6.00 1996 program , mono substituted fulvenes with Cl, SH, PH_2, and SiH_3 substituents

الخلاصة

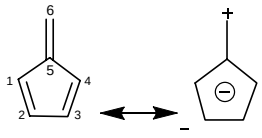
أجريت حسابات الميندو/ 3-فورسيز المتضمنة الحصول على الشكل الهندسي ذي الطاقة الأقل , على مركبات الفولفين - احادية التعويض للمعوضات:Cl, SH , PH_2, SiH_3 . ووجد إن جميع هـذه المعوضـات تؤدي آلي استقرار جريئة الفولفين .كما, إن جميع هذه المعوضات , بصورة عامة , تؤدي آلي زيـادة العـزم ثنائي القطب . أيضا ,تم تدوين المتغيرات الهندسية , حرارات التكوين , الطاقات المدارية ,الكثافات ألالكترونية للذرات في لجميع هذه الجزيئات.

Introduction

Fulvenes are a cross- conjugated molecules with some unique properties [1-3] Their structure and electronic distribution were investigated theoretically[4] and experimentally[5]. The halogenated substituted fulvenes were used to improve the octane quality of a fuel for an internal combustion engines[6] The fluorosubstituted fulvenes is relatively common ligand in the organometalic ; the low-valent titanium-pentafulvene complexes had been prepared[7].Theoretical study on monosubstituted fulvenes having substituents from first and second row elements had been reported[8-11]. However, no experimental and or theoretical studies are found for fulvenes having the Cl, SH , PH_2, SiH_3 substituents.

The aim of the present work is to study the X-monosubstituted fulvenes , where X is the substituent Cl, SH , PH_2, and SiH_3 at the carbon atoms C3, C4, and C6, by calculation based on the MINDO/3-FORCES[12-13] method. The molecular energy of the mono substituted fulvene , obtained from the

semi emperical MINDO/3 method[14] is completely minimized according to the Murtagh- Sargent minimization technique[15] .The derivative of the energy is calculated , analytically, according to Pulay's Force method[16]. The applications of the MINDO/3-FORCES method are well known[17-21]. The effect of X on the optimized geometry, heats of formation, dipole moments, HOMO-LUMO energies, electron densities and the stabilization of each molecule are, also, reported.



Structural detals

For the SH substituent , we assumed that SH is in the plane of the molecule according to the analogous calculation on fulvene molecule[8] .The geometric parameters(bond lengths and bond angles) for the studied molecules were listed in Table.1. It is obvious that when the Cl and SH substituents are introduced into the fulvene molecule , the adjacent bonds beccome shorter and the bond angles, to which the subtituents are attached, are greater than the corresponding ones in the case of the introduction of PH_2 and SiH_3 substituents , Table 1.

Dipole moment

The dipole moment can be understood as a result from intramolecular charge transfer from exocyclic double bond to five membered ring thereby acquiring pseudoaromatic cyclopentadienide character[8]. All the substituents , in general , increase the dipole moment , Table 2, The more increment was shown for Cl group due to the high electro negativity of Cl atom. For all the substituents , except PH_2, the lower dipole moment values are to be more pronounced at C_6 position, Table 2.

Electron densities

It can be seen from Tables.3 and 4 that Cl , SH , and PH_2 substituents decrease the electron densities on the carbon atom to which the substituent is attached and , in general, increase the electron density on the adjacent carbon atoms, i.e. they act as electron releasing. The SiH_3 substituent shows an opposite effect to that found for above three substituents , Table.4 , i.e. acts as electron with drawing.

Stabilization by substituents

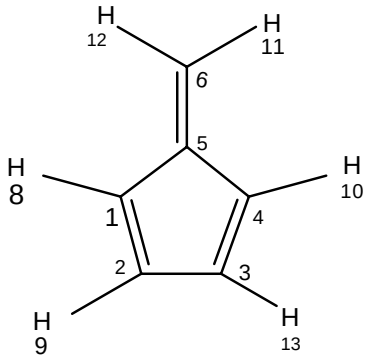
The stabilizing effect of a substituent is often assessed by using isodesmic reactions(conserved bond type)[22]. A positive heat of formation (Table 5) indicates stabilization of the reactant by substituent. The results show that all the substituents are stabilizing. It is found that the substituents at C_6 position are the more stabilizing ones. The PH_2 stabilizes the fulvene molecule more than other substituents due to its contribution in the resonance within the fulvene ring by its lone paired electrons, Table 5.

Orbital Energies

According to Koopmans' theorem (the negative HOMO is equal to the ionization potential). The C_6 substituted fulvenes with the PH_2 and SiH_3 substituents are more easily to be reduced than that of the C_3 and C_4 substitution positions. This is may be due to the low values of the LUMO energy. The others two substituents, Cl and SH show the opposite effect. The easier reduction is the C_3-substituted fulvene with the Cl substituent . This is confirmed by the high dipole moment, Table 2. The low energy of LUMO suggests a high reactivity (Table 2). On the other side, the more easily substituted fulvene to be oxidized is with PH_2 at C_4 due to its low HOMO energy , Table 2.

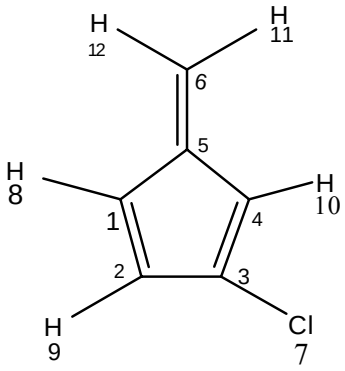
Table 1. Calculated geometric parameters (bond lengths in Angestrom and bond angles in degrees) of the mono substituted fulvene.

Fulvene molecule



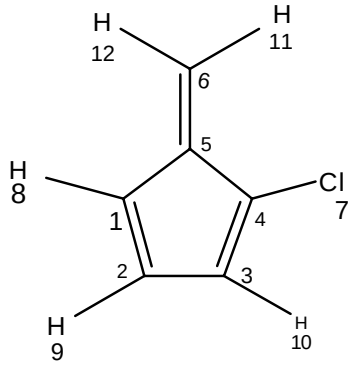
C_1C_2=1.358;C_2C_3=1.482; C_3C_4=1.358; C_4C_5 =1.505; C_5C_1=1.502; C_5C_6=1.333;
C_1H_8=1.099;C_2H_9=1.098;C_3H_{13}=1.099; C_4H_{10}=1.097;C_6H_{11}=1.093;C_6H_{12}=1.098;<$C_2C_1C_5$=108.9;<$C_1C_2C_3$=109.1;<$C_2C_3C_4$=109.1;<$C_3C_4C_5$=108.7;<$C_4C_5C_1$=104.1;<$C_6C_5C_1$=127.4;<$C_5C_1H_8$=122.8;<$C_1C_2H_9$=126.6;$C_4C_3H_{13}$=126.4;<$C_5C_4H_{11}$=123.5;<$C_5C_6H_{11}$=121.6; <$C_5C_6H_{12}$=124.8; <$H_{12}C_6H_{11}$=113.5

1



C_1C_2=1.358;C_2C_3=1.479; C_3C_4=1.357; C_4C_5 =1.507; C_5C_1=1.507; C_5C_6=1.338;
C_1H_8=1.100;C_2H_9=1.097;C_3Cl_7=1.751; C_4H_{10}=1.097;C_6H_{11}=1.100;C_6H_{12}=1.103;<$C_2C_1C_5$=110.2;<$C_1C_2C_3$=107.3;<$C_2C_3C_4$=110.8;<$C_3C_4C_5$=108.0;<$C_4C_5C_1$=119.1;<$C_6C_5C_1$=128.2;<$C_5C_1H_8$=122.6;<$C_1C_2H_9$=128.7;$C_4C_3H_{10}$=126.4;<$C_5C_4Cl_7$=123.7;<$C_5C_6H_{11}$=125.0; <$C_5C_6H_{12}$=124.7; <$H_{12}C_6H_{11}$=110.1

2



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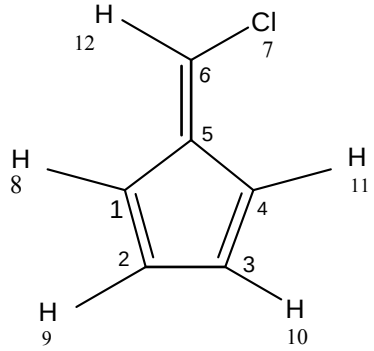
3



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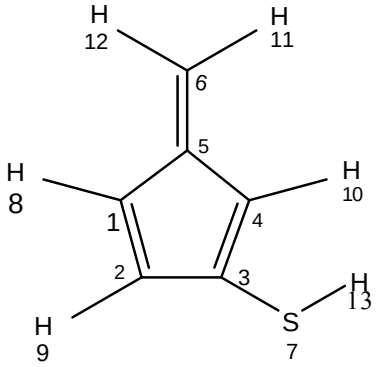
<$C_6C_5C_1$=126.4;<$C_5C_1H_8$=122.5; <$C_1C_2H_9$=127.3; $C_4C_3H_{10}$=127.5; <$C_5C_4Cl_7$=122.2; <$C_5C_6H_{11}$=128.2; <$C_5C_6H_{12}$=126.3; <$H_{12}C_6H_{11}$=105.4

4



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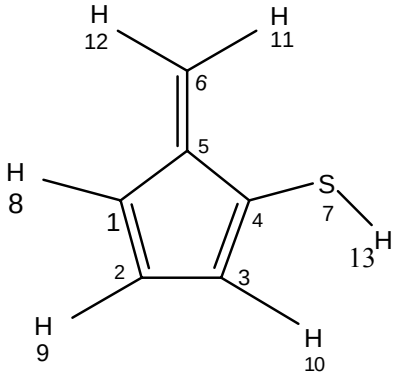
C_1H_8=1.100;C_2H_9=1.099;$C_3(S_H)$1.724; C_4H_{10}=1.098;C_6H_{11}=1.100;C_6H_{12}=1.101;<$C_2C_1C_5$=109.8;<$C_1C_2C_3$=108.6;<$C_2C_3C_4$=108.3;<$C_3C_4C_5$=109.4;<$C_4C_5C_1$=103.0;<$C_6C_5C_1$=128.3;<$C_5C_1H_8$=122.7;<$C_1C_2H_9$=128.0;C_4C_3(SH)=134.1;<C5C4H10=122.8;<$C_5C_6H_{11}$=125.0; <$C_5C_6H_{12}$=124.9; <$H_{12}C_6H_{11}$=110.0

5



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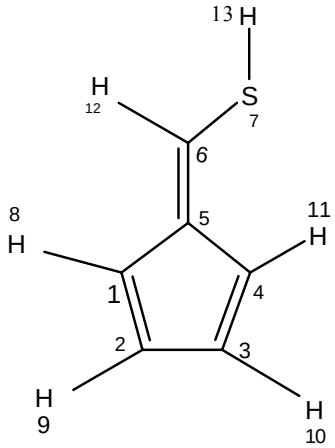
6



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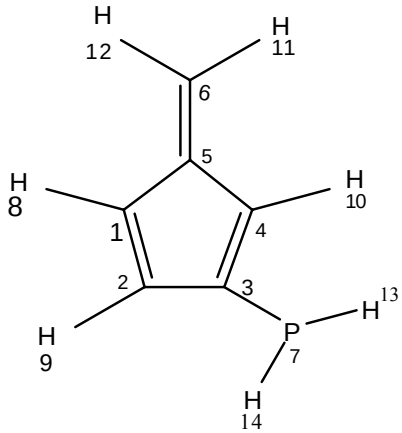
7



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C_1H_8=1.099;C_2H_9=1.103;C_3(PH2)=1.7

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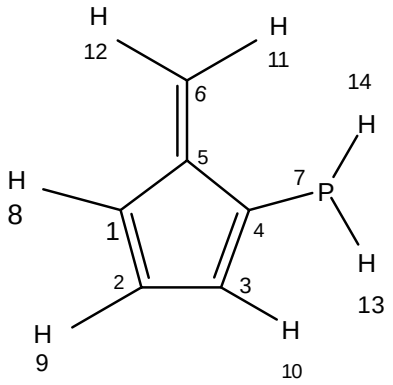
8



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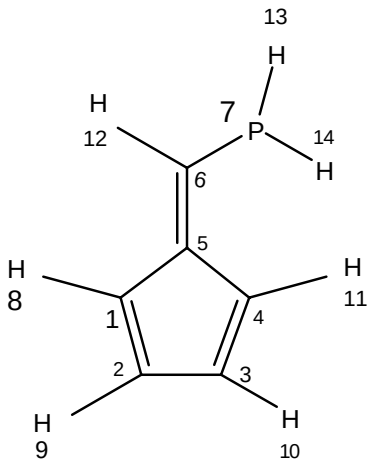
9



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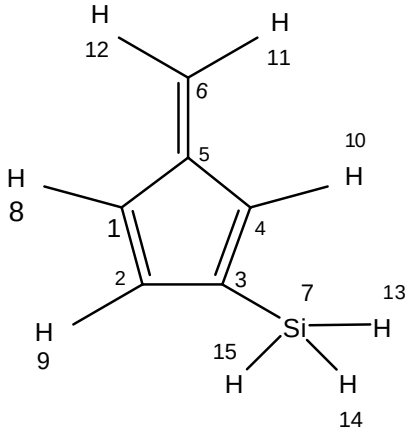
10



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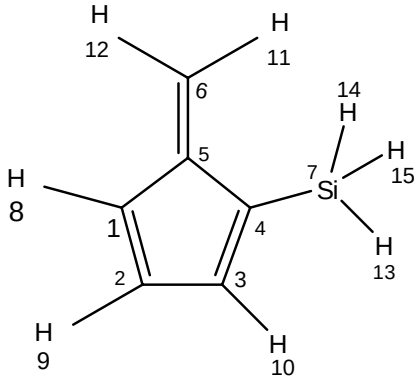
C_1H_8=1.099;C_2H_9=1.103;$C_3(SiH3)$=1.828;C_4H_{10}=1.104;C_6H_{11}=1.100;C_6H_{12}=1.100;<$C_2C_1C_5$=109.0;<$C_1C_2C_3$=111.8;<$C_2C_3C_4$=103.7;<$C_3C_4C_5$=113.2;<$C_4C_5C_1$=101.5;<$C_6C_5C_1$=129.2;<$C_5C_1H_8$=123.1;<$C_1C_2H_9$=125.2;$C_4C_3(SiH3)$=130.4;<$C_5C_4H_{10}$=119.9;<$C_5C_6H_{11}$=125.0;<$C_5C_6H_{12}$=125.0; <$H_{12}C_6H_{11}$=109.8

11



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C_1H_8=1.100;C_2H_9=1.099;C_3H_{10}=1.104; $C_4(SiH_3)$=1.829;C_6H_{11}=1.100;C_6H_{12}=1.101;<$C_2C_1C_5$=109.5;<$C_1C_2C_3$=107.6;<

$C_2C_3C_4$=112.8;<$C_3C_4C_5$=104.4;<$C_4C_5C_1$=105.4;<$C_6C_5C_1$=124.4;<$C_5C_1H_8$=122.6;<$C_1C_2H_9$=128.4;$C_4C_3H_{10}$=126.7;<$C_5C_4(SH_3)$=128.0;<$C_5C_6H_{11}$=127.3; <$C_5C_6H_{12}$=124.0; <$H_{12}C_6H_{11}$=109.0

C_1C_2=1.357;C_2C_3=1.480; C_3C_4=1.358; C_4C_5 =1.509; C_5C_1=1.513; C_5C_6=1.355; C_1H_8=1.100;C_2H_9=1.100;C_3H_{10}=1.100; C_4H11=1.100;$C_6(SiH_3)$=1.820;C_6H_{12}= 1.122;<$C_2C_1C_5$=110.2;<$C_1C_2C_3$=108.5 ;<$C_2C_3C_4$=108.8;<$C_3C_4C_5$=110.1;<$C_4C_5C_1$=102.1;<$C_6C_5C_1$=126.9;<$C_5C_1H_8$=122.5;<$C_1C_2H_9$=127.9;$C_4C_3H_{10}$=127.6;<$C_5C_4H_{11}$=123.3;<$C_5C_6(SiH_3)$=137.8; <$C_5C_6H_{12}$=111.0; <$H_{12}C_6(SiH_3)$=111.1

12

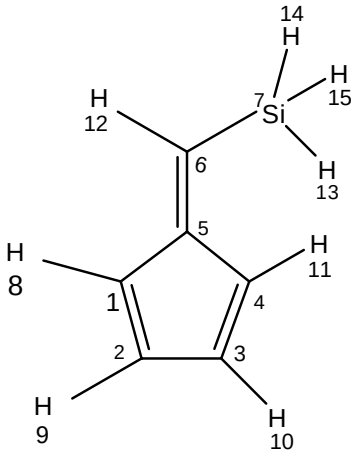


Table 2. Calculated heats of formation(in kcal/mole), dipole moments(in Debye) ,orbital energies(HOMO,LUOMO, in eV) and ionization energies (IP, in eV) for some mono substituted fulvenes.

Molecules	ΔH_f *(Kcal/mol)*	Dipole moment ,μ	HOMO*(eV)*	LUMO *(eV)*	IP *(eV)*
fulvene	67.343	0.345	-8.6742	0.3450	8.674
1	58.143	2.221	-8.8214	0.0299	8.821
2	58.606	1.715	-8.6416	0.0529	8.641
3	56.912	1.282	-8.8416	0.1214	8.841
4	58.106	1.968	-8.3554	0.2747	8.355
5	58.303	1.273	-8.1723	0.2978	8.172
6	59.143	1.124	-8.6157	0.3112	8.615
7	61.569	1.370	-8.1251	0.3449	8.125
8	65.459	1.343	-7.9718	0.3526	7.971
9	56.964	1.700	-8.3369	0.2865	8.336
10	55.108	0.568	-8.5990	0.2259	8.599
11	57.459	0.372	-8.5462	0.2318	8.546
12	54.527	0.306	-8.6365	0.1146	8.636

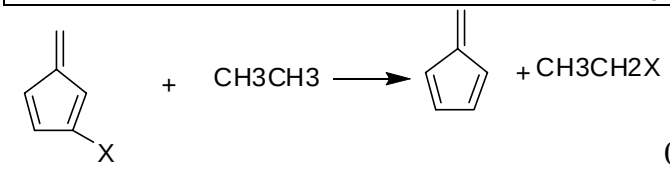
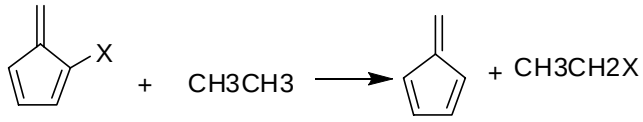
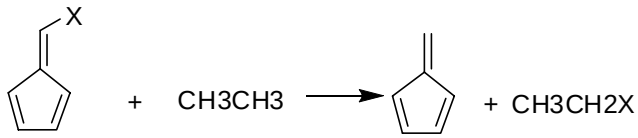
Table 3. Calculated electron densities for the fulvene and monosubstituted (Cl and SH) fulvenes .See Table 1 for numbering

Atom	fulvene	1	2	3	4	5	6
C1	4.034	4.008	4.049	4.021	4.019	4.053	4.017
C2	3.997	4.050	3.971	3.996	4.034	3.973	4.006
C3	3.997	3.753	4.090	4.004	3.816	4.090	4.001
C4	4.034	4.126	3.786	4.012	4.126	3.849	4.022
C5	3.959	3.949	4.003	4.043	3.945	3.987	4.048
C6	3.997	3.996	3.967	3.745	4.006	3.982	3.808
H8	1.099	0.992	0.988	0.996	0.995	0.991	1.001
H9	1.098	0.971	0.995	0.994	0.982	1.000	0.998
H10	1.099	0964	0.966	0.993	0.983	0.985	0.999
H11	1.093	0.989	0.984	0.988	0.993	0.986	1.005
H12	1.098	0.992	0.991	1.018	0.995	0.995	1.017
H13	1.093				0.882	0.884	0.879
H14							
H15							
Cl		7.208	7.211	7.189			
S					6.223	6.224	6.201

Table 4. Calculated electron densities for the monosubstituted (PH_2 and SiH_3) fulvenes .See Table 1 for numbering

Atom	7	8	9	10	11	12
C1	4.035	4.039	4.023	4.045	4.019	4.037
C2	4.010	3.996	4.010	3.989	4.020	4.000
C3	3.949	4.027	4.000	4.046	3.961	3.991
C4	4.064	3.986	4.032	3.997	4.083	4.046
C5	3.954	3.970	4.015	3.967	3.961	3.946
C6	4.005	4.000	3.912	3.991	4.001	4.023
H8	0.994	0.995	1.003	0.993	0.997	0.996
H9	1.008	0.997	1.000	1.009	0.993	0.999
H10	1.006	1.009	1.002	1.013	1.1015	1.000
H11	0.996	1.000	1.007	0.997	0.997	0.998
H12	0.997	0.996	1.038	0.997	0.997	1.027
H13	0.973	0.979	0.963	1.053	1.054	1.050
H14	0.974	0.975	0.961	1.053	1.057	1.046
H15				1.054	1.057	1.046
P	5.037	5.030	5.035			
Si				3.794	3.787	3.795

Table 5 .Evaluation of substituted effects using MINDO/3-forces calculations (energies Δ , in kcal/mol).

	Cl	SH	PH2	SiH3
	0.755	6.354	8.836	10.326
	0.292	6.156	4.946	7.977
	1.986	5.317	13.441	10.909

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