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MINDO/3-FORCES Study On Some Monosubstituted Triafulvalenes

دراسة الميندو/3 –فورسيز لبعض الترايفولفينات احادية التعويض

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Abstract:-

MINDO/3-FORCES calculations have been done after complete optimization of geometry on X-monosubstituted triafulvalene molecules , where X is CN, OH , NO_2, NH_2, CH_3, and cyclopropyl. It was found all these substituents are stabilizing . Also, all the substituents increase the dipole moment .Geometric parameters, heats of formation, orbital energies and the electron densities are reported

الخلاصة:-

أجريت حسابات الميندو/ 3-فورسيز المتضمنة الحصول على الشكل الهندسي ذي الأقل طاقة , على مركبات الترايفولفلين- احادية التعويض للمعوضات:- CN, OH , NO_2, NH_2, CH_3, cyclopropyl . ووجد إن جميع هذه المعوضات تؤدي آلي استقرار جريئة الترايفولفلين .كما, إن هذه المعوضات تؤدي آلي زيادة العزم ثنائي القطب . أيضا ,تم تدوين المتغيرات الهندسية , حرارات التكوين , الطاقات المدارية والكثافات ألالكترونية

Key words:-MINDO/3-FORCES version 6.00 1996 program , mono substituted triafulvalenes

Introduction:-

The fulvalenes are the class of hydrocarbons obtained by formally cross-conjugating two rings through a common exocyclic double bond[1]. The fulvalenes and their derivatives have wide industrial,biological and therapeutic conductivity applications[2].The ab initio calculations for triafulvalene were reported and it was found that the molecule is planar with D_{2h} symmetry[3] .However, there is no any experimental and or theoretical studies concerning the monosubstituted triafulvalene molecules.

The aim of present work is to study the X-monosubstituted triafulvalenes , where X is CN, OH , NO_2, NH_2, CH_3 , and cyclopropyl substituents by calculation based on the MINDO/3-FORCES[4-6] method. The molecular energy of the mono substituted triafulvalene , obtained from the semi emperical MINDO/3 method[7] was completely minimized according to the Murtagh- Sargent minimization technique[8] .The derivative of the energy was calculated , analytically, according to Pulay's Force method[9]. The applications the MINDO/3-FORCES method are well known[10-15]. The effect of X on the optimized geometry , heats of formation, dipole moments, HOMO-LUMO energies, electron densities and the stabilization of each molecule were reported..

Structural Detals

For the OH substituent , we assumed that OH is in the plane of the molecule according to the analogous calculation on fulvene molecule[16] .Introduction of substituent into the triafulvalene molecule increases the adjacent bond length (Table1) . This effect is more pronounced for NH_2 and NO_2, which is in agreement with the high dipole moment calculated (Table 2). All the substituent are found to produce a small decrease in bond angle to which the substituent is attached, with the exception of the OH substituent

Dipole Moments

All the substituents increase the dipole moment but the increment in case of the electron with drawing group NO_2, CN is more than that for the electron releasing OH, NH_2 , CH_3, cyclopropy, (Table 2)

Electron Densities

It can be seen from Table-3 that CN, OH, NH_2, CH_3 and the cyclopropyl 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. CH_3 and CN substituents are very weakly electron releasing. The NO_2 substituent shows an opposite effect to that found for OH, NH_2 , CH_3 and CN substituents, i.e. acts as electron with drawing. These results are in agreement with the calculations reported for the X- mono substituted fulvenes[16]

Stabilization by Substituents

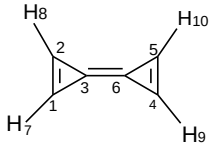
The stabilizing effect of a substituent is often assessed by using isodesmic reactions(conserved bond type)[17]. A positive heat of formation (Table 4) indicates stabilization of the reactant by substituent. The results show that all the substituents are stabilizing. It was found that NO_2 stabilizes the triafulvalene molecule more than other substituents because of the high dipole moment (Table 2).The CH_3 substituent shows slight stabilization, which may be due to the low dipole moment.

Orbital Energies

According to Koopmans' theorem (the negative HOMO is equal to to the ionization potential).The electron releasing NH_2, OH, CH_3 , and cyclopropy substituents are found to increase the energy of HOMO (Table-2) to a great extend .This effect is more pronounced in the case of NH_2 , which also increases the energy of the LUMO. The high energy of LUMO suggests a high stability. In the case of electron withdrawing substituents, such as CN and NO_2, the HOMO and LUMO decrease to a certain degree. The low energy of LUMO suggests a high reactivity (Table-2). . Conclusion:-The effect of X-substituent groups in the triafulvalene is resembles their effect in the fulvene[16].This is may be due to the similarity in structure in both of fulvenes and triafulvalenes .

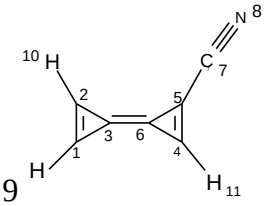
Table 1. Calculated geometric parameters (bond lengths are in Angestron and bond angles in degrees) of the mono substituted triafulvalenes..

1



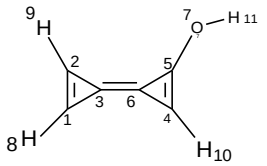
C1C2,1.321;C1C3,1.474;C2C3,1.474; C3C6,1.320 C4C5, 1.321; C5C6, 1.474; C4C6, 1.474; C1H7,1.088;C2H8,1.088;C4H9,1.088;C5H10,1.088
C1C2C3,63.4;C2C1C3,63.8;C1C3C2,53.2;C4C5C6,63.4;C5C4C6,63.4;C5C6C4,53.2;C2C3C6,153.4;C5C6C3,153.4;C1C3C6,153.4;C4C6C3,153.4;H8C2C1,150.5; H7C1C2 ,151.0;H10C5C4,151.0;H9C4C5,151.0.

2



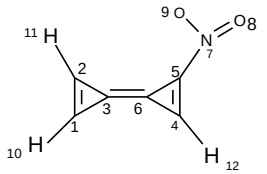
C1C2,1.322;C1C3,1.473;C2C3,1.473; C3C6,1.321 C4C5, 1.336 ; C4C6, 1.456; C5C6, 1.502; C1H9,1.088;C2H10;1.088;C4H11,1.089;C5C7,1.423;C7N8,1.161
C1C2C3,63.3;C2C1C3,63.3;C1C3C2,53.3;C4C5C6,61.4;C5C4C6,64.9;C5C6C4,53.7;C2C3C6,153.2;C5C6C3,151.7;C1C3C6,153.5;C4C6C3,154.5;H10C2C1,151.1;H9C1C2,151.0; H11C4C5,149.3;C7C5C4,152.1

3



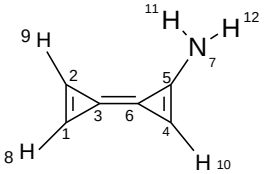
C1C2,1.321;C1C3,1.473;C2C3,1.474; C3C6,1.321 C4C5, 1.329 C5C6, 1.466; ; C4C6, 1.488; C1H8,1.088;C2H9,1.088;C4H10,1.086;C5O7,1.300;O7H11,0.954
C1C2C3,63.3;C2C1C3,63.3;C1C3C2,53.2;C4C5C6,64.1;C5C4C6,62.4;C5C6C4,53.4;C2C3C6,153.2;C5C6C3,153.3;C1C3C6,153.4;C4C6C3,153.1;H9C2C1,151.2;H8C1C2,151.1;O7C5C4,155.1;H10C4C5,153.2;H11O7C5,112.5.

4



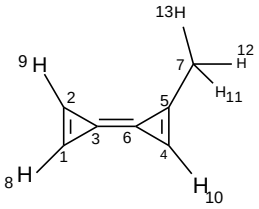
C1C2,1.323;C1C3,1.470;C2C3,1.470; C3C6,1.321 C4C5, 1.337; C5C6, 1.505; C4C6, 1.456;C1H10,1.087;C2H11,1.087;C5N7,1.391;N7O8,1.229;N7O9,1.228;C4H12,1.091
C1C2C3,63.2;C2C1C3,63.2;C1C3C2,53.4;C4C5C6,61.3;C5C4C6,65.0;C5C6C4,53.6;C2C3C6,153.2;C5C6C3,150.6;C1C3C6,153.2;C4C6C3,155.7;H11C2C1,151.2;H10C1C2,151.6;N7C5C4,152.2; H12C4C5,148.5;C8N7C5,113.7;O8N7O9,132.0

5



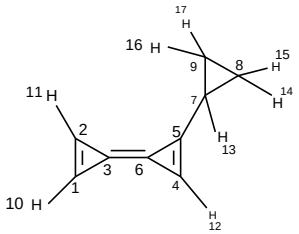
C1C2,1.320;C1C3,1.475;C2C3,1.475; C3C6,1.322;C4C5, 1.342; C5C6, 1.486; C4C6, 1.467;C1H8,1.088;C2H9,1.0882; C4H10,1.085;C5N7,1.324; N7H11 ,1.012 ;N7H12, 1.012
C1C2C3,63.4;C2C1C3,63.4;C1C3C2,53.1;C4C5C6,62.4;C5C4C6,63.4;C5C6C4,54.1;C2C3C6,153.2;C5C6C3,151.4;C1C3C6,153.6;C4C6C3,154.4;H9C2C1,151.1;H8C1C2 , 151.0;N7C5C4,151.6;H11N7C5,123.7;H12N7C5,235.9;H12N7H11,112.2

6



C1C2,1.321;C1C3,1.474;C2C3,1.474; C3C6,1.321 C4C5, 1.336 C5C6, 1.500; C4C6, 1.458;C1H8,1.088;C2H9,1.088;C4H10,1.089;C5C7,1.455;C7H11,1.112;C7H12,1.112 ;C7H13,1.112
C1C2C3,63.3;C2C1C3,63.4;C1C3C2,53.3;C4C5C6,61.5;C5C4C6,64.9;C5C6C4,53.6;C2C3C6,153 .2;C5C6C3,152.2;C1C3C6,153.4;C4C6C3,154.1;H9C2C1,150.9;H8C1C2,150.9;C10C4C5,149.6;C 7C5C4,152.4;C5C7H13,112.7;H13C7H12,105.6;H12C7H11,105.7

7



C1C2,1.321;C1C3,1.474;C2C3,1.474; C3C6,1.321; C4C5, 1.337; C5C6, 1.499; C4C6,1.458;C5C7,1.464;C7C8,1.516;C7C9,1.516;C8C9,1.484; C1H10,1.088;C2H11,1.088;C4H12,1.088; C7H13 , 1.119 ; C8H14 , 1.105 ; C8 H15 ,1.105;C9H16,1.105;C9H17,1.105
C1C2C3,63.3;C2C1C3,63.4;C1C3C2,53.2;C4C5C6,61.5;C5C4C6,64.7;C5C6C4,53.7;C2C3C6,153 .0;C5C6C3,152.6;C1C3C6,153.6;C4C6C3,153.6;C4C5C7,150.1;C5C7C8,128.1;C7C8C9,60.7;C8C 9C7,60.7;C8C7C9,58.6;H11C2C1,150.9;H10C1C2,150.9; C7C5C4,150.1;H14C8H15,107.6;H16C9H17,107.6;C5C7H13,108.5

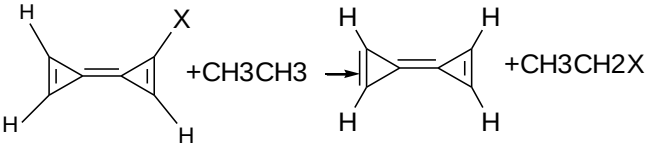
Table 2. Calculated heats of formation(in kcal/mole), dipole moments (in Debye) , orbital energies (HOMO, LUOMO, in eV) for the mono substituted triafulvalenes .See Table 1 for numbering

.molecule	ΔH_f	μ	.HOMO	LUMO
1	148.656	0.000	-6.9386	1.9911
2	159.047	2.053	-7.07500	1.2280
3	84.994	0.739	-6.7900	1.6340
4	117.414	5.530	-7.8140	-0.1100
5	128.896	1.569	-6.4450	1.7790
6	131.388	0.071	-6.8897	1.8121
7	152.601	0.288	-6.7920	1.7090

Table 3. Calculated electron densities for the mono substituted triafulvalenes .See Table 1 for numbering

Atom	1	2	3	4	5	6	7
C1	4.010	4.007	4.008	3.984	4.016	4.012	4.013
C2	4.010	4.009	4.006	4.004	4.001	4.010	4.010
C3	4.042	4.026	4.039	4.002	4.068	4.034	4.039
C4	4.042	3.986	4.221	3.854	4.185	4.014	4.028
C5	4.010	3.995	3.638	4.227	3.838	3.995	3.984
C6	4.010	4.057	4.049	4.030	4.020	4.057	4.054
C7		3.881				3.892	3.939
C8							3.982
C9							3.982
H7	0.969						
H8	0.969		0.966		0.973	0.969	
H9	0.969	0.964	0.966		0.971	0.969	
H10	0.969	0.965	0.941	0.945	0.947	0.970	0.970
H11		0.968	0.755	0.951	0.922	1.031	0.969
H12				0.967	0.919	1.023	0.969
H13						1.023	1.034
H14							1.006
H15							1.007
H16							1.007
H17							1.006
N7				3.855	5.140		
O8				6.592			
O9				6.587			
O7			6.411				
N8		5.143					

Table 4.Evaluation of substituted effects using MINDO-forces calculations (energies Δ ,in kcal/mol). $\Delta = \Delta H_{f,\text{product}} - \Delta H_{f,\text{reactant}}$



X	CN	OH	NO_2	NH_2	CH_3	cyclo.
Δ	11.348	19.236	29.57	23.645	10.664	11.101`

Acknowledgements

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