THEORETICAL STUDY OF THE INFLUENCE OF STERIC EFFECT TO THE ATE CONSTANT OF SOME DIELS- ALDER REACTIONS [+]

دراسة نظرية لتأثير الحشد الفراغي على معدل سرعة التفاعل لبعض تفاعلات ديلز – الدر

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Abstract

Computational studies with the factors affecting the steric energies of Diels-Alder addition and their correlation with the relevant physical properties of the product and reactant molecules were investigated. A single and multi – parametric linear regression analysis was applied with the rate constant as dependent and independent variables. One of the reactant (Dien or Dienophile) of four series was kept constant and the other reactants were varied. The products and reactants were influenced by all the molecular properties with different extent and different direction for these four serious of reactions. These properties included the total steric energy=E stretching +E bending +E torsion +E over lap +Evdw+E dipole-dipole. The polarity and the values of steric energies were increased due to high electrostatic repulsion power of Dienophile malic unhydride and hexachlorocyclopent-1-ene for series (i) and (ii) respectively. While the rate constants of tetracyanoethylene were increased with decreasing electrons affinity in series (iii) , and the low steric energies of anthracen in series (iv) as determined using MM2 program and this was due to its coplanarity.

المستخلص:

تم تحقيق دراسات بالحاسوب للعوامل المؤثرة على طاقات الحشد الفراغي لإضافة ديلز – الدر وترابط هذه العوامل الوثيق مع الصفات الفيزيائية للجزيئات المتفاعلة والناتجة من التفاعل.طبقت التحاليل الانحدارية المنفردة والمتعددة مع ثابت معدل سرع التفاعل كقيم معتمدة وغير معتمدة.عوملت احد المتفاعلات (الدايين آو الدايينوفيل) كمتفاعل ثابت بينما غيرت المتفاعلات الأخرى لأربع متسلسلات . كان تأثير الناتج بوساطة خصائص الجزئية بإشكال واتجاهات مختلفة شملت :طاقة الحشد الفراغي الكلية = طاقة (التمطى + الانحناء + الالتواء +التداخل + قوى فاندرفال + قوى ثنائية القطب). إن الاستقطابية وقيم طاقات الحشد تزداد بسبب زيادة قوة التنافر الكهروستاتيكية للداينوفايل انهيدريد الماليك وسداسي كلور–بنتين– الحلقي للمتسلسلتين (i و ii) على التوالي . أما معدل سرع

[+]Received on 17/6/2008 ,Accepted on 29/4/2009 .
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التفاعل لرباعي سيانو الاثلين فتزداد بنقص الألفة الاليكترونية فى المتسلسلة (iii) ،كما تقل قيم طاقة الحشد الفراغى للمتسلسلة(iv) حسب قياسات برنامج (MM2) وبسبب تسطح الجزيئة .

Introduction:

The Diels-Alder reaction was generally considered the "Mona Lisa" of reactions in organic chemistry since it required very little energy to create the very useful cyclohexene ring[1-2] . This reaction has been studied extensively both because of its importance in natural products synthesis and because it can be understood in detail by means of computational chemistry by MM2 molecular mechanic and semi-empirical methods. It involved the reaction between two linear π systems of length 2 and 4, respectively [3] The product was again a π system and thus might react again in Diels-Alder reaction. Recently, it has been used to synthesize particular classes of polymers [4] .

Fig.(1)displayed the reaction network obtained by repetitive Diels-Alder reactions of a simple initial mixture.

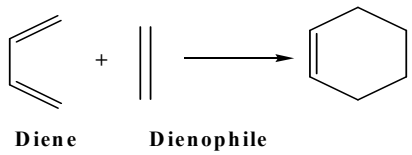


Fig (1) The Diels-Alder reaction

The structure of the Diels-Alder adducts have shed light on the respective role of steric and electronic factors on the stereo selectivity of the cyclo-addition [5]. As part of continuous program directed toward a computational studies with organic reactions [6], it was became of interest to investigate the influence of steric effect (the bulky group)of products on the rate constant of some Diels-Alder reactions.

Experimental:

All the simulations were calculated by MM2 molecular mechanic methods (force field) and semimperical methods in addition to the geometry (three dimensional structure) of compounds were established by Chem3D Ultra; Molecular Modeling and Analysis; (version 6.0.3); Cambridge Soft Corporation (2004).A statistical program that used for correlation analysis was Special Program for Social Sciences (SPSS).

Results and Conclusions:

Within the scope of the present search, the rate constants of some Diels-Alder reactions were correlated with the relevant physical properties of the products of reacting molecules with the aim to gain in to the factors that influenced this addition reaction and to obtain information about the molecular physical properties of products include the components of total steric energy[E total],which were attributed to bond stretching [E str.],angle bending[E bend], 1.4- bonded interaction and 1.4 non bonded interaction torsion interaction[E tor] and coupled energy terms[E cross-terms].The cross-terms combine two interrelated motions[7].

The single and multi-parameter linear regression analysis were applied for these reasons with the rate constants from literature as a dependent variables and the molecular physical properties as the independent variable [8].

One of the reactant dienophile table (1) or diene table(2) with each of four series of Diels-Alder reaction (Tables 3-6) was kept constant and the other was varied. The chemical structure of all products were listed in table (6). The stable relative position of atoms in the molecule was a function of through-bond and through –space interactions which may be described by relatively simple mathematical relationships.

Tables (7-10) gave the result of single and multi – parametric linear regression analysis of series(1-4) with the structures of all products, these tables were showed that all molecular properties previous mentioned influence the reaction, but with different extent and different direction for different series. A single parameter was not enough to describe the rate behavior of each series and more than one was necessary, in most cases a single parameter gives a correlation coefficient(R) lower than 0.9 while two parameters gave a correlation coefficient between (0.9-0.95). The correlation coefficient was increased to more than 0.95 when three parameters were chosen one of these parameters was belonging to steric energy which included ,stretching, bending stre-bend ,vdw ,torsion and dipole-dipol the relative weight of these parameters differed from series to series. Table (7) showed series 1,the reaction rate was increased with decrease of magnitude of a1 stretching and increase values of,a2 bending and a3 dipole dipole interaction according to higher polarities that form electro statistic repulsion. In Table (8) series 2,stretching, bending and torsion affecting reaction rate which gave correlation factors . R =0.450 and R2=0.203 . This caused decrease in reaction rate due to the compound having electron demand and six big chlorine group which have height steric energy . In Table (8) series 3 ,the affected factors of the dienophile tetracyanoethene were (a1 bending a2 torsion and a3vdw) which decreased with decreasing reaction rate due to correlation coefficient R, R2 which belong to compound possessing high resonance effect due to alternating the double bond of ethene and triple bond of cyano. In Table (10) series 4,, the factor influenced the reaction rate of the dien 9,10 dimethylanthracene were dipole-dipole interaction due to value of correlation coeifficient R=1,R2=0.999 and this belong to high resonance of bi bond in the dien. The results of regression analysis showed that the reaction was influenced by all factors (previous mentioned) with different extent and direction.

Table (1) The names and structures of all used dienophiles

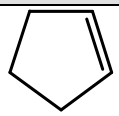
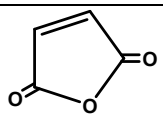
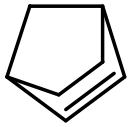
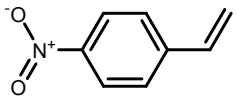
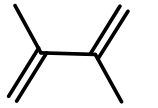
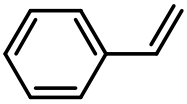
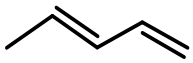
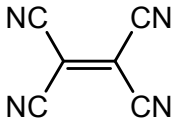
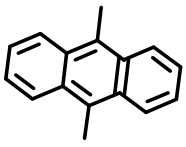
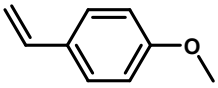
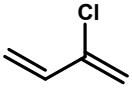
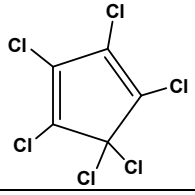
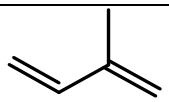
No.	Name	structure
1	Cyclopentene	
2	malic anhydride	
3	norbornene	

Table (2)The names and structures of all used dienes

No.	name	structure	No.	name	structure
4	p-nitrostyrene		12	2،3-dimethylbutadiene	
5	styrene		13	1-methoxybutadiene	
6	trans-1-methylbutadiene		14	tetracyanoethene	
7	1,3-cyclohexadiene		15	butadiene	
8	9.10-dimethylanthracene		16	cyclopentadiene	
9	p-methoxystyrene		17	furan	
10	2-chlorobutadiene		18	hexachloro cyclopentadiene	
11	2-methylbutadiene				

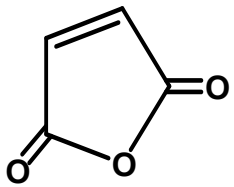


Table (3) :
The physical properties of malic anhydride (2) vs Dienes

Dienes	strech	bend.	strech. bend	torstion	Non 4VDW	1,4 VDW	Dipole/dipole	Total steric energy of product	rate constant
6	0.68944	3.6128	0.2225	5.3791	-1.7847	5.5287	14.4493	28.0918	22700E-8
7	80.7453	140.2725	1.6106	8.7346	25.3682	77. 6784	13.5777	347.9873	13200E-8
10	0.5832	2.8315	0.1902	4.4154	-2.0773	5.1059	15.6323	26.6813	690E-8
11	0.5619	2.8425	0.1825	5.0544	-2.2624	5.1720	14.1689	25.7199	15400 E-8
12	0.7132	3.8801	0.1756	4.8038	-2.0463	5.6205	14.0156	27.1623	33600 E-8
13	0.8966	4.4258	0.3323	6.2313	-2.1502	7.8894	15.2173	32.8426	84100 E-8
15	0.5412	2.7892	0.1848	5.2728	-1.7267	4.7609	14.4144	26.2365	6830 E-8
16	2.9716	41.547	-1.0500	6.4826	-0.6128	9.1431	14.0018	72.4840	22700 E-8

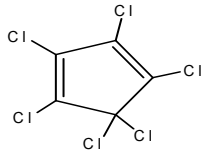


Table (4)The physical properties of hexachlorocyclopentadiene 18 vs. dienophile

dienophile	strech.	bend.	strech. bend	torstion	Non 4VDW	1,4 VDW	Dipole/dipole	Total steric energy of product	rate constant
1	3.2656	25.8874	-0.7571	6.3037	-1.7560	7.1782	27.4555	67.5774	59E-6
2	5.5986	46.8879	-0.8176	5.3314	-1.4512	11.4355	49.7448	116.7292	29E-6
3	4.6925	41.0233	-1.2081	13.828	-0.3353	12.3830	25.741	96.1162	72E-6
4	23.6970	151.9117	-9.5323	8.7017	1.9476	34.3353	22.8030	234.0322	538E-6
5	23.6767	151.7447	-9.5960	8.7750	1.6591	33.9604	22.8165	233.0364	739E-6
9	22.8523	151.7941	-9.1223	10.9403	0.7016	36.5889	22.7114	236.4664	1580E-6
16	3.2381	25.3077	-0.7525	9.9177	-2.0707	9.0143	25.7079	70.3625	15200E-6
17	3.3019	24.3849	-0.6738	9.1342	-2.3575	9.7537	28.8284	72.3717	333E-6

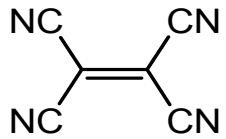


Table (5)The physical properties of tetracyanoethene 14 vs. dienes

Dienes	strech	bend	strech. bend	torstion	Non 4VDW	1,4 VDW	dipole/dipole	Total steric energy of product	rate constant
6	0.0879	0.2844	0.0165	-4.9598	-0.0441	1.9336		-2.6816	2060E-5
7	0.1427	0.2109	0.0210	1.0741	-0.5662	3.3557	0.0937	4.3319	7290 E-5
10	0.1051	0.6017	0.0292	-3.1798	0.4064	2.0131		-0.0242	1.0 E-5
11	0.1862	1.1891	-0.002	-3.6158	0.5587	1.9748		0.2927	1130 E-5
12	0.4569	1.1299	-0.0159	-3.9757	0.9843	2.8068		1.4830	24300 E-5
13	0.1967	0.7734	0.0651	-1.6452	-0.2751	4.2426		3.3575	598000 E-5
16	0.5749	1.7381	0.0223	-3.4494	0.2822	5.6861	0.0963	4.9506	123000 E-5
15	0.0471	0.1570	0.0088	-4.2398	-0.0241	1.5612		-2.4898	519 E-5

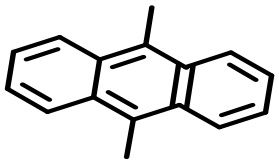


Table (6)The physical properties of 9,10-dimethylanthracene 8 vs. dienophile

dienophile	strech.	bend	strech. bend	torstion	Non 4VDW	1,4 VDW	Dipole/dipole	Total steric energy of product	rate constant
1	0.2192	5.6609	-0.0578	2.5324	-0.1500	0.6347	-0.4046	8.4348	7.8E-6
2	1.9098	14.6751	-0.4681	-2.2599	-0.8600	3.1256	14.7035	30.8260	141000 E-6
3	0.9226	16.6	-0.7085	5.4280	-0.7869	4.0315	0.1632	25.6498	36 E-6
4	7.7540	11.7728	-23.6780	-13.9700	-1.1413	2.4310	0000	-16.8315	602 E-6
5	0.2118	0.8797	0.0234	-10.7398	0.2272	4.4939	000	-4.9039	70 E-6
9	0.3821	1.7667	0.0136	-7.1164	-0.6147	7.3084	000	1.7398	56 E-6

Table (7):The result of single and multi – parametric linear regression analysis of series(1)

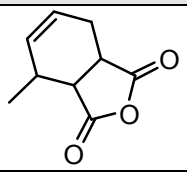
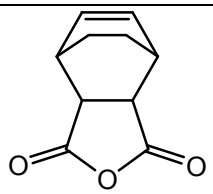
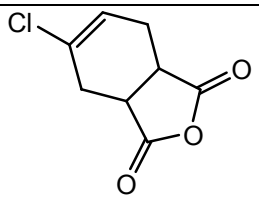
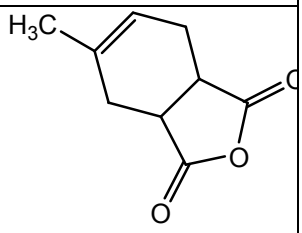
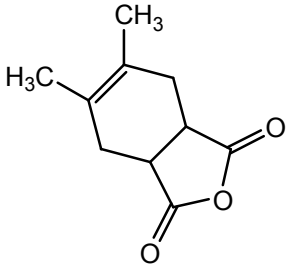
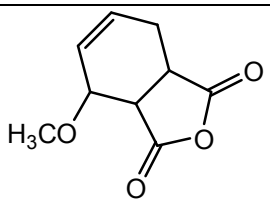
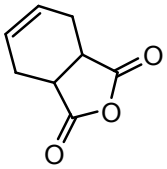
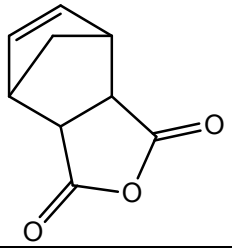
No. of Series	Reactants	Products	R	R^2	Std. Error	a_1	a_2	a_3
1	6 vs. 2		0.998	0.996	0.00172	-0.0108 strech	0.006 bend	0.006 Dipol-Dipol
	7 vs. 2							
	10 vs. 2							
	11 vs. 2							
	12 vs. 2							
	13 vs. 2							
	15 vs. 2							
	16 vs. 2							

Table (8):The result of single and multi – parametric linear regression analysis of series(2)

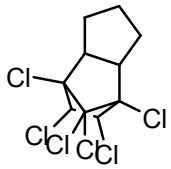
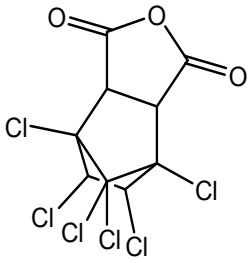
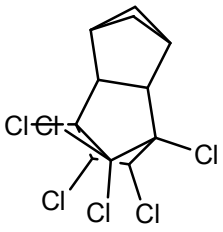
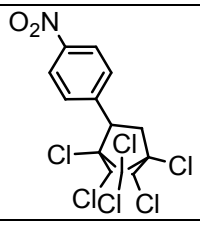
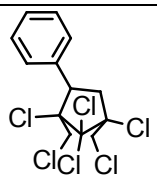
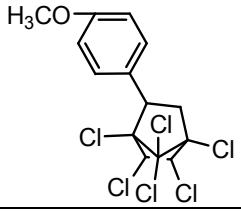
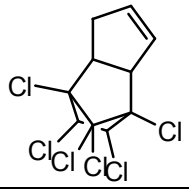
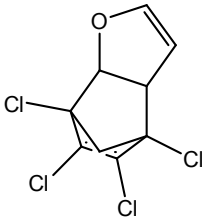
No. of Series	Reactants	Products	R	R^2	Std. Error	a_1	a_2	a_3
2	1 vs. 18		0.450	0.203	0.006272	0.003 Strech.	0.01 Bend	0.001 torstion
	2 vs. 18							
	13 vs. 8							
	4 vs. 18							
	5 vs. 18							
	9 vs. 18							
	16vs. 18							
	17 vs. 18							

Table (9):The result of single and multi – parametric linear regression analysis of series(3)

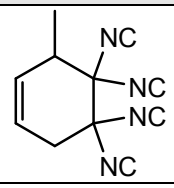
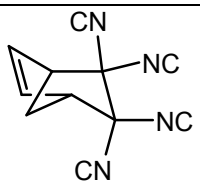
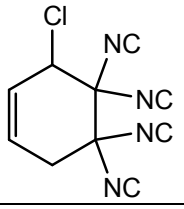
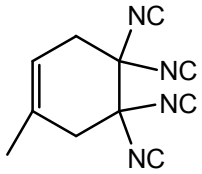
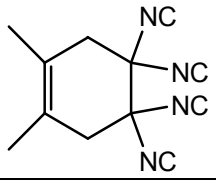
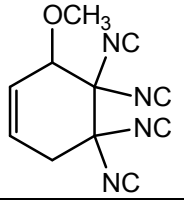
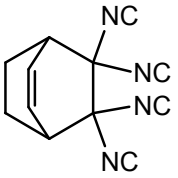
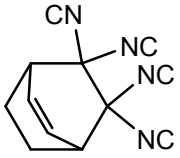
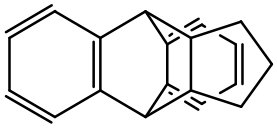
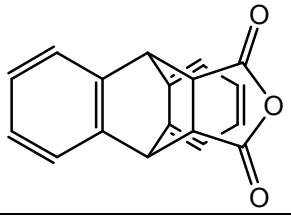
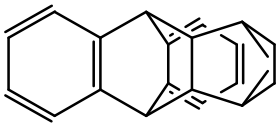
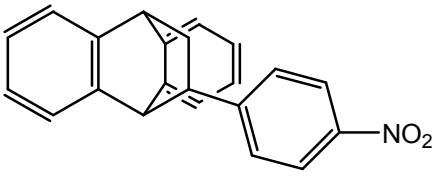
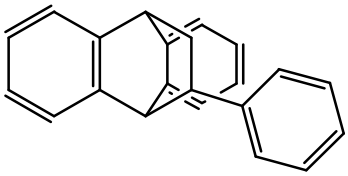
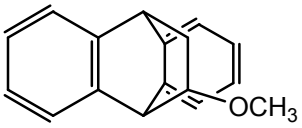
No. of Series	Reactants	Products	R	R^2	Std. Error	a_1	a_2	a_3
3	**6 vs. 14**		0.730	0.534	1.45391	-0.651 bend	-0.880 torstion	3.512- VDW
	7 vs. 14							
	10 vs. 14							
	11 vs. 14							
	12 vs. 14							
	13 vs. 14							
	15vs. 14							
	16 vs. 14							

Table (10):The result of single and multi – parametric linear regression analysis of series(4)

No. of Series	Reactants	Products	R	R^2	Std. Error	a_1	a_2	a_3
4	1 vs. 8		1.000	0.999	0.20143	0.095 Didipole - Didipole	-	-
	2 vs. 8							
	3 vs. 8							
	4 vs. 8							
	5 vs. 8							
	9vs. 8							

Conclusion:

The polarity was increased in addition to increase the reaction (appears from R correlation factors) by the high electrostatic repulsion power of dienophiles malic anhydride (furan-2,5-dione)(i) (in spite of its coplanarity)and this produced a high values of steric energies [9-10].

The hexechlorocyclopent-1-ene (ii) has high steric energies duo to their six substituted chloride atoms, these electrons withdrawing atoms decreased the electrons density and decreased the reaction rate [11-12] which is inverse electron demand appear from R value It was worthy to motioned that for the same reason, the rate constant of ethene-1, 1, 2, 2-tetracarbonitrile (iii) increased with decreasing electrons affinity represented by a lower electron density and a higher ionization potential [11-12].

Fig (1)
Coplanarity of 9,10-dimethylanthracen(iv)

The stretch and bend. Values of malic anhydride vs. diene 7(Table 3) was due to the structure of six membered unsaturated 1,3-cyclohexadiene [6].

Finally anthracen (iv) in these serious have low steric energies (as determined using MM2 program) ,and this was due to its coplanarity[6], Fig(1).

The benzene rings adopted a new role: instead of lying the structural basis for extended ð-conjugation, it only served as a stable, regularly shaped branching point and space filler. The consequences of this function for the design of shape-persistent 3D macromolecules was immense[13],although , individual ring may not be as well stabilized as an isolated benzene ring, because anthracene has only 14 pi electrons compered with 18 needed for three fully independed aromatic rings, but when its center ring reacted as a diene, the product has two fully aromatic rings, each with six pi electrons, as shown in Fig (2)[14]

As stereoselectivity study in Diels-Alder reactions, There were endo and exo products (at which the dienophiles substituted groups were near of or far from the unsaturated double bond). Interestingly the later was more preferable as a thermodynamic product of this reaction, the former as a kinetic product duo to the VandeWalles interactions [12]. Fig (2) showed a representative for these phenomenon by the reaction of cyclopentadien(16) with malic anhydride(2)[6,15]

The thermodynamic product was the lowest energy product, whereas the kinetic product is the most easily formed product. The thermodynamic product was found by comparing molecular energies of geometrically optimized two final product confirmations. The exo adduct has lower heat of formation (Kcal/mole) 81.17587 Kcal/mole, than endo 295.09296.Table (4).

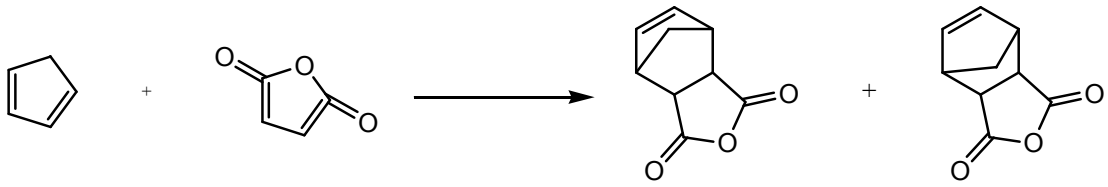


Fig (2): Exocyclopentadien(16) with malic anhydride(2)

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