Electronic Structure of Some Chalcone Derivatives.
I. Ground State Geometric Parameters and Charge Density Distributions, AM1-MO Treatment

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Abstract. The ground state geometries of 1,3-diphenyl–2- propene-1-one, 3-(3⁻-tolyl)–1- phenyl–2 - propene-1- one, 3-(4⁻-bromophenyl)–1 -(4⁻-methoxyphenyl)–2-propene-1-one, 3-(3⁻,4⁻ methylene dioxy phenyl–1–(4⁻-methoxyphenyl)–2-propene-1-one and 3-(3⁻,4⁻-methylene dioxy phenyl)–1-(4⁻-bromophenyl)–2- propene-1-one have been examined theoretically. Equilibrium geometries were determined using AM1-MO. All (3N-6) degrees of freedom were considered in the optimization process. The calculated geometric parameters of chalcone derivatives are analyzed in terms of total energy, electronic energy, core-core repulsion energy, ionization potential, electron affinity, energy gap, heat of formation, dipole moment, net charges, bond order and charge density maps (HOMO and LUMO). The substituents effect on geometry, energetics and relative stability of the studied derivatives are also analyzed.

Introduction

Chalcones are compounds of biological and industrial importance. They are currently the subject of extensive investigations and a wide range of their biological activities is being explored[1-14]. Chalcones are precursors to the flavonoids natural products, which play a significant role in the disease and parasite resistance of plants. In fact, there is interest in the use of chalcone derivatives for pharmaceutical agents including antibiotics, antitumor, antimicrobial, antifungal, antiinflammatory and antimalarial agents.

The stability of chalcone derivatives [Ar-(C = O)-C = C-Ar⁻] depends upon the various types of interactions between different moieties [Ar-(C = O)- and

C = C-Ar¯], the polarization of the –(C = O)-C = C group and the nature of the substituent Ar¯ and Ar.

Chalcones may exist in two forms trans –(s-cis)–1, 3-diphenyl-2-propene-1-one (a) and cis-(s-cis)-1, 3-diphenyl-2-propene-1-one (b):

(a)   (b)
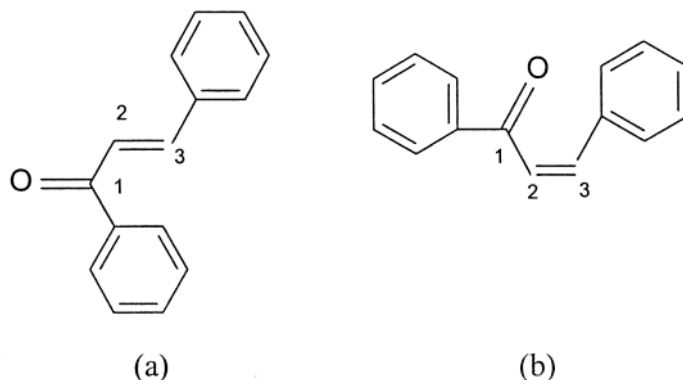
Chalcone is quasiplanar and can undergo quite large amplitude torsional motion[15]. Cis –(s-cis) structure (b) is expected to be nonplanar because of steric hindrance between the carbonyl oxygen and a phenyl ring[16].

The main objective of the present work is to investigate theoretically the electronic properties that underlie the activity of chalcones. Detailed investigation of the electronic structure is facilitated via the analysis of the charge density maps and the substituent effects on the geometry, energetic and relative stability of some chalcone derivatives.

Computational Procedure

AM1-MO semi-empirical quantum chemical method[17] has been used to calculate the theoretical electronic properties of the studied chalcones. Full geometry optimization of such large molecules would involve at least 110 degrees of freedom. This is computationally very expansive if one wants to utilize a reasonable basis set at the ab-initio level of the theory. Hence the use of the reliable semi-empirical AM1-MO method becomes essential since it takes a very good account of the directional character of bonding and describes the polar bond much more accurately than do any other methods.

Results and Discussion

a – Acrolein (CH$_2$ = CH – CHO)

Acrolein is a basic chromophore in the structure of chalcones, therefore, to study the electronic structure of chalcone derivatives, first, one studies the elec-
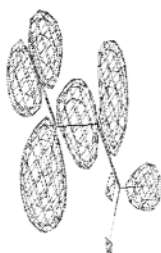
tronic structure and the ground state properties of acrolein as a reference. Optimized geometry and ground state properties are presented in Fig. 1 & 2. The charge density maps (HOMO and LUMO) are given in Fig. 1. Among the values given in Fig. 2 several remarks can be considered:
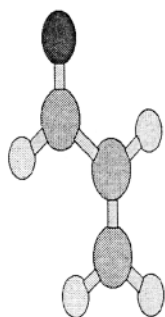
(a)   (b)
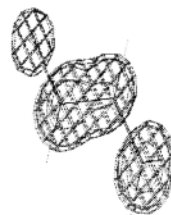
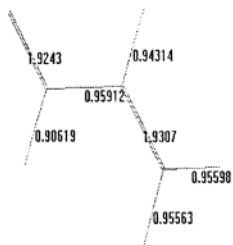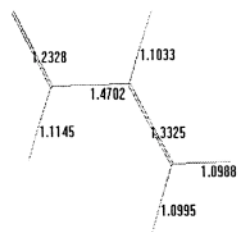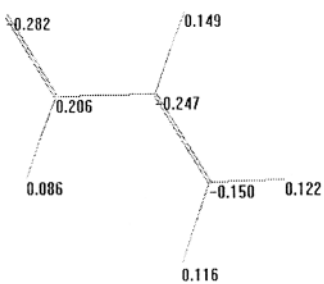(c)   (d)

Fig. 1. Final geometry (a) numbering system, (b) HOMO, (c) LUMO and (d) of acrolein.

(a)

(b)

(c)

Fig. 2. Bond order (a) bond length, (b) net charge and (c) of acrolein.

1 – The bond lengths computed theoretically for acrolein are consistent with that for aldehyde (C = O, 1.23 Å) and ethylene (C = C, 1.33 Å) molecules, indicating that no interaction between two moieties C = O and C = C groups.

2 – The computed bond order for C = O, C_1-C_3 and C_3-C_4 (c.f. Fig. 2) indicates no conjugations between these bonds and most of charge density localized on these bonds.

3 – The computed net charges on different centers indicating that acrolein is highly polar compared with the σ-frame polarized opposite to the π-frame (c.f. Fig. 2, net charges).

4 – The computed energy gap (ΔE = E_{LUMO} − E_{HOMO}) is 10.56 eV. The HOMO is of σ-type whereas, LUMO is of π-type.

b – Trans-(s-cis)-1,3-diphenyl-2-propen-1-one (I)

Final geometry, numbering system, HOMO and LUMO charge density maps are presented in Fig. 3. Ground state properties and geometric parameters are presented in Tables 1-3. Among the values given in these tables, some general remarks ought to be made:
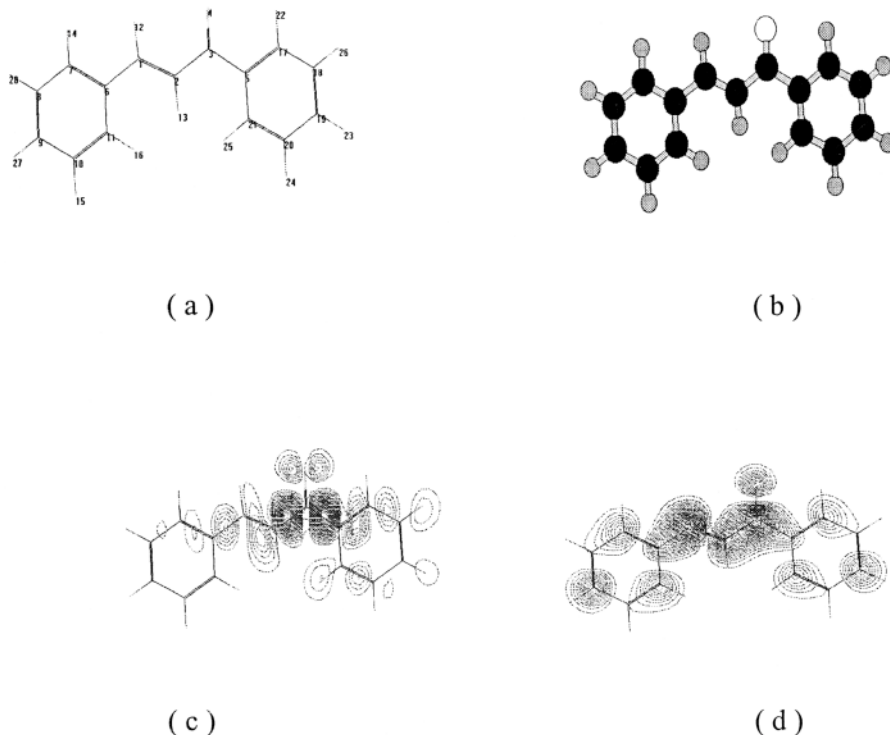

(a)

(b)

(c)

(d)

Fig. 3. Numbering system (a) final geometry, (b) HOMO, (c) LUMO and (d) charge density maps for: 1,3-diphenyl-2-propene-1-one.

Table 1. Heat of formation ΔH$_f$, total energy E$_T$, electronic energy E$_{elec}$, core-core energy E$_{core}$, ionization potential I.P., electron affinity E.A., energy gap ΔE and dipole moment μ for the studied chalcones.

Chalcone	I	II	III	IV	V
Parameter:					
ΔH$_f$, kcal	32.8414	25.2414	0.4962	−63.7567	−20.0288
E$_T$, eV	−2404.5191	−2560.3863	−3219.9595	−3648.5182	−3512.2202
E$_{elec}$, eV	−13573.4439	−15076.2490	−18417.2626	−21883.9837	−19998.9439
E$_{core}$, eV	11168.9248	12515.8627	15197.3032	18235.4655	16486.7236
I.P., eV	9.2830	9.2199	9.2662	8.9280	9.0378
E.V., eV	0.7446	0.7164	0.9834	0.8449	0.9877
ΔE, eV	8.5384	8.5035	8.2828	8.0831	8.0493
μ , D	2.859	2.780	3.417	4.008	2.554

Table 2. Bond order and their components and net charge on active centres for the studied chalcones.

Chalcone	I	II	III	IV	V
Bond order					
C$_1$ − C$_2$					
s − σ	0.0975	0.0975	0.0974	0.0976	0.0974
ρ − σ	0.3809	0.3808	0.3818	0.3803	0.3796
ρ − π	0.8709	0.8701	0.8763	0.8745	0.8820
C$_1$ − C$_6$					
s − σ	0.0771	0.0773	0.0767	0.0766	0.0762
ρ − σ	0.4256	0.4250	0.4266	0.4263	0.4282
ρ − π	0.0907	0.0912	0.0898	0.0907	0.0841
C$_2$ − C$_3$					
s − σ	0.0791	0.0789	0.0801	0.0793	0.0797
ρ − σ	0.3821	0.3819	0.3821	0.3827	0.3822
ρ − π	0.0778	0.0779	0.0746	0.0752	0.0747
C$_3$ − C$_5$					
s − σ	0.0821	0.0819	0.0842	0.0838	0.0817
ρ − σ	0.3785	0.3789	0.3736	0.3749	0.3776
ρ − π	0.0574	0.0558	0.0704	0.0669	0.0601
C$_5$ − C$_{17}$					
s − σ	0.0828	0.0829	0.0819	0.0823	0.0825
ρ − σ	0.4142	0.4134	0.4191	0.4169	0.4168
ρ − π	0.4285	0.4313	0.3904	0.3975	0.4250

Table 2. Contd.

Chalcone	I	II	III	IV	V
$C_6 - C_7$					
$s - \sigma$	0.0838	0.0851	0.0839	0.0845	0.0845
$\rho - \sigma$	0.4126	0.4099	0.4126	0.4073	0.4070
$\rho - \pi$	0.4140	0.4228	0.4136	0.3571	0.3569
Net charge					
C_1	0.0342	−0.0330	−0.0437	−0.0381	−0.0334
C_2	−0.2419	−0.2431	−0.2289	−0.2367	−0.2399
C_3	0.2969	0.2971	0.3024	0.3019	0.2959
C_4	−0.3021	−0.3007	−0.3116	−0.3091	−0.2987
H_{12}	0.1473	0.1465	0.1516	0.1503	0.1516
H_{13}	0.1367	0.1373	0.1315	0.1346	0.1389
C_5	−0.1408	−0.1406	−0.1803	−0.1802	−0.1321
C_6	−0.0700	−0.0660	−0.0524	−0.0678	−0.0772

Table 3. Geometric parameters (bond lengths, bond angles and dihedral angles) of the ground state for the studied chalcones.

Chalcone	I	II	III	IV	V
Bond length (Å)					
$C_1 - C_2$	1.3439	1.3439	1.3434	1.3446	1.3437
$C_2 - C_3$	1.4721	1.4721	1.4730	1.4731	1.4721
$C_3 - C_4$	1.2414	1.2404	1.2433	1.2426	1.2415
$C_3 - C_5$	1.4792	1.4801	1.4780	1.4777	1.4828
$C_1 - H_{12}$	1.1090	1.1091	1.1081	1.1086	1.1085
$C_1 - H_{13}$	1.1004	1.1104	1.0983	1.0994	1.1007
$C_3 - C_6$	1.4519	1.4520	1.4537	1.4529	1.4538
Bond angles (degrees)					
$< C_1 C_2 C_3$	121.57	121.54	122.11	121.26	121.38
$< O_4 C_3 C_2$	122.15	122.38	120.95	121.48	121.65
$< C_2 C_3 C_5$	116.66	116.28	118.38	117.60	117.63
$< C_2 C_1 C_6$	125.68	125.84	124.66	125.68	124.90
$< C_2 C_1 H_{12}$	118.96	118.81	119.47	119.19	119.61
$< C_1 C_2 H_{13}$	122.23	122.44	120.98	122.13	121.92
Dihedral angles					
$< C_1 C_2 C_3 O_4$	−2.9339	4.6201	0.0255	−7.6194	−15.6490
$< C_1 C_2 C_3 C_5$	−178.0987	−176.6703	−179.9745	172.3922	164.4280
$< C_3 C_2 C_1 C_6$	179.3616	−179.1550	−179.9745	179.4610	−178.3187
$< H_{12} C_1 C_2 C_3$	−1.0709	0.6089	0.0255	−0.1999	119.6064

1 – Replacement of the two hydrogen atoms (5&7) of acrolein by two phenyl groups (I) has a significant effect on the geometry of the acrolein moiety. The $r_{C=C}$, $r_{C=O}$, r_{C1-C6} and r_{C3-C5}, get longer. One can understand the elongation of these bonds as a result of the involvement of the two phenolic groups in a competitive conjugative interaction with the acrolein moiety, which results in a weakening of these bonds, and a consequent elongation is observed (c.f. Table 3).

2 – The involvement of the two phenyl groups in a competitive interaction with acrolein appears also with increase of negative charge on O, C_3 and C_4 atoms with a decrease of the bond order of C = O by 0.07 e and for C = C by 0.09 e.

3 – The two phenyl groups destabilize the HOMO and stabilize the LUMO of (I) and hence the energy gap of (I) decreases by 0.539 eV ($\approx$ 13 kcal). As the energy gap decreases, the reactivity of compound gets larger.

4 – The dipole moment computed for acrolein is 3.069 D. Phenyl substitution as in (I) decreases the dipole moment by 0.21 D. The decrease of dipole moment of (I) can be explained by the charge transfer in the opposite direction of the dipole moment vector of acrolein.

5 – The HOMO of (I) is π-type consisting of 62% on Ar, 3% on Ar$^-$ and 35% on acrolein moiety. The LUMO is also π-type consisting of 53% on acrolein moiety, *i.e.* about 20% of the charge transferred from phenyl moiety to acrolein. The reason why acrolein moiety, groups and atoms become the active centers for chalcone derivatives.

c- 3-(3¯-tolyl)-1-phenyl-2-propene-1-one (II)

Final geometry, HOMO and LUMO charge density maps are presented in Fig. 4. Ground state properties and geometric parameters are presented in Tables 1-3. Some general remarks ought to be made:

1 – If one H-atom of the phenyl attached to the ethylenic group is replaced by a methyl group as in (II), no change in the geometry of (I) is observed.

2 – The only traceable change in the geometry is the alteration of the bond angles. The observed alteration of the bond angles is associated with special rearrangement of the nuclear frame to minimize the steric hindrance caused by the bulky tolyl group.

3 – The ionization potential (IP) estimated theoretically for (II) is less than the IP of (I). Hence, the methyl substitution destabilizes the HOMO and decreases and energy gap of (II). Therefore, the reactivity of (II) is expected to be greater than (I).

4 – The computed dipole moment for (II) is 2.780 D, which is less than (I) by 0.08 D. Again, the methyl substitution increases the amount of charge transferred in the opposite direction of the dipole moment vector of acrolein moiety.

5 – The HOMO and LUMO of (II) both are of π-type. Methyl substitution increases the amount of charge transferred from aryl moiety to acrolein moiety.
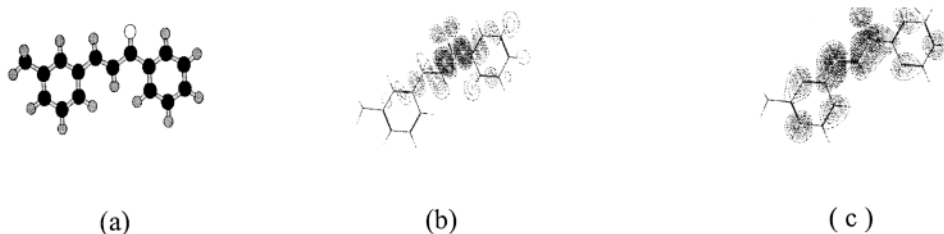

(a)   (b)   (c)

Fig. 4. Final geometry (a) HOMO, (b) LUMO and (c) charge density maps for: 3-(3⁻-tolyl)–1-phenyl–2-propene-1-one.

d- 3-(4⁻-bromophenyl)–1-(4⁻-methoxyphenyl)–2-propene-1-one (III)

One H-atom in phenyl attached to C = C group is replaced by Br and H-atom of phenyl attached to C = O group by OCH_3 in (I) to give (III). Final geometry, charge density maps and geometric parameters are given in Tables 1-3 and Fig. 5. The following remarks are considered:

1 – The dipole moment computed for (III) is greater than that of (I) by 0.6 D. The high polarization of the σ-frame seems to be responsible for the higher value of the dipole moment.

2 – Elongation of the C = C and C = O groups of acrolein is due to the increase of bond order of these bonds.

3 – Compound (III) becomes more polar due to the substituents (Br and OCH_3) as indicated from the net charge on acrolein moiety (atoms and bonds).

4 – Dramatic change in bond angles of (III) to accommodate the steric hindrance of the two bulky groups Br and OCH_3.

5 – Substitution of Br and OCH_3 destabilizes the HOMO of (III) and stabilizes LUMO. Hence, the energy gap of (III) is less than that of (I) by ≈ 0.3 eV and consequently the reactivity of (III) is greater than (I).

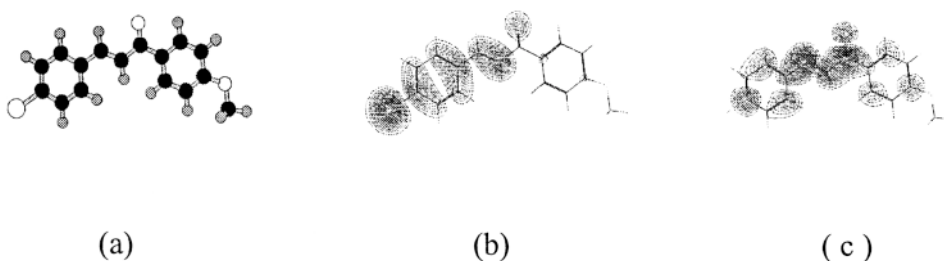(a)   (b)   (c)

Fig. 5. Final geometry (a) HOMO, (b) LUMO and (c) charge density maps for: 3-(4⁻bromophenyl)–1-(4⁻-methoxyphenyl)–2-propene-1-one.

e - 3-(3¯,4¯-methylenedioxyphenyl)-1-(4¯-methoxyphenyl)–2-propene-1-one (IV)

Replacement of *p*-Br in the ring attached to C = C group in (III) by phenyl dioxy methylene leads to (IV). Final geometry, charge density maps and geometric parameters are given in Fig. 6 and Tables 1-3. One can observe the following:

1 – The computed dipole moment of (IV) is greater than that of (III) by ≈ 0.6 D. The high polarization of the σ-frame of (IV) and the amount of the charge transferred in the same direction of the dipole moment vector of the acrolein moiety seem to be responsible for the high value of the dipole moment.

2 – The introduction of phenyl dioxy methylene moiety destabilizes the HOMO and stabilizes the LUMO and hence the energy gap decreases by about 0.2 eV than (III). Therefore, the reactivity of (IV) is greater than (III).

3 – The *p*-OCH$_3$ phenyl moiety is twisted out of the molecular plane (acrolein by an angle 172º. This is expected due to the steric hindrance of OCH$_3$ group and the polarity of the phenyl dioxy methylene with acrolein.

4 – Polarization of (IV) is greater than (III) as indicated from the net charge observed on C = C and C = O groups of acrolein moiety.
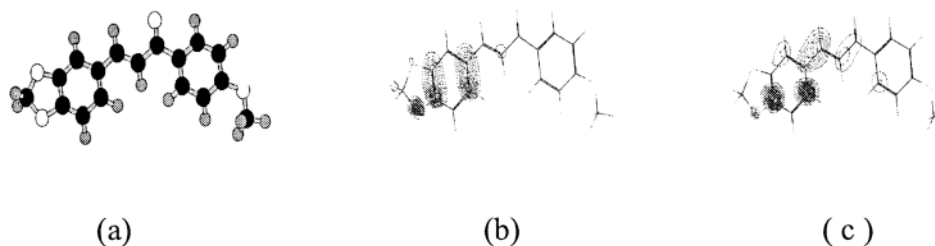

(a)   (b)   (c)

Fig. 6. Final geometry (a) HOMO, (b) LUMO and (c) charge density maps for: 3-(3¯,4¯methyl-ene dioxy phenyl)–1-(4¯-methoxyphenyl)–2-propene-1-one.

f - 3-(3¯,4¯-methylenedioxy phenyl)–1-(4¯-bromophenyl)–2-propene-1-one (V)

Replacement of OCH$_3$ group of (IV) by Br gives (V). Final geometry, charge density maps and the geometric parameters are given in Tables 1-3 and Fig. 7. The following can be considered:

1 – Increase of C$_1$-C$_6$ and C$_3$-C$_5$ bond lengths connected to Br- phenyl and phenyl dioxymethylene to acrolein. The increase of bond length is due to the involvement of two phenyl moieties in a competitive interaction with acrolein moiety.

2 – *p*-Br phenyl ring is twisted out of the molecular plane by an angle 15.6º whereas, dioxymethylene phenyl is still coplanar with acrolein moiety.

3 – The polarity of compound (V) is higher than (IV) as indicated from the net charge located on the different centers of acrolein moiety.
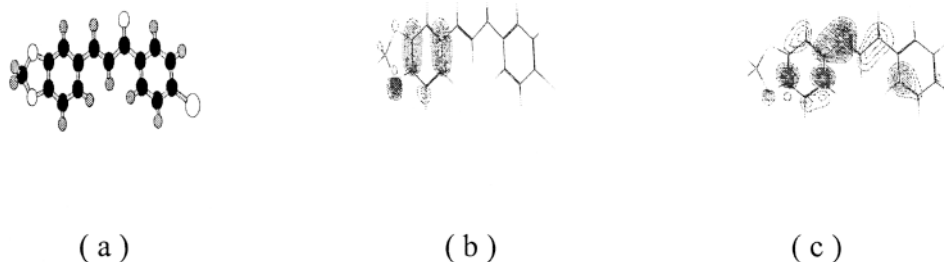
Fig. 7. Final geometry (a) HOMO, (b) LUMO and (c) charge density maps for: 3-(3⁻,4⁻-methylene dioxy phenyl)–1-(4⁻-bromophenyl)–2-propene-1-one.

4 – Dramatic change can be observed in (V) over all derivatives, which is the decrease in the computed dipole moment. The computed dipole moment of (V) is 2.55 D. The decrease in dipole moment can be explained as a result of the increase of charge transferred from the two phenyl moieties in opposite direction of the dipole moment vector of acrolein moiety.

Acknowledgement

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التركيب الإلكتروني لبعض مشتقات الشالكون
١– الخـواص الهندسيـة وتوزيـع الكثافـة الإلكترونيـة باستخدام AM1-MO

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المستـخلص . تمت دراسـة التركيب الإلكتـروني لبـعض مشـتقـات الشـالكون ، وذلك لحساب أفضل الأشكال الهندسـية لهـذه المركبات في الحالة الدنيا باستخدام نتائج حسابات الأفلاك الجزيئية . وقد تم تحليل ومناقشـة نتائج الحسابات الجزيئية للخواص الإلكترونية المختلفة : الطاقة الكليـة ، والطاقة الإلكترونية ، وطاقـة التنافـر ، وطاقة التأين ، والألفـة الإلكترونية ، وفجوة الطاقة ، وحرارة التكوين ، والعزم القطبي ، ورتبـة الرابطة ، وتوزيع الشـحنات على الذرات المختلفة. وتمت دراسـة خرائط كثافة الشـحنات على المركبـات باستخدام مـدار أعلى ممتلئ HOMO ، وكـذلك أقل مدار فـارغ LUMO . كمـا تمت دراسة تأثير إدخـال بعض الذرات والمجاميع الفعالة على التركـيب الإلكتروني للمـركبات تحت الدراسة .