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Structure-Stability and Energy Storage Capacity of Para Acetyl-Dichloro Chalcone and Chromen Isomers: A Density Functional Theory Investigation

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ABSTRACT

The present study investigates stability and energy storage capacity of E and Z isomers of chalcone 3-(x,y-dichlorophenyl)-1-(4-$COCH_3$-phenyl)prop-2-en-1-one, with x and y denoting positions of chlorine atoms. The considered values of (x,y) are (2,3), (2,4), (2,5), (2,6), (3,4), and (3,5). The investigation also includes 4-(i,j-dichloro-8aH-chromen-2-yl)acetyl-where (i,j) take values of (5,6), (5,7), (5,8), (5,8a), (6,7), and (6,8). Computations are performed using density functional theory in conjunction with the functional B3LYP and the basis set 6-311G (d,p) with and without dispersion correction. Results showed that the stability sequence of the studied isomers is E isomers > Z isomers > chromen isomers. Concerning the E and Z isomers, the most stable isomer is E (3,5). Results revealed that E (3,5) favors s-cis conformation over s-trans. Among chromen isomers, (5,8a) chromen is the most stable. The compounds investigated here have the highest energy storage capacity (0.41 MJ/kg) when the (6,7) chromen isomer converts to the *E* (3,4) chalcone isomer, which indicates they may be applied in solar thermal batteries.

Keywords: Chalcone, 8aH-chromene, DFT, Dispersion correction, Energy storage capacity, Solar thermal battery.

INTRODUCTION

Chalcones (1,3-diphenyl-2E-propene-1-one) consist of two benzene rings bridged by α, β-unsaturated carbonyl group. Chalcones exist in two geometric forms: trans (E) and cis (Z). Thermodynamically, the E isomer is more stable than the Z isomer[1]. Each geometry exists in two conformations-namely, s-cis and s-trans-in accordance to the two possible arrangements of the carbonyl and the vinyl groups around the sigma bond joining these two groups. Fig. 1 displays E-s-cis, E-s-trans and Z chalcones along with chromen.

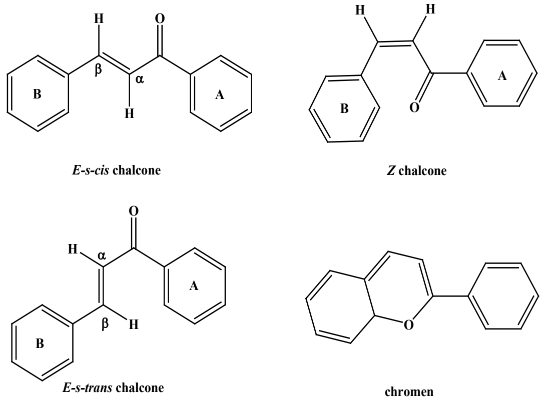

Fig. 1. E chalcone, Z chalcone, and chromen structures. A and B are used to differentiate the two benzene rings

The stability of a conformer, s-cis or s-trans, is determined by its total energy, steric effects between the substituents on the carbon atoms of vinyl and carbonyl groups as well as field effects between the two groups[2]. Density functional theory (DFT) investigations on planarity of s-cis and s-trans α,β-unsaturated carbonyl moiety revealed that s-cis conformation had better planarity[3,4]. The lower planarity of s-trans conformation was attributed to the steric effect between the hydrogen of the A and B rings[4]. The conformation s-cis exhibited greater stability than the s-trans and its total energy was lower by 2.0 kcal/mol[4]. However, in non-aromatic compounds with α,β-unsaturated moieties, such as 1,3-butadiene[5] and acrolein[6], it has been found that s-trans conformer is fully planar and has less steric effect and, thus, is more stable. Conformers s-cis and s-trans have different physical properties; for example, s-cis and s-trans (E)-pent-3-en-2-one chalcones present differences in the infrared spectrum[7]. It has been reported that the cis chalcone isomers have stronger antitumorigenic activity than the trans isomers[8].

The stability of dichloro amino chalcones have been investigated using DFT calculation[9]. The most stable conformation was found to be the s-cis. Furthermore, the stability ranking of the studied amino isomers and corresponding photo-chemical chromen isomers indicated that E dichloro amino isomers are more stable isomers and the dichloro amino chromens are less stable. Furthermore, the stability order within the E dichloro amino isomers revealed that (3,5)-amino isomer has the highest stability and (2,3) amino chalcone has the lowest. A similar order of stability was found for Z isomers. Meanwhile, the isomer that has the highest stability among the dichloro amino chromens is (5,8a), and The (6,7) isomer has the lowest stability.

In recent investigations, two chromens were photochemically synthesized from their chalcone isomers, 5,8a-dichloro-2-(4-methoxyphenyl)-8aH-chromene (abbreviated as methoxy chromen). This compound was synthesized from methoxy chalcone via solar simulated visible light irradiation[10]. Similarly, 4-(5,7-dichloro-8aH-chromene-2-yl)-N,N-dimethylaniline (abbreviated as dimethylamino chromen) was synthesized from E-3-(2,4-dichlorophenyl)-1-(4 (dimethylamino)phenyl)prop-2-en-1-one (abbreviated as dimethylamino chalcone)[11]. Both solar-simulated light syntheses of the above chromens from E chalcones revealed the capability of visible light to catalyze photo-isomerization of E chalcone to chromen. Interestingly, both photo-synthesized chromen isomers reverted to their corresponding chalcones when left in the dark. This finding agrees with the DFT stability investigation mentioned above[9]. The chromen isomer is less stable than the chalcone isomer; hence, it reverts back to the latter in the dark. A molecule capable of performing the cycle of E dichloro amino chalcone to dichloro amino chromen and back, called molecular photo-switching, can be utilized in a solar thermal battery, also known as a molecular solar thermal energy storage system (MOST). In this photo-switch, the metastable photo-isomer generates heat when it isomerizes to the E dichloro amino chalcone in the dark.

The estimated upper limit of ESC of a molecular photo-switch is 1 MJ/kg in actual applications[12]. For example, one of the most investigated photo-switches is the photo-induced dihydroazulene/vinylheptafulvene (DHA/VHF) photo/thermo-switch. Through photo-inducing action, DHA can be converted into the metastable s-cis-VHF which, due to thermal equilibrium, can be converted into the metastable s-trans-VHF. DHA/VHF has an energy storage capacity of 57.7 kJ/mol, which is equivalent to the wavelength of emission of $\lambda = 2074$ nm[13]. Using the same DFT method with different substituents, the calculated energy storage capacity is 85 kJ/mol (equivalent to the emitted wavelength of $\lambda = 1408$ nm; 0.28 MJ/kg)[14]. Other molecular photo-switches for use in MOSTs have been studied along with functionalized norbornadienes[15,16], fulvalene-diruthenium derivatives[17,18], azobenzenes[19,20], azopolymers[21], and a number of dihydroazulene/vinylheptafulvene (DHA/VHF) derivatives[13,14,22,23,24].

In the present work, the model compounds E and Z 3-(x,y-dicholophenyl)-1-(4-acetylphenyl) prop-2-en-1-one, with (x,y) = (2,3), (2,4), (2,5), (3,4), (3,5), and (2,6), and their chromen isomers are considered to investigate the relative stability of these isomers. Effect of acetyl, a group that withdraws electrons, on the stability of s-cis/s-trans conformation of E chalcone isomers is also explored. The results of s-cis/s-trans stability are compared with those of a similar isomer carrying an electron-donating group, namely, E dichloro amino chalcone. Calculations are performed utilizing DFT in conjunction with the functional B3LYP and the basis set 6-311G (d,p), which will be abbreviated as DFT/B3LYP/6-311G(d,p) in the forthcoming. Stability results obtained for the current isomers are compared with those of dichloro amino chalcone and chromen isomers. Furthermore, thermal energy storage of dichloro acetyl chalcones and chromens are investigated and compared with those of dichloro amino chalcone and chromen isomers. Finally, a comparison of the thermal energy storage of dichloro acetyl chalcone and chromen isomers with that of non-chalcone structure molecules-such as the previously investigated dihydroazulene/vinylheptafulvene (DHA/VHF) derivatives-is conducted.

Computational Details

Gaussian 09 was used to perform the calculations[25]. Gauss view 5[26] was utilised for drawing and inputting initial geometry, and the theory level DFT/B3LYP/6-311G(d,p) was employed to perform the subsequent calculations. The empirical dispersion correction (DC) function was used with the keyword (empiricaldispersion=gd3), in order to account for the steric interactions. The temperature that the parameter calculations were performed at was 293.15 K.

Geometric optimization utilizing the Berny optimization algorithm included in Gaussian09 was performed with DFT way. To verify that the optimized geometric structure is a true minimum, vibrational frequencies were calculated and checked for non-existing negative frequencies. To investigate which conformer (s-cis chalcone or s-trans chalcone) is more stable, a scan using DFT method was run for E (3,5) chalcone isomers while implementing internal redundant coordinates with the keyword (#opt=ModRedundant). This was carried out by changing the dihedral angle of (C7-C8-C9-O10), see Fig. 4, between 0° and 360° in steps of 10°. Optimization of (2,6) chromen presented a problematic elongation of the C6–Cl bond. To resolve this complication, the geometric optimization protocol was modified, first by applying a restricted semi-empirical PM6 model, then freezing the length of C6–Cl bond at 1.76 Ao, in accordance with its optimized value, and optimizing with DFT method employing the mod redundant keyword (# opt=(tight, modredundant) freq b3lyp/ 6-311g (d,p) nosymmgeom=connectivity)[9,10].

The ESC was calculated applying relative stability, which is the difference between Gibbs free energy of E chalcone isomer and that of the corresponding chromen isomer.

RESULTS AND DISCUSSION

Given that chalcones exist in multiple conformations due to variations in the dihedral angle of (-C=C-C=O), it was essential to do a scan of the geometry-optimised structure to identify the highest stability conformer to find the highest stable conformer employing DFT/B3LYP/6-311G(d,p) level of theory. With the two chlorine atoms bonded to different carbon atoms of ring B, the stability of the E isomers, Z isomers, and chromen isomers was examined. The conformational stabilities for E isomers, Z isomers, and chromen isomers at the same level of theory were also studied.

The 3D geometry-optimized (GO) structures with DC for the highest stability isomers of the studied chalcones and chromen are given in Table S1. The table also provides the geometrical parameters and the sum of electronic energy with zero-point, thermal and thermal free energies and thermal enthalpy of the isomers.

Trans Chalcone Isomers

Potential Energy Surface (PES)

Potential energy surface (PES) scanning is a procedure used to obtain different conformations of a molecule by calculating the energies associated with its rotation around a bond, such as the bonds the C=O and the C=C. To determine the more stable rotational conformers, potential energy surface (PES) scan was run for E (3,5) chalcone optimized-structure isomers while implementing internal redundant coordinates. The scan was done by calculating total energy for the values of the dihedral angle (7-8-9-10) equal 0° to 360° in 10° increments. Dihedral angle (7-8-9-10) is the angle formed by atoms C7, C8, C9, and O10 (Fig. 4). In forthcoming, dihedral angles are named according to atom numbering as given in Fig. 4 and Fig. 6. The calculated total energy versus the dihedral angle is given in Fig. 2. The conformer with the lowest energy (–1083.16045×10^3 kcal/mol) is the most stable and belongs to the s-cis conformation with (7-8-9-10) dihedral angle equal to 0° that is nearly planar. The highest local minimum energy of –1083.15778×10^3 kcal/mol is for (7-8-9-10) dihedral angle of 150° and conforms with s-trans chalcone. In particular, s-trans endures the most steric effect arising from the hydrogen and the hydrogen bonded to the ortho carbon of ring A.

The most stable conformers were those with dihedral angles of 0° and 360°, which matched with the s-cis chalcone conformer. For the s-trans and s-cis chalcone conformers illustrated in Fig. 2, the s-cis chalcone conformer is more planar, hence less steric, and a greater degree of π-bonds all over the molecule, when compared to the s-trans chalcone conformer. This result agrees with previous results obtained for E chloro amino chalcone[9] and E chloro methoxy chalcone[27].

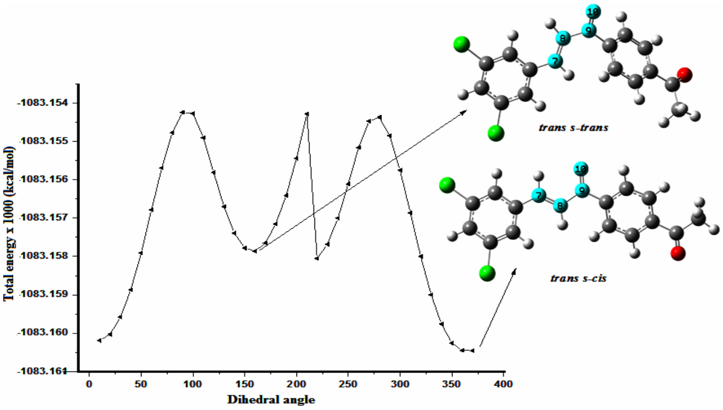

Fig. 2. Potential energy versus dihedral angle (7-8-9-10) curve of (E (3,5)) isomer

Stability of E chalcones

Conformation is decided according to the relative orientation of the two carbonyl groups, namely, the α,β-unsaturated carbonyl and the acetyl carbonyl. These two groups could have their oxygen atoms on the same side (syn conformation) or on opposite sides, as shown in supplementary materials (anti-syn confirmation). The total energy of E (2,4) dichloro acetyl chalcone was calculated with DFT, and it turns out that the syn conformation has a total energy of –1083.158751×10^3 kcal/mol, while the anti-syn conformation has a total energy of –1083.159097×10^3 kcal/mol. Hence, the two oxygens prefer to be in the anti-syn conformation, as it has lower energy. Therefore, all the E dichloro acetyl chalcones, with carbonyls in the anti-syn conformation, were geometry-optimized. For that reason, all the E dichloro acetyl chalcones were submitted for geometry optimization with the carbonyls in the anti-syn conformation.

The isomers of dichloro E chalcone can exist in two different conformations, as illustrated in Figure 3.

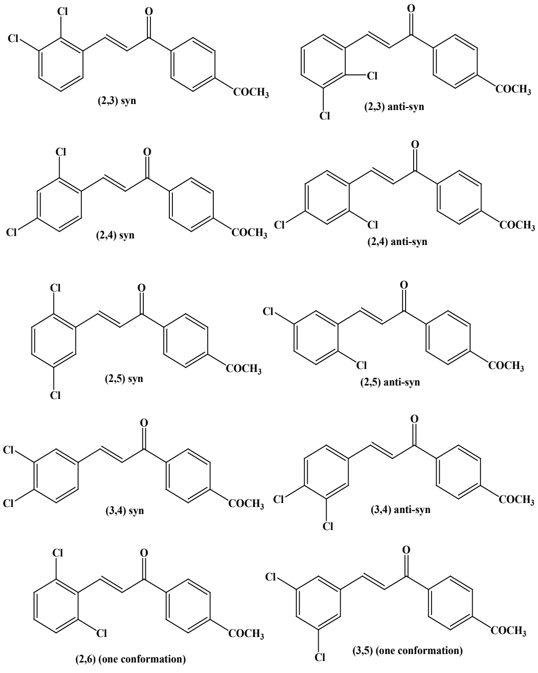

Fig. 3. Syn and anti-syn E chalcones

Conformation of a molecule is syn when either C2-Cl or C3-Cl bond is parallel to the C9-O10 bond and is anti-syn when the two bonds are anti-parallel, see Fig. 3. Dichloro E chalcones, except E (3,5) and E (2,6), exist in two conformations (syn and anti-syn).

The total energy of most stable isomer is shown in the footnote of Table 1. The relative energy (RE) (with and without DC) referenced to the most stable isomer, E (3,5) chalcone, and dipole moment (with DC) of the E chalcone isomers shown in Fig. 3 were calculated; the results are given in Table 1. Dipole moment values were the same in the cases with and without DC. According to Table 1, the total energy decreased when DC was used in the calculation, stability of the isomers presented the pattern (3,5) > (2,4) syn > (2,5) syn > (3,4) anti-syn > (2,3) syn > (2.6). However, after DC was applied, the stability trend was altered to (3,5) > (2,4) syn > (2,5) syn > (3,4) anti-syn > (2,6) > (2,3) syn, in which the least stable isomer was (2,3) syn while it was (2,6) without DC. The most stable isomer was (3,5), with and without DC. Regardless of applying DC, anti-syn conformers, except (3,4), were more stable than syn conformers.

Table 1: Relative energy* (RE) in kcal/mol and dipole moment (DM) in Debye of geometry-optimized E isomers

E isomer	RE Without DC	 With DC	DM
(2,3)-syn	4.5	4.21	2.6191
(2,3)-anti-syn	6.28	5.86	3.9311
(2,4)-syn	1.36	0.96	1.2492
(2,4)-anti-syn	2.64	2.04	1.8320
(2,5)-syn	1.56	1.10	1.0403
(2,5)-anti-syn	3.21	2.57	4.9773
(3,4)-syn	2.32	2.49	4.4314
(3,4)-anti-syn	1.94	2.11	2.0674
(2,6)	5.47	4.12	2.2745
(3,5)	0.00	0.00	0.9799

**The relative energy (RE) is calculated as the difference between the total energy of the (x,y) isomer and that of the (3,5) isomer.
-Total energy of the (3,5) isomer without DC: -1,083,160.46 kcal/mol.
-Total energy of the (3,5) isomer with DC: -1,083,180.09 kcal/mol.

The sequence of the RE values with DC was affected by the decrease in planarity and the stability of the isomers. The E (2,3) syn and (2,6) isomers had the largest and the second-largest RE values 4.21 kcal/mol and 4.12 kcal/mol, respectively, as they have high non-planarity. E (2,3) syn is less stable due to steric hindrance effects between chlorine atoms and between the hydrogen on carbon 7 and the chlorine on carbon 2 (see Figure 4).

The RE trend results shown in Table 1 are in full agreement with previously investigated para amino dichloro E chalcones[9] and para methoxy dichloro E chalcones[27].

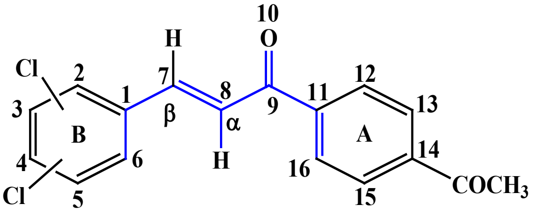

Fig. 4. Atoms numbering in E chalcone. Dihedral angles essential for geometry-optimization is shown in blue

The stability ranking is affected by many factors, such as steric effect embracing nearby chlorine atoms and chlorine and hydrogen atoms, the planarity (the dihedral angle value), and the existence of the chlorine atoms in ortho and para positions. As can be seen in Fig. 4, (6-1-7-8), (7-8-9-10), and (8-9-11-16) are the essential dihedral angles as far as the geometric optimization of E chalcone isomers is concerned. Therefore, their values in geometry-optimized E chalcone isomers were calculated and are given in Table 2.

Table 2: Dihedral angles in degrees in geometry-optimized E isomers with dispersion correction

E isomer	Dihedral angle 6-1-7-8	 7-8-9-10	 8-9-11-16
2,3-syn	-26.771	-7.340	-14.847
2,4-syn	18.097	5.458	13.700
2,5-syn	20.725	5.958	13.680
2,6	-41.070	-7.731	-9.432
3,4-anti-syn	-0.808	-3.182	-12.826
3,5	2.152	4.118	14.581

From Tables 1 and 2 and Figs. 3 and 4, the following can be deduced:

First, E (3,5) is the most stable isomer as it has the lowest total energy. Moreover, its angle (6-1-7-8) is the closest to zero, excluding that of the (3,4) isomer. The case of the (3,4) isomer is explained below. Higher planarity in the (3,5) isomer leads to more electron delocalization between ring B (Fig. 4) and the other parts of the molecule.

Second, E (2,4) is the second in stability order, as electron donation by the ortho and para positioned chlorine atoms stabilizes the isomer. In addition, the angle (6-1-7-8) of the isomer is 18.097°, and such a dihedral angle does not prevent electron delocalization between ring B and the other parts of the molecule.

Third, third-most stable isomer is E (2,5), which has a chlorine atom in ortho position. Thus, compared to the other isomers, it can more conveniently donate electrons from ring B and hence enhance conjugation to the carbonyl.

Fourth, E (3,4) is the fourth-most stable isomer because of the two chlorine atoms steric effect, which contributes to destabilisation. Table 2 shows that E (3,4) has lowest dihedral angles among all isomers. Subsequently, it has the highest planarity when compared to the other isomers, making its chlorine atoms capable of donating electrons. However, more is needed to make the (3,4) isomer more stable, namely, steric effect between the neighboring chlorine atoms themselves and them with hydrogen atoms are significant. For example, E (3,5) is more stable than E (3,4) because the chlorine atoms of the former are not adjacent, thus, lower steric effect.

Finally, a larger dihedral angle means larger non-planarity and less electron delocalization between ring A, carbonyl group, and the vinyl group, thus, lower stability. E (2,6) isomer has greatest (6-1-7-8) angle, -41.07°, which implies that the efficiency of electron delocalization between chlorine atoms and vinyl group is lower, when compared to the other isomers. E (2,3) isomer has relatively high (7-8-9-10) and (8-9-11-16) dihedral angles. The angle (6-1-7-8) of E (2,6) is greater than that of E (2,3). Notably, the stability of E (2,3) is less than that of E (2,6) because the chlorine atoms of the former are adjacent and, thus, higher steric effect. The same is true for the chlorine at carbon 2 and the β-hydrogen in E (2,3) isomer. As a result, E (2,3) is least stable, and E (2,6) is second-least stable.

Sums of Mulliken charges for the carbon atoms in the dichlorobenzene rings of the (3,5) and (2,6) isomers are -0.287 and -0.322, respectively. It is clear that there is more negative charge in the dichlorobenzene ring of the (2,6) than the (3,5) isomer. This agrees with the idea that the dichlorobenzene ring of (3,5) is more planar and delocalizes electrons with the rest of the molecule. While the dichlorobenzene ring in (2,6) is non-planar, there is less delocalization and higher Mulliken charges on carbon atoms than on carbon atoms of the same ring in (3,5).

Table 1 also shows the dipole moments of the investigated isomers with two possible conformations: syn and anti-syn; in particular, the most stable conformer, syn, has lower dipole moment compared to its anti-syn counterpart. However, E (3,4) anti-syn isomer, which is more stable than its syn counterpart, also has lower dipole moment compared to the less-stable syn isomer. Hence, most stable conformers tend to have lower dipole moments. Excluding the dipole moment of less-stable conformers, the highest dipole moment was determined for E (2,3) syn isomer. In contrast, the most minor dipole moment was that of E (3,5). E (3,5) having a chlorine in the opposite direction to the carbonyl group, possess minimum dipole moment. To the contrary, the chlorine at the number 2 position in the (2,3) syn isomer is aligned with the carbonyl group; hence, it acquires the highest dipole moment, disregarding the less-stable isomers from the comparison.

cis Chalcone isomers

The Z isomers can exist in two conformations, syn and anti-syn, as shown in Figure 5.

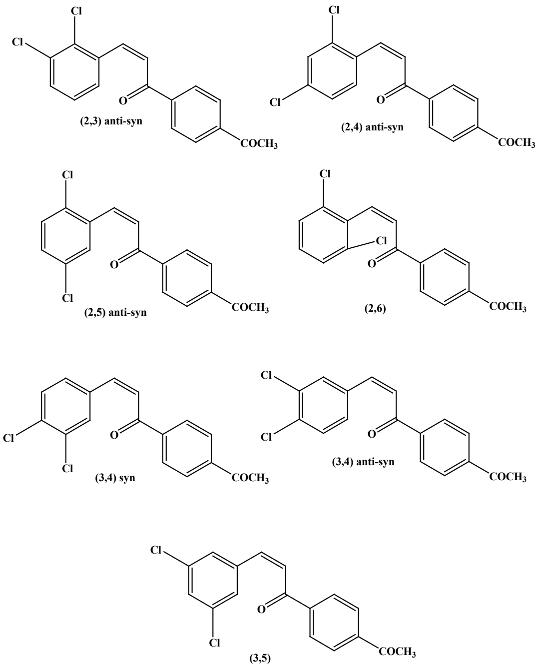

Fig. 5. Syn and anti-syn Z isomers

As yet, only the anti-syn conformations have been studied for the (2,3), (2,4), and (2,5) isomers while, for (3,4), both (3,4) syn and (3,4) anti-syn isomers have been studied. Total energy (with and without DC) and dipole moment (with DC) of the Z chalcone isomers shown in Fig. 5 were calculated, and the results are given in Table 3. In the table, relative energy (RE) with respect to the most stable isomer, Z (3,5), is given instead of total energy. The total energy decreased when DC was used to calculate the total energy, as indicated in the footnote of Table 3; hence, the isomer's stability increased when the DC was used to calculate the total energy. The syn conformations of the (2,3), (2,4) and (2,5) isomers were not calculated because, when their syn conformations were geometry-optimized, the outcome was anti-syn. This is due to steric effect between chlorine atom and carbonyl oxygen, which mainly prevents the presence of syn conformations. The Z (3,4) chalcone isomer showed a different behavior. The geometry optimization process preserved both conformation geometries; hence, Z (3,4) isomer exists in syn conformation as well as anti-syn. This can be attributed to the fact that carbonyl and chlorine atom on carbon 3 are more distant in anti-syn conformation than in syn conformation. Again, like E chalcones, one conformer appears for each of the Z (2,6) and Z (3,5) isomers.

Table 3: Relative energy* (RE) in kcal/mol and dipole moment (DM) in Debye of geometry-optimized Z isomers

	RE		
Z isomer	Without DC	With DC	DM
(2,3) anti-syn	4.19	3.65	2.8869
(2,4) anti- syn	0.83	0.34	1.7439
(2,5) anti-syn	1.34	0.65	0.4472
(2,6)	4.88	2.79	1.8645
(3,4) syn	1.77	1.95	2.3710
(3,4) anti-syn	1.66	1.92	1.9712
(3,5)	0.00	0.00	1.5263

* The relative energy (RE) is calculated as the difference between the total energy of the (x,y) isomer and the total energy of the (3,5) isomer.

- Total energy of the (3,5) isomer without DC: -1,083,155.94 kcal/mol.

- Total energy of the (3,5) isomer with DC: -1,083,176.00 kcal/mol.

The values of RE with DC followed the trend (3,5) < (2,4) anti-syn < (2,5) anti-syn < (3,4) anti-syn < (2,6) < (2,3) anti-syn. The order of the RE values was influenced by the decrease in planarity and the stability of the studied Z chalcones. The Z (2,3) anti-syn and Z (2,6) isomers had the largest and the second-largest RE values 3.65 and 2.79 kcal/mol, respectively, as they have high non-planarity and low steric effect among adjacent chlorine atoms in Z (2,3) and chlorine with hydrogen atoms.

Dihedral angles (6-1-7-8), (7-8-9-10), and (8-9-11-16) for geometry-optimized Z chalcone isomers (Fig. 6) were calculated, and the results are given in Table 4.

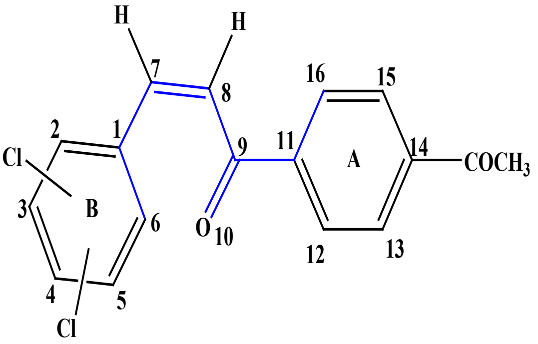

Fig. 6. Atoms numbering in Z chalcone. Dihedral angles essential for geometry-optimization are shown in blue

Table 4: Dihedral angles in degrees in geometry-optimized Z isomers with dispersion correction

Z isomer	Dihedral angle		
	6-1-7-8	7-8-9-10	8-9-11-16
(2,3) anti-syn	41.417	-36.601	-16.270
(2,4) anti-syn	30.483	-30.703	-19.145
(2,5) anti-syn	36.635	-33.573	-16.482
(2,6)	-68.077	-15.351	-17.521
(3,4) anti-syn	10.805	-16.889	-20.873
(3,5)	14.644	-19.947	-19.852

With and without DC, the stability of Z isomers followed the same trend as that of E isomers. The stability without DC presented the trend (3,5) > (2,4) anti-syn> (2,5) anti-syn > (3,4) anti-syn > (3,4) syn > (2,3) anti-syn> (2,6), with Z (3,5) being the most stable isomer and Z (2,6) as the least stable isomer. Including DC, the stability trend became: (3,5) > (2,4) anti- syn > (2,5) anti-syn > (3,4) anti-syn > 2,6)> (2,3) anti-syn, with the most and least stable isomers being Z (3,5) and Z (2,3), respectively (Table 3). Similar to the stability criteria used for E chalcone isomers (see Section 3.1.2), steric effect among adjacent chlorines and adjacent chlorines and oxygen reduce stability of the Z chalcone isomers. Furthermore, the dihedral angles between ring B and ring A also influences stability of the isomers, as the closer the angles to zero, the more significant is the electron donation from the B ring. According to Tables 3 and 4, the Z (3,5), (2,4), and (2,5) isomers are the three most stable isomers as, compared to the other isomers, they had the lowest total energy and highest planarity, as well as decreased steric effect among adjacent chlorines and them with oxygen. The Z (3,4) came fourth in stability ranking. Even though the Z (3,4) is more planar than Z (3,5), it does display an adjacent chlorine atoms steric effect that is not found in the Z (3,5) isomer, therefore making Z (3,5) more stable than Z (3,4). Finally, because of high steric effect among the adjacent chlorine atoms and adjacent chlorine and oxygen atoms non-planarity, the least-stable isomers were Z (2,6) and Z (2,3). These results agree with a previous investigation on Z dichloro para amino chalcones[9].

Table 3 also shows the dipole moment values for the Z isomers. Similar to the behavior of E chalcone isomers, the Z (3,4) anti-syn conformer has a lower dipole moment than its less-stable counterpart, namely, the Z (3,4) syn conformer. In a trend similar to that of E chalcones, the Z (2,3) anti-syn isomer has the highest dipole moment value, while the Z (2,5) anti-syn isomer has the lowest dipole moment.

Chromen isomers

The total energy, referenced to the lowest total energy isomer (5,8a) chromen, as RE and dipole moment of the chromen isomers shown in Fig. 7 were calculated with and without DC, and the results are given in Table 5.

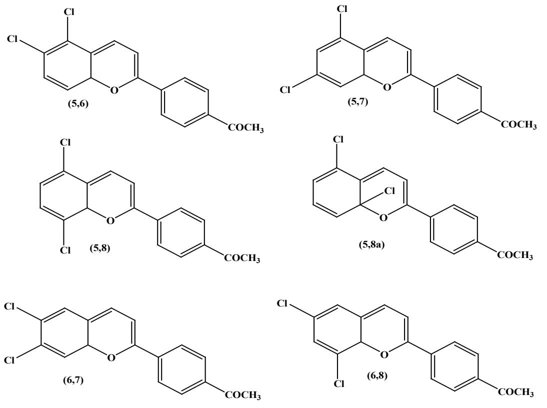

Fig. 7. Geometry-optimized structures of chromen isomers

Table 5 reveals that adding DC to the calculations decreases the total energy, as shown in Table 5 footnote, and increases the stability of the isomers. The stability of the isomers according to RE, without applying DC, follows the trend (5,8a) > (6,8) > (5,8) > (5,7) > (5,6) > (6,7); with DC, the stability trend becomes (5,8a) > (5,8) > (6,8) > (5,7) > (5,6) > (6,7). Steric hindrance affects the stability of isomers, so the isomers with the fewest adjacent chlorine atoms or adjacent chlorine and hydrogen interactions were the most stable. The (5,8a) isomer was the most stable, while (6,7) was the least stable. Furthermore, due to the steric hindrance effect, applying DC made the (5,8) chromen isomer more stable than the (6,8) chromen isomer. The (5,8) chromen isomer became more stable than the (6,8) chromen isomer as the (5,8) isomer has two hydrogen atoms separating the chlorine atoms, whereas the (6,8) isomer only has one. In other words, the (6,8) isomer is more affected by steric effect than the (5,8) isomer. This stability order of chromen isomers agrees satisfactorily with that observed for dichloro para amino chromen isomers [9].

According to Table 5, the (5,6) isomer had the most significant dipole moment (2.6574 Debye), while the (6,8) isomer has the lowest (1.0470 Debye). The dipole moment values followed the order (5,6)> (5,8a) >(5,8) > (5,7) > (6,7) > (6,8).

Table 5: Relative energy* (RE) in kcal/mol and dipole moment (DM) in Debye of the geometry-optimized chromen isomers.

	RE		
Chromen	Without DC	With DC	DM
(5,6)	9.68	11.28	2.6574
(5,7)	7.5	8.95	1.4988
(5,8)	7.34	8.24	1.7179
(5,8a)	0.00	0.00	2.2657
(6,7)	10.32	12.27	1.4173
(6,8)	7.22	8.49	1.0470

* The relative energy (RE) is calculated as the total energy of the (i,j) isomer minus the total energy of the (5,8a) isomer. The total energy of the (5,8a) isomer without DC is –1,083,139.31 kcal/mol, and with DC, it is -1,083,161.82 kcal/mol.

According to total energy values in the footnote of Tables 1, 3 and 5 of the most stable isomers, the E chalcone isomers have the lowest total energy, followed by the Z chalcone, while chromen isomers have highest; namely, the stability trend is E > Z > chromen. Table 6 lists the total energy variance (with DC) of these isomers. The total energy difference between the E and Z isomers is less than that between the Z and chromen isomers. Table 6 shows that the E and Z isomers are energetically comparable and far from the chromen isomers as both possess two aromatic rings. In contrast, the chromen isomers possess a single aromatic ring and, therefore, are least stable. Stability sequences of the studied isomers are similar to that of para dichloro amino E chalcone, Z chalcone, and chromen isomers[9].

Table 6: The difference (ΔE) in total energy* (with DC) in kcal/mol between E and Z chalcones and Z chalcone and chromen

Isomer	Energy difference ΔE(E-Z)	ΔE(Z-chromen)
(2,3)	3.53	21.81
(2,4)	3.47	22.79
(2,5)	3.64	21.77
(2,6)	2.76	11.39
(3,4)	3.9	24.53
(3,5)	4.09	22.67

* Total energy of E chalcones, Z chalcones, and chromens can be calculated from the footnotes of Tables 1, 3 and 5, respectively

Energy Storage Capacity

When an isomer converts to another having higher Gibbs free energy (G), the difference between their Gibbs free energies is the energy storage capacity (ESC):

$$ESC = \Delta G = G_{high} – G_{low} \quad (1)$$

Obviously, the greater the value of G, the greater the ESC. The Gibbs free energies for all E and Z chalcones, and chromen were calculated using the same DFT method. basis set. Equation (1) was used to calculate ESCs of the chromen isomers relative to the corresponding E chalcone isomers:

$$ESC = G_{chromen} – G_{E\text{-}chalcone} \quad (2)$$

The calculated Gibbs free energies and energy storage capacities are given in Table 7.

Table 7: Gibbs free energies for the geometry-optimized E isomers, Z isomers, and chromen isomers (with dispersion correction), as well as the energy storage capacity

	Gibbs free energy (kJ/mol)				Energy storage capacity			
Isomer		Present work			Present work		Others*	
	E	Z	Isomer	Chromen	kJ/mol	MJ/kg	kJ/mol	MJ/kg
2,3	-4531505.32	-4531490.33	5,6	-4531390.54	115	0.362	120	0.392
2,4	-4531519.94	-4531504.89	5,7	-4531400.40	120	0.378	124	0.405
2,5	-4531519.49	-4531503.19	5,8	-4531401.12	118	0.372	123	0.401
2,6	-4531506.62	-4531495.17	5,8a	-4531460.09	47	0.148	148	0.483
3,4	-4531515.70	-4531497.74	6,7	-4531386.63	130	0.410	135	0.441
3,5	-4531524.52	-4531506.82	6,8	-4531402.09	122	0.384	130	0.424

*Calculated from Gibbs free energies in the Supporting Information of reference[9]

Table 7 shows that all isomers had close ESC values, except for E chalcone (2,6) and chromen (5,8a), for which the ESC value was about half that of the others. The highest ESC for the currently investigated compounds was obtained for converting the (6,7) chromen isomer to the (3,4) chalcone isomer. From Table 7, the conversion of (6,8) chromen isomer to the corresponding (3,5) E chalcone isomer (the most stable) releases 122 kJ/mol (0.384 MJ/kg), which corresponds to an emitted energy of 981 nm. The emitted energy for the process of (5,8a) chromen to the corresponding E (2,6) chalcone (the least stable) is 2540 nm, and the ESC is 47 kJ/mol (0.148 MJ/kg). Comparing these, results at the same level of DFT calculations, to similar isomers but with an electron-donating group, such as NH_2, the last two columns of Table 7 reveal the ESC of the (5,8a) dichloro amino chromen to E (2,6) dichloro amino chalcone process, which produces a maximum emission of around 806 nm (148 kJ/mol). The other photo-switch of the (6,8) dichloro amino chromen to E (3,5) dichloro amino chalcone process emits around 917 nm (130 kJ/mol. An amino group (which is an electron-donating group) increases the ESC compared with the acetyl group (an electron-withdrawing group).

The present DFT-calculated ESC and the corresponding emitted wavelength of the process chromen to chalcone is in good agreement with the DFT calculations for other MOST system molecules, such as dihydroazulene/vinylheptafulvene (DHA/VHF), with an ESC of 57.7 kJ/mol (λ = 2074 nm; 0.25 MJ/kg)[13] and dihydroazulene/vinylheptafulvene with three different substituents, with ESCs of 85 kJ/mol (λ = 1408 nm; 0.28 MJ kg), 76 kJ/mol (λ = 1575 nm; 0.15 MJ/kg), and 105 kJ/mol (λ = 1135 nm; 0.21 MJ/kg)[14].

CONCLUSION

The computations indicated that stability of considered E isomers follows order (3,5) > (2,4) syn > (2,5) syn > (3,4) anti-syn > (2,3) syn > (2,6). After applying dispersion correction (DC), the stability trend was altered to the following: (3,5) > (2,4) syn > (2,5) syn > (3,4) anti-syn > (2,6) > (2,3) syn. The Z chalcones have a stability trend similar to that of E chalcones. The stability ranking is affected by many factors, such as steric effect among adjacent chlorine atoms and chlorine and hydrogen atoms, the planarity (i.e., the dihedral angle) between the chlorophenyl group and the other parts of the molecule, and the existence of chlorine atoms in the ortho and para positions. Therefore, the E (3,5) chalcone was found to be the most stable isomer because its (6-1-7-8) angle is close to zero, which indicates higher planarity of E (3,5), allowing greater electron delocalization between ring B and other parts of the molecule. Z (2,3) anti-syn is the least stable isomer among E and Z isomers sequences. Stability order of chromen isomers was found to be (5,8a) > (6,8) > (5,8) > (5,7) > (5,6) > (6,7). However, their stability order changed after dispersion correction, as follows: (5,8a) > (5,8) > (6,8) > (5,7) > (5,6) > (6,7). Because of steric effect among adjacent chlorine atoms and between them and hydrogen atoms, most stable chromen isomer was (5,8a), and least stable was (6,7). The Stability order of the dichloro acetyl chalcones, when compared with the stability order results calculated in the literature using the same level of calculations, showed a very good agreement. Hence, replacing amino (a group that donates electron) with acetyl (a group that withdraws electron) does not affect the stability order of the isomers.

The calculated ESC values for the isomers were close to each other, except for that of (5,8a) chromen. The highest ESC was obtained from the isomerization of (6,7) chromen to E (3,4) chalcone. The effect of changing the electron-withdrawing group (acetyl) to an electron-donating group (amino) increases the ESC. The ESC results obtained in this investigation are comparable to those obtained for the DHA/VHF system.

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Conflicts of Interest

The authors declare no conflict of interest.

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