IRANIAN JOURNAL OF CATALYSIS

Structure and isomeric studies of 1,3-diaryl-*H*-benzo[f]chromene, catalyst effect or thermodynamic stability? An *ab initio* study

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Received 10 Jane 2013; received in revised form 13 October 2013; accepted 10 December 2013

ABSTRACT

Two possible isomers of some 1,3-diaryl-H-benzo[f]chromene have been studied using density functional theory. Structures of E1 and E2 isomers were optimized at the B3LYP and MP2 levels with different basis sets. The total electronic energies show that E2 isomer is about 3-5 kcal/mol more stable than E1 isomer and this energy difference is attributed to the planarity of heterocyclic ring and more establishment resonance in E2 isomer, that is confirmed by second order interaction energies $E^{(2)}$ of NBO results. The calculated geometry for both chromene isomers were also compared with the experimental data. The X-ray data indicate the E1 isomer as the stable structure for 1,3-diaryl-1H-benzo[f]chromene, while the E2 isomer is fixed for 3-phenyl-1-p-tolyl-1H-benzo[*f*]chromene. The compared dihedral angles of both isomers show that phenyl (I) group in E2 isomer has more contribution in resonance with the heterocyclic and naphthalene rings than that in E1, while in E1 isomer phenyl (II) group is more engaged in resonance than that in E2.

***Keywords**: 1,3-Diaryl-H-benzo[f]chromene; 3-Phenyl-1-p-tolyl-1H-benzo[f]chromene; DFT, NMR; Isomerization analysis.*

1. Introduction

Naphtopyrans (known as benzo[f]chromene) are an important class of photochromic compounds and classical molecules which have the ability to generate a yellow color on being irradiated with UV light [1, 2]. There has been considerable interest in chromenes and their benzo-derivatives, because of their value for a variety of industrial, biological and chemical synthetic uses [3]. In particular, benzo[f]chromene have been used in photochromic lenses, electronic display device, optical switches, and impermanent or permanent memories [4]. The chromenes have anti-trypanocidal activities, vasodilatory properties, and they use as a new and more potent drugs for the treatment of Chagas disease [5]. 2-Amino-4*H*-chromenes and their derivatives are of considerable interest as they possess a wide range of biological properties [6,7] such as spasmolytic, diuretic, anticoagulant, anticancer [8], anti-helminthic, hypothermal, antiviral, novobiocin, and antianaphylactic activities [9,10]. The synthesis of chromenes and their derivatives is of high interest in organic chemistry.

Consequently, there have been some reports on the preparation of benzo[*f*]chromene [11-13]. The effects of various metal halide catalysts such as $FeCl_3$, $BiCl_3$, $ZnCl_2$, $InCl_3$, and $CeCl_3.7H_2O$ and metal triflates such as $In(OTf)_3$, $Bi(OTf)_3$,$Yb(OTf)_3$, and $Sc(OTf)_3$ were screened by Yadav et al. [11] for this conversion. Surprisingly, none of these catalysts gave the desired product under the reaction conditions. The reaction was successful only with $GaCl_3$. Furthermore, Bronsted acids such as montmorillonite K10, heteropoly acid and ion-exchange resins also failed to produce the desired product. In the absence of catalyst, no reaction was observed even after long reaction time (12 h) under reflux conditions. However, $InCl_3.4H_2O$ [14] and concentrated H_2SO_4 [15] were reported as efficient catalysts.

Yadav et al. [11] based on a gallium (III) chloride catalyzed reaction, introduced 1,3-diphenyl-3H-benzo[*f*]chromene (E1, see Fig.1) as the main product, which was confirmed by X-ray crystal analysis [12].

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Eshghi et al. suggested the other isomer (1,3-Diaryl-1H-benzo[*f*]chromene (E2, see Fig.1)) as the dominant product in a ferric hydrogen sulfate catalyzed condition [13]. 3-Phenyl-1-p-tolyl-1H-benzo[*f*]chromene was synthesized by Xue et al. [15] as the sole product, and its structure was emphasized by X-ray data as E2 isomer.

Since the Csp^3-O bond is cleaved by UV irradiation, so the E1 is considered as a photochromic molecule. The aim of the present paper is study of isomerational analysis and prediction the effect of substitution on the direction of isomerization by means of density functional theory (DFT) methods. For this purpose, we studied the effect of different substitution (X=H, CH_3, OCH_3, and Cl) on the theoretical geometrical parameters, proton chemical shifts, and energies of both aforementioned isomers. The calculated results compared with the X-ray diffraction and NMR data as the experimental results. The theoretical study of two isomers gives a clear understanding for the resonance, electron donating, and steric effects of the substituted groups on the stability of isomers.

2. Method of analysis

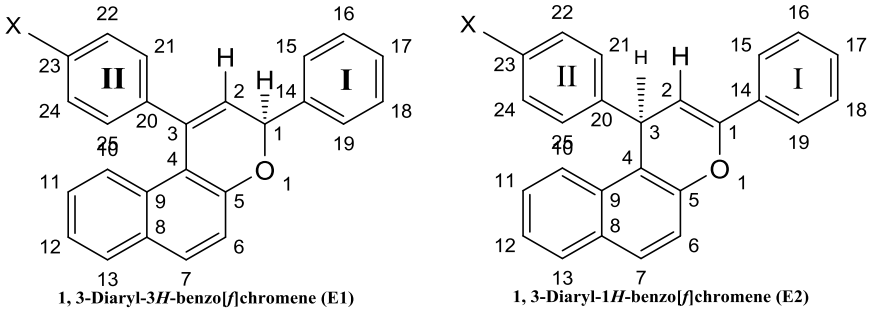
All theoretical calculations were performed using Gaussian 03W program [17] package without any constraint on the geometry. Two possible isomers of 1,3-diaryl-H-benzo[*f*]chromenes were fully optimized at the B3LYP [18] level, using 6-31G*, 6-311G**, and 6-311++G** basis sets, and second-order Moller-Plesset (MP2) level [19], using 6-31G* basis set. The second order interaction energies ($E^{(2)}$) [18] were performed at the B3LYP/6-311G** level using NBO (3.0) implemented in Gaussian 03. The absolute shielding for two isomers and tetramethylsilane (TMS) have been obtained using the gauge-including atomic orbital (GIAO) method [21,22] achieved at the B3LYP/6-311G** level. The predicted ^1H and ^{13}C chemical shifts are derived from equation $\delta = \sigma_0 - \sigma$, where δ is the chemical shift, σ is the absolute shielding, and σ_0 is the absolute shielding of TMS.

3. Results and Discussion

3.1. Optimized structure

According to the theoretical point of view, by considering the position of double bond in the heterocyclic ring of 1,3-diaryl-*H*-benzo[*f*]chromenes (X=H), and X= CH_3, OCH_3, and Cl substitutions, with respect to the phenyl groups, two isomers can be drawn for desired molecule (E1 and E2 isomers). The structure of these isomers with different substitutions in the para position of the phenyl (II) group, (hereafter PII), and the atom numbering of the system are shown in Fig. 1. Also, the optimized structure, obtained at the B3LYP/6-311G** level, for the E1 and E2 isomers of 1,3-diaryl-*H*-benzo[*f*]chromenes are shown in Fig. 2.

The calculated total electronic energies and the energy difference between E1 and E2 isomers for X=H, CH_3, OCH_3, and Cl substitutions, calculated at the B3LYP with 6-311G**, 6-311++G** basis sets and MP2/6-31G* level, are listed in Table 1. Our calculations show that the E2 is more stable than E1. According to Table 1, the energy difference between these two isomers in X=H species, similar to others substitutions, is high (3.55-5.09 kcal/mol). This energy difference could be attributed to the planarity of heterocyclic ring with the naphthalene fragment in E2 isomer, which facilitates the establishment of resonance between heterocyclic and naphthalene rings.



X= H (1, 3-Diphenyl-*H*-benzo[*f*]chromene)

X= CH_3 (3-Phenyl-1-p-tolyl-*H*-benzo[*f*]chromene)

X= Cl (1- (4-Chlorophenyl)-3-phenyl-*H*-benzo[*f*]chromene)

X= OCH_3 (3- (4-Metoxyphenyl)-1-phenyl-*H*-benzo[*f*]chromene)

Fig. 1. The two possible isomers of 1, 3–diaryl- *H*-benzo[*f*]chromene (atom numbering for calculations are different with IUPAC numbering).

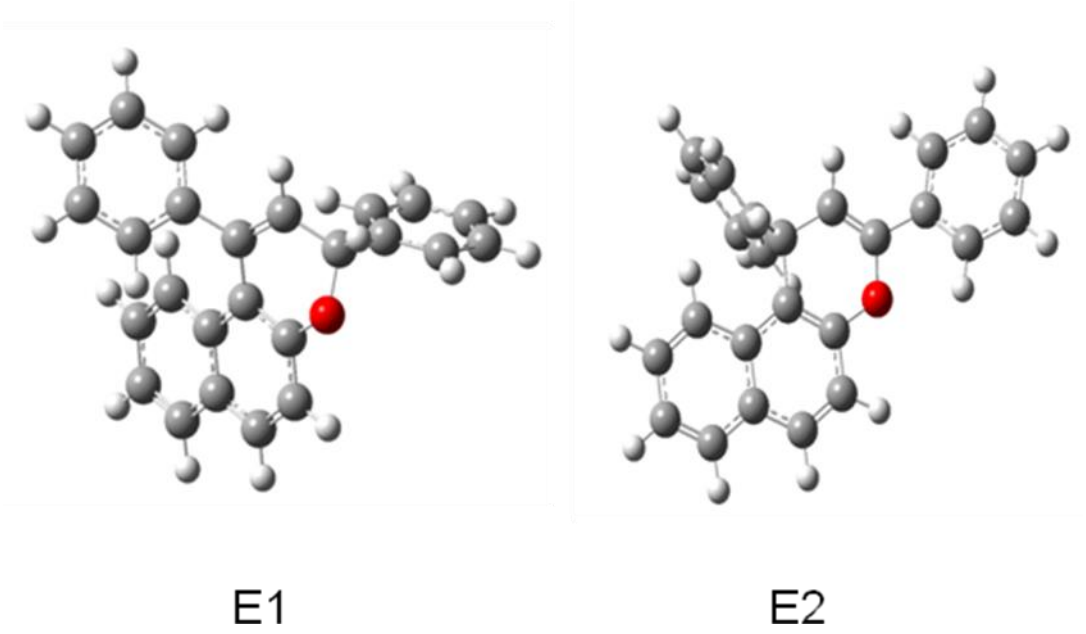


Fig. 2. The optimized structure at B3LYP/6-311G** level for the E1 and E2 isomers of 1,3-diaryl-*H*-benzo[*f*]chromenes.

This planarity of heterocyclic ring is explained by NBO results. The electronic energy difference between two isomers in the case of CH_3, OCH_3, and Cl substitutions is in the range of about 3-5 kcal/mol, similar to X=H substitution, as shown in Table 1. The stability of E2 isomer is due to planarity of heterocyclic ring with the naphthalene fragment, as explained previously.

The fully optimized structural parameters of E1 and E2 isomers at the B3LYP/6-311G**, B3LYP/6-311++G** and MP2/6-31G* levels, and the corresponding experimental values for X=H and $X=CH_3$, are summarized in Tables 2 and 3, respectively. For comparison, the optimized geometrical parameters in E1 and E2 isomers of X=Cl and OCH_3 substitutions calculated at B3LYP-6-311G** and MP2/6-31G* levels are listed in Table 4. According to this table the optimized geometry of X=Cl and OCH_3 substitutions are also almost the same as those in X=H, CH_3 substitutions. This is due to the same deviation between the dihedral angles of phenyl and heterocyclic ring in the mentioned substitutions.

Table 1. The calculated total electronic energies (in Hartree) of E1 and E2 isomers and the energy differences (in kcal/mol) between E1 and E2 isomers of 1,3-diaryl-H-benzo[f]chromenes obtained at different levels and basis.[a]

	MP2/6-31G*			B3LYP/6-311++G**			B3LYP/6-311G**		
	E			E			E		
X	E1	E2	ΔE	E1	E2	ΔE	E1	E2	ΔE
H	-1035.40166	-1035.40733	3.55	-1038.96448	-1038.97260	5.09(4.39)	-1038.97594	-1038.98356	4.78
CH_3	-1074.57274	-1074.57833	3.51	-1078.29216	-1078.30017	5.02(4.87)	-1078.30355	-1078.31112	4.74
OCH_3	-1150.53754	-1150.54256	3.15	-1153.51801	-1153.52576	4.86(4.68)	-1153.53233	-1153.53960	4.56
Cl	-1494.43463	-1494.44035	3.58	-1498.60594	-1498.59887	4.43	-1498.59886	-1498.60661	4.85

[a] E, absolute electronic energy for E1 and E2 isomers; ΔE, energy difference between E2 and E1, the corrected values for the ZPE are given in parenthesis.

Table 2. The selected bond experimental and calculated distances (Å), angles and dihedral angles (°) for 1, 3-diphenyl-3*H*-benzo[*f*]chromene (X=H) in different levels and basis sets.[a]

	MP2/6-31G*		B3LYP/6-311G**		B3LYP/6-311++G**		
	E1	E2	E1	E2	E1	E2	Exp[b]
O1-C5	1.371	1.383	1.362	1.375	1.363	1.376	1.389(9)
O1-C1	1.453	1.384	1.448	1.380	1.449	1.379	1.462(9)
C1-C2	1.499	1.346	1.507	1.337	1.506	1.337	1.474(10)
C1-C14	1.499	1.469	1.511	1.477	1.510	1.476	1.519(11)
C3-C20	1.478	1.521	1.490	1.536	1.490	1.536	1.462(9)
C2-C3	1.356	1.501	1.347	1.509	1.347	1.509	1.344(10)
C3-C4	1.468	1.509	1.480	1.520	1.497	1.519	1.484(8)
C4-C5	1.398	1.384	1.394	1.357	1.394	1.378	1.375(10)
C5O1C1	111.7	117.1	114.1	118.7	113.8	118.7	111.2(5)
O1C1C2	108.2	122.6	108.5	121.7	108.3	121.7	108.4(5)
O1C1C14	107.1	111.6	108.4	112.0	108.4	112.0	108.1(6)
C2C1C14	113.0	125.6	113.6	126.3	113.8	126.2	113.1(6)
C3C2C1	117.9	122.9	119.2	123.7	119.0	123.6	120.5(6)
C2C3C20	120.5	109.9	119.2	109.5	119.3	109.5	121.4(6)
C2C3C4	117.3	109.5	117.6	109.9	117.5	109.9	115.7(6)
C20C3C4	121.5	112.1	122.6	114.3	122.5	114.2	121.8(6)
C5O1C1C2	56.9	9.7	52.8	8.2	53.2	8.6	55.4(8)
O1C1C2C3	-43.8	7.3	-39.7	5.4	-40.1	5.2	-42.7(9)
C1C2C3C4	3.6	-20.2	2.3	-15.2	2.5	-15.3	3.8(10)
C2C3C4C5	24.5	17.9	23.8	12.7	23.7	13.1	23.1(9)
C2C1C14C15	70.8	-144.9	82.1	-154.3	78	-153.6	61.2(9)
C2C3C20C21	49.1	104.7	51.1	96	51.4	95.3	47.7(10)
C1O1C5C4	-31.9	-11.6	-30	-10.3	-30.2	-10.5	-32.4(9)
R^2	0.99980	0.98748	0.99964	0.98807	0.99967	0.98807	-
a	0.996	1.006	1.003	1.012	1.002	1.012	-
b	0.0217	0.315	0.0327	0.294	0.0346	0.298	-
SD	0.858	2.896	1.152	2.767	1.107	2.763	-

[a] R^2: regression coefficient; a: slope; b: intercept and SD: standard deviation between experimental and theoretical bond lengths and bond angles.
[b] Data from ref. [12].

Table 3. The selected experimental and calculated bond distances (Å), angles (°) and dihedral angles (°) for 3-Phenyl-1-p-tolyl-*H*-benzo[*f*]chromene (X=CH_3) in different levels and basis set[a].

	MP2/6-31G*		B3lyp/6-311G**		B3lyp/6-311++G**		
	E1	E2	E1	E2	E1	E2	Exp[b]
O1-C5	1.371	1.383	1.362	1.375	1.363	1.376	1.392(5)
O1-C1	1.454	1.384	1.448	1.38	1.450	1.380	1.386(4)
C1-C2	1.499	1.346	1.506	1.336	1.506	1.337	1.325(5)
C1-C14	1.499	1.469	1.511	1.476	1.510	1.476	1.484(5)
C3-C20	1.477	1.520	1.489	1.535	1.489	1.535	1.523(5)
C2-C3	1.356	1.501	1.347	1.509	1.347	1.509	1.495(5)
C3-C4	1.468	1.509	1.479	1.520	1.479	1.520	1.498(5)
C5O1C1	111.7	117.1	114.1	118.6	113.9	118.6	117.0(3)
O1C1C2	108.3	122.6	108.4	121.7	108.3	121.7	120.9(4)
O1C1C14	107.1	111.6	108.3	111.9	108.3	112.0	110.8(4)
C2C1C14	113.1	125.6	113.6	126.2	113.8	126.2	128.3(4)
C3C2C1	117.9	122.9	119.1	123.7	119.0	123.6	123.8(4)
C2C3C20	120.5	109.9	119.3	109.5	119.4	109.5	111.7(3)
C2C3C4	117.3	109.5	117.5	109.8	117.5	109.8	109.1(3)
C20C3C4	121.5	112.1	122.5	114.2	122.0	114.2	111.9(3)
R^2	0.99804	0.99983	0.99827	0.99981	0.99830	0.99982	-
a	0.996	1.006	1.003	1.012	1.002	1.012	-
b	0.0212	0.315	0.0327	0.294	0.0346	0.298	-
SD	2.527	0.735	2.375	0.771	2.355	0.762	-

[a] R^2, regression coefficient; a, slope; b, intercept; and SD, standard deviation, between experimental and theoretical geometrical parameters.
[b] Data from ref. [16]

The selected calculated second order interaction energies ($E^{(2)}$) between the donor–acceptor orbitals in E1 and E2 isomers of 1,3-diaryl-H-benzo[f]chromenes are collected in Table 5. According to this table, the only significant difference between the interaction energies of the compared species is π C4-C5 bond (of naphthalene ring, (hereafter NR)) to the π* C2-C3 bond (of heterocyclic ring, (hereafter HR)) and vice versa in E1 isomer, and π C14-C15 bond (of phenyl (I) group, (hereafter PI)) to the π* C2-C1 bond (of HR), and vice versa, in E2 isomer. These interactions are relatively large, about 8-13 kcal/mol. Therefore, stabilization through the resonance of heterocyclic ring with the naphthalene and phenyl groups is expected for E1 and E2 isomers, respectively. It is noteworthy that the ($E^{(2)}$) of LP(1) and LP(2) O1→ σ* and π* (C1–C2) in E2 isomer could be well related to stabilization of this isomer through resonance with the HR. This may explain the almost coplanarity of the HR in E2 isomer. The planarity of HR in E2 isomer causes establishment of resonance between naphthalene ring and C5-O1-C1-C2 residue. The difference between dihedral angle of PI and PII with respect to the HR shows that in E2 isomer resonance of PII with HR is much less than PI with HR (dihedral angle of PI and PII in E2 isomer is 25.6º and 96.0º for X=H substitution, respectively). The longer C3-C20 bond length (1.521-1.536Å) in E2 isomer compared to C1-C14 (1.469-1.477Å) confirms the mentioned resonance.

Table 4. The selected calculated bond distances (Å), angles (°) and dihedral angles (°) of 1-(4-chlorophenyl)-3-phenyl-*H*-benzo[*f*]chromene (X=Cl) and 3-(4-metoxyphenyl)-1-phenyl-H-benzo[f]chromene (X=OMe) in different levels and basis set.

	X=Cl				X=OMe	
	MP2/6-31G*		B3lyp/6-311G**		B3lyp/6-311++G**	
	E1	E2	E1	E2	E1	E2
O1-C5	1.371	1.383	1.364	1.383	1.363	1.376
O1-C1	1.454	1.384	1.449	1.384	1.450	1.380
C1-C2	1.499	1.346	1.508	1.347	1.506	1.337
C1-C14	1.499	1.469	1.512	1.470	1.510	1.476
C3-C20	1.477	1.520	1.490	1.520	1.489	1.535
C2-C3	1.356	1.501	1.351	1.500	1.347	1.509
C3-C4	1.468	1.510	1.480	1.509	1.479	1.520
C5O1C1	111.7	117.1	114.2	117.0	114.0	118.7
O1C1C2	108.3	122.6	108.4	122.6	108.4	121.7
O1C1C14	107.1	111.7	108.0	111.8	108.3	112.0
C2C1C14	113.1	125.6	113.6	125.6	113.6	126.3
C3C2C1	117.9	122.9	119.3	122.7	119.1	123.8
C2C3C20	120.5	110.0	119.0	110.3	119.4	109.7
C2C3C4	117.6	109.5	117.6	109.4	117.5	109.8
C20C3C4	121.5	112.0	122.8	111.8	122.4	114.2

The calculation results show, because of non-planar HR in E1 isomer, the resonance occurs between HR with NR via C4-C3-C2 atoms. In E1 isomer, PII group has more contribution in resonance compared to PI group. The dihedral angle between PII and HR, (dihedral angle of Ph (I) and Ph (II) in E1 isomer are 95.6º and 51.1º for X=H substitution, respectively), confirms our claim. The aforementioned resonance makes E2 isomer more stable than E1 isomer. Similar results obtained for other substitutions (See Table 1 for the CH_3, OCH_3, and Cl substitutions). As it is shown in Table 1, the energy difference between E1 and E2 is in the 5.09-3.55 kcal/mol range (calculated at different levels) for X=H. The corresponding values for X=Cl, CH_3, and OCH_3, with different substitution effects such as electron withdrawing and electron donating are in the 4.85-3.58, 5.02-3.51, and 4.86-3.15 kcal/mol ranges, respectively. However, these energy differences reduce to 4.39, 4.87, and 4.68 kcal/mol, respectively, upon ZPE corrections (Table 1).

According to theoretical and experimental results and above issues about mentioned resonance, the C3-C4 bond length in E1 isomer is shorter compared to the corresponding value in E2 isomer that confirms the resonance between naphthalene and C4-C3-C2, as mentioned previously. The C3-C20 bond length is also shorter compared to C1-C14 in E1 isomer which this is due to conjugation between Ph (II) and naphthalene in E1 isomer. As Tables 2 and 3 show, the O1-C1 bond length in E2 is about 0.07Å shorter than the corresponding value in E1 isomer, which is the result of resonance. The increase of O1-C5 and decrease of O1-C1 bond lengths in E2 relative to E1 can be a reason for existing the resonance between naphthalene ring with the C5-O1-C1-C2 fragment.

According to Table 2, the most of theoretical results which obtained for E1 isomer, as the O1-C1, C1-C14, C3-C20, and C2-C3 bond lengths, O1C1C2, C2C1C14, and C2C3C4 bond angles, are in good agreement with the X-ray results, while O1-C5 and C2C3C20 are in agreement with the corresponding value in other isomer, and the averaged amount of C3-C4 bond length in two isomers is close to that in observed results. So, the above comparison indicates

Table 5. Selected second order perturbation energies $E^{(2)}$ (donor/acceptor) for E1 and E2 isomers of 1,3-diaryl-*H*-benzo[*f*]chromenes obtained at B3LYP/6-311G** level.[a]

Donor	Type	Acceptor	Type	E1	E2
C4-C5	π	C2-C3	π*	12.5	-
C2-C3	π	C4-C5	π*	8.1	-
O1	LP (1)	C4-C5	σ*	6.4	6.5
O1	LP (2)	C4-C5	π*	25.4	26.1
O1	LP (1)	C1-C2	σ*	-	5.5
O1	LP (2)	C1-C2	π*	-	26.6
C1-C2	π	C14-C15	π*	-	9.5
C14-C15	π	C1-C2	π*	-	13
C1-C2	Σ	C1-C14	σ*	-	5.6
C1-C2	Σ	C1-C14	σ*	-	5.4

[a] Energy in kcal/mol.

that the E1 isomer for X=H substitution is more stable calculated results and the mentioned resonance. It is noteworthy that the theoretical results, obtained at all level of calculations, for $X=CH_3$ show good agreement with the experimental data for E2 isomer, within the limit of experimental error, as shown in Table 3. The regression coefficients R^2, and standard deviations (SD) are listed in Tables 2 and 3 for both isomers. The best values for scaling factors have been obtained by B3LYP level with 6-311G** and 6-311++G** basis sets and MP2/6-31G* level.

3.2. ^1H and ^{13}C NMR spectra study

The study of NMR results is favorable to find out the presence of a particular atom in a particular position of a molecule. Since each nucleus is associated with the electrons of the nearest atoms, so atoms show a different chemical shift (δ) value when they are in different environments. In the present study, the chemical shift of hydrogen and carbon atoms in 1, 3 diaryl-*H*-benzo[*f*]chromenes with X= (H, CH_3, OCH_3, and Cl) substitution are calculated at the B3LYP/6-311G** level of theory. The selected experimental and theoretical ^1H and ^{13}C-NMR data for the E1 and E2 isomers (in $CDCl_3$ solvents at room temperature) are listed in Table 6. The experimental proton NMR spectra of the 1,3-diaryl-*H*-benzo[*f*]chromenes (X=H) consist of two doublet signals at the range of about 4.9-6.04 ppm (representative 1H NMR spectral data for a: Yadav et al [11]. is; 6.0 (d,1H) and 5.34 (d,1H) ppm; b) Xue et al. [14] and Eshghi et al. [13] are; 5.96 (d,1H), 5.71 (d,1H) and 5.9 (d,1H), 4.9 (d,1H) ppm; respectively), which are related to H_1, H_2, and H_3 protons in both isomers. Our calculations show that the protons on the C_1 and C_2 atoms of E1 isomer occurs at the range of about 6.53-6.27 ppm while the protons on the C_2 and C_3 atoms of E2 isomer occur at the range of about 6.50-6.14 ppm. The comparison experimental and theoretical ^1H-NMR results shows that both isomers can be related to the same experimental results. So, we try to make a comparison between experimental and theoretical ^{13}C-NMR results for distinguishing between the two isomers.

We have used density functional theory to predict the ^{13}C-NMR chemical shifts for two isomers of 1,3-diaryl-*H*-benzo[*f*]chromenes. The better correlation between experimental and theoretical ^{13}C-NMR results is observed in the E1 isomer as a main product in Xu procedure [12], while the results of our calculations, as shown in Table 1, show that E2 isomer is the stable isomer. The calculated chemical shift of C1 in E1 isomer with sp^3 hybridization is 86 ppm that is in good agreement with the experimental value of 76.5 ppm, while corresponding carbon with sp^3 hybridization in E2 isomer (C3) is predicted to occur at the 50.0 ppm. As well as, the chemical shift of C2 in E1 isomer is about 23 ppm higher than E2 isomer and it is closer to the experimental value (126.5 ppm). Although detailed comparison needs to reach a definite assignment but the distribution of the peaks shows that there is good agreement between theoretical results of E1 isomer and experimental data [12].

Table 6. The theoretical (at B3LYP/ 6-311G** level) and experimental ^{1}HNMR, ^{13}CNMR chemical shifts (ppm) for benzo[*f*]chromenes in $CDCl_3$.

	X=H		X=CH_3		X=OMe		X=Cl	
	E1	E2	E1	E2	E1	E2	E1	E2
H_1	6.32 (5.96[a], 6.04[b], 5.9[c])	–	6.43 (5.93[a])	–	6.12 (5.68[a])		5.94 (5.69[a])	–
H_2	6.12 (5.71[a], 5.34[b], 4.9[c])	6.38 (5.96[a], 6.04[b], 5.9[c])	6.15 (5.69[a])	6.47 (5.93[a])	6.40 (5.90[a])	6.49 (5.90[a])	6.11 (5.94[a])	6.51 (5.94[a])
H_3	–	6.05 (5.71[a], 5.34[b], 4.9[c])	–	6.09 (5.69[a])	–	6.07 (5.68[a])	–	6.20 (5.69[a])
C_{sp3}	86.6 (76.5[a])	50.0	86.2 (76.6[a])	48.9	86.45 (76.6[a])	48.5	86.9 (76.5[a])	49.9
C_2	134.2 (126.5[a])	111.4	134.1 (125.1[a])	112.1	133.04 (125.2[a])	112.3	136.3 (127.2[a])	111.8
C_{sp2}	151.3 (138.2[a])	157.8	150.7 (138.1[a])	157.2	150.26 (137.6[a])	157.1	149.8 (133.4[a])	158.2

[a, b, c]: The experimental values are given in parenthesis from refs. [12], [11], and [13], respectively.

It seems that some of the NMR and X-ray results are not in agreement with the theoretical calculations data for the most stable isomer. This disagreement could be attributed to the synthesis conditions, since the isomerization of E1 to E2 is a forbidden sigmatropic reaction. Therefore, after formation of E1 its conversion to the E2 is not possible and the less stable compound will be the predominant isomer. Moreover a simple protonation- deprotonation reaction does not isomerize these alkenes in heterocycle rings. Accordingly, different experimental results obtained by different researchers [12-16] may be due to consequence dehydrometallation- hydrometallation of E1 isomer by some transition metals used as catalyze.

4. Conclusions

DFT (B3LYP) and MP2 calculations have been performed for total energies, optimized geometry, and NMR calculations of two isomers of 1,3-diaryl-*H*-benzo[*f*]chromene at the levels. The total electronic energies, indicates that E2 is more stable than E1. The comparison of X-ray data with the calculated geometrical parameters for X=CH_3 is in agreement with E2, while for X=H the X-ray data is in agreement with the E1 isomer. The comparison of calculated ^{13}CNMR spectrum with the experimental results shows that E1 isomer is in good agreement with the available experimental data. By considering the experimental and theoretical evidences it is concluded that formation of E1 and E2 depends on the preparation conditions.

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