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Hydroarylation of cinnamic acid with phenols catalyzed by acidic ionic liquid [H-NMP]HSO_4: computational assessment on substituent effect

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Abstract Hydroarylation of cinnamic acid with different substituted phenols, in the presence of acidic ionic liquid, *N*-methyl-2-pyrrolidonum hydrosulfate ([H-NMP]HSO_4) gave the corresponding dihydrocoumarins in high yields and excellent selectivity. Among these substituted phenols, while methyl phenol afforded the corresponding dihydrocoumarin, nitrophenol under the same reaction conditions diverted the course of reaction, affording 3-(4-nitrophenyl)-3-phenyl-propanoic acids. We investigated this behavior from the energetic and electronic points of view, using quantum chemistry computational methods. In this respect, the electronic energy change values for the conversion reaction of substituted phenyl cinnamate esters to dihydrocoumarin compounds have been obtained via density functional theory calculations. We demonstrated that the conversion reaction in the presence of CH_3 substituent is more favorable energetically than NO_2 substituent. Moreover, we have concentrated on topological analysis of electron density on some key bond and ring critical points and their associated bond paths to assess the conversion of substituted phenyl cinnamate esters to dihydrocoumarins. Our calculated results showed that *para*-methyl phenyl cinnamate has more of electronic tendency to undergo the intramolecular cyclization step and, consequently, generate the corresponding dihydrocoumarin.

Keywords Dihydrocoumarins · 3-(4-Nitrophenyl)-3-phenylpropanoic acids · Ionic liquid · Phenols · Cinnamic acid · DFT methods · QTAIM analysis

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Introduction

Coumarin derivatives as a molecule or scaffold exist extensively in plants. They exhibit a wide scope of pharmacological activities [1, 2] such as anti-cancer, anti-aging, anti-inflammatory and anti-oxidative [3]. For instance, tannin-containing plant extracts contain the 4-aryldihydrocoumarin moiety and have traditionally been used for the treatment of infection diseases for centuries in China [4–10]. The anti-fungal and anti-TB potencies of several coumarin derivatives as a new class of pharmacophore have also been studied [11–14]. They have also been widely employed as additives in perfumes, cosmetics, pharmaceuticals, and food, as well as optical brighteners, dispersed fluorescents, and laser dyes [15].

4-Aryl-3,4-dihydrocoumarins are natural products [16–18], which show some significant biological activities such as aldose reductase inhibition [8], antiherpetics [19], protein kinases [9]. They are also used as intermediates in the synthesis of more complicated targets, showing biological activities. For instance 4-aryl-3, 4-dihydrocoumarins has been employed as starting materials for the synthesis of *N*-diaryl (aryl) substituted amides, showing antiarrhythmic properties [20].

The most common strategy for the synthesis of dihydrocoumarins is acid-catalzed hydroarylation of cinnamic acids with differently substituted phenols [21–23]. Other methods include: the catalytic hydrogenation of coumarins [24, 25], Lewis acid catalyzed reaction of activated phenols with acrylonitrile [26, 27], the Fischer carbene complex reaction with ketene acetals [28], *p*-TSA catalyzed hydroarylation of cinnamic acids with various phenols [29], $AlCl_3$ catalyzed C–C coupling reaction between hydroxyketene *s*,*s*-acetals and arenes [30], [4 + 2] cycloaddition reaction of *o*-quinone methides with silyl ketene acetals [31], bio-conversion of coumarins by certain kind of microorganisms [32], microwave-promoted reaction of phenols and cinnamoyl chloride in the presence of montmorillonite K-10 as heterogeneous catalyst in solvent-free conditions [33], microwave-assisted reaction of phenols and cinnamic acids mediated by silica supported Wells–Dawson heteropolyacid [34], *p*-TSA mediated hydrolysis of aryl cinnamic esters [35], and trifluoroacetic acid-catalyzed hydroarylation of cinnamic esters with tyroso [36]. There is also the preparation of trifluoromethylated dihydrocoumarins, by tandem super acidic activation of 2-(trifluoromethyl)acrylic acid with arenes that have been accomplished and reported [37]. Also, solvent-free synthesis of 4-aryl-3, 4-dihydrobenzopyran-2-ones through [3 + 3] cyclo-coupling of phenols with cinnamic acid mediated by molecular iodine has been reported [38, 39].

These methods have their own merits and drawbacks such as the deficiency of substrate generality and the use of a large excess of expensive chemicals such as trifluoroacetic acid [23], and the general concerns regarding the transition metals-catalyzed reactions [23, 40, 41].

In the few past decades, ionic liquids have attracted much attention and interest in the context of green synthesis of organic compounds due to their adaptable physical and chemical properties [42]. Because of these properties, such as high thermal and chemical stability, low vapor pressure, good solvating ability, ease of recovery, reusability, and controlled miscibility, they are suitable for being used as an

alternative green reaction media [43–49]. Perhaps, one of the most important features of ionic liquid is its dual role, both as solvent and catalyst [50–54]. These unique properties are the result of being molten salts, liquefied below 100 °C, which generally consist of a cation (such as imidazolium, pyrrolidinium, pyridinium, tetraalkyl ammonium or tetraalkyl phosphonium) and or an anion (e.g., tetrafluoroborate, hexafluorophosphate, and bromide). In addition, after the first economically feasible industrial process employing ionic liquids by BASF (BASIL10 process) in 2003 [55, 56], the applicability of various ionic liquids for other reactions have become well-known and widely accepted. Thus, it is worthwhile, to examine inexpensive commercially available or readily accessible ionic liquids in the synthesis of useful compounds as catalyst or/and solvent.

Since most compounds are soluble in ionic liquids, acidic ILs can be used in several reactions, both as catalyst and solvent. In this context, acidic Brönsted ionic liquid, pyrrolidinium bisulfate [HNMP] HSO_4, can be considered as a good candidate, being examined in reactions leading to useful organic compounds [57–59]. Noticeably, it can be prepared by a facile method, just upon treatment of 1-methyl-2-pyrrolidone with sulfuric acid (Scheme 1) [57].

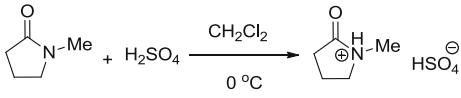
We are interested in heterocyclic chemistry [60–66] and especially in the synthesis of coumarins [67, 68]. We have also used ionic liquids as solvents and catalysts [69–80]. In the context of consideration of green chemistry, and moving towards rational drug design [81], recently, we have also tried to combine our obtained experimental data, with computational analysis to interpret the experimental results, or vice versa, which have been promising and fulfilled [82–87].

Due to the significance of coumarin derivatives and the importance of ionic liquids as green catalyst/solvents and in order to support computational methods as rational and sound tools for interpretation and also prediction of experimental data, in this paper we wish to reveal our investigation on developing hydroarylation of cinnamic acids with phenols mediated by acidic ionic liquid, namely *N*-methyl-2-pyrrolidonum hydrosulfate ([H-NMP] HSO_4) as a highly chemoselective, inexpensive commercially available, and efficient catalyst as a mild proton source. Moreover, we have assessed our observed experimental results on substituent effect using density functional theory (DFT) methods [88] and quantum theory of atoms in molecules (QTAIM) approach [89, 90] and found a reliable agreement between experimental results and our obtained computational energetic and electronic interpretations.

Results and discussion

Initially, a mixture of cinnamic acid **1a** and phenol **2a** in the presence of acidic ionic liquid [H-NMP]HSO_4 was heated under reflux conditions. After a standard workup procedure, the corresponding dihydrocoumarin **3a** was obtained in 95 % yield

Scheme 1 Synthesis of ionic liquid



(Scheme 2). Encouraged by this result, we established the scope and generality of the reaction by using differently substituted phenols (Table 1). As depicted in Table 1, several differently substituted phenols **2a–j**, bearing different groups such as Me, Cl, and *t*-Bu undergo esterification with various cinnamic acids **1a–c** with subsequent intramolecular hydroarylation to give the corresponding dihydrocoumarins **3a–j** in good to excellent yields.

In this developed approach, several phenols bearing electron releasing groups such as Me, *t*-Bu were easily converted into the corresponding dihydrocoumarins in satisfactory yields in relatively short reaction times. Phenol **2a** without any substituent gave product **3a** in 95 % yield. The dihydrocoumarins **3g** was obtained in 88 % using α-naphthol. Phenol with an electron withdrawing group such as the chloro group at *para* position afforded the desired product **3e** in high yield (Table 1).

The suggested mechanism for the reaction of cinnamic acid with phenols mediated by ionic liquid, involves the formation of phenolic esters via trans esterification with subsequent intramolecular Friedel–Crafts type cyclization resulting in the formation of corresponding dihydrocoumarin derivatives **3** [21].

Noticeably, following the aforementioned protocol, and under identical reaction conditions, 4-nitrophenol did not produce the expected corresponding coumarin. Actually, in the presence of [H-NMP]HSO_4, under reflux conditions, the reaction of cinnamic acid with 4-nitrophenol **2k** (R = NO_2) proceeded smoothly, but just ended up in esterification to give the ester **4** (R = NO_2) as sole product, the corresponding nitro phenyl cinnamates (linear ester **4**) (R = H), even after prolonged reaction time (24 h) in low yield (35 %).

In the following section, we reveal the results of our computational studies trying to rationalize the aforementioned observed behavior in the experimental affordance of coumarins, using phenols, bearing CH_3 as electron donating and NO_2 as electron-withdrawing groups at the *para* position.

Computational section

In the present section, we have concentrated on computational assessment of substituent effects on the formation of dihydrocoumarin compounds via DFT [88] and QTAIM [89, 90] approaches. In this respect, the reaction of *para*-substituted phenols (containing CH_3 as electron-donating and NO_2 as electron-withdrawing groups) with cinnamic acid have been modeled for the synthesis of dihydrocoumarins. The aforementioned reaction model is depicted in Scheme 3.

Scheme 2 Hydroarylation of cinnamic acid with phenols catalyzed by ionic liquid

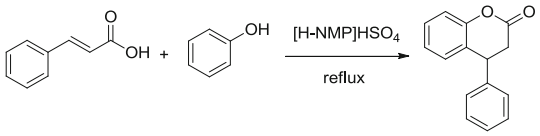
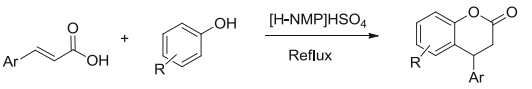


Table 1 Hydroarylation of cinnamic acid with phenols catalyzed by ionic liquid



1 2 3

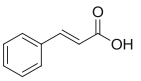
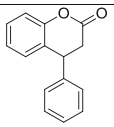
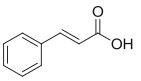
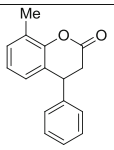
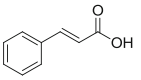
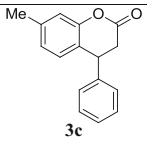
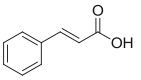
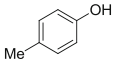
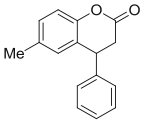
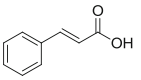
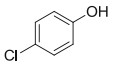
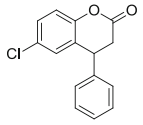
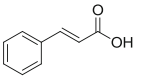
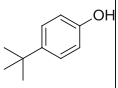
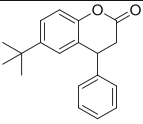
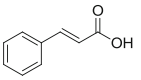
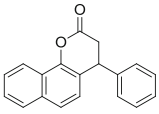
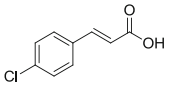
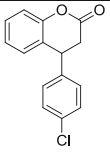
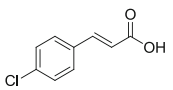
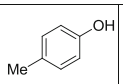
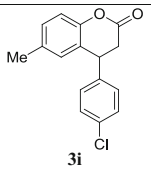
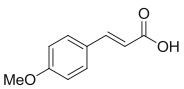
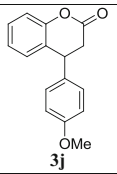
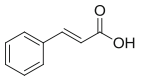
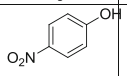
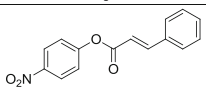
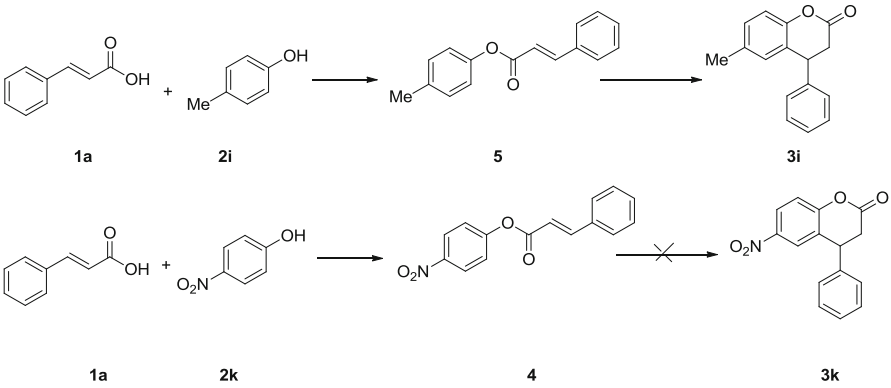
Entry	Cinnamic acid (1)	Phenols (2)	Product (3)	Time (h)	Yield %
1	 **1a**	 **2a**	 **3a**	5	95
2	 **1a**	 **2b**	 **3b**	4	90
3	 **1a**	 **2c**	 **3c**	3	92
4	 **1a**	 **2d**	 **3d**	2	94
5	 **1a**	 **2e**	 **3e**	3	84
6	 **1a**	 **2f**	 **3f**	2.5	84
7	 **1a**	 **2g**	 **3g**	2	88
8	 **1b**	 **2h**	 **3h**	3.5	82

Table 1 continued

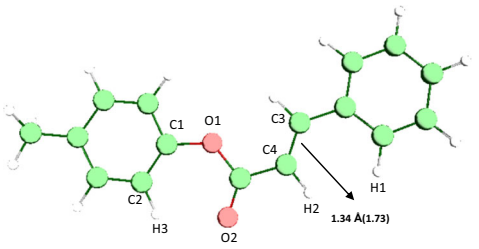
9	 **1b**	 **2i**	 **3i**	4.5	89
10	 **1c**	 **2j**	 **3j**	4	84
11	 **1a**	 **2k**	 **4**	24	35



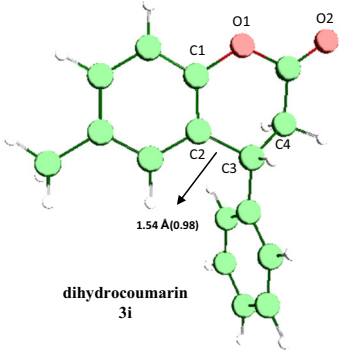
Scheme 3 The effective reaction models for the assessment of substituent effect

From the mechanistic point of view, the reaction of *para*-methyl phenol **2i** with cinnamic acid **1a** leads to the formation of phenolic ester compound **5** followed by intramolecular Friedel-Craft type cyclization to generate dihydrocoumarin **3i**, while this intramolecular cyclization step does not occur in the case of 4-nitro phenol **2k**.

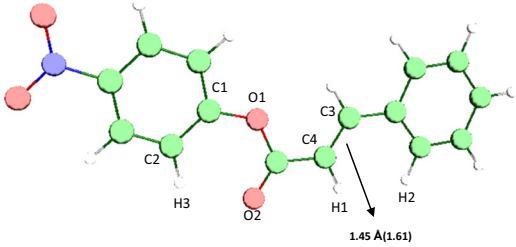
In this context, we have first determined the ground state structures of *para*-methyl and *para*- nitro substituted dihydrocoumarins **3i** and **3k** and their corresponding esters **5** and **4** at the M06/6-311+G** level of theory [91] with no symmetry restrictions in geometry optimization procedure. Then, the stationary points were analyzed by vibrational frequency calculations to confirm the found optimized structures corresponding to true minima. It is important to mention that



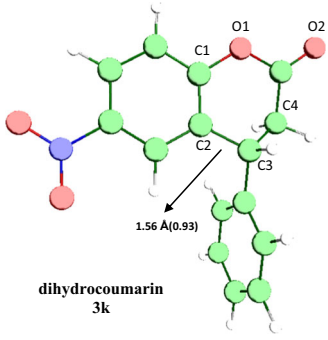
Phenyl cinnamate ester
5



dihydrocoumarin
3i



phenyl cinnamate ester
4



dihydrocoumarin
3k

Fig. 1 The optimized geometry of substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k** were obtained at the M06/6-311+G* level of theory. Notably, the M06/6-311+G** calculated bond length (and bond order) values of some key bonds have been also presented

the M06 functional has been introduced as a hybrid meta-GGA (generalized gradient approximation) exchange–correlation functional that was recommended for application in organometallic and inorganometallic thermochemistry, kinetic studies, and noncovalent interactions [91]. All DFT computations have been performed using the GAMESS suite of programs [92]. In Fig. 1, we have illustrated the theoretical optimized structures of two substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k** obtained at the M06/6-311+G** level of theory in the gas phase together with the atomic numbering. It should be noticed that in Fig. 1, we have also presented M06/6-311+G** calculated bond length and bond order values of some key bonds for substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k**. As it can be seen in Fig. 1, the C=C bond (C3–C4) in *para*-methyl phenyl cinnamate is richer electronically than that of *para*-nitro phenyl cinnamate with the higher bond order. This electronic property significantly facilitates the intramolecular cyclization step to produce dihydrocoumarin. On the other hand, the calculated bond order of C2–C3 (forming via the intramolecular cyclization step) is higher in dihydrocoumarins **3i** than that of dihydrocoumarins **3k,** which is in agreement with the obtained results.

The electronic energy change values for the conversion of substituted phenyl cinnamate esters to dihydrocoumarin compounds have been calculated at M06/6-31G* and M06/6-311+G** levels of theory and reported in Table 2. The reported values of electronic energy changes demonstrate that the conversion reaction in the presence of CH_3 substituent is more favorable energetically by about 2 kcal mol^{-1} than in the presence of NO_2 substituent. It should be noted that the difference between the values of reaction electronic energy in the presence of CH_3 and NO_2 substituent are approximately the same at both levels of theory, while the M06/6-311+G** calculated reaction electronic energy is more negative than the M06/6-31G* calculated ones. Since the difference between electronic energy of conversion reaction is too small for description of CH_3 and NO_2 substituent effect, in the next step, we focused on topological analysis of electron density via QTAIM computations to interpret this issue more distinctly.

In this respect, the obtained M06/6-311+G** wave function files for the optimized structures of substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k** were used as inputs to AIM2000 program [93]. Then, we calculated some selected bond and ring critical points

Table 2 The electronic energy change values for the conversion reaction of *para*-CH_3 and *para*-NO_2 substituted phenyl cinnamate esters to dihydrocoumarin compounds, calculated at the M06/6-31G* and M06/6-311+G** levels of theory

Substituent	M06/6-31G*	M06/6-311+G**
CH_3	−14.15	−17.07
NO_2	−12.18	−15.22

Note that all values have been reported in kcal mol^{-1}

(BCPs and RCPs, respectively) and their associated bond paths to assess the conversion of substituted phenyl cinnamate esters to dihydrocoumarins from the electronic point of view. In Table 3, we have listed the calculated values of electron density, ρ_b, its laplacian, $\nabla^2\rho_b$, electronic kinetic energy density, G_b, electronic potential energy density, V_b, total electronic energy density, H_b and $|V_b|/G_b$ of some selected CPs for substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k**. It should be mentioned that the magnitude of $\rho(r)$ and the magnitude and sign of its Laplacian $\nabla^2\rho(r)$ at BCPs are useful indicators for the nature of chemical bonding between atoms. Densities of local electronic energy, $H(r)$, its components [kinetic energy $G(r)$ and potential energy $V(r)$; as $H(r) = G(r) + V(r)$] and their ratio ($|V_b|/G_b$)at BCPs determine whether accumulation of charge at a given point, r, is stabilized, $H(r) < 0$, or destabilized, $H(r) > 0$ [89, 90].

QTAIM molecular graphs of substituted phenyl cinnamate esters **5** and **4** and dihydrocoumarins **3i** and **3k** are also presented in Fig. 2. The comparative analysis of the reported results of Table 3 clearly shows the following facts: (1) a comparison between the calculated electron density properties and indicators on C3–C4 BCP in substituted phenyl cinnamate esters show that the C=C bond in *para*-methyl phenyl cinnamate is electron-richer than its corresponding BCP in *para*-nitro phenyl cinnamate (with 0.3342 and 0.3202 electron density values for C3–C4 BCPs in substituted phenyl cinnamate esters **5** and **4**, respectively), and, consequently, the C=C bond in *para*-methyl phenyl cinnamate more readily undergoes the intramolecular cyclization step to produce the corresponding dihydrocoumarin; (2) at C2–C3 BCP (that is formed mechanistically through the intramolecular cyclization step), the calculated values of $\rho(r)$ in dihydrocoumarin compound **3i** are

Table 3 Mathematical properties of critical points associated with the key bonds in esters and their corresponding dihydrocoumarin compounds

Substituent	ρ_b	$\nabla^2\rho_b$	G_b	V_b	H_b	$\lvert V_b\rvert/G_b$
CH_3						
Cinnamate BCP(C3–C4)	0.3342	−0.9384	0.1295	−0.4938	−0.3643	3.8131
Cinnamate BCP(O2–H3)	0.0182	0.0686	0.0148	−0.0126	0.0022	0.8513
Cinnamate BCP(H1–H2)	0.0099	0.0376	0.0076	−0.0058	0.0017	0.7644
Coumarin BCP(C2–C3)	0.2499	−0.5760	0.0582	−0.2605	−0.2023	4.4759
Coumarin RCP1	0.0197	0.1320	0.0269	−0.0208	0.0061	0.7732
NO_2						
Cinnamate BCP(C3–C4)	0.3202	−0.9344	0.1284	−0.4906	−0.3622	3.8208
Cinnamate BCP(O2–H3)	0.0199	0.0721	0.0155	−0.0131	0.0023	0.8477
Cinnamate BCP(H1–H2)	0.0109	0.0380	0.0076	−0.0058	0.0018	0.7631
Coumarin BCP(C2–C3)	0.2380	0.5764	0.0586	−0.2615	−0.2029	4.4620
Coumarin RCP1	0.0176	0.1316	0.0268	−0.0207	0.0061	0.7723

The properties have been obtained via QTAIM analysis on the M06/6-311+G** calculated wave function of electron density. Note that numbering of atoms is in accordance with Fig. 1

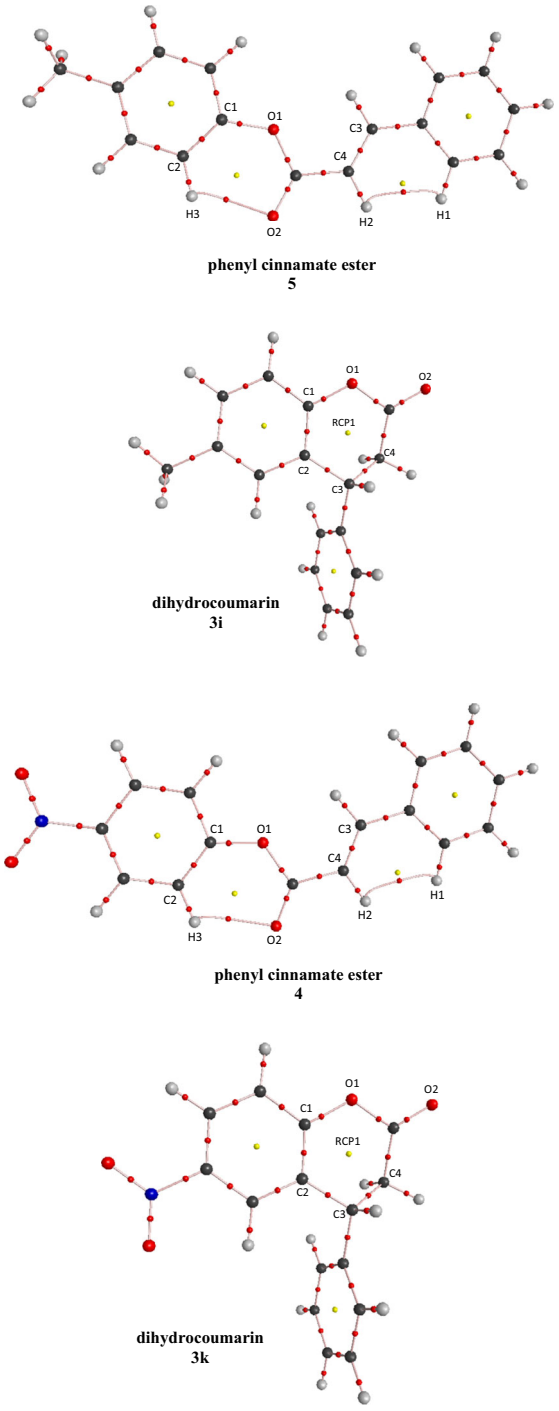


Fig. 2 Complete molecular graphs (MGs) of substituted phenyl cinnamate esters **5** and **4** and their corresponding dihydrocoumarins **3i** and **3k** obtained by QTAIM analysis of M06/6-311+G** electron density functions. Bond critical points: *red circles*; ring critical points: *yellow circles*; bond paths: *pink lines*. (Color figure online)

larger than that of the dihydrocoumarin compound **3k** that is in confirmation with the experimental production of dihydrocoumarin **3i** in high yield with the presence of the CH_3 electron-donating group at the *para* position of phenol; (3) a more stringent analysis of QTAIM molecular graphs demonstrate the presence of two C–H–H–C and C–H–O–C intramolecular interactions [94] between H1 and H2 and also O2 and H3 in substituted phenyl cinnamate esters **5** and **4**, while these H–H and O–H bonds are not present in dihydrocoumarins **3i** and **3k** that confirms the mechanistical interpretations. Moreover, the presence of H–H and O–H bonds results in formation of additional 6-member rings with the requisite ring critical points (RCP) very close to the BCP of H–H and O–H bonds. The comparison of the corresponding values of ρ_b and $\nabla^2\rho_b$ for H1–H2 and O2–H3 BCPs in substituted phenyl cinnamate esters **5** and **4** (with 0.0182 and 0.0199 ρ_b values for O2–H3 BCPs and also 0.0099 and 0.0109 ρ_b values for H1–H2 BCPs in substituted phenyl cinnamate esters **5** and **4**, respectively) corroborate that these C–H–H–C and C–H–O–C intramolecular interactions are stronger in *para*-nitro phenyl cinnamate **4** than *para*-methyl phenyl cinnamate **5** and leads to the more electronic stable *para*-nitro phenyl cinnamate **4.** While, these C–H–H–C and C–H–O–C intramolecular interactions in *para*-methyl phenyl cinnamate **5** are weaker and, consequently, facilitate the intramolecular cyclization step to afford the respected dihydrocoumarin **3i** in high yield and (4) the intramolecular cyclization step leads to the formation of new RCP denoted as RCP1. On the basis of the calculated electron density values of RCP1 (with 0.0197 and 0.0176 ρ_b values for RCP1 in dihydrocoumarin compounds **3i** and **3k**, respectively), we can deduce that formation of this new ring is more favorable in the presence of CH_3 than the NO_2 substituent. Our obtained DFT and QTAIM results on energetic and electronic features of the model reaction is in confirmation with the experimental production of dihydrocoumarin compounds from the different *para*-substituted phenyl cinnamates.

Experimental

Materials and methods

Experimental procedures and characterization

Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. IR spectra were recorded from a KBr disk on the FT-IR Bruker Tensor 27. All products were known and characterized by comparison of their IR spectra and physical data with those of authentic samples, which were found to be identical.

Preparation of acidic ionic liquid [H-NMP]HSO_4 [57]

In a 25-mL round bottom flask, a 0.97 mL (10 mmol) of 1-methyl-2-pyrrolidon in dichloromethane (15 mL) was placed, while cooling in an ice bath and with stirring.

Then 0.53 mL of sulfuric acid 98 % (10 mmol) was added drop wise to the reaction mixture within 10 min, and stirring was continued for 4 h at ambient temperature. The dichloromethane was removed under reduced pressure and the product was dried at 70 °C under vacuum for 30 min in an appropriate vacuum oven.

Synthesis dihydrocoumarins: general procedure

To a 25 mL round bottomed flask equipped with a reflux condenser, phenol (1 mmol), cinnamic acid (1 mmol), and acidic ionic liquid *N*-methyl-2-pyrrolidonum hydrosulfate ([H-NMP]HSO_4) (3 mmol) were placed. The reaction mixture was heated at 120 °C for a period of time as indicated in Table 1 (2–5 h). After completion of the reaction (monitored by TLC), the reaction mixture was cooled and poured in water. The mixture was extracted with ethyl acetate (2 × 10 mL). The organic layer was separated, washed with water and brine and separated again, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product. This crude product was column chromatographed over silica gel (230–400 mesh) using ethyl acetate and petroleum ether as eluent to give the highly pure products in satisfactory yield (Table 1).

Conclusion

In conclusion, we have developed a facile, operational, metal and solvent-free reaction for hydroarylation of cinnamic acids with phenols mediated by acidic ionic liquid *N*-methyl-2-pyrrolidonum hydrosulfate ([H-NMP]HSO_4) affording dihydrocoumarins **3**, and 4-nitro esters **4** a, in good to high yields. Easy handling, broad substrate scope, and the use of ionic liquid as an efficient and eco-friendly solvent are some of the merits of our protocol. In addition, this approach can be considered advantageous from the green chemistry point of view, since hydroarylation offers perfect atom economy. Moreover, we have performed a comparative analysis on the substituent effect via DFT and QTAIM approaches to interpret computationally the experimental observations.

Experimental data

Various 4-aryl-3,4-dihydrobenzopyran-2-one derivatives and 4-nitro-phenyl cinnamate

1. 4-Phenyl-3,4-dihydrobenzopyran-2-one (**3a**); [95] mp:79–81 °C; Lit. [95] 78 °C; IR (KBr): $\upsilon_{max} = 1759\ cm^{-1}$; ^{1}HNMR ($CDCl_3$, 400 MHz): $\delta = 3.02–3.14$ (m, 2H), 4.37 (t, $J = 7.2$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.15 (s, 1H), 8.40 (d, $J = 7.2$ Hz, 2H), 7.32–7.35 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = 37.0$ (CH_2), 40.7 (CH), 117.2 (CH),

124.7 (CH), 125.8 (Cq), 127.6 (2 × CH), 127.7 (CH), 128.4 (CH), 128.8 (CH), 129.2 (2 × CH), 140.3 (Cq), 151.7 (Cq), 167.7 (Cq) [38, 39].

2. 8-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3b**); [96] mp: 107–109 °C; Lit. [96] 108 °C; IR (KBr): $\upsilon_{max} = 1764\ cm^{-1}$; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.36$ (s, 3H), 2.99–3.10 (m, 2H), 4.32 (t, $J = 6.8$ Hz, 1H), 6.81 (d, $J = 7.6$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 3H), 7.26–7.33 (m, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = 15.9$ (CH_3), 36.9 (CH_2), 40.8 (CH), 124.2 (CH), 125.6 (Cq), 125.9 (CH), 126.5 (Cq), 127.6 (2 × CH), 127.6 (CH), 129.1 (2 × CH), 130.3 (CH), 140.5 (Cq), 150.0 (Cq), 167.9 (Cq) [38, 39].
3. 7-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3c**); [95] mp: 123–125 °C; Lit. [95] 124 °C; IR (KBr): $\upsilon_{max} = 1778,\ 1764\ cm^{-1}$; ^{1}HNMR ($CDCl_3$, 400 MHz): $\delta = 2.38$ (s, 3H), 2.99–3.11 (m, 2H), 4.33 (t, $J = 6.8$ Hz, 1H), 6.89 (q, $J = 8.0$ Hz, 2H), 6.97 (s, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 7.28–7.32 (m, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = 21.1$ (CH_3), 37.2 (CH_2), 40.4 (CH), 117.5 (CH), 122.7 (Cq), 125.5 (CH), 127.6 (2 × CH), 127.6 (CH), 128.1 (CH), 129.1 (2 × CH), 139.2 (Cq), 140.6 (Cq), 151.6 (Cq), 167.9 (Cq) [38, 39].
4. 6-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3d**); [97] mp:81–84 °C; Lit. [97] 83 °C; IR (KBr): $\upsilon_{max} = 1757\ cm^{-1}$; ^{1}HNMR ($CDCl_3$, 400 MHz) $\delta = 2.28$ (s, 3H), 2.99–3.11 (m, 2H), 4.32 (t, $J = 6.8$ Hz, 1H), 6.81 (s, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 7.2$ Hz, 2H), 7.29–7.40 (m, 3H); ^{13}CNMR($CDCl_3$, 100 MHz): $\delta = 20.8$ (CH_3), 37.2 (CH_2), 40.7 (CH), 116.9 (CH), 125.3 (Cq), 127.6 (2 × CH), 127.6 (CH), 128.7 (CH), 129.2 (2 × CH), 129.3 (CH), 134.4 (Cq), 140.5 (Cq), 149.7 (Cq), 167.9 (Cq) [38, 39].
5. 43.1.12. 6-Chloro-4-phenyl-3,4-dihydrobenzopyran-2-one (**3e**); [98] mp:102–105 °C; Lit. [98] 103–104 °C; IR (KBr): $\upsilon_{max} = 1770\ cm^{-1}$; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.00$–3.12 (m, 2H), 4.33 (t, $J = 6.8$ Hz, 1H), 6.96 (s, 1H), 7.10 (d, $J = 8.8$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 7.30 (s, 1H), 7.35–7.40 (m, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): d 36.6 (CH_2), 40.6 (CH), 118.5 (CH), 127.5 (2 × CH), 127.6 (Cq), 128.0 (CH), 128.2 (CH), 128.9 (CH), 129.4 (2 × CH), 129.8 (Cq), 139.4 (Cq), 150.2 (Cq), 166.9 (Cq) [38, 39].
6. 7,8-Benzo-4-phenyl-3,4-dihydrobenzopyran-2-one (**3g**); [96] mp: 111–113 °C; Lit. [96] 112 °C; IR (KBr): $\upsilon_{max} = 1762\ cm^{-1}$; ^{1}HNMR ($CDCl_3$, 400 MHz): $\delta = 3.14$–3.26 (m, 2H), 4.51 (s, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.20 (d, $J = 6.4$ Hz, 2H), 7.32 (s, 1H), 7.35 (d, $J = 6.8$ Hz, 2H), 7.57 (s, 1H), 7.60 (d, $J = 10.4$ Hz, 2H), 7.85 (d, $J = 7.2$ Hz, 1H), 8.33 (d, $J = 7.6$ Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = 37.3$ (CH_2), 41.1 (CH), 119.9 (Cq), 121.4 (CH), 123.7 (Cq), 124.3 (CH), 125.3 (CH), 126.8 (CH), 126.9 (CH), 127.5 (2 × CH), 127.6 (CH), 127.7 (CH), 129.2 (2 × CH), 133.7 (Cq), 140.7 (Cq), 146.8 (Cq), 167.5 (Cq) [38, 39].
7. 4-Nitro-phenyl cinnamate (**4**) [35]; mp: 143–145 °C; Lit [35] 142–146 °C; IR (KBr): $\upsilon_{max} = 1735\ cm^{-1}$; ^{1}HNMR ($CDCl_3$, 400 MHz): d 6.56 (d, $J = 16.0$ Hz, 1H), 7.31 (d, $J = 8.8$ Hz, 2H), 7.37–7.39 (m, 3H), 7.53–7.55 (m, 2H), 7.85 (d, $J = 16.0$ Hz, 1H), 8.24 (d, $J = 8.8$ Hz, 2H); ^{13}CNMR ($CDCl_3$, 100 MHz): d 115.1 (CH), 121.4 (2 × CH), 124.2 (2 × CH), 127.5

(2 × CH), 128.1 (2 × CH), 130.2 (CH), 132.7 (Cq), 144.2 (Cq), 147.0 (CH), 154.6 (Cq), 163.3 (Cq) [38, 39].

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