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Cyclohexane-1,4-diyl bis (hydrogen sulfate) as an efficient homogeneous catalyst for one-pot multi-component synthesis of dihydropyrimidones via Biginelli reaction

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Abstract

A green methodology for the development of the synthesis of dihydropyrimidinones via a clean multi-component Biginelli reaction by using cyclohexane-1,4-diyl bis (hydrogen sulfate) (CDBH) as an effective catalyst in water and solvent-free conditions was reported. This sulfonated catalyst is an efficient and environmentally benign homogeneous catalysts which characterized by using different techniques such as FT-IR and 1H NMR spectra and also titrimetric curves. Finally, we did the density functional and atom in molecules (AIM) study to have a better understanding about the electronic properties and intra molecular hydrogen bonds of this new catalyst. To show the merit of the present work in comparison with reported results in the literature, we compared the results of CDBH catalyst with reported sulfonated catalysts in the Biginelli reaction. Easy preparation of the catalyst, short reaction times, and good to high yields of the products and reusability of the catalyst are some of the advantages of this novel method.

Keywords: Cyclohexane-1,4-diylbis (hydrogen sulfate); Biginelli reaction; DFT study

Introduction

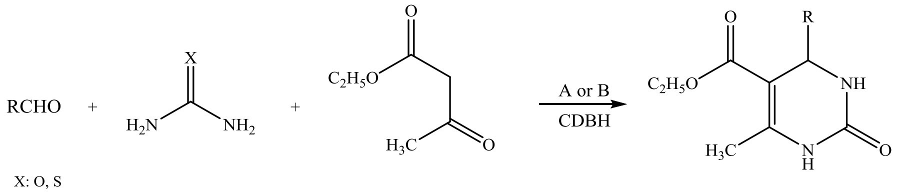
Multi-component coupling reactions (MCRs) are the efficient and powerful tool for the rapid formation of heterocyclic complex compounds [1]. One of the outstanding examples of MCR is Biginelli reaction. More than a century ago, Biginelli introduced a straight procedure of one-pot three components condensation of an aldehyde, α, β-ketoester, and urea [2]. Unfortunately, this reaction had some limitations such as low yield, long reaction time, and severe reaction conditions. Later on, Biginelli reaction has been improved by using a number of catalysts including ionic liquids or supported ionic liquids [3], Gly(NO_3) [4], pineapple juice [5] and Lewis acids or metal-based catalysts such as $H_4PMo_{11}VO_{40}$ [6], Fe_3O_4-MWCNT [7], CaF_2 [8], $MgBr_2$ [9], $NbCl_5$ [10], $Ce(C_{12}H_{25}SO_3)_3$ [11], $ErCl_3$ [12], Mo/γ-Al_2O_3 [13], Fe_3O_4@Nb_2O_5 [14], and graphite-$LaCl_3$ [15]. Another type of catalysts is Bronsted acids such as concentrated H_2SO_4 [16], SiO_2-H_2SO_4 [17], HBF_4 [18], chloroacetic acid [19], 12-molybdophosphoric acid [20], chiral phosphoric acid [21], and mesoporous SiO_2-H_2PO_3 [22]. Recently, some of the new catalysts such as IBX [23], EPZ10 [24], TMSCl [25] and, Amberlyst-70 [26], have been used for Biginelli reaction. It has been proved that sulfonated acid catalysts such as SBA-15-$PrSO_3H$ [27], bentonite/PS-SO_3H [28], PS-PEG-SO_3H [29], carbon-SO_3H [30], Fe_3O_4/PAA-SO_3H [31], nano-γ-Fe_2O_3-SO_3H [32], sulfonated β-CD [33] and, silica sulfuric acid [34] behave as an efficient catalyst for Biginelli reaction.

On the other hand, Biginelli reaction used to produce a remarkable class of nitrogen heterocycles compounds such as 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs). DHPMs have also synthesized under microwave [35, 36] and ultrasound irradiations [7, 37]. The range of possible applications for DHPM derivatives involves an extended area of biological and pharmacological properties such as antibiotic, antiviral, anticarcinogenic, antihypertensive, and calcium channel modulators [38].

Sulfonated compounds are the oxidative products of the carbon materials by sulfur acid [39] or oleum [40] which used to produce sulfonic acid groups on the surface. After Nagasawa's report on the preparation of sulfamic acid derivatives with chlorosulfonic acid, this procedure has been considered as an efficient procedure for preparation of heterogeneous and homogeneous sulfonated acid catalysts [41]. Homogeneous catalysts in organic reactions usually show significant activity; however, unlike heterogeneous catalyst they are not isolated from the reaction mixture as easily as possible [42].

Nevertheless, heterogeneous catalytic systems still have to express the little efficiency of mass transfer in multiphase reaction [43].

Based on the above necessary attentions and in continuing our efforts towards the progress of efficient and environmentally benign homogeneous catalysts [44], we describe a simple and effective synthesis method of dihydropyrimidinones via a one-pot multicomponent Biginelli condensation of different aromatic aldehydes, urea (thiourea), ethyl acetoacetate, using a catalytic amount of cyclohexane-1,4-diyl bis (hydrogen sulfate) (CDBH) in water (method A) as well as under solvent-free conditions (method B) (Scheme 1). To the best of our knowledge, this is the first report describing the use of CDBH in Biginelli reaction. Additionally, geometry optimization performed by using the Gaussian 09 package to have a better understanding of the structural and electronic properties of the cyclohexane-1,4-diyl bis (hydrogen sulfate) compound. Useful parameters such as electronic density $\rho(r)$ at the bond critical point (BCP) and its Laplacian $\nabla^2\rho(r)$ were calculated using atom in molecule theory (AIM) to determine the strength of the intramolecular hydrogen bond.



Scheme 1. Synthesis of Biginelli DHPMs.

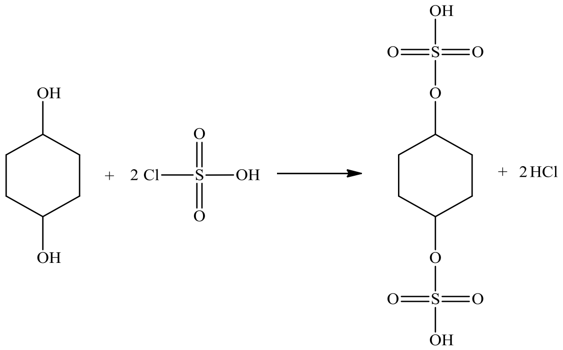
Experimental

General

All chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Melting points of all products were determined in open glass capillaries on a Mettler 9100 melting point apparatus. Infrared (IR) spectra were recorded using a 4300 Shimadzu FT-IR spectrometer. ^{1}H spectra were recorded on a Bruker 400MHz spectrometer. Elemental analysis was performed on a Horeaus CHN Rapid analyzer.

Preparation of cyclohexane-1,4-diyl bis (hydrogen sulfate)

Chlorosulfonic acid (2.32 g, 20 mmol) was added to a suspension of the powdered 1, 4-cyclohexanediol (0.23 g, 2 mmol) in 10 mL dry CH_2Cl_2 over a period of 30 min in an ice bath. After the addition was completed, the mixture was concentrated under vacuum, washed with ether (10 mL) three times, and dried under vacuum. CDBH (0.47 g, 1.70 mmol) was obtained as yellow oil, which was kept in a capped bottle.



Scheme 2. Synthesis of cyclohexane-1,4-diyl bis (hydrogen sulfate).

General procedure for the synthesis of dihydropyrimidones derivatives

Method A: A mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), CDBH (0.1 g, 0.03 mol%), and 5 mL of water was stirred at 80 ℃ for the appropriate time (monitored by TLC). After completion of the reaction, the reaction mixture was cooled to room temperature. The obtained solid product was filtered using a pump and dried. The solution of CDBH was dried under vacuum for recycling catalyst in the next run. Pure dihydropyrimidinones were recrystallized from ethanol to yield pure products.

Method B: In the second procedure, the components as mentioned above were mixed thoroughly and heated in an oil bath maintained under solvent-free conditions at 80 ℃ for an appropriate time. The reaction mixture was then cooled to the room temperature. Hot water was added to the solid mass and the reaction was worked-up as described in Method A.

Results and discussion

Characterization of cyclohexane-1,4-diyl bis (hydrogen sulfate)

CDBH was prepared by adding the chlorosulfonic acid to 1, 4-cyclohexanediol while keeping the temperature at 0°C (Scheme 2). It was identified by FT-IR spectroscopy, ^{1}H NMR, elemental analysis and, titration. The geometry of this molecule was fully optimized through density functional calculation using B3LYP/6-31G level of theory to get a better knowledge about the electronic properties. The FT-IR spectra of 1, 4-cyclohexanediol and cyclohexane-1,4-diyl bis (hydrogen sulfate) (Fig. 1), showed distinct absorption bands for all samples at 1032 cm^{-1}, 1066 cm^{-1} 2939 cm^{-1}, and 2938 cm^{-1} due to the existence of the C–O and aliphatic C–H stretching vibration respectively. In the CDBH spectrum, the bands at 1066 cm^{-1} and 1201 cm^{-1} were related to sulfonic acid groups on the ring [11].

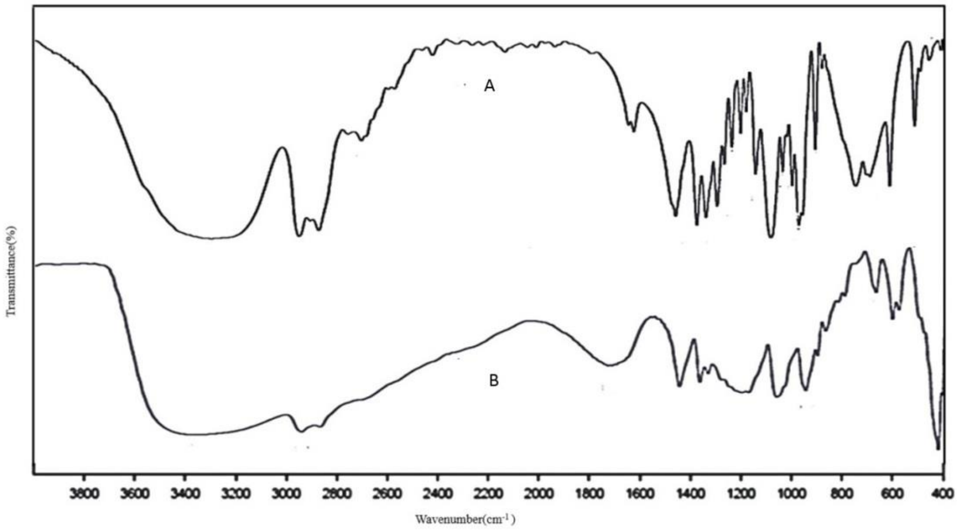


Fig. 1. FT-IR spectra of 1, 4-cyclohexanediol (A) and cyclohexane-1,4-diyl bis (hydrogen sulfate) (B)

Based on the titrimetric curves (Fig 2, 3), it is clearly that in spite the use of the same analytical concentrations for the titrant, there is a significant difference at the end points during the titration of the reagents. This result clearly points the presence of the major difference between the acidity of these reagents. This difference is attributed to the different acidities of -OH and –SO_3H functional groups.

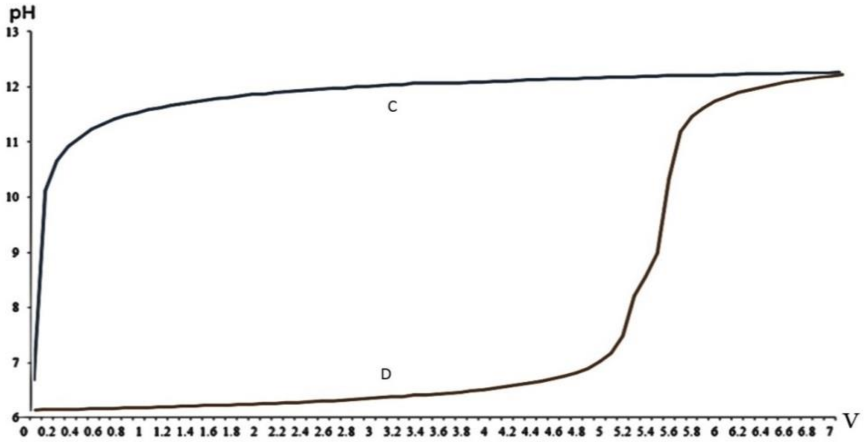


Fig. 2. Titrimetric curves of 1, 4-cyclohexanediol (C) and cyclohexane-1,4-diyl bis (hydrogen sulfate) (D)

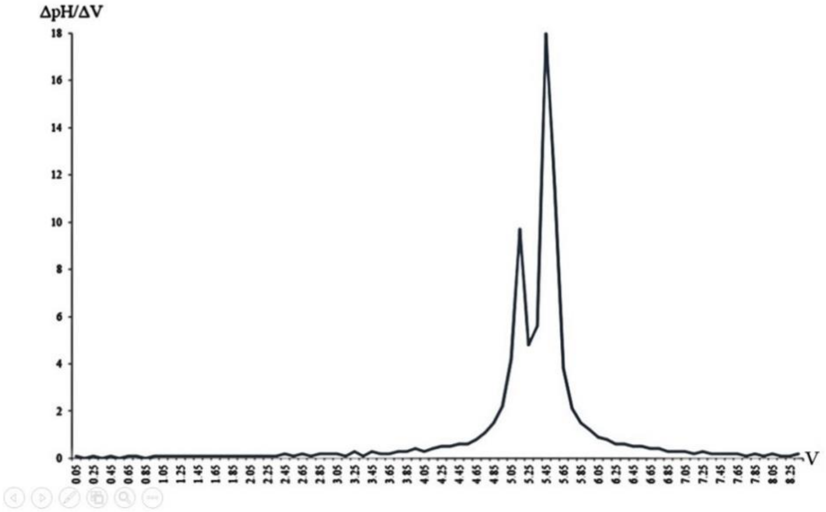
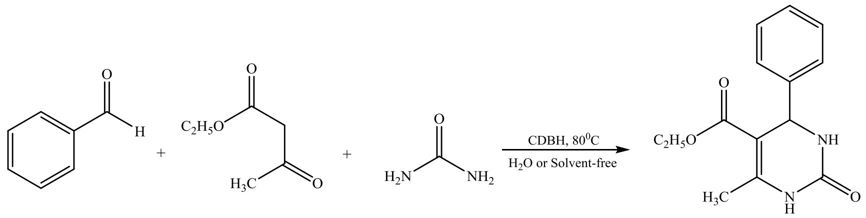


Fig. 3. First derivative titration curve of cyclohexane-1,4-diyl bis (hydrogen sulfate)

Catalytic synthesis of dihydropyrimidin-2(1H)-ones or thiones

In order to achieve the optimal condition of the reaction, we performed the reaction of benzaldehyde, ethyl acetoacetate, and urea in the ratio of 1:1:1.2 mmol with adding 10 mL of water. In the absence of the catalyst and 80 ℃, the reaction yield was only 15% even after 180 minutes with the recovery of starting material (entry 1, Table 1). Whilst, the higher yield (50%) was observed upon catalyst by CDBH (0.01 mol%) within 60 minutes (entry 2, Table 1). Further investigation shows that 0.03 mol% of CDBH will increase the reaction yield up to 90% only in 20 minutes (entry 4, Table 1). Among different solvents such as H_2O, EtOH, CH_3CN, THF, and $CHCl_3$, water is the best for model reaction (entries 5–9, Table 1). It was found that the solvent polarity has a strong effect on the reaction yield, such a way that, THF and $CHCl_3$ with low polarity have low yield, and reasonable yield was obtained for CH_3CN with modest polarity. Though, polar and protic solvents such as EtOH and H_2O provide high yield in a shorter time. 90% of the 3, 4-dihydropyrimidinone derivative was obtained in the presence of H_2O. The hydrophilicity of the catalyst in water might associate it to interact with starting materials for the smooth conversion to the desired product. Furthermore, the model reaction had more yield under solvent-free conditions (entry 10, Table 1).



Scheme 3. Biginelli reaction of benzaldehyde, ethyl acetoacetate, and urea

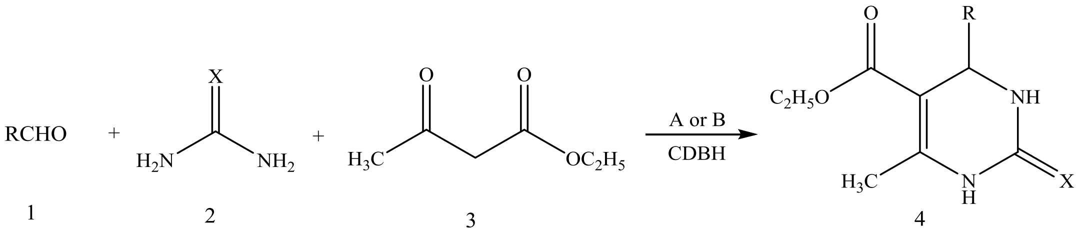
Table 1. The effect of various solvents on the Biginelli reaction[a]

Entry	CDBH (wt %)	Condition/solvent	Time (min)/yield[b] (%)
1	-	80 °C/ H_2O	180/15
2	0.01	80 °C/ H_2O	60/50
3	0.02	80 °C/ H_2O	30/75
4	0.03	80 °C/ H_2O	20/90
5	0.03	Reflux/ H_2O	15/90
6	0.03	Reflux/ EtOH	60/75
7	0.03	Reflux/ CH_3CN	120/70
8	0.03	Reflux/ THF	120/40
9	0.03	Reflux/ $CHCl_3$	180/45
10	0.03	80 °C/solvent free	15/95

[a] Reaction condition: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.2 mmol), catalyst: CDBH solvent (10mL) or solvent-free.

[b] Isolated yield.

By using different starting materials such as aromatic aldehydes carrying either electron-donating or electron withdrawing substituent, different 1,3-dicarbonyls and urea/thiourea overview and possibility of this protocol were demonstrated. Moderate-to-good yields of the desired products under optimized reaction conditions were obtained.



X: O, S

Scheme 4. Synthesized dihydropyrimidinone derivatives by using ethyl acetoacetate

Table 2. Synthesis of DHPMs derivatives by using ethyl acetoacetate catalyzed by CDBH[a]

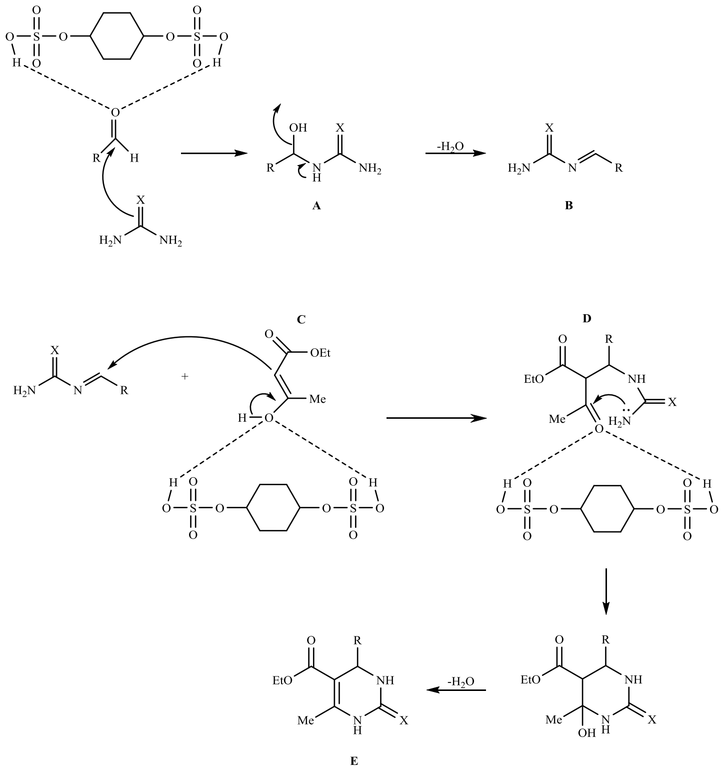
Entry	R	X	product	Method A		Method B		M.p. (°C)	
				Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]	Found	Reported
1	C_6H_5	O	**4a**	20	90	15	80	192-194	198-200 [25]
2	2-ClC_6H_4	O	**4b**	20	85	15	80	226-228	231–233 [5]
3	3-$O_2NC_6H_4$	O	**4c**	20	80	15	80	220-222	227–228 [5]
4	4-$CH_3C_6H_4$	O	**4d**	15	90	15	85	210-212	212-214 [19]
5	2,4-$(Cl)_2$-C_6H_3	O	**4e**	20	80	15	80	245–247	248–250 [9]
6	Ph CH=CH	O	**4f**	30	80	25	80	226-228	232-235 [20]
7	2-Furyl	O	**4g**	30	75	25	75	195-197	201-203 [26]
8	C_6H_5	S	**4h**	25	85	25	85	204-206	208-210 [21]
9	4-ClC_6H_4	S	**4i**	25	80	25	85	214-216	208-210 [35]
10	4-$CH_3OC_6H_4$	S	**4j**	25	90	25	90	143-145	150-152 [21]

[a] Reaction condition: Aldehydes (1 mmol), ethyl acetoacetate (1 mmol), urea or thiourea (1.2 mmol), CDBH (0.1 g, 0.03 mol%), 80 ℃.

[b] Isolated yield.

The results showed that the catalyst had no significant effect on some of the sensitive functional groups such as Cl, NO_2, and OCH_3 (entries 2, 3, and 10, Table 2). Furfural as an acid-sensitive aldehyde operated well with CDBH without leading to the formation of any side products (entry 6, Table 2). Thiourea such as urea was used successfully to produce the corresponding dihydropyrimidin-2-(1H)-thiones in high yields (entries 8–10, Table 2).

According to the literature, a possible mechanism is proposed in Scheme 5. Aldehyde is activated by CDBH which act as a BrØnsted acid through a nucleophilic addition of urea or thiourea forming the *N*-acylimine intermediate **A**. Then, generation of the iminium intermediate **B** which is the key rate-determining step occurred. This intermediate acts as an electrophile for the nucleophilic addition of the enol form of the *β*-dicarbonyl compound **C**. The ketone carbonyl of the resulting open-chain of the resulting open-chain ureide adduct **D** undergoes intramolecular cyclocondensation with the urea NH_2 followed by dehydration to give the cyclized product **E**.



Scheme 5. Plausible mechanism of the reaction

The efficiency of CDBH was compared with the reported other sulfonic acid in the synthesis of compound **4a** from benzaldehyde, ethyl acetoacetate and urea in Table 3.

Table 3. Comparison of different sulfonic acid catalysts for the synthesis of **4a**

Entry	Catalyst	Condition	Time (min)	Yield (%)	Reference
1	$Ce(C_{12}H_{25}SO_3)_3$	EtOH/80 ℃	240	93	11
2	Bentonite/PS-SO_3H	Solvent-free/120 ℃	30	89	28
3	PS-PEG-SO_3H	Dioxane/80 ℃	600	86	29
4	Carbon-SO_3H	CH_3CN/80 ℃	240	90	30
5	Fe_3O_4/PAA-SO_3H	Solvent-free/rt.	120	90	31
6	nano-γ-Fe_2O_3-SO_3H	Solvent-free/60 ℃	180	95	32

7	β-CD-SO_3H	Solvent-free/100 ℃	120	83	33

In this Table, the following facts should be considered: Although the same reaction can be carried out using lower amounts of some of the reported catalysts, the reaction time is very long (Table 3, entries 1, 3, 4). The other main drawback is that catalyst and solvent are expensive (Table 3, entries3, 4, 6, 7).

The reusability of the catalyst was evaluated under the optimized reaction conditions by model reaction. This process was carried out over five runs and all reactions led to the desired products with high efficiency (Table 4).

Table 4. Efficiency of the recovered catalyst in the model reaction

Entry	No. of runs	Yield (%)[a]
1	First	90
2	Run 1	88
3	Run 2	85
4	Run 3	82
5	Run 4	80

[a] Isolated yield.

Geometry Optimization of cyclohexane-1,4-diyl bis (hydrogen sulfate)

A single molecule of cyclohexane-1,4-diyl bis (hydrogen sulfate) is modeled using Gauss View 5.0. [45] and geometry optimized by applying the density functional theory (DFT) using Gaussian 09 package [46] to calculate the structural and electronic properties of this molecule. We employ the B3LYP hybrid functional, including Becke's three parameters nonlocal exchange potential and the nonlocal correlation functional of Lee-Yang-Parr [47], using the 6-31G basis set. The optimized structure on the potential energy surface (PES) was real minimum stationary point due to the absence of negative frequency in normal mode analysis. Furthermore, using the results obtained from the calculation, the structural and electronic properties such as ionization potentials (I), HOMO energies $\varepsilon_{\mathrm{HOMO}}$, LUMO energies $\varepsilon_{\mathrm{LUMO}}$, electron affinity ($A$), chemical hardness ($\eta$), electronic chemical potential (μ) and electrophilicity index (ω) were reported.

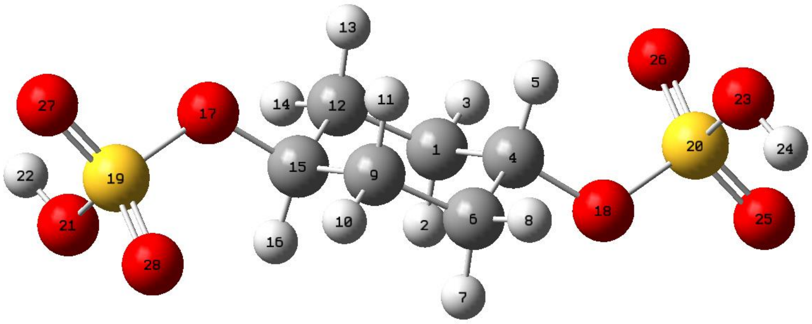


Fig. 4. The fully optimized geometrie of cyclohexane-1,4-diyl bis(hydrogen sulfate)

Table 5. Calculated highest occupied molecular orbital ε_{HOMO} and lowest unoccupied molecular orbital ε_{LUMO}, energies, band gap, ionization energy (*I*), electron affinity (A), chemical hardness *(η)*, electronic chemical potential (*μ*), electrophilicity index (ω), softness (S) Electronic energy (E), Enthalpy *(*Δ*H*°) and Gibbs free energy *(*Δ*G*°)of cyclohexane-1,4-diyl bis (hydrogen sulfate), at the B3LYP/6-31G level of theory

Electronic properties	cyclohexane-1,4-diyl bis (hydrogen sulfate)
Energy of LUMO (eV)	-8.7822
Energy of HOMO (eV)	-0.3905
Band gap (eV)	8.3917
Ionization energy (eV)	8.7822
Electron affinity (eV)	0.3905
Chemical hardness (eV)	4.1959
Electron chemical potential (eV)	-4.5863
Electrophilicity index (eV)	5.0132
Softness (1/eV)	0.2383
E(kcal/mol)	-1024789.5932
Δ*H*°(kcal/mol)	-1024648.2438
Δ*G*°(kcal/mol)	-1024687.0616

Hydrogen bond (HB) is one of the most significant interactions playing a vital role in many biochemical and chemical processes [48]. This bond is considered as non-covalent interaction involving a polarized proton donor (HX) and a high electronegative moiety (Y), which in general is formed by atoms containing lone pair orbital or π-electrons [49]. Technically, there are many definitions for a hydrogen bond and these have been reviewed recently. The above given definition for the hydrogen bonding is considered as normal hydrogen bonding. Contrarily, there is another type of hydrogen bonding and it is called unusual hydrogen bonding (unconventional) [50,51] where the HB occur between C—H groups and an electronegative element like C—H···O [52-53].

Bader's theory of atoms in molecules (AIM) provides a very useful tool to analyze the bond type via parameters, such as electron density $\rho\ (r)$, the Laplacian of the electron density $\nabla^2 \rho\ (r)$, and the ellipticity, (ϵ), which are computed at the bond critical point (BCP). According to this theory, when two neighboring atoms are chemically bonded, a bond critical point appears between the hydrogen atom of donor group and acceptor. At the bond critical point, the Laplacian of the charge density $\nabla^2 \rho\ (r)$, is the sum of the curvature in the charge density along any orthogonal coordinate axes. Negative values for Laplacian of the electron density ($\nabla^2 \rho\ (r) < 0$) reveals that the charge density is concentrated, as in covalent bond and positive values ($\nabla^2 \rho\ (r) > 0$) shows depleted in the charge density, as in a closed shell (electrostatic) interactions. If hydrogen bond exists, the range of $\rho\ (r)$ and $\nabla^2 \rho\ (r)$ are within 0.002-0.035 and 0.024-0.139 a.u., respectively. Accordingly, two intramolecular hydrogen bonds in cyclohexane-1,4-diyl bis (hydrogen sulfate) with the values of $\rho(r)$=0.0083 and $\nabla^2\rho(r)$=0.0291 are classified as weak hydrogen bonds.

Figure 5 shows that the equatorial orientation of the aglycons on C1 and C4 in cyclohexane-1,4-diyl bis (hydrogen sulfate) lead to the formation of two six member rings (Fig. 5) through unconventional HBs (HC6···O9 and HC3···O15), which make the molecules become more stable.

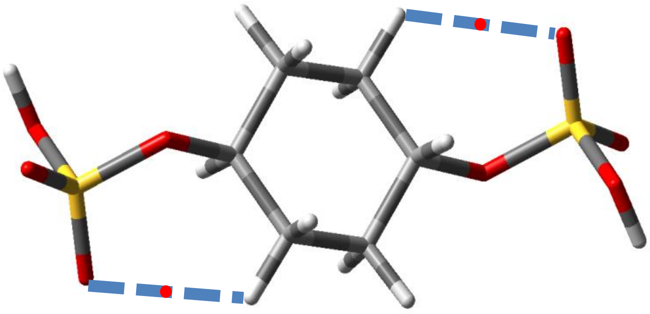


Fig. 5. Hydrogen bonding for cyclohexane-1,4-diyl bis(hydrogen sulfate), Small read spheres and blue lines correspond to the bond critical points (BCP) and the bond paths, respectively.

The total electron energy density $H(r)$, and the Laplacian $\nabla^2\rho(r)$, at BCP are two topological parameters often applied to classify and characterize the hydrogen bonds. Hydrogen bond is characterized by $H(r)<0$ and $\nabla^2\rho(r)<0$ for strong hydrogen bonds, while medium hydrogen bonds with $H(r)<0$ and $\nabla^2\rho(r)>0$, and $H(r)>0$ with $\nabla^2\rho(r)>0$ are established for weak ones. [54] The signs of $\nabla^2\rho(r)$ and $H(r)$ for the HB in cyclohexane-1,4-diyl bis (hydrogen sulfate) are positive. Therefore, these bonds are classified as van der Waals interaction.

Conclusion

In summary, we have synthesized cyclohexane-1,4-diyl bis (hydrogen sulfate) (CDBH) and characterized with different techniques such as FT-IR spectroscopy, ^{1}H NMR, elemental analysis, titration and also a DFT study to know more about the electronic properties. In continuation, this catalyst was used for the one-pot synthesis of dihydropyrimidinones from a multi-component reaction of aldehydes, 1, 3-dicarbonyl compounds and urea or thiourea. The important advantages of this method are high catalytic activity, short reaction time, excellent yields, reusability of catalyst, simple work-up, and mild reaction conditions.

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