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An efficient and simple approach for the synthesis of pyranopyrazoles using imidazole (catalytic) in aqueous medium, and the vibrational spectroscopic studies on 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole using density functional theory

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ABSTRACT

We describe a one-pot four component synthesis of pyranopyroles from aryl aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate in the presence of catalytic amounts of an organocatalyst imidazole in water as medium. A plausible mechanism for the formation of imidazole catalyzed pyranopyrazoles has been envisaged. This method is rapid, simple, provides products in good yield, and is eco-friendly. In addition, based on the optimized geometry, the frequency and intensity of the vibrational bands of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole were obtained by the density functional theory (DFT) calculations using 6-31G(d,p) basis set. The vibrational frequencies were calculated and the scaled values have been compared with experimental FT-IR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement.

1. Introduction

Pyranopyrazoles are fused heterocyclic compounds that possess many biological properties such as fungicidal [1], bactericidal [2], vasodilatory activities [3] and act as anticancer agents [4]. They also find application as pharmaceutical ingredients and biodegradable agrochemicals [5–8]. Apart from this, pyrano[2,3-*c*]pyrazoles have been shown to act as potential insecticidal [9a] and molluscicidal agents [9b]. As a result, considerable attention has been focused on the development of new methodologies for the synthesis of these heterocycles.

Multi-component reactions (MCRs), are those reactions in which three or more reactants react together to give the product in a single step under suitable reaction conditions [10]. MCRs offer the advantage of simplicity and synthetic efficiency over conventional chemical reactions. The MCRs have the additional advantages of selectivity, synthetic convergency, and atom-economy [11a,b]. Further, use of water as a solvent is an active area of research in green chemistry. A number of classic reactions which were carried out strictly under anhydrous conditions, in hazardous and toxic organic solvents, can also be carried out in water with proper use of catalysts and reaction conditions. MCRs which are carried out in water as a medium offer better environmental protection, hence, are considered as clean and green reactions.

Pyranopyrazole was first synthesized by the reaction between 3-methyl-1-phenylpyrazolin-5-one and tetracyanoethylene [5]. Sharanin et al. later reported a one-pot three component reaction between pyrazolone, aromatic aldehyde and malononitrile in the presence of triethyl amine as a catalyst in ethanol to get pyranopyrazoles [7]. Another method has been reported by the condensation of *N*-methylpiperidone, pyrazoline-5-one and malononitrile in absolute ethanol [12]. Nadia et al. reported a method using a mixture of 5-methyl-2,4-dihydro-3*H*-pyrazol-3-one, malononitrile and different aromatic aldehydes in the presence of ammonium acetate in ethanol [4]. A four component reaction of aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate in water and catalytic β-cyclodextrin was reported by Vasuki and Kandhasamy [8] and the same reaction is carried out by Shestopalov et al. using catalytic amounts of triethyl amine in ethanol [13]. However, all the reported

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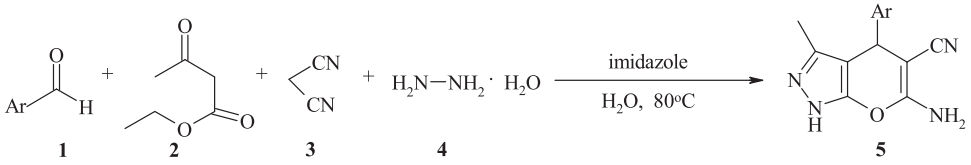


Scheme 1.

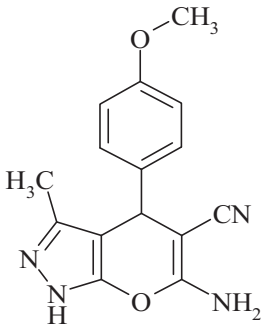
methods are associated with disadvantages such as: use of expensive and environmentally hazardous reagents, low yields of products, drastic reaction conditions and tedious work-up procedures.

In continuation of our work on the synthesis of biologically active heterocyclic organic compounds [14a–e]; herein, we are reporting a simple and efficient synthesis of pyranopyrazoles by a four component reaction of aromatic aldehydes (**1**), ethyl acetoacetate (**2**), malononitrile (**3**) and hydrazine hydrate (**4**) in the presence of an organocatalyst imidazole in water at 80 °C (Scheme 1). The method is environmentally friendly as it is carried out in water, involves the use of an inexpensive ecofriendly organocatalyst and gives high yield of the products within 30 min.

2. Results and discussion

For a detailed exploration, the reaction between *p*-anisaldehyde and ethyl acetoacetate, malononitrile and hydrazine hydrate in the presence of imidazole was considered for the optimization of amount of catalyst used; and to study the effect of solvents on the rate of the reaction. Initially, when the reaction was carried out in the absence of any catalyst, no product was found even after 30 min. Addition of 0.2 mmol imidazole afforded the product in low yield, an increase in the amount of imidazole to 0.5 mmol gave 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (**5a**) in 88% yield; further increase in the amount of catalyst did not increase the product yield. Next, in order to investigate the effect of solvents, the above reaction was carried out in conventional organic solvents such as DCM, CH_3CN, ethanol and in water. Water as a solvent provided the best yields compared to DCM, CH_3CN and ethanol.

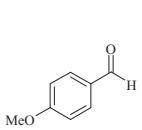
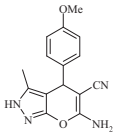
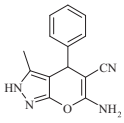
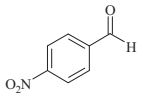
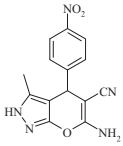
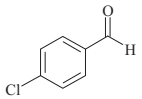
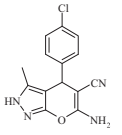
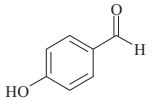
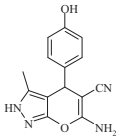
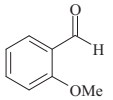
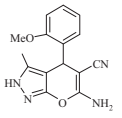
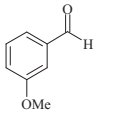
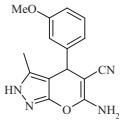
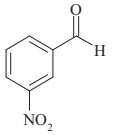
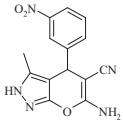
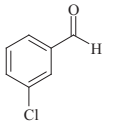
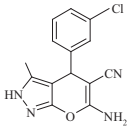
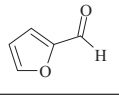
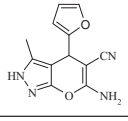
In order to establish the generality, the catalyst was successfully applied to the reaction of various araldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate and the results of this study are presented in Table 1. It is clear from this table that, excellent product yields were obtained with aryl and heteroaryl aldehydes. Furthermore, the reaction is compatible in the presence of various functional groups such as –Cl, $–OCH_3$, $–NO_2$ and –OH.



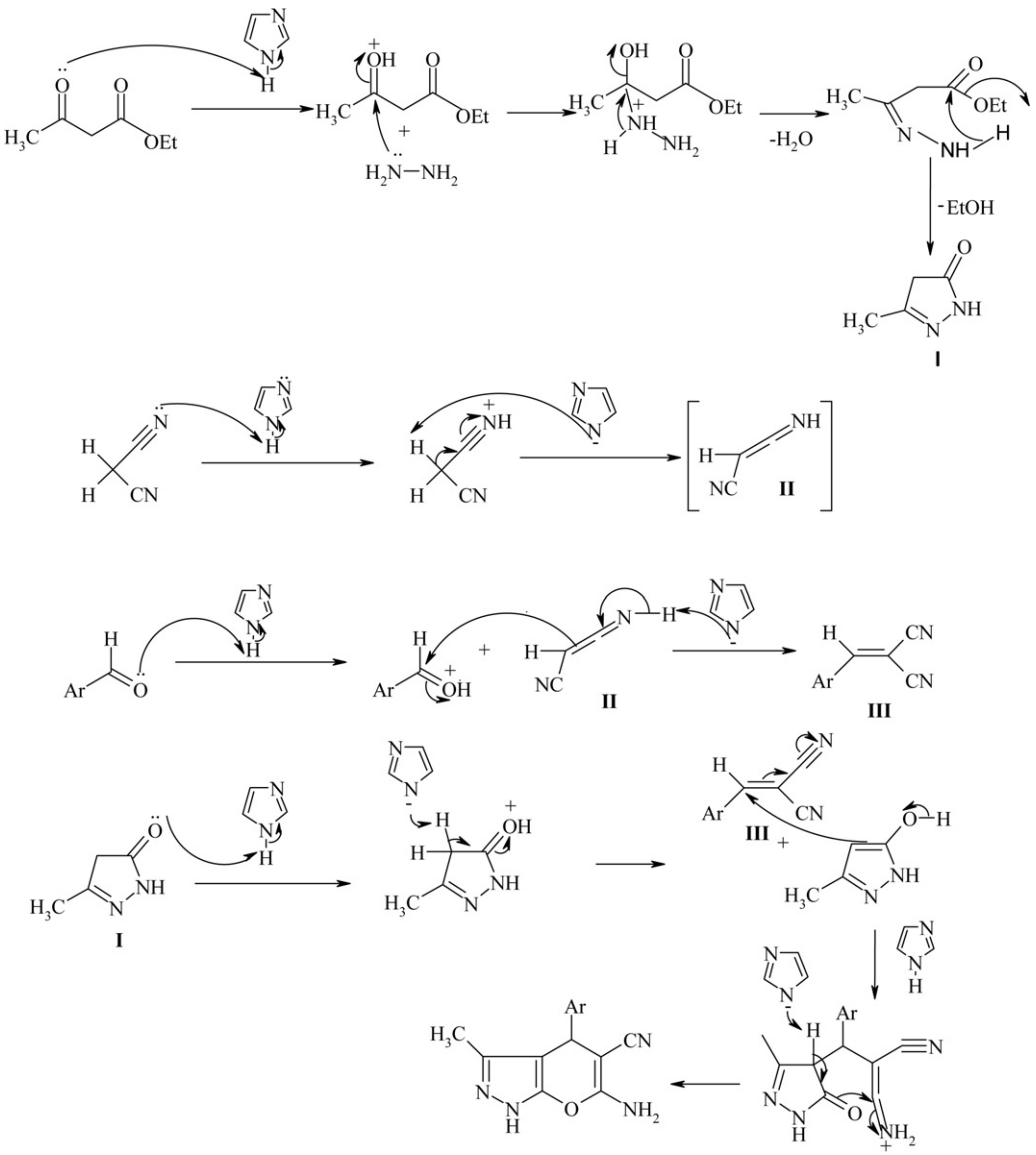
5a

Fig. 1. Structure of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole ($C_{15}H_{14}N_4O_2$).

Table 1
Synthesis of pyranopyrazoles from various aromatic aldehydes, malononitrile, ethyl acetoacetate and hydrazine hydrate.

Entry	Aromatic aldehydes (**1**)	Product[a] (**5**)[c]	Time (min)	Yield (%)[b]
a			20	88
b			20	89
c			20	85
d			20	90
e			20	90
f			30	89
g			30	85
h			30	90
i			30	85
j			30	89

[a] All the products are known and were identified by either comparison of their IR spectra, or by their melting points or on TLC with the authentic samples prepared by known methods.
[b] Isolated yield.
[c] Compounds **5a**, **5b** and **5i** were characterized by ^{1}H NMR spectral analysis.



Scheme 2. A plausible mechanism for the formation of pyranopyrazoles.

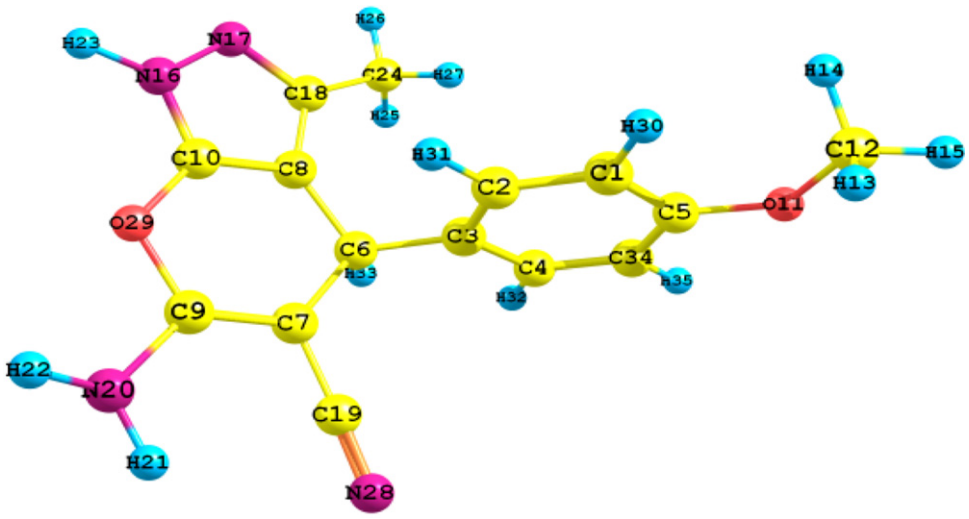


Fig. 2. Numbering system adopted for the optimized structure of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole.

Table 2
Optimized bond lengths and bond angles of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole.

Bond	Length	Angle	(°)
C1–C2	1.396	C2–C1–C5	119.6
C1–C5	1.401	C2–C1–H30	119.4
C1–H30	1.083	C1–C2–C3	121.6
C2–C3	1.397	C1–C2–H31	119.0
C2–H31	1.087	C5–C1–H30	121.0
C3–C4	1.401	C1–C5–O11	124.7
C3–C6	1.530	C1–C5–H34	119.5
C4–H32	1.087	C3–C2–H31	119.5
C4–C34	1.390	C2–C3–C4	118.0
C5–O11	1.365	C2–C3–C6	121.5
C5–C34	1.401	C4–C3–C6	120.5
C6–C7	1.539	C3–C4–H32	119.5
C6–C8	1.504	C3–C4–H34	121.3
C6–H33	1.100	C3–C6–C7	112.0
C7–C9	1.368	C3–C6–C8	113.8
C7–C19	1.419	C3–C6–H33	106.6
C8–C10	1.370	H32–C4–H34	119.2
C8–C18	1.426	C4–H34–C5	120.0
C9–N20	1.367	O11–C5–H34	115.8
C9–O29	1.373	C5–O11–C12	118.3
C10–N16	1.349	C5–H34–H35	118.6
C10–O29	1.363	C7–C6–C8	106.8
O11–C12	1.419	C7–C6–H33	107.9
C12–H13	1.098	C6–C7–C9	125.1
C12–H14	1.098	C6–C7–C19	118.8
C12–H15	1.091	C8–C6–H33	109.6
N16–N17	1.366	C6–C8–C10	121.9
N16–H23	1.007	C6–C8–C18	134.7
N17–C18	1.334	C9–C7–C19	116.1
C18–C24	1.496	C7–C9–O20	126.3
C19–N28	1.167	C7–C9–O29	123.8
N20–H21	1.010	C7–C19–N28	177.9
N20–H22	1.010	C10–C8–C18	103.4
C24–H25	1.096	C8–C10–N16	109.1
C24–H26	1.092	N8–N10–O29	128.5
C24–H 27	1.095	N8–C18–N17	111.5
C34–H35	1.085	N8–C18–N24	128.1
		N20–C9–O29	109.9
		C9–N20–H21	116.2
		C9–N20–H22	116.0
		C9–O29–C10	113.9

Table 3
Optimized dihedral angles of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole.

Dihedral angle	(°)	Dihedral angle	(°)
H30–C1–C2–C3	179.8	C7–C6–C8–C18	−178.7
C5–C1–C2–H31	−179.8	H33–C6–C8–C10	118.2
H30–C1–C2–H31	0.13	H33–C6–C8–C18	−62.09
C2–C1–C5–O11	179.8	C6–C7–C9–N20	176.2
C2–C1–C5–C34	0.058	C6–C7–C9–O29	−1.01
H30–C1–C5–O11	−0.11	C19–C7–C9–N20	−3.30
H30–C1–C5–C34	−179.9	C19–C7–C9–O29	179.4
C1–C2–C3–C4	0.19	C6–C8–C10–N16	179.75
C1–C2–C3–C6	179.2	C6–C8–C10–O29	−1.026
H31–C2–C3–C4	179.9	C18–C8–C10–N16	−0.05
H31–C2–C3–C6	−1.0841	C18–C8–C10–O29	179.18
C2–C3–C4–H32	179.7	C6–C8–C18–N17	−179.7
C2–C3–C4–C34	−0.12	C6–C8–C18–C24	0.26
C6–C3–C4–H32	0.63	C10–C8–C18–N17	0.01
C6–C3–C4–C34	−179.2	C10–C8–C18–C24	−180.
C2–C3–C6–C7	−71.72	C7–C9–N20–H21	14.32
C2–C3–C6–C8	49.55	C7–C9–N20–H22	155.5
C2–C3–C6–H33	170.5	O29–C9–N20–H21	−168.1
C4–C3–C6–C7	107.3	O29–C9–N20–H22	−26.91
C4–C3–C6–C8	−131.4	C7–C9–O29–C10	1.682
C4–C3–C6–H33	−10.49	N20–C9–O29–C10	−176.0
C3–C4–C34–C5	0.02	C8–C10–N16–N17	0.07
C3–C4–C34–H35	179.9	C8–C10–N16–H23	179.1
H32–C4–C34–C5	−179.8	O29–C10–N16–N17	−179.2
H32–C4–C34–H35	0.15	O29–C10–N16–H23	−0.23
C1–C5–O11–C12	0.72	C8–C10–O29–C9	−0.71
C34–C5–O11–C12	−179.5	N16–C10–O29–C9	178.4
C1–C5–C34–C4	0.01	C5–O11–C12–H13	60.89
C1–C5–C34–H35	−180.0	C5–O11–C12–H14	−61.53
O11–C5–C34–C4	−179.8	C5–O11–C12–C15	179.7
O11–C5–C34–H35	0.25	C10–N16–N17–C18	−0.06
C3–C6–C7–C9	124.6	H23–N16–N17–C18	−179.1
C3–C6–C7–C19	−55.90	N16–N17–C18–C8	0.03
C8–C6–C7–C9	−0.64	N16–N17–C18–C24	−180.0
C8–C6–C7–C19	178.9	C8–C18–C24–H25	62.10
H33–C6–C7–C9	−118.4	C8–C18–C24–H26	−177.9
H33–C6–C7–C19	61.10	C8–C18–C24–H27	−57.39
C3–C6–C8–C10	−122.6	N17–C18–C24–H25	−117.9
C3–C6–C8–C18	57.2	N17–C18–C24–H26	2.06
C7–C6–C8–C10	1.54	N17–C18–C24–H27	122.6

3. Experimental

All chemicals are commercial and were used without further purification. Progress of the reactions was monitored using Silica gel-H TLC plates. The synthesized compounds were characterized by ^{1}H NMR spectral analysis; by comparing the products on TLC or by the comparison of melting points with products prepared by known methods. NMR spectra were recorded on a Brucker spectrophotometer. FT-IR spectra were recorded on a Bruker Optics Alpha-P FT-IR spectrophotometer with attenuated total reflectance (ATR) module. The FT-Raman were recorded in solid phase on Bruker Optics MultiRAM FT-Raman spectrophotometer using Nd-YAG laser operating at 1064 nm as an excitation source at the resolution of 4 cm^{-1}. Vibrational spectroscopic studies of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (**5a**) was done by recording FT-IR, FT-Raman spectra in the region 4000–400 cm^{-1} and 3500–100 cm^{-1}, respectively.

3.1. Typical procedure for the preparation of pyranopyrazole

The aromatic aldehyde (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol) hydrazine hydrate (1 mmol) and imidazole (0.5 mmol) were taken in water (5 ml) and heated on a preheated hot plate at 80 °C for 20–30 min. Various aromatic aldehydes used, yield of the products and time taken for completion of the reactions is summarized in Table 1.

3.2. Mechanism

A plausible mechanism for the formation of imidazole catalyzed pyranopyrazoles is envisaged. The formation of pyranopyrazoles catalyzed by imidazole may involve the protonation of ethyl acetoacetate by imidazole, followed by intermolecular attack by hydrazine hydrate. Subsequent loss of water, and intramolecular nucleophillic attack by –NH_2 group on the carbonyl carbon to give 5-methyl-2,4-dihydro-pyrazol-3-one (**I**). Similarly protonation of aldehyde by imidazole and reaction with 3-imino-acrylonitrile (**II**) may afford 2-benzylidene-malononitrile (**III**). Addition of **I** to **III** in the presence of imidazole followed by rearrangement may give the expected pyranopyrazole as shown in Scheme 2.

4. Vibrational spectroscopic studies on 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (5a)

Determination of the molecular structure of the organic molecules provides insight into the important molecular properties. Knowledge of the electronic structure and the spectral properties help in understanding the biological activity. Density functional theory (DFT) is a quantum mechanical theory used

Table 4
Comparison of the calculated and experimental vibrational frequencies of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole.

Mode	Calculated			Experimental		%PED	Approximate character
	Freq (cm^{-1})	IR intensity (cm^{-1})	Raman intensity (cm^{-1})	IR freq (cm^{-1})	Raman freq (cm^{-1})		
11	521	6.60	0.69	523	511	τ N28C19C7C6–25, τ O11C1C34C5–17	Torsion of nitrile group
13	552	3.09	2.24	565	567	δ C1C5C34–17, δ C12O11C5–10, τ N28C19C7C6–12	Phenyl ring def
14	618	2.09	7.81	614	613	δ C4C34C5–18, δ C2C1C5–24	In plane bending phenyl ring
15	631	7.69	0.97	630	634	δ N28C19C7–10, δ C19C7C9–20	NCC bending of nitrile group
19	671	1.40	0.50	668	678	τ N17N16C10C8–18, τ H26C24C18C8–11, τ C18N17N16C10–16	Pyrazole ring torsion
20	697	1.13	1.03	721	706	τ C4C34C5C1–10, τ C2C1C5C34–10, τ C3C2C1C5–24,	Phenyl ring torsion
22	760	5.33	3.05	750	748	ν C1C5–11, ν O11C5–15, δ C3C2C1–10	OC stretch ether Linkage + CC Stretching
30	966	22.6	2.86	971	936	ν N17C18–10, δ C18N17N16–14, δ H25C24H27–11, τ N25C24C18C8–21, τ H27C24C18C8–20	Methyl ring wagging attached to pyrazole ring
32	1006	49.27	0.97	1001	1003	ν O29C9–32, δ H22N20C9–23	O–C stretch of pyran ring
34	1035	48.8	2.49	1029	1.57	ν O11C12–72	O–C stretch of ether attached to phenyl ring
36	1092	3.10	2.87	1073	1083	ν N17N16–41	NN stretch of pyrazole ring
42	1164	7.29	5.03	1169	1169	δ H14C12H13–15 τ H13C12O11C5–28, τ H14C12O11C5–29	Out of plane bending + torsion of methyl group attached to ether linkage
45	1235	1.36	7.14	1223	1222	ν C3C2–15, δ H33C6C3–31	CC stretching in phenyl ring + HCC asym bending
49	1291	19.3	1.69	1301	1313	δ H30C1C2–13, δ H31C2C3–14, δ H32C4C34–14, δ H35C34C5–11	Phenyl ring bending
51	1362	2.2	8.16	1328vw	1363vw	H27C24H26–25, H26C24H25–22, H25C24H27–23	HCH in plane bending methyl group attached to pyrazole
53	1384	60.59	37.58	1392	1390	ν N17C18–26, δ C18N17N16–11, δ H23N16N17–18	NC stretch + CNN bend in pyrazole ring (def)
56	1436	5.54	19.98	1442	1392	δ H27C24H26–44 δ H26C24H25–31 τ H26C24C18C8–1	HCC sym bending methyl group attached to pyrazole ring
57	1440	5.9	20.37	1443	1441	δ H25C24H27––37, δ H26C24H25–15	HCC asym bending CH_3 group attached to pyrazole ring
59	1460	31.29	7.15	1465	1440	δ H14C12H13–39	Methyl group bending (methoxy group)
62	1513	173.13	12.52	1512	1549	ν N16C10–31, ν O29C10–17, δ H23N16N17–15, δ N16C10C8–14	NC stretch + HNN bending in pyrazole ring + OC stretching pyran ring
65	1595	9.63	4.64	1582	1542	ν C10C8–23, δ H21N20H22–24	CC stretch of pyran ring + out of plane NH_2 bend
66	1605	86.17	82.16	1597	1584	ν C4 C34–30, ν C2C1–11, ν C3C2–11	Phenyl ring breathing
67	1640	444.70	55.44	1641	1628	ν C7 C9–36, ν C10C8–11, ν N20C9–11, δ H21N20H22–13	Ring breathing of pyran ring + NH_2 bend

Table 4 (*Continued*)

Mode	Calculated			Experimental		%PED	Approximate character
	Freq (cm^{-1})	IR intensity (cm^{-1})	Raman intensity (cm^{-1})	IR freq (cm^{-1})	Raman freq (cm^{-1})		
68	2222	66.95	192.72	2191vs	2191vs	ν N28C19–89, ν C19 C7–11	CN sym stretch of nitrile group
69	2884	22.49	65.68	2856m	2839m	ν C6H33 100	CH stretch
70	2898	56.53	123.49	2836	2882	ν C12H13–45, ν C12H14–47	CH sym stretch of methyl group attached to ether linkage
71	2929	17.17	122.53	2925	2937	ν C24 H25, ν C24 H26–17, ν C24 H27–30	CH sym stretch of methyl group attached pyrazole ring
72	2957	40.72	48.80	2962	2935	ν C12H13–51, ν C12H14–49	CH asym stretch of methyl group attached to ether linkage.
76	3054	11.02	59.77	3053	3050	ν C4H32 95	CH asym stretch phenyl ring
79	3097	11.28	88.90	3104	3078	ν C1–H30 95	CH sym stretch phenyl ring
80	3445	63.14	175.11	3481	3482	ν N20H21–57, ν N20–H22–43	NH sym stretch of NH_2 group attached to pyran ring
81	3545	119.74	165.22	3565		ν N16–H23–100	NH stretch of pyrazole ring
82	3562	42.35	78.67	3587		ν N20H21 43, νN20–H22 57	NH asym stretch of NH_2 group attached to pyran ring

δ, bend; τ, torsion; ν, stretch; asym, asymmetric; sym, symmetric; def, deformation.

to investigate the electronic structure in the ground state of many-body systems, in particular atoms and molecules. Raman spectroscopy has recently been proved to be a valuable tool in the investigation of complex molecules of biological interest [15–17].

Recently, vibrational spectral studies and theoretical computations related to natural coumarin derivatives [18,19], ginkgolide [20], cresyl violet perchlorate [21], and molecules like 2,4-dichloro-6-nitrophenol [22] have appeared in the literature. Atalay et al. [23,24] have reported the theoretical studies on molecular structure and vibrational spectra of 2-amino-5-phenyl-1,3,4-thiadiazole and 1-amino-5-benzoyl-4-phenylpyrimidin-2(1*H*). Yakuphanoglu et al. [25] and Sekerci et al. [26] have successfully used Hartree–Fock and density functional methods to study the spectral properties of molecules like *N*-phenyl-*N*′-(2-thienylmethylene) hydrazine and 1-(thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole.

In this paper, we report the interpretation of vibrational spectra and computations related to the structure of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (**5a**, Fig. 1) using density functional theory.

4.1. Computational details

Density functional theory calculations were carried out using Gaussian 09 package [27]. Equilibrium structure and vibrational frequencies were optimized using Becke-3-Lee-Yang-Parr (B3LYP) functional with 6-31g** basis set [28,29]. Frequency calculations were carried out on the optimized structure using the program available in the Gaussian software itself. Equilibrium symmetry predicted is C1 with energy of −1392.97 Hartrees. Potential energy distribution was carried out using VEDA 4.0 program [30]. Opti-

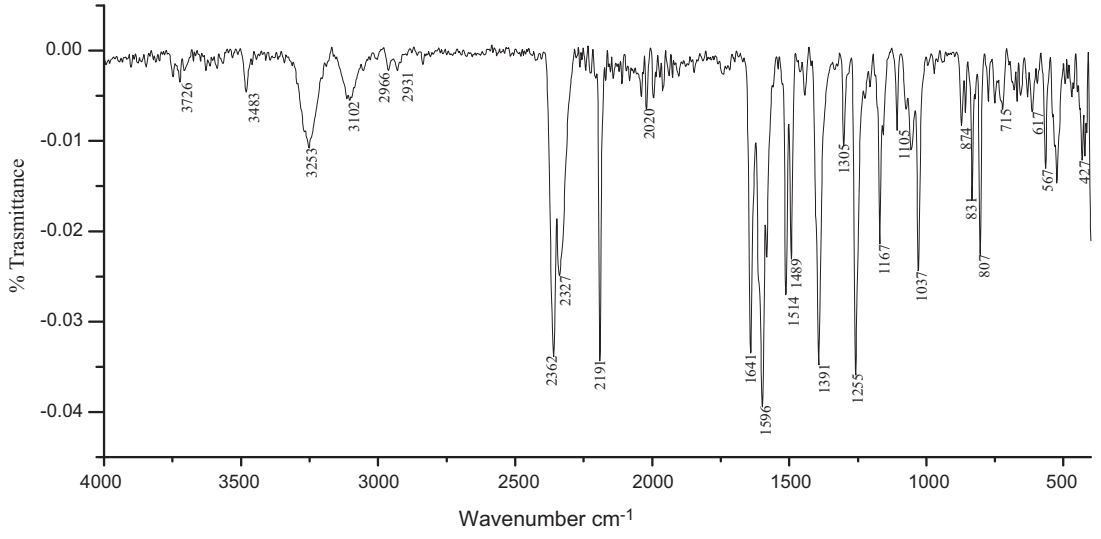


Fig. 3. FT-IR spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 400–4000 cm^{-1}.

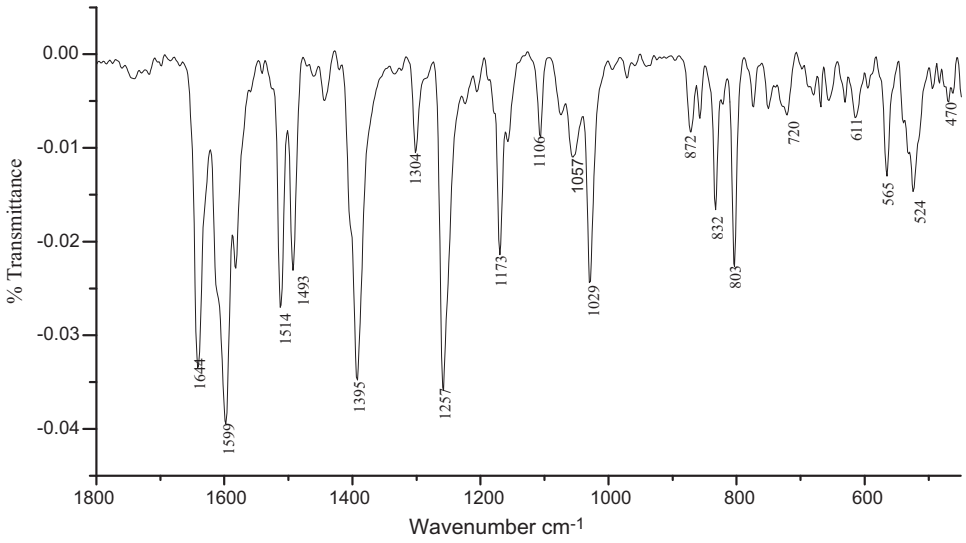


Fig. 4. FT-IR spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 1800–400 cm^{-1}.

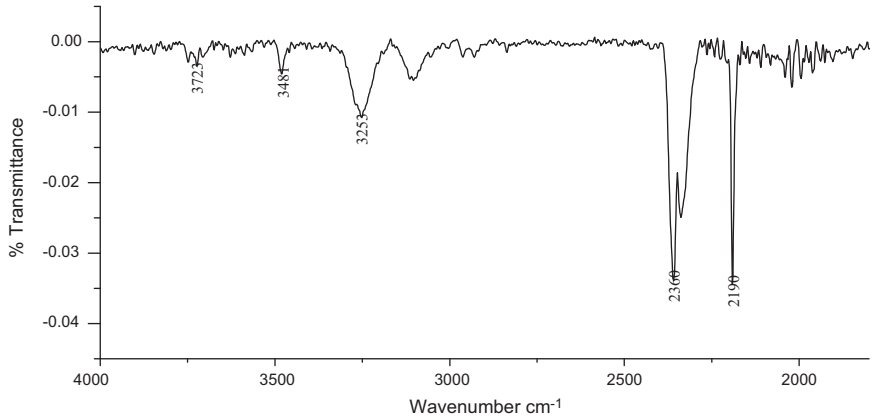


Fig. 5. FT-IR spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 4000–1800 cm^{-1}.

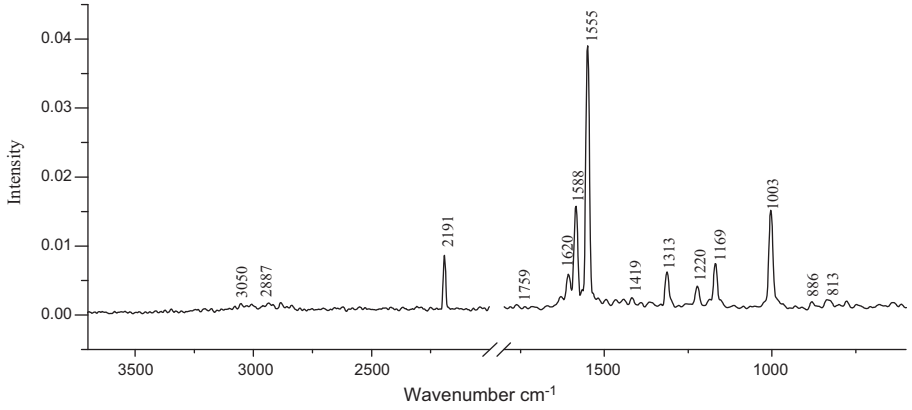


Fig. 6. FT-Raman spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 3700–600 cm^{-1}.

mized geometry of the molecule and the numbering system is given in Fig. 2, optimized bond lengths and bond angles are presented in Table 2 and optimized dihedral angles are given in Table 3.

5. Vibrational analysis

6-Amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole has 35 atoms, hence, 99 modes of fundamental vibrations are possibe. Predicted equilibrium symmetry for this molecule is C1 with energy of −1392.97 hartrees. A detailed vibrational analysis has been carried out and assignments of the observed fundamental bands have been proposed on the basis of peak positions and the relative intensities. The PED contribution to each of the observed frequencies gives the reliability and precision of the spectral analysis. The calculated harmonic-vibrational frequencies and the observed FT-IR and FT-

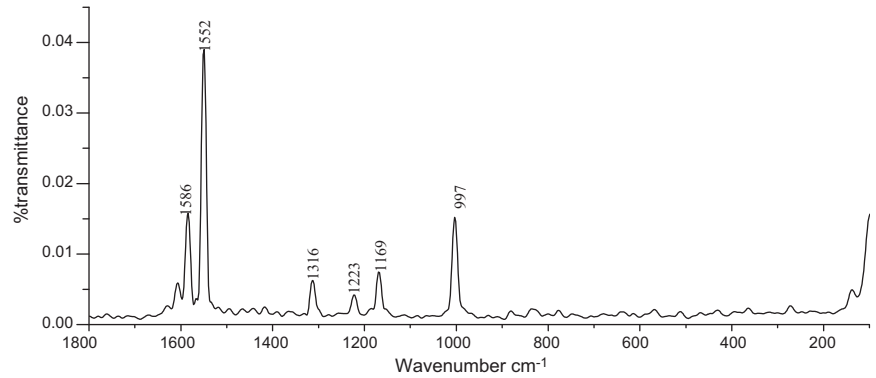


Fig. 7. FT-Raman spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 1800–100 cm^{-1}.

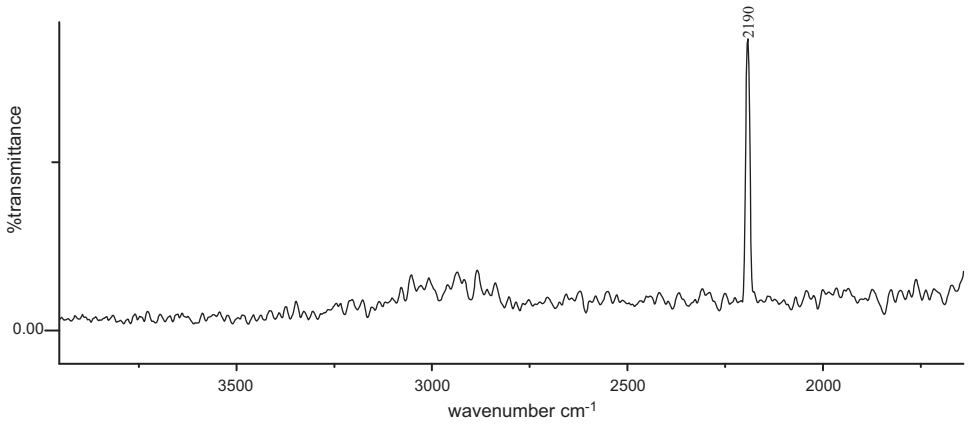


Fig. 8. FT-Raman spectrum of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole in 3700–1800 cm^{-1}.

Raman frequencies for various modes of vibrations are presented in Table 4. A comparison of the calculated frequencies with the experimental values indicates the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Hence, computed frequencies were multiplied with scale factor 0.9614 to offset the systematic error caused by neglecting anharmonicity giving a good agreement with the observed frequencies. These calculations provide a valuable insight into the vibrational spectrum and molecular parameters.

6-Amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (**5a**) has a pyrazole ring with a methyl substituent, pyran ring has a nitrile, an amino group and a phenyl ring with a *p*-methoxy substituent. The pyran (C10–C8–C6–C7–C9–O29) and the pyrazole(C10–C8–C18–N16–N17) are fused together and lie in one plane. The phenyl ring (C1–C2–C3–C4–C34–C5) lies perpendicular to the plane of the fused rings (∟ C3–C6–C7 = 112°, Fig. 2). Hence, the vibrational spectral analysis was performed based on the characteristic vibrations of the methyl group, amino group, nitrile group, methoxy group, and a phenyl ring. The FT-IR and FT-Raman spectra are shown in Figs. 3–8.

5.1. Methyl group vibrations

The molecule under consideration has two methyl groups, one attached to the pyrazole ring and the other to the side chain phenyl ring as methoxy substituent. The asymmetric stretching mode of methyl group is expected to be around 2980 cm^{-1} and symmetric stretching at 2870 cm^{-1} [31,32]. In our molecule, C–H symmetric stretch of methyl group vibrations recorded at 2836 cm^{-1}, 2925 cm^{-1} (FT-IR) and 2882 cm^{-1}, 2937 cm^{-1} (FT-Raman) are consistent with the predicted values of 2898 cm^{-1}, 2929 cm^{-1}. C–H asymmetric stretching vibrations computed at 2957 cm^{-1} and 2984 cm^{-1} match with the 2963 cm^{-1}, 3005 cm^{-1} in IR and 2957 cm^{-1}, 3007 cm^{-1} in Raman spectrum.

The symmetric and asymmetric bending vibrations of methyl group are normally expected in the regions 1465–1440 cm^{-1} and 1390–1370 cm^{-1}, respectively. The asymmetric bending of methyl group observed at 1465 cm^{-1} (IR) and 1440 cm^{-1} (Raman) are in good agreement with the theoretically calculated value of 1460 cm^{-1}. The symmetric bending calculated at 1436 cm^{-1} is observed as a medium band at 1442 cm^{-1} (IR) and 1392 cm^{-1} (Raman). Out of plane bending with torsion of methyl group attached to ether linkage is calculated at 1164 cm^{-1} and is experimentally seen at 1169 cm^{-1} in IR and Raman.

5.2. NH_2 and NH group vibrations

The NH_2 wagging was computed at 496 cm^{-1} and is observed at 519 cm^{-1} in FT-IR and at 512 cm^{-1} in FT-Raman. NH sym stretch of NH_2 group attached to pyran ring is calculated at 3445 cm^{-1} is in good agreement with the experimental values of 3481 cm^{-1} and 3482 cm^{-1} in FT-IR and FT-Raman, respectively. NH asym stretch of NH_2 group attached to pyran ring which is calculated to appear at 3562 cm^{-1} is observed only in FT-IR at 3581 cm^{-1} and not in FT-Raman. NH stretch of pyrazole ring is calculated as 3545 cm^{-1} is also seen only in FT-IR at 3565 cm^{-1}.

5.3. C=N, C–N, N–N and the nitrile group

C=N and C–N stretching vibrations generally occur in the region 1382–1266 cm^{-1}, and it is difficult to assign these bands as they

get mixed with several other bands. In our study, the pyrazole ring contains the C=N and C–N bonds, which show stretching vibrations at 1392, 1512 cm^{-1} in IR and at 1390, 1549 cm^{-1} in Raman. These are consistent with the calculated frequencies at 1384 cm^{-1} and 1513 cm^{-1} along with the bending vibrations.

A characteristic band for the nitrile group attached to the pyran ring is observed at 2191 cm^{-1} in both FT-IR and FT-Raman spectra, which is in very good agreement with the computed value of 2222 cm^{-1}. Torsion of nitrile group calculated at 521 cm^{-1} agrees with the observed values of 523 cm^{-1} in IR and 511 cm^{-1} in Raman.

N–N Stretch of pyrazole ring was calculated at 1092 cm^{-1} and is consistent with the experimental values of 1073 cm^{-1} in IR and 1083 cm^{-1} in Raman spectrum.

5.4. C–H vibrations

Generally, C–H stretching, C–H in-plane bending and C–H out-of-plane bending vibrations appear in the range 3100–3000 cm^{-1}, 1300–1000 cm^{-1} and 1000–750 cm^{-1} [33]. HCH in plane bending of methyl group attached to pyrazole ring is calculated at 1362 cm^{-1} is experimentally observed at 1328 cm^{-1} (IR) and 1363 cm^{-1} (Raman) as very weak bands. CH stretch of hydrogen attached to pyran ring is observed at 2856 cm^{-1} in IR and at 2839 cm^{-1} in Raman spectrum matches the predicted frequency of 2884 cm^{-1}.

5.5. C–O group vibrations

$C_{15}H_{14}N_4O_2$ has two ether linkages, one in the form of cyclic ether in pyran ring and the other one as methoxy group attached to the phenyl ring. O–C stretch of these two are calculated at 1035 cm^{-1} (O–CH_3) and 1044 cm^{-1} (cyclic ether). These have been found to be consistent with the recorded values at 1029 cm^{-1}, 1057 cm^{-1} (IR) and 1038 cm^{-1} (Raman). The calculated O–C Stretch of pyran ring (O–C–NH_2) at 1006 cm^{-1} coincides very well with the observed values of 1001 cm^{-1} and 1003 cm^{-1} in the IR and Raman spectra.

5.6. Phenyl ring vibrations

C–H asymmetric stretching of phenyl ring is calculated at 3054 cm^{-1} and experimental value is at 3053 cm^{-1} and 3050 cm^{-1} in IR and Raman respectively. C–H symmetric stretching of phenyl ring which is calculated at 3097 cm^{-1} is in good agreement with the value 3104 cm^{-1} in IR and 3078 cm^{-1} in Raman spectrum. Phenyl ring breathing observed at 1641 cm^{-1} and 1628 cm^{-1} agreed with the computed value of 1605 cm^{-1}. Phenyl ring deformation computed at 552 cm^{-1} agreed with the recorded values of 565 cm^{-1} and 567 cm^{-1} in IR and Raman. In-plane bending of phenyl ring is calculated at 618 cm^{-1} and was observed at 614 cm^{-1} in IR and 613 cm^{-1} in Raman. Computed phenyl ring torsion at 697 cm^{-1} is in agreement with the observed values of 721 cm^{-1} and 706 cm^{-1} in IR and Raman spectra.

6. Conclusions

A convenient and efficient protocol has been developed for the synthesis of pyranopyrazoles in high yields using catalytic amounts of imidazole as an organocatalyst, in water. We have demonstrated that, the synthesis is milder, fast and does not require any tedious work-up procedure. An effort has been made in the present study to optimize the structure of 6-amino-4-(4′-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (**5a**, $C_{15}H_{14}N_4O_2$). The geometric parameters and vibrational frequencies of **5a** were calculated using B3LYP method with 6-31g** basis set. To fit the theoretical results, the experimental values were multiplied by 0.9614. The gained multiplication factors were found to be in good agreement with the experimental values for both FT-IR and FT-Raman. These results confirm the validity of potential energy distribution to each of the observed frequencies.

Organic molecules possessing similar functional groups have been synthesized and their structures have been studied using DFT calculations and vibrational spectral analyses [34,35]. It has been found by us that, the vibrational frequency values reported for the corresponding functional groups are consistent with the values which we have observed for the functional groups present in pyranopyrazoles.

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