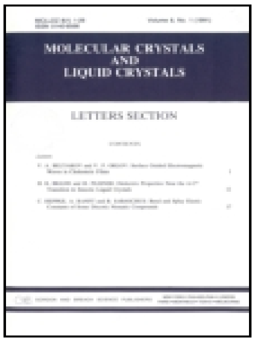

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ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Abdullah Aydin, Hakan Arslan, Murat Şüküroğlu, Mehmet Akkurt & Orhan Büyükgüngör (2015) Crystal Structure and Vibrational Spectra of 3-Chloro-4-Phenyl-6-(Morpholine-4-yl)-Pyridazine by Hartree-Fock and Density Functional Methods, Molecular Crystals and Liquid Crystals, 606:1, 216-236, DOI: 10.1080/15421406.2014.915664

To link to this article: http://dx.doi.org/10.1080/15421406.2014.915664

Mol. Cryst. Liq. Cryst., Vol. 606: pp. 216–236, 2015

ISSN: 1542-1406 print/1563-5287 online
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Crystal Structure and Vibrational Spectra of 3-Chloro-4-Phenyl-6-(Morpholine-4-yl)-Pyridazine by Hartree-Fock and Density Functional Methods

ABDULLAH AYDIN,[1,*] HAKAN ARSLAN,[2] MURAT ŞÜKÜROĞLU,[3] MEHMET AKKURT,[4] AND ORHAN BÜYÜKGÜNGÖR[5]

[1]Department of Science Education, Faculty of Education, Kastamonu University, Kastamonu, Turkey
[2]Department of Chemistry, Faculty of Arts and Science, Mersin University, Mersin, Turkey
[3]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Gazi University, Ankara, Turkey
[4]Department of Physics, Faculty of Sciences, Erciyes University, Kayseri, Turkey
[5]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, Samsun, Turkey

The title compound, 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine (I), was prepared and characterized using elemental analysis and FT-IR and ^{1}H NMR spectroscopy studies. The crystal and molecular structure of the title compound was determined from single-crystal X-ray diffraction data. It crystallizes in the orthorhombic space group *$P2_12_12_1$, $Z = 8$ with $a = 7.5743$ (3) Å, $b = 14.8922$ (8) Å, $c = 23.3472$ (9) Å, $V = 2633.5$ (2) Å^3, and $D_x = 1.391$ Mg/m^3. The title compound, $C_{14}H_{14}ClN_3O$, crystallizes with two independent molecules A and B in the asymmetric unit, wherein the morpholine ring adopts a distorted chair conformation. The 1,6-dihydropyridazine ring creates dihedral angles of 47.0(3)° (in molecule A) and 47.9(2)° (in molecule B) with the phenyl ring, respectively. The crystal studied was an inversion twin with a 0.56(12):0.44(12) domain ratio. The molecular structure, vibrational frequencies, and intensities of the title compound were calculated using Hartree-Fock and density functional theory methods (BLYP, B3LYP, B3PW91, and mPW1PW91) using the 6-31G(d,p) basis set. The calculated geometric parameters were compared to the corresponding single crystal X-ray structure of the title compound. Comparison of the theoretical and experimental geometries of the title compound show that the X-ray parameters are in good agreement with the optimized molecular structure of the title compound. In addition, the harmonic vibrations computed for this compound using the B3LYP/6-31G(d,p) method are in good agreement with the observed vibrational spectral data. Theoretical vibrational spectra of the title compound were interpreted using PEDs and the VEDA 4 program. The superior performance of these investigated methods was calculated using the PAVF 1.0 program.*

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[*] Address correspondence to Abdullah Aydin, Department of Science, Faculty of Education, Kastamonu University 37200, Kastamonu, Turkey. E-mail: aaydin@kastamonu.edu.tr

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Keywords Ab initio calculations; alkanoic acids; B3LYP; DFT; infrared spectrum; non-steroidal anti-inflammatory drugs; vibrational frequencies

Introduction

A series of 6-morpholino-4-aryl-3(2*H*)-pyridazinone alkanoic acids their ester and amide derivatives were prepared and tested for their in vivo analgesic activity using the *p*-benzoquinone-induced writhing test [1]. In recent years, the 3(2*H*)-pyridazinone system has attracted a great deal of attention due to its structural relationship to pyrazolone derivatives such as aminopyrine and dipyrone, themselves derived from ring enlargement of pyrazolone to pyridazinone. These drugs possess analgesic and anti-inflammatory activities but have limited clinical use due to serious side effects such as blood dyscrasias [1, 2]. Studies focusing on 3(2*H*)-pyridazinones indicate that 2-substituted 4,5-functionalised 6-phenyl-3(2*H*)-pyridazinone derivatives possess potent analgesic activity and lack the general side effects, i.e., gastric irritation and renal suppression, of currently used non-steroidal anti-inflammatory drugs [3].

Our literature survey reveals that neither the complete vibrational spectra nor the quantum mechanical calculations for the title compound have been reported. Therefore, we have undertaken a detailed theoretical and experimental investigation of the vibrational spectra of this molecule. We calculated the vibrational frequencies and geometric parameters of the title compound in the ground state to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters using the density functional with the HF, BLYP, B3LYP, B3PW91, and mPW1PW91 methods and the standard 6-31G(d,p) basis set. A detailed interpretation of the vibrational spectra of the title compound has been made on the basis of the calculated potential energy distribution (PED). In the present work, we continued our theoretical studies, checking the relative performance of the B3PW91, BLYP, and B3LYP methods for comparison at the 6-31G(d,p) level, using the title compound as a test compound.

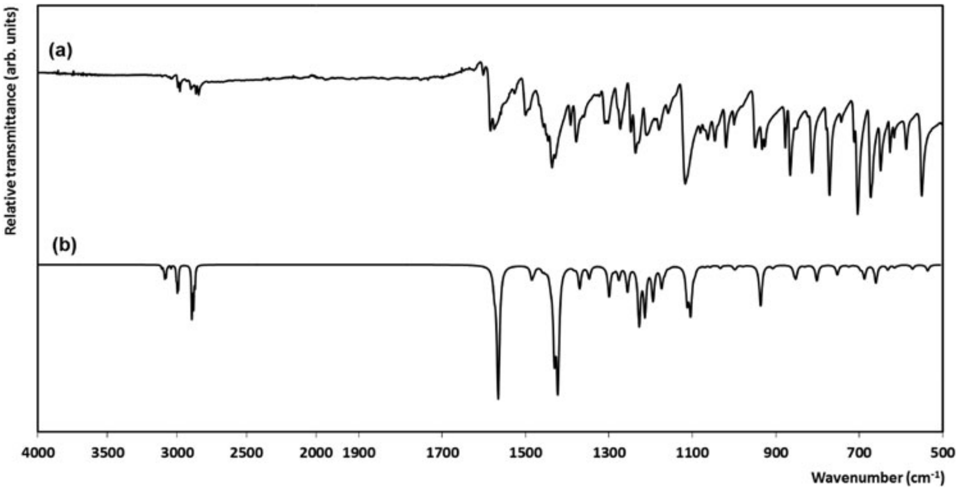


Figure 1. Experimental (a) and theoretical (b) FT-IR spectrum of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine.

Experimental

Instrumentation

^{1}H NMR spectra were recorded on a Bruker 400 FT-NMR spectrometer (Bruker, Rheinstetten, Germany) using TMS as the internal standard in $CDCl_3$. Elemental analyses of C, H, and N were performed at the Scientific and Technical Council of Turkey, Instrumental Analysis Center (Ankara, Turkey) and were within ±0.4% of the theoretical values.

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of the title compound were recorded using a Perkin Elmer Spectrum 100 series spectrometer with a ATR prism (4000–525 cm^{-1}; number of scans: 250; resolution: 1 cm^{-1}) (Fig. 1).

The FT-Raman spectrum of the title compound was recorded using a Nicolet Spectrometer 6700 in 4000–400 cm^{-1} range at the room temperature with a laser wavelength of 780 nm. The recorded FT-Raman spectrum of the title compound is shown in Fig. 2.

Synthesis of Compound 3-Chloro-4-Phenyl-6-(Morpholine-4-yl)-Pyridazine (I)

A mixture of 0.02 mol 4-phenyl-3,6-dichloropyridazine, 0.04 mol morpholine and 0.04 mol triethylamine in 2-propanol was refluxed for 12 hr. After cooling the mixture at room temperature, the precipitated crystals were filtered and washed with ice-cold ethanol (Scheme 1). 3-Chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine (**I**): Recrystallized from ethanol. Yield: 88%. M.p.: 181–183°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.43 (m, 5H, phenyl-H2-6), 6.76 (s, 1H, pyridazine-H5), 3.77 (t, 4H, morpholine-H2, H6), and 3.56 (t, 4H, morpholine-H3, H5). Anal. calcd. for $C_{14}H_{14}ClN_3O$: C, 60.98; H, 5.12; N, 15.24. Found: C, 61.02; H, 5.68; N, 15.09% [1].

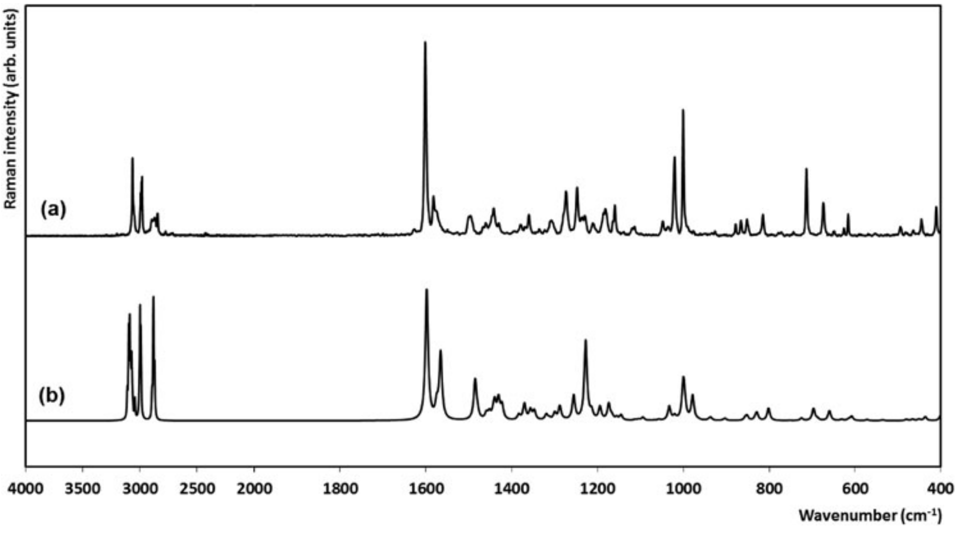
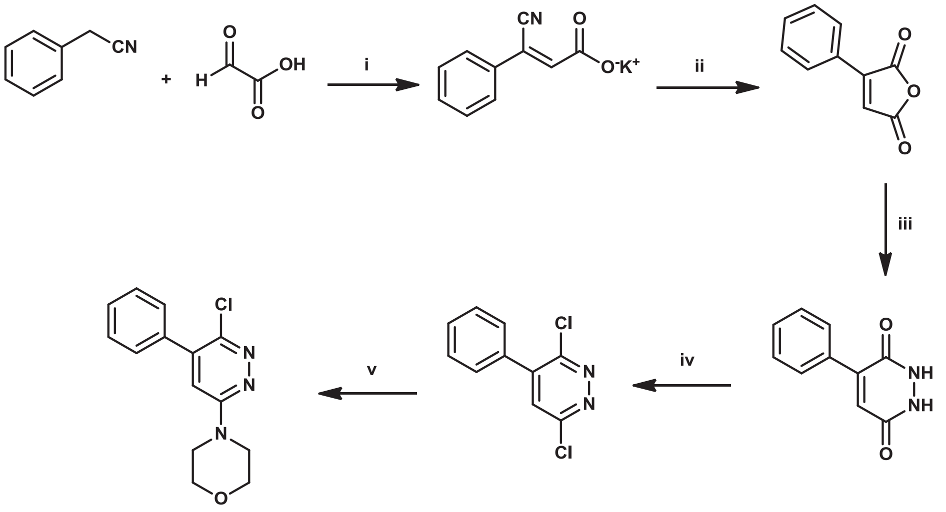


Figure 2. Experimental (a) and theoretical (b) FT-Raman spectrum of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine.



i; K_2CO_3, MeOH, r.t. 24 h, ii; $HCOOH/H_2SO_4$, reflux, iii; NH_2NH_2, water, reflux, iv; $POCl_3$, v; Morpholine, isopropanol, reflux

Scheme 1. Synthesis of the title compound.

Crystal Structure Analysis

In this study, single crystal X-ray data were performed at 296 K on a STOE IPDS 2 X-AREA [4] diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) to $\theta_{\max} = 26.5°$. Cell parameters were obtained from 22079 reflections. The cell was refined on a STOE X-AREA and the data were reduced on a X-RED32 and corrected for absorption using integration of 20482 measured reflections; 5443 were independent ($R_{\text{int}} = 0.061$) [4]. The structure was solved using direct methods using SIR-97 [5] and refined with a full-matrix least-squares procedure using the program SHELXL-97 [6]. All non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically and refined using a riding model with C-H = 0.93 and 0.97 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The crystal studied was an inversion twin with a 0.56(12):0.44(12) domain ratio. The number of Freidel pairs in the data set is 2336. A molecular plot was prepared with ORTEP-3 for Windows [7]. The programs used to prepare material for publication were WINGX [8] and PLATON [9]. Further details concerning data collection and refinement [10] are given in Table 1.

Calculations Details

All calculations were performed using Gaussian 03W on a double Xeon/3.2 GHz processor with 8 GB Ram [11]. The molecular structure of the title compound in the ground state was optimized by using HF, BLYP, B3LYP, B3PW91, and mPW1PW91 methods with the standard 6-31G(d,p) basis set. The vibrational frequencies were also calculated using these methods. The frequency values computed at these levels contain known systematic errors [12]. Therefore, we used the scaling factor values of 0.8992, 1.0072, 0.9614, 0.9573, and 0.9500 for HF, BLYP, B3LYP, B3PW91, and mPW1PW91, respectively [13–16].

We have also calculated optimal scaling factors for all investigated methods. The assignment of the calculated wave numbers is aided by the animation option in GaussView

Table 1. Crystal and experimental data of the title compound

Crystal data	
$C_{14}H_{14}ClN_3O$	$D_x = 1.391$ Mg m^{-3}
$M_r = 275.73$	Mo $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	Cell parameters from 22,079 reflections
$a = 7.5743$ (3) Å	$\theta = 1.4$–$27.3°$
$b = 14.8922$ (8) Å	$\mu = 0.28$ mm^{-1}
$c = 23.3472$ (9) Å	$T = 296$ (2) K
$V = 2633.5$ (2) Å^3	Thin plate, pink
Formula $Z = 8$	0.66 × 0.37 × 0.03 mm
Space group $Z = 4 \Rightarrow Z' = 8/4 = 2.0$	
Data collection	
STOE IPDS 2 diffractomer	3352 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.061$
Absorption correction: integration	$\theta_{\max} = 26.5°$
$T_{\min} = 0.880$, $T_{\max} = 0.991$	$h = -9 \rightarrow 9$
20482 measured reflections	$k = -18 \rightarrow 18$
5443 independent reflections	$l = -29 \rightarrow 29$
Refinement	
Refinement on F^2	Calculated weights $w = 1/[\sigma^2(F_o{}^2) + (0.0792P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.069$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.159$	$\Delta\rho_{\max} = 0.53$ e Å^{-1}
$S = 1.00$	$\Delta\rho_{\min} = -0.21$ e Å^{-1}
5443 reflections	Extinction correction: none
344 parameters	Absolute structure: [10], 2336 Freidel pairs
H atoms constrained to parent site	Flack parameter: 0.56 (12)

3.0, which gives a visual presentation of the shape of the vibration modes [17]. Furthermore, the theoretical vibrational spectra of the title compound were interpreted using PEDs and the VEDA 4 program [18]. The improved performance of the density functional methods versus HF was quantitatively characterized using the PAVF 1.0 program [19, 20].

Results and Discussion

Description of Crystal Structure of $C_{14}H_{14}ClN_3O$

The title compound, $C_{14}H_{14}ClN_3O$, crystallizes with two independent molecules A and B in the asymmetric unit, in which the morpholine ring adopts a distorted chair conformation (Fig. 3). The bond lengths and bond angles of the title compound are given in Table 2.

The bond lengths and angles are in the normal range [21]. The C9–N3, O1–C12, and O1–C13 bond lengths were 1.384 (6), 1.432 (7), and 1.439 (6) Å, respectively. In addition,

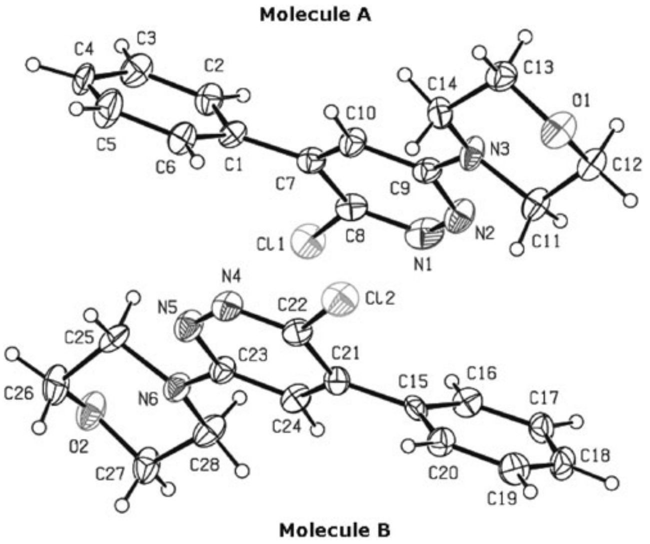


Figure 3. Two molecules (A and B) of the title compound in the asymmetric unit with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) of the title compound

*Bond lengths**	Molecule A	Molecule B	*Bond lengths*	Molecule A	Molecule B
Cl1–C8	1.753(5)	1.732(5)	N3–C14	1.447(7)	1.468(8)
C1–C2	1.398(8)	1.404(7)	N3–C9	1.384(6)	1.389(6)
O1–C13	1.439(6)	1.422(7)	N3–C11	1.468(6)	1.462(7)
O1–C12	1.432(7)	1.387(8)	C2–C3	1.382(7)	1.377(7)
C1–C7	1.465(7)	1.481(7)	C3–C4	1.447(9)	1.411(8)
C11–C12	1.476(7)	1.511(9)	C4–C5	1.358(10)	1.328(8)
N1–N2	1.275(7)	1.338(6)	C5–C6	1.402(9)	1.374(7)
N1–C8	1.378(7)	1.326(6)	C6–C1	1.366(8)	1.413(8)
N2–C9	1.342(6)	1.347(6)	C13–C14	1.483(7)	1.498(9)
*Bond angles**			*Bond angles*		
C12–O1–C13	109.1(4)	107.2(4)	N2–C9–N3	115.5(4)	114.7(4)
N2–C9–C10	121.7(4)	121.6(4)	N3–C9–C10	122.8(4)	123.7(4)
N2–N1–C8	119.6(5)	119.7(4)	N3–C11–C12	110.2(4)	109.4(5)
N1–N2–C9	121.1(5)	119.5(4)	O1–C12–C11	113.4(4)	107.1(5)
C9–N3–C11	118.5(4)	121.8(4)	O1–C13–C14	111.9(5)	112.4(5)
C11–N3–C14	114.9(4)	112.6(5)	N3–C14–C13	110.5(4)	109.9(5)
C9–N3–C14	120.3(4)	119.6(4)	C1–C7–C8	125.6(4)	124.8(4)
N1–C8–C7	124.1(4)	124.8(5)	C3–C4–C5	119.8(5)	121.0(5)
Cl1–C8–N1	114.6(4)	113.8(4)	C2–C1–C6	118.2(4)	118.2(4)
Cl1–C8–C7	121.2(4)	121.4(4)	C7–C10–C9	119.9(5)	120.6(5)

*See Fig. 3 for the corresponding atom names in molecule B.

Table 3. Hydrogen bond parameters (Å, °)

	D-H	H... A	D... A	D-H... A
C4-H4... O1^{i}	0.93	2.59	3.279 (7)	131
C26-H26B... O2^{ii}	0.97	2.55	3.260 (7)	130
C2-H2... Cg6^{iii}	0.93	2.98	3.794 (6)	147
C20-H20... Cg3^{iv}	0.93	2.91	3.730 (7)	148

Symmetry codes: (i) 5/2-*x*, 1-*y*, −1/2+*z*; (ii) 1/2+*x*, 3/2-*y*, -*z*; (iii) 1-*x*, −1/2+*y*, 1/2-*z*; and (iv) 2-*x*, 1/2+*y*, 1/2-*z*. Cg3 and Cg6 are the centroids of the C1–C6 and C15–C20 rings, respectively.

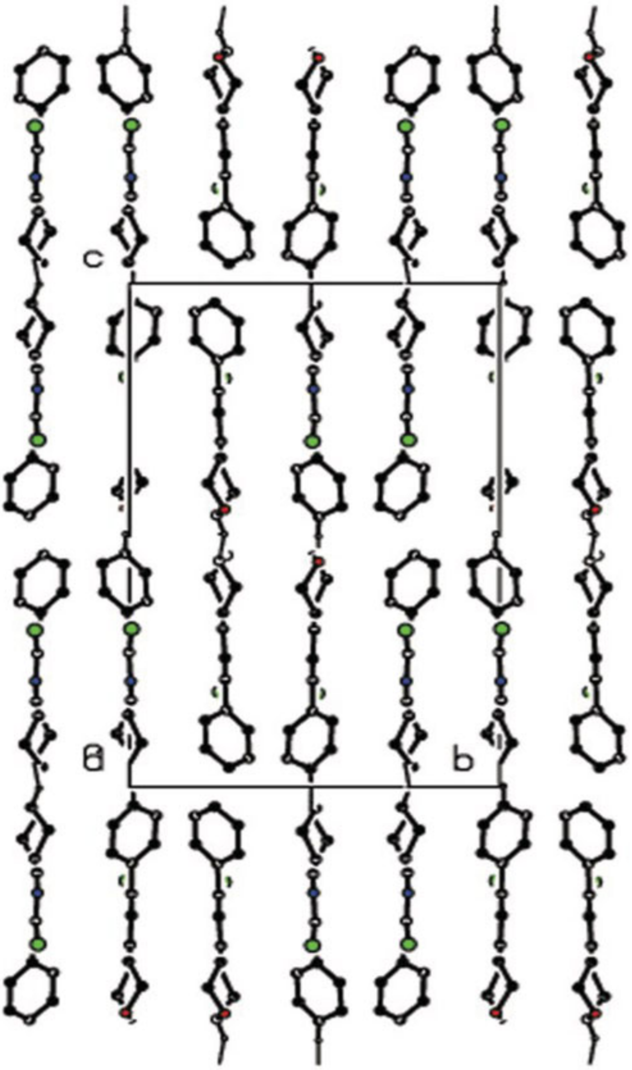


Figure 4. Packing and hydrogen bonding interactions of the title compound viewed down the *a*-axis. H atoms not participating in hydrogen bonding have been omitted for clarity.

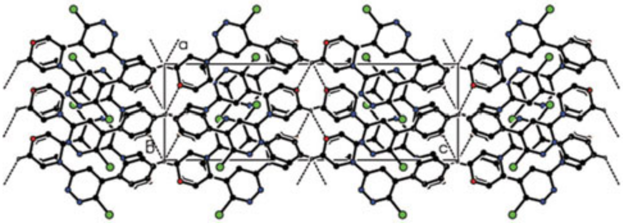


Figure 5. Packing and hydrogen bonding interactions of the title compound viewed down the *b*-axis. H atoms not participating in hydrogen bonding have been omitted for clarity.

the Cl1-C8 bond length was 1.753 Å. These values were consistent with those reported previously: 1.388 (2), 1.424 (2) and 1.417 (2) Å [22], and 1.733 (2) Å [23].

In the crystal structure, molecules are linked by C—H . . . O interactions, in a parallel to (010). Furthermore, C—H . . . π interactions contribute to the stability of the structure. A

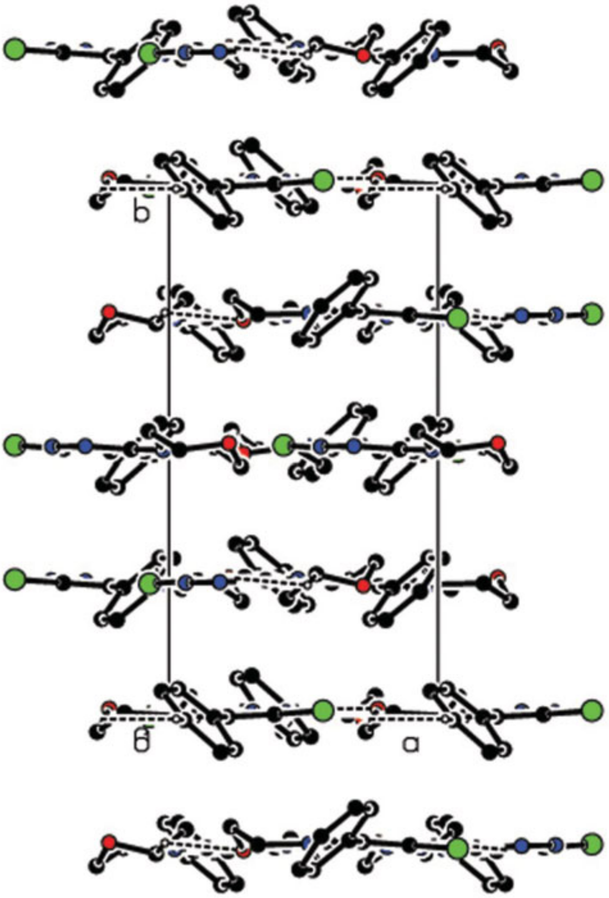


Figure 6. Packing and hydrogen bonding interactions of the title compound viewed down the *c*-axis. H atoms not participating in hydrogen bonding have been omitted for clarity.

weak π–π interaction [centroid-centroid distance = 3.931(3) Å] is also observed between the 1,6-dihydropyridazine rings of molecules A and B in the asymmetric unit.

In molecules A and B of the title compound, the morpholine ring adopts a distorted chair conformation. The puckering parameters [24] are $Q_T = 0.528(6)$ Å, $\theta = 7.8(5)°$, $\phi = 345(5)°$ for (N3/O1/C11-C14) and $Q_T = 0.587(6)$ Å, $\theta = 167.1(6)°$, $\phi = 216(3)°$ for (N6/O2/C25-C28). In molecule A, the 1,6-dihydropyridazine ring (N1/N2/C7-C10) makes dihedral angles of 47.0(3)° with the phenyl ring (C1-C6), while in molecule B the corresponding angle is −47.9(2)°.

The crystal structure is stabilized by C—H... O interactions and C—H... π interactions (Table 3). In addition, a weak π–π interaction [Cg2... Cg5(x, y, z) = 3.931(3) Å] exists between the Cg2 and Cg5 centroids of the (N1/N2/C7-C10) and (N4/N5/C21-C24) 1,6-dihydropyridazine rings of molecules A and B in the asymmetric unit. Figures 4–6 show the packing and hydrogen bonding of the title compound.

Theoretical Studies

Molecular Geometry

The optimized structure parameters of the title compound calculated using ab initio and DFT methods listed in Table 4 are in accordance with the atom numbering scheme given in Fig. 7. In addition, Table 4 compares the calculated geometric parameters with the experimental data. Based on this comparison, the bond lengths and angles calculated for the title compound are in good agreement with the experimental values. However, according to our calculations, the optimized bond lengths and bond angles obtained using the B3LYP method show the best agreement with the experimental values. The largest difference between experimental and calculated DFT/B3LYP-6-31G(d,p) bond lengths and bond angles were 0.071 Å and 2.01°, respectively.

Morpholine is a six-member heterocyclic aliphatic rings. The morpholine ring can exist in the chair and boat conformations. The chair conformation was found to be the most stable conformer [25]. We obtained the morpholine ring in a normal chair conformation, where the four carbon atoms C11, C12, C13, and C14 form a plane and the opposing nitrogen N3 and oxygen O1 atoms are located 46.66° above and 53.80° below the ring plane in our calculations. The C—C, C—O, and C—N bond lengths in the morpholine ring are found at approximately 1.52(1), 1.41(1), and 1.46(1) Å, respectively. The morpholine ring endohedral angles lie between 109.96° and 111.90°. These results are in agreement with single crystal X-ray diffraction results and literature values [25].

Vibrational Assignments

The title compound is a nonplanar molecule with C_1 point group symmetry. The molecule has 33 atoms and 93 normal modes of fundamental vibration [26]. All 93 vibrations are active in both IR and Raman. The FT-IR and RAMAN spectra of the title compound are given in Figs. 1 and 2. Table 5 lists the vibrational frequencies obtained using the B3LYP method with the standard 6-31G(d,p) basis set calculations together with the experimental frequencies and the approximate description of each normal modes. All other obtained data are given in the Supplemental Data, Table S1. The vibrational band assignments were made using both the animation option of the GaussView 3.0 graphical interface for Gaussian programs [17] and the VEDA 4 program [18]. Several calculated thermodynamic

Table 4. Optimized and experimental geometries of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine in the ground state[a]

Bond lengths (Å)	Exp.[b]	B3LYP	BLYP	B3PW91	mPW1PW91	HF
C1–C2	1.398(8)	1.415	1.403	1.401	1.399	1.391
C1–C6	1.366(8)	1.415	1.403	1.401	1.399	1.389
C1–C7	1.465(7)	1.493	1.486	1.482	1.480	1.491
C2–C3	1.382(7)	1.403	1.393	1.391	1.389	1.383
C3–C4	1.447(9)	1.406	1.396	1.394	1.392	1.386
C4–C5	1.358(10)	1.405	1.395	1.393	1.391	1.384
C5–C6	1.402(9)	1.404	1.394	1.392	1.390	1.386
C7–C8	1.415(6)	1.427	1.417	1.414	1.412	1.418
C7–C10	1.380(7)	1.398	1.385	1.383	1.381	1.361
C8–N1	1.378(7)	1.331	1.318	1.317	1.314	1.286
C8–Cl1	1.753(5)	1.783	1.759	1.745	1.740	1.739
C9–C10	1.408(6)	1.424	1.415	1.412	1.410	1.414
C9–N2	1.342(6)	1.367	1.348	1.346	1.342	1.306
C9–N3	1.384(6)	1.392	1.382	1.376	1.374	1.388
C11–C12	1.476(7)	1.535	1.524	1.519	1.517	1.518
C11–N3	1.468(6)	1.484	1.470	1.462	1.460	1.460
C12–O1	1.432(7)	1.442	1.424	1.417	1.414	1.401
C13–C14	1.483(7)	1.543	1.530	1.526	1.523	1.520
C13–O1	1.439(6)	1.434	1.416	1.410	1.407	1.395
C14–N3	1.447(7)	1.474	1.462	1.454	1.452	1.460
N1–N2	1.275(7)	1.346	1.329	1.321	1.318	1.318
R		0.9522	0.9512	0.9512	0.9507	0.9338
Bond angles (°)	Exp.	B3LYP	BLYP	B3PW91	mPW1PW91	HF
C2–C1–C6	118.20(4)	118.71	118.85	118.95	119.01	119.19
C2–C1–C7	120.60(5)	121.63	121.54	121.51	121.51	121.10
C6–C1–C7	121.00(5)	119.60	119.55	119.48	119.42	119.66
C1–C2–C3	121.30(5)	120.44	120.39	120.33	120.30	120.29
C2–C3–C4	118.60(5)	120.38	120.34	120.33	120.33	120.22
C3–C4–C5	119.80(5)	119.67	119.71	119.74	119.76	119.80
C4–C5–C6	119.00(6)	120.09	120.06	120.05	120.04	120.03
C1–C6–C5	122.70(5)	120.70	120.64	120.59	120.57	120.45
C1–C7–C8	125.60(4)	125.50	125.26	125.17	125.11	124.59
C1–C7–C10	120.80(4)	119.88	119.93	119.90	119.91	120.64
C8–C7–C10	113.60(4)	114.62	114.81	114.93	114.97	114.76
C7–C8–N1	124.10(4)	124.42	123.92	123.77	123.70	123.45
C7–C8–Cl1	121.20(4)	121.21	121.32	121.32	121.32	121.00
N1–C8–Cl1	114.60(4)	114.32	114.71	114.86	114.93	115.54
C10–C9–N2	121.70(4)	120.93	120.73	120.73	120.75	121.02
C10–C9–N3	122.80(4)	123.19	123.08	123.16	123.11	120.92
N2–C9–N3	115.50(4)	115.85	116.16	116.09	116.13	117.98
C7–C10–C9	119.90(5)	119.78	119.62	119.47	119.39	119.18
C12–C11–N3	110.20(4)	109.92	109.97	109.92	109.88	109.16
C11–C12–O1	113.40(4)	111.65	111.61	111.58	111.55	111.52

(Continued on next page)

Table 4. Optimized and experimental geometries of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine in the ground state[a] *(Continued)*

Bond lengths (Å)	Exp. [b]	B3LYP	BLYP	B3PW91	mPW1PW91	HF
C14–C13–O1	111.90(5)	111.97	111.90	111.96	111.92	111.10
C13–C14–N3	110.50(4)	109.95	110.01	109.90	109.86	109.52
C8–N1–N2	119.50(4)	120.49	120.81	120.88	120.91	121.21
C9–N2–N1	121.10(5)	119.76	120.09	120.21	120.25	120.37
C9–N3–C11	118.50(4)	119.25	118.86	119.10	118.92	116.80
C9–N3–C14	120.30(4)	122.01	121.47	121.78	121.56	117.97
C11–N3–C14	114.90(4)	113.52	113.58	113.75	113.76	111.88
C12–O1–C13	109.10(4)	109.87	110.24	109.94	109.94	111.99
R		0.9756	0.9744	0.9729	0.9727	0.9410

[a] Atom numbering scheme of the molecular structure is given in Fig. 7.
[b] Obtained from single crystal structure data of the title compound.

parameters are shown in Table 6. The total energies and the changes in the total entropy of the title compound at room temperature with different methods are also presented.

The characteristic ν_{CH} stretching vibrations of heteroaromatic structure are expected to appear in the 3000–3100 cm^{-1} frequency range [27–29]. The ν_{CH} stretching vibrations of the title compound were assigned to four bands observed at 3107, 3096, 3066, and 3047 cm^{-1} in the infrared spectrum. The B3LYP calculated wave numbers of these bands reproduced the experimental values well. The differences between experimental and calculated ν_{CH} values were approximately 3, 1, 5, and 17 cm^{-1}, respectively.

For the assignments of CH_2 group frequencies, six fundamentals can be associated with each CH_2 group: an asymmetric stretch, a symmetric stretch, and polarized scissoring and rocking modes. The wagging and twisting modes of the CH_2 group would be expected to be depolarized for out-of-plane bending vibrations. The CH_2 bending modes follow the following order scissoring > wagging > twisting > rocking [25].

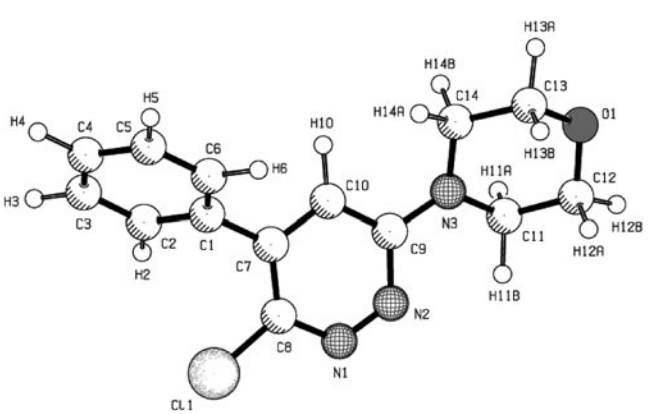


Figure 7. Optimized molecular structure of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine showing the atom numbering scheme.

Table 5. Vibrational wave numbers for the title compound[a]

No	Exp. IR	Exp. RAMAN	B3LYP	B3LYPxSF	B3LYPxSF	IR int.	RAMAN act.	Assignments, %PED,[b]
1	3107	—	3230	3105	3110	5.98	51.39	νC15-H16, 72
2	3096	—	3217	3093	3097	5.98	166.73	νCH, sym, Ring 3, 83
3	—	3078	3208	3084	3088	22.63	179.78	νCH, sym, Ring 3, 85
4	—	3075	3198	3075	3079	20.82	79.40	νCH, asym, Ring 3, 83
5	3066	3062	3189	3066	3071	2.66	114.32	νCH, asym, Ring 3, 81
6	3047	3054	3182	3059	3064	1.54	27.48	νCH, asym, Ring 3, 80
7	3042	3046	3160	3038	3043	6.20	41.36	νCH2, asym, Ring 1, 58
8	2999	2993	3121	3000	3004	18.56	42.39	νCH2, asym, Ring 1, 57
9	2993	2984	3113	2993	2997	39.94	193.06	νCH2, asym, Ring 1, 64
10	2979	2979	3106	2986	2991	36.70	141.39	νCH2, asym, Ring 1, 65
11	2899	2870	3005	2889	2893	95.52	44.88	νCH2, asym, Ring 1, 73
12	2886	-	2994	2878	2882	50.29	107.67	νCH2, sym, Ring 1, 70
13	2864	2862	2992	2876	2880	27.93	141.17	νCH2, sym, Ring 1, 69
14	2844	2843	2981	2866	2870	35.20	89.38	νCH2, sym, Ring 1, 65
15	1601	1602	1660	1596	1598	0.07	189.66	νCC, Ring 3, 33 + δCH, Ring 3, 42
16	1584	1582	1636	1573	1575	33.50	20.42	νCC, Ring 2,3, 25 + δCH, Ring 2,3, 36
17	1575	1574	1626	1563	1566	250.10	95.91	νCC, Ring 2,3, 22 + δCH, Ring 2,3, 34
18	1500	1497	1543	1483	1485	23.79	56.58	νCC, Ring 2,3, 18 + δCH, Ring 2,3, 34
19	1467	1465	1537	1478	1480	8.65	7.09	νCC, Ring 2,3, 17 + δCH, Ring 2,3, 21
20	1457	1459	1515	1457	1459	6.93	8.48	δCH2, Scis, Ring 1, 48

(Continued on next page)

Table 5. Vibrational wave numbers for the title compound[a] *(Continued)*

No	Exp. IR	Exp. RAMAN	B3LYP	B3LYPxSF	B3LYPxSF	IR int.	RAMAN act.	Assignments, %PED,[b]
21	1450	1449	1508	1450	1452	5.07	9.55	δCH2, Scis, Ring 1, 41
22	1446	1445	1499	1441	1443	0.89	6.52	δCH2, Scis, Ring 1, 46
23	1440	1441	1495	1438	1440	18.53	22.37	δCH2, Scis, Ring 1, 44
24	1437	1436	1486	1429	1431	152.50	27.72	νCC, Ring 3, 8 + δCH, Ring 3, 20 + δCH2, Scis, Ring 1, 19 + νCN, 7
25	1429	1428	1478	1421	1423	218.13	19.33	νCC, Ring 3, 9 + δCH, Ring 3, 21 + δCH2, Scis, Ring 1, 16 + νCN, 8
26	1392	1394	1437	1381	1383	4.17	7.21	δCH2, wagg, Ring 1, 67
27	1379	1378	1423	1368	1370	42.33	22.33	δCH2 wagg, Ring 1, 60 + νCC, 8 + + νCN, 5
28	1360	1360	1409	1354	1356	1.23	13.60	δCH2, wagg, Ring 1, 69
29	1330	1335	1399	1345	1347	23.87	12.46	δCH2 wagg, Ring 1, 68
30	1323	1322	1370	1317	1319	0.14	7.84	δCH2 wagg, Ring 1, 81
31	1309	1308	1363	1310	1312	0.78	2.39	δCH, Ring 3, 61
32	1302	1306	1350	1298	1300	57.92	9.36	δCH2, twist, Ring 1, 48 + δCC-H16, 5 + δCH Ring 3, 10
33	1279	1279	1338	1286	1288	4.87	18.46	δCH2 twist, Ring 1, 67
34	1273	1274	1326	1274	1276	24.64	0.63	νCC, Ring 3, 18 + δCH2, twist, Ring 1, 44 + δCC-H16, 6
35	1248	1248	1304	1254	1256	47.32	32.45	δCH2, twist, Ring 1, 64
36	1236	1236	1275	1226	1228	108.86	105.53	νCC, Ring 3, 7 + δCH2, twist, Ring 1, 43 + δCC-H16, 7
37	1229	1229	1261	1212	1214	89.37	10.11	δCH2, twist, Ring 1, 68 + δCC-H16, 4
38	1189	1186	1241	1193	1194	63.73	17.07	δCH2, twist, Ring 1, 70
39	1180	1181	1219	1172	1174	39.13	21.25	νNN, 7 + νCN, 14 + νCC, 16 + δCH2, twist, Ring 1, 28
40	1158	1160	1211	1165	1166	9.10	4.61	δCH Ring 3, 58
41	1145	1148	1200	1154	1155	2.45	3.74	νCN 10 + νCC, 27

42	1140	1139	1189	1144	1145	0.01	6.70	δCH Ring 3, 67 + νCC, 12
43	1117	1117	1155	1111	1112	64.24	1.23	νCO, 11 + νCC, 10 + δCCC 20
44	1111	1114	1147	1103	1104	85.65	1.41	δCC-H16, 6 + νCC, 12 + δCCH, 14
45	1081	1086	1137	1093	1094	9.87	3.99	δCH2, rock, Ring 1, 80
46	1071	1078	1111	1068	1070	2.28	0.35	δCH, Ring 3, 41 + νCC, ring 3, 17
47	1063	1068	1098	1056	1057	2.96	1.31	δCH2, rock, Ring 1, 90
48	1046	1047	1073	1031	1033	5.94	17.53	δCCH, 34 + Deformation, Ring 2, 10
49	1019	1020	1060	1019	1020	0.48	5.22	δCH, Ring 3, 21 + νCC, Ring 3, 13 + νCC, 11
50	1000	1001	1039	999	1000	4.28	46.93	δCH2, rock, Ring 1, 41 + Deformation, Ring 3, 11, + νCN, 5
51	993	989	1035	995	997	5.76	13.09	δCH2, rock, Ring 1, 54 + νCC, 11 + δCOC, 24
52	981	982	1016	977	978	2.22	30.65	δCCC, Ring 3, 32 + δCH, Ring 3, 23
53	954	959	1002	964	965	0.15	0.63	γCH, Ring 3, 91
54	950	950	977	939	941	0.54	1.21	γCH, Ring 3, 90
55	949	948	973	935	936	77.98	3.40	νCN, 7 + νCO, 5 + νCC, 12 + γCH, Ring 3, 22
56	933	931	942	906	907	5.23	0.34	γCH, Ring 3, 30 + δCH, 11
57	926	925	938	902	903	0.63	2.62	γCH, Ring 3, 74
58	877	877	889	855	856	11.05	2.91	γCH16, 42
59	865	866	885	850	852	21.33	5.36	Deformation, Ring 1, 46
60	849	851	864	831	832	1.00	2.44	δCH2, rock, Ring 1, 80
61	823	819	861	828	829	1.32	8.68	γCH, Ring 3, 89
62	813	815	833	800	802	30.21	14.87	νCN, 6 + δCH2, rock, Ring 1, 38
63	771	776	781	751	752	18.34	0.28	γCH, Ring 3, 87
64	743	742	753	724	725	2.72	2.86	γC-H16, Ring 3, 20 + γC, Ring 3, 31

(Continued on next page)

Table 5. Vibrational wave numbers for the title compound[a] *(Continued)*

No	Exp. IR	Exp. RAMAN	B3LYP	B3LYPxSF	B3LYPxSF	IR int.	RAMAN act.	Assignments, %PED, [b]
65	712	713	724	696	697	6.52	14.11	δCCC Ring 3, 10 + δCH Ring 3, 7 + δCNN, 18 + νC-Cl, 23
66	704	706	714	686	687	25.05	1.95	γCH, Ring 3, 86
67	672	674	685	659	660	33.82	11.35	γC, 27 + δCH2, rock, Ring 1, 31
68	648	648	656	630	631	8.74	1.47	γCH, Ring 3, 21 + δCH2, rock, Ring 1, 14
69	626	626	639	614	615	4.56	1.76	δCCC Ring 3, 16 + δCH Ring 3, 10 + δCCC Ring 3, 16
70	615	616	631	607	608	0.85	4.84	δCCC Ring 3, 20 + δCH Ring 3, 21
71	588	587	594	571	572	7.59	1.18	γCH, Ring 3, 28 + δCCC, 6 + δCH2, rock, Ring 1, 27
72	551	550	556	535	536	11.07	0.93	γC, Ring 3, 26 + δCH2, rock, Ring 1, 30
73	—	494	499	480	480	2.65	1.46	γC, Ring 3, 31 + γC, 20 + γN, 29
74	—	464	484	465	466	0.27	1.67	δCH2, rock, Ring 1, 53
75	—	448	469	450	451	2.83	1.67	γC, 24 + τCC, 31
76	—	444	453	436	436	6.70	4.29	γC, 24 + τCC, 40
77	—	411	416	400	401	0.63	5.42	γC Ring 3, 92
78	—	—	405	389	390	1.58	0.12	δCH2, rock, Ring 1, 76
79	—	—	389	374	374	2.69	0.40	γC, 44 +γN, 11
80	—	—	357	343	344	0.17	1.03	γC, 48 +γN, 28
81	—	—	298	286	287	12.81	5.67	τCC, 30 + τCN, 35 + τCO, 9
82	—	—	278	267	267	7.42	1.23	τCC, 46 + τCN, 26
83	—	—	250	241	241	0.80	4.84	δCH2, rock, Ring 1, 66
84	—	—	244	234	234	3.81	2.69	δCH2, rock, Ring 1, 58 + τCC, 20
85	—	—	221	212	213	3.32	2.70	δCH2, rock, Ring 1, 42 + τCC, 29
86	—	—	220	212	212	1.86	0.30	δCH2, rock, Ring 1, 72

87	—	—	146	140	140	0.93	1.77	τCC, 39 + τCN, 20 (Skelatal vib.)
88	—	—	109	104	105	0.25	1.39	τCN, 39 + τCC, 25 (Skelatal vib.)
89	—	—	92	88	88	4.12	1.54	τCN, 40 + τCC, 36 (Skelatal vib.)
90	—	—	67	65	65	0.22	8.19	τCC, 37 + τCN, 32 (Skelatal vib.)
91	—	—	53	51	51	0.24	9.34	τCN, 35 + τCC, 33 (Skelatal vib.)
92	—	—	37	36	36	0.18	2.33	τCN, 56 + τCN, 23 (Skelatal vib.)
93	—	—	25	24	24	0.06	0.31	τCN, 55 (Skelatal vib.)
r	—	—	0.9999	0.9999	0.9999	—	—	
Mean absolute percentage error			3.3496	0.9217	0.8859	—	—	
Mean absolute error			51.8607	9.3826	9.2831	—	—	
RMS_{ov}			54.6629	9.856	9.6505	—	—	
RMS_{mol}			63.3443	11.4213	11.1831	—	—	
Scaling factor, SF			1.0000	0.9614	0.9628	—	—	

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[a] Harmonic frequencies (in cm^{-1}), IR intensities (km/mol), Raman activity (Å/amu).

[b] ν, stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; sym, symmetric; asym, asymmetric; Ring1: C1-C2-C3-C4-C5-C6; Ring2: C7-C8-N1-N2-C9-C10; and Ring3: N3-C11-C12-O1-C13-C14. PED less than 10% are not shown.

Table 6. Theoretically computed energies, zero-point vibrational energies, entropies, and dipole moment for the title compound

Thermodynamic parameters (298 K)	B3LYP	BLYP	B3PW91	mPW1PW91	HF
SCF energy (a.u.)	−1241.565	−1241.240	−1241.218	−1241.395	−1235.966
Total energy (Thermal) E_{total} (kcal/mol)	174.690	169.525	175.174	176.328	186.309
Heat capacity at const. volume, C_v (cal/mol.K)	61.224	63.590	61.097	60.616	56.175
Entropy, S (cal/mol.K)	130.502	132.719	130.486	129.925	125.368
Vibrational energy, E_{vib} (kcal/mol)	172.913	167.747	173.397	174.551	184.532
Zero-point vibrational energy, E_o (kcal/mol)	164.79027	159.29618	165.28112	166.50446	177.13704
Rotational constant (GHz)					
A	0.62604	0.61379	0.63065	0.63380	0.64040
B	0.17997	0.17726	0.18090	0.18153	0.18102
C	0.14534	0.14303	0.14634	0.14684	0.14829
Dipole moment (Debye)					
μx	−0.2551	0.0368	−0.2373	−0.3062	−1.2444
μy	−4.9311	−4.8960	−4.9470	−4.9450	−5.0728
μz	0.5424	0.4843	0.5181	0.5384	0.7452
μTotal	4.9674	4.9200	4.9797	4.9836	5.2761

The C—H stretching vibration of the methylene group is at lower frequencies than those of the aromatic C-H ring stretching. The asymmetric CH_2 stretching vibration generally observed in the 3000–2900 cm^{-1} region while the CH_2 symmetric stretch appears between 2900 cm^{-1} and 2800 cm^{-1} [30, 31]. The bands at 3037 (3047), 2999 (2993), 2993 (2984), 2979 (2979), and 2899 (2870) cm^{-1} in FT-IR (FT-Raman) are assigned to CH_2 asymmetric stretching vibrations. The computed anharmonic frequencies using the B3LYP method for CH_2 asymmetric and symmetric stretching vibrations show good correlation with recorded spectral data and are in close agreement with the literature values [30,31].

The bond angle bending (HCH) vibrational modes (scissoring, wagging, twisting, and rocking) are well defined in all the calculations. As seen in Table 5, the bands observed at 1457 (1459), 1450 (1449), 1446 (1445), and 1440 (1441) cm^{-1} in the FT-IR (FT-Raman) spectrum correspond to scissoring deformation of -CH_2- groups in the title compound [32,33]. The theoretically computed values for the scissoring deformation vibration modes show good agreement with the experimental values. The wagging, twisting, and rocking vibrational modes are distributed over a wide range [32–35]. Twisting and wagging vibrational modes for the –CH_2- groups were assigned in the 1392–1180 cm^{-1} range. The above result is in close agreement with the literature values [36]. These vibrational modes are described in the tables by mean of the general symbol δ_{CH2}. The rocking –CH_2- is assigned in the of 1081–813 cm^{-1} range [33, 34]. These bands are assigned using calculated PED.

The bands due to the δ_{CH} in-plane ring bending vibration interacting with the ν_{CC} stretching vibration are observed in the region 1601–1019 cm^{-1}. γ_{CH} Out-of-plane bending vibrations are strongly coupled vibrations that occur in the region 954–648 cm^{-1} region

Table 7. Mullikan atomic charges calculated using B3LYP/6-31G(d,p)

	Charge				
Atom	B3LYP	BLYP	B3PW91	mPW1PW91	HF
C1	0.038447	0.060431	0.014059	0.006285	−0.032104
C2	−0.085915	−0.070693	−0.108420	−0.110197	−0.115811
H2	0.106766	0.078946	0.142526	0.148556	0.172431
C3	−0.092183	−0.064878	−0.130160	−0.136178	−0.151562
H3	0.095145	0.067656	0.130902	0.136905	0.159613
C4	−0.077713	−0.050605	−0.112538	−0.118245	−0.141941
H4	0.092538	0.064826	0.128253	0.134321	0.157746
C5	−0.090473	−0.063272	−0.128162	−0.134198	−0.149392
H5	0.092491	0.064779	0.128426	0.134486	0.157501
C6	−0.104228	−0.086860	−0.129099	−0.131347	−0.136865
H6	0.091394	0.062689	0.128213	0.134411	0.160433
C7	0.075410	0.096086	0.056200	0.049635	−0.000283
C8	0.054229	0.052294	0.035212	0.034295	0.080985
C9	0.537061	0.501141	0.554982	0.563843	0.615264
C10	−0.113178	−0.098196	−0.136747	−0.138312	−0.140821
H10	0.104408	0.073884	0.139759	0.146643	0.188726
C11	−0.044944	−0.032640	−0.100268	−0.102861	−0.012572
H11A	0.157337	0.141011	0.188122	0.191440	0.160330
H11B	0.109054	0.095898	0.137470	0.140796	0.128571
C12	0.042606	0.050514	−0.011831	−0.014444	0.096870
H12A	0.111794	0.095832	0.141275	0.144974	0.133273
H12B	0.095016	0.082384	0.121257	0.124677	0.106745
C13	0.056315	0.063479	0.001943	−0.000582	0.111830
H13A	0.093484	0.080299	0.119543	0.123171	0.107063
H13B	0.108729	0.092746	0.138224	0.141955	0.130057
C14	−0.049486	−0.036719	−0.101009	−0.104399	−0.038038
H14A	0.112357	0.099129	0.140413	0.143707	0.127663
H14B	0.111663	0.099266	0.139361	0.142696	0.119798
N1	−0.252648	−0.249057	−0.251061	−0.251274	−0.249090
N2	−0.375084	−0.356096	−0.382214	−0.386528	−0.418784
N3	−0.528716	−0.466142	−0.551682	−0.568497	−0.732696
O1	−0.479554	−0.440895	−0.476351	−0.484467	−0.633747
Cl1	0.007879	−0.007239	0.033403	0.038733	0.038806

[37, 38]. The δ_{CH} and γ_{CH} bending vibrations of the CH group have also been identified for the title compound and are presented in Table 5.

Silverstein et al. [33] assigned C-N stretching absorption in the 1382–1266 cm^{-1} region for aromatic amines. The identification of $\nu_{\text{C–N}}$ vibrations is difficult because of possible overlap in this region. However, with the help of theoretical calculations (VEDA 4) the $\nu_{\text{C–N}}$ vibrations were identified and assigned. The infrared (Raman) bands appearing at 1437 (1436), 1429 (1428), and 1379 (1378) cm^{-1} were designated as $\nu_{\text{C–N}}$ stretching vibrations. The slight shift in wave number results from the increase in force constants of the C—N bond due to resonance.

C—Cl stretching vibrations generally give strong bands in the 710–500 cm^{-1} region. For simple organic chlorine compounds, C—Cl absorptions lie in the 750–700 cm^{-1} region. Thus, the band observed (calculated) at 712 (697) cm^{-1} in the FT-IR spectrum was assigned to a C-Cl stretching vibration in the present investigation. The above result is in close agreement with the literature values [39–41].

The most characteristic vibration of cyclic ethers is in the 1150–1085 cm^{-1} region and corresponds to C—O—C asymmetric stretching [42, 43]. The computed C—O—C asymmetric stretching vibrations at 1112 cm^{-1} are found to be in perfect agreement with the experimental FT-IR value of 1117 cm^{-1} and FT-Raman value of 1117 cm^{-1}. The modes observed at 993 cm^{-1} in the infrared and at 989 cm^{-1} in the Raman spectrum are assigned to the C—O—C in-plane bending mode of the title compound. The Raman frequencies observed at 712 cm^{-1} in IR and 713 cm^{-1} are assigned to the in-plane bending of C—N—N.

To investigate the performance and vibrational frequencies for the title compound, the mean deviation, mean absolute deviation, average absolute error, root mean square (RMS) value, and correlation coefficient between the calculated harmonic and observed fundamental vibrational frequencies for each method were calculated and are given in Table 5. The RMS values were obtained in this study using the following equation [44]:

$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\nu_i^{\mathrm{calc}} - \nu_i^{\mathrm{exp}}\right)^2} \qquad (1)$$

These results indicate that the B3LYP calculations approximate the observed fundamental frequencies much better than other methods. A small observed difference between experimental and calculated vibrational modes can be attributed to hydrogen bond vibrations present in the crystal that lead to strong perturbation of the infrared frequencies (and intensities) of many other modes. We state that the experimental results are solid-phase and theoretical calculations are in the gaseous phase.

Atomic charges for the title compound calculated using the B3LYP/6-31G(d,p) method are given in Table 7. The morpholine nitrogen (N3) possesses more negative charge than the other nitrogen atoms due the lone pair electron delocalization. This also contributes to a positive charge on the carbon atom (C9) of the pyridazine ring.

Conclusions

In this study, we have determined the crystal structure of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine using single crystal X-ray diffraction analysis. We calculated the geometric parameters and vibrational frequencies of the title compound using HF, BLYP, B3LYP, B3PW91, and mPW1PW91 methods with the standard 6-31G(d,p) basis set. The optimized geometric parameters (bond lengths and bond angles) agree with the experimental values for 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine. Comparison of the observed fundamental vibrational frequencies of the title compound and the calculated results from the density functional (BLYP, B3LYP, B3PW91, and mPW1PW91) and HF methods indicate that B3LYP is superior to the scaled HF, BLYP, B3PW91, and mPW1PW91 approach for molecular vibrational problems.

Acknowledgments

The authors wish to acknowledge the Faculty of Arts and Sciences, Ondokuz Mayis University, Turkey, for the use of the Stoe IPDS II diffractometer (purchased under grant F.279 of the University Research Fund).

Supplementary Information

Crystallographic data for the structural analysis of 3-chloro-4-phenyl-6-(morpholine-4-yl)-pyridazine have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 924535. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk.

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