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Spectroscopic investigations of 1-benzylpiperazine

C. YOHANNAN PANICKER[1], HEMA TRESA VARGHESE[2],
SUNIL. B.[3] and P.L. ANTO[3]

[1]Department of Physics, TKM College of Arts and Science, Kollam, Kerala (INDIA)
[2]Department of Physics, Fatima Mata Natinal College, Kollam, Kerala (INDIA)
[3]Department of Physics, St. Thomas's College, Thrissur, Kerala (INDIA)

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Abstract

FT-IR and FT-Raman spectra of 1-benzylpiperazine were recorded and analyzed. The vibrational wavenumbers were computing at B3LYP/6-31G* level. The data obtained from theoretical calculations are used to assign vibrational bands obtained experimentally. The results indicate that B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. The geometrical parameters, the predicted infrared intensities and Raman activities are reported.

Key words: FT-IR, FT-Raman, DFT calculations, piperazine.

Introduction

Piperazine is a potent anthelmintic used in the therapy of ascariasis (roundworm) and oxyuriasis (threadworm) infestations. The piperazines were originally named because of their chemical similarity with piperadine, a constituent of piperine in the black pepper plant. Piperazine owes its anthelmintic activity to its ability to produce flaccid paralysis of the muscles of the parasite[1]. Piperazines have been reported in gene transfer reactions[2] and quaternary piperazinium salts have shown spasmolytic, anthelmintic and germicidal activity. Polycationic ligands having piperidine and piperazine rings have been reported to exhibit a substantial degree of selective RNA binding[3]. Replacement of the piperazinyl nitrogen with carbon, oxygen or sulfur, corresponding to the piperidino, morpholino, or thimorpholino group, respectively, enhances the activity against Gram-positive bacteria, but reduces the activity against Gram-negative bacteria[4]. Some piperazine derivatives possess high biological activity for multidrug resistance in cancer and malaria[5]. Dorsey *et al.*,[6] reported the synthesis and biological evaluations of piperizine derivatives as serotonin-selective reuptake inhibitors with a potentially improved adverse reaction profile. Gunasekaran and Anita[7] reported the spectral investigation and normal coordinate analysis of piperazine.

Experimental

The FT-IR spectrum was recorded on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets, number of scans 16, resolution 2 cm^{-1}. The FT-Raman spectrum was obtained on a BRUKER RFS 100/S, Germany. For excitation of the spectrum the emission of a Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement of solid sample. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm^{-1}.

Computational details :

Calculations of the title compound were carried out with Gaussian03 software program[8] using the B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Therefore, a scaling factor of 0.9613 was uniformly applied to the DFT calculated wavenumbers[9]. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes[10,11]. The optimized geometrical parameters are given in Table 1.

Results and Discussion

The observed IR, Raman and calculated (scaled) wavenumbers and the assignments are given in Table 2. The CN stretching vibration[12] coupled with δNH, is moderately to strongly active in the region 1325-1175 cm^{-1}. El-Shahawy *et al.*[13] observed a band at 1320 cm^{-1} in the IR spectrum as this υCN mode. In the present case, the υCN bands are observed at 1303, 1262, 1208 cm^{-1} in the IR spectrum and at 1303, 1209 cm^{-1} in the Raman spectrum and at 1292, 1265, 1233, 1225, 1203 cm^{-1} theoretically.

For bridging methylene groups[14], the CH_2 vibrations are observed in the region 2800-3000, 1200-1400, 875-1150 and 600-850 cm^{-1}. The vibrations of the CH_2 group (the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch υ_sCH_2, the scissoring vibration and wagging vibration) appear in the regions 2940-3005, 2870-2940, 1420-1480 and 1320-1380 cm^{-1}, respectively[12,15]. The stretching bands of the CH_2 groups are observed at 2955, 2938, 2806, 2769 cm^{-1} in the IR spectrum, 2951, 2804 cm^{-1} in the Raman spectrum and in the range 2989-2788 cm^{-1} theoretically (DFT) for the title compound. According to literature[16] scissoring mode of the CH_2 group give rise to characteristic band near 1485 cm^{-1} in IR and Raman spectra. These modes are unambiguously correlated with the strong bands in the region of 1499-1467 cm^{-1} theoretically. The wagging modes are observed at 1362, 1355, 1339, 1324 cm^{-1} in the IR spectrum and in the range 1372-1328 cm^{-1} theoretically. The twisting and rocking vibrations of the CH_2 group appear in the region[12] of 1050-1200 and 740-900 cm^{-1}, respectively. These modes are also assigned (Table 2). For the title compound the twisting vibrations are observed at 1143, 1124, 1074 cm^{-1} in the IR spectrum, 1140 cm^{-1} in the Raman spectrum and in the range of 1146-1077 cm^{-1} theoretically. The rocking deformations are assigned in the range of 879-726 cm^{-1} theoretically. For the title compound, the CC stretching modes are observed at 1030, 982, 970 cm^{-1} theoretically and 1029, 979 cm^{-1} in the IR spectrum and at 1035 cm^{-1} in the Raman spectrum[16].

The N-H stretching vibrations[12,17] generally give rise to bands at 3500-3300 cm^{-1}. In the present study, the NH stretching band is observed in the IR spectrum at 3272 cm^{-1} and the calculated value (DFT) is 3444 cm^{-1}. The downshift in the IR spectrum is due to weakening of the NH bond. N-H group show bands[14] at 1510-1500 cm^{-1}, 1335-1250 cm^{-1} and 840-600 cm^{-1}. According to literature if N-H is a part of a closed ring[12,14] the C-N-H deformation band is absent in the region 1510-1500 cm^{-1}. For the title compound the C-N-H deformation band is assigned at 1386 cm^{-1} (DFT) theoretically. The DFT calculations give wagging mode of NH at 612 cm^{-1}.

The phenyl CH stretching modes occurs above 3000 cm^{-1} and is typically exhibited as multiplicity of weak to moderate bands compared with the aliphatic CH stretching[18]. In the present case, the DFT calculations give υCH modes of the phenyl rings in the range 3098-3056 cm^{-1}. The bands observed at 3085, 3062, 3040 cm^{-1} in the IR spectrum and at 3067 cm^{-1} in the Raman spectrum are assigned as CH stretching modes of the phenyl rings. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring near 1600, 1580, 1490 and 1440 cm^{-1}) are good group vibrations[12]. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers. In the absence of ring conjugation, the band at 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1}. In the case of C=O substitution, the band near 1490 cm^{-1} can be very weak. The fifth ring stretching vibration is active near 1315 ± 65 cm^{-1}, a region that overlaps strongly with that of the CH in-plane deformation[12]. The sixth ring stretching vibration, or the ring breathing mode, appears as a weak band near 1000 cm^{-1}, in mono-, 1,3-di- and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation[12,19]. The phenyl ring modes are observed at 1580, 1445 cm^{-1} in the IR spectrum, 1607, 1587, 1451 cm^{-1} in the Raman spectrum and in the range 1454-1599 cm^{-1} theoretically. The ring breathing mode is observed at 1005 cm^{-1} in the IR spectrum, 1004 cm^{-1} in the Raman spectrum and at 996 cm^{-1} theoretically as expected[12]. The in-plane and out-of-plane deformation CH bands of the phenyl ring are expected above and below 1000 cm^{-1} according to literature[12]. The in-plane CH modes are observed at 1319, 1182, 1013 cm^{-1} in the IR spectrum and at 1182, 1024 cm^{-1} in the Raman spectrum. The out-of-plane CH modes are observed at 906, 749 cm^{-1} in the IR spectrum and at 902, 823, 750 cm^{-1} in the Raman spectrum. These modes are assigned in the range 1024-1314 (in-plane) and 759-995 cm^{-1} (out-of-plane) theoretically[12]. The substituent sensitive modes of the phenyl and piperazine rings[12] are also identified and assigned (Table 2).

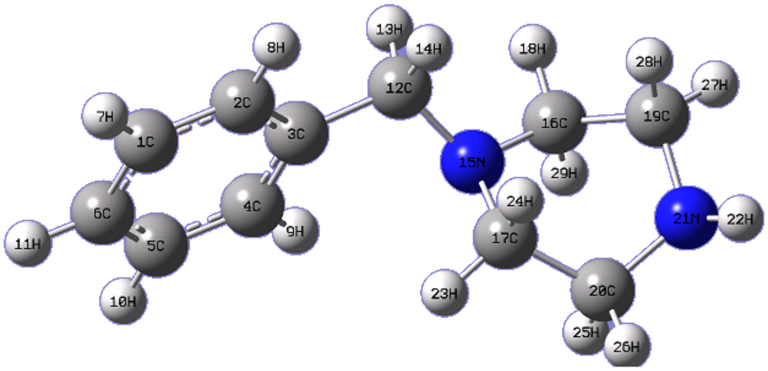

Table 1. Geometrical parameters

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C_1-C_2	1.4002	A(2,1,6)	120.0	D(6,1,2,3)	0.4
C_1-C_6	1.3991	A(2,1,7)	119.8	D(6,1,2,8)	-179.4
C_1-H_7	1.0859	A(6,1,7)	120.1	D(7,1,2,3)	180.0
C_3-C_2	1.4029	A(1,2,3)	120.8	D(7,1,2,8)	0.1
C_2-H_8	1.0872	A(1,2,8)	119.8	D(2,1,6,5)	0.0
C_3-C_4	1.4048	A(3,2,8)	119.4	D(2,1,6,11)	179.7
C_3-C_{12}	1.5227	A(2,3,4)	118.8	D(7,1,6,5)	-179.5
C_5-C_4	1.3982	A(2,3,12)	120.6	D(7,1,6,11)	0.2
C_4-H_9	1.0851	A(4,3,12)	120.6	D(1,2,3,4)	-0.6
C_5-C_6	1.4013	A(3,4,5)	120.5	D(1,2,3,12)	177.5
C_5-H_{10}	1.0860	A(3,4,9)	118.6	D(8,2,3,4)	179.2
C_6-H_{11}	1.0857	A(5,4,9)	120.9	D(8,2,3,12)	-2.7
C_{12}-H_{13}	1.0982	A(4,5,6)	120.3	D(2,3,4,5)	0.4
C_{12}-H_{14}	1.1101	A(4,5,10)	119.8	D(2,3,4,9)	-178.7
C_{12}-N_{15}	1.4663	A(6,5,10)	120.0	D(12,3,4,5)	-177.7
C_{16}-N_{15}	1.4822	A(1,6,5)	119.6	D(12,3,4,9)	3.2
C_{17}-N_{15}	1.4806	A(1,6,11)	120.2	D(2,3,12,13)	-99.4
C_{16}-H_{18}	1.0943	A(5,6,11)	120.2	D(2,3,12,14)	16.2
C_{16}-C_{19}	1.5375	A(3,12,13)	108.8	D(2,3,12,15)	141.2
C_{16}-H_{29}	1.0980	A(3,12,14)	108.4	D(4,3,12,13)	78.7

C_{17}-C_{20}	1.5359	A(3,12,15)	113.1	D(4,3,12,14)	-165.8
C_{17}-H_{23}	1.0969	A(13,12,14)	106.6	D(4,3,12,15)	-40.7
C_{17}-H_{24}	1.1089	A(13,12,15)	107.5	D(3,4,5,6)	0.1
C_{19}-N_{21}	1.4736	A(14,12,15)	112.2	D(3,4,5,10)	-179.9
C_{19}-H_{27}	1.0986	A(12,15,16)	117.0	D(9,4,5,6)	179.1
C_{19}-H_{28}	1.1061	A(12,15,17)	113.6	D(9,4,5,10)	-0.9
C_{20}-N_{21}	1.4753	A(16,15,17)	114.5	D(4,5,6,1)	-0.3
C_{20}-H_{25}	1.0987	A(15,16,18)	108.7	D(4,5,6,11)	-179.9
C_{20}-H_{26}	1.0949	A(15,16,19)	112.8	D(10,5,6,1)	179.7
N_{21}-H_{22}	1.0125	A(15,16,29)	109.7	D(10,5,6,11)	0.0
		A(18,16,19)	110.1	D(3,12,15,16)	154.5
		A(18,16,29)	107.1	D(3,12,15,17)	-68.6
		A(19,16,29)	108.4	D(13,12,15,16)	34.4
		A(15,17,20)	110.0	D(13,12,15,17)	171.3
		A(15,17,23)	109.6	D(14,12,15,16)	-82.4
		A(15,17,24)	110.8	D(14,12,15,17)	54.5
		A(20,17,23)	110.7	D(12,15,16,18)	-19.4
		A(20,17,24)	108.9	D(12,15,16,19)	102.9
		A(23,17,24)	106.9	D(12,15,16,29)	-136.2
		A(16,19,21)	108.5	D(17,15,16,18)	-155.9
		A(16,19,27)	109.8	D(17,15,16,19)	-33.6
		A(16,19,28)	108.7	D(17,15,16,29)	87.3
		A(21,19,27)	110.0	D(12,15,17,20)	-162.6
		A(21,19,28)	112.9	D(12,15,17,23)	75.5
		A(27,19,28)	107.0	D(12,15,17,24)	-42.2
		A(17,20,21)	112.4	D(16,15,17,20)	-24.5
		A(17,20,25)	108.7	D(16,15,17,23)	-146.5
		A(17,20,26)	109.8	D(16,15,17,24)	95.9
		A(21,20,25)	110.2	D(15,16,19,21)	61.1

	A(21,20,26)	108.8	D(15,16,19,27)	-178.6
	A(25,20,26)	106.7	D(15,16,19,28)	-61.9
	A(19,21,20)	116.0	D(18,16,19,21)	-177.4
	A(19,21,22)	114.1	D(18,16,19,27)	-57.1
	A(20,21,22)	114.1	D(18,16,19,28)	59.6
			D(29,16,19,21)	-60.6
			D(29,16,19,27)	59.7
			D(29,16,19,28)	176.4
			D(15,17,20,21)	59.1
			D(15,17,20,25)	-63.2
			D(15,17,20,26)	-179.7
			D(23,17,20,21)	-179.7
			D(23,17,20,25)	58.0
			D(23,17,20,26)	-58.4
			D(24,17,20,21)	-62.4
			D(24,17,20,25)	175.2
			D(24,17,20,26)	58.8
			D(16,19,21,20)	-26.1
			D(16,19,21,22)	-161.9
			D(27,19,21,20)	-146.2
			D(27,19,21,22)	78.0
			D(28,19,21,20)	94.3
			D(28,19,21,22)	-41.5
			D(17,20,21,19)	-31.2
			D(17,20,21,22)	104.5
			D(25,20,21,19)	90.3
			D(25,20,21,22)	-134.0
			D(26,20,21,19)	-153.0
			D(26,20,21,22)	-17.3

Table 2. Vibrational assignments

B3LYP υ(cm^{-1})	IR intensity	Raman activity	IR υ(cm^{-1})	Raman υ(cm^{-1})	Assignments
3444	0.32	123.54	3272		υNH
3098	17.31	268.03			υCH
3089	34.57	53.78	3085		υCH
3077	32.08	86.36			υCH
3066	0.76	97.29	3062	3067	υCH
3056	8.69	34.42	3040		υCH
2989	24.47	107.85			$\upsilon_{as}CH_2$
2980	48.30	62.91			$\upsilon_{as}CH_2$
2946	45.21	137.58	2955	2951	$\upsilon_{as}CH_2$
2933	38.02	108.28	2938		$\upsilon_{as}CH_2$
2927	115.62	141.89			$\upsilon_{as}CH_2$
2914	44.11	118.30			$\upsilon_{s}CH_2$
2909	15.03	19.01			$\upsilon_{s}CH_2$
2829	104.37	114.68			$\upsilon_{s}CH_2$
2803	58.62	49.47	2806	2804	$\upsilon_{s}CH_2$
2788	58.10	44.51	2769		$\upsilon_{s}CH_2$
1599	4.20	32.57	1580	1607	υPh
1581	0.60	9.21		1587	υPh
1511	2.32	18.49			υPh
1499	5.90	11.90	1500		δCH_2
1494	3.56	10.48	1494		δCH_2
1493	10.14	2.16			δCH_2
1476	4.95	13.61			δCH_2
1467	6.92	16.31	1464		δCH_2
1458	7.14	2.54			υPh
1454	8.62	2.48	1445	1451	υPh

1386	4.63	4.20			δNH
1372	1.97	1.50			ωCH$_2$
1366	14.49	6.22	1362		ωCH$_2$
1352	21.11	7.70	1355		ωCH$_2$
1341	20.38	15.41	1339		ωCH$_2$
1328	7.40	3.26	1324		ωCH$_2$
1314	6.80	10.22	1319		δCH
1292	6.24	13.91	1303	1303	υCN
1265	16.87	12.58	1262		υCN
1233	18.72	9.84			υCN
1225	4.01	7.52			υCN
1203	9.00	10.54	1208	1209	υCN
1194	2.11	10.95			δCH
1180	3.01	7.37	1182	1182	δCH
1172	1.26	7.07			δCH
1146	13.82	4.89	1143	1140	τCH$_2$
1131	21.11	5.80	1124		τCH$_2$
1105	38.75	5.44			τCH$_2$
1081	3.93	2.38			τCH$_2$
1077	11.24	1.16	1074		τCH$_2$
1063	12.30	5.24			δCH
1030	8.18	4.58	1029	1035	υCC
1024	13.68	5.37	1013	1024	δCH
996	0.32	28.72	1005	1004	υPh
995	4.32	2.02			γCH
982	16.44	1.90	979		υCC
970	11.16	4.00			υCC
965	0.38	0.12			γCH

909	4.10	2.04	906	902	γCH
879	6.47	1.89			ρCH$_2$
860	6.45	10.902			ρCH$_2$
851	0.32	5.02			ρCH$_2$
834	1.27	1.83		823	γCH
803	4.09	8.14	800	802	ρCH$_2$
759	29.68	8.36	749	750	γCH
726	25.40	10.53			ρCH$_2$
701	19.69	1.19	699		γPh
627	0.13	4.67		623	δPh(X)
612	10.52	1.74	611		γNH
601	27.21	1.51	590		δPh
525	26.62	3.76			γPh(X)
486	6.56	0.42	489	489	δPh(X)
465	30.48	1.05			δRing
423	73.64	2.34		428	γRing
411	1.41	0.08			γPh
360	1.94	0.46			tRing
332	4.46	1.19			tRing
300	3.58	1.75		298	δCX(X)
262	10.45	1.28		265	γCX(X)
206	0.80	4.85		219	tCH$_2$
185	10.21	1.05			tCH$_2$
102	0.81	2.66			tCH$_2$
50	0.43	3.08			tCH$_2$
44	0.20	3.15			tCH$_2$
33	0.61	5.87			tPh

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ω-wagging; τ-twisting; ρ-rocking; t-torsion; Ph-phenyl ring; Ring-Piperazine ring; as-asymmetric; s-symmetric.

Conclusion

The FT-IR and FT-Raman spectra of the title compound were recorded and analyzed. The molecular geometry and vibrational wavenumbers were calculated using DFT method. The predicted infrared intensities and Raman activities are reported. The downshift of the N-H stretching band in the IR spectrum is due to weakening of the NH bond.

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