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IR, Raman and Computational study of 1-(2-aminoethyl) piperazine

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Abstract

IR and Raman spectra of 1-(2-aminoethyl)piperazine were recorded and analyzed. Using Gaussian03 set of quantum chemistry codes, the vibrational wavenumbers and corresponding vibrational assignments were examined theoretically at the HF and DFT levels. The results indicate that the B3LYP method is able to provide satisfactory results for predicting vibrational wavenumbers. The predicted infrared intensities and Raman activities are reported.

Key words: HF, DFT, IR, Raman, 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 HF/6-31G* and 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 and 0.8929 were uniformly applied to the DFT and HF calculated wavenumbers[9]. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. 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].

Results and Discussion

The observed IR and Raman bands and calculated (scaled) wavenumbers with assignments are given in Table 1. The CN stretching vibration[12] coupled with δNH, is moderately to strongly active in the region 1275 ± 55 and 950-1050 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 band is observed at 1308,1275, 1267, 1059 cm^{-1} in the IR spectrum, 1303, 1064 in the Raman spectrum and at 1310, 1303, 1283, 1267, 1059, 1049 cm^{-1} theoretically (DFT).

The N-H stretching vibrations generally give rise to bands[12,14] at 3500-3300 cm^{-1}. In the present study, the NH stretching band is observed in the IR spectrum at 3388 cm^{-1} and the calculated value (DFT) is 3361 cm^{-1}. N-H group show bands[15] at 1510-1500 cm^{-1}, 1335-1250 cm^{-1} and 840-730 cm^{-1}. According to literature if N-H is a part of a closed ring[12,15] 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 observed at 1321 cm^{-1} in the IR spectrum and at 1318 cm^{-1} (DFT) theoretically. The DFT calculations give wagging mode of NH at 847 cm^{-1}.

For bridging methylene groups[15], 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 $\upsilon_{s}CH_2$, the scissoring vibration and wagging vibration) appear in the regions 2940-3005, 2870-2940, 1420-1480 and 1320-1380 cm^{-1}, respectively[12,16].

The stretching bands of the CH_2 groups are observed at 2944, 2878, 2815 cm^{-1} in the IR spectrum, 2945 cm^{-1} in the Raman spectrum and in the range 2968-2825 cm^{-1} theoretically (DFT) for the title compound. According to literature[17] 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 1436-1448 cm^{-1} theoretically. The bands at 1466 in the IR spectrum and at 1463, 1446 cm^{-1} in the Raman spectrum are assigned as δCH_2 modes of the title compound. The wagging modes are observed at 1351, 1338 cm^{-1} in the IR spectrum and in the range 1398-1318 cm^{-1} theoretically (DFT). The twisting and rocking vibrations of the CH_2 group appear in the region[12] of 1200-1280 and 800-1025 cm^{-1}, respectively. These modes are also assigned (Table 1). For the title compound the twisting vibrations are observed at 1180, 1143, 1126, cm^{-1} in the IR spectrum, 1192, 1149 cm^{-1} in the Raman spectrum and in the range of 1185-1110 cm^{-1} theoretically. The rocking deformations are assigned in the range of 891-1042 cm^{-1} theoretically.

For the title compound, the CC stretching modes are observed at 844, 783, 765 cm^{-1} theoretically, 837 cm^{-1} in the IR spectrum and at 801, 764 cm^{-1} in the Raman spectrum[17].

The NH_2 stretching mode[12] are expected in the region 3260-3390 cm^{-1} and in the present case the DFT calculation give this mode at 3407 cm^{-1}. Topacli and Topacli[18] reported the calculated wavenumbers in the range 3670-3920 cm^{-1} for NH_2 stretching modes. The bands corresponding to the δNH_2 vibrations[12] are expected in the region 1610 ± 30 cm^{-1}. The calculated value is 1632 cm^{-1}. The rocking/twisting mode of NH_2 is expected in the region 1195 ± 90 cm^{-1} and the DFT calculations give this mode at 1098 cm^{-1}. The wagging mode of NH_2 is expected[12] in the range 840 ± 55 cm^{-1} and is observed at 869 (IR). The DFT calculations give this mode at 877 cm^{-1}. The torsion NH_2 mode is expected in the range 355 ± 65 cm^{-1} and the band at 309 cm-1 (DFT) are assigned as this mode. For sulfonamide derivatives, the NH_2 modes are reported at[19] 3390, 3395, 3399 cm^{-1} and NH modes at 3253, 3230, 3255 cm^{-1}.

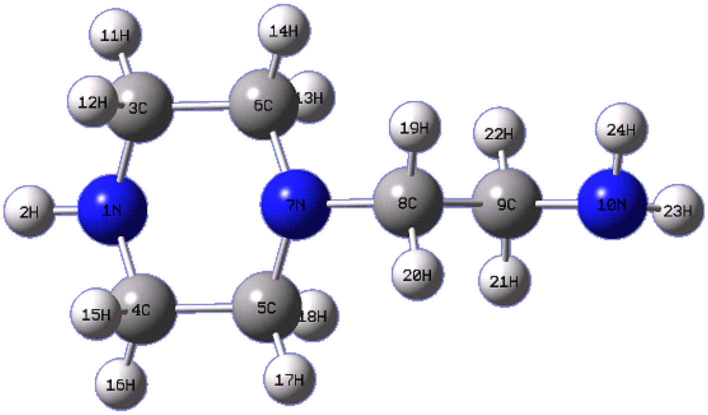

Table 1. Calculated vibrational wavenumbers, measured IR and Raman bands and assignments

HF/6-31G*			B3LYP/6-31G*			IR	Raman	Assignments
υ(cm^{-1})	I_{IR}	R_A	υ(cm^{-1})	I_{IR}	R_A	υ(cm^{-1})	υ(cm^{-1})	
3492	5.22	78.74	3407	0.94	97.97			$\upsilon_{as}NH_2$
3409	0.65	139.61	3361	2.24	161.39	3388		υNH
3387	0.86	116.03	3325	3.82	141.32	3315		$\upsilon_s NH_2$
2908	86.05	52.79	2968	73.92	39.61			$\upsilon_{as}CH_2$
2893	14.78	208.11	2962	18.29	179.42			$\upsilon_{as}CH_2$
2890	81.50	96.10	2960	64.44	88.46			$\upsilon_{as}CH_2$
2890	101.04	17.15	2956	55.81	67.48			$\upsilon_{as}CH_2$
2885	12.82	116.21	2951	0.36	82.77			$\upsilon_{as}CH_2$
2883	37.69	11.23	2950	43.64	29.98	2944	2945	$\upsilon_{as}CH_2$
2845	35.46	88.15	2901	39.51	91.99			$\upsilon_s CH_2$
2803	192.59	69.54	2857	122.79	91.20	2878		$\upsilon_s CH_2$
2794	105.53	78.20	2841	181.23	42.38			$\upsilon_s CH_2$
2791	20.01	65.43	2836	7.62	24.19			$\upsilon_s CH_2$
2786	10.68	157.86	2830	1.97	203.04			$\upsilon_s CH_2$
2783	32.74	4.40	2825	43.97	1.28	2815		$\upsilon_s CH_2$
1648	41.27	6.90	1632	24.80	12.09	1604		δNH_2
1500	0.97	7.28	1486	0.60	6.06			δCH_2
1492	1.25	7.13	1473	2.88	7.30			δCH_2
1488	10.62	4.27	1467	15.14	3.80	1466		δCH_2
1482	4.06	1.51	1460	1.84	1.11		1463	δCH_2
1478	0.02	34.59	1455	0.03	28.48			δCH_2
1472	2.62	5.70	1448	3.11	17.12		1446	δCH_2
1471	4.88	19.05	1443	0.52	6.33	1445		ωCH_2
1405	10.86	1.11	1398	0.05	5.92			ωCH_2
1402	1.24	4.31	1395	0.13	4.81			ωCH_2
1397	0.02	2.95	1377	11.80	0.34			ωCH_2
1369	3.11	1.47	1348	8.30	2.12	1351		ωCH_2
1347	13.47	1.64	1340	23.73	2.35	1338		ωCH_2
1346	36.94	3.20	1318	44.90	2.98	1321		δNH
1328	20.82	7.33	1310	5.40	13.50	1308		υCN
1321	9.71	19.47	1303	5.19	21.79		1303	υCN

1297	10.89	14.54	1283	9.70	7.86	1275		υCN
1285	8.78	8.66	1267	7.24	5.48	1267		υCN
1247	1.64	1.72	1232	3.12	1.89			τCH_2
1206	0.03	18.65	1185	0.11	19.25	1180	1192	τCH_2
1188	2.15	1.29	1169	2.83	1.78			τCH_2
1162	61.85	10.66	1149	40.49	4.38	1143	1149	τCH_2
1144	40.79	2.05	1124	30.00	1.51	1126		τCH_2
1113	17.49	5.31	1110	6.96	3.30			τCH_2
1097	13.39	6.07	1098	11.94	3.14	1087		τNH_2
1067	0.30	0.03	1059	15.40	5.87	1059	1064	υCN
1053	21.05	12.60	1049	3.87	1.31			υCN
1038	17.80	9.45	1042	10.95	8.55			ρCH_2
1034	11.00	9.29	1033	16.04	5.84	1030	1031	ρCH_2
997	23.00	9.36	995	13.20	4.09	1003		ρCH_2
926	6.27	5.66	933	3.48	5.59	925		ρCH_2
893	2.55	0.22	891	7.81	0.38	891		ρCH_2
853	0.06	1.77	877	0.28	4.48	869		ωNH_2
848	4.24	5.71	847	84.91	1.60			ωNH
770	0.47	1.30	844	53.23	4.10	837		υCC
745	5.47	18.33	783	95.10	1.91		801	υCC
697	85.16	1.25	765	10.24	0.92		764	υCC
597	181.73	1.19	758	7.38	12.71			δRing
583	151.54	8.25	616	2.93	2.47	607		δRing
475	92.53	0.78	496	33.57	0.61	502	490	δRing
467	0.04	2.50	466	0.05	1.94		451	γRing
378	2.19	0.39	393	1.24	0.84			γRing
369	0.50	0.02	360	0.59	0.03			γRing
308	18.18	0.66	330	7.11	1.01			tNH
305	4.80	4.00	309	18.40	2.20			tNH_2
240	0.40	0.04	255	1.06	0.17			tCH_2
210	3.22	0.31	247	32.66	1.60			tCH_2
195	43.71	3.08	219	3.13	0.23			tCH_2
89	2.90	0.44	98	1.61	0.21			tCH_2
82	3.21	0.19	94	3.17	0.44			tCH_2
80	1.38	0.17	78	4.51	0.34			tCH_2

υ-stretching; δ-in-plane deformation; ω-wagging; ρ-rocking; γ-out-of-plane deformation; t-torsion; τ-twisting.

Conclusion

The IR and Raman spectra of 1-(2-aminoethyl)piperazine were recorded and analyzed. The wavenumbers were calculated theoretically using Gaussian03 software package. The observed wavenumbers were found to be in agreement with calculated (B3LYP) values. The predicted infrared intensities and Raman activities are reported.

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