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Vibrational spectroscopic and computational study of 1-methyl-1,4-diazacycloheptane

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Abstract

IR and Raman spectra of 1-methyl-1,4-diazacycloheptane were recorded and analyzed. Using Gaussian03 set of quantum chemistry codes, the vibrational wavenumbers and corresponding vibrational assignments were examined theoretically. 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: DFT calculations, IR, Raman, cycloheptane.

Introduction

Cycloheptane is used as a non-polar solvent for the chemical industry and as an intermediate in the manufacture of chemicals and pharmaceutical drugs. Cycloheptane vapour is irritating to the eyes and may cause respiratory depression if inhaled in large quantity[1]. Heterocycles are of interest because of their interesting pharmacological and biological activities[2-7]. Rehman *et al.*,[8] reported the preparation of a number of diazacyclooctane derivates and the structures of these complexes were elucidated on the basis of various physical techniques. The surface reactions of cyclic hydrocarbons on transition metal surfaces have received considerable attention[9,10].

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[11] 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[12]. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes[13,14].

Results and Discussion

The observed IR and Raman bands with their relative intensities and calculated (scaled) wavenumbers and assignments are given in Table 1. The N-H stretching vibrations generally give rise to bands[15-17] at 3500-3300 cm^{-1}. For the title compound, the band observed at 3362 cm^{-1} in the IR spectrum is assigned as NH stretching mode. The calculated values are 3418 (HF) and 3364 (DFT) cm^{-1}. N-H group show bands[18] at 1510-1500 cm^{-1}, 1235-1165 cm^{-1} and 740-730 cm^{-1}. The C-N stretching modes are reported[19] in the range 1100-1300 cm^{-1}. In the present case the C-N stretching modes are also observed at 1206, 1159, 1118 cm^{-1} in the IR spectrum and at 1191, 1150, 1120, 1115, 1084 cm^{-1} (DFT) theoretically. According to literature if N-H is a part of a closed ring[15,18] 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 1232 cm^{-1} in the IR spectrum and at 1230 cm^{-1} (DFT) theoretically.

In aromatic compounds the asymmetric stretching vibrations of CH_3 are expected in the range 2905-3000 cm^{-1} and symmetric CH_3 vibrations in the range15,20 of 2860-2900 cm^{-1}. The first of these results from the asymmetric stretching $\upsilon_{as}CH_3$ mode in which two C-H bonds of the methyl group are extending while the third one is contracting. The second arises from the symmetrical stretching $\upsilon_{s}CH_3$ in which all three of the C-H bonds extend and contract in phase. The asymmetric stretching modes of the methyl group are calculated (DFT) to be 2990, 2944 cm^{-1} and the symmetric mode at 2894 cm^{-1}. The bands observed at 2940, 2890 cm^{-1} in the IR spectrum and 2943 cm^{-1} in the Raman spectrum are assigned as stretching modes of the methyl group. Two bending can occur within a methyl group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending vibration, involves out-of-phase bending of the C-H bonds. The asymmetrical deformations are expected in the range[15] 1400-1485 cm^{-1}. The calculated values (DFT) of $\delta_{as}CH_3$ modes are at 1488, 1475 cm^{-1}. In many molecules, the symmetric deformations $\delta_{s}CH_3$ appears with an intensity varying from medium to strong and expected in the range15 1380 ± 25 cm^{-1}. The band observed at 1362 cm^{-1} in the

IR spectrum is assigned as the $\delta_s CH_3$ mode. The DFT calculations give $\delta_s CH_3$ mode at 1361 cm^{-1}. Aromatic molecules display a methyl rock in the neighborhood[15] 1045 cm^{-1}. The second rock in the region[15] 970 ± 70 cm^{-1} is more difficult to find among the C-H out-of-plane deformations. In the present case, these ρCH_3 modes are calculated at 1066 and 1035 cm^{-1}. The bands observed at 1071, 1029 cm^{-1} in the IR spectrum and at 1031 cm^{-1} in the Raman spectrum are assigned as rocking modes of the methyl group. The methyl torsions often assigned in the region15 185 ± 65 cm^{-1}.

For bridging methylene groups[18], 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[15, 20]. The stretching bands of the CH_2 groups are observed at 2969, 2843, 2798 cm^{-1} in the IR spectrum and in the range 2967-2793 cm^{-1} theoretically (DFT) for the title compound. According to literature[21] 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 1479-1452 cm^{-1} theoretically. The wagging modes are observed at 1379, 1336 cm^{-1} in the IR spectrum, 1436 cm^{-1} in the Raman spectrum and in the range 1441-1334 cm^{-1} theoretically. The twisting and rocking vibrations of the CH_2 group appear in the region15 of 1200-1280 and 740-900 cm^{-1}, respectively. These modes are also assigned (Table 1). For the title compound the twisting vibrations are observed at 1302, 1260, 1224 cm^{-1} in the IR spectrum, 1211 cm^{-1} in the Raman spectrum and in the range of 1324-1216 cm^{-1} theoretically(DFT). The rocking deformations are assigned in the range of 517-938 cm^{-1} theoretically and the lowering of wavenumber values are due to steric repulsion between the adjacent CH_2 groups. For the title compound, the CC stretching modes are observed in the range of 803-1011 cm^{-1} theoretically (DFT) and at 1014, 955 cm^{-1} in the IR spectrum[21].

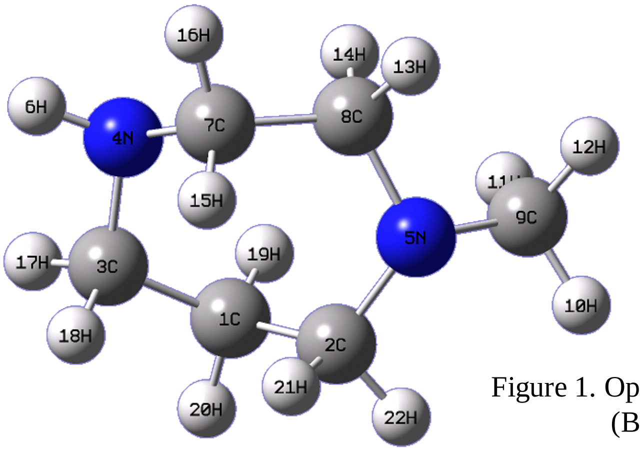

Figure 1. Optimized geometry (B3LYP)

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

HF/6-31G*			B3LYP/6-31G*			IR $\upsilon(cm^{-1})$	Raman $\upsilon(cm^{-1})$	Assign-ment
$\upsilon(cm^{-1})$	I_{IR}	R_A	$\upsilon(cm^{-1})$	I_{IR}	R_A			
3418	1.71	114.01	3364	1.40	139.18	3362		υNH
2917	59.34	100.22	2990	43.86	87.95			$\upsilon_{as}CH_3$
2895	49.74	68.00	2967	40.10	41.85	2969		$\upsilon_{as}CH_2$
2890	37.03	111.45	2965	7.56	189.29			$\upsilon_{as}CH_2$
2886	73.57	72.73	2962	70.01	21.90			$\upsilon_{as}CH_2$
2881	64.16	111.78	2948	61.79	118.05			$\upsilon_{as}CH_2$
2874	68.04	80.95	2944	49.57	91.41	2940	2943	$\upsilon_{as}CH_3$
2845	71.28	161.14	2920	17.51	84.54			$\upsilon_{as}CH_2$
2838	91.45	60.89	2905	59.91	98.71			$\upsilon_{s}CH_2$
2834	17.80	76.05	2894	56.47	91.39	2890		$\upsilon_{s}CH_3$
2805	85.14	14.41	2845	112.05	4.31	2843		$\upsilon_{s}CH_2$
2798	12.38	111.18	2834	10.52	118.03			$\upsilon_{s}CH_2$
2773	83.31	66.96	2815	84.96	60.81			$\upsilon_{s}CH_2$
2748	85.20	78.87	2793	79.70	77.66	2798		$\upsilon_{s}CH_2$
1503	4.63	18.93	1488	4.06	19.90			$\delta_{as}CH_3$
1499	7.28	2.88	1479	4.13	3.71			δCH_2
1494	6.81	6.13	1475	9.33	6.47			$\delta_{as}CH_3$
1491	4.35	5.12	1468	0.70	4.90			δCH_2
1486	5.93	16.46	1463	8.35	10.61	1460	1463	δCH_2
1476	9.40	38.56	1456	13.21	24.14			δCH_2
1474	6.25	6.87	1452	0.33	16.22			δCH_2
1460	4.27	8.64	1441	3.60	6.35		1436	ωCH_2
1450	0.30	13.15	1428	0.87	11.77			ωCH_2
1406	1.00	5.17	1397	0.37	10.31			ωCH_2
1403	14.32	2.73	1375	23.05	1.69	1379		ωCH_2
1376	18.77	5.03	1361	20.00	7.27	1362		$\delta_{s}CH_3$
1363	8.54	2.36	1334	11.27	4.65	1336		ωCH_2
1354	10.21	6.09	1324	14.52	9.41			τCH_2
1329	37.01	5.06	1313	2.23	15.28			τCH_2

1324	3.61	18.05	1306	31.49	6.14	1302		τCH$_2$
1275	12.93	1.56	1256	4.52	2.24	1260		τCH$_2$
1249	21.49	1.93	1230	23.18	1.54	1232		δNH
1236	5.69	9.96	1216	3.06	7.79	1224	1211	τCH$_2$
1212	1.36	7.73	1191	1.23	5.06	1206		υCN
1174	21.95	1.66	1150	18.20	0.94	1159		υCN
1133	42.05	8.52	1120	2.37	7.63	1118		υCN
1131	15.95	8.29	1115	42.68	5.26			υCN
1088	11.15	11.17	1084	16.56	6.88			υCN
1084	12.47	3.71	1066	6.95	2.47	1071		ρCH$_3$
1052	9.40	3.32	1035	6.50	2.16	1029	1031	ρCH$_3$
1014	8.45	14.26	1011	5.75	9.42	1014		υCC
989	0.97	3.55	978	4.08	2.74			υCC
970	8.53	5.01	966	6.03	2.03	955		υCC
942	24.64	2.80	938	14.27	1.98	937		ρCH$_2$
872	4.56	2.41	867	2.04	2.03			ρCH$_2$
821	2.18	0.72	827	2.23	1.13			ρCH$_2$
790	10.76	4.21	803	1.71	2.21			υCC
689	1.43	18.19	741	88.55	3.15		737	ρCH$_2$
615	47.81	2.55	700	1.27	11.57			γNH
506	13.01	1.71	517	26.46	0.75	520		ρCH$_2$
462	64.31	2.56	494	0.85	1.28			δRing
425	15.64	0.64	433	6.01	0.52	438		γRing
386	22.13	1.26	394	4.63	1.02			tCH$_2$
356	12.71	2.00	379	2.93	1.63			tCH$_2$
322	3.64	0.73	325	0.31	0.80			tCH$_2$
277	1.91	0.33	283	1.83	0.50			tCH$_2$
234	3.86	0.12	252	1.06	0.22			tCH$_2$
196	1.36	0.24	233	1.57	0.49			tCH$_3$
140	2.42	0.42	157	0.89	0.58			tRing
48	1.78	0.42	69	1.47	0.41			tRing

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; ω-wagging; t-torsion; I$_{IR}$ - IR intensity; R$_A$-Raman activity.

Conclusion

The IR and Raman spectra of 1-methyl-1,4-diazacycloheptane 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.

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