Vibrational spectroscopic and theoretical study of Barbituric acid

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ABSTRACT

The vibrational frequencies and corresponding vibrational assignments of barbituric acid are examined theoretically using the Gaussian03 set of quantum chemistry codes. Comparison of the observed IR and Raman spectra with the calculated values by density functional theory is found in agreement with the experimental data. Theoretical infrared intensities, Raman activities and first hyperpolarizability values are reported. The calculated geometrical parameters are in agreement with reported values.

Key words: IR, Raman, DFT, pyrimidine, hyperpolarizability.

INTRODUCTION

Barbituric acid (pyrimidine,2,4,6 (1H,3H,5H) -trione) is an important compound with a heterocyclic structure and possibility of existing in several tautomeric forms because of mobility of the hydrogen atoms in its molecules. Some experimental investigations of this compound and its derivatives mainly tuned to its application in medicine and as dye in some branches of chemical industry are reported.[1,2] The pyrimidine compounds are one of the most important classes though the literature.[3-5] The pyrimidine nuclei, along with purine derivatives are highly important constituents of nucleic acids. These are physiologically important essential for the biosynthesis of proteins.[6,7] The crystal structure of barbituric acid dihydrate was reported by several authors.[8-10] Barbituric acid is a simple molecule which has been much studied in recent times due to its propensity to form polymorphs and, as a result, it has been used as a model compound for developing computational polymorph prediction techniques.[11] Phenobarbital and mephobarbital[12] are well known barbituric acid derivatives which are used for the treatment of epilepsy. Substituted heterocyclic/substituted aryl systematic variation at the 5-position of barbituric[13-15] or thiobarbituric[16-18] acids nucleus remarkably increases the antiepileptic activity. In the present work, the IR, Raman and theoretical calculations of the vibrational frequencies of the title compound are reported.

EXPERIMENTAL

The FT-IR spectrum was recorded using a Perkin-Elmer spectrum one FT-IR spectrometer. The spectral resolution was 2 cm^{-1}. Raman spectra were recorded on a Bruker RFS100/s FT instrument (Nd:YAG laser, 1064 nm excitation).

Computational details

Calculations of the title compound were carried out with Gaussian03 software program[19] using the HF/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. At the optimized structure of the examined species, no imaginary wavenumber

modes were obtained, proving that a true minimum on the potential surface was found. 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.[20]

RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers, infrared bands and the corresponding assignments are given in table 1. The vibrations of the CH_2 group, the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch υCH_2, scissoring vibration δCH_2 and wagging vibration ωCH_2 appear in the regions 3000 ± 50, 2965 ± 30, 1445 ± 55 and 1350 ± 85 cm^{-1}, respectively.[21,22] The CH_2 stretching bands are observed at 2987, 2955 cm^{-1} in IR spectrum and at 3000 cm^{-1} in the Raman spectrum. The scissoring and wagging vibrations are observed at 1420, 1382 (IR), 1421, 1379 (Raman) and at 1408, 1384 cm^{-1} theoretically. The twisting mode ρCH_2 is observed at 1260 in IR, 1256 in Raman and 1268 cm^{-1} theoretically as expected.[21] The rocking mode[21] ρCH_2 is expected in the range 895 ± 85 cm^{-1} and the band at 928 (DFT), 935 (IR), 920 cm^{-1} (Raman) is assigned as this mode. The torsional mode of CH_2 is seen the low wavenumber range.[21] The CH_2 modes are reported at 2994, 2961 (stretching) and at 1143, 1168 cm^{-1} (twisting) by Chandra *et al.*[23] The methylene wagging exhibits absorption bands in the range[24-26] 1360 ± 25 cm^{-1} and twisting mode in the range 1290± 40 cm^{-1}.
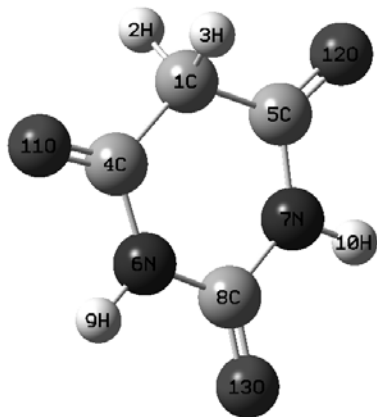
For the title compound the $\upsilon C=O$ stretching modes are observed at 1764, 1727, 1709 (IR), 1737, 1716 (Raman) and at 1784, 1769, 1751 cm^{-1} theoretically. Chandra *et al.*[23] reported reported the $\upsilon C=O$ stretching modes at 1755, 1744, 1712 cm^{-1} in the IR spectrum, 1735, 1713, 1700 cm^{-1} in the Raman spectrum and at 1762, 1723, 1705 cm^{-1} theoretically. The NH ring stretching vibrations[27] generally give rise to bands at 3500-3300 cm^{-1}. The DFT calculations give 3460 and 3458 cm^{-1} as NH stretching vibrations. In cyclic compounds the NH deformation bands are expected in the region[28] 1350 ± 50 cm^{-1} and the out-of-plane NH wag absorbs near 650 cm^{-1}. In the present case NH deformation bands are also identified and assigned. The NH in-plane and out-of-plane deformations[29] are reported at around 1378, 1371, 1320 and 865, 850, 662, 658 cm^{-1}. The deformation bands of C=O group are reported[29] at 767, 754, 650,648, 421, 395 cm^{-1}. According to Roeges[21] the pyrimidine ring stretching vibrations are expected in the region 1250-1590 cm^{-1} and ring breathing mode is in the region 985 ± 10 cm^{-1}. The in-plane ring deformations are expected in the regions 795 ± 75, 380 ± 110 cm^{-1} and out-of-plane deformations in the ranges 630 ± 10, 485 ± 40, 400 ± 15 cm^{-1}. The pyridimine ring vibrations are reported at 1424, 1420 (stretching modes), 753, 764, 721, 694, 695, 686 (out of-plane deformations), 938, 964, 918, 686, 685, 669, 611 cm^{-1} (in-plane deformations)[23]. The ring breathing mode is reported at 628 (IR), 634 (Raman) and at 599 cm^{-1} theoretically[23]. All the pyridimidine ring vibrations are identified and assigned (Table 2). The lowering of the wavenumbers were due to the presence of triones in the title compound. Chandra *et al.*[23] reported C=O bond lengths as 1.217 and C-N bond lengths in the range 1.392-1.401 and CC bond lengths as 1.512 Å. The reported values of the bond angles of the ring are C_4-C_1-C_5 = 118.9, C_1-C_5-N_7 = 116.3, C_5-N_7-C_8 = 125.0, N_7-C_8-N_6 = 118.1, C_8-N_6-C_4 = 125.0, N_6-C_4-C_1 = 116.3[923] and for the title compound the corresponding values are, 118.0, 115.6, 128.1, 114.6, 128.1 and 115.6[9]. The present calculations give the bond angles N_6-C_8-O_{13} = 122.7, N_7-C_8-O_{13} =122.7, C_1-C_4-O_{11} = 123.0, N_6-C_4-O_{11} =121.4, C_1-C_5-O_{12} =123.6 and N_7-C_5-O_{12} =121.4, whereas the reported values are 120.9, 120.9, 118.9, 122.3, 121.3, 122.3[923]. According to Nichol and Clegg[10] the geometrical parameters of the title compound are: bond lengths, N_6-C_4 = 1.3643, N_6-

$C_8 = 1.3810$, N_7-C_8= 1.3728, N_7-C_5 = 1.3670, C_4-C_1= 1.5034, C_5-C_1 = 1.5034Å; the bond angles, O_{11}-C_4-C_1 = 121.6, N_6-C_4-C_1 = 117.6, O_{12}-C_5-C_1= 123.0, N_7-C_5-C_1 = 117.3, C_4-C_1-C_5 = 115.9º and torsion angles, C_8-N_6-C_4-C_1 = -4.7, C_8-N_7-C_5-C_1 = 6.2, O_{11}-C_4-C_1-C_5= -172.5, N_6-C_4-C_1-C_5 = 9.1, N_7-C_5-C_1-C_4 = -9.8º and these values are in agreement with our calculated results. The calculated first

Table 1: Calculated vibrational wavenumbers (scaled), measured infrared and Raman band positions and assignments

HF/6-31G(d)			B3LYP/6-31G(d)			$\upsilon_{(IR)}$	$\upsilon_{(Raman)}$	Assig-
υ cm^{-1}	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	υ cm^{-1}	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	cm^{-1}	cm^{-1}	nments
3434	69.04	91.07	3460	43.18	125.52			υNH
3431	150.98	28.68	3458	97.66	35.59	3400		υNH
2945	0.63	62.36	2998	0.45	68.68	2987	3000	υ_{as}CH$_2$
2907	0.72	2.69	2965	0.92	107.05	2955		υ_sCH$_2$
1827	10.78	34.06	1784	130.31	44.59	1764		υCO
1804	1132.95	1.29	1769	644.19	4.71	1727	1737	υCO
1802	698.56	13.66	1751	474.22	12.25	1709	1716	υCO
1435	106.40	6.08	1408	33.77	11.86	1420	1421	δCH$_2$
1412	287.03	4.69	1384	72.25	3.15	1382	1379	ωCH2
1396	23.86	7.09	1374	301.25	3.70			υRing
1385	56.31	0.01	1352	5.38	0.75	1345		δNH
1328	396.88	0.48	1305	289.89	1.21	1299		δNH
1300	58.21	0.14	1268	9.20	0.79	1260	1256	τCH$_2$
1224	95.23	0.65	1192	100.08	0.40	1202		υRing
1192	0.00	3.45	1177	0.00	3.90	1180	1182	υRing
997	9.60	0.51	983	5.01	1.45			υRing
961	31.53	0.00	928	12.51	0.04	935	920	ρCH$_2$
893	2.37	0.41	886	0.74	0.38			υRing
888	0.29	2.05	881	0.00	1.44			υRing
760	143.48	0.50	719	98.22	0.05	725		δRing
674	0.00	0.06	679	155.79	2.08			ωNH
668	211.99	1.63	666	0.00	0.39	661	657	ωNH
618	1.57	13.09	611	0.87	18.50		614	υRing
604	6.49	0.09	594	7.27	0.12			δCO
578	0.00	6.30	569	0.00	6.57	558		δCO
473	8.93	1.48	469	12.16	2.70		646	δCO
467	46.24	0.95	463	0.81	0.12			δRing
466	1.75	0.04	461	36.78	1.90			δRing
373	26.03	2.79	365	15.26	3.29			γRing
372	45.06	0.79	364	33.04	0.84			γCO
141	1.84	0.01	136	1.37	0.00		128	γCO
113	0.00	0.02	114	0.00	0.00			γCO
43	11.61	0.01	28	10.08	0.00			tCH$_2$

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-twisting; ρ-rocking; ω -wagging; t- torsion; Ring-pyrimidine ring; subscripts: as – asymmetric, s- symmetric.

hyperpolarizability of the title compound is 0.64 × 10^{-30} esu, which is comparable with the reported values of similar derivatives and experimental evaluation of this data is not readily available.

We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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