



Vibrational Assignments, First-Order Hyperpolarizability and Molecular Structure of 5-(2-Chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepine-2-one by Hartree-Fock and Density Functional Theory Calculations

M. PRASATH^{1,2} and S. MUTHU^{3,*}

¹Department of Physics, Aksheyaa College of Engineering, Puludivakkam, Maduranthagam Taluk, Kancheepuram-603 314, India

²Department of Physics, Manonmaniam Sundaranar University, Tirunelveli-627 012, India

³Department of Physics, Sri Venkateshwara College of Engineering, Sriperumbudur-602 105, India

*Corresponding author: E-mail: muthu@svce.ac.in

(Received: 28 September 2012;

Accepted: 31 May 2013)

AJC-13568

Vibrational analysis of the 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one (5C7NB2) compound was carried out by using FT-Raman and FT-IR spectroscopic techniques. The equilibrium geometry, various bonding features and harmonic vibrational frequencies of 5C7NB2 have been investigated by Hartree-Fock (HF) and density functional B3LYP methods with the 6-31G (d,p) basis set. The geometry and normal modes of vibration obtained from the HF and DFT methods are in good agreement with the experimental data. The first order hyperpolarizability (β total) of this novel compound and related properties (β , μ and $\Delta\alpha$) are calculated using HF/6-31G (d,p) and B3LYP/6-31G(d,p) methods based on the finite-field approach.

Key Words: Benzodiazepine, FT-IR, FT-Raman spectra, Vibrational analysis, Hyperpolarizability.

INTRODUCTION

The benzodiazepines, are a class of psychoactive drugs with varying hypnotic, sedative, anxiolytic, anticonvulsant, muscle relaxant and amnesic properties, which are mediated by slowing down the central nervous system¹. Benzodiazepines are molecularly similar to several groups of drugs, some of which share similar pharmacological properties, including the quinazolinones, hydantoines, succinimides, oxazolinediones, barbiturates and glutarimides^{2,3}.

Clonazepam (also known by its brand name klonopin or Rivotril) is a benzodiazepine drug with short to medium duration of action. The molecular formula for lorazepam is $C_{15}H_{10}N_3O_3Cl$ and its molecular mass is 315.7 g/mol. According to the Scottish Intercollegiate Guidelines Network (SIGN), 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one (5C7NB2) may be used for refractory myoclonic seizures⁴. As with many benzodiazepines, 5C7NB2 can have drug interactions and can cause a number of unwanted physical symptoms upon withdrawal such as faintness, dizziness, sweating, tremors, etc.^{5,6}.

Literature survey reveals that to the best of our knowledge, neither the complete Raman and IR spectra nor Gyperpolarizability properties for 5C7NB2 have been reported so far. The goal of the present study is to give a complete

description of the molecular geometry and molecular vibrations of the title compound for the first time. For that purpose quantum chemical computations were performed on 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one using HF and density functional theory (DFT). Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity.

All the calculations were performed using the Gaussian 03 program⁷. Using Chemcraft program⁸ with symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy. The Raman activities were transformed into Raman intensities using RaInt program⁹ by the expression:

$$I_i = 10^{-12} (n_o - n_i)^4 \left(\frac{1}{n_i} \right) S$$

where I_i is the Raman intensity, S is the Raman scattering activities, n_i is the wavenumber of normal modes and n_o denotes the wavenumber of the excitation laser¹⁰. Next, the spectra were analyzed in terms of the P.E.D. contributions by using the VEDA program¹¹.

EXPERIMENTAL

A pure sample of 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one (5C7NB2) was purchased from Sigma Aldrich Chemical Company, USA and used as such for spectral measurements. The Fourier transform infrared (FT-IR) spectrum of this compound was recorded in the region 4000-400 cm^{-1} on a Bruker model IFS 66 V spectrophotometer using the KBr pellet technique. The Fourier Transform Raman (FTR) spectrum of 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one was recorded using Nd-YAG laser in the region 4000-100 cm^{-1} on the same spectrophotometer equipped with FRA 106 FTR module accessory.

RESULTS AND DISCUSSION

Molecular geometry: In order to give detailed assignment of the vibrational spectra and consequently to solve the molecular structure, we applied quantum mechanical calculations in frame of DFT and HF methods. The labeling of atoms in 5C7NB2 in this investigation is shown in Fig. 1. The optimized geometrical parameters have been listed in Table-1. Comparing the HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods, most of the bond lengths and bond angles of HF/6-31(d,p) are slightly shorter due to the neglect of electron correlation. Due to larger atomic radius of chlorine the Cl-C bond possess higher value comparing to other bond length values [1.74, 1.76 and 1.72 Å

TABLE-1
OPTIMIZED GEOMETRICAL PARAMETERS OF 5C7NB2 MOLECULES, BOND LENGTH (Å), INTERFACIAL ANGLES (°)

Parameters	Expt (Ref 12)	HF/ 6- 31G(d,p)	B3LYP/ 6- 31G(d,p)	Parameters	Expt (Ref 12)	HF/ 6- 31G(d,p)	B3LYP/ 6- 31G(d,p)
Bond length				Bond angle			
O ₁ -C ₂	1.20	1.19	1.21	N ₃ -C ₄ -C ₁₂	120	122.5	122.5
C ₂ -N ₃	1.37	1.38	1.40	C ₅ -C ₄ -C ₁₂	120	119.8	119.7
C ₂ -C ₂₂	1.51	1.51	1.52	C ₄ -C ₅ -C ₆	120	121	121.2
N ₃ -C ₄	1.35	1.39	1.40	C ₄ -C ₅ -H ₂₄	120	119.2	118.9
N ₃ -H ₂₃	1.01	0.99	1.02	C ₄ -C ₁₂ -C ₁₁	120	118.6	118.3
C ₄ -C ₅	1.42	1.39	1.41	C ₄ -C ₁₂ -C ₁₃	120	122.1	122.3
C ₄ -C ₁₂	1.42	1.40	1.42	C ₆ -C ₅ -H ₂₄	120	119.8	119.8
C ₅ -C ₆	1.42	1.37	1.38	C ₅ -C ₆ -C ₇	120	118.7	118.6
C ₅ -H ₂₄	1.1	1.08	1.09	C ₅ -C ₆ -H ₂₅	120	121.1	121.7
C ₆ -C ₇	1.42	1.39	1.40	C ₇ -C ₆ -H ₂₅	120	120.2	119.7
C ₆ -H ₂₅	1.1	1.07	1.08	C ₆ -C ₇ -N ₈	120	119.3	119.2
C ₇ -N ₈	1.50	1.45	1.47	C ₆ -C ₇ -C ₁₁	120	121.4	121.5
C ₇ -C ₁₁	1.42	1.38	1.39	N ₈ -C ₇ -C ₁₁	120	119.3	119.3
N ₈ -O ₉	1.32	1.19	1.23	C ₇ -N ₈ -O ₉	119.9	117.4	117.4
N ₈ -O ₁₀	1.13	1.19	1.23	C ₇ -N ₈ -O ₁₀	120	117.8	117.8
C ₁₁ -C ₁₂	1.42	1.39	1.40	C ₇ -C ₁₁ -C ₁₂	120	120.4	120.6
C ₁₁ -H ₂₆	1.10	1.07	1.08	C ₇ -C ₁₁ -H ₂₆	120	119.3	119.1
C ₁₂ -C ₁₃	1.50	1.49	1.49	O ₉ -N ₈ -O ₁₀	119.9	124.8	124.8
C ₁₃ -C ₁₄	1.50	1.50	1.50	C ₁₂ -C ₁₁ -H ₂₆	120	120.2	120.3
C ₁₃ -N ₂₁	1.26	1.25	1.28	C ₁₁ -C ₁₂ -C ₁₃	120	119.2	119.2
C ₁₄ -C ₁₅	1.42	1.39	1.41	C ₁₂ -C ₁₃ -C ₁₄	120	116.8	116.8
C ₁₄ -C ₁₉	1.42	1.39	1.41	C ₁₂ -C ₁₃ -N ₂₁	120	125.9	126.1
C ₁₅ -C ₁₆	1.42	1.38	1.39	C ₁₄ -C ₁₃ -N ₂₁	120	117.3	117.0
C ₁₅ -H ₂₇	1.1	1.08	1.09	C ₁₃ -C ₁₄ -C ₁₅	120	118.9	118.9
C ₁₆ -C ₁₇	1.42	1.39	1.40	C ₁₃ -C ₁₄ -C ₁₉	120	123	123.4
C ₁₆ -H ₂₈	1.1	1.08	1.09	C ₁₃ -N ₂₁ -C ₂₂	108	120.5	119.5
C ₁₇ -C ₁₈	1.42	1.38	1.39	C ₁₅ -C ₁₄ -C ₁₉	120	118.1	117.7
C ₁₇ -H ₂₉	1.1	1.08	1.09	C ₁₄ -C ₁₅ -C ₁₆	120	121.3	121.7
C ₁₈ -C ₁₉	1.42	1.39	1.40	C ₁₄ -C ₁₅ -H ₂₇	120	118.9	118.6
C ₁₈ -H ₃₀	1.1	1.07	1.09	C ₁₄ -C ₁₉ -C ₁₈	120	121.1	121.1
C ₁₉ -Cl ₂₀	1.72	1.74	1.76	C ₁₄ -C ₁₉ -Cl ₂₀	118.8	121.1	121.6
N ₂₁ -C ₂₂	1.47	1.45	1.46	C ₁₆ -C ₁₅ -H ₂₇	120	119.8	119.8
C ₂₂ -H ₃₁	1.11	1.09	1.10	C ₁₅ -C ₁₆ -C ₁₇	120	119.6	119.5
C ₂₂ -H ₃₂	1.11	1.08	1.09	C ₁₅ -C ₁₆ -H ₂₈	120	120	120.0
Bond angle				C ₁₇ -C ₁₆ -H ₂₈	120	120.4	120.5
O ₁ -C ₂ -N ₃	122.6	120.4	120.4	C ₁₆ -C ₁₇ -C ₁₈	120	120	120.0
O ₁ -C ₂ -C ₂₂	122.5	124	124.8	C ₁₆ -C ₁₇ -H ₂₉	120	120.4	120.5
N ₃ -C ₂ -C ₂₂	114	115.6	114.7	C ₁₈ -C ₁₇ -H ₂₉	120	119.6	119.5
C ₂ -N ₃ -C ₄	114	127.9	128.5	C ₁₇ -C ₁₈ -C ₁₉	120	119.8	120.0
C ₂ -N ₃ -H ₂₃	117.4	112.7	112.2	C ₁₇ -C ₁₈ -H ₃₀	120	120.7	120.8
C ₂ -C ₂₂ -N ₂₁	113.9	111.9	112.0	C ₁₉ -C ₁₈ -H ₃₀	120	119.5	119.3
C ₂ -C ₂₂ -H ₃₁	108.8	108.7	108.4	C ₁₈ -C ₁₉ -Cl ₂₀	118.8	117.8	117.3
C ₂ -C ₂₂ -H ₃₂	108.8	107	107.0	N ₂₁ -C ₂₂ -H ₃₁	120	111.4	111.5
C ₄ -N ₃ -H ₂₃	110	116.8	116.8	N ₂₁ -C ₂₂ -H ₃₂	107.5	108.9	109.1
N ₃ -C ₄ -C ₅	120	117.6	117.7	H ₃₁ -C ₂₂ -H ₃₂	109.4	108.7	108.7

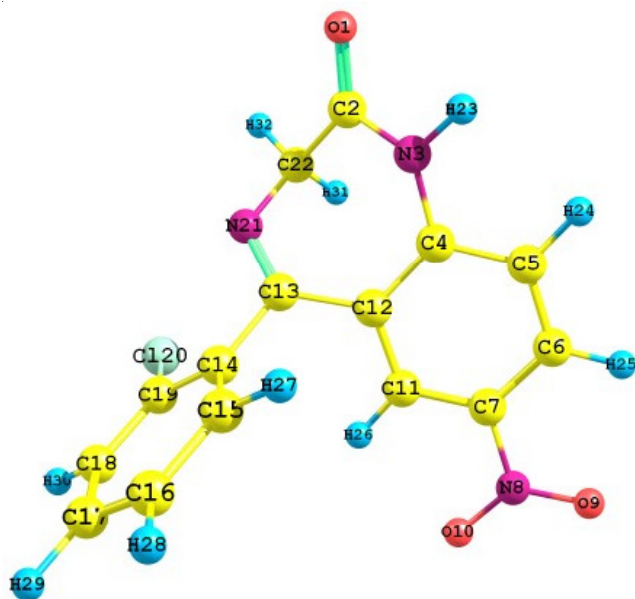


Fig. 1. Atom numbering system adopted in this study for 5C7NB2

by HF/6-31G(d,p), B3LYP/6-31G(d,p) and experimental], respectively. When comparing bond angles of experimental¹² to that of theoretical (*i.e.*, both DFT and HF) the values correlate well with the experimental result of the molecules in solid phase. This deviation can be attributed to the fact that the theoretical calculations were aimed at the isolated molecules in the gaseous phase and the experimental results were aimed at the molecule in the solid state. Despite these differences, the calculated geometrical parameters represent a good approximation and they are the basis for the calculation of other parameters such as polarizability, vibrational frequencies and thermodynamic properties.

Vibrational assignments: The vibrational frequency and approximate description of each normal modes obtained using HF and DFT/B3LYP methods with 6-31G(d,p) basis set are given for 5C7NB2 in Table-2. The detailed vibrational assignment of the experimental wavenumbers is based on normal mode analyses and a comparison with theoretically scaled wavenumbers with PED by B3LYP and HF methods. The observed and computed infrared and Raman spectra of 5C7NB2 are shown in Figs. 2 and 3, respectively. Comparison of the frequencies calculated at HF and B3LYP with the experimental values (Table-2) reveals the over estimation of the calculated vibrational modes due to neglect of anharmonicity in real system. According to the theoretical calculations, 5C7NB2 has a planar structure of C_s point group symmetry. The molecule has 32 atoms and 90 normal modes of fundamental vibrations. A brief analysis is given for the substituent in the present work.

C=O stretching vibrations: This band is reasonably easy to be recognized due to its high intensity¹³. The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiple bonded group is highly polar and therefore gives rise to an intense infrared absorption band. Carbonyl group vibrations gives rise to characteristic bands in vibrational spectra and for this reason, such bands have been subject of extensive studies^{14,15}. The FT-IR and FT Raman band (mode No: 80) appeared at 1725 and 1755 cm^{-1} ,

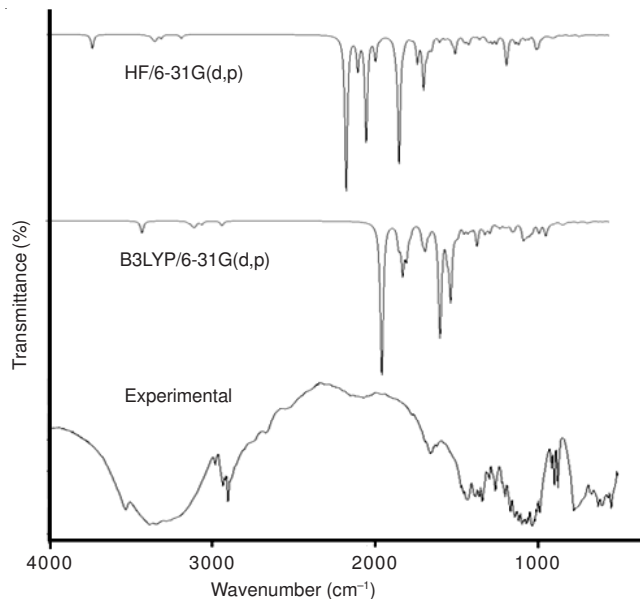


Fig. 2. Experimental and calculated FTIR spectrum of 5C7NB2

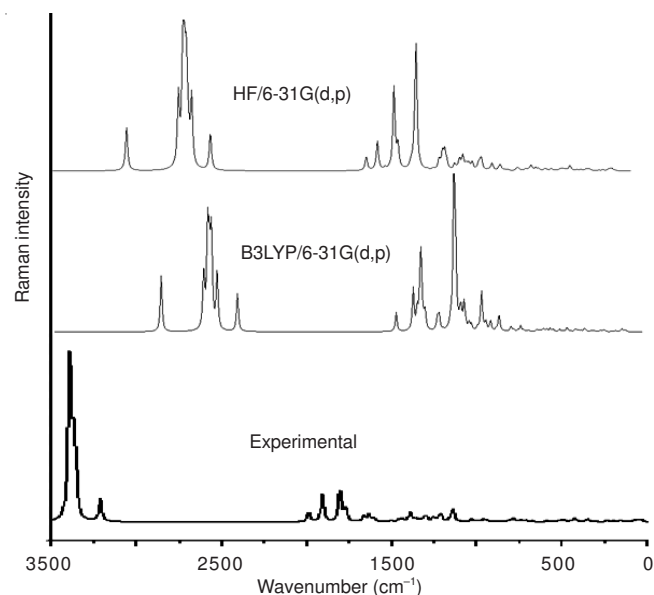


Fig. 3. Experimental and calculated FT-Raman spectrum of 5C7NB2

respectively have been designated to C=O stretching and is in excellent agreement with theoretically predicted frequency obtained in both HF and B3LYP/6-31G(d,p) basis set with PED contribution of 85 %.

C=N, C-N vibrations: The designation of C=N and C-N vibrations is a difficult task, since mixing of several other bands are possible in this region. Silverstein *et al.*¹⁶ assigned C-N stretching absorption in the region 1382-1266 cm^{-1} for aromatic amines. Kahovec and Kohlreusch¹⁷ identified the stretching frequency of the C=N band in salicylic aldoxime at 1617 cm^{-1} . In the present study, the bands observed at 1018 and 1277 cm^{-1} in FT-Raman spectrum have been assigned to C=N and C-N stretching vibrations, respectively. The corresponding bands in FTIR spectrum for the above C=N and C-N vibrations are 1004 and 1298 cm^{-1} , respectively. The theoretically calculated values of C=N and C-N stretching vibrations (mode No: 50 and 63) are presented at 1005 and 1269 cm^{-1} by B3LYP/6-

TABLE-2
CALCULATED SCALED IR WAVENUMBERS AND RELATIVE INTENSITIES
FOR 5C7NB2 USING HF/6-31G (d,p) AND B3LYP/6-31G(d,p)

Species	Observed wavenumbers (cm ⁻¹)		Computed wavenumbers (cm ⁻¹)								Vibrational assignments (PED, %)
	FTIR	FT-Raman	HF/6-31G(d,p)				B3LYP/6-31G(d,p)				
			Unscaled frequency	Scaled frequency	IR intensity	Raman intensity	Unscaled frequency	Scaled frequency	IR intensity	Raman intensity	
W(90)	3440	3425	3837	3469	9	36	3572	3432	7	38	NH stretching (100)
W(89)	–	–	3442	3112	0	12	3256	3129	0	29	CH stretching (98)
W(88)	–	–	3441	3110	0	44	3254	3127	0	11	CH stretching (99)
W(87)	–	–	3407	3080	1	83	3228	3102	1	62	CH stretching (96)
W(86)	–	–	3394	3068	3	61	3216	3091	3	44	CH stretching (76)
W(85)	–	–	3381	3056	1	40	3202	3077	2	26	CH stretching (92)
W(84)	–	–	3378	3054	2	35	3198	3073	1	31	CH stretching (98)
W(83)	–	–	3366	3043	0	17	3193	3069	0	11	CH stretching (98)
W(82)	–	–	3340	3019	2	55	3154	3031	2	39	CH stretching (97)
W(81)	–	–	3198	2891	3	30	3006	2889	3	26	CH ₂ stretching (97)
W(80)	1725	1755	2011	1818	100	12	1826	1755	100	12	C=O stretching (85)
W(79)	1659	1625	1927	1742	21	24	1700	1633	13	27	CC stretching (77)
W(78)	–	1601	1866	1687	68	2	1670	1605	29	12	NO ₂ stretching (45) (9645)
W(77)	–	–	1802	1629	6	28	1650	1585	3	23	NO stretching (49)
W(76)	1471	–	1799	1627	9	39	1641	1577	18	42	ON stretching (50)
W(75)	1456	–	1770	1600	1	15	1623	1560	1	3	CC stretching (54)
W(74)	–	1536	1768	1598	1	5	1612	1549	5	12	ON stretching (56)
W(73)	–	–	1670	1509	1	5	1527	1468	6	1	δ HCC (50)
W(72)	–	–	1655	1496	4	2	1520	1460	3	3	δ HCC (42)
W(71)	–	–	1650	1491	0	1	1518	1458	3	5	δ HCH (79)
W(70)	1436	–	1646	1488	1	6	1508	1449	12	10	δ HNC (54)
W(69)	–	–	1631	1474	81	100	1477	1420	4	0	CC stretching (47)
W(68)	1360	1378	1602	1448	3	0	1424	1368	0	5	δ HNC (53)
W(67)	1341	–	1545	1397	1	1	1395	1341	60	100	ON stretching (82)
W(66)	–	–	1500	1356	16	1	1385	1331	15	48	CC stretching (55)
W(65)	1297	–	1456	1316	32	8	1350	1297	2	8	t HCNC (75)
W(64)	–	–	1430	1293	8	14	1343	1290	15	9	CC stretching (43)
W(63)	1298	1277	1413	1277	4	14	1321	1269	44	18	CN stretching (41)
W(62)	1261	–	1401	1266	3	4	1309	1258	3	3	CH stretching (14)
W(61)	–	–	1396	1262	4	2	1295	1245	0	0	δ HCC (44)
W(60)	–	1230	1339	1211	4	4	1285	1235	3	5	δ HCC (46)
W(59)	1203	–	1323	1196	0	1	1266	1217	7	4	δ HNC (49)
W(58)	1168	1182	1301	1176	2	9	1223	1175	6	2	δ HCN (55)
W(57)	–	–	1275	1153	1	12	1198	1151	0	2	δ HCC (65)
W(56)	1143	–	1251	1131	2	3	1191	1144	5	25	δ HCN (10)
W(55)	–	–	1248	1128	2	2	1170	1125	1	1	δ HCC (68)
W(54)	1116	–	1230	1112	11	5	1158	1113	2	6	δ HCC (43)
W(53)	1095	–	1203	1087	0	6	1123	1079	14	7	δ CCC (40)
W(52)	1058	–	1169	1057	2	1	1083	1040	1	1	δ CCC (38)
W(51)	1019	–	1154	1043	3	6	1063	1022	6	11	δ CCC (46)
W(50)	1004	1018	1138	1029	3	9	1045	1005	2	0	C=N stretching (50)
W(49)	988	–	1127	1019	4	2	1027	987	6	0	δ CNC (48)
W(48)	–	–	1125	1017	0	0	991	952	0	0	t CCCC (77)
W(47)	–	–	1117	1009	0	0	981	943	0	0	t HCCN (89)
W(46)	–	–	1085	981	0	0	974	936	2	3	δ CNC (12)
W(45)	–	–	1083	979	1	1	956	919	1	0	t CCCC (60)
W(44)	915	–	1052	951	3	6	952	914	3	1	t HCCC (69)
W(43)	899	–	1003	906	1	1	922	886	2	1	δ NCC (10)
W(42)	876	–	996	900	2	3	901	866	2	4	δ ONO (11)
W(41)	–	–	985	890	3	2	882	848	0	1	t HCCC (75)
W(40)	–	–	958	866	4	1	864	830	4	0	t HCCN (20)
W(39)	–	–	933	844	5	1	843	810	4	1	t HCCN (49)
W(38)	778	790	863	781	6	1	783	753	2	1	γ NCCC (37)
W(37)	–	–	859	777	7	2	779	749	7	1	δ ONO (27)
W(36)	–	–	857	775	7	0	767	737	4	0	δ CH (33)
W(35)	–	–	846	765	1	0	754	725	5	1	γ NCCC (82)

W(34)	–	–	821	743	1	0	740	711	1	1	t CCCC (36)
W(33)	–	–	796	719	4	1	732	703	5	1	δ CCC (12)
W(32)	672	–	770	696	5	1	711	683	5	2	δ CCC (30)
W(31)	–	–	754	681	0	4	686	659	0	2	γ NCCC (10)
W(30)	–	–	723	654	3	2	665	639	3	1	t CCCC (10)
W(29)	632	–	702	634	2	2	657	632	4	1	δ CCC (42)
W(28)	–	–	649	587	7	2	613	589	9	2	t HNCC (41)
W(27)	551	–	632	571	6	1	587	564	1	1	δCH ₂ +CCH (35)
W(26)	–	–	604	546	1	1	557	535	1	2	δ CNC (15)
W(25)	–	–	594	537	0	0	550	528	0	1	δ ONC (28)
W(24)	503	–	574	519	0	0	527	507	0	0	γ NCCC (37)
W(23)	–	–	543	491	1	1	501	482	1	1	δ ONC (34)
W(22)	–	–	530	479	1	1	487	468	1	1	γ CCCCC (12)
W(21)	–	–	511	462	1	1	471	452	1	1	γ CCCCC (30)
W(20)	–	–	490	443	0	1	453	435	0	1	δ NCC (20)
W(19)	–	–	463	419	0	4	428	411	0	2	δ NH (35)
W(18)	–	–	453	409	0	1	417	401	0	1	C=N bending (39)
W(17)	–	–	408	369	1	1	377	363	1	1	γ NH (38)
W(16)	–	–	379	343	0	1	356	342	0	1	δ CICC (41)
W(15)	–	–	340	308	1	1	313	300	0	1	CN bending (11)
W(14)	–	–	334	302	1	0	308	296	1	0	γ NCCC (13)
W(13)	–	–	317	287	0	1	289	278	0	1	δ NO ₂ (19)
W(12)	–	–	305	276	0	1	281	270	0	1	γ CCCCC (36)
W(11)	–	–	239	216	0	1	224	215	0	0	δ CCC (13)
W(10)	–	–	210	190	0	1	195	188	0	1	γ CCCCC (42)
W(9)	–	–	166	150	0	1	157	151	0	1	δ CICC (47)
W(8)	–	–	155	140	0	1	145	140	0	1	t CCCC (25)
W(7)	–	–	137	124	0	2	127	122	0	1	t CCCC (25)
W(6)	–	–	118	107	0	0	112	108	0	0	t CNCC (24)
W(5)	–	–	71	64	0	1	72	69	0	1	t CCCC (56)
W(4)	–	–	69	62	1	1	65	63	1	1	γ CCCC (48)
W(3)	–	–	50	45	0	2	50	48	0	2	t CCCC (75)
W(2)	–	–	43	39	0	2	42	40	0	2	γ CCCC (48)
W(1)	–	–	19	17	0	3	22	22	0	2	t CCCC (88)

γ: Out-of-plane bending; δ: in plane bending; ω: wagging; t: torsion.

31G(d,p) method which coincides well with the experimentally recorded spectrum. These assignments are also supported by PED values.

NH Vibrations: Tsuboi¹⁸ reported the N-H stretching frequency at 3481 cm⁻¹ in aniline. In line with his observation (N-H) stretching is assigned to the band at 3425 cm⁻¹ in the present work. The theoretically calculated value by B3LYP/6-31G(d,p) at 3432 cm⁻¹ (mode No. 90) shows excellent agreement with experimentally observed FT-IR value at 3440 cm⁻¹ with a large contribution of 100 % PED. The N-H in-plane bending and N-H out-of-plane bending are assigned to the bands at 411 and 363 cm⁻¹ which agrees well with Venkateswaran and Pandya¹⁹ and Evans²⁰.

Non-linear optical effects: Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields²¹. Non-linear optical property is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections²²⁻²⁵.

The second-order polarizability or first hyperpolarizability β, dipole moment μ and polarizability α of the title compound

are calculated using HF and B3LYP 6-31G(d,p) basis set on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment μ, the mean polarizability α₀, the anisotropy of the polarizability Δα and the mean first polarizability β₀, using the x, y, z components from Gaussian 03W output is as follows

$$\mu_{\text{tot}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 6\alpha_{xx}^2]^{1/2}$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yzz}$$

The calculated hyperpolarizability values of 5C7NB2 are given in Table-3. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems and frequently used as a threshold value for comparative purposes. The computed first hyperpolarizability, β_{tot} of 5C7NB2 molecule are 42.62 × 10⁻³¹ cm⁵/esu and 128.1 × 10⁻³¹ cm⁵/esu in HF and B3LYP methods, respectively which is very higher than that of urea (β of urea is 3.7289 × 10⁻³¹ cm⁵/esu). Total

TABLE-3
 AB INITIO HF AND B3LYP/6-31G (d,p) CALCULATED μ , α AND β FOR 5C7NB2

Parameters	HF	B3LYP	Parameters	HF	B3LYP
μ_x	-0.0042	0.0397	β_{xxx}	73.11	587.75
μ_y	-0.4665	-0.0367	β_{xxy}	-116.02	-397.14
μ_z	4.9652	4.618	β_{xyy}	275.56	385.96
μ (D)	4.9871	4.6183	β_{yyy}	-164.51	-624.78
α_{xx}	231.1	258.06	β_{xxz}	-127.06	-168.81
α_{xy}	-11.4	-11.88	β_{xyx}	83.98	137.5
α_{yy}	214.68	236.61	β_{yyz}	-16.03	-44.15
α_{xz}	22.21	21.12	β_{zzx}	59.03	101.83
α_{yz}	-7.54	-7.59	β_{yzz}	23.7	13.32
α_{zz}	116.45	120.63	β_{zzz}	37.08	61.33
α (a.u)	187.41	205.1	β_{tot} (esu)	42.62×10^{-31}	128.1×10^{-31}
$\Delta\alpha$ (a.u)	414.431	464.956	–	–	–

dipole moment of title molecule is approximately 10 times greater than those of urea. Thus, the above results indicate that 5C7NB2 is one of the best material for non-linear optical property applications.

Conclusion

The optimized molecular geometry, hyperpolarizability, harmonic vibrational wave numbers and intensities of vibrational bands of 5-(2-chlorophenyl)-7-nitro-2,3-dihydro-1,4-benzodiazepin-2-one (5C7NB2) were calculated at DFT levels invoking two different methods HF and B3LYP/6-31G(d,p) basis set using Gaussian 03W program. A complete assignment of the fundamentals was proposed on the basis of the PED calculations. Furthermore, non-linear optical, first-order hyperpolarizabilities and total dipole moment properties of the compound have been calculated in order to get an insight into the compound. We hope that the results are of assistance in the quest for experimental and theoretical evidence for the title molecule is reaction intermediates and for non-linear optical and photo-elastic materials.

REFERENCES

- R.M. McKernan, T.W. Rosahl, D.S. Reynolds, C. Sur, K.A. Wafford, J.R. Attack, S. Farrar, J. Myers, G. Cook, P. Ferris, L. Garrett, L. Bristow, G. Marshall, A. Macaulay, N. Brown, O. Howell, K.W. Moore, R.W. Carling, L.J. Street, J.L. Castro, C.I. Ragan, G.R. Dawson and P.J. Whiting, *Nature Neurosci.*, **3**, 587 (2006).
- P. Danneberg and K.H. Weber, *Br. J. Clin. Pharmacol.*, **16**, 231 (1983).
- J.V. Earley, R.I. Fryer and R.Y. Ning, *J. Pharm. Sci.*, **68**, 845 (1979).
- Diagnosis and Management of Epilepsy in Adults, A National Clinical Guideline, Scottish Intercollegiate Guidelines Network 70. April 2003.
- Drugs.com Klonopin. www.drugs.com/ pdr/klonopin.html. Accessed 1/4/2010.
- D.S. Charney, S.J. Mihic and R.A. Harris, In eds.: L.L. Brunton, J.S. Lazo and K.L. Parker, *Hypnotics and Sedatives*, Goodman and Gilman's The Pharmacological Basis of Therapeutics, McGraw Hill, New York, edn. 11, Ch. 16, p. 412 (2006).
- Gaussian 03 Program, Gaussian Inc., Wallingford CT (2004).
- G.A. Zhurko and D.A. Zhurko, Chemcraft Program, Academic Version 1.5 (2004).
- D. Michalska, RAIN Program, Wroclaw University of Technology, Poland (2003).
- D. Michalska and R. Wysokinski, *Chem. Phys. Lett.*, **403**, 211 (2005).
- M.H. Jamroz, Vibrational Energy Distribution Analysis, VEDA 4 Program, Warsaw (2004).
- P. Chananont, T.A. Hamor and I.L. Martin, *Acta Cryst.*, **B37**, 1371 (1981).
- R. Meenakshi, J. Lakshmi, S. Gunasekaran and S. Srinivasan, *J. Mol. Simul.*, **36**, 425 (2010).
- G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, New York (1980).
- N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York (1990).
- M. Silverstein, G.C. Basseler and C. Morill, *Spectrometric Identification of Organic Compounds*, Wiley, New York (1981).
- L. Kahovec and K.W.F. Kohlreusch, *Monatsh. Chem.*, **74**, 333 (1941).
- M. Tsuboi, *Spectrochim. Acta*, **16**, 505 (1960).
- C.S. Venkateswaran and N.S. Pandya, *Proc. Indian Acad. Sci.*, **A15**, 390 (1942).
- J.C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).
- Y.X. Sun, Q.L. Hao, W.X. Wei, Z.X. Yu, L.D. Lu, X. Wang and Y.S. Wang, *J. Mol. Struct. (Theochem.)*, **904**, 74 (2009).
- C. Andraud, T. Brotin, C. Garcia, F. Pelle, P. Goldner, B. Bigot and A. Collet, *J. Am. Chem. Soc.*, **116**, 2094 (1994).
- V.M. Geskin, C. Lambert and J.L. Bredas, *J. Am. Chem. Soc.*, **125**, 15651 (2003).
- M. Nakano, H. Fujita, M. Takahata and K. Yamaguchi, *J. Am. Chem. Soc.*, **124**, 9648 (2002).
- D. Sajan, I.H. Joe, V.S. Jayakumar and J. Zaleski, *J. Mol. Struct.*, **785**, 43 (2006).