



FT-IR and Computational Study of 4-[(2Z)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]amino}Benzoic Acid

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ABSTRACT

Fourier transform infrared spectrum of 4-[(2Z)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]amino}benzoic acid was recorded and analyzed. The vibrational wavenumbers were examined theoretically using the Gaussian03 set of quantum chemistry codes. The calculated first hyperpolarizability is reported and the title compound is an attractive object for future studies of nonlinear optics. Optimized geometrical parameters of the title compound are in agreement with that of similar reported structures. Predicted infrared intensities are also reported.

Key words: FTIR, DFT calculations, benzoic acid, cyclohexane.

INTRODUCTION

Camphor is a white transparent waxy crystalline solid with a strong penetrating pungent aromatic odour and it is a terpenoid and its uses include as a plasticizer for cellulose nitrate, as a moth repellent, as an antimicrobial substance, in embalming and in fire works¹. Schwerdtfeger *et al.*² reported the vibrational spectrum of camphor from ab initio and density functional theory. A recent patent reported that benzoic acid derivatives have

good anti tumor properties, their activity being related to novel synergistic compositions that selectively control tumor tissue³. Beevi *et al.*^{4,5} reported the synthesis, characterization, antimicrobial activity and physico-chemical studies of Schiff base complexes of camphor and para aminobenzoic acids. In this work, by using HF and B3LYP methods we calculated the vibrational wavenumbers of the title compound in the ground state to distinguish the fundamentals from the many experimental vibrational wavenumbers and

geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

EXPERIMENTAL

All the chemicals were procured from Merck, India. Equimolar solutions of camphor in ethanol and para-aminobenzoic acid in ethanol are mixed together and refluxed for six hours. The resulting solution is evaporated. The FT-IR spectrum was recorded using KBr pellets on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets. The spectral resolution was 2 cm^{-1} .

Computational details

Calculations of the title compound were carried out with Gaussian03 program⁶ using the HF/6-31G (d) and B3LYP/6-31G (d) basis sets to predict the molecular structure and vibrational wave numbers. The wave number values computed contain known systematic errors and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets⁷. The absence of imaginary values of wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{8,9}.

RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers and observed wavenumbers and assignments are given in Table 1. In the vibrations of the CH_2 group, the asymmetric stretching $\nu_{\text{as}}\text{CH}_2$, symmetric stretching $\nu_{\text{s}}\text{CH}_2$, scissoring vibration δCH_2 appear in the regions 2940 ± 20 , 2885 ± 45 , 1440 ± 10 cm^{-1} respectively^{10,11}. The DFT calculations give $\nu_{\text{as}}\text{CH}_2$ at 2997, 2988, 2978 cm^{-1} and $\nu_{\text{s}}\text{CH}_2$ at 2957, 2954, 2948 cm^{-1} . The scissoring modes δCH_2 are assigned at 1462, 1455, 1444 cm^{-1} theoretically. Absorption of hydrocarbons due to CH_2 twisting and wagging vibration is observed in the region 1350-1150 cm^{-1} . These bands are generally appreciably weaker than those resulting from CH_2 scissoring vibrations. These modes are assigned at 1270, 1247, 1211 cm^{-1} in IR, and at 1267, 1247, 1232, 1208, 1189, 1175 cm^{-1}

¹ theoretically. The band calculated at 826, 808, 802 cm^{-1} were assigned to the rocking modes¹¹ of CH_2 .

In esters the vibrations of CH_3 are expected in the range^{11,12} 2900-3000 cm^{-1} . The first of these result from asymmetric stretching $\nu_{\text{as}}\text{CH}_3$ modes in which two C-H bonds of the methyl group are extending while the third one is contracting and the other result from symmetric stretching $\nu_{\text{s}}\text{CH}_3$ in which all three of the C-H bonds extend and contract in-phase. The asymmetric stretching modes of methyl group are calculated to be at 3022, 3019, 3010, 2999, 2991, 2984 cm^{-1} and the symmetric mode at 2939, 2936, 2931 cm^{-1} . The bands at 3015, 2903 cm^{-1} in the IR spectrum of the title compound are assigned as CH_3 stretching vibrations. Two bending can occur within a methyl group. The first of these, the symmetrical bending vibration, involves out-of-phase bending of the C-H bonds. The asymmetric deformations are expected in the range¹¹ 1400-1485 cm^{-1} . The calculated values of $\delta_{\text{as}}\text{CH}_3$ modes are at 1498, 1486, 1482, 1476, 1467, 1463 cm^{-1} . Experimentally the bands are observed a 1504 cm^{-1} in IR spectrum. In many molecules the symmetric deformation $\delta_{\text{s}}\text{CH}_3$ appears with an intensity varying from medium to strong and expected in the range¹¹ of 1380 ± 25 cm^{-1} . Bands at 1398 cm^{-1} in the IR spectrum and at 1400, 1387, 1378 cm^{-1} (DFT) were assigned as $\delta_{\text{s}}\text{CH}_3$ modes for the title compound. Esters display a methyl rock¹¹ in the neighborhood of 1045 cm^{-1} . The second rock¹¹ in the region 970 ± 70 cm^{-1} is more difficult to find among the C-H out-of-plane deformations. For the title compound, these modes ρCH_3 are calculated at 1113, 1089, 1035, 1002, 974, 933 cm^{-1} . The bands at 1111, 1021, 1000, 964 cm^{-1} in the IR spectrum are assigned as ρCH_3 modes.

The $-\text{C}(=\text{O})\text{OH}$ group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation as well as the C-O stretch and the OH in-plane deformation. In the present case the DFT calculations give the OH stretch at 3468 cm^{-1} . The C=O stretching vibration gives rise to characteristic bands in the IR and Raman spectra and the intensity of these bands can increase due to conjugation or the formation of hydrogen bonds¹³. C=O stretching vibration¹¹ gives rise to a strong band in the region 1725 ± 65 cm^{-1} . Rippon *et al.*¹⁴ reported a value of 1647 cm^{-1} for the carbonyl stretching

Table 1: Calculated (Scaled) wavenumbers, observed IR bands and assignments

HF/6-31G*		B3LYP/6-31G*		IR $\nu_{(\text{cm}^{-1})}$	Assignments
$\nu_{(\text{cm}^{-1})}$	IR intensity	$\nu_{(\text{cm}^{-1})}$	IR intensity		
3623	65.90	3597	17.92		νOH
3040	2.01	3101	2.15		νCH
3029	8.39	3085	8.44	3087	νCH
3020	6.52	3078	6.91		νCH
2996	17.13	3046	21.22	3040	νCH
2948	32.72	3022	28.79		$\nu_{\text{as}}\text{Me}$
2935	20.30	3019	10.11		$\nu_{\text{as}}\text{Me}$
2935	21.10	3010	30.54	3015	$\nu_{\text{as}}\text{Me}$
2926	96.68	2999	53.92		$\nu_{\text{as}}\text{Me}$
2920	32.50	2997	32.66		$\nu_{\text{as}}\text{CH}_2$
2918	5.50	2991	56.16		$\nu_{\text{as}}\text{Me}$
2915	75.15	2988	9.54		$\nu_{\text{as}}\text{CH}_2$
2908	44.26	2984	1.02		$\nu_{\text{as}}\text{Me}$
2904	1.31	2981	23.42		νCH
2899	0.83	2978	25.40		$\nu_{\text{as}}\text{CH}_2$
2887	7.30	2957	29.19		$\nu_{\text{s}}\text{CH}_2$
2883	39.57	2954	12.00		$\nu_{\text{s}}\text{CH}_2$
2872	31.26	2948	24.20		$\nu_{\text{s}}\text{CH}_2$
2861	29.60	2939	31.66		$\nu_{\text{s}}\text{Me}$
2855	39.83	2936	18.64		$\nu_{\text{s}}\text{Me}$
2849	14.95	2931	11.49	2903	$\nu_{\text{s}}\text{Me}$
1747	409.27	1772	311.13		$\nu\text{C=O}$
1717	556.30	1719	413.63	1705	$\nu\text{C=N}$
1612	294.58	1594	262.48	1610	νPh
1562	21.01	1542	10.87	1576	νPh
1508	27.05	1498	4.31	1504	$\delta_{\text{as}}\text{Me}$
1507	22.78	1487	12.47		νPh
1498	7.88	1486	6.29		$\delta_{\text{as}}\text{Me}$
1492	0.38	1482	0.73		$\delta_{\text{as}}\text{Me}$
1489	4.40	1476	4.21		$\delta_{\text{as}}\text{Me}$
1481	4.26	1467	1.94		$\delta_{\text{as}}\text{Me}$
1478	11.03	1463	5.55		$\delta_{\text{as}}\text{Me}$
1476	9.66	1462	10.74		δCH_2
1469	2.54	1455	1.96		δCH_2
1462	7.05	1444	5.48	1427	δCH_2
1424	14.23	1403	16.32		νPh
1414	5.45	1400	7.72	1398	$\delta_{\text{s}}\text{Me}$
1409	20.89	1387	3.19		$\delta_{\text{s}}\text{Me}$
1404	6.46	1378	3.48		$\delta_{\text{s}}\text{Me}$
1330	3.02	1305	5.73	1318	νPh
1324	6.05	1299	155.92		δOH
1323	12.66	1297	137.74		νCC
1317	3.72	1292	0.75		δCH
1287	1.55	1280	56.00		δCH

1269	214.71	1279	365.88		ν CO
1263	262.43	1267	5.44	1270	ω CH ₂
1250	16.78	1247	54.10	1247	ω CH ₂
1232	9.43	1232	3.44		ω CH ₂
1221	87.26	1216	26.62		ν CN
1210	22.71	1208	12.50	1211	ν CH ₂
1206	13.95	1189	5.31		τ CH ₂
1199	7.61	1178	22.40	1179	ν CC
1182	110.72	1175	8.25		τ CH ₂
1163	39.85	1162	80.77		δ CH
1162	19.78	1149	15.98		ν CC
1144	176.35	1133	2.00		ν CC
1133	8.61	1113	3.26	1111	ρ Me
1116	2.57	1102	2.66		δ CH
1110	3.77	1089	5.32		ρ Me
1101	4.77	1076	10.37	1082	ν CC
1060	44.82	1061	45.78		ν CC
1055	18.51	1035	42.53	1021	ρ Me
1039	0.35	1009	15.29		ν CC
1029	22.31	1002	3.73	1000	ρ Me
1020	4.16	988	5.07		δ CH
1017	0.37	974	1.08	964	ρ Me
1009	4.55	943	1.11		γ CH
984	2.03	933	2.36		ρ Me
948	1.53	929	1.16		ν CC
938	0.87	918	0.56		γ CH
935	3.79	915	2.08		γ OH
921	3.67	914	0.44		ν CC
902	4.51	895	0.42		ν CC
890	47.24	853	4.46	861	ν CC
868	1.72	842	6.54	853	γ CH
853	5.26	829	21.82		γ CH
842	0.46	826	5.53		ρ CH ₂
827	6.99	808	4.16	812	ρ CH ₂
804	5.86	802	6.44		ρ CH ₂
777	37.44	744	11.35	756	Ring breath
745	8.78	737	8.76	741	δ C=O
734	4.98	719	8.91		γ CH
697	57.30	684	34.54	681	γ Ph
685	4.61	671	2.09		δ Ring
652	0.80	635	0.46	634	δ Ph(X)
637	1.66	627	7.32		δ Ring
628	17.40	615	5.61	604	γ Ring
587	6.15	583	11.63		δ Ph
574	2.73	563	4.32		γ C=O
555	2.59	547	1.89		ρ C(=O)O
523	7.77	512	7.22	526	γ Ph(X)
494	6.42	489	39.45		δ Ring
474	4.29	475	53.92	478	γ Ring

447	12.87	465	0.86		δ Ring
437	29.96	438	13.59		γ Ring
423	1.19	425	3.78	418	δ Ring
406	62.85	404	0.56		γ Ph
396	81.47	398	1.08		γ Ring
389	15.59	381	2.75		δ Ph(X)
380	5.04	379	2.09		δ Ring
334	1.79	329	2.98		γ Ring
289	0.33	286	0.37		γ Ring
276	3.18	273	0.53		δ CX(X)
273	0.96	269	0.98		γ CX(X)
254	3.81	248	1.85		δ CX(X)
243	0.32	241	0.21		γ CX(X)
229	0.25	232	0.14		τ Me
212	7.27	213	2.66		τ Me
202	13.49	200	9.98		τ Me
193	0.25	192	0.29		tCH ₂
156	0.33	160	0.36		tCH ₂
117	4.92	114	2.43		tCH ₂
97	0.53	91	0.68		tPh
72	5.03	72	3.10		tRing
39	2.09	41	2.21		tRing
38	2.48	36	1.782		tRing
31	2.13	27	1.30		tCOOH

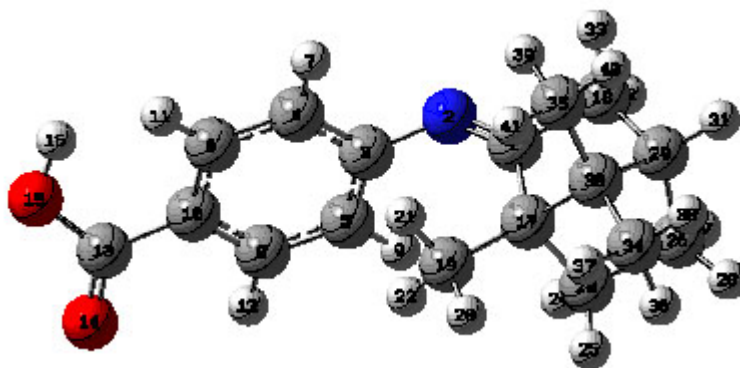
ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; ρ -rocking; t-torsion; τ -twisting; Ph-phenyl ring; X-substituent sensitive; Me-methyl; Ring-cyclohexane ring moiety.

mode. The band calculated at 1772 cm⁻¹ (DFT) is assigned as ν C=O mode. The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region 1390 \pm 55 cm⁻¹. The C(=O)O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region 1250 \pm 80 cm⁻¹. The DFT calculations give OH in-plane deformation at 1299 and C-O stretch at 1279 cm⁻¹. The out-of-plane deformation¹⁵ OH exhibits a moderate band in the region 905 \pm 65 cm⁻¹. The C=O in-plane deformation is weakly to moderately active in the region 725 \pm 95 cm⁻¹. Most carboxylic acid display γ C=O in the region 595 \pm 85 cm⁻¹ in the vicinity of methyl and ethyl esters. The -C(=O)O deformation or rock has a weak to moderate intensity and appears in the region 445 \pm 125 cm⁻¹. The C=O deformation bands are identified assigned (Table 1).

For the title compound, the CC stretching modes are observed in the range of 1297-853 cm⁻¹ theoretically and 1179, 1082, 861 cm⁻¹ in the IR spectrum¹⁶. For the para substituted phenyl ring, the CH stretching modes are assigned in the range 3101-3046 cm⁻¹ theoretically, which is expected in the region¹¹ 3000-3115 cm⁻¹. The CH stretching modes of the phenyl ring are observed at 3087 and 3040 cm⁻¹ in the IR spectrum. For the para disubstituted phenyl ring, the phenyl ring stretching modes δ Ph are expected in the range¹¹ 1280-1620 cm⁻¹ and the bands observed at 1610, 1576, 1318, cm⁻¹ in the IR spectrum and at 1594, 1542, 1487, 1403, 1305 cm⁻¹ (DFT) are assigned as these modes. The ring breathing mode for the para substituted benzenes with entirely different substituents¹⁷ have been reported to be strongly IR active with typical bands in the interval 780-840 cm⁻¹. For the title compound, this is confirmed by the

strong band in the infrared spectrum at 756 cm^{-1} which finds support from computational results (744 cm^{-1} theoretically). Ambujakshan *et al.*¹⁸ reported a value 792 cm^{-1} (IR) and 782 cm^{-1} (calculated) as

ring breathing mode for para substituted benzenes. For para disubstituted benzenes the δCH modes are seen in the range¹¹ $995\text{--}1315\text{ cm}^{-1}$.



The DFT calculations give these modes at $1292, 1280, 1162, 1102\text{ cm}^{-1}$. The out-of-plane CH deformations¹¹ of para substituted benzenes are observed below 1000 cm^{-1} . The bands observed at 853 cm^{-1} in the IR spectrum and at $943, 918, 842, 829\text{ cm}^{-1}$ (DFT) are assigned as the out-of-plane deformation CH bands. Two very strong CH out-of-plane deformation bands, occurring at $840 \pm 50\text{ cm}^{-1}$ is typical for 1,4-disubstituted benzenes¹¹. Again according to literature^{11,12} a lower γCH absorbs in the neighborhood $820 \pm 45\text{ cm}^{-1}$, but is much weaker or infrared inactive. The DFT calculations give a γCH at 829 cm^{-1} and no band is experimentally observed for this mode. The substituent sensitive modes of the phenyl rings are also identified and assigned (Table 1).

The cyclohexane ring fragment is a sterically strained system. Presumably, this is the reason for elongation of skeletal C-C bonds, $C_{26}\text{--}C_{23} = 1.5592, C_{17}\text{--}C_{23} = 1.5681, C_{18}\text{--}C_{29} = 1.5407, C_{29}\text{--}C_{26} = 1.5465\text{ \AA}$. The C-C bond lengths in the methyl bridge ($C_{30}\text{--}C_{35} = 1.5405, C_{30}\text{--}C_{34} = 1.5387\text{ \AA}$) are elongated to a lesser extent. These may be explained by change of the substitution pattern in cyclohexane ring as reported by Tarabara *et al.*¹⁹. The change in bond lengths $C_1\text{--}C_{18} = 1.5306$ and $C_{17}\text{--}C_{30} = 1.5830\text{ \AA}$ are due to the adjacent methyl group and azomethane group. The methylene groups, $C_{23}\text{--}H_{24,25}$ (106.7°), $C_{26}\text{--}H_{27,28}$ (106.9°), $C_{18}\text{--}H_{32,33}$ (106.8°) inclined almost equally with respect to the other parts of the six membered ring. For

the cyclohexane ring, Teimouri *et al.*²⁰ reported the bond lengths $C_{17}\text{--}C_{23} = 1.508, C_{26}\text{--}C_{29} = 1.510, C_{18}\text{--}C_1 = 1.566, C_1\text{--}C_{17} = 1.56, C_{18}\text{--}C_{29} = 1.557\text{ \AA}$ and the corresponding bond lengths of the title compound are $1.5681, 1.5465, 1.5306, 1.5399, 1.5407\text{ \AA}$. The bond angles reported by Teimouri *et al.*²⁰ are $C_{17}\text{--}C_1\text{--}C_{18} = 105.3, C_{17}\text{--}C_{23}\text{--}C_{26} = 88.2, C_{23}\text{--}C_{17}\text{--}C_1 = 112.4, C_{29}\text{--}C_{18}\text{--}C_1 = 103.8, C_{29}\text{--}C_{26}\text{--}C_{23} = 89.8, C_{18}\text{--}C_{29}\text{--}C_{26} = 117.7^\circ$ where as the corresponding calculated (DFT) values of the title compound are $106.3, 104.6, 103.5, 102.5, 102.7, 106.8^\circ$. There are three types of CC bonds involved in the title compound, strained CC bonds in cyclohexane, methyl bridge and in the phenyl ring. The CC bond lengths are in the range $1.5306\text{--}1.5681\text{ \AA}, 1.3875\text{--}1.4092\text{ \AA}$ and $1.5230\text{--}1.5405\text{ \AA}$, cyclohexane, phenyl and methyl bridge, respectively.

Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties²¹. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing^{22,23}. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The calculated first hyperpolarizability of the title compound is 5.56×10^{-30} esu and the title compound is an attractive object for future studies of nonlinear optical properties.

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