

Computational investigation for molecular spectra of 4-tricyanovinyl-N,N-diethylaniline (TCVA)

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ABSTRACT

In this work, a computational study for the molecular structure of TCVA is reported. The equilibrium geometry, harmonic vibrational frequencies, infrared intensities and thermodynamic functions for TCVA are calculated by Hatree-Fock (HF) and Density Functional Theory (DFT) using Becke's three parameter exchange functional with Lee-Yang-Parr (B3LYP) theories utilizing 6-31G(d,p) and 6-311G(d,p) basis sets. Our computational FT-IR spectra for TCVA molecule have been constructed. Our scaled computational wavenumbers and FT-IR spectra have showed a comparable agreement with the experimental results obtained by M.M. El-Nahass et al.^[1]. PACS 31.15.A-, 33.20.Ea, 33.20.Tp, 36.40.Mr
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KEYWORDS

TCVA;
FT-IR;
HF;
DFT;
Vibrational spectra;
Thermodynamics functions.

INTRODUCTION

Tricyanovinyl derivative compounds are of much interest both as molecular systems, having high charge transferability in the electronic ground state and as promising semiconducting organic materials. One of them is the 4-tricyanovinyl-N,N-diethylaniline (TCVA) which is disubstituted benzenes of the donor-acceptor type with an electron donor D (diethylamino group) and an electron acceptor A (tricyanovinyl group)^[2,3]. The molecular structure of TCVA is given in Figure (1). This dye belongs to a class of organic compounds known as molecular rotors^[3,4], which have great importance as fluorescence probes of surrounding media^[2,4]. It is also used for coloring synthetic polymer fibers^[5]. Also, it is applied as sublimeable dye in heat-transfer recording materials^[6] and in photoconductive recording materials^[7]. It has received some interest as a cytotoxic agent

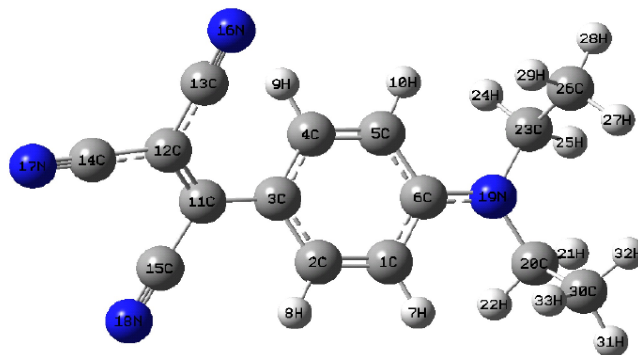


Figure 1 : The molecular structure of TCVA in powder form against tumors, as X-ray protective agent and as stabilizer in plastics against ultraviolet radiation^[8]. The computationally investigated spectra were interpreted with aid of normal coordinate analysis followed by geometry optimization and force field calculations based on B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) levels. Up to our knowledge no ab initio HF and DFT

calculations have been performed on 4-tricyanovinyl-N,N-diethylaniline molecule.

COMPUTATIONAL DETAILS

The entire calculations were performed at HF and DFT B3LYP levels on a Pentium IV/2.8 GHz personal computer using Gaussian 03W^[9] program package, invoking gradient geometry optimization^[10]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at HF level, adopting the standard 6-31G(d,p) basis set. This geometry was then re-optimized again at DFT B3LYP level, using basis set 6-311G (d,p), for better description of polar bonds of N–H and C–H groups. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT B3LYP levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of TCVA were used for harmonic vibrational frequency calculations resulting in IR spectra. Vibrational frequencies computed at B3LYP level have been adjusted to be more reliable than those obtained by the computationally demanding Møller–Plesset perturbation methods. DFT offers electron correlation frequently comparable to second-order Møller–Plesset theory (MP2). Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics. By combining the results of the GaussView (4.1) program^[11] with symmetry considerations, vibrational frequency assignments are made with a high degree of accuracy.

RESULTS AND DISCUSSION

Optimized geometry

TCVA optimized structure parameters calculated by *ab initio* HF and DFT B3LYP levels with the 6-31G(d,p) and 6-311G(d,p) basis sets are listed in TABLES (1 and 2) in accordance with atom numbering scheme given in Figure (1), the optimized structure can be compared with the experimental results and also with other similar systems for which the crystal structures have been solved. For example, the optimized bond lengths of C–C in phenyl ring fall in the range

from 1.3713 Å for C1–C2 to 1.4118 Å for C5–C6 using HF/6-31G(d,p), 1.3706 Å to 1.4118 Å for HF/6-311G(d,p), 1.3784 Å to 1.4237 Å for B3LYP/6-31G(d,p) and 1.376 Å to 1.422 Å for B3LYP/6-311G(d,p) methods which are in a comparable agreement with those of the experimental results^[1] in the range 1.3627 Å to 1.4123 Å. Similarly the optimized C11–C12 bond length in the attached vinyl group is found to be 1.3512 Å using HF/6-31G(d,p), 1.3493 Å for HF/6-311G(d,p), 1.3903 Å for B3LYP/6-31G(d,p) and 1.3862 Å for B3LYP/6-311G(d,p) which are in a comparable agreement with the experimental result^[1] of 1.3340 Å.

The optimized C6–N19 bond length is found to be 1.3646 Å using HF/6-31G(d,p), 1.3625 Å for HF/6-311G(d,p), 1.3706 Å for B3LYP/6-31G(d,p) and finally 1.3678 Å for B3LYP/6-311G(d,p) which are in a comparable agreement with the experimental result^[1] of 1.354 Å. The optimized C1–C6–C5 bond angle is found to be 116.3938° using HF/6-31G(d,p), 113.3295° for HF/6-311G(d,p), 116.3315° for B3LYP/6-31G(d,p) and finally 116.2692° for B3LYP/6-311G(d,p) which are in a comparable agreement with the experimental result^[1] of 116.58°. The optimized C4–C5–C6 bond angle is found to be 121.6197° using HF/6-31G(d,p), 121.6310° for HF/6-311G(d,p), 121.8623° for B3LYP/6-31G(d,p) and finally 121.8672° for B3LYP/6-311G(d,p) which are in a comparable agreement with the experimental result^[1] of 121.03°. The optimized C1–C2–C3 bond angle is found to be 122.0589° using HF/6-31G(d,p), 122.1135° for HF/6-311G(d,p), 122.3741° for B3LYP/6-31G(d,p) and finally 122.3787° for B3LYP/6-311G(d,p) which are in a comparable agreement with the experimental result^[1] of 122.97°. Based on above comparison, although there are some differences between the theoretical values and the experimental values, the optimized structural parameters can well reproduce the experimental ones and they are the bases for thereafter discussion.

Vibrational assignments

TCVA molecule has 33 atoms and 93 normal vibrations are distributed as $58A_1 + 35A''$ considering C_s symmetry. All the calculated modes are numbered from the smallest to the largest frequency within each

TABLE 1 : The Optimized Calculated Bond Lengths in (Å) of TCVA using HF and B3LYP.

Parameters	HF		B3LYP	
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)
	Bond Length (Å)			
C1-C2	1.3713	1.3706	1.3784	1.376
C1-C6	1.4111	1.4109	1.4221	1.4203
C1-H7	1.0699	1.0695	1.0815	1.0798
C2-C3	1.3990	1.3981	1.4172	1.4147
C2-H8	1.0748	1.0744	1.0845	1.0829
C3-C4	1.3989	1.3982	1.4164	1.4141
C3-C11	1.4637	1.4631	1.4529	1.4518
C4-C5	1.3711	1.3702	1.3785	1.376
C4-H9	1.0719	1.0716	1.0809	1.0792
C5-C6	1.4118	1.4118	1.4237	1.422
C5-H10	1.0698	1.0695	1.0816	1.0799
C6-N19	1.3646	1.3625	1.3706	1.3678
C11-C12	1.3512	1.3493	1.3903	1.3862
C11-C15	1.4526	1.4503	1.4414	1.4378
C12-C13	1.4391	1.4366	1.4261	1.4228
C12-C14	1.4403	1.4379	1.4300	1.4263
C13-N16	1.1358	1.1298	1.1652	1.1568
C14-N17	1.1355	1.1295	1.1644	1.1561
C15-N18	1.1347	1.1287	1.1628	1.1546
N19-C20	1.4583	1.4586	1.4676	1.4677
N19-C23	1.4590	1.4592	1.4680	1.4683
C20-H21	1.0824	1.0823	1.0933	1.0916
C20-H22	1.0829	1.0830	1.0949	1.0929
C20-C30	1.5286	1.5289	1.5339	1.5335
C23-H24	1.0837	1.0836	1.0946	1.0929
C23-H25	1.0820	1.0820	1.0934	1.0915
C23-C26	1.5288	1.5290	1.5338	1.5333
C26-H27	1.0840	1.0844	1.0935	1.0918
C26-H28	1.0860	1.0864	1.0948	1.0935
C26-H29	1.0836	1.0839	1.0934	1.0918
C30-H31	1.0860	1.0865	1.0948	1.0936
C30-H32	1.0841	1.0845	1.0934	1.0919
C30-H33	1.0840	1.0842	1.0933	1.0918

fundamental wavenumber. TCVA harmonic vibrational frequencies calculated for HF level using 6-31G(d,p) and 6-311G(d,p) basis sets have been collected in TABLES (3 and 4) while those for DFT B3LYP level using 6-31G(d,p) and 6-311G(d,p) basis sets have been collected in TABLES (5 and 6). Comparison of the frequencies calculated at HF and DFT B3LYP with the experimental values^[1] reveals the overestimation of the

calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in DFT to a certain extent makes DFT frequency values smaller in comparison with that of HF frequency ones. Reduction in the computed harmonic vibrations, though the basis set sensitive are only marginal as observed in the DFT values using 6-311G(d,p). Any way not withstanding the level of calculations, it is

TABLE 2 : The Optimized Calculated Bond Angles in (°) of TCVA using HF and B3LYP.

Parameters	HF		B3LYP	
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-11G(d,p)
	Bond Angle (°)			
C2-C1-C6	121.3243	121.3271	121.3334	121.3699
C2-C1-H7	117.8273	117.8222	118.037	118.0451
C6-C1-H7	120.8486	120.8507	120.6296	120.585
C1-C2-C3	122.0589	122.1135	122.3741	122.3787
C1-C2-H8	117.9737	117.9237	118.1612	118.1261
C3-C2-H8	119.9605	119.9557	119.4638	119.4923
C2-C3-C4	116.8168	116.7611	116.2718	116.2498
C2-C3-C11	120.0023	120.0055	119.5791	119.6379
C4-C3-C11	123.1760	123.2280	124.1491	124.1117
C3-C4-C5	121.7651	121.8139	121.8175	121.8557
C3-C4-H9	120.6295	120.6412	120.6848	120.7103
C5-C4-H9	117.5888	117.5289	117.4974	117.4311
C4-C5-C6	121.6197	121.6310	121.8623	121.8672
C4-C5-H10	117.6468	117.6366	117.732	117.7303
C6-C5-H10	120.732	120.7315	120.4057	120.4022
C1-C6-C5	116.3938	116.3295	116.3315	116.2692
C1-C6-N19	121.8677	121.8976	121.9068	121.9362
C5-C6-N19	121.7298	121.7653	121.757	121.7892
C3-C11-C12	128.3949	128.3756	129.6622	129.3247
C3-C11-C15	115.3166	115.3031	115.7642	115.6915
C12-C11-C15	116.2871	116.3198	114.5736	114.9837
C11-C12-C13	123.5397	123.5744	124.9029	124.6226
C11-C12-C14	121.9617	121.9683	121.0689	121.2115
C13-C12-C14	114.4758	114.4349	114.0266	114.1590
C6-N19-C20	121.219	121.2388	121.1021	121.1866
C6-N19-C23	121.2251	121.2681	121.2130	121.2885
C20-N19-C23	117.5300	117.4841	117.6288	117.5060
N19-C20-H21	107.2691	107.1974	107.0187	106.9898
N19-C20-H22	109.2427	109.2580	108.8995	108.8953
N19-C20-C30	114.7678	114.8597	114.7122	114.7169
H21-C20-H22	105.6775	105.6901	105.9095	105.9300
H21-C20-C30	109.1985	109.1701	109.5884	109.5895
H22-C20-C30	110.2539	110.2269	110.3008	110.3078

customary to scale down the calculated harmonic frequencies in order to improve the comparable agreement with the experiment. Vibrational frequencies calculated at DFT B3LYP level were scaled by 0.96^[12], and those calculated at HF level were scaled by 0.89^[13]. Our FT-IR spectra of TCVA at HF levels utilizing 6-31G(d,p) and 6-311G(d,p) basis sets using Gaussian 03W and Gauss View (4.1) program package have

been shown in Figure (2) while Those for TCVA at DFT B3LYP levels utilizing 6-31G(d,p) and 6-311G(d,p) basis sets using Gaussian 03W and Gauss View (4.1) program package have been shown in Figure(3).

C–H Vibrations

The aromatic C-H stretching vibrations are in general observed in the region 3000.0 – 3100.0 cm⁻¹^[14].

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TABLE 3 : The Calculated Vibrational Wavenumbers (Harmonic Frequency) (cm^{-1}) and IR Intensities are obtained for TCVA at HF/6-31G(d,p).

No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.
1	18.0	16.0	0.10	0.02
2	35.9	32.0	1.85	0.33
3	42.9	38.1	0.23	0.04
4	72.8	64.8	0.83	0.15
5	104.1	92.6	1.90	0.34
6	114.0	101.4	1.89	0.34
7	119.9	106.7	1.92	0.34
8	133.3	118.6	8.51	1.52
9	148.5	132.2	3.12	0.56
10	158.3	140.9	5.11	0.91
11	201.2	179.1	0.57	0.10
12	202.5	180.3	7.03	1.26
13	229.1	203.9	0.67	0.12
14	238.0	211.8	2.75	0.49
15	271.3	241.4	3.83	0.68
16	310.8	276.6	2.19	0.39
17	338.3	301.1	13.42	2.40
18	371.3	330.4	6.97	1.25
19	397.3	353.6	7.30	1.31
20	433.1	385.5	5.24	0.94
21	467.4	416.0	3.70	0.66
22	479.8	427.0	12.56	2.25
23	512.7	456.3	0.64	0.11
24	517.2	460.3	3.36	0.60
25	546.1	486.1	1.02	0.18
26	559.0	497.5	3.06	0.55
27	585.9	521.4	6.60	1.18
28	590.1	525.2	19.29	3.45
29	640.4	569.9	1.21	0.22
30	664.0	591.0	4.43	0.79
31	677.1	602.6	0.26	0.05
32	697.5	620.8	1.50	0.27
33	784.6	698.3	9.25	1.66
34	791.6	704.5	16.32	2.92
35	824.6	733.9	15.48	2.77
36	849.1	755.7	2.71	0.49
37	858.7	764.3	6.36	1.14
38	909.0	809.0	6.43	1.15
39	930.0	827.7	71.34	12.76
40	974.9	867.6	6.39	1.14
41	980.9	873.0	0.53	0.09
42	992.7	883.5	0.54	0.10
43	1086.0	966.5	6.72	1.20
44	1096.7	976.0	19.04	3.41
45	1105.9	984.2	8.83	1.58
46	1108.8	986.9	16.45	2.94
47	1125.9	1002.1	4.95	0.88
48	1179.5	1049.7	2.05	0.37
49	1196.9	1065.3	59.42	10.63
50	1210.1	1077.0	27.55	4.93
51	1271.5	1131.6	16.78	3.00
52	1275.8	1135.5	538.50	96.30

No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.
53	1296.4	1153.8	26.63	4.76
54	1304.4	1161.0	67.56	12.08
55	1339.3	1191.9	255.96	45.78
56	1360.2	1210.6	7.73	1.38
57	1412.5	1257.1	401.20	71.75
58	1429.1	1271.9	14.34	2.56
59	1451.1	1291.5	51.20	9.16
60	1486.1	1322.6	20.31	3.63
61	1509.0	1343.0	60.21	10.77
62	1516.7	1349.8	281.27	50.30
63	1552.2	1381.5	41.63	7.45
64	1553.2	1382.3	135.98	24.32
65	1565.4	1393.2	50.96	9.11
66	1597.4	1421.7	34.33	6.14
67	1615.5	1437.8	3.35	0.60
68	1622.2	1443.8	1.00	0.18
69	1624.9	1446.1	0.49	0.09
70	1631.8	1452.3	19.13	3.42
71	1647.5	1466.3	4.11	0.74
72	1669.0	1485.4	15.64	2.80
73	1689.2	1503.4	559.16	100.00
74	1717.3	1528.4	137.72	24.63
75	1744.1	1552.2	556.17	99.47
76	1796.3	1598.7	340.55	60.90
77	2604.3	2317.8	25.87	4.63
78	2609.5	2322.4	73.23	13.10
79	2615.6	2327.9	21.27	3.80
80	3191.1	2840.1	15.68	2.80
81	3194.3	2842.9	37.14	6.64
82	3221.4	2867.0	13.39	2.39
83	3230.3	2874.9	48.89	8.74
84	3251.8	2894.1	4.53	0.81
85	3260.6	2901.9	61.21	10.95
86	3263.1	2904.2	26.67	4.77
87	3265.2	2906.0	35.61	6.37
88	3277.8	2917.3	12.34	2.21
89	3288.3	2926.6	115.89	20.73
90	3370.1	2999.4	2.54	0.45
91	3401.1	3027.0	1.98	0.35
92	3419.3	3043.1	13.54	2.42
93	3423.1	3046.6	10.44	1.87

TABLE 4 : The Calculated Vibrational Wavenumbers (Harmonic Frequency) (cm^{-1}) and IR Intensities are obtained for TCVA at HF/6-311G(d,p).

No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.
1	18.0	16.0	0.15	0.03
2	35.8	31.9	1.83	0.30
3	42.7	38.0	0.21	0.04
4	72.9	64.8	0.92	0.15
5	103.9	92.5	1.87	0.31
6	112.6	100.2	1.37	0.23

No	Wave number		IR Intensity		No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.		Unscaled	Scaled	Rel.	Abs.
7	118.1	105.1	1.94	0.32	51	1263.4	1124.5	22.17	3.66
8	133.4	118.7	7.54	1.24	52	1267.6	1128.2	579.17	95.56
9	150.1	133.6	2.54	0.42	53	1284.3	1143.1	38.62	6.37
10	159.6	142.0	4.73	0.78	54	1297.4	1154.7	53.17	8.77
11	200.5	178.5	0.62	0.10	55	1331.6	1185.1	254.28	41.96
12	202.0	179.8	6.70	1.11	56	1352.6	1203.8	8.74	1.44
13	228.7	203.6	0.48	0.08	57	1405.7	1251.1	424.70	70.08
14	238.3	212.1	2.90	0.48	58	1423.0	1266.5	10.62	1.75
15	271.4	241.6	4.16	0.69	59	1445.3	1286.3	46.62	7.69
16	310.6	276.4	2.11	0.35	60	1480.0	1317.2	21.65	3.57
17	338.0	300.9	13.13	2.17	61	1501.7	1336.5	46.02	7.59
18	371.1	330.3	7.08	1.17	62	1510.3	1344.2	273.58	45.14
19	399.3	355.4	7.99	1.32	63	1540.7	1371.3	20.18	3.33
20	433.3	385.6	5.39	0.89	64	1542.3	1372.7	157.97	26.07
21	465.9	414.6	4.52	0.75	65	1558.3	1386.9	75.40	12.44
22	478.1	425.5	11.37	1.88	66	1585.2	1410.8	35.73	5.89
23	510.8	454.6	0.58	0.10	67	1605.2	1428.6	3.28	0.54
24	521.3	464.0	3.32	0.55	68	1612.1	1434.8	1.91	0.31
25	546.7	486.6	1.58	0.26	69	1614.7	1437.1	0.23	0.04
26	559.2	497.7	2.76	0.46	70	1622.2	1443.8	17.40	2.87
27	587.2	522.6	10.45	1.72	71	1639.3	1458.9	3.29	0.54
28	589.7	524.9	22.44	3.70	72	1661.0	1478.3	33.16	5.47
29	639.5	569.2	1.25	0.21	73	1678.5	1493.9	564.87	93.20
30	664.4	591.3	3.88	0.64	74	1706.3	1518.6	122.81	20.26
31	680.8	605.9	0.33	0.05	75	1733.4	1542.7	606.07	100.0
32	695.2	618.7	1.55	0.26	76	1783.2	1587.0	307.58	50.75
33	782.9	696.8	15.07	2.49	77	2588.2	2303.5	27.24	4.49
34	789.6	702.8	13.21	2.18	78	2593.1	2307.8	72.47	11.96
35	824.8	734.1	12.88	2.12	79	2599.4	2313.5	20.45	3.37
36	846.1	753.0	3.32	0.55	80	3170.3	2821.6	16.31	2.69
37	856.2	762.0	5.34	0.88	81	3173.4	2824.3	37.79	6.24
38	902.4	803.1	5.74	0.95	82	3203.5	2851.1	9.90	1.63
39	925.2	823.5	68.16	11.25	83	3211.6	2858.4	38.50	6.35
40	971.3	864.4	6.57	1.08	84	3227.2	2872.2	11.91	1.96
41	976.5	869.1	1.29	0.21	85	3235.7	2879.7	59.49	9.82
42	988.1	879.4	0.51	0.08	86	3238.0	2881.8	45.10	7.44
43	1078.9	960.3	5.59	0.92	87	3241.4	2884.9	27.04	4.46
44	1087.6	968.0	15.01	2.48	88	3253.8	2895.9	14.34	2.37
45	1099.9	978.9	21.87	3.61	89	3266.0	2906.7	127.43	21.03
46	1102.4	981.1	11.20	1.85	90	3350.6	2982.1	2.19	0.36
47	1119.4	996.3	4.11	0.68	91	3380.9	3009.0	2.25	0.37
48	1173.4	1044.3	2.41	0.40	92	3398.3	3024.5	12.22	2.02
49	1191.2	1060.2	53.43	8.82	93	3402.2	3027.9	9.13	1.51
50	1204.7	1072.2	26.98	4.45					

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TABLE 5 : The Calculated Vibrational Wavenumbers (Harmonic Frequency) (cm^{-1}) and IR Intensities are obtained for TCVA at B3LYP/6-31G(d,p)

No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.
1	12.2	11.7	0.16	0.02
2	38.9	37.3	0.28	0.04
3	40.6	39.0	0.09	0.01
4	68.7	66.0	0.31	0.05
5	89.1	85.5	0.50	0.08
6	106.6	102.3	0.14	0.02
7	118.0	113.3	1.90	0.29
8	125.5	120.5	5.23	0.79
9	139.0	133.5	1.34	0.20
10	149.8	143.8	7.84	1.19
11	184.8	177.4	6.79	1.03
12	187.4	179.9	0.81	0.12
13	213.2	204.7	0.25	0.04
14	222.9	214.0	0.54	0.08
15	264.3	253.7	2.11	0.32
16	284.9	273.5	0.88	0.13
17	309.8	297.4	3.91	0.59
18	345.4	331.5	4.90	0.74
19	369.6	354.8	0.45	0.07
20	404.8	388.6	4.28	0.65
21	427.5	410.4	0.66	0.10
22	446.3	428.5	9.61	1.46
23	469.7	450.9	2.80	0.42
24	477.4	458.3	0.63	0.10
25	507.5	487.2	0.89	0.13
26	523.9	503.0	2.83	0.43
27	534.4	513.0	9.31	1.41
28	539.5	518.0	10.52	1.60
29	600.1	576.1	0.54	0.08
30	603.2	579.1	1.67	0.25
31	624.6	599.6	0.30	0.05
32	651.6	625.5	0.49	0.07
33	705.0	676.8	4.47	0.68
34	739.8	710.2	22.65	3.44
35	752.7	722.6	6.28	0.95
36	792.9	761.2	2.47	0.37
37	800.4	768.4	7.42	1.13
38	812.0	779.5	0.41	0.06
39	840.1	806.5	44.63	6.78
40	915.9	879.2	3.50	0.53
41	917.7	881.0	0.37	0.06
42	930.5	893.3	0.49	0.07
43	972.8	933.9	0.10	0.01
44	978.0	938.9	0.33	0.05
45	1014.4	973.8	3.82	0.58
46	1029.4	988.2	36.12	5.48
47	1063.8	1021.2	2.62	0.40
48	1089.6	1046.0	1.42	0.22
49	1107.2	1062.9	66.31	10.07
50	1117.8	1073.1	24.60	3.73
51	1185.6	1138.2	5.50	0.84
52	1190.7	1143.0	76.70	11.64

No	Wave number		IR Intensity	
	Unscaled	Scaled	Rel.	Abs.
1	12.2	11.7	0.16	0.02
53	1216.9	1168.3	121.48	18.44
54	1230.6	1181.4	25.55	3.88
55	1257.2	1206.9	225.95	34.30
56	1319.8	1267.0	122.12	18.54
57	1321.6	1268.8	43.91	6.67
58	1329.6	1276.4	16.78	2.55
59	1374.4	1319.4	121.55	18.45
60	1380.9	1325.7	64.80	9.84
61	1389.4	1333.8	14.41	2.19
62	1398.5	1342.6	244.44	37.11
63	1425.1	1368.1	8.82	1.34
64	1430.2	1373.0	36.71	5.57
65	1453.0	1394.9	168.80	25.62
66	1490.9	1431.2	143.88	21.84
67	1502.1	1442.0	19.95	3.03
68	1506.9	1446.6	37.39	5.68
69	1510.1	1449.7	3.08	0.47
70	1516.6	1455.9	18.72	2.84
71	1519.8	1459.0	43.75	6.64
72	1533.8	1472.4	349.29	53.02
73	1540.5	1478.9	248.90	37.78
74	1573.4	1510.5	39.12	5.94
75	1577.8	1514.7	30.37	4.61
76	1666.9	1600.2	658.89	100.02
77	2319.5	2226.7	13.57	2.06
78	2335.6	2242.2	64.46	9.78
79	2347.8	2253.9	26.35	4.00
80	3054.7	2932.5	10.50	1.59
81	3056.4	2934.2	34.64	5.26
82	3060.4	2937.9	15.85	2.41
83	3064.7	2942.1	66.39	10.08
84	3099.1	2975.1	2.07	0.31
85	3107.5	2983.2	15.36	2.33
86	3127.3	3002.2	37.79	5.74
87	3130.0	3004.8	34.95	5.30
88	3138.1	3012.6	4.84	0.73
89	3142.4	3016.7	54.67	8.30
90	3212.1	3083.6	0.36	0.06
91	3236.8	3107.3	6.92	1.05
92	3242.0	3112.3	11.82	1.79
93	3260.1	3129.7	5.31	0.81

TABLE 6 : The Calculated Vibrational Wavenumbers (Harmonic Frequency) (cm^{-1}), IR Intensities and Vibrational Assignments are obtained for TCVA at B3LYP/6-311G(d,p).

No	Wave number		IR Intensity		Vibrational Assignment
	Unscaled	Scaled	Rel.	Abs.	
1	14.5	14.0	0.28	0.04	β C-H+ γ C-C-C
2	38.0	36.5	0.13	0.02	β C-H+ γ C-C-C
3	39.9	38.3	0.20	0.03	β C-H+ γ C-C-C
4	67.3	64.6	0.31	0.05	β C-H+ γ C-C-C
5	90.0	86.4	0.68	0.10	β C-H+ γ C-C-C

No	Wave number		IR Intensity		Vibrational Assignment	No	Wave number		IR Intensity		Vibrational Assignment
	Unscaled	Scaled	Rel.	Abs.			Unscaled	Scaled	Rel.	Abs.	
6	101.1	97.0	0.13	0.02	β C-H+ γ C-C-C	40	913.7	877.2	1.34	0.21	β C-C-C+ ring breath
7	113.1	108.6	1.06	0.16	β C-H+ γ C-C-C	41	916.9	880.2	2.42	0.37	β C-N-C+ β C-C-C
8	125.1	120.0	5.22	0.80	γ C-N-C + γ C-C-C	42	926.3	889.3	0.67	0.10	ν C-C
9	139.7	134.1	1.32	0.20	β N-C-C + β C-H	43	979.5	940.3	0.47	0.07	γ C-C-C
10	150.2	144.2	7.01	1.07	β N-C-C + β C-H	44	982.3	943.0	0.30	0.05	γ C-C-C
11	184.8	177.4	6.08	0.93	β N-C-C + β C-H	45	1012.1	971.6	3.85	0.59	ν C-C+ ν C-H
12	186.7	179.3	0.67	0.10	γ N-C-C + β C-H	46	1022.6	981.7	40.39	6.19	γ C-H
13	211.9	203.4	0.09	0.01	β C-H + β N-C-C	47	1059.7	1017.3	2.48	0.38	ν C-C+ β C-H
14	220.2	211.4	0.77	0.12	β C-H + β N-C-C	48	1082.8	1039.5	2.75	0.42	β C-C-C+ β C-H
15	260.9	250.4	2.31	0.35	β C-H + β N-C-C	49	1102.0	1057.9	58.78	9.01	β C-C-C+ β C-H
16	284.7	273.4	1.10	0.17	β C-H + β N-C-C	50	1111.8	1067.3	23.95	3.67	β C-H
17	310.9	298.5	4.62	0.71	β C-C-C+ γ C-N-C	51	1178.5	1131.4	6.70	1.03	β C-H
18	346.0	332.2	4.95	0.76	γ N-C-C + γ C-C-C	52	1183.4	1136.0	92.38	14.15	ring breath
19	369.2	354.4	0.71	0.11	γ N-C-C + γ C-C-C	53	1212.9	1164.4	134.93	20.67	ν C-C
20	405.7	389.5	4.50	0.69	γ N-C-C + γ C-C-C	54	1222.4	1173.5	25.76	3.95	β C-C-C+ β C-H
21	428.9	411.7	0.76	0.12	γ C-C-C	55	1250.0	1200.0	221.14	33.88	β C-C-C+ β C-H
22	446.5	428.7	10.99	1.68	γ C-N-C + γ C-C-C	56	1311.4	1258.9	78.16	11.97	β C-N-C+ ν C-C
23	471.0	452.2	1.26	0.19	γ C-N-C + γ C-C-C	57	1315.2	1262.6	93.16	14.27	γ C-H+ ν C-C
24	476.3	457.3	0.98	0.15	γ C-N-C + γ C-C-C	58	1324.2	1271.2	19.11	2.93	γ C-H+ ν C-C
25	509.5	489.1	1.19	0.18	β N-C-C + β C-N-C	59	1368.0	1313.3	193.61	29.66	γ C-H+ ν C-C
26	524.7	503.7	2.95	0.45	β N-C-C + β C-C-C	60	1372.4	1317.5	0.95	0.15	γ C-H+ ν C-C
27	534.3	512.9	13.20	2.02	β N-C-C + γ C-C-C	61	1382.7	1327.4	19.93	3.05	γ C-H
28	544.9	523.1	14.25	2.18	β N-C-C + γ C-C-C	62	1391.7	1336.1	236.49	36.23	γ C-H
29	600.2	576.2	0.86	0.13	β C-N-C + β C-C-C	63	1413.9	1357.4	8.41	1.29	γ C-H
30	604.1	579.9	0.88	0.14	γ C-N-C + γ C-C-C	64	1418.9	1362.1	25.47	3.90	γ C-H
31	630.4	605.2	0.37	0.06	β C-N-C + β C-C-C	65	1446.0	1388.2	170.99	26.20	ν C-N+ β C-H
32	651.6	625.6	0.56	0.09	β C-C-C	66	1479.3	1420.1	145.33	22.27	ν C-C + β C-H
33	712.9	684.4	5.71	0.87	ν C-N + β C-C-C	67	1491.2	1431.6	17.37	2.66	CH ₃ deformation
34	738.6	709.1	24.15	3.70	ν C-N + β C-C-C	68	1496.0	1436.1	16.22	2.48	CH ₃ deformation
35	762.8	732.2	5.98	0.92	γ C-C-C	69	1498.3	1438.4	7.63	1.17	CH ₃ deformation
36	790.0	758.4	2.89	0.44	γ C-H	70	1505.7	1445.5	18.79	2.88	CH ₃ deformation
37	798.0	766.1	5.78	0.88	γ C-H	71	1510.3	1449.8	32.50	4.98	CH ₂ deformation
38	810.1	777.7	1.45	0.22	γ C-C-C	72	1524.6	1463.6	381.22	58.40	CH ₂ deformation
39	841.8	808.1	48.43	7.42	β C-C-C	73	1531.9	1470.7	254.92	39.05	ν C-C
40	913.7	877.2	1.34	0.21	β C-C-C+ ring breath	74	1563.2	1500.7	39.72	6.09	ν C-C
						75	1566.9	1504.2	40.60	6.22	ν C-C
						76	1652.4	1586.3	652.78	100.01	ν C-C
						77	2312.3	2219.8	12.45	1.91	ν C-N
						78	2327.3	2234.2	63.38	9.71	ν C-N
						79	2339.7	2246.1	28.01	4.29	ν C-N
						80	3036.7	2915.2	13.07	2.00	ν_s C-H
						81	3038.5	2917.0	34.54	5.29	ν_s C-H

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No	Wave number		IR Intensity		Vibrational Assignment
	Unscaled	Scaled	Rel.	Abs.	
82	3046.3	2924.5	10.16	1.56	ν_s C-H
83	3049.8	2927.8	66.81	10.24	ν_s C-H
84	3078.6	2955.5	1.05	0.16	ν_{as} C-H
85	3087.9	2964.4	11.56	1.77	ν_{as} C-H
86	3101.6	2977.6	41.88	6.42	ν_{as} C-H
87	3104.6	2980.4	41.77	6.40	ν_{as} C-H
88	3113.8	2989.3	6.22	0.95	ν_{as} C-H
89	3119.0	2994.2	62.75	9.61	ν_{as} C-H
90	3192.0	3064.3	0.31	0.05	ν C-H
91	3217.3	3088.6	6.20	0.95	ν C-H
92	3222.7	3093.8	10.54	1.61	ν C-H
93	3240.7	3111.0	4.42	0.68	ν C-H

ν , stretching; ν_s , sym. stretching, ν_{as} , asym. stretching; β , in plane bending; γ , out of plane bending

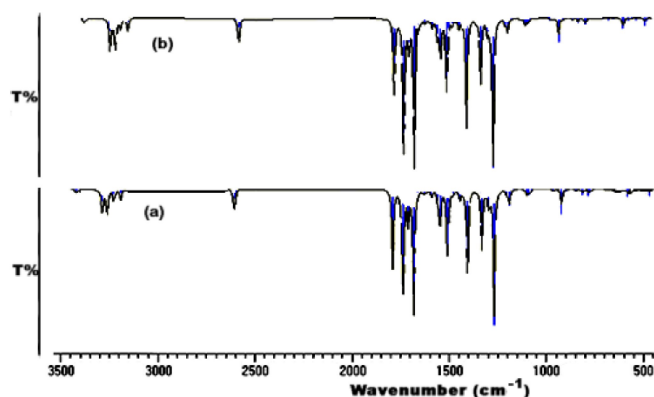


Figure 2 : (a) Simulated FT-IR-spectrum calculated for TCVA at HF/6-31G(d,p); (b) Simulated FT-IR-spectrum calculated for TCVA at HF/6-311G(d,p).

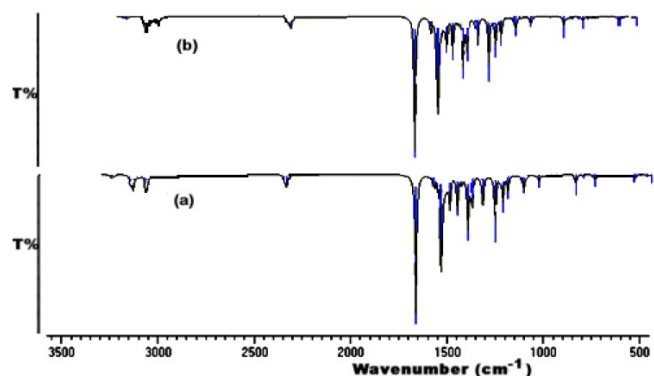


Figure 3 : (a) Simulated FT-IR-spectrum calculated for TCVA at B3LYP/6-31(d,p); (b) Simulated FT-IR-spectrum calculated for TCVA at B3LYP/6-311G(d,p)

In our work using Gaussian View (4.1) program, we found that vibrations 90 – 93 are assigned to the aromatic C-H stretching vibrations in the range 3064.3 - 3111.0 cm^{-1} for B3LYP/6-311G(d,p) are in a com-

parable agreement with experimental assignment 3100.0 cm^{-1} [1]. Also vibrations 84 - 89 are assigned to anti-symmetric aliphatic C-H stretching (ethyl group) in the region 2955.5 – 2994.2 cm^{-1} for B3LYP/6-311G(d,p) are in a comparable agreement with experimental assignments 2931.3 - 2977.6 cm^{-1} [1] and vibrations 80 - 83 are assigned to symmetric aliphatic C-H stretching in the region 2915.2 – 2927.8 cm^{-1} for B3LYP/6-311G(d,p). The C-H out of plane bending vibrations are in general observed in the region 690.0 – 850.0 cm^{-1} [14,15] while the C-H in plane bending vibrations are in general observed in the region 1025.0 – 1280.0 cm^{-1} [14,15]. In our work using Gauss View (4.1) program, we found that vibrations 36 – 37 are assigned to C-H out of plane bending in the range 758.4 – 766.1 cm^{-1} for B3LYP/6-311G(d,p) are in a comparable agreement with the experimental assignment 819.6 cm^{-1} [1] while vibrations 50 – 51 are assigned to C-H in plane bending in the range 1067.3 – 1131.4 cm^{-1} for B3LYP/6-311G(d,p) are in a comparable agreement with the experimental assignment 1278.6 cm^{-1} [1].

Ca¹³N Vibrations

It is known that Ca¹³N group stretching vibrations are in general observed in range 2210.0 – 2260.0 cm^{-1} [15,16]. In our work using Gauss View (4.1) program, we found that vibrations 77-79 are assigned to Ca¹³N stretching vibrations are in the region 2219.8 - 2246.1 cm^{-1} for B3LYP/6-311G(d,p) are in a comparable agreement with the experimental assignment 2210.0 cm^{-1} [1].

C=C Vibrations

It is known that C=C group stretching vibrations are in general observed in range 1480.0 – 1630.0 cm^{-1} [14,15]. In our work using Gauss View (4.1) program, we found that vibrations 73-76 are assigned to C=C group stretching vibrations in the region 1470.7 – 1586.3 cm^{-1} for B3LYP/6-311G(d,p) are in a comparable agreement with the experimental assignment 1602.6 cm^{-1} [1].

Methyl Group vibrations

It is known that CH₂ deformation modes are in general observed in the range 1450.0 - 1470.0 cm^{-1} while CH₃ deformation modes are observed in the range 1410.0 - 1440.0 cm^{-1} [14,15]. In our work using Gauss View (4.1) program, we found that vibrations 71 – 72

are assigned to CH_2 deformations in the region $1449.8 - 1463.6 \text{ cm}^{-1}$ are in a comparable agreement with experimental assignment 1449.9 cm^{-1} while vibrations $67 - 70$ are assigned to CH_3 deformations in the region $1431.6 - 1445.5 \text{ cm}^{-1}$ are in a comparable agreement with the experimental assignment 1423.2 cm^{-1} .

Other Molecular properties

Several calculated thermodynamic parameters are presented in TABLE (7). Scale factors have been recommended for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, $S_{\text{vib}}(T)$. The variations in the ZPVEs seem to be insignificant. The total energies and the change in the

total entropy of TCVA at room temperature using different methods are also presented. Generally the calculated thermal parameters indicate the stability of the studied structure.

Furthermore TCVA possesses higher dipole moment value (10 ~12 debye) so that higher dipole moment increases its ability to interact with surrounding molecules. This is in a good agreement with the finding of M. Ibrahim^[17,18]. Correlating this with the studied vibrational frequencies one can conclude that, the studied molecule is chemically active through its hydrogen bonding, thermal stability and finally higher dipole moment value. This dedicates the studied structure as a promising one for many applications.

TABLE 7 : The Optimized Calculations of Total Energies (a.u), Zero Point Vibrational Energies (kcal mol⁻¹), Rotational Constants (GHz), Entropies (cal k⁻¹) and Dipole Moment (Debye) for TCVA.

Parameters	HF		B3LYP	
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)
Total Energy	-793.9400257	-794.0896521	-798.9841318	-799.1623148
Zero Point Energy	175.04901	174.0929	163.59747	162.80882
	0.79283	0.7949	0.78844	0.79117
Rotational constants	0.18541	0.1854	0.18246	0.18305
	0.15743	0.15754	0.15247	0.15325
Entropy				
	Total	139.083	139.069	143.907
Translational	42.451	42.451	42.451	42.451
Rotational	33.896	33.892	33.949	33.937
Vibrational	62.736	62.726	67.507	67.477
Dipole Moment	10.5329	10.7156	12.1933	12.3127

CONCLUSION

TCVA molecule has 33 atoms and 93 normal vibrations distributed as $58A_1 + 35A''$ considering C_s symmetry. Our computed structural parameters, harmonic vibrational frequencies and IR-intensities using both HF and DFT B3LYP theories utilizing 6-311G(d,p) basis sets for TCVA have shown a comparable agreement with the experimental ones. TCVA is chemically active as it possesses a high dipole moment value (10~12 debye) which increases its ability to interact with the surrounding matrix. Therefore, TCVA is a promising structure for many applications.

Any discrepancy between the observed and the calculated frequencies may be due to the fact that the cal-

culations have been actually done on a single molecule in the gaseous state in contrary to the experimental values recorded in the solid state. Therefore, the assignments made at higher levels for both HF and DFT B3LYP theories with only reasonable deviations from the experimental values seem to be correct.

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