



Molecular structure and vibrational spectra of 2, 4, 6 -trimethylbenzene sulphonyl chloride (FTIR & Raman) by quantum chemical calculations

K Sambathkumar*

Department of Physics, (Computational and Theoretical Divisions), A Govt Arts College, Villupuram 605 602, India

Received 1 November 2018; accepted 18 June 2020

The 2, 4, 6-trimethylbenzene sulphonyl chloride was characterized using IR and Raman spectral data. The molecular electrostatic potential surface of the 2,4,6-trimethylbenzene sulphonyl chloride (TMBS) has been visualized in electropositive potential in the region of the CH_3^+ group and most electronegative potential in the two oxygen atom has strong binding group. The HOMO and LUMO energies and electronic charge transfer confirms that local reactivity and global reactivity descriptors. The rate constant of 2, 4, 6-trimethylbenzene sulphonyl chloride shows strong temperature dependence. Molecular electrostatic potential (MEP) were also calculated for identification. Temperature dependence of various thermodynamic properties like ($C_{p,m}^\circ$, S_m° and (H_m°)) is increase with increase in temperature for the structure.

Keywords: TMBS, NMR, UV, HOMO – LUMO, MEP.

1 Introduction

Methyl benzene sulphonyl chlorides are mostly used as laboratory reagents. They are used as initiators in polymerization of methyl methacrylate. The substituent in benzene sulphonyl chloride leads to the variation of charge distribution among the molecule, the consequently affects the structural, electronic and vibrational parameters. The most important organo-sulfur compound is helpful to make organic synthesis of catalytic actions. TMBS possesses in biological activities, such as pesticides, pigment, fluorescent brighteners and also useful in dye industry for the bright colors as well as pharmaceutical use. It is used for disinfecting skin and for the treatment of minor wounds and abrasions, purification of drinking water in case of amoebicidal and bactericidal emergencies. It is highly toxic and harmful and affects the blood and central nervous system. Now-a-days TMBS is mainly used as an intermediate for agricultural chemicals in the manufacturing of insecticides. Due to its wide application and structural simplicity, a detailed spectral investigation of the molecule has been taken for the present study. In an earlier approach by Caminati *et al.*, the free jet millimeter wave spectrum of benzene sulphonyl chloride has been investigated in the 60–66 GHz frequency range. The NQR frequencies of trimethylbenzene sulphonyl chloride are investigated in the temperature range 100–240 K. The nuclear quadrupole resonance spectrum of sulphonyl chloride

has been measured over the temperature range 80–285 K. The empirical method is suggested for estimating the NQR frequencies of substituted sulphonyl chlorides¹⁻⁷. But electron diffraction structure analysis was carried out on benzene sulphonyl chloride, utilizing data from vibrational spectroscopic calculations. The proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. For this purpose, several theoretical ways are useful in analyzing vibrational spectra of organic molecules⁸⁻¹⁰. *Ab initio* molecular orbital calculation is relatively successful approach to the calculation of vibrational spectrum of closed shell organic molecules. However, the Hartree – Fock *ab initio* methods are able to give good results provided a reasonable basis set and an appropriate correlation treatment is taken into account. The most popular and accurate scaled *ab initio* approach is scaled quantum mechanical (SQM) force field procedure, which employs different scale factors for different coordinates^{11,12}. On the other hand, DFT methods, particularly hybrid functional method^{13,14} have evolved to powerful quantum chemical tool for the determination of the electronic structure of molecules. In the frame work of DFT approach, different exchange and correlation functionals are routinely used. Among these, the B3LYP combination is widely used. Since, it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard basis set

*Corresponding author: (E-mail: sa975kumar@gmail.com)

(6-311++G(d,p)) provide an excellent agreement between accuracy and computational efficiency of vibrational spectra for large and medium size molecules¹⁵⁻¹⁸. The aim of this work is to check the performance of B3LYP density functional force field for simulation of the IR and Raman spectra of title compound with the use of the standard 6-311++G(d,p) basis set.

2 Experimental Analysis

All chemicals were purchased from Sigma–Aldrich or Fluka Chemical Company with a stated purity of greater than 99% and it was used as such without further purification. The FT-IR spectra were recorded in the region of 400–4000 cm^{-1} on Perkin-Elmer Spektrum 100 BX, FT-IR spectrophotometer. The Raman spectrum is recorded in the wavenumber region 3500–100 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory operating at 1.5W power with Nd:YAG laser of wavelength 1064 nm is used as an excitation source.

3 Computational Details

For the all calculations, gaseous phase conditions have been considered at 1 ATM pressure and temperature of 298 K. Initially, primary structures have been designed by *Gauss view* software and for performing the final optimization, Gaussian 09 program package has been used¹⁹. Density functional theory (DFT) method at the level, B3LYP, with basis set of 6-311++G(d,p), has been used for performing the calculation. The routine work has been considered for the calculation of chemical displacement values modality, for which the related structure was optimized first and in the following the values of chemical displacement were calculated. For investigation of vibrational parameters modality and potential energy distribution (PED) structure analysis, VEDA 4 program was used²⁰. The values of electrostatic potential for different structures were studied which for this purpose, *Molekel* software package was used²¹.

4 Results And Discussion

4.1. Molecular Geometry

The molecular structure of TMBS having Cs symmetry is shown in Fig. 1. The global minimum energy obtained by DFT structure optimization for TMBS is calculated as -1357.968 Hartrees. The calculated optimized geometrical parameters obtained

in this study for the title compound is presented in Table 1. Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose the full set of 81 standard

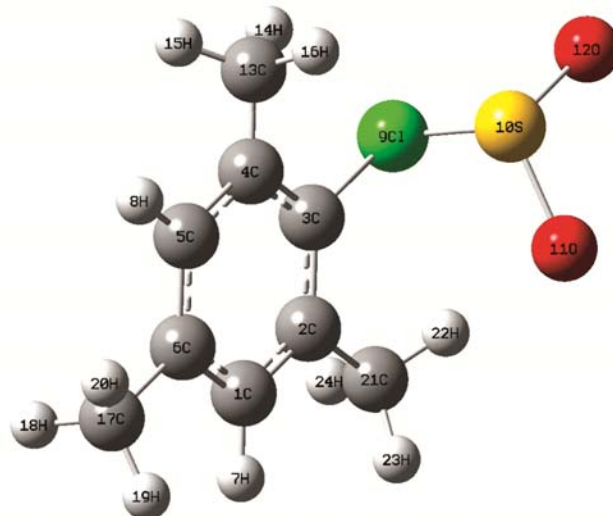


Fig. 1 — Optimized molecular structure of 2, 4, 6-trimethylbenzene sulphonylchloride.

Table 1 — Optimized geometrical parameters of 2,4,6-trimethylbenzene sulphonyl chloride obtained by B3LYP/6-311++G(d,p) density functional calculations

Bond length	Value(Å)	Bond angle	Value ⁰
C1–C2	1.40	C1–C2–C3	120.19
C2–C3	1.39	C2–C3–C4	120.05
C3–C4	1.40	C3–C4–C5	120.10
C4–C5	1.40	C4–C5–C6	119.68
C5–C6	1.40	C5–C6–C1	120.08
C6–C1	1.40	C2–C1–C17	119.22
C1–C7	1.76	C6–C1–C17	120.93
C17–S8	2.00	C17–S8–O9	109.86
S8–O9	1.66	C17–S8–O10	110.00
S8–O10	1.66	C1–C2–C11	119.67
C2–C11	1.54	C3–C2–C11	120.13
C11–H12	1.06	C2–C11–H12	109.12
C11–H13	1.06	C2–C11–H13	109.87
C11–H14	1.06	C2–C11–H14	109.65
C3–H15	1.06	C2–C3–H15	119.70
C4–C16	1.53	C4–C3–H15	120.24
C16–H17	1.06	C3–C4–C16	120.11
C16–H18	1.06	C5–C4–H16	119.78
C16–H19	1.06	C4–C16–H17	109.51
C5–H20	1.06	C4–C16–H8	109.40
C6–C21	1.53	C4–C16–H19	109.56
C21–C22	1.06	C4–C5–H20	120.27
C21–C23	1.06	C6–C5–H20	120.04
C21–C24	1.06	C5–C6–C21	119.82
		C1–C6–C21	120.09
		C6–C21–H22	109.93
		C6–C21–H23	109.61
		C6–C21–H24	108.99

For numbering of atom refer Fig. 1

internal coordinates (containing 15 redundancies) for the title compound are defined in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this set of vibrational coordinates and used in all subsequent calculations.

5 Vibrational Spectra

The structure of TMBS consists of 24 atoms and 66 normal vibrational parameters. FT-IR and Raman calculations on the structure were obtained using theoretical and experimental methods. The modality of vibrational peaks has been shown in Figs 2–3. Vibratory parameters of TMBS structure by DFT method at theoretical level, B3LYP were calculated and investigated in which for matching of obtained results with experimental results, appropriate conversion factors were used respectively²². As seen

in Table 4, theoretical and experimental results are consistent.

C-H vibrations — Vibratory parameters of C-H are observed in tensional and flexural forms. Usually, tensional vibrations appear in the range of 2850 to 3200 cm^{-1} . Depending on hybridization, vibrational

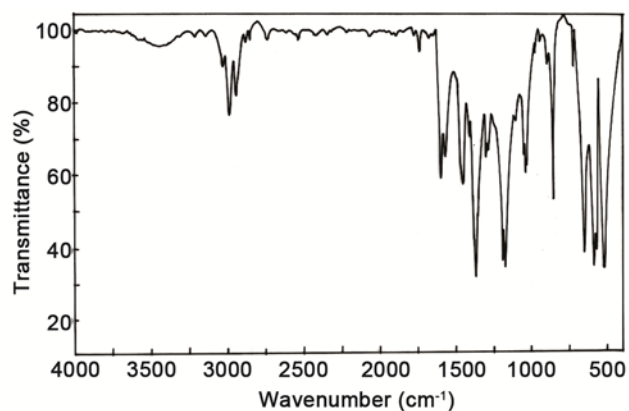


Fig. 2 — FTIR Spectrum of 2, 4, 6-trimethylbenzene sulphonylchloride.

Table 2 — Definition of internal coordinates of 2,4,6-trimethyl benzene sulphonyl chloride

No (i)	Symbol	Type	Definition
Stretching			
1 – 2	r_i	C-H	C3-H15, C5 – H20
3 – 11	R_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C2-C11, C4-C16, C6-C21
12-20	r_i	C-H (methyl)	C11-H12, C11-H13, C11-H11, C16-H17, C16-H18, C16-H19, C21-H22, C21-H23, C21-H24
21	Q_i	C-Cl	C1-C17
22	P_i	Cl-S	C17-S8,
23-24	U_i	S-O	S8-O9, S8-O10
Bending			
25–30	β_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
31-34	α_i	C-C-H	C2-C3-H15, C4-C3-H15, C4-C5-H20, C6-C5-H20
35-43	α_i	C-C-H (Methyl)	C2-C11-H12, C2-C11-H13, C2-C11-H14, C4-C16-H17, C4-C16-H18, C4-C16-H19, C6-C21-H22, C6-C21-H23, C6-C21-H24
44-52	δ_i	H-C-H	H12-C11-C2, H13-C11-C2, H14-C11-C2, H17-C16-C4, H18-C16-C4, H19-C16-C4, H22-C21-C6, H23-C21-C6, H24-C21-C6,
53-54	σ_i	Cl-S-O	C17-S8-O9, C17-S8-O10,
55	σ_i	O-S-O	O9-S8-O10
56-57	Σ_i	C-C-Cl	C2-C1-C17, C6-C1-C17,
58	ν_i	C-Cl-S	C1-C17-S8
59-64	λ_i	C-C-C	C1-C2-C11, C3-C2-C11, C3-C4-C16, C5-C4-C16, C5-C6-C21, C1-C6-C21
Out – of – plane bending			
65-66	ω_i	C-H	H15-C3-C2-C4, H20-C5-C4-C6,
67-69	ψ_i	C-C	C11-C2-C1-C3, C16-C4-C3-C5, C21-C6-C5-C1
70	ϕ_i	C-Cl	C17-C1-C2-C6
71	ρ_i	Cl-S	C17-S8-C1-C2
Torsion			
72-77	τ_i	t Ring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3
78	τ_i	tC-Cl-SO ₂	(C2-C6)-Cl-C17-S8-O9-O10
79-81	τ_i	tC-CH ₃	(C1-C3)-C2-C11-H12-H13-H14, (C3-C5)-C4-C16-H17-H18-H19, (C5-C1)-C6-C21-H22-H23-H24

For numbering of atom refer Fig. 1

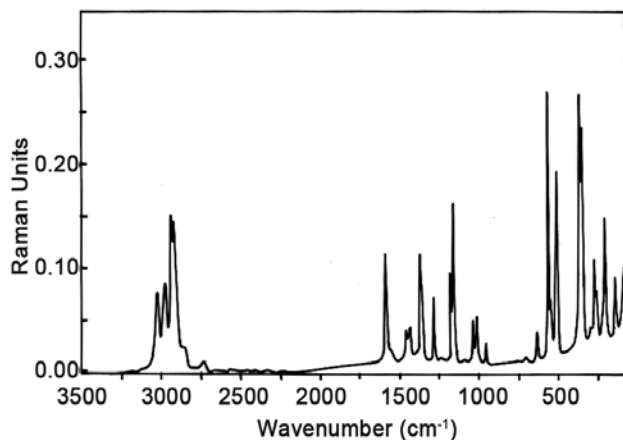


Fig. 3 — FT-Raman Spectrum of 2, 4, 6-trimethylbenzene sulphonylchloride.

parameter of CH with SP^3 , SP^2 and SP hybridization appear below the range of 3000, 3100 and 3200 cm^{-1} respectively. But it is expected that the flexural vibrations appear in the range of 1000 to 1300 cm^{-1} . But for TMBS structure, flexural vibrations have appeared in the range of 3188 and 3099 cm^{-1} , with different intensities, using FT-IR experimental method. The C-H in-plane and out-of-plane bending vibrations have also been identified and listed in Table 4.

C-C vibrations — The carbon-carbon stretching vibrations²² of the title compound are observed at 1660, 1638, 1595, 1564, 1295 and 1258 cm^{-1} in FTIR and 1598, 1470, 1292 cm^{-1} in FT-Raman. The in-plane and out-of-plane bending vibrations of carbon-carbon group are presented in Table 4. These assignments are in good agreement with the literature²³.

C-Cl vibrations — Tensional vibrations of C-Cl appear in the range of 800-600 cm^{-1} . It should be noted that aerial chlorine are expected to appear in the range of 1100 to 1305 cm^{-1} . Based on this, in the present study, the FTIR band identified at 886 cm^{-1} has been assigned to C-Cl stretching mode of vibration. The in-plane and out-of-plane bending vibrations have also been identified and presented in Table 4.

CH₃ group vibrations — For the assignments of the CH₃ group frequencies, nine fundamental vibrations can be associated to each CH₃ group. Three stretching, three bending, two rocking modes and a single torsional mode describe the motion of methyl group. The above modes are defined in Table 4. The CH₃ symmetric stretching frequency is identified at 2993, 2985, 2974 cm^{-1} and CH₃ in-plane stretching is established at 3062, 3033, 3015 cm^{-1} .

Table 3 — Definition of local symmetry coordinates and values of corresponding scale factors used to correct the refined B3LYP/6-311++G(d,p) force field for 2,4,6-trimethyl benzene sulphonyl chloride.

No	Symbol ^a	Definition ^b
1-2	CH	r_1, r_2
3-11	C-C	$R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11},$
12-14	CH ₃ ss	$(r_{12}+r_{13}+r_{14})/\sqrt{3}, (r_{15}+r_{16}+r_{17})/\sqrt{3},$ $(r_{18}+r_{19}+r_{20})/\sqrt{3}$
15-17	CH ₃ ips	$(2r_{12}+r_{13}+r_{14})/\sqrt{6}, (2r_{15}+r_{16}+r_{17})/\sqrt{6},$ $(2r_{18}+r_{19}+r_{20})/\sqrt{6},$
18-20	CH ₃ ops	$(r_{13}-r_{14})/\sqrt{2}, (r_{16}-r_{17})/\sqrt{2}, (r_{19}-r_{20})/\sqrt{2}$
21	C-Cl	Q_{21}
22	Cl-S	P_{22}
23	SO ₂ ss	$(U_{23}+U_{24})/\sqrt{2}$
24	SO ₂ ass	$(U_{23}-U_{24})/\sqrt{2}$
25	Rtrigd	$(\beta_{25}-\beta_{26}+\beta_{27}-\beta_{28}+\beta_{29}-\beta_{30})/\sqrt{6}$
26	Rsymd	$(-\beta_{25}-\beta_{26}+2\beta_{27}-\beta_{28}-\beta_{29}+2\beta_{30})/\sqrt{12}$
27	Rasymd	$(\beta_{25}-\beta_{26}+\beta_{28}-\beta_{29})/\sqrt{2}$
28-29	bCH	$(\alpha_{31}-\alpha_{32})/\sqrt{2}, (\alpha_{33}-\alpha_{34})/\sqrt{2}$
30-32	CH ₃ sb	$(-\alpha_{35}-\alpha_{36}-\alpha_{37}+\alpha_{44}+\alpha_{45}+\alpha_{46})/\sqrt{6}, (-\alpha_{38}-\alpha_{39}-$ $\alpha_{40}+\alpha_{47}+\alpha_{48}+\alpha_{489})/\sqrt{6}, (-\alpha_{41}-\alpha_{42}-$ $\alpha_{43}+\alpha_{50}+\alpha_{51}+\alpha_{52})/\sqrt{6}$
33-35	CH ₃ ipb	$(\delta_{44}-\delta_{45}-2\delta_{46})/\sqrt{6}, (-\delta_{47}-\delta_{48}-2\delta_{49})/\sqrt{6}, (\delta_{50}-$ $\delta_{51}-2\delta_{52})/\sqrt{6}$
36-38	CH ₃ opb	$(\delta_{44}-\delta_{45})/\sqrt{2}, (-\delta_{47}-\delta_{48})/\sqrt{2}, (\delta_{50}-\delta_{51})/\sqrt{2}$
39-41	CH ₃ ipr	$(2\alpha_{35}-\alpha_{36}-\alpha_{37})/\sqrt{6}, (2\alpha_{38}-\alpha_{39}-\alpha_{40})/\sqrt{6},$ $(2\alpha_{41}-\alpha_{42}-\alpha_{43})/\sqrt{6}$
42-44	CH ₃ opr	$(\alpha_{36}-\alpha_{37})/\sqrt{2}, (39-\alpha_{40})/\sqrt{2}, (\alpha_{42}-\alpha_{43})/\sqrt{2},$
45	SO ₂ rock	$(\sigma_{53}-\sigma_{54})/\sqrt{2}$
46	SO ₂ twist	$(\sigma_{53}+\sigma_{54})/\sqrt{2}$
47	SO ₂ sciss	$(2\sigma_{55}-\sigma_{53}-\sigma_{54})/\sqrt{6}$
48	bC-Cl	$(\Sigma_{56}-\Sigma_{57})/\sqrt{2}$
49	bCl-S	v_{58}
50-52	bCC	$(\lambda_{59}-\lambda_{60})/\sqrt{2}, (\lambda_{61}-\lambda_{62})/\sqrt{2}, (\lambda_{63}-\lambda_{64})/\sqrt{2},$
53-54	ω CH	ω_{65}, ω_{66}
55-57	ω CC	$\pi_{67}, \pi_{68}, \pi_{69}$
58	ω CCl	ϕ_{70}
59	ω Cl-S	ρ_{71}
60	t Rtrigd	$(\tau_{72}-\tau_{73}+\tau_{74}-\tau_{75}+\tau_{76}-\tau_{77})/\sqrt{6}$
61	t Rsym	$(\tau_{72}-\tau_{74}+\tau_{75}-\tau_{77})/\sqrt{2}$
62	t Rasym	$(-\tau_{72}+2\tau_{73}-\tau_{74}-\tau_{75}+\tau_{76}-\tau_{77})/\sqrt{12}$
63	SO ₂ wag	τ_{78}
64-66	tCH ₃	$\tau_{79}, \tau_{80}, \tau_{81}$

^a These symbols are used for description of normal modes by TED in Table 4

^b The internal coordinates used here are defined in Table 2

The CH₃ symmetric bending and CH₃ in-plane bending frequencies are attributed at 1379, 1368, 1365 cm^{-1} and 1456, 1446, 1442 cm^{-1} , respectively.

Table 4 — Assignment of fundamental vibrations of 2,4,6-trimethyl benzene sulphonyl chloride normal mode analysis based on SQM force field calculations using selectively scaled B3LYP/6-311++G(d,p) force field

Species Symmetry	Observed fundamentals (cm ⁻¹)		Calculated frequencies using B3LYP/ 6-311+G** force field (cm ⁻¹)		TED (%) among types of internal coordinates ^b
	FTIR	FT-Raman	Unscaled	Scaled ^a	
C _s					
A'	3188 (w)	--	3313	3192	v C-H (99)
A'	3099 (w)	--	3208	3097	v C-H (94)
A'	3062 (vw)	--	3149	3066	CH ₃ ips (93)
A'	--	3033 (w)	3137	3031	CH ₃ ips (95)
A'	3015 (vw)	--	3129	3015	CH ₃ ips (94)
A'	2993 (ms)	--	3083	2995	CH ₃ ss (92)
A'	--	2985 (w)	3067	2988	CH ₃ ss (91)
A'	--	2974 (w)	3050	2976	CH ₃ ss (90)
A'	1660 (vw)	--	1730	1655	vCC (90)
A'	1638 (vw)	--	1704	1634	vCC (89)
A'	--	1598(s)	1658	1596	vCC (88)
A'	1595 (ms)	--	1649	1591	vCC (87)
A'	1564 (vw)	--	1607	1569	vCC (86)
A'	--	1470(vw)	1511	1480	vCC (87)
A'	--	1456(vw)	1492	1452	CH ₃ ipb (86)
A'	--	1446(vw)	1478	1442	CH ₃ ipb (85)
A'	1442 (w)	--	1470	1440	CH ₃ ipb (84)
A'	1379 (ms)	--	1443	1374	CH ₃ sb (82)
A'	--	1368(vw)	1389	1365	CH ₃ sb (81)
A'	1365 (ms)	--	1385	1364	CH ₃ sb (83)
A'	1295 (w)	--	1310	1293	vCC (80)
A'	--	1292(ms)	1302	1290	vCC (81)
A'	1258 (w)	--	1276	1258	vCC (79)
A'	--	1251(vw)	1261	1249	bCH (78)
A'	1214 (w)	--	1246	1211	bCH (76)
A'	--	1198(w)	1232	1197	SO ₂ ass (75)
A'	--	1192(w)	1221	1185	SO ₂ ss (74)
A'	--	1153(w)	1176	1155	Rtrigd (72)
A'	1139 (w)	--	1163	1143	Rsymd (73)
A'	--	1120(vw)	1143	1118	Rasynd (71)
A'	1050 (vw)	1049 (w)	1070	1048	CH ₃ ipr (70)
A'	1042 (vw)	--	1059	1036	CH ₃ ipr (69)
A'	1033 (vw)	--	1045	1029	CH ₃ ipr (68)
A'	886 (w)	--	898	888	vCCl (67)
A'	--	846 (vw)	859	845	vClS (66)
A'	700 (ms)	700 (vw)	721	702	SO ₂ sciss (67)
A'	636 (vw)	--	645	636	bCC (68)
A'	628 (s)	--	633	623	bCC (69)
A'	--	619 (w)	627	615	bCC (67)
A'	555 (w)	558 (vw)	563	550	SO ₂ rock (65)
A'	--	548 (w)	555	545	bCCl (64)
A'	517 (s)	517 (vs)	530	515	bClS (63)
A''	2965 (ms)	--	3041	2970	CH ₃ ops (65)
A''	2952 (vw)	--	3024	2950	CH ₃ ops (63)
A''	2941 (vw)	--	3009	2935	CH ₃ ops (64)
A''	1189 (w)	1188 (w)	1211	1180	CH ₃ opb (61)
A''	1176 (w)	--	1203	1176	CH ₃ opb (62)
A''	--	1172 (v)	1197	1169	CH ₃ opb (60)
A''	--	984 (w)	994	980	CH ₃ opr (59)
A''	--	967 (w)	980	967	CH ₃ opr (58)
A''	955 (w)	--	964	953	CH ₃ opr (57)

Contd.

Table 4 — Assignment of fundamental vibrations of 2,4,6-trimethyl benzene sulphonyl chloride normal mode analysis based on SQM force field calculations using selectively scaled B3LYP/6-311++G(d,p) force field (Contd.)

Species Symmetry	Observed fundamentals (cm ⁻¹)		Calculated frequencies using B3LYP/ 6-311+G** force field (cm ⁻¹)		TED (%) among types of internal coordinates ^b
	FTIR	FT-Raman	Unscaled	Scaled ^a	
C _s					
A''	--	873 (w)	881	875	ωCH (59)
A''	859 (vs)	--	865	861	ωCH (60)
A''	665 (vw)	--	661	662	SO ₂ wag (59)
A''	581 (s)	581 (vs)	592	578	tRtrigd (59)
A''	--	575 (vw)	583	573	tRsymd (57)
A''	569 (w)	--	576	567	tRasynd (55)
A''	373 (vw)	374 (vs)	374	374	ωCC (56)
A''	368 (vw)	--	363	366	ωCC (54)
A''	--	359 (s)	356	358	ωCC (55)
A''	--	332 (vw)	328	334	ωCCl (56)
A''	319 (vw)	320 (vw)	320	320	ωClS (57)
A''	280 (vw)	280 (w)	288	278	SO ₂ twist (58)
A''	268 (vw)	268 (vw)	265	266	tCH ₃ (54)
A''	233 (vw)	--	231	232	tCH ₃ (55)
A''	--	215 (s)	218	214	tCH ₃ (52)

Abbreviations

v-stretching; ss-symmetric stretching; ass-antisymmetric stretching; b-bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; ω-out-of-plane bending; t-torsion; ips-in-plane stretching; ops-out-of-plane stretching; sb-symmetric bending; ipb-in-plane bending; opb-out-of-plane bending; ipr-in-plane rocking; opr-out-of-plane rocking; vs – very strong; s – strong; ms – medium strong; m – medium; w-weak; vw-very weak.

These assignments are also supported by literature²². The in-plane rocking and out-of-plane rocking modes of CH₃ group are found at 1050, 1042, 1033 cm⁻¹ and 984, 967, 955 cm⁻¹ respectively. The bands obtained at 2965, 2952, 2941 cm⁻¹ in IR and 1189, 1176, 1172 cm⁻¹ are assigned to CH₃ out-of-plane stretching and CH₃ out-of-plane bending modes, respectively. The assignment of the bands at 268, 233, 215 cm⁻¹ is attributed to methyl twisting mode.

SO₂ group vibrations — Sulfoxides, sulfones, sulfonyl chlorides, sulfates and sulfonamides have exhibit the S-O stretching vibrations around 1375-1300 cm⁻¹ and 1200–1140 cm⁻¹ at 1198 and 1192 cm⁻¹ are assigned to the asymmetric and symmetric stretching modes of SO₂ group, respectively. The band appeared at 700 cm⁻¹ in both IR and Raman spectra are assigned to the scissoring modes of SO₂ group for the title compound. The SO₂ rocking modes have been assigned at 555 cm⁻¹ and 558 cm⁻¹ in IR and Raman spectra, respectively. The IR and Raman band for wagging and twisting modes of SO₂ group are assigned at 665 cm⁻¹ and 280 cm⁻¹, respectively.

Ring vibrations — Most of the ring modes are affected by the substitutions in the aromatic ring of the title compound. In the present study, the bands identified at 1153, 1139, 1120 cm⁻¹ and 581, 575, 569 cm⁻¹ have been designated to ring in-plane and out-of-

plane bending modes, respectively, by careful consideration of their quantitative descriptions. A small changes in force constant / reduced mass ratio, resulting mainly due to addition of sulfonyl group to benzene and from different extents of mixing between ring and substituent group vibrations.

5.1. Transport properties

The spatial distribution of the frontier orbital is a three dimensional representation of local electron density of the molecule. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) are the frontier orbital's, the difference between them are known as HOMO-LUMO gap (HLG). HLG determines the transport properties of the molecule. Large decrease in the HLG predicts the possibility of having reasonable conduction through the molecule, since, the conductivity increases with decreases in HLG. So the field increases the HLG extensively decreases by using Gaussian 09 programme package. Figure 4 illustrates the spatial distribution of the molecular orbital of the molecule. Table 5, shows the small HLG exists in this molecular system, the possibility of conduction through the molecules is found to be very less, therefore, it almost act as an insulator.

Electric fields on HOMO-LUMO analysis

The analysis of the wave function is mainly described by one-electron excitation from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital. HOMO-LUMO analysis of these compound is done at B3LYP/6-311++G(d,p) level. HOMO is delocalized mainly on ring carbons; the oxygen of Cl also takes part in the formation of HOMO of TMBS Fig.4. The strong electron withdrawing group O of benzene ring attracts the charge density while on other hand electron donating group Cl is attached on left hand of TMBS which would strengthen the donor ability. Hence LUMOs are distributed on the benzene ring group. In TMBS, HOMO is delocalized mainly on ring carbons and there is no distribution of HOMO on benzene

Table 5 — HOMO - LUMO energy gap and related molecular properties of 2,4,6-trimethylbenzene sulphonyl chloride.

Molecular Properties	B3LYP/6-311++G(d,p)
HOMO	-0.3739a.u
LUMO	-0.1871a.u.
Energy gap	-0.1868 a.u.
Ionisation Potential (I)	0.3739 a.u.
Electron affinity(A)	0.1871a.u.
Global softness(s)	10.7066 a.u.
Global Hardness (η)	0.0934 a.u.
Chemical potential (μ)	-0.2805 a.u.
Global Electrophilicity (ω)	0.4207 a.u.

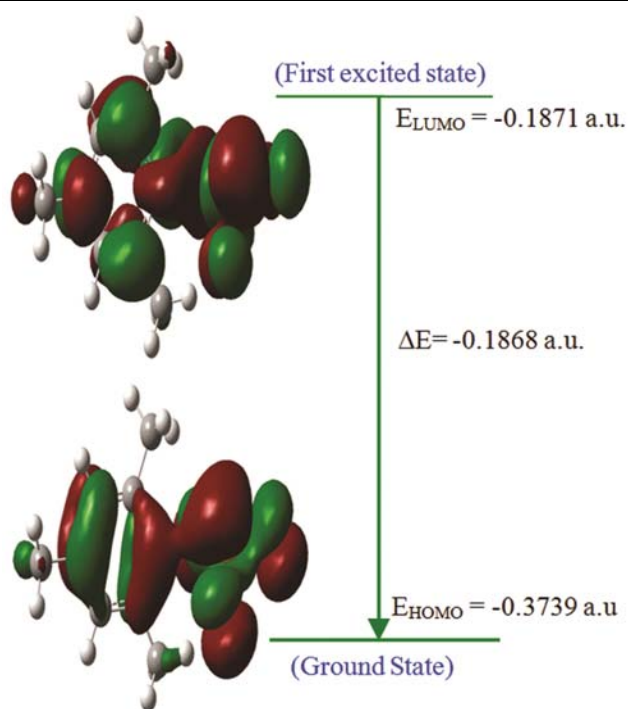


Fig. 4 — Homo-Lumo of 2, 4, 6-trimethylbenzene sulphonylchloride.

ring. Fig. 4 shows that there is no electronic projection in HOMO and LUMO over the ring hydrogen atoms of the compound in zero fields. The values of HOMO energy, LUMO energy and HLG are used as an indicator of kinetic stability of the molecule. This shows that substituted Cl has no effect on the title compound when the HOMO-LUMO gap (HLG) extensively decreases from -0.3739 (a. u.) to -0.1871 (a. u.) for TMBS, respectively (Table 5). This large decrease in the HLG implies that the possibility of having reasonable conduction through the molecule, hence the conductivity increases with decreases in HLG.

5.2. Mulliken charges

The Mulliken psychoanalysis is the finest population analysis method. The electron population of each atom of the molecules is identifying, because of calculating the Mulliken charges are explained by the density functional methods. The charge distribution of the TMBS gives the Carbon and Hydrogen charges had both signs. Oxygen atoms have negative charges in all basic sets, which are donor atoms. Mulliken atomic charge computation play a vital role in the relevance of quantum chemical calculation to molecular system because of atomic charge effect, dipole moment, molecular polarizability, electronic structure of the molecular systems. By using the Gaussian output shown in the Table.6. The molecule has different charge distribution with respect to the dynamic basic sets for quantum calculations. The predicted atomic charges are in graphical representation (Fig. 5). To change the basic set, the charge distribution should be changed. The charge change with origin set due to polarization For illustration, the charge of H(17) and H(19) atoms are

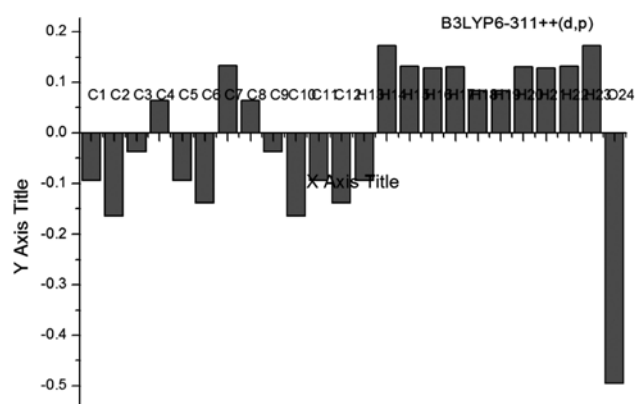


Fig. 5 — Mulliken plot of 2, 4, 6-trimethylbenzene sulphonylchloride.

0.130662, 0.083890 at B3LYP/6-311+G(d,p) in the title compound TMBS. Thus the charges of the atoms are not varied according to electric field.

5.3 Molecular electrostatic potential (MEP)

Electrostatic potential indicates molecule charge distribution in three-dimensions. Indeed this map enables people to diagnose and investigate the distribution of atoms charge in the different parts of the molecule. However, the prediction of behavior and performance of the molecule in chemical reactions could be done by this map²³. For calculating and displaying this map, initially the related structure has been optimized using density functional theory and in the following the electrostatic potential map has been calculated and recorded by *Molekel* program. As this map shows the modality of charge distribution for different parts of molecule is at the theoretical level of B3LYP. Hydrogen atoms in this map have the minimum level of electrostatic potential and oxygen atoms have the maximum level of electrostatic potential. In addition, chlorine atom is seen in green color and is in the middle range of electrostatic potential level. In addition, sulphur atom related to the benzene group is seen approximately yellow in the electrostatic potential map and approximately have more negative level than chlorine

Table 6 — The charge distribution calculated by the Mulliken atomic charges method for 2,4,6-trimethylbenzene sulphonyl chloride DFT/6-311+(d,p) basis set.

Atoms	B3LYP/6-311++G(d,p)
C1	-0.094848
C2	-0.165242
C3	-0.037782
C4	0.064479
C5	-0.094767
C6	-0.138847
Cl7	0.133699
S8	0.064479
O9	-0.037782
O10	-0.165242
C11	-0.094848
H12	-0.138847
H13	-0.094767
H14	0.173397
H15	0.131973
C16	0.127852
H17	0.130662
H18	0.083890
H19	0.083890
H20	0.130662
C21	0.127852
H22	0.131973
H23	0.173397
H24	-0.495232

atom. The potential increases in the order red < orange < yellow < green < cyan < blue. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Figs.6-8. As

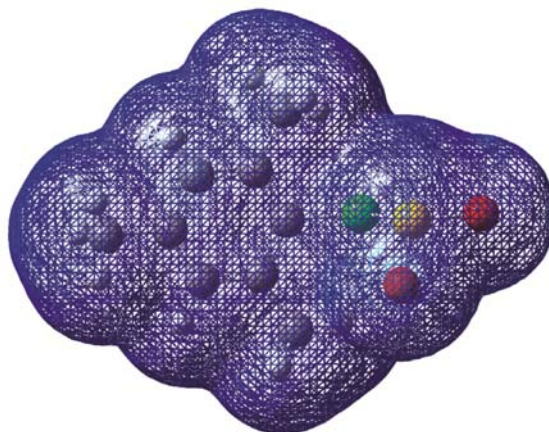


Fig. 6 — The total electron density surface of 2, 4, 6-trimethylbenzene sulphonylchloride.;

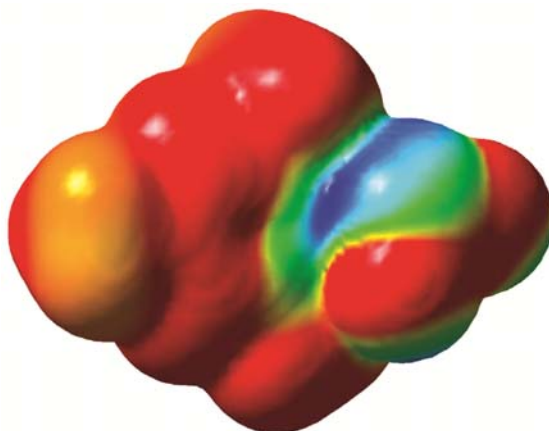


Fig. 7 — The molecular electrostatic potential surface of 2, 4, 6-trimethylbenzene sulphonylchloride.

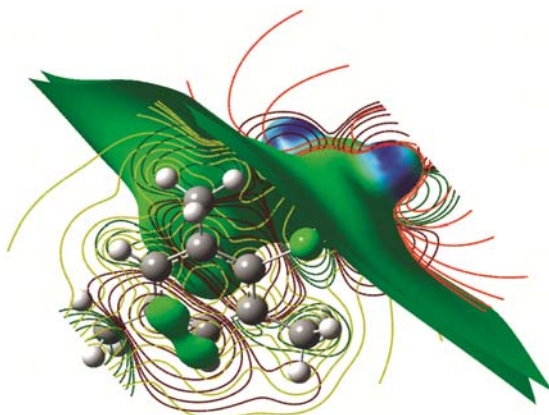


Fig. 8 — The contour map of electrostatic potential surface of 2, 4, 6-trimethylbenzene sulphonylchloride.

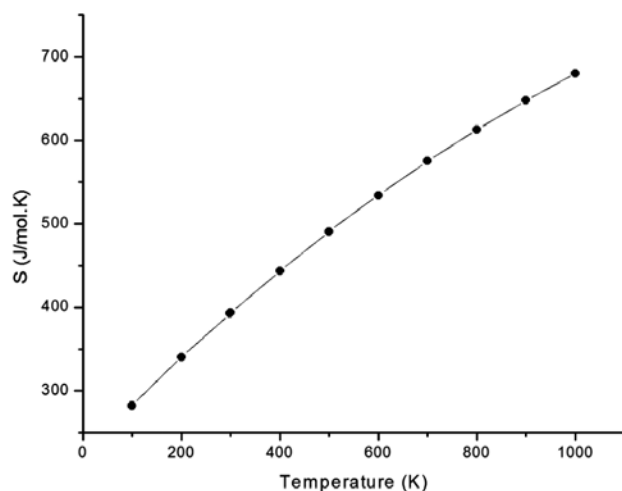


Fig. 9 — The effect of temperature on entropy (S) of 2, 4, 6-trimethylbenzene sulphonylchloride.

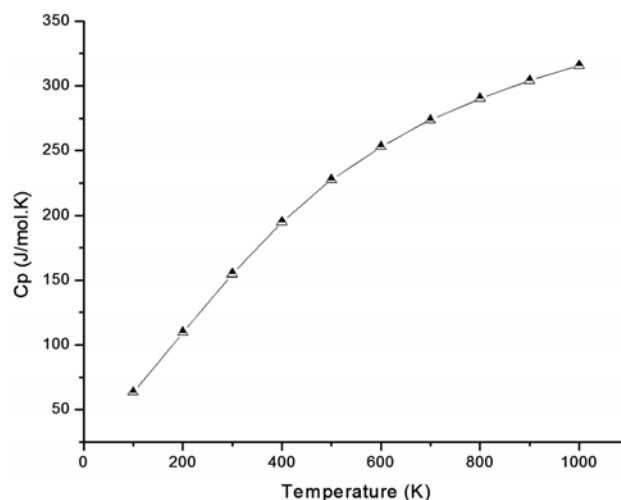


Fig. 10 — The effect of temperature on heat capacity (C_p) of 2, 4, 6-trimethylbenzene sulphonylchloride.

Table 7 — Thermodynamic properties of 2,4,6-trimethylbenzene sulphonyl chloride determined at different temperatures with B3LYP/6-311++G(d,p) level.

T (K)	S (J/mol.K)	C_p (J/mol.K)	$\Delta H_{0 \rightarrow T}$ (kJ/mol)
100.00	275.97	58.87	4.19
200.00	330.74	107.40	12.37
298.15	384.56	167.23	25.79
300.00	385.60	168.40	26.11
400.00	442.49	228.95	46.02
500.00	499.33	280.77	71.60
600.00	499.33	280.77	71.60
700.00	554.37	322.69	101.85
800.00	656.17	383.77	172.91
900.00	702.72	406.41	212.45
1000.00	746.55	425.35	254.07

can be seen from the figure, this molecule has several possible sites, C and O atoms for electrophilic attack.

5.4 Thermodynamic properties

Standard statistical thermodynamics function, heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy changes (H_m^0) (monomer and dimer) were computed at B3LYP/6-311++G(d,p) basis set by using perl script THERMO.PL²⁴ and are listed in Table 7. Thermodynamic functions are all values increasing with temperature ranging from 100 to 1000K due to the fact that the molecular vibrations intensities increase with temperature. The correlation equation among heat capacities, entropies, enthalpy changes with temperatures were fitted by quadratic formulas and the corresponding fitting factors (R^2) these thermodynamic properties are respectively. The correlations plot of those shown in Figs 9-11.

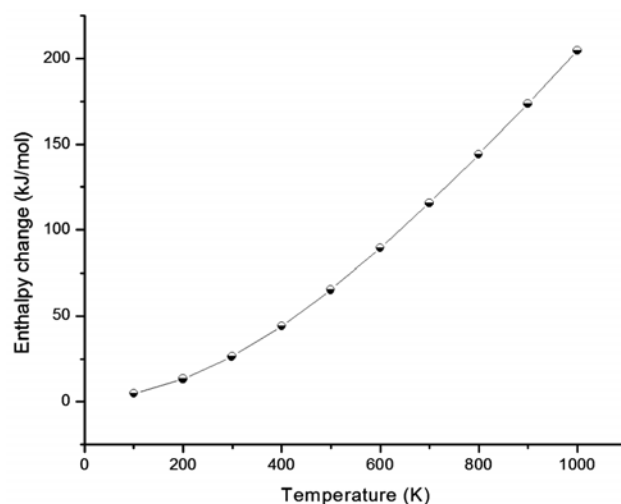


Fig. 11 — The effect of temperature on enthalpy change ($\Delta H_{0 \rightarrow T}$) of 2, 4, 6-trimethylbenzene sulphonylchloride.

$$S_m^0 = 215.23396 + 0.64772T - 0.00338 \times 10^{-5} T^2 \quad (R^2 = 0.99884)$$

$$C_{p,m}^0 = 8.94698 + 0.58974T + 3.63885 \times 10^{-5} T^2 \quad (R^2 = 0.99886)$$

$$H_m^0 = -2.8146 + 0.51434T - 2.72041 \times 10^{-5} T^2 \quad (R^2 = 0.9994)$$

Conclusion

A complete vibrational, molecular structure analysis of TMBS has been performed, based on the quantum chemical approach by DFT (B3LYP) calculations. The spectral characterization studies such as FTIR, FT-Raman for TMBS have been

carried out. A good agreement between experimental and theoretical normal modes of vibrations has been observed. The vibrational frequencies of the fundamental modes of the compound are precisely assigned and analysed and the theoretical results are compared with the experimental frequencies. The energies of important MO's, absorption wavelength, oscillator strength and excitation energies of the compound are also determined from TDDFT method and compared with the experimental values. The electric field influence is noticed in HOMO-LUMO gaps of TMBS. The HOMO-LUMO gap values are -0.1868 a.u.. for TMBS, respectively as the electric field increases. MEP study shows that the electrophilic attack takes place at the O position of TMBS.

Reference

- Rimmer S & Ebdon J R, *J Polym Sci Part A Polym Chem*, 34 (1996) 3585.
- www.chemicaland21.com/specialty_chem/Benzenesulfonyl_chloride.html.
- www.frankmckinnon.com/benzenesulfonyl_chloride.htm.
- Caminati W, Maris A, Millemaggi A & Favero P G, *Chem Phys Lett*, 243 (1995) 302.
- Brunetti A H & Pusiol D J, *J Mol Struct*, 96 (1983) 293.
- Pusiol D J & Brunetti A H, *J Mol Struct*, 81 (1982) 131.
- Srihari D, Rarnanamurthi, Venkatacharplu P & Pmmaswarup D, *Indian J Pure Appl Phys*, 20 (1982) 71.
- Shin D N, Hahn J W, Jung K H & Ha T K, *J Raman Spectrosc*, 29 (1998) 245.
- Hetre W J, Radom L O, Schleyer P V R & Pople J A, *Abinitio Molecular Orbital Theory*, Wiley, New York, 1986.
- Ziegler T, *Chem Rev*, 91 (1991) 651.
- Jones R O & Gunnarsson D, *Rev Mol Phys*, 61 (1989) 689.
- Handy N C, Murray C W & Amos R D, *J Phys Chem*, 97 (1993) 4392.
- Zhengyu Z & Dongmet D. *J Mol Struct Theochem*, 505 (2000) 247.
- Zhengyu Z, Aiping D & Nongmei, *Int J Quant Chem*, 78 (2000) 186.
- Healy E F & Holder H, *T Molstruct*, 281 (1993) 141.
- Harris N J, *J Phys Chem*, 99 (1995) 14689.
- Finley J W & Stephens P J, *J Mol Strut Theochem*, 157 (1995) 225.
- Jones M, Organic Chemistry, (Norton Company).
- Frisch M J, Trucks G W, Schlegel H B, et al, GAUSSIAN 09, Revision A.02, Gaussian, Inc, Wallingford CT, 2009.
- Jamroz M H, Vibrational Energy Distribution Analysis, VEDA 4, Warsaw, (2004).
- Zarei G, Soleymani R, Dehghaniyan R & Dejeje N M R, *J Chem*, 28 (2012) 1229.
- Sambathkumar K, *Density Functional Theory Studies of Vibrational Spectra, Homo- Lumo, NBO and NLO Analysis of Some Cyclic and Heterocyclic Compounds*, Bharathidasan University, Tiruchirappalli, 2014.
- Sambathkumar K, *Spectrochim Acta A*, 147 (2015) 51.
- Sambathkumar K & Nithiyanantham S, *J Mater Sci: Mater Electron*, 28 (2017) 6529.