

Molecular structure, vibrational spectroscopic (FT-IR, FT-Raman), and NBO analysis of 4-acetylthioanisole by density functional method

G.Saravanan¹, F.Liakath Ali Khan², A.Md. Sabeelullah Roomy³

¹Research Scholar, Department of Physics, Islamiah College (Autonomous), Vaniyambadi, India
phone: 09360224696

²Associate Professor, Department of Physics, Islamiah College (Autonomous), Vaniyambadi, India.
phone: 09445913721

³Research Scholar, Department of Physics, Islamiah College (Autonomous), Vaniyambadi, India
Phone: 09487105224

ABSTRACT

The molecular structure, vibrational frequencies, corresponding vibrational assignments of 4-acetylthioanisole (4ATA) have been investigated by using density functional theory (B3LYP) methods at 6-311G(d,p) and 6-311++G(d,p) basis sets. The vibrational band assignments have been made by using normal coordinate vibrational analysis. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The theoretical NMR spectra of the 4ATA molecule were carried out by using B3LYP functional with 6-311G(d,p) and 6-311++G(d,p) basis sets. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. Besides, Mulliken charges were also calculated by the DFT method and the infrared and Raman intensities have also been reported.

Keywords: B3LYP, HOMO, LUMO, NBO

Corresponding author: G.Saravanan

1.Introduction

Anisole is an aromatic compound containing an ether group. The IUPAC name of thioanisole is methyl phenyl sulphide. Its molecular formula is $C_6H_5SCH_3$. Its molecular weight is 124.20. Anisole and its derivatives are used as solvents and in perfumery, insect repellent, oxide, photo indicators and agrochemicals. Decontamination of toxic chemicals [1,2] is done by oxidation of thioanisole.

The title is about 4-acetylthioanisole used as solvent of both extraction and reaction as well as an intermediate for the synthesis of textile chemicals, pharmaceuticals and agrochemicals.

Agathe et al[3] discovered a reaction for new thio substituted compounds. The minimum energy structures were fully utilized and the MP2 method was used to analyse the DFT results. The equilibrium geometries IR and Raman scattering intensity were computed using the Gaussian 03 package.

Information from various sources shows that DFT calculation on 4-acetylthioanisole have not been reported so far. The molecular parameters (bond length, bond angle, dihedral angles), the HOMO energy[E HOMO], the LUMO [E LUMO], the energy gap between E HOMO and E LUMO of the title compound were studied by DFT(B3LYP) method with 6-311G(d,p) and 6-311++G(d,p) as basis sets. The redistribution of electron density in different bonding and antibonding orbitals and E2 energies are calculated by Natural bondorbital(NBO) analysis using DFT method to give a clear proof of stabilization starting from the hyper conjugation of various intra molecular interactions. The theoretical NMR spectra and the Mulliken charge were calculated by the DFT method.

2. Computation details:

To have accuracy and to get the desired result, theoretical methods and basis sets are employed. DFT is useful in finding the electronic structure of molecules. The density functional theory uses B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) as basis sets. This method was also used to calculate the properties of studied molecules in this work. All the calculation were done using the Gaussian 03W program packages[4] with the default convergence criteria without any constraint on the geometry[5]. For B3LYP functional selected as the one which gives the most accurate results with the expanded 6-311G(d,p) and 6-311++G(d,p) as basis set.

3. Results and Discussion.

3.1 Molecular Geometry

The optimized molecular structure of 4 ATA is shown in figure-1. Since no experimental values are available, the geometrical parameters of 4 ATA have been investigated by theoretical methods such as B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) as basis set and the values are tabulated in Table-1.

Due to larger atomic radius of sulphur, the S11-C12 bond possesses higher value comparing to other bond length values(1.8209 Å and 1.8211 Å by B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) respectively).

The highest bond angle possessed by C4-C3-S11 (124.49 and 124.51 at B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) respectively). In the absence of experimental values, the theoretically calculated bond lengths, bond angles and dihedral angles are mutually correlate with each other.

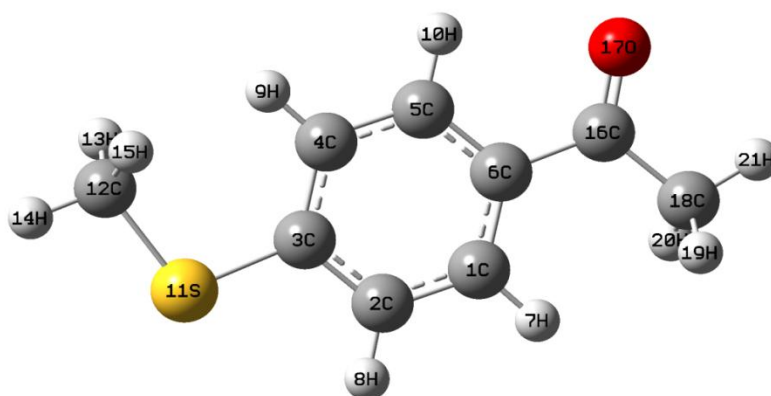


Fig.1.Optimized structure of 4-acetylthioanisole

Table 1 : Comparison of geometrical parameters of 4-ATA performed at theB3LYP 6-311G(d,p) and B3LYP 6-311++G(d,p)

Parameters	B3LYP 6-311 G(d,p)	B3LYP 6 -311++G(d,p)
Bond length		
C1-C2	1.3861	1.3867
C2-C3	1.4031	1.4038
C3-C4	1.4014	1.4022
C4-C5	1.3875	1.3882
C5-C6	1.3994	1.4003
C1-C6	1.4026	1.4034
C1-H7	1.0833	1.0833
C2-H8	1.0844	1.0844
C4-H9	1.0818	1.0818
C5-H10	1.0833	1.0834
C3-S11	1.7764	1.7744
S11-C12	1.8209	1.8211
C12-H13	1.0902	1.0903
C12-H14	1.0901	1.0902
C12-H15	1.0902	1.0903
C6-C16	1.4958	1.4949
C16-O17	1.2164	1.2185
C16-C18	1.5194	1.5186
C18-H19	1.0939	1.0940
C18-H20	1.0939	1.0940
C18-H21	1.0886	1.0887
Bond Angle		
C2-C1-C6	120.95	121.00
C2-C1-H7	118.63	118.58
C6-C1-H7	120.42	120.42

C1-C2-C3	120.41	120.41
C1-C2-H8	119.85	119.82
C3-C2-H8	119.75	119.77
C2-C3-C4	119.01	118.96
C2-C3-S11	116.50	116.53
C4-C3-S11	124.49	124.51
C3-C4-C5	120.10	120.15
C3-C4-H9	120.10	120.15
C5-C4-H9	119.13	119.09
C4-C5-C6	121.31	121.30
C4-C5-H10	120.58	120.37
C6-C5-H10	118.11	118.33
C1-C6-C5	118.23	118.19
C1-C6-C16	123.29	123.03
C5-C6-C16	118.48	118.78
C6-C16-O17	120.78	120.80
O17-C16-C18	120.50	120.40
C16-C18-H19	111.00	110.96
C16-C18-H20	111.00	110.96
C16-C18-H21	108.53	108.71
C3-S11-C12	103.81	103.89
S11-C12-H13	111.45	111.49
S11-C12-H14	105.24	105.20
S11-C12-H15	111.45	111.49
Dihedral Angle		
C6-C1-C2-C3	0.0	0.0
C6-C1-C2-H8	180.0	-180.0
H7-C1-C2-C3	180.0	180.0
H7-C1-C2-H8	0.0	0.0
C2-C1-C6-C5	0.0	0.0
C2-C1-C6-C16	-180.0	180.0
C1-C6-C16-C18	-0.00494	0.0
C1-C6-C16-O17	180.0	-180.0
C5-C6-C16-O17	-0.00491	0.0
C5-C6-C16-C18	180.0	-180.0
C6-C16-C18-H19	-59.71	-59.71
C6-C16-C18-H20	59.74	59.71
C6-C16-C18-H21	-180.0	180.0
O17-C16-C18-H19	120.28	120.29
O17-C16-C18-H20	-120.26	-120.29
O17-C16-C18-H21	0.0	0.0
C1-C2-C3-C4	0.0	0.0
H8-C2-C3-C4	-180.0	-180.0
H8-C2-C3-S11	0.0	0.0
C1-C2-C3-S11	-180.0	-180.0
C2-C3-S11-C12	-180.0	180.0

C4-C3-S11-C12	0.0	0.0
C3-S11-C12-H13	62.08	62.10
C3-S11-C12-H14	180.0	-180.0
C3-S11-C12-H15	-62.08	-62.10
C2-C3-C4-C5	0.0	0.0
C2-C3-C4-H9	-180.0	180.0
C3-C4-C5-C6	0.0	0.0
C3-C4-C5-H10	180.0	-180.0
H9-C4-C5-C6	180.0	180.0
H9-C4-C5-H10	0.0	0.0

3.2 HOMO and LUMO analysis:

HOMO and LUMO are very useful parameters in quantum chemistry. They are known as frontier orbitals because of their interaction with other species. HOMO is an electron donar, while LUMO is an electron acceptor[6]. The HOMO and LUMO energy calculated by B3LYP/6-311G(d,p) and B3LYP/6-311++G(g,p) method are mentioned in Table-2. This electronic transition absorbtion corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from HOMO to LUMO. In the present study the HOMO values at B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) are -0.221 and -0.221 respectively. The LUMO values for the above mentioned parameters are -0.299 and -0.299 respectively as tabulated in Table-2. The atomic compositions of the frontier molecular orbital are shown in Figure-2.

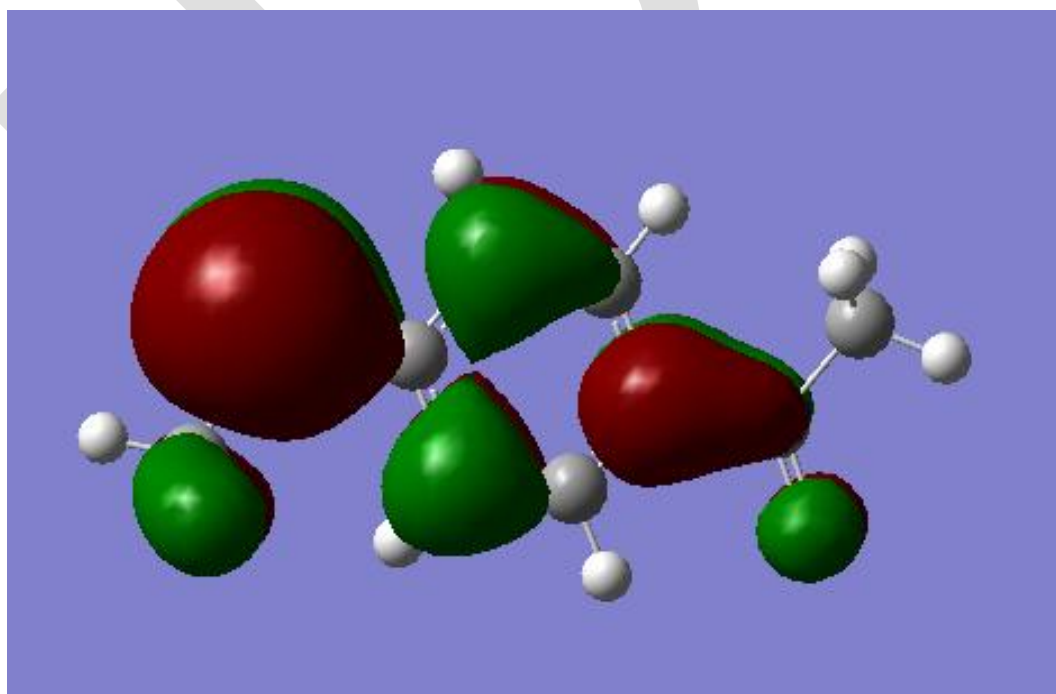


Fig2: HOMO, LUMO values of 4-acetyl thioanisole computed at B3LYP6-311++g(d,p)

Table 2 Theoretically computed values of HOMO and LUMO energy for 4-ATA

Methods	B3LYP 6-311 G(d,p)	B3LYP 6-311++G(d,p)
HOMO	-0.221	-0.221
LUMO	-0.299	-0.299
ENERGY GAP(ΔE)	-0.078	-0.078

3.3. NBO Analysis

NBO analysis gives the accurate possible natural Lewis structure picture of ϕ , because all orbitals are mathematically chosen to include the highest possible percentage of the ED. Interaction between both filled and virtual orbital spaces information is correctly explained by the NBO analysis and it could enhance the analysis of intra and inter-molecular interactions. The second order Fock matrix was carried out to evaluate donor (i) – acceptor (j) i.e. donor level bonds to acceptor level bonds interaction in the NBO analysis [7]. The result of interaction is a loss of occupancy from localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E(2)$ associates with the delocalization $i \rightarrow j$ is estimated as:

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, ϵ_j and ϵ_i are diagonal elements; and $F(i, j)$ is the off diagonal NBO Fock matrix element.

NBO analysis provides an efficient method for studying intra and inter-molecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second-order micro-disturbance theory are reported [8,9]. The larger $E(2)$ value the more intensive is the interaction between electron donors and acceptors i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [10]. Delocalization of ED between occupied Lewis – type (bond or lone pair) NBOs and formally unoccupied (anti bond or Rydberg) non Lewis NBOs correspond to a stabilizing donor-acceptor interaction.

NBO analysis has been performed on the 4-ATA molecule at the DFT/B3LYP/6-311++G(d,p) level in order to elucidate, the intra-molecular rehybridization and delocalization of ED within the molecule. The C2-H8 donar orbital has 1.98e as ED, which stabilizes the maximum energy of 4.61kJ/mol during σ electron interaction with antibonding C3-C4 orbital. There occurs a strong intra-molecular hyperconjugative interaction of π^* (C5-H10) which has a value of ED as 1.67e, that weakens the respective bond. The increased ED transfers less energy during the intra-molecular interaction. The $E(2)$ values and types of the transition are shown in Table-3.

Table 3: Second order perturbation theory analysis of Fock matrix in NBO basis for 4-ATA using B3LYP/6-311++G(d,p)

Donor (i)	Type	ED/e	Acceptor (j)	Type	E(2) ^a (kJmol ⁻¹)	E(j)-E(i) ^b (a.u)	F(i,j) ^c (a.u)
C1-C2	σ	1.97	C1-C6	σ*	3.25	1.27	0.057
C1-C2			C1-H7		0.84	1.12	0.027
C1-C2			C2-H8		0.96	1.11	0.029
C1-C2	σ	1.97	C5-S11	σ*	4.55	0.91	0.057
C1-C6			C5-H10		2.44	1.12	0.047
C1-H7	σ	1.98	C5-C6	σ*	4.51	1.09	0.063
C2-H8	σ	1.98	C3-C4	σ*	4.61	1.08	0.063
C3-C4	π	1.67	C5-H10	π*	2.15	1.13	0.044
C4-H9	σ	1.98	C5-C6	σ*	3.43	1.09	0.055
C5-C6	σ	1.97	C16-O17	σ*	0.86	1.29	0.030
C6-C16	σ	1.98	C1-C2	σ*	2.52	1.21	0.049
S11-C12	σ	1.99	C2-C3	σ*	2.27	1.20	0.047
C16-O17	σ	1.99	C18-H20	σ*	1.51	0.80	0.031
C18-H21		1.99	C16-O17	σ*	0.84	1.09	0.027

^aE(2) means energy of hyper conjugative interaction (stabilization energy)

^bE(j)-E(i) Energy difference between donor and acceptor i and j NBO orbitals.

^cF(i,j) is the Fock matrix element between i and j NBO orbitals.

3.4. NMR Spectra Analysis

The molecular structure of 4-ATA is optimized by using B3LYP method with 6-311G(d,p) and 6-311++G(d,p). GIAO ¹³C and ¹H chemical shift calculations of the title compound is made by using B3LYP method in conjunction with 6-311G(d,p) and 6-311++G(d,p) basis set [11]. The theoretical NMR Spectra calculations were performed by using the Gaussian03 program package.

The Spectral value of all the atoms like Carbon, Sulphur, Hydrogen, Oxygen shows different values for basis sets. In Carbon atom C12 has the maximum value of 170.236 and 171.718 by using B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) respectively. In Hydrogen atom H21 has the maximum value of 30.291 and 30.339. In Oxygen atom, O17 has values -376.564 and -379.372 by using B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) respectively. This shows that both the basis sets are in close agreement with each other. The calculated values of NMR spectra are shown in Table-4.

Table 4: Theoretical NMR spectra of 4-ATA(all values in ppm)

Atoms	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
C1	49.761	54.107
C2	53.529	55.745
C3	28.332	32.010
C4	51.727	56.299
C5	50.867	54.047
C6	40.925	35.142
C12	170.236	171.718
C16	-29.583	-39.771
C18	157.347	145.524
H7	24.331	24.584
H8	24.774	24.470
H9	24.764	24.654
H10	23.985	24.633
H13	30.274	30.228
H14	30.453	30.307
H15	29.784	30.224
H19	30.018	30.195
H20	30.043	30.210
H21	30.291	30.339
S11	472.493	457.277
O17	-376.564	-379.372

3.5 Vibrational Assignment:

The Vibrational assignment were performed on the basis of recorded FT-IR and FT-Raman spectra based on theoretically predicted wave numbers by density functional B3LYP/6-311++G(d,p) method are shown in the Table-5. We know that ab initio HF and DFT potentials systematically overestimate the vibrational wavenumbers. These discrepancies are corrected by introducing proper scale factors [12,13]. There are 57 modes of vibrations in the molecule.

Literature survey reveals that C-H stretching, in-plane and out-of-plane bending appeared in the range 3100-3000 cm^{-1} , 1300-1000 cm^{-1} , 1000-750 cm^{-1} respectively. The vibrational frequencies are in the range 3192-3170 cm^{-1} [mode nos:54-56] by B3LYP/6-311++G(d,p) method are assigned to C-H asymmetrical stretching vibrations. The C=O asymmetrical

stretching vibrations appear to be at 1737 cm^{-1} C-S asymmetrical stretching vibrations appear to be at 1110 cm^{-1} . The computed values are in good correlation with the literature value[14].

Table 5: Vibrational wave numbers obtained for 4-ATA at B3LYP/6-311++G(d,p) (Harmonic Frequency (cm-1),IR intensities (km-mol-1) Raman Intensities.

Mode Number	Frequency Scaled	Intensity		Assignments
		IR	Raman	
1	40	5	0	C12-S11 twisting
2	64	2	0	C12-S11 rocking
3	83	1	0	CH2 scissoring
4	145	5	1	C-S scissoring
5	152	0	0	CH2 rocking
6	210	0	0	CH2 rocking
7	224	1	4	C-S scissoring
8	259	0	1	CH2 rocking
9	298	0	2	C-S symmetric stretch
10	354	2	2	C-S scissoring
11	413	0	0	CCC symmetric stretch
12	452	5	2	C-CH2 scissoring
13	471	7	0	CH2 rocking
14	516	20	3	C=O scissoring
15	594	12	0	CH2 rocking
16	624	10	3	C=O scissoring
17	644	1	7	CH2 asymmetric stretch
18	714	1	13	C-S symmetric stretch
19	722	3	0	CH2 rocking
20	772	14	14	CH2 scissoring
21	825	37	0	CH2 rocking
22	841	8	0	CH2 rocking
23	957	60	24	C-CH2 symmetric stretch
24	965	3	1	C-S rocking
25	972	2	3	CH2 rocking
26	989	6	11	CH2 rocking
27	994	1	0	CH2 twisting
28	1028	7	2	CCC scissoring
29	1043	1	0	CCC asymmetric stretch
30	1082	32	161	CCC symmetric stretch
31	1110	70	28	C-S asymmetric stretch

32	1146	7	0	CCC symmetric stretch
33	1210	58	39	CH2 scissoring
34	1281	229	71	CCC asymmetric stretch
35	1318	6	17	CCC asymmetric stretch
36	1334	13	7	CCC asymmetric stretch
37	1362	4	8	CH2 wagging
38	1385	58	3	CH2 symmetric stretch
39	1433	17	3	CCC asymmetric stretch
40	1468	10	16	CH2 scissoring
41	1471	14	5	CH2 scissoring
42	1480	17	9	CH2 scissoring
43	1486	28	5	CH2 scissoring
44	1521	6	5	CCC asymmetric stretch
45	1586	16	7	CCC asymmetric stretch
46	1627	243	492	CCC asymmetric stretch
47	1737	246	184	C=O asymmetric stretch
48	3033	3	182	CH2 symmetric stretch
49	3043	20	185	CH2 symmetric stretch
50	3090	8	46	CH2 asymmetric stretch
51	3127	7	58	CH2 asymmetric stretch
52	3135	3	118	CH2 asymmetric stretch
53	3142	14	110	CH2 asymmetric stretch
54	3170	4	54	C-H asymmetric stretch
55	3180	1	35	C-H asymmetric stretch
56	3192	8	99	C-H asymmetric stretch
57	3203	5	108	C-H symmetric stretch

3.6 Mulliken Charges

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems [15]. Our interest here is in the comparison of different methods to describe the electron distribution in 4-ATA as broadly as possible, and to assess the sensitivity of the calculated charges to changes in (i) the choice of the basis set; (ii) the choice of the quantum mechanical method. Mulliken charges are calculated by determining the electron population of each atom as defined in the basis functions. The Mulliken charges calculated at different levels and at B3LYP/ 6-311++G(d,p) basis set are listed in the Table -6. The Mulliken charges at the C₁ and S₁₁ atoms show more negative due to the attached acetyl group and C₆ possesses more positive charge.

Table -6 : Calculated Mulliken Charges of 4ATA by DFT method

Charges	B3LYB/6-311++G(d,p)
1 C	-0.970120
2 C	-0.827731
3 C	1.025781
4 C	-0.057907
5 C	-0.118325
6 C	1.452784
7 H	0.153219
8 H	0.175964
9 H	0.147965
10 H	0.216687
11 S	-0.715004
12 C	-0.464366
13 H	0.178462
14 H	0.183496
15 H	0.194546
16 C	-0.370003
17 O	-0.261097
18 C	-0.455913
19 H	0.159637
20 H	0.145334
21 H	0.206590

4. Conclusion

The spectral studies such as FT-IR, FT-Raman, and NMR for 4-ATA was carried out for the first time. A complete vibrational and molecular structure analysis has been performed based on the quantum mechanical approach by (DFT) B3LYP calculations. Correlation between the ^1H , ^{13}C of theoretical values and the GIAO NMR calculations are found by using 6-311 G(d,p) and 6-311++G(d,p) are coinciding well. NBO shows the transfer of charge within the molecule during the intra-molecular interaction. Lewis and non-Lewis structure of NBOs show occupancy in s and p orbitals. HOMO and LUMO orbitals have been visualized and the energy band gap is calculated. Finally the Mulliken charges is also been determined.

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