

Simulation of Structure, Molecular Orbitals, Electron Density and Reactivity Aspects of Rubber Vulcanization Accelerator 2-Mercaptobenzothiazole by Density Functional Theory

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In this study, insights on the charge transfer and reactivity properties of 2-mercaptobenzothiazole are presented. The structural parameters are determined by B3LYP method. Delocalization of the lone pair electrons of S3 towards N1=C2 is possible and thereby decreases in force constant and increase in C2–S3 bond length than C2–S14. The C8–C9 bond distance increases due to the electron withdrawing nature of nitrogen. Negative electrostatic potentials reside on nitrogen whereas positive electrostatic potentials lie on hydrogen in S–H group. The LUMO–HOMO energy gap determines the charge transfer capacity and is equal to 5.1370 eV. The $n_s \rightarrow \pi^*_{NC}$ interaction between the sulphur (S3) lone pair and the N1=C2 antibonding orbital gives strong stabilization by 26.70 kcal mol⁻¹. The $n_s \rightarrow \pi^*_{NC}$ interaction between the sulphur (S14) lone pair and the N1=C2 antibonding orbital gives stabilization by 23.77 kcal mol⁻¹. The atoms C2, C8 and C9 are most prone to nucleophilic attack while the electrophilic attack on C2, C4 and C8 atoms. The C2, C4, C8 and C9 are more susceptible to free radical attack. The high first-order polarizability tensor reveals inductive interactions and second order polarizability tensors characterize the electron acceptor properties.

Keywords: 2-Mercaptobenzothiazole, DFT, Natural bond orbital, Hyperpolarizability, Reactivity descriptors.

INTRODUCTION

Accelerator, in the rubber industry, that causes vulcanization of rubber to occur more rapidly or at lower temperatures. Accelerators are basically amine derivatives and there are different classes of accelerators, aldehyde amines guanidines, thiazoles, sulfenamides, dithiocarbamates, thiuram sulfides, xanthates, thiocarbamyl sulfonamides. The most important accelerators being organic materials containing sulphur and nitrogen, especially derivatives of benzothiazole. 2-Mercaptobenzothiazole (MBT) is used primarily as a vulcanization accelerator in the production of natural and synthetic rubbers. 2-Mercaptobenzothiazole is also used in water treatment, lubricants and petroleum products as a corrosion inhibitor by inhibiting the formation of organic layers on metal surfaces. Other applications of 2-mercaptobenzothiazole include using it as a free radical polymerization initiator, as a chain transfer agent, as a reforming agent and as an assisting agent of photo-

polymerization initiators for resins. 2-Mercaptobenzothiazole is also used as a reactant for various pharmaceuticals and pesticides.

During vulcanization the accelerators apparently converts the sulfur into a compound that reacts rapidly with rubber than does sulphur itself. An alternative possibility is that the accelerator reacts first with the rubber, changing it into a form that combines rapidly with sulfur. The first step in sulfur vulcanization is the formation of an active sulfurating species, which is a prerequisite for the formation of a crosslink precursor. A sulfurating species is a molecule that is able to insert sulfur in the form of crosslinks into the elastomer, where it has been long recognized that accelerator polysulfide complexes are better sulfurating species than molecular sulfur. These accelerator polysulfides are formed by the interaction of the accelerator molecule with molecular sulfur [1-3]. So, during that cross-linking formation, the mobility or the flexibility of the segments in between two cross-links are gradually changed

with the introduction of more and more sulfur cross-link bonds.

Studies have been carried out on the mechanism of 2-mercaptobenzothiazole accelerated sulfur vulcanization of rubber with carbon black as filler. Results indicate that sulfuration by 2-mercaptobenzothiazole and sulfur proceed by a free radical mechanism but it becomes polar when ZnO and stearic acid are also present [4]. In this paper the role of thiol intermediates in 2-mercaptobenzothiazole accelerated sulfur vulcanization of rubber have been investigated. Density functional theory (DFT) has been becoming a useful tool used to investigate the charge density distribution, topological properties, electrostatic potential, frontier molecular orbitals, *etc.* The present investigation would be able to give some insight to the understanding of the charge transfer property of 2-mercaptobenzothiazole and to the influence of the functionalized moiety on the vulcanizing properties.

COMPUTATIONAL METHODS

The quantum chemical calculations have been performed with Gaussian-09 [5] program, invoking gradient geometry optimization [6]. The density functional theory (DFT) [7] with three parameter hybrid functional (B3) [8,9] for the exchange part and the Lee–Yang–Parr (LYP) correlation functional [10] have been used for the computation of molecular structure and reactivity parameters using the standard 6-31G**, 6-311++G** and cc-pVDZ basis sets.

Isoelectronic molecular electrostatic potential (MEP) and electron density [11] are calculated by using B3LYP/6-311++G** method. The MEP explains hydrogen bonding, reactivity and structure–activity relationship of molecules including biomolecules and drugs [12]. The electron density surface mapped with electrostatic potential depicts the shape, size, charge density distribution and the sites of chemical reactivity of a molecule. GaussView 5.0.8 visualization program [13] has been utilized to construct the MEP surface and the shape of frontier molecular orbitals.

The stabilization energy $E^{(2)}$ associated with i (donor) $\rightarrow j$ (acceptor) delocalization is estimated from the second-order perturbation approach [14–17]. Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, softness, electrophilicity, nucleophilicity and the appropriate local reactivity descriptors are determined by employing the different kind of atomic charges (Mullikan charges, natural charges, electrostatic potential derived charges, Hirshfeld charges, Chelpg charges) of the neutral, cationic and anionic species of 2-mercaptobenzothiazole molecule.

The site-selectivity of a chemical system, can be determined by using Fukui functions [18,19]. The vertical ionization potential (I), electron affinity (A) and the electron populations are determined on the basis of B3LYP/6-311++G** method. The energy calculations of the N-electron species are done using restricted B3LYP method while the energies of the N–1 and N+1 electronic species are calculated using open shell restricted B3LYP method by using B3LYP/6-311++G** optimized geometry of the N-electron species. The local reactivity descriptors of the individual atoms of the molecule $s_k^a = f_k^a S$, $\omega_k^a = \omega_k^a f_k^a$ and f_k^a , where, $a = +, -$ and 0 represents local philicity

quantities describing nucleophilic, electrophilic and free radical attack, respectively.

The static dipole moment (μ), the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$) and the mean hyperpolarizability (β_0) using x, y and z components are determined.

RESULTS AND DISCUSSION

Structural properties: The optimized geometry and the total electron density mapped electrostatic potential surface of the 2-mercaptobenzothiazole is shown in Fig. 1(a-b). The molecule belongs to C_s point group. The optimized structural parameters namely bond length, bond angle and the dihedral angle for the stable geometry of 2-mercaptobenzothiazole molecule determined by B3LYP methods are given in Table-1. No significant differences are observed in the C–C bond lengths of aromatic benzene ring. The bond length C2–S3 is 0.01 Å longer than the C2–S14 bond distances of the thiazole moiety. Easy delocalization of the lone pair electrons of S3 towards N1=C2 is possible and thereby decreases in force constant and increase in C2–S3 bond length than C2–S14. Similarly, the C8–C9 bond distance increases due to the electron withdrawing nature of nitrogen by the partial ionic nature. The shorter S3–C9 bond (1.76 Å) is in favour of the delocalization of sulphur (S3) lone pair of electrons towards the aromatic ring.

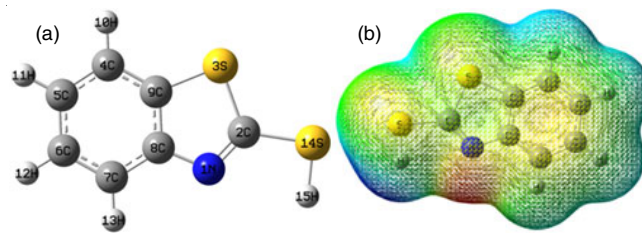


Fig. 1. (a) Optimized geometry and (b) Total electron density mapped electrostatic potential surface of 2-mercaptobenzothiazole

Analyzing the bond angle of aromatic ring of 2-mercaptobenzothiazole, the geometry of the benzene ring is relatively perturbed due to the presence of nitrogen and sulphur attachments. The bond angles C4–C5–C6 (120.9°), C5–C6–C7 (121°) and C4–C9–C8 (121.7°) are greater than 120° whereas the bond angles C5–C4–C9 (118°), C6–C7–C8 (119°) and C7–C8–C9 (119.5°) are less than 120° indicates the electron withdrawing/donating influence of nitrogen and sulphur atoms. The present theoretical structural parameters of 2-mercaptobenzothiazole are well correlated with the XRD values of 1,2-bis(benzothiazol-2-ylthio)ethane [*bis*(BT-NS)Et] [20]. The slight distortions from the X-ray geometry of *bis*(BT-NS)Et may arise from the packing effects in the solid state. The C–H bond length of aromatic ring is also well agreed with the neutron diffraction measurements that are known to obtain more accurate C–H bond lengths that is 1.09 Å [21] (Table-1), similar to the present computational results.

Analysis of molecular electrostatic potential: The total electron density mapped electrostatic potential surface of 2-mercaptobenzothiazole is presented in Fig. 1(b). Local negative electrostatic potentials (red) reside on nitrogen which corresponds to the most nucleophilic regions, whereas local positive

TABLE-1
STRUCTURAL PARAMETERS OF
2-MERCAPTOBENZOTHAZOLE DETERMINED BY B3LYP
METHOD WITH 6-31G**, 6-311++G** and cc-pVDZ BASIS SETS

Structural parameters	B3LYP/6-31G**	B3LYP/6-311++G**	B3LYP/cc-pVDZ	Expt. ^a
Internuclear distance (Å)				
N1–C2	1.29	1.29	1.29	1.293
N1–C8	1.39	1.39	1.39	1.399
C2–S3	1.78	1.78	1.78	1.751
C2–S14	1.77	1.77	1.77	1.744
S3–C9	1.76	1.76	1.76	1.729
C4–C5	1.39	1.39	1.40	1.374
C4–C9	1.40	1.39	1.40	1.389
C5–C6	1.40	1.40	1.41	1.389
C6–C7	1.39	1.39	1.39	1.378
C7–C8	1.40	1.40	1.40	1.384
C8–C9	1.42	1.41	1.42	1.406
C–H(ring) ^b	1.09	1.08	1.09	1.09
S14–H15	1.35	1.35	1.36	–
Bond angle (°)				
C2–N1–C8	110.7	111.0	110.7	110.1
N1–C2–S3	116.6	116.4	116.6	116.6
N1–C2–S14	124.7	125.0	124.8	127.3
S3–C2–S14	118.6	118.6	118.6	116.1
C2–S3–C9	87.9	88.0	87.8	88.8
C5–C4–C9	118.0	118.0	118.0	118.3
C5–C4–H10	120.8	120.8	120.8	–
C9–C4–H10	121.2	121.3	121.2	–
C4–C5–C6	121.0	120.9	120.9	121.2
C4–C5–H11	119.3	119.4	119.3	–
C6–C5–H11	119.7	119.7	119.7	–
C5–C6–C7	120.9	121.0	120.9	120.6
C5–C6–H12	119.5	119.4	119.5	–
C7–C6–H12	119.6	119.6	119.6	–
C6–C7–C8	119.0	119.0	119.1	119.3
C6–C7–H13	121.8	121.7	121.8	–
C8–C7–H13	119.3	119.4	119.2	–
N1–C8–C7	124.9	125.2	125.0	125.4
N1–C8–C9	115.5	115.4	115.6	114.9
C7–C8–C9	119.5	119.5	119.4	119.7
S3–C9–C4	129.2	129.1	129.1	129.5
S3–C9–C8	109.3	109.3	109.2	109.6
C4–C9–C8	121.6	121.7	121.7	–
C2–S14–H15	93.6	93.5	93.2	–

^aValues are taken from [Ref. 20]; ^bValues are taken from [Ref. 21].

electrostatic potentials (blue) lie on hydrogen in S–H group which represents the most electrophilic regions. Green areas cover parts of the molecule where electrostatic potentials are close to zero (C–C bonds). The MEP of the molecule lie in the range $+1.238\text{e} \times 10^{-2}$ to $-1.238\text{e} \times 10^{-2}$. The total electron density of 2-mercaptobenzothiazole lie in the range $+3.143\text{e} \times 10^{-2}$ to $-3.143\text{e} \times 10^{-2}$. The MEP and total electron density shows

that the 2-mercaptobenzothiazole is more polar and reactive. Electrostatic potential is used to find the electrophilic or nucleophilic sites that play a crucial role in molecular recognition. It is noteworthy that the electrostatic forces have a long-distance character and they determine the path along which the reactant molecules approach each other.

Analysis of frontier molecular orbitals: The energies of HOMO, LUMO, LUMO+1 and HOMO–1 and the LUMO–HOMO energy gap are calculated by using B3LYP/6–311++G** method. The calculated LUMO–HOMO energy gap explains the ultimate charge transfer interface within the molecule. The hardness and softness of the molecule depends on the frontier molecular orbital energies. The LUMO–HOMO energy gaps of 2-mercaptobenzothiazole determined by B3LYP/6–311++G** method is 5.1370 eV. The molecular orbital energies and global reactivity properties of 2-mercaptobenzothiazole determined by B3LYP/6–311++G** method are summarized in Table-2.

According to the frontier molecular orbital theory (FMO) of chemical reactivity, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reacting species [22,23]. The energy of the HOMO is directly related to the ionization potential and characterises the susceptibility of the molecule towards attack by electrophiles. The HOMO–LUMO gap, *i.e.* the difference in energy between the HOMO and LUMO, is an important stability index [24]. A large HOMO–LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions [25]. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule [26].

Natural bond orbital (NBO) analysis: The hyperconjugative interaction energy was deduced from the second-order perturbation approach of Fock Matrix in NBO basis between donor–acceptor orbitals [27]. The NBO method demonstrates the bonding concepts like atomic charge, Lewis structure, bond type, hybridization, bond order, charge transfer and resonance possibilities. The bonding concepts such as type of bond orbital, their occupancies, the natural atomic hybrids of which the NBO is composed, giving the percentage of the NBO on each hybrid, the atom label and a hybrid label showing the hybrid orbital (sp^x) composition (the amount of *s*-character, *p*-character, *etc.*) of 2-mercaptobenzothiazole determined by B3LYP/6–311++G** method. All bonding donor orbitals have two electrons. The bonding orbital for C4–C5 has 50.78 % C4 character in a $sp^{1.76}$ hybrid and has 49.22 % C5 character in a $sp^{1.80}$ hybrid orbital. The bonding orbital for C5–C6 has 50.06 % C5 character in a $sp^{1.79}$ hybrid and has 49.94 % C6 character in a $sp^{1.81}$ hybrid orbital. The bonding orbital for N1–C2 with

TABLE-2
CALCULATED MOLECULAR ORBITAL ENERGIES AND GLOBAL REACTIVITY
PROPERTIES OF 2-MERCAPTO BENZOTHAZOLE BY B3LYP/6–311++G** METHOD

$E_{\text{LUMO}+1}$ (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	$E_{\text{HOMO}-1}$ (eV)	$E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	Ionization potential, I (eV)
–0.7617	–1.3372	–6.4742	–6.8086	5.1370	8.2737
Electron affinity, A (eV)	Electronegativity (χ)	Chemical potential (μ)	Electrophilicity (ω)	Hardness (η)	Softness (S)
–0.3417	3.9660	–3.9660	1.8257	4.3077	0.1161

1.9894 electrons has 59.61 % N1 character and 40.39 % C1 character in a $sp^{1.62}$ hybrid orbital. The bonding orbital for C2–S3 has 52.70 % C2 character and 47.30 % S3 character. The C–C bonds of the benzene ring possess more p character than s character. This clearly indicates the delocalization of π electrons among all the carbon atoms.

The Fock matrix analysis yield different types of donor–acceptor interactions and their stabilization energy. This bonding–antibonding interactions can be quantitatively described in terms of the NBO approach that is expressed by means of second–order perturbation interaction energy $E^{(2)}$ [14–17]. This energy represents the estimation of the off–diagonal NBO Fock matrix element. Second order perturbation theory analysis of Fock matrix of 2-mercaptobenzothiazole using NBO analysis are presented in Table-3. The lone pair donor orbital, $n_s \pi^*_{NC}$ interaction between the sulphur (S3) lone pair and the N1=C2 antibonding orbital gives strong stabilization by 26.70 kcal mol⁻¹. The lone pair donor orbital, $n_s \pi^*_{NC}$ interaction between the sulphur (S14) lone pair and the N1=C2 antibonding orbital gives strong stabilization by 23.77 kcal mol⁻¹. The bond pair donor orbital, $\pi_{CC} \pi^*_{CC}$ interaction between the C6–C7 bond pair and the antiperiplanar C8=C9 antibonding orbital give stabilization of 21.25 kcal mol⁻¹.

TABLE-3
SECOND ORDER PERTURBATION THEORY ANALYSIS OF
FOCK MATRIX OF 2-MERCAPTO BENZOTHIAZOLE BY
B3LYP/6–311++G** METHOD USING NBO ANALYSIS

Donor (i) – Acceptor (j) interaction	$E^{(2)a}$ (kcal mol ⁻¹)	$E(j) - E(i)^b$ (a.u.)	$F(i, j)^c$ (a.u.)
$\pi(N1-C2) \rightarrow \pi^*(C8-C9)$	14.62	0.35	0.071
$\pi(C4=C5) \rightarrow \pi^*(C6=C7)$	18.90	0.29	0.066
$\pi(C4=C5) \rightarrow \pi^*(C8=C9)$	18.78	0.27	0.066
$\pi(C6=C7) \rightarrow \pi^*(C4=C5)$	19.82	0.28	0.067
$\pi(C6=C7) \rightarrow \pi^*(C8=C9)$	21.25	0.26	0.07
$\pi(C8=C9) \rightarrow \pi^*(N1=C2)$	12.44	0.25	0.050
$\pi(C8=C9) \rightarrow \pi^*(C4=C5)$	19.47	0.3	0.068
$\pi(C8=C9) \rightarrow \pi^*(C6=C7)$	16.19	0.3	0.063
$n(N1) \rightarrow \sigma^*(C2-S3)$	17.38	0.52	0.086
$n(S3) \rightarrow \pi^*(N1=C2)$	26.70	0.24	0.072
$n(S3) \rightarrow \pi^*(C8=C9)$	17.61	0.27	0.064
$n(S14) \rightarrow \pi^*(N1=C2)$	23.77	0.25	0.073

Analysis of structure–reactivity descriptors

Topological charge distribution analysis: The different kind of atomic charges (Mullikan charges, natural charges, electrostatic potential derived charges, Hirschfeld charges, Chelpg charges) of 2-mercaptobenzothiazole are calculated by using B3LYP/6–311++G** method and presented in Table-4. The chemical information obtained from charge density analysis enables us to know how the structure can exist, how the compound exhibits chemical and biological reactivity and where the interaction sites/regions localize. All the charges except Mulliken shows the nitrogen (N1) atom of thiazole moiety in neutral, cationic and anionic species possess negative charge due to its more electronegativity. In the neutral molecule, the sulphur (S3) has positive charge and very small negative charge by Chelpg method. This reveals the possibility of the nucleophilic attack at S3 on sulphurization process. Instead the sulphur atom S14 possesses negative charge except NBO method and these suggest that electrophilic attack predominate at this sulphur atom. In the cationic and anionic species of 2-mercaptobenzothiazole both the sulphur atoms possess positive and negative charges, respectively.

The C2 and C8 have positive charges due to the electronic effect of N1 atom. All these charge distribution in 2-mercaptobenzothiazole provides better understanding of chemical reactivity and clearly favours the sulphurization process and 2-mercaptobenzothiazole is considered the best vulcanization accelerator. The charge density of 2-mercaptobenzothiazole provides important and meaningful chemical information for better understanding the inherent properties of the compound. The calculated σ – and π –electron densities on a particular atom also characterize the possible orientation of the chemical interactions and, thus, are often considered to be directional reactivity indices. In contrast, overall electron densities and net charges on atoms are considered as non–directional reactivity indices [17]. Atomic charges are also used for the description of the molecular polarity of molecules.

Dipole moment and polarity indices: The polarity of a molecule is well known to be important for various physico-chemical properties and many descriptors have been proposed to quantify the polarity effects. The most obvious and most often used quantity to describe the polarity is the dipole moment

TABLE-4
ATOMIC CHARGES OF 2-MERCAPTOBENZOTHIAZOLE DETERMINED BY B3LYP/6–311++G** METHOD

Atom	Mulliken	NBO	ESP	Hirshfeld	Chelpg
N1	0.1613	–0.5073	–0.5928	–0.1614	–0.5964
C2	0.5549	–0.0753	0.1652	0.0533	0.3114
S3	–0.5200	0.3769	0.0372	0.0195	–0.0344
C4	0.1157	–0.2139	–0.1081	–0.0397	–0.0802
C5	–0.1140	–0.1988	–0.2780	–0.0423	–0.1774
C6	–0.2939	–0.2033	–0.0383	–0.0428	–0.0094
C7	–0.8454	–0.1870	–0.4239	–0.0407	–0.2987
C8	–1.7812	0.1162	0.6679	0.0362	0.5079
C9	2.1734	–0.2003	–0.1707	–0.0198	–0.0922
H10	0.1748	0.2143	0.1781	0.0525	0.1327
H11	0.1650	0.2079	0.1677	0.0453	0.1012
H12	0.1699	0.2079	0.1365	0.0453	0.0828
H13	0.1875	0.2199	0.1947	0.0501	0.1429
S14	–0.2412	0.0902	–0.1675	–0.0357	–0.1957
H15	0.0930	0.1526	0.2320	0.0803	0.2057

of the molecule [28,29]. The total dipole moment, reflects only the global polarity of a molecule. The total dipole moment of 2-mercaptobenzothiazole is determined by B3LYP/6-311++G** method is 1.0102 D shows that the polar nature of 2-mercaptobenzothiazole molecule.

Fukui reactivity descriptors: Fukui functions and local softness are extensively applied to probe the local reactivity and site selectivity. The formal definitions of all these descriptors and working equations for their computation have been described [30,31]. The Fukui functions (f_k) of the individual atoms of the neutral, cationic and anionic species of 2-mercaptobenzothiazole calculated by B3LYP/6-311++G** method. In the present study, both the local reactivity and multiphlicity descriptors are used to probe the nature of attack/reactivity at a particular site in the molecule. The Fukui dual reactivity descriptor (Δf_k), the dual local softness (Δs_k) and the multiplicity descriptors ($\Delta \omega_k$) which can concurrently characterize both nucleophilic and electrophilic nature of a chemical species.

The Fukui dual reactivity descriptors (Δf_k) (Table-5), the dual local softness (Δs_k) (Table-6) and the multiplicity descriptors ($\Delta \omega_k$) (Table-7) have also been determined to predict the reactive sites of the 2-mercaptobenzothiazole molecule. The relative thermodynamic and kinetic stabilities are discussed through the hardness and softness of the molecule. The hardness of 2-mercaptobenzothiazole determined by B3LYP/6-311++G** method is 4.3077 eV while the softness is 0.1161 eV.

In the present investigation the atoms C2, C8 and C9 are most prone to nucleophilic attack while the electrophilic attack is more on C2, C4 and C8 atoms. The sites C2, C4, C8 and C9 are more susceptible to free radical attack.

If Δf_k , Δs_k and $\Delta \omega_k$ are greater than zero, then the site k is favoured for a nucleophilic attack, whereas if these are less than zero, then the site k may be favoured for an electrophilic attack. From Fukui dual reactivity descriptor (Δf_k), the dual local softness (Δs_k) and the multiplicity descriptors ($\Delta \omega_k$) one can understand that the atoms C8, C9 and S14 are more favourable for nucleophilic attack. The atoms N1, S3, C2 and

TABLE-5
FUKUI DUAL DESCRIPTORS (Δf_k) OF 2-MERCAPTOBENZOTHAZOLE BY B3LYP/6-311++G** METHOD

Atom	Mulliken	NBO	ESP	Hirshfeld	Chelppg
N1	-0.0068	-0.0149	-0.0754	-0.0135	-0.0794
C2	0.0281	-0.1435	0.0531	-0.0586	0.0271
S3	-0.0798	-0.0360	-0.1138	-0.0423	-0.1112
C4	-0.0192	-0.0510	0.0002	-0.0136	-0.0521
C5	-0.0306	0.0119	-0.0044	0.0099	0.0752
C6	0.0333	0.0360	0.0585	0.0141	0.0204
C7	-0.0381	-0.0591	-0.1135	-0.0167	-0.0639
C8	0.0009	0.0502	0.1155	0.0253	0.1057
C9	0.0663	0.0502	0.0379	0.0289	0.0690
S14	0.0318	0.1444	0.0447	0.0757	0.0649

TABLE-6
DUAL LOCAL SOFTNESS DESCRIPTORS (Δs_k) OF 2-MERCAPTOBENZOTHAZOLE BY B3LYP/6-311++G** METHOD

Atom	Mulliken	NBO	ESP	Hirshfeld	Chelppg
N1	-0.0008	-0.0017	-0.0088	-0.0016	-0.0092
C2	0.0033	-0.0167	0.0062	-0.0068	0.0031
S3	-0.0093	-0.0042	-0.0132	-0.0049	-0.0129
C4	-0.0022	-0.0059	0.0000	-0.0016	-0.0061
C5	-0.0036	0.0014	-0.0005	0.0012	0.0087
C6	0.0039	0.0042	0.0068	0.0016	0.0024
C7	-0.0044	-0.0069	-0.0132	-0.0019	-0.0074
C8	0.0001	0.0058	0.0134	0.0029	0.0123
C9	0.0077	0.0058	0.0044	0.0034	0.0080
S14	0.0037	0.0168	0.0052	0.0088	0.0075

TABLE-7
MULTIPHILICITY DESCRIPTORS ($\Delta \omega_k$) OF 2-MERCAPTOBENZOTHAZOLE BY B3LYP/6-311++G** METHOD

Atom	Mulliken	NBO	ESP	Hirshfeld	Chelppg
N1	-0.0125	-0.0271	-0.1377	-0.0247	-0.1450
C2	0.0513	-0.2621	0.0969	-0.1070	0.0494
S3	-0.1456	-0.0657	-0.2078	-0.0772	-0.2030
C4	-0.0351	-0.0932	0.0004	-0.0247	-0.0952
C5	-0.0559	0.0217	-0.0080	0.0181	0.1372
C6	0.0608	0.0656	0.1067	0.0258	0.0373
C7	-0.0696	-0.1079	-0.2072	-0.0304	-0.1166
C8	0.0016	0.0917	0.2108	0.0461	0.1930
C9	0.1210	0.0916	0.0691	0.0529	0.1259
S14	0.0580	0.2636	0.0816	0.1382	0.1184

C7 are more favourable for electrophilic attack. The Fukui functions which represent the relative nucleophilic and electrophilic are shown in the Figs. 2(a) and (b). The free radical

descriptors and the Fukui dual descriptor (Δf_k), the dual local softness (Δs_k) and the multiplicity descriptors ($\Delta \omega_k$) of mercaptobenzothiazole are shown in Figs. 3(i) and (ii).

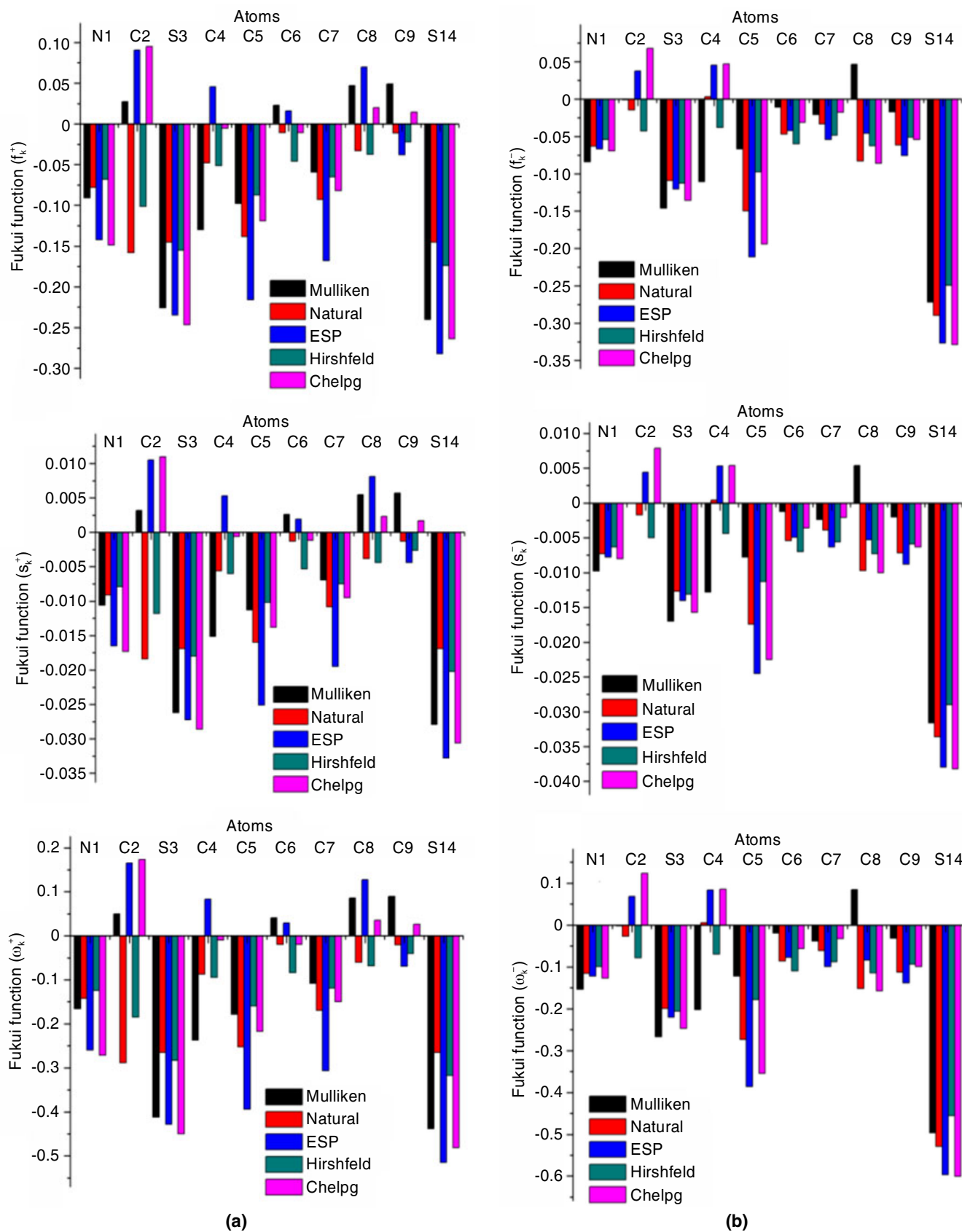


Fig. 2. (a) Relative nucleophilic and (b) relative electrophilic descriptors of mercapto benzothiazole

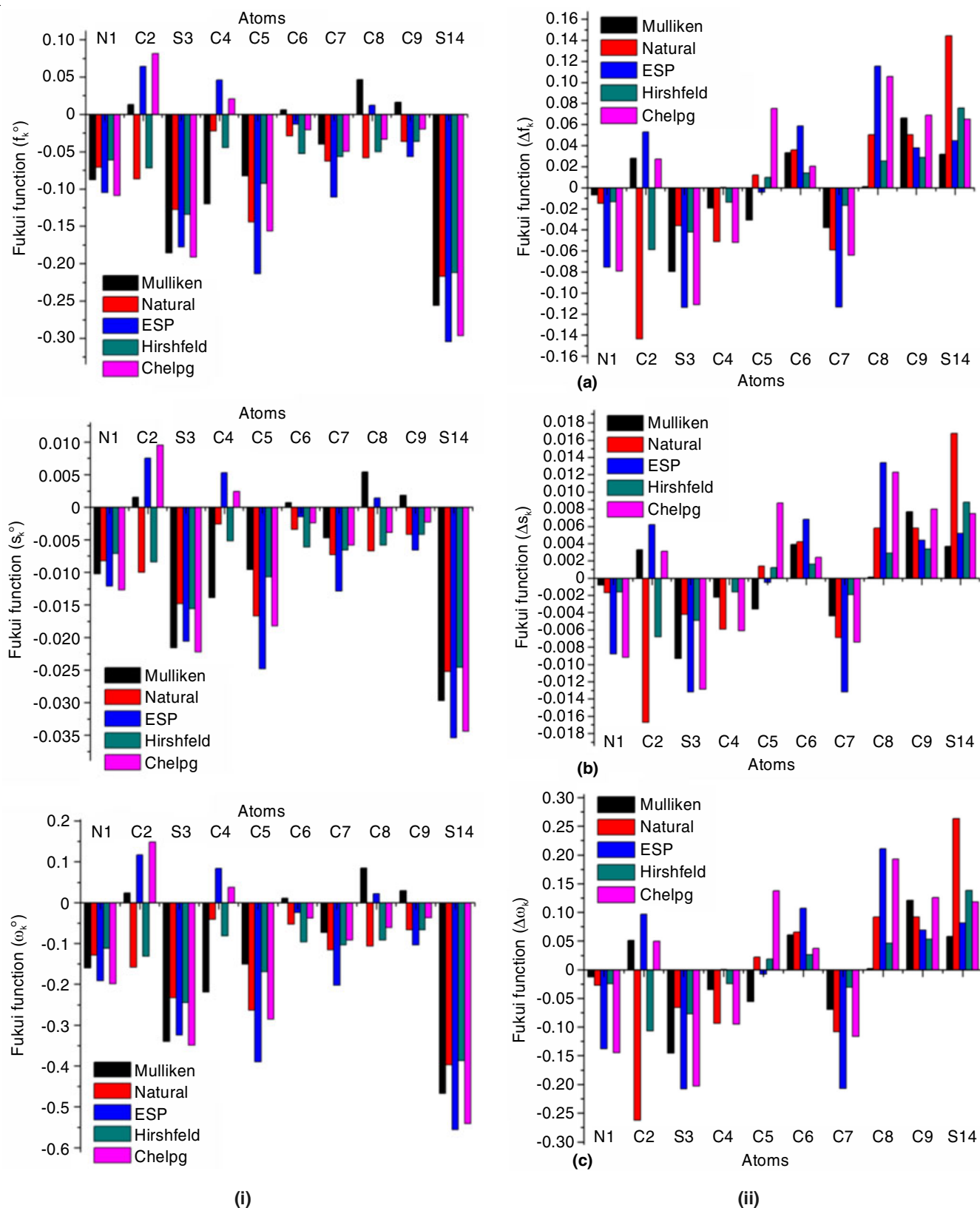


Fig. 3. (i) Relative free radical descriptors and (ii) (a) dual descriptor (Δf_k), (b) the dual local softness (Δs_k) and (c) the multiplicity descriptors ($\Delta \omega_k$) of mercaptobenzothiazole

Molecular polarizability and hyperpolarizability analysis:

The polarizabilities are related to hydrophobicity and other biological activities [32]. The first hyperpolarizability of 2-mercaptobenzothiazole computed by B3LYP/6-311++G**

method are presented in the Table-8. The hyperpolarizability (β) which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement through

TABLE-8
DIPOLE MOMENT, AVERAGE POLARIZABILITY, FIRST POLARIZABILITY AND HYPERPOLARIZABILITY TENSORS OF 2-MERCAPTOBENZOTHAZOLE DETERMINED BY B3LYP/6-311++G(d,p) METHOD

$\mu_{\text{total}} (\text{D})$	1.0102	$\alpha_{\text{total}} (\text{e.s.u})$	57.1418×10^{-24}	β_{yyz}	19.3551
α_{xx}	193.9302	$\Delta\alpha (\text{a.u})$	108.0139	β_{zzz}	0.0313
α_{xy}	-0.9530	β_{xxx}	486.9225	β_x	470.2948
α_{yy}	123.0201	β_{xxy}	36.6944	β_x^2	22.1177×10^4
α_{xz}	0.0030	β_{xyy}	2.8191	β_y	59.1596
α_{yz}	0.0009	β_{yyz}	3.1101	β_y^2	34.9986×10^2
α_{zz}	69.6334	β_{xzz}	-0.3184	β_z	-0.2794
$\alpha_0 (\text{a.u})$	128.8612	β_{xyx}	0.0116	β_z^2	78.0644×10^{-3}
$\alpha_0 (\text{e.s.u})$	19.0941×10^{-24}	β_{yyz}	0.0077	$\beta_0 (\text{a.u})$	22.4677×10^4
$\alpha_{\text{total}} (\text{a.u})$	385.6345	β_{zzz}	-19.4468	$\beta_0 (\text{e.s.u})$	19.4119×10^{-28}

π conjugated frame work from electron donor to electron acceptor groups. Molecules with high hyperpolarizability have chromophores, since the compound 2-mercaptobenzothiazole is a conjugative system with S-H chromophore and hence its hyperpolarizability values determined are in the order of more than 10×10^{-24} e.s.u. [33]. The asymmetric molecule 2-mercaptobenzothiazole has large values of molecular hyperpolarizability, β due to the electron delocalization along a conjugated backbone.

Furthermore, the electronic polarizability of molecules shares common features with the electrophilic super delocalizability. The first-order polarizability tensor contains information about possible inductive interactions in the 2-mercaptobenzothiazole molecule. The total anisotropy of the polarizability (second-order term) characterize the electron acceptor properties of 2-mercaptobenzothiazole molecule.

Conclusion

The following observations are made from the present investigations:

- The structure of 2-mercaptobenzothiazole is optimized and the bond length, bond angle and dihedral angle are determined by using B3LYP method with 6-31G**, 6-311++G** and cc-pVDZ basis sets.
- The C=N and S-H are syn with respect to C2-S14 bond. The intramolecular hydrogen bonding of the type S-H...N is the power of enforcing the existence of syn conformation.
- Local negative electrostatic potentials (red) reside on nitrogen which corresponds to the most nucleophilic regions, whereas local positive electrostatic potentials (blue) lie on hydrogen in S-H group which represents the most electrophilic regions.
- The MEP of the molecule lie in the range from $+1.238e \times 10^{-2}$ to $-1.238e \times 10^{-2}$. The total electron density of 2-mercaptobenzothiazole lie in the range from $+3.143e \times 10^{-2}$ to $-3.143e \times 10^{-2}$.
- The LUMO-HOMO energy gap of 2-mercaptobenzothiazole is 5.1370 eV. The energy gap is not too high and the molecule is reactive enough.
- The bonding orbital for N1-C2 with 1.9894 electrons has 59.61 % N1 character and 40.39 % C1 character in a $sp^{1.62}$ hybrid orbital. The bonding orbital for C2-S3 has 52.70 % C2 character and 47.30 % S3 character.
- The lone pair donor orbital, $n_s \pi^*_{\text{NC}}$ interaction between S3 and N1=C2 antibonding orbital gives strong stabilization

by 26.70 kcal mol⁻¹, while between the sulphur (S14) lone pair and the N1=C2 antibonding orbital gives strong stabilization by 23.77 kcal mol⁻¹.

• In the neutral molecule, the sulphur (S3) has positive charge and very small negative Chelpg charge. This reveals the possibility of the nucleophilic attack at S3 on sulphurization process. Instead another sulphur atom S14 possesses negative charge except NBO method and these suggest that electrophilic attack predominate at this sulphur atom.

• The local philicity quantities represents the atoms C2, C8 and C9 are most prone to nucleophilic attack while the electrophilic attack is more on C2, C4 and C8 atoms. The sites C2, C4, C8 and C9 are more susceptible to free radical attack.

• Fukui dual reactivity descriptor (Δf_k), the dual local softness (Δs_k) and the multiphlicity descriptors ($\Delta \omega_k$) reveal that the atoms C8, C9 and S14 are more favourable for nucleophilic attack while N1, S3, C2 and C7 are more favourable for electrophilic attack.

• High total first-order polarizability tensor α_{total} (e.s.u) = 57.1418×10^{-24} reveals the possible inductive interactions in 2-mercaptobenzothiazole molecule.

• Total anisotropy of the polarizability (second-order term) β_0 (e.s.u) = 19.4119×10^{-28} characterize the electron acceptor properties of 2-mercaptobenzothiazole molecule.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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