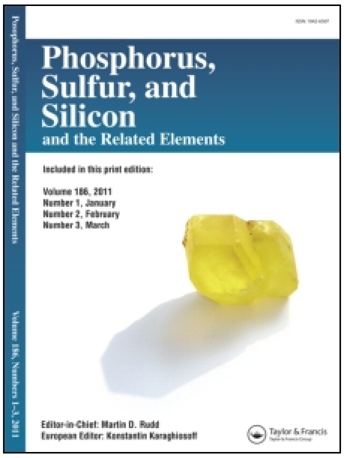

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Electronic Structure and Barrier to Internal Rotation of Sulfenamide, (N,N-Disubstituted and N-aryl)benzsulfenamide and N-aryl Methylsulfenamide Derivatives

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ELECTRONIC STRUCTURE AND BARRIER TO INTERNAL ROTATION OF SULFENAMIDE, (N,N-DISUBSTITUTED AND N-ARYL) BENZSULFENAMIDE AND N-ARYL METHYLSULFENAMIDE DERIVATIVES

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*The ground geometries of sulfenamide, N,N-disubstituted benzsulfenamide, N-aryl benzsulfenamide, and N-aryl methylsulfenamide derivatives have been examined theoretically. Equilibrium geometries were determined using 6-311G** and 6-311G**+MP2 basis sets for sulfenamide (**I**) and 6-31G* for the derivatives at the level of RHF method. The calculated geometric parameters of sulfenamide (**I**)are analyzed. Detalied investigation of the electronic structure of sulfenamide (**I**) is facilitated via the analysis of charge density maps (total, HOMO, and LUMO). The substituents effect on geometry, energetics, and relative stability of the studied derivatives also are analyzed. The investigated nature of the hindered rotation about the N—S bond of some N,S-disubstituted sulfenamide derivatives has been computed theoretically using 6-31G* and 6-31G*+MP2 theory level.*

Keywords: Ab initio calculations; charge density; substituents effect; sulfenamide; torsional barrier

Sulfenamides are compounds of biological and industrial importance. They are currently the subject of extensive investigation and a wide range of biological activities are being explored.[1–11] Sulfenamides have been used as additives in the rubber industry,[12] as growth regulators of plant,[13] insecticides,[14] fungicides,[15] ovicides,[16] and some of them have potential medicinal values.[17]

The stability of sulfenamide derivatives [ArNHSR] depends upon the various types of interactions between different moieties, the

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polarization of the N—S bond, the nature of amines, mercaptide ratio, pH, and temperature. Most sulfenamides give low melting solids or liquids that are rapidly decomposed within few weeks under ordinary conditions.[18]

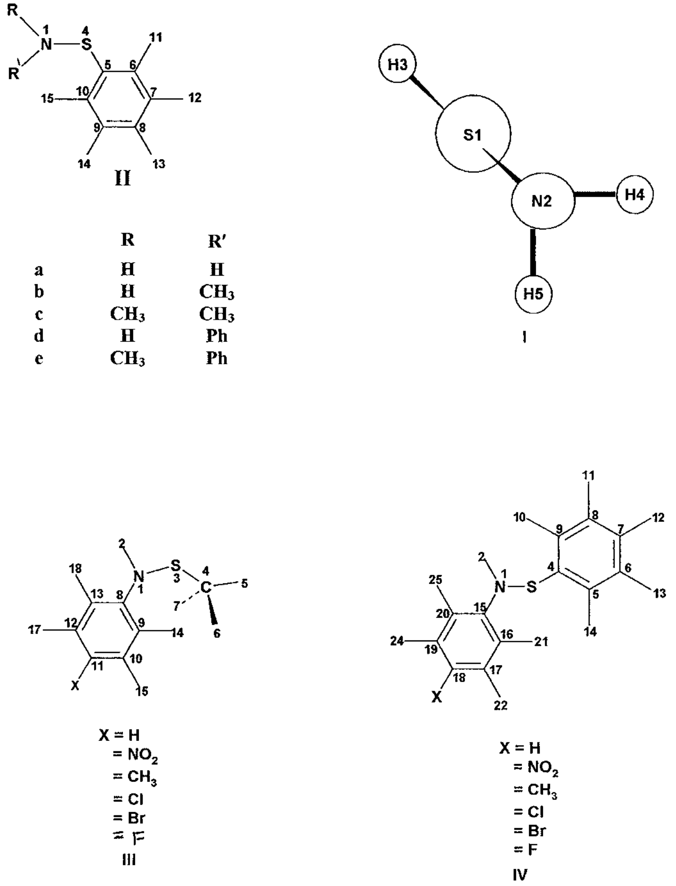
Sulfenamides may exist in R- and S-conformations. The N-chiral center in sulfenamides is parallel to the asymmetric carbon atom and can be assigned R- and S-chiralities using Chain, Ingold, and prelog (CIP) rules.[19]

Roban et al.[20–22] and Blanca et al.[23] established the existence of a significant barrier to the rotation around the N—S bond in N-alkyl-N-benzyl trichloro (fluoro)methanesulfenamide and dinitro(trinitro) benzsulfenamides using dynamic NMR techniques. As the number of substituents on nitrogen are increased, the magnitude of the observed barrier becomes greater. Polar substituents attached to the sulfenyl phenyl ring increase the torsional barriers about the N—S bond. The barrier is greatly increased when the substituent is electron withdrawing in the para-position. Theortical calculations[24–26] and experimantal microwave methods[27] were carried out on the parent sulfenamide. Nevertheless, in the absence of any systematic study of the electronic properties and bonding characteristics of this class of compounds, most conclusions that correlate their activities and application to structural factors remain qualitative in nature.

The main objective of the present work is to investigate theoretically the electronic properties that may underly the activity of sulfenamides. Ab-initio MO-techniques are used to study: (1) The electronic structure of the parent sulfenamide (**I**) in its planar and pyramidal configuration. Detailed investigation of the electronic structure is facilitated via the analysis of the charge density maps, (2) the substituent effects on the geometry, energetices and relative stability of some arenesulfenamides derivatives, and (3) compute theoretically the barrier to internal rotation about the N—S bond for some N,S-disubstituted sulfenamides.

COMPUTATIONAL PROCEDURE

All computations are carried out at the Hartree-Fock ab initio level of theory. The extended 6-31G**, 6-311G**, and TZV** basis sets[28] were used for the parent sulfenamide, whereas 6-31G* was used for all derivatives. Correlation energies were estimated at the MP2 level for the parent sulfenamide and in barrier calculations. Charge densities were computed using Mulliken analysis. The Gamess[29] software package was used for all computations performed in the present work. The molecular geometries of the studied compounds were fully optimized



II

	R	R'
a	H	H
b	H	CH_3
c	CH_3	CH_3
d	H	Ph
e	CH_3	Ph

I

X = H
= NO_2
= CH_3
= Cl
= Br
= F
III

X = H
= NO_2
= CH_3
= Cl
= Br
= F
IV

FIGURE 1 Geometries and numbering adopted for studied compounds.

using the gradient minimization technique.[30] Numbering systems for the geometric representations of the studied compounds are systematically presented in Figure 1.

RESULTS AND DISCUSSION

Sulfenamide (I)

The ground state energies for the planar and pyramidal structures of sulfenamide (**I**) are presented in Table I for the basis sets used with correlation energies at the MP2 level. Optimized geometry bond length, bond angle, bond order, net charge, total energy, dipole moments, and

TABLE I Ground State Energy for the Planar and Pyramidal Sulfenamide Using Different Basis Sets

	Total energy, au		Correlation energy, au	
Basis sets	Planar	Pyramidal	Planer	Pyramidal
6-31G**	−453.660	−453.685		
6-31G**+MP2	−453.96	−453.989	0.301	0.304
6-311G**	−453.700	−453.726		
6-311G**+MP2	−454.023	−454.050	0.323	0.324
TZV**	−453.707	−453.729		
TZV**+MP2	−454.030	−454.055	0.323	0.326

the available experimental[27] data for the pyradidal structure of sulfenamide (**I**) are presented in Table II. Analysis of the data reveals the following:

1. In all levels of calculations, the pyramidal structure of sulfenamide (**I**) is more stable than the planar one. In case of 6-31G** the energy difference is 0.025 au (∼15 Kcal). MP2 calculation increase the energy difference to 0.028 au (∼18 Kcal) with a correlation energy of 0.3 au (∼19 Kcal). As the extent of basis sets increases, the stabilization enegry and correlation energy increases. This results would suggest the necessity for using polarization functions in any meaningful study of the structure of sulfenamide derivatives.

TABLE II Equilibrium Bond Length, Bond Angle, Net Charge, Bond Order, and Theoretical Dipole Moment for the Pyramidal Form of Sulfenamide

Parameter	631G**	6-31G**+MP2	6-311G**	6-311G**+MP2	Expt.[a]
Bond length, A					
N—S	1.706	1.731	1.707	1.726	1.705
N—H	0.997	1.011	0.997	1.012	1.008
S—H	1.327	1.332	1.332	1.336	1.351
Bond angle					
<HSN	98.0	96.7	98.0	96.5	101.9
<HNH	137.0	141.2	137.6	140.4	112.6
<HSNH	117.9	120.6	118.4	120.5	
<HNSH	124.3	118.8	123.2	119.0	
Net charge					
N—	−0.794	−0.789	−0.631	−0.632	
S	0.138	0.131	0.118	0.113	
Bond order					
N—S	0.924	0.919	0.912	0.909	
μ, D	1.057	1.029	0.959	0.941	0.994

[a] See Lovas et al.,[27] no other experimental values are available.

2. The computed dipole moments at the different levels of calcuations are ~5% greater than the experimentally reported value (0.994). The 6-311G** basis set seems to be much more capable of reproducing the experimental dipole moment.
3. Both basis sets 6-31G** and 6-311G** are in general good agreement with the experimental data and indicate the reliability of the present computational level in comparsion with B3LY/6-31G(p,d).[26] It is interesting to note the importance of including the d-function in describing the electronic environment of the sulfur atom.
4. The <HSN bond angle is much better reproduced by 6-31G** and 6-311G** than the <HNH angle. This is due to the presence of d-functions on heavy atoms(N and S) and p-functions on H-atoms, which increase the extension of the charge densities in space.
5. Sulfenamidde (**I**) is a highly polar molecule showing polarization of the σ- and π-frameworks. The computed Mulliken charge densities on S- and N-atoms and the bond order of the N—S bond are given in Table II. The magnitude of the net charge and bond order decreases as the polarization functions increase. This may be attributed to the lone pair orbital of the S-atom which shows a relatively large s- and d-contribuations indicative of its diffuse nature and a much more lower directional character.

Molecular Charge Distribution

The charge distribution of sulfenamide is analyzed in terms of the total molecular density, HOMO and LUMO-molecular density maps. The charge density maps of sulfenamide are presented in Figure 2.

1. Total molecular charge density. To get the total electron density map, the MOs are presumed to be unrenormalized, that is the sum of the squares of the coefficients of the MOs, add to unity. The first step, therefore, is to renormalize the MOs. this is done by multiplying the starting eigen vector matrix by the inverse square root of the overlap matrix. If renormalization is not done, the total electron density would be too large, and the map would be quite incorrect. The total charge density is shown in Figure 2. Careful examination reveals the following:

a) There is an accumulation of negative charge around the nitrogen atom (−0.794), which is almost equally distribuated, idicating the polarization of the N—S bond.
b) The spacing and magnitude of the contours in the non-bonded side of the two atoms (N- and S-) show a very steep density gradient. The steep density gradient around the two atoms is clearly different. This

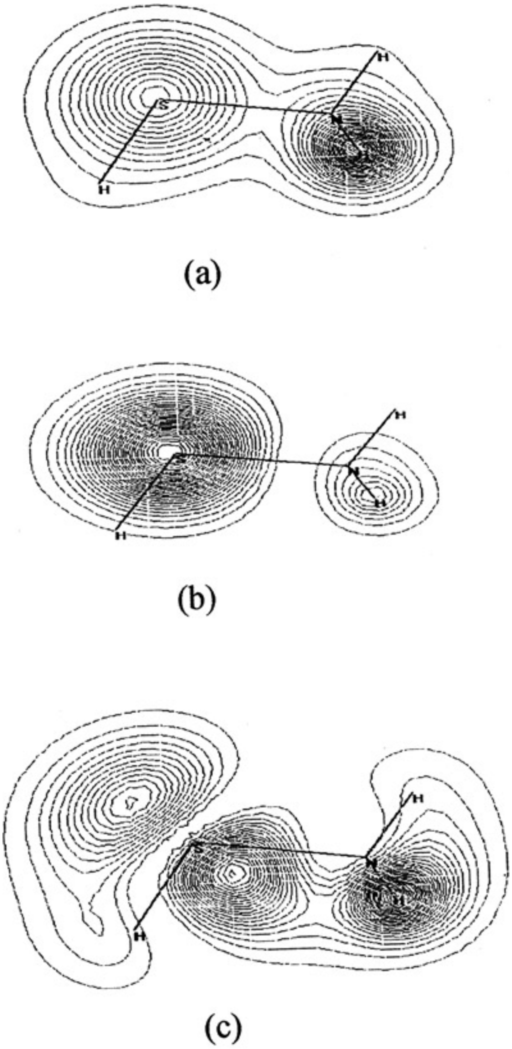


FIGURE 2 Charge density maps, (a) total, (b) HOMO, and (c) LUMO of sulfenamide.

difference may be attributed to two reasons: The different characteristics of the atomic like cores K and LK of nitrogen and sulfur atoms and the different properties of the nonbonding orbitals on the two atoms.

2. HOMO and LUMO charge density maps. Figure 2 represents the denisty maps of the highest occupied and lowest unoccupied molecular orbitals. The HOMO is π-type and is 70% localized on the P_z of S-atom and 30% on Pz of N-atom. On the other hand, The LUMO is a delocalized MO with 46% on S-atom, 24% on N-atom, 16% on H(S), and 14% on H(N). Therefore, the ionic character of the N—S bond is pronounced and the magnitude of charges that occur follow the simple electronegativity order S < N. This arises mainly from the very high polarization of the cores K and KL relative to the free atom situation.

Substituted Sulfenamides

The N—S bond is very sensitive to the electronic properties of the side group attached to it. It has been fairly well established that the electronic properties of the side groups dominate the electronic behavior, dynamics, and biological activity of the N—S bond. Compounds obtained from replacement of the H-atom attached to S-atom in (**I**) by a phenyl or methyl groups and one or two of the H-atoms on the N-atom by alkyl, phenyl or aryl are presented in Figure 1. These systems are studied aiming with the intension of exploring their trends rather than reporting exact values of observable quantities for the sulfenamide derivatives

*1. N,N-Disubstituted benzsulfenamides (**IIa–c**).* The minimum energy geometrical parameters, bond length, bond order, net charge, heat of formation, total energy, electronic energy, core-core repulsion energy, ionization potential, electron affinity, energy gap, and dipole moments are computed theoretically using 6-31G* basis set for **IIa–c** Tables III and IV. Some general remarks ought to be made:

a) Replacement of one or two H-atoms on N-atom by methyl-group (**IIb** and **IIc**) increases the N—S bond length. Substituation by methyl

TABLE III Optimized Geometries Bond Order and Net Charge of N,N-Disubstituted Benzsulfenamides

Substituents		Bond length				Bond order				Net charge	
R	R′	N—S	S—C_5	N—R	N—R′	N—S	S—Ph	N—R	N—R′	N—	S—
H	H	1.7492	1.8420	0.9922	0.9921	0.828	0.904	0.992	0.992	−1.0434	0.5389
H	CH_3	1.7578	1.8418	0.9941	1.4542	0.833	0.908	0.994	0.785	−0.9533	0.5289
CH_3	CH_3	1.7739	1.8409	1.4571	1.4574	0.826	0.918	0.797	0.791	−0.8662	0.5216
H	Ph	1.7635	1.8064	1.3704	0.9698	0.821	0.998	0.776	0.934	−0.9567	0.4451
CH_3	Ph	1.6461	1.7899	1.3813	1.4596	0.815	0.993	0.923	0.868	−0.8095	0.4459

TABLE IV Heat of Formation, Total Energies, Electronic Energies, Core-Core Repulsion Energies, Ionization Potential, Electron Affinity, Energy Gap, and Dipole Moments of N,N-Disubstituted Benzsulfenamides

Substituents										
R	R′	ΔH_f kcal mol^{-1}	E_T, au	E_{elec}, au	E_{core}, au	IP, au	E.A., au	ΔE, au	μ, D
H	H	125.68	−683.08	−1085.84	402.76	0.3072	0.1444	0.4516	1.169
H	CH_3	31.49	−722.08	−1210.48	488.39	0.3057	0.1445	0.4502	1.335
CH_3	CH_3	33.29	−761.09	−1346.78	585.69	0.3052	0.1441	0.4493	1.310
H	Ph	61.61	−912.73	−1789.59	876.86	0.2589	0.1304	0.3893	1.801
CH_3	Ph	68.04	−951.73	−1960.69	1008.97	0.2536	0.1339	0.3875	1.254

group is expected to introduce perturbation via inductive effects, i.e., the methyl group decreases the electronic charge on the N-atom causing lengthing of the N—S bond (c.f. Table III). Conjugative effects are not involved.

b) Replacement of one H-atom on N-atom by a phenyl group (**IId**) increases the N—S bond length. This is associated with a special rearranement of the nuclear frame to minimize the steric hindrance caused by the bulky phenyl group. In case of (**IIe**) the presence of methyl and phenyl attached to N-atom tends to slightly overestimate the tightness of binding leading to slightly shorter bond length.

c) The bond angles $\theta_{SNR'}$, θ_{SNR}, θ_{C_5SN}, and θ_{C_5SNR} are significantly affected by substitution on both the nitrogen and sulfur atoms. This is associated with the rearrangement of the nuclear frame to minimize the steric hindrance caused by the bulky substituents.

d) The ionic character of the N—S bond decreases on replacing the two H-atoms of nitrogen by a methyl or a phenyl group and reaches a minimum in case of (**IIc**). The change in bond order parallels the aforementioned change in bond length, indicating the sensitive response of the charge density to the substiruent effect. The net charge on N- and S-atoms show, however, a more localized response. Thus, the net charges on the S- and N-atoms are hardly affected by the nature of subsitituents.

e) As the size of the substituent at N-atom increases the compounds get more and more stable. This explains why low molecular weight sulfenamides are unstable and decompose at ordinary conditions.

f) Replacement of one or two H-atoms on N-atoms by methyl- or phenyl-groups decreases the energy levels HOMO/LUMO and hence decreases the ionization potential and electron affinity of compounds (**IIb–e**).

g) In spite of the symmetry conditions, the interaction between different moieties of the studied compounds (**IIa–e**) depends on the energy gap, $\Delta\varepsilon$, the estimated value for (**I**) is 13.7 eV, decreases to 12 eV in case of **IIa**. Replacement of one or two H-atoms on nitrogen by one or two methyl or phenyl groups decreases the energy gap. As the energy gap decreases the competitive interaction between different moities increases and hence the reactivity increases (c.f. Table IV).

h) The computed dipole moment for I is1.057D, replacement of the H on S-atom by a phenyl group, **IIa**, increases the dipole moment to 1.169D. The high polarization of the σ-frame seems to be responsible for the high value of dipole moment. Replacement of one or two H-atoms on nitrogen,by methyl- or phenyl-groups (**IIb–e**), increases the value of dipole moment and reaches a maximum in case of (**IId**). The electron donating power of the substituents has a pronounced effect not only on the magnitude, but also on the direction of the computed dipole moments.

*2. N-Arylbenzsulfenamides (**IV**).* Table V includes the optimized geometrical and ground state bonding properties of N-arylbenzsulfenamide. Careful inspection of Table V reveals the following:

a) The most stable conformer of all the studied compounds is the nonplanar form, with the aryl ring twisted out of the molecular plane ($HNSCH_3$) by an angle dependent on the electron attracting or donating power of the substituent in the para-position.

b) The ionization potential (IP) estimated theoretically for the studied N-arylbenzsulfenamides **IV** vary in a systematic way with the electron-donating-attracting power of substituents. Strong electron-withdrawing ($-NO_2$) increases the energy of HOMO and hence raises the IP, whereas, the CH_3-group, as an electron releasing substituent, has the opposite effect.

c) The variation of IP's with the Hammett σ_p value [31] is linear and fits the equation:

$$\text{I.P.} = 1.037\sigma_p + 7.1944.$$

This linear relationship (correlation coefficient 0.962) is presented in Figure 3.

TABLE V Optimized Geometries (Bond Lengths, Bond Order, and Net Charges) Heat of Formation, Total Energies, Electronic Energies, Core-Core Repulsion Energies, Ionization Potential, Electron Affinity, Energy Gap, and Dipole Moments of N-Arylbenzsulfenamides

Aryl Parameters	—H	p—CH_3	p—NO_2	p—Cl	p—F	p—Br
Bond length A						
N1—S	1.7315	1.7026	1.7389	1.7557	1.7320	1.7261
N—C_{15}	1.3688	1.3745	1.3598	1.3684	1.3705	1.4283
N—H	1.0126	0.9736	1.0056	0.9738	1.0051	0.9664
S—C_4	1.7856	1.7489	1.7943	1.8015	1.7877	1.7932
C_{18}—X	1.0795	1.5073	1.4563	1.7835	1.3292	1.9093
Bond order						
N—S	0.814	0.818	0.804	0.819	0.820	0.811
S—C_4	0.976	0.982	0.971	0.996	0.997	0.971
N—C_{15}	0.911	0.918	0.965	0.942	0.933	0.929
Net charge						
N—	−0.9918	−0.9787	−0.9861	−0.9568	−0.9574	−0.9893
S—	0.4511	0.4509	0.4592	0.4455	0.4434	0.4483
ΔH, Kcal mol^{-1}	61.61	33.16	52.92	70.60	17.91	47.50
E_T, au	−912.74	−951.78	−1116.22	−1371.63	−1011.57	−3482.06
E_{elec}, au	−1788.38	−1927.03	−2287.40	−2426.29	−1986.70	−4711.74
E_{core}, au	875.64	975.26	1171.18	1054.66	975.13	1229.68
IP, au	0.2645	0.2587	0.2942	0.2646	0.2625	0.2724
EA, au	0.1305	0.1313	0.0759	0.1238	0.1245	0.1252
ΔE, au	0.3950	0.3900	0.3701	0.3884	0.3870	0.3976
μ, D	2.5039	2.1252	9.1372	3.3147	3.7495	5.9043

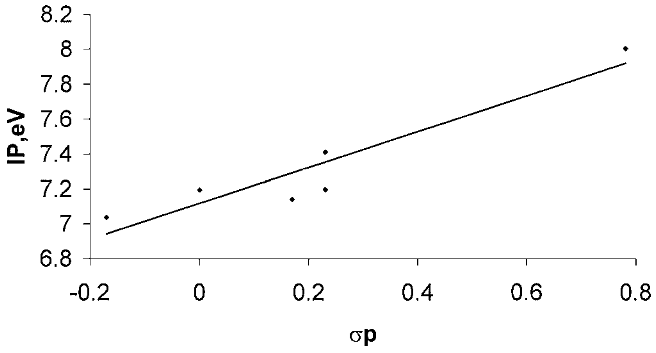


FIGURE 3 Variation of IP with Hammett constant.

TABLE VI Optimized Geometries (Bond Lengths, Bond Order, and Net Charges) Heat of Formation, Total Energies, Electronic Energies, Core-Core Repulsion Energies, Ionization Potential, Electron Affinity, Energy Gap, and Dipole Moments of N-Arylmethylsulfenamide

Aryl Parameters	—H	p—NO_2	p—CH_3	p—Cl	p—Br	p—F
Bond length A						
N—S	1.7241	1.7393	1.7316	1.7369	1.7477	1.7368
C_4—S	1.7886	1.7875	1.8122	1.8148	1.8305	1.7877
C_8—N	1.3766	1.3509	1.3915	1.3867	1.3751	1.3606
N—H	0.9915	0.9825	0.9896	0.9862	1.0037	0.9876
C_{11}—X	1.0628	1.4388	1.3880	1.7489	1.8589	1.3282
Bond order						
N—S	0.979	0.784	0.817	0.793	0.811	0.793
S—C_4	0.985	0.984	0.986	0.986	0.971	0.985
N—C_8	0.907	0.968	0.887	0.908	0.929	0.903
Net charge						
N—	−0.9655	−0.9574	−0.9696	−0.9679	−0.9794	−0.9697
S—	0.3447	0.3646	0.3332	0.3415	0.3629	0.3497
ΔH, kcal mol^{-1}	25.59	38.72	16.84	20.16	35.02	96.41
E_T, au	−722.22	−925.70	−761.26	−1181.12	−3291.53	−821.07
E_{elec}, au	−1211.55	−1678.08	−1335.74	−1820.26	−4120.62	−1397.17
E_{core}, au	489.32	752.37	574.48	639.74	811.08	576.10
IP, au	0.2627	0.2968	0.2586	0.2736	0.2720	0.2652
EA, au	0.1507	0.0758	0.1482	0.1321	0.1391	0.1340
$\Delta\varepsilon$, au	0.4134	0.3726	0.4008	0.4057	0.4111	0.3992
μ, D	0.8997	6.8582	0.7884	2.6933	2.5269	2.2325

d) The value of dipole moment for **IV**, X=H is 2.5039D. Electron withdrawing group (—NO_2) increases the dipole moment, whereas, electron donating group (—CH_3) has the opposite effect (c.f. Table V).

*3. N-Aryl methylsulfenamides (**III**)*. Table VI includes the optimized parameters and ground state properties of the studied derivatives. Data in hand, indicate that:

a) The most stable conformer of all the studied compounds **III** is the nonplanar configuration, with aryl moiety twisted out of the molecular plane ($HNSCH_3$) by an angle that depends on the electron attracting or donating power in the para-position.

b) The interaction between subsystems S—CH_3, N-aryl and sulfenamide moieties can be explained by the frontier orbital theory, namely, the HOMO, LUMO and energy gap, $\Delta\varepsilon$, of the compound.

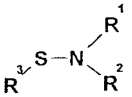
The estimated values of $\Delta\varepsilon$ decreases in the order H > Br > Cl > CH_3 > F > NO_2 respectively.

c) The $\Delta\varepsilon$ values show that the p-NO_2 aryl moiety enjoys the greater conjugative interaction with the sulfenamide moiety and has the smallest $\Delta\varepsilon$ value, whereas, the unsubstituted compound (X=H) shows the least conjugative interaction and hence largest $\Delta\varepsilon$ value.

d) The computed dipole momoent for **III** (X=H) is 0.8997D. The dipole momoent is sensitive to the replacement of the H in the para position by electron donating or withdrawing groups. Thus, methyl substituation perturbs the dipole moments. Due to its +I effect the dipole moment decreases by ~0.11D. The strong-withdrawing group show, however, a completely different trend (c.f. Table VI).

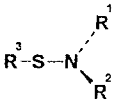
Barrier to Internal Rotatio

The N,S-disubstituted sulfenamide derivatives considered in the present calculations are presented below:

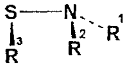


	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	CH_3	H	CH_3
d	Ph	H	H
e	CH_3	H	Pb
f	pH	H	CH_3

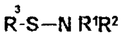
The rotational angle θ was taken to be 0° for the S-form, 180° for the R-form and 90° for the transition state. We represent the transition state as:



nitrogen inversion



S-N torsional



sulfur inversion

The energies of N,S-disubstituted sulfenamides have been calculated as functions of the angle θ, about the N—S bond, using 6-311G** and 6-311G**+MP2 basis sets. The rotation barrier height was obtained as the difference between the energies of the two conformers where $\theta = 90°$ and $\theta = 0°$. The calculated energies and barrier heights for N,S-disubstituted sulfenamides are presented in Table VII which shows:

TABLE VII Calculated Energies and Barriers Height for Sulfonamide Derivatives Using 6-311G** and (6-311G**+MP2)

Compound	S-form (0°)	TS (90°)	R-form (180°)	ΔE^*, Kcal mol^{-1}
a	−453.660	−453.639	−453.660	13.2
	(−453.961)	(−453.946)	(−453.961)	9.4
b	−492.732	−492.712	−492.708	12.45
	(−493.211)	(−493.196)	(−493.186)	9.4
c	−531.729	−531.702	−531.725	16.9
	(−532.319)	(−532.301)	(−532.316)	9.4
d	−683.217	−683.197	−683.215	12.5
	(−684.298)	(−684.287)	(−684.297)	6.9
e	−722.227	−722.169	−722.231	20.1
	(−723.459)	(−723.433)	(−723.471)	16.3
f	−722.242	−722.210	−722.231	19.4
	(−723.468)	(−723.442)	(−723.471)	16.3

a) The computed barrier for sulfenamide (**a**) is 13.2 Kcal/mol. On using MP2-level the barrier decreases to 9.4 kcal. Replacement of the H-atom on N-atom by a methyl or a phenyl group as in compound (**b and d**) increases the energy content of the almost planar ground state as well as the transition state. However, the energy difference between the two states is not affected by substituation at N-atom (c.f. Table VII).
b) Replacement of the two H-atoms at N- and S-atoms by a methyl group as in compound (**c**) increases the barrier height by 4 Kcal over (**a**). The increase in the barrier height of compound (**c**) may be attributed to the steric effect of two methyl groups at the transition state.
c) The magnitude of the barrier for compounds (**e**) and (**f**) are the same, indicating that the extent of interaction between methyl and phenyl with sulfenamide, moiety is the same regardless of the position of the methyl or phenyl group on S- and/or N-atom.
d) One can attribute the lower ground state energy in comparsion to transition state energy to: 1. The nodal plane of the sulfur lone-pair in the ground state is approximately at right angles to the lone-pair on nitrogen-atom, minimizing the repulsive interaction, 2. In the transition state, the local symmetry axis of the orbitals lies in the same plane or nearly so and the inter orbital repulsion is at maximum. 3. The steric hindrance provides one contribution to the destabilization of the transition state.

CONCLUSIONS

MO calculations predict that the pyramidal structure of sulfenamide is more stable than the planar structure. The planar configuration is more polarized than the pyramidal one as depicted from the total energy and dipole moment. The total charge density maps show a very steep density gradient. This may be attributed to different characteristics of atomic like core K and KL of N- and S-atoms and different properties of the non-bonding orbitals on the two atoms. The HOMO of sulfenamide (**I**) is of π-type which is 70% localized on S-atom. On the other hand, The LUMO is a delocalized MO consisting of 24% on N-atom, 46% on S-atom, 16% on H(s), and 14% on H(N). The most stable conformers of all the studied compounds **II**, **III**, **IV** are the non planar ones, with the substituent at N-atom or S-atom twisted out of the molecular plane by an angle that depends upon the electron attracting or donating power. The electron donating power has a pronounced effect not only on the magnitude, but also on the direction of the computed dipole moments. The estimated IP, theoretically, for all the studied compounds vary in a systematic way with electron donating-attracting power of substituents. Strong electron-withdrawing NO_2 group increases the energy of the HOMO and hence raises the IP, whereas, the CH_3 group as an electron releasing substituents has the opposite effect.

The data of the barrier to internal rotation of N,S-substituted sulfenamide computed, theoretically, are best accommodated by postulating three contributions: overlap repulsion between non-bonding electrons on S- and N-atom, steric hindrance at the transition state and dependence of the N—S bond strength on dihedral angle.

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