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SCF MO Calculations for 1,3-Thiazole and 2-Phenyl-1,3-thiazole and Rotational Barriers in 2-Phenyl-1,3-thiazole and Its Protonated Form

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SCF MO calculations show that 2-phenyl-1,3-thiazole exists in *planar* configuration, while protonated 2-phenyl-1,3-thiazole tends to stabilize in a *non-planar* form.

The reactivity and aromaticity of the 1,3-thiazole, a five-membered aromatic compound containing two different heteroatoms (S,N), is a problem of current interest¹. The reactivity of 2-phenyl-1,3-thiazole was also the object of extended studies²⁻⁴, particularly the transmission of the effects of the substituents from one ring to the other, which is considered as a measure of the mutual conjugation between the two rings. In order to obtain further information about the π -interaction between the rings in 2-phenyl-1,3-thiazole, we carried out molecular orbital calculations for rotational barrier in this molecule and its protonated form.

THEORETICAL APPROACH

Calculations were carried out using recent Dewar's variant^{5,6} of Pople's SCF MO method⁷. In Dewar's variant the essential parameter of the theory: one-electron core resonance integral (β_{ij}^c) is given as follows:

$$\beta_{ij}^c = kS_{ij} \quad (1)$$

$$k = k_{ij} \frac{I_i + I_j}{2} \quad (2)$$

where S_{ij} is the overlap integral estimated from the Slater-Zener orbitals, while k_{ij} is a parameter characteristic for a particular bond. The following bond parameters were used in the present work:

$$k_{C-C} = 0.6207 \quad (3)$$

$$k_{C-N} = 0.5507 \quad (4)$$

$$k_{C-S} = 0.9240 \quad (5)$$

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Since the standard π -approximations are unable to calculate the strain and non-bonded interactions, the problem of rotational barrier cannot be studied by this kind of approach, which is, therefore, limited to planar structures. In the case of two π -electron rings linked together by one bond, the π -interaction between the rings tends to keep the molecule coplanar; the non-bonded interactions, on the other hand, are smallest when the terminal units are perpendicular to each other. It is, therefore, necessary to include both effects in order to obtain a more realistic estimate for the potential function of rotation. In the present work a procedure similar to the one used in the case of biphenyl⁵ was made use of, *i. e.* the effects of non-planarity in the π -bonding energy was estimated by assuming that the core resonance integral shows a cosine dependence on the angle of twist (Θ):

$$\beta_{\Theta}^c = \beta_{ij}^c \cos \Theta \quad (6)$$

The energy minimization was carried out as a function not only of the twist angle but also of the inter-ring distance. For both molecules we carried out the minimization twice: first we started with a very long distance [1.540 Å], and then with a rather short one [1.350 Å]. In both minimization procedures we obtained for 2-phenyl-1,3-thiazole the same value of the inter-ring distance of 1.466 Å, while this distance for the case of the protonated 2-phenyl-1,3-thiazole was 1.426 Å. Similarly, the energies converged to the same values of 56.62 eV for 2-phenyl-1,3-thiazole and to 57.75 eV for the protonated form of 2-phenyl-1,3-thiazole. This procedure was repeated throughout our calculations for various twist angles. The contribution of non-bonded interactions in the case of the protonated 2-phenyl-1,3-thiazole was estimated using the expressions of Bartell⁸ for non-bonded interactions between carbon-carbon, carbon-hydrogen, and hydrogen-hydrogen.

The geometry was first calculated from the Dewar SCF MO treatment using (6) for each value of Θ and then the non-bonded interactions were estimated from Bartell's potential functions by using the calculated geometries; the C—H bond lengths were assumed to be 1.082 Å.

DISCUSSION AND RESULTS

The method used^{5,6} here gives good estimates of heats of atomization, as well as of geometries of conjugated molecules. The calculated heats of atomization ($-\Delta H_a$) for investigated molecules together with the calculated values of total energy (E_{tot}), vertical ionization potentials [(IP)_v] and aromatic stabilization (A_s) are given in Table I. The calculated bond lengths and electron densities of thiophene, 1,3-thiazole, 2-phenyl-1,3-thiazole and protonated forms of 1,3-thiazole and 2-phenyl-1,3-thiazole are given in Fig. 1. Unfortunately there are as yet no experimental data available for 1,3-thiazole and 2-phenyl-1,3-thiazole to test our calculations. On the other hand, the agreement with experiment for the thiophene is very good indeed.

Our calculations imply that the aromaticity of 1,3-thiazole is of the order of the one of thiophene; 1,3-thiazole having a slightly higher value of aromatic stabilization than thiophene. Aromatic stabilization is calculated in the manner described earlier^{5,6,9}. Calculated vertical ionization potentials of thiophene and thiazole are almost identical. It was pointed out earlier¹⁰ that the stabilization of isoconjugated molecules reflects in the higher value of

TABLE I
 Calculated Energy Values

Compound	$-\Delta H_a$ at 25° C (eV)		$-E_{\text{tot}}$ (eV) ^a	(IP) _v (eV) ^b		A _s (kcal/mole)
	Calc.	Obs.		Calc.	Obs.	
Thiophene (1)	40.32	40.32 ^c	22.57	8.93	9.0 ^d	6.5
1,3-Thiazole (2)	35.05		21.74	8.94		7.2
Protonated 1,3-Thiazole (3)			22.21			
2-Phenyl-1,3-thiazole (4)	87.68		56.62	8.54		28.8
Protonated 2-phenyl-1,3-thiazole (5)			57.75			

^a $E_{\text{tot}} = E_G + E_\pi$; ^b From Koopmans theorem; ^c G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith, and H. M. Huffman, *J. Am. Chem. Soc.* 71 (1949) 797; S. Sunner, *Acta Chem. Scand.* 9 (1955) 847; ^d H. D. Hartough, in *The Chemistry of Heterocyclic Compounds*, Vol. 3, A. Weissberger, Editor, Interscience Publishers, Inc., New York 1952, p. 94.

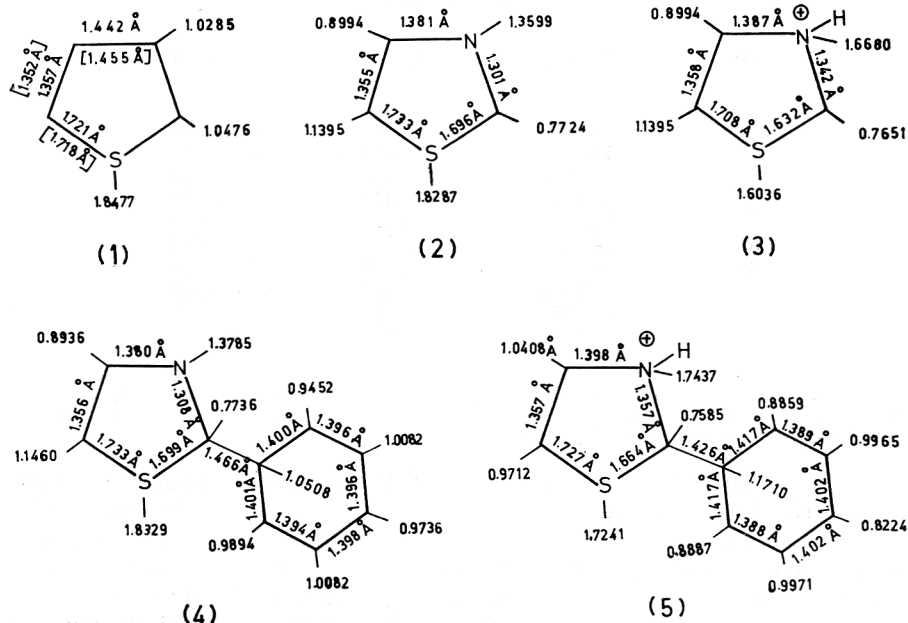


Fig. 1. Molecular orbital diagrams (bond lengths and charge densities) of thiophene, thiazole, protonated thiazole, 2-phenylthiazole, and protonated 2-phenylthiazole. The observed bond lengths of thiophene [B. Bak, D. Christensen, J. Rastrup-Andersen, and L. Tannenbaum, *J. Chem. Phys.* 25 (1956) 892] are given in brackets

the first π -ionization potential. Therefore, our calculated value of vertical ionization potential for thiazole of 8.94 eV might be quite close to the experimental value; the deviation from experiment may be of the order of 0.1–0.2 eV. Note that the sum (29.8 kcal/mole) of aromatic stabilization for 1,3-thiazole (7.2 kcal/mole) and benzene (22.6 kcal/mole) is nearly equal to the calculated value for 2-phenyl-1,3-thiazole (28.8 kcal/mole) and this is in agreement with the earlier prediction¹¹ that if aromatic components A and B are linked together by an essential single bond (1.46 Å), the following relationship is valid:

$$A_s(A-B) \cong A_s(A) + A_s(B) \quad (8)$$

The validity of the above relation was earlier confirmed for biphenyl⁵, and 2,2'-bithiophene⁶.

Table II shows the results of calculation for the rotation of 2-phenyl-1,3-thiazole, where the non-bonded interactions are neglected, because no H-atom is attached to the N or S atoms and there is also no potential function presently available for the interaction of hydrogen with a lone pair. The planar configuration of 2-phenyl-1,3-thiazole is the most stable form of this molecule, showing a difference of 9.2 kcal/mole from the perpendicular configuration ($\Theta = 90^\circ$). Apparently, 2-phenyl-1,3-thiazole is more stable in planar configuration than, for example, biphenyl, because of the lack of any direct hydrogen-hydrogen non-bonded interactions. These interactions are in the case of biphenyl over balancing conjugation and keeping biphenyl in configuration with the dihedral angle of 42° between two rings.

TABLE II
Rotation of Phenyl Group Around the Central Carbon-Carbon Bond in 2-Phenyl-1,3-thiazole

Θ^a	$-E_\pi$ (eV) ^b	$-E_{tot}$ (eV) ^c	ΔE_{tot} (eV) ^d
0°	14.6002	56.6156	-0.3969
10°	14.5781	56.4904	-0.3717
20°	14.5193	56.5230	-0.3043
30°	14.4421	56.4340	-0.2153
40°	14.3673	56.3475	-0.1288
50°	14.3103	56.2810	-0.0623
60°	14.2761	56.2411	-0.0244
70°	14.2612	56.2236	-0.0049
80°	14.2557	56.2191	-0.0004
90°	14.2557	56.2187	0.0000

^a dihedral angle of rotation; ^b π -bonding energy for each dihedral angle of rotation; ^c total energy for each dihedral angle of rotation; ^d stability of each conformation relative to the perpendicular configuration ($\Theta = 90^\circ$).

Similar calculations for the protonated 2-phenyl-1,3-thiazole are reported in Table III. The calculated angle of the twist in the protonated 2-phenyl-1,3-thiazole is about 10° and is expected to be of lower value than the angle of twist deduced for biphenyl (42°) by Bastiansen *et al.*¹² Perhaps the experimental value is somewhat greater because the non-bonded interactions with lone pairs on the sulphur atom were neglected. Note the slow change of energy at the minimum (around 10°), implying that torsional vibrations should have large amplitudes.

TABLE III

Rotation of Phenyl Group Around the Central Carbon-Carbon Bond in Protonated 2-Phenyl-1,3-thiazole

Θ^a	$-E_{\text{tot}}$ (eV) ^b	ΔE_{tot} (eV) ^c	V_{IJ} (eV) ^d	$\Delta E_{\text{tot}} + V_{\text{IJ}}$ (eV)
0°	57.8091	-0.8961	0.4771	-0.4179
10°	57.7571	-0.8441	0.4177	-0.4264
20°	57.6154	-0.7024	0.2863	-0.4161
30°	57.4219	-0.5089	0.1574	-0.3515
40°	57.2254	-0.3124	0.0772	-0.2352
50°	57.0678	-0.1548	0.0339	-0.1209
60°	56.9701	-0.0571	0.0137	-0.0434
70°	56.9262	-0.0132	0.0045	-0.0087
80°	56.9143	-0.0013	0.0009	-0.0004
90°	56.9130	-0.0000	0.0000	0.0000

^a dihedral angle of rotation; ^b total energy for each dihedral angle of rotation; ^c stability of each configuration relative to the perpendicular configuration ($\Theta = 90^\circ$); ^d non-bonded interactions calculated using Bartell's expressions.

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IZVOD

SCF MO računi za 1,3-tiazol i 2-fenil-1,3-tiazol i rotacijske barijere u 2-fenil-1,3-tiazolu i protoniranom 2-fenil-1,3-tiazolu

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SCF MO računi pokazuju da 2-fenil-1,3-tiazol postoji u *planarnoj* konfiguraciji, dok se protonirani 2-fenil-1,3-tiazol nastoji stabilizirati u *neplanarnoj* formi.

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