MOLECULAR MECHANICAL AND QUANTUM-CHEMICAL STUDY OF SOME ALDEHYDE THIOSEMICARBAZONES

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Abstract

Conformational analysis and quantum-chemical calculations were carried out by means of the methods *MMP2* and *SCF MO LCAO* in *CNDO/2* approximation for a group of aldehyde thiosemicarbazones. The analysis of the electron density distribution depending on the substituents' nature was done on the basis of the data obtained. The structural comparence were made between *MO* calculations on the molecules. The net charge distribution, dipole moments and heat of formation were listed.

BAZI ALDEHİT TİYOSEMİKARBAZONLARIN MOLEKÜLER MEKANİKSEL VE KUANTUM KİMYASAL ARAŞTIRILMASI

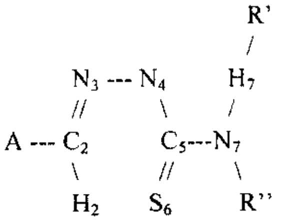
Özet

Bir grup aldehit tiyosemikarbazonun *MMP2* ve *CNDO/2* yaklaşımı ile *SCF MO LCAO* yöntemleri yardımıyla konformasyon ve kuantum kimyasal hesaplamaları yapıldı. Substituent doğasına bağlı elektron yoğunluğu analizi elde edilen veriler esas alınarak yapıldı. Moleküllerin *MO* hesaplamaları arasında yapısal kıyaslamalar yapıldı. Net yük dağılımı, dipol momentler ve oluşum ısıları listelendi.

Introduction

Recently, some aldehyde thisemicarbazones are polyfunctionalyzed compounds which easily cyclize by action of bases, acids oxidants; therefore they are useful and versatile synthons for the preparation of five or six-membered heterocyclic compounds [1,2].

It is important to study their electronic structures with the aim of receiving information on the electron distribution in the systems and its dependence on the nature of substituents. This allows for deeper understanding of the processes occuring in the molecules and gives possibility of purposeful syntheses of new compounds. In this study, the results of the electron structure investigations are presented for a group of compounds aldehyde thiosemicabazones in Figure 1.



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	A	*R'*	*R''*
a	*COOMe*	*Ph*	*Ph*
b	*COOMe*	*Me*	*Ph*
c	*COOMe*	*H*	*Ph*
d	*COOMe*	*Me*	*Me*
e	*COOMe*	*Me*	*H*
f	*COOMe*	*H*	*H*
g	*COPh*	*Me*	*Ph*
h	*Me*	*Me*	*Ph*
i	*Ph*	*Me*	*Ph*
j	*Ph*	*Me*	*Me*
k	*COPh*	*Me*	*H*

Figure 1. The skeleton of the compounds investigated.

Methodology

At the first stage we optimized the geometry of the molecule by the *MMP2* method for molecular mechanics. The optimized values of atomic coordinates were used for further quantum-chemical calculations. Systematic calculations were made by the method *MO LCAO SCF* in the *CNDO/2* approximation [3-4]. The *CNDO/2* method has been systematically parameterized for the most part of the periodical system [5].

Results and Discussion

In the table 1, optimized geometrical characteristics calculated by means of *MMP2* are given for the molecules ***1a-k***. The spatial disposition of atoms for the molecules ***1a-k*** is shown in Figure 2.

The self-consistent energy values and wave functions were obtained as a result. Based on the data, the rest of the electron structure parameters necessary for analysing the electron density distribution in the systems was calculated. The accuracy of self-consistency is equal to 0.01 electron charge unit *(e^-)*.

Table 1. Optimized structural parameters of the compounds ***1a-k***.

Geometric Parameters(A , °)	*Compounds*										
	1a	*1b*	*1c*	*1d*	*1e*	*1f*	*1g*	*1h*	*1i*	*1j*	*1k*
C1(A)-C2	1.36	1.36	1.36	1.36	1.36	1.36	1.36	1.50	1.28	1.28	1.36
C2-H2	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.35	1.35	1.10
C2-N3	1.27	1.27	1.27	1.27	1.27	1.27	1.28	1.27	1.10	1.10	1.27
N3-N4	1.44	1.44	1.43	1.44	1.44	1.43	1.44	1.44	1.44	1.44	1.44
N4-R'	1.38	1.47	0.97	1.47	1.47	0.97	1.48	1.47	1.47	1.47	1.47
N4-C5	1.36	1.36	1.35	1.36	1.36	1.35	1.37	1.37	1.36	1.37	1.36
C5-S6	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68
C5-N7	1.36	1.36	1.35	1.35	1.35	1.34	1.36	1.36	1.36	1.36	1.35
N7-H7	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.97	0.96	0.96
N7-R''	1.37	1.37	1.37	1.47	0.96	0.95	1.38	1.37	1.37	1.46	0.96
C1(A)-C2-N3	121.1	121.3	121.6	121.1	121.2	121.5	117.0	120.2	119.6	119.8	121.3
C1(A)-C2-H2	118.2	117.9	117.6	118.0	117.9	117.8	120.2	116.5	116.9	117.0	117.1
N3-C2-H2	120.8	120.8	120.8	120.9	120.9	120.8	122.8	123.3	123.5	123.2	121.6
C2-N3-N4	128.8	128.8	129.1	129.5	129.6	129.6	135.8	132.5	129.7	131.1	131.7
N3-N4-R'	114.5	114.0	114.3	113.7	113.8	113.9	110.5	111.8	127.7	129.1	112.7
R'-N4-C5	121.1	120.7	115.1	120.6	120.1	114.2	118.4	118.4	113.2	112.4	117.9
N3-N4-C5	124.3	125.3	130.7	125.6	126.1	132.0	131.1	129.8	119.0	118.4	129.4
N4-C5-S6	118.2	118.6	113.5	119.9	121.0	116.4	122.5	123.0	121.4	123.2	126.7
N4-C5-N7	120.0	119.6	122.0	135.4	124.0	127.5	116.9	117.9	118.7	118.7	120.4
N7-C5-S6	121.7	121.9	124.5	119.2	114.2	116.1	120.6	119.0	119.8	118.0	112.9
C5-N7-H7	116.8	116.6	116.0	117.6	122.2	123.2	115.1	116.4	127.0	125.4	122.1
C5-N7-R''	127.4	127.8	128.9	125.3	120.6	120.0	130.8	128.1	117.2	118.1	121.0
H7-N7-R''	115.8	115.6	115.1	116.9	117.0	116.7	114.0	115.4	115.8	116.5	117.0

In the table 2, the efective charge distributions in *"the active zones"* and on the atoms adjusted are given.

Table 2. Efective charges on atoms for the systems calculated *(e⁻)*.

Atoms	*Compounds*										
	1a	*1b*	*1c*	*1d*	*1e*	*1f*	*1g*	*1h*	*1i*	*1j*	*1k*
C1(A)	0.411	0.417	0.380	0.388	0.388	0.383	0.250	-0.020	0.023	0.023	-0.011
C2	-0.009	0.009	-0.009	0.005	0.010	0.002	0.060	0.129	0.130	0.093	0.059
H2	0.001	0.002	-0.004	-0.000	0.001	-0.002	0.019	0.015	-0.008	-0.007	0.243
N3	-0.004	-0.012	0.020	0.001	-0.002	0.014	-0.035	-0.091	-0.093	-0.079	-0.026
N4	-0.034	-0.061	-0.110	-0.107	-0.101	-0.109	-0.104	-0.100	-0.103	-0.021	-0.116
R'	-0.011	0.087	0.014	0.095	0.093	0.155	0.076	0.078	0.080	0.074	0.079
C5	0.326	0.318	0.295	0.284	0.300	0.313	0.282	0.287	0.287	0.328	-0.301
S6	-0.466	-0.451	-0.421	-0.407	-0.423	-0.443	-0.409	-0.426	-0.420	-0.485	-0.428
N7	-0.150	-0.140	-0.176	-0.152	-0.197	-0.201	-0.173	-0.174	-0.176	-0.151	-0.195
H7	0.112	0.112	0.120	0.118	0.122	0.126	0.114	0.112	0.113	0.108	0.117
R''	0.162	0.164	0.132	0.104	0.158	0.158	0.144	0.145	0.143	0.095	0.155

As it seen in table 2, calculated net charges can be compared experimental values which can be derived the difference structure *(N - X),* that are obtained *X-ray* and *neutron* diffraction data. Presently, we do not have both diffraction data for these molecules.

The thiosemicarbazones *1* are more reactive under photochemical than under thermal conditions. However the structure of the products obtained from the thiosemicarbazone cyclization is independent of the adopted reaction condition, either photochemical or thermal [1]. The formation of the cyclization *(triazin ring)* is independent of the nature of the *R'* and *R''* groups of the thiosemicarbazone chain, the *R'* and *R''* groups influencing only the reaction yield. The reaction probably consists of a nucleophilic attack of the *N3* nitrogen atom of the thiosemicarbazone chain on the carbon atom of the carbo-methoxy group followed by the departure of the leaving alkoxy group from a cyclic intermediate, subsequent deprotonation of the *N3* nitrogen atom and eventually by the formation of a double bond between carbon and oxygen atoms [1].

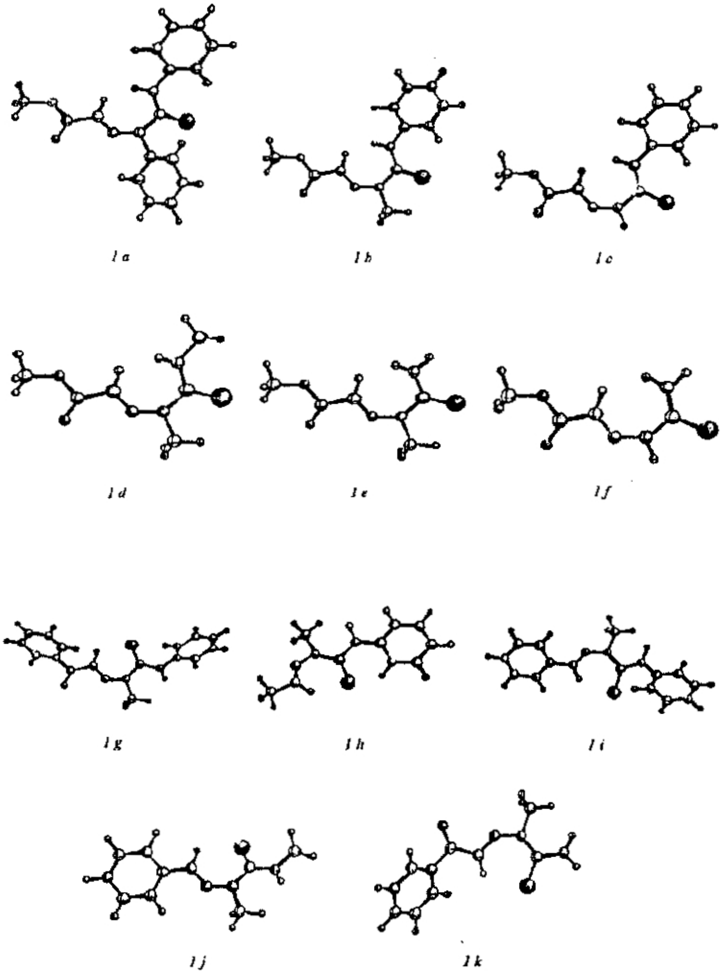

Figure 2. The spatial disposition of atoms for the molecules ***1a-k***.

An analysis of the effect of the nature of *R'* group on the reactivity has shown that the effect of this group on the reaction yield is less important that of the *R''* group, the methyl group being, among those examinated, the most efficient group.

The influence of the aldehydic residue *A* on the photohetero cyclization has also been investigated in thiosemibarbazones ***Ig-i***. These compounds have the same thiosemicarbazidic chain structure, characterized by a methyl group on *N4*, a terminal *NHPh* group and a residue *A* having different electronic effects ; electron-withdrawing the benzoyl group, electron-repelling the methyl group and the electronic effect of the phenyl group depending on its position with respect to the reaction centre and the reaction type. These different behaviours can be displaied by the σ^+ *(-0.18)* and σ^- *(0.08)* values of the phenyl group [6].

Substituion of *H*, for methyl or phenyl group, *R''*, in compound *I* determined a dramatic lowering of the reaction yield or even a complete loss of reactivity. The above results show that the mechanism of the photo induced cyclization is not influenced by the electronic density on the aldehydic carbon. According to the afore interpretation the activation of *N3* nitrogen atom is the main factor affecting the photocyclization of thiosemicarbazones *I*.

In conclusion the data obtained indicate that: *i)* the terminal group of the thiosemicarbazone chain operates as a chromophore, *ii)* the nature of the heterocyclic ring synthesized depends only on the chemical structure of the residue *A*, while the electronic properties of *A*, in contrast to what was observed for the oxidative cyclization reaction, are important.

The analysis of the electron density distributions on bonds is given in table 3 in the form of the *Wiberg*'s indices W_{ij}. Index W_{ij} may be considered as a quantum-chemical analogoue of the bond *(i-j)* multiplicity and characterizes the strength of the bond. The energy levels disposition for the molecular orbitals entering into *"the active zones"* is presented in table 4.

Table 3. The *Wiberg*'s indices for the bonds of in *'the active zone'*.

Bonds	*Compounds*										
	1a	*1b*	*1c*	*1d*	*1e*	*1f*	*1g*	*1h*	*1i*	*1j*	*1k*
C1(A)-C2	1.12	1.12	1.11	1.11	1.11	1.11	1.08	1.05	1.11	1.11	1.11
C2-N3	1.83	1.38	1.84	0.84	1.84	1.84	1.86	1.92	1.84	1.84	1.84
C2-H2	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.95	0.94	0.94	0.94
N3-N4	1.01	1.01	1.02	1.00	1.00	1.02	0.99	0.97	0.97	0.99	0.99
N4-R'	0.99	1.00	0.95	1.00	1.00	0.95	1.01	1.01	1.01	1.02	1.01
N4-C5	1.19	1.20	1.23	1.20	1.21	1.25	1.23	1.24	1.22	1.25	1.20
C5-C6	1.22	1.23	1.22	1.24	1.23	1.20	1.24	1.23	1.24	1.23	1.31
C5-N7	1.29	1.29	1.27	1.28	1.29	1.29	1.24	1.24	1.25	1.26	1.26
N7-H7	0.94	0.95	0.94	0.95	0.96	0.96	0.94	0.94	0.94	0.95	0.96
N7-R''	0.99	1.00	0.99	1.01	0.96	0.96	1.00	1.00	1.00	1.02	0.96

Table 4. Some informations about the molecules derived molecular orbital calculations by *CNDO* method.

Compounds	Total Energy *(a.u.)*	E_{el} *(eV)*	μ *(Debye)*	*HOMO (eV)*	*LUMO (eV)*
1a	-207.5	-1063.4	6.4	-9.9	1.7
1b	-170.5	-767.5	6.2	-10.2	1.5
1c	-161.8	-688.6	6.4	-10.2	1.2
1d	-133.6	-511.5	6.1	-10.3	1.2
1e	-124.9	-449.5	6.0	-10.3	1.2
1f	-116.2	-386.7	6.6	-10.4	1.1
1g	-189.0	-940.6	4.6	-9.9	1.5
1h	-126.7	-560.8	5.6	-9.7	2.9
1i	-163.6	-811.5	5.8	-9.8	2.0
1j	-126.7	-556.1	6.2	-9.7	2.1
1k	-143.4	-612.6	4.7	-10.0	1.4

On the basis quantum calculations, the data were obtained on the spatial (complete optimization of all the geometrical parameters) and electron structure (charges on atoms, bond indices and their components *MO* energies and composition) of the complexes between the compounds ***1a-k***. The obtained information enables to draw the conclusions about the relative strength and the ionicity of the *S-C* bond, as well as about the effect of the substituent R on the structure of the compounds.

Table 5. Main Orbital Components for *HOMO-LUMO* Energy Levels of Compounds ***1a-k***

Compounds	*Main Orbital Components**
1a	$\Psi_{HOMO} \approx .32p_z^{N4} + .35p_y^{S6} - .76p_z^{S6} + .19p_z^{N7}$ $\Psi_{LUMO} \approx -.38p_z^{C1} - .37p_z^{C2} + .21p_z^{N3} + .54p_z^{N3} - .21p_z^{C5} + .39p_z^{O9}$
1b	$\Psi_{HOMO} \approx -.18p_z^{N4} + .87p_z^{S6} - .25p_z^{N7}$ $\Psi_{LUMO} \approx -.36p_z^{C1} - .38p_z^{C2} - .22p_x^{N3} + .54p_z^{N3} - .23p_z^{C5} + .39p_z^{O5}$
1c	$\Psi_{HOMO} \approx -.33p_x^{S6} + .50p_y^{S6} + .73p_z^{S6}$ $\Psi_{LUMO} \approx .31p_x^{C1} + .39p_z^{C2} - .25p_x^{N3} - .52p_z^{N3} + .28p_z^{C5} - .37p_z^{O5}$
1d	$\Psi_{HOMO} \approx .34p_x^{S6} - .85p_y^{S6} - .20p_z^{S6}$ $\Psi_{LUMO} \approx -.32p_z^{C1} - .40p_z^{C2} + .23p_x^{N3} + .53p_z^{N3} - .28p_z^{C5} + .37p_z^{O9}$
1e	$\Psi_{HOMO} \approx .48p_x^{S6} - .79p_y^{S6} + .31p_z^{S6}$ $\Psi_{LUMO} \approx -.32p_z^{C1} - .40p_z^{C2} + .21p_x^{N3} + .55p_z^{N3} - .18p_y^{C5} - .18p_z^{C5} + .37p_z^{O9}$
1f	$\Psi_{HOMO} \approx -.63p_x^{S6} + .72p_y^{S6} - .21p_z^{S6}$ $\Psi_{LUMO} \approx ..32p_z^{C1} + .39p_z^{C2} - .19p_x^{N3} - .19p_y^{N3} + .22p_z^{C5} - .38p_z^{O9}$
1g	$\Psi_{HOMO} \approx -.92p_x^{S6} - .13\,p_z^{S6} + .14\,p_z^{N7}$ $\Psi_{LUMO} \approx -.24p_y^{C1} - .27p_z^{C1} - .31p_z^{C2} + .43p_z^{N3} - .30p_z^{C5} + .30p_y^{O8} + .32p_z^{O8}$
1h	$\Psi_{HOMO} \approx -.14p_z^{N4} - .92p_x^{S6} - .14p_z^{N7}$ $\Psi_{LUMO} \approx -.29p_z^{C2} + .21p_z^{N4} - .64p_z^{C5} + .30p_z^{S6} + .23p_z^{N7}$
1i	$\Psi_{HOMO} \approx -.12p_x^{N4} - .81p_x^{S6} - .48p_z^{S6} - .11p_x^{N7}$ $\Psi_{LUMO} \approx .36p_z^{C2} + .25p_x^{N3} + .39p_z^{N3} + .31p_z^{C5} - .26p_z^{C25} - .25p_z^{C25} + .32p_z^{C22}$
1j	$\Psi_{HOMO} \approx -.17p_z^{C2} + .21p_x^{N4} - .30p_z^{N4} + .30p_y^{S6} + .78p_z^{S6}$ $\Psi_{LUMO} \approx -.36p_z^{C2} - .24p_x^{N3} + .44p_z^{N3} + .28p_z^{C11} - .32p_z^{C1} + .28p_z^{C13} - .36p_z^{C15}$
1k	$\Psi_{HOMO} \approx .85p_x^{S6} - .39p_y^{S6} - .20p_z^{S6}$ $\Psi_{LUMO} \approx -.26p_y^{C2} + .31p_z^{C2} + .38p_y^{N3} - .41p_z^{N3} + .19p_z^{C5} - .22p_y^{C1} + .31p_z^{C1} + .27p_y^{O17}$ $-.38p_z^{O17}$

**C1 = C(A), O5, O8, O9, O17 = O(A) ; C11, C13 = C(R') ; C22, C25 = C(R')*

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