HÜCKEL MO CALCULATIONS FOR THE PRODUCTS OF THE OXIDATIVE DESULFURATION OF THIOBENZANILIDE TO BENZANILIDE

Bogdan Bogdanov

Faculty of Chemistry, University „Kiril and Metodij" — Skopje

The oxidation of thiobenzanilide proceeds by its desulfuration and formation of benzanilide. The first stage of this reaction goes through the formation of thiobenzanilide-S-oxide, a stable intermediate which can be further oxidized to thiobenzabilide-S,S-dioxide, an unstable intermediate which decomposes to benzanilide[1,2].

The aim of this paper is to report the results of the Hückel MO calculations for thiobenzanilide, thiobenzanilide-S-oxide, thiobenzanilide-S, S-diohxide and benzanilide and determine their reactivity and stability in this reaction.

The values for the Coulomb integrals α_X and resonance integrals β_{XY} were calculated from[3,4],

$$\alpha_X = \alpha_0 + h_X$$

$$\beta_{XY} = K_{XY}\,\beta_0$$

The values of the Hückel MO parametars h_X and K_{XY} are given in table. 1.

The π-electronic energy levels as well as the energy diference between HOMO — LUMO for thiobenzanilide, thiobenzanilide-S-oxide, thiobenzanilide-S,S-dioxide and benzanilide are shown in Figure 1.

Table 1. Hückel's MO Parameters[3,4]

atom type	no. of elektrons	h_X for $\alpha_X = \alpha_0 + h_X$	K_{XY} for $\beta_{XY} + K_{XY}\,\beta_0$
G	1	0,00	$K_{\dot{C}-\dot{C}} = 1{,}00$
N	2	1,40	$K_{\dot{C}-\dot{N}} = 0{,}90$
O	1	1,00	$K_{\dot{C}-\dot{O}} = 1{,}06$
S	1	0,46	$K_{\dot{C}-\dot{S}} = 0{,}81$
S	2	1,10	$K_{\dot{C}-\ddot{S}} = 0{,}69$
			$K_{\ddot{S}-\dot{O}} = 0{,}85$

It can be seen from Fig. 1. that benzanilide is the most stable among these compounds. It is the final product of the oxidation and cannot be furtxher oxidized under the given experimental conditions[1,2]. The calculated stability decreases in the following order: thiobenzanilide, thiobenzanilide-S-oxide and thiobenzanilide-S,S-dioxide, which is in agreement wit the experoimental results[1,2]. Thiobenzanilide-S,S-dioxide is the least stable compound and cannot be isolated as it easily decomposes to benzanilide.

Figure 2 schows the calculated π-charge densities, π-bond order and free valencies for thiobenzanilide, thiobenzanilide-S-oxide, thiobenzani lide-S,S-dioxide and benzanilide. The MO diagram for thiobenzanilide-S, S-dioxide, where the π-elektron order is smaller (0,278) compared to thio benzanilide (0,720) and thiobenzanilide-S-oxide (0,595), predicts the insta bility of the C — S bond.

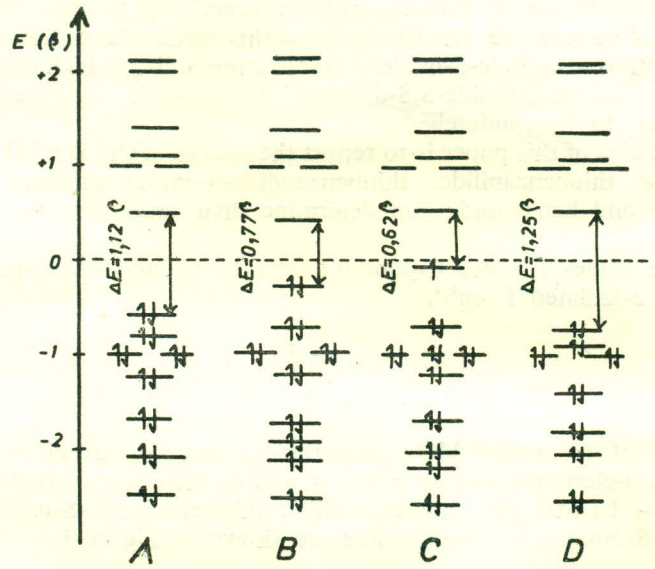

Figure 1. — Electron energy levels and HOMO — LUMO separations fo Thiobenzanilide (A), Thiobenzanilide-S-oxide (B), Thiobenzanilide-S,S-dioxide (C) and Benzanilide (D).

Also, the greater positive charges of the carbon sulfur atoms in the C — S bond of thiobenzanilide-S, S-dioxide tham those of thiobenzanilide and thiobenzanilide-S-oxide, lead to the same conclusions.

Finnaly, the value of the free valence of the carbon atom in the C — S bond for thiobenzanilide (0,146) as compared to benzanilide-S,S-dioxid (0,357) points out that the latter is more reactive and the SO_2 group is easily replaced by oxygen in the oxidation reaction yielding benzanilide.

The Hückel MO calculations were performed using a standard computer program.

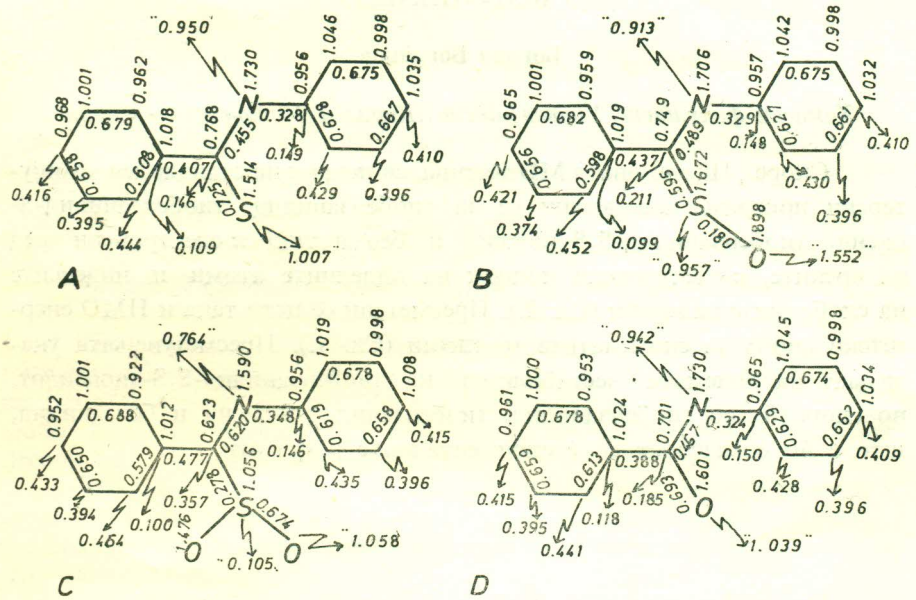

Figure 2. Calculated Charge densities, bond orders and free valences for Thiobenzanilide (A), Thiobenzanilide-S-oxide (B), Thiobenzanilide-S,S-dioxide (C) and Benzanilide (D).

ACKNOWLEDGEMENT: The author si very grateful to the electronic calculating center ELEKTROSKOPJE for permission to use their compauter Honeywell 64/20.

REFERENCES

1. W. Walter, O. H. Bauer : Liebigs Ann. Chem. 305 (1975).
2. B. Podolešov, B. Bogdanov : Glasnik Hem. Društva Beograd 46, 11 (1981).
3. A. Streitwieser, Jr. „Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p. 135.
4. F. A. Van-Catledge : J. Org. Chem. 45, 4801 (1980).

HÜCKEL MO ПРЕСМЕТУВАЊА НА ПРОДУКТИТЕ НА ОКСИДАТИВНОТО ДЕСУЛФУРИРАЊЕ НА ТИОБЕНЗАНИЛИД ДО БЕНЗАНИЛИД

Богдан Богданов

Хемиски факултет, Универзитет „Кирил и Методиј" — Скопје

Според Hückel-овата МО теорија, со помош на стандарден компјутерски програм, пресметани се за тиобензанилид, тиобензанилид-S-оксид, тиобензанилид-S,S-диоксид и бензанилид π-електронски ред на врските, π-електронски полнеж на одделните атоми и индексите на слободните валенции (Сл. 2.). Пресметани се исто така и НМО енергетски нивоа за споменатите молекули (Сл. 1.). Пресметувањата укажуваат на големата нестабилност на тиобензанилид-S,S-диоксидот, во споредба со тиобензанилид, тиобензанилид-S-оксид и бензанилид, што е во согласност со експерименталните резултати.