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ARTICLES

Structure of Sulfophthalexons, Chelating Analytical Reagents

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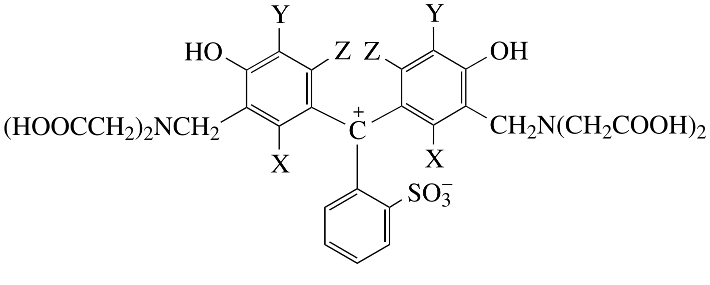
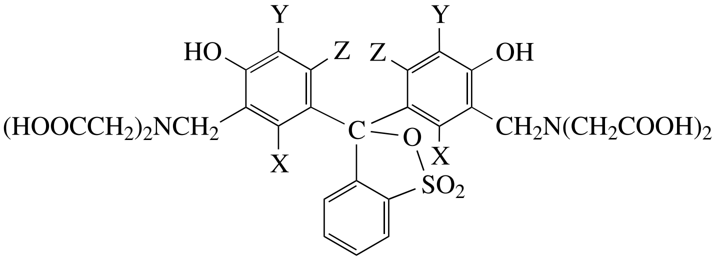
Abstract—On the basis of quantum-chemical calculations, it is demonstrated that, for isolated sulfophthalexon molecules, the heterocyclic form is thermodynamically more stable than the open zwitterionic form. On the contrary, the latter is predominant in aqueous solutions.

A research are related to the synthesis, investigation, and analytical application of phthalexons was developed at Saratov State Pedagogical Institute under the direction of Prof. Cherkasov [1]. Phthalexons are compounds of the triphenylmethane series whose molecules involve iminodiacetate fragments. A specific feature of the structure of sulfophthalexons is that they can exist both as inner complex salts (zwitterions) (A) and as the form with the closed heterocycle (B).



A



B

(**I**) X = Y = Z = H; (**II**) X = Z = H, Y = Cl; (**III**) X = Z = H, Y = Br; (**IV**) X = Z = H, Y = CH_3; (**V**) X = Y = CH_3, Z = H; (**VI**) X = CH_3, Y = $CH(CH_3)_2$, Z = H; (**VII**) X = Y = H, Z = CH_3.

The aim of this work was to solve the problem of revealing the structure of sulfophthalexon molecules using quantum-chemical methods. The compounds under study were phthalexon S (**I**), *ortho*-chlorophthalexon S (**II**), *ortho*-bromorophthalexon S (**III**), *ortho*-cresolphthalexon S (Xylenol Orange) (**IV**), *para*-xylenolphthalexon S (**V**), thymolphthalexon S (Methylthymol Blue) (**VI**), and *meta*-cresolphthalexon S (**VII**).

EXPERIMENTAL

Calculations were performed by the PM3 method [2] using the HyperChem program (HyperChem (TM), HyperCube Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA) with full geometry optimization (Polak–Ribiere procedure [3]). In quantum-chemical calculations, the gradient norm was no higher than 0.02 kcal mol^{-1} $Å^{-1}$ for isolated phthalexon molecules and 1 kcal mol^{-1} $Å^{-1}$ for supermolecular systems containing water. For clusters involving 197 water molecules, the minimum distance between the molecules of water and the dissolved compound was 1.7 Å.

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Table 1. Heats of formation (ΔH_f) and dipole moments (μ) of molecules **I–VII** and Mulliken charges (*q*) on the central carbon atom

Compound	Form	ΔH_f, kcal/mol	μ, D	*q*
I	A	–424.3	7.23	0.406
I	B	–464.9	3.88	0.321
II	A	–432.5	6.42	0.408
II	B	–460.6	5.04	0.335
III	A	–404.1	6.46	0.409
III	B	–432.5	5.32	0.335
IV	A	–436.8	6.70	0.414
IV	B	–480.8	3.76	0.320
V	A	–446.1	6.24	0.376
V	B	–474.9	4.81	0.333
VI	A	–460.5	6.18	0.375
VI	B	–490.4	5.21	0.333
VII	A	–442.7	7.34	0.392
VII	B	–478.3	5.17	0.332

Table 2. Characteristics of the computation procedure for estimating the heats of formation of **IA** $197H_2O$ and **IB** $197H_2O$ clusters

Form	Edge of the cubic cell, Å	Number of water molecules in the unit volume of the cubic cell, Å^{-3}	Gradient norm, kcal mol^{-1} Å^{-1}
A	18.684	0.0302	0.882
B	18.758	0.0298	0.946
$729H_2O$	28.000	0.0332	–

RESULTS AND DISCUSSION

We calculated the electronic structure of molecules **I–VII** in the forms A and B. Molecular systems of type A exhibit the trigonal structure of the central carbon atom. Its tetragonalization occurs on the change to cyclic forms B. It was found that for isolated molecules of **I–VII** the cyclic structure (B) is thermodynamically more favorable than the bipolar structure (A) (Table 1).

The difference between the formation enthalpies of forms A and B $\Delta H_f(A) - \Delta H_f(B)$ decreases in the series (energies in kcal/mol are given in parentheses) **IV** (44.0) $\gtrsim$ **I** (40.6) > **VII** (35.6) > **VI** (29.9) ≈ **V** (28.8) ≈ **III** (28.4) ≈ **II** (28.1), which largely corresponds to the increase in the total steric loading (not necessary in the *ortho* positions) of aromatic rings containing chelating groups. It is interesting that the geometry optimization by the PM3 method for the parent system $2\text{-}^{-}O_3SC_6H_4C^{+}(C_6H_5)_2$ constructed using the HyperChem program leads to the rearrangement into the heterocyclic isomer.

Frequently the molecules whose canonical structures are written as zwitterions are actually less polar in the gas phase because of the significant compensation of formal π-electron charges by the shift of the electron density of the σ core in the opposite direction, and, as a result, the charge separation can be smaller than that observed in solutions [4]. The above is true for the molecules of **I–VII** in form A; this is illustrated by the values of the Mulliken charge on the central carbon atom, which is rather close to those for molecular systems B (Table 1). Dipole moments of all of the studied molecules are high, and the systems of type A have higher the dipole moments (Table 1). Therefore, water as a highly polar solvent must favor the charge separation in open A-type structures, which leads to the stabilization of the molecular systems A due to hydration.

The latter fact was confirmed by quantum-chemical calculations with the explicit inclusion of water medium [5–7]; for this purpose, we studied clusters containing molecular systems **IA** and **IB** and 197 water molecules. The more water molecules are included in the cluster (up to 729 in a cubic cell with the edge of 28.00 Å, which corresponds to the density of liquid water [8]), the more adequately is the water medium taken into account. The results in Table 2 indicate that in our case the density distribution of water molecules in the cell is close to that in liquid water even if we ignore that a part of the cell volume is occupied by the molecule of **IA** or **IB**.

We found that the difference ΔH_f (**IB**$197H_2O$) – ΔH_f (**IA**$197H_2O$) = 60.6 kcal/mol. Thus, in the aqueous medium, in contrast to the gas phase, the open zwitterionic form A of sulfophthalexon S (**I**) actually is more thermodynamically stable than the cyclic structure B.

Evidently, the formation of sulfophthalexon zwitterions in aqueous solutions, on the one hand, is among the factors responsible for the color of the analytical reagents and, on the other hand, favors their complexation with inorganic cations and appearance of the analytical signal in the photometric determination of metals. Thus, the negative charge of the SO_3^- group can facilitate the approach of the metal cation to the reagent molecule. The positive charge substantially localized at the central carbon atom of the triarylmethane system must favor the elimination of the proton from the phenol hydroxyl group yielding the quinoid structure of the aromatic ring accompanied by the bathochromic shift of the long-wave absorption band in the electronic absorption spectrum of the reagent [1, 9]. In addition, the carbonyl center (oxygen atom), which appears on the deprotonation of the reagent, facilitates the coordination with the metal cation in the formation of the chelate [1, 9].

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