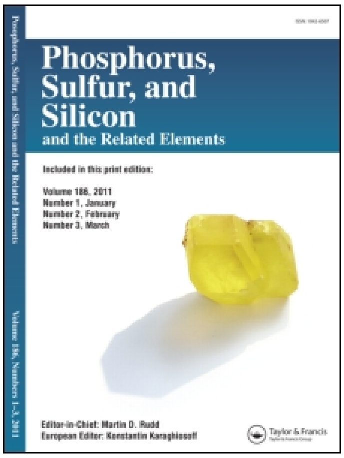

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A QUANTUM CHEMICAL STUDY OF BISMUTH COMPOUNDS THERMODYNAMIC PROPERTIES AND CONFIGURATION OF PENTACOORDINATED ORGANOBISMUTH MOLECULES

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By the PM3 method, standard values of entropy, heats, and free energies of formation have been computed for a series of inorganic and organic bismuth compounds. Linear dependences $P_{exper} = \boldsymbol{b}P_{theor}$ *(where P is any of the mentioned properties) have been stated, allowing a priori evaluation of thermodynamic characteristics of Bi-containing substances. A quantum chemical calculation reproduces well the adiabatic ionization potential of* BiH_3*. Triphenyldichlorobismuth and triphenyldinitratobismuth existence in benzene solutions in the form of trigonal bipyramid with two axial chloro and nitrato ligands has been concluded.*

Keywords: Bismuth compounds; configuration; quantum chemical evaluation; thermodynamic properties; theory—experiment correlation

INTRODUCTION

Metallic bismuth is a component of fusible alloys, solders, babbits, etc., additive to steels, another alloys, aluminium. Bismuth alloys with manganese are used for manufacturing powerful permanent magnets.[1] Bismuth inorganic compounds can serve as anticeptic agents and astringents, components of thermoelectric generators, flux in the production

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of enamels, ceramics, porcelain, crystal, special glasses, cosmetics.[1] Bismuth (V) fluoride is strong fluorinating agent.[1] Bismuth (III) chloride is used as catalyst of olefins hydration, alkenes binding with HCl and chloroorganic compounds, substitution to form C—C and C—Cl bonds.[1] Bismuth (III) bromide is a catalyst of HBr binding with unsaturated organic substances.[1] Bismuth (III) iodide has found its application in analytical chemistry for determining caesium.[1]

Organic bismuth compounds are of interest as the potential components of alkenes polymerization catalysts, polyvinylchloride stabilizers, methylmetacrilate polymerization inhibitors, additives to fuels, antimicrobial preparations, etc.[1] The above aspects of bismuth organic chemistry require further development.

Research into bismuth compounds' resistivity to different effects, as well as into their chemical reactions mechanisms, calls for information on relevant thermodynamic properties.

Entropies, heats, and free energies of formation and dipole moments are fundamental physicochemical characteristics of substances and molecules. Their measurements involve experimental difficulties and are not always feasible, and the corresponding methods have substantial restrictions.

It is of value to show a possibility of a priori estimation of the above characteristics, namely to establish quantitative interrelations possessing predictive power, between experimental and theoretical manifestations of the physicochemical properties under study.

For evaluating the energy characteristics, promising are methods of quantum chemistry. As for ab initio computations, in relation to compounds of bismuth and other heavy elements only low level of sophistication is available in a number of cases. Therewith the results of such treatment depend significantly and not always monotonically on the selected basis and consideration of correlation effects.[2,3]

For rather simplified obtaining predictive quantitative relations, the semiempirical quantum chemical methods would be reasonable to use.

For the series of organic and inorganic compounds belonging to different classes and possessing various functional groups, we have established a correctness of the most important thermodynamic and molecular characteristics reproduction by the MNDO, AM1 and PM3 methods,[4–13] as well as of electronegativity, inductive and mesomeric parameters of atomic groups.[14] Therewith the PM3 scheme[15,16] is the only among the mentioned ones which involves a set of parameters for bismuth,[16] Stewart[16] pointing out that the average absolute error of Bi-containing substances' heats of formation consists 10.9 kcal/mol.

All the aforesaid has determined a choice of the PM3 method[15,16] for solving the problems of the present work, which is aimed at the evaluation of the standard gaseous-phase entropies (S), heats (ΔH_f), and free energies (ΔG_f) of formation, as well as first ionization potentials (I), dipole moments (μ) of the molecules of inorganic, and organic bismuth compounds in order to establish the correlations, having a predicting power, between the said values and experimental ones.

It is to be accentuated that in this paper not only $P = \Delta H_f$ (value usually treated), but also $P = S$, ΔG_f have been considered. For bismuth-containing species, the heats of formation were only tested earlier.[16]

COMPUTATIONAL METHODS

The computations were performed using the software from the *MOPAC* package[17,18] with the complete geometry optimization (Broyden–Fletcher–Goldfarb–Shanno function minimizer[19] involving Thiel's fast minimization algorithm.[20] The preliminary optimization was realized by the molecular mechanics method (the MMX procedure)[21] with the software of the *PCMODEL* complex.[21] In quantum chemical computations, the condition of the gradient norm not exceeding 0.02 kcal/(mol Å) was preset. In some cases, the sufficient decrease in gradient norm was achieved by means of abandonment of the Thiel's fast minimization routine (the keyword NOTHIEL of the *MOPAC* package was applied), or under optimization with the Davidon–Fletcher–Powell method (keyword DFP),[19] or using combined approaches involving the keywords NOTHIEL and DFP.

For molecules with closed electronic shells, the restricted Hartree–Fock (RHF) formalism was used. Computations of the systems with open shells or the species, spin state of which was not so obvious, were conducted both in accordance with the RHF ideas and by the unrestricted Hartree–Fock (UHF) method.[2,18]

In calculating the rotational contributions to thermodynamic functions the symmetry number was taken as unity.

The regression analysis was performed with the confidence level of 0.95.

RESULTS AND DISCUSSION

The ΔG_f values were calculated from the relationship:

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

where the standard entropies of formation ΔS_f were calculated by the formula:

$$\Delta S_f = S - \sum_i S_i,$$

in which S_i are the entropies of the elements constituting molecule in their standard states[22–26] in view of hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, iodine being the two-atomic molecules; $T = 298.15$ K.

The results obtained are presented in Tables I–III.

For $P = \Delta H_f$, S, ΔG_f we have established linear dependences of the type

$$P_{\text{exper}} = \mathbf{b} P_{\text{theor}}.$$

In Table IV the values of **b**, correlation coefficients **r**, as well as the following conventional quantities: MS (mean signed); average value for $P_{\text{theor}} - P_{\text{exper}}$; and MU (mean unsigned); average value for $|P_{\text{theor}} - P_{\text{exper}}|$ are shown.

TABLE I Experimental and Computed Values of Standard Heats of Formation

Compound	$\Delta H_{f\ \text{exper}}$, kcal/mol	Ref.	$\Delta H_{f\ \text{theor}}$, kcal/mol	
			RHF	UHF
Bi^+	219.418	23	237.91	229.60
Bi^{2+}	605.4	24	588.84	588.84
BiH	43.008	23	49.93	41.62
BiF	−7.023	23	7.08	−0.644
BiS	43	24, 25	64.07	61.63
BiS^+	229	24	232.52	226.82
BiCl	7	24	17.76	10.36
$BiCl_2$	−22.6	26	−19.73	−22.39
BiSe	42.0	16, 24, 25	56.22	50.59
BiBr	12.765	23	17.33	9.45
BiTe	42.8	16, 24, 25	49.63	47.15
BiI	17.819	23	24.57	16.58
$(CH_3)_2Bi$	56	27	41.80	40.87
$BiCl_3$	−63.5	16, 24–26	−42.62	
$BiBr_3$	−24.4	26	−43.70	
BiI_3	4.0	26	−23.85	
Sb_3Bi	46.9	26	13.66	
$(CH_3)_3Bi$	46.05	23	43.07	
$(C_2H_5)_3Bi$	51.6	16	26.66	
$(C_6H_5)_3Bi$	138.6	16	137.64	

TABLE II Experimental and Computed Values of Standard Entropies

Compound	S_{exper}, cal/(mol·K)	Ref.	S_{theor}, cal/(mol·K) RHF	UHF
Bi_2	65.40	25	63.61	63.61
BiH	51.27	24	51.11	51.11
BiO	58.81	25	57.29	57.55
BiF	58.2	24	57.99	58.00
BiS	61.7	23	59.43	59.66
BiCl	60.9	24	61.45	61.59
BiSe	63.037	25	62.24	62.70
BiBr	63.9	24	64.40	64.38
BiTe	65.160	25	63.73	63.85
BiI	65.8	23	65.10	65.20
$BiCl_3$	85.74	24, 25	91.83	
BiI_3	99.77	24	99.53	

Tendencies in changing the experimental and theoretical entropies, heats and free energies of formation of bismuth compounds agree with each other (**r** > 0.96) in spite of the fact that the difference $\Delta H_{f\,exper} - \Delta H_{f\,theor}$ is equal to 27.85 kcal/mol for BiI_3 and to 33.24 kcal/mol for Sb_3Bi.

The RHF consideration leads to positive deviations of all the computed ΔG_f values from the experimental ones, and MU = MS.

For bismuth (III) hydride BiH_3, we have calculated the Koopmans and adiabatic ionization potentials equal to 10.01 and 9.64 eV, respectively. Thus the quantum chemical evaluation reproduces well the experimental value of the BiH_3 adiabatic ionization potential (9.5 eV) measured by the electron impact technique.[23,27]

TABLE III Experimental and Computed Values of Standard Free Energies of Formation

Compound	$\Delta G_{f\,exper}$, kcal/mol	Ref.	$\Delta G_{f\,theor}$, kcal/mol RHF	UHF
BiH	36.415	23	39.35	31.03
BiF	−13.134	23	−2.99	−10.71
BiS	29	24, 25	47.49	44.98
BiCl	−0.170	23	7.39	−0.064
BiSe	30.3	25	40.68	34.92
BiBr	3.191	23	3.55	−4.324
BiTe	31.0	25	34.17	31.66
BiI	6.394	23	9.30	1.28
$BiCl_3$	−60.364	23	−46.161	

TABLE IV Coefficients **b** in Equations $P_{exper} = \mathbf{b}P_{theor}$ and the **r**, MU, MS Values

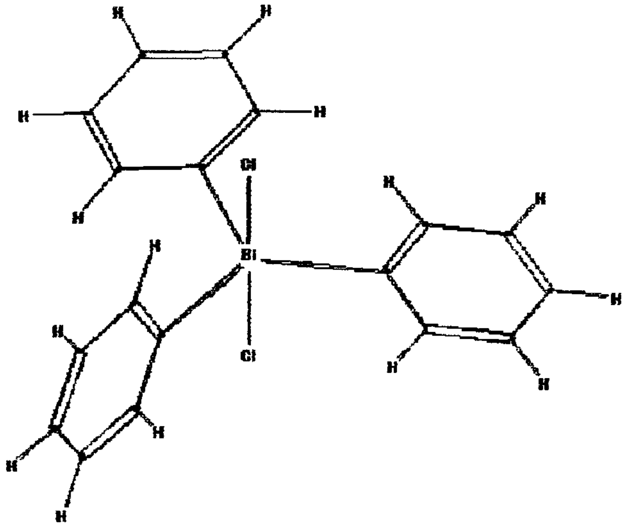
P	Number of compounds	**b**	**r**	Error MU	Error MS
ΔH_f^a	20	1.0052 ± 0.0493	0.9934	13.55	−0.45
ΔH_f^b	20	1.0156 ± 0.0450	0.9948	11.06	−3.85
S^a	12	0.9989 ± 0.0203	0.9908	1.35	−0.16
S^b	12	0.9975 ± 0.0197	0.9910	1.27	−0.06
ΔG_f^a	9	0.8966 ± 0.2353	0.9804	7.79	7.79
ΔG_f^b	9	0.9895 ± 0.2301	0.9625	6.22	2.22

[a] For molecular systems, the properties of which were computed in the RHF and UHF versions (Tables I–III), the RHF formalism is applied in the given case.

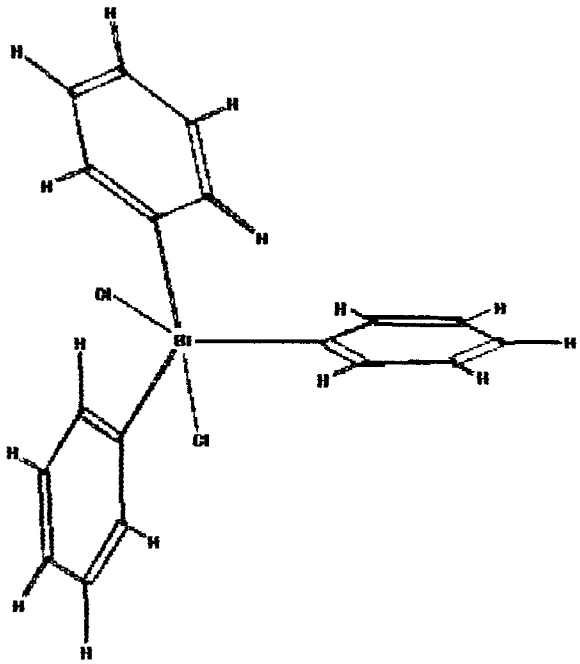
[b] For molecular systems, the properties of which were computed in the RHF and UHF versions (Tables I–III), the UHF formalism is applied in the given case.

The computations of thermodynamic characteristics and dipole moments has allowed us to conclude on geometry of triphenyldichlorobismuth $(C_6H_5)_3BiCl_2$ and triphenyldinitratobismuth $(C_6H_5)_3Bi(ONO_2)_2$ molecules as solutes.

In the both cases, two kinds of trigonal-bipyramidal configurations were investigated, namely, the structures (**I**, **III**) with two axial chloro or nitrato ligands, and the configurations (**II**, **IV**) in which one inorganic



I



II

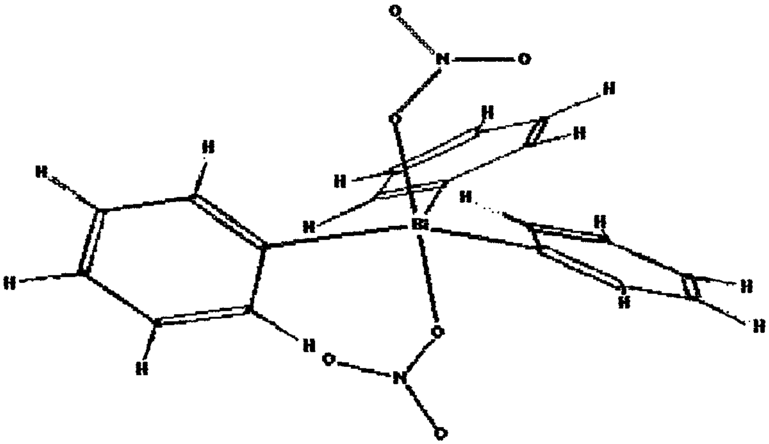
ligand occupies equatorial, and another axial position. The hypothetical structures with two equatorial Cl or ONO_2 groups unlikely exist. Being simulated by means of the *PCMODEL* package, they rearrange into the systems **I**, **III** on optimization by the molecular mechanics (MMX) or quantum chemistry (PM3) method.

Experiments[28] give for the molecules $(C_6H_5)_3BiX_2$ in benzene at 298 K the dipole moments equal to zero (X = Cl) and 3.26 D (X = ONO_2).

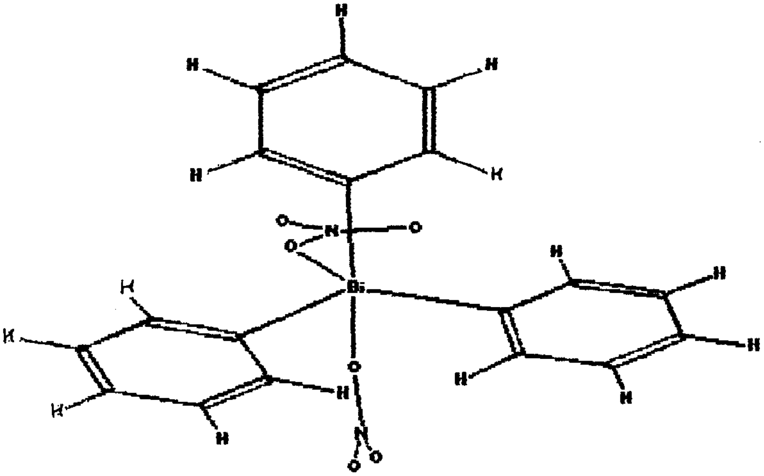
It is configuration **I** or **III** that is realized in benzene solution. Three factors that stipulate this are:

1. The forms **I**, **III** are more stable thermodynamically as compared to **II**, **IV** and, likely, to the structures with two equatorial inorganic ligands (Table V).
2. The computed dipole moments of the configurations **I**, **III** correspond to the experimental data,[28] in the contrast to the computational results for the structures **II**, **IV** (Table V).
3. Solvent is nonpolar.

Configuration preference of trigonal-bipyramidal molecules $(C_6H_5)_3BiCl_2$ and $(C_6H_5)_3Bi(ONO_2)_2$ could be explained by the



III



IV

sterically hindered axial positions pointed out in monograph.[29] In this connection the bulky phenyl groups tend to occupy equatorial positions. According to x-ray diffraction[29–32] and IR, Raman spectroscopic[33,34] studies, the analogous spatial structure with three equatorial phenyl groups is peculiar for the $(C_6H_5)_3BiX_2$ (X = $COOCH_3$, NCO, ONO_2, F, Cl, Br),[34] $(C_6H_5)_4BiY$ (Y = CO_2, CCl_3, NCO, NCS, ONO_2),[33] $(C_6H_5)_3BiCl_2$[29–32] molecules in crystal state.

TABLE V Computed Values of Standard Heats of Formation (ΔH_f), Entropies (S), Free Energies of Formation (ΔG_f), and Molecular Dipole Moments (μ) for Different Configurations of Triphenyldichlorobismuth and Triphenyldinitratobismuth

Configuration	ΔH_f, kcal/mol	S, cal/(mol·K)	ΔG_f, kcal/mol	μ, D
I	170.20	160.75	215.26	0.208
II	186.51	160.06	231.77	7.68
III	172.28	188.02	250.79	1.28
IV	194.13	183.02	274.14	13.7

Thus, the results of the present work along with the literature data show that the configuration of the $(C_6H_5)_3BiCl_2$ and $(C_6H_5)_3Bi(ONO_2)_2$ molecules is just the same either as crystals or as solutes.

CONCLUSION

The existence of quantitative relations P_{exper} *vs* P_{theor} as such (different from previous[15,16,35–44] analysis of absolute errors by the data of the MNDO, MNDO/d, AM1, PM3, SAM1 methods) shows that the semiempirical quantum chemical PM3 method does reproduce correctly alteration trends of thermodynamic properties of bismuth compounds.

Using the correlations found one could predict the properties not always available to the experimental measurement. In doing so, the computed values have to be corrected by the multiplier **b**. For $P = \Delta H_f$, S, the **b** values are close to unity, that allows one to calculate the corresponding characteristics directly, without any correlation equations.

A priori evaluation of the said parameters by quantum chemical methods is important for molecular design of compounds with given properties, may serve as a base for expert decision on reasonability of synthesis that is sometimes labor—and time—consuming, requiring complicated device, rigid conditions, expensive, and toxic chemicals.

The trigonal bipyramidal configuration of the triphenyldichlorobismuth and triphenyldinitratobismuth molecules in solutions has been revealed. Success extended to pentavalent bismuth compounds therewith, although only species with the bismuth valence not exceeding 3 were included in the selection of the PM3 parameters.

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