UNELE PROPRIETĂȚI FIZICO-CHIMICE ALE n-ALCANII CU LANȚ SCURT CAUZATE DE ORBITALII LOR MOLECULARI SPECIFICI

SOME PHYSICOCHEMICAL PROPERTIES OF SHORT CHAIN n-ALKANES CAUSED BY THEIR SPECIFIC MOLECULAR ORBITALS

***Mihail Gorbaciov**, dr., cercet. șt. superior, USM, Institutul de Chimie*
Natalia Gorincioi, dr., cercet. șt. coord., USM, Institutul de Chimie
Iolanta Bălan, dr., cercet. șt. superior, lector univ., USM, Institutul de Chimie
Ion Arsene, dr., cercet. șt. superior, USM, Institutul de Chimie
conferențiar universitar, UPS „Ion Creangă" din Chişinău

***Mikhai**l **Gorbachev**, PhD, senior researcher, MSU, Institute of Chemistry*
ORCID: 0009-0005-3058-5497, mikhailgorbaciov778@gmail.com
Natalia Gorinchoy, PhD, leading researcher, MSU, Institute of Chemistry
ORCID: 0000-0003-4529-9061
Iolanta Balan, PhD, senior researcher, lecturer, MSU, Institute of Chemistry
ORCID: 0000-0002-8704-1344
Ion Arsene, PhD, senior scientific researcher, MSU, Institute of Chemistry
associate professor UPS "Ion Creanga" from Chisinau
ORCID:0000-0003-3102-3507

Rezumat. *Se arată că diferite proprietăți fizico-chimice ale n-alcanilor cu lanț scurt (tensiunea lor superficială și solubilitatea lor în apă) pot fi descrise în mod adecvat pe baza așa-numiților „orbitali moleculari specifici" identificați prin metoda DFT. Valorile energetice ale acestor orbitali sunt incluse în ecuațiile de corelație găsite, care fac posibilă descrierea cantitativă a proprietăților lor menționate mai sus.*
Cuvinte cheie: *tensiune de suprafață, solubilitate în apă, n-alcani, proprietăți orbitale controlate, calcule DFT*

Abstract. *It is shown that various physicochemical properties of short-chain n-alkanes (their surface tension and their solubility in water) can be adequately described on the basis of the so-called "specific molecular orbitals" identified by the DFT method. The energy values of these orbitals are included in the found correlation equations, which make it possible to quantitatively describe their above-mentioned properties.*
Keywords: *surface tension, solubility in water, n-alkanes, orbital controlled properties, DFT calculations.*

Introduction

Basing on the DFT calculations, it has been shown in our previous work [1] that the surface tension σ of various organic near-boiling liquids, whose molecules possess the $\pi\sigma^*$-hyperconjugation between their π-electronic systems and the antibonding σ^*-type molecular orbitals of methyl groups depends linearly on the specific molecular parameter of these liquids which includes the one-particle binding energy as a multiplier. This energy is proportional to both the sum of all p_z- and σ^*-orbitals taking part in the one-particle $\pi\sigma^*$-hyperconjugation phenomenon and the energy E_{orb} of the occupied molecular orbital which enters the surface supramolecular electron $\pi\sigma^*$-system. The found in [1] linear regression equation allows one to calculate the surface tension of the above liquids. In the connection with the above-mentioned it seems to us very interesting to try to expend the main results (ideas) received in the work [1] for the case of some short chain n-alkanes.

Computational details

The electronic and geometrical structures of all the considered n-alkanes (C1-C10) have been investigated by means of the DFT method, including Becke's three-parameter non local-exchange functional [2] with the correlation functional of Lee, Yang and Parr (B3LYP) [3]. For each of the compounds considered, a full geometry optimization was carried out using the 6-31G* basis sets including polarization functions for all the atoms in the systems [4]. The calculations were performed with the GAUSSIAN 09 program package [5].

Results and Discussion

Surface tension of the boiling C2- C10 n-alkanes

It is to be noted here, that we have considered monomolecular surface layers of the studied boiling n-alkanes (from ethane to n-decane) as the systems whose properties determine their surface tension (see the work [9]). This choice was done on the basis of the fact that in boiling liquids the molecules of their surface layers practically do not interact with the molecules in their bulk [9]). In addition, the structure of the surface layers of the studied n-alkanes, used in theoretical calculations, was considered by us on the basis of known experimental data (see Refs. [6, 7]). So, for the wide temperature range of liquid n-alkanes it has been shown experimentally [6, 7] that the hydrocarbon chains of their molecules, forming these monolayers, are oriented normal to their planes.

Also, we have considered that the intermolecular interaction, existing between the molecules of the surface layers of the boiling n-alkanes under study, is being realized by means of the intermolecular dispersion attraction, which involves all the hydrogen atoms, entering the structures of their molecules. In its turn, the energy of the given attraction is directly proportional [8] to the value (the module) of $|E_{orb}|$, where E_{orb} is the energy of those MOs which contribute essentially to dispersion attraction. Usually, the given MOs are the HOMOs or the nearest to the HOMOs occupied molecular orbitals [8]. Moreover, as was shown in Ref. [9], the atoms participating in the dispersion interaction under consideration enter, with large values of the coefficients of their atomic orbitals, into these MOs (usually with the same "+" or "-" sign).

Further, using the above particularities of the considered physicochemical models (the surface layers of the boiling n-alkanes), the following equation, describing their surface tension σ, was obtained in [9]:

$$\sigma \times 10^3 = 0.0448G + 0.8333, \qquad (1)$$
$$(n = 9, R^2 = 0.983)$$

where the quantity G has the following form:
$$G = |E_{orb}|(1 - T_b/T_c). \qquad (2)$$

In Eq. (2) T_b and T_c are respectively the boiling and critical temperatures of the n-alkane under study. Table 1 (taken from [9]) contains the values of σ calculated by means of Eqs. (1) and (2). The last column of Table 1 contains the values of σ calculated by means of the so-called "Leave-one-out" Cross-Validation Scheme (LOOCV).

Table 1. The usage of Eqs. (1) and (2) for the calculation of σ of the studied boiling n-alkanes.

No	n-Alkane	T_b (˚K)	T_c (˚K)	$\|E_{orb}\|$ (kJ/mol)	G (kJ/mol)	σ × 10^3 (N/m) Exper.	Calc.	LOOCV
1	Ethane	184.55	305.32	893.58	353.4580	16.31	16.67	16.99
2	Propane	231.11	369.83	873.56	327.6656	15.50	15.51	15.53
3	Butane	272.65	425.12	863.34	309.6393	14.93	14.71	14.67
4	Pentane	309.22	469.70	845.16	288.7624	14.07	13.77	13.72
5	Hexane	341.88	507.60	841.27	274.6572	13.41	13.14	13.12
6	Heptane	371.58	540.20	837.02	261.2699	12.45	12.54	12.57
7	Octane	398.83	568.70	835.47	249.5532	12.09	12.01	11.99
8	Nonane	423.97	594.60	833.73	239.2533	11.53	11.55	11.56
9	Decane	447.30	617.70	833.00	229.7927	10.75	11.13	11.29

The clear view of the specific molecular orbitals SMOs responsible for the dispersive attraction between n-alkane molecules, belonging to their surface liquid layers, is shown in Figure 1. It is easy to see that for any of the investigated n-alkanes the atomic 1s-orbitals of all its hydrogen atoms, entering the LCAO of its SMO, have the same sign.
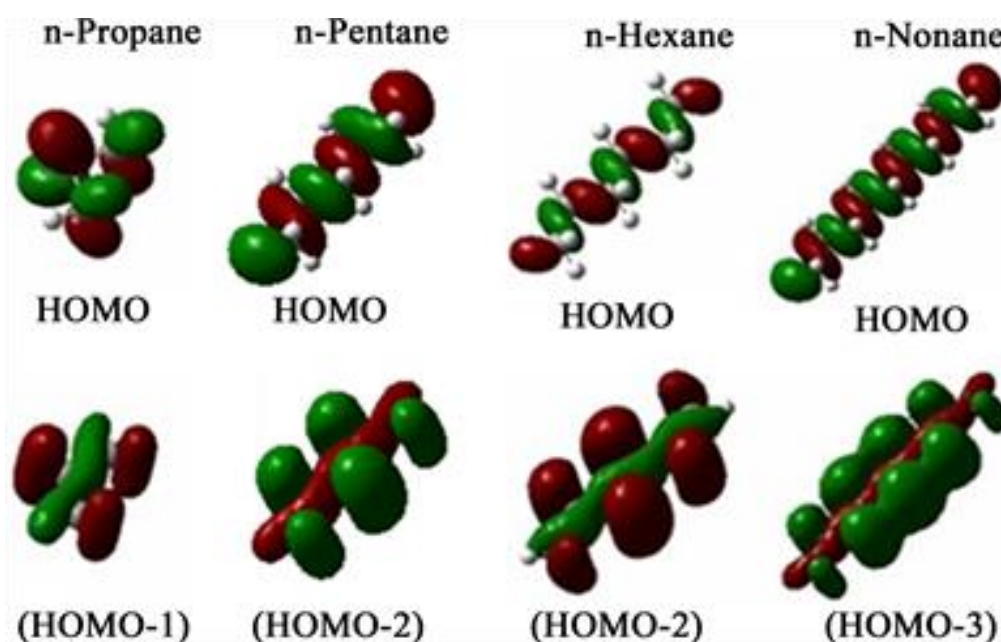

Fig. 1. The view of the HOMOs (the upper row) and the SMOs (the lower row) for some of the studied n-alkanes

Thus, taking into account the specific molecular orbitals (their energies) of the studied n-alkanes really allows one the adequate description of their surface tension.

Solubility of the C1-C10 n-alkanes in water

In order to consider the above property of the studied n-alkanes (from CH_4 to $n-C_{10}H_{12}$) we have used the van't Hoff isochore equation written in its logarithmic form:

$$\log_{10}S = A + B\Delta H/RT = A + B'\Delta H \tag{3}$$

Here S is solubility of a chemical compound (in our case any of the considered n-alkanes). The quantity S is usually expressed in molar fraction. ΔH is the partial molar enthalpy connected with formation of a saturated aqueous solution for each of the studied n-alkanes. R is the gas constant. A, and B' are some constant quantities depending on the nature of the considered n-alkane. T is the absolute temperature at that the dissolution of the n-alkanes takes place. Further, basing on Equation (3), we have received (see the work [10]) the following final equation for the quantity $\log_{10}S$:

$$\log_{10}S = A + \xi \cdot n_m + \mu E_{orb} \cdot n_m \cdot n_H \tag{4}$$

In Equation (4), the constants ξ and μ do not depend on the nature of the n-alkanes under study. For any of the studied n-alkanes, n_m is the number of its methylene groups and n_H is the number of its hydrogen atoms.

In order to verify Equation (4) we have investigated the n-alkanes presented in Table 2.

Table 2. The data necessary to obtain Equation (5) and the subsequent calculation of $-\log_{10}S$.

No	Alkane	n_m	n_H	E_{orb} (kJ/mol)	$-\log_{10}S$ Exp.	$-\log_{10}S$ Calc.	$-\log_{10}S$ LOOCV
1	Methane	1	4	309.63	0.90	0.89	0.89
2	Ethane	2	6	275.17	1.36	1.40	1.42
3	Propane	3	8	252.37	1.94	1.94	1.94
4	n-Butane	4	10	249.27	2.57	2.53	2.52
5	n-Pentane	5	12	246.01	3.18	3.15	3.15
6	n-Hexane	6	14	243.72	3.84	3.82	3.81
7	n-Heptane	7	16	241.63	4.53	4.52	4.52
8	n-Octane	8	18	240.06	5.24	5.26	5.27
9	n-Nonane	9	20	238.80	5.88	6.04	6.10
10	n-Decane	10	22	237.84	6.98	6.86	6.67

Beginning from ethane, all these compounds possess linear hydrocarbon chains. The geometry optimization of all the considered systems shows that their molecules have the planar carbon chains in which any four consecutive carbon atoms are in the trans-configuration. The subsequent analysis of the virtual MOs of the given n-alkanes (see Ref. [10]) shows that namely their LUMOs satisfy all the above-mentioned in Section 3.1 criteria for their consideration as the sought SMOs. Indeed, these LUMOs contain 1s-AOs of all the hydrogen atoms and, moreover, with one common sign ("+" or "−") of the corresponding MO coefficients. For the case of methane, propane, n-pentane, and n-octane their LUMOs (i.e. their SMOs) are shown in Figure 2.
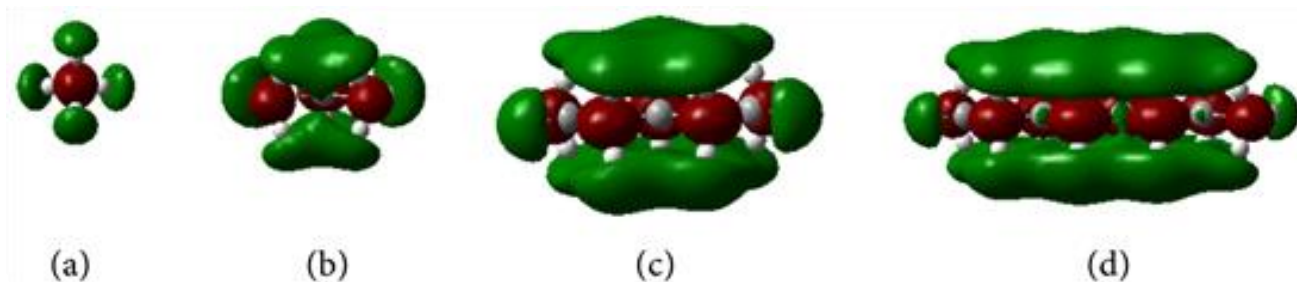

(a)   (b)   (c)   (d)

Fig. 2. The SMOs (the LUMOs) of some studied n-alkanes responsible for their solubility S: methane (a), propane (b), n-pentane (c), and n-octane (d)

In order to demonstrate that namely the considered virtual orbitals are responsible for the interaction of n-alkanes with neighboring water molecules, we have calculated the interaction between the two molecules: n-pentane and water. The results of this DFT calculation are presented in Figure 3. One can see that there is a clear-cut interaction between the lone electronic pairs of the oxygen atom of the water molecule and the SMO (the LUMO) of the n-pentane one. For each of the studied n-alkanes, Table 2 contains the quantities: n_m, n_H, and E_{orb}, along with the experimental values $-\log_{10}S$ at $T = 298.15$ K (see the work [10]).

Further, the numerical values of the constants A, ξ, and μ (see Equation (4)) were defined by means of the least square method applied to the data set in Table 2. The usage of the found values of A, ξ, and μ in Equation (4) allows one to write it in the following final form:

$$-\log_{10}S = 0.4220 + 0.4198n_m + 4.28287 \times 10^{-5} E_{orb} \cdot n_m \cdot n_H \tag{5}$$

The last but one column of Table 2 contains the values of $-\log_{10}S$ of the studied n-alkanes calculated by means of Equation (5). The comparison of the values of $-\log_{10}S$ presented in the last three columns of Table 2 shows that these values are very close to each other and to the corresponding experimental ones. It means that Equation (5) (and, therefore, Equation (4)) describes the solubility of the studied n-alkanes in water adequately.
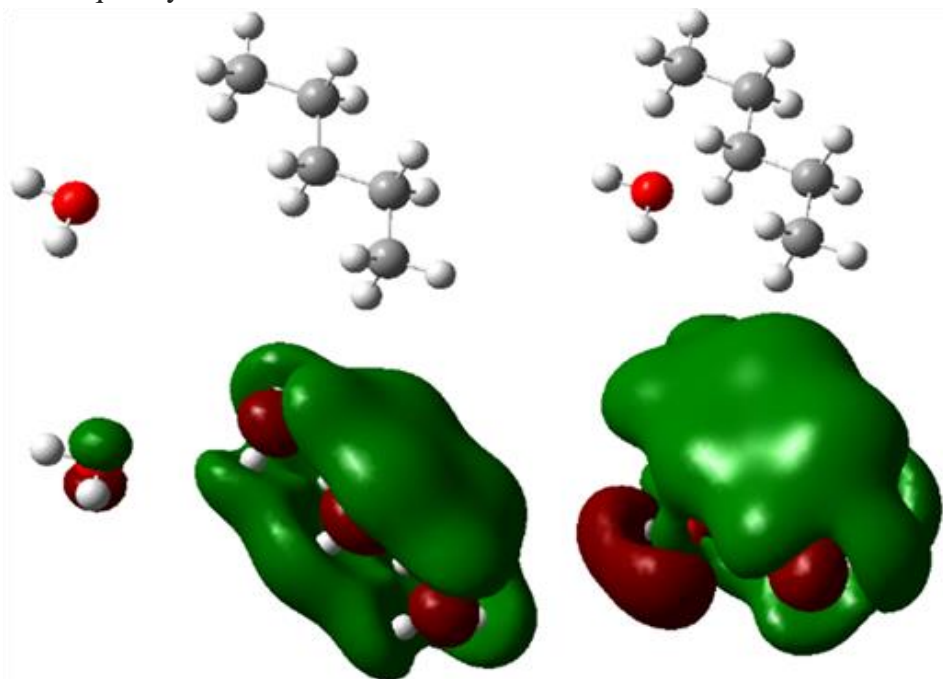

Fig. 3. **The interaction of the lone electronic pair of a molecule of water with the virtual SMO (the LUMO) of n-pentane**

Conclusions

Thus, the following conclusions can be drawn. Various specific molecular orbitals of the studied n-alkanes are responsible for their various physicochemical properties. For a quantitative description of the properties studied in this work (surface tension and solubility in water), the energies of these orbitals are of fundamental importance. The numerical values of the energies of these orbitals calculated by the DFT method can be used in the corresponding correlation equations that quantitatively describe the above properties.

Acknowledgment

References

1. GORBACHEV, M.Yu.; GORINCHOY, N.N.; ARSENE, I. *Surface tension of near-boiling liquids with intramolecular πσ*-hyperconjugation: DFT calculations.* J. Molecular Liquids, 2017, 237, pp. 108-112.

2. KOHN, W.; BECKE, A.D. PARR, R.G. *Density functional theory of electronic structure.* Journal of Physical Chemistry, 1996,

3. LEE, C. ; YANG, W.; PARR, R.G. *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density.* Physical Review B, 1988, 37, pp. 785-789.

4. HEHRE, W.J.; RADOM, L.; SCHLEYER, P.V.R.; POPLE, J.A. *Ab Initio molecular orbital theory.* Wiley: New York, 1986, 548 p.

5. FRISCH, M.J.; TRUCKS, G.W.; SCHLEGEL, H.B.; et al. Gaussian 09, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

6. ESENTURK, O.; WALKER, R.A. *Surface vibrational structure at alkane liquid/vapor interface*, Journal of Chemical Physics, 2006, 125, Article ID: 174701.

7. WU, X.Z.; SIROTA, E.B.; SINHA, S.K.; OCKO, B.M. *Surface crystallization of liquid normal-alkanes.* Physical Review Letters, 1993, 70, pp. 958-961.

8. GAVEZZOTTI, A. *Supramolecular interactions: Energetic consideration.* In: Braga, D. and Grepioni, F., Eds., Making Crystals by Design: Methods, Techniques and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, pp. 1-24.

9. GORBACHEV, M.Yu.; GORINCHOY, N.N.; ARSENE, I. *Key role of some specific occupied molecular orbitals of short chain n-alkanes in their surface tension and reaction rate constants with hydroxyl radicals: DFT study*, Int. J. Org. Chem., 2021, 11, pp. 1-13.

10. GORBACHEV, M.Yu.; GORINCHOY, N.N. *Molecular orbital nature of solubility of shot chain n-alkanes in water and their reaction rate constants with nitronium cations: a DFT study.* Int. J. Org. Chem., 2022, 12, pp. 92-101.