

# The effect of solvent polarity on solubility of HMX and FOX-7: A DFT study

Mohammad Eghdamtalab<sup>a</sup> & Ayoub Kanaani<sup>b\*</sup>

<sup>a</sup>Malek Ashtar University of Technology, Tehran, Iran

<sup>b</sup>School of Chemistry, Damghan University, Damghan 36716 41167, Iran

Received 22 May 2016; accepted 3 January 2017

Production of micro and submicron-sized particles with a narrow particle size distribution (PSD) is gaining interests in materials technology especially in specialty chemicals. There are many conventional methods for the size reduction of particles such as milling, grinding, crushing, spray drying, and recrystallization from liquid solutions. A new, promising process for particulation of materials employs environmentally benign compressed gases as either solvents or anti-solvents. The molecular geometry of HMX and FOX-7 has been calculated by using the density functional method (B3LYP) invoking 6-311++G(d,p) basis set. The solvent effect was treated using a continuum model as modeled in hexane, benzene, chloroform, tetrahydrofuran, acetone, ethanol, methanol, dimethylformamide, acetonitrile and DMSO. Furthermore, dipole moment ( $D$ ), polarizability ( $\alpha$ ), molecular electrostatic potential map (MEP), thermodynamic, frontier molecular orbital analysis (HOMO–LUMO), hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), global electrophilicity index ( $\omega$ ) and  $\Delta G_{\text{solv}}$  properties for HMX and FOX-7 in several solvents have been investigated and discussed. It is found that with an increasing solvent dielectric constant, the dipole moment of the molecules under study also increases.

**Keywords:** HMX, FOX-7, Solubility, DFT, Polarizability

## 1 Introduction

The properties of explosives are closely related to the properties of their particles. Especially particle size, particle size distribution, and morphology have great influence on the performance and stability of the explosives. Although properties of nano-sized explosive particles are not much known, a lot of research has been going on the micron-sized explosives<sup>1-3</sup>, and within this range, small particles and narrow particle size distribution and spherical morphology is desired.

The army is interested in developing a green process to produce nanocrystalline ( $\leq 300$  nm) particles of the high energy explosive compounds HMX (cyclo tetramethylenetetranitramine) and FOX-7 (1,1-Diamino-2,2-dinitroethene). HMX is also known as: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane; cyclotetramethylene tetranitramine; or octogen. The combustion and detonation characteristics of the HMX and FOX-7 can be improved if it is formed into nanoparticles of uniform size.

It is envisaged that computational approach based on density functional theory (DFT) could be an important and effective method for understanding the relative solubility/reactivity of these compounds<sup>4</sup>.

Theoretical calculations provide a reliable tool to analyze the kinetic and thermodynamic stability of organic compounds by providing the nearly accurate estimation of energy values of highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO and LUMO). The energy separation between these frontier orbitals has been extensively used as a reliable indicator of stability<sup>5-10</sup>. Though this approach may not suffice to understand the absolute solubility and reaction pathways of these precursors but does provide a rationale behind their markedly different solubility and reactivity behavior. Our objective has been to correlate the solubility and reactivity to theoretically calculated parameters like HOMO–LUMO gap ( $\Delta E_{\text{gap}}$ ), dipole moment, optimized energies, and so forth.

In this work, quantum-chemical descriptors<sup>11-13</sup> including the dipole moment ( $\mu$ ), polarizability ( $\alpha$ ), thermochemical parameters, ( $\Delta G_{\text{solv}}$ ), and solubility properties of two explosive compound (HMX and FOX-7) in different solvents were studied via density functional theory (DFT) using B3LYP density functional and 6-311++G(d,p) basis sets.

## 2 Computational Details

Quantum chemistry may be applied to the calculation of optimized geometric parameters

\*Corresponding author (E-mail: a.kanaani@std.du.ac.ir)

(structure), charge distribution and solvent effects of isolated molecules. In this work, the Gaussian 03 program package<sup>14</sup> was applied with the DFT B3LYP functional and the 6-311++G(d,p) basis set<sup>15,16</sup>. Harmonic vibrational frequency analysis suggested that optimized geometries belong to the minima at the respective potential energy surface.

Polarizable continuum model<sup>17,18</sup> (PCM) was used for evaluating the bulk solvent effects, in which the problem is divided into a solute part (HMX and FOX-7) lying inside a cavity and a solvent part (in our case, DMSO, acetonitrile, DMF, methanol, ethanol, acetone, THF, chloroform, benzene and hexane, respectively) represented as a structure-less material, characterized by its dielectric constant as well as other parameters<sup>19</sup>. To perform calculations, the commands “B3LYP/6-311++G(d,p) fopt=calcall scf=verytight” were typed in the route section for optimization of structures, obtaining energies and frequencies and “B3LYP/6-311++g(d,p) scrf=(solvent=!,pcm) scf=verytight” (instead of !, the name of solvent was inserted) were typed in the route section to calculate solvation effects. It is noticeable that when we use two diffuse functions (++ after 6-311), the “scf=verytight” keyword is necessary to obtain exact data.  $\Delta G_{\text{solv}}$  was obtained as the difference between the Gibbs free energies of the compounds in solvent (PCM) and vacuum (gas phase) as<sup>20</sup>:

$$\Delta G_{\text{solv}} = G_{\text{solvent}} - G_{\text{gas}} \quad \dots (1)$$

### 3 Results and Discussion

#### 3.1 Molecular structure

The optimized structures of HMX and FOX-7 are presented in Figs 1 and 2. To see how the solubility will affect the geometry, the geometry optimization of HMX and FOX-7 were performed using the PCM at B3LYP/6-311++G(d,p) level. Solvation process only slightly changed the molecule in the space, re-optimized geometry parameters in the dielectric continuum corresponding to the different solvent-explosive solutions ( $\epsilon = 46.826, 35.688, 37.219, 32.613, 24.852, 20.493, 7.426, 4.711, 2.271$  and 1.882, respectively) leading to small changes in bond lengths and dihedral angles, which means that introduction of a solvent reaction field has slight effect on the geometry of HMX and FOX-7 structures (supporting data may be obtained from the author).

Actually, the atoms that constitute such molecules have different electro negativities such that when a covalent bond is created, the two bonding electrons are

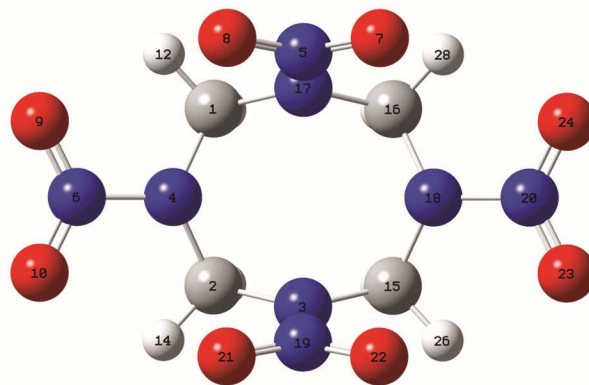


Fig. 1 — Theoretical optimized geometric structure with atoms numbering of HMX

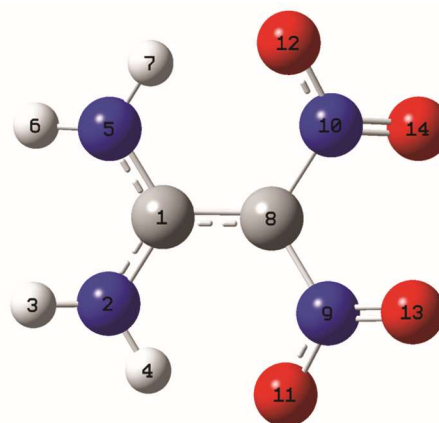


Fig. 2 — Theoretical optimized geometric structure with atoms numbering of FOX-7

engrossed to different ability by atoms that share. The molecular orbital loses its symmetry, and the possibility of finding the electrons is greater in the proximity of the more electronegative atom. Even so, it still maintains the overall electrical neutrality; however, the more electronegative atom has a predominance of negative charge, and the less electronegative atom has a predominance of positive charge, which gives rise to the formation of a dipole. The bigness of the dipole is specified by what is known as the dipole moment ( $\mu$ ) and is the product of the fractional charge on each atom present and the spacing that separates them. The charge separation in a covalent bond is greater as the difference in electronegativity between the atoms that form it.

#### 3.2 Polarizability

The polarizability is defined as the linear coefficient between an applied electric field and the induced dipole moment. Molecular polarizability of a molecule reflects the global polarity of the molecular structure<sup>7</sup>

that results from the uneven partial charge distribution over all the atoms of the molecule. Normally, highly polar compounds with sensible inter-molecular electrostatic interplays are more polar soluble<sup>21,22</sup>. As well as, it was displayed that polarizability is important in the modeling of solubility<sup>23</sup>. The polarizabilities for HMX and FOX-7 in various solvents are listed in Table 1. We observed that as the solvent dielectric constant increases, the polarizabilities of the molecules under study also increase. For example, for compound HMX the order of polarizabilities is as follow:

DMSO> DMF> CH<sub>3</sub>CN> CH<sub>3</sub>OH> Ethanol> Acetone> THF> Chloroform> Benzene> Hexane

### 3.3 Dipole moment

Dipole moment is the product of all the charges on a molecule and the distance of separation between them. There is also a direct relationship between polarizability and dipole moment<sup>24-26</sup>. The size of the molecular dipole moment influences the solubility of the compound in various solvents. Ground-state dipole moment is an important factor in measuring solvent effect on the molecule under study; a large ground-state dipole moment gives rise to a strong solvent polarity effects<sup>27</sup>. The dipole moments of HMX and FOX-7 vary just from 10.70 D to 14.26 D and 9.82 D to 12.29 D when the values change from the  $\epsilon=1.882$  to  $\epsilon=46.68$ , which also demonstrate that the solvent effects on two compounds are important. As be seen in Table 1 with increasing polarity of the solvent, the dipole moment is constantly rising. This means that with increasing polarity of the solvent increases the solubility of the title compounds. Molecules that have a greater dipole moment, most influence the polarity of solvent. So the change dipole moment in HMX is more than FOX-7 by increasing the polarity of the solvent. Whatever the calculated dipole moment ( $D$ ) for at the compound is further show that the compound easier and faster solved in solvents with higher polarity.

Hence, the solubility of HMX is more than of FOX-7 in the same solvent.

### 3.4 Molecular electrostatic potential (MEP) surface

Molecular electrostatic potential (MEP) is used for relative reactivities towards electrophilic attack and nucleophilic reactions<sup>28</sup>. To predict reactive sites for electrophilic and nucleophilic attack for HMX and FOX-7, the MEP at the B3LYP/6-311++G(2d,p) method was calculated. These sites give data about the area where the compound can have intermolecular interaction. As can be seen in Fig. 3, these molecules

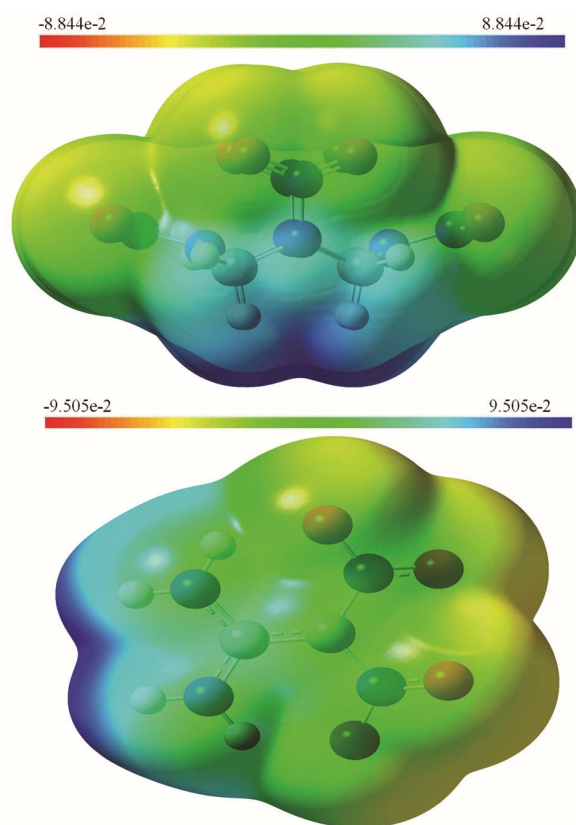


Fig. 3 — Molecular electrostatic potential map (MEP) of HMX and FOX-7

Table 1 — Molecular dipole moments and molecular polarizabilities for HMX and FOX-7 in gas phase and different solvents calculated with the B3LYP density functional and the 6-311++G(d,p) basis set

Compound	Parameter	Gas	Hexane	Benzene	CHCl <sub>3</sub>	THF	Acetone	Ethanol	CH <sub>3</sub> OH	DMF	CH <sub>3</sub> CN	DMSO
HMX	Dipole moment (D)	9.34	10.70	11.10	12.46	13.07	13.87	13.95	14.06	14.10	14.09	14.16
	Molecular polarizability (Bohr <sup>3</sup> )	-18.643	-18.775	-18.809	-18.917	-18.972	-19.049	-19.058	-19.068	-19.072	-19.071	-19.078
FOX-7	Dipole moment (D)	8.54	9.82	10.15	11.23	11.63	12.12	12.01	12.07	12.25	12.25	12.29
	Molecular polarizability (Bohr <sup>3</sup> )	-8.477	-8.450	-8.445	-8.427	-8.427	-8.428	-8.365	-8.365	-8.428	-8.428	-8.429

have several possible sites for the electrophilic attacks over the oxygen atoms. For the feasible nucleophilic reaction, the maximum positive region is located on hydrogen bonded to C atoms. The hydrocarbon parts of the structure provide significant nonpolar regions, while the presence of oxygen and nitrogen creates electronegative areas suitable for hydrogen bond acceptance. The procedure of solvation depends in an intricate way on a many of other molecular properties of the solvent and the solute, such as the relative sizes of solute and solvent molecules, their polarizability, and their mutual ability to form strong and efficient interacting aggregates. Dimethyl sulfoxide and acetonitrile, the more polar solvents investigated, should be capable of forming electrostatic interaction with the polar parts of the HMX and FOX-7 molecules.

### 3.5 Electrochemical properties

Molecular polarizability and atomic electron densities/charges are directly linked to the frontier molecular orbitals<sup>29,30</sup>. The latter is therefore also linked to solubility<sup>31-34</sup>.  $E_{HOMO}$  describes the tendency of the molecule to donate electrons (charge density). In general: the higher the  $E_{HOMO}$  energy the greater the ability of the molecule to donate electrons. The energy gap between the HOMOs and LUMOs is the critical parameters of chemical reactivity<sup>35</sup>. Large  $E_{HOMO-LUMO}$  energy differences indicate that the available electrons in these molecules have less tendency to move to the excited state and such compounds are chemically more inert<sup>22</sup>. HOMO, HOMO-1 and LUMO, LUMO+1 for both compounds were shown in Figs 4 and 5.

On the basis of Koopman's theorem, global reactivity descriptors such as electronegativity ( $\chi$ ) =  $-1/2(\epsilon_{LUMO} + \epsilon_{HOMO})$ , chemical potential ( $\mu$ ) =  $1/2(\epsilon_{LUMO} + \epsilon_{HOMO})$ , global hardness ( $\eta$ ) =  $1/2(\epsilon_{LUMO} - \epsilon_{HOMO})$  and electrophilicity index ( $\omega$ ) =  $\mu^2/2\eta$  are calculated using the energies of frontier molecular orbitals<sup>36</sup>.  $\epsilon_{HOMO}$ ,  $\epsilon_{LUMO}$  of HMX and FOX-7 in different solvents have been given in Tables 2 and 3.

The chemical hardness is quite useful to explain the chemical stability. The molecules having a great HOMO-LUMO energy gap will be more stable and less reactive than soft molecules having small HOMO-LUMO energy gap<sup>37</sup>. According to Table 2, for HMX with increasing polarity of the solvent  $E_{HOMO-LUMO}$  gap reduced, so the global hardness ( $\eta$ ) decreases and solubility increases. But for FOX-7 (Table 3) the process changes the chemical potential is as follow:

Hexane < Benzene < Chloroform < THF < Ethanol < Methanol < Acetone < Acetonitrile < DMF < DMSO

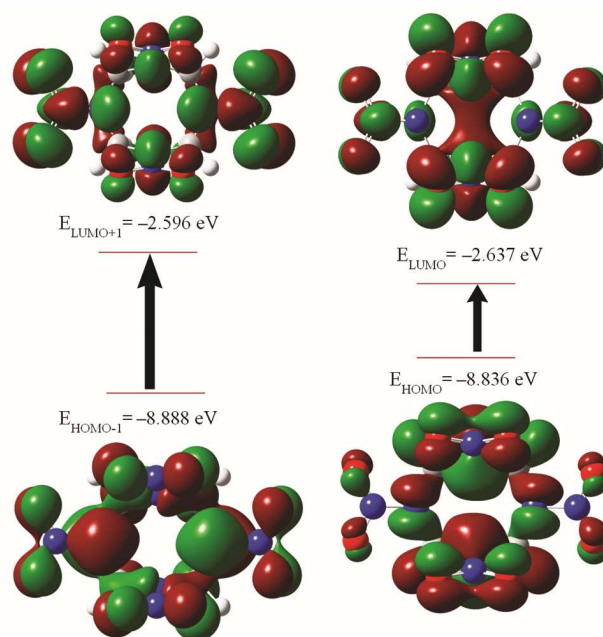


Fig. 4 — Atomic orbital compositions of the frontier molecular orbital for HMX

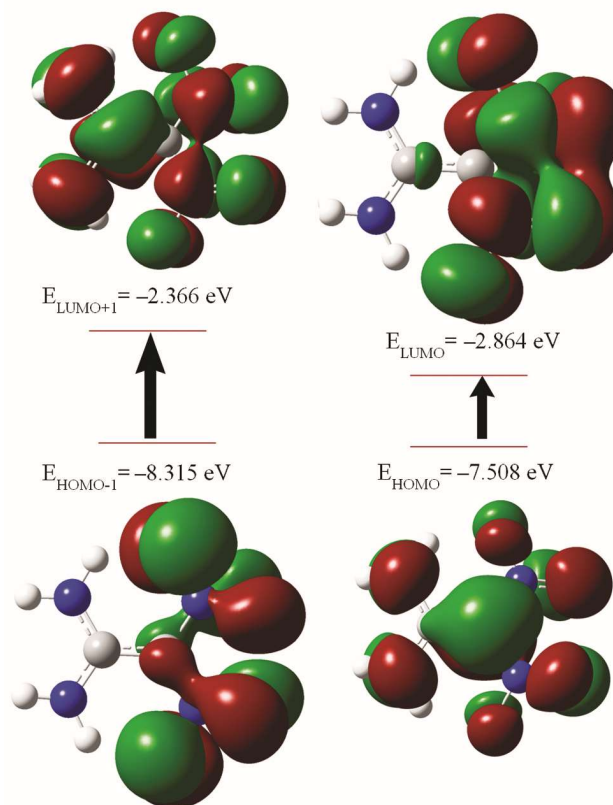


Fig. 5 — Atomic orbital compositions of the frontier molecular orbital for FOX-7

Table 2 —  $\Delta E_{\text{gap}}$ , chemical potential ( $\mu$ ), molecular hardness ( $\eta$ ), electronegativity ( $\chi$ ) and electrophilicity indices ( $\omega$ ) of HMX in gas phase and different solvents, at B3LYP/6-311++G(d,p) level

	Gas	Hexane	Benzene	Chloroform	THF	Acetone	Ethanol	Methanol	DMF	Acetonitrile	DMSO
$E_{\text{HOMO}}$ (eV)	-8.863	-8.726	-8.697	-8.616	-8.586	-8.552	-8.548	-8.544	-8.543	-8.543	-8.540
$E_{\text{HOMO-1}}$ (eV)	-8.888	-8.755	-8.726	-8.644	-8.613	-8.577	-8.574	-8.569	-8.568	-8.568	-8.566
$E_{\text{LUMO}}$ (eV)	-2.637	-2.561	-2.549	-2.527	-2.523	-2.523	-2.524	-2.524	-2.524	-2.524	-2.525
$E_{\text{LUMO+1}}$ (eV)	-2.596	-2.494	-2.470	-2.407	-2.387	-2.367	-2.365	-2.364	-2.327	-2.363	-2.362
$E_{\text{HOMO-LUMO gap}}$ (eV)	6.226	-6.165	-6.147	-6.090	-6.063	-6.028	-6.024	-6.020	-6.018	-6.018	-6.015
Chemical potential ( $\mu$ )	5.750	5.644	5.623	5.571	5.554	5.537	5.536	5.534	5.533	5.534	5.532
Global hardness ( $\eta$ )	3.113	3.082	3.074	3.045	3.032	3.014	3.012	3.010	3.009	3.009	3.008
Electronegativity ( $\chi$ )	-5.750	-5.644	-5.623	-5.571	-5.554	-5.537	-5.536	-5.534	-5.533	-5.534	-5.532
Electrophilicity indices ( $\omega$ )	5.310	5.167	5.143	5.097	5.088	5.086	5.087	5.087	5.088	5.088	5.088

Table 3 —  $\Delta E_{\text{gap}}$  (eV), chemical potential ( $\mu$ ), molecular hardness ( $\eta$ ), electronegativity ( $\chi$ ) and electrophilicity indices ( $\omega$ ) of FOX-7 in gas phase and different solvents, at B3LYP/6-311++G(d,p) level

	Gas	Hexane	Benzene	Chloroform	THF	Acetone	Ethanol	Methanol	DMF	Acetonitrile	DMSO
$E_{\text{HOMO}}$ (eV)	-7.508	-7.474	-7.472	-7.460	-7.464	-7.470	-7.433	-7.434	-7.472	-7.472	-7.473
$E_{\text{HOMO-1}}$ (eV)	-8.315	-8.295	-8.294	-8.289	-8.301	-8.317	-8.248	-8.250	-8.322	-8.321	-8.323
$E_{\text{LUMO}}$ (eV)	-2.864	-2.922	-2.941	-3.004	-3.037	-3.080	-3.022	-3.027	-3.092	-3.091	-3.095
$E_{\text{LUMO+1}}$ (eV)	-2.366	-2.284	-2.269	-2.185	-2.174	-2.162	-2.089	-2.088	-2.159	-2.160	-2.159
$E_{\text{HOMO-LUMO gap}}$ (eV)	4.644	-4.552	-4.530	-4.456	-4.427	-4.390	-4.411	-4.407	-4.380	-4.381	-4.378
chemical potential ( $\mu$ )	5.186	5.198	5.206	5.232	5.250	5.275	5.227	5.231	5.282	5.282	5.284
global hardness ( $\eta$ )	2.322	2.276	2.265	2.228	2.213	2.195	2.206	2.203	2.190	2.191	2.189
Electronegativity ( $\chi$ )	-5.186	-5.198	-5.206	-5.232	-5.250	-5.275	-5.227	-5.231	-5.282	-5.282	-5.284
Electrophilicity indices ( $\omega$ )	5.792	5.935	5.983	6.143	6.227	6.338	6.195	6.209	6.370	6.367	6.378

Ionization potential (IP) and electron affinity (EA) are commonly calculated via; (i) differences of total energies of the neutral ( $E_{\text{neutral}}$ ) and ionic systems ( $E_{\text{cation}}$ ,  $E_{\text{anion}}$ ) obtained from optimized molecular configurations; (ii) Koopman's theorem in which IP and EA are approximated as the negative value of the energy for the lowest unoccupied molecular orbital (HOMO), and the negative value of the highest occupied molecular orbital (LUMO), respectively, (i.e.,  $\text{IP} = -E_{\text{HOMO}}$ ,  $\text{EA} = -E_{\text{LUMO}}$ ).

The EAs and IPs were obtained via the  $\Delta\text{SCF}$  method in which the energies of ions (the anion and cation) are separately calculated as follow:

$$\text{IP} = E_{\text{cation}} - E_{\text{Neutral}} \quad \dots (2)$$

$$\text{EA} = E_{\text{neutral}} - E_{\text{anion}} \quad \dots (3)$$

For neutral ground state the restricted B3LYP functional was used in computing the total energy, while unrestricted (UB3LYP) formalism was used for radical cations and anions. Because the title compound has strong electron-negative atoms such as oxygen and nitrogen, therefore EA will be less than the IP. The numerical values of above-mentioned parameters were

listed in Table 4. From Table 4, we can conclude that the IP obtained by PCM method increase with the increasing polarity of the solvent, while the EA will decrease with the increase in the polarity of the solvent.

### 3.6 Gibbs solvation free energy

Ten different solvents (hexane, benzene, chloroform, tetrahydrofuran, acetone, ethanol, methanol, dimethylformamide, acetonitrile and DMSO) were used to compute free energies of solvation for title compounds. The results for the calculation of the  $\Delta G_{\text{solv}}$  of the HMX and FOX-7 as it is continuously updated with several solvents with the B3LYP density functional and the 6-311++G(d,p) basis set are presented in Table 5. As shown in Table 5, by the increase of solvent's dielectric constant, the absolute amount of  $\Delta G_{\text{solv}}$  and solubility of title compound increased. Table 5 shows that the order of absolute value of  $\Delta G_{\text{solv}}$  for both compounds was found to be as follow:

DMSO > dimethylformamide > acetonitrile > Methanol > ethanol > acetone > tetrahydrofuran > chloroform > benzene > hexane.

Table 4 — Ionization potential (eV) and electron affinity (eV) of HMX and FOX-7 in gas phase and different solvents, at B3LYP/6-311++G(d,p) level

Compound	Parameter	Gas	Hexane	Benzene	Chloroform	THF	Acetone	Ethanol	Methanol	DMF	Acetonitrile	DMSO
HMX	IP	242.37	242.37	249.56	251.65	258.64	261.84	262.83	263.33	263.80	263.98	263.93
	EA	-24.86	-17.72	-15.64	-9.84	-6.77	-2.67	-2.21	-1.68	-1.46	-1.53	-1.15
FOX-7	IP	219.91	224.75	226.10	230.21	232.05	234.38	234.49	234.67	235.02	235.01	235.21
	EA	-19.79	-14.42	-13.01	-8.38	-6.54	-4.25	-3.96	-3.64	-3.591	-3.55	-3.45

Table 5 —  $\Delta G_{\text{solv}}$  (kcal/mol), of HMX and FOX-7 in different solvents, at B3LYP/6-311++G(d,p) level

	Hexane $\epsilon=1.88$	Benzene $\epsilon=2.27$	Chloroform $\epsilon=4.81$	THF $\epsilon=7.58$	Acetone $\epsilon=20.70$	Ethanol $\epsilon=24.50$	Methanol $\epsilon=32.70$	DMF $\epsilon=36.71$	Acetonitrile $\epsilon=37.50$	DMSO $\epsilon=46.68$
HMX	-6.66	-8.54	-14.75	-17.59	-21.38	-21.80	-22.29	-22.49	-22.43	-22.77
FOX-7	-5.09	-6.42	-10.54	-12.26	-14.41	-14.61	-14.87	-15.00	-14.97	-15.16

#### 4 Conclusions

The molecular geometry of HMX and FOX-7 in gas phase and solutions have been investigated by using DFT approach at B3LYP/6-311++G(d,p) level, while the solvents values were obtained with the PCM method. It has been concluded that the solvent effects on the molecular structure of two compounds are not obvious. The dipole moments of HMX and FOX-7 vary just from 10.70 D to 14.26 D and 9.82 D to 12.29 D when the values change from the  $\epsilon=1.882$  to  $\epsilon=46.68$ , which also demonstrate that the solvent effects on two compounds are important. The MEP map shows that the negative potential sites are on electronegative atoms, while the positive potential sites are around the hydrogen atoms. We observed that as the solvent dielectric constant increases the dipole moment of the molecules under study increases. The theoretical calculations for discussed explosive compounds in various solvents show a correlation between polarity and solubility. With the increment of solvent's dielectric constant, the absolute amount of  $\Delta G_{\text{solv}}$  of title compound increased. Results show that the order of absolute value of  $\Delta G_{\text{solv}}$  for both compounds was found to be DMSO > dimethylformamide > acetonitrile > Methanol > ethanol > acetone > tetrahydrofurane > chloroform > benzene > hexane.

#### Acknowledgment

Authors are grateful to the Damghan University for financial support.

#### References

- Teipel U, Förster-Barth U & Krause H H, *Propellants Explos Pyrotech*, 24 (1999) 195.
- Teipel U, Kröber H & Krause H H, *Propellants Explos Pyrotech*, 26 (2001) 168.
- Teipel U & Mikonsaari I, *Propellants Explos Pyrotech*, 27 (2002) 168.
- Domingo L R & Domingo L R, *J Org Chem*, 66 (2001) 3211.
- Zhang G & Musgrave C B, *J Phys Chem*, 111A (2007) 1554.
- Bouachrine M, Bouzzine S, Hamidi M, Lère-Porte J, Serein-Spirau F, Sotiropoulos J & Miqueu K, *J Mater Environ Sci*, 1 (2010) 78.
- Aihara J I & Aihara J I, *Phys Chem Chem Phys*, 2 (2000) 3121.
- Yoshida M & Aihara J I, *Phys Chem Chem Phys*, 1 (1999) 227.
- Ghosh A, Sarkar A, Mitra P, Banerji A, Banerji J, Mandal S & Das M, *J Mol Struct*, 980 (2010) 7.
- Aihara J I & Aihara J I, *J Phys Chem*, 103A (1999) 7487.
- Lameira J, Alves C, Moliner V & Silla E, *Eur J Med Chem*, 41 (2006) 616.
- Lameira J, Medeiros I, Reis M, Santos A & Alves C, *Bioorg Med Chem Lett*, 14 (2006) 7105.
- Wong K Y, Mercader A G, Saavedra L M, Honarparvar B, Romanelli G P & Duchowicz P R, *J Biomed Sci*, 21 (2014) 1.
- Frisch M J, Trucks G W & Schlegel H B, *Gaussian*, (Inc., Wallingford CT), 2009.
- Becke A D & Becke A D, *Phys Rev*, 38A (1988) 3098.
- Lee C, Yang W & Parr R G, *Phys Rev*, 37B (1988) 785.
- Aguilar M, Del Valle F O & Tomasi J, *J Chem Phys*, 98 (1993) 7375.
- Cossi M, Barone V, Cammi R & Tomasi J, *Chem Phys Lett*, 255 (1996) 327.
- Preat J, Jacquemin D, Wathélet V, André J-M & Perpète E A, *J Phys Chem*, 110A (2006) 8144.
- Mananghaya M, Rodulfo E, Santos G N, Villagrancia A R & Ladines A N, *J Nanomater*, 2012 (2012) 62.
- Chenzhong C & Zhiliang L, *J Chem Inform Comput Sci*, 38 (1998) 1.
- Li F Y & Zhao J J, *J At Mol Sci*, 1 (2010) 68.
- Docherty H, Dyer P J & Cummings P T, *Mol Simul*, 37 (2011) 299.
- Hatua K & Nandi P K, *J Chem Theory Comput*, 12 (2013) 1250099.
- Lin T Y, Chaudhari A & Lee S L, *J Mol Model*, 19 (2013) 529.
- Blair S A & Thakkar A J, *J Chem Phys*, 141 (2014) 074306.
- Masternak A, Wenska G, Milecki J, Skalski B & Franzen S, *J Phys Chem*, 109A (2005) 759.
- Scrocco E & Tomasi J, *Adv Quantum Chem*, 11 (1979) 115.
- Dumont R S & Dumont R S, *Can J Chem*, 92 (2013) 100.
- Jung I H, Lo W Y, Jang J, Chen W, Zhao D, Landry E S, Lu L, Talapin D V & Yu L, *Chem Mater*, 26 (2014) 3450.
- Gallagher S H, Armstrong R S, Lay P A & Reed C A, *J Phys Chem*, 99 (1995) 5817.

- 32 Makovskaya V, Dean JR, Tomlinson WR & Comber M, *Anal Chim Acta*, 315 (1995) 193.
- 33 Farah J P S, Lima G A R & Quina F H, *Comp Theor Chem*, 394 (1997) 267.
- 34 Yin C, Liu X, Guo W, Lin T, Wang X & Wang L, *Water Res*, 36 (2002) 2975.
- 35 Pearson R G, *J Org Chem*, 54 (1989) 1423.
- 36 Padmanabhan J, Parthasarathi R, Subramanian V & Chattaraj P, *J Phys Chem*, 111A (2007) 1358.
- 37 Özbek N, Kavak G, Özcan Y, İde S & Karacan N, *J Mol Struct*, 919 (2009) 154.