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DFT Prediction of Radiolytic Stability of Conformationally Flexible Ligands

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Abstract: Radiolytic stability is one of the main requirements of the ligands for the reprocessing of spent nuclear fuel. The prediction of radiation stability based only on the 2D molecular structural formula allows us to accelerate and simplify the development of new ligands. Here, we used quantum chemistry to investigate the radiolytic behavior of water-soluble diglycolamides as one of the most popular ligands for spent nuclear fuel reprocessing. The accurate accounting of conformational mobility in the descriptors based on the Frontier Orbital Fukui theory allowed us to obtain a good correlation between theoretical and experimental data.

Keywords: spent nuclear fuel; extraction; diglycolamides; DFT; irradiation; radiolytic stability

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1. Introduction

Today, approximately 11% of the world's electricity is produced with nuclear power, which is third in the world after coal and hydropower [1]. Due to the high efficiency of nuclear power plants, their total number in the world is growing every year [2]. This fact also relates to the accessibility of nuclear energy generation in various climatic zones, regardless of natural conditions. In the context of the world's decarbonization strategy, the nuclear industry is able to reduce carbon dioxide emissions into the atmosphere.

However, a critical problem of the nuclear industry is the accumulation of radioactive waste and spent nuclear fuel (SNF). The reprocessing of SNF first allows for the return of uranium and plutonium to the nuclear fuel cycle. In addition, an important step is the extraction of minor actinides (Am, Cm, and Np), which determines the requirements for storage facilities and repositories in the long term [3]. Despite being extracted from the SNF, these metals also need to be separated from each other and from the lanthanides, which possess similar chemical behavior.

A family of diglycolamides (DGAs) is a promising class of organic ligands for various strategies of SNF reprocessing using liquid-liquid extraction. N,N,N0,N0-tetraoctyldiglycolamide (TODGA) plays a crucial role in numerous partitioning processes for advanced fuel cycles, including DIAMEX [4], 1cycle-SANEX [5], and GANEX [6]. A replacement of n-octyl fragments by a short branch with 1–2 carbon atoms makes the molecule water-soluble [7]. These DGAs are widely used in the ALSEP [8] and EXAm [9] processes. On the one hand, the DGAs are the focus of a large number of radiochemical investigations that provide the theoreticians with a sufficient amount of experimental information to be placed in the basement of new theories. On the other hand, it also raises questions about the origins of the ligands' efficiency, selectivity, and radiation stability.

Due to the high activity of the separated elements, the radiation stability of the extractants is one of the most important requirements for the ligands. The radiolytic degradation of water-soluble DGA molecules has been investigated experimentally and theoretically in numerous studies [10–13]. The summary information on radiolytic products is presented in Table S1 (Supplementary information). In general, the key points of the DGAs radiolysis are: (a) the main way of the DGA degradation process is the breaking of the C-O bond except TMDGA; (b) the C breaking in the DGA skeleton is not observed; (c) the stability of molecules increases with the methylation of the ether bonds. The latter fact, at first glance, looks counterintuitive and does not correlate with the increase in the stability of the more branched radical, which could be assumed from the general knowledge of organic chemistry.

Theoretical modeling of the radiolysis process allows us to estimate the radiolytic stability of the molecules and suggest modifications in the ligand design process prior to experimental studies, thus reducing the doses of the number of staff. Furthermore, the search for new effective and radiolytically stable ligands may be significantly simplified and accelerated by computing the properties of the molecule based only on its structural formula before the synthesis [14].

Theoretical investigations of radiolysis in similar systems are based on the assumption that indirect radiolysis is dominant due to a low concentration of ligands in the solvent, which has also been experimentally confirmed [15–17]. Firstly, ionizing radiation generates radicals and ions from the solvent molecules. Next, the formed particles attack the ligand molecules. Therefore, to predict the ligand stability, we need to estimate its reactivity regarding the ions and radicals produced by solvent radiation. A set of quantum chemical approaches is used for the DGAs' property simulation. Koubsky et al. [11,18,19] suggested using the Fukui Frontier Orbital Theory [20,21] and to calculate the electrophilic, nucleophilic, and radical Fukui functions to determine the most reactive sites in the molecule regarding the corresponding particles [22]. The authors also calculated the bond orders (using Mayer and natural population analyses) to identify the weakest bonds. The same approach was used in the work of Verlinden and colleagues [23], where they continued the discussion about less reactive hydrogen atoms near the ether bond regarding the N-alkyl substitutional groups in relation to the radical attack. Although the theoretical data in most of the cases described the experimental results qualitatively well, the theoretical quantum chemical technique was not used for the determination of all class tendencies and for the further prediction of the required modifications of the molecule.

Earlier, we showed the significance of taking into account the conformational mobility of the ligand when modeling its properties, including the quantitative estimation of the radiolitic stability [14,24]. The aim of this study is to optimize the approaches to the radiolysis theoretical investigation. We investigated a set of water-soluble DGA molecules' radiation stability by quantum chemical approaches, using the experimental data from [10] for theory validation.

2. Materials and Methods

The general idea of the model building is based on the concept of local reactivity, or the so-called conceptual density functional theory (DFT). According to the concept, we can predict the reactivity of the molecule or its parts based on the electron density distribution and alteration. We considered two regions of interest: the electron density condensed on atoms and between them. The first region can be described with a local reactivity index, showing its probability to perform as the center of a chemical reaction. The second one can be described as a non-integer variant of the well-known bond order. The investigation of both regions can be performed during the analysis of the Schrodinger equation solution (e.g., using the Kohn-Sham approach).

We used the local reactivity descriptors (atom indices) based on the Fukui border orbitals theory to determine the most reactive atom. The indices show the variation of local electron density as a reaction of adding or removing an electron from the whole system. Due to the large number of possible particles created during the irradiation in the solution, we preferred to use a condensed dual descriptor (CDD) as the local reactivity index [25,26]. Moreover, it was observed that the influence of the orbital relaxation was smaller in the case of the CDD calculation, and hence this descriptor is more accurate than the Fukui indices [27]. The CDD is a linear combination of condensed Fukui indices and is defined as follows:

$$\Delta f_A = 2q_N^A - q_{N+1}^A - q_{N-1}^A$$

The greater the reactivity of the atom is, the greater the absolute value of the CDD becomes, while the sign of the CDD shows the type of the attacking particle.

We also estimated the influence of conformation errors and steric factors on the calculated indices and bond orders.

All initial molecules were created from their 2D-molecular formulas. We performed three single-point calculations for each molecule with charges −1, 0, +1 for the condensed dual descriptor calculations by using ORCA 5.0 [28]. We used the natural population analysis for the bond order and charge calculating realized in the Janpa package [29]. The SASA (Solvent-Accessible Surface Area) approach realized in the MDTraj library [30] was used to estimate the steric accessibility of different sites in molecules. This method was based on the Golden section helix algorithm to generate the sphere with a radius equal to the sum of the atom's and the attacking particle's van der Waals radii. A proton was chosen as the smallest possible attacking particle. We introduced a new descriptor, $\mathrm{SASA_k}$, which was equal to the SASA for atom k in a molecule divided on all the surface of atom k considering the attacking particle. Since the main radiolytic products of DGAs were produced by C-C, C-O and C-N bonds, all electronic properties were calculated for non-hydrogen atoms.

We estimated molecule electronic properties in two ways—for the optimized molecule geometry (opt-approach) and for the confrontation set (conf-approach):

- "Opt-approach": We provided the optimization of molecules in two steps: (1) conformational analysis by the PM7 semiempirical Hamiltonian [31] in the MOPAC2016 package [32]; (2) the obtained conformation was optimized in the ORCA package on the D3-B3LYP/def2-TZVPP RIJCOSX [33–37] level of theory.
- "Conf-approach": For the conformation error estimation, we selected 20 conformations for each molecule by the following method. We generated 200 conformations for each structure using the rdkit open library. Next, the energy of each molecule considering solvation energy (where the solvent is water) was computed using the GFN2-xTB [38]. We chose the conformation with minimal energy and then we selected 19 other conformations with energy less than the minima energy adding 20 kcal/mol (to select only those conformations that thermodynamically can exist in solution) and with the maxima of the RMSD of atom coordinates (to cover the potential energy surface as widely as possible). We calculated the electronic structure of each conformation with charges −1, 0, +1 in the ORCA at the same D3-B3LYP/def2-TZVPD RIJCOSX level of theory. The MBOs, NBOs and CDD values were averaged for each molecule over all conformations, considering the probability of this conformation existing in the solution. This probability was calculated based on the Gibbs energy obtained by XTB for each conformation. It should be mentioned that despite the long description of the process, its automatization together with the absence of DFT geometry optimization led to significant time saving compared to the first one. It also excluded the human factor and solved the issue with the symmetric atoms.

3. Results and Discussion

The general structure of DGAs investigated in this study with marked atoms is presented in Figure 1. First, we compared the experimental results of the main degradation products of the molecules with the theoretical ones predicted based on the bond orders obtained by different methods. We also compared each molecule using the CDD and SASA calculations with experimental values of the radiolysis constant.

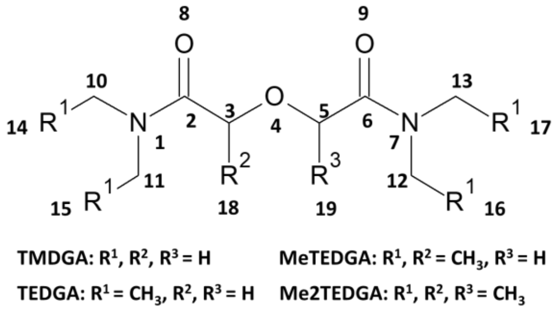

Figure 1. The structural formula of the investigated DGAs molecules.

Concerning the applied side of the issue, the calculation of Mayer bond orders is much faster compared to the natural ones, thus, these calculations are the most common, and the construction of the computational approach based on MBOs would be time-saving. Calculated Mayer and Natural bond orders for opt- and conf- approaches are presented in Figure 2 (and Table S1, supplementary information). First, the MBOs obtained for the optimized geometries presented abnormally small values in all cases (0.56 for TMGA, 0.49 for TEDGA, 0.21 for MeTEDGA and 0.19 for Me_2TEDGA). Such bond orders rather indicated the absence of covalent bonds between atoms, which was impossible in our case. Nonetheless, the comparison of the MBOs revealed the lowest bond orders (and predicted the leakage) of the ether bond for the TMDGA molecule and the elimination of the methyl group (by C3-C18 bond breaking). Since these processes were not observed in the experiments, we concluded that the approach was inapplicable.

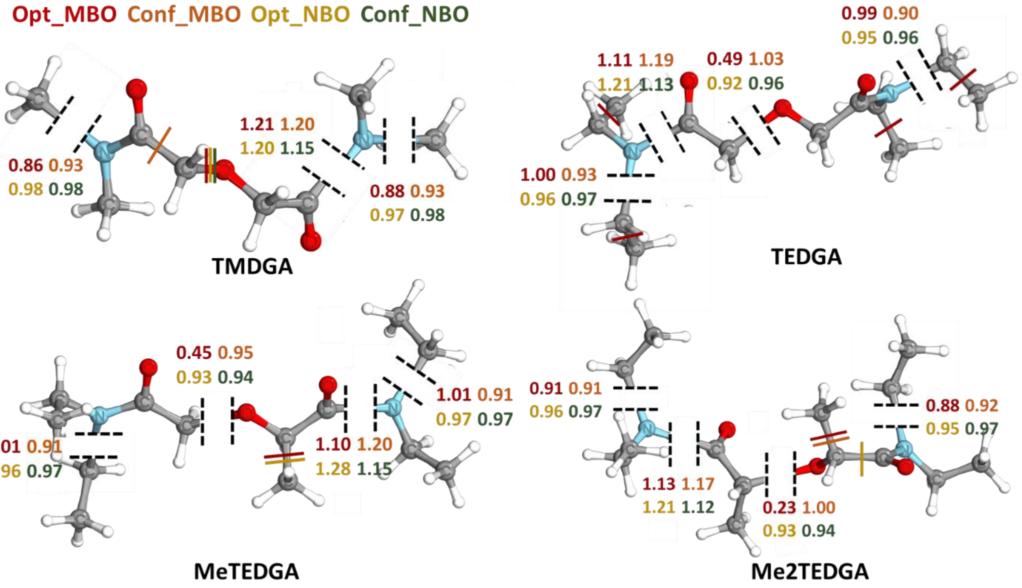

Figure 2. The breaking bonds from the experimental data (black lines) and the values of bond orders obtained by different calculation methods (color lines).

Moreover, we noted the significant difference between the symmetric bonds in some cases, which also could not be explained by anything other than the imperfection of the proposed computational method. Though a flexible molecule could be stable in non-symmetric conformations, the overall properties of the molecule should be a result of the properties of the whole set of stable 3D structures. The conformationally corrected property, in its turn, should generally reproduce the symmetry of the structure.

The MBOs determined by using the conf-approach did not show extremely low values. Furthermore, the bond orders were very similar for the symmetrical atoms in the molecules. However, again, the most reactive sites were not obtained correctly. In the case of TMDGA, the method predicted the C2-C3 bond breaking, which was not observed experimentally. The removal of the methyl group was again calculated for the Me_2TEDGA molecule. Thus, we finally excluded this approach from further investigation.

Unfortunately, the NBOs simulated for the opt-approach still predicted the removal of the methyl group for the MeTEDGA as well as C2-C3 and C5-C6 bond breaking for the Me_2TEDGA molecules. However, the conf-approach showed results closest to the experimental ones. We predicted ether bond breaking in all cases with good values of bond orders. Meanwhile, the C3-O4 and C5-O4 bonds were strong in the TMDGA substances. At this step, we may conclude that the analysis of bond leakage (even when using the accurate computational approach and considering the conformational mobility) cannot be used solely as a predictive tool for the estimation of the radiolitic stability. It can be explained by comparing the probabilities of the irradiation interaction with the ligand in the solution. Considering the volumes of the ligand molecule and the solvent one, as well as the typical concentrations in the radiochemical processes, the probabilities ratio can be estimated as nearly 10^2–10^3, and the solvent irradiation appeared to be the most probable one. The computational approach should preferably consider the probable reactions with the products of the solvent radiolysis rather than the direct ligand degradation. Thus, we decided to try other descriptors for the DGAs radiolytic behavior explanation using the NPA analysis and conf-approach.

The proposed extended approach was based on the following assumptions; We considered the radiolitic stability as a reciprocal of the reactivity of the atoms, i.e., the probable targets of the solvent fragments. We calculated the CDD and $SASA_k$ values for each molecule in each conformation and then averaged CDD × $SASA_k$ values, considering the probability of encountering this conformation in the water solution. The results are presented in Table 1.

Table 1. CDD × $SASA_k$ values $\times 10^{-3}$ obtained for each non-hydrogen atom in the DGAs molecules.

Atom	**N1**	**C2**	**C3**	**O4**	**C5**	**C6**	**N7**	**O8**	**O9**	**C10**
TMDGA	−1.56	4.97	0.59	0.41	0.50	5.07	−1.53	−7.83	−7.64	0.99
TEDGA	−0.008	1.66	−0.06	0.01	−0.05	1.81	−0.001	−6.39	−6.45	0.20
MeTEDGA	−0.31	1.14	0	8.1	−0.006	0.79	−0.02	−1.26	−8.46	0.15
Me_2TEDGA	−0.01	0.25	0	3.1	0	0.27	−0.45	−1.45	−5.58	0.16
Atom	**C11**	**C12**	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**	**C19**	**-**
TMDGA	1.09	1.00	1.12	-	-	-	-	-	-	-
TEDGA	0.11	0.01	0.24	0.18	−0.03	−0.03	0.17	-	-	-
MeTEDGA	0.25	0.16	0.19	0.16	−0.04	−0.06	0.14	0.07	-	-
Me_2TEDGA	0.23	0.29	0.32	0.01	−0.04	−0.15	0.34	0.18	0.32	-

First, it is important to note that the calculated CDD × $SASA_k$ values for the C3 atom in the MeTEDGA molecule as well as the C3 and C5 positions in the Me_2TEDGA structure were equal to zero. This fact meant that these molecular sites were not sterically accessible for the attacking particle. Thus, the DGA's methylation led to the ether bonds' protection, and therefore the stability of molecules increased in the row TEDGA < MeTEDGA < Me_2TEDGA.

Moreover, the CDD × $SASA_k$ values were decreased for the C2 and C6 atomic positions. The attack of these sites leads to the breaking of bonds between the nitrogen and carbonyl atoms in the structure. While the products of N1-C2 and C6-N7 bond breaking were presented in the experimental data of radiolytic degradation, the decrease in C2 and C6 CDD × $SASA_k$ values in the rows TMDGA, TEDGA, MeTEDGA, Me_2TEDGA was by accompanied by the increase in radiation stability in this row.

The CDD × $SASA_k$ values were small for C10–C17 for all molecules with ethyl groups. This fact allowed us to make a suggestion about the same tendency for all carbon atoms in the long N-alkyl branches in lipophilic DGAs (such as TODGA, TEHDGA, etc.). Therefore, the main radiolytic degradation processes were taking place in positions 1–7 for all the DGAs molecules except TMDGA. This result was confirmed by the results of gamma irradiation experiments for lipophilic DGAs, where no products of the N-alkyne chain rupture were observed [39–41]. Moreover, the increase in radiation stability in the case of methylation in the C3 and C5 positions was validated by the TODGA and its methylating derivative, gamma-radiolysis [42].

Next, we applied the conformational reactivity descriptor (CRD) presented in our previous work [12]. The calculated CRD descriptor appeared to be linearly correlated with the experimental values of the dose constants (Table S3, Figure 3). While the TMDGA molecule has the lowest radiolytic stability, this ligand has the highest value of CRD. The radiolysis dose constants obtained by experimental investigation decrease in the row TMDGA > TEDGA > MeTEDGA > Me_2TEDGA, and the CRD has the same behavior in this series. The coefficient of linear determination (R^2) between the CRD and dose constant values is equal to 0.82. This fact validates the possibility of using the CRD descriptor for the estimation of the organic molecule's radiolytic stability.

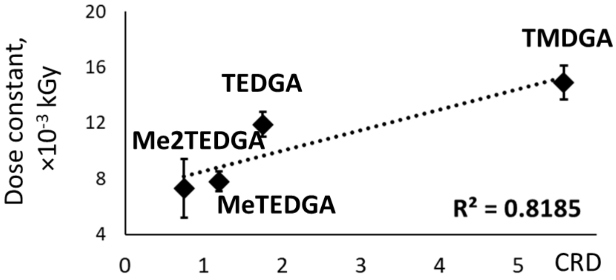

Figure 3. Correlation between the experimental radiolysis constants and the calculated CRD values.

We may also note the decrease in model accuracy compared to our previous work, where the R^2 value was 0.97. Though the average flexibility of the molecules was the same, here, we used automated subsampling together with semiempirical quantum chemistry in the first stage instead of the computationally expensive DFT calculations. Thus, we may consider the current computational scheme as much more helpful for the ligand design, as it reduces the required computational time several times.

4. Conclusions

In summary, we showed that the previously proposed approach using CDD × SASA and CRD as descriptors of reactivity allows us to obtain a qualitative and quantitative estimation of the organic ligand radiolytic stability. In addition, our method made it possible to critically reduce the human factor in determining the molecule's electronic properties by starting automated modeling from a 2D structural formula. It should be noted that, despite the long description of the process of the conf-approach calculation, its automation, combined with the lack of optimization of the DFT geometry, leads to significant time savings compared to the traditional quantum chemistry way of geometry optimization.

We also showed that the methods using only optimized geometry for the molecule electronic structure calculation do not allow to simulate the properties of conformationally flexible molecules accurately. In particular, the bond orders calculated in this way do not correlate with the experimentally detected radiolysis products. Regarding the DGA synthesis, the fact that the radiolytic stability grows during the methylation of the ether bonds becomes the general recommendation for the new ether-containing ligands development. It is the steric protection of the C-O bond that leads to a decrease in the probability of its breaking despite the seemingly more stable radicals formed. We could also propose an increase in radiolytic stability after increasing the lengths of the alkyl chains. Though it is important to control the solubility of DGA in the corresponding solvent, these recommendations remain the same for water- and organic-soluble molecules.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en16010257/s1, Table S1: Summary of radiolysis products of water-soluble DGAs; Table S2: Calculated Mayer and natural bond orders for TMDGA, TEDGA, MeTEDGA and Me_2TEDGA molecules by opt- and conf- approaches; Table S3: Dose constants for the investigated molecules and CRD value (0.85 quantile of CDD $\times$ $SASA_k$).

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