

Structural and Spectral (IR, NMR and UV/Visible) Properties of Newly Designed Boronic Acid Derivatives Containing DO3A Sensitive to Uranyl Ion: A DFT and TD-DFT Study

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Abstract

In this study, the structural, electronic and optical properties of DO3A-based boronic acid derivates with and without UO_2^{2+} ion are studied by density functional calculations with M062X/6 - 31 g + (d) method, in aqueous media. The quantum chemical properties such as E_{HOMO} , E_{LUMO} , the energy gap (ΔE), chemical potential (μ), hardness (η) are also performed. The theoretical essential UV-Vis. bands of DO3A-UO₂(VI)-APB-o are at 392 and 687 nm. DO3A-UO₂ (VI)-ABB-o structure has two main bands at 393 and 650 nm. In general, the bathochromic shift occurs and the HOMO-LUMO energy gap decreases to about 2 eV, by binding UO_2^{2+} ion in three different media. The notable shifts in NMR spectrums have been found on *a*-carbon of carbonyl group, ring carbons and amide protons. In IR-spectrums, the prominent peaks belong to BO-H and N-H of amide stretching vibrations of calculated structures.

Keywords

Uranium, DO3A, Benzimidazole, DFT

1. Introduction

Boronic acid derivatives have attracted attention from many applications due to their unique properties and are widely used in Diels Alder reactions [1], asymmetric synthesis [2], cross-coupling reactions [3], activation of carboxylic acids and pattern in synthesis [4]. Due to the binding properties of boronic acid derivatives, they have been used in sensor studies [5]. Since using 2-arylboronic acid as a chemosensor for polyols, it has been used as a fluorescence probe in many studies [6]. Some organoboron compounds have been developed for fluoride ion sensors [7]. Carotenoid derivatives containing $B(OH)_2$ groups have been used as potential sugar sensor [8].

On the other hand, DO3A (tetraazacyclododecane-1,4,7,-three acetic acid) molecules in the scope of this study is a compound known as a cyclin size macro and they can be seen as a chelating agent with higher affinity because of the carbonyl groups [9]. Since these molecules have been synthesized, they often used in several ions complexes as Ni²⁺, Cu²⁺, Ca²⁺ and Gd³⁺ and also particularly yttrium complexes are investigated in a variety of research and applications like therapeutic radiopharmaceuticals [10], positron emission tomography [11], magnetic resonance imaging and medical diagnosis and treatment as high thermodynamic stability features [12].

One of the main applications of these molecules is the formation of the lanthanide complexes clingy by DOTA (tetraazacyclododecane-1,4,7,10-tetra acetic acid) lanthanides bound to the amino and carboxyl groups [13]. DOTA and their complexes have been subjected to various experimental work and theoretical studies in the literature. The study was conducted by Iglesias and different isomers of DOTA and related lanthanide complexes have been investigated in the solvent medium and stable geometries and energies specified with the DFT method [14]. In another study, structural properties of Ln (III) complexes with a tetrapyridine pendant-armed macrocyclic ligand have been investigated by DFT method [15].

As can be seen from the above some mentioned studies, quick and versatile quantitative determination of molecular diagnostics of the mutated gene associated with human disease plays an important role in modern clinical treatment and genomic studies. On the other hand, radioactive waste, such as the uranyl ions consisting of the fuel nuclear power plant and ore beneficiation are carried to the living systems on through land, water and food chains. To solve the uranyl chemistry in living systems, specifically, understanding of interactions with biomolecules can be achieved by calculation studies at the molecular level.

In this sense, new designed DO3A-based sensors containing benzimidazole and phenyl group with boronic acid have been shown in **Figure 1**. Their stability of uranyl ion and possible structures with DO3A have been calculated in water media and also chemical properties such as E_{HOMO} , E_{LUMO} , the energy gap (ΔE), chemical potential (μ), hardness (η), softness (S), the absolute electronegativity (χ) and the electrophilicity index (ω) have been predicted. Moreover, detections of these complexes in water phase spectroscopic properties (UV-Vis, IR and NMR) have been given.

2. Method

All calculations were performed with using the Gaussian [16] 09W and Gauss



Figure 1. Designed DO3A-based sensors containing benzimidazole and phenylgroup.

View 5.0.8 molecular modeling software [17]. Also, ChemCraft program [18] was used to determine the diameter of the examined structures. M062X [19], B3LYP [20] and B3PW91 [21] methods that can be suitable for calculations are selected and compared with experimental absorption value of reference uranium complex [22]. First of all, U (IV) DO3A complex was optimized with selected three methods in the gas phase. Optimization in the solvent phase (methanol) was then carried out and the UV-Vis spectrum was obtained. The calculation results compared with experimental value and show that (Table S1 given in Supporting information) M062X functional was found better than the other selected methods. After determination of the appropriate method, all subsequent calculations performed with M062X functional and 6 - 31 + G(d) [23] basis set. The SARC ZORA basis set was used for the uranium atom [24]. The SMD Solvation Model Density [25] method was chosen to reflect the effect of the water phase on the calculations. The dielectric constant was chosen as the standard value for water ε = 78.39). Calculations corresponding to acidic medium implemented with nitrogen protonation. The basic medium is provided by the removal of hydrogen atoms in the carboxylic groups on DO3A.

3. Results and Discussion

3.1. DO3A-Based Aminophenol and Aminobenzo Imidazolyl Boronic Acid Derivatives with and without UO₂²⁺

3.1.1. Stabilities

After selecting the appropriate method for the calculations, boronic acid-containing derivatives of ortho, para and meta positions of DO3A based sensors have been investigated. **Table 1** shows that energy values of DO3AAPB and DO3A-ABB derivatives in gas and water phases.

The calculated energy results show that the o-boronic acid structure, DO3A-APB-o

Compound	Gaz phase	Stability	Water phase	Stability
DO3A-APB-o	-1,150,397.88	-	-1,150,446.42	-
DO3A-APB-m	-1,150,394.81	3.07	-1,150,444.17	2.25
DO3A-APB-p	-1,150,395.47	2.41	-1,150,444.03	2.39
DO3A-ABB-a	-1,242,992.44	-	-1,243,051.98	-
DO3A-ABB- β	-1,242,990.76	1.68	-1,243,049.84	2.14
DO3A-ABB- γ	-1,242,989.14	3.30	-1,243,050.51	1.47

Table 1. Total energies of DO3A-APB and DO3A-ABB structures (kcal/mol).

is the more stable than the other positions in the gas phase, about of 2 - 3 kcal/mol energy values. In the water phase, the same trend was found about 2 kcal/mol. When the energy of structures in water and gas phases is compared, it has been found that the presence of water in the environment brings about the solvation stability.

Table 1 shows that DO3A-ABB-*a* structure is more stable than the other positions in the gas and water phases, about of 1.5 - 3 kcal/mol energy values.

As a result, DO3A-APB-o and DO3A-ABB- α have been found the most stable within calculated structures and so by choosing these compounds, further calculations have been continued. Optimized DO3A-APB-o and DO3A-ABB- α structures have been presented in Table S2 and Table S3.

3.1.2. Structural Properties and Molecular Orbitals

Ortho structures with and without uranyl ion have been examined in terms of their structural, electronic and spectroscopic properties in acidic, basic and neutral media. While the acidic medium was formed by protonation of the nitrogen (N6), the basic medium was formed by the removal of the carboxylic proton located on DO3A. The numbered structures of some selected atoms of all calculated of DO3A-based sensors with/without uranyl ion are presented, acidic, neutral and basic media, in **Figure 2** and **Table 2**.

C-C bond lengths of the target compounds are in the range of 1.530 - 1.534 Å. This bond length with uranyl ion is changed from 1.564 to 1.576 Å. For compound without uranyl ion, the bond length between nitrogen and carbon in that fragment vary from 1.455 to 1.476 Å. For a compound with uranyl ion it increases to 1.464 - 1.528 Å.

The bond length between uranyl and nitrogen are between 2.246 and 1.2684 Å. For uranyl-free structures, the bond length of boron and hydroxide is between 1.363 and 1.371 Å, while bond length with uranium slightly increased to range of 1.377 and 1.399 Å, within indicates three media. Diameters of related structures in the water medium have been determined theoretically and given in Table S4. DO3A-APB-oand DO3A-ABB- α structures have been found to be about 11 Å in three mediums. The diameter of the structures with uranyl ion is wider than the others, 1 Å.

When the charges of the DO3A-APB-o structures in Table 3 are examined,

Compound	DO3A-APB-o (Neutral)	DO3A-ABB-o (Acidic)	DO3A-APB-o (Basic)	DO3A-UO ₂ (VI) APB-o (Neutral)	DO3A-UO ₂ (VI) APB-o (Acidic)	DO3A-UO ₂ (VI) APB-o (Basic)
d (N1-C5)	1.446	1.441	1.446	1.476	1.469	1.370
d (N1-C10)	1.463	1.464	1.463	1.506	1.521	1.511
d(C10-C11)	1.534	1.532	1.535	1.564	1.571	1.577
d (N2-C11)	1.475	1.474	1.468	1.522	1.524	1.527
d (N2-C12)	1.455	1.457	1.456	1.477	1.479	1.482
d (N6-C14)	1.353	1.517	1.353	1.355	1.506	1.357
d (C5-C14)	1.527	1.517	1.528	1.535	1.505	1.533
d (N6-C7)	1.411	1.471	1.409	1.414	1.488	1.413
d (N8-C7)	-	-	-	-	-	-
d (N9-C7)	-	-	-	-	-	-
d (O-C13)	1.218	1.217	1.258	1.226	1.226	1.271
d (OH-C13)	1.330	1.331	-	1.363	1.363	-
d (B-OH)	1.370	1.364	1.370	1.377	1.362	1.377
d (N1-U)	-	-	-	2.544	2.570	2.543
d (N2-U)	-	-	-	2.685	2.654	2.550
d (N3-U)	-	-	-	2.549	2.507	2.484
d (N4-U)	-	-	-	2.544	2.507	2.492

Table 2. Optimized bond lengths (Å) of DO3A-APB-o and DO3A-ABB- α structures at M062X/6 – 31 + G (d) level of theory.

Compound	DO3A-ABB- <i>a</i> (Neutral)	DO3A-ABB- <i>a</i> (Acidic)	DO3A-ABB- <i>a</i> (Basic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Neutral)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Acidic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Basic)
d (N1-C5)	1.450	1.445	1.453	1.477	1.469	1.474
d (N1-C10)	1.463	1.467	1.465	1.515	1.522	1.514
d(C10-C11)	1.534	1.530	1.533	1.569	1.568	1.576
d (N2-C11)	1.476	1.473	1.469	1.521	1.514	1.528
d (N2-C12)	1.456	1.457	1.456	1.469	1.464	1.483
d (N6-C14)	1.364	1.554	1.365	1.373	1.577	1.375
d (C5-C14)	1.524	1.507	1.525	1.532	1.505	1.531
d (N6-C7)	1.385	1.437	1.388	1.384	1.445	1.383
d (N8-C7)	1.364	1.352	1.362	1.325	1.310	1.382
d (N9-C7)	1.310	1.298	1.310	1.382	1.367	1.325
d (O-C13)	1.218	1.214	1.267	1.226	1.225	1.271
d OH-C13)	1.330	1.347	-	1.365	1.365	-
d (B-OH)	1.368	1.371	1.371	1.390	1.390	1.378
d (N1-U)	-	-	-	2.534	2.591	2.555
d (N2-U)	-	-	-	2.677	2.658	2.555
d (N3-U)	-	-	-	2.532	2.506	2.476
d (N4-U)	-	-	-	2.604	2.603	2.488

Compound	DO3A-APB-o (Neutral)	DO3A-APB-o (Acidic)	DO3A-APB-o (Basic)	DO3A-UO ₂ (VI) APB-o (Neutral)	DO3A-UO ₂ (VI) APB-o (Acidic)	DO3A-UO ₂ (VI) APB-o (Basic)
N1	-0.41	-0.35	-0.45	-0.52	-0.53	-0.52
N2	-0.62	-0.60	-0.40	-0.50	-0.51	-0.50
N3	-0.31	-0.24	-0.39	-0.53	-0.53	-0.50
N4	-0.12	-0.05	-0.10	-0.52	-0.52	-0.50
C5	-0.12	-0.42	-0.33	-0.30	-0.29	-0.30
N6	-0.45	-1.13	-0.47	-0.75	-0.83	-0.75
C7	0.02	0.44	0.06	0.22	0.12	0.23
N8	-	-	-	-	-	-
N9	-	-	-	-	-	-
C10	0.12	-0.19	-0.03	-0.18	-0.19	-0.18
C11	-0.61	-0.24	-0.54	-0.17	-0.17	-0.19
C12	-0.38	-0.31	-0.54	-0.30	-0.30	-0.30
C13	0.51	0.47	0.63	0.63	0.63	0.55
C14	0.34	0.56	0.55	0.62	0.61	0.62
В	1.08	0.95	1.09	0.54	0.58	0.54
U	-	-	-	1.76	1.76	1.62

Table 3. Optimized Mulliken charges (Debye) of DO3A-APB-o and DO3A-ABB- α structures.

DO3A-UO₂ DO3A-UO₂ DO3A-UO₂

Compound	DO3A-ABB- <i>a</i> (Neutral)	DO3A-ABB- <i>a</i> (Acidic)	DO3A-ABB- <i>a</i> (Basic)	(VI) ABB- <i>a</i> (Neutral)	(VI) ABB- <i>a</i> (Acidic)	(VI) ABB- <i>a</i> (Basic)
N1	-0.44	-0.07	-0.49	-0.52	-0.53	-0.52
N2	-0.66	-0.48	-0.38	-0.50	-0.51	-0.50
N3	-0.32	-0.02	-0.38	-0.53	-0.53	-0.50
N4	-0.07	-0.21	0.05	-0.52	-0.51	-0.50
C5	-0.06	0.57	0.05	-0.30	-0.28	-0.30
N6	-0.47	-0.27	-0.47	-0.75	-0.82	-0.73
C7	1.05	0.78	0.06	0.20	0.12	0.70
N8	-0.66	-0.63	-0.66	-0.74	-0.68	-0.76
N9	-0.45	-0.30	-0.45	-0.53	-0.47	-0.53
C10	-0.25	0.41	-0.27	-0.20	-0.20	-0.18
C11	-0.19	0.12	-0.20	-0.20	-0.18	-0.19
C12	-0.36	0.18	-0.53	-0.29	-0.82	-0.30
C13	0.55	0.54	0.69	0.63	0.64	0.55
C14	0.19	0.32	0.06	0.62	0.62	0.62
В	1.04	1.07	1.10	0.50	0.50	0.50
U	-	-	-	1.81	1.81	1.62

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Figure 2. Schematic structures of DO3A-based sensors with/without uranyl ion.

the charges of nitrogen atoms in theDO3A ring reduce in the acidic medium and are in the range of -0.60 to -0.05, when the nitrogen charges in the other medium are compared. For all three medium, these charges are close to reaching -0.50 after the bonded with the uranyl ion. The charge of amide nitrogen is about -0.40 in the neutral and basic medium while it increases to -1.13 in the acidic medium. In the DO3A-UO₂ (VI)-APB-0 complexes, it increases to -0.75 in the neutral and basic medium while it decreases to -0.85 in the acidic medium. The charge of C5 carbon atom linking DO3A to amide falls from -0.40 in the acidic medium to -0.29 in the UO₂ complexes. The charge of the boron atom in the DO3A-APB-0 structures decreases from -1.00 to -0.55 in DO3A-UO₂ (VI)-APB-0 structures. The uranium (VI) ion charge is in the range of 1.75 to 1.61. Similar tends and values have been found forDO3A-ABB- α and DO3A-UO₂ (VI)-ABB- α structures in all three mediums.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters as a measure of relative stability and reactivity. The energies of frontier orbitals, total energies (E_T), chemical hardness (η), electronic chemical potentials (μ), chemical softness (S) and electrophilicity (ω) values are listed in **Table 4**.

When the total energy values of the DO3A-APB-o are examined, it can be seen that the energy stability decreases in these order DO3A-APB-o acidic > DO3A-APB-o neutral > DO3A-APB-o basic media. The same trend has been for the DO3A-ABB-*a*, DO3A-UO₂ (VI)-ABB-*a* and DO3A-UO₂ (VI)-APB-o series structures. The most stable structures are in acidic media.

When the total energy values of the DO3A-APB-o are examined, it can be seen that the energy stability decreases in these order DO3A-APB-o acidic > DO3A-APB-o neutral > DO3A-APB-o basic media. The same trend has been seen for the DO3A-ABB-*a*, DO3A-UO₂ (VI)-ABB-*a* and DO3A-UO₂ (VI)-APB-o series structures. The most stable structures have been found in the acidic media.

A large HOMO-LUMO energy gap has been associated with high stability of structures. For DO3A-APB-0 and DO3A-ABB- α series, the HOMO-LUMO energy gap of all calculated structures decrease to about 2 eV by binding uranyl ion and their lower one is counter to neutral medium. On the other hands, their uranyl structures have a largest band gap in acidic medium. Among the calcu-

Compound	E_{T}	E _{HOMO}	E _{lumo}	$\mathbf{E}_{\mathrm{GAP}}$	Ι	А	χ	η	S	μ	ω
DO3A-APB-o (N)	-1,150,446.42	-7.31	-0.19	7.12	7.31	0.19	3.75	3.56	0.28	-3.75	1.97
DO3A-APB-o (A)	-1,150,690.41	-7.47	-0.83	6.64	7.47	0.83	4.15	3.32	0.30	-4.15	2.60
DO3A-APB-o (B)	-1,149,613.33	-6.97	-1.24	5.73	6.97	1.24	4.10	2.86	0.35	-4.10	2.94
DO3A-UO ₂ (VI)-APB-o (N)	-17,342,528.18	-7.51	-3.11	4.40	7.51	3.11	5.31	2.20	0.45	-5.31	6.41
DO3A-UO ₂ (VI)-APB-o (A)	-17,342,776.59	-8.17	-3.22	4.95	8.17	3.22	5.70	2.48	0.40	-5.70	6.55
DO3A-UO ₂ (VI)-APB-o (B)	-17,341,682.81	-7.34	-2.64	4.70	7.34	2.64	4.99	2.35	0.43	-4.99	5.30
DO3A-ABB-a (N)	-1,243,051.98	-7.44	-0.36	7.08	7.44	0.36	3.90	3.54	0.28	-3.90	2.15
DO3A-ABB-a (A)	-1,243,294.62	-7.52	-0.69	6.83	7.52	0.69	4.10	3.41	0.29	-4.10	2.47
DO3A-ABB- $a(B)$	-1,242,223.34	-7.08	-0.25	6.83	7.08	0.25	3.67	3.42	0.29	-3.67	1.97
DO3A-UO ₂ (VI)-ABB-a (N)	-17,435,128.24	-7.26	-3.19	4.07	7.26	3.19	5.23	2.04	0.49	-5.23	6.71
DO3A-UO ₂ (VI)-ABB- a (A)	-17,435,369.38	-7.95	-3.31	4.64	7.95	3.31	5.63	2.32	0.43	-5.63	6.83
DO3A-UO ₂ (VI)-ABB- α (B)	-17,434,284.04	-7.21	-2.66	4.55	7.21	2.66	4.93	2.27	0.44	-4.93	5.35

Table 4. Values of the global reactivity descriptors of the systems (eV).

lated chemical hardness (η), DO3A-APB-o in basic media, DO3A-ABB-a in acidic media and both DO3A-UO₂ (VI)-APB-o and DO3A-UO₂ (VI)-ABB-a structures in neutral media have lower values than the rest of the their series and these result indicating that they are kinetically more stable and less reactive than the other their structures.

3.2. Absorption Spectra Analysis

The absorption spectrum of structures has been calculated using Time-Dependent DFT calculations same levels of theory in water phase three indicated media. The calculated absorption bands are summarized in **Figure 3**.

For DO3A-APB-0 compound in the indicated mediums absorption bands outside the visible region and are range of 205 nm - 230 nm. It can be seen from the **Figure 3**, when DO3A-APB-0 bonded with uranyl ion, DO3A-UO₂ (VI)-APB-0, oscillator strength decreases and shift to long wavelength. At the beginning, a single peak has seen and two flattened peaks have formed at with the addition of uranyl ion. These peaks are in the range of 384 - 392 nm and 645 - 695 nm. For DO3A-ABB-*a*, calculated absorption bands are range in 200 - 264 nm within three indicated media. DO3A-UO₂ (VI)-ABB-*a* gives the same trend and these peaks are in the range of 374 - 393 nm and 645 - 688 nm. Consequently, when DO3A-APB-0 structure bonds with uranyl ion, the maximum shift is in the neutral medium, whereas maximum shifts of DO3A-ABB-*a* with uranyl ion are in the basic medium.

3.3. Infrared and NMR Spectra Analysis

In this section, the changes in ¹³C-NMR and ¹H-NMR chemical shift values of the all the calculated complexes formed by the binding of uranyl ions have been summarized in Table 5 and Table 6.

Compound	DO3A-APB-o (Neutral)	DO3A-APB-o (Acidic)	DO3A-APB-o (Basic)	DO3A-UO ₂ (VI) APB-o (Neutral)	DO3A-UO ₂ (VI) APB-o (Acidic)	DO3A-UO ₂ (VI) APB-o (Basic)
C5	62.9	63.8	63.6	59.8	64.6	60.7
C7	158.6	145.2	158.3	158.7	152.3	159.7
C10	57.4	58.0	56.6	59.1	56.2	53.8
C11	46.7	48.7	45.9	64.6	65.1	59.6
C12	61.8	62.9	66.2	71.4	70.5	70.2
C13	191.3	189.7	182.6	189.3	189.2	191.4
C14	18.3	196.5	187.9	185.3	195.7	185.7

Table 5. ¹³C-NMR chemical shifts (ppm) of DO3A-APB-0 and DO3A-ABB-a and their structures with uranyl ion.

Compound	DO3A-ABB- <i>a</i> (Neutral)	DO3A-ABB- <i>a</i> (Acidic)	DO3A-ABB- <i>a</i> (Basic)	DO3A-UO ₂ (VI) ABB- α (Neutral)	DO3A-UO ₂ (VI) ABB- α (Acidic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Basic)
C5	64.5	63.9	64.3	61.8	64.5	61.0
C7	149.2	142.4	154.5	61.8	144.6	155.3
C10	52.0	53.7	49.0	54.1	54.4	54.6
C11	63.7	62.6	61.6	54.7	56.8	60.6
C12	61.1	62.3	65.9	61.9	62.8	70.8
C13	190.1	189.9	192.1	188.0	187.7	191.2
C14	185.0	184.0	186.6	188.0	184.3	184.0

Table 6. ¹H-NMR chemical shifts (ppm) of DO3A-APB-0 and DO3A-ABB-a and their structures with uranyl ion.

Compound	DO3A-APB-o (Neutral)	DO3A-APB-o (Acidic)	DO3A-APB-o (Basic)	DO3A-UO ₂ (VI) APB-o (Neutral)	DO3A-UO ₂ (VI) APB-o (Acidic)	DO3A-UO ₂ (VI) APB-o (Basic)
BO-H	4.9	5.4	4.8	6.0	6.7	5.7
N6-H	11.0	6.4	11.2	12.4	8.1	11.8
N8-H	-	-	-	-	-	-
C14-H	7.0	7.5	-	8.3	8.3	-
С10-Н	2.3	2.6	2.2	3.5	3.3	3.8
С11-Н	3.1	2.9	3.3	3.9	4.1	3.9
С15-Н	9.3	7.8	9.2	8.3	8.4	9.5

Compound	DO3A-ABB- <i>a</i> (Neutral)	DO3A-ABB- <i>a</i> (Acidic)	DO3A-ABB- <i>a</i> (Basic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Neutral)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Acidic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Basic)
BO-H	5.1	6.1	5.1	5.9	5.9	5.8
N6-H	9.4	11.1	9.5	8.4	8.3	8.0
N8-H	9.9	10.6	10.2	10.0	11.1	9.8
C14-H	9.4	11.5	-	8.3	8.3	-
С10-Н	3.6	2.4	2.2	3.7	3.3	3.8
С11-Н	3.0	2.5	3.3	3.3	3.9	2.7
C15-H	8.5	9.0	8.6	8.1	8.4	8.0



Figure 3. Computed UV-Vis absorption bands. The λ_{max} values of structures also have been indicated on the graphs.

Firstly, the chemical shift of TMS (tetramethylsilane) has been calculated with the same level of theory in order to carry out the NMR calculations. Subsequently, the NMR spectrum of the structures has been calculated and the difference between the two values gives the final result. In the calculated ¹³C-NMR spectra, a chemical shift in the C5 atom ca. 0.5 - 3 ppm is observed in the high field while C11 carbon (ca. 14 - 18 ppm) has low field for DO3A-APB-0 structures. The same trend exists for C12 (ca. 10 ppm). Similarly, C5 and C11 carbon atoms belong to DO3A-ABB- α structures have been found in the high field ca. 1 ppm and ca. 5 - 9 ppm, respectively. There is no significant change in other carbon atoms, but there is a low shift in C10 atom, ca. 2 - 5 ppm. In the calculated ¹H-NMR spectra, the corresponding proton peaks connected to C10, C11 (ca. 1 ppm) and N6 (ca. 2 ppm) of DO3A-APB-0 structures have shifted to the low field. In the DO3A-ABB- α structures, there are only high field shift in N6-H and C10-H peaks, ca. 1 - 2 ppm, there is no big differences for the other peaks.

The calculated harmonic vibrations and most characteristic peaks of the compounds are also included in this part and given in **Table 7**. The main effect on DO3A-UO₂ (VI)-APB-0 on calculated IR-spectrum is seen at the BO-H and N6-H stretching vibrations for all mediums. The bond stretching vibrations of BO-H and N6-H occur in the region of 3565 cm⁻¹ and 3234 cm⁻¹ in the neutral

Compound	DO3A-APB-o (Neutral)	DO3A-APB-o (Acidic)	DO3A-APB-o (Basic)	DO3A-UO ₂ (VI) APB-o (Neutral)	DO3A-UO ₂ (VI) APB-o (Acidic)	DO3A-UO ₂ (VI) APB-o (Basic)
BO-H	3787	-3777	3789	3565	3545	3535
C13-OH	3436	3475	-	3448	3456	-
Aromatic C-H	3245	3247	3241	3309	3274	3263
N6-H	3473	3396	3469	3234	3282	3248
C10-H	3129	3175	3163	3200	3202	3100
C13-O	1795	1800	1583	1755	1750	1591
C14-O	1711	1920	1709	1682	1800	1684
Aromatic C-C	1687	1660	1687	1641	1701	1643
C14-N6	1584	1550	1521	1607	1659	1606
U-O	-	-	-	864	861	825
U-N	-	-	-	742	740	756
B-C	1379	1381	1367	1372	1383	1367

Table 7. Selected and calculated vibrational frequency (cm⁻¹).

Compound	DO3A-ABB- <i>a</i> (Neutral)	DO3A-ABB- <i>a</i> (Acidic)	DO3A-ABB- <i>a</i> (Basic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Neutral)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Acidic)	DO3A-UO ₂ (VI) ABB- <i>a</i> (Basic)
BO-H	3799	3712	3782	3541	3533	3539
C13-OH	3476	3450	-	3441	3452	-
Aromatic C-H	3236	3235	3232	3267	3265	3252
N6-H	3491	3366	3489	3495	3282	3501
С10-Н	3160	3167	3194	3188	3184	3151
C13-O	1786	1799	1587	1742	1746	1587
C14-O	1755	1959	1756	1712	1871	1751
Aromatic C-C	1686	1697	1690	1689	1679	1688
C14-N6	1589	1591	1584	1590	1506	1572
U-O	-	-	-	867	880	824
U-N	-	-	-	724	740	767
B-C	1405	1412	1382	1382	1379	1385
N8-H	3613	3583	3533	3533	3476	3530

medium. The differences in between DO3A-APB-o and DO3A-UO₂ (VI)-APB-o of BO-H stretching modes are among 222 and 254 cm⁻¹ and the N6-H one is in between 114 - 239 cm⁻¹ in neutral and acidic medium, appears in a lower frequency. In DO3A-UO₂ (VI)-ABB- α structures, the bond stretching vibrations of BO-H and N6-H occur in the region of 3541 cm⁻¹ and 3495 cm⁻¹ in the neutral

medium. When the stretching mode of BO-H passing from DO3A-APB-o to DO3A-UO₂ (VI)-ABB-*a* structures have been shifted to lower frequency (180 - 258 cm⁻¹). There is no significant difference in the basic medium at N8-H stretching vibration frequency, whereas a shift has been found at about 80 - 100 cm⁻¹ in the neutral and acidic medium.

4. Conclusion

Our theoretical work represents structural and spectral properties of newly designed DO3A-based structures sensitive to UO_2^{2+} . The structures have been optimized in the gas phase and water phase at three levels of theory (M062X, B3LYP and B3PW9/6 - 31 g + (d)) for comparison with experimental value, after that M062X/6 - 31 g + (d) method has been chosen for all remaining calculations. The calculations have been shown that ortho position of boronic acid is the most stable within all calculated structures. By examining the diameter dimension of the structural features, it has been seen that the linking of the uranium causes the increase of the total diameter up to about 1 Å. The relative stability of the studied structures showed that all series are more stable in the acidic medium. The calculated HOMO-LUMO gap results manifest that linking of UO_2^{2+} ion to designed structures has caused the decrease. The theoretical electronic spectrum of DO3A-UO₂ (VI)-APB-o gives bands at 392 and 687 nm in neutral medium. DO3A-UO₂ (VI)-ABB-a structure has two main bands at 393 and 650 nm. Both structures show red shift and are located within the visible region by binding UO_2^{2+} ion. The notable shifts in NMR spectrums have been found on α -carbon of carbonyl group, ring carbons and amide protons. In IR spectrum, the prominent peaks belong to BO-H and N6-H stretching vibrations of calculated structures.

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