Supplementary Materials

Bioactive Coating on Titanium Dental Implants for Improved Anticorrosion Protection: A Combined Experimental and Theoretical Study

Jozefina Katić [1], Ankica Šarić [2,*], Ines Despotović [3], Nives Matijaković [4], Marin Petković [5] and Željka Petrović [4,*]

[1] Department of Electrochemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia; jkatic@fkit.hr
[2] Division of Materials Physics, Centre of Excellence for Advanced Materials and Sensing Device, Ruđer Bošković Institute, Bijenička cesta 54, 10002 Zagreb, Croatia
[3] Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10002 Zagreb, Croatia; Ines.Despotovic@irb.hr
[4] Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10002 Zagreb, Croatia; Nives.Matijakovic@irb.hr
[5] Adentro dental studio, Petrova ul. 67, 10000 Zagreb, Croatia; info@adentro.hr
* Correspondence: Ankica.Saric@irb.hr (A.Š.); Zeljka.Petrovic@irb.hr (Ž.P.)

Computational modeling. All calculations were performed by means of quantum chemical calculations at the density functional theory (DFT) level using the Gaussian 09 program (revision D1) [1]. The $(TiO_2)_n$ clusters were employed, as proposed by Allard et al. [2] and Qu and Kroes [3], with n = 10 using the polarizable solvatation model.

The M06 functional designed by the Truhlar's group, which provides very accurate thermodynamic parameters, being particularly successful in nonbonding interactions treatment, was selected [4–6]. The 6−31+G(d,p) + LANL2DZ mixed basis set was utilized. The Pople's 6−31+G(d,p) double−ξ basis set was chosen for O, H, C atoms and the LANL2DZ basis (LANL2 pseudopotential for inner electrons and its associated double−ξ basis set (DZ)) was used for the transition−metal (Ti) atoms [7]. This gave rise to the M06/6−311++G(2df,2pd) + LANL2DZ// M06/6−31+G(d,p) + LANL2DZ model utilized for geometry optimization which has been frequently used for studies of transition−metal containing systems. The geometric structures of the molecules were optimized by minimizing energies with respect to all geometrical parameters without imposing any molecular symmetry constraints and using a tight convergence condition. The Berny algorithm using redundant internal coordinates was employed. Frequency calculations were made under the harmonic approximation on all the optimized structures at the same level of theory with no scaling in order to confirm that the structures correspond to the true minima confirm the true minima of the structures, meaning that no imaginary frequencies were present, as well as to extract thermal Gibbs free energy corrections. The final single point energies were obtained using a highly flexible 6−311++G(2df,2pd) basis set for the O, H, C atoms, while the same LANL2DZ ECP type basis set for titanium atoms was employed.

The self−consistent field (SCF) calculations were conducted under a tight condition imposing the threshold value of 10–8 hartree to total energy difference during the iteration process. The integration grid was set to FineGrid having 75 radial shells and 302 angular points per shell. The 2−electron integral accuracy esd set to 10–13. The FoFCou algorithm with NoSymm option was utilized. Geometry optimizations, frequency calculations, and single point energy evaluations were performed by taking solvent effects into account. To evaluate the bulk solvent effects (1,2−ethandiol as a glycerol aproximation,

ε = 40.245), the implicit SMD polarizable continuum solvation model [8] was employed. The conformational space was manually sampled for the (TiO2)10—cholecalciferol, taking into account various donor and acceptor sites of the (TiO2)10 cluster and cholecalciferol molecule. Only the most thermodynamically stable (TiO2)10—cholecalciferol structure is reported here. The starting structure of the cholecalciferol was taken from the literature [9].

The interaction Gibbs free energies, ΔG^*_{INT}, were computed as the difference between the total free energy (G^*_{AB}) of the $(TiO_2)_{10}$—cholecalciferol structure and the sum of the total free energies ($G^*_A + G^*_B$) of the associating units A and B using the supramolecular approach:

$$\Delta G^*_{INT,AB} = G^*_{AB} - G^*_A - G^*_B \quad (1)$$

The species total free energy in the liquid was calculated using the expression:

$$G^*_X = E^{Tot}_{soln} + \Delta G^*_{VRT,soln} \quad (2)$$

where E^{Tot}_{soln} corresponds to the basic energy of a density functional theory calculation using the SMD model, while $\Delta G^*_{VRT,soln}$ encompasses vibrational, rotational, and translational contribution to the solution free energy, being computed by applying the ideal gas partition functions to the frequencies calculated in the dielectric medium and the 1M standard state. A more negative value of the binding energy implied the more stable formed species. No BSSE correction of binding energies was applied.

The topological analysis of the charge density distribution using the Bader's quantum theory of atoms in molecules (QTAIM) [10] was performed by employing AIMALL software package [11] using the SMD/M06/6−311++G(2df,2pd) + LANL2DZ// M06/6−31+G(d,p) + LANL2DZ wave function obtained from optimization. Within the QTAIM analysis the electron density was analysed for two major characteristics: (a) The existence of critical points (CPs), where electron density exhibits maximum, minimum, or a saddle point in space, and (b) for the bond paths [12], the maximum electron density line connecting two interacting atoms in the energetic minimum structure (the two atoms are bonded). The point of the electron density minimum value along that line called the bond critical point (BCP) and values of topological parameters, like electron density $\rho(r_c)$, Laplacian $\nabla^2\rho(r_c)$, electronic kinetic energy $G(r_c)$, electronic potential energy density $V(r_c)$, total energy density $H(r_c)$ at that point explain interatomic interaction features. $\nabla^2\rho(r_c) < 0$ indicates locally concentrated charge density, while locally depleted charge density is indicated by $\nabla^2\rho(r_c) > 0$. The chemical bond nature can be described qualitatively concerning signs and values of the electron density Laplacian $\nabla^2\rho(r_c)$ and the electron energy density $H(r_c)$ at the cbond critical point, according to the following criteria.

The interactions characterized by $\nabla^2\rho(r_c) < 0$ and $H(r_c) < 0$ (shared interaction) are characteristic for weakly polar and nonpolar covalent bonds. On the other hand, $\nabla^2\rho(r_c) > 0$ and $H(r_c) > 0$ (closed shell interactions) point to ionic bonds, weak hydrogen bonds, and van der Waals interactions. The intermediate interactions likely include strong hydrogen bonds, and most of the coordinate bonds are characterized by $\nabla^2\rho(r_c) > 0$ and $H(r_c) < 0$ [13,14]. A very high negative value of the $\nabla^2\rho(r_c)$ is an indication of a strong covalent bond, while a high positive value corresponds to a strong noncovalent bond. The energies of the coordinate bonds (Ti–O) and of other intra− and intermolecular hydrogen bonds are calculated by Espinosa's equation [15–20]:

$$E = 0.5\, V(r_c) \quad (3)$$

where E is the bond energy (a.u.), and $V(r_c)$ is potential energy density (a.u.) at the corresponding critical point [21].

References

1. Gaussian 09, Revision D.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J.A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.;. Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. Gaussian, Inc., Wallingford CT, 2013.
2. Allard, M.M.; Merlos, S.N.; Springer, B.N.; Cooper, J.; Zhang, G.; Boskovic, D.S.; Kwon, S.R.; Nick, K.E.; Perry, C.C. Role of TiO_2 Anatase Surface Morphology on Organophosphorus Interfacial Chemistry. *J. Phys. Chem. C* **2018**, *122*, 29237–29248, doi: 10.1021/acs.jpcc.8b08641.
3. Qu, Z.; Kroes, G.−J. Theoretical Study of Stable, Defect−Free $(TiO_2)_n$ Nanoparticles with n = 10−16. *J. Phys. Chem. C* **2007**, *111*, 16808–16817, doi: 10.1021/jp073988t.
4. Zhao, Y.; Thrular, D.G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06−class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 2151241, doi: 10.1007/s00214−007−0310−x.
5. Zhao, Y.; Truhlar, D.G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167, doi:10.1021/ar700111a.
6. Zhao, Y.; Truhlar, D.G. Density Functional Theory for Reaction Energies: Test of Meta and Hybrid Meta Functionals, Range−Separated Functionals, and Other High−Performance Functionals. *J. Chem. Theory Comput.* **2011**, *7*, 669–676, doi:10.1021/ct1006604.
7. Wadt, W.R.; Hay, P.J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298, doi:10.1063/1.448800.
8. Marenich, A.V.; Cramer, C.J.; Truhlar, D.G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396, doi.org/10.1021/jp810292n.
9. Avilable Online: http://webbook.nist.gov/chemistry, (accessed on 15th March 2019)
10. Bader, R.F.W. *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, New York, USA, 1994.
11. Keith, T.A. *AIMAll (Version 17.01.25)*, TK Gristmill Software, Overland Park KS, USA, 2017 (aim.tkgristmill.com)
12. Bader, R.F.W. A Bond Path: A Universal Indicator of Bonded Interactions. *J. Phys. Chem. A.* **1998**, *102*, 7314–7323, doi:10.1021/jp981794v.
13. Bader, R.F.W.; Essén, H. The characterization of atomic interactions. *J. Chem. Phys.* **1984**, *80*, 1943–1960, doi:10.1063/1.446956.
14. Cremer, D.; Kraka, E. A Description of the Chemical Bond in Terms of Local Properties of Electron Density and Energy. *Croat. Chem. Acta* **1984**, *57*, 1259–1281.
15. Espinosa, E.; Alkorta, I.; Rozas, I.; Elguero, J.; Molins, E. About the evaluation of the local kinetic, potential and total energy densities in closed−shell interactions. *Chem. Phys. Lett.* **2001**, *336*, 457–461, doi:10.1016/S0009−2614(01)00178−6.
16. Borissova, A.O.; Antipin, M.Y.; Karapetyan, H.A.; Petrosyan, A.M.; Lyssenko, K.A. Cooperativity effects of H−bonding and charge transfer in an L−nitroarginine crystal with Z′ > 1. *Mendeleev Commun.* **2010**, *20*, 260–262, doi:10.1016/j.mencom.2010.09.006.
17. Baryshnikov, G.V.; Minaev, B.F.; Minaeva, V.A.; Nenajdenko, V.G. Single crystal architecture and absorption spectra of octathio[8]circulene and *sym*−tetraselenatetrathio[8]circulene: QTAIM and TD−DFT approach. *J. Mol. Model.* **2013**, *19*, 4511–4519, doi:10.1007/s00894−013−1962−1.

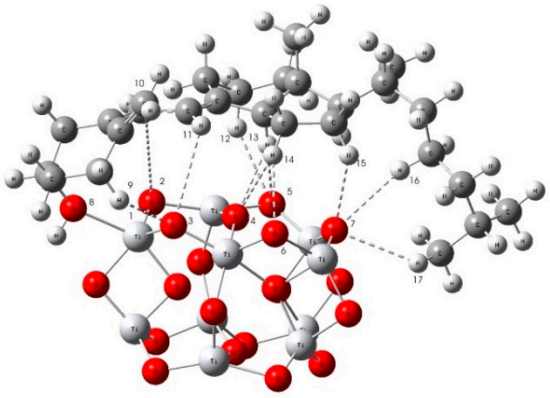
18. Baryshnikov, G.V.; Minaev, B.F.; Korop, A.A.; Minaeva, V.A.; Gusev, A.N. Structure of zinc complexes with 3−(pyridin−2−yl)−5−(arylideneiminophenyl)−1HH−1,2,4−triazoles in different tautomeric forms: DFT and QTAIM study. *Russ. J. Inorg. Chem.* **2013**, *58*, 928–934, doi:10.1134/S0036023613080032.
19. Shahangi, F.; Chermahini, A.N.; Farrokhpour, H.; Teimouri, A. Selective complexation of alkaline earth metal ions with nanotubular cyclopeptides: DFT theoretical study. *RSC Adv.* **2014**, *5*, 2305–2317, doi:10.1039/C4RA08302D.
20. Puntus, L.N.; Lyssenko, K.A.; Antipin, M.Y.; Bünzli, J.C.G. Role of Inner− and Outer−Sphere Bonding in the Sensitization of EuIII−Luminescence Deciphered by Combined Analysis of Experimental Electron Density Distribution Function and Photophysical Data. *Inorg. Chem.* **2008**, *47*, 11095–11107, doi:10.1021/ic801402u.
21. Espinosa, E.; Molins, E.; Lecomte, C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem. Phys. Lett.* **1998**, *285*, 170–173, doi:10.1016/S0009−2614(98)00036−0.

Table S1. Formation of the most stable $(TiO_2)_{10}$–cholecalciferol[(a)], $(TiO_2)_{10}$–cholecalciferol–glycerol[(b)] and $(TiO_2)_{10}$–glycerol species[(c)]. Standard state (1M) free energies of interaction $\Delta_r G^*_{INT}$ computed by using the SMD solvation model at the M06/6–311++G(2df,2pd) + LANL2DZ// M06/6–31+G(d,p) + LANL2DZ level of theory.

Species	**$\Delta_r G^*_{INT}$ / kcal mol^{-1}**
$(TiO_2)_{10}$–cholecalciferol	−6.64
$(TiO_2)_{10}$–cholecalciferol–glycerol	5.51
$(TiO_2)_{10}$–glycerol	−0.24

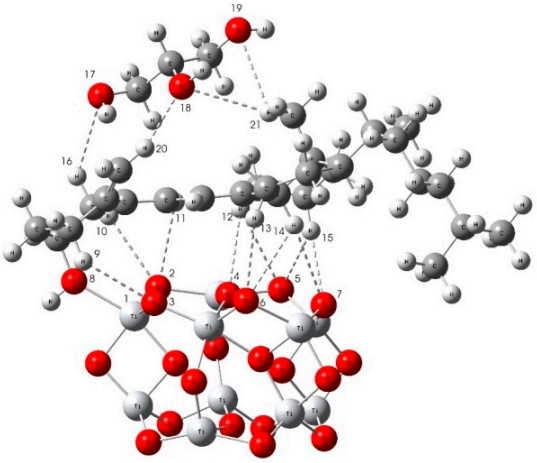
(a): According to the reaction: $(TiO_2)_{10}$ + cholecalciferol → $(TiO_2)_{10}$–cholecalciferol; (b): According to the reaction: $(TiO_2)_{10}$–cholecalciferol + glycerol → $(TiO_2)_{10}$–cholecalciferol–glycerol; (c): According to the reaction: $(TiO_2)_{10}$ + glycerol → $(TiO_2)_{10}$–glycerol.

Table S2. Bond lengths (d), energies (E) and QTAIM properties of the selected bonds in the most stable $(TiO_2)_{10}$–cholecalciferol, $(TiO_2)_{10}$–cholecalciferol–glycerol and $(TiO_2)_{10}$–glycerol structures.



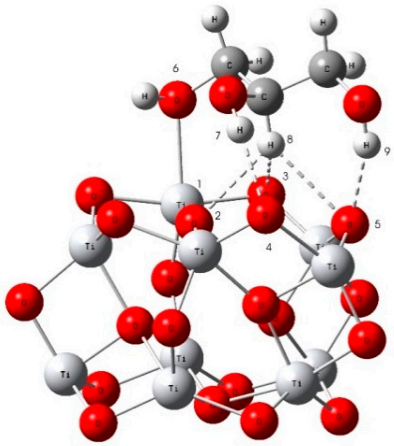
$(TiO_2)_{10}$–cholecalciferol

Bond	d / Å	$\rho(r_c)$ / $e\times a_0^{-3}$	$\nabla^2\rho(r_c)$ / $e\times a_0^{-5}$	$V(r_c)$ / a.u.	$G(r_c)$ / a.u.	$H(r_c)$ / a.u.[a]	E / kcal mol^{-1}[b]
Ti(1)—O(8)	2.252	4.208×10^{-2}	0.1930	−0.0468	0.0475	0.0007	−14.68
O(2)—C(10)	3.295	6.634×10^{-3}	0.0188	−0.0037	0.0042	0.0005	−1.15
O(3)–H(9)	2.358	1.318×10^{-2}	0.0399	−0.0096	0.0098	0.0002	−2.99
O(3)–H(11)	3.149	3.781×10^{-3}	0.0129	−0.0019	0.0026	0.0006	−0.61
O(4)–H(13)	2.459	1.204×10^{-2}	0.0372	−0.0082	0.0088	0.0006	−2.57
O(4)–H(14)	2.866	5.601×10^{-3}	0.0203	−0.0034	0.0042	0.0008	−1.07
O(5)–H(12)	2.554	9.540×10^{-3}	0.0290	−0.0062	0.0067	0.0005	−1.93
O(5)–H(13)	2.710	7.739×10^{-3}	0.0243	−0.0046	0.0053	0.0007	−1.43
O(6)–H(14)	2.488	1.055×10^{-2}	0.0318	−0.0071	0.0075	0.0004	−2.24
O(7)–H(15)	2.791	6.321×10^{-3}	0.0210	−0.0037	0.0045	0.0008	−1.15
O(7)–H(16)	2.813	5.611×10^{-3}	0.0189	−0.0032	0.0040	0.0008	−1.02
O(7)–H(17)	2.758	7.019×10^{-3}	0.0230	−0.0041	0.0049	0.0008	−1.30



$(TiO_2)_{10}$–cholecalciferol–glycerol

Bond	*d* / Å	$\rho(r_c)$ / $e\times a_0^{-3}$	$\nabla^2\rho(r_c)$ / $e\times a_0^{-5}$	$V(r_c)$ / a.u.	$G(r_c)$ / a.u.	$H(r_c)$ / a.u.	*E* / kcal mol^{-1}
Ti(1)—O(8)	2.194	4.968×10^{-2}	0.2348	−0.0570	0.0578	0.0008	−17.89
O(2)—H(10)	2.751	6.634×10^{-3}	0.0237	−0.0041	0.0050	0.0009	−1.29
O(2)—H(11)	2.864	6.780×10^{-3}	0.0219	−0.0038	0.0046	0.0008	−1.19
O(3)–H(9)	2.728	6.582×10^{-2}	0.0224	−0.0040	0.0048	0.0008	−1.27
O(4)–H(12)	3.000	5.133×10^{-3}	0.0174	−0.0028	0.0036	0.0008	−0.89
O(5)–H(12)	3.024	4.451×10^{-3}	0.0154	−0.0023	0.0031	0.0008	−0.72
O(5)–H(15)	2.753	7.520×10^{-3}	0.0243	−0.0044	0.0052	0.0008	−1.38
O(5)–H(12)	2.554	9.540×10^{-3}	0.0290	−0.0062	0.0067	0.0005	−1.93
O(6)–H(13)	2.823	5.424×10^{-3}	0.0190	−0.0031	0.0039	0.0008	−0.99
O(6)–H(14)	2.987	4.636×10^{-3}	0.0158	−0.0025	0.0032	0.0007	−0.79
O(7)–H(14)	2.989	4.301×10^{-3}	0.0141	−0.0021	0.0028	0.0007	−0.67
O(7)–H(15)	2.562	9.262×10^{-3}	0.0283	−0.0060	0.0065	0.0005	−1.89
H(16)–O(17)	2.831	5.379×10^{-3}	0.0194	−0.0032	0.0040	0.0008	−1.01
O(18)–H(20)	2.524	8.719×10^{-3}	0.0291	−0.0059	0.0066	0.0007	−1.86
O(18)–H(21)	2.963	4.776×10^{-3}	0.0159	−0.0026	0.0033	0.0007	−0.82
O(19)–H(21)	2.826	5.912×10^{-3}	0.0211	−0.0036	0.0044	0.0008	−1.14



$(TiO_2)_{10}$–glycerol

Bond	d /Å	$\rho(r_c)$ / $e\times a_0^{-3}$	$\circledcirc^2\rho(r_c)$ / $e\times a_0^{-5}$	$V(r_c)$ / a.u.	$G(r_c)$ / a.u.	$H(r_c)$ / a.u.	E / kcal mol^{-1}
Ti(1)–O(6)	2.316	3.992×10^{-2}	0.1584	−0.0429	0.0412	−0.0016	−13.45
O(2)–H(8)	2.373	1.325×10^{-2}	0.0437	−0.0095	0.0102	0.0007	−2.98
O(3)–H(8)	2.523	1.104×10^{-2}	0.0353	−0.0075	0.0081	0.0007	−2.34
O(4)–H(7)	2.041	2.109×10^{-2}	0.0564	−0.0159	0.0150	−0.0009	−4.99
O(5)–H(8)	2.445	1.190×10^{-2}	0.0377	−0.0085	0.0089	0.0004	−2.65
O(5)–H(9)	2.004	2.245×10^{-2}	0.0620	−0.0173	0.0164	−0.0009	−5.42

[a]$H(r_c) = V(r_c) + G(r_c)$; [b]$E = 0.5 \times V(r_c)$

Table S3. Total electronic energy, E^{Tot}_{soln}, obtained at the SMD/M06/6−311++G(2df,2pd) + LANL2DZ//SMD/M06/6−31+G(d,p) + LANL2DZ level of theory, thermal correction to the Gibbs free energy, $\Delta G^*_{VRT,soln}$, obtained at the SMD/M06/6−31+G(d,p) + LANL2DZ level of theory, and total free energy, G^*_X, ($G^*_X = E^{Tot}_{soln} + \Delta G^*_{VRT,soln}$) in 1,2−ethandiol media of the investigated species (all energies in hartree).

Species	E^{Tot}_{soln}	$\Delta G^*_{VRT,soln}$	G^*_X
$(TiO_2)_{10}$	−2087.37939	0.01770	−2087.36169
Cholecalciferol	−1130.06908	0.59431	−1129.47477
Glycerol	−344.73968	0.08645	−344.65324
$(TiO_2)_{10}$–cholecalciferol	−3217.49205	0.64499	−3216.84706
$(TiO_2)_{10}$–cholecalciferol–glycerol	−3562.24267	0.75117	−3561.49150
$(TiO_2)_{10}$–glycerol	−2432.14832	0.13301	−2432.05131

Table S4. Cartesian coordinates of the calculated systems

$(TiO_2)_{10}$

O	0.012556	0.037487	−0.031374
Ti	−0.762637	1.720520	−0.735570
O	−1.550151	3.055293	−1.970692
Ti	−2.173639	4.497664	−1.093928
O	−0.982278	4.561211	0.322316
Ti	−0.366138	6.278490	0.135196

O	−1.117115	6.847631	1.679921
Ti	−1.899621	5.510007	2.795092
O	−2.316802	3.769763	2.072609
Ti	−2.292265	1.789824	2.420889
O	−4.046551	2.095193	2.345897
Ti	−4.034566	4.013518	1.668519
O	−3.779276	5.627194	2.503345
Ti	0.021619	−0.001144	1.762820
O	−1.669245	0.007542	2.503132
O	1.597635	0.024270	2.805346
Ti	1.634535	1.834461	3.162622
O	1.080049	2.620589	4.722896
Ti	−0.479092	3.646902	4.460171
O	−1.703190	2.385319	4.200464
O	0.073602	1.861577	2.123353
Ti	0.847733	3.819316	1.153342
O	0.721485	2.710588	−0.338996
O	2.332328	3.118277	2.035497
O	1.320731	5.467090	0.536924
O	−0.050232	4.434930	2.860570
O	−1.499160	6.221991	−1.366952
O	−3.771756	4.307500	−0.120483
O	−1.669150	5.253167	4.547605
O	−2.062476	1.776451	0.404561

Cholecalciferol

C	7.002686	6.531137	2.191559
C	6.429546	5.294193	2.930340
C	5.021312	5.221203	2.285607
C	5.265578	5.429981	0.797893
C	6.472363	6.387255	0.745552
C	6.277309	5.436704	4.462424
C	4.893284	5.018753	4.977942
C	4.324969	3.806041	4.248015
C	4.248813	4.027782	2.753339
C	3.576880	3.213793	1.910743
C	2.826413	2.044232	2.318683
C	2.216046	1.143490	1.514122
C	1.414456	0.004473	2.090186
C	0.001880	−0.043865	1.516570
C	0.041315	−0.079407	−0.004739
C	0.838421	1.088000	−0.585419
C	2.209155	1.197669	0.034789
O	−0.788260	1.047832	1.998682
C	3.322714	1.290869	−0.704010
C	7.237430	4.037614	2.597018
C	8.515842	6.765749	2.246368
C	8.948380	7.967515	1.393042
C	8.398929	9.326827	1.810235
C	8.900186	10.433244	0.889687
C	8.471618	11.858755	1.249129
C	9.045814	12.316109	2.584510
C	9.053239	6.899529	3.668185

C	6.957807	12.029502	1.230660
H	6.509034	7.405173	2.654734
H	4.491476	6.120333	2.655157
H	6.202902	7.365562	0.327054
H	7.257038	5.980759	0.091276
H	4.382363	5.829575	0.284533
H	5.506719	4.474410	0.310005
H	6.465601	6.474913	4.770123
H	7.044027	4.828099	4.964488
H	8.999918	5.884972	1.788843
H	6.752719	3.131740	2.983619
H	7.376857	3.898077	1.517124
H	8.234718	4.084556	3.052939
H	4.187213	5.855363	4.873118
H	4.948050	4.808874	6.053735
H	4.955417	2.925111	4.457375
H	3.333651	3.561053	4.653865
H	8.682412	7.788373	0.339285
H	10.049772	8.017528	1.414297
H	8.962255	5.965357	4.235320
H	10.118447	7.168815	3.653686
H	8.525321	7.679644	4.233921
H	3.591889	3.441741	0.844222
H	8.692335	9.542122	2.849654
H	7.298054	9.305064	1.796289
H	8.564025	10.211692	−0.137213
H	10.002188	10.395327	0.861604
H	2.728148	1.874331	3.393979
H	8.888524	12.514903	0.467318
H	1.371208	0.074572	3.184973
H	1.900716	−0.952759	1.841181
H	8.604089	11.761485	3.423898
H	8.841244	13.380822	2.758350
H	10.134311	12.174523	2.627025
H	6.479848	11.467081	2.044925
H	6.677572	13.083501	1.357821
H	6.521558	11.680469	0.284582
H	−0.507416	−0.941345	1.889496
H	0.289472	2.024945	−0.393902
H	0.923658	0.992810	−1.674853
H	−0.983555	−0.075972	−0.397424
H	0.503133	−1.029703	−0.311189
H	3.274753	1.302636	−1.792781
H	4.311934	1.346482	−0.250723
H	−0.289878	1.872064	1.896934

Glycerol

C	−0.003781	0.000157	0.000329
C	1.431888	0.003255	−0.465949
C	1.517717	−0.061316	−1.971312
O	2.855263	−0.183367	−2.426508
O	0.004820	0.028600	1.420687
O	2.099353	1.195619	−0.062570

H	1.951731	−0.870743	−0.037387
H	2.130685	1.219015	0.904204
H	−0.524727	0.882689	−0.402136
H	−0.510857	−0.903503	−0.370448
H	0.978004	−0.943731	−2.332521
H	1.040772	0.832759	−2.404156
H	−0.895646	0.175195	1.737804
H	3.340806	0.607906	−2.153392

$(TiO_2)_{10}$–cholecalciferol

C	−3.823346	1.278730	7.550665
C	−4.022857	0.449830	6.253333
C	−2.838154	0.993617	5.431879
C	−1.653992	0.996133	6.385310
C	−2.289376	1.298217	7.753797
C	−5.334512	0.718680	5.478938
C	−5.132823	0.933332	3.968870
C	−3.989873	0.113976	3.376314
C	−2.681330	0.412443	4.064313
C	−1.461464	0.284312	3.494768
C	−1.216736	0.050253	2.090140
C	−0.017178	−0.024735	1.467756
C	0.048199	0.073074	−0.033015
C	1.025436	1.147527	−0.469411
C	2.406777	0.884162	0.101097
C	2.380812	0.789145	1.623268
C	1.291603	−0.116593	2.147216
C	1.516819	−0.968190	3.159687
O	0.524423	2.438499	−0.038360
Ti	−0.312602	3.771617	1.572806
O	0.641387	3.219923	3.072175
Ti	0.264870	4.390544	4.489321
O	−1.676899	3.832572	4.306672
Ti	−3.014405	3.976817	3.238725
O	−4.392068	4.346282	4.615958
Ti	−3.833091	5.471432	5.890312
O	−4.720319	7.081494	6.219266
Ti	−3.614649	8.179906	5.169230
O	−2.188749	8.862823	6.029005
Ti	−0.621451	7.732255	6.005179
O	−0.586812	6.862723	7.696416
Ti	−0.746710	5.118721	7.123010
O	0.471767	3.812444	6.176492
C	−3.866209	−1.047578	6.525828
C	−4.579792	0.868200	8.816250
C	−4.194186	1.756722	10.008631
C	−4.579487	3.230107	9.891185
C	−3.853566	4.083075	10.925286
C	−4.320304	5.537150	11.047355
C	−5.735116	5.638864	11.605963
C	−6.093557	0.845461	8.633040
O	0.232380	4.998247	0.150342
Ti	0.112375	6.548193	1.088443

O	−1.494011	7.491992	1.139601
Ti	−2.175843	7.126265	2.820100
O	−0.602485	7.773600	3.845156
Ti	1.215016	7.444989	3.780472
O	1.042347	8.224528	5.646114
O	−1.988196	3.221787	1.636600
O	−0.448124	5.496931	2.479866
O	1.451963	7.538102	1.943518
O	1.617256	5.758362	4.177000
O	−0.623961	5.875603	5.506752
O	−2.532467	4.777423	7.073459
O	−2.783549	6.569347	4.852080
O	−3.361203	8.427779	3.287870
O	−3.169311	5.595793	2.438058
C	−4.204716	6.297396	9.730084
H	−4.144326	2.303167	7.286899
H	−3.089839	2.057840	5.255470
H	−1.953213	2.268074	8.150231
H	−1.995245	0.543118	8.497397
H	−0.897627	1.736717	6.099170
H	−1.155228	0.015571	6.384593
H	−5.840821	1.605114	5.888639
H	−6.026589	−0.123035	5.630734
H	−4.256553	−0.155654	9.076178
H	−3.852048	−1.627220	5.592781
H	−2.942763	−1.284324	7.070937
H	−4.705930	−1.426026	7.124125
H	−4.931433	1.997589	3.769046
H	−6.065243	0.703752	3.437168
H	−4.217281	−0.960980	3.476005
H	−3.924254	0.299291	2.295197
H	−3.108440	1.686627	10.177893
H	−4.659573	1.343186	10.918399
H	−6.414238	0.076449	7.919524
H	−6.594581	0.635166	9.588510
H	−6.474119	1.810642	8.270285
H	−0.584840	0.509747	4.106707
H	−5.669681	3.335887	10.003680
H	−4.338157	3.605824	8.884709
H	−2.776264	4.072624	10.683284
H	−3.946371	3.602871	11.914507
H	−2.091618	0.075518	1.435205
H	−3.645623	6.021561	11.772474
H	−0.946190	0.271293	−0.453163
H	0.408983	−0.869783	−0.474515
H	−6.480263	5.245669	10.900118
H	−6.003641	6.683490	11.811930
H	−5.837201	5.077783	12.544934
H	−4.897423	5.894726	8.976316
H	−4.452754	7.359125	9.863177
H	−3.186984	6.242628	9.316588
H	1.066715	1.179358	−1.565720
H	2.204126	1.796030	2.028852

H	3.355365	0.460164	2.004332
H	3.100416	1.672972	−0.218129
H	2.769863	−0.057326	−0.337187
H	2.497724	−1.033495	3.630901
H	0.741607	−1.634691	3.536156
H	0.904269	3.137016	−0.596287

$(TiO_2)_{10}$−cholecalciferol−glycerol

C	−3.279742	−0.178154	7.996131
C	−3.519092	−0.647906	6.537330
C	−2.603343	0.348271	5.784232
C	−1.312129	0.382250	6.593023
C	−1.763392	0.117666	8.043174
C	−4.962380	−0.506298	6.007636
C	−5.037225	0.112613	4.603676
C	−3.871256	−0.268012	3.695114
C	−2.537281	0.085433	4.312358
C	−1.381334	0.170489	3.618293
C	−1.258881	−0.006324	2.188482
C	−0.124119	−0.019211	1.449672
C	−0.207866	−0.121836	−0.054481
C	0.748042	0.795741	−0.792980
C	2.160563	0.670465	−0.254738
C	2.211877	0.923930	1.247963
C	1.246524	0.044148	2.001837
C	1.642367	−0.661320	3.074421
O	0.288517	2.168080	−0.675867
Ti	−1.068645	3.417608	0.511407
O	−0.299039	3.320907	2.194597
Ti	−1.434953	4.231297	3.400552
O	−2.992357	3.048348	2.835754
Ti	−4.005592	2.782405	1.472118
O	−5.740794	2.678084	2.469577
Ti	−5.899976	3.928659	3.719286
O	−7.334300	5.130106	3.621867
Ti	−6.402277	6.576525	2.878479
O	−5.541504	7.703475	4.010274
Ti	−3.755489	7.060016	4.347442
O	−3.831882	6.251248	6.088562
Ti	−3.253094	4.575054	5.656292
O	−1.465460	3.701381	5.095515
C	−3.033738	−2.085549	6.334695
C	−3.749434	−1.090676	9.134062
C	−3.296546	−0.586537	10.511905
C	−3.807759	0.786968	10.933048
C	−3.277729	1.180906	12.307235
C	−3.680018	2.569156	12.813136
C	−5.187900	2.711322	12.979217
C	−5.256940	−1.326431	9.122586
O	−0.576632	4.728661	−0.785238
Ti	−1.462535	6.173397	−0.062495
O	−3.226623	6.585817	−0.459051
Ti	−4.181406	6.023408	1.025134

O	−3.176798	7.140847	2.314278
Ti	−1.395907	7.474502	2.724347
O	−2.356184	8.148023	4.407205
O	−2.518117	2.392969	0.233157
O	−1.998271	5.000491	1.226841
O	−0.743227	7.548314	0.978824
O	−0.598590	6.034029	3.352225
O	−2.957925	5.309213	4.058963
O	−4.792463	3.698483	5.231496
O	−5.008358	5.369443	2.936779
O	−5.809686	6.864611	1.099935
O	−4.537068	4.268590	0.559130
C	−3.129876	3.687710	11.936071
O	0.392489	−3.406528	1.308519
C	−0.962172	−3.617871	1.665830
C	−1.112554	−4.219398	3.044285
C	−2.565533	−4.495929	3.350292
O	−2.631906	−5.084528	4.640502
O	−0.560604	−3.293287	3.974240
H	−3.821071	0.782049	8.088383
H	−3.094271	1.335554	5.913489
H	−1.542982	0.965500	8.704765
H	−1.223311	−0.744312	8.460994
H	−0.783399	1.336456	6.476989
H	−0.621833	−0.402781	6.248861
H	−5.556414	0.119244	6.690077
H	−5.447493	−1.493823	5.999262
H	−3.255820	−2.068555	8.993876
H	−3.055736	−2.363326	5.273254
H	−2.008510	−2.243587	6.694936
H	−3.681715	−2.796373	6.864869
H	−5.055602	1.207803	4.693844
H	−5.985013	−0.163592	4.122846
H	−3.901105	−1.350687	3.475641
H	−3.993250	0.223104	2.716263
H	−2.196424	−0.580315	10.559640
H	−3.620215	−1.324959	11.264632
H	−5.586537	−1.877142	8.233542
H	−5.563781	−1.909568	10.002107
H	−5.814574	−0.379746	9.144847
H	−0.470306	0.425071	4.162397
H	−4.908845	0.789856	10.944330
H	−3.504521	1.542196	10.191294
H	−2.176265	1.121526	12.287910
H	−3.608822	0.427923	13.042228
H	−2.194917	−0.086979	1.628279
H	−3.224678	2.679286	13.811409
H	−1.236226	0.042460	−0.400558
H	0.070386	−1.144487	−0.362539
H	−5.702493	2.691984	12.008283
H	−5.442649	3.664178	13.462041
H	−5.605906	1.902726	13.594544
H	−3.617884	3.706394	10.951597

H	−3.298928	4.669391	12.398323
H	−2.049060	3.578159	11.771232
H	0.725764	0.549501	−1.862918
H	1.950922	1.977146	1.437985
H	3.229556	0.774435	1.628339
H	2.825176	1.363985	−0.786978
H	2.511700	−0.347825	−0.479535
H	2.670510	−0.601006	3.431265
H	0.964303	−1.311920	3.626560
H	0.845575	2.742408	−1.223345
H	−0.547044	−5.166619	3.090244
H	−0.651579	−3.662144	4.864241
H	−3.130634	−3.548600	3.324751
H	−2.984299	−5.170902	2.587929
H	−1.382309	−4.306175	0.923032
H	−1.529804	−2.671774	1.615787
H	−3.553325	−5.112644	4.928828
H	0.761773	−2.712019	1.876752

$(TiO_2)_{10}$–glycerol

C	−0.111462	−5.226199	0.998346
O	0.923479	−5.662448	1.866070
C	−1.119174	−4.370599	1.736797
C	−2.320338	−4.046368	0.886453
O	−3.398344	−3.514320	1.667851
Ti	−4.044088	−4.460648	3.681056
O	−3.616623	−6.232214	2.951436
Ti	−2.623228	−7.258485	4.010891
O	−3.393979	−8.853936	4.546143
Ti	−3.860357	−8.357061	6.293387
O	−2.594795	−8.466936	7.561195
Ti	−1.649907	−6.766462	7.514618
O	−0.008669	−7.364230	6.624234
Ti	0.144960	−6.108283	5.346021
O	−1.193473	−5.279582	6.268845
Ti	−1.003849	−3.438227	5.654602
O	−1.022399	−3.101017	7.543653
Ti	−2.285692	−4.132255	8.367884
O	−3.612769	−3.638497	6.829102
Ti	−4.770822	−5.550381	6.753855
O	−5.316726	−7.303860	6.862566
O	−0.539429	−3.155465	2.199220
Ti	−3.671724	−2.211050	5.434043
O	−4.633685	−2.606201	3.966747
O	−5.141367	−5.111470	4.974352
O	−2.572545	−4.033003	4.523971
O	−0.773366	−6.844766	3.968639
O	−3.082179	−6.731064	5.748391
O	0.444357	−4.075593	4.869911
O	−1.925374	−1.735679	5.290620
O	−4.774346	−1.462180	6.779549
Ti	−4.838079	−2.835444	7.994757
O	−5.870306	−4.332748	7.683545

O	−3.494440	−3.108989	9.287082
O	−1.097733	−5.705720	8.844340
O	−3.344067	−5.737115	8.039333
H	−1.476286	−4.943242	2.601024
H	−0.070121	−3.351934	3.031727
H	−2.065300	−3.329578	0.093848
H	−2.703289	−4.958147	0.415606
H	−0.626910	−6.089501	0.545741
H	0.365643	−4.653032	0.192438
H	−3.194863	−2.598864	1.915474
H	0.501684	−6.195406	2.565972