

Theoretical Determination of Structures of Terpenoids 18 α -Oleanane and A-Neo-18 α -oleanene

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(Received: 12 March 2012;

Accepted: 9 January 2013)

AJC-12679

The purpose of this study was to determine which of the quantum chemistry methods PM3, HF and DFT/B3LYP evaluate more accurately the geometric parameters of two terpenoids 18 α -oleanane (**1**) and A-neo-18 α -oleanene (**2**). The theoretical results were compared to experimental data generated by X-ray diffraction. Compound **1**, C₃₂H₅₂O₃, crystallizes in space group C2 with a = 13.3520 (2), b = 6.54000 (10), c = 32.4439(5) Å, V = 2798.13(7) Å³ and Z = 4. The structure was refined to a final R = 0.027 for the structure factors observed with I \geq 3 σ (I). The second molecule **2**, C₃₀H₄₆O₂, crystallizes in the monoclinic space group with a = 13.2214 (4), b = 6.4962 (2), c = 29.8420(9) Å, V = 2558.00(13) Å³ and Z = 4. The structure was refined to a final R = 0.061 for the structure factors observed with I = 2 σ (I). A comparative study using *ab initio* calculation (HF/6-31G**), semi empirique (PM3) and DFT(B3LYP/6-31G**) shows a high correlation with the geometric data of X-ray diffraction. The difference between the calculated and experimental values is very insignificant.

Key Words: PM3, HF, DFT, Terpenoids, X-Ray.

INTRODUCTION

Plants produce a wide range of natural products, including terpenoids, steroids, saponins, alkaloids, flavonoids, coumarins and tannin. Many of which possess potent biological activity. Several molecules isolated from nature are currently under study at an advanced stage of clinical trials, either directly or in the form of analogues deduced from structure-activity relationships¹. A vast series of natural terpenoids are widely distributed in nature and exhibit great structural and biological diversity and are commonly found in vascular plants from various families. They are present at different levels of abundance in all plant parts. Terpenoids are of considerable pharmacological and clinical interest and are used as models for the design of molecules having useful activities (antitumor, antiviral, antibacterial, hepatoprotective, antioxidant, antiulcer and anti-allergen)². During the last decade, increasing attention has focused on new and appropriate methods for the analysis of terpenoids from plant sources. Conventional chromatographic methods, HPLC, LC-NMR GC-MS still remain the most useful and most commonly applied techniques³. Although structural elucidation of terpenoids is not a difficult task, the similarities between the structures can create problems. In particular, the determination of stereochemistry requires NOE/NOESY NMR

experiments and/or X-ray analyses. Multidisciplinary efforts of chemist, biochemists and medicinal chemists have led to new developments in the field of terpenoids, which are based primarily on the physical and chemical properties include selective reactivity towards various reagents and the possibilities for functionalization and derivatization of these natural compounds⁴. However, to the best of our knowledge, there is little published information describing the X-ray crystallography of these compounds⁵. Compared to flavonoids which have been widely investigated⁶⁻⁸.

In continuation of our work to the characterization of natural products⁹⁻¹¹, we present in this study a theoretical determination of the geometric parameters of 18 α -oleanane and A-neo-18 α -oleanene at semi-empirical PM3¹², *ab initio* HF¹³ and DFT levels¹⁴. We used 6-31G(d,p) bases set. The functional B3LYP¹⁵ was used in DFT calculation. This procedure has been efficiently employed in the structural determination of diterpenoids¹⁶ and other organic compounds^{17,18}. The studied terpenoids were selectively prepared by Salvador *et al.*⁴ under Wagner-Meerwein rearrangement of lupane terpenoid by using bismuth(III) salts as catalysts. The physical data (IR, MS, NMR and X-ray crystallography) of obtained compounds were indicated⁴. So, we have used the experimental X-ray diffraction data in our theoretical approach.

COMPUTATIONAL METHOD

All the calculations were carried out using software package Gaussian 98¹⁹. Quantum chemical methods at the PM3, DFT and HF level were used to determine the optimal geometry and energies of two terpenoids 18 α -oleanane and A-neo-18 α -oleanene. In DFT calculations the functional B3LYP was used with standard Pople's split valence 6-31G(d,p) basis set¹⁵. Such combination is being used with good results for organic hydrogen-bonded systems^{20,21}. It represents a good compromise between economy of computational resources, accuracy and applicability to many-atoms molecules. The 6-31G(d,p) basis set was used in the HF calculations. The optimized geometries were characterized as true minima on the potential energy surface (PES) since all harmonic frequencies were real. *Ab initio* geometry optimization on 18 α -oleanane (C₃₂H₅₂O₃) and A-neo-18 α -oleanene (C₃₀H₄₆O₂) was performed starting from the geometry found in the X-ray refinement.

RESULTS AND DISCUSSION

Structure of the compound 1 (C₃₂H₅₂O₃): The displacement ellipsoid plot with the numbering scheme for the compound **1** is shown in Fig. 1. Selected X-ray diffraction data summarize bond lengths, bond angles and torsion angles in Tables 1-3, respectively.

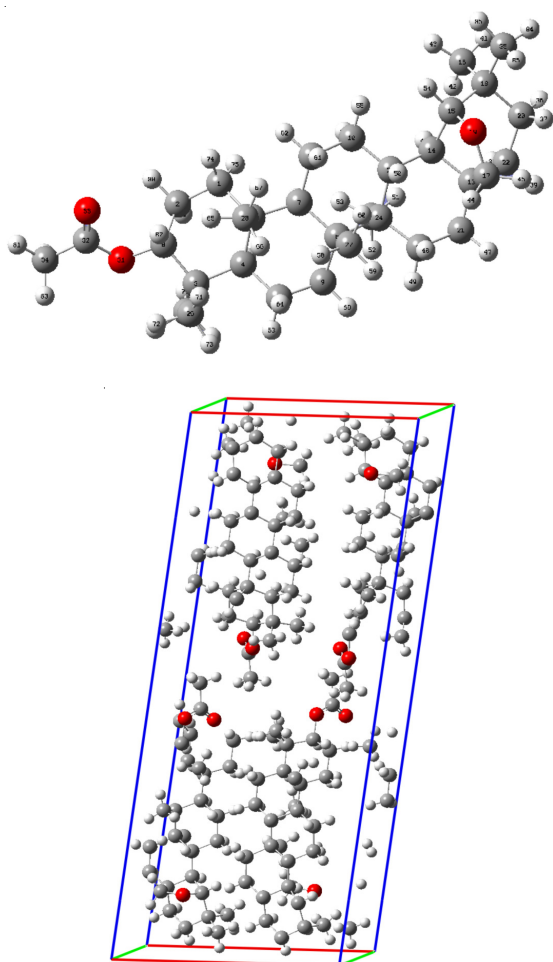


Fig. 1. Perspective view of the molecule **1** and the crystal packing in the unit cell (displacement ellipsoids are drawn at the 50 % probability level, H atoms of arbitrary sizes)

In order to establish the accuracy of HF/6-31G (d,p), PM3 and B3LYP/6-31G (d,p) models chemistry in the reproducibility of structural properties of the 18 α -oleanane, the computational data were compared with the experimental data taken from work of Salvador *et al.*⁴. The computational data are generated for the gas phase and compared with the solid state ones because the only experimental data found in the literature were from an X-ray study. Molecules optimized with B3LYP/6-31G (d,p) model indicating that both molecules are into their minimum values of energy.

The results showed in Tables 1 and 2 reveal a general similitude between theoretically and experimentally calculated bond distances and bond angles for 18 α -oleanane. The theoretical and experimental C-C and C-O bond distances present small differences; using HF/6-31G (d,p) method data in the order of 0.00-0.03 Å, in the order of 0.001-0.02 Å using DFT/B3LYP/6-31G (d,p) method data and in the order of 0.001-0.03 Å using PM3 method data, while the C-H bond distances show noticeable differences using the three methods of calculation, respectively in a range of 0.102-0.127, 0.115-0.136 and 0.130-0.148 Å.

The large differences in the solid state can be attributed to the fact that C-H groups constituted the site for the intermolecular interactions and hydrogen bonds with the water of the crystal lattice. Oppositely, in the simulation is modeled a single molecule free of intermolecular interactions, therefore the bond distances are almost not modified.

The theoretical and experimental bond angles between carbon atoms in first molecule present differences about 0.02 to 1.92° used HF/6-31G (d,p) 0.00 to 2.55° used B3LYP/6-31G (d,p) and around of 0.03 to 4.44° used PM3, when the PM3 method over estimates the bond angles. The presence of an oxygen atom diverted the experimental values around 0.4-1.6° with respect to the theoretical bond angle, such as the bond distances. Nevertheless the variations found, the standard deviations for bond distances and bond angles of two molecules were small (Tables 1 and 2), thus the B3LYP/6-31G (d,p) method give a good agreement between theoretical and experimental data. The torsion angles showed in Table-3, regularly are utilized to define the molecular planarity. However, their values tended to be 0° or 180°. The presence of oxygen atom originates a great deviation of the angle in a range of 4-8°.

Structure of the compound 2 (C₃₀H₄₆O₂): The displacement ellipsoid plot with the numbering scheme for the title compound **2** is shown in Fig. 2. Selected X-ray diffraction data summarize bond lengths in Table-4, bond angles in Table-5 and torsion angles in Table-6.

The geometry of compound **2** has been fully optimized using PM3, the DFT method with the help of Becke's three parameter hybrid density functional, B3LYP/6-31G(d,p) and HF/6-31G(d,p), using Gaussian 98 program¹⁹. The results were compared with the X-ray data and show an excellent agreement (Tables 4-6), where the molecular structure is shown in Fig. 2. The largest deviation of the DFT optimized bond-lengths/angles from the corresponding X-ray experimental values is 14.06 % for C-H and 1.94 % for H-C-H. However the HF method data give the deviation between 14.85 % and

TABLE-1
BOND LENGTHS [\AA] FOR THE SIMULATED $\text{C}_{32}\text{H}_{52}\text{O}_3$ COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Bond lengths	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C1 C2	1.533(3)	1.52964	0.26	1.53463	0.08	1.51719	1.05
C2 C3	1.505(3)	1.51851	0.87	1.52406	1.24	1.53414	1.91
C3A C3B	1.496(3)	1.50461	0.55	1.51126	0.99	1.50405	0.51
C4 C23	1.536(3)	1.53949	0.20	1.54302	0.43	1.52585	0.68
C4 C5	1.556(3)	1.56618	0.62	1.57193	1.00	1.55461	0.10
C5 C10	1.557(3)	1.56414	0.43	1.57071	0.86	1.54973	0.48
C8 C26	1.545(3)	1.54798	0.16	1.55103	0.36	1.53244	0.83
C8 C9	1.569(2)	1.57256	0.21	1.57832	0.57	1.55637	0.82
C8 C14	1.587(3)	1.60426	1.06	1.61279	1.600	1.57744	0.62
C14 C27	1.540(3)	1.55151	0.72	1.55349	0.85	1.53192	0.54
C17 C28	1.524(3)	1.53913	0.97	1.54619	1.43	1.54736	1.50
C19 C20	1.546(3)	1.54627	0.00	1.55598	0.62	1.55755	0.72
C20 C29	1.526(4)	1.53575	0.60	1.53957	0.85	1.52795	0.09
C20 C21	1.531(3)	1.54681	1.01	1.55364	1.46	1.54231	0.71
C3O3A	1.463(2)	1.43322	2.05	1.45659	0.46	1.43689	1.804
O3A C3A	1.330(3)	1.32500	0.39	1.35349	1.73	1.36374	2.51
C3A O3B	1.197(3)	1.18921	0.67	1.21230	1.25	1.21568	1.52
C19 O19	1.438(3)	1.41768	1.43	1.44337	0.34	1.43596	0.16
O19 C28	1.432(3)	1.41007	1.55	1.43485	0.17	1.43110	0.08
C1 H1A	0.9700	1.08417	11.76	1.09482	12.86	1.11233	14.67
C3 H3	0.9800	1.08234	10.43	1.09551	11.78	1.11954	14.23
C24H24A	0.9600	1.08186	12.68	1.09354	13.90	1.09739	14.30
C5 H5	0.9800	1.09129	11.34	1.10278	12.52	1.12417	14.70
C9 H9	0.9800	1.08428	10.63	1.09744	11.97	1.12740	15.04
C12H12A	0.9700	1.08545	11.89	1.09599	12.97	1.10725	14.14
C13 H13	0.9800	1.08504	10.71	1.09680	11.91	1.12477	14.76
C27H27A	0.9600	1.08104	12.60	1.09175	13.71	1.10162	14.75
C30H30A	0.9600	1.08381	12.89	1.09361	13.91	1.10251	14.84
C28H28A	0.9700	1.08417	11.76	1.09691	13.08	1.10481	13.89

TABLE-2
BOND ANGLES [$^\circ$] FOR THE SIMULATED $\text{C}_{32}\text{H}_{52}\text{O}_3$ COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Bond angles	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C2C1C10	113.04(15)	113.88532	0.74	113.74956	0.62	110.81220	1.97
C3C2C1	110.15(15)	111.57127	1.28	111.19503	0.94	109.48833	0.60
C3C4C23	111.56(17)	111.84748	0.25	111.79507	0.20	110.77040	0.70
C23C4C24	108.49(17)	107.17171	1.23	107.50357	0.91	108.63274	0.12
C3C4C5	106.69(14)	106.36907	0.30	106.41392	0.26	106.82162	0.12
C6C5C4	113.41(15)	114.60128	1.04	114.46517	0.92	113.57345	0.14
C4C5C10	117.90(15)	117.51600	0.32	117.45202	0.33	115.68533	1.87
C7C6C5	110.56(16)	110.50219	0.05	110.62825	0.06	109.74763	0.73
C6C7C8	113.69(17)	114.20655	0.45	114.15842	0.41	111.21777	2.17
C26C8C7	107.33(19)	106.93246	0.37	107.12642	0.19	107.82816	0.46
C7C8C9	108.43(15)	108.26870	0.15	108.50358	0.06	109.33280	0.83
C8C9C10	116.77(14)	117.47856	0.60	117.28589	0.44	115.52603	1.06
C25C10C1	107.13(16)	107.39615	0.24	107.67072	0.50	108.64580	1.41
C27C14C15	106.80(18)	106.81816	0.01	107.10718	0.28	108.52058	1.60
C15C14C8	111.36(16)	111.29607	0.05	111.21781	0.12	110.65427	0.63
C13C18C17	113.94(16)	114.16598	0.19	114.35243	0.36	114.48260	0.47
C29C20C21	108.8(2)	109.29300	0.43	109.31144	0.45	109.15830	0.31
C21C22C17	112.81(18)	112.86340	0.04	112.81594	0.00	113.04737	0.20
O19C28C17	106.5(2)	106.01939	0.47	106.51770	0.00	106.98700	0.43
O3AC3C2	109.77(15)	109.35649	0.37	109.53822	0.21	109.55500	0.19
O3AC3C4	107.14(14)	108.30564	1.08	108.20797	0.99	107.55479	0.38
O3AC3H3	108.2	107.58958	0.56	107.14403	0.97	110.38835	2.02
C3AO3AC3	118.74(16)	119.23973	0.41	117.36475	1.15	119.73322	0.83
O3BC3AO3A	123.89(19)	124.20452	0.25	124.29414	0.32	120.71556	2.56
O3BC3AC3B	124.5(2)	124.58072	0.04	125.10138	0.46	127.14129	2.10
C29C20C21	108.8(2)	109.29300	0.43	109.31144	0.45	109.15830	0.31

TABLE-3
 TORSION ANGLES [°] FOR THE SIMULATED C₃₂H₅₂O₃ COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Torsion angles	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C10 C1 C2 C3	-58.0(2)	-55.20295	4.85	-55.84187	3.75	-62.81247	8.25
C1 C2 C3 C4	58.0(2)	56.83759	2.03	57.10729	1.58	63.13292	8.80
C2 C3 C4 C23	72.9(2)	72.49876	0.58	72.20640	0.98	67.37180	7.61
C3 C4 C5 C6	-177.24(18)	-173.81807	1.93	-174.53532	1.52	-178.93151	0.95
C23 C4C5C10	-72.7(2)	-70.70069	2.77	-70.98060	2.39	-68.26320	6.13
C4 C5 C6 C7	162.17(18)	161.52070	0.40	161.80457	0.22	163.54149	0.84
C10 C5 C6 C7	-62.7(2)	-62.73089	0.01	-62.63138	0.14	-65.96454	5.16
C5 C6 C7 C8	58.3(3)	58.60312	0.46	58.24794	0.15	62.13529	6.51
C4C5 C10 C25	66.3(2)	66.26531	0.09	66.66210	0.51	66.14255	0.27
C12C13C14C7	65.0(2)	66.57046	2.38	65.68780	1.01	60.07306	7.73
C27C14C15C16	61.4(2)	60.81349	0.99	61.28786	0.22	61.19647	0.37
C8 C14C15C16	-176.82(19)	-177.63025	0.45	-177.08599	0.14	-177.62846	0.45
C15C16C17C18	-45.9(3)	-43.84531	4.55	-44.29081	3.57	-46.69778	1.65
C12C13C18C19	72.2(2)	71.47184	1.03	71.30680	1.27	77.02715	6.64
C16C17C22C21	-174.1(2)	-173.43194	0.39	-173.59319	0.30	-175.98346	1.06
C28C17C22C21	-47.6(3)	-47.45044	0.37	-47.29925	0.71	-49.61850	4.15
C18C17C22C21	61.1(3)	60.90315	0.37	61.12906	0.01	60.05037	1.76
C2 C3O3A C3A	92.0(2)	84.92607	7.70	85.36260	7.23	90.14941	2.04
C4C3 O3A C3A	-142.38(19)	-149.99579	5.34	-149.21740	4.80	-149.49429	4.99
C3O3AC3AC3B	174.8(2)	179.90729	2.90	179.77083	2.83	178.91010	2.33
O3A C3 C4 C23	-49.5(2)	-49.63466	0.22	-50.24512	1.45	-52.27299	5.55
O3A C3 C4 C24	69.2(2)	67.50774	2.48	67.27607	2.81	67.37379	2.67
O3A C3 C4 C5	-174.95(16)	-175.72474	0.44	-175.85331	0.51	-176.19862	0.71
C1 C2 C3 O3A	178.98(17)	178.39401	0.32	178.83354	0.08	-178.43160	0.30
O19C19C20C29	-63.9(2)	-63.09122	1.29	-62.31185	2.51	-63.43493	0.76
O19C19C20C21	54.0(2)	55.52818	2.77	56.15222	3.94	56.61896	4.79
C18C19C20C21	-61.8(3)	-59.63100	3.68	-59.40388	3.93	-59.07090	4.46
O19C19C20C30	175.4(2)	177.91034	1.41	178.44430	1.72	177.99157	1.46
C16C17C28O19	-150.38(16)	-150.69526	0.20	-149.80710	0.38	-148.42409	1.30
C22C17C28O19	84.7(2)	84.41106	0.36	84.99180	0.31	87.19798	2.91
C18C17C28O19	-29.0(2)	-28.60485	1.44	-28.04899	1.44	-25.72492	12.68

TABLE-4
 BOND LENGTHS [Å] FOR THE SIMULATED C₃₀H₄₆O₂, COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Bond lengths	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C1 C2	1.542(5)	1.53628	0.40	1.54342	0.05	1.53498	0.49
C1 C10	1.543(5)	1.55355	0.64	1.56146	1.15	1.55653	0.84
C10 C25	1.544(5)	1.54593	0.09	1.55079	0.40	1.52598	1.20
C3 C4	1.489(5)	1.51343	1.60	1.51220	1.52	1.49193	0.16
C3 C5	1.331(5)	1.32672	0.36	1.34465	0.98	1.34440	0.96
C4 C23	1.511(6)	1.53535	1.56	1.54141	1.97	1.52065	0.59
C6 C7	1.522(4)	1.53728	0.97	1.54426	1.43	1.52083	0.10
C8 C14	1.585(4)	1.60272	1.09	1.61094	1.60	1.57615	0.58
C19 C20	1.536(5)	1.54395	0.48	1.55196	1.00	1.55613	1.27
C21 C22	1.525(5)	1.53991	0.94	1.54390	1.20	1.52802	0.16
C1 H1A	0.9700	1.08533	11.88	1.09486	12.86	1.10682	14.10
C2 H2A	0.9700	1.08884	12.24	1.09664	13.05	1.10682	14.10
C4 H4	0.9800	1.08499	10.70	1.09696	11.92	1.12620	14.91
C6 H6A	0.9700	1.08361	11.71	1.09475	12.85	1.11198	14.62
C7 H7A	0.9700	1.08394	11.74	1.09454	12.83	1.11317	14.75
C15 H15B	0.9700	1.08517	11.86	1.09535	12.91	1.11230	14.67
C16 H16A	0.9700	1.08502	14.85	1.09569	12.94	1.10679	14.09
C21 H21A	0.9700	1.08635	11.98	1.09623	13.01	1.10800	14.22
C22 H22B	0.9700	1.08671	12.03	1.09729	13.11	1.10935	14.36
C23 H23A	0.9600	1.08563	13.08	1.09467	14.02	1.09725	14.29
C24 H24C	0.9600	1.08536	13.05	1.09446	14	1.09729	14.29
C25 H25A	0.9600	1.08491	13.01	1.09458	14.01	1.09848	14.41
C25 H25C	0.9600	1.08535	13.05	1.09506	14.06	1.09814	14.38
C27 H27A	0.9600	1.08066	12.56	1.09133	13.67	1.10460	15.06
C27 H27B	0.9600	1.08378	12.88	1.09368	13.91	1.10194	14.78
C30 H30B	0.9600	1.08528	13.04	1.09491	14.05	1.09769	14.33
C19 O19	1.475(4)	1.43480	2.75	1.46247	0.88	1.44712	1.91
C28 O28	1.199(4)	1.18316	1.35	1.20532	0.49	1.20604	0.55
C28 O19	1.346(4)	1.33465	0.87	1.36558	1.41	1.38057	2.53

TABLE-5
BOND ANGLES [°] FOR THE SIMULATED C₃₀H₄₆O₂, COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Bond angles	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C2 C1 C10	105.1(3)	105.20307	0.06	105.26561	0.12	106.24329	1.05
C5 C3 C4	127.8(3)	127.84605	0.00	127.65174	0.14	125.11316	2.12
C5 C3 C2	109.9(3)	110.70784	0.7	110.57555	0.58	111.36061	1.30
C4 C3 C2	122.3(3)	121.43371	0.73	121.75153	0.47	123.52246	0.97
C3 C4 C24	111.9(4)	111.64695	0.26	111.75335	0.16	111.22733	0.64
C3 C5 C6	128.9(3)	129.54770	0.47	129.45538	0.40	127.80427	0.87
C3 C5 C10	112.9(3)	112.79360	0.12	112.62435	0.27	112.61996	0.28
C6 C5 C10	118.2(3)	117.64323	0.49	117.90268	0.27	119.43807	1.01
C5 C6 C7	111.0(3)	110.14373	0.80	110.34404	0.62	108.58137	2.20
C6 C7 C8	113.9(3)	114.08179	0.13	113.91924	0.01	111.66971	1.99
C7 C8 C26	108.1(3)	107.51306	2.20	107.78012	0.32	108.40005	0.24
C10 C9 C8	116.3(2)	117.11079	0.67	116.95000	0.54	114.93416	1.19
C5 C10 C1	101.0(3)	101.27065	0.23	101.32630	0.28	102.88932	1.83
C5C10 C25	109.4(3)	109.98796	0.51	110.07480	0.58	109.66167	0.21
C1C10 C25	107.7(3)	107.65993	0.07	107.92855	0.17	108.89141	1.07
C1 C10 C9	111.6(3)	110.71285	0.82	110.94974	0.61	111.40044	0.20
C25C10 C9	115.1(3)	115.93933	0.69	115.27944	0.12	114.45129	0.59
C27C14C13	110.0(3)	110.64465	0.55	110.59230	0.50	110.87069	0.76
C15C14 C13	106.9(3)	106.86773	0.06	107.12041	0.17	108.60941	1.56
C27 C14 C8	111.3(3)	111.19587	0.12	111.21195	0.10	110.40868	0.83
C16C15 C14	113.4(3)	113.69812	0.22	113.74394	0.27	111.90489	1.34
C28C17 C16	112.9(3)	112.30666	0.55	111.90318	0.91	114.90381	1.74
C28C17 C18	100.9(3)	100.21670	0.71	100.47503	0.45	100.43107	0.49
C16C17 C18	114.8(3)	115.60596	0.67	115.64596	0.70	114.35916	0.41
C28C17 C22	106.4(3)	107.03688	0.56	107.18845	0.70	108.12280	1.58
C19C18 C17	97.9(3)	97.83961	0.10	98.12072	0.19	98.29956	0.36
C29C20 C21	109.7(3)	109.36903	0.33	109.39228	0.30	109.13528	0.54
C21C20 C30	111.2(3)	111.26739	0.02	111.30126	0.06	110.44838	0.71
C21C20 C19	108.2(3)	108.23076	0.00	108.08861	0.13	109.86860	1.50
C22C21 C20	113.8(3)	114.42923	0.51	114.51780	0.59	114.99400	1.01
C21C22 C17	112.6(3)	112.83162	0.17	112.83848	0.17	112.84989	0.18
C2 C1 H1A	110.7	112.68339	1.68	112.85281	1.89	111.69196	0.81
C10 C1 H1A	110.7	112.79389	1.80	112.83576	1.89	111.70763	0.9
H1AC1 H1B	108.8	107.29907	1.47	107.32329	1.37	105.62907	3.03
C3 C2 C1	102.4(3)	103.17643	0.72	103.26476	0.81	104.86511	2.37
C3 C2 H2A	111.3	110.83879	0.44	110.83126	0.44	111.30678	0.00
C3 C4 H4	107.5	108.19700	0.55	108.08034	0.46	106.69760	0.83
C5 C6 H6A	109.4	111.24628	1.64	111.30801	1.73	110.03838	0.54
H6AC6 H6B	108.0	106.17030	1.75	105.93104	1.94	107.26952	0.92
C9C11 H11B	109.4	111.06365	1.51	110.74239	1.18	109.65993	0.18
C11C12H12A	109.3	109.25230	0.09	109.50602	0.18	110.42280	1.00
C16C15H15A	108.9	107.32460	1.46	107.22746	1.56	110.53635	1.46
C17C16 C15	112.4(3)	112.15605	0.24	112.03590	0.35	112.36393	0.06
C17C16H16A	109.1	108.56204	0.54	108.30137	0.73	109.98190	0.73
C13 C18 H18	110.1	109.24285	0.81	109.20337	0.81	108.91628	1.08
C4 C23 H23A	109.5	111.13134	1.46	111.25744	1.55	111.33206	1.64
C4 C23 H23B	109.5	110.52112	0.91	110.69377	1.00	111.05237	1.36
O28 C28 O19	121.5(3)	122.99954	1.20	122.54219	0.83	115.18920	5.22
O28 C28 C17	129.3(4)	128.40560	0.95	128.73900	0.47	134.52172	4.00
O19 C28 C17	109.2(3)	108.58305	0.59	108.70696	0.48	110.28894	0.96
C20C29H29A	109.5	110.97319	1.27	111.07738	1.36	111.18600	1.46
C28 O19 C19	108.3(3)	110.18346	1.70	108.88495	0.50	107.46948	0.80

2.20 %, respectively. But using PM3 method data the difference is around 15.06 and 5.22 %. The differences observed between the theoretical and experimental results are probably due to packing effects. When we whereas the PM3 method over estimates the torsion angle.

Conclusion

We have tested the PM3, HF and DFT methods to determine geometric parameters of two terpenoids 18 α -oleanane (**1**) and A-neo-18 α -oleanene (**2**). DFT/B3LYP/6-31G(d,p)

model chemistry can be considered as the most appropriate method to facilitate the reproducibility of structural properties in terpenoids compounds, because the bond distances, bond angles and torsion angles of the simulated molecules are generally adjusted to the experimental conformations taken from literature into a strict range of variation. The larger values than the corresponding experimental ones, due to the fact that theoretical calculations imply isolated molecules in gaseous phase state while experimental results refer to molecules in

TABLE-6
TORSION ANGLES [°] FOR THE SIMULATED C₃₀H₄₆O₂, COMPARED WITH X-RAY DATA TAKEN FROM REF.⁴

Torsion angles	X-Ray	HF/6-31G**	Error (%)	B3LYP/6-31G**	Error (%)	PM3	Error (%)
C1C2C3C5	16.0(4)	15.76398	1.74	16.03395	0.06	7.96247	52.24
C2C3C4C24	68.4(5)	70.72388	3.31	67.68825	1.12	60.43578	11.71
C2C3C4C23	-56.4(5)	-53.84021	4.62	-56.80069	0.62	-63.33288	12.18
C3C5C10C25	93.6(4)	97.58022	4.20	98.02684	4.67	106.26100	13.47
C2C1C10C5	28.3(3)	24.68919	12.88	24.82692	12.38	13.71782	51.60
C11C9C10C5	-175.7(3)	-177.91139	1.24	-177.35699	0.92	-171.58982	2.36
C18C13C14C15	56.2(3)	56.22264	0.01	55.72534	0.90	55.67419	1.05
C26C8C14C15	51.7(3)	49.34631	4.62	50.71532	1.97	57.57378	11.28
C13C14C15C16	-59.5(4)	-59.89303	0.58	-59.80998	0.43	-60.84135	2.18
C15C16C17C28	70.6(4)	70.74859	0.14	70.69248	0.35	69.53906	1.57
C12C13C18C19	73.2(3)	73.35554	0.16	73.36718	0.17	77.85678	6.30
C22C17C18C13	169.2(3)	168.54865	0.40	168.52102	0.41	165.41471	2.25
C13C18C19O19	77.2(3)	77.96332	0.94	77.79146	0.72	79.06261	2.36
C17C18C19O19	-43.9(3)	-42.52486	3.20	-43.07594	1.95	-41.93332	4.55
O19C19C20C29	-65.5(4)	-64.33877	1.84	-63.63706	2.91	-64.55094	1.51
O19C19C20C21	53.7(4)	54.53836	1.47	55.20085	2.71	55.39618	3.07
O19C19C20C30	175.0(3)	176.67768	0.93	177.15162	1.21	176.79477	1.00
C16C17C28O28	33.4(5)	31.72751	5.17	31.62976	5.47	32.68792	2.30
C18C17C28O28	156.3(4)	154.99892	0.86	154.90930	0.92	155.90749	0.28
C22C17C28O28	-90.5(5)	-92.22515	1.84	-92.24785	1.86	-92.23923	1.85
C16C17C28O19	-148.6(3)	-149.50876	0.58	-149.61535	0.65	-147.16232	0.98
C18C17C28O19	-25.6(3)	-26.23734	2.34	-26.33581	2.76	-23.94274	6.59
C22C17C28O19	87.5(3)	86.53858	1.14	86.50704	1.17	87.91054	0.3
O28C28O19C19	175.4(3)	177.50500	1.17	177.51755	1.18	177.36439	1.10
C18C19O19C28	30.4(3)	28.68997	5.75	28.82138	5.29	28.77545	5.45
C20C19O19C28	-90.7(3)	-91.93305	1.32	-92.09491	1.49	-88.44740	2.52

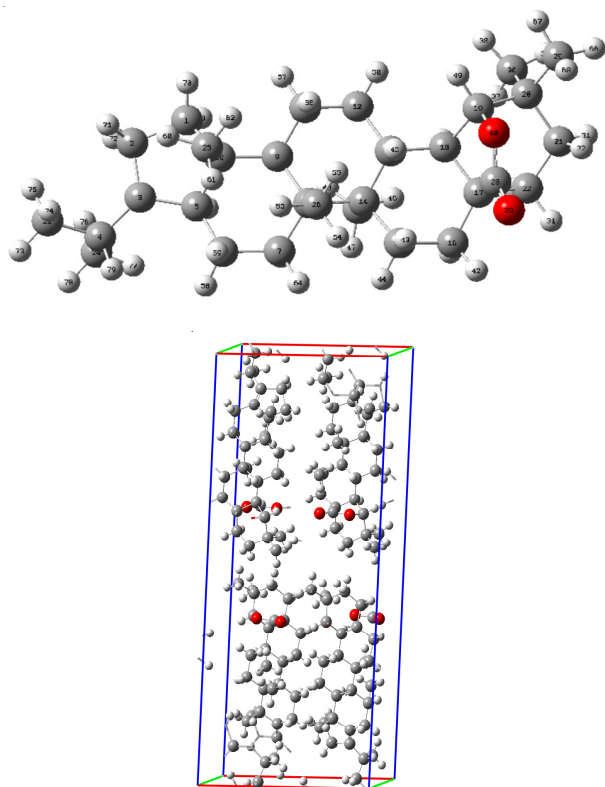


Fig. 2. Perspective view of the molecule **2** and the crystal packing in the unit cell (displacement ellipsoids are drawn at the 50 % probability level, H atoms of arbitrary sizes)

the solid state. In spite of the differences, calculated geometric parameters represent a good approximation and can provide a starting point to calculate other parameters, such as vibrational wave numbers.

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