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Ab initio and DFT study of Octanitrocubane.

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Abstract

The molecular stability, structure, dipole moment, charge transfer, polarizability and energy of Octonitrocubane have been studied by using ab- initio Quantum Mechanical calculations. We have used the Restricted Hartree-Fock (RHF) and density functional Becke3LYP (B3LYP) theories by employing 6-31G, 6-31++G** and 6-311++G** basis sets for inclusion of electron correlation.

Key words: Octonitrocubane, ab-initio Quantum mechanical calculations, Restricted Hartree-Fock (RHF) and DFT (B3LYP).

1.0 Introduction

Cubane (C_8H_8) is a synthetic hydrocarbon molecule which consists of eight carbon atoms arranged at the corners of a cube. It is a solid crystalline substance. It was first synthesized in 1964 by Philip Eaton [1] from 2-cyclopetanone. Cubane is kinetically stable due to lack of readily available decompositions of paths.

Cubane and its derivatives compounds have many important properties. The 90 degree bond angle of the carbon atoms in cubane means that the bonds are highly strained. Due to the high reactivity of cubane compounds, they can be used as high density; high energy fuels (Propellants) and explosives. These compounds can also be use in medicine, nanotechnology and as polymer example Octanitrocubane and Heptanitrocubane (cubane derivatives). Molecular mechanical calculations, semi-empirical and ab initio quantum mechanical treatments of cubane have been carried out but such studies have not yet been carried out on it derivatives [2].

Octanitrocubane (C_8NO_2) is a stable, white solid with a density of 1.98g/cm^3. It is a powerful high explosive and it is shock insensitive. Octanitrocubane was synthesized by Philip Eaton and Mao-Xi Zhang at the University of Chicago in 1999 [3]. Its crystalline structure was proven by the crystallographer Richard Gilardi of the United States Naval Research laboratory [3]. It is believed to be one of the World's most energetic substances and potentially powerful non-nuclear explosive. Military is interested in this molecule because it is said to be powerful than HMX (Octogen) [4]. This increase in power is due to its highly expansive breakdown into CO_2 and N_2, as well as to the presence of strained chemical bonds in the molecule which have stored
potential energy. In addition, Octanitrocubane produces no water vapour making it less visible, and both the chemical itself and its decomposition products are considered non-toxic. Although some works have been carried out on the chemical and physical properties of this molecule [3], yet detail works are required to understand the physio-chemical properties of Octanitrocubane. For this we have used ab initio methods and the results are presented in the present work. We could not compare our results with other theoretical results because we did not find any results on Octanitrocubane obtained by employing the same basis sets.

2.0 Computational Methodology

The molecular structure of Octanitrocubane has been fully optimized by using ab- initio quantum mechanical calculations at the Restricted Hartree-Fock (RHF) level of theory without using any symmetry constraints. Initial geometry optimization was performed using the ab-initio RHF method with 3-21G basis set. Subsequently, its results were utilised to the basis set 6-31G basis set, to the 6-31++G** basis set and final calculation were carried out with 6-311++G** level. The structure was refined further using Density Functional Theory which is a cost effective method for inclusion of electron correlations with the three-parameter density functional generally known as Becke3LYP (B3LYP), which includes Becke's gradient exchange corrections [5], the Lee, Yang and Parr correlation functional [6] and the Vosko, Wilk and Nusair correlation functional [7] with a 6-31++G** and 6-311++G** basis sets. At the first step geometry optimization was carried out then the IR and Raman frequencies were calculated.

The optimized molecular structure was tested by computing the second derivatives and checking that all the harmonic vibrational frequencies are found to be real at all level of calculations. All calculations in the present work were performed on Pentium M PC using Windows version of Gaussian 03 [8] suit of ab initio quantum chemical program.

RESULT AND DISCUSSION

3.1 Molecular structure

The geometrical parameters (bond lengths and bond angles) of Octanitrocubane at the RHF/6-31G, RHF/6-31++G**,RHF/6-311++G** and B3LYP/6-31++G** levels of theories are listed in Table 1 while the molecular structure is shown in Figure 1. There are slight variations in some of the geometrical parameters while some are the same at the two levels of theories. The calculated bond lengths at RHF level are slightly (0.01Å to 0.02Å) smaller than the corresponding values obtained at the DFT/B3LYP level for the 6-31++G** basis set. The bond angles vary from 0.1 to 0.4 degree at both levels of theories. The angles between the atoms in the Cubane ring vary from 89.99 to 90.36 degree at both levels of theory which is approximately equal to 90 degree as obtained experimentally. The Cubane ring makes the molecule more stable. The Oxygen atoms play a major role in the electron density configuration. The bond lengths and bond angles obtained at the RHF/6-31G basis set are slightly greater than their corresponding values obtained at RHF for the 6-31++G** and 6-311++G** basis sets.

3.2 Energies and Dipole moments

The dipole moments in Debye and total electronic energies (a.u) without zero point correction (E_1), with zero point correction (E_2), with thermal energy correction (E_3) and with enthalpy correction (E_4) for the molecule at the RHF/6-31G, RHF/6-31++G**,RHF/6-311++G** and B3LYP/6-31++G** level of theories are listed in Table 2. The scaling factor for the zero-point vibrational energy is 0.9877 for the 6-311++G** basis set and 0.8929 for the 6-31G basis set [9]-[10].

The dipole moment of the molecule gives the strength of the polarity of the molecule. The magnitude of the dipole moment obtained at B3LYP/6-31++G** and B3LYP/6-31++G** levels are smaller as compared to the corresponding values of the dipole moment at RHF/6-31G, RHF/6-31++G** and RHF/6-311++G** levels. Oxygen atoms draw more electrons from their neighbouring carbon atoms, become highly electronegative in this molecule and attract electrons more strongly than the other atoms both in the 6-31++G** and 6-311++G** basis sets. Thus we can say that an anisotropic impact on the molecule makes the electron transfer from Carbon and Nitrogen atoms to the Oxygen atoms.

3.3 Charge Transfer and Polarizability.

The electrostatic potential derived Charges on different atomic positions of Octanitrocubane at the RHF/6-31G, RHF/6-31++G**, RHF/6-311++G** and B3LYP/6-31++G** levels of theories are listed in Table 3. From Table 3 it is clear that the values of charges on all the Oxygen atoms are negative while that on the Carbon and Nitrogen atoms are positive at RHF/6-31++G**, RHF/6-311++G** and B3LYP/6-31++G** basis sets except for the RHF/6-31G basis set. Here, the charges on all the Oxygen atoms and the Carbon C3, C5, C6, C8 atoms are negative while those on all Nitrogen atoms andC1, C2, C4, C6 are negative.

The polarizability tensor components of Octanitrocubane obtained at RHF/6-31G, RHF/6-31++G**,RHF/6-311++G** and B3LYP/6-31++G** basis sets are listed in Table 2. The polarizability tensor components of Octanitrocubane molecule xx, yy and zz corresponding components increases significantly as we move from RHF/6-31G, RHF/6-31++G**, RHF/6-311++G** to B3LYP/6-31++G** levels. The xy, xz and yz component are not significant.

Table 1: Optimized geometrical parameters of Octanitrocubane molecule obtained at RHF and B3LYP methods by employing 6-31G, 6-31++G and 6- 311++G** basis sets. Bond Lengths are given in (Å) and Bond Angles (˚).**

Geomet. Parameters		RHF/6-31G	/6-31++G**	/6-311++G**	B3LYP/6-31++G**
R1	R(1,3)	1.5632	1.5544	1.5555	1.5697
R2	R(1,5)	1.5611	1.5544	1.5555	1.5697
R3	R(1,6)	1.5606	1.5511	1.5523	1.5652
R4	R(1,28)	1.4507	1.4641	1.4687	1.4864
R5	R(2,3)	1.5606	1.5511	1.5523	1.5652
R6	R(2,6)	1.5632	1.5544	1.5555	1.5697
R7	R(2,8)	1.5611	1.5544	1.5555	1.5697
R8	R(2,11)	1.4507	1.4641	1.4687	1.4864
R9	R(3,4)	1.5611	1.5544	1.5555	1.5698
R10	R(3,9)	1.4506	1.4641	1.4687	1.4864
R11	R(4,5)	1.5632	1.5544	1.5555	1.5697
R12	R(4,8)	1.5606	1.5511	1.5523	1.5652
R13	R(4,10)	1.4507	1.4641	1.4687	1.4864
R14	R(5,7)	1.5606	1.5511	1.5523	1.5651
R15	R(5,12)	1.4506	1.4641	1.4687	1.4863
R16	R(6,7)	1.5611	1.5544	1.5555	1.5697
R17	R(6,31)	1.4506	1.4641	1.4687	1.4864

R18	R(7,8)	1.5632	1.5544	1.5555	1.5697
R19	R(7,13)	1.4507	1.4641	1.4687	1.4864
R20	R(8,14)	1.4506	1.4641	1.4687	1.4864
R21	R(9,16)	1.2161	1.184	1.1768	1.2203
R22	R(9,18)	1.2163	1.1851	1.1778	1.2215
R23	R(10,15)	1.2153	1.184	1.1768	1.2203
R24	R(10,17)	1.2168	1.1851	1.1778	1.2215
R25	R(11,19)	1.2168	1.1851	1.1778	1.2214
R26	R(11,32)	1.2153	1.184	1.1768	1.2204
R27	R(12,24)	1.2161	1.184	1.1768	1.2203
R28	R(12,26)	1.2163	1.1851	1.1778	1.2215
R29	R(13,21)	1.2153	1.184	1.1768	1.2203
R30	R(13,23)	1.2168	1.1851	1.1778	1.2215
R31	R(14,20)	1.2163	1.1851	1.1778	1.2215
R32	R(14,22)	1.216	1.184	1.1768	1.2203
R33	R(25,28)	1.2168	1.1851	1.1778	1.2215
R34	R(27,28)	1.2153	1.184	1.1768	1.2203
R35	R(29,31)	1.2163	1.1851	1.1778	1.2215
R36	R(30,31)	1.2161	1.184	1.1768	1.2204
A1	A(3,1,5)	90.1345	89.9993	89.9982	90.0015
A2	A(3,1,6)	90.1916	89.9993	90.2815	90.395
A3	A(3,1,28)	126.8417	127.2868	127.3021	127.2462
A4	A(5,1,6)	89.6343	89.7411	89.7152	89.6013
A5	A(5,1,28)	124.3916	123.5159	123.5487	123.6584
A6	A(6,1,28)	124.5498	124.9308	124.8827	124.823
A7	A(3,2,6)	90.1905	90.2567	90.2821	90.3939
A8	A(3,2,8)	89.635	89.7414	89.7156	89.6037
A9	A(3,2,11)	124.5404	124.9275	124.8724	124.8386
A10	A(6,2,8)	90.1343	90.0006	90.0025	89.9988
A11	A(6,2,11)	126.8403	127.2883	127.3079	127.2355
A12	A(8,2,11)	124.403	123.5165	123.5492	123.655
A13	A(1,3,2)	89.8077	89.7412	89.7159	89.5979
A14	A(1,3,4)	89.8649	90.0007	90.0018	89.9999
A15	A(1,3,9)	124.1251	123.5172	123.5504	123.6531
A16	A(2,3,4)	90.3604	90.2565	90.2823	90.3889

A17	A(2,3,9)	125.6655	124.9255	124.8703	124.8239
A18	A(4,3,9)	125.9553	127.2897	127.309	127.258
A19	A(3,4,5)	90.1341	89.9993	89.9982	89.9984
A20	A(3,4,8)	89.6348	89.9993	89.7147	89.6042
A21	A(3,4,10)	124.3987	123.5159	123.5478	123.6439
A22	A(5,4,8)	90.1933	90.2565	90.2815	90.3868
A23	A(5,4,10)	126.8397	127.2868	127.3033	127.2603
A24	A(8,4,10)	124.5435	124.9308	124.8827	124.829
A25	A(1,5,4)	89.8648	90.0007	90.0018	90.0002
A26	A(1,5,7)	90.3616	90.2565	90.2819	90.3908
A27	A(1,5,12)	125.9455	127.2897	127.3101	127.2662
A28	A(4,5,7)	89.8055	89.7412	89.716	89.6063
A29	A(4,5,12)	124.1205	123.5173	123.5519	123.6447
A30	A(7,5,12)	125.6805	124.9254	124.8679	124.8164
A31	A(1,6,2)	89.8071	89.741	89.7149	89.6023
A32	A(1,6,7)	90.3609	90.2564	90.2815	90.3923
A33	A(1,6,31)	125.6781	124.9287	124.8793	124.8284
A34	A(2,6,7)	89.8648	89.9994	89.9975	90.0028
A35	A(2,6,31)	124.1255	123.5166	123.5494	123.6506
A36	A(7,6,31)	125.9424	127.2883	127.3054	127.2488
A37	A(5,7,6)	89.6348	89.7414	89.7159	89.6048
A38	A(5,7,8)	90.1934	90.2566	90.2816	90.3901
A39	A(5,7,13)	124.5536	124.9275	124.8706	124.8207
A40	A(6,7,8)	90.1338	90.0006	90.0025	89.9999
A41	A(6,7,13)	124.3878	123.5165	123.5512	123.6678
A42	A(8,7,13)	126.8406	127.2883	127.308	127.242
A43	A(2,8,4)	90.3615	90.2564	90.2818	90.3924
A44	A(2,8,7)	89.8655	89.9994	89.9974	89.9985
A45	A(2,8,14)	125.9595	127.2882	127.3034	127.2379
A46	A(4,8,7)	89.8047	89.741	89.7153	89.606
A47	A(4,8,14)	125.6657	124.9288	124.8812	124.8255
A48	A(7,8,14)	124.1214	123.5166	123.5491	123.6656
A49	A(3,9,16)	116.0589	116.4115	116.4086	116.7776
A50	A(3,9,18)	115.8251	114.5683	114.5726	114.578

A51	A(16,9,18)	128.0695	128.9995	128.9964	128.6249
A52	A(4,10,15)	116.8077	116.409	116.4038	116.7791
A53	A(4,10,17)	115.1066	114.5707	114.5772	114.5763
A54	A(15,10,17)	128.0848	128.9994	128.9965	128.6233
A55	A(2,11,19)	115.1073	114.5695	114.5734	114.5765
A56	A(2,11,32)	116.8107	116.4103	116.4076	116.7681
A57	A(19,11,32)	128.0811	128.9995	128.9964	128.6343
A58	A(5,12,24)	116.0513	116.4114	116.409	116.7846
A59	A(5,12,26)	115.8328	114.5682	114.5719	114.5729
A60	A(24,12,26)	128.0693	128.9994	128.9965	128.6239
A61	A(7,13,21)	116.8097	116.4103	116.4076	116.7778
A62	A(7,13,23)	115.1068	114.5696	114.5736	114.5731
A63	A(21,13,23)	128.0826	128.9994	128.9962	128.6272
A64	A(8,14,20)	115.8216	114.5695	114.5769	114.5763
A65	A(8,14,22)	116.0609	116.4103	116.4044	116.7689
A66	A(20,14,22)	128.0705	128.9994	128.9962	128.632
A67	A(1,28,25)	115.1064	114.5707	114.5779	114.5812
A68	A(1,28,27)	116.8102	116.4089	116.4032	116.7745
A69	A(25,28,27)	128.0825	128.9993	128.9962	128.6221
A70	A(6,31,29)	115.8323	114.5695	114.5758	114.5695
A71	A(6,31,30)	116.0512	116.4103	116.4053	116.7802
A72	A(29,31,30)	128.0696	128.9995	128.9963	128.6305

In the above Table, in column 1, $R_{1,2,3,....}$ represents the bond lengths and serial numbers and $A_{1,2,3,....}$ represents the bond angles and serial numbers. In column 2, for example R(1,3) represents the bond length between atoms 1 and 3 and A(1,3,5) represents the bond angle between atoms 1,3 and 5. Columns 3,4 and 5 represents the calculated bond lengths and bond angles at the RHF level of theory using the 6-31G, 6-31++G** and 6-311++G** basis sets respectively. Column 6 represents the calculated bond lengths and bond angles at the B3LYP level of theory using the 6-31++G** basis set.
μ =Dipole moment
E_1=Total Electronic Energy without zero point correction.
E_2=Total Electronic Energy with zero point correction.
E_3=Total Electronic Energy with Thermal energies.
E_4=Total Electronic Energy with enthalpies.
P= Polarizability of the Tensor components.

Row 1 represents the values of the dipole moment calculated at the RHF level of theory using the 6-31G, 6-31++G**, 6-311++G** basis sets and at the B3LYP level of theory using the 6-31++G** basis set. Rows 2,3,4 columns 2,3,4 represents the energy values calculated at the RHF level of theory using the 6-31G, 6-31++G** and 6-311++G** basis sets respectively. Row 2,3,4 column 5 represents the energy values calculated at the B3LYP level of theory using the 6-31++G** basis set.
Below the Polarizability (P), column 1 represents the Polarizability tensor components. Columns 2,3,4 represents the Polarizability calculated at the RHF level of theory using the 6-31G, 6-31++G** and 6-311++G** basis sets respectively. Column 5 represents the Polarizability calculated at the B3LYP level of theory using the 6-31++G** basis set.

Table 3: **Electrostatic Potential Derived Charges on different atomic positions of Octanitrocubane**

	Method/basis set	RHF/		B3LYP/	
S.N		**6-31G**	**6-31++G****	**6-311++G****	**6-31++G****
1	C	0.238449	0.069785	0.049945	0.052739
2	C	0.232654	0.063023	0.053506	0.037458
3	C	-0.127905	0.058693	0.053719	0.067124
4	C	0.232173	0.061558	0.053050	0.049610
5	C	-0.136421	0.064579	0.058231	0.044338
6	C	-0.138011	0.058103	0.054590	0.046325
7	C	0.243353	0.065079	0.053052	0.052473
8	C	-0.131621	0.070094	0.053818	0.052977
9	N	0.824607	0.646757	0.693498	0.533660
10	N	0.779469	0.637004	0.690554	0.541478
11	N	0.777428	0.641679	0.696138	0.542895
12	N	0.821546	0.637276	0.689793	0.544546
13	N	0.774862	0.637819	0.695057	0.544740
14	N	0.823444	0.637320	0.695762	0.539233
15	O	-0.417087	-0.347069	-0.368058	-0.294659
16	O	-0.425527	-0.350145	-0.368058	-0.293446
17	O	-0.434737	-0.354171	-0.377258	-0.297742
18	O	-0.429116	-0.357637	-0.378043	-0.296146
19	O	-0.433978	-0.356269	-0.377863	-0.297686
20	O	-0.428445	-0.354973	-0.377497	-0.297519
21	O	-0.416811	-0.347811	-0.371103	-0.295061
22	O	-0.424725	-0.348170	-0.371317	-0.292573
23	O	-0.433519	-0.354908	-0.377379	-0.299042
24	O	-0.424165	-0.347988	-0.368501	-0.294924
25	O	-0.433991	-0.357719	-0.378450	-0.298239
26	O	-0.427175	-0.354515	-0.377173	-0.298616
27	O	-0.417656	-0.351047	-0.369750	-0.294720
28	N	0.777644	0.644569	0.695285	0.541847
29	O	-0.428302	-0.356582	-0.377591	-0.300027
30	O	-0.425288	-0.348765	-0.371163	-0.295616
31	N	0.825297	0.643127	0.695471	0.547601
32	O	-0.416446	-0.348694	-0.371360	-0.293028

In this table (3), column 1 represents the serial number of the atoms as shown on the diagram; column 2 represents the symbols for the atoms. Columns 3,4,5 represents the charges calculated at the RHF level of theory using the 6-31G, 6-31++G** and 6-311++G** basis sets respectively. Column 6 represents the charges calculated at the B3LYP level of theory using the 6-31++G** basis set.

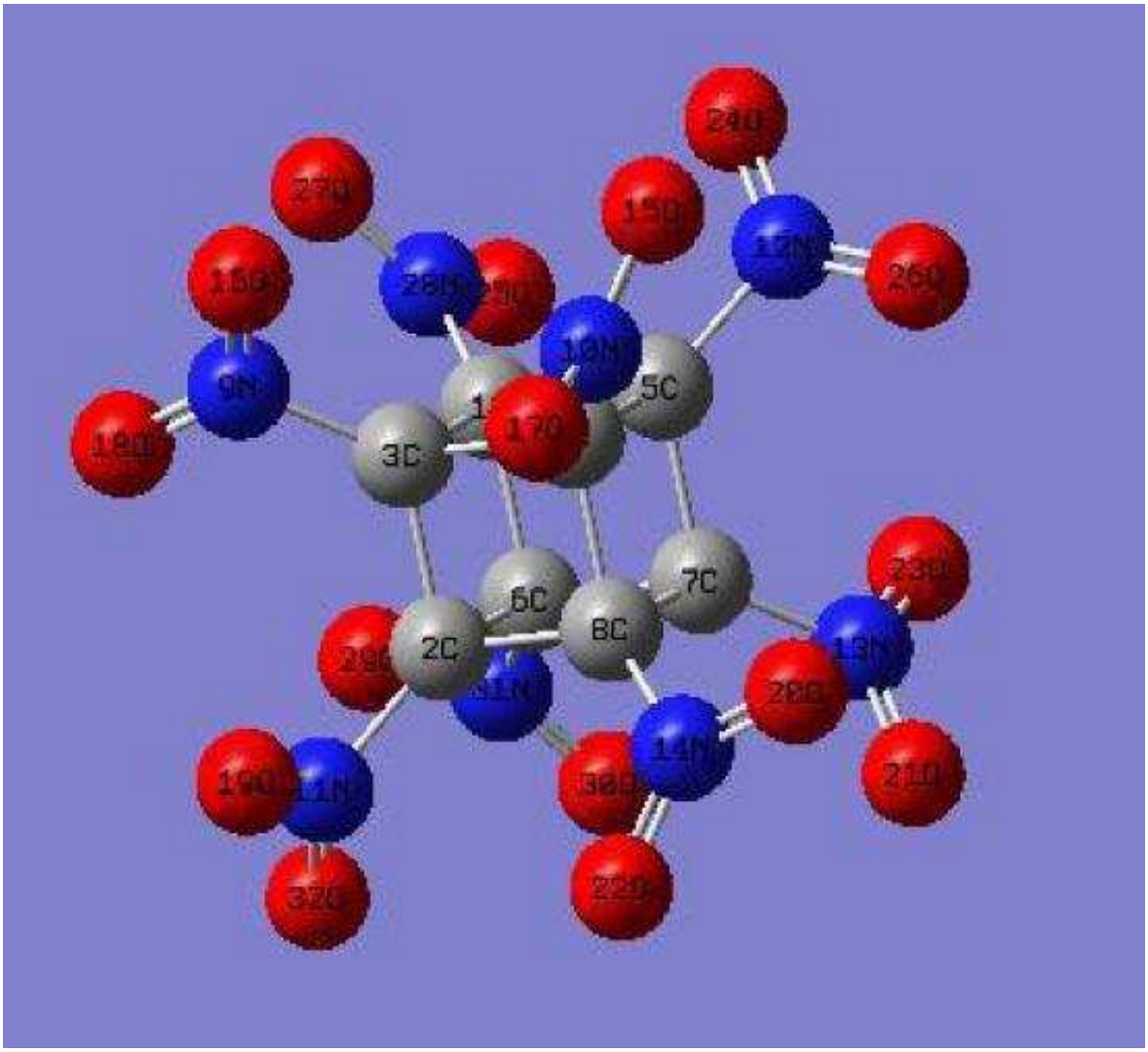

Fig. 1 Molecular Structure of octanitrocubane.

Conclusions

Ab-initio quantum mechanical and density functional calculations have been performed with different basis sets for the Octanitrocubane. We have studied the structure, energy, charges dipole moment and Polarizability Octanitrocubane molecule. We have seen that the charges on the same label atoms have same sign both at RHF and
B3LYP levels for of theories except for the 6-31G basis set. The mulliken populations analysis obviously demonstrates that the C-C bonds are the weakest, indicating that the cubic cage skeleton is the most reactive part of the molecule. The high electronic density at the centre of the cubic cage attributes some stabilization to the molecule. The magnitude of the dipole moment is higher in the RHF level and the Polarizability of the tensor components is greater at the B3LYP level.

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