Electronic Supplementary Information (ESI):

Application of silver nanoparticles for highly selective colorimetric assay of endrin in water and food samples based on stereoselective endo-recognition

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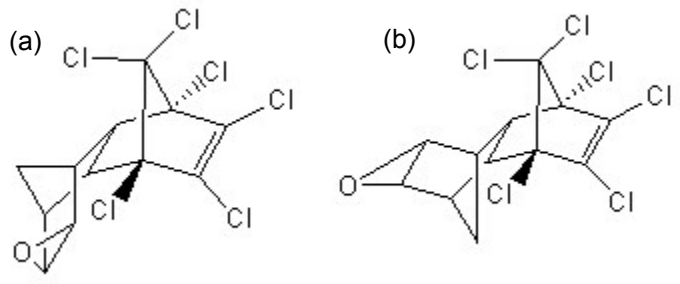


Fig. S1. Structure of (a) endrin (1R, 2S, 3R, 6S, 7R, 8S, 9S, 11R)-3, 4, 5, 6, 13, 13-Hexachloro-10-oxapentacyclo [6.3.1.13,6.02,7.09,11] tridec-4-eneis) and (b) dieldrin pesticide (1a*R*, 2*R*, 2a*S*, 3*S*, 6*R*, 6a*R*, 7*S*, 7a*S*)-3, 4, 5, 6, 9, 9-hexachloro-1a, 2, 2a, 3, 6, 6a, 7, 7a-octahydro-2, 7:3 ,6-dimethanonaphtho [2,3-*b*]oxirene)

Sample preparation for determination of endrin in food samples

Food samples such as rice, wheat and potato were collected from nearby region of Bilaspur, city for the detection of endrin. The obtained samples were dried in oven at 80 ^{o}C overnight and 5 g of samples was grounded into a fine powder with help of grinder. The fine powder (1 g) of food samples was mixed with 1:1 acetone and water solution. The solution mixture was filtered and obtained food sample was used for the detection of endrin and recovery studies using AgNPs as a colorimetric probe.

Optimization for the detection of endrin using AgNPs-based colorimetric assay

Metal NPs are found unstable if the surface is not stabilized by capping agent and consequently, a surface stabilizer is required to prevent the self aggregation of NPs in aqueous solution.[1] Therefore, the surface of AgNPs was modified with glucose or sucrose for detection of endrin by mixing an equal volume of NPs and aqueous solution containing a pesticide (1.0 μgmL^{-1}). The results are shown in ESI Fig S2. The sucrose capped AgNPs showed a higher value of LSPR absorption ratio for the detection of endrin compared to bare and glucose capped NPs. The reason for obtaining a higher value of LSPR absorption ratio with sucrose capped AgNPs was due to the presence of higher number of carbon atom in molecule compared to glucose capped NPs. The increase in absorption ratio was because of the number carbon atom present in capping agent that also reported elsewhere in the literature.[2] Thus, further experiments were performed using sucrose capped AgNPs as a colorimetric probe for detection of endrin.

Next, addition of different organic solvent such as methanol, ethanol and acetone in to the aqueous solution were tested for detection of endrin using sucrose capped AgNPs as a colorimetric probe. For this, 0.5 mL of methanol, ethanol and acetone were added to separate glass bottle containing a 0.5 mL aqueous solution of endrin (1.0 μgmL^{-1}) followed by the

addition AgNPs. The optimum LSPR absorption ratio was obtained when acetone used as an organic solvent. The reason for obtaining a higher value of LSPR absorption ratio was due to the solubility of the pesticide when acetone was used as an organic solvent compared to methanol and ethanol.[3] We have also performed blank experiment in the absence of endrin to test whether the addition of acetone cause the aggregation of NPs. We found there was no any color change and shift in LSPR absorption band of AgNPs in UV-visible region, only decrease in the color intensity was obtained due to the dilution of the NPs solution. The results are shown in ESI Fig. S3 (a) and S3(b). Therefore, the use of acetone did not cause any aggregation of NPs. The use of organic solvent along with aqueous solution containing an endrin caused a synergic effect to interact with NPs surface to enhance the LSPR absorption ratio. Afterwards, the volume ratio of aqueous to organic solvent (acetone) was optimized for better detection of pesticide. Different volume ratio of aqueous/acetone from 10:0 to 1:9 was added to the separate glass bottle containing endrin and AgNPs. The results are shown in ESI Fig. S4. The absorption ratio was increased with increasing the volume ratio of aqueous and acetone from 10:0 to 7:3. The increase in volume of organic solvent could increase the solubility of pesticide that induced the interactions of endrin to the NPs surfaces. After, more addition of aqueous to acetone volume ratio from 6:4 to 1:9 caused a decrease in the absorption ratio. Therefore, 7:3 volume ratio of aqueous to acetone was fixed to get an optimum detection of endrin.

Finally, the different sets of experiments were implemented to check the effect of pH on detection of endrin. For this, the pH of the sample solution (1.0 μgmL^{-1} of endrin) was changed from 2.0 to 11.0 using 0.1 M HCl and 0.1 M NaOH solution. After, 1 mL of AgNPs was added to the sample solution and kept for 5 min of reaction time at room temperature. The solution mixture containing NPs solution and endrin with different pH are shown in Fig. S5(a) to S5(f), along with their respective UV-visible spectra. The LSPR absorption ratio was enhanced when

the pH of the sample solution increased from 2.0 to 7.0 and after decrease in their ratio was obtained. At pH 7.0, the optimum increase in LSPR absorption ratio was obtained, because the neural pH favored the interactions of endrin to surface of AgNPs and result the maximum aggregation of NPs. At higher acidic pH (2.0), the color of solution mixture changed to bluish due to the self agglomeration of NPs. The self aggregation of NPs at higher pH is also reported elsewhere in the literatures.[4,5] Higher basic solution was not found good for the detection of endrin because decrease in LSPR absorption ratio. Therefore, 7.0 pH was found good for effective detection of endrin from sample solution.

1 B. Zargar and A. Hatamie, *Sens. Actuators B*, 2013, **182**, 706– 710.

2 S. K. Ghosh, S. Nath, S. Kundu, K. Esumi and T. Pal, *J. Phys. Chem. B*, 2004, **108**, 13963-13971.

3 The United Nations Environment Programme, The International Labour Organisation, The World Health Organization, (http://www.inchem.org/documents/ehc/ehc/ehc130.htm), 1992.

4 S. K. Laliwala, V. N. Mehta, J. V . Rohit and S. K. Kailasa, *Sens. Actuators B*, 2014, **197,** 254–263.

5 S. Basu, S. K. Ghosh, S. Kundu, S. Panigrahi, S. Praharaj, S. Pande, S. Jana and T. Pal, *J. Colloid Interface Sci.*, 2007, **313**,724–734.

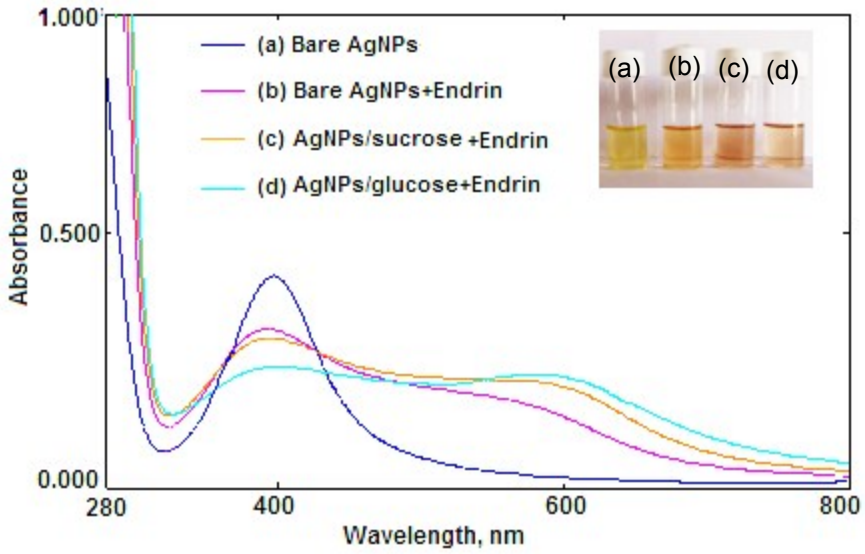


Fig. S2. Effect of (a) bare, (b) glucose and (c) sucrose capped AgNPs for the detection of endrin witht pH 7.0 for 5 min of reaction time at room temperature

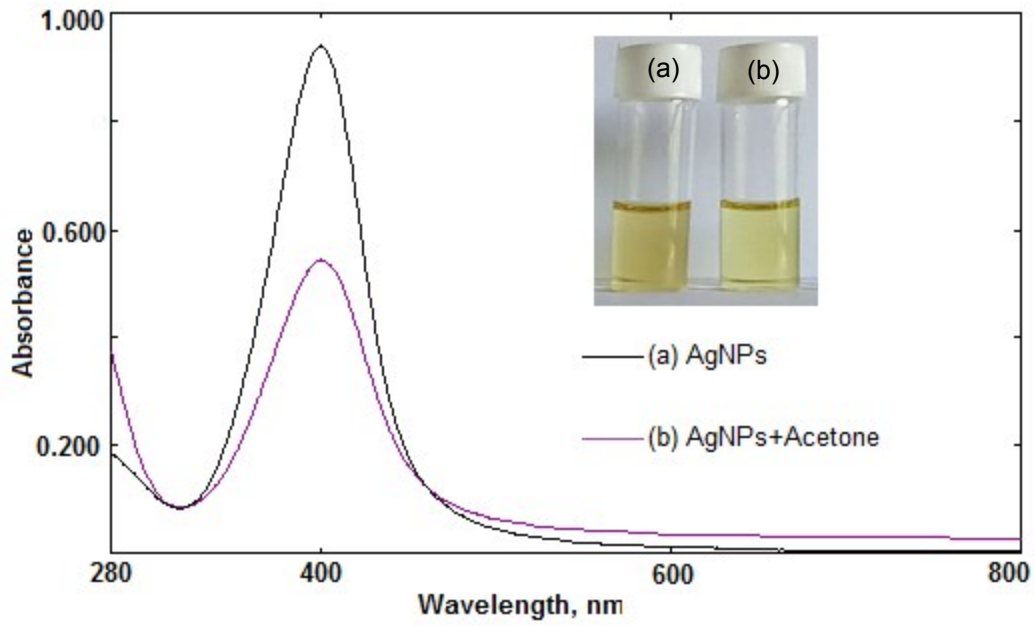


Fig. S3. Photographs of glass vials containing (a) 2 mL of AgNPs, (b) 1 mL of AgNPs and 1 mL acetone without addition of endrin

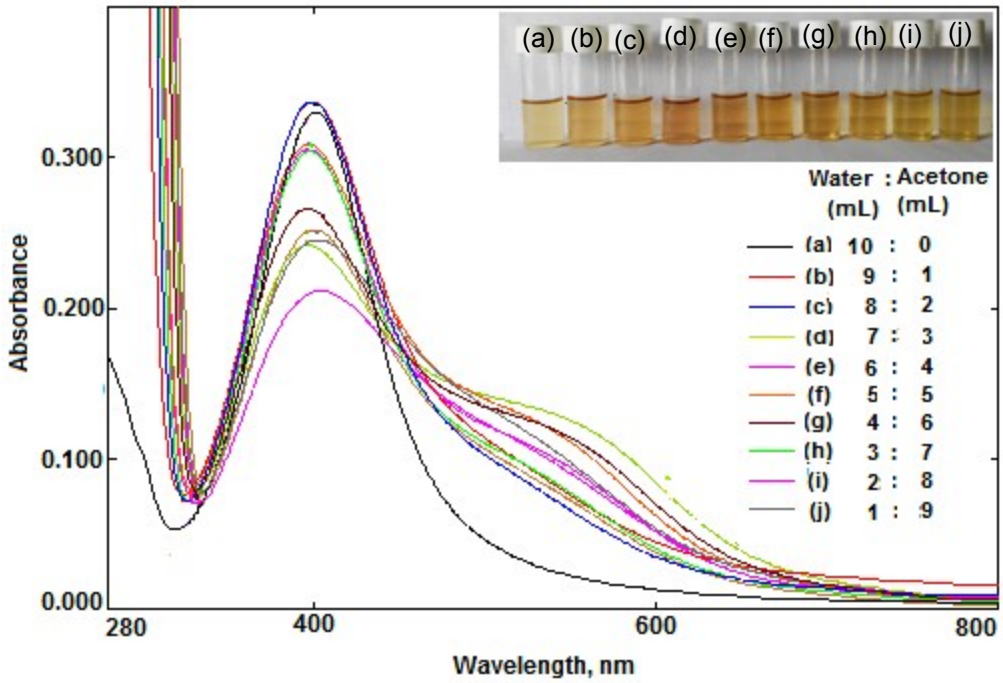


Fig. S4 Photographs of glass vials containing AgNPs and different volume ratios of water and acetone from 10:0 to 1:9 for the detection of endrin (1 μgmL^{-1}) using NPs as a colorimetric probe at pH 7.0 for 5 min of reaction time at room temperature

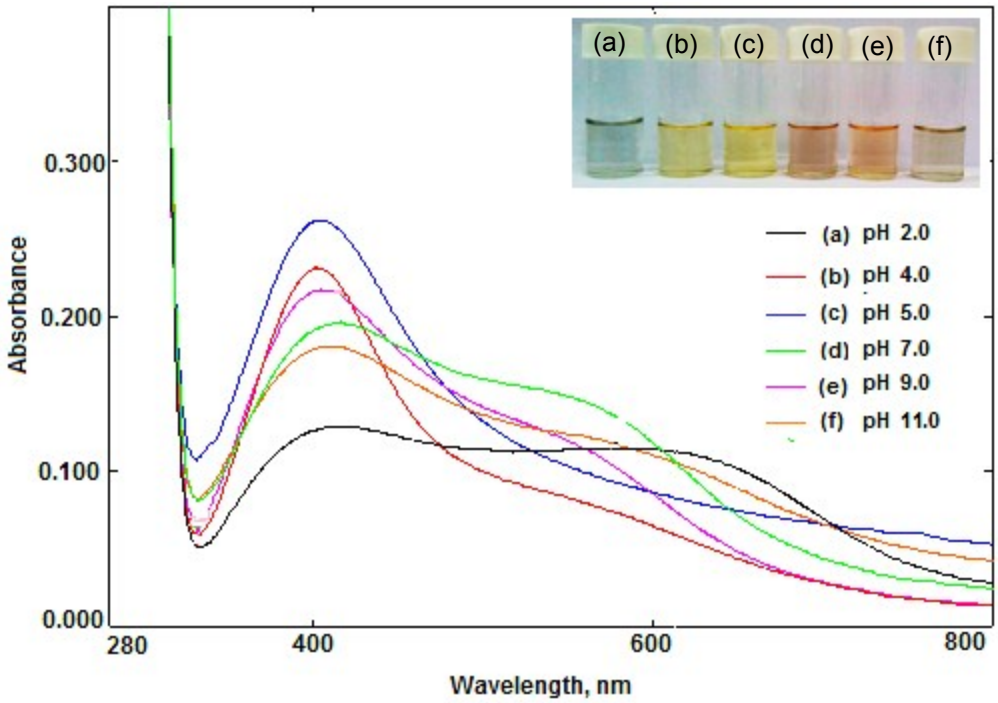


Fig. S5. Photographs of glass vials containing AgNPs and pH solution (2.0, 4.0, 5.0, 7.0, 9.0 and 11.0) for detection of endrin (1 μgmL^{-1}) using AgNPs as a colorimetric probe with pH 7.0 for 5 min of reaction time at room temperature

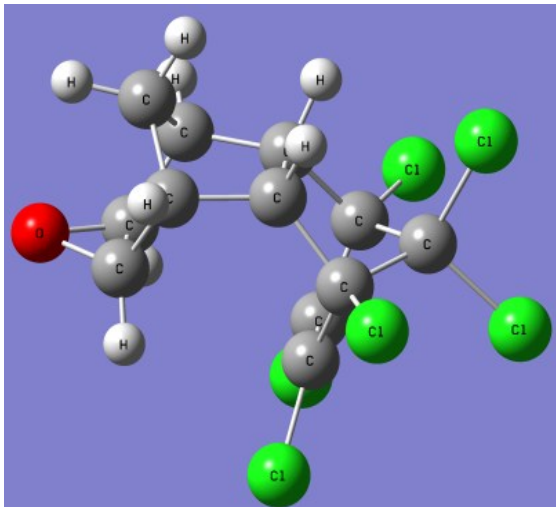
Gaussian 09 Program with DFT method (B3LYP and 6-31(d) basis set) was used for theoretical calculations of geometry optimization, charge distribution of endrin and dieldrin, sucrose and interaction between NPs and silver atom.

Structure of Endrin:

Optimized at B3LYP/6-31(d), Cartesian coordinates in Å

Symbol	X	Y	Z
C	2.718125	-0.005521	-2.111867
C	-0.444974	-1.133921	-0.23607
C	-0.063974	-0.666135	1.152783
C	2.177559	-1.136107	-1.184172
C	-0.064289	0.673857	1.148192
C	2.176256	1.131885	-1.190135
C	-0.446277	1.132071	-0.242027
C	-1.499694	-0.002902	-0.548858
C	0.666263	0.78643	-1.281524
C	2.779155	0.745557	0.146541
C	2.780351	-0.744438	0.150413
C	0.667471	-0.792564	-1.277412
H	0.336732	1.12872	-2.273873
H	2.276186	-0.008276	-3.114681
H	3.808615	-0.005636	-2.210322
H	2.432773	2.140042	-1.518203
H	2.569819	-1.350159	1.009955
H	2.568456	1.355831	1.002816
H	0.338166	-1.141269	-2.266913
H	2.433362	-2.146942	-1.506685
O	4.006097	0.000673	0.127925
Cl	-2.948537	-0.000192	0.53391
Cl	-2.152951	-0.007483	-2.220781
Cl	0.145562	1.709461	2.477391
Cl	0.147021	-1.693527	2.486403
Cl	-1.04953	-2.77238	-0.373798
Cl	-1.052667	2.769593	-0.3914

Charge: 0
Multiplicity: 1
Solvation: gas phase
Electronic energy: -3298.36079942 a.u.



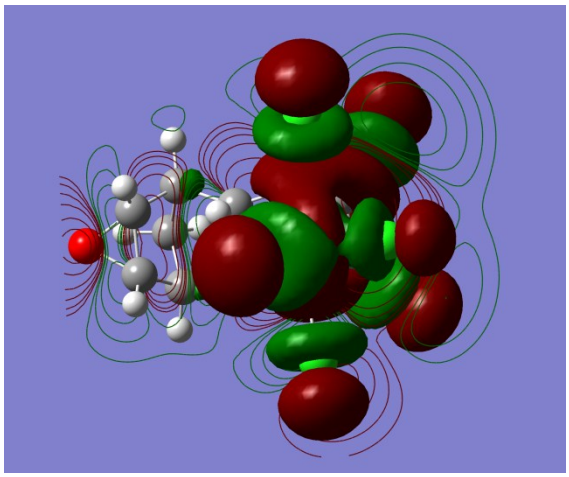
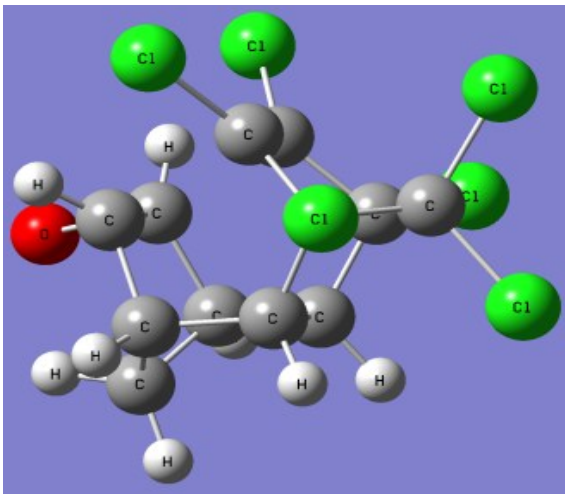


Fig1 : HOMO and LUMO of endrin

Structure of Dieldrin:

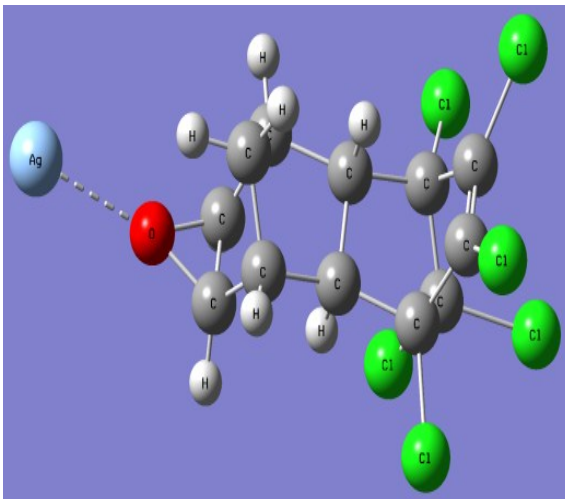
Optimized at B3LYP/6-31(d), Cartesian coordinates in Å



Charge: 0
Multiplicity: 1
Solvation: gas phase
Electronic energy: -3298.11467076 a.u.

Symbol	X	Y	Z
Cl	1.2961	-2.627317	0.058972
Cl	1.089516	2.874369	0.129703
Cl	2.741701	0.074004	1.422467
Cl	2.443416	-0.098802	-1.475845
Cl	-1.07891	-1.764953	-1.983265
Cl	-1.36002	1.802122	-1.969031
O	-3.31258	-0.262884	0.449483
C	-0.03914	-0.738617	1.581006
C	-0.15182	0.818141	1.534594
C	-1.48212	-1.259025	1.583877
C	-1.69218	0.995062	1.63397
C	-2.10954	-0.927229	0.20149
C	-2.22782	0.626467	0.229279
C	-2.13413	-0.199815	2.4443
C	0.592255	-1.021871	0.221953
C	0.533514	1.200111	0.183253
C	1.617739	0.104916	0.069125
C	-0.46899	-0.593297	-0.81817
C	-0.44391	0.73206	-0.909318
H	0.590361	-1.089762	2.440446
H	0.358631	1.34558	2.390216
H	-1.59599	-2.293803	1.906933
H	-2.00696	2.002797	1.97559
H	-2.15183	-1.601556	-0.657382
H	-2.90278	1.317681	-0.275449
H	-1.78273	-0.122098	3.473173
H	-3.21195	-0.287397	2.307439

Structure of Eldrin with silver

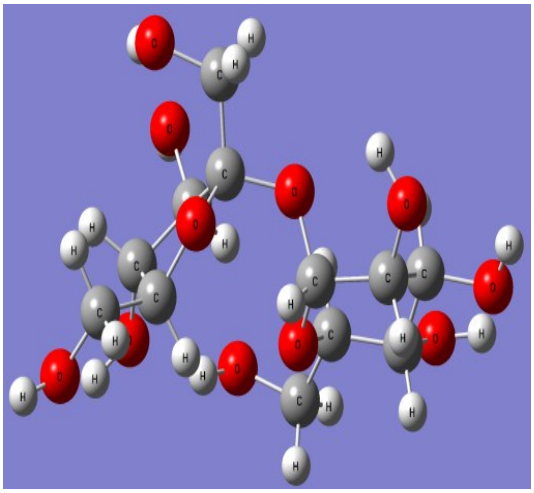


Optimized at HF/6-21G, Cartesian coordinates in Å

Charge: 0
Spin: Doublet
Solvation: gas phase
Electronic energyUHF : -8448.35058332 a.u.

Symbol	X	Y	Z
C	0.309478	-0.553476	-0.557073
C	1.764404	-1.112826	-0.258855
C	2.557302	-0.226821	-1.228316
C	2.501718	1.00513	-0.788191
C	0.255454	0.66306	0.376359
C	1.75857	1.012545	0.532359
C	2.217758	-0.411364	1.037026
Cl	4.025988	-0.520263	1.342172
Cl	1.429051	-1.075172	2.562136
Cl	2.111032	2.390092	1.660409
Cl	3.104603	2.459344	-1.582724
Cl	3.221868	-0.802634	-2.752839
C	-1.159663	1.287794	0.011862
C	-1.209067	-0.938306	-0.657826
C	-1.957912	0.533973	1.102189
C	-1.624604	0.471427	-1.227699
C	-1.894698	-0.890947	0.708422
O	-3.184077	-0.147546	0.657735
Cl	2.034902	-2.897612	-0.37586
H	0.460375	-0.192874	-1.557948
H	0.071655	0.294387	1.362641
H	-1.257568	2.357418	-0.021648
H	-1.435569	-1.790474	-1.27464
H	-1.965906	0.869126	2.117419
H	-1.10565	0.720375	-2.138854
H	-2.683525	0.561305	-1.383933
H	-1.870317	-1.703786	1.399593
Ag	-5.459998	0.055529	-0.26749

Structure of Sucrose



Optimized at RB3LYP/6-31(+), Cartesian coordinates in Å

Charge: 0
Multiplicity: singlet
Solvation: gas phase
Electronic energy: -1297.57061481 a.u.

Symbol	X	Y	Z
O	0.903611	0.719874	-0.800009
C	1.814096	1.30404	0.222462
C	0.91359	-0.717717	-0.918289
C	1.510544	2.79218	0.264842
C	3.23993	0.905478	-0.153961
O	4.139399	1.48867	0.827413
C	3.331675	-0.618377	-0.127741
C	2.339113	-1.256454	-1.100933
O	4.70162	-0.95833	-0.492113
O	2.384077	-2.707066	-0.989865
O	0.356915	-1.369577	0.254287
O	0.270103	3.051755	0.980426
C	-1.097923	-1.233647	0.477908
C	-1.438146	0.134066	1.143348
O	-1.794906	-1.248739	-0.792345
C	-1.478429	-2.48008	1.274678
C	-2.508783	0.764052	0.251064
O	-1.897646	-0.074857	2.515891
C	-2.32154	0.089214	-1.113091
O	-2.313288	2.206213	0.17241
C	-3.614964	-0.066002	-1.889856
O	-2.855764	-2.443893	1.717258
O	-4.141876	1.308221	-1.965938
H	1.575624	0.874169	1.20258
H	0.287322	-0.937284	-1.781642
H	2.293509	3.296657	0.832842
H	1.478214	3.199711	-0.753876
H	3.491916	1.275056	-1.157414
H	5.031735	1.098776	0.717302
H	3.130972	-0.966644	0.894803
H	2.661786	-1.03434	-2.122047
H	4.802527	-1.929304	-0.567228
H	1.766586	-2.989057	-0.280297
H	-0.547663	2.869548	0.457702

H	-0.558604	0.771007	1.166086
H	-1.388333	-3.344948	0.616364
H	-0.788787	-2.583538	2.119083
H	-3.500816	0.547919	0.663426
H	-1.686023	0.696116	3.076039
H	-1.582529	0.648989	-1.696665
H	-2.988632	2.582943	-0.431187
H	-3.435615	-0.469206	-2.891872
H	-4.308924	-0.716622	-1.346235
H	-2.942492	-1.738658	2.396146
H	-4.944716	1.370014	-2.515811

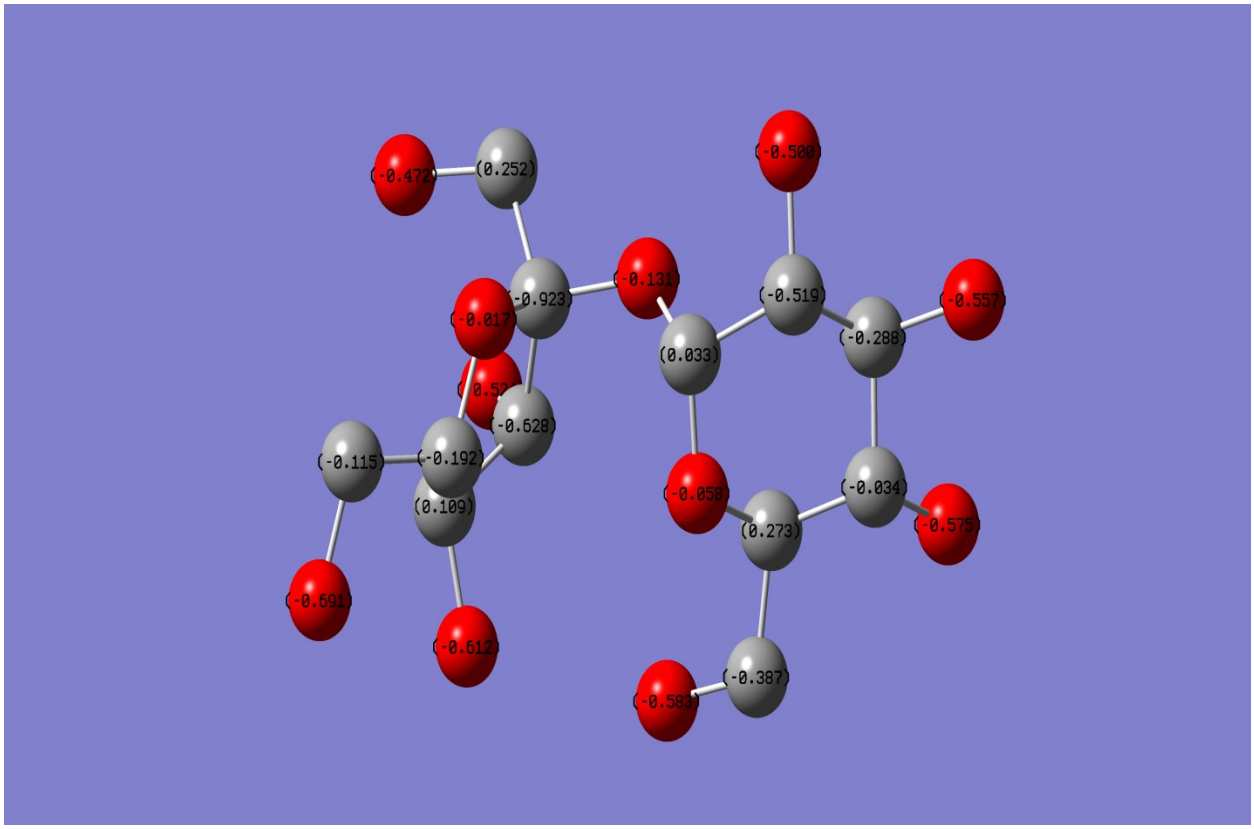


Fig. S6. Gaussian 09 Program with DFT method (B3LYP and 6-31(d) basis set) was used for theoretical calculations of geometry optimization and electron charge distribution. Optimized structure of sucrose with charge distribution on each atom varied from -0.017 to -0.691.