Structural and electronic properties of some derivatives of C_{20}

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Full geometry optimizations are accomplished without any symmetry constraints by means of hybrid functional B3LYP [1-3] and the 6-31+G* basis set, as implemented in Gaussian 98 [4]. The applied basis set is comprised of Pople's well known 6-31G* basis set [5,6] and an extra plus due to the importance of diffuse functions [7,8]. Vibrational frequency computations confirm that the fully optimized structures are indeed minima (NIMAG = 0). To obtain more accurate energetic data, single point calculations are performed at B3LYP/6-311++G** level. As a stability criterion of different configurations, binding energies are calculated according to the following expression:

$$E_b = 20EC + 8EX – E$$

where E is the total energy of the $C_{20}X_8$ heterofullerene. Systems with larger binding energies are more stable. The electronic conductivity of the fullerenes which is related to the HOMO-LUMO energy gaps were considerably influenced by exohedral derivatives. The NBO population analysis on optimized structures is accomplished at the B3LYP/6-311++G**//B3LYP/6-31+G* level [9].

The smallest possible fullerenes cage, i.e. C_{20}, taken into account of exohedral derivatives through our previously reported isolation strategy. The exohedral derivatives atoms are replaced at eight selected symmetric positions of C_{20}. Probing heterofullerenes $C_{20}X_8$ where X = H, OH, CN, F, Cl and Br reveals that all the systems are true minima. Calculated binding energy of 216.54 eV show $C_{20}(CN)_8$ as the most stable heterofullerene followed by $C_{20}(OH)_8$ with the binding energy of 185.32 eV. The binding energies of the other heterofullerenes ranges from 138.45 to 153.55 eV. Exohedral derivatives leads to a high charge distribution on the surfaces of all heterofullerenes with the highest distribution on $C_{20}(OH)_8$ with +0.197 charged carbons and -0.711 charged O atoms. These high point charges upon the heterofullerenes surface can improve the storage capacity since make them worthy of investigation for hydrogen storage. All exohedral derivatives increase the HOMO-LUMO gap leading to the enhanced stability against electronic excitations. On the other hand, all exohedral derivatives decrease the conductivity of fullerene through increasing their HOMO-LUMO gap.

Table1.Point groups (PG), total energies (E_{tot} in a.u.), ranges of C-C and X–C bond lengths (Å) and C–C–X angles (º) for the scrutinized heterofullerenes along with C_{20} at the B3LYP/6-31+G* level. Binding energies (B.E.) and the smallest vibrational frequencies (v_{min}) , HOMO-LUMO energy gaps (ΔE_{H-L} (eV)) at B3LYP/6-311++G**.

Species	PG	E_{tot} (a.u.)	C-C	X-C	C-C-X	B.E. (eV)	v_{min} (cm^{-1})	ΔE_{H-L} (eV)
C_{20}	C_i	-761.6	1.40-1.53	-	-	121.27	32	1.89
$C_{20}H_8$	T_h/C_1	-766.7	1.35-1.54	1.09	118.8	152.25	474	5.67
$C_{20}(OH)_8$	T_h/C_1	-1368.6	1.35-1.54	1.40	120.7	185.32	182	5.08
$C_{20}(CN)_8$	T_h/C_1	-1504.7	1.34-1.54	1.16	119.2	216.54	85	5.60
$C_{20}F_8$	T_h/C_1	-1560.8	1.35-1.53	1.37	118.1	153.54	192	5.11
$C_{20}Cl_8$	T_h/C_1	-4443.7	1.35-1.53	1.79	118.6	142.38	108	5.06
$C_{20}Br_8$	T_h/C_1	-21355.1	1.35-1.52	1.96	118.3	138.44	61	4.74

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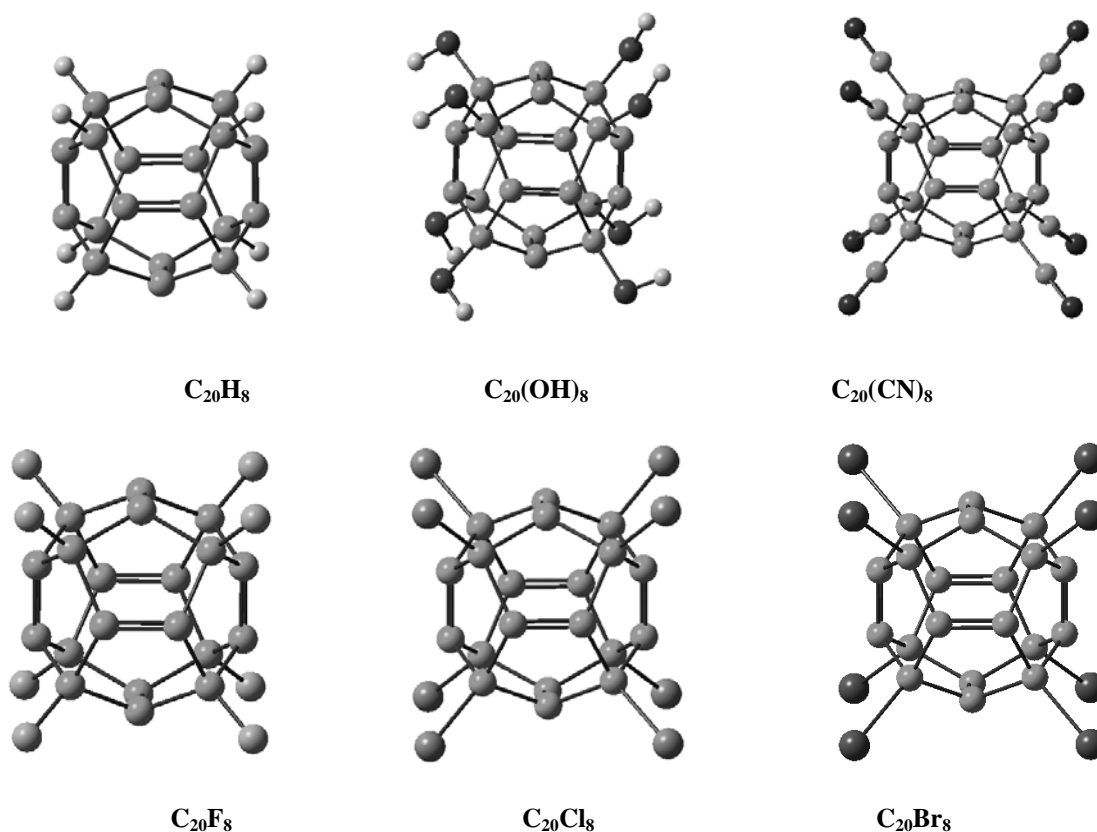[9] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1.

$C_{20}H_8$ $\qquad$ $C_{20}(OH)_8$ $\qquad$ $C_{20}(CN)_8$

$C_{20}F_8$ $\qquad$ $C_{20}Cl_8$ $\qquad$ $C_{20}Br_8$

Fig. 1. Optimized heterofullerenes at B3LYP/6-31+G.