Supplementary Information

An exotic 3-center/4-electron carbon-carbon *pi* long-bond: Is it tangible?

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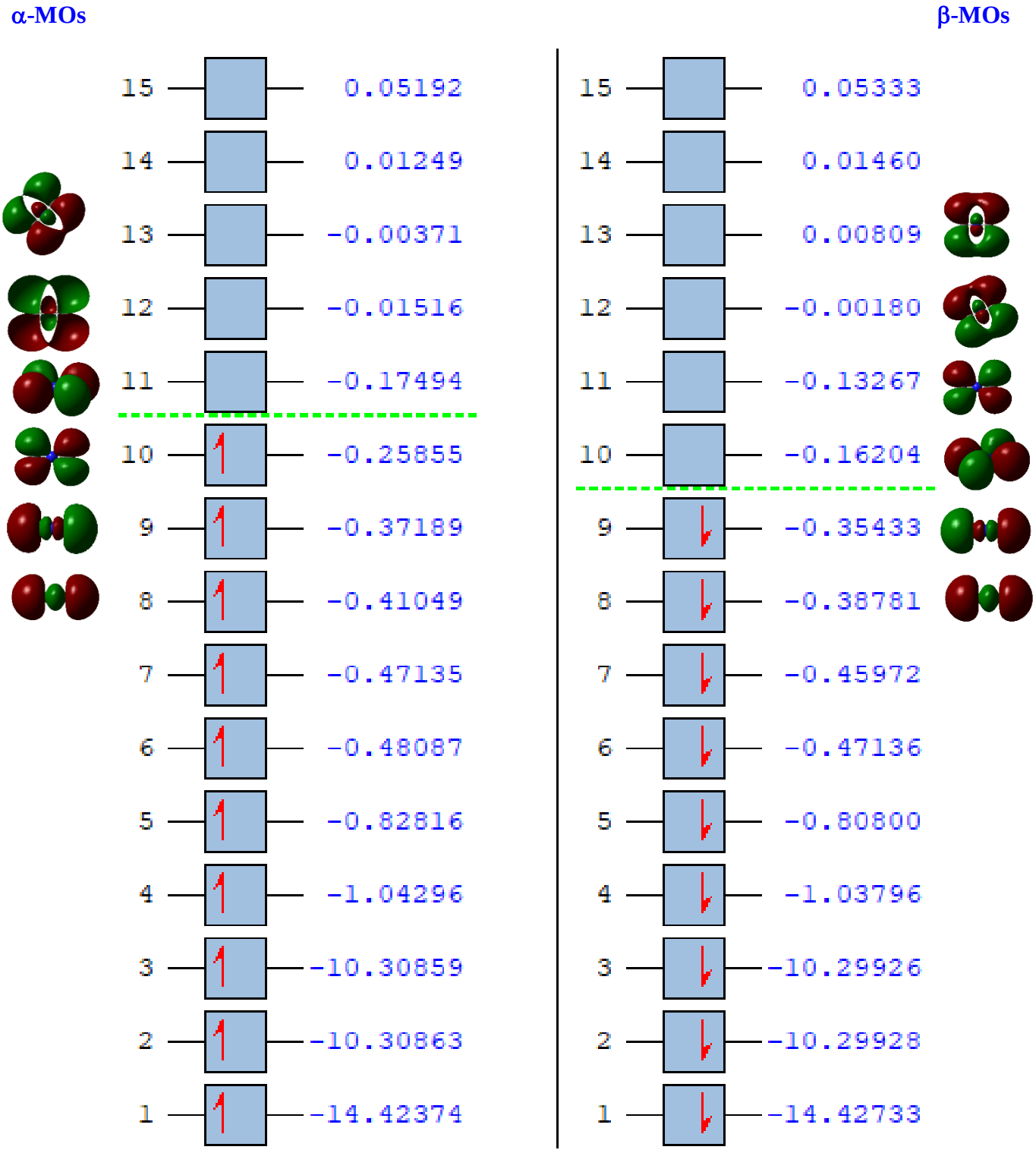
Table S1. T1 diagnostic values for C_2N, C_2O at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) level of the theory, and for C_6N, C_6O, C_8N at CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of the theory.

Species[a]	T1
C_2N (doublet)	0.031
C_2O (singlet)	0.022
C_2O (triplet)	0.031
C_6N (doublet)	0.042
C_6O (singlet)	0.024
C_8N(3,5) (doublet)	0.062

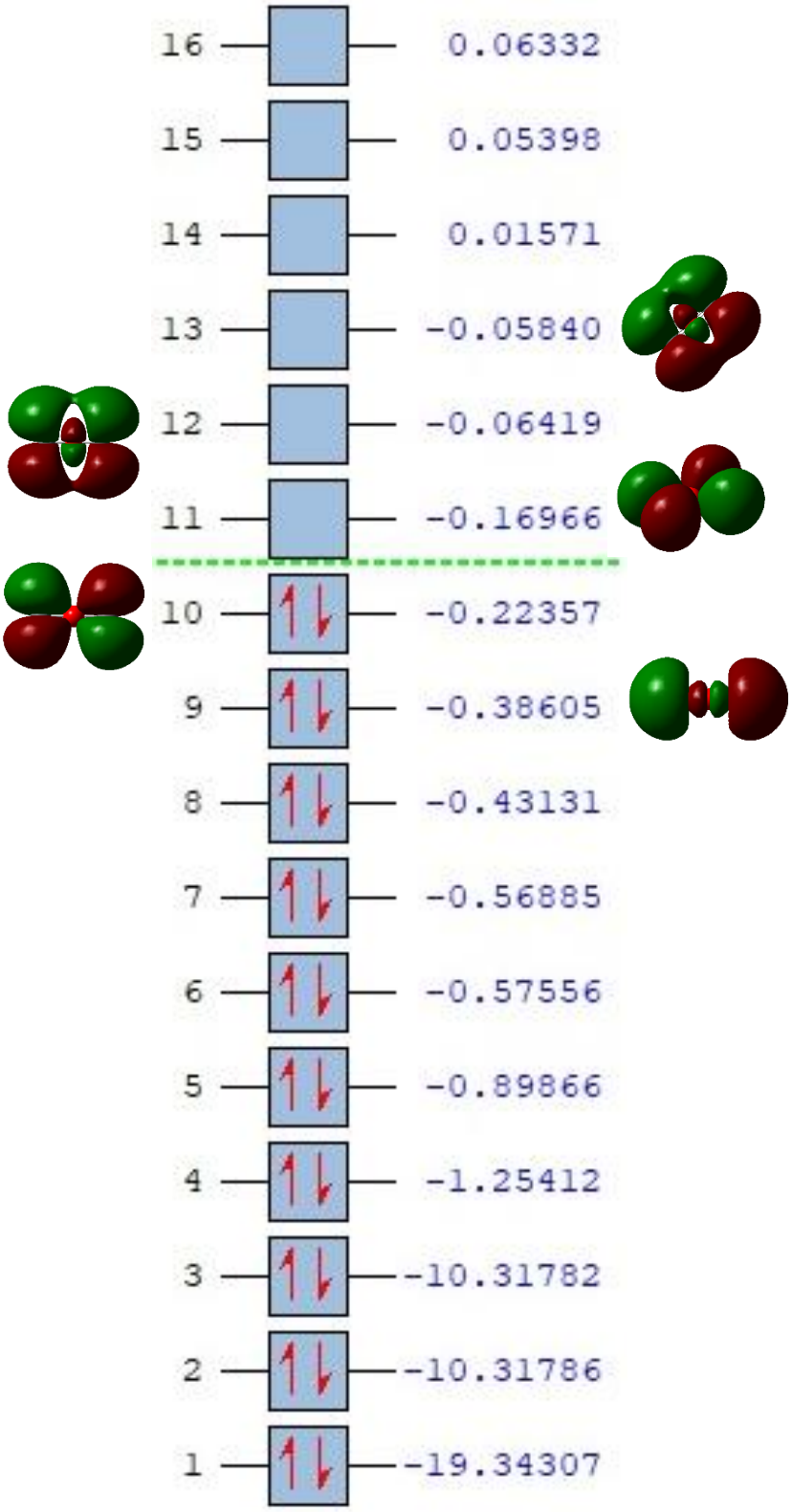
[a] For species with spin-multiplicity other than singlet, the diagnostics were performed at unrestricted, UCCSD(T), level of the theory.

Figure S1. Molecular Orbital (MO) diagrams of C_2N (doublet), C_2O (singlet), and C_2O (triplet) at the DFT/(U)B3LYP/6-311++G(d,p) level of the theory. The surface plots of only most relevant MOs are depicted (the isovalue of plots has been adjusted between 0.01-0.02 to have a best view of MOs). The orbital energies are in a.u., and plots are generated at DFT/(U)B3LYP/6-311++G(d,p) level of the theory (except for species with singlet spin multiplicity where restricted RB3LYP was utilized).

(a) C_2N (doublet)



(a) C_2O (singlet)



(c) C_2O (triplet)

Degenerate MOs (involved in long-bonding): # 10 & 11, # 12 & 13

α-MOs **β-MOs**

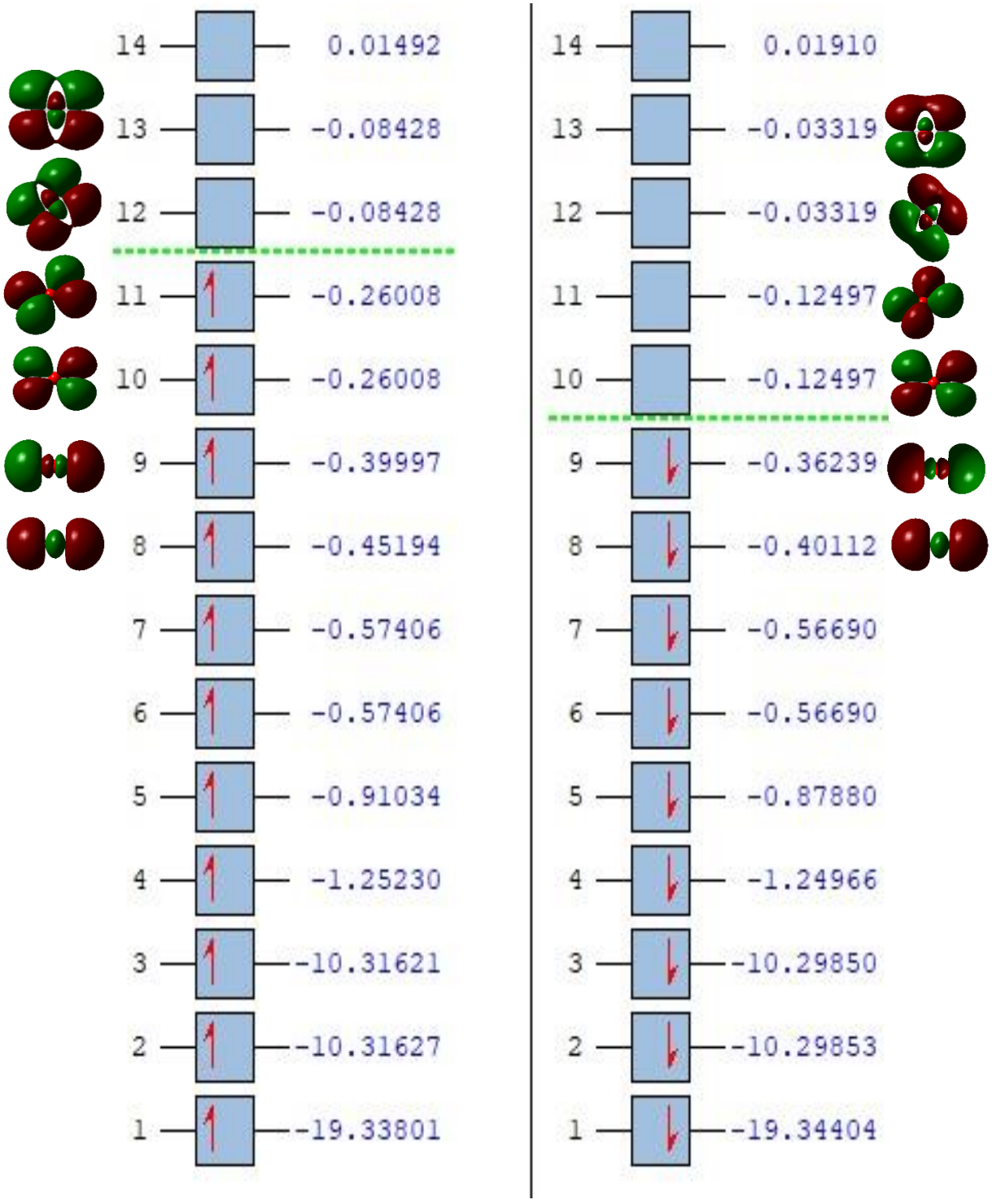
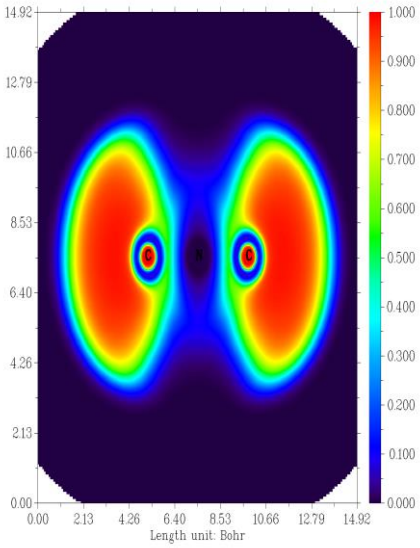
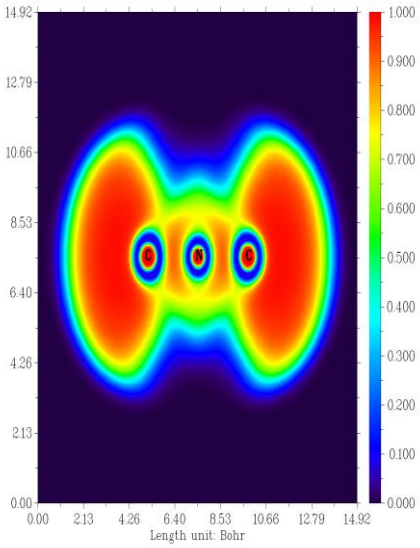
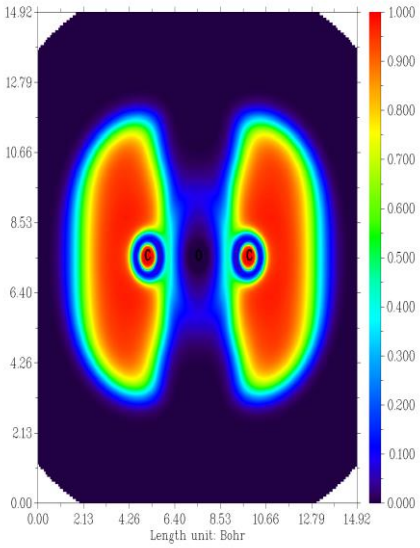
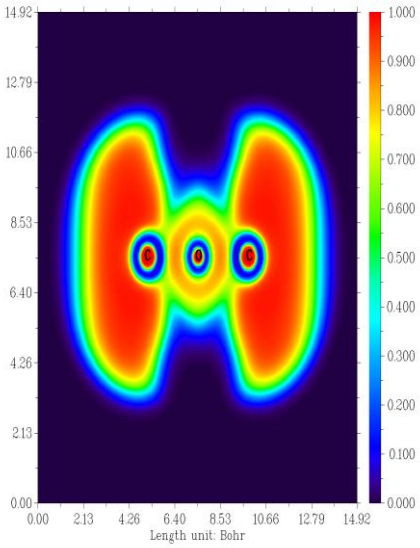
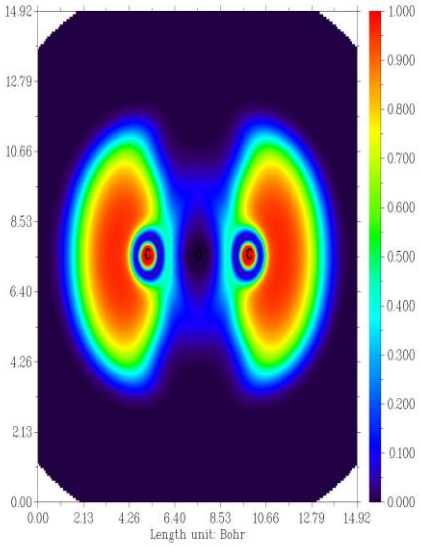
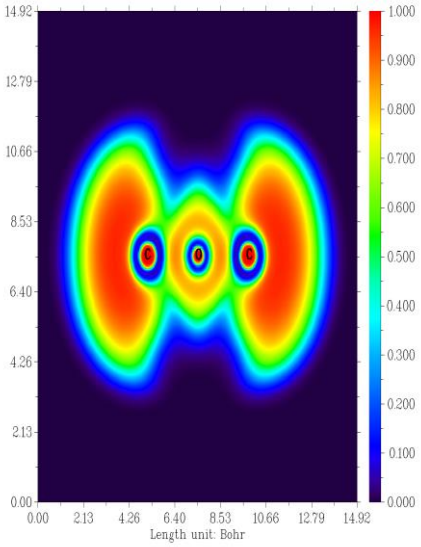
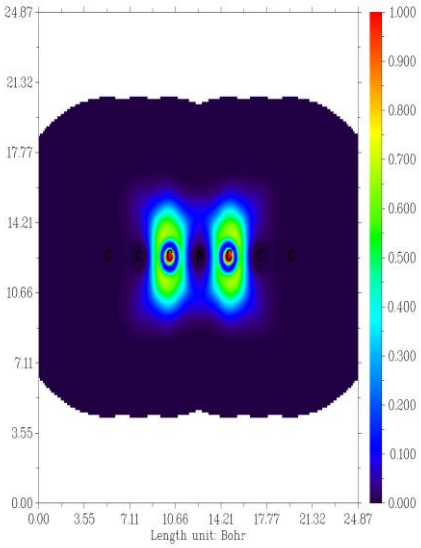
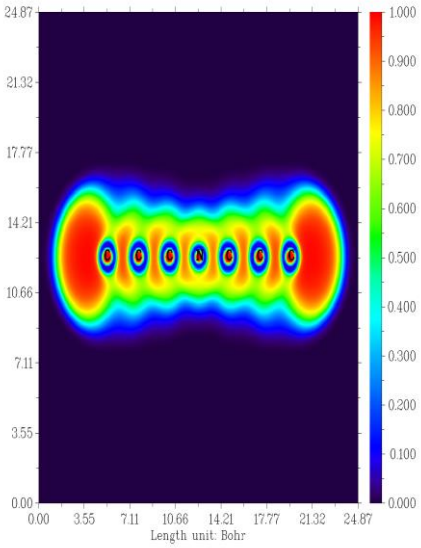
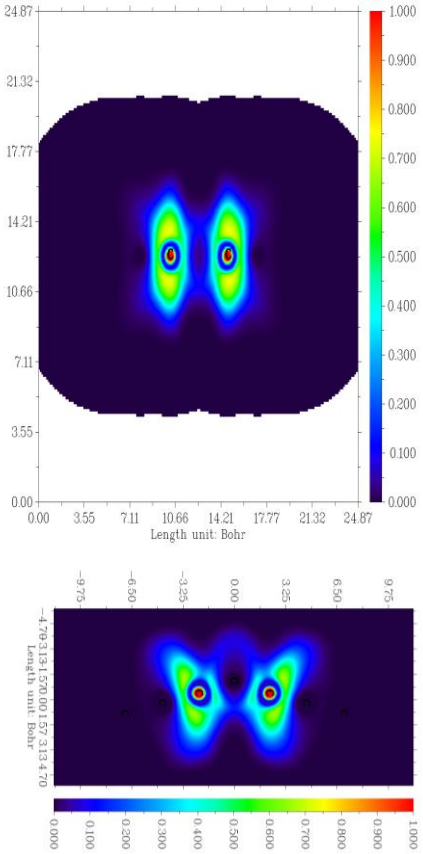
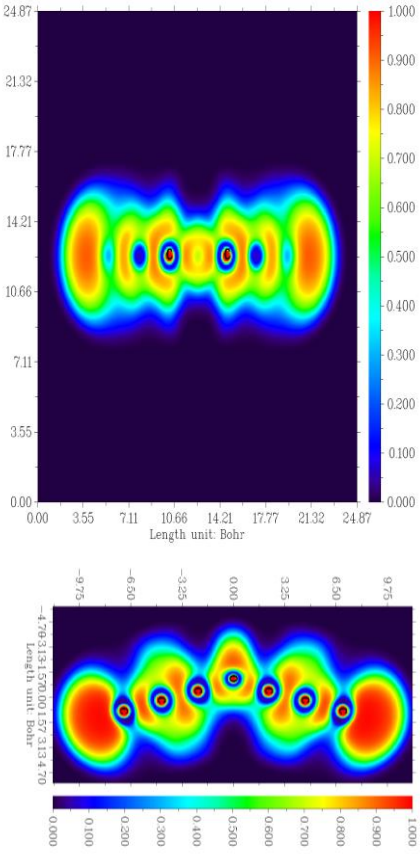


Figure S2. Plots of projected map of Electron Localization Function (ELF) in the relevant species being investigated: (a) ELF around two carbon atoms involved in $\hat{\pi}_{CC}$ long-bonding, (b) ELF around all the atoms. The projections are parallel to $\hat{\pi}_{CC}$ long-bond in the plane defined by C-X-C (besides this, in case of C_6O, maps in XY plane are additionally provided). The units of length are in Bohr and plots are generated at DFT/(U)B3LYP/6-311++G(d,p) level of the theory (except for species with singlet spin multiplicity where restricted RB3LYP was utilized).

Species	**(a)**	**(b)**
C_2N (doublet)		
C_2O (singlet)		

C_2O (triplet)		
C_6N (doublet)		

C_6O (singlet)	 (in XY plane)	 (in XY plane)
$C_8N(3,5)$ (doublet)