

Role of donor-acceptor functional groups in N₃P₃ cyclic-triphosphazene backbone. Unraveling bonding characteristics from natural orbitals within an extended transition state-natural orbital for the chemical valence scheme

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The formation of cyclophosphazenes containing several ligands or substituent groups gives rise to an attractive derivative set, for development of novel applications, with variable properties. Here, it is possible to unravel the role of different functional groups attached to the N₃P₃ backbone, to reach a better understanding of the bonding character in the cyclic [P₃N₃] skeleton. We employed the extended transition state-natural orbital for the chemical valence scheme to unravel the σ and π orbital kernels that are involved in the assembling of such structures, by varying the acceptor-donor characteristics of the -CF_3 , -NO_2 , -COOH , -CN , -NH_2 , -OH , and -OCH_3 groups, where -NO_2 behaves as a stronger electron-withdrawing substituent rather than -CF_3 , -COOH , and -CN , denoting that the nature of the ligand-phosphazene interaction contributes to some degree to the bond strength of the cyclic [P₃N₃] backbone. Our results reveal that the electron-withdrawing -NO_2 group leads to higher σ and π [P₃N₃] orbital-energy contributions, which is reflected in a shortening of the [P₃N₃] distance, contrasting with the case of electron-donating groups such as -NH_2 , -OH , and -OCH_3 within the phosphazene set. These insights allow further variation and modulation of the bonding in the [P₃N₃] ring. © 2019 Wiley Periodicals, Inc.

cyclic-phosphazene

ETS-NOCV

sigma and pi contributions

Ligands

Nitrogen oxides

Bonding characteristics

Electron-donating group

Electron-withdrawing substituents

Electronwithdrawing

ETS-NOCV

Novel applications

Phosphazenes

sigma and pi contributions

Bond strength (chemical)