Elusive cyanoform: computational probing its stability and reactivity with accurate ab initio methods.

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Streszczenie

We have applied the CCSD(T)-F12a/cc-pVTZ-F12//CCSD(T)/cc-pVTZ level of theory to calculate energies for 22 reactions pertinent to the stability and reactivity of hardly isolable cyanoform ($HC(CN)_3$). A number of exothermic processes has been indicated, especially the hydration. In the predicted mechanism for the gas-phase hydration of cyanoform, the H_2O addition to the C≡N bond corresponds to a rate-limiting step, which is aided by an extra molecule of water. Also, for the cyanoform dihydrate ($H_2NC(OH)C(CN)CONH_2$) product, the experimentally identified compound, the more stable planar isomer exhibits intramolecular O–H···O═C (not N–H···O═C) H-bonding. Our calculated structures, binding energies, and NBO data for $[HC(CN)_3]_n$ (n = 2,4) clusters suggest that the non-conventional C–H···N H-bonds contribute to their stability. Among the surveyed structures of the C≡N group incorporating products of reactions examined, the CCSD(T)/cc-pVTZ molecular parameters of cyanocarbons $C_2(CN)_4$, $C_2(CN)_6$, and $C_6(CN)_6$ can be regarded as the most accurate gas-phase values up-to-date.

Słowa kluczowe

Chemical reactions, Energy, Molecular structure, Mathematical methods, Molecules

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