Quantum Chemical Calculation on the Dimerisation of Anionic Organic Radical $[TCNE]_2^{2-}$ and $[DDQ]_2^{2-}$ in Solution

Kraiwan Punyain, Anne-Marie Kelterer, Günter Grampp

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Technikerstrasse 4/I,

A-8010 Graz, Austria

Abstract

Anionic organic radicals form dimers in solution and exhibit unusually long C-C bond between two fragments. The long C-C bonds are shorter than the sum of van der Waals radii but longer than a normal covalent bond.

Density Functional Theory (DFT) was used to investigate the $[TCNE]_2^{2-}$ and $[DDQ]_2^{2-}$ dimers in solution using the program ORCA. The generalized gradient approximation (GGA) and hybrid functional with inclusion of dispersion interaction have been used to calculate the optimized geometry with double and triple zeta basis set with continuum and explicit solvation model. Inclusion of the counterion is necessary for a proper description of the potential energy surface. The PBE-D functional with double and triple zeta basis result in good structural parameter corresponding to the experimental data from X-ray crystallography [1].

The energetic has also been investigated via single point MP2, CASSCF and MRMP2 calculations. The results are discussed in comparison to experimental (EPR, UV-VIS) [1,2,3] and theoretical [4] data.

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