A DFT study of the interresidue dependencies of scalar J- coupling and magnetic shielding in the hydrogen-bonding regions of a DNA triplex

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Author(s) Barfield, M; Dingley, AJ; Feigon, J; Grzesiek, S
Author(s) at UniBasel Grzesiek, Stephan ;
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Scalar coupling constants and magnetic shieldings in the imino hydrogen-bonding region of Hoogsteen-Watson-Crick T A-T and Ct G-C triplets have been calculated as a function of the distance between proton donor and acceptor nitrogen atoms. The Fermi contact contributions to (h2)J(N-15-H . . . N-15), (1)J(N-15-H- 1), and (h1)J(H-1 . . . N-15) were computed using density functional theory/finite perturbation theory (DFT/ FPT) methods for the full base triplets at the unrestricted B3PW91/6-311G** level. Chemical shifts B(H-1) and delta(N-15) were obtained at the same level using the gauge including atomic orbital (GIAO) method for magnetic shielding. All three scalar couplings and all three chemical shifts are strongly interrelated and exhibit monotonic changes with base pair separation. These correlations are in conformity with experimental data for a 32-nucleotide DNA tripler. The results suggest that both chemical shifts and coupling constants can be used to gain information on H-bond donor-acceptor distances in nucleic acids. In addition to the DFT/FPT calculations, a simple three-orbital model of the N-H H bond and a sum-over-states analysis is presented. This model reproduces the basic features of the H-bond coupling effect. In accordance with this model and the DFT calculations, a positive sign for the (h2)J(NN) coupling is determined from an E.COSY experiment.
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