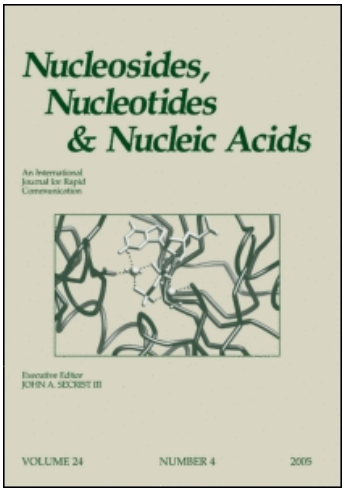

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EVALUATION OF SEVERAL ECONOMICAL COMPUTATIONAL METHODS FOR GEOMETRY OPTIMISATION OF PHOSPHORUS ACID DERIVATIVES

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ABSTRACT

Several economical methods for geometry optimisation, applicable to larger molecules, have been evaluated for phosphorus acid derivatives. MP2/cc-pVDZ and B3LYP/6-31+G(d) geometry optimisations are used as reference points, results from geometry optimisations for other methods and their subsequent single point energy calculations are compared to these references. The geometries from HF/MIDI! optimisations were close to those of the references and subsequent single point energies with B3LYP/6-31+G(d,p) or EDF1/6-31+G(d) gave a mean average deviation (MAD) of less than 0.5 kcal mol^{-1} from those obtained with the reference geometries.

The use of quantum mechanical calculations as a tool in chemical research has increased dramatically. The level of accuracy that can be afforded is often quite limited, since the computational cost of even small model systems can be substantial. Recently HF calculation with the MIDI! (1) basis set has been forwarded as a cost-efficient method for achieving geometries of good quality (near MP2-quality). Since the HF/MIDI! method performs very well with phosphorus containing compounds it seems promising for use in nucleic acid chemistry. In this study we have in more detail assessed how geometries are affected and especially how this influences the energies, as obtained from subsequent single point calculations. HF/MIDI! (1)

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geometries are compared to those obtained from several other, more widely used, methods.

The methods/basis sets used for geometry optimisation were MP2/cc-pVDZ (2,3), B3LYP/6-31+G(d), B3LYP/6-31G(d), HF/6-31G(d) (4–6), HF/3-21G(d) (7–9), B3LYP/MIDI! and HF/MIDI! (1). All geometry optimisations and B3LYP/6-31+G(d,p) single point energy calculations were carried out using Gaussian98 (rev. A7). The EDF1/6-31+ G(d) calculations were performed using Q-Chem (v. 1.2). Geometries are evaluated using MP2/cc-pVDZ and B3LYP/6-31G(d) as reference methods. Subsequent single point energy calculations was carried out using the B3LYP functional (10,11) with the 6-31+G (d,p) basis set and also the new EDF1 functional (12) with 6-31+G(d) as basis set. The test set used for evaluation was an extension of the HCOP test set (1), as presented in Figure 1.

The greatest deviations from MP2 geometries are found for HF/3-21G(d) and HF/6-31G(d) geometries. Also B3LYP/MIDI! performs relatively poorly. Unsurprisingly, B3LYP/6-31G(d) and B3LYP/6-31+G(d) give very similar results and the geometries are close to those of the MP2 calculations. Overall HF/MIDI! gives even smaller deviations (although slightly) in bond angles from the MP2 geometries and mean bond length deviations are of similar quality to those obtained with the B3LYP methods. Thus, the HF/MIDI! geometries deviate only slightly from the geometries obtained with the more costly MP2 and B3LYP methods and are clearly superior to the HF/3-21G(d), HF/6-31G(d) and B3LYP/MIDI! geometries.

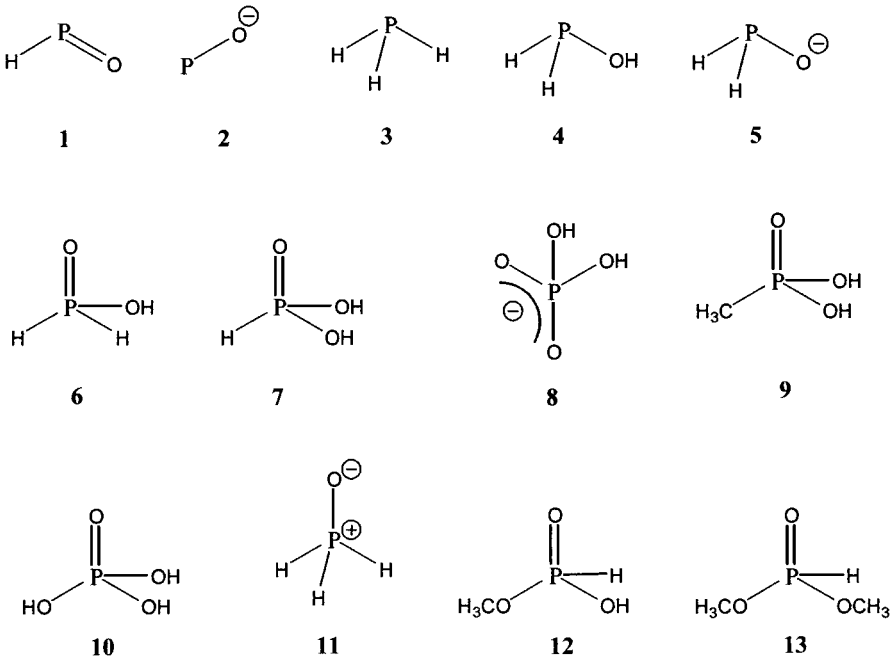

Figure 1. The extended HCOP test set.

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When comparing the outcome of subsequent single point energy calculations on the differently geometry optimised structures it is seen that the MP2/cc-pVDZ, B3LYP/6-31G(d) and B3LYP/6-31+G(d) geometries give very similar energies. The B3LYP/6-31+G(d,p) energies generally are within one kcal mol^{-1} (MAD 0.6–0.7 kcal mol^{-1}) and the EDF1 energies are within a few tenths of a kcal mol^{-1} (MAD 0.11–0.13 kcal mol^{-1}). HF/3-21G(d), HF/6-31G(d) and B3LYP/MIDI! geometries consistently give too high energies using both B3LYP/6-31+G(d,p) (MAD 1.3–1.9 kcal mol^{-1}) and EDF1 (MAD 1.2–3.9 kcal mol^{-1}). The single point energies calculated from HF/MIDI! geometries are, however, quite close to those from the MP2 and B3LYP geometries, usually within one kcal mol^{-1} (MAD 0.46–0.49 kcal mol^{-1}) and in many cases within a few tenths of a kcal mol^{-1}.

Already in our test set of very small molecules we see a considerable difference in computational cost (9 h for MP2/cc-pVDZ and 30 min using HF/MIDI! for **13**). In order to get a rough estimate of the computational time for some molecules of interest in nucleic acid chemistry, using the MP2, B3LYP and HF/MIDI! methods, we have correlated the number of heavy atoms against CPU time (on a Compaq/Digital XP1000, 500MHz EV6 running True64 Unix). According to this crude estimate, geometry optimisation of isopropyl pivaloyl H-phosphonate would take about 11 hours with HF/MIDI!, 5–14 days with B3LYP methods and 1 month for the MP2 calculation. With a purine nucleoside the corresponding estimate is a couple of days, 1–5 months and one year respectively.

Geometry optimisations using HF/MIDI! on phosphorus acid derivatives are computationally inexpensive and give geometries that are close to those obtained with more costly MP2 and B3LYP methods and clearly superior to those obtained with HF/3-21G(d) and HF/6-31G(d). Most importantly, the HF/MIDI! geometries lead to B3LYP/6-31+G(d,p) and EDF1/6-31+G(d) single point energies of a mean absolut deviation (MAD) of only 0.4–0.5 kcal mol^{-1} from those obtained with MP2/cc-pVDZ, B3LYP/6-31G(d) and B3LYP/6-31+G(d) geometries. Since the much used combination B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) gives energies with a MAD of 4 kcal mol^{-1}, relative to experimental data (for the large G2 test set) (13), one can assume that B3LYP/6-31+G(d,p)//HF/MIDI! should mostly be within about 4–5 kcal mol^{-1}. This deviation is as small as one can hope for in many applications and, especially considering the small increase in accuracy that would be achieved with more costly methods, HF/MIDI! is clearly of choice for geometry optimisation of molecules with more than 10 heavy atoms.

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