Physico-Chemical Properties of 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) Diazonium Ion: A Theoretical Investigation: Supporting Information[†]

Christos Deligkaris,[*a‡], Evan Millam,[b‡], Edmir Wade,[b‡], Maverick L. Grayer,[*] David M. Wahl[*]

(a) PDI anti (B3LYP/6-311G**)

(b) PDI gauche (B3LYP/6-311G**)

(c) PDI anti (CCSD(T)/cc-pVTZ)

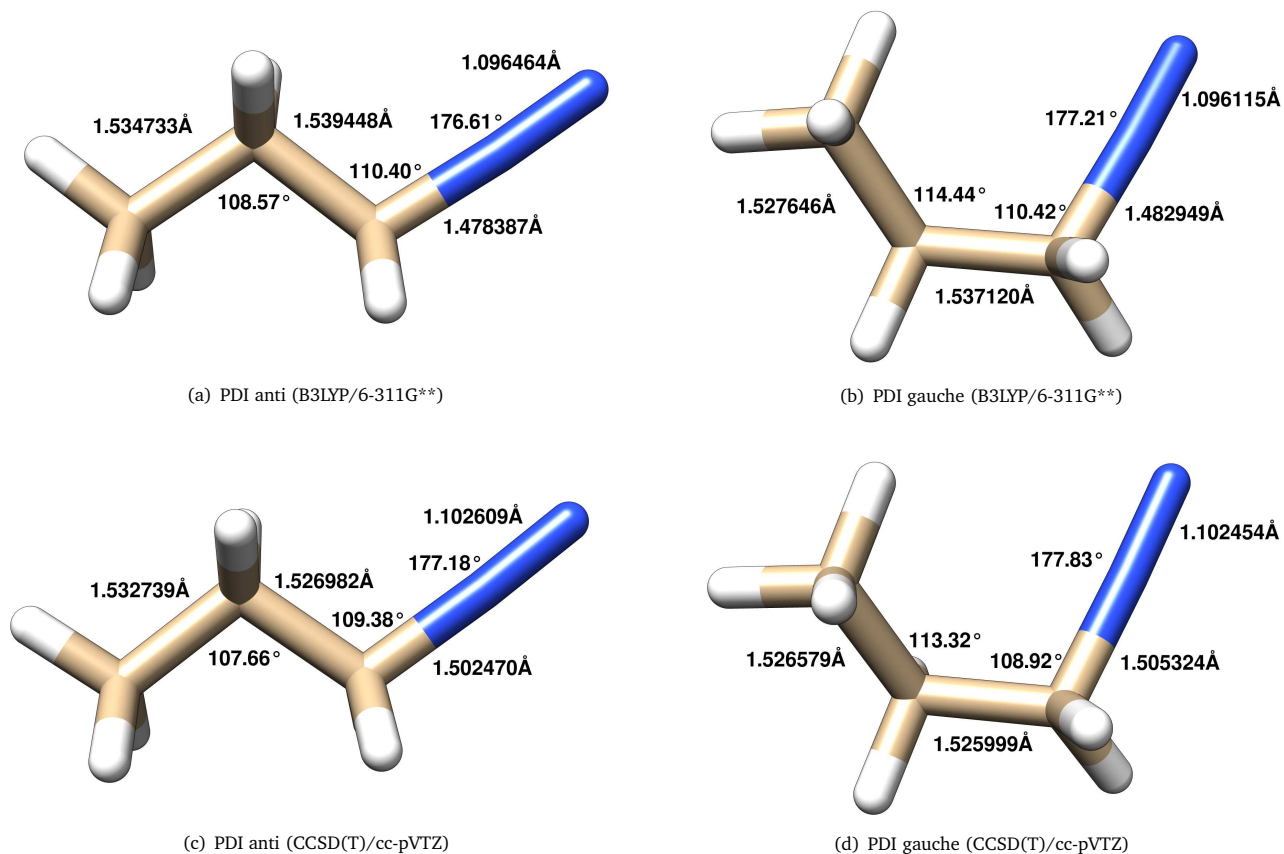(d) PDI gauche (CCSD(T)/cc-pVTZ)

Fig. 1 Energy minima at the CCSD(T)/cc-pVTZ level of theory (top) and B3LYP/6-311G** (bottom).

[a] Department of Geology and Physics, University of Southern Indiana, 8600 University Blvd, Evansville, USA. Tel: (812) 228-5056; E-mail: Dr.Deligkaris@usi.edu

[b] Department of Chemistry, University of Southern Indiana, 8600 University Blvd, Evansville, USA.

(a) TCTT
(b) TCG'T
(c) TCG'G
(d) TCGT
(e) TCGG'
(f) TCGG
(g) TGTG'
(h) TCTG'
(i) TCTG
(j) CCTT
(k) CCGG'
(l) CCGT
(m) CCGG
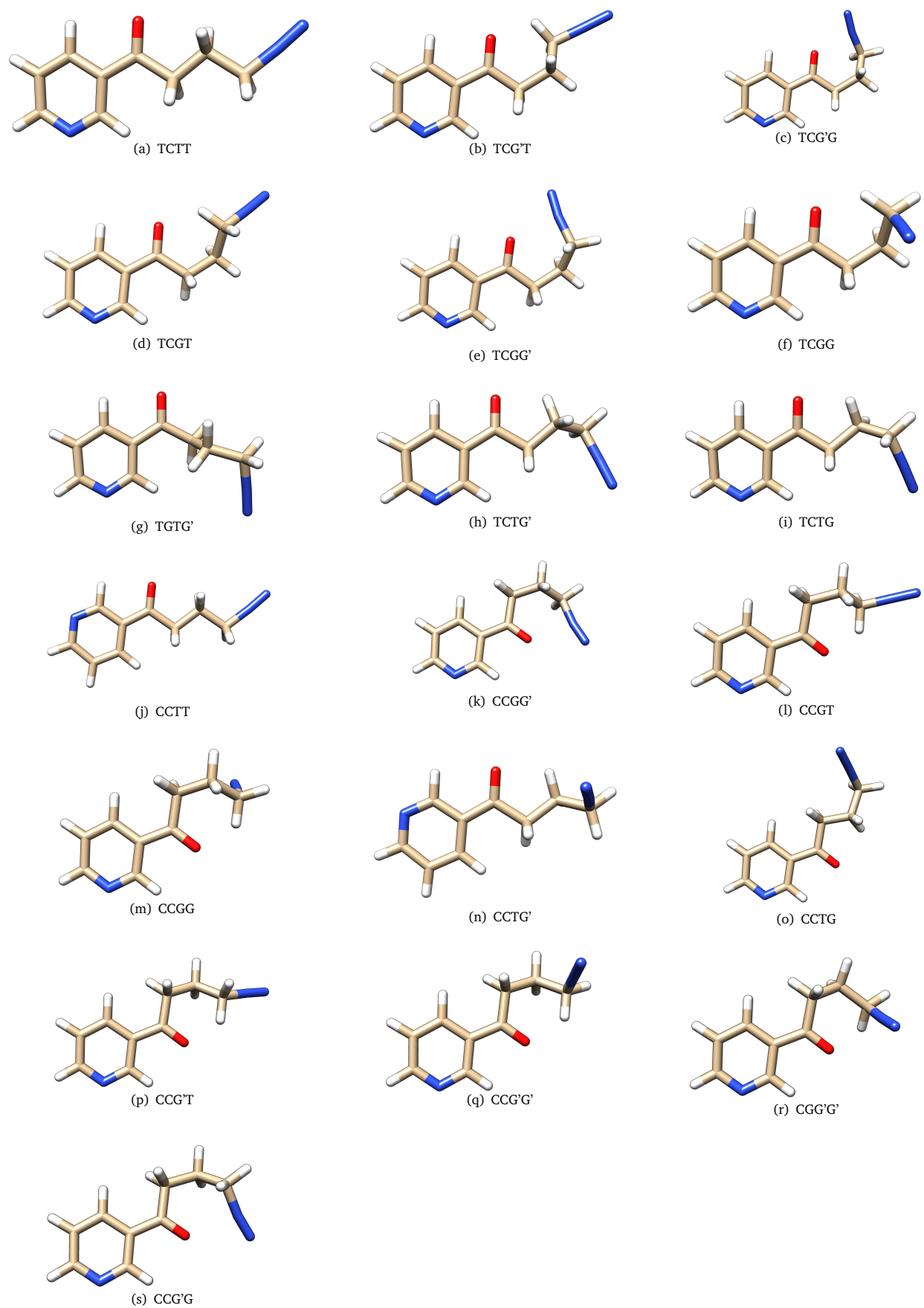(n) CCTG'
(o) CCTG
(p) CCG'T
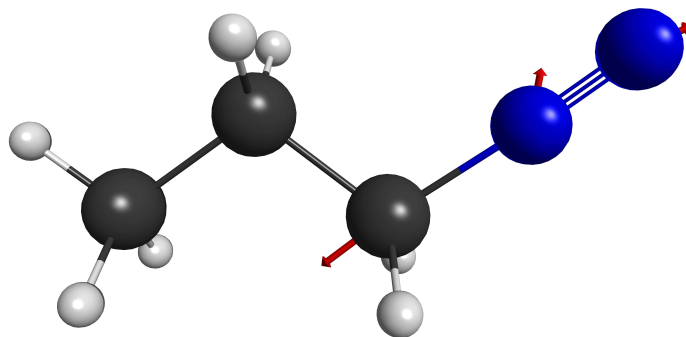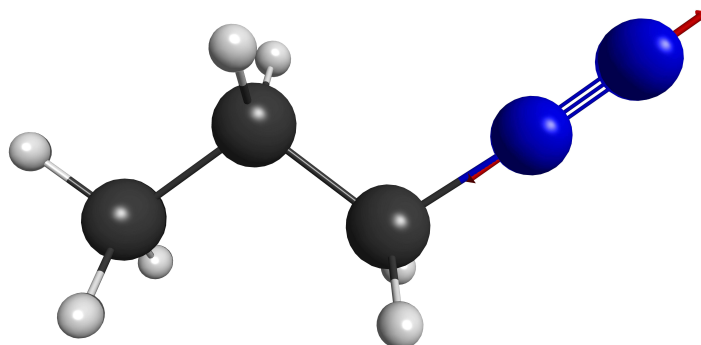(q) CCG'G'
(r) CGG'G'
(s) CCG'G

Fig. 2 NNKDI conformations that correspond to energy minima at B3LYP/6-311G** level of theory.
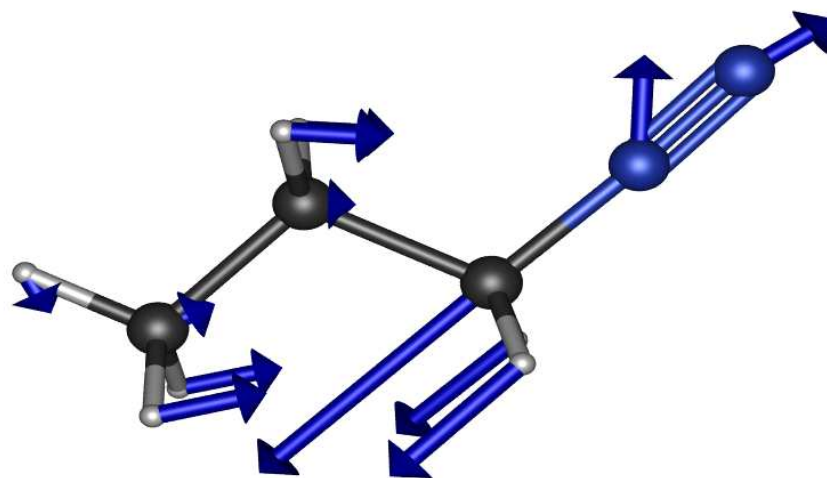
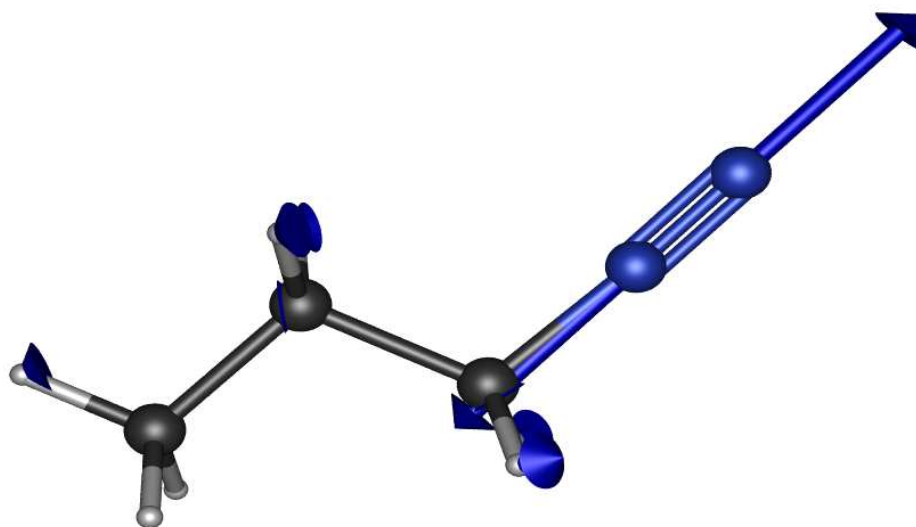(a) CCSD(T)/cc-pVTZ, 669 cm^{-1}

(b) CCSD(T)/cc-pVTZ, 2367 cm^{-1}

Fig. 3 Selected PDI anti vibrational modes predicted at the CCSD(T)/cc-pVTZ level of theory.
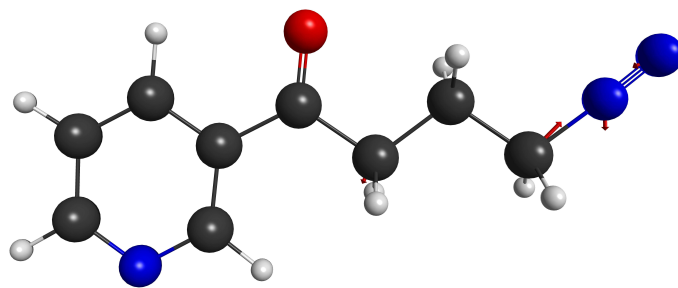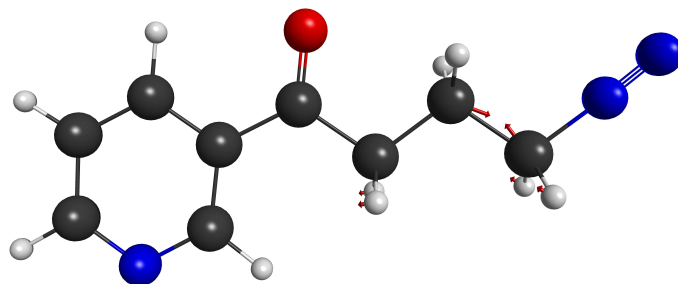
(a) B3LYP/6-311G**, 669 cm^{-1}
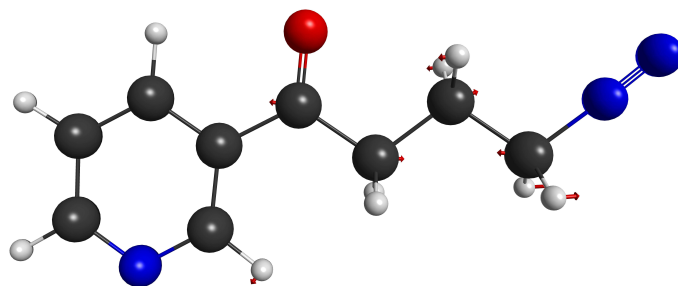

(b) B3LYP/6-311G**, 2435 cm^{-1}

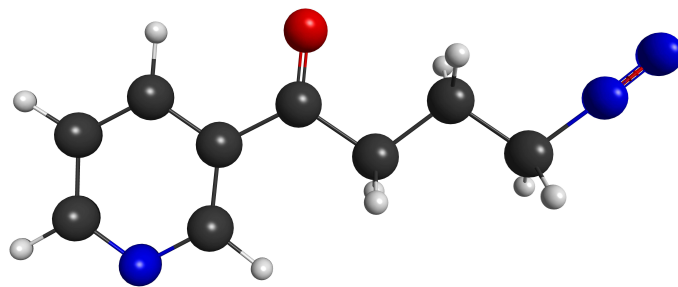**Fig. 4** Selected PDI anti vibrational modes predicted at the B3LYP/6-311G** levels of theory.

(a) 664.39 cm^{-1}, CCSD/6-31G*
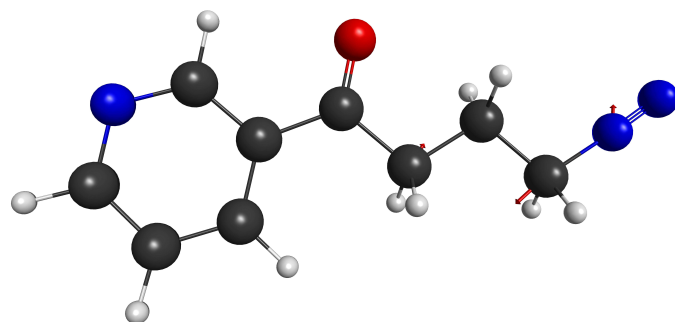

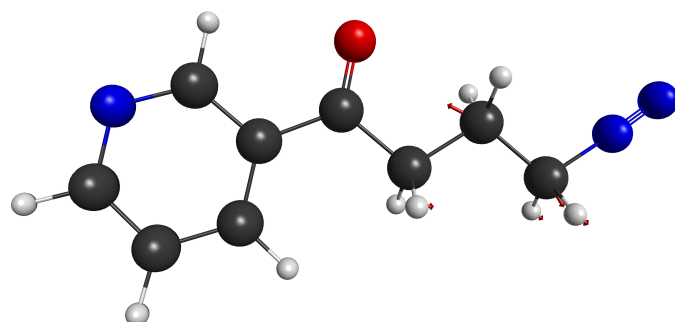(b) 1060.24 cm^{-1}, CCSD/6-31G*

(c) 1389.14 cm^{-1}, CCSD/6-31G*

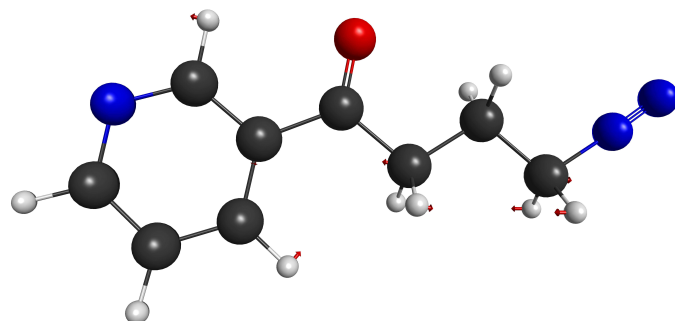(d) 2443.48 cm^{-1}, CCSD/6-31G*

Fig. 5 Selected NNKDI TCTT vibrational modes predicted at the CCSD/6-31G* level of theory.

(a) 663.72 cm^{-1}, CCSD/6-31G*

(b) 1060.39 cm^{-1}, CCSD/6-31G*

(c) 1385.24 cm^{-1}, CCSD/6-31G*

(d) 2443.21 cm^{-1}, CCSD/6-31G*

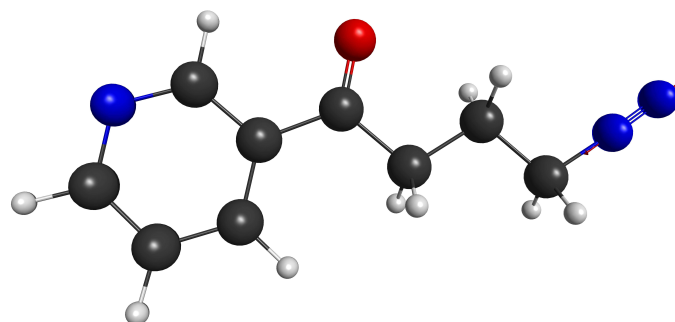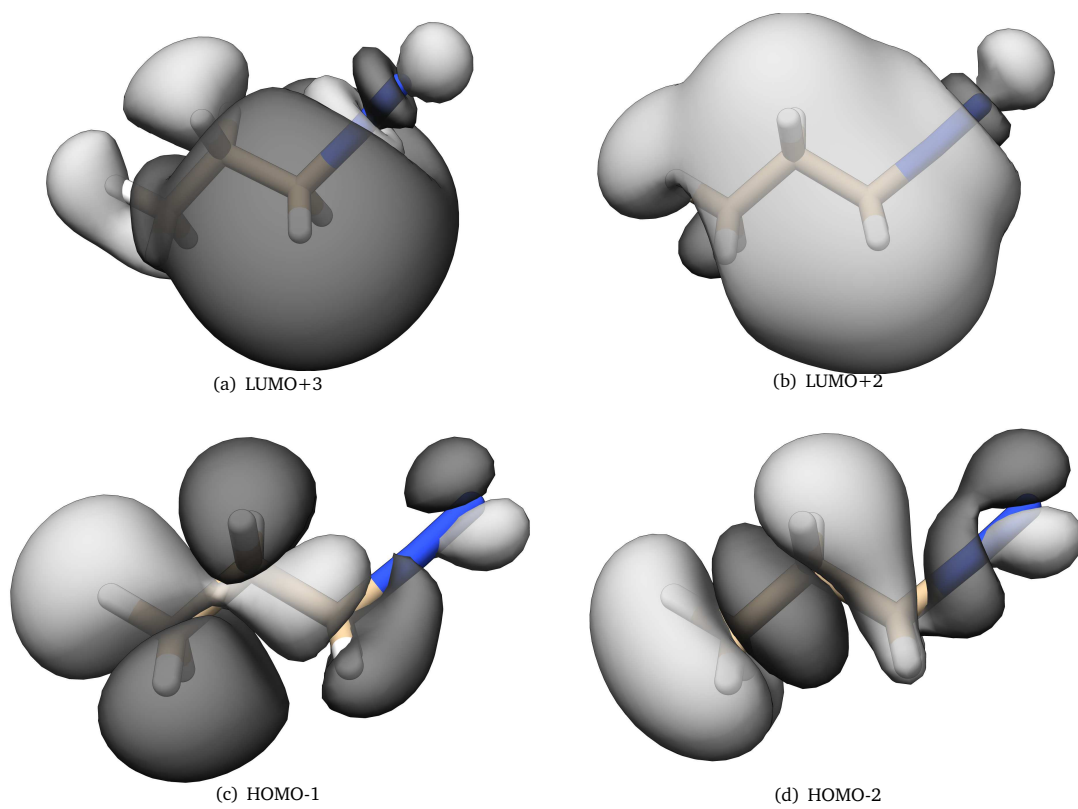**Fig. 6** Selected NNKDI CCTT vibrational modes predicted at the CCSD/6-31G* level of theory.

(a) LUMO+3

(b) LUMO+2

(c) HOMO-1

(d) HOMO-2

Fig. 7 PDI anti molecular orbitals as calculated at the B3LYP/6-311G** level of theory.

(a) LUMO+3

(b) LUMO+2

(c) HOMO-1

(d) HOMO-2

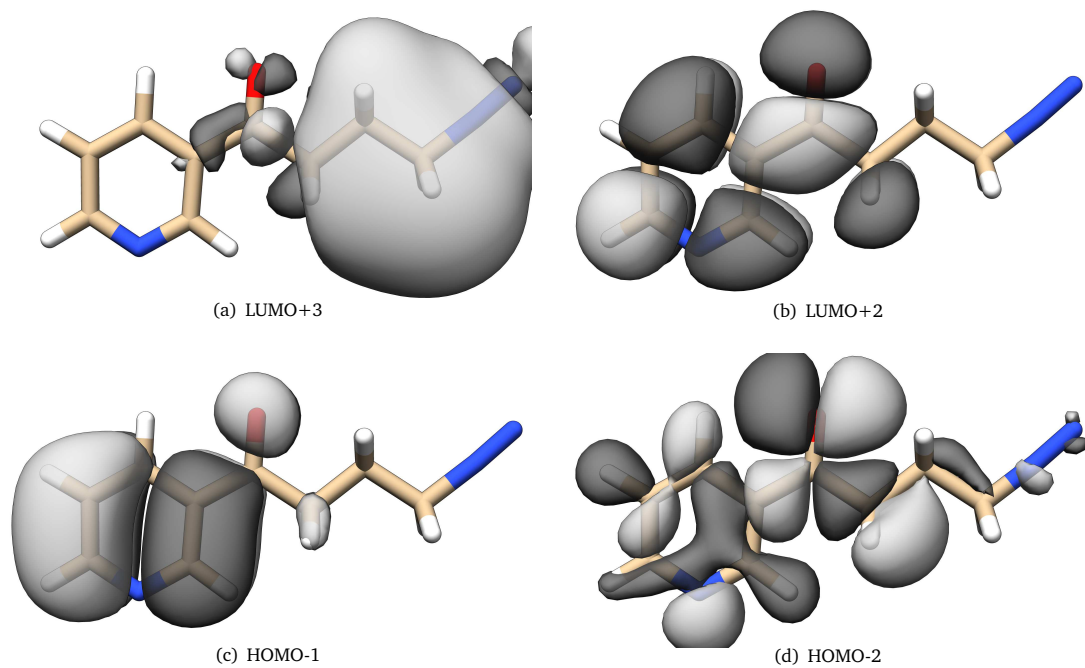**Fig. 8** NNKDI molecular orbitals as calculated at the B3LYP/6-311G** level of theory.

Table 1 Energies for B3LYP/6-311G** calculations of NNKDI conformation TCTT.

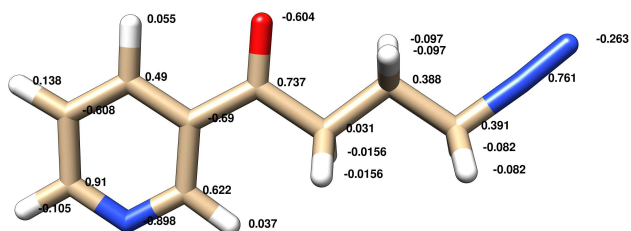| Calculation	Energy [Hartree]
Restricted Singlet	-588.289936119991
Unrestricted Sinlet	-588.289936356757
Restricted Triplet	-588.173957026897

Fig. 9 RESP charges of the NNKDI conformation TCTT as calculated at the HF/6-31G* level of theory.
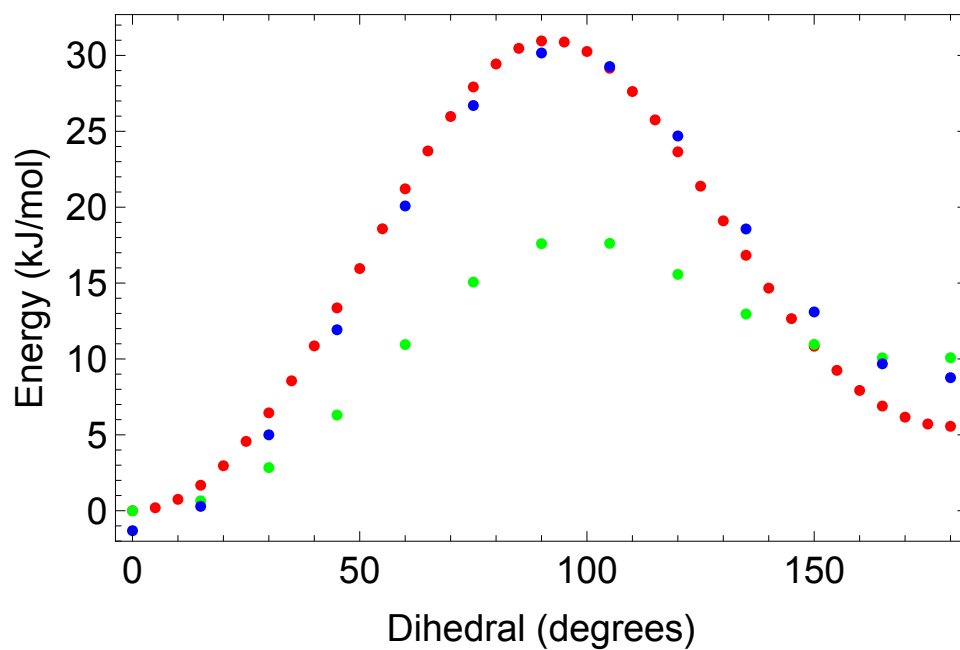
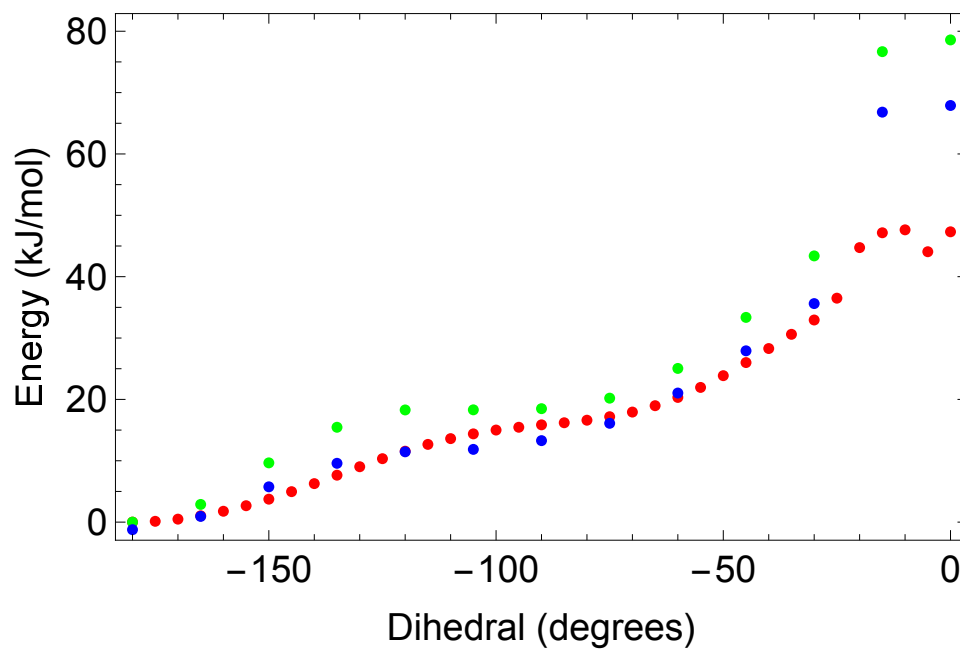**Fig. 10** Potential energy surface for the C1-C3' torsion. Red is QM, green is GAFF2, blue is this work.

Fig. 11 Potential energy surface for the C2-C1 torsion. Red is QM, green is GAFF2, blue is this work.
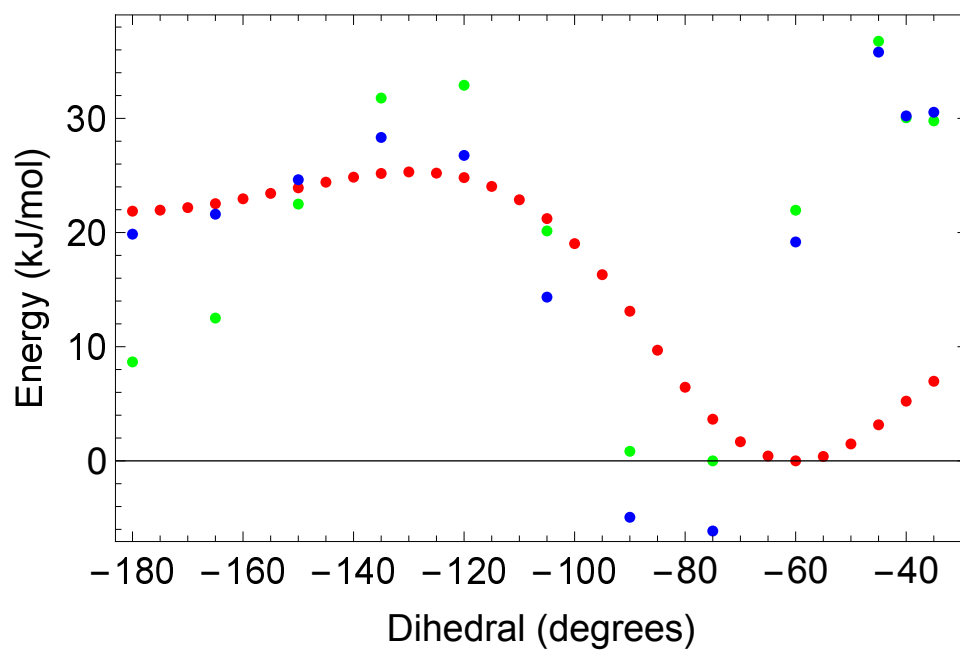
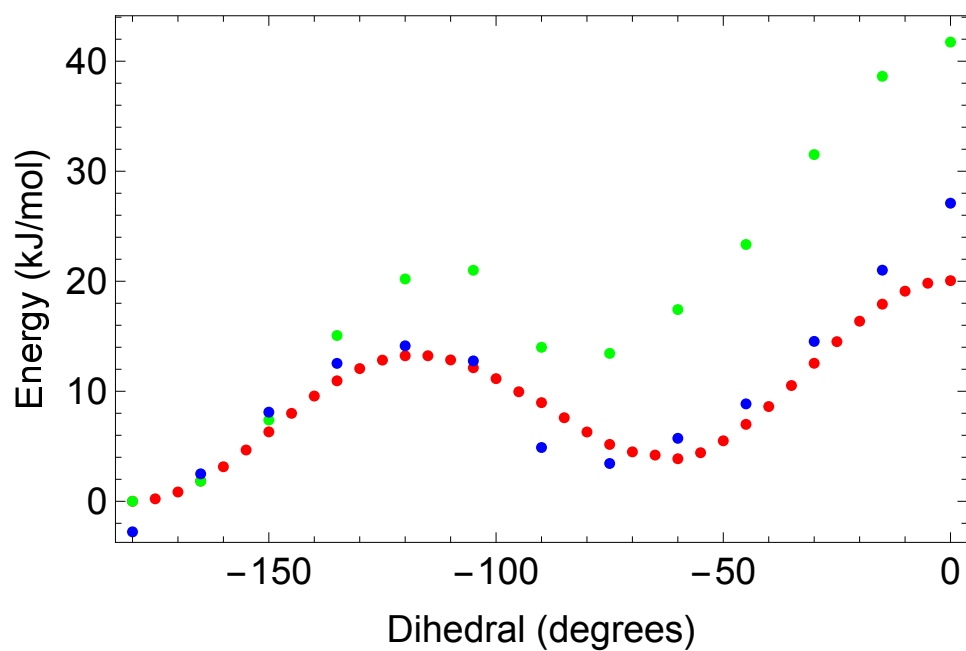**Fig. 12** Potential energy surface for the C3–C2 torsion. Red is QM, green is GAFF2, blue is this work.

Fig. 13 Potential energy surface for the C4–C3 torsion. Red is QM, green is GAFF2, blue is this work.
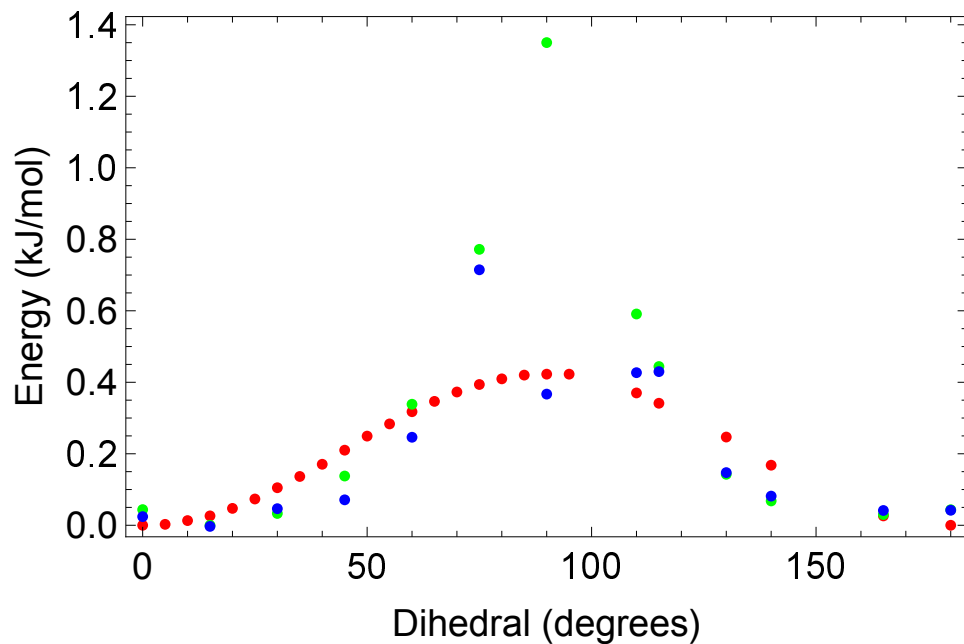
Fig. 14 Potential energy surface for the N5-C4 torsion. Red is QM, green is GAFF2, blue is this work.
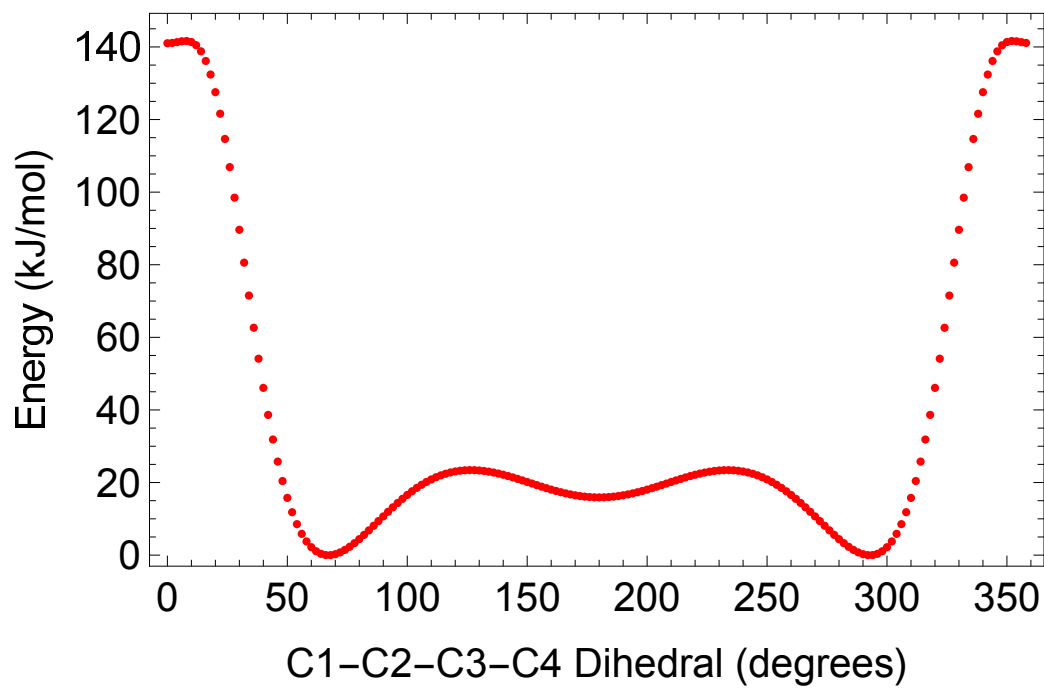

Fig. 15 Single point energies (no structural relaxation was allowed) at the MP2/6-311G** level of theory around the C2-C3 torsion.
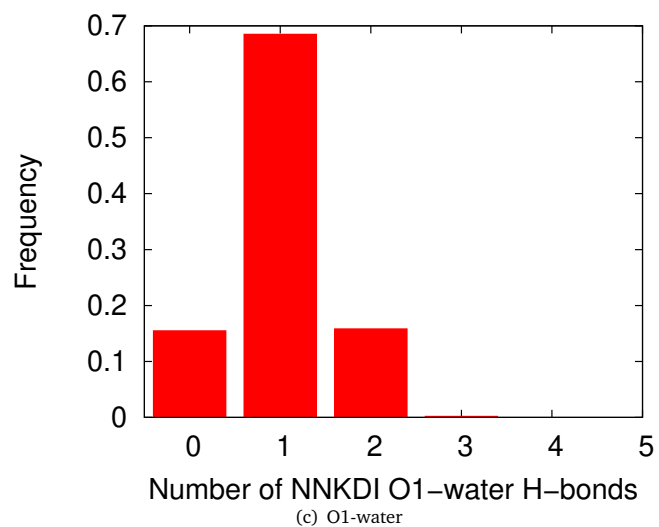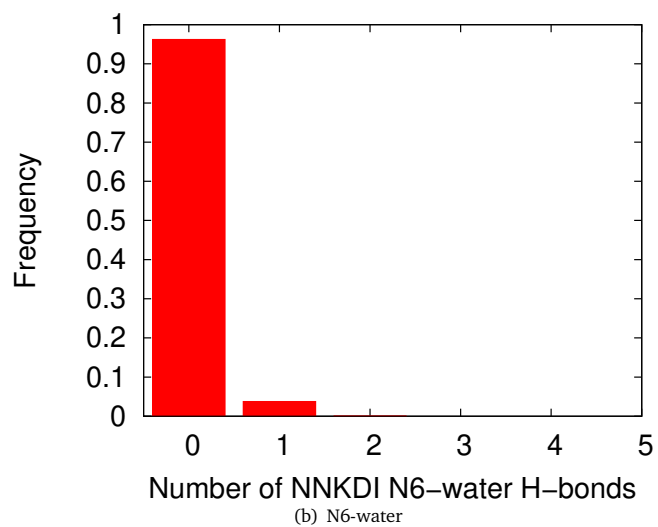
(a) N1-water

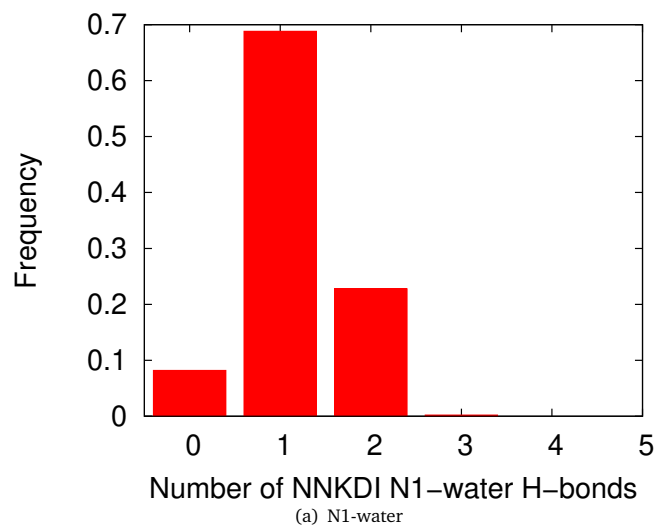(b) N6-water

(c) O1-water

Fig. 16 Frequency distribution of NNKDI hydrogen bonds with water during a 1.5 μs MD simulation.
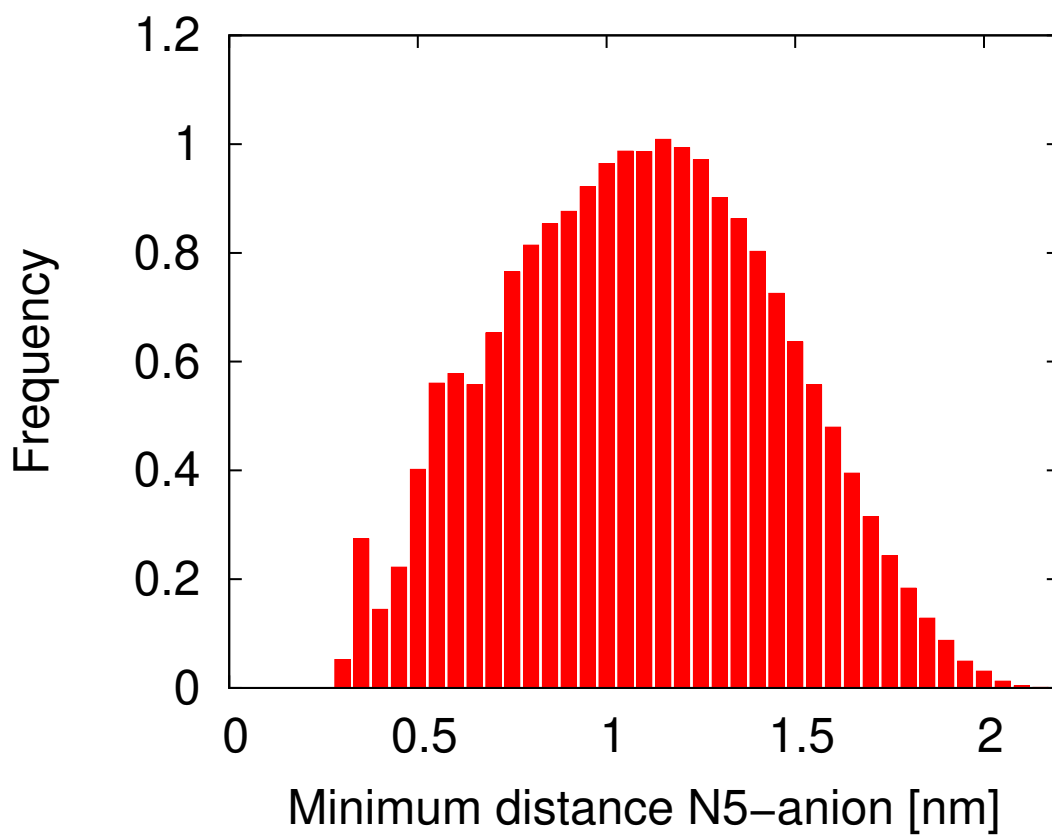
Fig. 17 Minimum distance between NNKDI atom N5 and all anions during a 1.5 μs MD simulation.
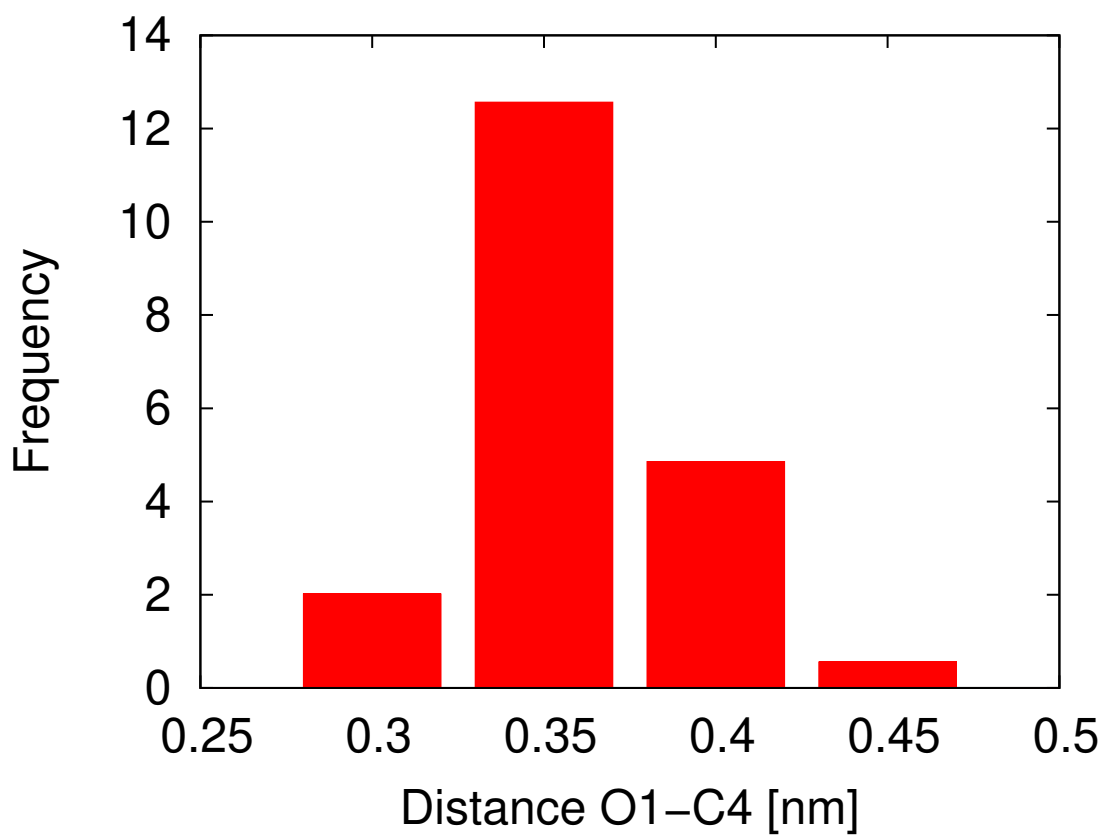
Fig. 18 Frequency distribution of the O1-C4 distance during a 1.5 μs MD simulation.
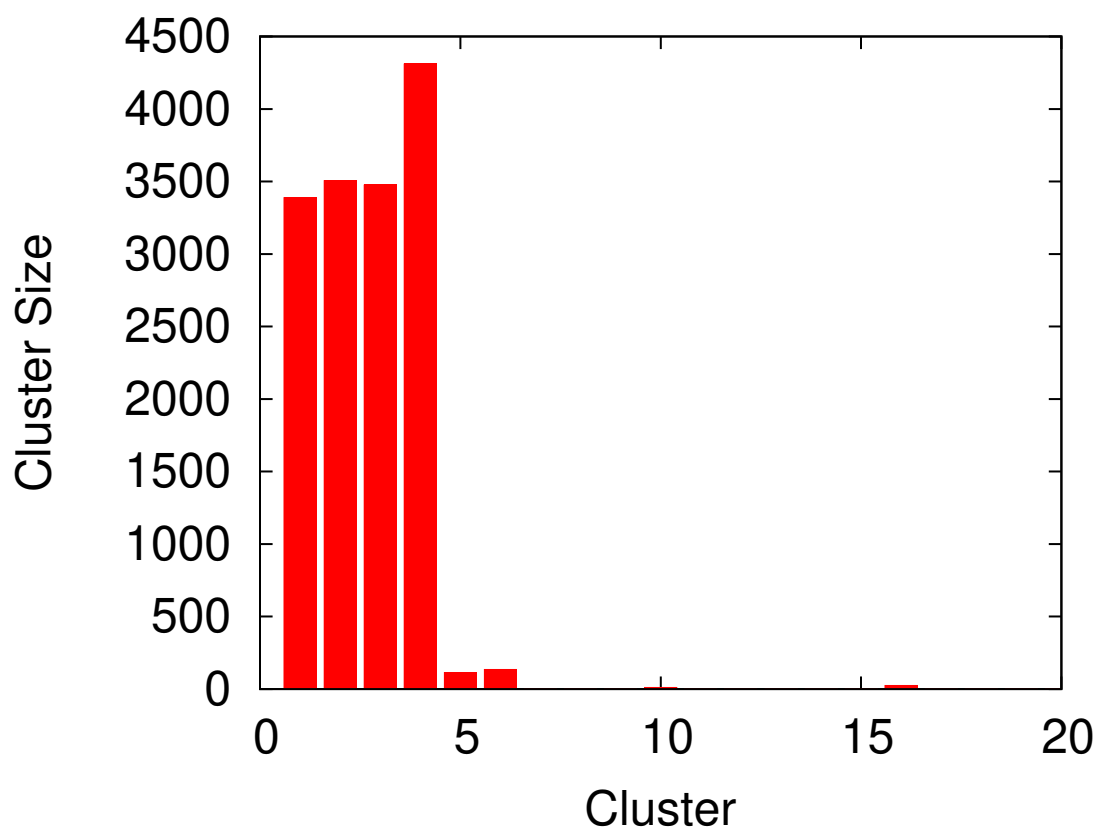
Fig. 19 Frequency distribution of the clusters found in a NNKDI MD simulation of $1.5\ \mu$ s. The RMSD cutoff used was 0.03 nm, and there were 42 clusters found in total. Only four clusters were significantly populated. The cluster analysis was performed for every 10-th frame of the MD simulation.
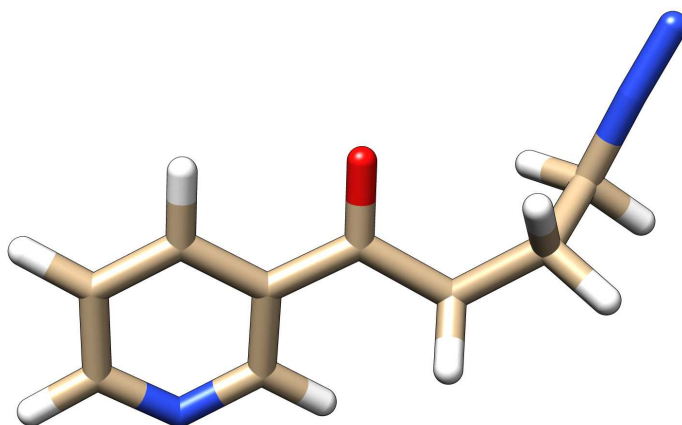

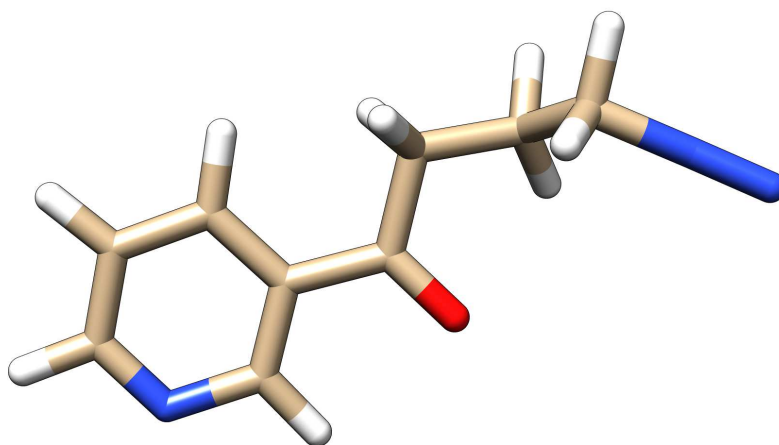**Fig. 20** This NNKDI conformation represents the center of cluster 1. Dihedrals are a: $173.7°$, b: $14.0°$, c: $-99°$, d: $144°$

Fig. 21 This NNKDI conformation represents the center of cluster 2. Dihedrals are a: $-3.0°$, b: $22.4°$, c: $-109.5°$, d: $144.6°$
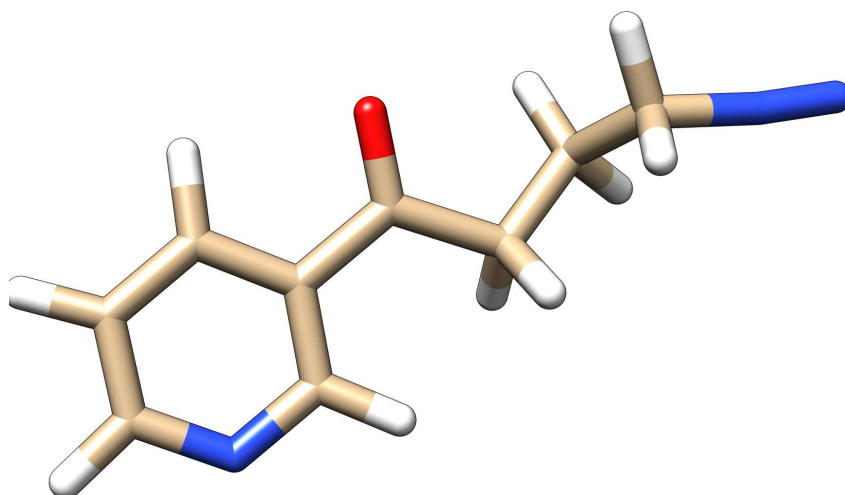

Fig. 22 This NNKDI conformation represents the center of cluster 3. Dihedrals are a: $-174.4°$, b: $-16.7°$, c: $102.1°$, d: $129.9°$
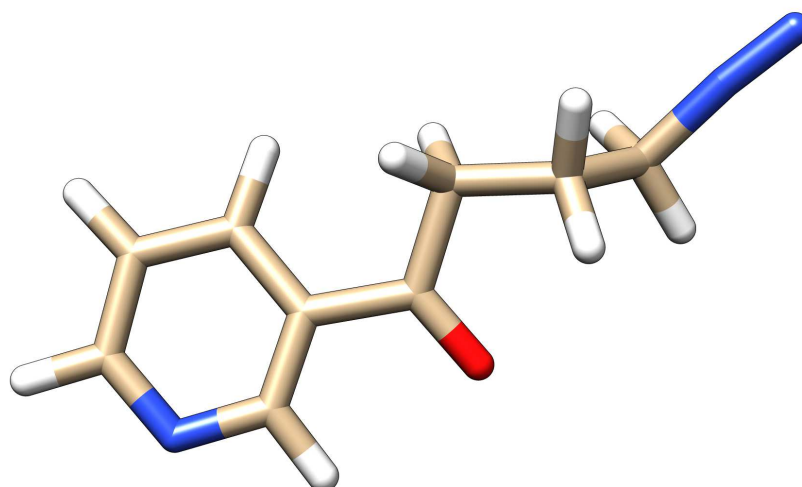

Fig. 23 This NNKDI conformation represents the center of cluster 4. Dihedrals are a: $9.2°$, b: $-17.6°$, c: $98.7°$, d: $136.8°$