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Is “Frank” DNA-Strand Breakage via the Guanine Radical Thermodynamically and Sterically Possible?

Supporting information

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Table 1: Angles (degrees) formed by the C-H bonds added to the nucleotide shown in Figure 1 [a]

H-C1`-N	106.6	H-C3`-C4`	119.1
H-C1`-O	113.0	H-C4`-O	112.6
H-C1`-C2`	108.9	H-C4`-C3`	113.9
H2a-C2`-H2b	109.5	H-C4`-C5`	102.8
H2a-C2`-C1`	112.0	H5a-C5`-H5b	109.6
H2a-C2`-C3`	112.1	H5a-C5’-O	109.5
H2b-C2`-C1`	111.8	H5a-C5`-C4`	109.3
H2b-C2`-C3`	112.0	H5b-C5`-O	109.4
H-C3`-O	100.8	H5b-C5`-C4`	109.0
H-C3`-C2`	110.3		

[a] All bond lengths were taken to be 1.0 Å.

Table 2: Experimental and calculated bond lengths (Å) of guanosine and the difference (Δ = X-ray – B3LYP).

Bonds	Length		
	X-ray[a]	B3LYP	Δ
O6-C6	1.230	1.243	0.013
O3'-C3'	1.447	1.451	0.004
O4'-C1'	1.415	1.468	0.053
O4'-C4'	1.442	1.476	0.034
O5'-C5'	1.449	1.454	0.004
N1-C6	1.400	1.445	0.045
N1-C2	1.368	1.381	0.013
N2-C2	1.337	1.364	0.027
N3-C2	1.327	1.327	0.000
N3-C4	1.349	1.365	0.015
N7-C5	1.390	1.396	0.005
N7-C8	1.300	1.323	0.023
N9-C4	1.376	1.382	0.006
N9-C8	1.370	1.406	0.035
N9-C1'	1.458	1.457	-0.001
C4-C5	1.378	1.398	0.020
C5-C6	1.418	1.433	0.014
C1'-C2'	1.515	1.543	0.028
C2'-C3'	1.510	1.540	0.030
C3'-C4'	1.525	1.533	0.008
C4'-C5'	1.507	1.521	0.014

[a] Taken from L. H. Koole, H. M. Buck, J. A. Kanters, A. Schouten, *Can. J. Chem.* **1988**, *66*, 2634-2639.

Table 3: Selected experimental and calculated bond angles (°) of guanosine and the difference (Δ = X-ray – B3LYP).

Bonds	Angle		
	X-ray[a]	B3LYP	Δ
C'1-O4'-C4'	109.8	110.8	-1.0
C2-N1-C6	125.4	125.9	-0.5
C4-N3-C2	111.8	113.6	-1.8
C5-N7-C8	104.5	105.2	-0.7
C1'-N9-C4	125.6	124.9	0.7
C4-N9-C8	106.4	106.1	0.3
N3-C2-N1	123.8	122.7	1.1
N9-C4-C5	105.4	106.1	-0.7
N3-C4-C5	128.9	128.1	0.8
C4-C5-C6	118.9	119.4	-0.5
C4-C5-N7	110.5	110.3	0.2
N1-C6-C5	111.1	110.2	0.9
N1-C6-O6	119.9	118.8	1.1
N7-C8-N9	113.1	112.3	0.8
C2'-C1-'O4'	105.8	105.6	0.2
O4'-C1'-N9	107.0	109.4	-2.4
C3'-C2'-C1'	102.6	101.4	1.2
O3'-C3'-C2'	106.2	114.3	-8.1
C2'-C3'-C4'	102.8	103.1	-0.3
O4'-C4'-C3'	106.6	105.3	1.3
O4'-C4'-C5'	109.6	107.4	2.2
C4'-C5'-O5'	108.4	111.2	-2.8
N1-C2-N2	116.5	118.1	-1.6

[a] Taken from L. H. Koole, H. M. Buck, J. A. Kanters, A. Schouten, *Can. J. Chem.* **1988**, *66*, 2634-2639.

Table 4: Selected experimental and calculated bond angles (°) of guanosine and the difference (Δ = X-ray – B3LYP).

	Torsion angle		
Bonds	X-ray[a]	B3LYP	Δ
O4'-C1'-C2'-C3'	33.7	21.4	12.3
C1'-C2'-C3'-C4'	-33.4	-31.3	-2.1
C3'-C4'-C5'-O5'	57.8	60.8	-3.0
C8-N9-C1'-O4'	49.4	57.2	-7.8
C1'-N9-C8-N7	173.9	178.6	-4.7
C5-N7-C8-N9	-0.8	-0.1	-0.7
C8-N7-C5-C4	0.7	0.3	0.4
C2-N3-C4-C5	-1.7	-0.6	-1.1
C6-N1-C2-N3	1.3	-0.2	1.5
C2-N1-C6-C5	-0.9	-0.2	-0.7
C2-N1-C6-O6	179.7	179.8	-0.1
C4-N3-C2-N2	-179.9	-179.6	-0.3

[a] Taken from L. H. Koole, H. M. Buck, J. A. Kanters, A. Schouten, *Can. J. Chem.* **1988**, *66*, 2634-2639.

Comments:

The total root mean square (rms) error was calculated for the deviations according to the equation:

$$rms = \sqrt{\frac{\sum_{i}^{N}\left(\omega_i^{th} - \omega_i^{\exp}\right)^2}{N}}$$

N is the number of parameters used and ω_i^{th} and ω_i^{exp} are the theoretical and experimental bond lengths and angles, respectively. The rms values are 0.024 Å for the bond lengths, 2.1˚ for the angles and 4.6˚ for the torsion angles.

The bond length deviations range from 0.000 to 0053 Å. It is apparent that a polarized basis set is required to obtain a better correlation between the crystal structure and the DFT calculation but that is beyond the computational capacity available here.

The angle for the O3'-C3'-C2' bonds has the largest deviation of 8.1˚. The crystal structure is acetylated whereas the calculation is simply performed with a hydrogen atom in its place, which in turn causes this substantial deviation. When excluded from the rms value the number of 1.2˚ is obtained, which reflects a good correlation between theory and experimental results.

The torsion angle of the O4'-C1'-C2'-C3' bonds is not well represented by the calculation and as in the case of the bond lengths the absence of polarization function in the basis set is most likely the source of this error. Also the C8-N9-C1'-O4' and C1'-N9-C8-N7 angles are quite off. Both of these angles represent the spatial arrangement between the guanine and sugar moieties. The theoretical calculations relate to the situation of the molecule in vacuum; hence its structure is not affected by a crystal lattice like with the experimental results.

Summary

The overall correlation between the optimised theoretical minimum of the parent compound and the experimental crystal structure (L. H. Koole, H. M. Buck, J. A. Kanters, A. Schouten, *Can. J. Chem.* **1988**, *66*, 2634-2639) (molecule II) is reasonably good and therefore it is concluded that the global minimum is reached. Also the calculations of the normal modes revealed no imaginary frequencies for the calculated derivatives, which verifies that the structures are minima.