S2: Analysis of the simulations

Average Cremer-Pople parameters for each 10μs simulation

Key: "alpha-D"=1-OH (else 1-OMe) $^{1}C_4$=$^{1}C_4$-initiated (else $^{4}C_1$-initiated)

Cremer-Pople θ

$^{4}C_1$ conformers (θ<60)	AVE θ°	SD
alpha-D-GlcNAc-1C4.ave	10.06	5.48
alpha-D-GlcNAc.ave	10.05	5.48
alpha-D-GlcNS-1C4.ave	9.46	5.16
alpha-D-GlcNS3S-1C4.ave	9.55	5.20
alpha-D-GlcNS3S.ave	9.52	5.18
alpha-D-GlcNS6S-1C4.ave	9.50	5.20
alpha-D-GlcNS6S3S-1C4.ave	9.62	5.26
alpha-D-GlcNS6S3S.ave	9.63	5.27
alpha-D-GlcNS6S.ave	9.50	5.20
alpha-D-GlcNS.ave	9.46	5.15
glcNAc-1C4.theta.ave	9.73	5.32
glcNAc.theta.ave	9.70	5.30
glcNS-1C4.theta.ave	9.47	5.19
glcNS3S-1C4.theta.ave	9.65	5.30
glcNS3S.theta.ave	9.66	5.30
glcNS6S-1C4.theta.ave	9.46	5.24
glcNS6S3S-1C4.theta.ave	9.68	5.37
glcNS6S3S.theta.ave	9.65	5.36
glcNS6S.theta.ave	9.45	5.24
glcNS.theta.ave	9.47	5.19

$^{1}C_4$ conformers (θ>120)	AVE θ°	SD
alpha-D-GlcNAc-1C4.ave	166.41	6.55
alpha-D-GlcNAc.ave	166.26	6.39
alpha-D-GlcNS6S.ave	164.88	6.54
glcNAc-1C4.theta.ave	166.11	6.54
glcNAc.theta.ave	165.91	7.95
glcNS-1C4.theta.ave	164.90	6.28
glcNS3S-1C4.theta.ave	163.39	7.23
glcNS6S-1C4.theta.ave	165.13	6.29
glcNS6S3S-1C4.theta.ave	162.53	7.52

Cremer-Pople *Q*

$^4C_1$ conformers (θ<60)	AVE *Q*	SD
data_4C1/alpha-D-GlcNAc-1C4.ave	0.54	0.04
data_4C1/alpha-D-GlcNAc.ave	0.54	0.04
data_4C1/alpha-D-GlcNS-1C4.ave	0.55	0.04
data_4C1/alpha-D-GlcNS3S-1C4.ave	0.54	0.04
data_4C1/alpha-D-GlcNS3S.ave	0.54	0.04
data_4C1/alpha-D-GlcNS6S-1C4.ave	0.55	0.04
data_4C1/alpha-D-GlcNS6S3S-1C4.ave	0.54	0.04
data_4C1/alpha-D-GlcNS6S3S.ave	0.54	0.04
data_4C1/alpha-D-GlcNS6S.ave	0.55	0.04
data_4C1/alpha-D-GlcNS.ave	0.55	0.04
data_4C1/glcNAc-1C4.q.ave	0.56	0.04
data_4C1/glcNAc.q.ave	0.56	0.04
data_4C1/glcNS-1C4.q.ave	0.56	0.04
data_4C1/glcNS3S-1C4.q.ave	0.56	0.04
data_4C1/glcNS3S.q.ave	0.56	0.04
data_4C1/glcNS6S-1C4.q.ave	0.56	0.04
data_4C1/glcNS6S3S-1C4.q.ave	0.56	0.04
data_4C1/glcNS6S3S.q.ave	0.56	0.04
data_4C1/glcNS6S.q.ave	0.56	0.04
data_4C1/glcNS.q.ave	0.56	0.04

$^1C_4$ conformers (θ>120)	AVE *Q*	SD
data_1C4/alpha-D-GlcNAc-1C4.ave	0.52	0.04
data_1C4/alpha-D-GlcNAc.ave	0.52	0.04
data_1C4/alpha-D-GlcNS-1C4.ave	0.48	0.00
data_1C4/alpha-D-GlcNS3S-1C4.ave	0.53	0.05
data_1C4/alpha-D-GlcNS6S.ave	0.55	0.04
data_1C4/alpha-D-GlcNS.ave	0.54	0.00
data_1C4/glcNAc-1C4.q.ave	0.52	0.04
data_1C4/glcNAc.q.ave	0.52	0.04
data_1C4/glcNS-1C4.q.ave	0.55	0.04
data_1C4/glcNS3S-1C4.q.ave	0.55	0.04
data_1C4/glcNS6S-1C4.q.ave	0.55	0.04
data_1C4/glcNS6S3S-1C4.q.ave	0.55	0.04
data_1C4/glcNS.q.ave	0.56	0.00

Populations of hydroxyl orientation

Hexosamine	Hydroxyl	conformation	% occupancy
glcNAc-ome	OH4.dat	*t*	78.59
glcNAc-ome	OH4.dat	*+g*	11.86
glcNAc-ome	OH4.dat	*-g*	9.55
glcNAc-ome	OHM.dat	*t*	62.30
glcNAc-ome	OHM.dat	*+g*	22.02
glcNAc-ome	OHM.dat	*-g*	15.69
glcNAc-ome	OH3.dat	*t*	60.41
glcNAc-ome	OH3.dat	*+g*	25.00
glcNAc-ome	OH3.dat	*-g*	14.59
glcNAc-roh	OH1.dat	*t*	68.84
glcNAc-roh	OH1.dat	*+g*	19.08
glcNAc-roh	OH1.dat	*-g*	12.08
glcNAc-roh	OH4.dat	*t*	70.97
glcNAc-roh	OH4.dat	*+g*	17.56
glcNAc-roh	OH4.dat	*-g*	11.47
glcNAc-roh	OHM.dat	*t*	66.53
glcNAc-roh	OHM.dat	*+g*	20.22
glcNAc-roh	OHM.dat	*-g*	13.26
glcNAc-roh	OH3.dat	*t*	65.41
glcNAc-roh	OH3.dat	*+g*	21.41
glcNAc-roh	OH3.dat	*-g*	13.18
glcNS-roh	OH1.dat	*t*	67.95
glcNS-roh	OH1.dat	*+g*	18.85
glcNS-roh	OH1.dat	*-g*	13.21
glcNS-roh	OH4.dat	*t*	69.00
glcNS-roh	OH4.dat	*+g*	18.20
glcNS-roh	OH4.dat	*-g*	12.80
glcNS-roh	OHM.dat	*t*	66.38
glcNS-roh	OHM.dat	*+g*	19.86
glcNS-roh	OHM.dat	*-g*	13.76
glcNS-roh	OH3.dat	*t*	64.71
glcNS-roh	OH3.dat	*+g*	21.68
glcNS-roh	OH3.dat	*-g*	13.62
glcNS6S-roh	OH1.dat	*t*	66.53
glcNS6S-roh	OH1.dat	*+g*	19.99
glcNS6S-roh	OH1.dat	*-g*	13.48
glcNS6S-roh	OH4.dat	*t*	66.28
glcNS6S-roh	OH4.dat	*+g*	19.50
glcNS6S-roh	OH4.dat	*-g*	14.22
glcNS6S-roh	OH3.dat	*t*	64.67
glcNS6S-roh	OH3.dat	*+g*	21.20
glcNS6S-roh	OH3.dat	*-g*	14.13
glcNS3S-roh	OH1.dat	*t*	66.09
glcNS3S-roh	OH1.dat	*+g*	19.85
glcNS3S-roh	OH1.dat	*-g*	14.07
glcNS3S-roh	OH4.dat	*t*	67.25

glcNS3S-roh	OH4.dat	*+g*	19.22
glcNS3S-roh	OH4.dat	*-g*	13.53
glcNS3S-roh	OHM.dat	*t*	65.79
glcNS3S-roh	OHM.dat	*+g*	20.15
glcNS3S-roh	OHM.dat	*-g*	14.06
glcNS6S3S-roh	OH1.dat	*t*	66.98
glcNS6S3S-roh	OH1.dat	*+g*	19.09
glcNS6S3S-roh	OH1.dat	*-g*	13.93
glcNS6S3S-roh	OH4.dat	*t*	67.44
glcNS6S3S-roh	OH4.dat	*+g*	18.63
glcNS6S3S-roh	OH4.dat	*-g*	13.93

Populations of hydroxylmethyl orientations (O6-C6-C5-O5)

Hexosamine	orientation	% occupancy
glcNAc-ome	+g	1.78
glcNAc-ome	gt	39.70
glcNAc-ome	gg	58.52
glcNAc-roh	+g	1.78
glcNAc-roh	gt	38.61
glcNAc-roh	gg	59.61
glcNS-roh	+g	1.79
glcNS-roh	gt	38.50
glcNS-roh	gg	59.70
glcNS6S-roh	+g	3.99
glcNS6S-roh	gt	35.15
glcNS6S-roh	gg	60.86
glcNS3S-roh	+g	3.54
glcNS3S-roh	gt	35.70
glcNS3S-roh	gg	60.76
glcNS6S3S-roh	+g	4.44
glcNS6S3S-roh	gt	34.19
glcNS6S3S-roh	gg	61.37

Conformer populations (from 20 μs)

Pucker	GlcNAc	1-OMe-GlcNAc
4C1	99.6146%	99.7559%
OE	0.0004%	0.0012%
OH1	0.0012%	0.0020%
E1	0.0031%	0.0047%
2H1	0.0065%	0.0105%
2E	0.0106%	0.0063%
2H3	0.0118%	0.0029%
E3	0.0063%	0.0011%
4H3	0.0023%	0.0002%
4E	0.0018%	0.0001%
4H5	0.0027%	0.0007%
E5	0.0042%	0.0015%
OH5	0.0015%	0.0014%
3OB	0.0018%	0.0015%
3S1	0.0011%	0.0009%
B14	0.0002%	0.0001%
5S1	0.0010%	0.0006%
25B	0.0010%	0.0003%
2SO	0.0121%	0.0068%
B3O	0.0144%	0.0116%
1S3	0.0092%	0.0130%
14B	0.0049%	0.0040%
1S5	0.0070%	0.0026%
B25	0.0069%	0.0002%
OS2	0.0133%	0.0021%
EO	0.0000%	0.0000%
1HO	0.0000%	0.0000%
1E	0.0000%	0.0000%
1H2	0.0000%	0.0000%
E2	0.0000%	0.0000%
3H2	0.0000%	0.0000%
3E	0.0000%	0.0000%
3H4	0.0000%	0.0000%
E4	0.0003%	0.0001%
5H4	0.0002%	0.0005%
5E	0.0002%	0.0000%
5HO	0.0000%	0.0000%
1C4	0.2586%	0.1661%

Pucker	GlcNS	GlcNS3S	GlcNS6S	GlcNS6S3S
4C1	99.9729%	99.9729%	99.1278%	99.9445%
OE	0.0002%	0.0002%	0.0001%	0.0001%
OH1	0.0008%	0.0008%	0.0007%	0.0012%
E1	0.0032%	0.0032%	0.0040%	0.0083%
2H1	0.0064%	0.0064%	0.0100%	0.0146%
2E	0.0078%	0.0078%	0.0108%	0.0104%
2H3	0.0048%	0.0048%	0.0057%	0.0033%
E3	0.0010%	0.0010%	0.0011%	0.0008%
4H3	0.0003%	0.0003%	0.0002%	0.0002%
4E	0.0000%	0.0000%	0.0000%	0.0000%
4H5	0.0000%	0.0000%	0.0002%	0.0000%
E5	0.0001%	0.0001%	0.0002%	0.0002%
OH5	0.0003%	0.0003%	0.0000%	0.0001%
3OB	0.0000%	0.0000%	0.0000%	0.0000%
3S1	0.0000%	0.0000%	0.0000%	0.0000%
B14	0.0001%	0.0001%	0.0005%	0.0001%
5S1	0.0010%	0.0010%	0.0041%	0.0072%
25B	0.0003%	0.0003%	0.0012%	0.0033%
2SO	0.0007%	0.0007%	0.0050%	0.0034%
B3O	0.0000%	0.0000%	0.0010%	0.0012%
1S3	0.0000%	0.0000%	0.0013%	0.0006%
14B	0.0000%	0.0000%	0.0005%	0.0000%
1S5	0.0000%	0.0000%	0.0013%	0.0000%
B25	0.0000%	0.0000%	0.0003%	0.0000%
OS2	0.0000%	0.0000%	0.0002%	0.0000%
EO	0.0000%	0.0000%	0.0000%	0.0000%
1HO	0.0000%	0.0000%	0.0000%	0.0000%
1E	0.0000%	0.0000%	0.0000%	0.0000%
1H2	0.0000%	0.0000%	0.0000%	0.0000%
E2	0.0000%	0.0000%	0.0000%	0.0000%
3H2	0.0000%	0.0000%	0.0000%	0.0000%
3E	0.0000%	0.0000%	0.0000%	0.0000%
3H4	0.0000%	0.0000%	0.0001%	0.0000%
E4	0.0000%	0.0000%	0.0003%	0.0000%
5H4	0.0000%	0.0000%	0.0017%	0.0000%
5E	0.0000%	0.0000%	0.0010%	0.0000%
5HO	0.0000%	0.0000%	0.0003%	0.0000%
1C4	0.0000%	0.0000%	0.8196%	0.0000%