Supporting Information for:

Conical-Intersection Topographies Suggest That Ribose Exhibits Enhanced UV Photostability

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Computational Methods *(continued)*

For the CASSCF(2,2) calculations preceding the MRCISD calculations no molecular orbitals were frozen at the SCF level. For the MRCISD calculations the ten 1s molecular orbitals of the carbon and oxygen atoms were frozen. All calculations were performed for two roots (S_0–S_1). The MS-CASPT2 calculations employed a level shift of 0.2 a.u.

For the O−H and the endocyclic C−O bond-elongation reaction paths, the last two points were obtained by rigid scan originating from the minimum-energy conical intersection. For the endo- and exocyclic C−O bond-elongation reaction paths, the first two points of the $n\sigma^*$ state are not shown, since the σ^* molecular orbital is not clearly defined in the short-bond-length region. Here, the S_1 state exhibits strong Rydberg character, hence the reaction path of that state exhibits an artefactual kink due to the inconsistent description of the $n\sigma^*$ state in that region. In the elongated-bond-length region the second molecular orbital in the active space is a well-defined σ^* orbital with no contributions anywhere else in the molecule and the Rydberg character has vanished.

Table S1 Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of the first few singlet excited states of ribose computed at the TDDFT/aug-cc-pVTZ and the CC2/aug-cc-pVTZ levels of theory.

state	TDDFT	CC2
S_1	5.91 (0.0062)	6.29 (0.0088)
S_2	6.19 (0.0154)	6.58 (0.0211)
S_3	6.44 (0.0124)	6.75 (0.0162)
S_4	6.53 (0.0016)	6.82 (0.0006)
S_5	6.83 (0.0041)	7.15 (0.0158)
S_6	6.90 (0.0086)	7.27 (0.0061)
S_7	6.97 (0.0017)	7.41 (0.0181)
S_8	7.08 (0.0070)	7.49 (0.0025)
S_9	7.14 (0.0042)	7.52 (0.0076)
S_{10}	7.24 (0.0041)	7.59 (0.0085)

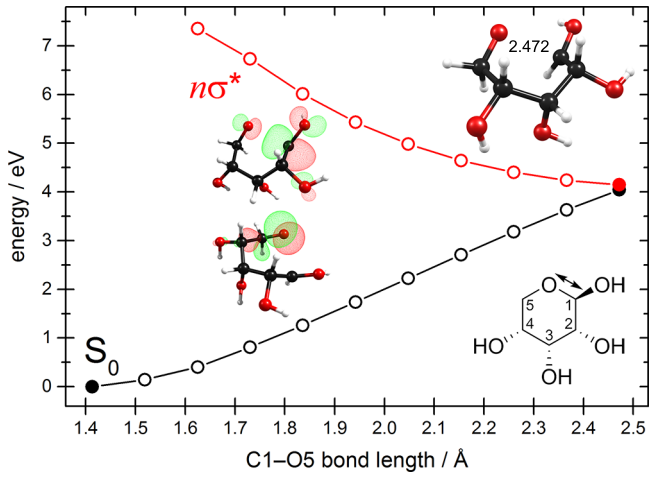

Figure S1 Analogous to Fig. 4 in the article: energy profiles, conical intersection, and molecular orbitals for the endocyclic C1−O5 bond-elongation process.

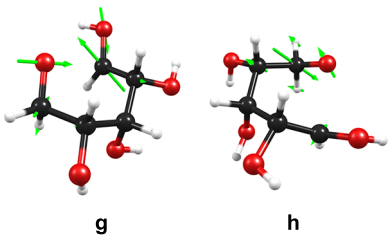

Figure S2 Analogous to Fig. 5 in the article: orthogonalized branching-space vectors ($|\mathbf{g}_{orth}| = 0.0825$ and $|\mathbf{h}_{orth}| = 0.0604\ E_h/a_0$) of the conical intersection for the endocyclic C1−O5 bond-elongation process.

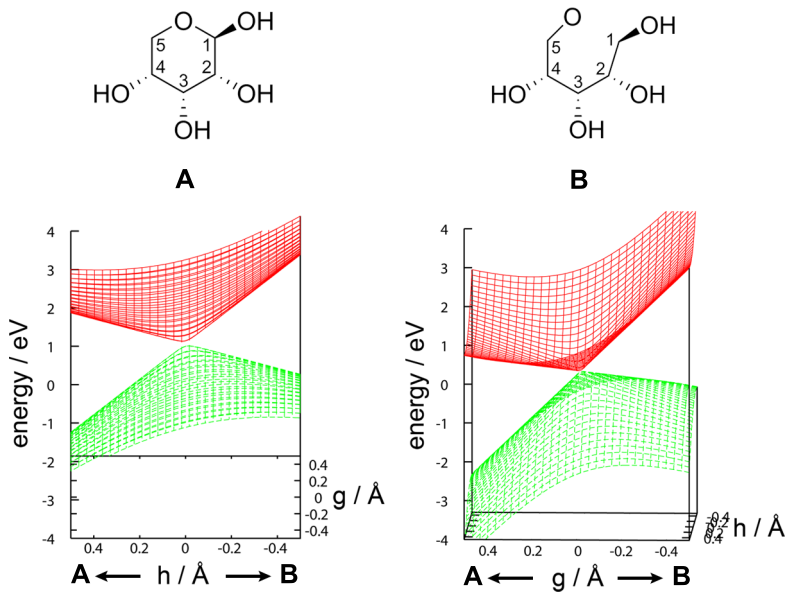

Figure S3 Local topography of the S_1 and S_0 potential-energy surfaces in the branching space of the $n\sigma^*/S_0$ conical intersection for the endocyclic C1−O5 bond-elongation process (shown from two perspectives). The positive direction of both the nonadiabatic-coupling vector **h** and the gradient-difference vector **g** corresponds to the reaction direction toward ring-closure (marked with **A**), whereas the negative direction of both **h** and **g** corresponds to the reaction direction toward ring-opening (marked with **B**, illustrated by the structural formulas). The topography of this conical intersection is peaked, yet it is slightly tilted toward ring-closure along both branching-space vectors.

Table S2 Topographical parameters (δ_{gh}, s_x, and s_y in E_h/a_0, Δ_{gh} dimensionless) of the minimum-energy conical intersection for the C1-O−H elongation process (see Figs. 1 or 2 in the article).

δ_{gh}	Δ_{gh}	s_x	s_y
0.07738	0.42336	−0.08490	0.06076

Table S3 Topographical parameters (δ_{gh}, s_x, and s_y in E_h/a_0, Δ_{gh} dimensionless) of the minimum-energy conical intersection for the endocyclic C5−O5 bond-elongation process (see Figs. 4 or 5 in the article).

δ_{gh}	Δ_{gh}	s_x	s_y
0.08259	−0.47154	−0.02785	0.03598

Table S4 Topographical parameters (δ_{gh}, s_x, and s_y in E_h/a_0, Δ_{gh} dimensionless) of the minimum-energy conical intersection for the endocyclic C1−O5 bond-elongation process (see Figs. S1 or S2).

δ_{gh}	Δ_{gh}	s_x	s_y
0.10220	0.30169	−0.04421	−0.02928

Table S5 Topographical parameters (δ_{gh}, s_x, and s_y in E_h/a_0, Δ_{gh} dimensionless) of the minimum-energy conical intersection for the exocyclic C1−O1 bond-elongation process (see Figs. 7 or 8 in the article).

δ_{gh}	Δ_{gh}	s_x	s_y
0.07282	0.90214	−0.02449	0.01780

Table S6 Cartesian coordinates of the MRCISD//CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the C1-O−H elongation process (energy: $-570.51337\ E_h$).

```
20

C    0.053837   1.006239  -0.897589
C   -0.411011  -0.255881  -0.175887
C   -1.909332  -0.490506  -0.309070
C   -2.703416   0.797957  -0.153500
C   -2.120286   1.852701  -1.076747
O   -0.790080   2.101619  -0.673356
O    0.206853  -1.416115  -0.686284
O   -2.232016  -0.992662  -1.582966
O   -4.061279   0.578653  -0.391228
O    1.200364   1.468138  -0.282590
H    1.147997  -1.364258  -0.554969
H   -1.624149  -1.704478  -1.767021
H   -0.165507  -0.095433   0.878330
H   -2.214121  -1.203717   0.466293
H   -2.599027   1.167234   0.869934
H   -2.163262   1.521006  -2.120971
H   -2.655348   2.796422  -0.983117
H   -4.115547  -0.001482  -1.147015
H    1.907262   2.548525  -1.736669
H    0.121356   0.826242  -1.984477
```

Table S7 Cartesian coordinates of the MRCISD//CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the endocyclic C5−O5 bond-elongation process (energy: −570.58400 E_h).

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20

C    0.171442   0.948311  -1.021321
C   -0.461303  -0.149296  -0.144180
C   -1.931988  -0.415535  -0.401592
C   -2.887555   0.744467  -0.166260
C   -2.706688   1.869219  -1.130614
O   -0.345038   2.147361  -0.753097
O    0.185021  -1.367714  -0.399769
O   -2.141664  -0.853888  -1.722531
O   -4.213736   0.260359  -0.238170
O    1.549922   0.843689  -0.761455
H    1.122800  -1.189674  -0.411643
H   -1.546197  -1.585756  -1.866746
H   -0.321701   0.162722   0.898435
H   -2.228030  -1.203458   0.302229
H   -2.756812   1.109669   0.854089
H   -2.599573   1.651999  -2.185847
H   -2.930279   2.884647  -0.833949
H   -4.279791  -0.219435  -1.061436
H    1.975310   1.610599  -1.132450
H   -0.029342   0.693312  -2.077919
```

Table S8 Cartesian coordinates of the MRCISD//CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the endocyclic C1−O5 bond-elongation process (energy: −570.57709 E_h).

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20

C    0.345927   0.509488  -1.178140
C   -0.332586  -0.333729  -0.168299
C   -1.831754  -0.443843  -0.392494
C   -2.666368   0.806672  -0.151812
C   -2.257423   2.038272  -0.995782
O   -1.033509   2.476716  -0.597082
O    0.123370  -1.683303  -0.216727
O   -2.098453  -0.870120  -1.710907
O   -4.010694   0.501624  -0.388741
O    1.547768   0.975496  -0.827384
H    1.073284  -1.678649  -0.147972
H   -1.676363  -1.718293  -1.820952
H   -0.134135   0.096355   0.820516
H   -2.194892  -1.196787   0.316805
H   -2.581661   1.085840   0.900718
H   -2.258403   1.716192  -2.049390
H   -3.052617   2.780357  -0.848275
H   -4.037700   0.026811  -1.216556
H    1.848691   1.608111  -1.473389
H    0.034270   0.548619  -2.212297
```

Table S9 Cartesian coordinates of the MRCISD//CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the exocyclic C1−O1 bond-elongation process (energy: −570.55628 E_h).

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20

O   -0.716954   2.054100  -0.768964
O    2.325042   1.349908  -0.492077
O    0.275360  -1.396986  -0.460117
O   -2.161695  -0.934494  -1.638745
O   -4.058797   0.569493  -0.470169
C   -0.014555   0.932551  -0.995010
C   -0.403061  -0.223328  -0.128102
C   -1.901397  -0.500988  -0.326478
C   -2.716093   0.769586  -0.134963
C   -2.131979   1.900013  -0.976697
H    1.210054  -1.214774  -0.397879
H   -1.621207  -1.702673  -1.804203
H   -0.255855   0.056697   0.924342
H   -2.227883  -1.260469   0.394872
H   -2.691633   1.052149   0.920204
H   -2.323078   1.699722  -2.035308
H   -2.582933   2.852830  -0.706885
H   -4.071695   0.046368  -1.269507
H    2.619454   2.082903  -1.046274
H    0.338559   0.749415  -2.002204
```