Supplementary Informations

Tautomers of cytosine and their excited electronic states: a matrix isolation spectroscopic and quantum chemical study

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Table S1. Experimental, and computational data used for calculating tautomer distribution

ν_{fit}	$(\Sigma)A_{fit}$	$(\Sigma)I_{1}$	$(\Sigma)I_{2a}$	$(\Sigma)I_{2b}$	$(\Sigma)I_{3a}$	$\Sigma I_i n_i$
709.2 710.8	37.1	–	5.4	5.0	–	49.4
716.8	135.8	36.2	–	–	–	110.8
743.0	74.7	–	–	–	34.4	37.3
747.2	40.1	5.3	–	–	–	16.3
751.2	10.2	–	–	–	5.7	6.2
767.3	57.2	6.6	–	–	–	20.2
780.7 782.0	301.1	39.0	16.0	10.4	–	239.4
806.3 807.6	417.9	–	48.3	51.5	–	484.5
818.1 820.9	124.0	–	–	–	92.3	99.8
1082.4 1083.7	373.8	–	20.1	48.7	–	365.9
1087.4 1090.3	166.7	50.2	–	–	–	153.8
1107.7 1110.3	210.9	–	29.0	37.5	–	330.4
1124.6	166.6	–	–	–	162.6	175.9
1195.2 1210.3 1223.5	1036.9	47.1	170.3	30.3	74.1	1018.5
1243.1	92.2	27.7	–	–	–	84.8
1251.2 1256.8	215.3	–	–	16.8	–	101.2
1292.3	47.7	–	–	–	25.1	27.1
1303.1 1319.8 1332.7	1038.7	–	–	222.8	–	1344.2
1337.5	225.5	65.3	–	–	–	200.0
1372.8 1374.3 1379.0 1381.3 1382.8 1385.1	587.2	–	60.3	52.1	23.3	556.2
1417.1 1419.3 1422.5 1426.0 1428.1	1807.3	85.8	441.0	–	103.4	1958.0
1437.6 1439.4	2017.0	–	–	376.5	–	2271.5
1474.5	817.9	171.9	–	–	68.2	600.5
1492.2 1496.0	571.0	–	60.4	41.1	–	464.4
1538.5	354.4	148.8	–	–	–	455.9
1561.1 1569.1 1574.2	1190.3	–	131.9	62.6	–	851.4
1589.3 1594.4 1599.2	1980.0	111.4	273.7	256.2	–	2869.4
1612.8 1620.8 1623.4	4976.7	–	392.3	497.4	30.0	4441.0
1655.8	1237.7	479.7	–	–	–	1470.2
1666.0 1671.9 1674.4	574.9	–	–	–	478.4	517.4
1716.9 1719.8	2400.2	737.1	–	–	–	2259.1
1747.3 1751.8 1757.1	735.8	–	–	–	791.6	856.2
3440.8 3445.6 3452.1	1617.1	80.2	55.7	62.6	62.5	891.2
3470.7	359.6	–	–	–	–	223.2
3496.1	142.1	–	–	–	110.7	119.8
3560.4 3563.4 3565.8	1014.4	47.4	40.4	43.1	–	550.3
3592.0	966.3	–	–	96.1	–	579.6
3600.9	182.5	–	84.1	–	–	302.0

Table S2. Optimized geometry of the oxo (**1**) tautomer of cytosine obtained under planarity constraint from CCSD/cc-pVDZ calculations: Cartesian coordinates in Angströms. This geometry was used in all calculations.

	X	Y
N(1)	1.19541	0.98259
C(2)	1.17082	-0.43691
N(3)	-0.07917	-1.03604
C(4)	-1.16010	-0.28230
C(5)	-1.15536	1.17243
C(6)	0.07438	1.75798
N(7)	-2.36098	-0.91931
O(8)	2.22814	-1.03772
H(9)	2.12025	1.39759
H(10)	-2.07376	1.76064
H(11)	0.22392	2.84139
H(12)	-2.36243	-1.93050
H(13)	-3.23219	-0.41226

Table S3. Parameters of the LVC calculations for the oxo (**1**) tautomer of cytosine. Vibrational frequencies (ω in cm^{-1}) obtained at the CCSD/cc-pVDZ level, intrastate couplings (τ in cm^{-1} $bohr^{-1}$) by the EOMEE-CCSD/cc-pVDZ method.

ω	τ (2A')	τ (3A')	τ (4A')
781.9	477.8	613.9	627.8
1134.3	558.3	639.9	136.3
1302.1	1350.6	179.0	227.1
1377.1	681.3	81.1	663.5
1471.1	800.9	1068.2	251.2
1538.0	278.2	42.0	584.6
1621.9	2181.4	2631.5	334.5
1650.1	718.3	391.2	527.4
1745.5	149.1	21.9	970.1
1853.9	1317.6	531.7	1604.4

Table S4 Optimized geometry of the hydroxy (**2b**) tautomer of cytosine obtained under planarity constraint from CCSD/cc-pVDZ calculations: Cartesian coordinates in Angströms. This geometry was used in all calculations.

	X	Y
N(1)	-1.26360	-1.01268
N(2)	0.07688	0.99686
N(3)	2.37131	0.92657
C(4)	-1.07138	0.31193
C(5)	1.19260	0.24829
C(6)	1.14509	-1.17223
C(7)	-0.12234	-1.73512
O(8)	-2.17852	1.07608
H(9)	2.05036	-1.78337
H(10)	-0.24556	-2.82469
H(11)	2.34352	1.93657
H(12)	3.25678	0.44486
H(13)	-2.91052	0.44101

Table S5. Parameters of the LVC calculations for the hydroxy (**2b**) tautomer of cytosine. Vibrational frequencies (ω in cm^{-1}) obtained at the CCSD/cc-pVDZ level, intrastate couplings (τ in cm^{-1} $bohr^{-1}$) by the EOMEE-CCSD/cc-pVDZ method.

ω	τ (2A')	τ (3A')	τ (4A')
803.4	1001.6	761.4	547.4
1001.4	512.7	158.9	141.2
1008.5	506.8	713.4	307.7
1113.0	471.0	299.0	1.7
1135.5	477.8	52.5	299.6
1268.8	648.0	740.7	203.7
1439.3	1173.0	385.0	538.6
1652.5	377.5	833.2	837.3
1666.2	293.4	964.4	688.3
1710.6	481.5	564.9	356.0

Table S6. Ground state optimized geometry of the imino (**3**) tautomer of cytosine obtained under planarity constraint from CCSD/cc-pVDZ calculations: Cartesian coordinates in Angströms. This geometry was used in all calculations.

	X	Y
N(1)	-1.17751	-1.01463
N(2)	2.34932	1.06016
N(3)	0.04854	0.95568
C(4)	-1.20658	0.37863
C(5)	1.30154	0.31517
C(6)	1.21149	-1.15479
C(7)	-0.00440	-1.75055
O(8)	-2.24407	1.01097
H(9)	-2.08288	-1.46626
H(10)	0.06189	1.97120
H(11)	2.12658	-1.74873
H(12)	-0.12945	-2.83640
H(13)	3.17944	0.45672

Table S7. Parameters of the LVC calculations for the imino (**3**) tautomer of cytosine. Vibrational frequencies (ω in cm^{-1}) obtained at the CCSD/cc-pVDZ level, intrastate couplings (τ in cm^{-1} $bohr^{-1}$) by the EOMEE-CCSD/cc-pVDZ method.

ω	τ (2A')	τ (3A')	τ (4A')
378.9	64.3	685.7	281.4
778.1	429.3	467.6	420.5
1179.1	440.2	628.2	170.1
1427.7	579.9	38.6	152.2
1438.9	716.1	38.2	673.4
1473.6	468.4	1237.4	516.2
1541.6	480.9	1363.2	1085.4
1707.4	679.0	272.2	344.2
1784.0	2691.9	2153.6	2370.3
1877.8	313.7	870.8	325.5