Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 660–662

Molecular structure of 5-fluorouracil from gas-phase electron diffraction data and quantum-chemical calculations

Natalja Vogt, Denis N. Ksenafontov, Denis Savelev and Anatoliy N. Rykov

Table S1 Conditions of the GED experiment for 5-fluororacil (5FU).

Nozzle-to-film distance, mm	362.3 (LD)	193.9 (SD)
Beam current, μA	2.4	2.4
Exposure time, sec	60, 50, 50	23, 25, 25
Nozzle temperature, K	485	483
Residual gas pressure, mm Hg	$2.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$
Number of the diffraction patterns (substance)	3	3
Number of the diffraction patterns (standard CCl_4)	2	2
Wavelength of electrons (λ), Å	0.0500675	0.0504375
Interval of scattering angles (s), $Å^{-1}$	3.6 – 17.4 (Δs = 0.2)	6.6 – 32.0 (Δs = 0.2)

Table S2 Experimental total intensity curves $I(s)$ for 5FU with background lines $G(s)$.

a) Long nozzle-to-film distance (LD), L = 362.3 mm

s, $Å^{-1}$	$I(s)$ [a]	$G(s)$ [b]
3.6	0.42702747	0.46531632
3.8	0.42722429	0.48208942
4.0	0.41033283	0.49886251
4.2	0.39929020	0.51332873
4.4	0.39978018	0.52444557
4.6	0.42356428	0.53168096
4.8	0.46357614	0.53513786
5.0	0.51669055	0.53559165

5.2	0.57048963	0.53385646
5.4	0.61431601	0.53056889
5.6	0.64109867	0.52629644
5.8	0.64754037	0.52157000
6.0	0.63377728	0.51674487
6.2	0.60226096	0.51187967
6.4	0.56116450	0.50682706
6.6	0.52112259	0.50139668
6.8	0.49086844	0.49546148
7.0	0.47001902	0.48899419
7.2	0.45645092	0.48211861
7.4	0.44415745	0.47498634
7.6	0.43174571	0.46773981
7.8	0.42084452	0.46048309
8.0	0.41440201	0.45329236
8.2	0.41352244	0.44623288
8.4	0.41680012	0.43935739
8.6	0.42124561	0.43269137
8.8	0.42430912	0.42624269
9.0	0.42503821	0.42001860
9.2	0.42248761	0.41402238
9.4	0.41649034	0.40826004
9.6	0.40699533	0.40272748
9.8	0.39586534	0.39741673
10.0	0.38646129	0.39231712
10.2	0.38178211	0.38742137
10.4	0.38325825	0.38273878
10.6	0.38883926	0.37827626
10.8	0.39431133	0.37402738
11.0	0.39570186	0.36997051
11.2	0.39085259	0.36607101
11.4	0.38050344	0.36229738
11.6	0.36730469	0.35862523
11.8	0.35401159	0.35503361
12.0	0.34292204	0.35151342
12.2	0.33474112	0.34807346
12.4	0.32972338	0.34474775
12.6	0.32646120	0.34157440
12.8	0.32431901	0.33859214
13.0	0.32246739	0.33580578

13.2	0.32139638	0.33318228
13.4	0.32200971	0.33065917
13.6	0.32469433	0.32818054
13.8	0.32898640	0.32574126
14.0	0.33312655	0.32338547
14.2	0.33470102	0.32117494
14.4	0.33231056	0.31916399
14.6	0.32657436	0.31737965
14.8	0.31934934	0.31581082
15.0	0.31323929	0.31442538
15.2	0.30959311	0.31319156
15.4	0.30865804	0.31210877
15.6	0.30981991	0.31120602
15.8	0.31159010	0.31051595
16.0	0.31310567	0.31006840
16.2	0.31379489	0.30987755
16.4	0.31331322	0.30994425
16.6	0.31177832	0.31027984
16.8	0.30977871	0.31092079
17.0	0.30805472	0.31191325
17.2	0.30800994	0.31325893
17.4	0.31055678	0.31460460

[a] Averaged taking into account scales factor of each experimental curve;
[b] Experimental background was approximated by cubic splines using algorithm of the UNEX program written by Y V Vishnevsky (http://unexprog.org).

b) Short nozzle-to-film distance (SD), L = 193.9 mm

s, Å^{-1}	$I(s)$ [a]	$G(s)$ [b]
6.6	0.43926619	0.42456197
6.8	0.41636907	0.42009955
7.0	0.39997936	0.41563714
7.2	0.38834410	0.41105366
7.4	0.37835728	0.40633724
7.6	0.36954114	0.40148228
7.8	0.36161817	0.39647016
8.0	0.35631945	0.39128860
8.2	0.35712443	0.38594573
8.4	0.36099305	0.38045895
8.6	0.36540984	0.37486626
8.8	0.36711311	0.36923597

9.0	0.36676085	0.36366102
9.2	0.36540770	0.35822224
9.4	0.35977499	0.35296295
9.6	0.35181703	0.34790329
9.8	0.34142138	0.34304681
10.0	0.33294822	0.33839349
10.2	0.32887007	0.33393770
10.4	0.33023533	0.32967010
10.6	0.33503840	0.32558072
10.8	0.33978894	0.32166033
11.0	0.34096640	0.31789764
11.2	0.33661313	0.31427829
11.4	0.32681389	0.31078859
11.6	0.31506560	0.30741716
11.8	0.30351616	0.30414711
12.0	0.29328465	0.30096036
12.2	0.28593427	0.29784670
12.4	0.28158007	0.29480010
12.6	0.27855546	0.29181586
12.8	0.27613442	0.28889506
13.0	0.27419912	0.28604114
13.2	0.27270493	0.28325359
13.4	0.27275033	0.28052816
13.6	0.27488243	0.27785837
13.8	0.27815187	0.27524014
14.0	0.28136971	0.27267653
14.2	0.28216451	0.27017494
14.4	0.27931058	0.26774572
14.6	0.27340921	0.26540008
14.8	0.26621112	0.26314718
15.0	0.25972805	0.26099401
15.2	0.25563409	0.25894580
15.4	0.25402828	0.25700414
15.6	0.25384452	0.25516723
15.8	0.25417382	0.25343138
16.0	0.25438438	0.25178834
16.2	0.25333611	0.25022362
16.4	0.25162245	0.24871986
16.6	0.24868229	0.24725700
16.8	0.24524761	0.24581933

17.0	0.24186197	0.24439889
17.2	0.23902646	0.24299673
17.4	0.23745740	0.24162025
17.6	0.23671921	0.24027636
17.8	0.23637545	0.23896973
18.0	0.23579008	0.23770382
18.2	0.23526308	0.23648270
18.4	0.23452192	0.23530999
18.6	0.23422378	0.23418968
18.8	0.23423452	0.23312286
19.0	0.23449275	0.23210669
19.2	0.23441723	0.23113502
19.4	0.23396607	0.23020118
19.6	0.23298468	0.22929839
19.8	0.23116312	0.22842168
20.0	0.22891378	0.22757026
20.2	0.22658280	0.22674497
20.4	0.22432807	0.22594582
20.6	0.22269164	0.22517156
20.8	0.22175905	0.22441851
21.0	0.22143605	0.22368153
21.2	0.22120523	0.22295640
21.4	0.22119911	0.22224136
21.6	0.22088925	0.22153460
21.8	0.22051640	0.22083486
22.0	0.21999513	0.22014089
22.2	0.21959361	0.21945252
22.4	0.21924236	0.21877083
22.6	0.21886095	0.21809922
22.8	0.21842923	0.21744323
23.0	0.21816838	0.21680773
23.2	0.21769646	0.21619418
23.4	0.21695352	0.21560316
23.6	0.21592176	0.21503670
23.8	0.21500020	0.21449773
24.0	0.21403163	0.21398739
24.2	0.21331232	0.21350513
24.4	0.21282873	0.21304725
24.6	0.21262883	0.21260579
24.8	0.21231116	0.21216893

25.0	0.21176750	0.21172499
25.2	0.21078354	0.21126620
25.4	0.20965170	0.21079075
25.6	0.20872655	0.21030022
25.8	0.20799337	0.20979642
26.0	0.20759841	0.20928191
26.2	0.20732361	0.20876105
26.4	0.20734292	0.20824105
26.6	0.20745904	0.20772987
26.8	0.20742675	0.20723574
27.0	0.20751939	0.20676694
27.2	0.20723491	0.20633048
27.4	0.20709973	0.20593350
27.6	0.20685926	0.20558091
27.8	0.20674081	0.20527560
28.0	0.20651195	0.20501816
28.2	0.20637158	0.20480772
28.4	0.20600572	0.20464178
28.6	0.20540902	0.20451826
28.8	0.20494997	0.20443549
29.0	0.20438163	0.20439046
29.2	0.20389890	0.20438110
29.4	0.20357836	0.20440703
29.6	0.20343631	0.20446948
29.8	0.20346460	0.20457104
30.0	0.20364966	0.20471555
30.2	0.20377068	0.20490856
30.4	0.20395214	0.20515820
30.6	0.20437616	0.20547296
30.8	0.20467637	0.20585960
31.0	0.20513472	0.20632334
31.2	0.20605624	0.20686309
31.4	0.20718096	0.20746679
31.6	0.20861986	0.20811378
31.8	0.20955090	0.20878164
32.0	0.21040759	0.20944950

[a] Averaged taking into account scales factor of each experimental curve;
[b] Experimental background was approximated by cubic splines using algorithm of the UNEX program written by Y V Vishnevsky (http://unexprog.org).

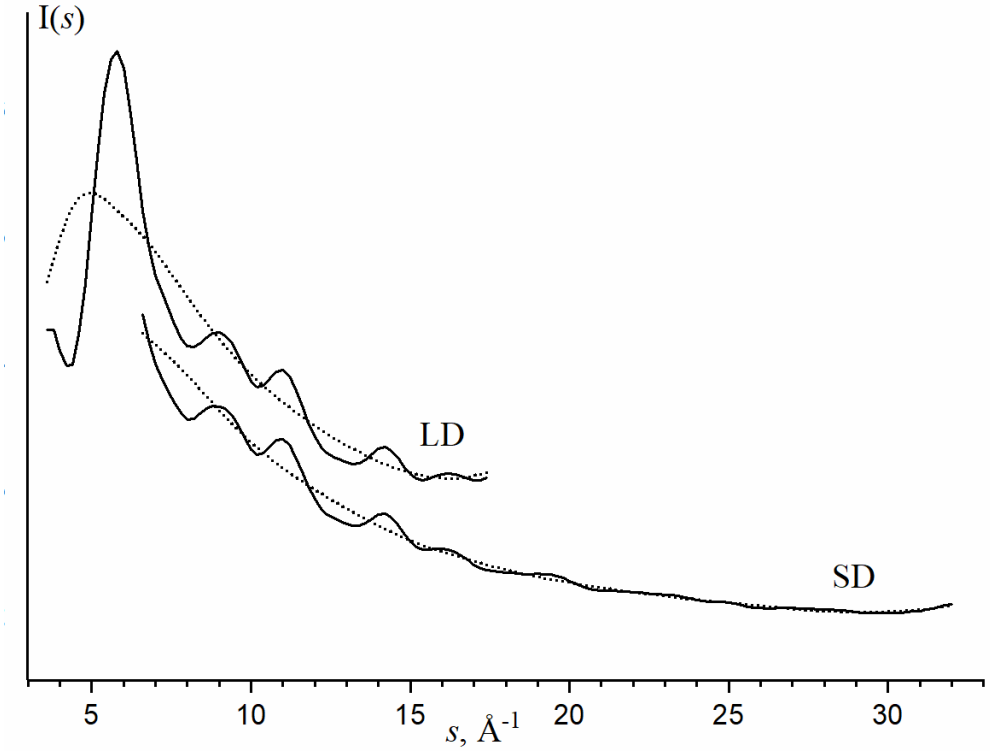


Figure S1 Experimental average total intensity curves *I*(*s*) (solid line) of 5FU with background lines *G(s)* (short dot) at the long (LD) and short (SD) nozzle-to film distances.

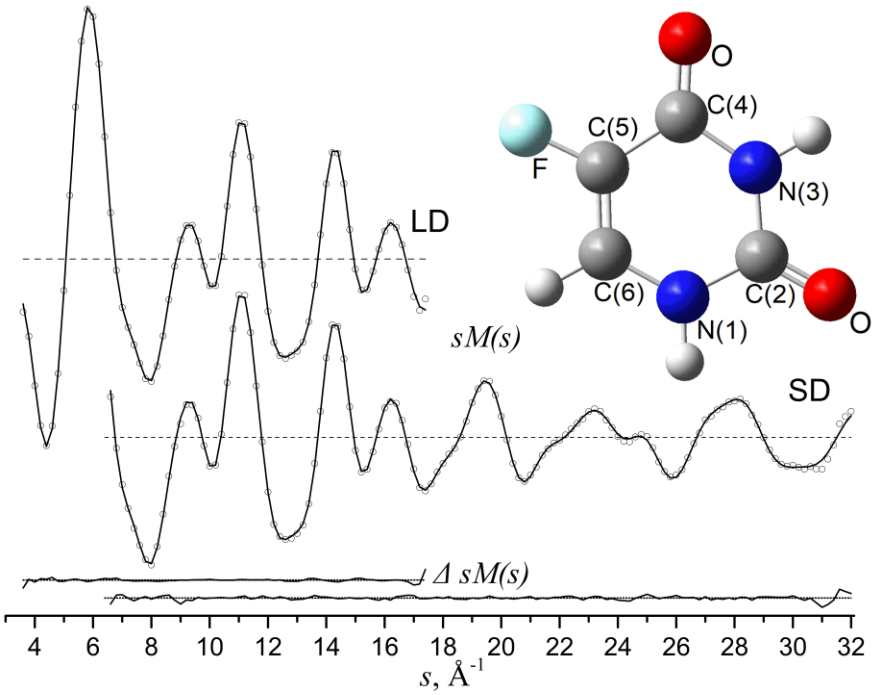


Figure S2 Experimental (open circles) and theoretical (solid line) *sM*(*s*) curves for the long (LD) and short (SD) nozzle-to-film distances and their differences $\Delta sM(s) = sM(s)_{exp} - sM(s)_{theor}$ (R_f=3.07%).

Table S3 Relative energy of tautomers of 5FU.

Method	Relative energy in kcal mol^{-1}					
	U1	U2	U3	U4	U5	U6
B3LYP/6-31G**	0.0	17.9	16.8	14.4	17.8	20.6
MP2/6-31G**	0.0	18.2	17.8	13.6	17.5	22.0
B3LYP/cc-pVTZ	0,0	17.3	16.4	14.6	17.2	20.7
MP2/cc-pVTZ	0,0	15.9	15.7	10.9	15.5	20.6

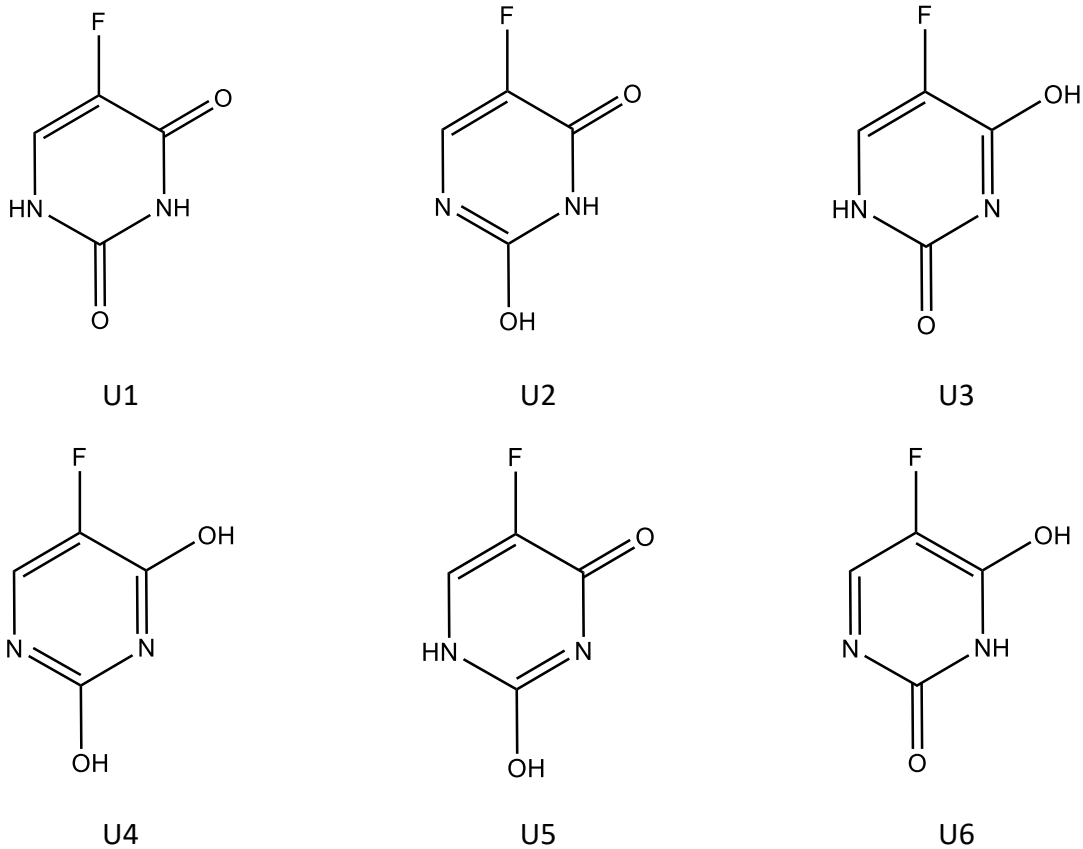


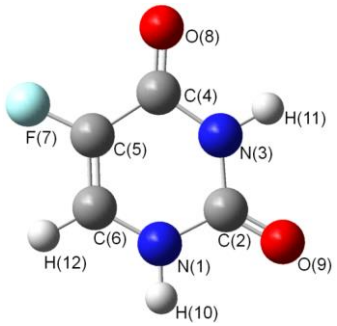
Figure S3 Different tautomers of 5FU.

Table S4 The r_e^{BO} structure of 5FU.

Parameters	CCSD(T)/cc-pVTZ	MP2_AE/cc-pwCVQZ	MP2/cc-pwCVQZ	MP2/aug-cc-pVQZ	MP2/cc-pVTZ	r_e^{BO} (see Eq.1)
N(1)–C(2)	1.3833	1.3738	1.3765	1.3773	1.3795	1.3784
C(2)–N(3)	1.3885	1.3797	1.3825	1.3830	1.3859	1.3828
N(3)–C(4)	1.3984	1.3916	1.3945	1.3953	1.3975	1.3932
C(4)–C(5)	1.4661	1.4529	1.4561	1.4561	1.4589	1.4601
C(5)=C(6)	1.3455	1.3386	1.3419	1.3429	1.3446	1.3405
C(5)–F	1.3326	1.3269	1.3291	1.3301	1.3310	1.3295
C(4)=O(8)	1.2129	1.2104	1.2125	1.2141	1.2152	1.2097
C(2)=O(9)	1.2129	1.2102	1.2124	1.2140	1.2146	1.2101
N(1)–H	1.0056	1.0042	1.0053	1.0059	1.0059	1.0045
N(3)–H	1.0105	1.0094	1.0104	1.0111	1.0111	1.0094
C(6)–H	1.0800	1.0766	1.0780	1.0786	1.0786	1.0786
N(1)C(2)N(3)	112.85	112.91	112.88	112.94	112.72	113.10
C(2)N(3)C(4)	129.04	129.04	129.09	129.00	129.27	128.72
N(3)C(4)C(5)	112.34	112.03	111.99	112.03	111.91	112.51
C(4)C(5)C(6)	121.15	121.47	121.49	121.54	121.45	121.22
C(4)C(5)F	117.36	117.34	117.35	117.34	117.37	117.33
N(3)C(4)O(8)	122.02	122.16	122.15	122.13	122.21	121.94
N(3)C(2)O(9)	123.60	123.59	123.60	123.58	123.68	123.49
C(2)N(1)H	115.55	115.36	115.36	115.36	115.41	115.50
C(2)N(3)H	115.21	115.18	115.15	115.18	115.06	115.36
C(5)C(6)H	122.20	121.84	121.90	121.95	121.86	122.22

Table S5 The experimental internuclear distances $r_{a,ij}$, calculated total corrections $\Delta r_{ij} = r_{a,ij} - r_{e,ij}^{se}$ and calculated harmonic root-mean-square vibrational amplitudes ($u_{ij,calc}$).

Distances	$r_{a,ij}$	Δr_{ij}	$u_{ij,calc}$
N1H10	1.020200	-0.015700	0.070100
N3H11	1.024900	-0.015500	0.070600
C6H12	1.094300	-0.015700	0.074700
C4O8	1.214914	-0.003400	0.038100
C2O9	1.215214	-0.003300	0.038000
C5F7	1.336638	-0.007600	0.046169
C5C6	1.347638	-0.006100	0.045069
N1C2	1.390314	-0.012300	0.049169
N1C6	1.390714	-0.011300	0.047969
C2N3	1.392214	-0.009800	0.049469
N3C4	1.403614	-0.010800	0.051069
C4C5	1.467525	-0.009600	0.051969



C2H10	2.029592	-0.004800	0.099800
C2H11	2.041178	-0.010100	0.100700
C4H11	2.057199	-0.010600	0.101400
C5H12	2.079342	-0.009800	0.098000
C6H10	2.086608	-0.006700	0.097300
N1H12	2.174713	-0.017700	0.099400
N3O8	2.289534	-0.010700	0.068980
N1O9	2.291599	-0.009600	0.067780
N3O9	2.295538	-0.008900	0.068180
N1N5	2.321813	-0.018800	0.067880
C6F7	2.337280	-0.007000	0.072880
N1C5	2.376309	-0.012200	0.067080
C5O8	2.384457	-0.009000	0.072680
N3C5	2.385231	-0.013300	0.071580
C4F7	2.391404	-0.010000	0.080080
C2C6	2.439972	-0.007400	0.069880
C4C6	2.448725	-0.009700	0.068980
O9H10	2.480455	-0.000200	0.136700
H10H12	2.482986	-0.015400	0.161800
O8H11	2.487129	-0.009000	0.140100
O9H11	2.492524	-0.007100	0.138700
C2C4	2.506101	-0.004300	0.071580
F7H12	2.536769	-0.002600	0.143800
N3C6	2.705652	-0.015000	0.079703
F7O8	2.787460	-0.009700	0.125203
N1C4	2.812412	-0.012900	0.077703
C2C5	2.834418	-0.004300	0.075503
N3H10	3.214771	-0.008600	0.093500
N1H11	3.226022	-0.017000	0.093800
C5H10	3.274115	-0.001900	0.093800
C5H11	3.300107	-0.011800	0.095900
C4H12	3.414287	-0.012900	0.096800
C2H12	3.425473	-0.013900	0.098500
C6O9	3.548333	-0.003000	0.073319
C6O8	3.569856	-0.005100	0.072919
C2O8	3.584781	-0.001700	0.075219
C4O9	3.597829	-0.000800	0.076919
N3F7	3.598249	-0.012000	0.077719
N1F7	3.602559	-0.012900	0.072819
C6H11	3.712434	-0.012400	0.097000
N3H12	3.788215	-0.019100	0.099000
C4H10	3.804326	-0.000500	0.096300
N1O8	4.017518	-0.007700	0.075275
H10H11	4.031117	-0.003900	0.128600
C5O9	4.040827	0.001200	0.073575
C2F7	4.162692	-0.003600	0.074775

F7H10	4.406605	-0.001900	0.107000
F7H11	4.414725	-0.008300	0.109600
O8H12	4.442609	-0.005100	0.106600
O9H12	4.442844	-0.007800	0.110100
O8O9	4.562037	0.002900	0.094712
H11H12	4.792814	-0.014300	0.120100
O8H10	5.005820	0.007900	0.098000
F7O9	5.366106	0.004900	0.091685

[a] See Figure S2 for atom numbering.

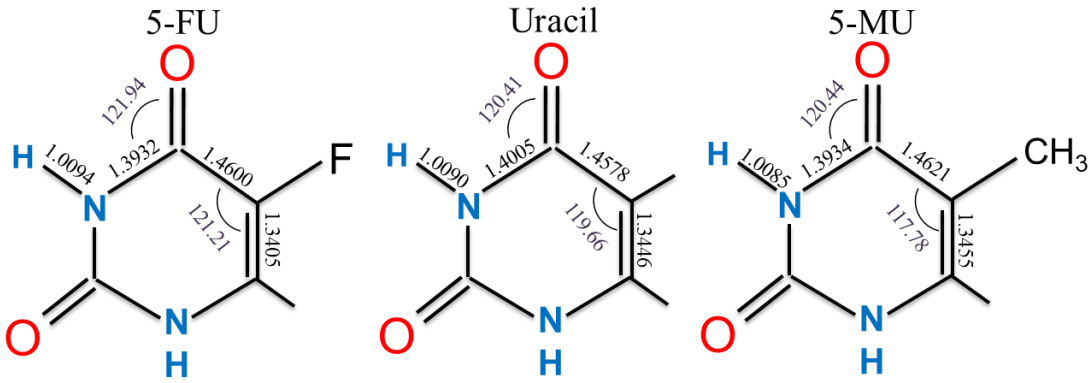


Figure S4 Comparison of the geometrical parameters for molecules 5-FU, uracil and thymine (5-MU).

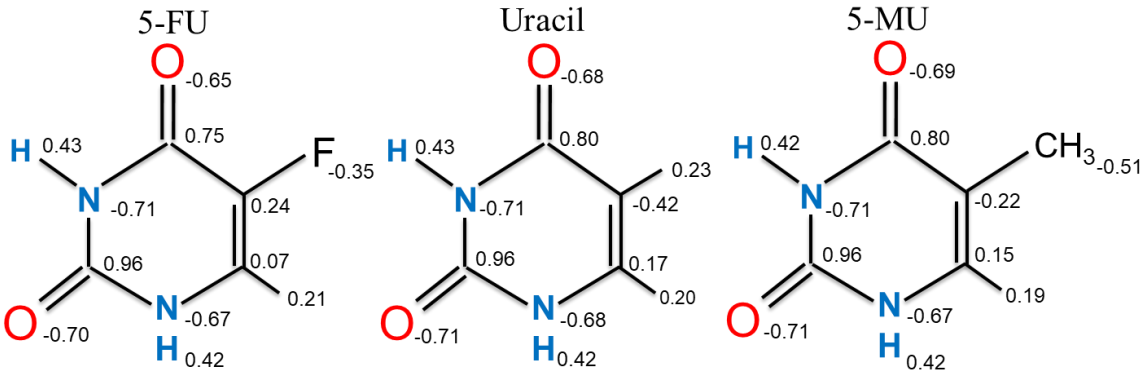


Figure S5 Partial charge distribution in 5FU, uracil and thymine according to natural bond orbital (NBO) calculations (MP2/cc-pVTZ).