Dispersion corrected DFT approaches for Anharmonic Vibrational Frequency Calculations: Nucleobases and their Dimers

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Electronic Supplementary Information

Table 1. Experimental, harmonic and anharmonic vibrational frequencies (cm^{-1}) and intensities for adenine molecule.

Exp.		**Calculated**												
Argon matrix[a]		B3LYP				B3LYP-D3				B3LYP-DCP				Assignment[b]
Mode		harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	
1	3569[d]	3731	57	3536	45	3730	57	3534	45	3746	65	3552	44	$\nu_{asym}NH_2$
2	3508[d]	3647	87	3482	72	3648	87	3482	72	3651	89	3484	74	νN_9H
3	3452[d]	3598	85	3445	74	3596	85	3443	75	3608	102	3449	97	$\nu_{sym}NH_2$
4		3243	0	3116	2	3241	0	3112	1	3272	0	3149	1	νC_8H
5	3057	3171	17	3045	21	3169	17	3042	21	3195	16	3068	18	νC_2H
6	1633	1660	599	1621	163	1662	593	1624	273	1714	600	1678	348	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6
7	1612	1639	112	1594	67	1638	112	1594	79	1683	111	1641	91	νN_3C_4, νC_5C_6
8	1599	1608	6	1565	2	1609	9	1565	2	1631	58	1586	80	$\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6
9	1482	1518	9	1483	9	1517	6	1482	7	1555	22	1521	25	νN_7C_8, δC_8H
10	1474	1503	76	1463	38	1503	79	1463	25	1539	35	1498	7	νN_1C_6, δC_2H, νC_2N_3, νC_6N_6
11	1419	1435	31	1406	19	1435	30	1406	19	1483	45	1453	29	νC_4C_5, νC_4N_9, δC_2H
12	1389	1417	8	1381	6	1416	8	1379	7	1455	23	1419	10	δN_9H, δC_2H, νC_4N_9, νC_8N_9
13	1345	1368	48	1337	24	1367	45	1337	22	1416	66	1384	38	δC_2H, νC_8N_9, δC_8H, νC_6N_6
14	1328	1359	27	1330	33	1357	31	1328	34	1398	29	1370	18	νN_1C_2, νC_5N_7, νC_4C_5

15	1290	1333	58	1298	51	1331	58	1296	55	1377	37	1348	36	νC_2N_3, νN_1C_2
16	1240	1266	23	1240	19	1264	24	1239	20	1290	19	1267	18	δC_8H, νN_7C_8, δN_9H
17	1229	1245	13	1224	3	1245	13	1224	7	1269	12	1250	8	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3
18	1127	1144	22	1124	11	1144	21	1122	1	1175	18	1155	11	νC_4N_9, δr, νC_6N_6
19	1061	1078	19	1054	7	1078	19	1054	9	1107	19	1083	14	νC_8N_9, δN_9H
20	1017	1016	7	994	7	1019	7	995	5	1021	3	998	1	$\delta_{rock}NH_2$, νN_1C_6
21	958	973	4	953	3	972	4	953	3	994	3	976	3	γC_2H
22	927	944	15	929	12	944	15	929	11	955	14	942	11	δr, νC_4C_5
23	887	898	11	886	9	898	11	885	8	906	13	894	7	δ R
24	848	854	4	814	20	853	3	813	19	884	2	867	2	γC_8H
25	802	825	14	778	6	825	14	779	6	856	13	840	12	γC_8H, τR, τr, γC_6N_6
26	717	725	3	715	2	725	3	715	2	741	3	732	3	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing)
27	678	692	1	666	2	691	1	665	2	710	0	699	0	γC_6N_6, τr, τR
28	655	666	7	651	10	666	7	651	10	680	6	668	7	τr
29	610	618	0	610	1	618	0	609	1	625	1	618	1	δr, νC_5C_6, δR
30	566	581	61	545	6	580	60	544	0	591	61	578	50	γN_9H, γC_2H, τR, τr
31		534	29	487	141	534	18	498	214	537	3	532	3	δ R, γN_9H
32	513	532	17	515	60	532	24	505	15	554	1	514	75	τNH_2, γN_9H
33		527	22	493	4	527	25	491	41	528	4	523	3	τNH_2, δR, δC_6N_6, νC_4N_9
34	503	512	3	487	45	513	3	486	60	542	53	528	36	τNH_2, γN_9H
35		300	0	293	0	300	0	292	0	306	0	302	0	τRr
36	276	277	15	274	14	281	14	277	13	282	12	280	12	δC_6N_6, δR, δr
37	214	240	134	240[c]	107	239	128	239[c]	103	228	1	228[c]	0	τRr, $\gamma_{wagg}NH_2$
38	184[f]	207	94	208[c]	77	205	100	205[c]	81	104	158	105[c]	101	$\gamma_{wagg}NH_2$, τRr
39		165	1	158	1	165	1	157	1	168	38	153	30	τRr, γC_6N_6

[a]From Ref.[34].

[b]Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; R and r refer to the 6-membered ring and 5-membered ring, respectively.

[c]Modes excluded from the anharmonic calculation.

[d]From Ref.[146].

[f]From Ref.[144].

Table 2. Experimental, harmonic and anharmonic vibrational frequencies (cm^{-1}) and intensities for cytosine molecule.

	Exp.	**Calculated**												
	Argon matrix[a,b] (amino-oxo form)	B3LYP				B3LYP-D3				B3LYP-DCP				Assignment[c]
Mode		harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	
1	3563	3733	48	3540	37	3732	48	3538	37	3750	56	3562	24	$\nu_{asym}NH_2$
2	3471	3617	71	3450	53	3617	72	3451	56	3623	70	3457	49	νN_1H
3	3440	3597	83	3438	76	3595	84	3433	74	3608	104	3455	121	$\nu_{sym}NH_2$
4		3221	2	3086	3	3220	2	3083	3	3270	0	3137	1	νC_5H
5		3196	2	3047	4	3194	2	3043	3	3247	1	3109	2	νC_6H
6	1734	1766	759	1736	469	1766	754	1738	442	1794	801	1761	381	νC_2O
7	1656	1686	471	1647	255	1685	480	1649	283	1738	421	1702	203	νC_5C_6, νN_3C_4
8	1595	1629	138	1586	95	1631	129	1585	156	1641	267	1596	296	$\delta_{sciss}NH_2$
9	1538	1568	151	1524	55	1567	149	1534	124	1617	148	1579	118	νN_3C_4, νC_4C_5
10	1475	1502	148	1461	51	1503	150	1460	126	1538	125	1498	59	νN_3C_4, νC_4N_4, δC_6H
11	1422	1442	78	1412	58	1443	77	1412	60	1472	53	1435	36	δN_1H
12	1337	1355	52	1328	29	1355	55	1327	30	1377	34	1351	13	δC_6H, νC_4N_4, δC_5H
13	1244	1260	23	1225	24	1260	27	1226	28	1310	30	1271	25	νC_2N_3
14	1195	1213	50	1192	39	1220	50	1193	38	1236	49	1213	38	δC_6H, δN_1H, νC_6N_1
15	1090	1125	2	1111	5	1131	3	1113	5	1139	3	1121	5	δC_5H, νC_6N_1, νC_5C_6
16	1088	1092	44	1066	39	1093	44	1065	38	1108	31	1085	23	$\delta_{rock}NH_2$
17		989	1	970	0	988	1	969	0	1005	1	989	1	δ ring, νC_4C_5
18		970	0	941	1	969	0	940	1	993	0	971	0	γC_6H
19		926	3	898	5	925	4	897	5	950	2	927	2	νN_1C_2, νC_4C_5, $\delta_{rock}NH_2$
20	781	793	47	772	38	793	46	772	38	815	43	804	39	γC_2O, τ ring
21	768	777	3	759	4	776	3	759	3	797	0	785	1	γC_5H, γC_4N_4, γC_2O
22	743	769	4	751	4	768	4	750	4	793	3	780	2	ring breathing
23	717	728	37	709	33	727	37	708	33	739	32	723	32	γC_5H, τ ring, γC_4N_4, γN_1H
24	615	641	53	607	53	638	53	606	53	647	55	637	49	γN_1H
25	576	578	3	572	2	578	2	571	2	585	2	579	2	δ ring

26	537	546	3	536	4	546	3	537	3	553	3	545	24	δ ring, τNH_2
27	529	534	3	518	16	537	3	535	5	543	4	534	5	δ ring, τNH_2, δC_2O
28		526	13	498	22	526	13	494	12	550	4	517	20	τNH_2, δC_2O
29	400	408	16	393	17	407	17	392	18	418	15	413	15	τ ring
30	330	359	3	357	2	363	3	358	3	364	4	363	4	δC_4N_4, δC_2O
31		216	214	218[d]	171	212	205	213[d]	164					$\gamma_{wagg}NH_2$
32		203	5	194	3	202	13	187	7	204	15	198	8	$\gamma_{wagg}NH_2$, τ ring
33		141	2	135	2	140	2	134	2	136	2	134	2	τ ring

[a]From Ref.[35].

[b]From Ref.[147].

[c]Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric.

[d]Modes excluded from the anharmonic calculation.

Table 3. Experimental, harmonic and anharmonic vibrational frequencies (cm^{-1}) and intensities for uracil molecule.

Exp.		**Calculated**												
Ar matrix[a]		B3LYP				B3LYP-D3				B3LYP-DCP				Assignment[b]
Mode		harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I (anh)	
1	3482	3639	105	3473	88	3639	106	3473	88	3643	113	3475	86	νN_1H
2	3433	3594	68	3427	17	3595	68	3430	55	3598	69	3429	56	νN_3H
3	3130	3246	1	3111	0	3246	1	3109	0	3293	4	3162	3	νC_5H
4		3205	2	3062	3	3203	2	3060	3	3252	1	3118	1	νC_6H
5	1762	1798	623	1771	347	1799	630	1770	492	1832	644	1801	113	νC_2=O
6	1733	1764	771	1749	436	1765	761	1749	232	1801	796	1773	417	νC_4=O
7	1644	1673	61	1640	63	1672	62	1638	64	1728	32	1694	42	νC_5=C_6
8	1473	1499	88	1463	55	1500	82	1463	52	1535	128	1492	88	ν ring, δN_1H
9	1401	1381	33	1349	14	1383	48	1350	15	1401	9	1362	11	δN_3H + δCH
10	1389	1417	13	1386	9	1417	8	1386	8	1430	21	1396	17	ν ring, δN_1H, δN_3H
11	1359	1403	93	1372	73	1405	87	1371	69	1450	67	1418	49	ν ring, δN_3H, δCH

12	1219	1227	2	1202	20	1230	8	1204	26	1225	84	1203	82	ν ring, δNH, δCH
13	1186	1195	107	1167	87	1199	106	1165	81	1277	11	1242	5	ν ring, δNH, δCH
14	1076	1085	5	1064	5	1087	5	1062	7	1109	8	1091	7	ν ring, δCH, δN_1H
15	987	992	7	977	8	991	8	976	8	1005	6	979	5	δ ring
16	963	964	9	942	9	968	9	946	9	994	68	973	49	ν ring, δN_3H, δCH
17	958	973	0	949	0	972	0	948	0	1005	0	981	0	γCH
18	806	822	65	803	50	822	65	803	50	845	41	830	42	γC_4=O, γCH
19	757	769	34	746	32	769	34	745	32	792	5	778	4	γC_2=O
20	759	770	3	753	2	769	3	752	2	794	7	780	7	ring breathing
21	718	731	17	713	14	731	17	712	14	745	5	732	5	γCH
22	662	689	66	643	58	687	66	641	61	699	20	679	19	γN_3H
23	562	571	43	530	31	569	43	528	31	581	22	577	19	γN_1H
24	551	559	5	550	5	561	4	560	3	572	59	563	57	δ ring
25	537	542	7	535	7	542	9	535	8	555	2	548	1	δC=O
26	516	521	21	515	20	523	21	516	20	531	29	525	29	δ ring
27	391	387	21	387	19	389	21	387	19	396	18	395	14	δC=O, δ ring
28	411	401	22	391	24	400	22	390	24	411	22	407	20	torsion
29	185	170	0	163	0	170	0	162	0	170	0	168	0	torsion
30		155	2	147	2	154	2	146	2	153	2	152	2	torsion

[a] From Ref.[145,154,155].

[b] Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric.

Table 4. Experimental, harmonic and anharmonic vibrational frequencies (cm^{-1}) and intensities for hypoxanthine molecule.

	Exp.	**Calculated**												
	Argon matrix[a] (oxo-N_1H-N_9H)	B3LYP				B3LYP-D3				B3LYP-DCP				Assignment[b]
Mode		harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	
1	3465	3641	86	3475	71	3641	86	3478	71	3644	89	3479	74	νN_9H
2	3428	3588	67	3421	52	3588	67	3422	48	3592	73	3422	58	νN_1H
3		3248	0	3120	1	3245	0	3116	1	3275	0	3150	1	νC_8H
4		3182	3	3051	5	3180	3	3047	4	3211	2	3083	1	νC_2H
5	1753/1742	1790	719	1755	570	1791	718	1756	562	1829	703	1799	452	νC_6O
6	1608	1626	85	1590	54	1625	85	1590	54	1673	87	1635	52	νC_2N_3, δC_2H
7	1556	1590	71	1549	53	1590	72	1549	26	1637	70	1598	58	νN_3C_4, νC_4C_5
8	1472	1526	29	1494	24	1525	28	1493	24	1571	16	1538	15	νN_7C_8, νC_4C_5
9	1424	1479	5	1441	2	1480	4	1440	1	1515	3	1474	2	νN_7C_8, δN_1H
10	1400	1432	6	1398	2	1433	6	1397	2	1474	16	1436	8	δN_1H, δC_2H, νC_4C_5
11	1342	1403	19	1367	12	1402	19	1367	12	1439	26	1395	17	δN_9H, δC_2H
12	1338	1372	32	1336	28	1371	32	1336	27	1416	39	1379	35	νC_5N_7, δC_2H, νC_2N_3
13	1332	1355	5	1329	6	1356	5	1331	4	1387	3	1360	3	νC_4N_9, νC_5C_6, δC_8H
14		1293	5	1265	3	1292	6	1264	3	1323	10	1293	4	δC_8H
15	1173	1188	77	1162	62	1189	78	1162	63	1225	69	1197	56	δC_8H
16	1100	1135	10	1110	15	1138	10	1111	13	1165	8	1139	12	νN_1C_2, δN_1H
17		1074	14	1048	18	1075	15	1048	18	1104	16	1079	16	νC_8N_9, δN_9H
18	1049	1063	42	1032	41	1062	42	1031	41	1110	28	1083	21	νN_1C_6, δC_6O
19	919	947	6	932	4	947	6	934	2	957	6	942	4	δr
20	906	935	3	911	3	934	3	910	3	953	3	935	3	γC_2H
21	877	902	9	887	7	901	9	886	7	911	11	899	6	δR
22	808	842	6	813	20	841	6	811	19	874	4	855	0	γC_8H
23	786	810	19	766	8	810	19	766	10	843	17	826	17	γC_6O, τR, τr
24	701	741	40	709	31	740	39	708	29	755	33	742	31	γN_1H, γC_6O
25	687	701	10	689	11	700	10	689	11	723	8	712	9	νN_3C_4, νN_1C_6
26	663	675	24	650	19	674	24	649	20	685	22	673	27	τr, γN_1H
27	624	658	6	635	13	657	6	634	14	665	15	652	12	γN_1H, τr

28	581	607	8	599	7	608	8	600	7	619	8	611	7	δr, νC_5C_6
29	560	581	115	524	86	580	114	526	86	590	111	578	101	γN_9H
30	529	537	11	531	10	537	11	531	10	546	11	539	11	δR, δC_6O
31	510	539	5	501	79	538	5	501	79	548	4	540	5	γN_9H
32		509	2	503	2	510	2	503	2	519	2	512	1	δR
33		322	1	318	1	322	1	318	1	326	1	323	1	δC_6O, δrR
34		271	0	262	0	270	0	262	0	277	0	273	0	τrR
35		209	16	202	15	208	16	201	15	213	17	211	16	τrR
36		156	2	149	1	155	2	149	1	154	2	151	1	τrR

[a] From Ref.[36].

[b] Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; R and r refer to the 6-membered ring and 5-membered ring, respectively.

Table 5. Experimental, harmonic and anharmonic vibrational frequencies (cm^{-1}) and intensities for thymine molecule.

Exp.		**Calculated**												
Argon matrix[a]		B3LYP				B3LYP-D3				B3LYP-DCP				Assignment[b]
Mode		harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	harm	I(harm)	anharm	I(anh)	
1	3479	3640	103	3473	86	3640	103	3472	85	3645	111	3472	72	νN_1H
2	3432	3595	67	3430	50	3596	67	3431	53	3600	69	3430	50	νN_3H
3		3196	4	3064	4	3194	4	3059	6	3244	2	3115	1	νC_6H
4	2992	3111	14	2964	7	3110	14	2963	10	3173	7	3029	6	$\nu_{asym}CH_3$
5	2969	3089	9	2945	12	3088	9	2943	12	3141	2	2997	4	$\nu_{out\text{-}of\text{-}plane}CH_3$
6	2939	3030	22	2937	18	3028	22	2934	18	3076	15	2969	11	$\nu_{sym}CH_3$
7	1767	1795	764	1767	499	1795	768	1768	492	1828	797	1794	222	νC_2O, νC_2N_3, νN_1C_2
8	1711	1748	637	1718	382	1749	629	1719	449	1788	661	1752	438	νC_4O, νN_3C_4
9	1668	1699	39	1662	35	1700	38	1662	18	1759	2	1725	59	νC_5C_6, δC_6H, νC_4O, νN_1C_6
10	1472	1499	79	1456	35	1499	76	1456	44	1540	126	1495	83	νC_6N_1, δN_1H, $\delta_{sciss}CH_3$
11	1455	1488	10	1452	4	1488	7	1450	4	1488	1	1451	1	$\delta_{sciss}CH_3$
12	1431	1465	7	1428	6	1464	7	1428	5	1464	10	1430	7	γCH_3

13	1405	1419	61	1386	5	1419	70	1384	30	1463	44	1433	32	inv CH_3, δN_1H, νC_2N_3
14	1388	1421	32	1388	140	1423	25	1389	97	1432	21	1402	17	inv CH_3, δN_1H, νC_2N_3
15	1367	1399	7	1365	4	1405	8	1367	5	1418	5	1386	7	δN_3H, δC_6H
16	1357	1373	6	1343	9	1375	8	1344	5	1399	8	1370	4	δC_6H, δN_3H
17	1220	1230	11	1198	12	1228	11	1196	13	1290	7	1258	11	νC_5-CH_3, νN_1C_6
18	1183	1197	142	1173	66	1203	146	1174	81	1239	113	1211	62	δC_6H, δN_1H, νN_1C_6
19	1139	1155	4	1127	5	1156	4	1126	5	1193	17	1170	11	νN_3C_4, νN_1C_6
20	1046	1069	1	1043	1	1068	1	1043	1	1076	3	1053	3	$\delta_{rock}CH_3$, $\gamma_{wagg}C_5$-CH_3
21	1004	1022	2	1003	2	1024	2	1005	2	1031	3	1014	1	$\delta_{rock}CH_3$, δ ring
22	959	965	13	947	12	969	13	948	12	987	12	964	9	$\delta_{rock}CH_3$, δN_3H, νN_1C_2, νC_2N_3
23	889	911	16	889	9	910	16	886	5	931	11	911	8	$\gamma_{wagg}C_6H$, γ ring
24	799	804	5	794	5	805	6	794	4	821	6	807	6	δ ring, νC_5-CH_3, νN_1C_2
25	763	786	35	760	19	786	34	761	19	813	34	798	31	$\gamma_{wagg}C_4O$, $\gamma_{wagg}C_5$-CH_3, $\gamma_{wagg}N_3H$, γ ring
26	754	762	28	742	16	762	28	743	18	784	24	774	23	$\gamma_{wagg}C_2O$, $\gamma_{wagg}N_3H$, $\gamma_{wagg}N_1H$, γ ring
27	727	734	5	722	4	736	5	722	4	767	5	755	4	νC_4C_5, νC_5-CH_3, δ ring
28	662	691	61	633	77	689	62	631	79	699	62	676	57	$\gamma_{wagg}N_3H$, γ ring, $\gamma_{wagg}N_1H$, $\gamma_{wagg}C_2O$
29	601	606	1	601	1	610	1	604	1	618	1	613	1	δC_2O, δC_4O, δC_5-CH_3, δ ring
30	545	570	59	507	36	567	59	504	38	576	56	566	54	$\gamma_{wagg}N_1H$, $\gamma_{wagg}N_3H$, $\gamma_{wagg}C_4O$, γ ring
31	540	547	7	539	7	548	8	539	7	560	8	554	7	δ ring, δC_4O
32	455	461	19	458	19	463	19	459	18	472	17	461	16	δ ring
33		406	17	389	21	405	17	388	22	416	17	410	16	γ ring
34		389	20	387	19	391	20	389	19	398	20	397	19	δC_2O, δC_4O, νN_3C_4
35		303	0	293	0	301	0	292	0	308	1	310	1	$\gamma_{wagg}C_5$-CH_3, γ ring
36		278	3	279	3	283	3	282	2	287	3	292	2	δC_5-CH_3, δC_4O
37		159	1	151	1	158	1	150	1	158	2	158	2	γ ring
38		153	1	148	0	150	1	151	1	166	0	172	0	τ CH_3
39		113	0	110	0	113	0	110	0	114	0	113	0	γ ring

[a] From Ref.[39].

[b] Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; inv= inversion; asym = asymmetric; sym = symmetric.

Table 6. Deviations between computed anharmonic vibrational frequencies (in cm^{-1}) of nucleobases and experimental data[a].

	adenine	**cytosine**	**uracil**	**hypoxanthine**	**thymine**	**all**
	MAE[b]					(weighted average)
B3LYP	12.0	11.2	11.8	11.3	9.3	11.1
B3LYP-D3	12.3	11.0	12.3	11.2	9.9	11.4
B3LYP-DCP	24.0	18.4	18.7	31.9	20.3	22.6
	MIN[c]					(minimum value)
B3LYP	-34	-23	-32	-36	-38	-38
B3LYP-D3	-35	-25	-34	-34	-41	-41
B3LYP-DCP	-80	-14	-17	-6	-7	-80
	MAX[d]					(maximum value)
B3LYP	26	27	18	26	7	27
B3LYP-D3	25	28	16	25	8	28
B3LYP-DCP	55	46	72	66	57	72

[a] From Ref.[31,32,34-36,39,145,147].

[b]Mean absolute error to the experimental results.

[c]Minimum negative deviation to the experimental results.

[d]Maximum positive deviation to the experimental results.

Table 7. Deviations of harmonic and anharmonic vibrational frequencies (in cm^{-1}) of nucleobases computed with B3LYP-D3 and B3LYP-DCP respect to the B3LYP method.

	MAE[a]			MIN[b]			MAX[c]		
	Δharm[d]	Δanharm[e]	ΔGVPT2[f]	Δharm[d]	Δanharm[e]	ΔGVPT2[f]	Δharm[d]	Δanharm[e]	ΔGVPT2[f]
adenine									
D3	1.7	2.2	2	-14	-17	-19	15	18	20
DCP	18.7	29.1	6.8	-103	-102	-23	53	62	42
cytosine									
D3	1.4	2.4	2.3	-4	-7	-6	7	17	14
DCP	21.2	24.0	4.8	-5	-1	-8	52	62	24
uracil									
D3	1.3	1.5	1.2	-2	-3	-6	4	10	8
DCP	22.8	24.7	6.1	-2	1	-13	82	75	37
hypoxanthine									
D3	0.8	1.0	0.7	-2	-4	-2	3	3	3
DCP	22.8	27.5	6.2	-2	1	-8	46	60	44
thymine									
D3	1.7	1.4	1.4	-3	-5	-6	6	4	6
DCP	22.9	26.1	6.3	-1	-2	-14	61	65	52
all									
D3	1.4	1.7	1.5	-14	-17	-19	15	18	20
DCP	21.6	26.4	6.1	-103	-102	-23	82	75	52

[a]Mean absolute error.

[b]Minimum negative deviation.

[c]Maximum positive deviation.

[d]Deviation between harmonic frequencies.

[e]Deviation between anharmonic frequencies.

[f]Deviation of anharmonic shift for the selected method respect to B3LYP method.

Table 8. Counterpoise-corrected binding energy (ΔE_{bind}) of hydrogen-bonded and stacked dimer structures in kcal mol-1 compared to reference values.

ΔE_{bind}	Ref	Optimized geometry
Uracil-Uracil hydrogen-bonded		
B3LYP	-11.4	-13.5
B3LYP-D3	-14.9	-16.7
B3LYP-DCP	-13.8	-15.8
Ref a (CBS)	-15.7	
Uracil-Uracil stacked		
B3LYP-D3	-5.8	-9.3
B3LYP-DCP	-3.9	-7.8
Ref a (CBS)	-7.9	
Adenine-Adenine hydrogen-bonded		
B3LYP	-9.3	-10.2
B3LYP-D3	-13.1	-13.9
B3LYP-DCP	-11.8	-12.9
Ref b (CBS)	-13.2	
Adenine-Adenine stacked		
B3LYP-D3	-5.6	-7.3
B3LYP-DCP	-4.5	-6.6
Ref c (CBS)	-8.3	
Adenine-Naphthalene stacked		
B3LYP-D3	-2.3	-7.9
B3LYP-DCP	+3.6	-7.1
Ref d (CBS)	-8.5	

[a] Ref.[137]

[b] Ref.[138]

[c] Ref.[139]

[d] Ref.[140]

Table 9. Rotational constants in cm^{-1} of optimized dimer structures, computed with B3LYP, B3LYP-D3 and B3LYP-DCP methods, compared with reference structures.

	B3LYP	B3LYP-D3	B3LYP-DCP	Ref[b]
Uracil-Uracil hydrogen-bonded				
A	0.046747	0.046663	0.047372	0.046977
B	0.007470	0.007558	0.007619	0.007910
C	0.006441	0.006505	0.006563	0.006770
MAE[a], %	3.6	3.0	2.5	
Uracil-Uracil stacked				
A		0.022792	0.023083	0.022812
B		0.018301	0.018077	0.020433
C		0.017017	0.017235	0.019037
MAE[a], %		7.0	7.4	
Adenine-Adenine hydrogen-bonded				
A	0.038408	0.038394	0.038869	0.038507
B	0.004313	0.004369	0.004408	0.004399
C	0.003878	0.003923	0.003959	0.003948
MAE[a], %	1.3	0.5	0.5	
Adenine-Adenine stacked				
A		0.016851	0.017303	0.015827
B		0.013524	0.013326	0.014517
C		0.011780	0.011765	0.012261
MAE[a], %		5.7	7.2	
Adenine-Naphthalene stacked				
A		0.019729	0.019946	0.020394
B		0.011048	0.011366	0.011999
C		0.010480	0.010740	0.011592
MAE[a], %		6.9	4.9	
All				
AVERAGE MAE[a], %	2.5	4.7	4.5	

[a] Mean absolute error.

[b] Ref.[137-140]

Table 10. Structural parameters of optimized hydrogen-bonded and stacked dimer structures compared to reference structures[137-140].

	B3LYP	B3LYP-D3	B3LYP-DCP	Ref	Error, % B3LYP	Error, % B3LYP-D3	Error, % B3LYP-DCP
Uracil-Uracil hydrogen-bonded							
r N3-O'2	2.85978	2.82872	2.82865	2.68192	-6.6	-5.5	-5.5
r O4-N'1	2.7975	2.7743	2.76913	2.62376	-6.6	-5.7	-5.5
r H3-O'2	1.82963	1.79574	1.79794	1.65586	-10.5	-8.4	-8.6
r O4-H'1	1.76572	1.74032	1.73641	1.59862	-10.5	-8.9	-8.6
α N3-H3-O'2	172.59961	173.77026	173.09168	173.86721	0.7	0.1	0.4
α H3-O'2-C'2	126.714	125.55512	125.97066	125.2688	-1.2	-0.2	-0.6
α C4-O4-H'1	128.91291	127.49196	127.72335	127.42064	-1.2	-0.1	-0.2
α O4-H'1-N'1	175.2903	176.39592	175.80687	176.12931	0.5	-0.2	0.2
Uracil-Uracil stacked							
r N3-C'2		3.04174	3.12506	2.77937		-9.4	-12.4
r C2-N'3		3.04174	3.12506	2.77937		-9.4	-12.4
r N1-C'4		3.40125	3.38928	3.08074		-10.4	-10.0
r C4-N'1		3.40125	3.38928	3.08074		-10.4	-10.0
r C5-C'6		3.87457	3.75362	3.47734		-11.4	-7.9
r C6-C'5		3.87457	3.75362	3.47735		-11.4	-7.9
Adenine-Adenine hydrogen-bonded							
r H_{am}-N'1	1.97256	1.91889	1.93355	1.92463	-2.5	0.3	-0.5
r N6-N'1	3.00103	2.9498	2.96206	2.94839	-1.8	0.0	-0.5
r N1-H'_{am}	1.97255	1.91889	1.93355	1.92297	-2.6	0.2	-0.6
r N1-N'6	3.00103	2.9498	2.96206	2.9466	-1.8	-0.1	-0.5
α N6-H_{am}-N'1	178.78511	178.53519	177.83965	178.17496	-0.3	-0.2	0.2
α H_{am}-N'1-C'6	119.96032	120.1782	120.40863	120.29665	0.3	0.1	-0.1
α N1-H'_{am}-N'6	178.78511	178.53511	177.83968	178.16992	-0.3	-0.2	0.2
α C6-N1-H'_{am}	119.96037	120.17823	120.4088	120.34323	0.3	0.1	-0.1
Adenine-Adenine stacked							
r N1-C'8		3.5519	3.51297	3.32667		-6.8	-5.6
r C2-N'7		3.39262	3.35714	3.30988		-2.5	-1.4
r N3-N'7		3.69738	3.76167	3.53667		-4.5	-6.4
r C4-C'5		3.58781	3.63799	3.42621		-4.7	-6.2
r C5-C'4		3.62091	3.63801	3.42621		-5.7	-6.2
r C6-N'9		3.66363	3.65277	3.40615		-7.6	-7.2
r N6-H'9		3.82444	3.78039	3.4561		-10.7	-9.4
r N7-C'2		3.29564	3.35714	3.30988		0.4	-1.4
r N7-N'3		3.74249	3.76169	3.53667		-5.8	-6.4
r C8-N'1		3.41169	3.51296	3.32667		-2.6	-5.6
r N9-C'6		3.55295	3.65275	3.40615		-4.3	-7.2
r H9-N'6		3.50834	3.78037	3.4561		-1.5	-9.4
Adenine-Naphthalene stacked							
r N1-C'3		3.65537	3.54329	3.23751		-12.9	-9.4
r C2-C'4		3.53176	3.50262	3.21905		-9.7	-8.8
r N3-C'10		3.53101	3.55512	3.28405		-7.5	-8.3
r C4-C'10		3.29891	3.29056	2.98317		-10.6	-10.3
r C5-C'9		3.79718	3.69504	3.37665		-12.5	-9.4
r C5-C'1		3.7135	3.60016	3.30096		-12.5	-9.1

r C6-C'2	3.73934	3.58268	3.26696	-14.5	-9.7
r N6-C'2	3.97407	3.77379	3.39036	-17.2	-11.3
r N7-C'1	3.57398	3.47089	3.1805	-12.4	-9.1
r N7-C'9	3.69806	3.60085	3.31383	-11.6	-8.7
r C8-C'8	3.40076	3.38853	3.12415	-8.9	-8.5
r N9-C'7	3.62581	3.67613	3.42655	-5.8	-7.3
r N9-C'6	3.5546	3.60922	3.36418	-5.7	-7.3
r N9-C'5	3.40637	3.45271	3.23149	-5.4	-6.8

Legend: Atoms of monomer 2 are indexed with apostrophe; r = distance between atoms in Å; α = angle between atoms in degree units. Uracil dimers: O2 = oxigen bonded to C2; O4 = oxigen bonded to C4; H3 = hydrogen bonded to N3; H1 = hydrogen bonded to N1. Adenine dimers: Ham = amino group hydrogen atom.

Table 11. Mean absolute errors (MAE) of structural parameters of optimized dimer structures, computed with B3LYP, B3LYP-D3 and B3LYP-DCP methods, compared to reference structures[137-140].

	MAE, % B3LYP	MAE, % B3LYP-D3	MAE, % B3LYP-DCP
Uracil-Uracil hydrogen-bonded	4.7	3.6	3.7
Uracil-Uracil stacked		10.4	10.1
Adenine-Adenine hydrogen-bonded	1.2	0.2	0.3
Adenine-Adenine stacked		4.8	6.0
Adenine-Naphthalene stacked		10.5	8.9

Table 12. Anharmonic vibrational frequencies (cm^{-1}) of hydrogen-bonded uracil dimer, computed using B3LYP, B3LYP-D3 and B3LYP-DCP approaches, and corresponding shifts respect to the isolated molecule (Δhb).

	B3LYP		B3LYP-D3		B3LYP-DCP		Assignment[a]
Mode	anharm	Δhb	anharm	Δhb	anharm	Δhb	
1	3473	0.2	3472	-1.3	3473	-1.5	νN1H (M1)
2	3429	2.2	3427	-2.9	3432	3.1	νN3H (M2)
3	3111	0.2	3098	-10.2	3163	1.5	νC5H (M1)
4	3116	5.6	3117	8.0	3163	0.8	νC5H (M2)
5	3002	***-424.6, -470.4***	2926	***-503.1, -546.4***	2947	***-482.0, -527.5***	νN3H (M1), νN1H (M2)
6	3068	5.7	3066	6.6	3120	1.9	νC6H (M1)
7	3072	9.6	3072	12.4	3127	9.2	νC6H (M2)
8	2897	***-530.0, -575.8***	2870	***-559.7, -546.4***	2880	***-549.4, -594.9***	νN3H (M1), νN1H (M2)
9	1782	11.0	1783	13.5	1815	13.5	νC2=O (M1)
10	1743	-6.4	1746	-2.7	1759	-14.0	νC2=O, νC4=O, ν ring, δN1H (M2)
11	1700	***-49.9***	1699	***-49.4***	1735	***-38.4***	νC2=O, νC4=O, δNH (M2)
12	1679	***-70.8***	1676	***-72.4***	1715	***-58.1***	νC4=O, ν ring, δN3H (M1)
13	1635	-4.2	1635	-3.8	1695	0.9	νC5=C6 (M2)
14	1625	-14.1	1624	-14.8	1685	-8.7	νC5=C6 (M1)
15	1511	***48.6***	1515	***52.3***	1535	***42.3***	δN1H (M2)
16	1474	***102.0***	1475	***104.9***	1514	***95.4***	ν ring, δN1H, δN3H (M1)
17	1434		1445		1457		δN3H (M1)
18	1404		1403		1453		ν ring, δN1H, δCH (M2)
19	1390		1390		1429		ν ring, δN1H, δCH (M1)
20	1387	1.3	1382	-3.6	1409	12.9	δN3H + δCH (M2)
21	1360	11.1	1356	6.6	1381	19.1	δN3H (M2), ν ring, δCH (M1)
22	1356	6.9	1352	1.9	1371	8.9	δN3H, ν ring (M2), δCH (M1)
23	1231		1232		1248		δN1H, ν ring, δCH (M2)
24	1202		1204		1262		ν ring (M1)
25	1181	-21.4	1183	-21.8	1239	-2.9	ν ring, δN3H, δCH (M2)
26	1188	20.9	1187	21.9	1211	7.4	δN1H, ν ring, δCH (M1)
27	1076		1074		1101		δCH (M2)
28	1074	10.3	1073	11.5	1096	5.7	δCH, δN1H (M1)
29	980	2.4	981	5.0	1012	33.3	δ ring (M1, M2)
30	978	0.4	978	2.2	997	18.4	δ ring (M2, M1)
31	917		880		993		γCH, γN1H (M2), γN3H (M1)
32	958	-18.8	964	-11.4	984	5.1	δ ring (M1)
33	944	-4.8	943	-5.1	985	4.2	γCH (M1)
34	957	14.3	957	10.3	981	8.3	ν ring, δN3H, δCH (M2)
35	797		832		922		γN3H (M1), γN1H, γCH (M2)
36	728		738		877		γN1H, γCH (M2), γN3H (M1)
37	800	-3.0	796	-6.3	833	3.2	γC4=O, γCH (M1)
38	811	7.7	809	6.2	834	4.4	γC4=O, γCH (M2)
39	768	14.5	767	15.2	791	11.0	ring breathing (M1, M2)
40	764	10.4	763	11.4	788	7.7	ring breathing (M1, M2)
41	740	-5.7	740	-5.1	788	10.1	γC2=O (M2)
42	729	-16.7	729	-16.1	776	-1.9	γC2=O (M1)
43	713	-0.3	711	-1.9	737	5.5	γCH (M1)
44	711		708		730		γ ring (M2)
45	645	2.6	634	-6.6	685	6.1	γN3H (M2)

46	504	-25.2	536	8.3	599	21.9	γN1H (M1)
47	570	20.4	572	12.3	586	22.7	δ ring (M2)
48	556	21.1	558	23.0	572	24.0	δC=O (M1)
49	552	36.8	551	35.1	568	43.7	δ ring (M1, M2)
50	519	3.9	520	4.0	530	5.7	δ ring (M2)
51	543	***156.1***	543	***155.8***	558	***162.1***	δC=O, δ ring (M2), δ ring (M1)
52	527	***140.0***	527	***139.9***	539	***143.2***	δC=O, δ ring (M1), δ ring (M2)
53	402	11.3	400	10.3	422	14.6	τ (M2)
54	377	-13.6	380	-9.5	422	15.1	τ (M1)
55	411		416		425		δC=O (M1, M2)
56	396		399		407		δC=O (M1, M2)
57	170		169		190		τ (M1, M2)
58	159		163		178		τ (M1, M2)
59	152	-11.4	152	-10.2	170	1.7	τ (M1, M2)
60	145	-2.2	148	1.5	164	12.1	τ (M1, M2)
61	130		135		141		intermolecular mode
62	83		86		85		intermolecular mode
63	48		53		72		τ (M1, M2)
64	62		62		69		intermolecular mode
65	14		9		25		τ (M1, M2)
66					21		τ (M1, M2)

[a] Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; M1 = Monomer 1; M2 = Monomer 2.

Table 13. Anharmonic vibrational frequencies (cm^{-1}) of stacked uracil dimer, computed using B3LYP-D3 and B3LYP-DCP approaches, and corresponding shifts respect to the isolated molecule (Δstacked).

	B3LYP-D3		B3LYP-DCP		Assignment[a]
Mode	anharm	Δstacked	anharm	Δstacked	
1	3362	***-111.1***	3465	-9.6	νN1H (M1, M2)
2	3374	***-98.5***	3465	-9.5	νN1H (M1, M2)
3	3394	-35.7	3401	-28.3	νN3H (M1, M2)
4	3396	-33.8	3400	-29.3	νN3H(M1, M2)
5	3113	3.9	3163	0.7	νC5H (M1, M2)
6	3113	4.0	3162	0.5	νC5H (M1, M2)
7	3068	8.7	3125	6.8	νC6H (M1, M2)
8	3068	8.6	3125	7.1	νC6H (M1, M2)
9	1763	-7.1	1803	1.7	νC2=O (M1, M2)
10	1762	-7.9	1797	-4.2	νC2=O (M1, M2)
11	1727	-21.6	1745	-27.9	νC4=O (M1, M2)
12	1689	***-59.3***	1734	-39.2	νC4=O (M1, M2)
13	1634	-4.0	1694	0.2	νC5=C6 (M1, M2)
14	1635	-3.3	1692	-2.1	νC5=C6 (M1, M2)
15	1474	11.4	1503	10.7	ν ring, δN1H (M1, M2)
16	1478	15.5	1501	8.6	ν ring, δN1H (M1, M2)
17	1385	-0.4	1401	5.1	ν ring, δN3H, δCH (M1, M2)
18	1386	0.0	1399	3.7	ν ring, δN3H, δCH (M1, M2)
19	1384	13.4	1425	6.8	ν ring, δN1H, δN3H (M1, M2)
20	1376	5.7	1420	1.3	ν ring, δN1H, δN3H (M1, M2)

21	1358	7.9	1371	9.5	ν ring, δNH, δCH (M1, M2)
22	1347	-2.5	1371	9.1	ν ring, δNH, δCH (M1, M2)
23	1211	6.4	1245	3.1	ν ring, δCH, δNH (M1, M2)
24	1211	6.7	1243	1.6	ν ring, δCH, δNH (M1, M2)
25	1170	4.4	1211	8.2	ν ring, δNH, δCH (M1, M2)
26	1170	5.2	1208	4.5	ν ring, δNH, δCH (M1, M2)
27	1073	10.9	1093	2.1	ν ring, δCH, δN1H (M1, M2)
28	1073	11.5	1093	2.5	ν ring, δCH, δN1H (M1, M2)
29	985	9.6	987	7.9	δ ring (M1, M2)
30	986	10.0	985	5.9	δ ring (M1, M2)
31	948	-0.8	981	0.9	γCH (M1, M2)
32	946	-2.3	981	0.2	γCH (M1, M2)
33	956	9.5	978	5.3	ν ring, δN3H, δCH (M1, M2)
34	953	6.9	978	5.4	ν ring, δN3H, δCH (M1, M2)
35	808	5.7	832	2.3	γC4=O, γCH (M1, M2)
36	806	3.7	829	-0.5	γC4=O, γCH (M1, M2)
37	772	26.6	791	12.7	γC2=O (M1, M2)
38	750	4.4	775	-2.8	γC2=O (M1, M2)
39	759	7.4	785	4.4	ring breathing (M1, M2)
40	756	4.4	785	5.2	ring breathing (M1, M2)
41	716	3.3	733	1.0	γCH (M1, M2)
42	720	7.6	730	-1.1	γCH (M1, M2)
43	700	***59.1***	687	7.9	γN3H (M1, M2)
44	686	***44.9***	690	11.1	γN3H (M1, M2)
45	824	***296.1***	587	10.4	γN1H (M1, M2)
46	651	***123.7***	584	7.5	γN1H (M1, M2)
47	565	4.7	564	0.7	δ ring (M1, M2)
48	558	-1.9	563	0.3	δ ring (M1, M2)
49	536	1.2	549	0.9	δC=O (M1, M2)
50	536	0.6	548	0.3	δC=O (M1, M2)
51	523	7.0	521	-3.5	δ ring (M1, M2)
52	526	10.0	521	-3.3	δ ring (M1, M2)
53	411	21.2	419	11.8	τ (M1, M2)
54	405	15.1	412	4.8	τ (M1, M2)
55	389	1.1	395	-0.7	δC=O, δ ring (M1, M2)
56	383	-4.0	396	0.1	δC=O, δ ring (M1, M2)
57	195		188		τ (M1, M2)
58	171		179		τ (M1, M2)
59	170	8.1	173	4.3	τ (M1, M2)
60	165	19.2	149	-2.8	τ (M1, M2)
61	82		66		intermolecular mode
62	47		49		intermolecular mode
63	34		29		intermolecular mode
64	17		16		intermolecular mode
65					intermolecular mode
66					intermolecular mode

[a] Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; M1 = Monomer 1; M2 = Monomer 2.

Table 14. Anharmonic vibrational frequencies (cm^{-1}) of hydrogen-bonded adenine dimer, computed using B3LYP, B3LYP-D3 and B3LYP-DCP approaches, and corresponding shifts respect to the isolated molecule (Δhb).

	B3LYP		B3LYP-D3		B3LYP-DCP		Assignment[a]
Mode	anharm	Δhb	anharm	Δhb	anharm	Δhb	
1	3500	-36.2	3502	-32.3	3498	***-54.2***	$\nu_{asym}NH_2$ (M1, M2)
2	3500	-35.3	3502	-31.7	3499	***-53.8***	$\nu_{asym}NH_2$ (M1, M2)
3	3482	-0.9	3484	1.7	3479	-4.5	νN_9H (M1, M2)
4	3481	-1.0	3483	1.6	3479	-4.6	νN_9H (M1, M2)
5	3001	***-443.6***	2965	***-478.0***	2979	***-470.4***	$\nu_{sym}NH_2$ (M1, M2)
6	2980	***-464.7***	2897	***-546.0***	2919	***-530.6***	$\nu_{sym}NH_2$ (M1, M2)
7	3112	-4.6	3102	-10.1	3149	-0.4	νC_8H (M1, M2)
8	3111	-4.8	3101	-11.0	3149	0.0	νC_8H (M1, M2)
9	3034	-10.5	3029	-13.6	3062	-5.6	νC_2H (M1, M2)
10	3034	-10.8	3030	-12.1	3063	-4.7	νC_2H (M1, M2)
11	1648	26.5	1647	23.6	1705	26.6	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6 (M1, M2)
12	1644	22.2	1645	21.6	1579	***-99.8***	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6 (M1, M2)
13	1604	-17.0	1605	-18.5	1529	***-149.6***	νC_5C_6, νC_6N_6, $\delta_{sciss}NH_2$ (M1, M2)
14	1591	-30.9	1592	-31.7	1652	-26.4	νC_5C_6, νC_6N_6, $\delta_{sciss}NH_2$ (M1, M2)
15	1584	-9.9	1584	-10.3	1647	6.5	νN_3C_4, νC_5C_6 (M1, M2)
16	1584	19.6	1583	18.6	1629	43.5	$\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6 (M1, M2)
17	1492	***-72.4***	1495	***-69.9***	1533	***-52.4***	$\delta_{sciss}NH_2$, νC_6N_6 (M1, M2)
18	1490	6.9	1490	7.8	1536	14.5	νN_7C_8, δC_8H (M1, M2)
19	1480	-2.7	1481	-1.4	1521	-0.3	νN_7C_8, δC_8H (M1, M2)
20	1470	7.0	1468	5.2	1509	11.7	νN_1C_6, δC_2H, νC_2N_3, νC_6N_6 (M1, M2)
21	1418	12.1	1418	11.4	1467	14.8	νC_4C_5, νC_4N_9, δC_2H (M1, M2)
22	1417	11.1	1414	8.3	1467	13.9	νC_4C_5, νC_4N_9, δC_2H (M1, M2)
23	1380	-0.6	1380	0.8	1430	10.4	δN_9H, δC_2H, νC_4N_9, νC_8N_9 (M1, M2)
24	1380	-0.8	1380	0.4	1427	7.5	δN_9H, δC_2H, νC_4N_9, νC_8N_9 (M1, M2)
25	1342	5.3	1342	5.1	1393	9.7	δC_2H, νC_8N_9, δC_8H, νC_6N_6 (M1, M2)
26	1340	3.0	1340	3.0	1393	9.6	δC_2H, νC_8N_9, δC_8H, νC_6N_6 (M1, M2)
27	1324	-5.7	1323	-4.3	1385	15.5	νN_1C_2, νC_5N_7, νC_4C_5 (M1, M2)
28	1324	-6.1	1324	-3.7	1383	13.3	νN_1C_2, νC_5N_7, νC_4C_5 (M1, M2)
29	1312	14.0	1312	16.4	1359	11.1	νC_2N_3, νN_1C_2 (M1, M2)
30	1310	12.5	1311	15.1	1357	9.2	νC_2N_3, νN_1C_2 (M1, M2)
31	1241	1.1	1239	0.5	1274	7.6	δC_8H, νN_7C_8, δN_9H (M1, M2)
32	1239	-0.8	1236	-28.0	1272	5.5	δC_8H, νN_7C_8, δN_9H (M1, M2)
33	1239	14.3	1242	17.1	1264	13.3	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3 (M1, M2)
34	1227	2.7	1229	4.9	1262	11.5	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3 (M1, M2)
35	1135	11.8	1135	12.6	1168	13.1	νC_4N_9, δr, νC_6N_6 (M1, M2)
36	1132	8.8	1134	11.5	1166	10.4	νC_4N_9, δr, νC_6N_6 (M1, M2)
37	1055	1.5	1055	1.5	1083	-0.5	νC_8N_9, δN_9H (M1, M2)
38	1052	-1.4	1055	1.4	1082	-0.8	νC_8N_9, δN_9H (M1, M2)
39	1026	32.7	1032	36.8	1052	***54.4***	$\delta_{rock}NH_2$, νN_1C_6 (M1, M2)
40	1018	24.6	1023	28.1	1043	45.4	$\delta_{rock}NH_2$, νN_1C_6 (M1, M2)
41	934	-19.4	939	-13.2	968	-8.5	γC_2H (M1, M2)
42	934	-19.0	941	-11.3	966	-10.7	γC_2H (M1, M2)
43	931	2.4	932	3.5	946	3.8	δr, νC_4C_5 (M1, M2)
44	931	1.8	932	3.0	946	3.7	δr, νC_4C_5 (M1, M2)
45	896	10.6	899	13.5	909	14.6	δ R (M1, M2)

46	894	8.2	895	10.5	906	11.1	δ R (M1, M2)
47	866[b]		891[b]		828[b]		τNH_2 (M1, M2)
48	749		633		751		γC_8H, τNH_2 (M1, M2)
49	827	12.8	826	13.2	845	-21.6	γC_8H (M1, M2)
50	716	***-97.6***	799	-14.2	805	***-61.9***	γC_8H, τNH_2 (M1, M2)
51	793	15.4	796	16.2	828	-11.3	γC_8H, τR, τr, γC_6N_6 (M1, M2)
52	673	***-105.1***	754	-25.0	802	-37.4	γC_8H, τR, τr, γC_6N_6 (M1, M2)
53	720	5.4	721	6.4	744	11.2	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing) (M1, M2)
54	718	3.5	719	4.3	745	12.7	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing) (M1, M2)
55	670	4.4	666	1.2	678	-21.3	γC_6N_6, τr, τR (M1, M2)
56	667	0.7	671	5.7	702	2.5	γC_6N_6, τr, τR (M1, M2)
57	649	-1.9	650	-0.5	663	-4.4	τr (M1, M2)
58	646	-5.4	648	-2.5	661	-6.5	τr (M1, M2)
59	632	22.0	633	23.2	644	25.2	δr, νC_5C_6, δR (M1, M2)
60	624	14.6	626	16.7	635	17.1	δr, νC_5C_6, δR (M1, M2)
61	541	-3.9	551	6.9	570	-7.8	γN_9H, γC_2H, τR, τr (M1, M2)
62	544	-0.5	552	7.5	560	-17.5	γN_9H, γC_2H, τR, τr (M1, M2)
63	535	***47.3***	539	33.8	545	13.0	δ R ((M1, M2)
64	527	39.9	528	22.6	535	2.9	δ R (M1, M2)
65	464	***-51.0***	479	-18.8	536	21.8	γN_9H (M1, M2)
66	465	***-50.1***	479	-18.7	538	23.5	γN_9H (M1, M2)
67	528	1.2	531	45.2	540	16.8	$\delta_{rock}NH_2$, δR, δC_6N_6 (M1, M2)
68	525	31.3	528	42.1	538	15.2	$\delta_{rock}NH_2$, δR, δC_6N_6 (M1, M2)
69	460[b]	-26.3	469[b]	-21.7	471[b]	***-57.4***	τNH_2 (M1, M2)
70	459[b]	-27.9	467[b]	-23.7	469[b]	***-59.3***	τNH_2 (M1, M2)
71	284	-8.9	287	-5.5	299	-2.7	τRr (M1, M2)
72	284	-9.0	294	1.6	298	-4.0	τRr (M1, M2)
73	311	37.7	321	44.2	322	42.1	δC_6N_6, δR, δr (M1, M2)
74	308	34.5	315	37.8	317	36.8	δC_6N_6, δR, δr (M1, M2)
75	217	-23.2	208	-31.3	197	-31.6	τRr, $\gamma_{wagg}NH_2$ (M1, M2)
76	208	-32.7	211	-28.5	181	***-47.5***	τRr, τNH_2 (M1, M2)
77	145	***-62.2***	151	***-54.2***	128	22.9	$\gamma_{wagg}NH_2$, τRr (M1, M2)
78	151	***-56.4***	153	***-51.8***	148	***42.5***	$\gamma_{wagg}NH_2$, τRr (M1, M2)
79	93		104		95		intermolecular mode
80	77		86		82		intermolecular mode
81	10		23		51		τRr, γC_6N_6 (M1, M2)
82	39		51		37		intermolecular mode
83			3				intermolecular mode
84							intermolecular mode

[a]Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; R and r refer to the 6-membered ring and 5-membered ring, respectively; M1 = Monomer 1; M2 = Monomer 2.

[b]Modes excluded from the anharmonic calculation.

Table 15. Anharmonic vibrational frequencies (cm^{-1}) of stacked adenine dimer, computed using B3LYP-D3 and B3LYP-DCP approaches, and corresponding shifts respect to the isolated molecule (Δstacked).

	B3LYP-D3		B3LYP-DCP		Assignment[a]
Mode	anharm	Δstacked	anharm	Δstacked	
1	3521	-12.8	3532	-20.5	$\nu_{asym}NH_2$ (M2)
2	3506	-27.7	3532	-20.7	$\nu_{asym}NH_2$ (M1)
3	3491	9.0	3489	5.7	νN_9H (M2)
4	3487	4.6	3489	5.5	νN_9H (M1)
5	3423	-20.0	3430	-19.2	$\nu_{sym}NH_2$ (M2)
6	3422	-21.1	3430	-19.6	$\nu_{sym}NH_2$ (M1)
7	3115	3.8	3149	-0.2	νC_8H (M1)
8	3109	-2.6	3149	-0.5	νC_8H (M2)
9	3050	8.1	3080	12.3	νC_2H (M2)
10	3045	2.9	3080	12.4	νC_2H (M1)
11	1625	1.0	1679	1.1	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6 (M1, M2)
12	1625	1.1	1673	-5.6	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6 (M1, M2)
13	1599	4.3	1649	8.8	νN_3C_4, νC_5C_6 (M1, M2)
14	1595	0.5	1647	6.4	νN_3C_4, νC_5C_6 (M1, M2)
15	1566	1.4	1587	1.1	$\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6 (M1)
16	1565	0.2	1585	-0.5	$\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6 (M2)
17	1484	2.3	1521	-0.1	νN_7C_8, δC_8H (M1, M2)
18	1482	0.2	1520	-1.0	νN_7C_8, δC_8H (M1, M2)
19	1464	1.2	1496	-1.3	νN_1C_6, δC_2H, νC_2N_3, νC_6N_6 (M1, M2)
20	1463	-0.2	1495	-2.8	νN_1C_6, δC_2H, νC_2N_3, νC_6N_6 (M1, M2)
21	1406	0.3	1452	-1.0	νC_4C_5, νC_4N_9, δC_2H (M1, M2)
22	1406	-0.1	1452	-1.1	νC_4C_5, νC_4N_9, δC_2H (M1, M2)
23	1381	1.3	1415	-4.1	δN_9H, δC_2H, νC_4N_9, νC_8N_9 (M1, M2)
24	1378	-1.1	1415	-4.8	δN_9H, δC_2H, νC_4N_9, νC_8N_9 (M1, M2)
25	1338	1.2	1380	-3.4	δC_2H, νC_8N_9, δC_8H, νC_6N_6 (M1, M2)
26	1336	-1.0	1377	-6.6	δC_2H, νC_8N_9, δC_8H, νC_6N_6 (M1, M2)
27	1328	0.5	1366	-3.5	νN_1C_2, νC_5N_7, νC_4C_5 (M2)
28	1325	-2.7	1365	-4.4	νN_1C_2, νC_5N_7, νC_4C_5 (M1)
29	1299	3.3	1344	-3.9	νC_2N_3, νN_1C_2 (M1)
30	1297	1.1	1342	-5.3	νC_2N_3, νN_1C_2 (M2)
31	1244	5.7	1263	-3.5	δC_8H, νN_7C_8, δN_9H (M1, M2)
32	1242	3.6	1262	-5.2	δC_8H, νN_7C_8, δN_9H (M1, M2)
33	1227	2.2	1254	3.3	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3 (M1)
34	1228	3.2	1252	1.5	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3 (M2)
35	1125	3.2	1156	0.3	νC_4N_9, δr, νC_6N_6 (M1, M2)
36	1120	-1.6	1153	-2.6	νC_4N_9, δr, νC_6N_6 (M1, M2)
37	1053	-0.2	1080	-2.7	νC_8N_9, δN_9H (M1, M2)
38	1053	-0.4	1080	-2.8	νC_8N_9, δN_9H (M1, M2)
39	1010	14.8	1011	13.4	$\delta_{rock}NH_2$, νN_1C_6 (M1)
40	1005	10.6	1012	14.2	$\delta_{rock}NH_2$, νN_1C_6 (M2)
41	941	-11.5	973	-3.3	γC_2H (M1)
42	947	-5.1	973	-3.4	γC_2H (M2)
43	931	2.4	941	-1.0	δr, νC_4C_5 (M1)
44	931	1.8	941	-1.2	δr, νC_4C_5 (M2)
45	886	0.9	893	-1.9	δ R (M1)

46	887	1.8	893	-1.7	δ R (M2)
47	827	14.4	863	-3.6	γC_8H (M2)
48	829	15.8	862	-4.7	γC_8H (M1)
49	799	19.4	836	-4.1	γC_8H, τR, τr, γC_6N_6 (M1, M2)
50	798	18.5	836	-3.6	γC_8H, τR, τr, γC_6N_6 (M1, M2)
51	718	3.2	733	0.5	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing) (M2, M1)
52	717	2.2	732	-0.9	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing) (M1, M2)
53	674	8.8	696	-3.1	γC_6N_6, τr, τR (M1, M2)
54	669	4.0	691	-8.0	γC_6N_6, τr, τR (M1, M2)
55	647	-4.0	663	-5.3	τr (M1, M2)
56	647	-3.6	663	-4.9	τr (M1, M2)
57	611	1.7	616	-1.9	δr, νC_5C_6, δR (M1, M2)
58	611	1.4	616	-2.5	δr, νC_5C_6, δR (M1, M2)
59	558	13.3	573	-4.6	γN_9H, γC_2H, τR, τr (M1, M2)
60	558	13.9	575	-3.3	γN_9H, γC_2H, τR, τr (M1, M2)
61	526	20.6	529	-2.5	δ R (M1)
62	528	22.7	526	-5.9	δ R (M2)
63	513	14.8	519	4.7	τNH_2, γN_9H (M2), γN_9H (M1)
64	515	17.1	519	4.5	τNH_2, γN_9H (M1), γN_9H (M2)
65	493	6.7	520	-3.1	τNH_2, δR, δC_6N_6, νC_4N_9, γN_9H (M2), γN_9H (M1) (D3), $\delta_{rock}NH2$, δR, δC_6N_6, γN_9H (M1, M2) (DCP)
66	482	-9.0	518	-5.3	γN_9H, τNH_2 (M2, M1) (D3), $\delta_{rock}NH2$, δR, δC_6N_6, γN_9H (M1, M2) (DCP)
67	456	***-34.6***	477	***-51.8***	τNH_2 (M2), γN_9H (M1) (D3), τNH_2, γN_9H (M1, M2) (DCP)
68	425	***-66.4***	472	***-56.2***	τNH_2 (M1), γN_9H (M2) (D3), τNH_2, γN_9H (M1, M2) (DCP)
69	296	4.4	295	-6.4	τRr (M1, M2) (D3), $\gamma_{wagg}NH_2$, τRr (M1, M2) (DCP)
70	294	2.2	301	-1.0	τRr (M1, M2) (D3), $\gamma_{wagg}NH_2$, τRr (M1, M2) (DCP)
71	275	-1.8	276	-4.2	δC_6N_6, δR, δr (M1) (D3), δC_6N_6, δR, δr (M1, M2) (DCP)
72	213	-26.5	275	-5.6	τRr (M1, M2) (D3), δC_6N_6, δR, δr (M1, M2) (DCP)
73	203	-35.8	214	-14.1	τRr (M1, M2)
74	420[b]	***215.2***	202	-26.6	$\gamma_{wagg}NH_2$ (M1) (D3), τRr (M1, M2) (DCP)
75	290[b]	***84.8***	297[b]	***191.7***	$\gamma_{wagg}NH_2$ (M2) (D3), $\gamma_{wagg}NH_2$ (M1, M2) (DCP)
76	274[b]	***68.6***	291[b]	***186.1***	$\gamma_{wagg}NH_2$ (M2) (D3), $\gamma_{wagg}NH_2$ (M1, M2) (DCP)
77	164	7.2	167	14.3	τRr, γC_6N_6 (M1, M2)
78	158	1.1	163	9.8	τRr, γC_6N_6 (M1, M2)
79	66		68		intermolecular mode
80	54		55		intermolecular mode
81	37		39		intermolecular mode
82	27		25		intermolecular mode
83	9		14		intermolecular mode
84					intermolecular mode

[a]Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; R and r refer to the 6-membered ring and 5-membered ring, respectively; M1 = Monomer 1; M2 = Monomer 2.

[b]Modes excluded from the anharmonic calculation.

Table 16. Anharmonic vibrational frequencies (cm^{-1}) of adenine molecule in the stacked adenine-naphthalene dimer, computed using B3LYP-D3 and B3LYP-DCP approaches, and corresponding shifts respect to the isolated molecule (Δstacked).

	B3LYP-D3		B3LYP-DCP		Assignment[a]
Mode	anharm	Δstacked	anharm	Δstacked	
1	3520	-13.5	3537	-15.3	$\nu_{asym}NH_2$
2	3463	-18.5	3473	-10.7	νN_9H
3	3425	-18.0	3433	-15.9	$\nu_{sym}NH_2$
4	3117	5.2	3154	4.5	νC_8H
5	3034	-8.1	3049	-18.6	νC_2H
6	1627	3.4	1679	1.1	$\delta_{sciss}NH_2$, νC_5C_6, νC_6N_6
7	1601	7.0	1648	7.8	νN_3C_4, νC_5C_6
8	1562	-2.8	1584	-1.4	$\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6
9	1483	1.2	1519	-1.9	νN_7C_8, δC_8H
10	1464	0.4	1496	-1.5	νN_1C_6, δC_2H, νC_2N_3, νC_6N_6
11	1408	1.5	1452	-1.0	νC_4C_5, νC_4N_9, δC_2H
12	1379	-0.9	1421	1.7	δN_9H, δC_2H, νC_4N_9, νC_8N_9
13	1338	1.2	1386	2.1	δC_2H, νC_8N_9, δC_8H, νC_6N_6
14	1326	-1.2	1367	-2.9	νN_1C_2, νC_5N_7, νC_4C_5
15	1301	4.9	1347	-0.9	νC_2N_3, νN_1C_2
16	1242	3.1	1271	4.5	δC_8H, νN_7C_8, δN_9H
17	1227	2.5	1256	5.4	$\delta_{rock}NH_2$, νC_5N_7, νC_2N_3
18	1122	-0.1	1156	1.0	νC_4N_9, δr, νC_6N_6
19	1062	8.4	1089	6.0	νC_8N_9, δN_9H
20	1003	8.6	1011	13.1	$\delta_{rock}NH_2$, νN_1C_6
21	954	1.5	970	-6.3	γC_2H
22	931	2.2	944	1.5	δr, νC_4C_5
23	886	0.8	897	2.5	δ R
24	805	-8.4	872	5.1	γC_8H
	824	11.4			γC_8H
25	810	30.1	841	1.5	γC_8H, τR, τr, γC_6N_6
26	718	3.3	734	1.8	νN_3C_4, νC_5N_7, νC_4N_9 (ring breathing)
27	673	7.5	694	-5.4	γC_6N_6, τr, τR
28	654	3.1	665	-3.2	τr
29	612	2.8	618	0.0	δr, νC_5C_6, δR
30	567	22.7	573	-5.0	γN_9H, γC_2H, τR, τr
31	523	18.3	532	0.2	δ R, γN_9H
32	518	20.0	520	-8.1	τNH_2, γN_9H
33	522	30.5	520	5.8	γN_9H
34	461	-24.5	512	-11.2	τNH_2, δR
35	291	-0.6	307	5.6	τRr, $\gamma_{wagg}NH_2$
36	268	-8.6	275	-4.8	δC_6N_6, δR, δr
37	218	-21.2	203	-25.4	τRr, $\gamma_{wagg}NH_2$
38	168	-37.2			$\gamma_{wagg}NH_2$, τRr
	330[b]	***124.8***	265[b]	***159.4***	$\gamma_{wagg}NH_2$, τRr
39	164	7.4	166	13.6	τRr, γC_6N_6

[a]Abbreviations: ν = stretching; δ = in-plane bending; γ = out-of-plane bending; τ = torsional; sciss = scissoring; rock = rocking; wagg = wagging; asym = asymmetric; sym = symmetric; R and r refer to the 6-membered ring and 5-membered ring, respectively.

[b]Modes excluded from the anharmonic calculation.