Electronic Supplementary Material (ESI) for RSC Advances.
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Table S 1 Calculated total electronic energies (A.U), relative energies (kJ/mol) in parenthesis and dipole moment (Debye) of gaseous caffeine conformers**.**

Caffeine Conformers/ Rotamers	**MP2 Value**	**DFT Values**				
		M06	M06-2X	X3LYP	B3PW91	B3LYP
Conformer (A)	-678.7120497	-680.1279761	-680.2987337	-680.2748490	-680.2995226	-680.5638739
	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
	4.603	3.981	3.977	4.025	4.008	4.017
Conformer (B)	-678.7116155	-680.1277964	-680.2983148	-680.2745869	-680.2992887	-680.5635797
	(1.14)	(0.47)	(1.09)	(0.69)	(0.61)	(0.77)
	4.570	3.953	3.977	3.995	3.978	3.984
Conformer (C)	-678.7109422	-680.1272614	-680.2978019	-680.2741104	-680.2987934	-680.5631061
	(2.91)	(1.87)	(2.44)	(1.94)	(1.91)	(2.01)
	4.599	3.943	4.011	3.992	3.984	3.986
Conformer (D)	-678.7107405	-680.1270058	-680.2976344	-680.2741721	-680.2989309	-680.5631602
	(3.43)	(2.55)	(2.88)	(1.78)	(1.55)	(1.87)
	4.609	3.906	3.996	3.970	3.945	3.961
Conformer (E)	-678.7103569	-680.1268486	-680.2972702	-680.2739267	-680.2987085	-680.5629187
	(4.44)	(2.96)	(3.84)	(2.96)	(2.14)	(2.51)
	4.577	3.876	3.994	3.942	3.915	3.929
Conformer (F)	-678.7097658	-680.1263391	-680.2968476	-680.2734900	-680.2982505	-680.5624830
	(5.99)	(4.29)	(4.95)	(3.56)	(3.34)	(3.65)
	4.601	3.87	4.02	3.94	3.92	3.93

Table S 2 Selected structural parameters of the most stable conformers of caffeine

Strucutural Parameters	Experimental value*	Calculated value at MP2/6-311++G(d,p) level				
		Conformer **A**	Conformer **B**	Conformer **C**	Conformer **D**	Conformer **E**
Bond lengths (Å)						
N1-C2	1.410	1.4119	1.4138	1.4171	1.4117	1.4137
C2-N3	1.383	1.3831	1.3867	1.3876	1.3816	1.3852
N3-C4	1.376	1.3768	1.3754	1.3758	1.3770	1.3755
C4-C5	1.382	1.3870	1.3859	1.3853	1.3882	1.3871
C5-C6	1.446	1.4378	1.4373	1.4364	1.4404	1.4399
C6-N1	1.408	1.4101	1.4105	1.4074	1.4092	1.4099
C5-N7	1.373	1.3745	1.3738	1.3735	1.3768	1.3760
N7-C8	1.362	1.3637	1.3644	1.3647	1.3630	1.3638
C8-N9	1.297	1.3377	1.3382	1.3381	1.3374	1.3380
N9-C4	1.359	1.3591	1.3591	1.3595	1.3587	1.3587
N1-C10	1.464	1.4659	1.4664	1.4671	1.4663	1.4667
C2-O11	1.204	1.2241	1.2233	1.2229	1.2243	1.2234
N3-C12	1.458	1.4608	1.4604	1.4609	1.4609	1.4603
C6-O13	1.209	1.2279	1.2277	1.2282	1.2287	1.2285
N7-C14	1.456	1.4591	1.4592	1.4590	1.4638	1.4637
C8-H1	1.085	1.0819	1.0819	1.0820	1.0821	1.0821
Bond Angles (°)						
C2-N1-C6	127.8	127.5317	127.9410	127.9877	127.6807	128.1016
N1-C2-N3	116.5	116.9223	116.4823	115.8493	116.7886	116.3358
C2-N3-C4	120.3	120.0060	119.8588	120.3406	120.0362	119.8892
N3-C4-C5	121.5	121.0858	121.6437	121.7183	121.3712	121.9381
C4-C5-C6	122.9	123.8839	123.5615	123.0270	123.4024	123.0962
C5-C6-N1	111.0	110.5700	110.5126	111.0770	110.7209	110.6391
N9-C4-C5	111.6	111.8876	112.0082	111.9608	111.9463	112.0739
C4-C5-N7	104.7	105.3180	105.2978	105.3635	105.1540	105.1392
C5-N7-C8	105.6	106.9889	105.9938	105.9756	106.0535	106.0516
N7-C8-N9	114.2	113.3834	113.3857	113.3573	113.3851	113.3941
C8-N9-C4	103.8	103.4220	103.3146	103.3429	103.4610	103.3411
C5-C6-O13	125.9	126.0385	126.0561	126.8456	126.3374	126.3711
O13-C6-N1	-	123.3914	123.4313	122.0774	122.9417	122.9898
C6-N1-C10	-	118.0901	117.8570	114.8561	118.0360	117.7991
C10-N1-C2	114.4	114.3781	114.2020	117.1561	114.2833	114.0994
N1-C2-O11	-	121.0623	120.4011	121.6562	121.0884	120.4326
O11-C2-N3	122.2	122.0154	123.1165	122.4944	122.1228	123.2315
C2-N3-C12	-	118.0487	120.4150	120.2523	118.0297	120.4129
C12-N3-C4	121.8	121.9449	119.7261	119.4071	121.9341	119.6979
N3-C4-N9	-	127.0266	126.3481	126.3209	126.6825	125.9880
N9-C8-H1	-	125.0220	125.0588	125.0772	124.9324	124.9674
H1-C8-N7	-	121.5945	121.5555	121.5655	121.6825	121.6385
C8-N7-C14	-	127.2189	127.2355	127.3079	126.6690	126.7263
C14-N7-C5	126.7	126.7921	126.7707	126.7165	127.2775	127.2221
N7-C5-C6	-	130.7980	131.1408	131.6095	131.4435	131.7646

* T. Egawa, A. Kamiya, H. Takeuchi, S. Konaka, J. Mol. Struct. 825 (2006) 151–157.

Table S 3. Calculated NBO Charges of the most stable conformers of caffeine at MP2/6-311++G(d,p) level.

Atom No.	NBO Charge					
	Conformer A	Conformer B	Conformer C	Conformer D	Conformer E	Conformer F
O11	-0.731	-0.736	-0.741	-0.732	-0.736	-0.741
O13	-0.726	-0.725	-0.720	-0.732	-0.730	-0.725
N1	-0.624	-0.626	-0.626	-0.623	-0.625	-0.626
N3	-0.578	-0.580	-0.581	-0.578	-0.579	-0.580
N7	-0.443	-0.442	-0.443	-0.447	-0.447	-0.447
N9	-0.610	-0.602	-0.601	-0.603	-0.597	-0.596
C2	1.015	1.019	1.023	1.015	1.019	1.023
C4	0.477	0.472	0.472	0.471	0.467	0.467
C5	-0.084	-0.081	-0.080	-0.078	-0.075	-0.073
C6	0.821	0.822	0.818	0.823	0.823	0.819

Table S4 Selected ground state vibrational stretching frequencies (cm^{-1}) and IR intensity with tentative vibrational assignments of the most stable conformers of caffeine .

Assignment	Calculated values at B3LYP/6-311++G(d,p) level				
	Conformer **(A)**	Conformer **(B)**	Conformer **(C)**	Conformer **(D)**	Conformer **(E)**
NH str.	3225 (2)	3225 (2)	3225 (2)	3223 (2)	3223 (2)
CH_3 str. (+) at N_1	3051 (27)	3052 (27)	3050 (25)	3052 (27)	3052 (27)
CH_3 str. (+) at N_3	3044 (33)	3041 (37)	3042 (38)	3045 (28)	3041 (47)
CH_3 str. (+) at N_7	3049 (26)	3049 (27)	3049 (26)	3042 (51)	3042 (34)
$(C=O)_2$ sym. str.	1728 (447)	1730 (464)	1730 (468)	1727 (448)	1729 (465)
$(C=O)_2$ asym. str.	1687 (915)	1688 (898)	1688 (893)	1684 (920)	1685 (903)
C=C str.	1606 (90)	1607 (88)	1607 (83)	1604 (91)	1604 (90)
(C=N + C=C) str.	1578 (128)	1581 (132)	1580 (128)	1578 (115)	1581 (119)

Abbreviations used: (+), in phase; (-), out of phase.

Table S 5. Rotational constants (GHz) and zero-point vibrational energy (kcal mol^{-1}) of the most stable conformers of caffeine

Parameters	Calculated values at MP2/6-311++G(d,p) level					
	Conformer **(A)**	Conformer **(B)**	Conformer **(C)**	Conformer **(D)**	Conformer **(E)**	Conformer **(F)**
A (GHz)	1.0618291	1.0576225	1.0495598	1.0622487	1.0579730	1.0497040
B (GHz)	0.7037817	0.7060669	0.7094507	0.7011933	0.7036089	0.7073798
C (GHz)	0.4266568	0.4268161	0.4267240	0.4257872	0.4259891	0.4260128
ZPVE*	117.87432	117.84318	117.79519	117.75489	117.73767	117.70870

*values obtained at B3LYP/6-311++G(d,p) level using MP2/6-311++G(d,p) level optimized geometries.