SUPPORTING INFORMATION FOR
'SPECTROSCOPIC SIGNATURES AND STRUCTURAL MOTIFS of DOPAMINE: A COMPUTATIONAL STUDY'

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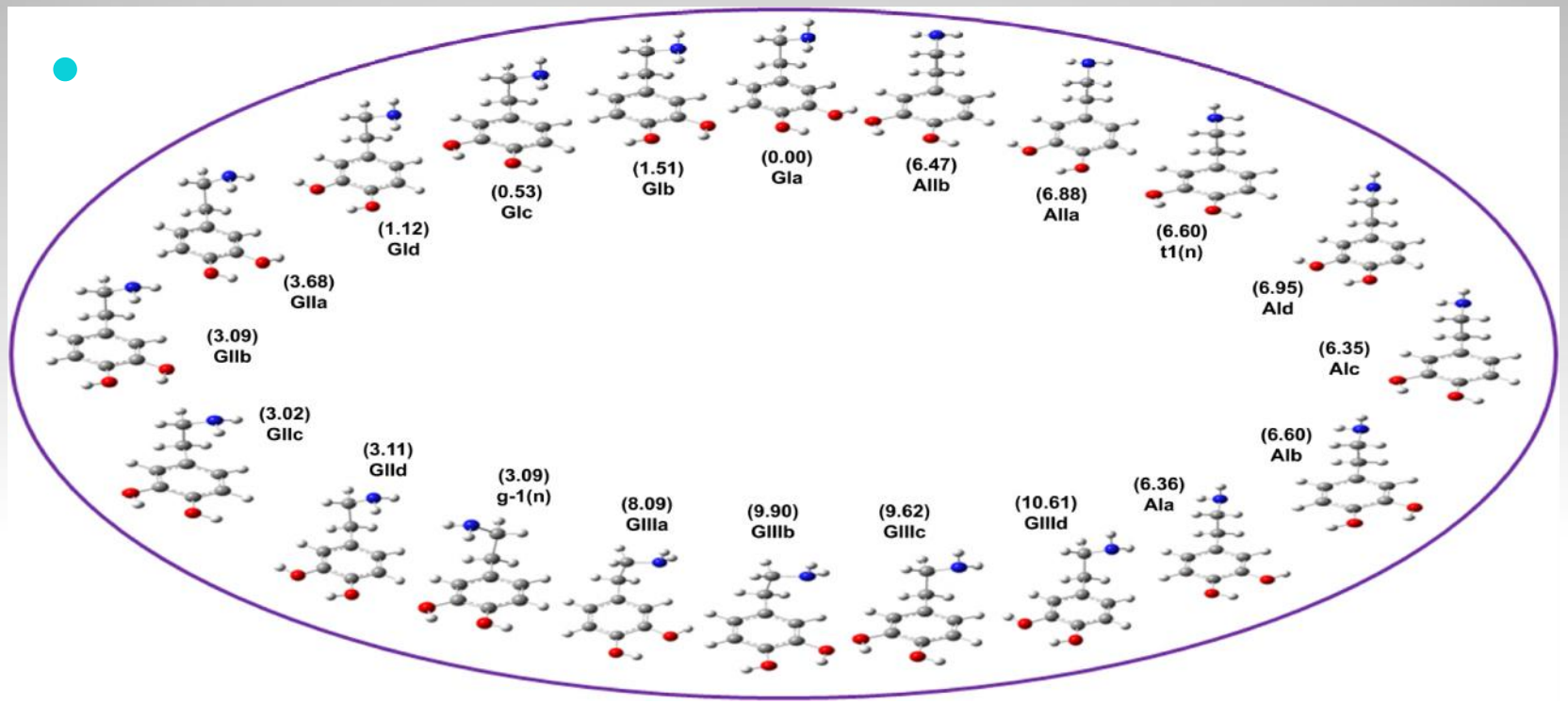

Table 1 Relative zero-point corrected energies (Δ*E*), free energies (Δ*G*) at 298 K (in kJ mol^{-1}) and dipole moments (D) in parenthesis of the twenty low-energy conformers of neutral dopamine in the gas phase at the MP2 level of theory

S. no.	description of the ethylamine side chain	MP2/6-311++G(d,p)		MP2/aug-cc-pVDZ	
		Δ*E*	Δ*G*	Δ*E*	Δ*G*
1	GIa	0.00 (1.9926)	0.00	0.00 (1.9395)	0.00
2	GIb	1.38 (3.6777)	1.17	1.51 (3.6225)	1.42
3	GIc	0.56 (1.5720)	0.38	0.53 (1.7193)	0.32
4	GId	1.21 (3.4452)	0.90	1.12 (3.3608)	0.98
5	GIIa	2.43 (3.3318)	1.40	3.68 (2.9473)	3.30
6	GIIb	1.95 (3.0539)	1.42	3.09 (2.6894)	2.76
7	GIIc	1.83 (3.6474)	1.31	3.02 (3.2194)	2.80
8	GIId	1.95 (2.2061)	1.33	3.11 (2.4738)	2.94
9	GIIIa	6.80 (4.3581)	5.83	8.09 (4.0810)	7.70
10	GIIIb	9.20 (2.7709)	7.57	9.90 (2.6872)	9.15
11	GIIIc	8.64 (2.9241)	6.47	9.62 (2.5915)	8.88
12	GIIId	9.66 (4.2992)	6.75	10.61 (4.0231)	9.84
13	AIa	5.57 (1.9445)	4.45	6.36 (2.0334)	5.39
14	AIb	5.72 (3.5082)	4.66	6.60 (3.5846)	5.67
15	AIc	5.49 (1.5824)	4.34	6.35 (1.7688)	5.42
16	AId	6.18 (3.3586)	5.01	6.95 (3.4389)	6.04
17	AIIa	6.32 (2.5240)	5.32	6.88 (2.7583)	6.05
18	AIIb	5.80 (2.7904)	4.65	6.47 (2.8936)	5.62
19	g-1(n)	1.95 (3.0549)	1.41	3.09 (2.6893)	2.76
20	t1(n)	5.71 (3.5080)	4.66	6.60 (3.5841)	5.67

[a] Zero-point corrections use the DFT B3LYP/6-311++G(d,p) and aug-cc-pVDZ harmonic frequencies respectively.

Table 2 Relative zero-point corrected energies [a] (Δ*E*), free energy (Δ*G*) at 298 K (in kJ mol^{-1}) and dipole moments (D) in parenthesis of the twenty low-energy conformers of neutral dopamine in the gas phase and aqueous solution (PCM) at MP2/6-311++G(d,p) level

S. no.	Conformer	Gas Phase		Aqueous Solution (PCM)	
		Δ*E*	Δ*G*	Δ*E*	Δ*G*
1	GIa	0.00 (1.9926)	0.00	1.38 (2.3983)	1.78
2	GIb	1.38 (3.6777)	1.17	1.39 (5.1723)	1.79
3	GIc	0.56 (1.5720)	0.38	1.15 (1.9578)	1.69
4	GId	1.21 (3.4452)	0.90	1.41 (4.8414)	1.95
5	GIIa	2.43 (3.3318)	1.40	0.56 (4.4242)	0.89
6	GIIb	1.95 (3.0539)	1.42	0.37 (3.9446)	0.59
7	GIIc	1.83 (3.6474)	1.31	0.00 (4.7108)	0.04
8	GIId	1.95 (2.2061)	1.33	0.09 (3.0907)	0.00
9	GIIIa	6.80 (4.3581)	5.83	5.07 (5.5320)	4.40
10	GIIIb	9.20 (2.7709)	7.57	4.88 (3.7319)	4.19
11	GIIIc	8.64 (2.9241)	6.47	4.05 (3.6229)	3.26
12	GIIId	9.66 (4.2992)	6.75	4.54 (5.5741)	4.12
13	AIa	5.57 (1.9445)	4.45	3.89 (2.5491)	4.01
14	AIb	5.72 (3.5082)	4.66	3.57 (4.7386)	3.39
15	AIc	5.49 (1.5824)	4.34	3.59 (2.1548)	3.05
16	AId	6.18 (3.3586)	5.01	3.80 (4.5958)	3.41
17	AIIa	6.32 (2.5240)	5.32	2.84 (3.4934)	2.74
18	AIIb	5.80 (2.7904)	4.65	2.74 (3.6798)	2.52
19	g-1(n)	1.95 (3.0549)	1.41	0.37(3.9445)	0.59
20	t1(n)	5.71 (3.5080)	4.66	3.57 (4.7388)	3.39

[a] Zero-point corrections use the DFT B3LYP/6-311++G(d,p) harmonic frequencies at MP2/6-311++G(d,p) level optimized geometries.

Table 3 Relative zero-point corrected energies [a] [E_{rel} (kJ mol^{-1})] and dipole moments (Debye) in parenthesis of the seven experimentally observed conformers of neutral dopamine in the gas phase computed at aug-cc-pVDZ levels

Conformer	E_{rel}^{CCSD} [b]	E_{rel}^{MP2}	$E_{rel}^{M06\text{-}2X}$	$E_{rel}^{\omega B97X\text{-}D}$	E_{rel}^{B3LYP}	E_{rel}^{MP2} [c]	E_{rel}^{CC2} [d]
GIa	**0.00** *(2.1033)*	**0.00** *(1.9395)*	**0.00** *(1.7436)*	**0.00** *(1.7419)*	**0.00** *(1.7035)*	**0.00** *(1.9189)*	**0.00**
GIb	2.00 *(4.0058)*	1.51 *(3.6225)*	1.08 *(3.3191)*	1.06 *(3.3334)*	0.91 *(3.2646)*	1.49 *(3.6039)*	1.52
GIc	0.77 *(1.8382)*	0.53 *(1.7193)*	0.27 *(1.7451)*	0.28 *(1.7174)*	0.18 *(1.7151)*	0.46 *(1.7101)*	0.49
GId	1.54 *(3.6320)*	1.12 *(3.3608)*	1.12 *(3.2001)*	1.18 *(3.2293)*	0.97 *(3.1450)*	1.00 *(3.3498)*	1.51
GIIb	3.32 *(2.9605)*	3.09 *(2.6894)*	1.63 *(2.5580)*	0.63 *(2.5706)*	1.04 *(2.5153)*	2.54 *(2.6793)*	1.06
GIIc	3.35 *(3.5438)*	3.02 *(3.2194)*	1.49 *(3.0349)*	0.44 *(3.0579)*	0.90 *(3.0127)*	2.46 *(3.2034)*	1.02
GIId	3.43 *(2.6853)*	3.11 *(2.4738)*	1.92 *(2.2170)*	0.77 *(2.2279)*	1.24 *(2.1487)*	2.52 *(2.4608)*	1.23

[a] Zero-point corrected energies at the MP2, M06-2X, ωB97X-D, B3LYP and CC2 optimized geometries as well as for CCSD single-point energies were obtained by including the zero-point corrections from B3LYP/aug-cc-pVDZ harmonic frequencies. [b] Single-point energy calculation with basis set 6-31+G(d). [c] Single-point energy calculation with basis set aug-cc-pVTZ.

[d] Optimized using the basis set def-TZVP.

Table 4 Relative zero-point corrected energies [a] [E_{rel} (kJ mol^{-1})] and dipole moments (Debye) in parenthesis of the protonated dopamine isomers g-1, g+1, t1, t2 and t3 in the gas phase calculated at the aug-cc-pVDZ level

	E_{rel}^{MP2}	$E_{rel}^{M06\text{-}2X}$	$E_{rel}^{\omega B97X\text{-}D}$	E_{rel}^{B3LYP}	$E_{rel}^{B3LYP-D3}$	$E_{rel}^{MP2\ b}$
g-1	0.00 *(9.6108)*	0.00 *(9.5089)*	0.00 *(9.3128)*	0.00 *(9.3681)*	0.00 *(11.70)*	0.00 *(9.5909)*
g+1	0.43 *(10.5710)*	0.10 *(10.0624)*	0.55 *(10.3859)*	0.20 *(10.5165)*	-	0.38 *(10.5458)*
t1	26.03 *(15.5552)*	22.80 *(14.8973)*	22.83 *(14.9932)*	17.14 *(14.9314)*	23.16 *(15.76)*	25.15 *(15.5367)*
t2	32.33 *(17.7135)*	29.39 *(17.0178)*	29.41 *(17.1279)*	23.41 *(17.0030)*	-	31.47 *(17.6876)*
t3	47.17 *(17.6553)*	-	-	38.03 *(16.9180)*	-	-

[a] Zero-point corrected energies at the MP2, M06-2X, ωB97X-D and B3LYP optimized geometries were obtained by including the zero-point corrections from B3LYP/aug-cc-pVDZ harmonic frequencies. [b] Single-point energy calculation with basis set aug-cc-pVTZ.

Table 5 Selected geometrical [a] (Å, degree) and energetic parameters [b] (kJ mol^{-1}) for various isomers of the dopamineH$^+$ in the gas phase and aqueous solution (PCM) calculated at the MP2/aug-cc-pVDZ level

	g-1		g+1		g-2		g+2		g-3		g+3	
	gas phase	aqueous solution	gas phase	aqueous solution	gas phase	aqueous solution	gas phase	aqueous solution	gas phase	aqueous solution	gas phase	aqueous solution
R(N-H)	1.0405	1.0295	1.0403	1.0301	1.0378	1.0294	1.0425	1.0302	1.0389	1.0295	1.0424	1.0301
	1.0271	1.0264	1.0269	1.0264	1.0270	1.0264	1.0270	1.0263	1.0270	1.0264	1.0269	1.0264
	1.0258	1.0252	1.0258	1.0254	1.0261	1.0252	1.0258	1.0254	1.0260	1.0252	1.0257	1.0254
$\theta_{C4C7C8N}$	-52	-58	51	58	-46	-58	52	58	-49	-58	52	58
$\theta_{C5C4C7C8}$	-79	-75	-103	-102	-62	-74	-95	-101	-69	-75	-98	-102
R(NH-π) [c]	2.30	2.65	2.41	2.63	2.70	2.67	2.27	2.62	2.50	2.65	2.31	2.63
Δ*E*	0.00	2.44	0.43	0.00	7.52	2.42	4.44	0.60	22.20	9.66	19.76	7.54
Δ*G*	0.00	3.63	0.33	0.00	6.54	3.50	4.84	0.80	21.41	10.80	19.87	7.63
atomic charges	0.487*	0.469*	0.487*	0.470*	0.487*	0.469*	0.488*	0.470*	0.487*	0.469*	0.488*	0.470*
(NBO) on	0.454	0.468	0.453	0.468	0.453	0.468	0.453	0.468	0.453	0.467	0.453	0.468
ammonium	0.460	0.475	0.460	0.475	0.460	0.475	0.460	0.475	0.460	0.475	0.460	0.475
hydrogen atoms												

Table 5 Continued

	t1		t2		t3	
	gas phase	aqueous solution	gas phase	aqueous solution	gas phase	aqueous solution
R(N-H)	1.0275 1.0278 1.0277	1.0261 1.0262 1.0260	1.0275 1.0278 1.0277	1.0262 1.0262 1.0260	1.0275 1.0278 1.0277	1.0261 1.0262 1.0260
$\theta_{C4C7C8N}$	-179	-179	178	-179	179	-179
$\theta_{C5C4C7C8}$	-94	-91	-84	-90	-87	-90
R(NH-π) [c]	-	-	-	-	-	-
Δ*E*	26.03	6.36	32.33	6.52	47.17	13.45
Δ*G*	24.92	6.03	31.25	6.19	45.94	12.87
atomic charges (NBO) on ammonium hydrogen atoms	0.459 0.458 0.463	0.468 0.468 0.475	0.459 0.458 0.463	0.468 0.468 0.475	0.459 0.458 0.463	0.468 0.468 0.475

[b] zero-point corrected energies and free energies were obtained by including the zero-point corrections from B3LYP/aug-cc-pVDZ harmonic frequencies. [c] R(NH–π) is the NH–π distance between the nearest carbon atom of the aromatic ring and the nearest NH proton. *H^+ pointed towards the aromatic rings.

Table 6 Natural atomic charges of the protonated dopamine isomers g-1, g+1, t1 and t2 in solution and gas phase calculated at the MP2/aug-cc-pVDZ level of theory

	NBO Charge							
atom number [a]	g-1		g+1		t1		t2	
	solution	gas phase	solution	gas phase	solution	gas phase	solution	gas phase
N1	-0.766	-0.787	-0.766	-0.786	-0.757	-0.768	-0.757	-0.769
O1	-0.795	-0.773	-0.794	-0.773	-0.796	-0.775	-0.787	-0.755
O2	-0.784	-0.756	-0.784	-0.753	-0.786	-0.759	-0.795	-0.773
C1	0.297	0.313	0.301	0.319	0.295	0.318	0.315	0.357
C2	0.335	0.370	0.338	0.376	0.331	0.363	0.311	0.322
C3	-0.277	-0.317	-0.262	-0.275	-0.261	-0.263	-0.273	-0.278
C4	-0.085	-0.105	-0.085	-0.112	-0.062	-0.091	-0.065	-0.102
C5	-0.227	-0.232	-0.245	-0.269	-0.227	-0.225	-0.224	-0.218
C6	-0.260	-0.245	-0.264	-0.259	-0.267	-0.259	-0.255	-0.235
C7	-0.419	-0.418	-0.419	-0.418	-0.417	-0.415	-0.416	-0.414
C8	-0.147	-0.150	-0.148	-0.152	-0.149	-0.152	-0.149	-0.152

[a] See fig. 1 for the atom numbering.

Table 7 Vertical excitation energies (eV) and oscillator strengths (in bracket) for the low-lying excited states of neutral dopamine in the gas phase

Conformational state	Calculated values at TD-DFT-B3LYP/aug-cc-pVDZ level		Calculated values at CC2/def-TZVP level		
	$^1\pi\pi^*$	$^1\pi\pi^*$	$^1\pi\pi^*$	$^1\pi\pi^*$	$^1\pi\pi^*$
GIa	4.712	6.039	4.832	5.998	6.746
	(0.051)	(0.166)	(0.044)	(0.141)	(0.198)
	4.64 [a]	*5.16* [a]	*4.64* [a]	*5.16* [a]	*6.20* [a]
GIb	4.728	6.079	4.846	5.996	6.728
	(0.050)	(0.117)	(0.044)	(0.073)	(0.391)
GIc	4.717	6.101	4.831	6.711	6.827
	(0.057)	(0.119)	(0.051)	(0.329)	(0.426)
GId	4.695	6.024	4.820	6.021	6.716
	(0.059)	(0.074)	(0.050)	(0.121)	(0.187)
GIIb	4.695	5.931	4.831	5.970	6.712
	(0.060)	(0.074)	(0.048)	(0.077)	(0.526)
GIIc	4.713	6.161	4.829	6.573	6.663
	(0.052)	(0.161)	(0.050)	(0.088)	(0.227)
GIId	4.688	6.104	4.812	6.002	6.681
	(0.055)	(0.059)	(0.050)	(0.114)	(0.304)

[a] **Corresponding experimental values.**

Vertical excitation energies (eV) and oscillator strengths (in bracket) for the low-lying excited states of dopamineH^+

Table 8a

conformational state	Calculated VEE at TD-DFT-B3LYP/aug-cc-pVDZ level	
	in gas phase	In Bulk solvation (PCM method)
	$^1\pi\pi^*$	$^1\pi\pi^*$
g-1	4.602 (0.068)	4.674 (0.069)
g+1	4.676 (0.053)	4.707 (0.077)
g-1(n) [a]	4.695 (0.060)	4.713 (0.072)

Table 8b

conformational state	Calculated VEE at CC2/def-TZVP level				
	$^1\pi\pi^*$	S2	S3	S4	S5
g-1	4.73 (0.0568)	5.39 (0.015)	5.726 (0.08)	6.236 (0.16)	6.41 (0.003)
g-1(n) [a]	4.838 (0.043)	5.895 (0.002)	5.975 (0.072)	6.592 (0.015)	6.718 (0.487)
t1	4.79 (0.052)	4.97 (0.002)	5.75 (0.088)	5.83 (0.015)	6.38 (0.016)

[a] neutral dopamine isomer corresponding to g-1 isomer of dopamine H^+.