

Supplementary Information

Barrier potentials, Molecular structure, force field calculations and quantum chemical studies of some bipyridine di-carboxylic acids using the experimental and theoretical using (DFT, IVP) approach

Jyothi Prashanth^{a*}, Ramaiah Konakanchi^b, Byru Venkatram Reddy^{a*}

^aDepartment of Physics, Kakatiya University, Warangal-506009, India

^bDepartment of Chemistry, National Institute of Technology, Warangal-506004, India

1. Raman intensities

The Raman activities (S_i) procured in the scaling method were transformed to respective Raman intensities (I_i) employing the following relationship obtained from the basic theory of Raman scattering [1,2]

$$I_i = f (v_0 - v_i)^4 S_i / \{v_i [1 - e^{-hc\nu/kT}]\}$$

where v_i is the frequency of i^{th} normal mode (cm^{-1}), v_0 is the exciting frequency (cm^{-1}), h is the Planck's constant, k is the Boltzmann's constant, c is the velocity of light and f is a suitably chosen common normalization factor for all peak intensities.

References

- [1] Kerezturny G, Holly S, Besenyei G. Vibrational Spectra of Monothiocarbamates-II. IR and Raman Spectra, Vibrational Assignment, Conformational Analysis and Ab Initio Calculations of S-Methyl-N,N-dimethylthiocarbamate. *Spectrochim Acta A*. 2007;49:2007-2026.
- [2] Kerezturny G, Chalmers JM, Griffith PR (Eds.). Raman Spectroscopy; Theory in Handbook of Vibrational Spectroscopy. Vol. 1, John Wiley and Sons Ltd. New York, 2002.

Table S1 Definition of internal coordinates of B3DA.

S. No.	Symbol	Description ^{a,b}	Definition
1-12	d _i	C-C (Ring)	C1-N2, N2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C7-N8, N8-C9, C9-C10, C10-C11, C11-C12, C12-C7
13	r'	C-C' (Ring-C')	C1-C7
14-19	r _i	C-H (Ring)	C3-H13, C4-H14, C5-H15, C9-H20, C10-H21, C11-H22
20-21	R _i	(C-C _α) ₁ , (C-C _α) ₂	C6-C16, C12-C23
22-23	R _i	(C _α =O) ₁ , (C _α =O) ₂	C16-O17, C23-O26
24-25	R _i	(C _α -O) ₁ , (C _α -O) ₂	C16-O18, C23-O24
26-27	R _i	(O-H) ₁ , (O-H) ₂	O18-H19, O24-H25
Bending			
28-39	θ _i	C-C-C, C-N-C (Ring)	C6-C1-N2, C1-N2-C3, N2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C12-C7-N8, C7-N8-C9, N8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C7
40-51	φ _i	C-C-H, N-C-H (Ring)	N2-C3-H13, C4-C3-H13, C3-C4-H14, C5-C4-H14, C4-C5-H15, C6-C5-H15, N8-C9-H20, C10-C9-H20, C9-C10-H21, C11-C10-H21, C10-C11-H22, C12-C11-H22
52-55	φ _i	C-C-C' (Ring-C')	N2-C1-C7, C6-C1-C7, N8-C7-C1, C12-C7-C1
56-59	φ _i	C-C-C _α	C5-C6-C16, C1-C6-C16, C11-C12-C23, C7-C12-C23
60	Δλ _i	(C-C _α =O) ₁	C6-C16-O17
61	Δλ _i	(C-C _α =O) ₂	C12-C23-O26
62	Δλ _i	(C-C _α -O) ₁	C6-C16-O18
63	Δλ _i	(C-C _α -O) ₂	C12-C23-O24
64	Δλ _i	(O-C _α =O) ₁	O17-C16-O18
65	Δλ _i	(O-C _α =O) ₂	O26-C23-O24
66	Δλ _i	(C _α -O-H) ₁	C16-O18-H19
67	Δλ _i	(C _α -O-H) ₂	C23-O24-H25
Wagging			
68-73	γ _i	π (CH)	C4-C3-N2-H13, C5-C4-C3-H14, C6-C5-C4-H15, C10-C9-N8-H20, C11-C10-C9-H21, C12-C11-C10-H22
74-75	γ _i	π (CC')	C6-C1-N2-C7, C12-C7-N8-C1
76-77	γ _i	π (C C _α)	C1-C6-C5-C16, C7-C12-C11-C23

78-79	ω_i	$\omega(\text{OH})_1, \omega(\text{OH})_2$	C6-C16-O18-H19, C12-C23-O24-H25
80-81	ω_i	$\omega(\text{C}_\alpha=\text{O})_1, \omega(\text{C}_\alpha=\text{O})_2$	O17-C16-O18-H19, O26-C23-O24-H25
Torsion			
82-93	δ_i	$\tau(\text{Ring})$	C6-C1-N2-C3, C1-N2-C3-C4, N2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-N2, C12-C7-N8-C9, C7-N8-C9- C10, N8-C9-C10-C11, C9-C10-C11-C12, C10-C11-C12-C7, C11-C12-C7-N8
94-97	τ_i	$\tau(\text{CC}')$	N2-C1-C7-N8, C6-C1-C7-C12, N2-C1-C7-C12, C6-C1-C7-N8
98-99	τ_i	$\tau(\text{CC}_\alpha)_1, \tau(\text{CC}_\alpha)_2$	C1-C6-C16-O17, C11-C12-C23-O26

^a: C' refers to Carbon atom (C7 in Fig. 4a) associated with the second pyridyl ring

^b: C_{αi} refers to Carbon atom of acid group.

Table S2 Definition of internal coordinates of B4DA.

S. No.	Symbol	Description ^{a,b}	Definition
1-12	d_i	C-C (Ring)	C1-N2, N2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C7-N8, N8-C9, C9-C10, C10-C11, C11-C12, C12-C7
13	r'	C-C' (Ring-C')	C1-C7
14-19	r_i	C-H (Ring)	C3-H13, C4-H14, C6-H19, C9-H20, C10-H21, C12-H26
20-21	R_i	(C-C _{α}) ₁ , (C-C _{α}) ₂	C5-C15, C11-C22
22-23	R_i	(C _{α} =O) ₁ , (C _{α} =O) ₂	C15-O16, C22-O25
24-25	R_i	(C _{α} -O) ₁ , (C _{α} -O) ₂	C15-O17, C22-O23
26-27	R_i	(O-H) ₁ , (O-H) ₂	O17-H18, O23-H24
Bending			
28-39	θ_i	C-C-C, C-N-C (Ring)	C6-C1-N2, C1-N2-C3, N2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C12-C7-N8, C7-N8-C9, N8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C7
40-51	ϕ_i	C-C-H, N-C-H (Ring)	N2-C3-H13, C4-C3-H13, C3-C4-H14, C5-C4-H14, C5-C6-H19, C1-C6-H19, N8-C9-H20, C10-C9-H20, C9-C10-H21, C11-C10-H21, C11-C12-H26, C7-C12-H26
52-55	ϕ_i	C-C-C' (Ring-C')	N2-C1-C7, C6-C1-C7, N8-C7-C1, C12-C7-C1
56-59	ϕ_i	C-C- C _{α}	C4-C5-C15, C6-C5-C15, C10-C11-C22, C12-C11-C22
60	$\Delta\lambda_i$	(C- C _{α} =O) ₁	C5-C15-O16
61	$\Delta\lambda_i$	(C- C _{α} =O) ₂	C11-C22-O25
62	$\Delta\lambda_i$	(C- C _{α} -O) ₁	C5-C15-O17
63	$\Delta\lambda_i$	(C- C _{α} -O) ₂	C11-C22-O23
64	$\Delta\lambda_i$	(O- C _{α} =O) ₁	O16-C15-O17
65	$\Delta\lambda_i$	(O- C _{α} =O) ₂	O25-C22-O23
66	$\Delta\lambda_i$	(C _{α} -O-H) ₁	C15-O17-H18
67	$\Delta\lambda_i$	(C _{α} -O-H) ₂	C22-O23-H24
Wagging			
68-73	γ_i	π (CH)	C4-C3-N2-H13, C5-C4-C3-H14, C1-C6-C5-H19, C10-C9-N8-H20, C11-C10-C9-H21, C7-C12-C11-H26
74-75	γ_i	π (CC')	C6-C1-N2-C7, C12-C7-N8-C1
76-77	γ_i	π (C C _{α})	C4-C5-C6-C15, C12-C11-C10-C22
78-79	γ_i	ω (OH) ₁ , ω (OH) ₂	C5-C15-O17-H18, C11-C22-O23-H24

80-81	γ_i	$\omega(C_{\alpha}=O)_1, \omega(C_{\alpha}=O)_2$	O16-C15-O17-H18, O25-C22-O23-H24
Torsion			
82-93	δ_i	τ (Ring)	C6-C1-N2-C3, C1-N2-C3-C4, N2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-N2, C12-C7-N8-C9, C7-N8-C9-C10, N8-C9-10-C11, C9-C10-C11-C12, C10-C11-C12-C7, C11-C12-C7-N8
94-97	τ_i	τ (CC')	N2-C1-C7-N8, C6-C1-C7-C12, N2-C1-C7-C12, C6-C1-C7-N8
98-99	τ_i	$\tau(CC_{\alpha})_1, \tau(CC_{\alpha})_2$	C6-C5-C15-O16, C10-C11-C22-O25

^a: C' refers to Carbon atom (C7 in Fig. 4b) associated with the second pyridyl ring

^b: C_{ai} refers to Carbon atom of acid group.

Table S3 Definition of internal coordinates of B5DA.

S. No.	Symbol	Description ^{a,b}	Definition
1-12	d_i	C-C (Ring)	C1-N2, N2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C7-N8, N8-C9, C9-C10, C10-C11, C11-C12, C12-C7
13	r'	C-C' (Ring-C')	C1-C7
14-19	r_i	C-H (Ring)	C3-H13, C5-H18, C6-H19, C9-H20, C11-H25, C12-H26
20-21	R_i	(C-C $_{\alpha}$) ₁ , (C-C $_{\alpha}$) ₂	C4-C14, C10-C21
22-23	R_i	(C $_{\alpha}$ =O) ₁ , (C $_{\alpha}$ =O) ₂	C14-O17, C21-O24
24-25	R_i	(C $_{\alpha}$ -O) ₁ , (C $_{\alpha}$ -O) ₂	C14-O15, C21-O22
26-27	R_i	(O-H) ₁ , (O-H) ₂	O15-H16, O22-H23
Bending			
28-39	θ_i	C-C-C, C-N-C (Ring)	C6-C1-N2, C1-N2-C3, N2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C12-C7-N8, C7-N8-C9, N8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C7
40-51	ϕ_i	C-C-H, N-C-H (Ring)	N2-C3-H13, C4-C3-H13, C4-C5-H18, C6-C5-H18, C5-C6-H19, C6-C5-H18, N8-C9-H20, C10-C9-H20, C10-C11-H25, C12-C11-H25, C7-C12-H26, C11-C12-H26
52-55	ϕ_i	C-C-C' (Ring-C')	N2-C1-C7, C6-C1-C7, N8-C7-C1, C12-C7-C1
56-59	ϕ_i	C-C- C $_{\alpha}$	C3-C4-C14, C5-C4-C14, C9-C10-C21, C11-C10-C21
60	$\Delta\lambda_i$	(C- C $_{\alpha}$ =O) ₁	C4-C14-O17
61	$\Delta\lambda_i$	(C- C $_{\alpha}$ =O) ₂	C10-C21-O24
62	$\Delta\lambda_i$	(C- C $_{\alpha}$ -O) ₁	C4-C14-O15
63	$\Delta\lambda_i$	(C- C $_{\alpha}$ -O) ₂	C10-C21-O22
64	$\Delta\lambda_i$	(O- C $_{\alpha}$ =O) ₁	O17-C14-O15
65	$\Delta\lambda_i$	(O- C $_{\alpha}$ =O) ₂	O24-C21-O22
66	$\Delta\lambda_i$	(C $_{\alpha}$ -O-H) ₁	C14-O15-H16
67	$\Delta\lambda_i$	(C $_{\alpha}$ -O-H) ₂	C21-O22-H23
Wagging			
68-73	γ_i	π (CH)	C4-C3-N2-H13, C6-C5-C4-H18, C1-C6-C5-H19, C10-C9-N8-H20, C12-C11-C10-H25, C7-C12-C11-H26
74-75	γ_i	π (CC')	C6-C1-N2-C7, C12-C7-N8-C1
76-77		π (C C $_{\alpha}$)	C3-C4-C5-C14, C9-C10-C11-C21
78-79	γ_i	ω (OH) ₁ , ω (OH) ₂	C4-C14-O15-H14, C10-C21-O22-H23

80-81	γ_i	$\omega(C_{\alpha}=O)_1, \omega(C_{\alpha}=O)_2$	O17-C14-O15-H16, O24-C21-O22-H23
Torsion			
82-93	δ_i	τ (Ring)	C6-C1-N2-C3, C1-N2-C3-C4, N2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-N2, C12-C7-N8-C9, C7-N8-C9- C10, N8-C9-10-C11, C9-C10-C11-C12, C10-C11-C12-C7, C11-C12-C7-N8
94-97	τ_i	τ (C'')	N2-C1-C7-N8, C6-C1-C7-C12, N2-C1-C7-C12, C6-C1-C7- N8
98-99	τ_i	$\tau(CC_{\alpha})_1, \tau(CC_{\alpha})_2$	C3-C4-C14-O17, C9-C10-C21-O24

^a: C' refers to Carbon atom (C7 in Fig. 4c) associated with the second pyridyl ring

^b: C_{oi} refers to Carbon atom of acid group.

Table S4 Second-order perturbation energies E(2) (kJ/mol) corresponding to the most important charge transfer interaction (donor-acceptor) in B3DA by DFT/B3LYP/6-311++G(d,p) method.

NBO(i)	Type	ED/e	NBO(j)	Type	ED/e	E(2) ^a (KJ/mol)	E(j)– E(i) ^b (a.u.)	F(i, j) ^c (a.u.)
C1-N2	σ	1.97965	C1-C6	σ*	0.04093	2.60	1.39	0.054
			C6-C16	σ*	0.06736	2.09	1.25	0.046
	π	1.70361	C3-C4	π*	0.29529	27.86	0.32	0.084
			C5-C6	π*	0.33605	12.03	0.32	0.056
C1-C6	σ	1.97394	C7-N8	σ*	0.02265	2.74	0.83	0.046
			C1-N2	σ*	0.02320	2.03	1.25	0.045
			C1-C7	σ*	0.04456	2.53	1.14	0.048
			C5-C6	σ*	0.01985	4.12	1.27	0.065
C1-C7	σ	1.96791	C5-H15	σ*	0.01381	2.18	1.16	0.045
			C1-C6	σ*	0.04093	2.23	1.20	0.046
			N2-C3	σ*	0.01540	3.89	1.19	0.061
			C5-C6	σ*	0.01985	2.29	1.20	0.047
N2-C3	σ	1.98404	C7-C12	σ*	0.03977	2.19	1.19	0.046
			N8-C9	σ*	0.02556	3.88	1.18	0.061
			C11-C12	σ*	0.02097	2.43	1.20	0.048
			C1-C7	σ*	0.04456	3.17	1.25	0.057
C3-C4	σ	1.98449	C4-C5	σ*	0.01472	2.49	1.30	0.051
			C5-H15	σ*	0.01381	2.85	1.16	0.051
	π	1.61547	C1-N2	π*	0.36797	16.03	0.27	0.059
			C5-C6	π*	0.33605	25.17	0.28	0.076
C3-H13	σ	1.98118	C1-N2	σ*	0.02320	4.81	1.06	0.064
			C4-C5	σ*	0.01472	3.37	1.010	0.055
C4-C5	σ	1.97906	C3-C4	σ*	0.02568	2.36	1.28	0.049
			C3-H13	σ*	0.02335	2.29	1.14	0.048
			C5-C6	σ*	0.01985	2.87	1.27	0.054
			C6-C16	σ*	0.06736	2.61	1.13	0.058
C4-H14	σ	1.97036	N2-C3	σ*	0.01540	4.25	1.07	0.060
			C5-C6	σ*	0.01985	3.47	1.09	0.055
			C1-C6	σ*	0.04093	4.44	1.26	0.067
			C1-C7	σ*	0.04456	3.73	1.13	0.058
C5-C6	σ	1.97670	C4-C5	σ*	0.01472	2.56	1.28	0.051
			C4-H14	σ*	0.01353	2.50	1.14	0.048
			C1-N2	π*	0.36797	30.35	0.27	0.081
			C3-C4	π*	0.29527	16.07	0.28	0.061
	π	1.61756	C16-O17	π*	0.23876	19.02	0.27	0.067
			C5-H15	σ	1.97279	C1-C6	σ*	0.04093
C5-H15	σ	1.97279	C3-C4	σ*	0.01540	3.22	1.09	0.053
			C6-C16	σ	1.98031	C1-N2	σ*	0.02320
C6-C16	σ	1.98031	C1-C6	σ*	0.04093	2.42	1.23	0.049
			C4-C5	σ*	0.01472	2.43	1.25	0.049
			O18-H19	σ*	0.01094	2.16	1.05	0.043
			C7-N8	σ	1.70320	C7-C12	σ*	0.03977
C7-N8	π	1.97246	C1-N2	σ*	0.02320	2.67	0.84	0.045
			C9-C10	π*	0.29232	27.89	0.32	0.084
			C11-C12	π*	0.33770	12.03	0.32	0.056
C7-C12	σ	1.98403	C1-C7	σ*	0.04456	2.47	1.14	0.048
			C11-C12	σ*	0.02097	4.15	1.27	0.065

			C11-H22	σ^*	0.01320	2.36	1.16	0.047
N8-C9	σ	1.98458	C1-C7	σ^*	0.04456	3.26	1.26	0.058
C9-C10	σ		C10-C11	σ^*	0.01543	2.48	1.16	0.051
			C11-H22	σ^*	0.01320	2.79	0.28	0.059
	π	1.62174	C7-N8	π^*	0.35487	15.54	0.28	0.059
			C11-C12	π^*	0.33770	24.86	0.28	0.076
C9-H20	σ	1.98119	C7-N8	σ^*	0.02265	4.76	1.10	0.055
			C10-C11	σ^*	0.01543	3.45	1.28	0.049
C10-C11	σ	1.97889	C9-C10	σ^*	0.02556	2.36	1.14	0.046
			C9-H20	σ^*	0.02333	2.28	1.27	0.055
			C11-C12	σ^*	0.02097	2.94	1.13	0.053
			C12-C23	σ^*	0.06645	3.09	1.07	0.060
C10-H21	σ	1.97986	N8-C9	σ^*	0.02256	4.27	1.09	0.055
			C11-C12	π^*	0.33770	3.50	1.14	0.057
C11-C12	σ	1.97248	C1-C7	σ^*	0.04456	3.50	1.26	0.067
			C7-C12	σ^*	0.03977	4.42	1.29	0.052
			C10-C11	σ^*	0.01543	2.60	1.29	0.048
			C10-H21	σ^*	0.01348	2.46	1.15	0.081
	π	1.62713	C7-N8	π^*	0.35487	29.25	0.28	0.081
			C9-C10	π^*	0.29232	15.98	0.28	0.061
			C23-O26	π^*	0.23282	19.41	0.28	0.068
C11-H22	σ	1.97887	C7-C12	σ^*	0.03977	4.21	1.08	0.061
			C9-C10	σ^*	0.02556	3.22	1.09	0.053
C12-C23	σ	1.97347	C7-N8	σ^*	0.02265	3.30	1.21	0.057
			C10-C11	σ^*	0.01543	2.03	1.25	0.045
			C11-C12	σ^*	0.02097	2.12	1.23	0.046
C16-O17	σ	1.99516	C6-C16	σ^*	0.06736	2.02	1.50	0.046
	π	1.98522	C5-C6	π^*	0.33605	2.73	0.41	0.050
O18-H19	σ	1.98562	C6-C16	σ^*	0.06736	3.81	1.17	0.033
C23-O26	π	1.98324	C11-C12	π^*	0.33770	3.65	0.41	0.060
O24-H25	σ	1.98702	C12-C23	σ^*	0.06645	3.61	1.17	0.038
LP(1)N2		1.91464	C1-C6	σ^*	0.04093	10.33	0.89	0.059
			C1-C7	σ^*	0.04456	2.62	0.77	0.087
			C3-C4	σ^*	0.02508	8.71	0.90	0.040
			C3-H13	σ^*	0.02335	4.20	0.77	0.080
LPN8	σ	1.91492	C1-C7	σ^*	0.04456	2.60	0.77	0.051
			C7-C12	σ^*	0.03977	10.36	0.89	0.040
			C9-C10	σ^*	0.02556	8.73	0.90	0.087
			C9-H20	σ^*	0.02333	4.20	0.77	0.080
LPO17	σ	1.97950	C6-C16	σ^*	0.06736	2.38	1.12	0.051
LP O17	π	1.85012	C6-C16	σ^*	0.06736	17.76	0.68	0.100
			C16-O18	σ^*	0.09554	32.82	0.61	0.129
LPO18	σ	1.97313	C16-O17	σ^*	0.01949	6.49	1.24	0.129
LPO18	σ	1.82249	C16-O17	π^*	0.23876	42.84	0.35	0.080
LPO24	σ	1.97787	C23-O26	σ^*	0.09877	6.39	1.24	0.111
LPO26	σ	1.97856	C12-C23	σ^*	0.06645	2.57	1.12	0.080
LPO26	σ	1.84131	C12-C23	σ^*	0.06645	17.45	0.68	0.100
			C23-O24	σ^*	0.09877	33.84	0.60	0.129

^a:E(2) means energy of hyper conjugative interaction (stabilization energy) .

^b:Energy difference between donor and acceptor i and j NBO orbitals.

^c:F_{i,j} is the Fock matrix element between i and j NBO orbitals.

Table S5 Second-order perturbation energies E(2) (kJ/mol) corresponding to the most important charge transfer interaction (donor-acceptor) in B4DA by DFT/B3LYP/6-311++G(d,p) method.

NBO(i)	Type	ED/e	NBO(j)	Type	ED/e	E(2) ^a (KJ/mol)	E(j)– E(i) ^b (a.u.)	F (i, j) ^c (a.u.)
C1-N2	σ	1.98356	C1-C6	σ*	0.03190	2.45	1.39	0.052
			C3-H13	σ*	0.02356	2.00	1.26	0.045
	π	1.69076	C3-C4	π*	0.27964	24.64	0.32	0.080
			C5-C6	π*	0.32281	14.08	0.33	0.061
C1-C6	σ	1.97829	C1-N2	σ*	0.02205	2.27	1.23	0.047
			C1-C7	σ*	0.4578	2.35	1.14	0.046
			C5-C6	σ*	0.02140	2.93	1.28	0.055
			C5-C15	σ*	0.06886	3.45	1.11	0.056
C1-C7	σ	1.97154	N2-C3	σ*	0.01465	3.42	1.19	0.057
			C7-C12	σ*	0.03021	2.27	1.20	0.047
			N8-C9	σ*	0.01460	3.48	1.19	0.058
N2-C3	σ	1.98624	C1-C7	σ*	0.04578	3.05	1.27	0.056
C3-C4	σ	1.98440	C4-C5	σ*	0.02151	2.65	1.28	0.052
			C5-C15	σ*	0.06886	3.08	1.12	0.053
	π	1.60723	C1-N2	π*	0.41151	18.80	0.27	0.064
			C5-C6	π*	0.32281	20.76	0.29	0.070
C3-H13	σ	1.98204	C1-N2	σ*	0.02205	4.78	1.05	0.063
			C4-C5	σ*	0.02151	3.43	1.09	0.055
C4-C5	σ	1.97361	C3-C4	σ*	0.02423	2.24	1.28	0.048
			C3-H13	σ*	0.02356	2.22	1.14	0.045
			C5-C6	σ*	0.02140	4.31	1.28	0.066
			C6-H19	σ*	0.01394	2.53	1.17	0.049
C4-H14	σ	1.97824	N2-C3	σ*	0.01465	4.29	1.14	0.061
			C5-C6	σ*	0.02140	4.19	1.28	0.061
C5-C6	σ	1.97496	C1-C6	σ*	0.03190	2.80	1.14	0.053
			C1-C7	σ*	0.04578	2.97	1.28	0.052
			C4-C5	σ*	0.02151	4.31	1.28	0.066
			C4-H14	σ*	0.01302	2.31	1.17	0.046
	π	1.62833	C1-N2	π*	0.41151	25.11	0.27	0.076
			C3-C4	π*	0.27964	18.58	0.29	0.067
C5-H15	σ	1.97513	C15-O16	π*	0.23213	19.56	0.27	0.067
			C3-C4	σ*	0.02423	2.13	1.24	0.046
			O17-H18	σ*	0.00975	2.03	1.06	0.042
C6-H19	σ	1.97522	C1-N2	σ*	0.02205	5.37	1.05	0.067
			C4-C5	σ*	0.02151	4.21	1.08	0.060
C7-N8	σ	1.98246	C7-C12	σ*	0.03021	2.68	1.37	0.054
			C9-H20	σ*	0.02364	2.06	1.25	0.045
C7-C12	σ	1.97761	C1-C6	σ*	0.03190	2.02	1.26	0.045
			C1-C7	σ*	0.04578	2.59	1.14	0.049
			C7-N8	σ*	0.02298	2.58	1.23	0.050
			C11-C12	σ*	0.02020	2.85	1.28	0.054
			C11-C22	σ*	0.06919	2.88	1.11	0.051
N8-C9	σ	1.98591	C1-C7	σ*	0.04578	3.39	1.27	0.059
C9-C10	σ	1.98412	C10-C11	σ*	0.02260	2.71	1.28	0.053
			C11-C22	σ*	0.06919	3.62	1.12	0.058
C9-H20	σ	1.98196	C7-N8	σ*	0.02298	4.83	1.05	0.064
			C10-C11	σ*	0.02298	3.47	1.08	0.055

C10-C11	σ	1.97542	C9-C10	σ^*	0.02517	2.29	1.28	0.048
			C9-H20	σ^*	0.02367	2.21	1.14	0.045
			C11-C12	σ^*	0.02020	4.27	1.29	0.066
			C12-H26	σ^*	0.01437	2.34	1.18	0.047
C10-H21	σ	1.97848	N8-C9	σ^*	0.01460	4.32	1.07	0.061
			C11-C12	σ^*	0.02020	4.06	1.11	0.060
C11-C12	σ	1.97298	C1-C7	σ^*	0.04578	3.31	1.15	0.055
			C7-C12	σ^*	0.03021	2.86	1.26	0.054
			C10-C11	σ^*	0.02260	4.29	1.27	0.066
			C10-H21	σ^*	0.01240	2.50	1.16	0.048
	π	1.62061	C22-O25	π^*	0.22875	19.02	0.27	0.066
			O23-H24	σ^*	0.00970	3.25	2.30	0.086
C11-C22	σ	1.97501	C7-C12	σ^*	0.03021	2.24	1.22	0.047
C12-H26	σ	1.97504	C7-N8	σ^*	0.02298	5.43	1.04	0.067
			C10-C11	σ^*	0.02260	4.31	1.08	0.061
C15-O16	σ	1.99561	C5-C15	σ^*	0.06886	2.03	1.50	0.050
	π	1.98274	C5-C6	π^*	0.32281	4.24	0.42	0.041
O17-H18	σ	1.98687	C5-C15	σ^*	0.06886	3.86	1.16	0.061
C22-O25	σ	1.99562	C11-C22	σ^*	0.06919	2.06	1.50	0.050
	π	1.98271	C11-C12	π^*	0.32033	3.30	0.42	0.036
O23-H24	π	1.98718	C11-C22	σ^*	0.06919	3.77	1.17	0.060
LPN2	σ	1.91697	C1-C6	σ^*	0.03190	10.01	0.90	0.086
			C1-C7	σ^*	0.04578	2.77	0.78	0.042
			C3-C4	σ^*	0.02423	8.83	0.91	0.081
			C3-H13	σ^*	0.02356	4.21	0.77	0.052
LPN8	σ	1.91710	C1-C7	σ^*	0.04578	3.14	0.78	0.045
			C7-C12	σ^*	0.03021	9.51	0.89	0.083
			C9-C10	σ^*	0.02517	8.93	0.91	0.082
			C9-H20	σ^*	0.02514	4.26	0.77	0.052
LPC10	σ	0.97186	N8-C9	π^*	0.36637	87.76	0.13	0.115
			C11-C12	π^*	0.32033	60.83	0.15	0.105
LPO16	σ	1.97963	C5-C15	σ^*	0.6886	2.48	1.11	0.048
LPO16	π	1.85026	C5-C15	σ^*	0.06886	17.66	0.68	0.100
			C15-O17	σ^*	0.0975	33.12	0.61	0.129
LPO17	σ	1.97701	C15-O16	σ^*	0.01840	6.67	1.24	0.081
LPO17	π	1.82327	C15-O16	π^*	0.23213	44.07	0.35	0.112
LPO23	σ	1.97741	C22-O25	σ^*	0.01819	6.56	1.24	0.081
LPO23	π	1.82645	C22-O25	π^*	0.22875	43.19	0.35	0.111
LPO25	σ	1.979557	C11-C22	σ^*	0.06919	2.53	1.11	0.048
LPO25	π	1.84784	C11-C22	σ^*	0.06919	17.81	0.68	0.100
			C22-O23	σ^*	0.09717	33.63	0.61	0.129

^a:E(2) means energy of hyper conjugative interaction (stabilization energy) .

^b:Energy difference between donor and acceptor i and j NBO orbitals.

^c:F(i,j) is the Fock matrix element between i and j NBO orbitals.

Table S6 Second-order perturbation energies E(2) (kJ/mol) corresponding to the most important charge transfer interaction (donor-acceptor) in B5DA by DFT/B3LYP/6-311++G(d,p) method.

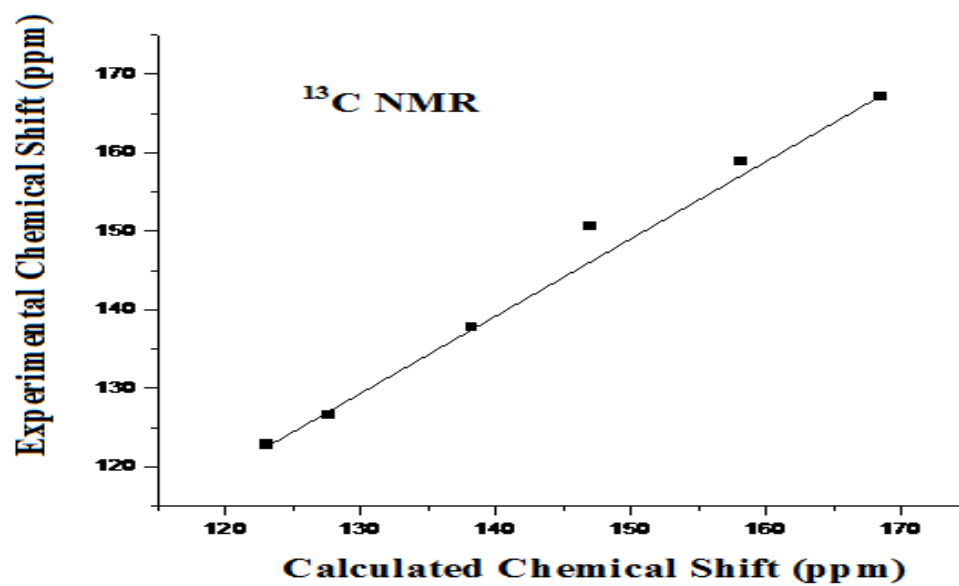
NBO(i)	Type	ED/e	NBO(j)	Type	ED/e	E(2) ^a (KJ/mol)	E (j)– E(i) ^b (a.u.)	F (i, j) ^c (a.u.)
C1-N2	σ	1.98347	C1-C6	σ*	0.03239	2.38	1.38	0.051
			C3-H13	σ*	0.02277	2.02	1.26	0.045
	π	1.68196	C3-C4	π*	0.34112	29.14	0.32	0.087
			C5-C6	π*	0.25170	11.27	0.33	0.055
C1-C6	σ	1.97929	C7-N8	π*	0.41878	12.11	0.31	0.056
			C1-N2	σ*	0.02259	2.10	1.23	0.045
			C1-C7	σ*	0.04511	2.40	1.14	0.047
			C5-C6	σ*	0.01368	2.64	1.29	0.052
C1-C7	σ	1.97215	C5-H18	σ*	0.01420	2.63	1.15	0.049
			C7-C12	σ*	0.03181	2.03	1.25	0.045
			N2-C3	σ*	0.01302	3.37	1.20	0.057
			C7-C12	σ*	0.03181	2.19	1.19	0.046
N2-C3	σ	1.98571	N8-C9	σ*	0.01313	3.46	1.20	0.058
C3-C4	σ	1.98046	C1-C7	σ*	0.04511	2.19	1.27	0.055
			C4-C5	σ*	0.02136	3.80	1.28	0.062
	π	1.60616	C5-H18	σ*	0.01420	2.45	1.17	0.048
			C1-N2	π*	0.41878	15.67	0.27	0.058
C3-H13	σ	1.98031	C5-C6	π*	0.25176	21.45	0.29	0.073
			C14-O17	π*	0.01855	21.85	0.27	0.071
C4-C5	σ	1.97360	C1-N2	σ*	0.02259	4.96	1.05	0.064
			C4-C5	σ*	0.02136	4.07	1.08	0.059
			C3-C4	σ*	0.03189	3.69	1.26	0.061
			C3-H13	σ*	0.02277	2.22	1.14	0.045
C4-C14	σ	1.97516	C5-C6	σ*	0.01368	2.55	1.29	0.051
			C6-H19	σ*	0.01449	2.51	1.16	0.048
			N2-C3	σ*	0.01302	2.26	1.23	0.047
			C5-C6	σ*	0.01368	2.19	1.26	0.047
C5-C6	σ	1.97888	O15-H16	σ*	0.00989	2.02	1.07	0.042
			C1-C6	σ*	0.03239	2.81	1.27	0.053
			C1-C7	σ*	0.04511	3.11	1.15	0.054
			C4-C5	σ*	0.02136	2.87	1.28	0.054
C5-H18	σ	1.97954	C4-C14	σ*	0.02136	2.79	1.14	0.051
			C1-N2	π*	0.41878	29.42	0.26	0.080
C6-H19	σ	1.97717	C3-C4	π*	0.3412	17.52	0.28	0.063
			C1-C6	σ*	0.03239	3.42	1.08	0.054
C7-N8	σ	1.98242	C3-C4	σ*	0.01302	3.98	1.08	0.059
			C1-N2	σ*	0.02259	5.43	1.04	0.067
	π	1.68196	C4-C5	σ*	0.02136	3.47	1.08	0.055
			C7-C12	σ*	0.03181	2.56	1.37	0.053
C7-C12	σ	1.97828	C9-H20	σ*	0.02276	2.06	1.26	0.045
			C1-N2	π*	0.41878	12.11	0.31	0.056
			C9-C10	π*	0.34112	29.14	0.32	0.087
C11-C12	σ	1.97828	C11-C12	π*	0.25170	11.22	0.33	0.055
			C1-C6	σ*	0.03239	2.08	1.26	0.046
			C1-C7	σ*	0.04511	2.60	1.14	0.049
			C7-N8	σ*	0.02317	2.41	1.22	0.048
			C11-C12	σ*	0.01370	2.61	1.29	0.052

			C11-H25	σ^*	0.01417	2.65	1.15	0.049
N8-C9	σ	1.98530	C1-C7	σ^*	0.04511	3.30	1.27	0.058
C9-C10	σ	1.98047	C10-C11	σ^*	0.02140	3.80	1.28	0.062
			C11-H25	σ^*	0.01417	2.47	1.16	0.048
	π	1.60616	C7-N8	π^*	0.41878	15.59	0.27	0.058
			C11-C12	π^*	0.25170	21.01	0.29	0.073
C9-H20		1.98033	C21-O24	π^*	0.01855	21.87	0.27	0.071
			C7-N8	σ^*	0.02317	4.98	1.04	0.064
			C10-C11	σ^*	0.02140	4.05	1.08	0.059
C10-C11	σ	1.97352	C9-C10	σ^*	0.03183	3.68	1.26	0.061
			C9-H20	σ^*	0.02276	2.25	1.14	0.045
			C11-C12	σ^*	0.01370	2.54	1.29	0.051
			C12-H26	σ^*	0.01455	2.50	1.16	0.048
C10-C21	σ	1.97515	N8-C9	σ^*	0.01313	2.27	1.23	0.047
			C11-C12	π^*	0.25170	2.18	1.26	0.047
C11-C12	σ	1.97868	C1-C7	σ^*	0.04511	3.46	1.15	0.057
			C7-C12	σ^*	0.03181	2.90	1.26	0.054
			C10-C11	σ^*	0.02140	2.89	1.28	0.054
			C10-C21	σ^*	0.06632	2.80	1.14	0.051
	π	1.62369	C7-N8	π^*	0.41878	29.43	0.26	0.079
			C9-C10	π^*	0.34112	17.59	0.28	0.063
C11-H25	σ	1.97949	O22-H23	σ^*	0.00990	3.63	2.29	0.090
			C7-C12	σ^*	0.03181	3.41	1.07	0.054
C12-H26	σ	1.97714	C9-C10	σ^*	0.03183	3.98	1.08	0.059
			C7-N8	σ^*	0.02317	5.49	1.04	0.067
C14-O17	σ	1.99580	C10-C11	σ^*	0.02140	3.45	1.08	0.054
			C4-C14	σ^*	0.06031	2.10	1.51	0.051
O15-H16	π	1.98334	C3-C4	π^*	0.34112	4.09	0.41	0.040
			C4-C14	σ^*	0.06031	3.74	1.18	0.060
C21-O24	σ	1.99580	C4-C14	σ^*	0.06031	3.74	1.18	0.060
			C10-C21	σ^*	0.06632	2.11	1.51	0.051
O22-H23	π	1.98334	C9-C10	π^*	0.34112	4.09	0.41	0.040
			C10-C21	σ^*	0.06632	3.74	1.18	0.060
LPN2	σ	1.91673	C10-C21	σ^*	0.06632	3.74	1.18	0.060
			C1-C6	σ^*	0.03239	9.82	0.90	0.085
			C1-C7	σ^*	0.04511	2.62	0.78	0.041
			C3-C4	σ^*	0.03189	9.08	0.89	0.082
LPN8	σ	1.91699	C3-H13	σ^*	0.02277	4.17	0.78	0.052
			C1-C7	σ^*	0.04511	3.06	0.78	0.044
			C7-C12	σ^*	0.03181	9.46	0.88	0.083
			C9-C10	σ^*	0.03183	9.05	0.90	0.081
LPO15	σ	1.97714	C9-H20	σ^*	0.02276	4.20	0.78	0.052
			C14-O17	σ^*	0.01855	6.58	1.24	0.081
LPO15	π	1.82841	C14-O17	π^*	0.24453	43.01	0.35	0.111
LPO17	σ	1.97955	C4-C14	σ^*	0.06030	2.48	1.13	0.048
			C4-C14	π^*	0.21220	17.41	0.69	0.100
LPO17	π	1.84915	C14-O15	π^*	0.09688	33.41	0.61	0.129
			C21-O24	σ^*	0.01855	6.58	1.24	0.081
LPO22	σ	1.97714	C21-O24	σ^*	0.01855	6.58	1.24	0.081
LPO22	π	1.82841	C21-O24	π^*	0.24433	43.01	0.35	0.111
LPO24	σ	1.97957	C10-C21	σ^*	0.06032	2.48	1.13	0.048
			C10-C21	π^*	0.06632	17.42	0.69	0.100
LPO24	π	1.84914	C21-O22	π^*	0.09688	33.39	0.61	0.129

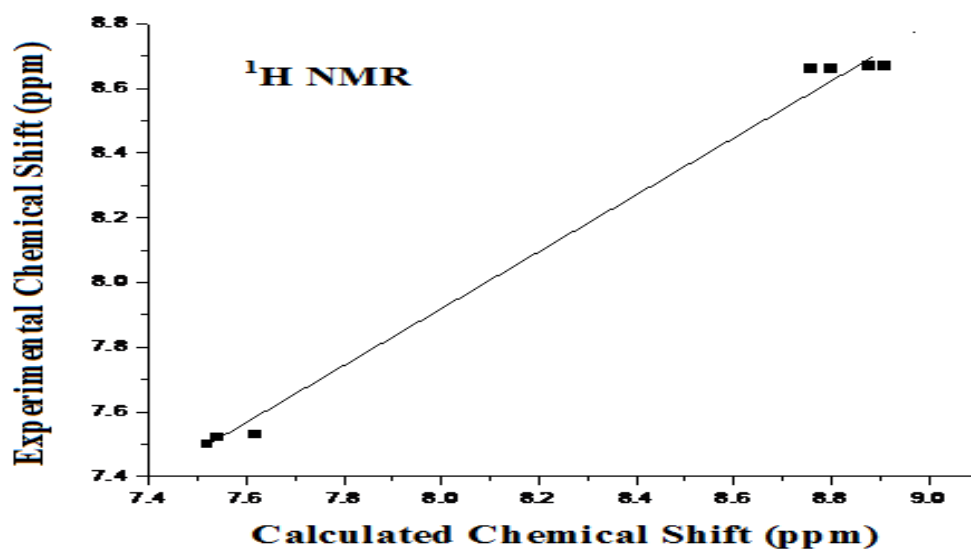
^a:E(2) means energy of hyper conjugative interaction (stabilization energy).

^b:Energy difference between donor and acceptor i and j NBO orbitals.

^c:F(i,j) is the Fock matrix element between i and j NBO orbitals.

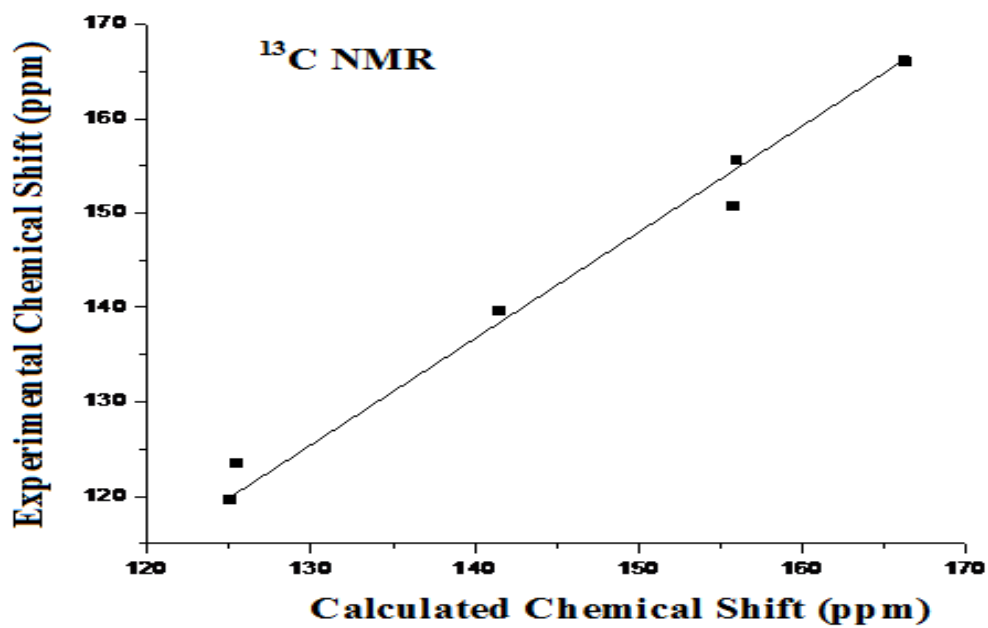


(a)

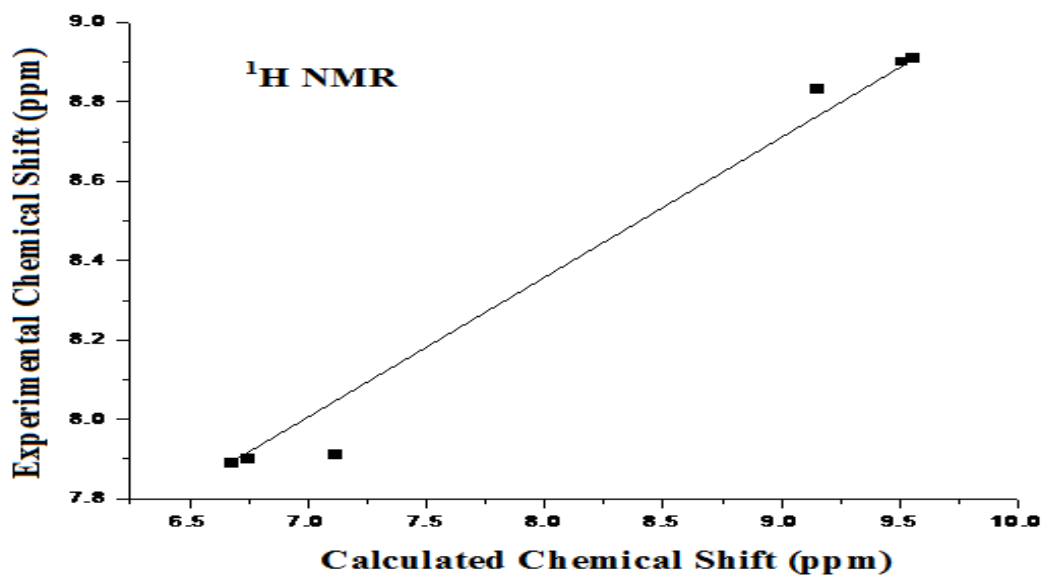


(b)

Fig. S1 Linear regression between the experimental and theoretical NMR chemical shifts of B3DA: (a) ¹³C NMR and (b) ¹H NMR.

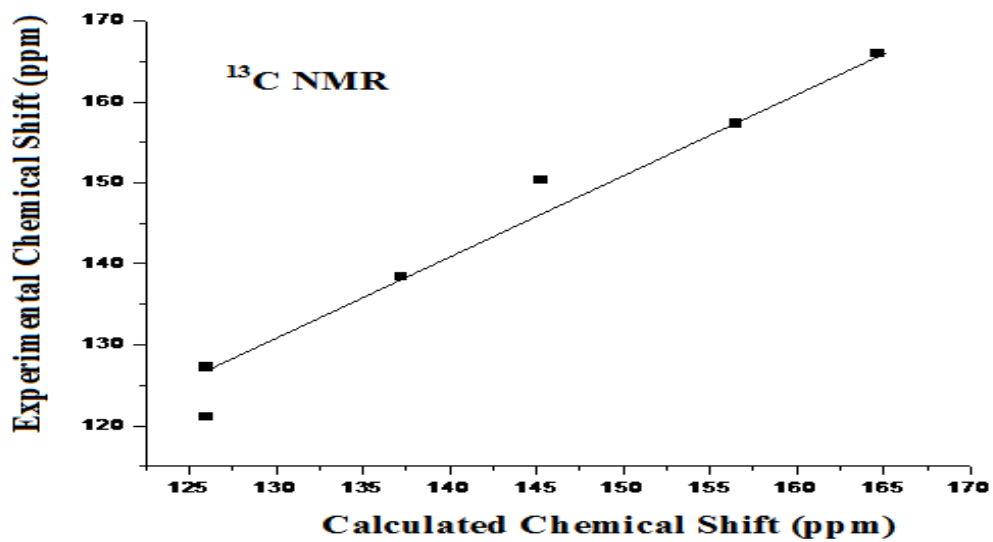


(a)

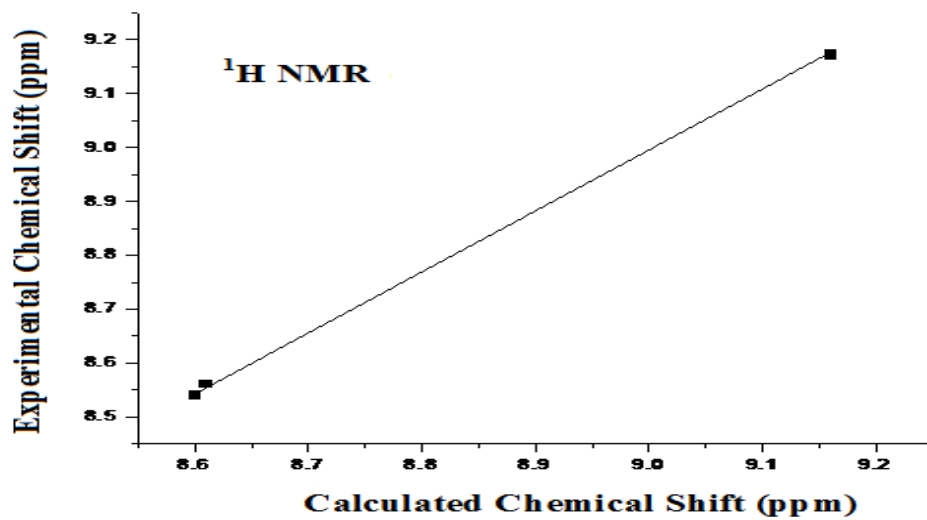


(b)

Fig. S2 Linear regression between the experimental and theoretical NMR chemical shifts of B4DA: (a) ¹³C NMR and (b) ¹H NMR.



(a)



(b)

Fig. S3 Linear regression between the experimental and theoretical NMR chemical shifts of B5DA: (a) ¹³C NMR and (b) ¹H NMR.