

Supporting Information

Quantum Chemical Study of Benzimidazole Derivatives to Tune the Second-order Nonlinear Optical Molecular Switching by Proton Abstraction

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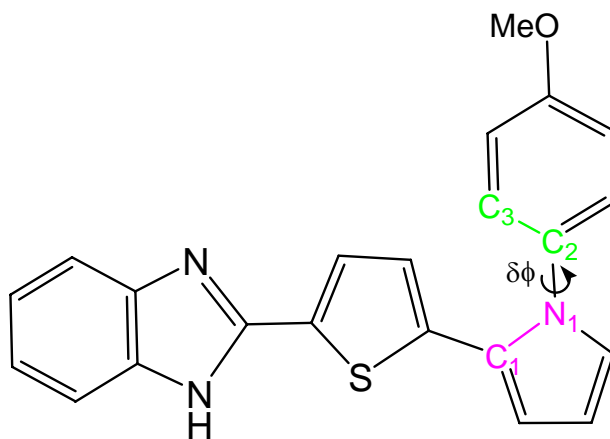


Fig. S1 Representation of dihedral angle in pristine molecule **1**

Table S1 The change in dihedral angles between neutral and anionic structures of pristine molecule **1** and its derivatives in Set II

Neutral	Dihedral angle (ϕ) C ₁ -N ₁ -C ₂ -C ₃	Anion	Dihedral angle (ϕ) C ₁ -N ₁ -C ₂ -C ₃	$\Delta \phi$
1	57.26	1⁻	47.85	9.41 ^o
1a	57.30	1a⁻	47.49	9.81 ^o
1b	43.92	1b⁻	37.18	6.74 ^o
1c	43.37	1c⁻	37.28	6.09 ^o
1d	43.71	1d⁻	38.72	4.99 ^o

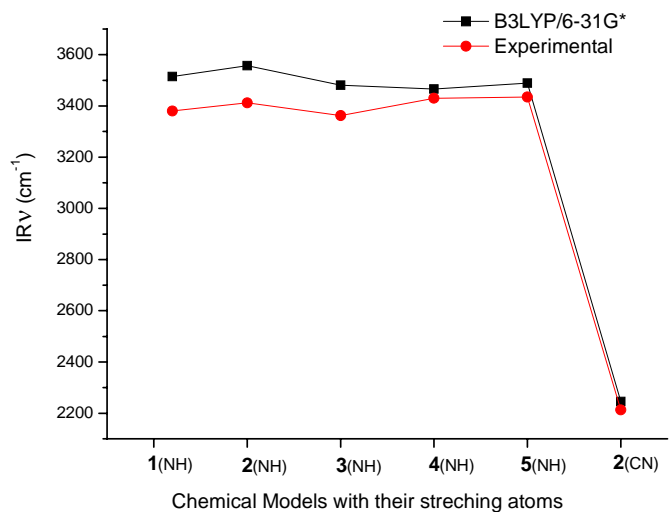


Fig. S2 The trend of calculated and experimental N-H and CN stretching frequencies for all systems in set I.

The origin of NLO response

The individual diagonal and off-diagonal components of parent compound **1** and its derivatives have been shown in Table S2. It can be seen that diagonal components β_{xxx} is significantly larger and dominant in all the systems except **1d** which has slightly higher off-diagonal component β_{xyy} . It is noteworthy that all the anionic species have small ratio $\eta = \beta_{xyy}/\beta_{xxx}$ which is called Cartesian nonlinear anisotropy and is a relevant factor for assessing the 2D character of the molecular β_{ijk} tensor. The values of η are very low even range from 0.037 to 0.081 which represents that all the anionic species prototype push-pull chromophores. The slightly higher ratios in neutral compounds might be due to the weak acceptor strength of benzimidazole moiety in push-pull configuration of neutral species. The similar trend of typical

push-pull chromophore can also be observed in electron density difference maps

given in Figure 5.

Table. S2 The individual components of β value along x-axis

Systems	β_{xzz}	β_{xyy}	β_{xxx}	$\eta = \beta_{xyy}/\beta_{xxx}$	β_X	β_0
1	0.15	3.26	19.11	0.170	13.53	14.38
1⁻	0.26	7.43	91.31	0.081	59.41	60.60
1a	0.09	1.68	7.22	0.233	5.40	5.86
1a⁻	0.00	4.73	61.27	0.077	39.60	40.24
1b	0.03	6.04	6.86	0.886	7.80	16.00
1b⁻	4.83	60.48	1601.61	0.037	1000.20	1014.00
1c	0.23	8.46	14.30	0.591	13.80	14.00
1c⁻	3.91	10.51	1832.79	0.057	1165.20	1189.00
1d	0.23	9.04	30.88	0.292	24.00	27.00
1d⁻	14.80	17.28	3123.98	0.055	1986.00	2028.00

Table. S3 The estimated change in dipole moments along x-axis, in neutral and anionic systems **1** and its derivatives

Neutral	μ_{ge} (B3LYP)	μ_{ge} (HF)	μ_{ee} (CIS)	$\mu_{ee}-\mu_{gg}$	$\mu_{ee}-\mu_{gg}$ (FF)
1	-1.34051	1.576551	2.884009	1.307458	-1.8700
1a	1.18944	1.622185	3.15359	1.531405	-1.9375
1b	0.974491	1.590005	5.353116	3.763111	4.986182
1c	1.148295	1.686941	6.20177	4.514829	6.805393
1d	-0.72185	-0.79636	0.661537	1.457897	3.44708
Anions					
1⁻	-5.26834	-6.57655	-3.58401	2.992542	-1.4663
1a⁻	-4.313503	-6.62218	-3.15359	3.468595	5.027143
1b⁻	4.56832	-8.5900	-4.35312	4.236889	7.288811
1c⁻	4.717063	6.786941	-3.90018	-10.6871	8.70775
1d⁻	-6.24247	-8.79636	-1.40154	7.394823	5.024041

First of all, a comparison between the results of both Hartree Fock (HF) and finite field (FF) methods shows no reasonable agreement with each other. The only trend we found common between two methods is that ($\mathbf{1c}$, $\mathbf{1c}^-$) pair and ($\mathbf{1}$, $\mathbf{1}^-$) pair have highest and lowest changes in dipole moments respectively which is same in both the methods. The results of HF method might be considered reasonable because ground state dipole moments calculated by HF and B3LYP methods are close to each other especially in case of neutral molecules.

In addition, the comparison of $\mu_{ee}-\mu_{gg}$ factors for neutral and anions shows no exact cancellation of each other because $\mu_{ee}-\mu_{gg}$ factors for anions are higher than in neutral compounds with both the methods. Although the higher values of $\mu_{ee}-\mu_{gg}$ factors in anions might attribute to enhance the β value but these might not be considered reliable due the inherited inconsistency in calculating the dipole moment of anions.

Table S 4 NBO analysis of three $\mathbf{1X}^-$ (X=F, Cl, Br) complexes

System	NBO charges		Wiberg bond index	
	N	X	N-H	H-X
$\mathbf{1}\cdot\text{F}^-$	-0.627	-0.631	0.137	0.527
$\mathbf{1}\cdot\text{Cl}^-$	-0.556	-0.858	0.621	0.157
$\mathbf{1}\cdot\text{Br}^-$	-0.555	-0.860	0.635	0.151