

Influence of methoxy groups on the properties of 1,1-bis(4-aminophenyl) cyclohexane based arylamines: experimental and theoretical approach

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5 Supporting information

Table S1. ^aValues of Δd parameter (Å) (defined here as sum of differences between every two consecutive bond lengths inside a Ph ring) calculated for the internal (un-substituted) and external (substituted) Ph rings. ^b $\Delta E(H-H_{i1})$ corresponds to the energy splitting between the HOMO and HOMO-1 orbitals for each neutral compound.

	1		2		3		4	
	neutral	cation	neutral	cation	neutral	cation	neutral	cation
Ph-internal ^a	0.050	0.102	0.050	0.050	0.050	0.100	0.054	0.086
Ph-external ^a	0.028	0.040	0.048	0.040	0.046	0.060	0.050	0.080
$\Delta E(H-H_{i1})$ (eV) ^b	0.156		0.230		0.164		0.140	

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Table S2. Transition energies and oscillator strengths obtained from the TDDFT calculations at the B3LYP/6-31+G* level.

Excited state	1		2		3		4	
	Energy (eV)	f ^a	Energy (eV)	f ^a	Energy (eV)	f ^a	Energy (eV)	f ^a
1	3.61	0.003	3.63	0.099	3.69	0.471	3.35	0.013
2	3.62	0.022	3.64	0.107	3.73	0.069	3.36	0.013
3	3.72	0.441	3.77	0.417	3.73	0.081	3.62	0.479
4	3.86	0.231	3.87	0.086	3.83	0.057	3.71	0.019
5	3.87	0.125	4.02	0.008	3.85	0.166	3.76	0.014
6	3.91	0.260	4.03	0.013	3.90	0.218	3.83	0.098
7	4.01	0.002	4.04	0.011	4.05	0.004	3.89	0.228
8	4.06	0.001	4.06	0.014	4.10	0.005	3.90	0.180
9	4.12	0.038	4.10	0.011	4.13	0.046	3.96	0.052
10	4.20	0.005	4.17	0.001	4.18	0.017	3.97	0.049

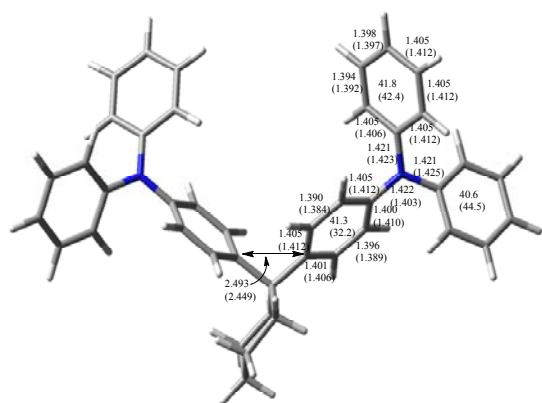
The excitation energies are in eV. ^aOscillator strengths.

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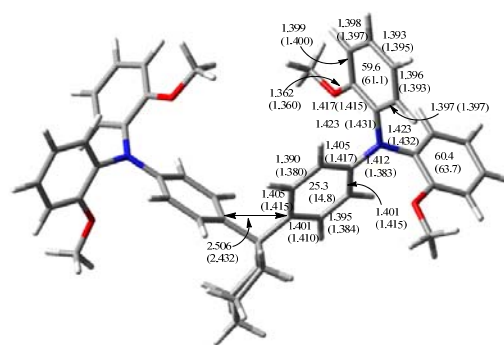
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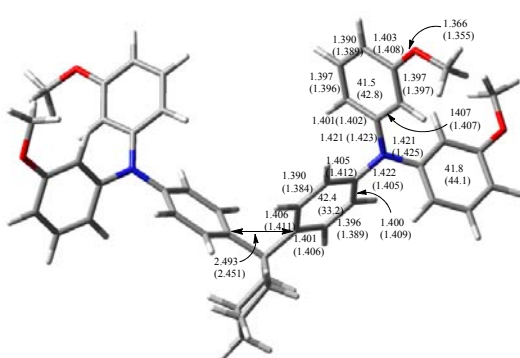
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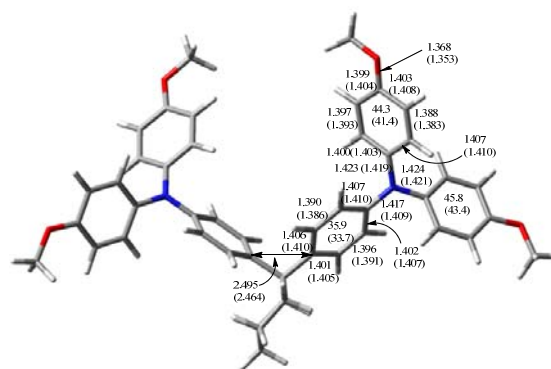
a Compound 1



b Compound 2



c Compound



3 Compound 4

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Figure S1. Optimized geometries for the compounds **1-4** along with some typical bond-lengths (Å) and dihedral angles between the Ph rings and the “N-plane” (absolute values in degrees, indicated inside the Ph rings). The values in parenthesis correspond to the radical cation state. Atoms in red, grey, blue, and white colors are oxygen, carbon, nitrogen, and hydrogen respectively.

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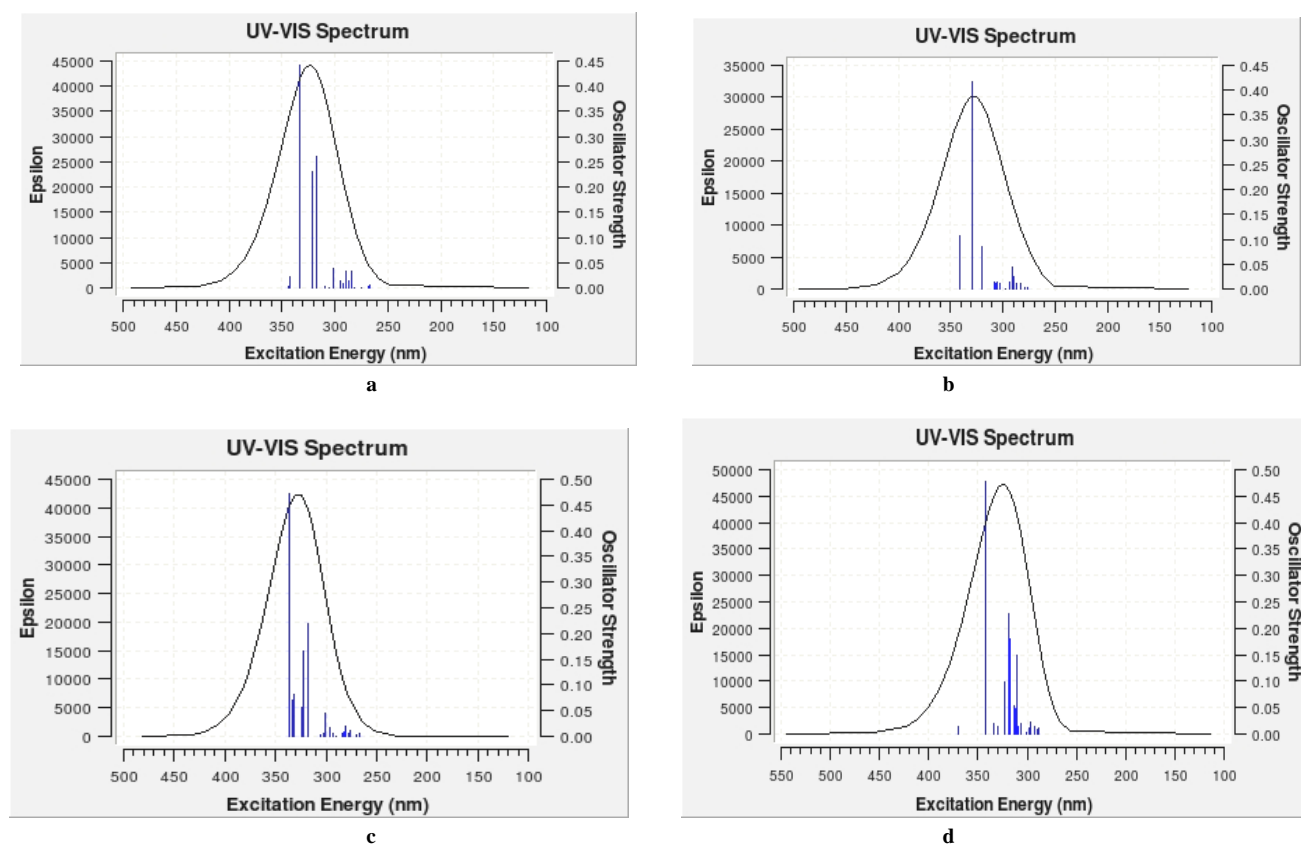


Figure S2. UV-VIS absorption spectra obtained from TDDFT calculations at the B3LYP/6-31+G* level: a, b c and d correspond to the compounds **1-4** respectively. The absorption bands are obtained by considering peak half-widths at half height of 0.333eV. It can be observed that the λ_{UVmax} for **1** and **4** are not due to the strongest transition but to the sum of some higher energy transitions which are very close in energy.

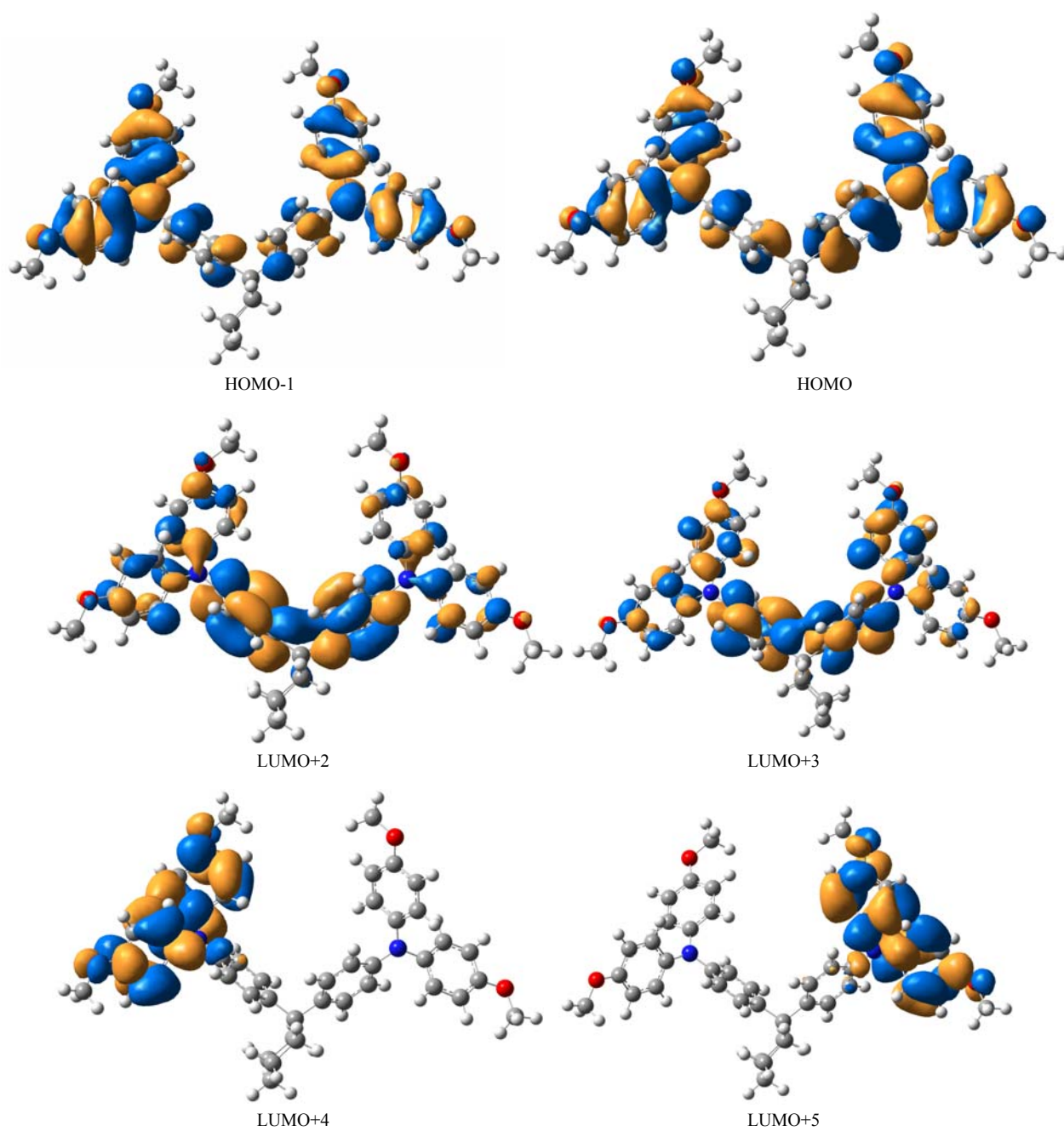


Figure S3. Pictograms of some relevant molecular orbitals for the compound **4**.

Some details on the estimation of k_{HT} values

The k_{HT} values are calculated on the basis of the Marcus-Levich-Jortner equation:

$$k_{CT} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda_s k_B T}} t^2 \sum_{n=0}^{\infty} \exp(-S) \frac{S^n}{n!} \exp\left[-\frac{-(\Delta G^\circ + \lambda_s + n\hbar\omega_i)^2}{4k_B\lambda_s T}\right] \quad (\text{eq. S1})$$

In this equation: t is the electronic coupling between two adjacent molecules, ΔG° is the CT reaction free energy (set to zero in the case of hole transfer between identical molecules), λ_s is the medium (outer) reorganization energy (set to 0.3 eV for all the compounds 1-4), $S_i = \frac{\hbar^2 \omega_i^2}{4k_B\lambda_s}$ is the Huang-Rhys factor characterizing the strength of the electron-vibration coupling for the internal mode i (in the products), $\hbar\omega_i$ represents the energetic effort due to the intra-molecular geometric relaxations related to the CT between two adjacent molecules.

In this calculation, the vibration mode $\hbar\omega_i$ has been set equal to 0.2 eV, which is a typical value for the energy of a carbon-carbon bond stretch in a conjugated system (V. Lemaur, M. Steel, D. Beljonne, J.L. Bredas, J. Cornil, *J. Am. Chem. Soc.* 2005, **127**, 6077-6086).

The transfer integrals between frontier orbitals of two monomers in a dimer were calculated on the basis of the following equation (E.F. Valeev, V. Coropceanu, D.A. da Silva, S. Salman, J.L. Bredas, *J. Am. Chem. Soc.* 2006, **128**, 9882):

$$t_{12} = \frac{\tilde{t}_{12} - \frac{1}{2}(\tilde{\epsilon}_1 + \tilde{\epsilon}_2)S_{12}}{1 - S_{12}^2} \quad (\text{Eq. S2})$$

The parameters involved in this formula are calculated as follows (for example in the case of the transfer integral between the HOMO orbitals of two monomers, noted here as M1 and M2):

$$\tilde{t}_{12} = \langle \psi_{HOMO}^{M1} | \hat{H}_{dimer} | \psi_{HOMO}^{M2} \rangle \quad (\text{Eq. S3})$$

$$\tilde{\epsilon}_{1(2)} = \langle \psi_{HOMO}^{M1(M2)} | \hat{H}_{dimer} | \psi_{HOMO}^{M1(M2)} \rangle \quad (\text{Eq. S4})$$

$$S_{12} = \langle \psi_{HOMO}^{M1} | \psi_{HOMO}^{M2} \rangle \quad (\text{Eq. S5})$$

In the above equations, $\psi_{HOMO}^{M1(M2)}$ represent the wave functions corresponding to HOMO_{M1} and HOMO_{M2} as calculated from the isolated monomers, whereas \hat{H}_{dimer} is the Hamiltonian in a given geometry of the dimer M1...M2.

The necessary matrices for these calculations (S_{12} and \tilde{t}_{12}) are produced by Gaussian09 program.