

Supporting Information

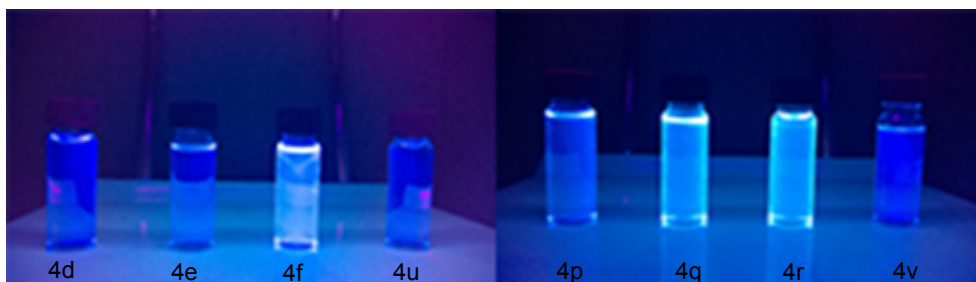
Novel 3, 6-Unsymmetrically Disubstituted-1, 2, 4, 5-Tetrazines: S-Induced One-Pot Synthesis, Properties and Theoretical Study

Chen Li, Haixia Ge, BingYin, Mengyao She, Ping Liu,* Xiangdong Li and Jianli Li*

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1. A photo of the emission of the tetrazines 4d, 4e, 4f, 4u, 4p, 4q, 4r, 4v in dichloromethane under a UV lamp



2. The calculation of fluorescence quantum yield

Fluorescence quantum yields (Φ_u) were determined using optically matching solutions of quinine sulfate ($\Phi_f = 0.55$ in 0.05 mol/L H_2SO_4) as the standard, and the quantum yields were calculated using Equation 1 according to the references.^[1, 2]

$$\Phi_u = \Phi_f \times \frac{I_u}{I_f} \times \frac{A_f}{A_u} \times \left(\frac{\eta_u}{\eta_f} \right)^2 \quad (\text{Equation 1})$$

Where Φ_u and Φ_f are the fluorescence quantum yields of the sample and standard, I_u and I_f are the integrated emission intensities of the spectra for the sample and standard, A_u and A_f are the absorbance of the standard and sample at the excitation wavelength (335 nm and 344 nm, in all cases), and η_u (1.4244) and η_f (1.33) are the indices of refraction of the sample (dichloromethane) and standard solutions (water), respectively.

References:

[1] Li, X.; Zhang, G.; Ma, H.; Zhang, D.; Li, J.; Zhu, D. *J. Am. Chem. Soc.* **2004**, *126*, 11543-11548.

[2] Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York, **1999**.

3. Theoretical calculation

3.1. Computational details

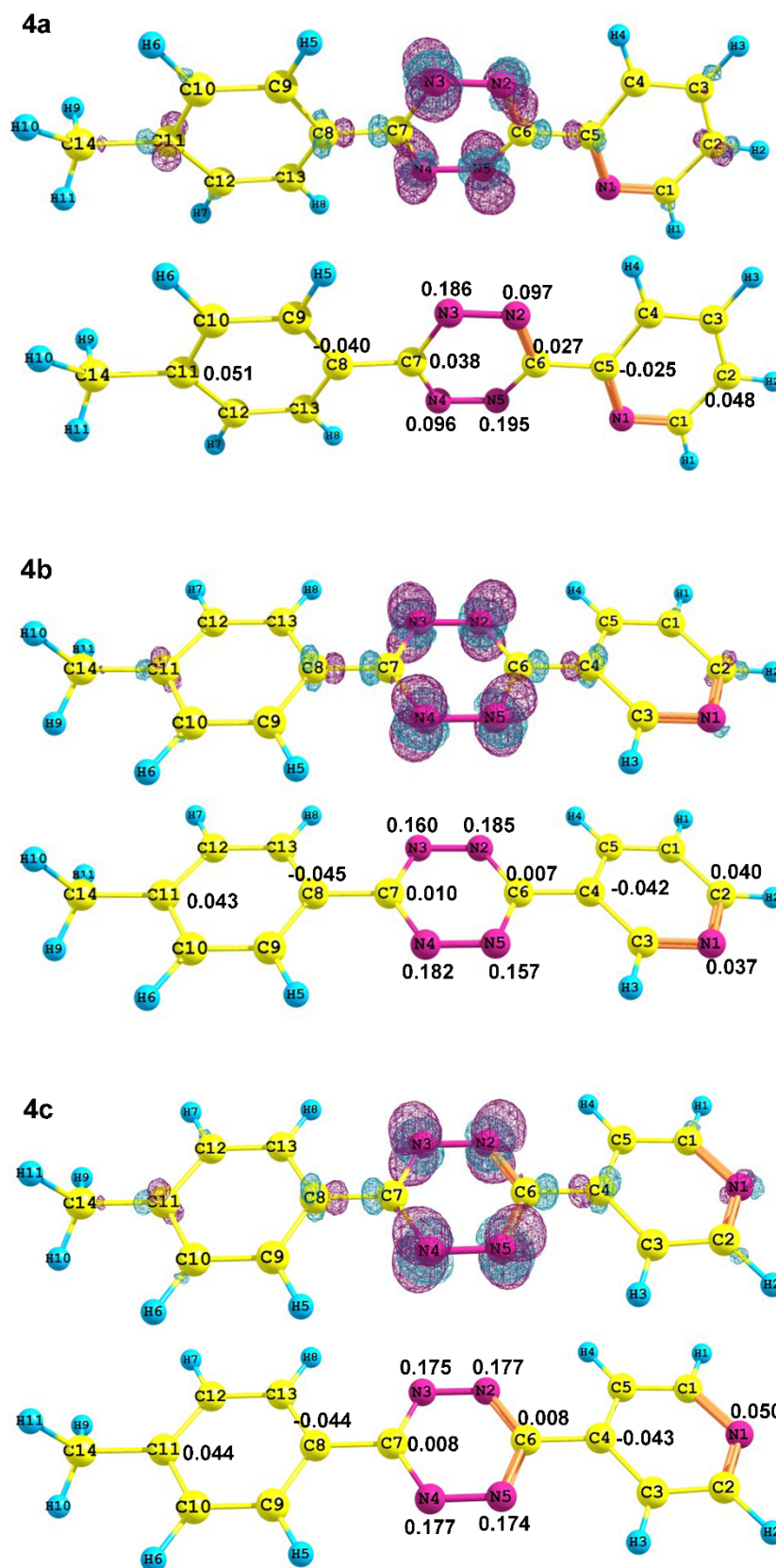
Gaussian 09 package has been employed for all the calculations.^[1] DFT method was exploited to obtain minimum energy structures. The optimized structure is proven to be the local minimum based

on the results of vibration analysis. Fukui function and the atom condensed Fukui function $f^+(r)$ ^[2] based on density functional theory (DFT) have been used to determine the site reactivity and site selectivity. Basis sets of double- ζ quality (6-31G** for C, H atoms, 6-31+G* for other atoms) are used for the geometry optimization. Theoretical calculation of **4a** is based on the crystal structure, and the others are based on simulate molecular structures drawn by Chem3D and GaussView. The single-crystal structure of **4a** was determined by X-ray crystallography. CCDC-973196 (for **4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

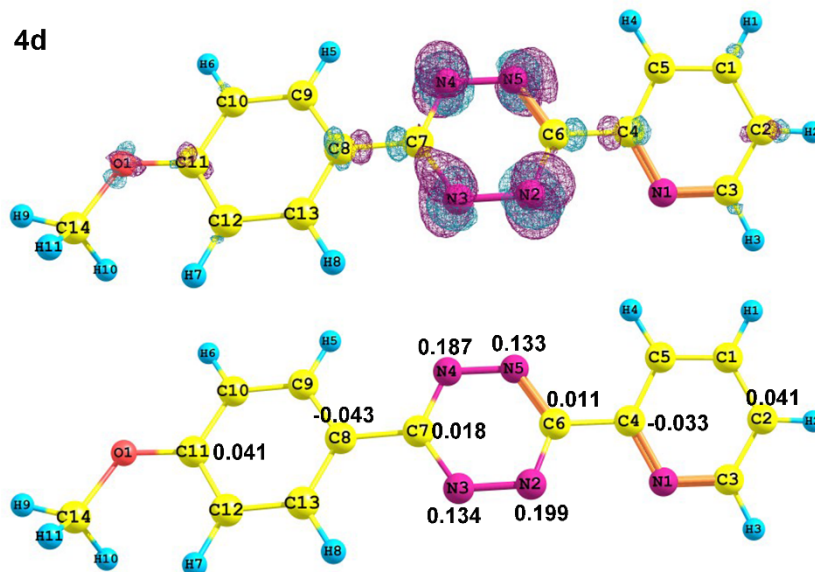
References:

- [1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Gaussian Inc: Pittsburgh*, **2003**.
- [2] a) Qi, D.; Zhang, L.; Wan, L.; Zhang, Y.; Bian, Y.; Jiang, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13277-13286; (b) Qi, D.; Zhang, L.; Zhao, L.; Cai, X.; Jiang, J. *ChemPhysChem* **2012**, *13*, 2046-2050.

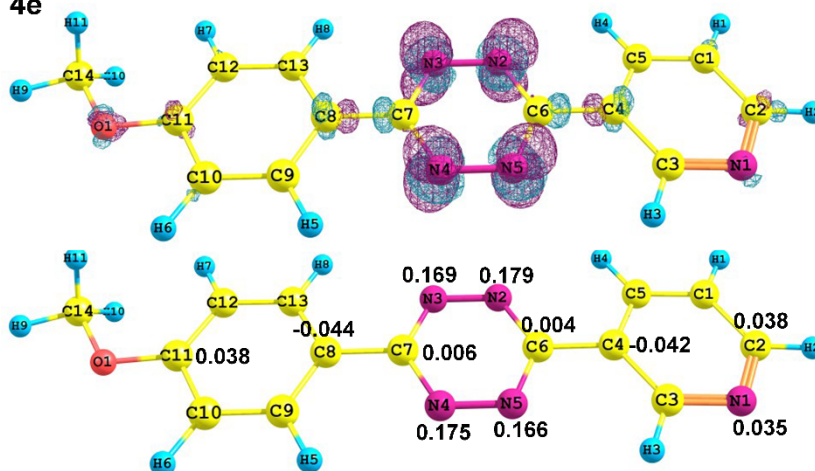
3.2. The 3D representation of the Fukui function $f^+(r)$ (positive in red color and negative in green color) and the condensed Fukui function $f^+(r)$ of N and surrounding C atoms of **4a-v**



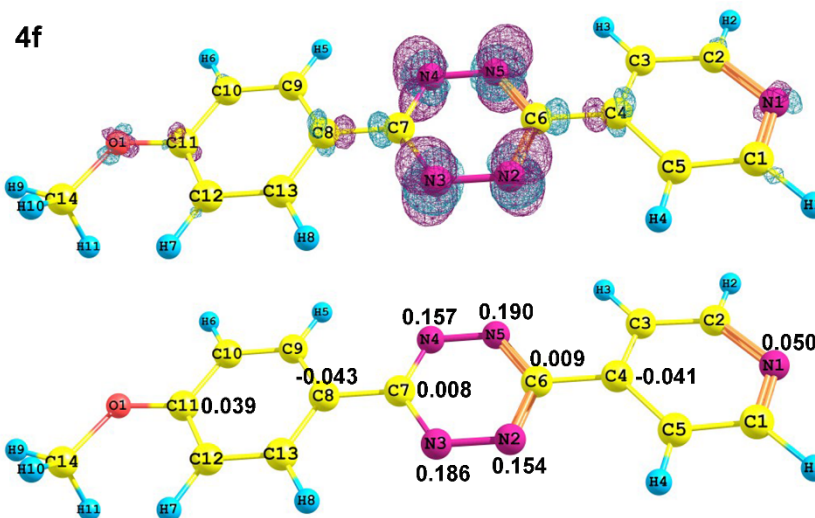
4d

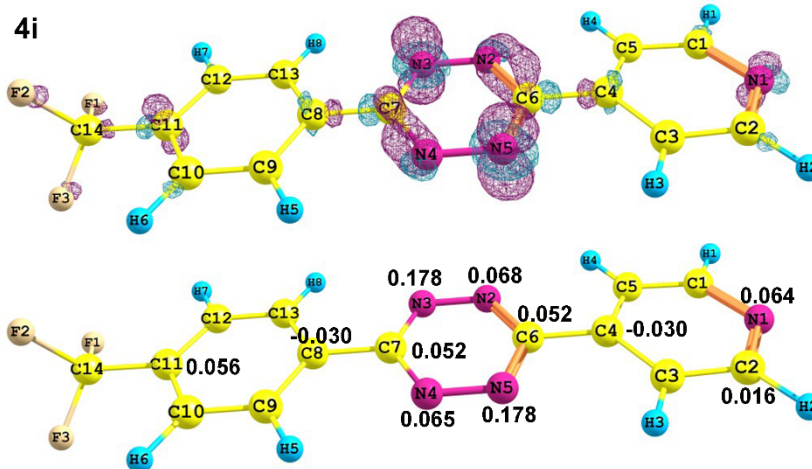
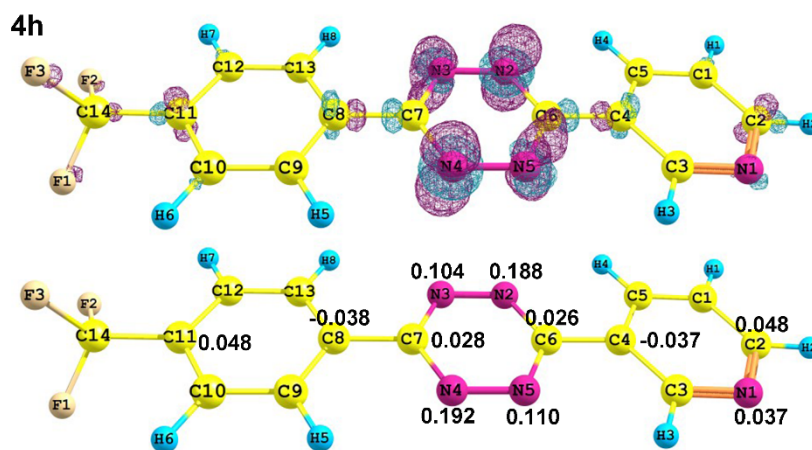
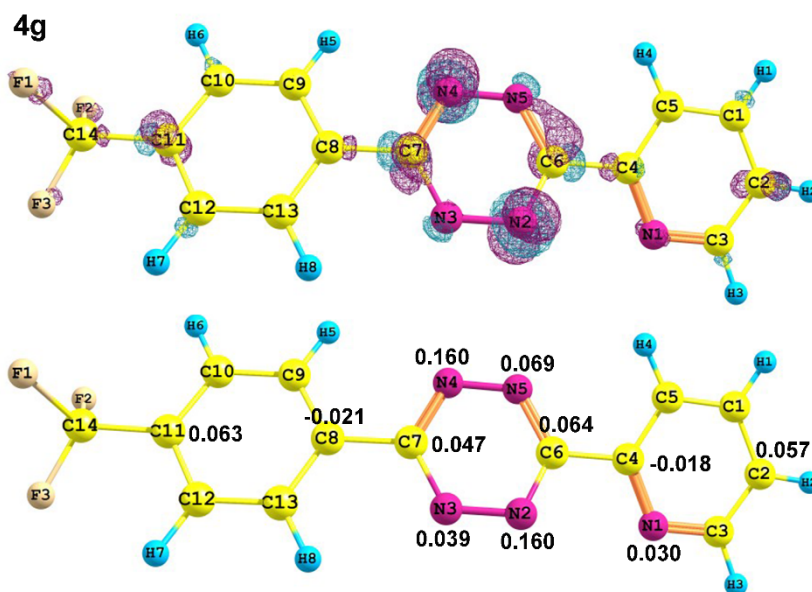


4e



4f





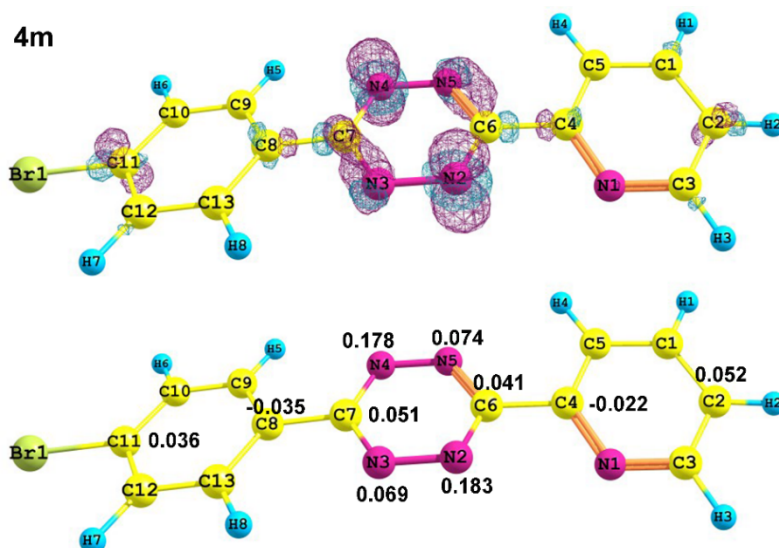
4j

ORTEP diagram of the crystal structure of compound 4j. The molecule consists of a 4-chlorophenyl group (C11-C13, Cl1) attached to a 1,3,5-triazine ring (C2-C7, N1-N5). The triazine ring is further substituted with a 4-cyanophenyl group (C4-C6, N2-N5). The structure is shown with thermal ellipsoids at the 50% probability level. Displacement ellipsoid coefficients are provided for the triazine ring atoms: N1 (0.025, 0.050, 0.037), N2 (0.077, 0.188, 0.046), N3 (0.077, 0.188, 0.046), N4 (0.183, 0.082, 0.037), and N5 (0.082, 0.037, 0.037).

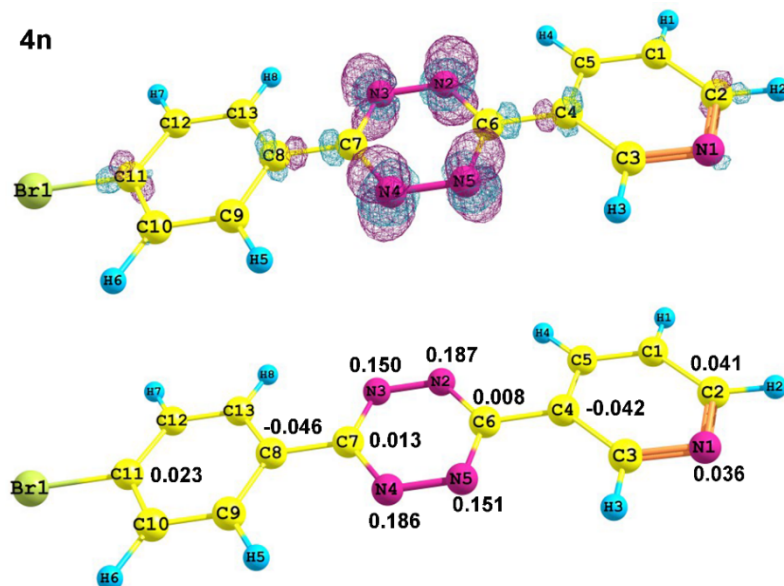
ORTEP diagram of the molecular structure of 4k, showing the molecule with thermal ellipsoids at the 50% probability level. The structure is a complex organic molecule with a central ring system and various substituents. Displacement ellipsoids are drawn at the 50% probability level. Bond lengths are given in Å and angles in degrees.

[illegible]

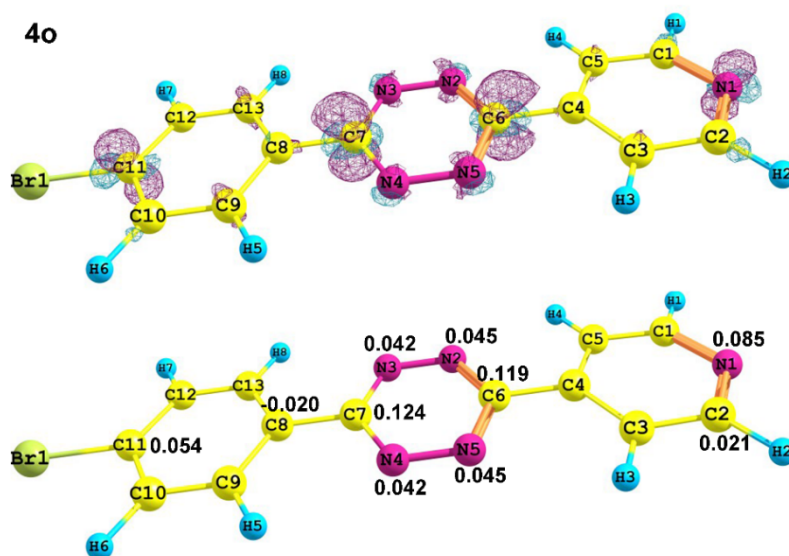
4m



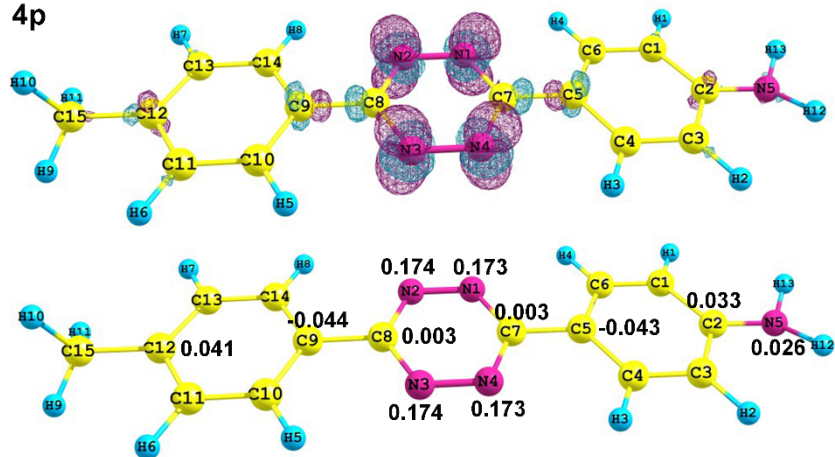
4n



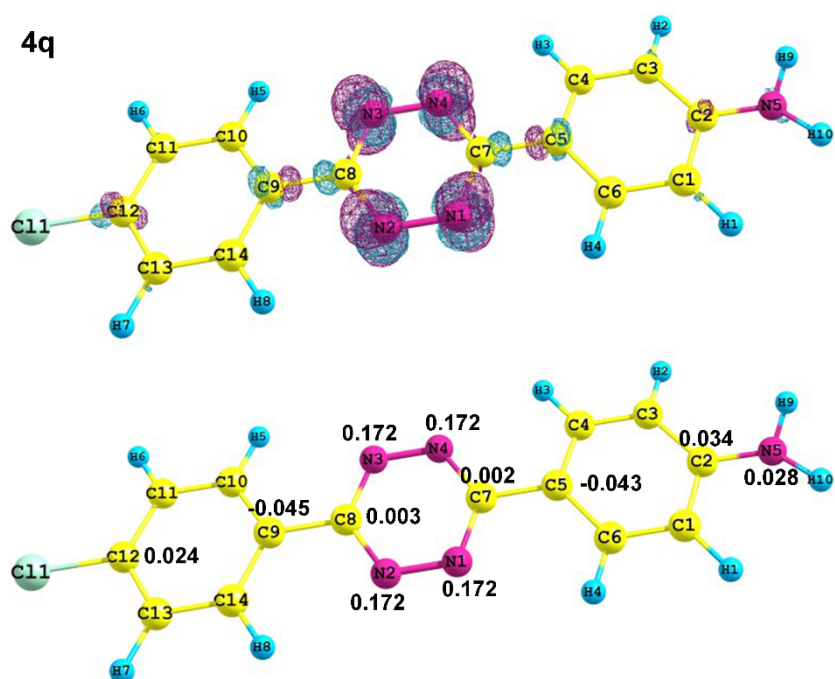
4o



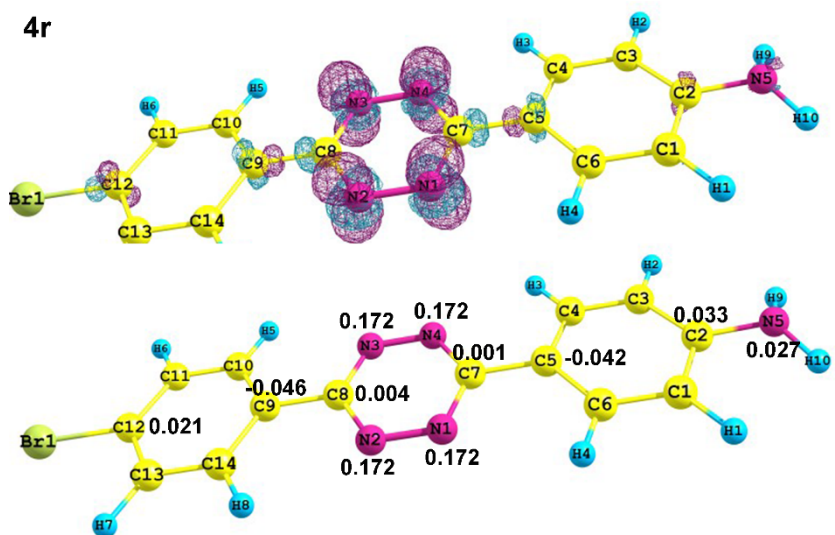
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4q



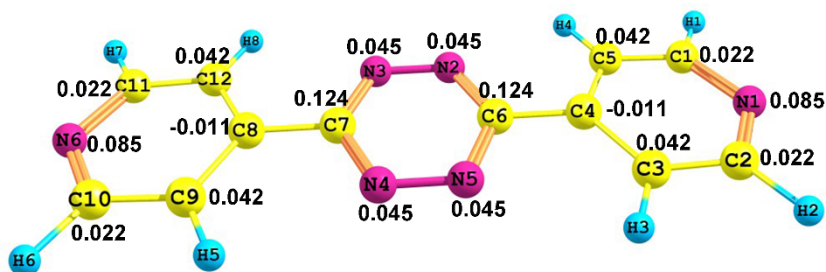
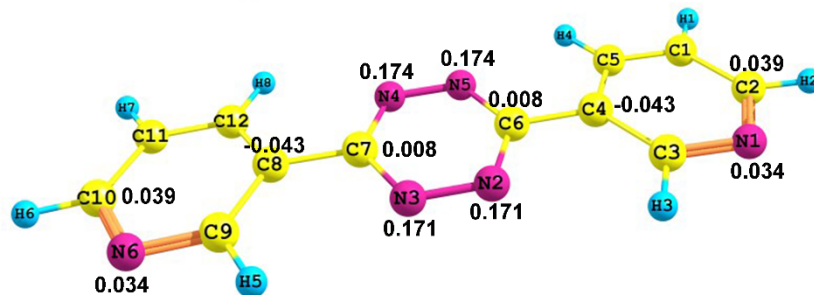
4r



4s



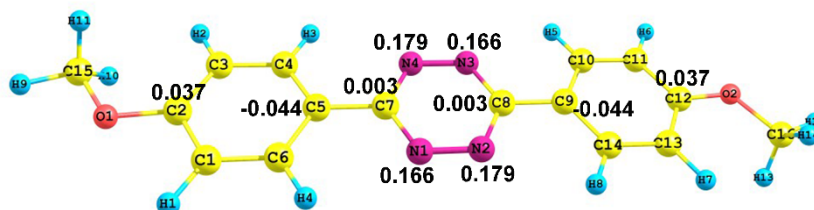
ORTEP diagram of the 4s molecule, showing the chemical structure with thermal ellipsoids at the 50% probability level. The molecule consists of a central benzene ring substituted with a 2-amino-2-methylpropyl group and a 2-amino-2-methylpropyl group. The atoms are labeled: C1-C6 for the benzene ring, N1 and N2 for the amino groups, and C7-C12 for the propyl groups. Hydrogen atoms are shown as small spheres of arbitrary radii. The structure is drawn with bond lengths and angles, and the thermal ellipsoids are shown at the 50% probability level.



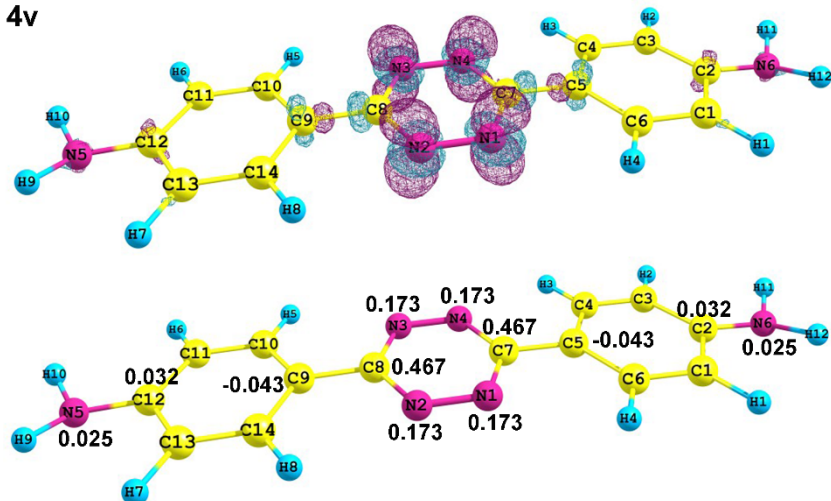
4u



ORTEP diagram of the molecular structure of compound 4u. The structure is a complex organic molecule with a central core consisting of two fused six-membered rings (C1-C6 and C7-C12) and a central six-membered ring (C13-C18). The central ring is substituted with two phenyl groups (C19-C24 and C25-C30). The molecule is shown with thermal ellipsoids at the 50% probability level. Displacement ellipsoid probabilities are given in Å²: N1 (0.010, 0.010, 0.010), N2 (0.010, 0.010, 0.010), N3 (0.010, 0.010, 0.010), N4 (0.010, 0.010, 0.010), C1 (0.010, 0.010, 0.010), C2 (0.010, 0.010, 0.010), C3 (0.010, 0.010, 0.010), C4 (0.010, 0.010, 0.010), C5 (0.010, 0.010, 0.010), C6 (0.010, 0.010, 0.010), C7 (0.010, 0.010, 0.010), C8 (0.010, 0.010, 0.010), C9 (0.010, 0.010, 0.010), C10 (0.010, 0.010, 0.010), C11 (0.010, 0.010, 0.010), C12 (0.010, 0.010, 0.010), C13 (0.010, 0.010, 0.010), C14 (0.010, 0.010, 0.010), C15 (0.010, 0.010, 0.010), C16 (0.010, 0.010, 0.010), C17 (0.010, 0.010, 0.010), C18 (0.010, 0.010, 0.010), C19 (0.010, 0.010, 0.010), C20 (0.010, 0.010, 0.010), C21 (0.010, 0.010, 0.010), C22 (0.010, 0.010, 0.010), C23 (0.010, 0.010, 0.010), C24 (0.010, 0.010, 0.010), C25 (0.010, 0.010, 0.010), C26 (0.010, 0.010, 0.010), C27 (0.010, 0.010, 0.010), C28 (0.010, 0.010, 0.010), C29 (0.010, 0.010, 0.010), C30 (0.010, 0.010, 0.010). Hydrogen atoms are shown as small spheres of arbitrary radii. The structure is drawn with bond lengths in Å and angles in degrees. The title of the figure is 'ORTEP diagram of the molecular structure of compound 4u'.

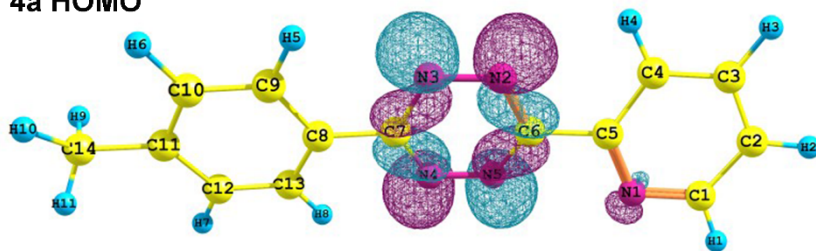


4v

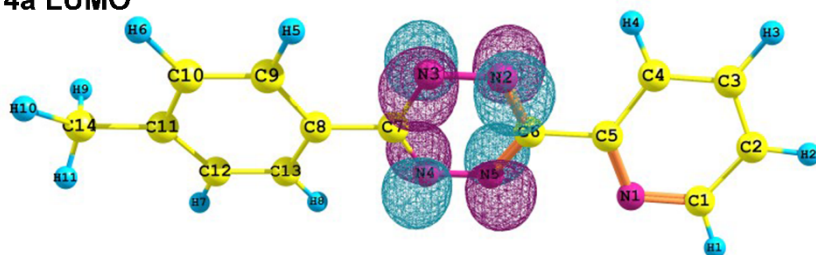


3.3. The shapes of HOMO and LUMO orbitals for the free molecules of 4a-v

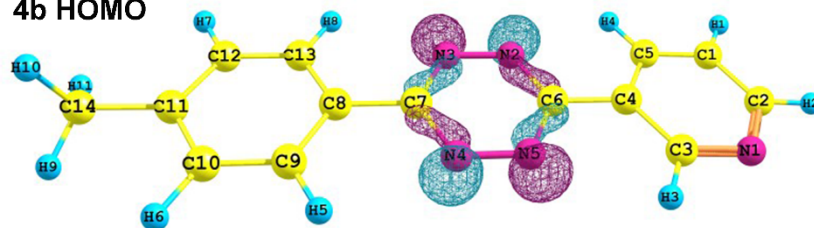
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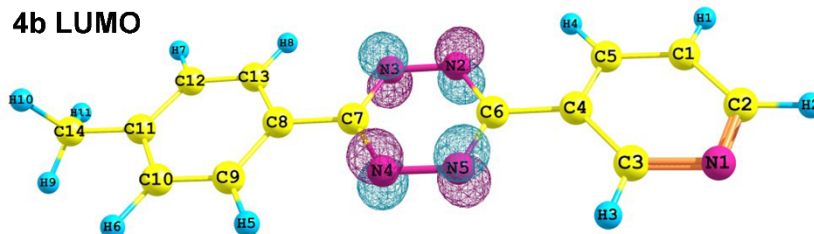
4a LUMO



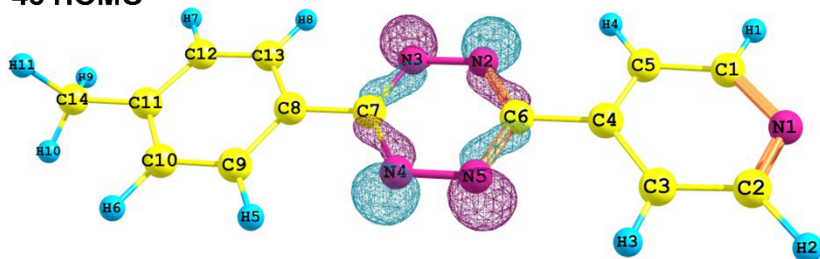
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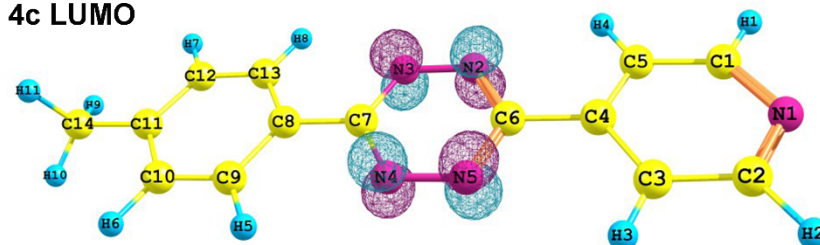
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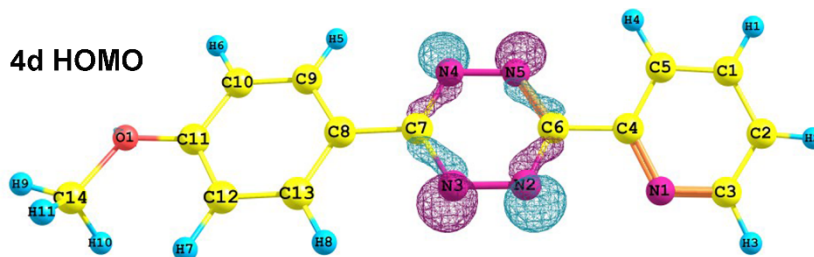
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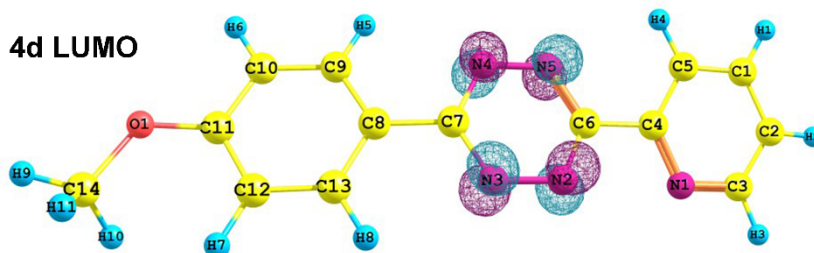
4c LUMO



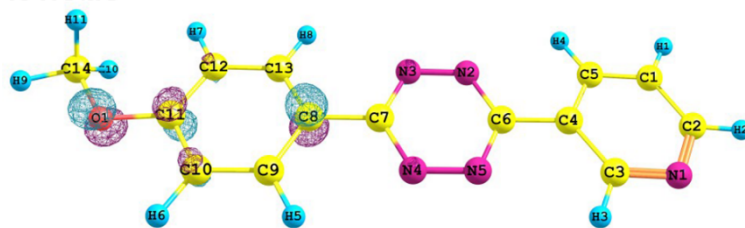
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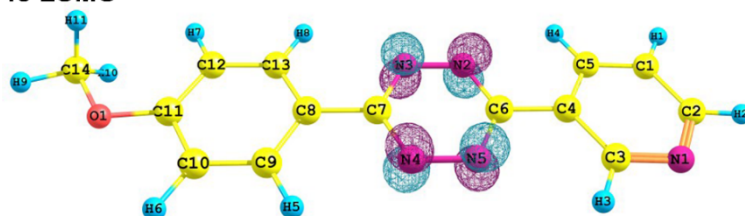
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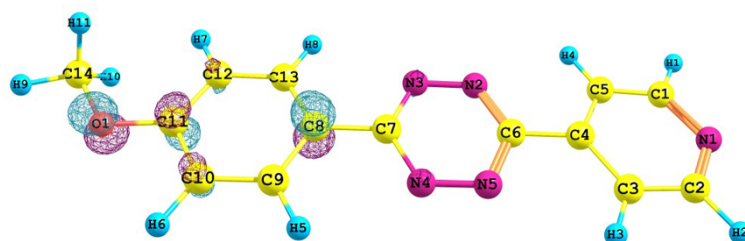
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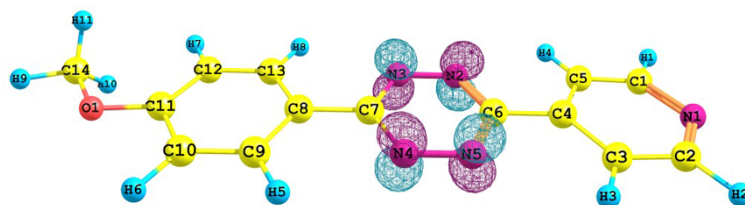
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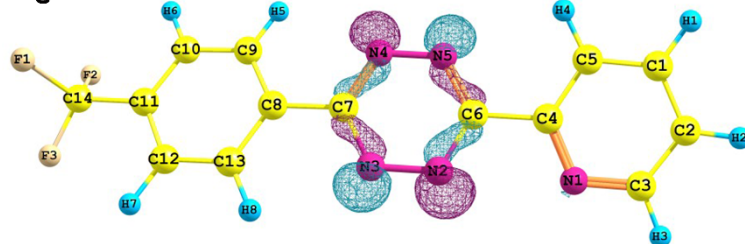
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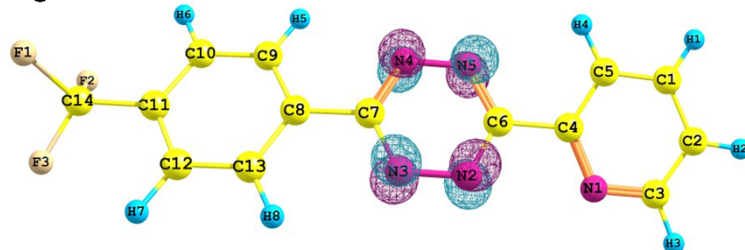
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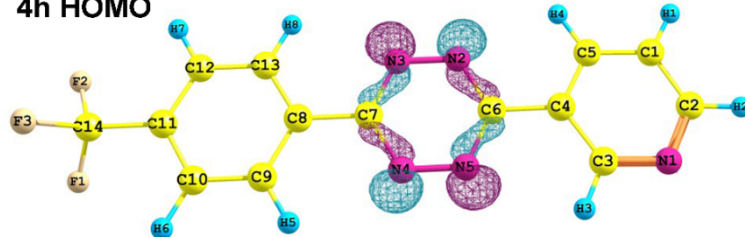
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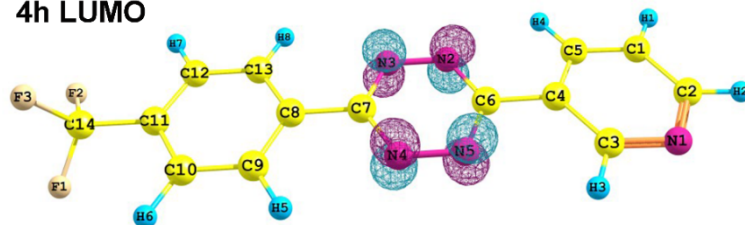
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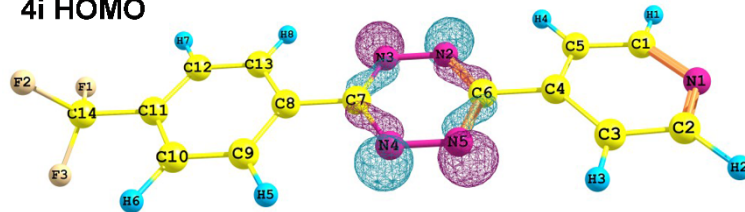
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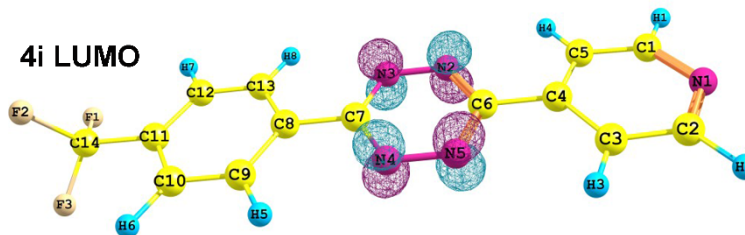
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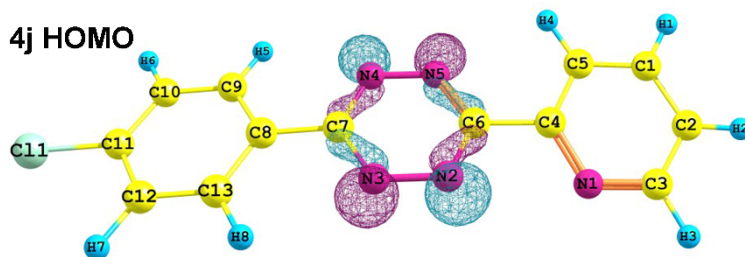
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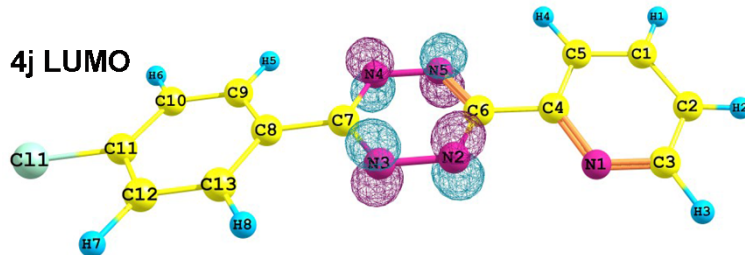
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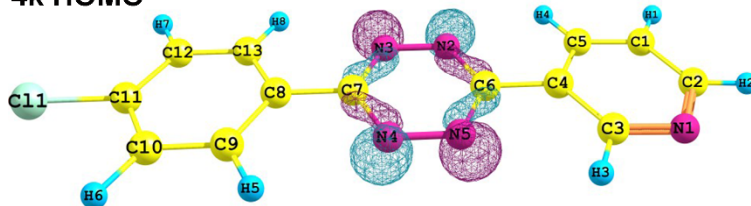
4j HOMO



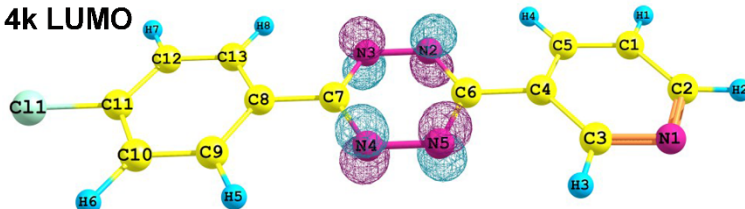
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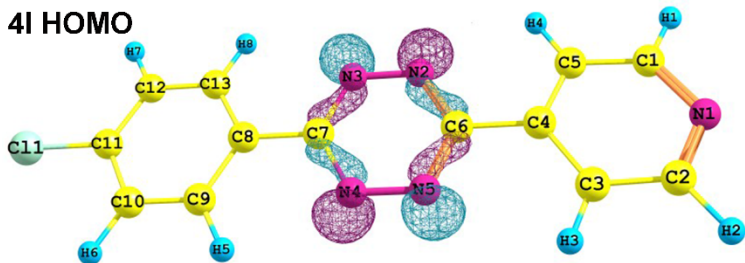
4k HOMO



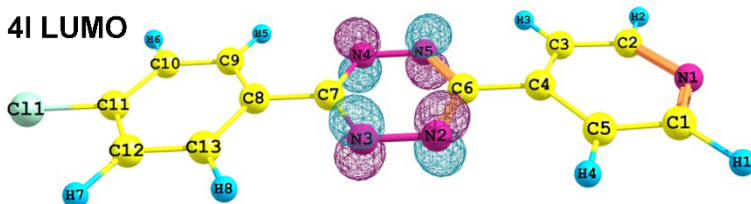
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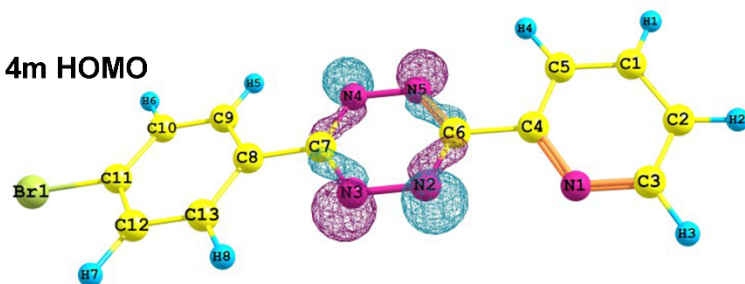
4l HOMO



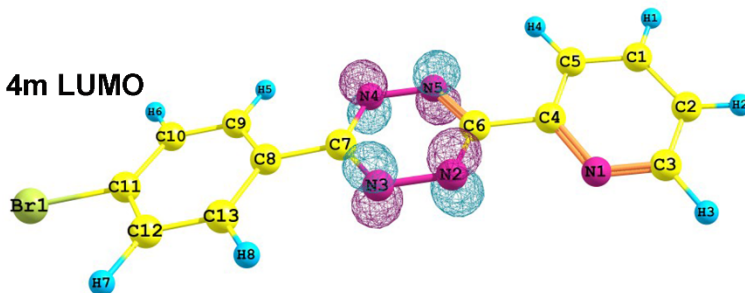
4l LUMO



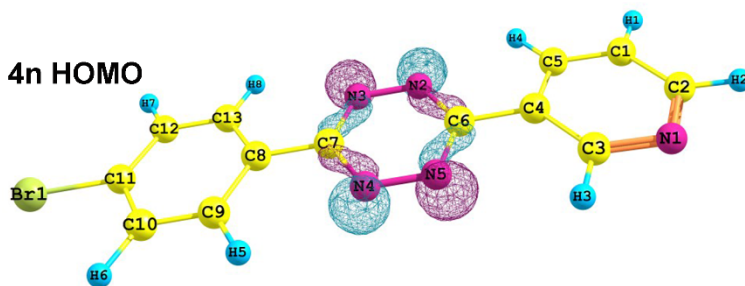
4m HOMO



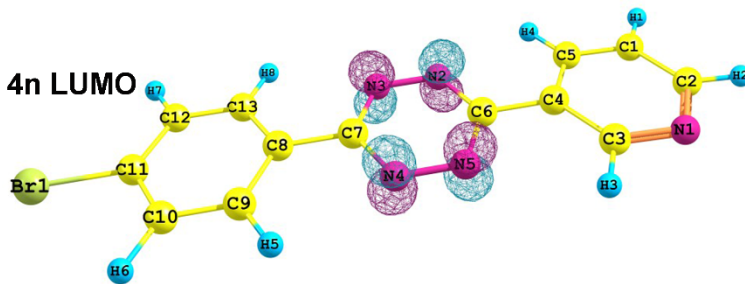
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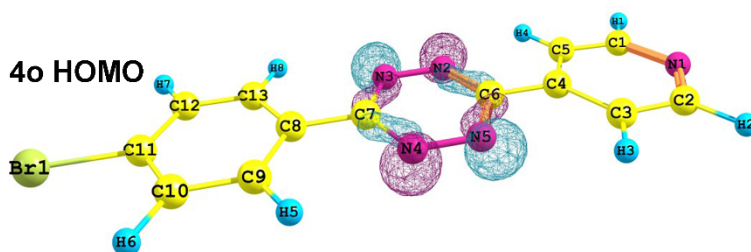
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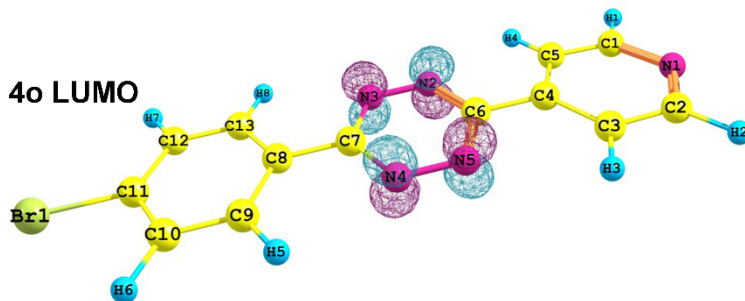
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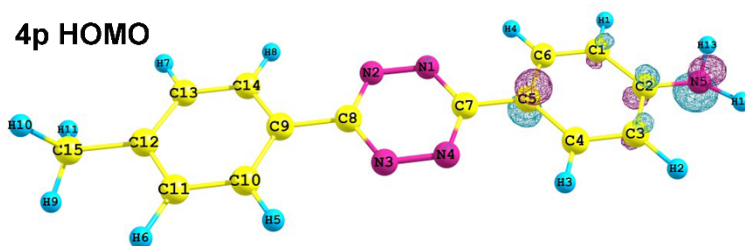
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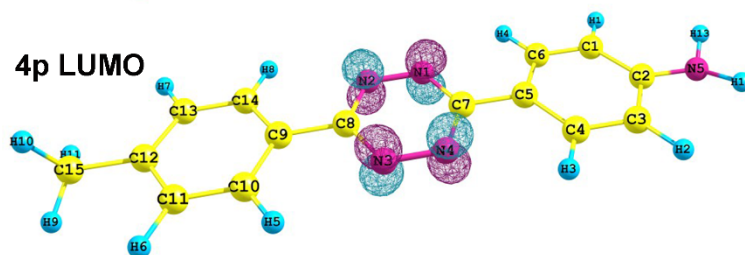
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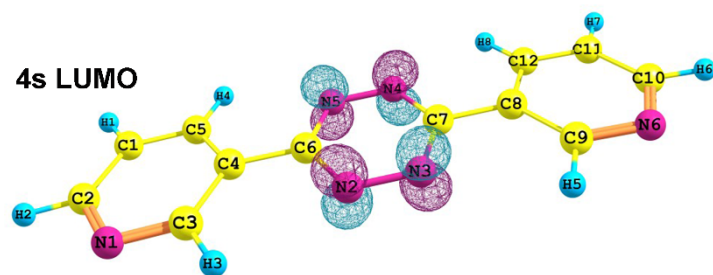
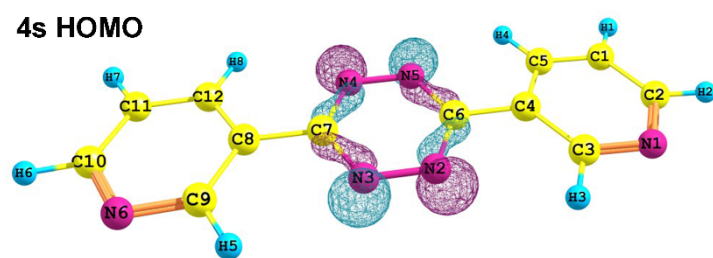
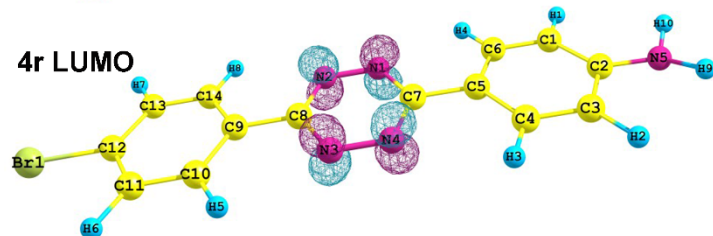
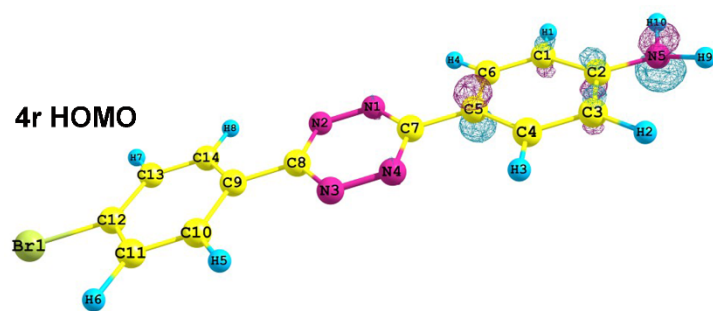
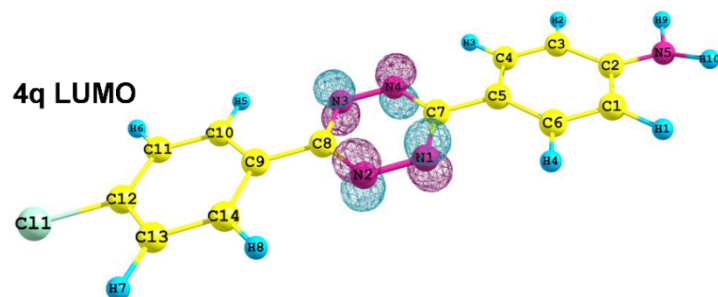
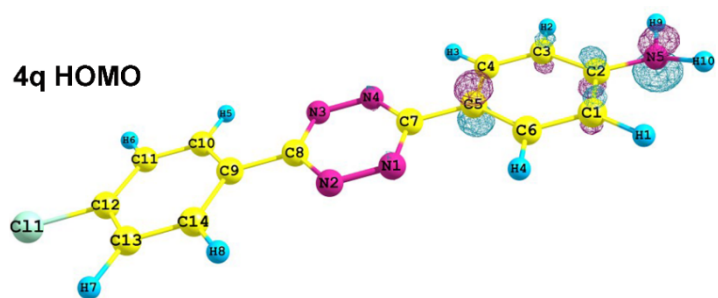


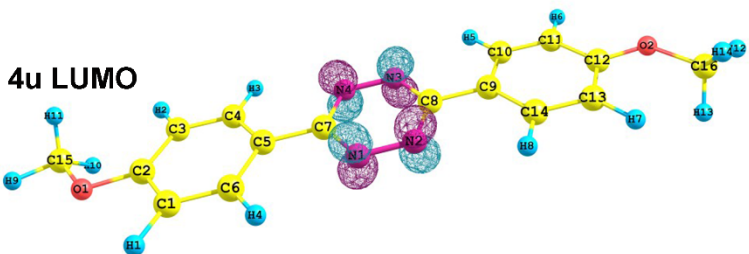
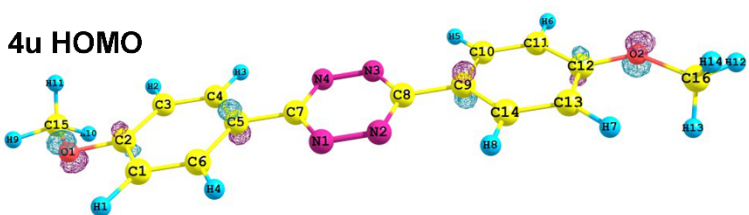
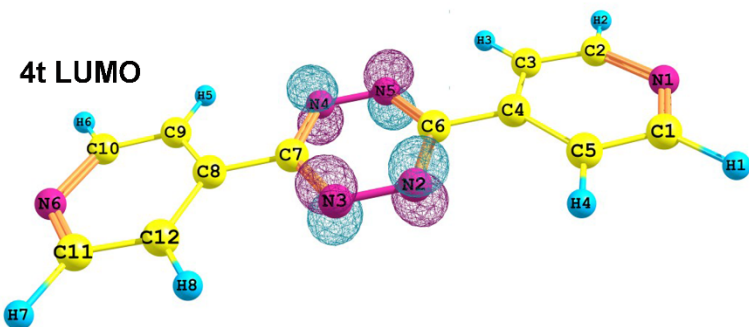
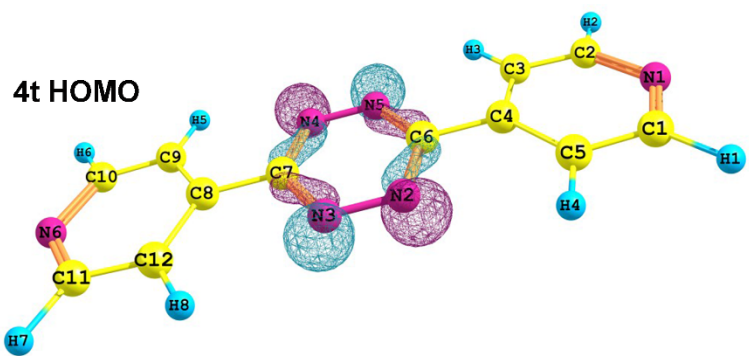
4p HOMO

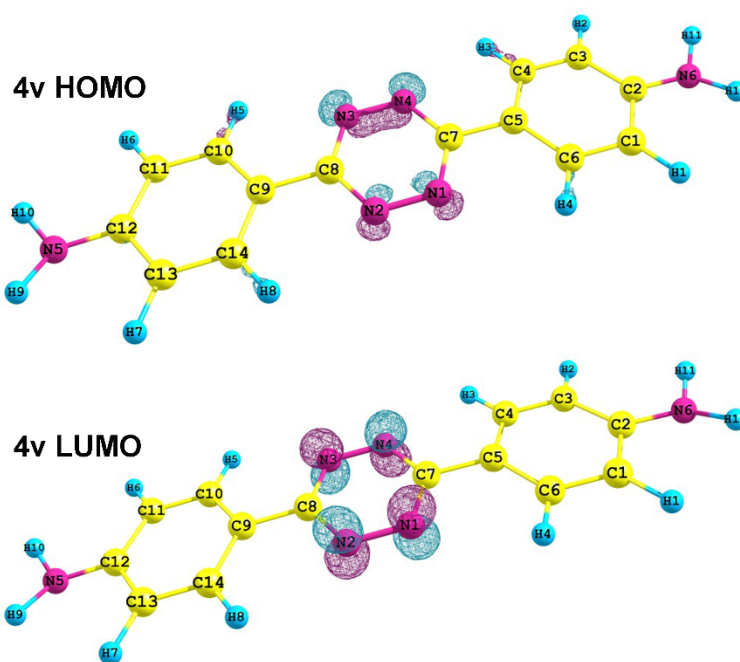


4p LUMO









4. ^1H NMR and ^{13}C NMR spectra, IR spectra of all compounds

