

Supporting Information

Excited State C–N Bond Dissociation and Cyclization of Tri-Aryl amine based OLED Materials: A Theoretical Investigation

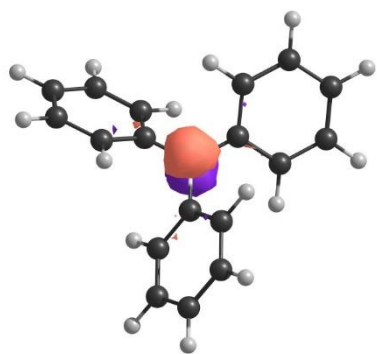
J. Vijaya sundar^{*a}, *V. Subramanian*^b and *B. Rajakumar*^a

^a *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036*

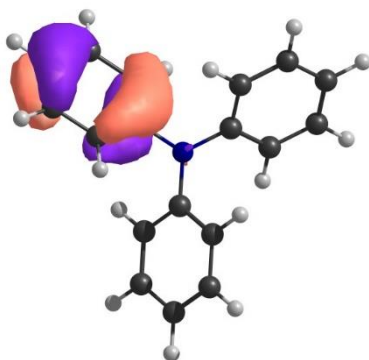
^b *Inorganic and Physical Chemistry Laboratory, Central Leather Research Institute, Chennai 600020*

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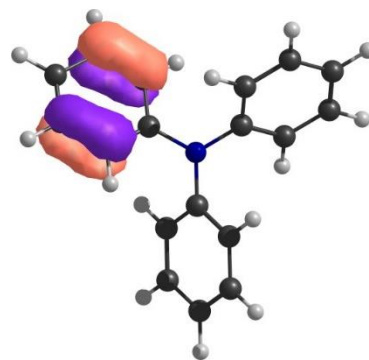
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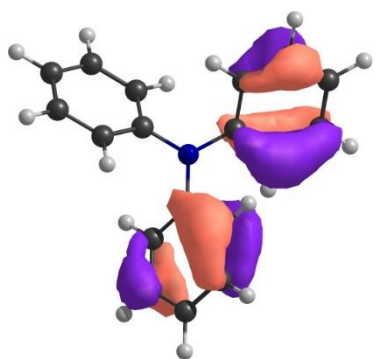
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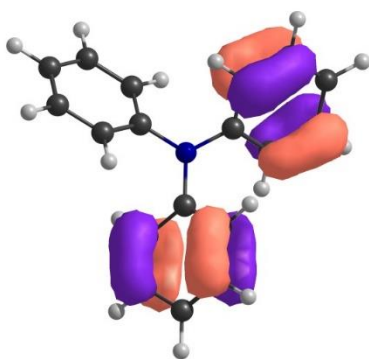
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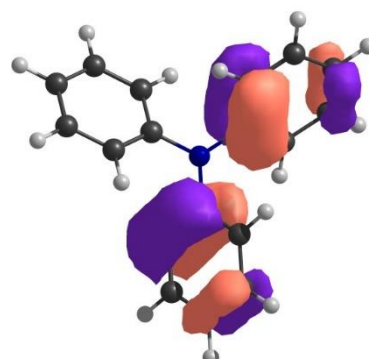
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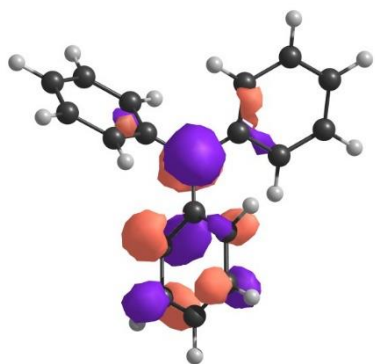
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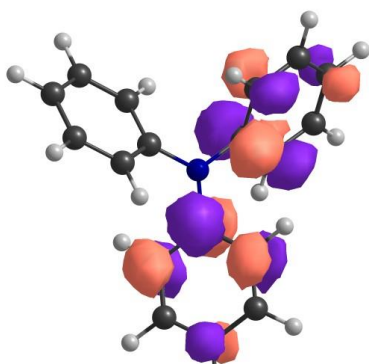
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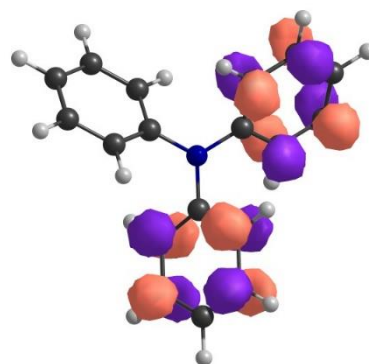
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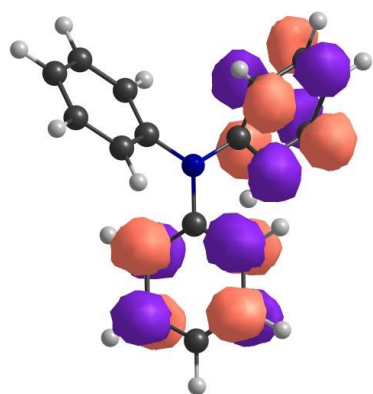
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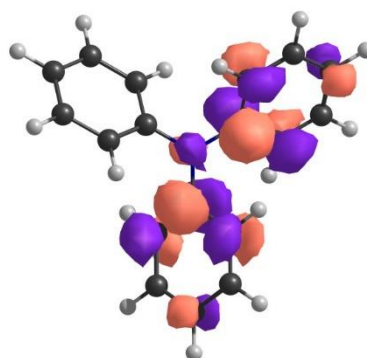
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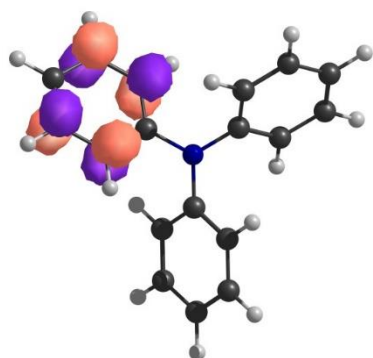
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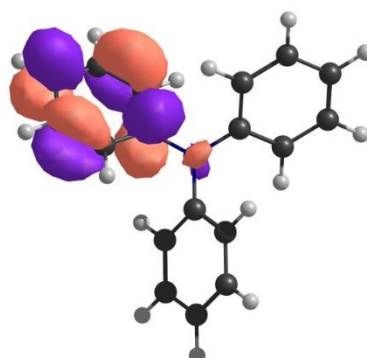
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LUMO+3

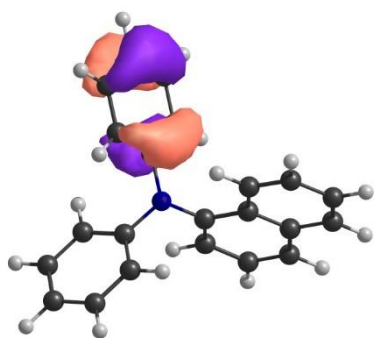


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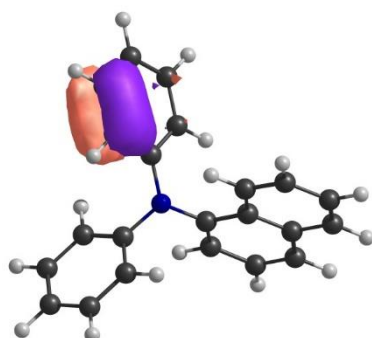


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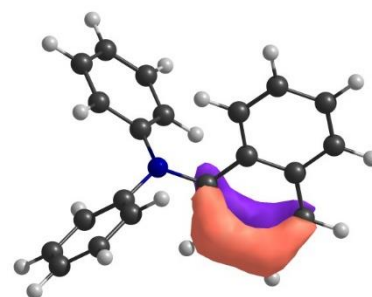
Figure S1. Contour representation of molecular orbitals used in the active space for CASSCF calculation of TPA.



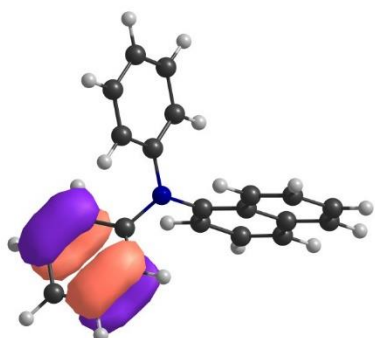
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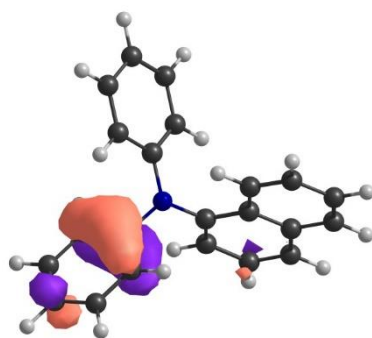
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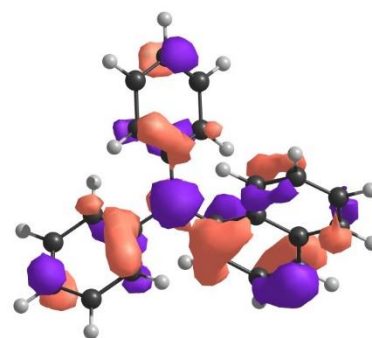
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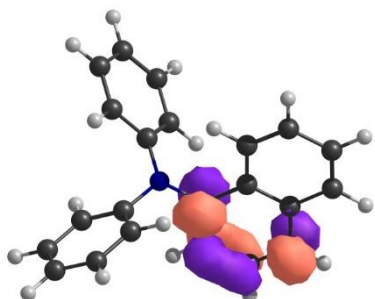
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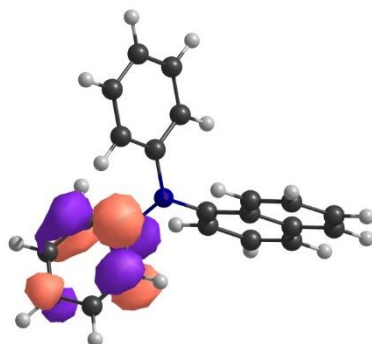
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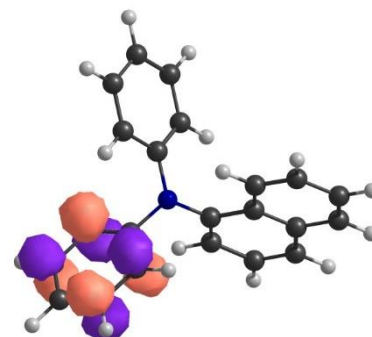
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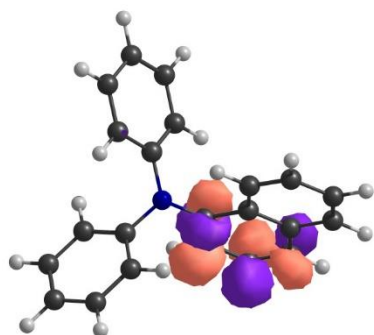
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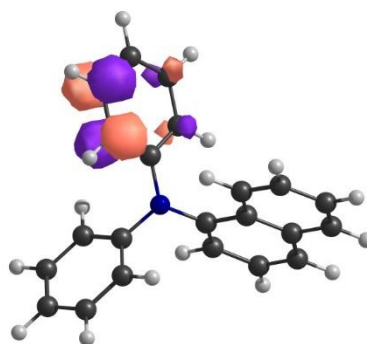
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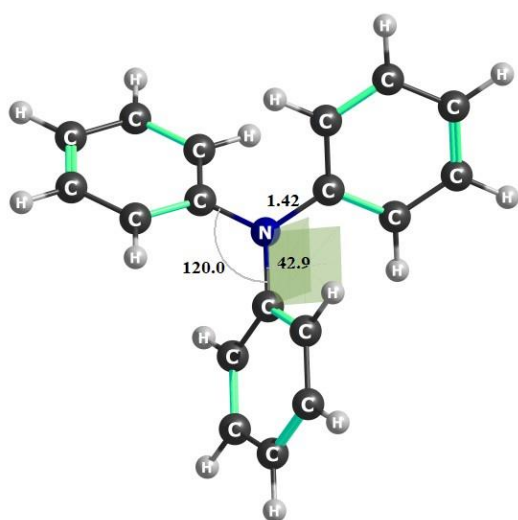


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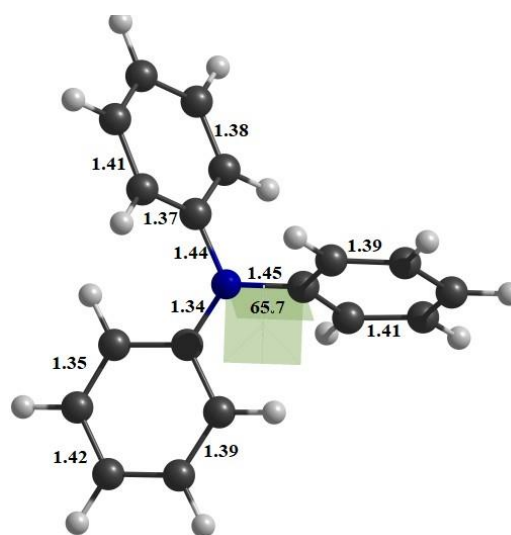


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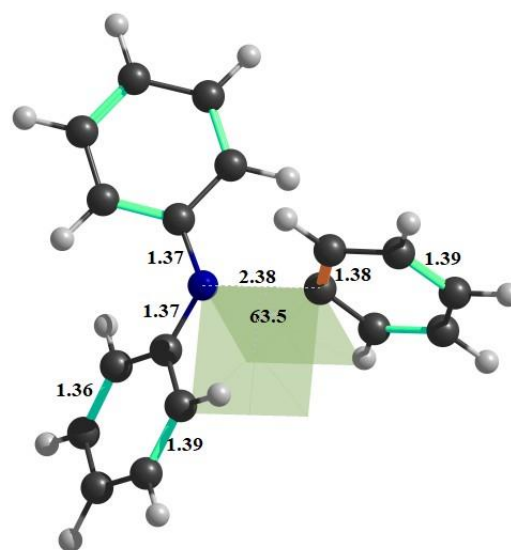
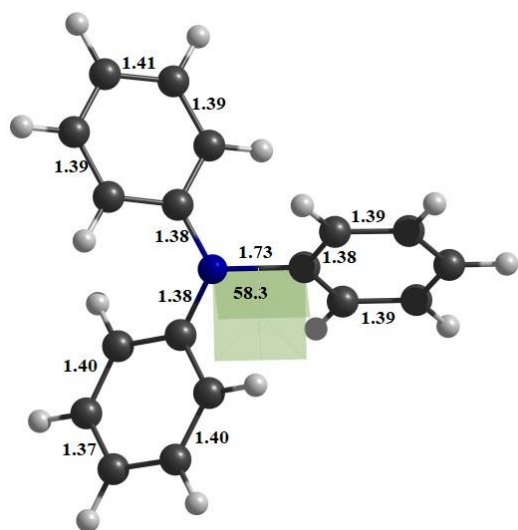
Figure S2. Contour representation of molecular orbitals used in the active space for CASSCF calculation of DNPA.



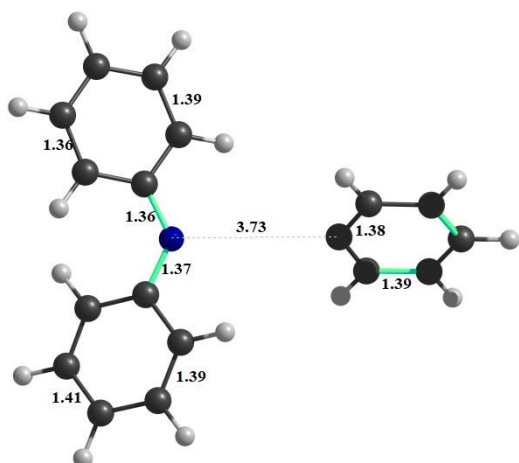
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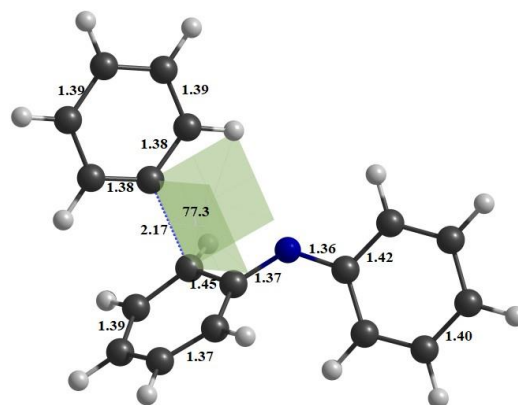
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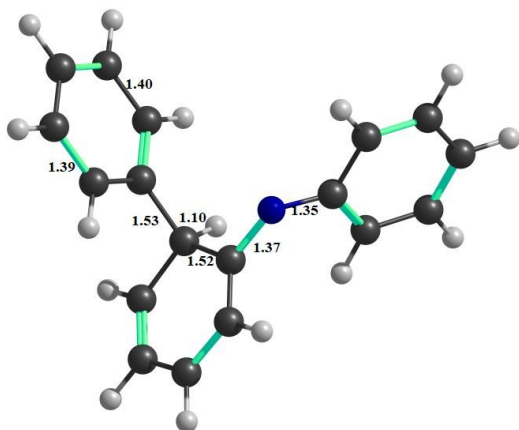
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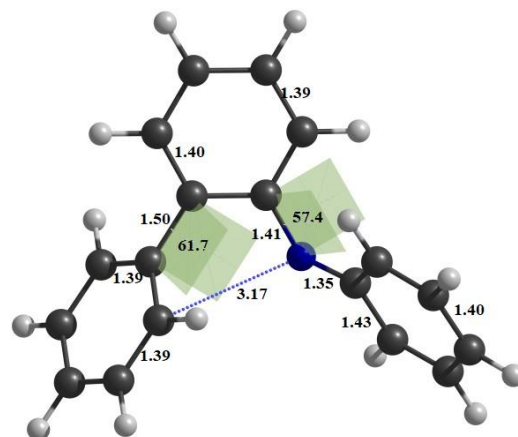
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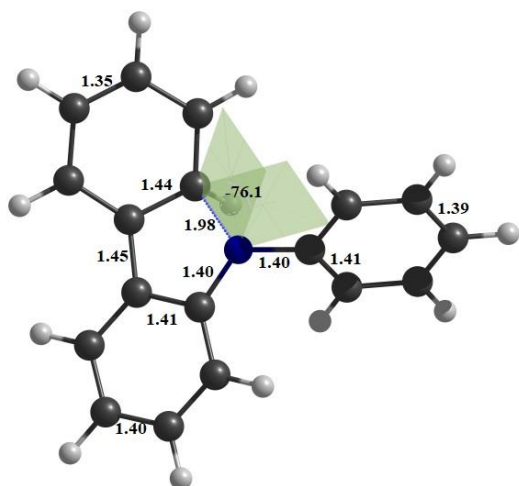
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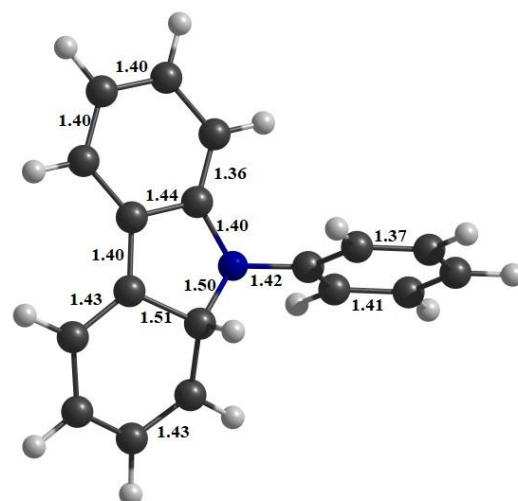
TS2



IM2

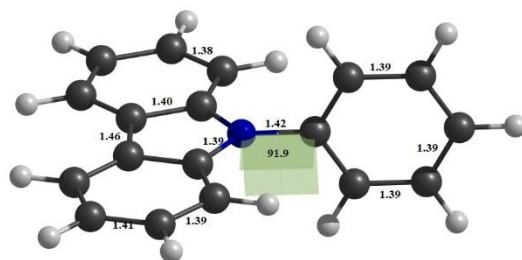


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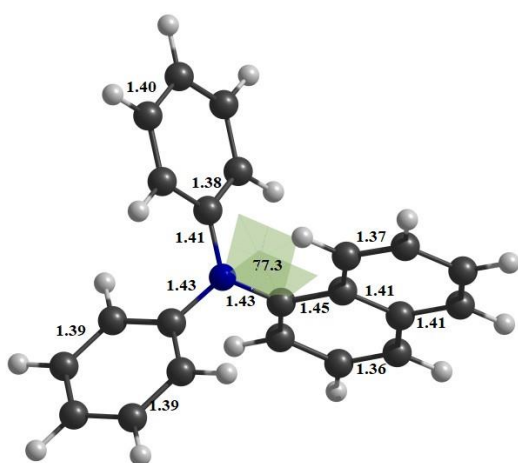
TS3

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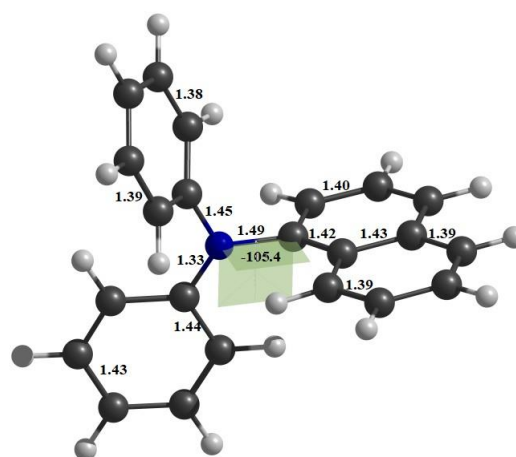


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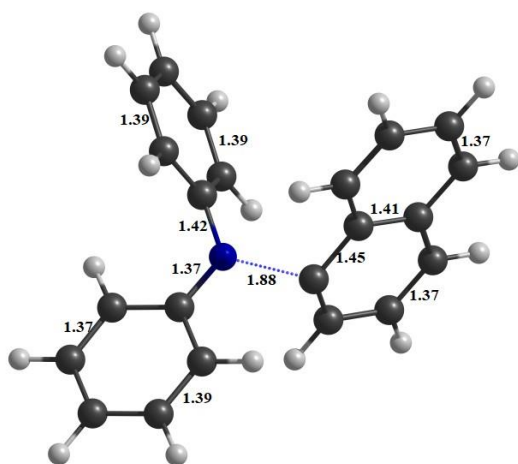
Figure S3. Optimized geometries of all the structures along the excited state degradation of TPA at CASSCF(14,13)/cc-pVTZ level of theory.



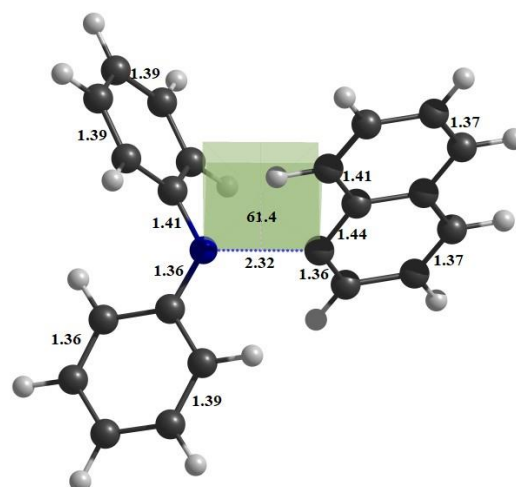
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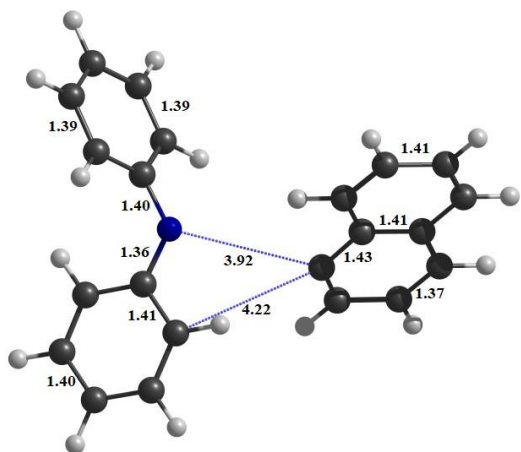
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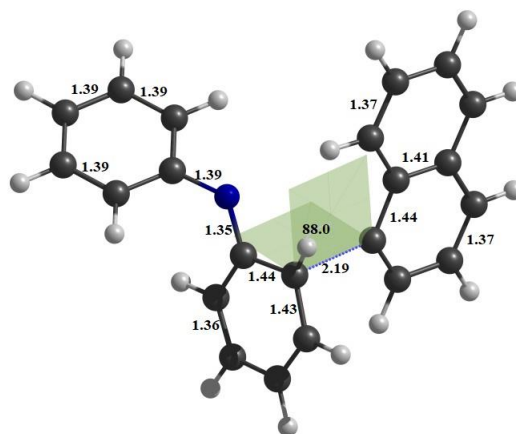
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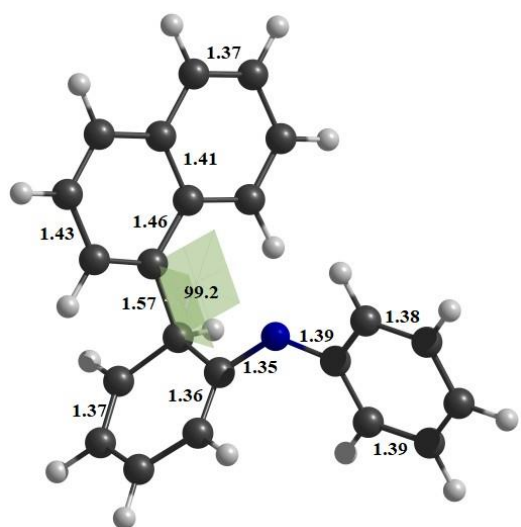
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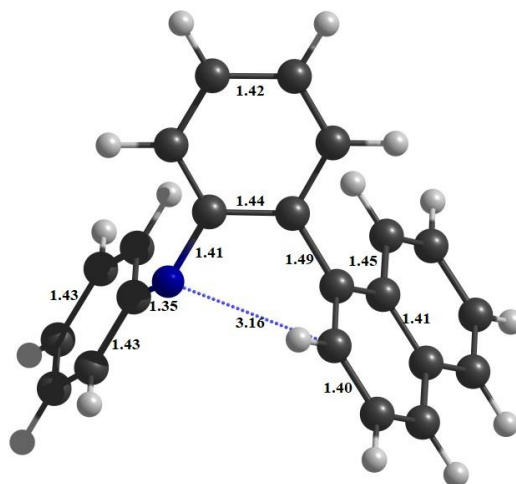
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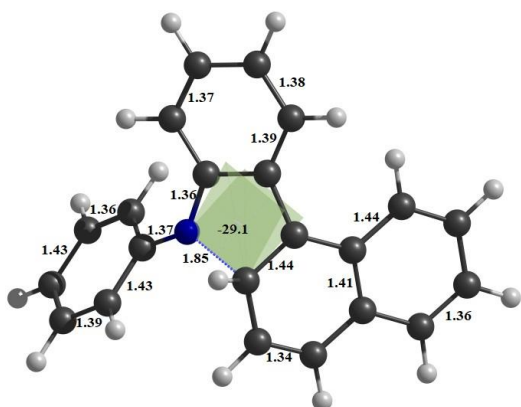
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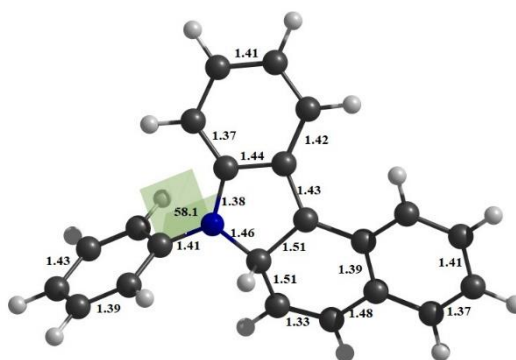
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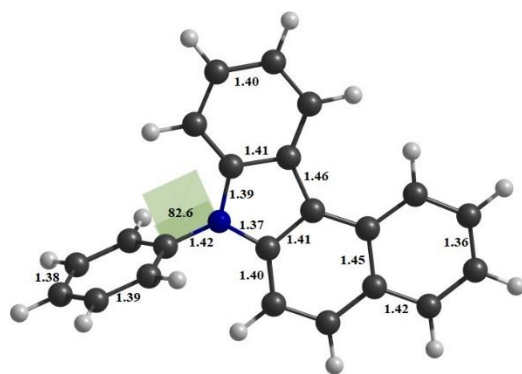
IM3



TS3

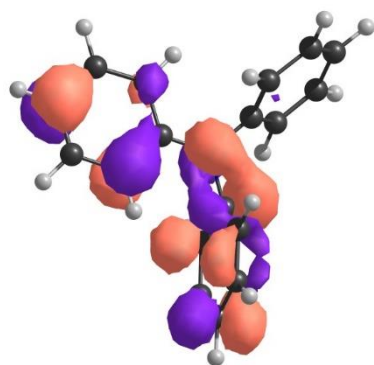


IM4

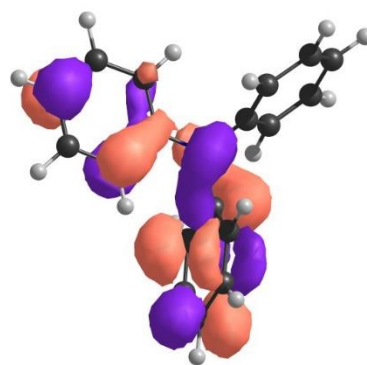


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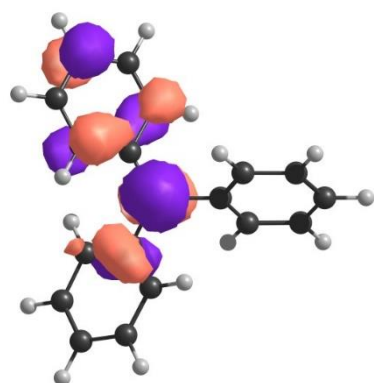
Figure S4. Optimized geometries of all structures along the excited state degradation of DNPA at CASSCF(12,11)/cc-pVTZ level of theory.



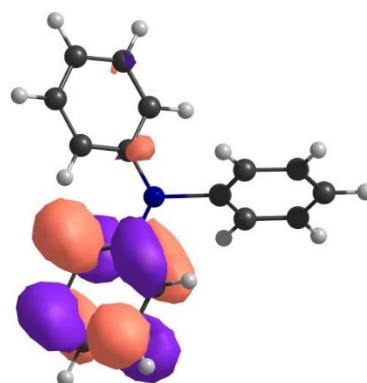
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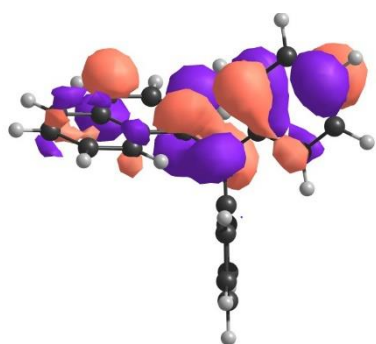
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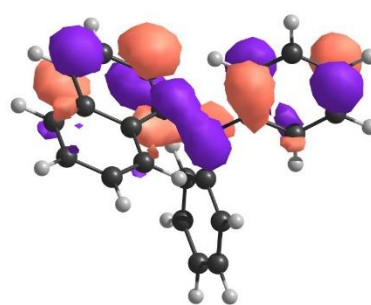
HOMO (TS1)



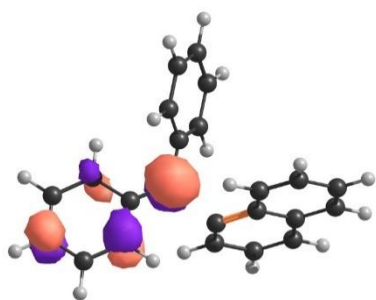
LUMO (TS1)



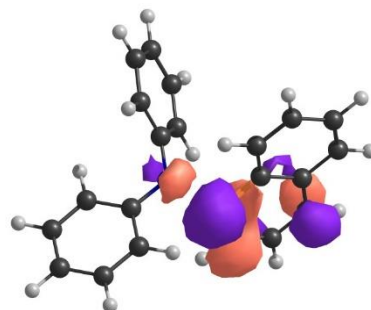
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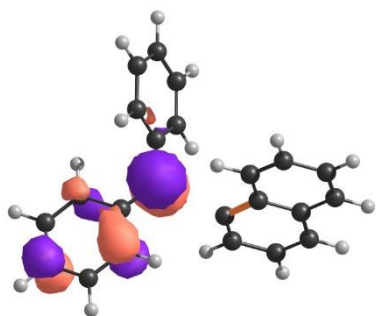
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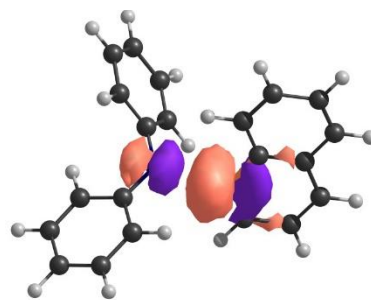
HOMO (TS1)



LUMO (TS1)



HOMO (CI)



LUMO (CI)

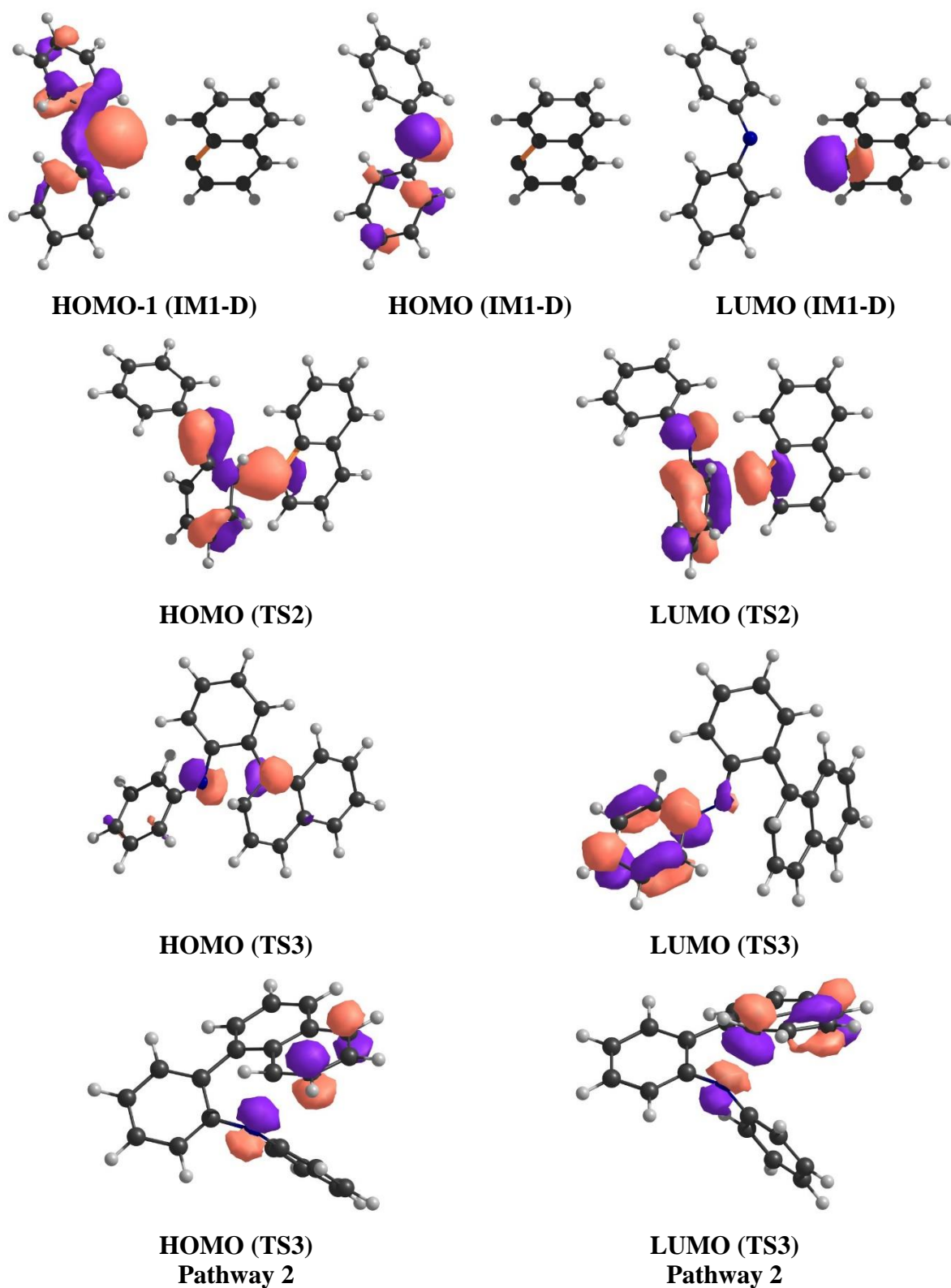


Figure S6. HOMO and LUMO contour images of important structures containing localized electron density (radical) as discussed for DPNA for pathway (1 & 2).

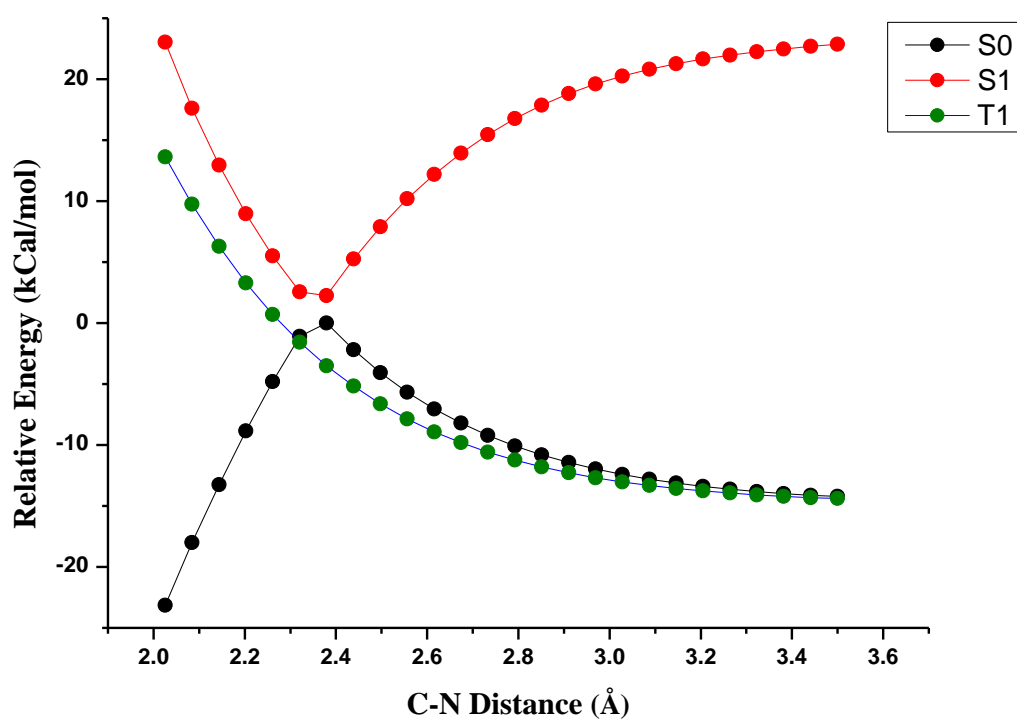


Figure S7. PES of TPA around the conical intersection (in kcal/mol)

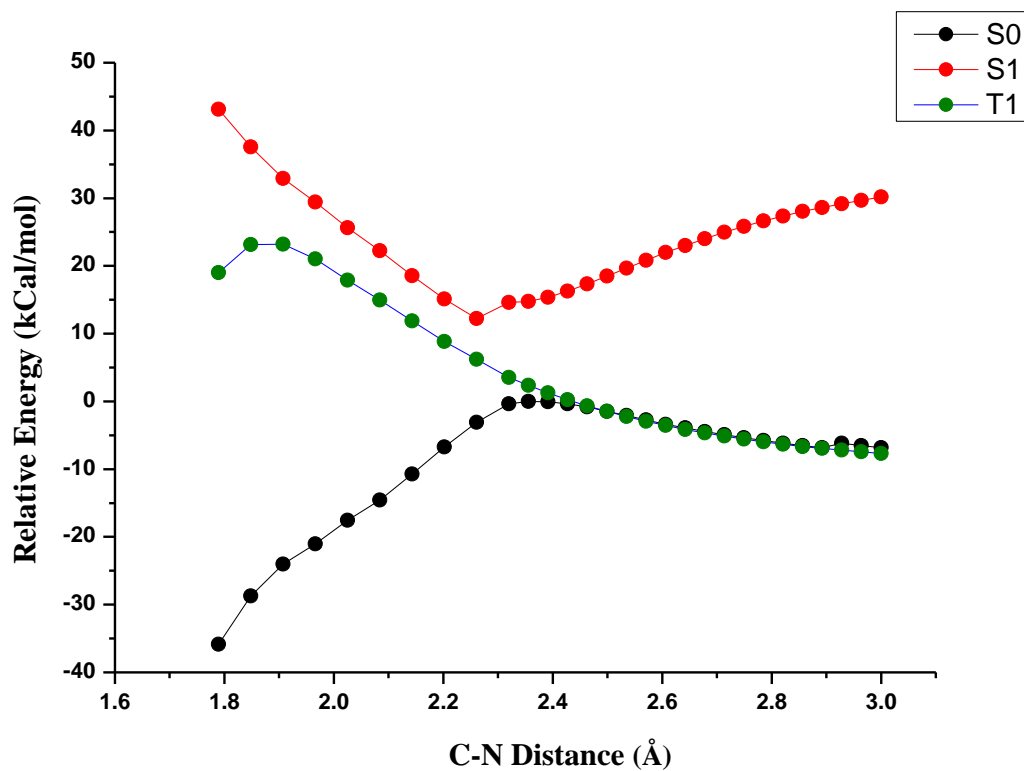


Figure S8. PES of DPNPA around the conical intersection (in kcal/mol)