Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Deciphering the cryptic role of catalytic electron in a photochemical bond dissociation using Aromaticity markers

Ambar Banerjee, Debabrata Halder, Gaurab Ganguly, and Ankan Paul *[a]

Contents

1. Additional Supporting Material

a. Table T1. Comparison of $S_0 \rightarrow S_1$ vertical excitation energy with different functional and methods.

b. Figure S1.

i. Energy profile for S_0 and S_1 vs time for BOMD with S_1 as initial surface**.**

ii. Snapshots from BOMD with S_1 as initial surface.

iii. Plot of N1-N2 distance, CN distance and CNN bond angle vs time for BOMD with S_1 as initial surface depicting the correlation between them.

c. Figure S2: Optimized geometry of 3* at CASSCF level of theory.

d. Figure S3: a) Plot of energy profile from surface hopping molecular dynamics using CASSCF employing SHARC b) Plot of the change of CNN bond angle along with the dynamics. c) Snapshots from the dynamics. d) Plot of T1 diagnostic value vs N1-N2 distance along the N1-N2 dissociation coordinate.

e. Figure S4: Optimized geometry of 4 at CASSCF level of theory.

f. Figure S5: a) Plot of energy profile from surface hopping molecular dynamics using CASSCF employing SHARC b) Plot of the change of CNN bond angle along with the dynamics. Figure S2. Relaxed Scan PES for N1-N2 bond dissociation of 1 in S_1 state and S_0 state at different levels of theory.

g. Figure S6. Relaxed Scan PES for N1-N2 bond dissociation of Cyano-Tetrazole in neutral and anionic state at different levels of theory.

h. Figure S7. The two integration planes for MICD computation of 1.

i. Figure S8. Ground (S_0) and Excited State (S_1) MICD computation of benzene.

j. Figure S9. Individual Pictures and discussions on Figure 3 of main manuscript.

k. Table T2. Table for MICD ring current integrations for CN-Tz , CN-$Tz^{-\cdot}$, Ph-CH=NH and Ph-$CH=NH^{+\cdot}$.

l. Table T3. Table for NICS shielding constant for CN-Tz , CN-Tz-. , Ph-CH=NH and Ph-$CH=NH^{+\cdot}$.

m. Figure S10. Plot of numerically integrated current densities in the S1 state for the phenyl moiety along the N1-N2 dissociation coordinate depicting shift from non-aromatic to aromatic transition.

n. Figure S11. Plot of dipole moment of S1 state along N1-N2 dissociation coordinate at different levels of theory.

o. Figure S12: Plot of numerically integrated current densities in the S1 state for the phenyl moiety along the N1-N2 dissociation coordinate depicting shift from non-aromatic to aromatic transition.

p. Supporting Video: V1

I. Supporting Movie M1: Video from the CPMD simulation on S_1 surface from 1* to N_2 evolution.

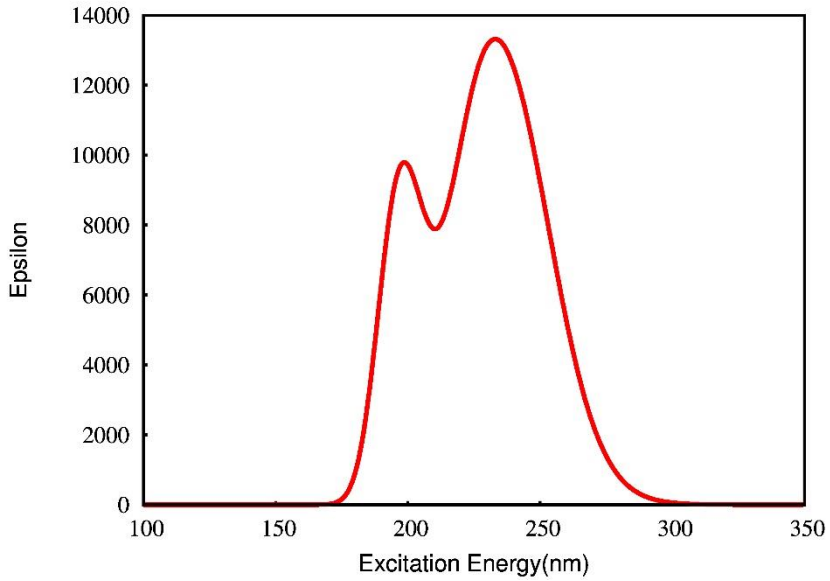
II. Supporting Movie M1: Video from the SHARC simulation on S_1 surface from 3* to N_2 evolution.

1. Additional Supporting Material.

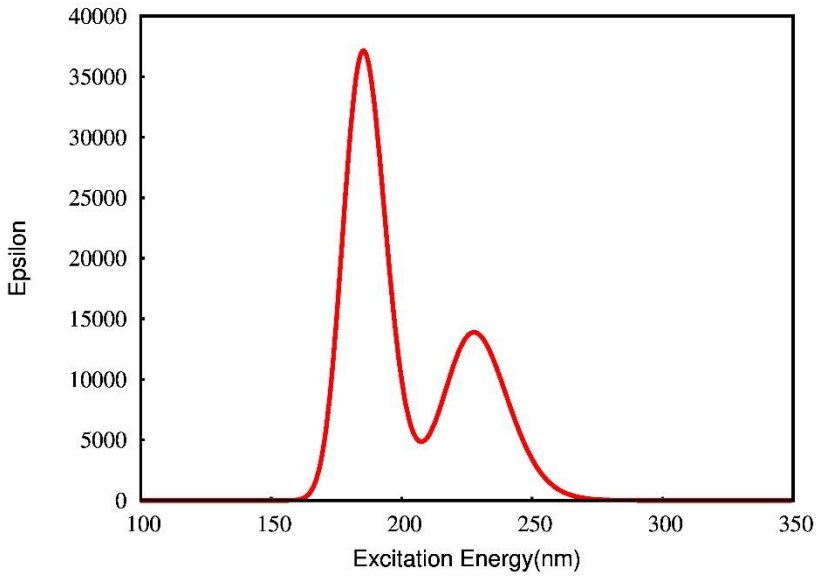
a. Table T1: Comparison of $S_0 \rightarrow S_1$ vertical excitation energy with different functional and methods. (computed UV-VIS spectra given below)

Method	Excitation Energy(S_0 to S_1)
B3LYP [6-311++g(d,p)]	253nm
ωb97XD [6-311++G(d,p)]	239nm
M062X[6-311++G(d,p)]	237nm
SA-CASSCF (aug-cc-pvdz)	221nm
SA-NEVPT2(aug-cc-pvdz)	237nm
MCQDPT (aug-cc-pvdz)	230nm

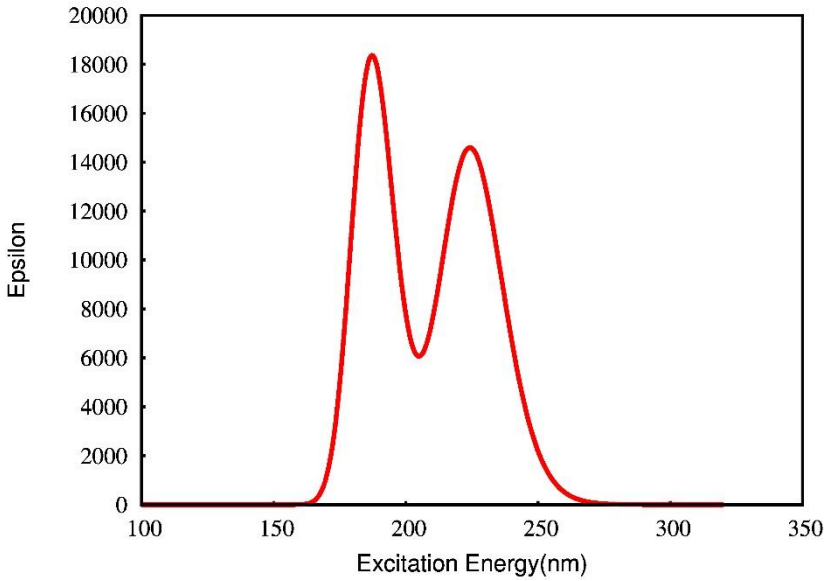
UV-VIS spectra of 1 at TD-B3LYP level of theory.



UV-VIS spectra of 1 at TD-wB97XD level of theory.

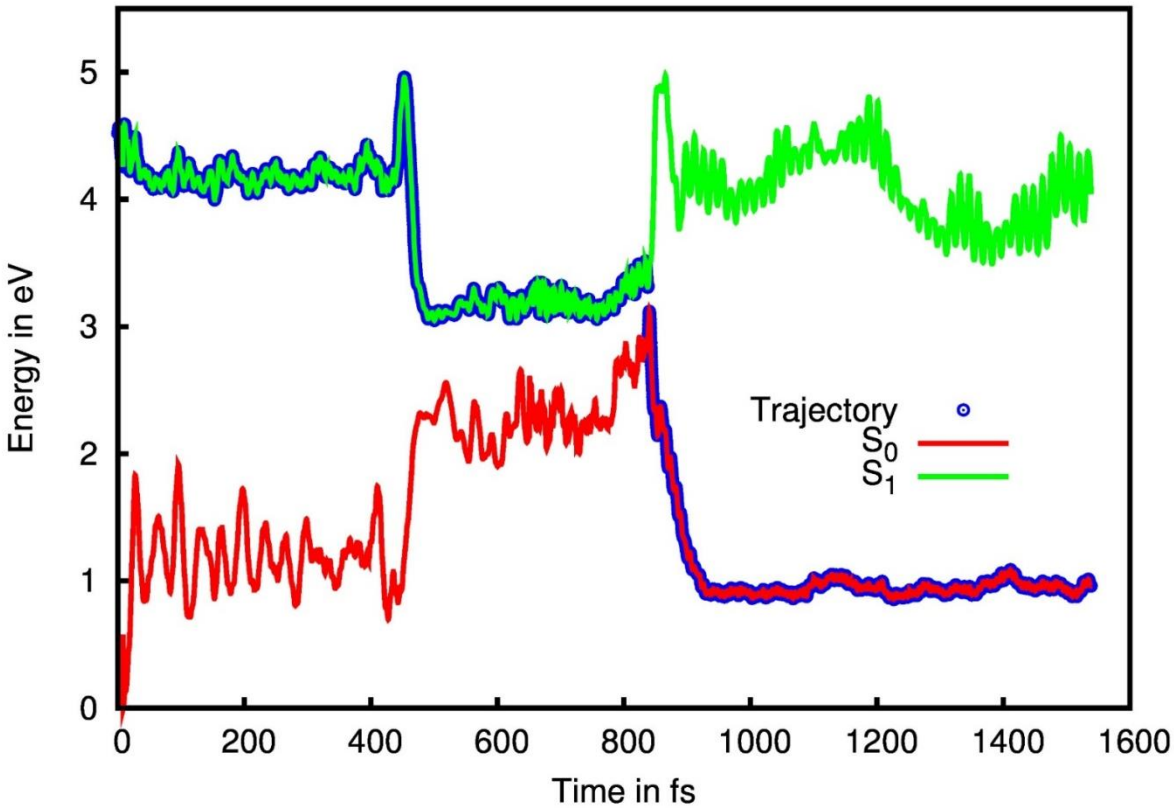


UV-VIS spectra of 1 at TD-M06-2X level of theory.

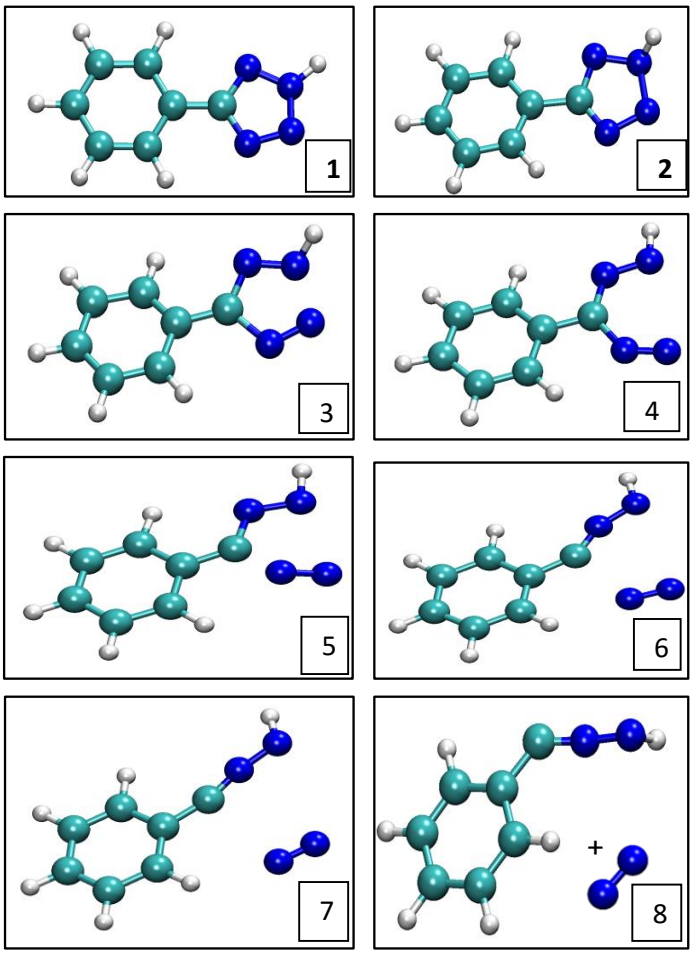


b. Figure S1:

i. Energy profile for S_0 and S_1 vs time for BOMD with S_1 as initial surface.

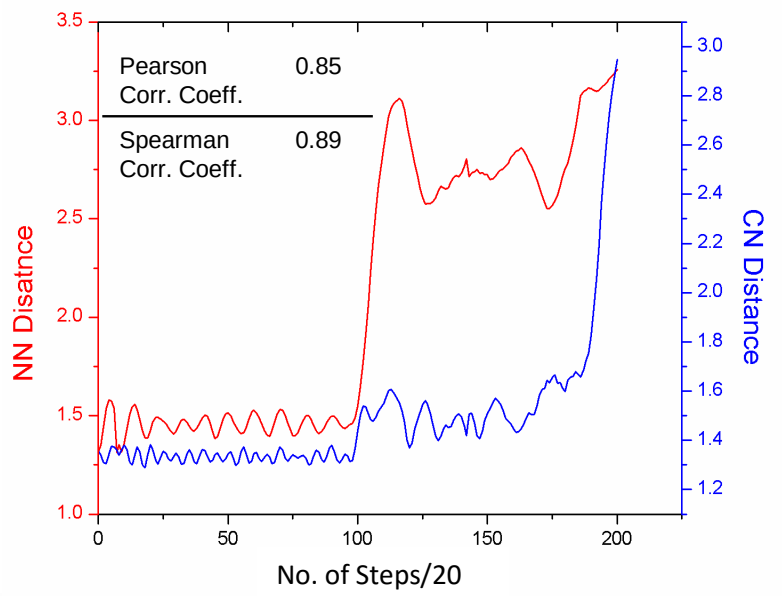


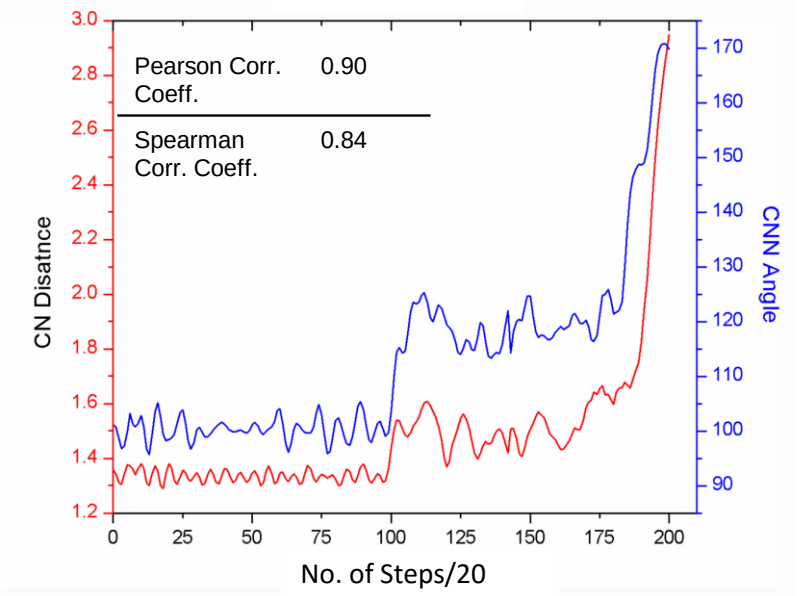
ii. Snapshots from BOMD with S_1 as initial surface.



(video of MD run separately in Supporting Movies Section)

iii. Plot of N1-N2 distance, CN distance and CNN bond angle vs time for BOMD with S_1 as initial surface depicting the correlation between them.

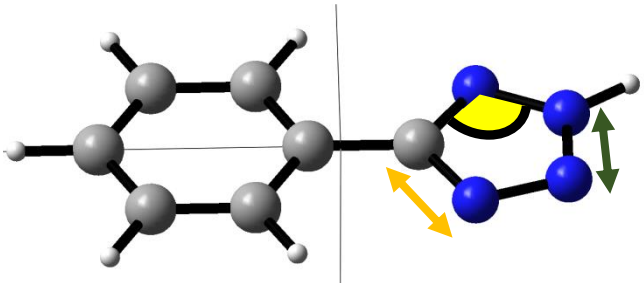




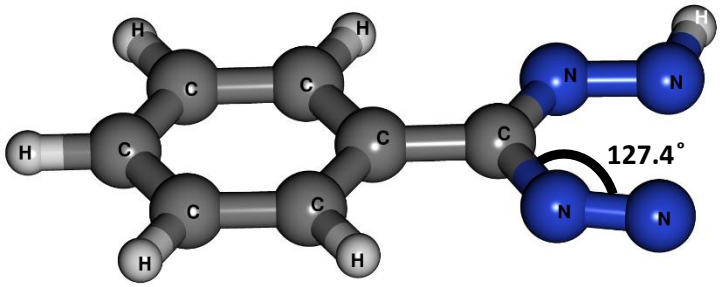
CN distance:

NN distance:

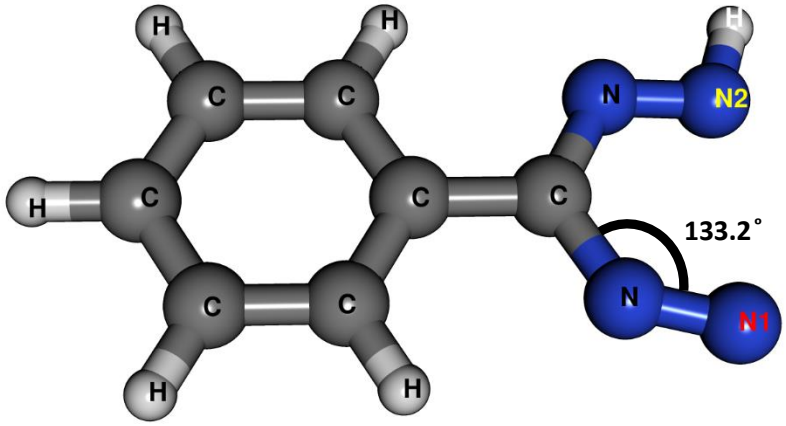
CNN bond angle:



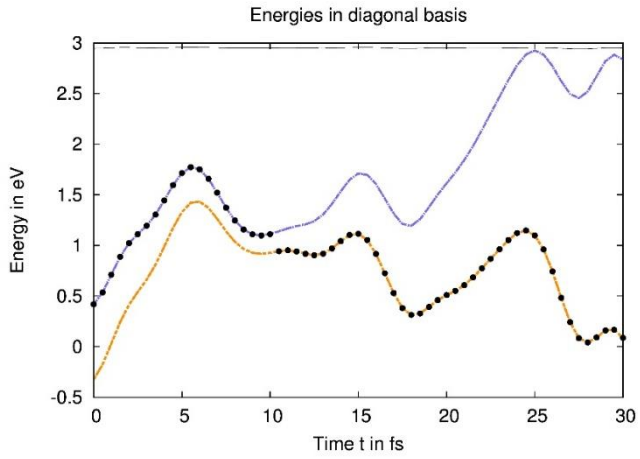
c. Figure S2: Optimized geometry of 3* at the CASSCF level of theory



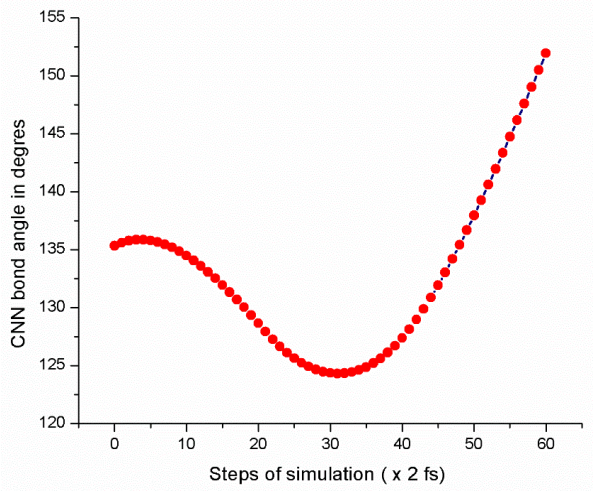
d. Figure S3: Optimized geometry of Conical Intersection with SA-CASSCF.



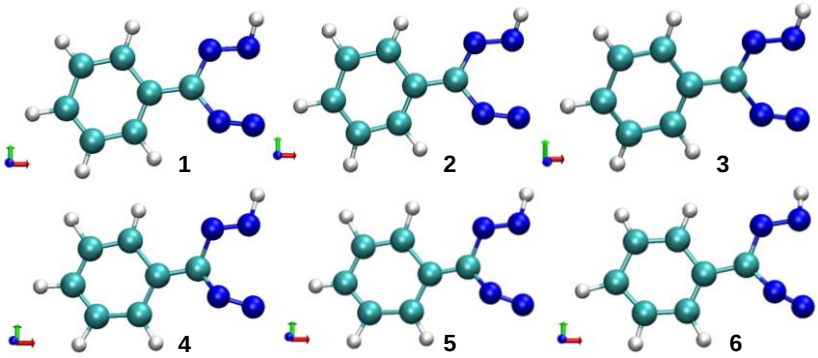
e. **Figure S4: a) Plot of energy profile from surface hopping molecular dynamics using CASSCF employing SHARC b) Plot of the change of CNN bond angle along with the dynamics. c) Snapshots from the dynamics. d) Plot of T1 diagnostic value vs N1-N2 distance along the N1-N2 dissociation coordinate.**



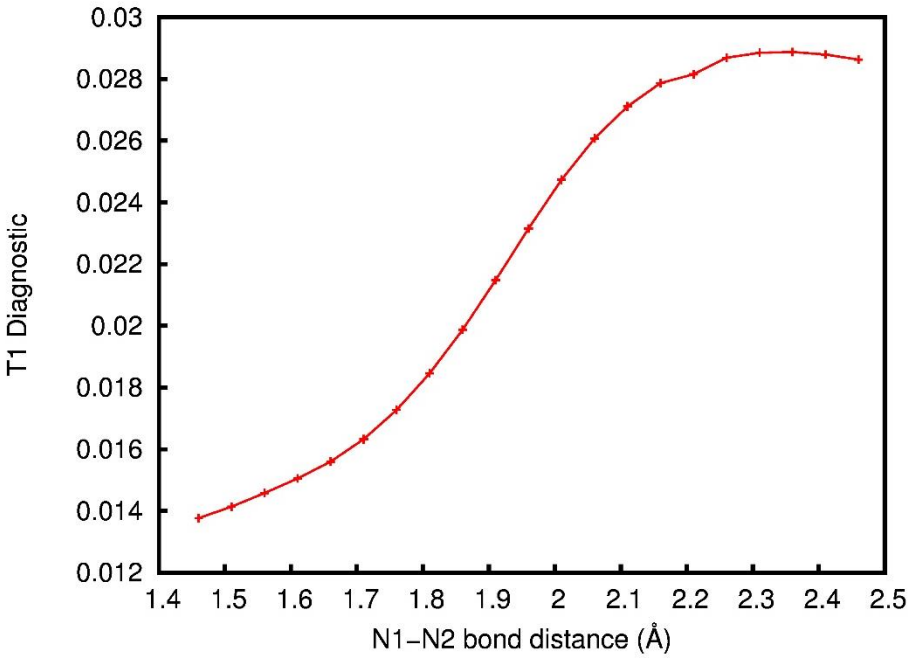
(a)



(b)

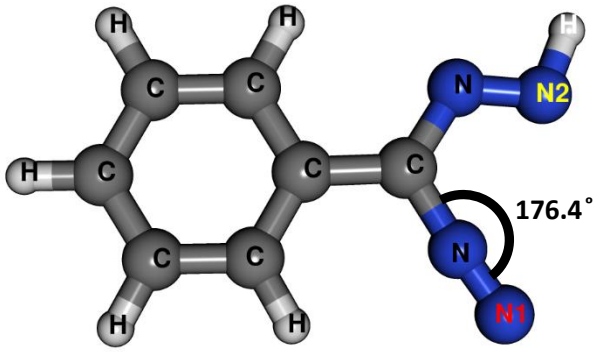


(c)

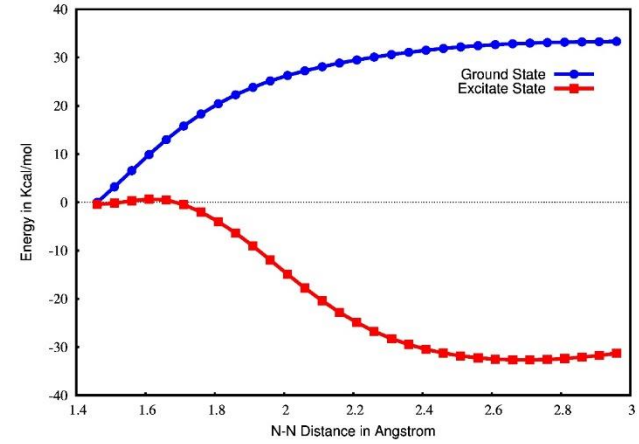


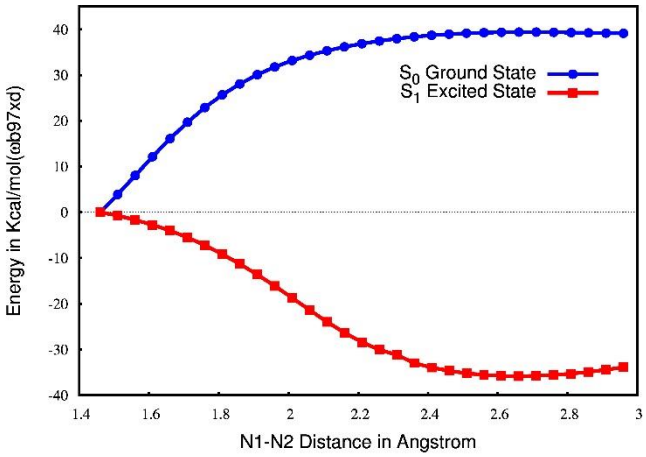
d)

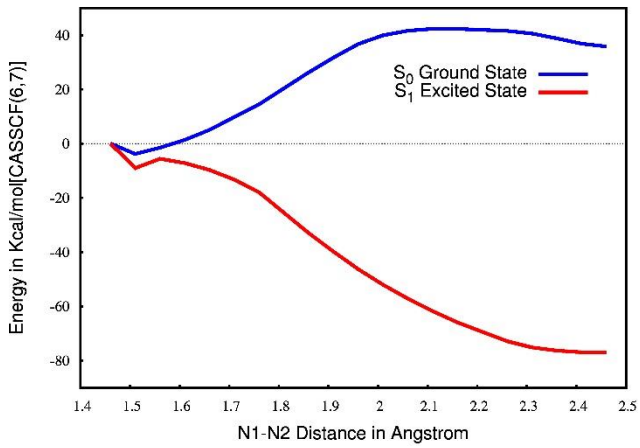
f. Figure S5: Optimized geometry of 4 at the CASSCF level of theory.



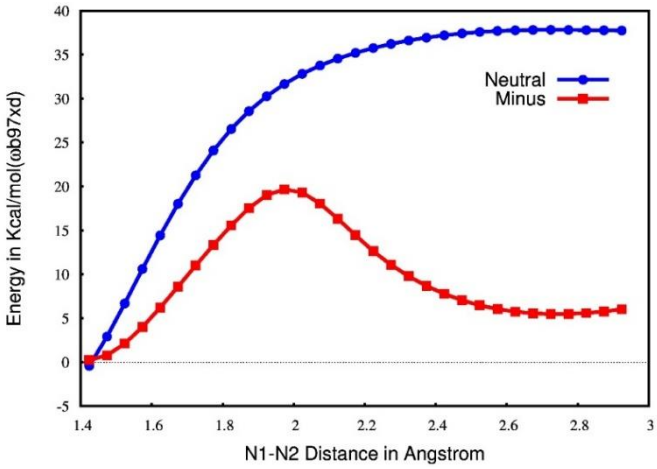
g. Figure S6: Relaxed Scan PES for N1-N2 bond dissociation of 1 in S_1 state and S_0 state at different levels of theory.



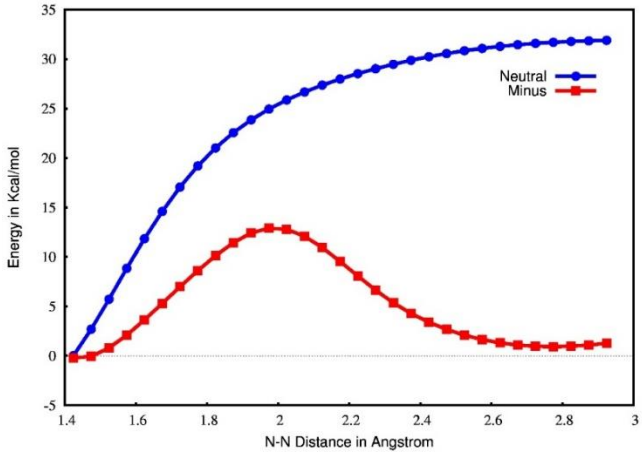




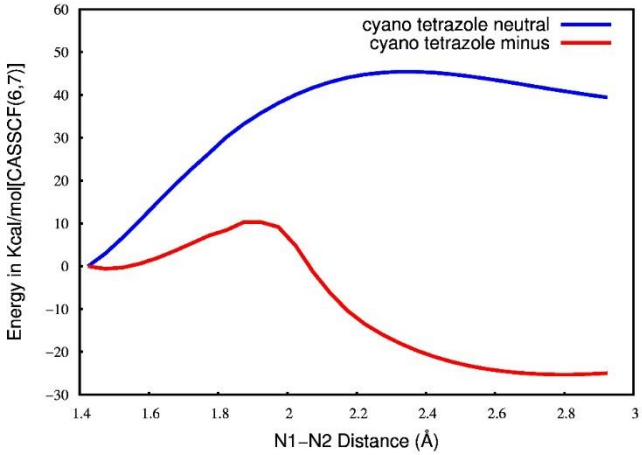
h. Figure S7: Relaxed Scan PES for N1-N2 bond dissociation of CyanoTetrazole in neutral and anionic state at different levels of theory.



a) At ωB97XD level of theory.

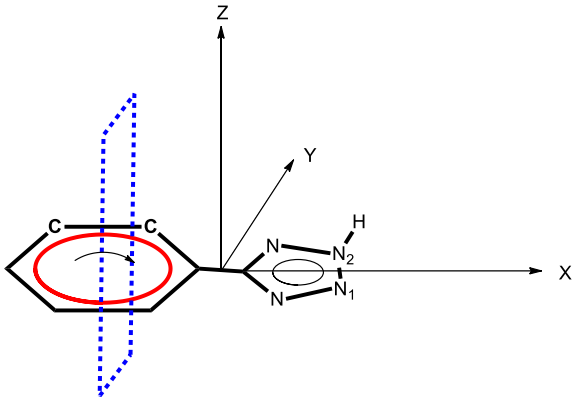


b) At B3LYP level of theory.

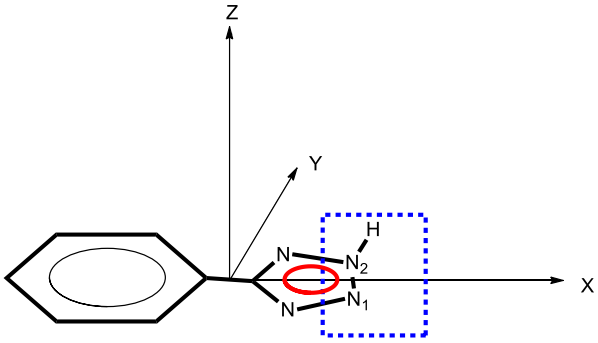


c) At CASSCF level of theory.

i. **Figure S8: The two integration planes for MICD computation of 1.**



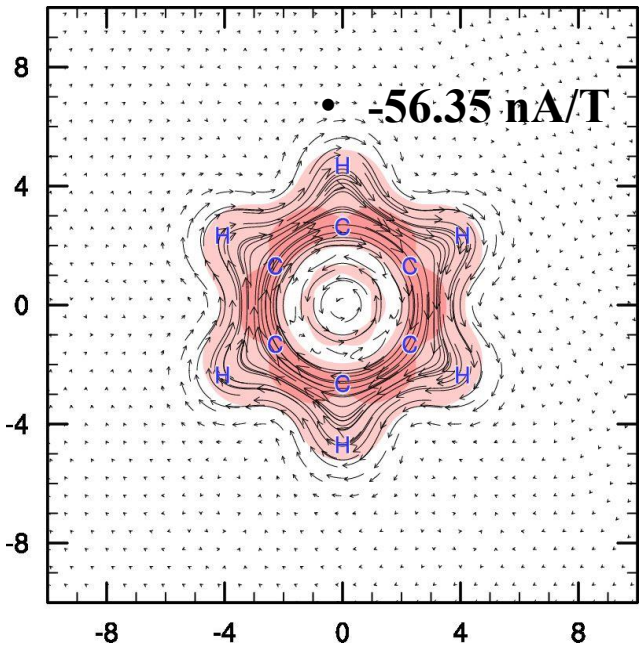
a) Integration plane for phenyl ring moiety



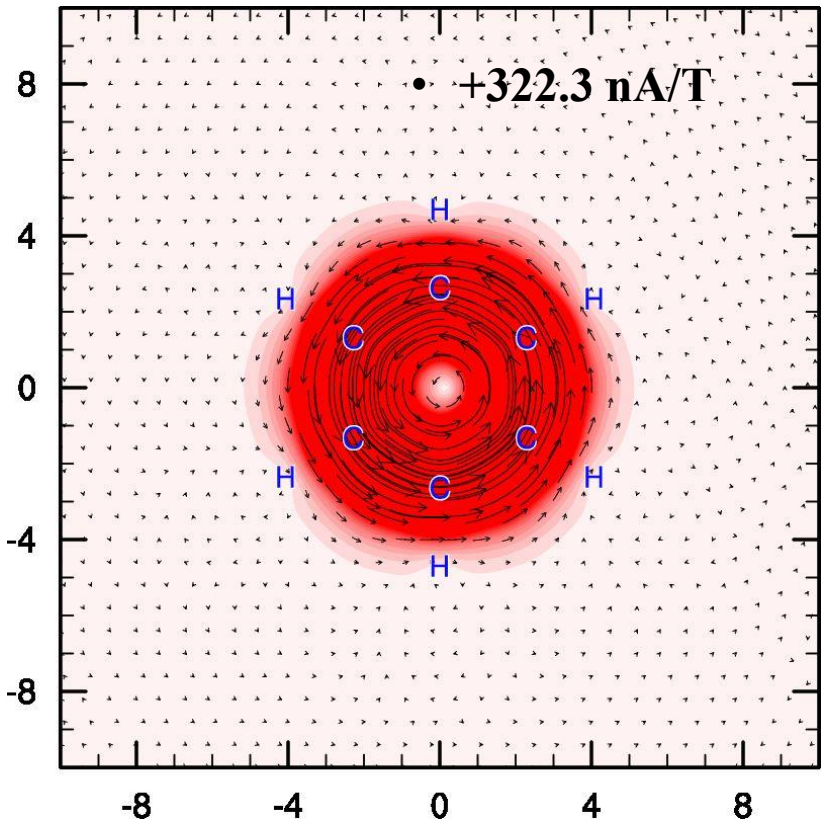
b) Integration plane for tetrazole ring moiety.

j. Figure S9: a) Ground (S_0) and b) Excited State (S_1) MICD computation of benzene.

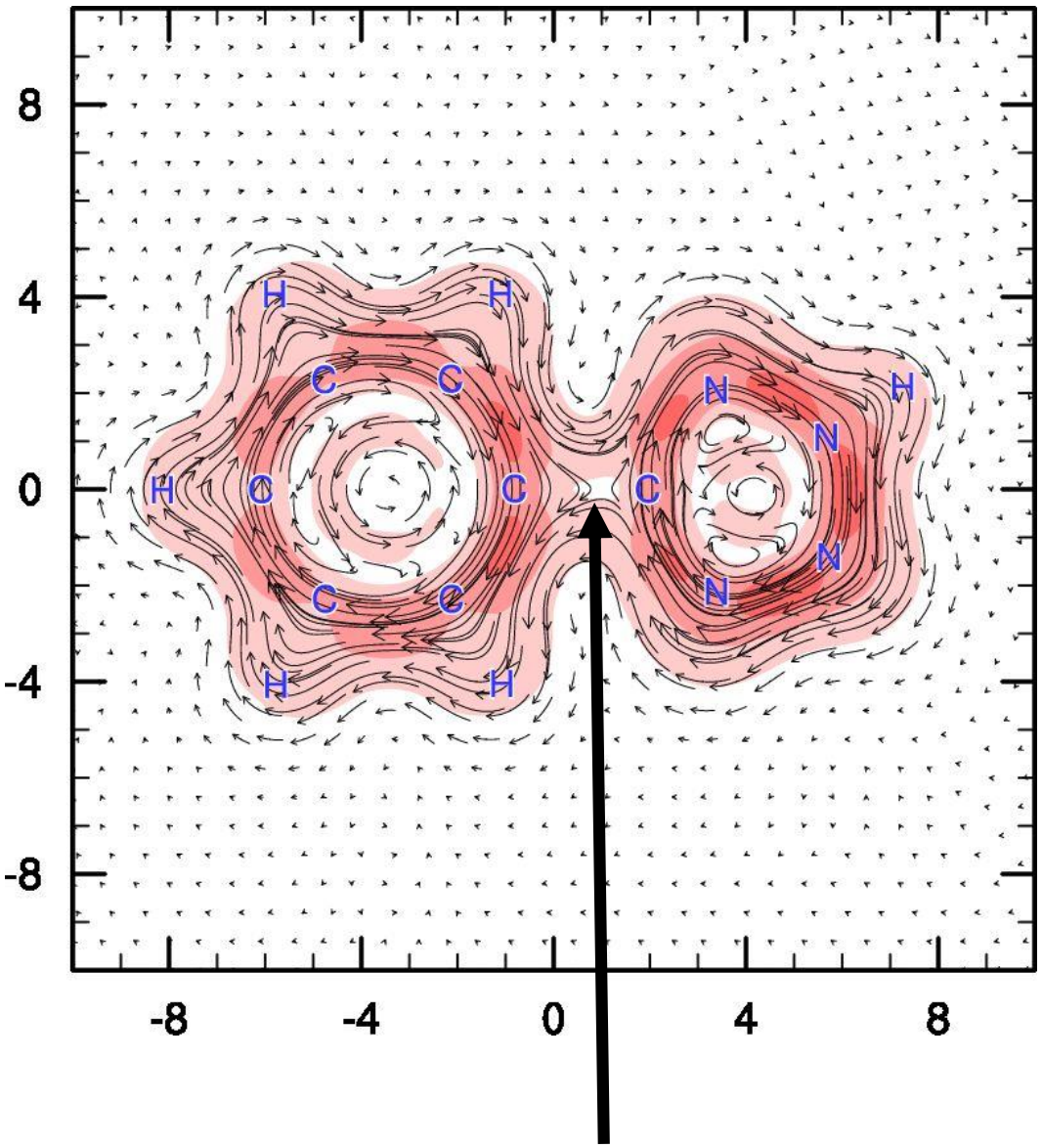
a)



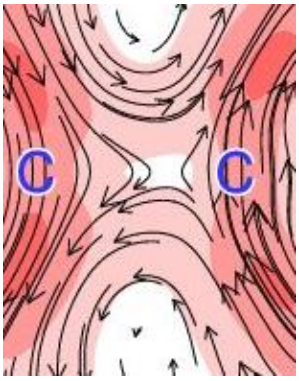
b)



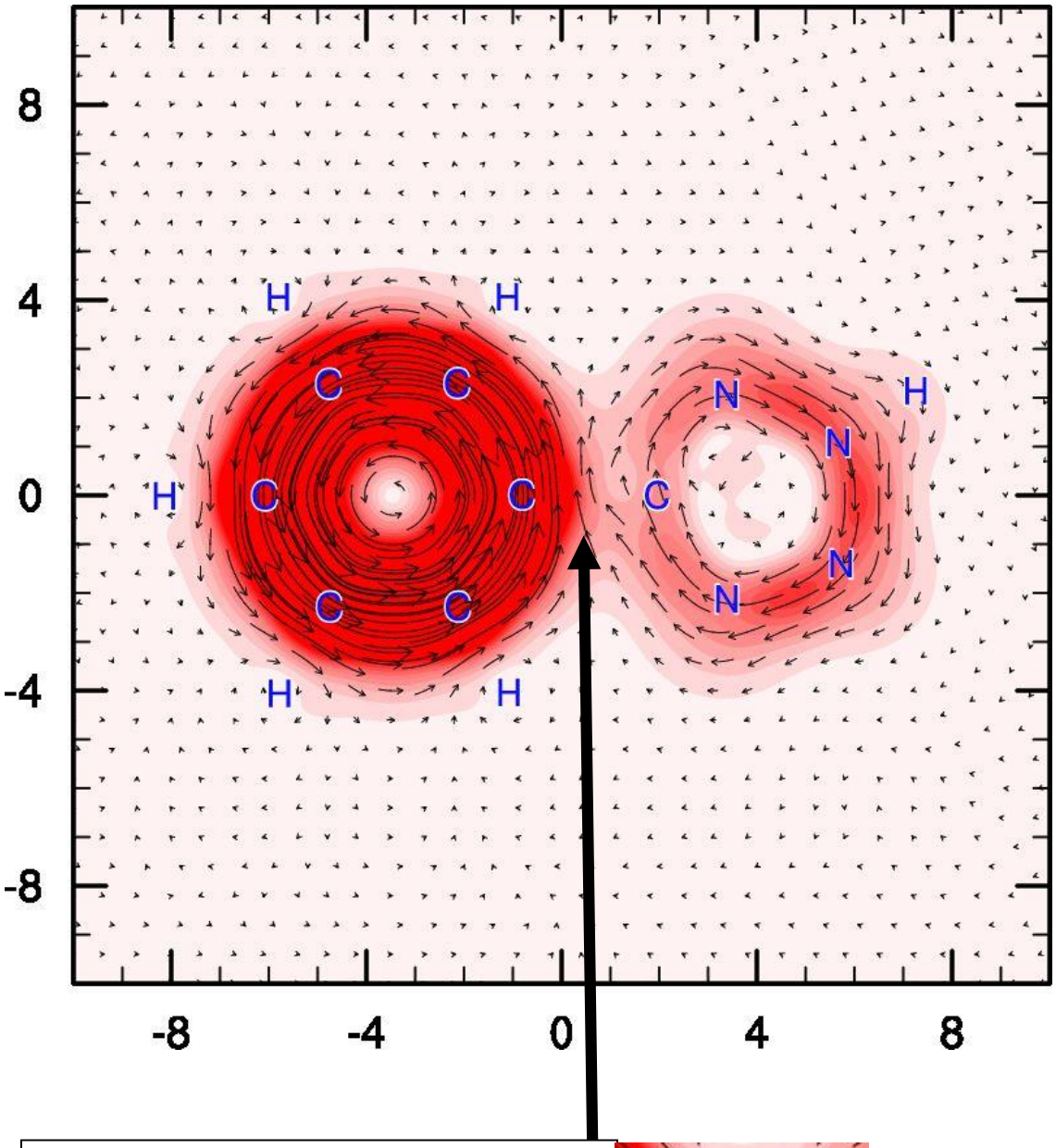
k. Figure S10: Individual Pictures and discussions on Figure 3 of main manuscript.



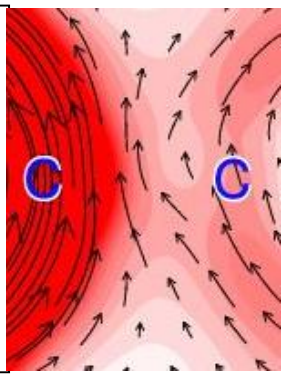
The clockwise ring current of phenyl ring and clockwise ring current on tetrazole ring are oppose each other here and hence cancel each other, depicted by the pointed white region as magnified here. **Cross Conjugation can be easily visualized herein.**



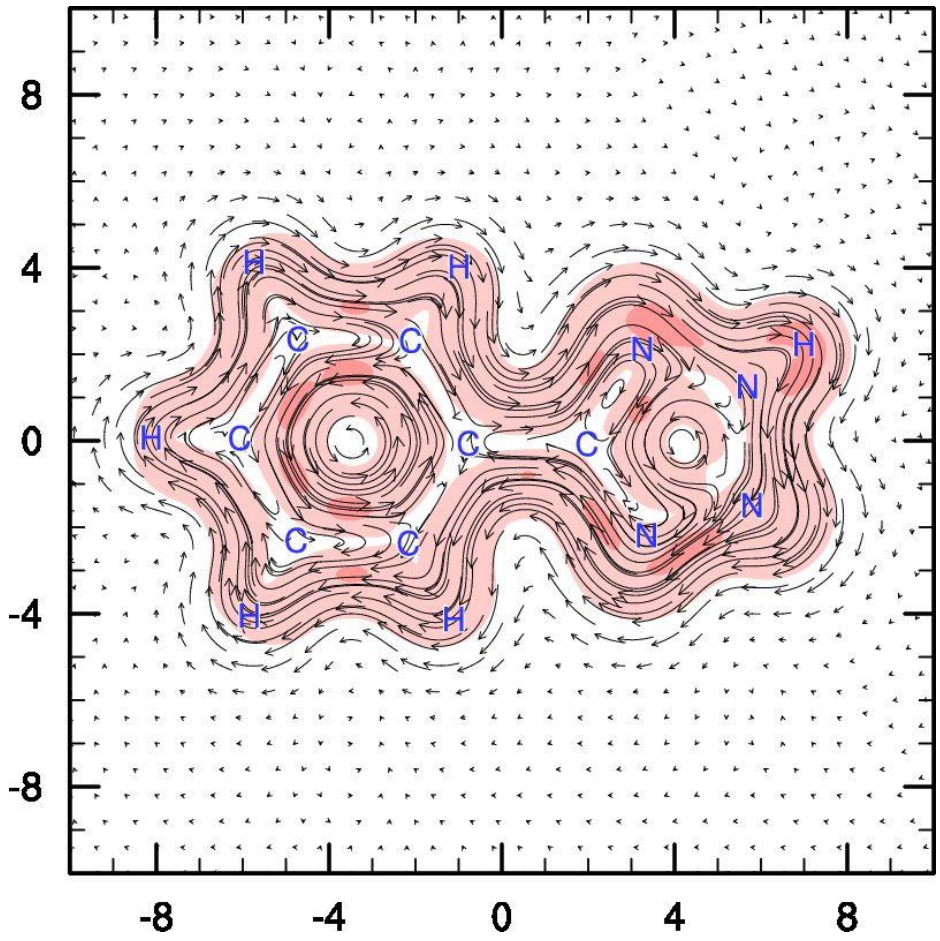
a) MICD plot for **1** in S_0 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the current



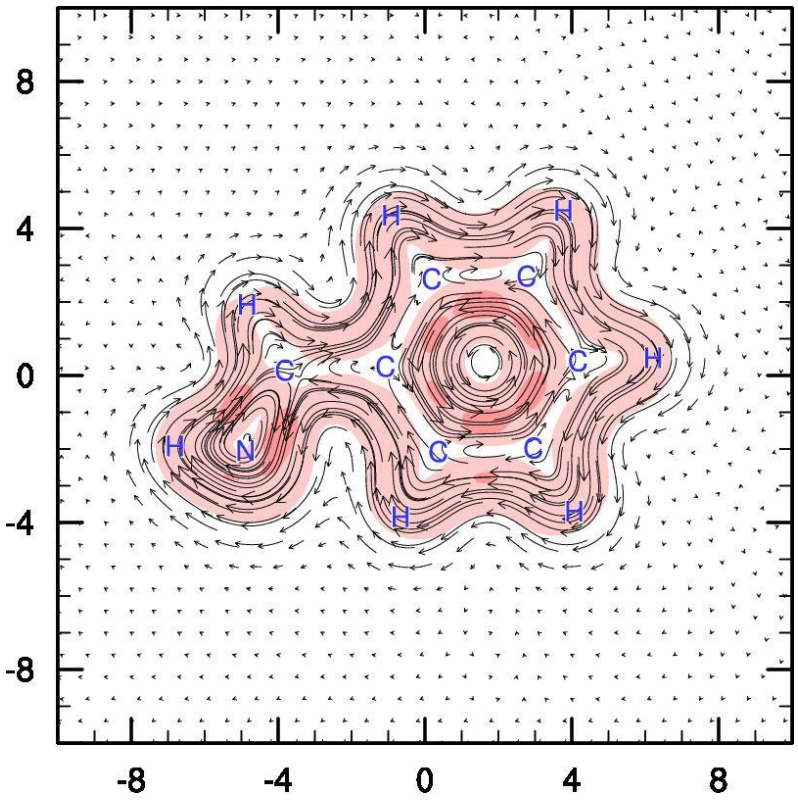
The anti-clockwise ring current of phenyl ring and clockwise ring current on tetrazole ring reinforce each other here and hence the above depicted white region has vanished and has turned red. **Cross Conjugation can be easily to be absent herein.**



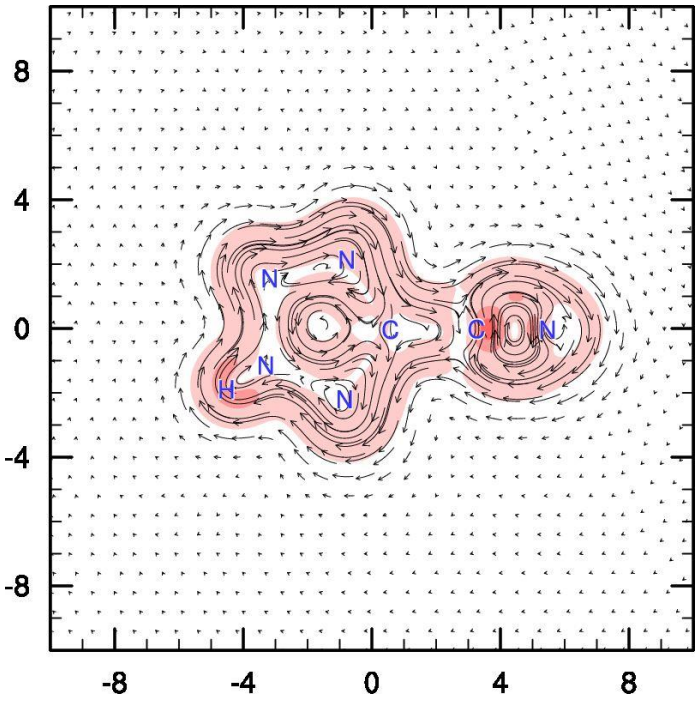
b) MICD plot for **1*** in S_1 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the curr



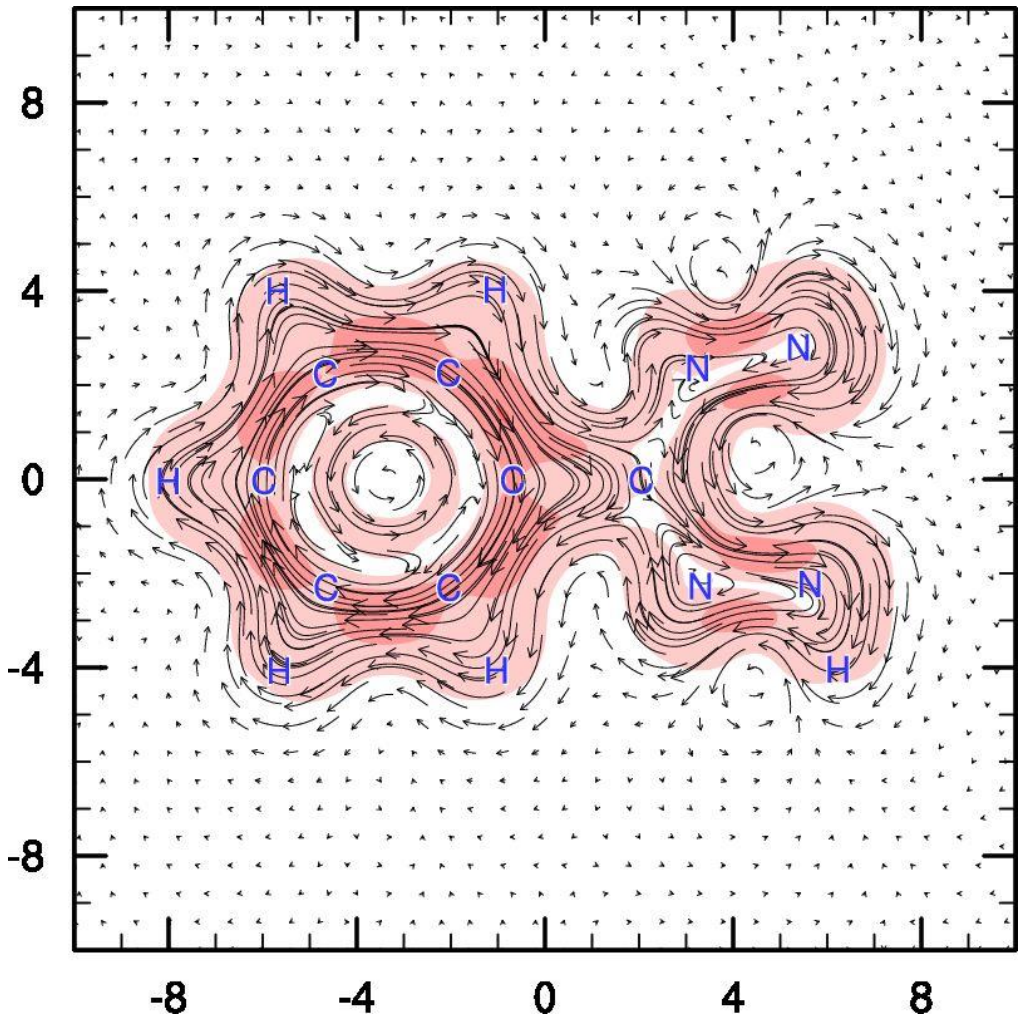
c) MICD plot for **2*** in S_1 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the current



d) MICD plot for **Ph-CH=NH$^{+\cdot}$ in S_0 state** in S_1 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the current

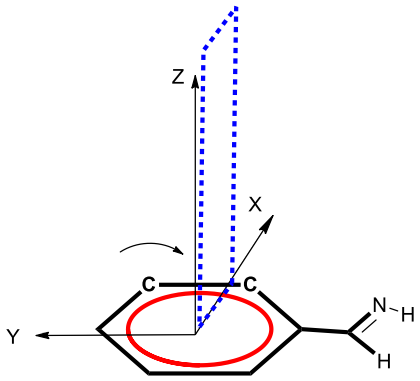


e) MICD plot for **CN-Tz$^{-\cdot}$ in S_0 state** in S_1 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the current.

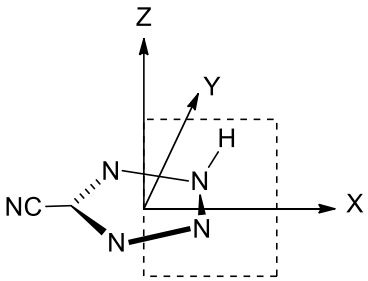


f) MICD plot for **3*** in S_1 state level of theory plotted 1.0 a0 above the molecular plane. The color intensity is proportional to the norm of the current.

l. **Table T2: Table for MICD ring current integrations for CN-Tz , CN-Tz$^{-\cdot}$, Ph-CH=NH and Ph-CH=NH$^{+\cdot}$.**



Species	2-D integration in +XZplane (Y-component) nA/T
Ph-CH=NH	-23.06
Ph-CH=NH$^{+\cdot}$	-1.68



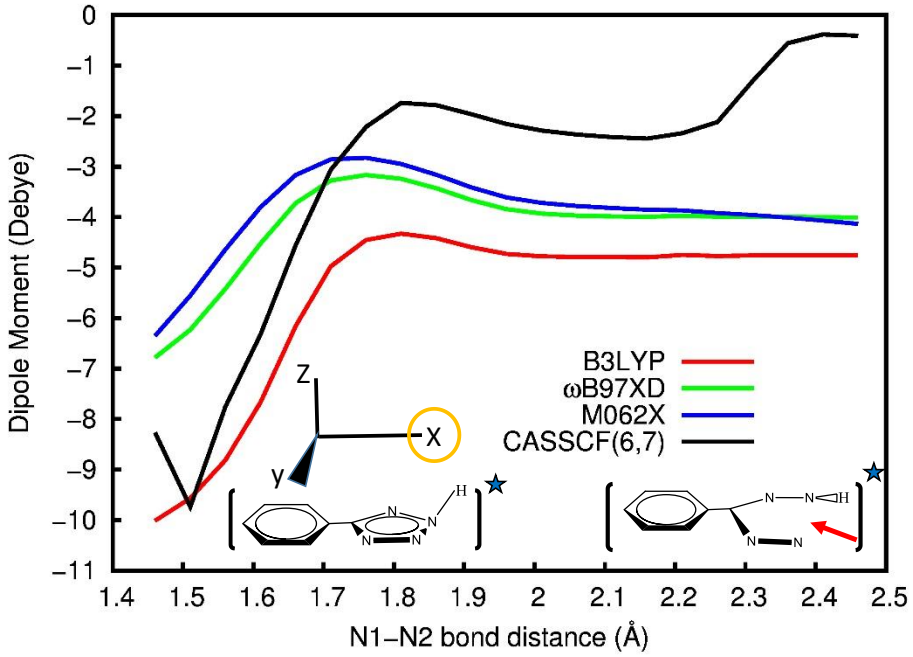
Species	2-D integration in +XZplane (Y-component) nA/T
CN-Tz	-20.6
CN-Tz$^{-\cdot}$	-4.34

m. Table T3: Table for NICS shielding constant for CN-Tz , CN-Tz-. , Ph-CH=NH and Ph-CH=$NH^{+\cdot}$.

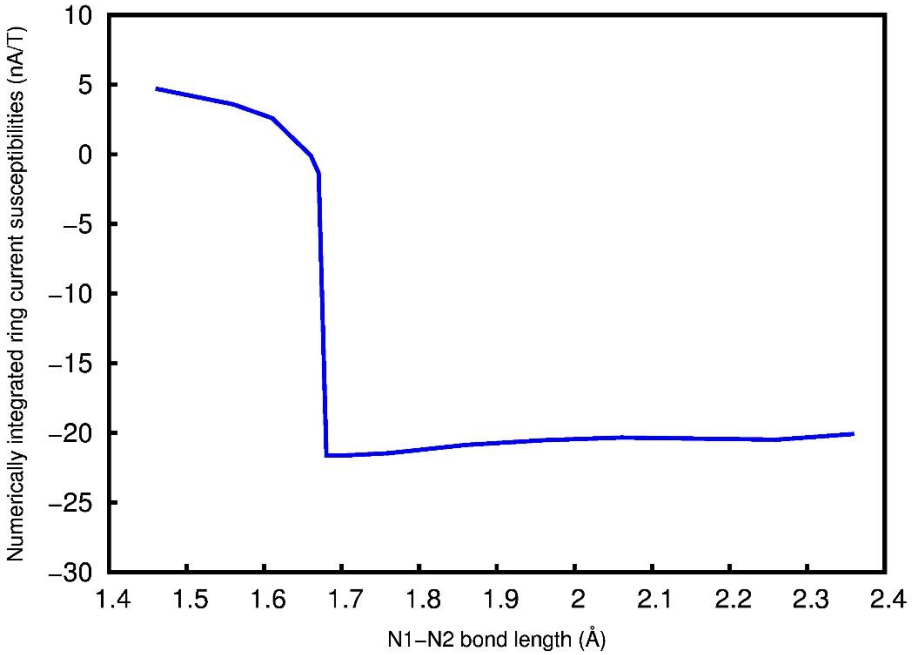
Species	$NICS(0)_{zz}$	$NICS(1)_{zz}$	$NICS(0)_{iso}$	$NICS(1)_{iso}$
CN-Tz	-23.4	-36.5	-16.1	-14.1
$CN\text{-}Tz^{-}$.	-32.2	-10.9	-10.1	-8.2

Species	$NICS(0)_{zz}$	$NICS(1)_{zz}$	$NICS(0)_{iso}$	$NICS(1)_{iso}$
Ph-CH=NH	-10.33	-26.83	-7.69	-9.89
$Ph\text{-}CH{=}NH^{+\cdot}$	+42.74	+18.08	+11.70	+4.91

n. **Figure S11: Plot of dipole moment of S_1 state along N1-N2 dissociation coordinate at different levels of theory.**



o. **Figure S12: Plot of numerically integrated current densities in the S_1 state for the phenyl moiety along the N1-N2 dissociation coordinate depicting shift from non-aromatic to aromatic transition.**



p. Supporting Video: V1

III. Supporting Movie M1: Video from the CPMD simulation on S_1 surface from 1* to N_2 evolution.

IV. Supporting Movie M1: Video from the SHARC simulation on S_1 surface from 3* to N_2 evolution.