Supporting Information

NO-induced adaptive antiaromaticity in cyclobutadiene

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1. Test the accuracy of the calculation method

Starting from the crystal structure of substituted CBD, we optimized the structure using the computational level of different density functional/6-311+G(d, p), and the key bond lengths are provided in **Table S1**. By comparison, the difference between the experimental results and the calculation results is only 0.29% when the computational level is M06-2X/6-311+G(d, p), which demonstrates that this functional is more suitable for this system.

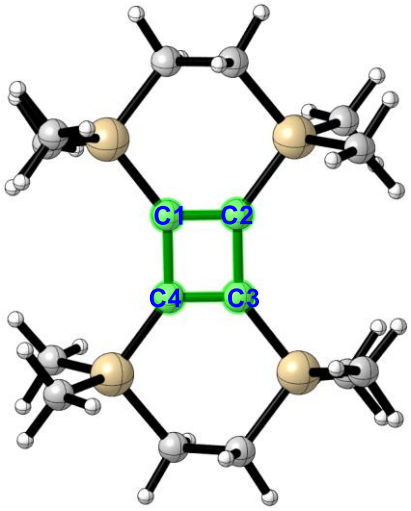


Figure S1. Structure of the experimentally synthesized substituted CBD. Highlighted bonds are used for evaluating the accuracy of DFT-optimized geometries in this work (Table S1).

Table S1. Optimized and experimental bond lengths (Å) and angles (°) of substituted CBD. The relative deviation is calculated by RD = $\sum[|(BL_{DFT}-BL_{Exp})|/BL_{Exp}]/n \times 100\%$ where BL_{DFT} and BL_{Exp} are DFT-optimized and experimental bond lengths, respectively (Unit: Å).

	C1-C2	C2-C3	C3-C4	C4-C1	<C1C4C3	<C2C3C4	RD(%)
Exp.	1.353	1.577	1.364	1.582	90.12	90.29	0.00
B3LYP	1.358	1.587	1.358	1.587	90.00	90.00	0.37
CAM-B3LYP	1.349	1.578	1.349	1.578	90.00	90.00	0.36
M06L	1.358	1.570	1.358	1.569	90.00	90.00	0.42
OPBE	1.366	1.576	1.366	1.576	90.00	90.00	0.33
PBE0	1.356	1.574	1.356	1.574	90.00	90.00	0.33
TPSS	1.367	1.591	1.367	1.591	90.00	90.00	0.53
M06-2X	1.352	1.577	1.352	1.577	90.00	90.00	0.29
wB97X-D	1.351	1.575	1.351	1.575	90.00	90.00	0.35

2. ΔE_{ST} (E_T - E_S) values of substituted CBD

The NO-substituted CBD shows antiaromaticity in the T_1 state whereas the other substituted CBDs display aromaticity, so it is expected that ΔE_{ST} of NO-substituted CBDs should be the largest, but the result is the smallest. We hypothesize that there may be strong chemical bonds stabilizing the T_1 state energy and thus leading to a small ΔE_{ST}. Since NO_2 and NO substituents are similar, and the ΔE_{ST} of NO_2-substituted CBD (NO_2-CBD) is larger (11.6 kcal/mol), so we made a comparison based on them. As shown in the Figure S2, firstly, we take NO-substituted CBD (NO-CBD) as a control, keeping the C4-N and N-O bonds unchanged, and make the four-membered ring (4MR) the same

as the 4MR of NO_2-CBD to obtain **1**. By comparison we find that the electronic energy of **1** is 2.9 kcal/mol higher than that of the compound NO-CBD. Secondly, we keep the 4MR unchanged and make the C4-N bond length 1.408 Å (C4-N bond length in compound NO_2-CBD) to obtain compound **2**, against which we find that the electronic energy of compound **2** is higher than that of compound NO-CBD by 6.6 kcal/mol. Finally, we keep both the 4MR and the C4-N bond length the same as those in the NO_2-CBD to obtain compound **3**, we find that the electronic energy of compound **3** is 7.8 kcal/mol higher than that of NO-CBD. Indeedy, the above results suggest that the approximate C4-N double bond (strong C4-N bond) is one of the key factors for stabilizing the energy of NO-CBD in the T_1 state, which results in a small ΔE_{ST}.

Table S2. ΔE_{ST} (E_T-E_S) values (kcal/mol) calculated of substituted CBD. Level of theory: CCSD/cc-pvtz//(U)M06-2X/6-311+G(d, p).

	H	CH_3	NH_2	$N(CH_3)_2$	OH	OCH_3	F	SiH_3	PH_2	SH
$\Delta E_{ST}(E_T\text{-}E_S)$	12.2	13.5	13.8	14.1	13.6	12.1	14.2	12.6	13.8	12.5
	Cl	NH_3^+	NO_2	NO	CHO	$COCH_3$	COOH	$COOCH_3$	$CONH_2$	CN
$\Delta E_{ST}(E_S\text{-}E_T)$	12.8	13.5	11.6	0.3	9.2	9.9	10.8	10.5	11.2	11.2

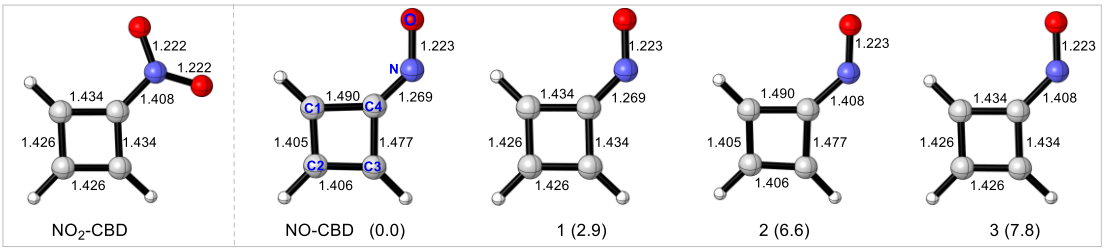


Figure S2. Some compounds obtained by changing some key bond lengths in NO-substituted CBD (NO-CBD) and their relative energies (kcal/mol) (relative energies are provided in parentheses).

3. Dipole moments of substituted CBD

As we all know, the dipole moment is the magnitude of the charge and the distance between the centers of the positive and negative charges, which has been denoted by the Greek letter 'μ'. Specifically, dipole moment (μ) = charge (q) * distance of separation (d). It is a vector quantity with the direction specified as pointing from the positive charge center to the negative charge center. For the system with charge, the separation of positive and negative charges is more serious, and the dipole moment tends to be larger.

As shown in Table S3, we provide dipole moment of different substituted CBD in the S_0 and T_1 states. For the convenience of the discussion, we have ordered the triplet dipole moments here. In general, electron-withdrawing substituents tend to separate positive and negative charges easily, those of electron-withdrawing substituted CBD that belong to the π-acceptor type substituted CBD possess larger dipole moments in our system. NO substituent is not the strongest π acceptor, so its dipole moment is not much larger than other systems. In a word, there would be a strong connection between the dipole moment and the type of substituent group in the current system.

Table S3. Dipole moments of substituted CBD in the S_0 and T_1 states (unit: D).

Substituent (R)	Dipole Moment (T_1)	Dipole Moment (S_0)
H	0.001	0.001
CH_3	0.632	0.537
SiH_3	0.663	0.596
PH_2	0.833	0.814
SH	0.945	0.900
Cl	1.277	1.432
F	1.321	1.571
OH	1.551	1.818
OCH_3	1.694	1.790
NH_2	2.094	1.935
$N(CH_3)_3$	2.277	2.215
NO	3.317	4.415
$COCH_3$	3.716	3.332
CHO	3.985	3.442
$CONH_2$	4.018	3.915
CN	4.572	4.430
$COOCH_3$	5.181	4.956
COOH	5.341	5.092
NO_2	5.640	5.041
NH_3^+	5.702	5.963

4. ACID plots of substituted CBD in the S_0 and T_1 states

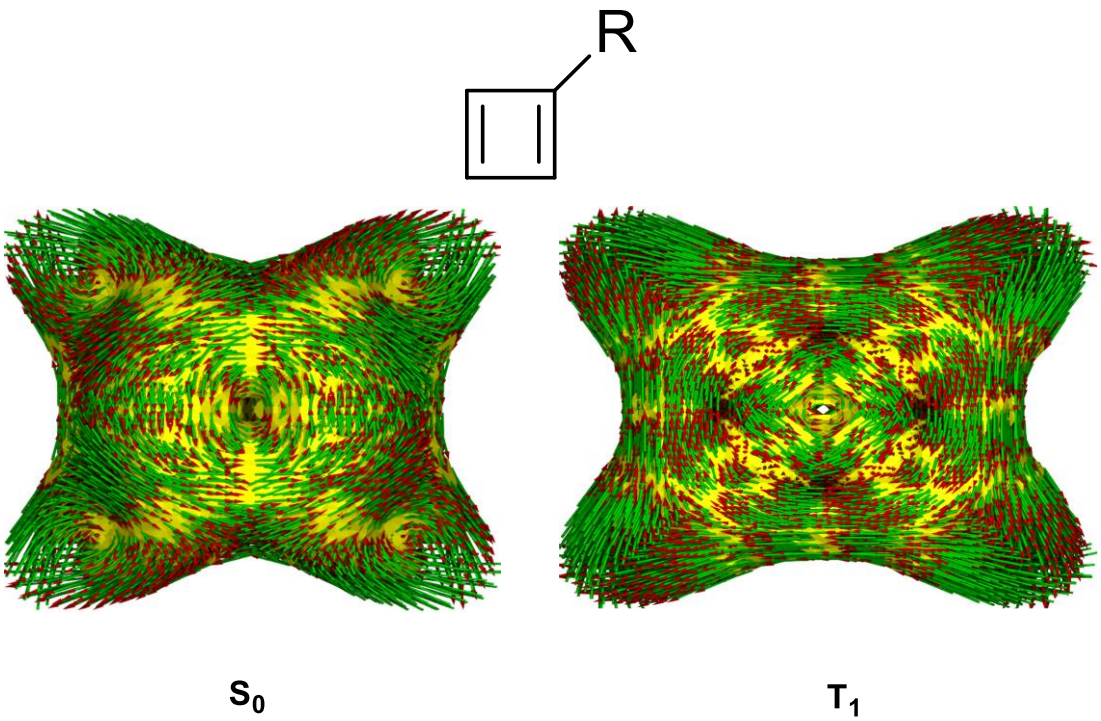


Figure S3. ACID plots in the S_0 and T_1 states when R = H. Isovalue for density surfaces: 0.035.

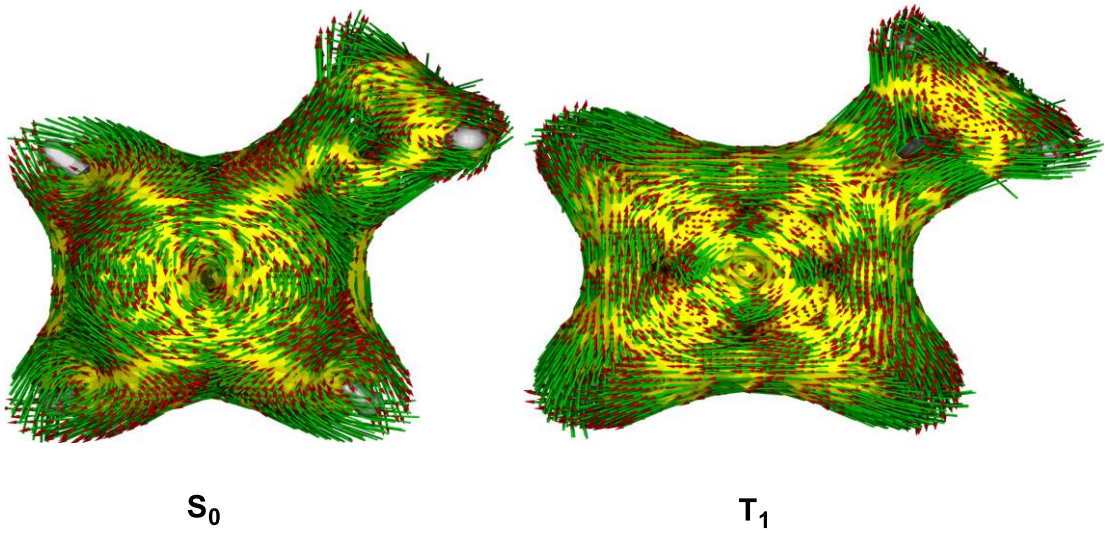


Figure S4. ACID plots in the S_0 and T_1 states when R = CH_3. Isovalue for density surfaces: 0.035.

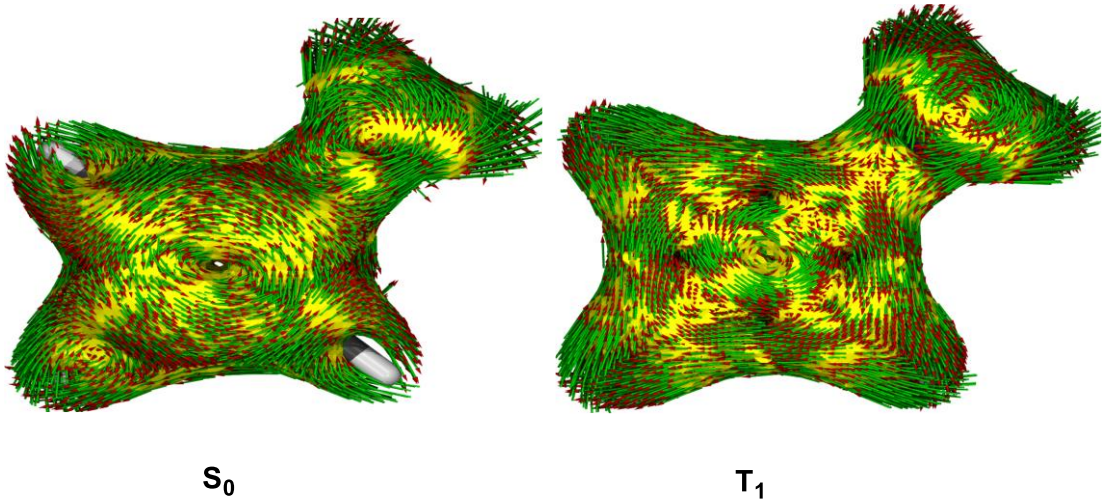


Figure S5. ACID plots in the S_0 and T_1 states when R = NH_2. Isovalue for density surfaces: 0.035.

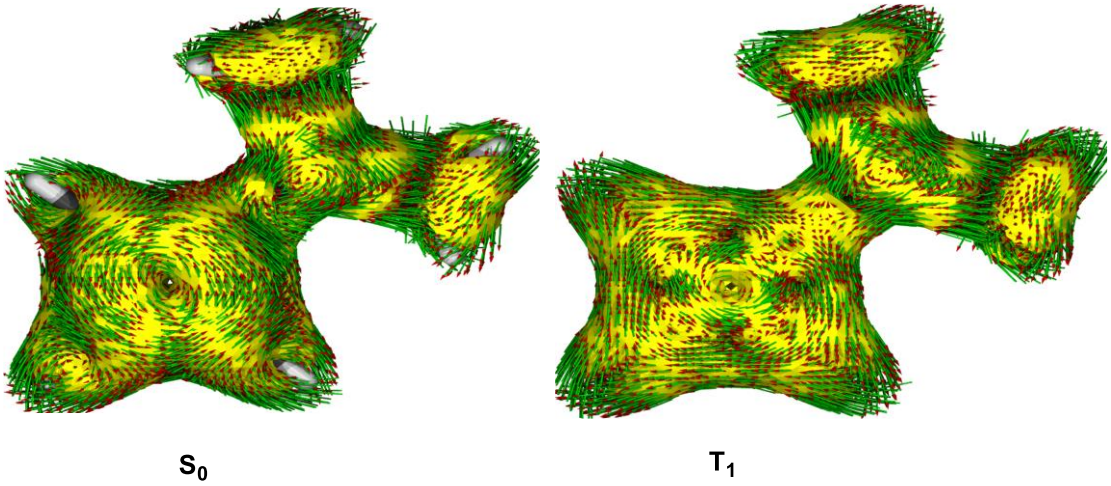


Figure S6. ACID plots in the S_0 and T_1 states when R = $N(CH_3)_2$. Isovalue for density surfaces: 0.035.

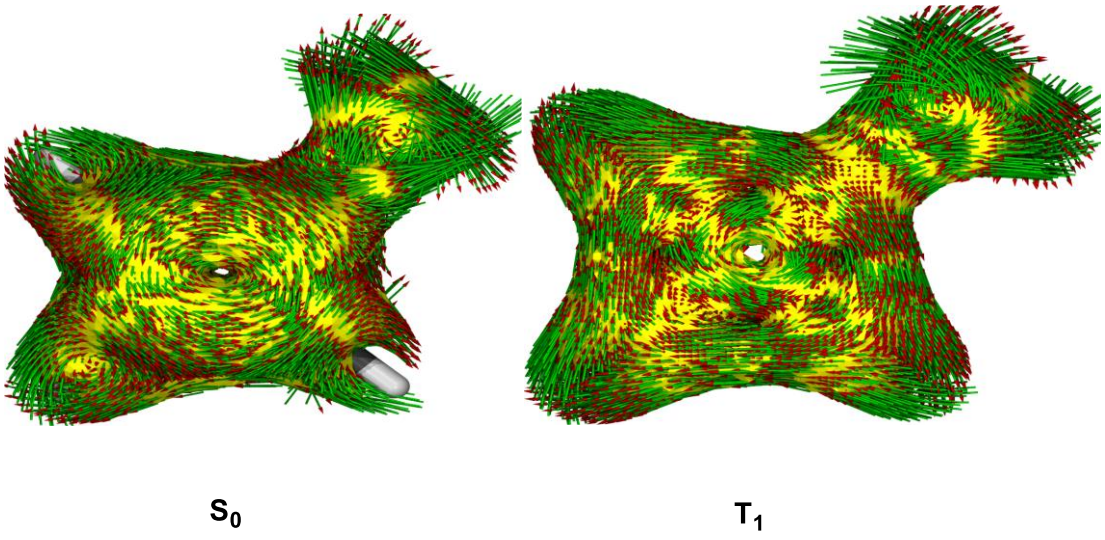


Figure S7. ACID plots in the S_0 and T_1 states when R = OH . Isovalue for density surfaces: 0.035.

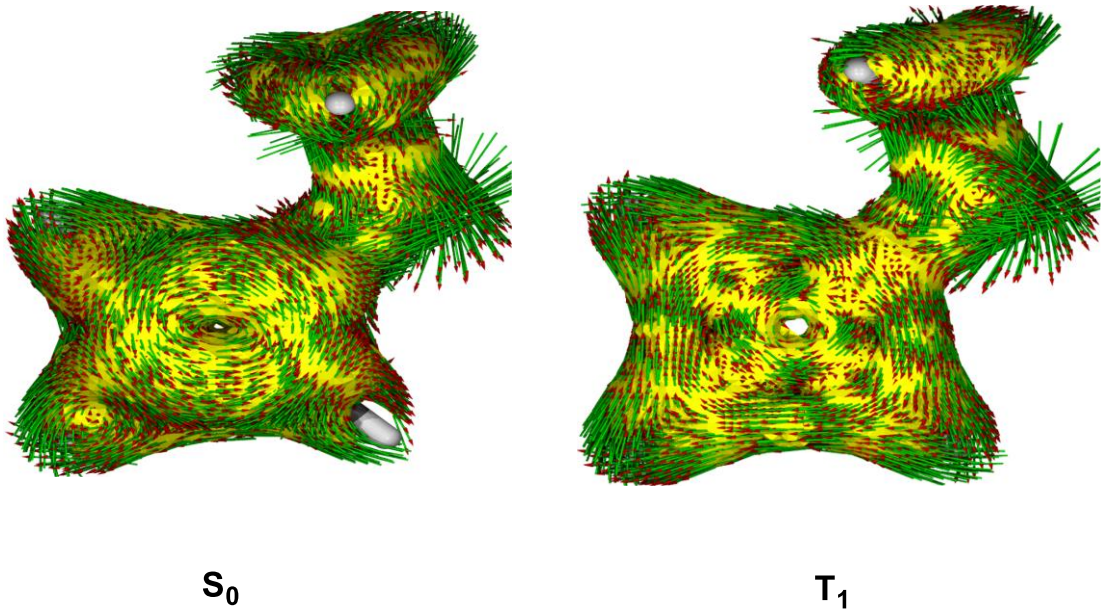


Figure S8. ACID plots in the S_0 and T_1 states when R = OCH_3 . Isovalue for density surfaces: 0.035.

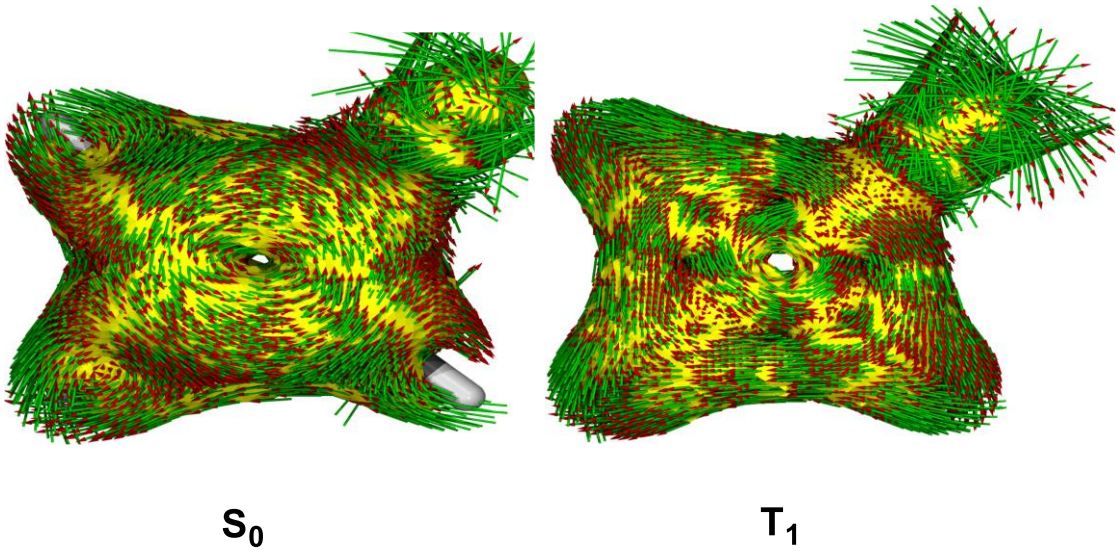


Figure S9. ACID plots in the S_0 and T_1 states when R = F . Isovalue for density surfaces: 0.035.

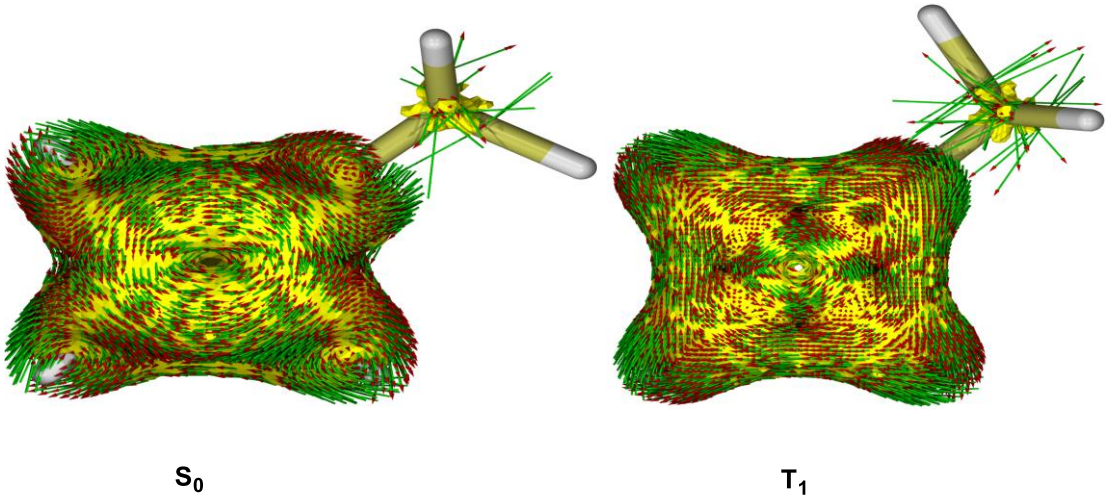


Figure S10. ACID plots in the S_0 and T_1 states when R = SiH_3. Isovalue for density surfaces: 0.035.

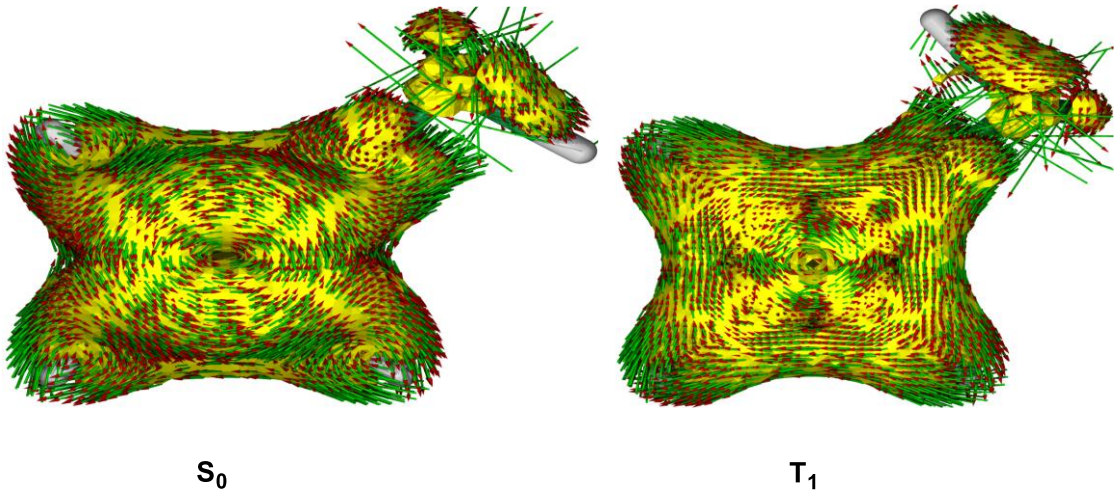


Figure S11. ACID plots in the S_0 and T_1 states when R = PH_2. Isovalue for density surfaces: 0.035.

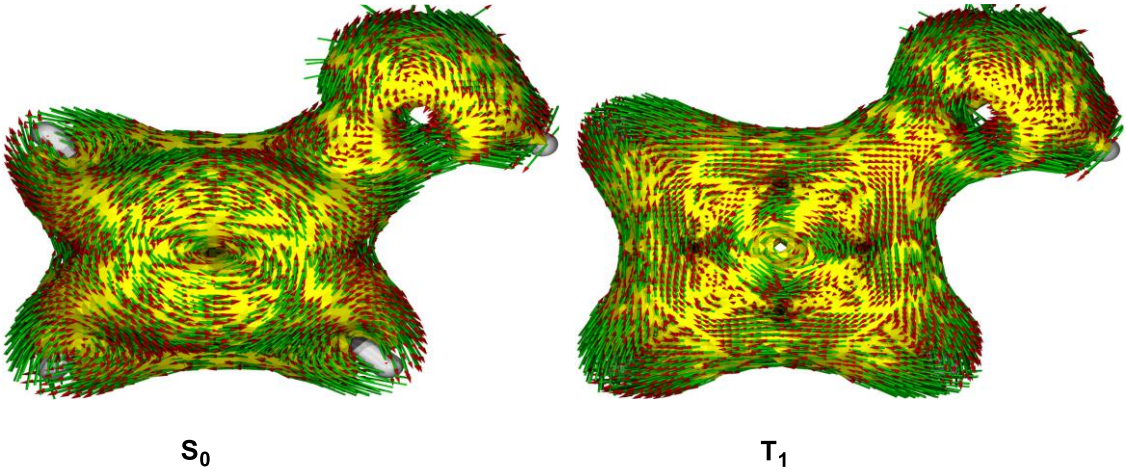


Figure S12. ACID plots in the S_0 and T_1 states when R = SH. Isovalue for density surfaces: 0.035.

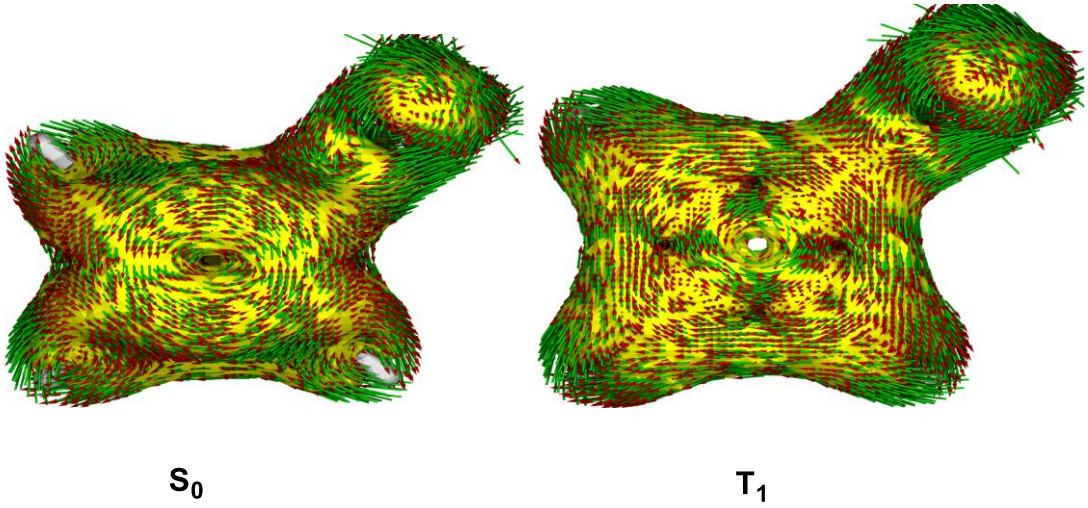


Figure S13. ACID plots in the S_0 and T_1 states when R = Cl. Isovalue for density surfaces: 0.035.

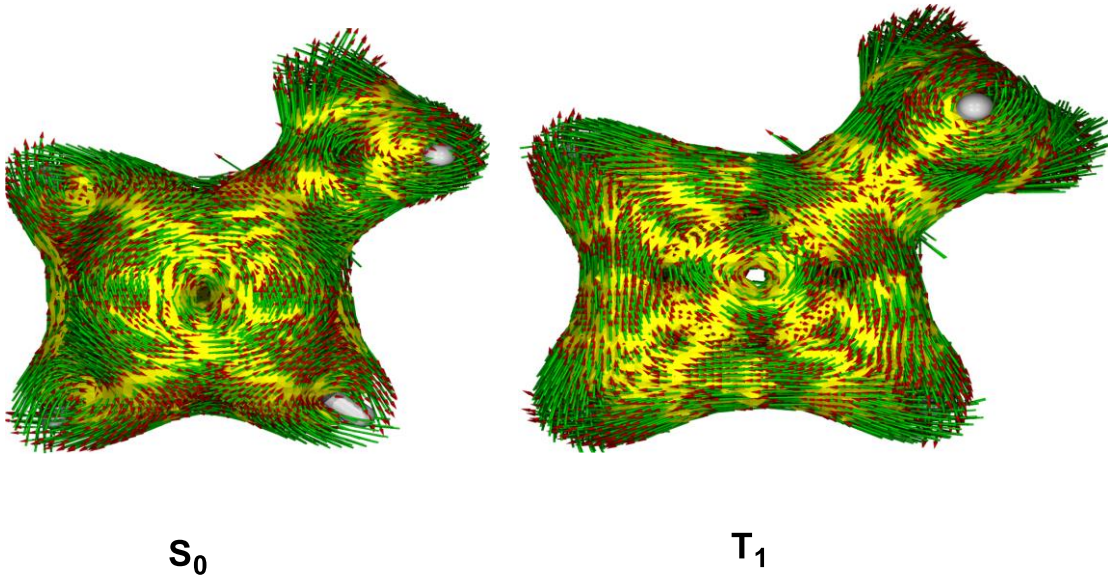


Figure S14. ACID plots in the S_0 and T_1 states when R = NH_3^+. Isovalue for density surfaces: 0.035.

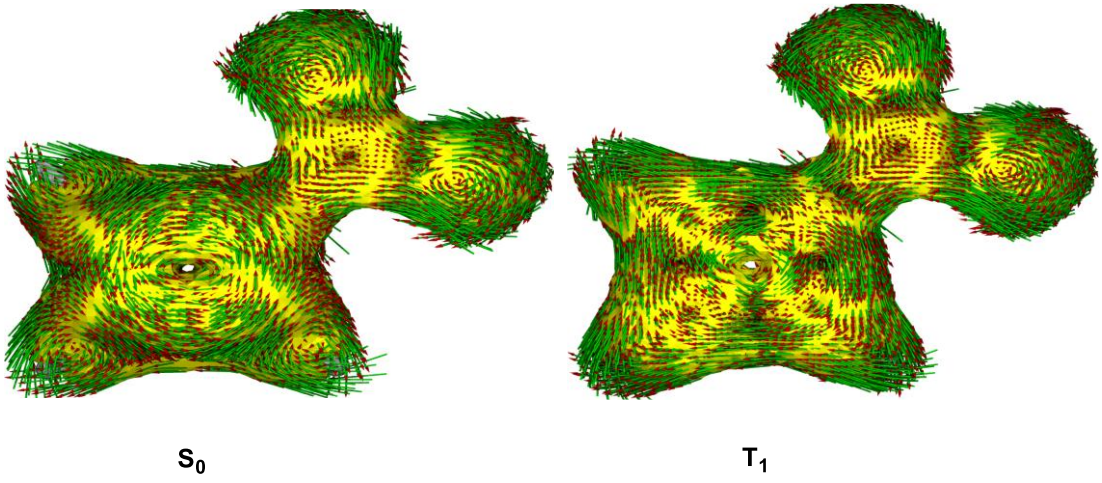


Figure S15. ACID plots in the S_0 and T_1 states when R = NO_2 . Isovalue for density surfaces: 0.035.

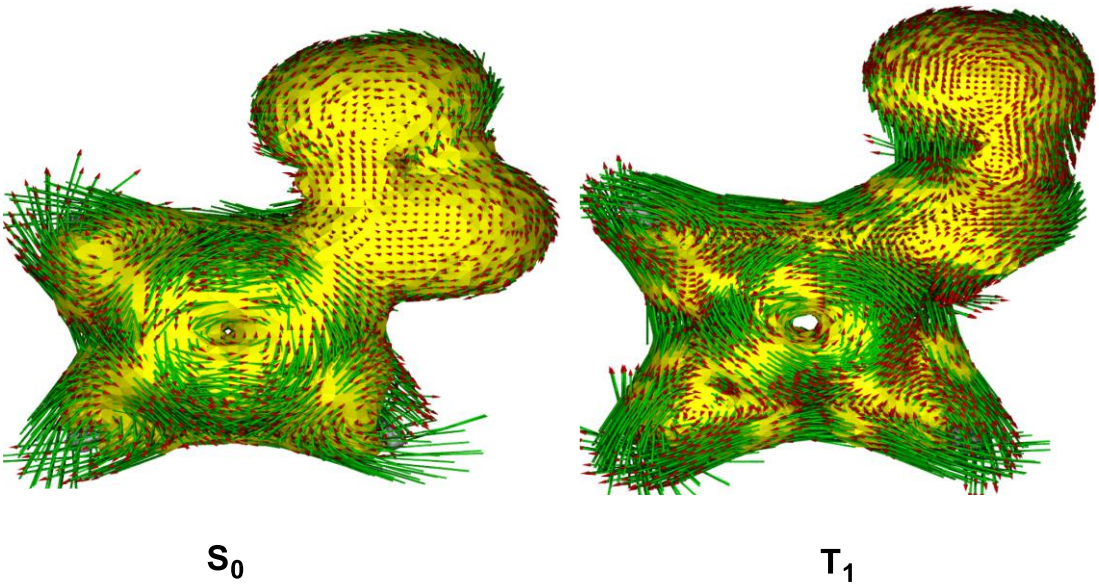


Figure S16. ACID plots in the S_0 and T_1 states when R = NO . Isovalue for density surfaces: 0.035.

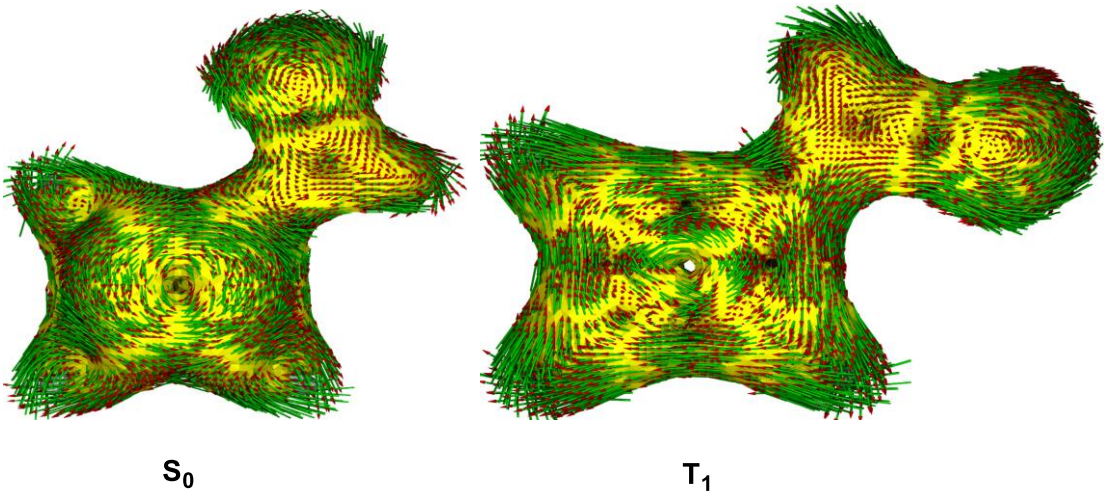


Figure S17. ACID plots in the S_0 and T_1 states when R = CHO . Isovalue for density surfaces: 0.035.

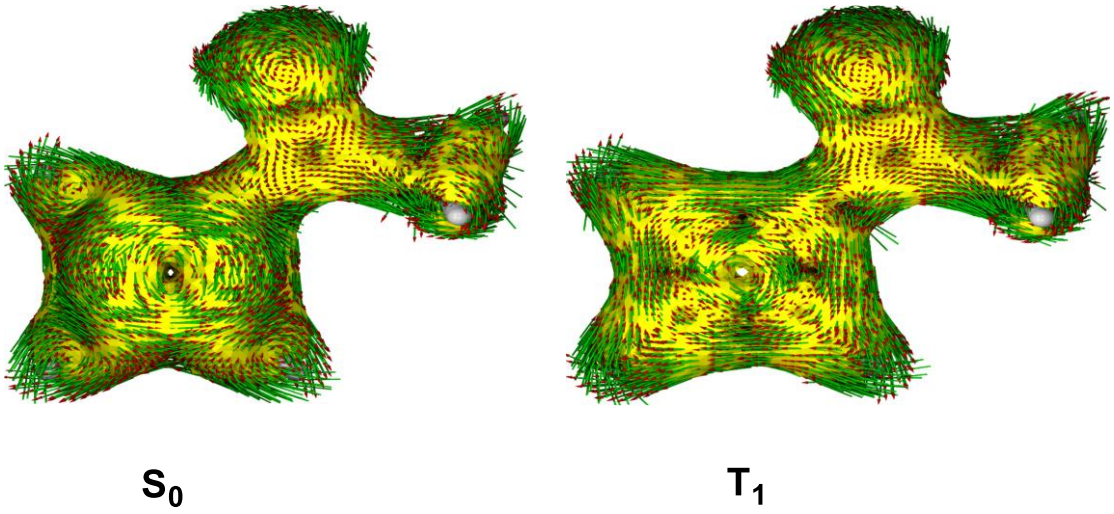


Figure S18. ACID plots in the S_0 and T_1 states when R = $COCH_3$. Isovalue for density surfaces: 0.035.

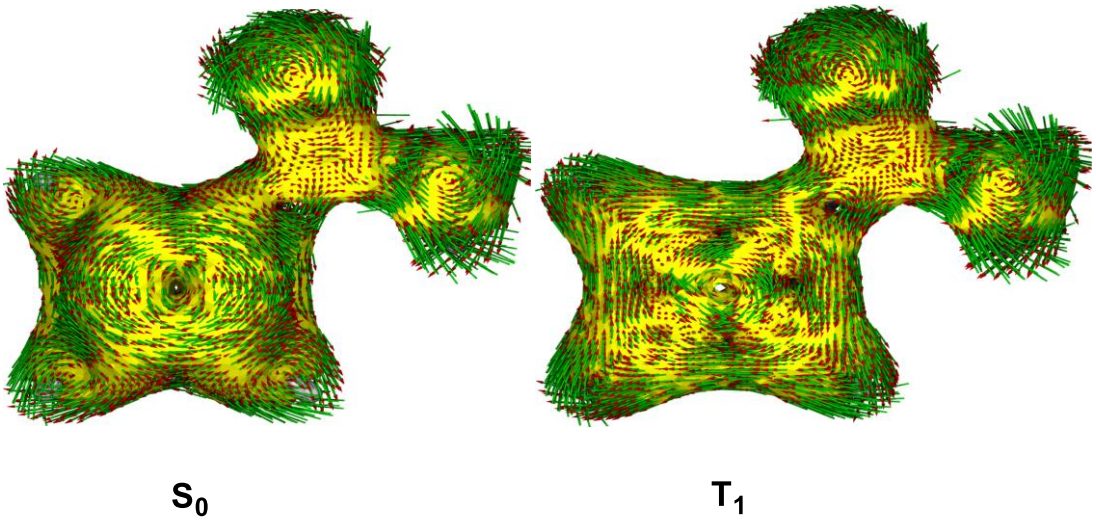


Figure S19. ACID plots in the S_0 and T_1 states when R = COOH . Isovalue for density surfaces: 0.035.

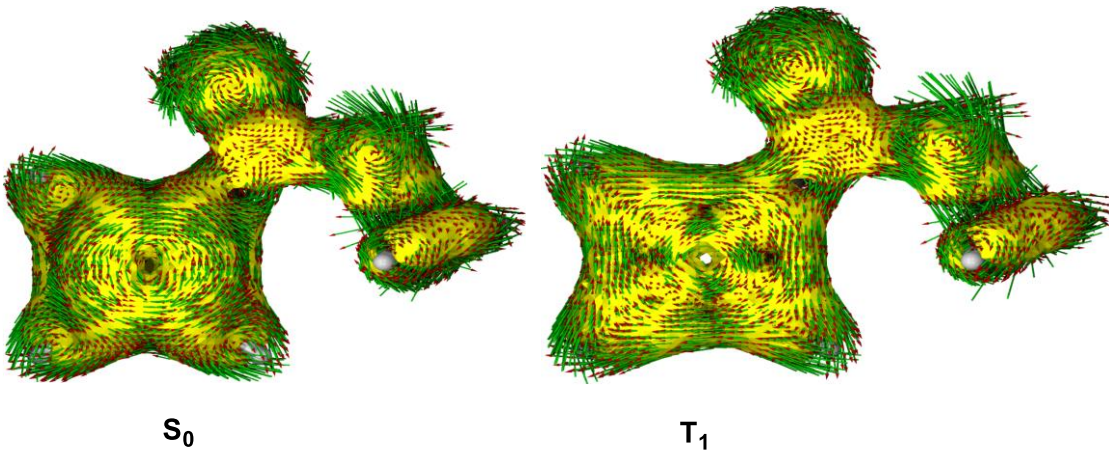


Figure S20. ACID plots in the S_0 and T_1 states when R = $COOCH_3$. Isovalue for density surfaces: 0.035.

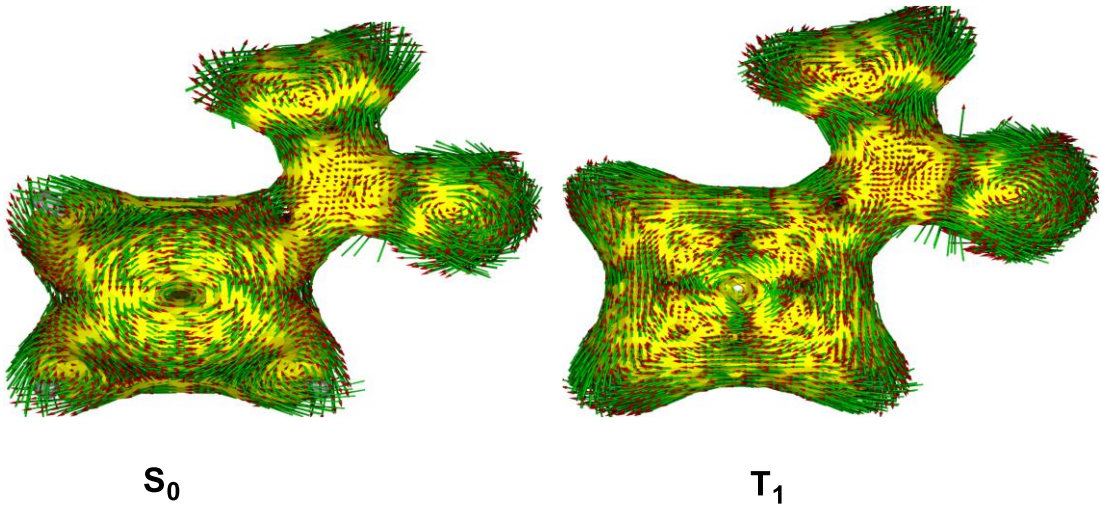


Figure S21. ACID plots in the S_0 and T_1 states when R = $CONH_2$. Isovalue for density surfaces: 0.035.

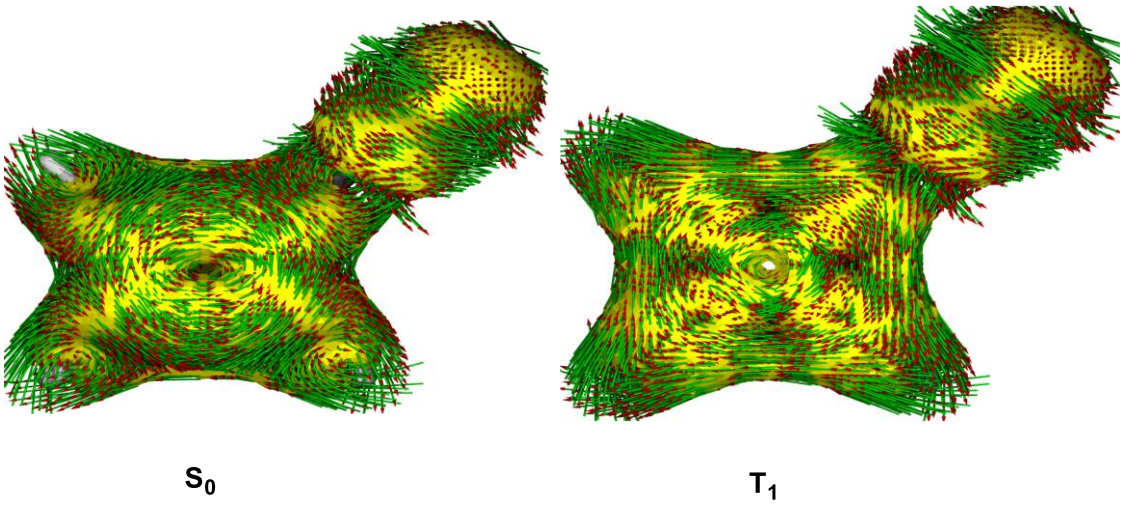


Figure S22. ACID plots in the S_0 and T_1 states when R = CN . Isovalue for density surfaces: 0.035.

5. PISO analysis for the β orbitals

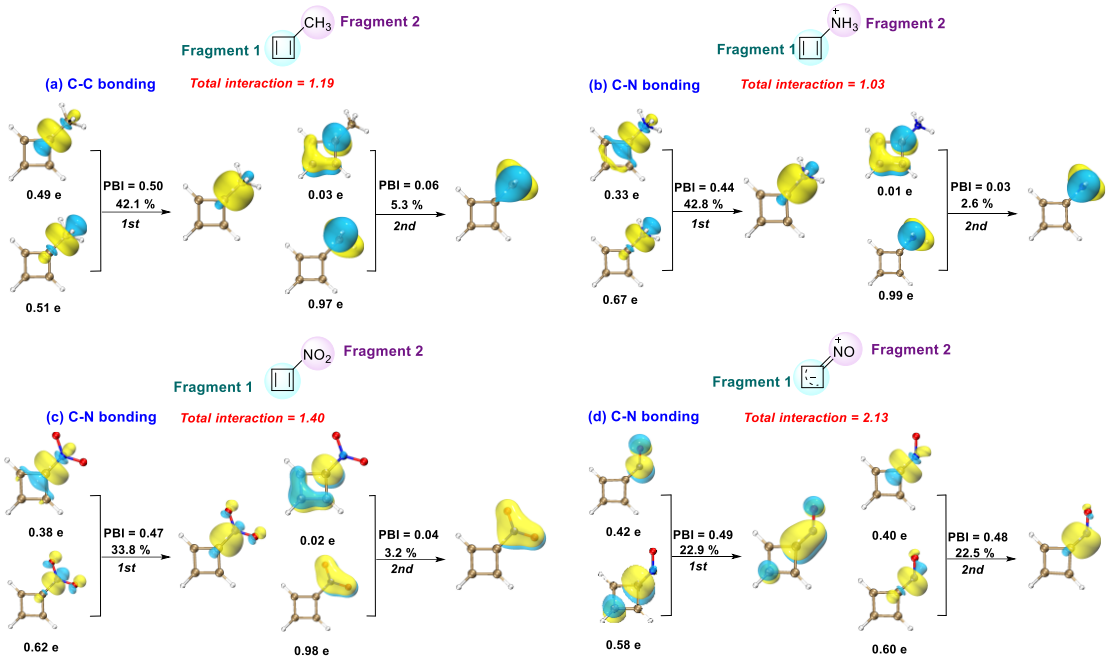


Figure S23. (a) PISO analysis for the β orbitals on the C–C bonding interactions in CH_3-substituted CBD, (b) PISO analysis for the β orbitals on the C–N bonding interactions in NH_3^+-substituted CBD, (c) PISO analysis for the β orbitals on the C–N bonding interactions in NO_2-substituted CBD, (d) PISO analysis for the β orbitals on the C–N bonding interactions in NO-substituted CBD. Isovalue: 0.05 a.u.

6. Resonance form and FBO order of parent CBD

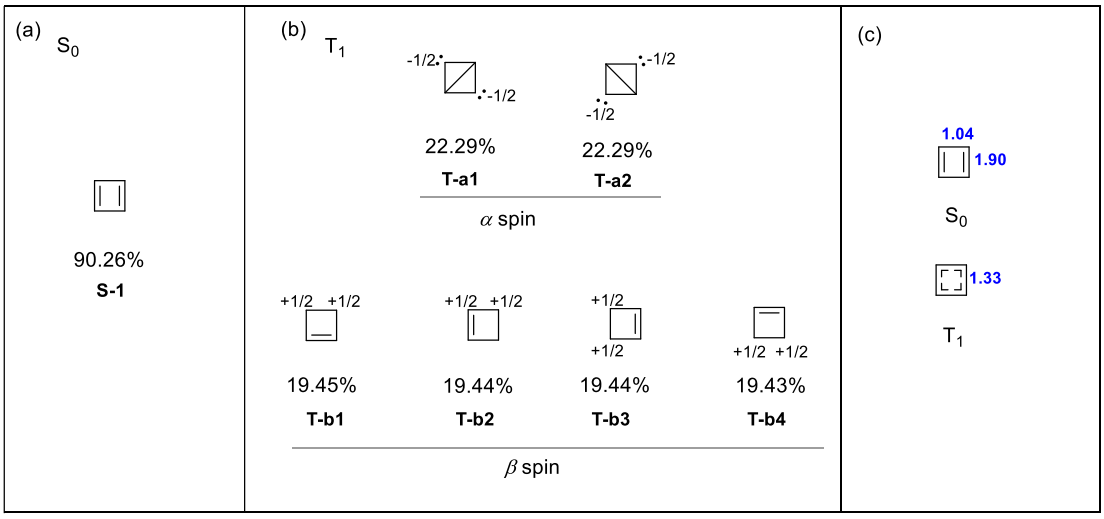
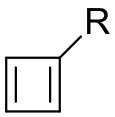


Figure S24. NRT analysis (a and b) and bond order (c) of parent CBD in the S_0 and T_1 states.

7. Cartesian coordinates of substituted CBD



R = H (S_0)

E (M06-2X) = -154.645579 a.u.

C	0.00000000	0.66483900	0.78508700
C	0.00000000	0.66483900	-0.78508700
C	0.00000000	-0.66478000	-0.78493700
C	0.00000000	-0.66478000	0.78493700
H	0.00000000	1.43065200	1.54752700
H	0.00000000	1.43065200	-1.54752700
H	0.00000000	-1.43100700	-1.54695300
H	0.00000000	-1.43100700	1.54695300

R = H (T_1)

E (M06-2X) = -154.627591 a.u.

C	0.00000000	0.71706400	0.71702800
C	0.00000000	0.71706400	-0.71702800
C	0.00000000	-0.71697600	-0.71694000
C	0.00000000	-0.71697600	0.71694000
H	0.00000000	1.47965900	1.48037100
H	0.00000000	1.47965900	-1.48037100
H	0.00000000	-1.48018700	-1.47967000
H	0.00000000	-1.48018700	1.47967000

R = CH_3 (S_0)

E (M06-2X) = -193.957997 a.u.

C	-0.44232400	-1.05652300	0.00014500
C	-1.62284000	-0.03072700	-0.00018100
C	-0.76064800	0.98144400	0.00000600
C	0.43105000	-0.05064800	0.00019800
H	-0.36345400	-2.13454800	-0.00035600
H	-2.70078600	-0.11372900	0.00012800
H	-0.84168600	2.05935800	0.00016800
C	1.90269400	0.10836300	-0.00008100
H	2.23057600	0.67080100	0.87981500
H	2.39769900	-0.86383700	0.00004400
H	2.23006000	0.67050900	-0.88032500

R = CH_3 (T_1)

E (M06-2X) = -193.937742 a.u.

C	-0.60160600	-1.01193400	-0.00426700
C	-1.61660200	-0.00000300	0.01083600
C	-0.60161100	1.01193500	-0.00426800
C	0.41894600	0.00000200	-0.01832300
H	-0.59938600	-2.09209200	-0.00619900
H	-2.69499600	-0.00000600	0.02067300
H	-0.59939700	2.09209300	-0.00619600
C	1.90237000	0.00000100	0.00594900
H	2.28249700	0.00007000	1.03410700
H	2.30114200	-0.88657200	-0.49091200
H	2.30115500	0.88649900	-0.49103600

R = NH_2 (S_0)

E (M06-2X) = -210.010220 a.u.

C	-0.43942400	-1.07849700	0.01790000
C	-1.55496300	-0.00822000	-0.00254800
C	-0.68328600	1.00122900	0.00035000
C	0.45191500	-0.06926300	0.01143600
H	-0.40231700	-2.15394600	-0.01062600
H	-2.63590400	-0.05825000	-0.01749400
H	-0.72677900	2.07888600	-0.01930200
H	2.16851800	0.99369900	0.23742800
H	2.39395900	-0.68972100	0.07914900
N	1.79386800	0.10826300	-0.06171200

R = NH_2 (T_1)

E (M06-2X) = -209.987786 a.u.

C	-0.56134200	-1.01495400	0.00133400
C	-1.58170300	-0.00016600	0.00352500
C	-0.56167400	1.01491200	0.00107200
C	0.44908100	0.00019400	0.00552500
H	-0.55079100	-2.09472500	-0.00886100
H	-2.65777100	-0.00010900	0.02209800
H	-0.55162000	2.09469400	-0.00759300
H	2.28302600	0.84264200	0.22730400
H	2.28207700	-0.84262400	0.22855100
N	1.81841500	0.00003000	-0.07574700

R = $N(CH_3)_2$ (S_0)

E (M06-2X) = -288.604748 a.u.

C	-1.24304000	1.08286700	0.12346400

C	-2.35223600	0.01813700	0.03373500
C	-1.48562000	-0.98816000	-0.10323600
C	-0.34762200	0.07950000	-0.03196600
H	-1.21014100	2.15576600	0.20238800
H	-3.43312400	0.06585400	0.06297700
H	-1.54424500	-2.05536800	-0.24632700
N	0.98555300	-0.03826800	-0.19128600
C	1.64785600	-1.28550700	0.14249100
H	2.53662400	-1.40532900	-0.48008300
H	1.95120000	-1.31308500	1.19693800
H	0.97069800	-2.11689900	-0.04701700
C	1.76836000	1.17263700	-0.04715000
H	2.75382900	1.02320700	-0.49041600
H	1.26292500	1.98490700	-0.57121300
H	1.88717300	1.45196800	1.00773300

R = N(CH$_3$)$_2$ (T$_1$)

E (M06-2X) = -288.582083 a.u.

C	-1.36029900	1.01604900	-0.00867700
C	-2.37457000	-0.00001300	0.06099800
C	-1.36009100	-1.01599100	-0.00810300
C	-0.34652200	0.00012600	-0.08184200
H	-1.35641700	2.09576700	-0.00139300
H	-3.44471100	-0.00018500	0.17630000
H	-1.35653800	-2.09571800	-0.00276600
N	1.00640200	0.00000500	-0.24828000
C	1.70364200	-1.22943700	0.07475800
H	2.70724100	-1.19839300	-0.35159400
H	1.78106000	-1.38328700	1.16033900
H	1.16972000	-2.07375300	-0.36184200
C	1.70385800	1.22935300	0.07483600
H	2.70741200	1.19821300	-0.35161100
H	1.16997400	2.07371600	-0.36170900
H	1.78134400	1.38308200	1.16041100

R = OH (S$_0$)

E (M06-2X) = -229.874262 a.u.

C	0.40601700	-1.08180200	-0.00002000
C	1.53112300	-0.00046000	-0.00001000
C	0.66237200	1.00687300	-0.00004300
C	-0.46948600	-0.07687900	-0.00002800
H	0.36714800	-2.15714400	0.00002600
H	2.61091300	-0.05669900	0.00013000
H	0.71264700	2.08482900	0.00023900

O	-1.80084400	0.01322400	0.00007000
H	-2.06410500	0.93682300	-0.00035200

R = OH (T_1)

E (M06-2X) = -229.853372 a.u.

C	0.55688100	-1.01750100	0.00013400
C	1.54917400	0.03018300	0.00012400
C	0.50680400	1.02533100	-0.00007900
C	-0.46203300	-0.02413200	-0.00018500
H	0.56928600	-2.09584600	-0.00090100
H	2.62477100	0.05886800	0.00021100
H	0.47342400	2.10441600	-0.00026700
O	-1.79873500	-0.11469600	0.00012000
H	-2.18255800	0.76684300	0.00003100

R = OCH_3 (S_0)

E (M06-2X) = -269.162135 a.u.

C	1.20598200	-1.01030800	0.10257200
C	1.96348500	0.35298300	0.05232200
C	0.84269300	1.05456200	-0.08886000
C	0.07468200	-0.32059400	-0.05153800
H	1.48579100	-2.04869100	0.15249700
H	3.01038100	0.61803500	0.10502000
H	0.59059400	2.09638700	-0.21043300
O	-1.20266300	-0.64022900	-0.22472000
C	-2.13823900	0.36279600	0.15488900
H	-1.90904300	1.31012400	-0.33864000
H	-3.11491200	0.00902800	-0.16575000
H	-2.13312100	0.50031300	1.23874600

R = OCH_3 (T_1)

E (M06-2X) = -269.162135 a.u.

C	1.33318900	-0.92481700	0.00054900
C	1.98810100	0.36339300	-0.00101300
C	0.70981600	1.02368500	-0.00006000
C	0.07358400	-0.25771400	0.00061300
H	1.64954900	-1.95569600	-0.00148800
H	3.01192100	0.69465400	0.00320000
H	0.37791400	2.05061100	-0.00057300
O	-1.17961900	-0.70503900	-0.00039600
C	-2.16247600	0.31934000	0.00013900
H	-2.06129400	0.94394200	-0.89192400
H	-3.12981900	-0.17627900	-0.00290100
H	-2.06460500	0.93975200	0.89548300

R = F (S_0)

E (M06-2X) = -253.888012 a.u.

C	-0.32879600	-1.08724700	-0.00000500
C	-1.51759300	-0.04624200	0.00000600
C	-0.69115600	0.99311800	-0.00000500
C	0.47263400	-0.03508400	0.00000100
H	-0.23499800	-2.15954100	-0.00000800
H	-2.59122000	-0.16355300	0.00001100
H	-0.77565500	2.06763600	-0.00001000
F	1.77681500	0.14535500	0.00000300

R = F (T_1)

E (M06-2X) = -253.888012 a.u.

C	-0.50998500	-1.02939400	-0.00000100
C	-1.52242200	0.00015300	0.00000100
C	-0.50963800	1.02907800	-0.00000100
C	0.46569900	-0.00009500	0.00000000
H	-0.49921100	-2.10701800	-0.00000200
H	-2.59852800	0.00133900	0.00000100
H	-0.49875600	2.10671200	-0.00000100
F	1.78384100	0.00005700	0.00000100

R = SiH_3 (S_0)

E (M06-2X) = -445.325536 a.u.

C	-0.94307200	-1.03293500	-0.00012600
C	-2.13924600	-0.04030600	0.00021700
C	-1.28420100	0.97758800	-0.00004100
C	-0.05765500	-0.02884200	-0.00037900
H	-0.84859900	-2.11174400	0.00017300
H	-3.21610700	-0.13650800	0.00025500
H	-1.37499300	2.05517100	-0.00018800
Si	1.79306100	0.05224000	0.00007300
H	2.28520800	0.77183900	1.19821300
H	2.31052000	-1.33493700	0.00020600
H	2.28614500	0.77178700	-1.19770500

R = SiH_3 (T_1)

E (M06-2X) = -445.306842 a.u.

C	-1.12158500	-1.01201400	-0.00001000
C	-2.11541100	0.01123700	0.00003300
C	-1.09904800	1.00759200	-0.00001200
C	-0.06916500	-0.01324100	-0.00004600
H	-1.13770800	-2.09156700	-0.00002000

H	-3.19586600	0.02435900	0.00007800
H	-1.08553700	2.08740400	-0.00002400
Si	1.78410200	-0.00061400	0.00000800
H	2.31745200	-0.68941000	1.19908800
H	2.31745100	-0.69166100	-1.19776800
H	2.23802900	1.40804000	-0.00125900

R = PH_2 (S_0)

E (M06-2X) = -496.582515 a.u.

C	-0.91829300	-1.05291900	0.02843900
C	-2.08067400	-0.01596000	-0.01570600
C	-1.20526300	0.98379400	-0.00303300
C	-0.02211100	-0.06271900	0.05165600
H	-0.85260300	-2.13184400	0.00794500
H	-3.15954300	-0.08451100	-0.03836200
H	-1.26141100	2.06270400	-0.01752800
H	2.01935100	0.66632400	1.16299700
H	2.08369000	-1.22017100	0.26532000
P	1.76857100	0.10628800	-0.11656700

R = PH_2 (T_1)

E (M06-2X) = -496.563942 a.u.

C	-1.04699800	1.01275900	0.01841100
C	-2.06523300	0.01582500	-0.00709500
C	-1.07373300	-1.01162700	-0.00686100
C	-0.02901900	-0.01254300	0.03866500
H	-1.02660500	2.09227600	0.02726600
H	-3.14462900	0.03089200	-0.00767300
H	-1.08813100	-2.09082300	-0.02533900
H	1.98062900	1.30312700	0.22443000
H	2.07392300	-0.54167100	1.18750000
P	1.76631400	-0.05468600	-0.11099300

R = SH (S_0)

E (M06-2X) = -552.837347 a.u.

C	0.90037600	-1.07219500	-0.00026300
C	2.02808500	0.00524500	0.00018600
C	1.13859300	0.99291800	0.00003800
C	0.00009500	-0.08561100	-0.00031100
H	0.86336100	-2.15011900	0.00070400
H	3.10844600	-0.04006600	0.00017200
H	1.16087100	2.07167600	0.00001800
H	-2.03713300	-1.16530000	0.00058600
S	-1.71865300	0.14010400	0.00003900

R = SH (T_1)

E (M06-2X) = -552.818249 a.u.

C	1.01073000	-1.01875000	-0.00342700
C	2.02755300	-0.01345400	-0.00269600
C	1.03107000	1.01282600	0.00485000
C	0.00249700	0.00736500	0.00593600
H	0.99003800	-2.09788800	-0.00776600
H	3.10545000	-0.02467400	-0.00266200
H	1.03427900	2.09164900	0.00766700
H	-1.92382200	-1.24192300	0.06122100
S	-1.72731600	0.08405700	-0.00540200

R = Cl (S_0)

E (M06-2X) = -614.249695 a.u.

C	-0.86260500	-1.07434500	-0.00000700
C	-2.00899900	0.00269700	0.00000900
C	-1.13192100	0.99881200	-0.00000700
C	0.00631200	-0.07246700	0.00000100
H	-0.80944100	-2.15114900	-0.00001100
H	-3.08734300	-0.06418000	0.00001700
H	-1.15862300	2.07704300	-0.00001300
Cl	1.70815800	0.05941800	0.00000200

R = Cl (T_1)

E (M06-2X) = -614.230325 a.u.

C	-0.99553600	-1.02383900	-0.00000100
C	-1.99973200	0.00005500	0.00000100
C	-0.99530700	1.02367800	-0.00000100
C	0.00290000	-0.00008200	0.00000000
H	-0.98322000	-2.10180700	-0.00000100
H	-3.07751500	0.00099700	0.00000200
H	-0.98288000	2.10165200	-0.00000100
Cl	1.70409800	0.00001700	0.00000000

R = NH_3^+ (S_0)

E (M06-2X) = -210.339281 a.u.

C	0.43889500	-1.07086100	0.00004500
C	1.64660400	-0.05346400	-0.00005500
C	0.82801600	0.98992400	0.00004300
C	-0.35998300	-0.02112700	0.00000600
H	0.33722300	-2.14691300	0.00005800
H	2.71646000	-0.19614800	-0.00011700
H	0.91844500	2.06504700	0.00007100

N	-1.81819600	0.11179400	-0.00002300
H	-2.15186000	0.62127100	0.82885000
H	-2.15183600	0.62124000	-0.82892500
H	-2.26225300	-0.81389100	-0.00001100

R = NH_3^+ (T_1)

E (M06-2X) = -210.319563 a.u.

C	-0.63046700	1.03290600	-0.00309500
C	-1.62819200	-0.00000600	0.02156400
C	-0.63047000	-1.03289000	-0.00309500
C	0.34881000	0.00000100	-0.05290100
H	-0.63790700	2.11143500	-0.00255700
H	-2.70687900	-0.00001300	0.02585600
H	-0.63789800	-2.11142100	-0.00255400
N	1.81002700	0.00000300	0.01732000
H	2.15943500	0.00182400	0.98618200
H	2.19735700	-0.82804600	-0.44990000
H	2.19761600	0.82612600	-0.45311200

R = NO_2 (S_0)

E (M06-2X) = -359.134427 a.u.

C	1.09075300	-1.07536400	0.00005800
C	2.26721600	-0.04223100	0.00001300
C	1.41194400	0.97627900	-0.00005400
C	0.24772000	-0.05066700	-0.00002000
H	0.98779700	-2.15055100	0.00009900
H	3.34110900	-0.14587400	0.00014500
H	1.46505600	2.05345000	-0.00036700
N	-1.17729900	0.03324600	0.00000200
O	-1.65331900	1.15349200	0.00010500
O	-1.80401400	-1.00822300	-0.00008800

R = NO_2 (T_1)

E (M06-2X) = -359.119092 a.u.

C	1.24496700	-1.03185300	-0.00010300
C	2.22927300	-0.00000500	-0.00044700
C	1.24498800	1.03185900	0.00025500
C	0.24892200	-0.00000800	0.00084400
H	1.23273100	-2.10852800	0.00084700
H	3.30906300	-0.00004000	-0.00084200
H	1.23275500	2.10853300	-0.00024200
N	-1.15932600	0.00000400	0.00009400
O	-1.71675400	1.08772300	-0.00022800
O	-1.71676800	-1.08771600	-0.00023700

R = NO (S_0)

E (M06-2X) = -283.938018 a.u.

C	1.01855600	1.02113900	-0.00031700
C	1.91278900	-0.23382400	-0.00001900
C	0.84460800	-1.03366400	-0.00045600
C	-0.07091900	0.23843400	-0.00001500
H	1.18074500	2.09090900	-0.00030800
H	2.98198000	-0.38212400	0.00016500
H	0.67221200	-2.09913200	-0.00065300
N	-1.41499400	0.54862700	0.00032500
O	-2.14502300	-0.42531900	0.00042000

R = NO (T_1)

E (M06-2X) = -283.948322 a.u.

C	0.79119700	1.04965600	-0.00010500
C	1.91837000	0.21164300	0.00078300
C	1.16686600	-0.97620800	-0.00028800
C	-0.06906500	-0.16674800	-0.00120600
H	0.60388900	2.11105800	-0.00215000
H	2.98007600	0.40924200	0.00181600
H	1.38079300	-2.03268100	0.00027800
N	-1.30910400	-0.43806100	0.00000500
O	-2.33065500	0.23359400	0.00061400

R = CHO (S_0)

E (M06-2X) = -267.963058 a.u.

C	-0.63197200	-1.01211700	-0.00003700
C	-1.99532700	-0.27318800	0.00011600
C	-1.36865800	0.90048400	0.00012700
C	0.02032200	0.15736200	0.00011200
H	-0.31153600	-2.04548700	0.00082500
H	-3.02661000	-0.59265900	-0.00151200
H	-1.68192900	1.93502700	-0.00025000
O	2.32149800	-0.31927800	-0.00014900
C	1.43806300	0.50595900	0.00004400
H	1.67352600	1.58633900	-0.00004200

R = CHO (T_1)

E (M06-2X) = -267.952571 a.u.

C	-0.76731200	-1.03369700	0.00029300
C	-1.95044200	-0.24811300	-0.00071200
C	-1.21469800	0.96104100	0.00013200
C	0.01799900	0.18727100	0.00132500

H	-0.53133100	-2.08528500	0.00124400
H	-3.00582600	-0.48215000	-0.00174800
H	-1.46172800	2.01099800	-0.00064600
O	2.28209200	-0.38489900	-0.00063600
C	1.42272400	0.48081500	0.00006400
H	1.69252500	1.55173000	-0.00037400

R = $COCH_3$ (S_0)

E (M06-2X) = -307.278784 a.u.

C	-1.27909600	-1.02253300	0.00032200
C	-2.36164100	0.09244600	0.00014600
C	-1.41335400	1.02540500	-0.00039800
C	-0.31045400	-0.10140300	-0.00028200
H	-1.28078700	-2.10421900	0.00131700
H	-3.44154500	0.09638800	0.00008900
H	-1.40353400	2.10657500	-0.00051700
O	1.72089900	-1.25956800	-0.00032900
C	1.15738100	-0.18701200	-0.00017600
C	1.89924600	1.12748600	0.00037300
H	1.61664000	1.71236100	-0.87953100
H	1.61737200	1.71092800	0.88150700
H	2.97216900	0.94816800	-0.00014100

R = $COCH_3$ (T_1)

E (M06-2X) = -307.266356 a.u.

C	-1.43142000	-0.96575700	-0.00000400
C	-2.32263600	0.14037000	0.00007600
C	-1.24906200	1.06803300	-0.00003400
C	-0.31324200	-0.04432600	-0.00011800
H	-1.52452400	-2.03964400	-0.00055600
H	-3.39891700	0.23843200	0.00045900
H	-1.16419900	2.14360000	-0.00012000
O	1.62007800	-1.32801900	0.00008400
C	1.12556200	-0.21230500	0.00000300
C	1.96328700	1.04730400	0.00000300
H	1.73737600	1.65159400	-0.88219400
H	1.73715500	1.65176000	0.88203100
H	3.01755300	0.77850100	0.00014700

R = COOH (S_0)

E (M06-2X) = -343.212548 a.u.

C	1.17323600	-1.05991900	-0.00012500
C	2.33149100	-0.02296300	-0.00024600
C	1.45572600	0.97675700	0.00015000

C	0.27490900	-0.07528900	0.00071400
H	1.09639500	-2.13850400	-0.00158900
H	3.40869600	-0.09508000	0.00001200
H	1.53168300	2.05566800	0.00005000
O	-1.83995100	-1.10683800	0.00013200
C	-1.19586700	-0.09873500	0.00017300
O	-1.80090300	1.11198400	-0.00049600
H	-1.14690300	1.81764200	0.00044400

R = COOH (T_1)

E (M06-2X) = -343.197811 a.u.

C	1.32707900	-1.01408000	-0.00000900
C	2.29765900	0.02508300	-0.00016500
C	1.28655500	1.02634800	0.00008800
C	0.28230500	-0.02084300	0.00029100
H	1.33905800	-2.09198300	-0.00044600
H	3.37733200	0.04934100	-0.00036000
H	1.28631800	2.10593000	0.00067700
O	-1.74823800	-1.18294600	0.00006600
C	-1.17103200	-0.12993700	0.00004600
O	-1.86155000	1.03667000	-0.00019800
H	-1.25980100	1.78749700	-0.00032100

R = $COOCH_3$ (S_0)

E (M06-2X) = -382.497282 a.u.

C	1.66906000	0.89836300	0.07210900
C	2.51366600	-0.40195600	0.00770300
C	1.40440200	-1.12734800	-0.07927400
C	0.53652900	0.19673100	-0.01263800
H	1.87841300	1.95644600	0.15393200
H	3.57095400	-0.61880400	0.02533500
H	1.18631500	-2.18238700	-0.16281800
O	-1.05866600	1.90107200	-0.03208400
C	-0.84499200	0.72035700	-0.02328600
O	-1.88172800	-0.14108200	-0.02264300
C	-1.65347800	-1.54124400	0.06283500
H	-1.15420800	-1.91557000	-0.83348300
H	-1.07045000	-1.79522300	0.95090600
H	-2.63900600	-1.99380600	0.13924300

R = $COOCH_3$ (T_1)

E (M06-2X) = -382.483273 a.u.

C	1.83052500	0.77105500	0.00001100
C	2.47158000	-0.49590100	0.00010100

C	1.22382700	-1.17364500	-0.00002600
C	0.54394100	0.11464100	-0.00016300
H	2.13942000	1.80397700	0.00006500
H	3.50179900	-0.82031900	0.00013700
H	0.92511600	-2.20903200	-0.00045500
O	-0.87796400	1.94387700	0.00004000
C	-0.77626800	0.74246900	-0.00002600
O	-1.89276400	-0.01471600	-0.00005200
C	-1.79581700	-1.43054400	0.00009400
H	-1.28403600	-1.79030000	-0.89576100
H	-1.28357200	-1.79006600	0.89576900
H	-2.81962800	-1.79598800	0.00039900

R = $CONH_2$ (S_0)

E (M06-2X) = -323.347343 a.u.

C	-1.21399800	-1.04656500	-0.00009300
C	-2.34946200	0.01930700	-0.00000500
C	-1.44862500	0.99706600	0.00010200
C	-0.29613400	-0.08115000	-0.00004200
H	-1.16203900	-2.12628600	-0.00005000
H	-3.42854300	-0.02551900	-0.00007000
H	-1.49701000	2.07735700	0.00016800
O	1.79726000	-1.16648300	0.00004500
C	1.17663200	-0.12312200	0.00001100
H	2.78635900	1.14065200	-0.00085000
H	1.25374100	1.95811100	-0.00109500
N	1.77984800	1.10204800	0.00024300

R = $CONH_2$ (T_1)

E (M06-2X) = -323.331611 a.u.

C	-1.36235500	-0.99237000	-0.02704500
C	-2.31922400	0.05997100	-0.00347200
C	-1.28972500	1.04427100	0.02641400
C	-0.30280700	-0.01658000	0.00120900
H	-1.38977200	-2.06977600	-0.05314700
H	-3.39843500	0.09980300	-0.00380400
H	-1.26726300	2.12230700	0.07251100
O	1.69708400	-1.23835100	0.02159200
C	1.15242300	-0.14985800	0.00399000
H	2.84964700	0.97107000	-0.11008300
H	1.39775100	1.90038300	-0.20331400
N	1.85164600	1.03006100	0.01693300

R = CN (S_0)

E (M06-2X) = -246.888444 a.u.

C	-0.81219400	-1.04304100	-0.00002900
C	-1.96459600	0.00040000	-0.00017600
C	-1.08219200	0.99400900	-0.00000400
C	0.08877800	-0.05812500	0.00024300
H	-0.74842800	-2.12202800	-0.00007100
H	-3.04156900	-0.06743600	-0.00037300
H	-1.11724100	2.07328700	0.00001900
C	1.49880500	0.01068100	0.00059600
N	2.64794700	0.09894600	-0.00048000

R = CN (T_1)

E (M06-2X) = -246.873520 a.u.

C	-0.94526900	-1.01952300	-0.00001200
C	-1.93526800	-0.00057900	-0.00020300
C	-0.94622200	1.01967500	-0.00001300
C	0.08315900	0.00031100	0.00028600
H	-0.93962600	-2.09749800	-0.00003000
H	-3.01463800	-0.00091200	-0.00044100
H	-0.94180400	2.09764100	-0.00002900
C	1.48147800	0.00030200	0.00063700
N	2.63839900	-0.00005000	-0.00052400