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

Supporting Information for : Effect of protein environment on the excited state phenomena in bacteriophytochrome

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S1 Orbitals included in the active space

The active space base calculation (CASSCF and CASPT2) are done using an active space of (6e,6o) with the 6-31G(d) basis set. The 6 orbitals of all the three important geometries (FC, CI_1, CI_2) are shown in the figures below. All the orbitals shown are the 3 state avaeraged CASSCF orbitals.

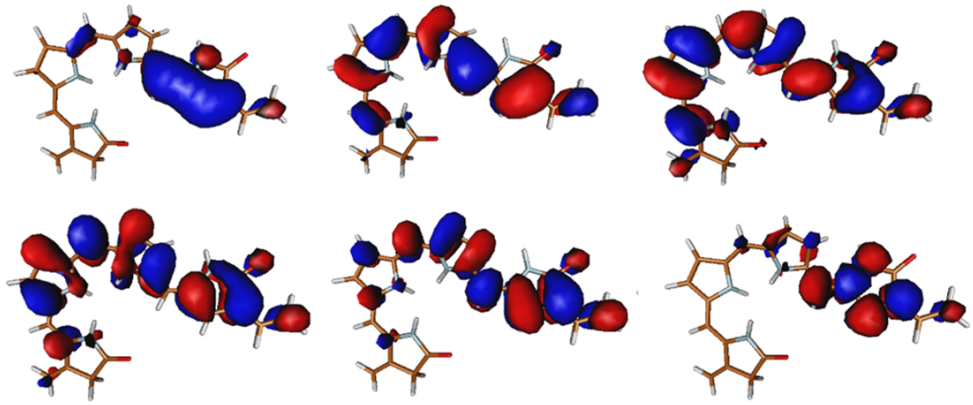


Figure S1: SA3-CASSCF orbitals at FC

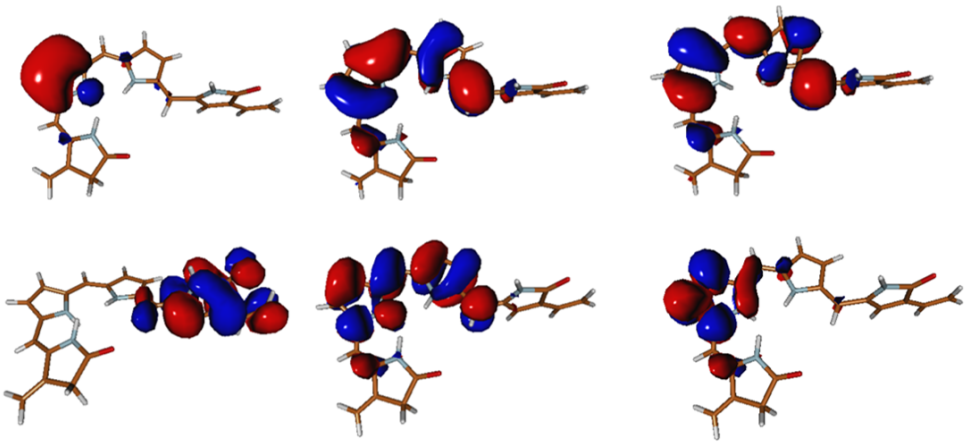


Figure S2: SA3-CASSCF orbitals at CI_1

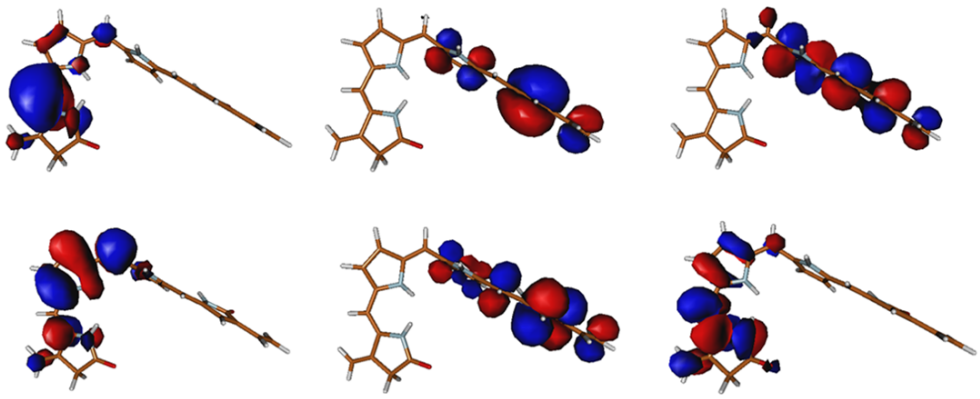


Figure S3: SA3-CASSCF orbitals at CI_2

S2 Vertical excitation energy : Effect of basis set and functional

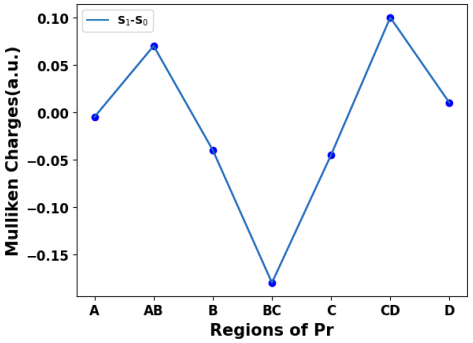
We have tested the effect of the excitation energy at the FC region with basis set and as well as with functional. Along with B3LYP, CAM-B3LYP functional is tested. For both the functional, along with 6-31G(d) basis set a more diffused basis set 6-311++G(d,p) is used. The following table shows that the vertical excitation energy does not change much with either the variation of the functional or the basis set. The S_1 state always remain the bright state involving the HOMO →LUMO transition. Given that both the HOMO and LUMO is of π nature extending the full chromophore this is unsurprising that the excitation energy change is minimal.

Table S1: The vertical excitation energies of the S_1 and S_2 states at the FC geometry. The excitatioin energies are reported in eV. The numbers in the brackets are the oscillator strengths.

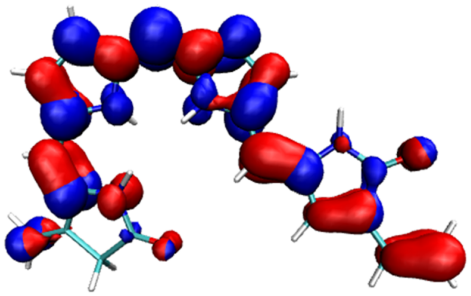
Excited state	B3LYP		CAM-B3LYP	
	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)
S1	1.99 (0.95)	1.95(0.95)	2.10 (1.04)	2.06 (1.02)
S2	2.47 (0.06)	2.45 (0.07)	3.24(0.24)	3.21(0.29)

S3 Charge transfer analysis at FC geometry

The Mulliken charges (in a.u.) calculated at B3LYP/6-31G(d) level of theory have been shown below in Fig. S4 (a). The attachment detachment density analysis has been shown in Fig. S4 (b).



(a)



(b)

Figure S4: Charge analysis for FC geometry (a) Redistribution of Mulliken charges on excitation (S_1-S_0) state (b) Optimized FC ; Blue : Attachment density, Red : Detachment density

S4 Geometry of optimized S_1-Min

The S_1-Min was obtained at TD-B3LYP/6-31g(d) level of theory.The same active space(6o,6e) is taken to calculate the excited states of S_1-Min geometry. CASPT2 calculations show comparable energies of the first bright state (1.65

eV) of the S_1-Min with that of the FC. S_1-Min is found to be a shallow minimum which lies very close to the FC geometry. Following figure is the geometry of S_1-Min along with its geometrical parameters.

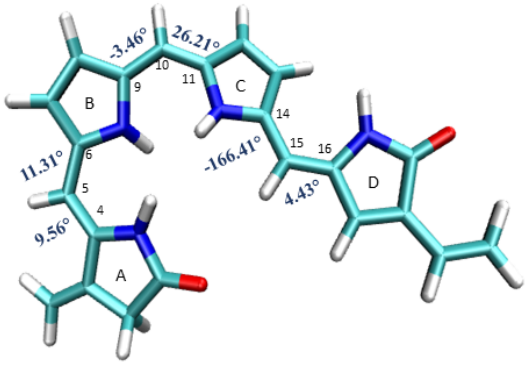


Figure S5: Geometrical parameters of FC, (a) Dihedral Angles τ_{A-B}, τ_{B-A}, τ_{B-C}, τ_{C-B}, τ_{C-D} and τ_{D-C} (in degrees)

S5 Comparison of dihedral angles at several geometries

The dihedral angles for the different geometries are tabulated below. The major change in dihedral in CI_1 with respect to the FC is that the D ring becomes perpendicular to the plane of the B and C rings. On the other hand the CI_2 has a rotation about the methine bridge between the B and C rings and there for major change occurs at τ_{C-B}.

Table S2: Dihedral angles at several geometries. The values are in degrees.

Geometry	τ_{A-B}	τ_{B-A}	τ_{B-C}	τ_{C-B}	τ_{C-D}	τ_{D-C}
FC	7.13	15.21	-9.30	-10.50	-165.66	4.72
S_1-Min	9.56	11.31	-3.46	-26.21	-166.41	4.43
CI_1	3.87	28.52	-12.07	-3.19	-179.89	90.64
CI_2	4.84	21.38	0.19	-90.74	-172.98	5.80

S6 Orbitals involved in the S_1 excitation near the CIs

The orbitals involved in the S_1 excitation for the two conical intersections. The direction of charge transfer is from B and C rings to the D ring for CI_1 whereas for CI_2 , it is the reverse i.e. from C and D ring to the A and B rings.

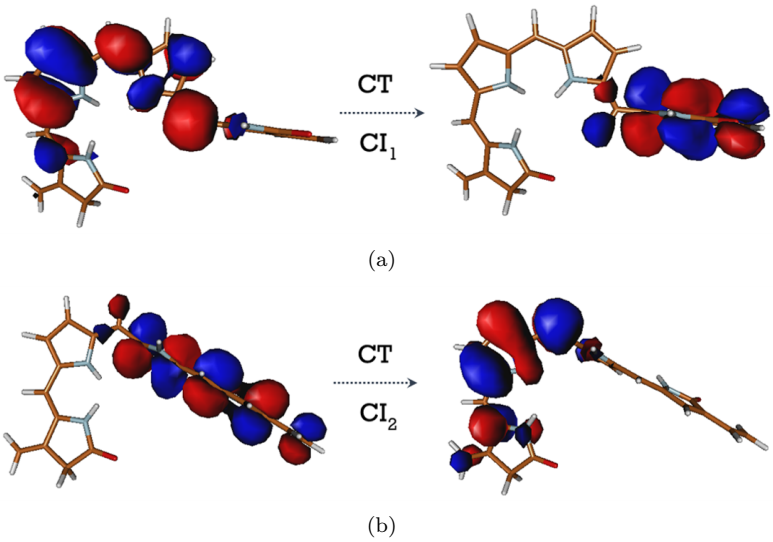
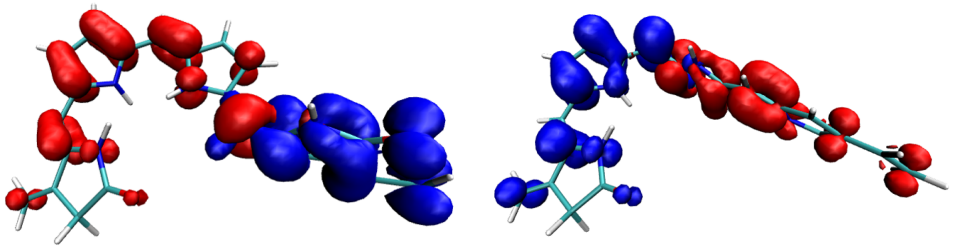


Figure S6: Orbitals involved in transition for S_1 state for (a) CI_1 and (b) CI_2

S7 Attachment detachment density analysis for CI_1 and CI_2

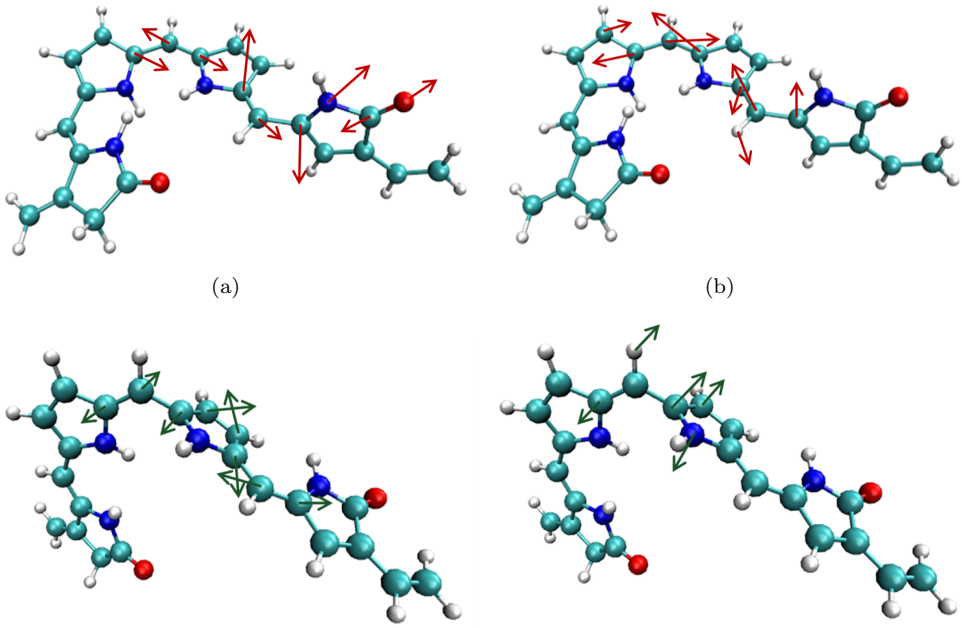
The above finding of the CT character for the two CIs is also shown through the attachment and detachment density analysis for the two CIs.



(a) (b)

Figure S7: Attachment detachment density for (a) CI_1 and (b) CI_2 ; Blue : Attachment density, Red : Detachment density

S8 The g and h vectors for CI_1 and CI_2



(a) (b)

(c) (d)

Figure S8: All the $\vec{g}$ and $\vec{h}$ vectors for the two conical intersections. 4(a) and 4(b) : $\vec{g}$ and $\vec{h}$ vectors of CI_1. 4(c) and 4(d) : $\vec{g}$ and $\vec{h}$ vectors of CI_2. The direction of arrows on different atoms refer to the direction of movement of the atoms for a particular vector.

S9 Residues near the chromophore

To ascertain which of the residues play major role in modulating the stability of the chromophore at several important regions on the potential energy surface, EDA analysis has been done. The important residues are selected mainly near the C and D ring positions as major differences happen at either at the D ring (CI_1) or at the CD ring (CI_2) with respect to the FC geometry. The following figures show the position of the important residues in the protein relative to the chromophore.

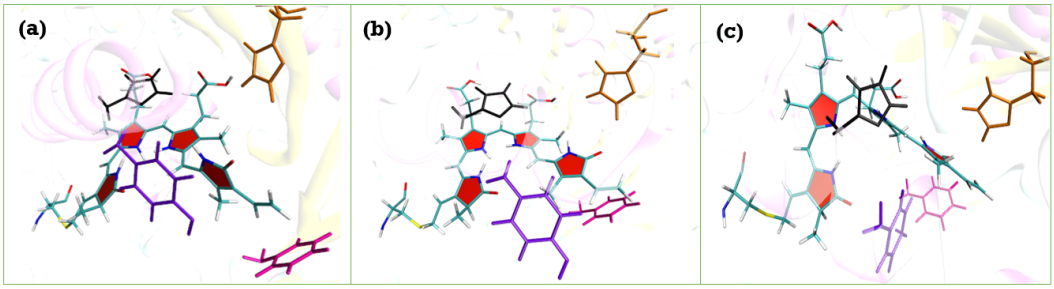


Figure S9: Chromophore with the important residues near the C and D ring inside the protein.(a) CI_1, (b) FC and (c) CI_2. Residue colour; black : HIS-260 , orange : HIS-290, violet : TYR-263 , pink : PHE-203. For clarity the chromphore pyrrole ring is shaded with the orange colour

S10 EDA analysis

Energy decomposition analysis is done to ascertain the effect of important residues. All the components of energy are given in the following table. The explanation is included in the main manuscript (Result and discusion section)

Table S3: EDA for the important residues

Residue	Energy component	CI-1	FC	CI-2
HIS-290	Dispersion	-2.30	-3.93	-15.04
	Polarisation	-1.14	-1.38	-1.59
	Charge transfer	-0.22	-2.91	-6.73
	Total	**7.91**	**8.18**	**-6.03**
TYR-263	Dispersion	-34.97	-21.60	-28.03
	Polarisation	-5.01	-1.42	-1.41
	Charge transfer	-17.95	-8.37	-10.40
	Total	**-48.86**	**-21.45**	**-19.82**
HIS-260	Dispersion	-41.29	-18.57	-44.41
	Polarisation	-4.33	-3.53	-10.13
	Charge transfer	-20.73	-8.33	-22.86
	Total	**-64.89**	**-34.97**	**-49.89**
PHE-203	Dispersion	-24.57	-16.89	-3.50
	Polarisation	-3.00	-0.80	-0.44
	Charge transfer	-11.20	-4.54	-0.32
	Total	**-18.32**	**-12.22**	**-0.89**

S11 Optimized geometries of FC, S_1-Min, CI_1 and CI_2

FC geometry optimized at B3LYP/6-31g(d) level of theory

```
C        -1.8408855746   -2.8176785591    0.1080497029
C        -4.3281227649    0.7791903542    0.2515722864
C        -0.5450073398    2.9652986816   -0.1530189557
C         3.2359498334    0.0404351528   -0.0157280381
C        -2.8926043389   -3.8450754485   -0.2907968270
C        -5.1166139640    1.8996127219    0.5992305545
C         0.5976741249    3.6782206944   -0.6011483290
C         3.8536300341   -1.2712746971    0.0728408705
C        -4.1969356195   -3.0638729771   -0.3237665220
C        -4.3105928792    3.0298656926    0.5582237782
C         1.6709014430    2.8058677329   -0.6527352881
C         5.2098772646   -1.1495721116    0.0731706869
C        -3.8838218480   -1.6575972745    0.0021669667
C        -3.0007080025    2.6359562233    0.1997368921
C         1.2300380801    1.5279936400   -0.2048582672
C         5.5173265350    0.3262892493    0.0097050764
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C	-5.4092852337	-3.5508349891	-0.6147926386
C	6.1974657031	-2.2037531162	0.1258254780
C	7.5290107901	-2.0120859165	0.1278040372
C	-4.7252603207	-0.5792094995	0.0813440826
C	-1.8551970045	3.4133328770	0.0142660597
C	1.8823946431	0.2793853107	-0.0234120192
N	-2.5142028996	-1.5967458378	0.2185760498
O	-0.6538283752	-2.9498027141	0.3090334933
N	-3.0321121746	1.2364773728	0.0607004075
N	-0.1180823737	1.6478421607	0.0428030696
N	4.2611281301	0.9591057455	-0.0918622993
O	6.5757741894	0.9137456476	0.0440938114
H	-6.2960961953	-2.9247618475	-0.6322745945
H	-5.7917068471	-0.7599628129	0.0116274286
H	-2.6344359817	-4.2860956624	-1.2603613292
H	-2.0736655202	-0.8212210106	0.6939386741
H	-2.4292579922	0.7872589825	-0.6204605104
H	-0.5993293838	1.0110304029	0.6620496764
H	4.1744778439	1.9562728309	0.0410691980
H	-2.0029593480	4.4887718213	-0.0156245337
H	1.2478973461	-0.5923045588	0.1224260112
H	5.7980653626	-3.2156797365	0.1672210584
H	8.2068412397	-2.8588103226	0.1709671376
H	7.9634050064	-1.0196669257	0.0886892126
H	-4.6031882672	4.0431596028	0.8007603431
H	0.5917726789	4.7156805979	-0.9088068429
H	-5.5546861361	-4.6018486687	-0.8443348788
H	-2.8933359824	-4.6600396833	0.4420185579
H	-6.1636196772	1.8570544557	0.8663803036
H	2.6550035152	3.0336696784	-1.0359259773
H	3.2790403954	-2.1888616806	0.1075166939

S_1-Min optimized geometry at TD-B3LYP/6-31g(d) level of theory

C	-1.5490195618	-2.6105187865	0.1065260083
C	-4.2757659812	0.7928994043	0.2104584885
C	-0.5959448255	3.0554476047	-0.1228511919
C	3.0926446031	-0.0029175688	0.0936003527
C	-2.5206507916	-3.7064070763	-0.3125881559
C	-5.1423524507	1.8849607996	0.5496758742
C	0.4723525202	3.6499984237	-0.7962850088
C	3.6343200729	-1.3297967645	0.2703647026
C	-3.8711476781	-3.0074666876	-0.3925350063
C	-4.4047697699	3.0402478191	0.5883985304
C	1.5492450000	2.7349861945	-0.8026629366
C	5.0019948139	-1.2900035688	0.1553052264
C	-3.6604958290	-1.6008958427	-0.0466657741
C	-3.0346786994	2.7253552691	0.2672250246
C	1.1444675898	1.5816075654	-0.1245973291
C	5.3834527723	0.1484793268	-0.0879275407
C	-5.0405811147	-3.5725733283	-0.7395723785
C	5.9157801142	-2.3943951396	0.2539722718
C	7.2626576334	-2.2983066953	0.1338094693
C	-4.5849658921	-0.5640810785	0.0395353476
C	-1.9373424183	3.5337996010	0.1358502123
C	1.7591541350	0.3101860330	0.1436654364
N	-2.3112260202	-1.4483517525	0.2154935463
O	-0.3545269470	-2.6564995059	0.3248434238
N	-2.9906179846	1.3199076947	0.0929486881
N	-0.1789141918	1.7854713173	0.2486699444

N	4.1673836863	0.8407630723	-0.1429370212
O	6.4824881706	0.6522892920	-0.2096841771
H	-5.9640642790	-3.0045225335	-0.7929970583
H	-5.6361740587	-0.8234334471	-0.0162503542
H	-2.2062071770	-4.1397445910	-1.2688486833
H	-1.9220763376	-0.6112419721	0.6273440151
H	-2.3632749498	0.9583670973	-0.6184985568
H	-0.6045614253	1.2881022534	1.0197978637
H	4.1335217915	1.8500676079	-0.1560536408
H	-2.0848372678	4.6077085947	0.1830897969
H	1.0941095861	-0.5165334515	0.3900455117
H	5.4643021475	-3.3677957103	0.4393329372
H	7.8868498132	-3.1820677727	0.2208547906
H	7.7483423981	-1.3461364459	-0.0487288186
H	-4.7570854173	4.0299633898	0.8476914567
H	0.4497047799	4.6212847580	-1.2711603146
H	-5.1064308532	-4.6287084806	-0.9812607730
H	-2.4957183726	-4.5138050569	0.4286562007
H	-6.1969930219	1.7792750386	0.7676688475
H	2.4870973761	2.8688519382	-1.3235170553
H	3.0153015568	-2.2029354751	0.4407410721

CI_1 optimized geometry at CASSCF/6-31g(d) level of theory with an active space (6,6)

C	2.2882758174	-1.9887737624	-0.1797048992
C	3.6684700454	2.0911267318	-0.3040654170
C	-0.5720590557	3.0143121713	0.2178429134
C	-3.5327338654	-0.6350510547	0.6726545232
C	3.5298304062	-2.7134450460	0.2970747154
C	4.0251284999	3.3142314669	-0.8350781639
C	-1.9356397611	3.4229644028	0.4830117718
C	-4.1593431364	-1.0106647728	1.8973782055
C	4.6060364296	-1.6418120971	0.3159523990
C	2.8888282659	4.1584442766	-0.7955122577
C	-2.6973195148	2.3325093025	0.6389122402
C	-5.4131820806	-1.4613359237	1.6394947162
C	3.9523298036	-0.3530811006	-0.0445255398
C	1.8354804600	3.4249337035	-0.2406544852
C	-1.8524024182	1.1534412597	0.4612282265
C	-5.6053529957	-1.3715876067	0.1496877396
C	5.8819797460	-1.8204002669	0.5978553483
C	-6.3962404215	-1.9385549895	2.5879854906
C	-7.6134520868	-2.3716333186	2.2705046575
C	4.4521481779	0.8823362791	-0.0549877934
C	0.4885783437	3.8230700681	-0.0327236400
C	-2.1735476832	-0.1496460451	0.4641452934
N	2.6284087322	-0.6758134706	-0.3451204793
O	1.1957539381	-2.4281486423	-0.3769029296
N	2.3056947552	2.1495721289	0.0209260223
N	-0.5812241064	1.6345804334	0.2638471401
N	-4.3934884776	-0.8465430026	-0.3310693888
O	-6.5300199960	-1.6516240520	-0.5309037014
H	6.5896802916	-1.0124694023	0.5897140913
H	5.4973041243	1.0199621985	0.1424905705
H	3.3461525300	-3.1429068558	1.2756277717
H	2.0305344963	-0.0569726513	-0.8419764454
H	2.0070256657	1.6815211765	0.8515995754
H	0.1455139485	1.0716678318	-0.1113201047
H	-4.2064777326	-0.7041059361	-1.3003356695
H	0.2862312786	4.8754145269	-0.1028144929

H	-1.4102441046	-0.8991660433	0.3171886954
H	-6.0827712601	-1.9303833184	3.6169718388
H	-8.2816104882	-2.7117191308	3.0391781658
H	-7.9710491912	-2.4006982584	1.2603663481
H	2.8190690577	5.1606072927	-1.1659207989
H	-2.2488893228	4.4450744185	0.5529337568
H	6.2668676920	-2.7927985924	0.8451042929
H	3.7488912250	-3.5276120718	-0.3836882646
H	4.9874899214	3.5641288676	-1.2317171921
H	-3.7448036560	2.2997164145	0.8574992742
H	-3.6785284075	-0.9369387886	2.8507182195

CI_2 optimized geometry at CASSCF/6-31g(d) level of theory with an active space (6,6)

C	-2.4382047537	-3.0408741368	-0.1954061325
C	-4.4087981907	0.8549019589	0.1549947723
C	-0.4481270209	2.5671726096	0.0861602216
C	3.6885264993	0.3106652213	0.5064671192
C	-3.5450145706	-3.8454565289	-0.8431590222
C	-5.0931133368	1.9451773815	0.6853802664
C	0.1608744585	2.5285314841	-1.1889205882
C	4.5994600975	-0.5656420062	1.2456774877
C	-4.7170045957	-2.8862480344	-0.9116977794
C	-4.1846627125	2.9580226683	0.9109810510
C	1.3450702502	1.8518786553	-1.0732999499
C	5.7370567778	-0.7620090936	0.5150050926
C	-4.2439166270	-1.5764582387	-0.3890067246
C	-2.9019464145	2.5036595239	0.5012698631
C	1.4940544402	1.4565878928	0.2874914674
C	5.5788596791	0.0421205037	-0.7438068430
C	-5.9252932768	-3.1609563166	-1.3645653479
C	6.8940684428	-1.5883755438	0.8651042567
C	7.9722736265	-1.7443093944	0.1170717712
C	-4.9401061544	-0.4214520630	-0.2604307172
C	-1.7104428951	3.1697544355	0.5218406682
C	2.4677469910	0.7133182106	0.9747590247
N	-2.8995207801	-1.7522556319	-0.0472364882
O	-1.3595438330	-3.4079347479	0.1452194277
N	-3.0839744859	1.1945610208	0.0801003263
N	0.3738223016	1.9110235407	0.9295100322
N	4.2954578907	0.6096297442	-0.6661384537
O	6.3201327276	0.2224320465	-1.6433959925
H	-6.7101085574	-2.4282980018	-1.3960664492
H	-5.9918404229	-0.4394197468	-0.4685078699
H	-3.2222151163	-4.1839144579	-1.8214575998
H	-2.4203581056	-1.1475569480	0.5818984520
H	-2.4544640157	0.7331262941	-0.5377496004
H	0.1952091952	1.8141523288	1.9058044976
H	4.0258710203	1.3224715367	-1.3046751851
H	-1.6850425797	4.1935513164	0.8459880401
H	2.2319175877	0.4145506499	1.9788163963
H	6.8196861171	-2.0911768842	1.8136061678
H	8.7757583109	-2.3722182929	0.4542726048
H	8.0925408728	-1.2643932281	-0.8342730976
H	-4.3791796184	3.9218565610	1.3339865185
H	-0.2605829653	2.9589643642	-2.0731427744
H	-6.1738160309	-4.1428870173	-1.7233644685
H	-3.7441187682	-4.7231829286	-0.2400833573
H	-6.1421477148	1.9631745770	0.8984568254

H	2.0134558306	1.6133219181	-1.8719832302
H	4.3564476701	-0.9887058388	2.1984485853