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

SUPPLEMENTARY INFORMATION:

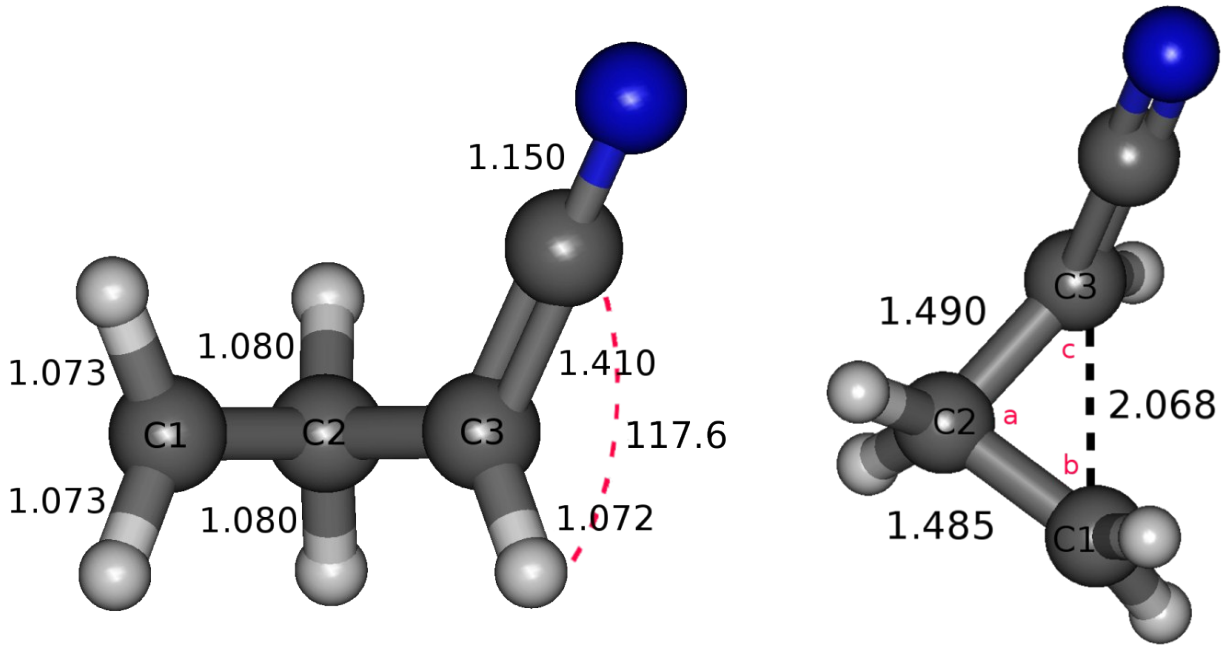

Figure I

Figure I: MP2 optimized structures of the transition state (ST) for the cyclopropyl cyanide opening reaction: side (left) and plan views (right) of the open cycle structure, respectively. Distances are given in angstroms, angles in degrees.

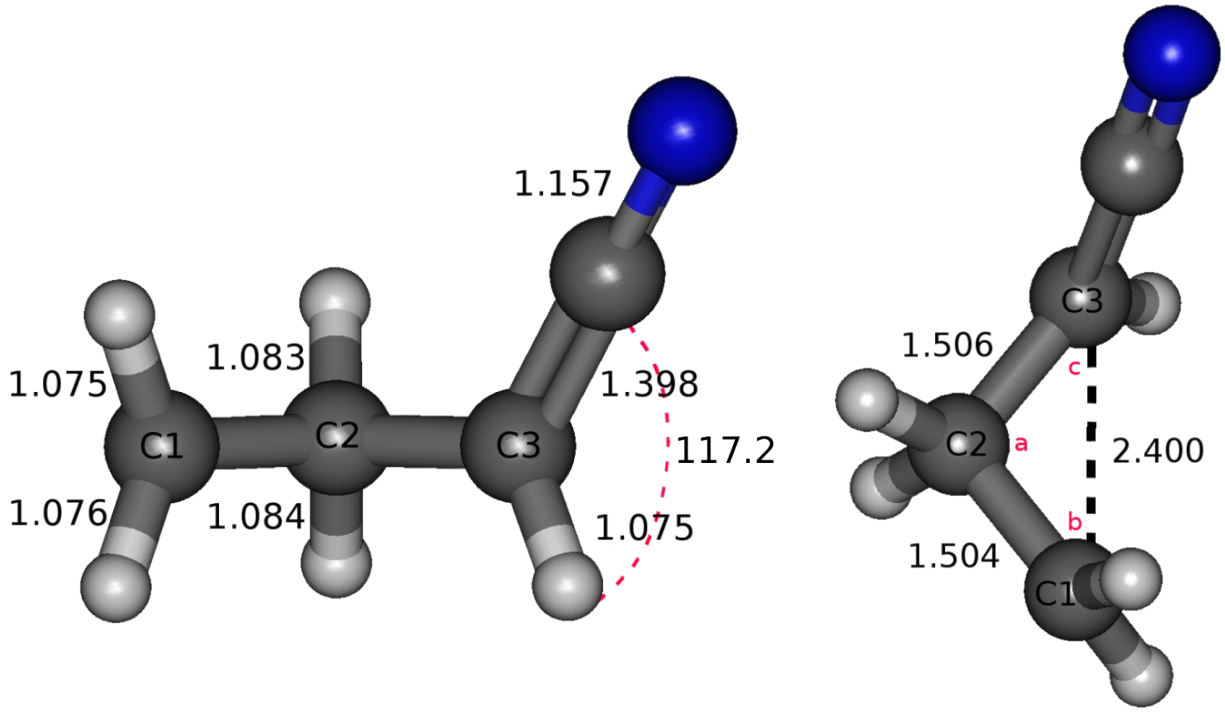

Figure II

Figure II: MP2 optimized structure of 1,3-biradical cyclopropyl cyanide corresponding to the potential energy minimum in the cyclopropyl cyanide opening reaction. Front view (left) and plan view (right) of the open cycle structure, respectively. Distances are given in angstroms, angles in degrees.

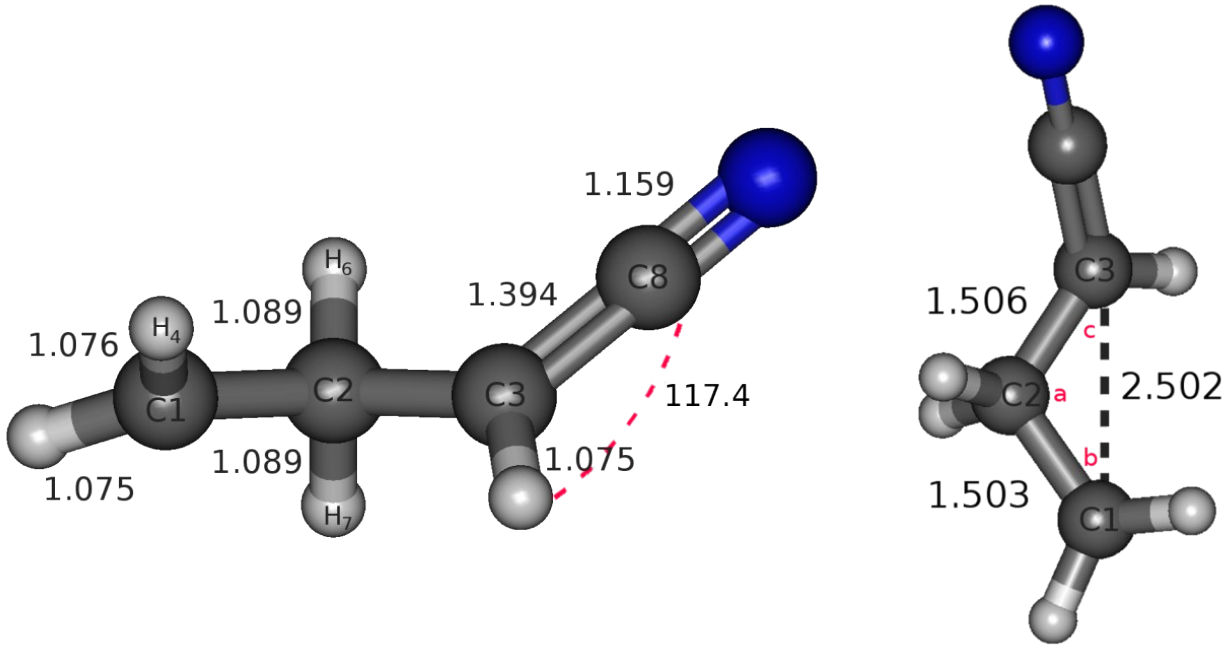

Figure III

Figure III: MP2 optimized structure of the 1,3-biradical cyclopropyl cyanide corresponding to the potential energy minimum for the first triplet state shown in Figure 7. Side (left) and plan (right) views of the open cycle structure, respectively. Distances are given in angstroms, angles in degrees.

	C_4H_5N	C_4H_5N(TS)	C_4H_5N(open)	Open C_4H_5N TRIPLET		
Angle	*UHF*	*UHF*	*UHF*		*Dihedral Angle*	
a	60.4	88.0	105.8	112.5	**[H7-C2-C3-C8]**	105.6
b	60.4	46.8	37.2	33.8	**[H7-C2-C1-H4]**	158.4
c	59.2	45.9	37.1	33.7	**[H6-C2-C3-C8]**	–9.8

Table A: Values of angles a, b and c of open, close, TS and open triplet optimized structures, in degrees (UHF, 6-31g(d,p)).

	C_4H_5N	C_4H_5N (TS)	C_4H_5N Open
Energy	0.0000	1.2639×10^2	1.1627×10^2
ZPE	2.2654×10^2	2.0933×10^2	2.0649×10^2
Total energy	0.0000	1.0937×10^2	9.6431×10^1

Table B: Energy, ZPE and total UHF energy (in kJ/mol) for the C_4H_5N opening reaction. Total energies are referred to the electronic energy of reactants including ZPEs.

	Reactants	**Adduct (1)**	**TS1**	**P1**
Energy	0.0000	-1.3786×10^2	1.9423×10^2	-2.3653×10^2
ZPE	4.6011×10^2	4.5494×10^2	4.4666×10^2	4.8215×10^2
Total energy	0.0000	-1.4329×10^2	1.8113×10^2	-2.1490×10^2

Table C: Energy, ZPE, and total energies (in kJ/mol) of the stationary points in

Reaction 1. Total energies are referred to the electronic energy of reactants including ZPEs.

Cartesian Coordinates (in Å) of each stationary points (minima and TS structures) described in the manuscript as given in the outputs of the GAMESS calculations.

C4H5N

		x	**y**	**z**
C	6.0	-1.3544809202	0.7471678186	-0.2176614066
C	6.0	-1.3542507976	-0.7471334778	-0.2181645093
C	6.0	-0.3144278604	0.0000028282	0.5886323335
H	1.0	-1.0112569617	1.2537415049	-1.1073055852
H	1.0	-2.1199907103	1.2653500457	0.3404460800
H	1.0	-1.0108300904	-1.2529145004	-1.1081766582
H	1.0	-2.1196447668	-1.2658939364	0.3395550488
C	6.0	1.0535743729	0.0000474098	0.1346477284
H	1.0	-0.4308129746	-0.0003328225	1.6634610669
N	7.0	2.1695190453	-0.0000689026	-0.2555461872

$C4H5NH^+$

		x	y	z
C	6.0	1.3528742513	0.8372889076	0.1000792483
C	6.0	1.4110792616	-0.5994542815	0.4367814581
C	6.0	0.3650160697	-0.1214390133	-0.5803737560
H	1.0	0.9481943947	1.5202185863	0.8330226956
H	1.0	2.0871340954	1.2563732908	-0.5717546721
H	1.0	1.0469048092	-0.9146856715	1.4039414989
H	1.0	2.1876979354	-1.2152964862	0.0081531178
C	6.0	-0.9883151218	-0.0832721463	-0.1834624107
H	1.0	0.5039387249	-0.3607704679	-1.6261166605
N	7.0	-2.1009880064	-0.0473059920	0.1596301814
H	1.0	-3.0704208540	-0.0229488497	0.4373549381

$[C8H10N2H]^+$ - Adduct (1)

		x	y	z
C	6.0	-4.7212128491	-0.5039154908	0.5742182028
C	6.0	-4.6570086901	-0.3049508267	-0.8957235928
C	6.0	-3.8128796276	0.5817650339	0.0110046294
H	1.0	-4.2431234897	-1.3780489985	0.9911138028
H	1.0	-5.5829988852	-0.1453748768	1.1164923419
H	1.0	-5.4732852210	0.1946106678	-1.3951424328
H	1.0	-4.1348978867	-1.0425848258	-1.4871403336
C	6.0	-2.4014748802	0.3767268451	0.0452082282
H	1.0	-4.1079816903	1.6138374837	0.1378531525
N	7.0	-1.2446006423	0.1929327530	0.0714140629
N	7.0	1.2424589176	-0.1528992271	0.1529713759
C	6.0	2.3987688048	-0.3340461724	0.2077973373
H	1.0	-0.0013748562	0.0198257287	0.1098977194
C	6.0	3.8097242474	-0.5365010868	0.2671693809
C	6.0	4.7120829893	0.6743936439	0.4682658568
C	6.0	4.6736984974	0.0134022034	-0.8606858476
H	1.0	4.0983547001	-1.4724940341	0.7242850167
H	1.0	5.5624518656	0.5108650758	1.1128025747
H	1.0	4.2300407689	1.6351658611	0.5732795667
H	1.0	5.4969404280	-0.6184391522	-1.1578966518
H	1.0	4.1654084768	0.5208212228	-1.6673107820

TS1

		x	y	z
C	6.0	0.0028640051	-1.8039321601	0.6050885118
C	6.0	-1.3612469810	-1.5799044300	0.0276448863
C	6.0	-2.1585479863	-0.4690405772	0.6077066110
H	1.0	0.1157012675	-1.7426165675	1.6775562228

H	1.0	0.5851124240	-2.5861765914	0.1459541244
H	1.0	-1.9006863978	-2.5038342326	0.2692507731
H	1.0	-1.3279177083	-1.5237217085	-1.0531746946
C	6.0	-3.0029679246	0.3370891183	-0.2077151162
H	1.0	-2.2963437291	-0.3963413395	1.6712801234
N	7.0	-3.5985237101	1.0433697654	-0.8722981445
N	7.0	0.0325396215	0.9163023204	0.1805227145
C	6.0	0.9314711514	0.1681321787	0.1785884394
H	1.0	-0.5647106680	1.7047383554	0.0663008429
C	6.0	2.3532794523	-0.1387174905	0.0633906213
C	6.0	3.1428433578	0.5996176343	-1.0076292470
C	6.0	3.3386845525	0.9662818625	0.4072439756
H	1.0	2.6192867707	-1.1501036506	0.2874213982
H	1.0	2.6056699174	1.2795882498	-1.6433686615
H	1.0	3.8907046356	0.0131251529	-1.5078840010
H	1.0	2.9386563596	1.9017329767	0.7536393909
H	1.0	4.2274592206	0.6419999265	0.9157948878

Product 1 (P1)

		x	y	z
C	6.0	3.2157077403	-0.3263499021	-0.4811028689
C	6.0	2.8795246550	-0.9191016259	0.8211227023
C	6.0	1.8317755693	-0.9718775054	-0.3086456560
H	1.0	3.2461796407	0.7497966412	-0.5690579685
H	1.0	3.8748260111	-0.8610736328	-1.1488118426
H	1.0	2.6719142627	-0.2672152431	1.6563855969
H	1.0	3.2886748161	-1.8835742585	1.0829509372
C	6.0	0.6805532772	-0.1226486004	-0.2171704746
H	1.0	1.6819672620	-1.9365975907	-0.7747509883
N	7.0	-0.5105036874	-0.4923891636	-0.6089442847
C	6.0	-1.5595582524	0.5472025606	-0.4641511466
C	6.0	0.6200703384	1.2966457415	0.2702388412
C	6.0	-0.8793942731	1.5280972071	0.5100823268
H	1.0	1.2309246755	1.4611134298	1.1557145010
H	1.0	1.0117817434	1.9371436234	-0.5257939597
H	1.0	-1.1910393451	2.5522683775	0.3238024871
H	1.0	-1.1454354461	1.2621166802	1.5317769437
H	1.0	-1.7342633336	0.9954295453	-1.4458430015
C	6.0	-2.7971841230	-0.0488935549	0.0348367237
N	7.0	-3.7902667357	-0.5378066245	0.4483484794
H	1.0	-0.7051826483	-1.4008079757	-1.0221314640

C4H5N biradical

x	y	z

C	6.0	1.8480963220	-0.8254705339	-0.5178282229
C	6.0	1.2925522070	0.5187983318	-0.1362300071
C	6.0	0.0935329825	0.2369114231	0.7313975850
H	1.0	1.3612026072	-1.3939562169	-1.2901842583
H	1.0	2.4588137011	-1.3661680634	0.1837098192
H	1.0	1.0049072452	1.0879413666	-1.0119269160
H	1.0	2.0197840512	1.1013968634	0.4174831927
C	6.0	-1.1931694396	0.1035533845	0.2003140917
H	1.0	0.2301887851	-0.0374976725	1.7614670705
N	7.0	-2.2582478211	0.0148204844	-0.2422943015

C4H5N biradical TS

		x	y	z
C	6.0	1.6056935778	-0.8085289521	-0.4292662801
C	6.0	1.3299786135	0.6232778061	-0.1460367298
C	6.0	0.1779336268	0.1829149249	0.6909798311
H	1.0	1.1153398967	-1.3029297917	-1.2451730620
H	1.0	2.2120008541	-1.3901466040	0.2383615998
H	1.0	1.0477203671	1.2066497849	-1.0099935611
H	1.0	2.1009963398	1.1295846923	0.4164648798
C	6.0	-1.1275984578	0.0652656306	0.1721190515
H	1.0	0.3304055652	-0.0809949910	1.7192276190
N	7.0	-2.1917916516	-0.0224157938	-0.2551846303

$[C8H10N2H]^+$ - Adduct (2)

		x	y	z
C	6.0	1.3820011833	0.5248473027	-1.6651781107
C	6.0	2.2416189192	-0.3780030057	-0.7754927845
C	6.0	3.5947230269	-0.0230058249	-0.5769643320
N	7.0	4.7089627483	0.3111191382	-0.5201512695
C	6.0	1.8044074985	-0.7945932582	-2.1829085299
N	7.0	3.3970672898	-1.0805378652	1.9834051328
C	6.0	3.4593577493	-1.5740998264	3.0554125792
C	6.0	3.5321639698	-2.1625341091	4.3642299325
C	6.0	3.7457586651	-1.2605547900	5.5657922702
C	6.0	2.4140833000	-1.8940479063	5.3545210924
H	1.0	0.3705219686	0.6579470124	-1.3119395698
H	1.0	1.8514341983	1.4080004284	-2.0736900296
H	1.0	2.5654440122	-0.8228749944	-2.9492140909
H	1.0	1.0963069874	-1.6093556748	-2.2016663398
H	1.0	1.8064954000	-0.8561793446	0.0887424620
H	1.0	5.6712589992	0.5483172860	-0.3480489308
H	1.0	3.9930889805	-3.1401317754	4.3859206632

H	1.0	2.1261596585	-2.7243843915	5.9813990265

$[C_8H_{10}N_2H]^+$ - Adduct (3)

		x	y	z
C	6.0	1.2341192563	0.5896080914	-1.9143909310
C	6.0	2.2272299101	0.1433567760	-0.8367853804
C	6.0	3.0699757301	-0.9633486858	-1.0800985174
N	7.0	3.8352795512	-1.8287016006	-1.2245194553
C	6.0	0.7165668807	-0.0708783236	-0.6989325126
N	7.0	1.2508717581	-2.5222871080	-2.7092935815
C	6.0	0.6527528287	-3.3299008145	-3.3325252595
C	6.0	-0.0749829612	-4.3027462374	-4.0992599105
C	6.0	0.0103019490	-4.2592685033	-5.6142479981
C	6.0	-1.2515968068	-3.8434507627	-4.9412000925
H	1.0	1.1520116486	1.6616462650	-2.0151868101
H	1.0	1.2328706533	0.0145972464	-2.8271963424
H	1.0	0.3682670154	-1.0870743949	-0.7993935518
H	1.0	0.2610752802	0.5245290924	0.0785127170
H	1.0	2.6991050999	0.9002987675	-0.2243479702
H	1.0	4.4068701397	-2.6326147747	-1.4209847950
H	1.0	-0.1463911766	-5.2744412869	-3.6307635566
H	1.0	-1.4912857542	-2.7907299182	-4.9189982203
H	1.0	-2.1017319097	-4.5081214692	-4.9695599140
H	1.0	0.0438988905	-5.2152450930	-6.1146070874
H	1.0	0.6296277464	-3.4895421355	-6.0503434584

$[C_8H_{10}N_2H]^+$ - Adduct (4)

		x	y	z
C	6.0	1.7960008319	0.7690827607	-0.7947465200
C	6.0	3.1152506250	0.0076138608	-0.6391368369
C	6.0	4.3038179279	0.7532156393	-0.4333212430
N	7.0	5.2516889128	1.3471909737	-0.2692222595
C	6.0	2.3924932677	0.1467363608	-1.9817046289
N	7.0	1.2150898035	-2.5026352920	-0.2586020739
C	6.0	0.6123830434	-3.4254139596	0.0209348926
C	6.0	-0.1551140507	-4.5995354124	0.3784408929
C	6.0	-0.1968351844	-5.7695084943	-0.5749095496
C	6.0	-1.4050427618	-4.9260595518	-0.4031639523
H	1.0	0.9712761731	0.2797744338	-0.3136189610
H	1.0	1.8275144958	1.8394277969	-0.7021522710
H	1.0	2.8436515606	0.7788894528	-2.7246950439
H	1.0	1.9886076222	-0.7815130980	-2.3370627037
H	1.0	3.1051991005	-0.9464277462	-0.1449988133
H	1.0	6.0892558341	1.8604605941	-0.1184898619
H	1.0	-0.1478310906	-4.8037881551	1.4331735469
H	1.0	-1.6786808929	-4.2612771040	-1.2017614064

H	1.0	-2.2314440646	-5.3119089690	0.1645556580
H	1.0	-0.1776159830	-6.7459254626	-0.1272663645
H	1.0	0.3579007961	-5.6831487954	-1.4910785908