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Charge-Induced Isomerization in Alkyl Imine Molecular Motors: A Reduced Energy Barrier Approach

Syed Bilal Ahmed[a], Hei Wun Kan[b], King-Cheong Lam[c,*] and Cho-Tung Yip[a,*]

[1] School of Science, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China
[2] Key Laboratory of Quantitative Synthetic Biology, Shenzhen Institute of Synthetic Biology, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China
[3] Division of Science, Engineering and Health Studies, The School of Professional Education and Executive Development, Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

Corresponding authors:
*Prof. Cho-Tung Yip, E-mail: h0260416@hit.edu.cn
*King-Cheong Lam, E-mail: antony.lam@cpce-polyu.edu.hk

Supplementary Information

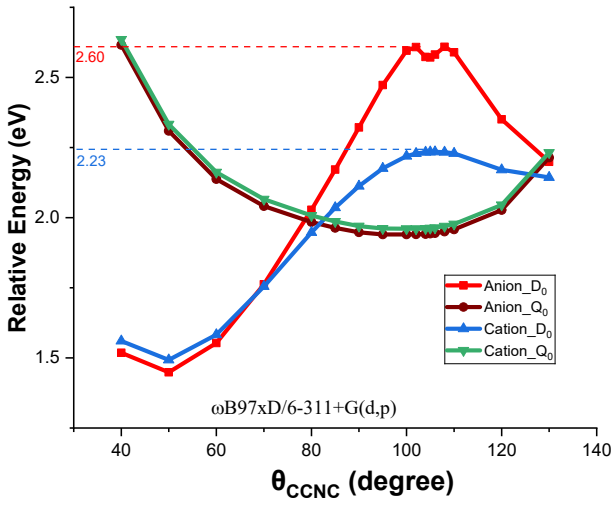
This document provides a comprehensive overview of the computational analyses conducted on the imine-based molecular rotary motor. It features graphical representations of energy profiles, spin density maps, and HOMO-LUMO gaps, all derived from various electronic structure calculations. Additionally, the Cartesian coordinates of the optimized key geometric structures used in this work are included.

Summary of Contents:

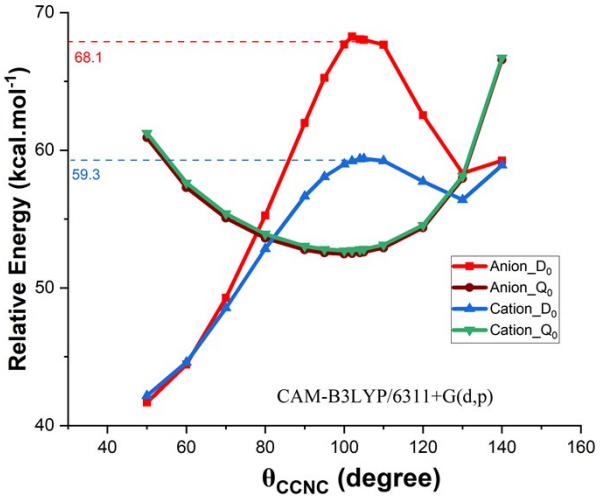
Methods	State	θ_{CCNC} (°)	C=N (Å)	θ_{CCCN} (°)
CASSCF/cc-pVTZ	Neutral	5.10	1.26	71.72
	Anion	29.77	1.32	41.18
	Cation	8.56	1.24	59.52
ωB97XD/6-311+G(d,p)	Neutral	5.36	1.26	72.63
	Anion	29.91	1.33	41.21
	Cation	8.43	1.24	59.72
CAM-B3LYP/6-311+G(d,p)	Neutral	6.48	1.26	69.16
	Anion	29.47	1.32	39.92
	Cation	6.87	1.26	65.87
M06-2X/6-311+G(d,p)	Neutral	6.40	1.26	70.45
	Anion	29.84	1.32	40.65
	Cation	7.06	1.26	66.86

Table S1: Comparison of key geometrical parameters for the (M)-*cis* isomer of the neutral (S_0) and charged (D_0) molecules. All geometries presented have been fully optimized, as calculated using various functionals and basis sets employed in this work.

(a)


2.60
2.23
Relative Energy (eV)
2.5
2.0
1.5
Anion_D0
Anion_Q0
Cation_D0
Cation_Q0
ωB97xD/6-311+G(d,p)
40
60
80
100
120
140
θCCNC (degree)

(b)


68.1
59.3
Relative Energy (kcal.mol-1)
70
60
50
40
Anion_D0
Anion_Q0
Cation_D0
Cation_Q0
CAM-B3LYP/6311+G(d,p)
40
60
80
100
120
140
160
θCCNC (degree)

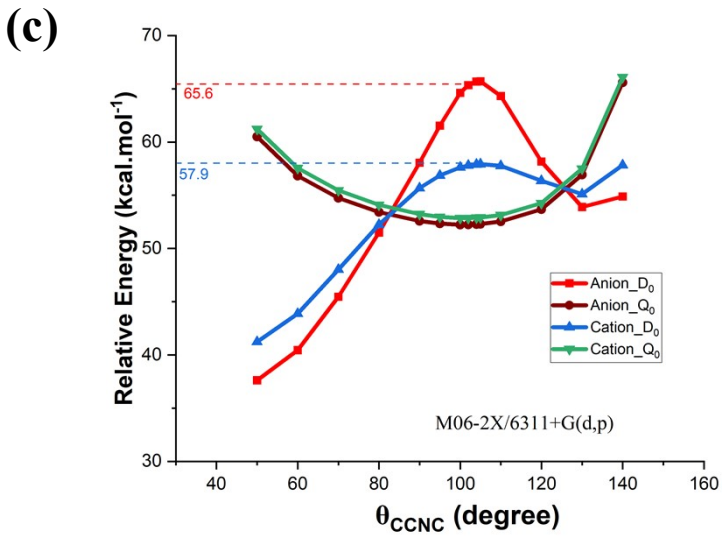


Figure S1: Relative energy profiles of the cationic and anionic imine-based molecular rotary motor in the region near the conical intersections calculated at (a) ωB97xD/6-311G+(d,p) (b) CAM-B3LYP/6-311G+(d,p) and (c) M062X/6-311G+(d,p) level of theories.

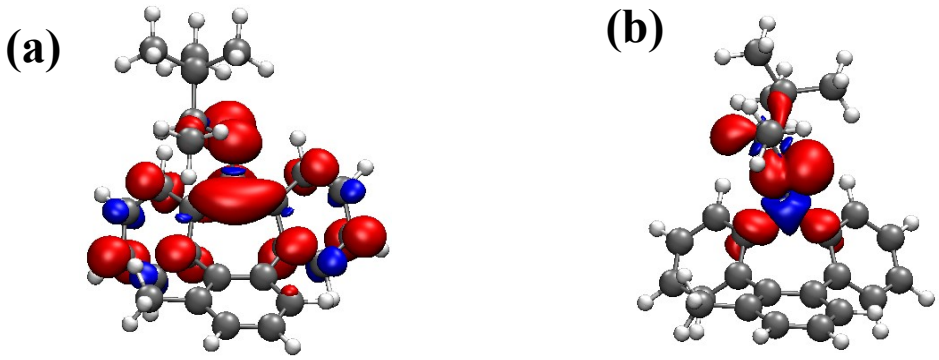
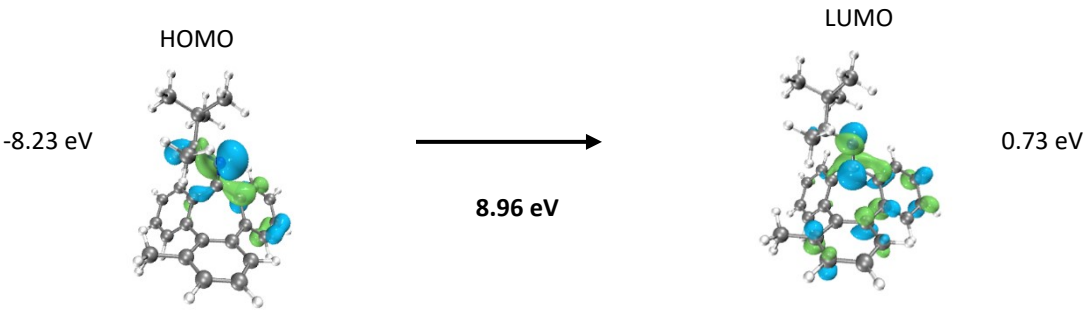
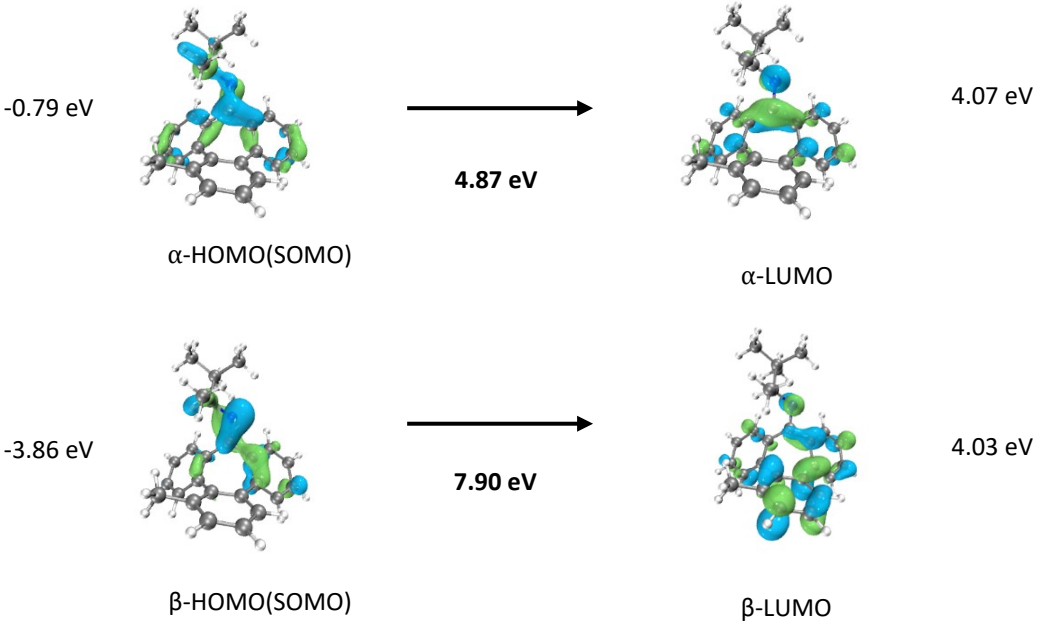


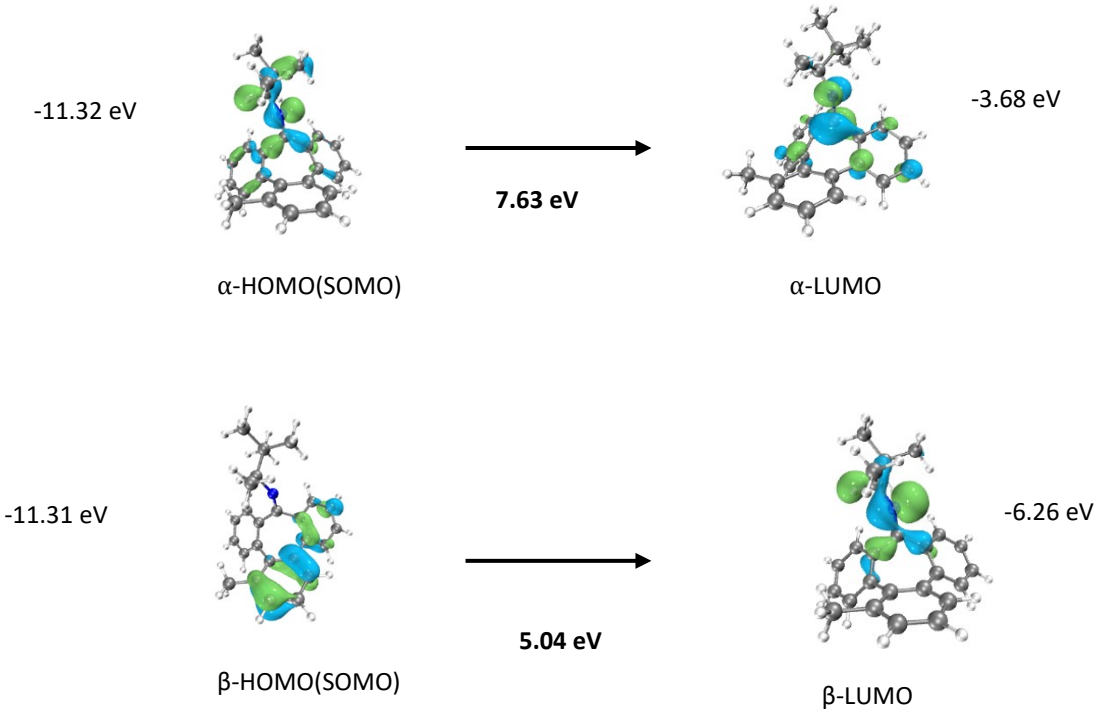
Figure S2: The spin density maps of the (a) anionic and (b) cationic molecular motors in the D_0 spin state. The θ_{CCNC} are 29.77° for the anionic molecule and 8.56° for the cationic molecule. The red color indicates the α-electron and the blue color represents the β-electron.



(a) Neutral



(b) Anion



(c) Cation

Figure S3: HOMO (SOMO) and LUMO energy gaps for the (a) neutral (S_0), (b) anion (D_0), and (c) cation (D_0) (M)-*cis* isomer of the imine-based molecular motor (isovalue = 0.05). The geometries are fully optimized (see Table S1). The energy gaps between the α-HOMO and α-LUMO are 8.96 eV for the neutral system, 4.87 eV for the anionic system, and 7.63 eV for the cationic system.

Cartesian coordinates of the optimized structures

(**M**)-***cis*** **isomer** (neutral_S_0 state) **Energy:** -1061.797

C	-1.85334000	-0.95723100	-0.15760900
C	-2.23170600	0.28157800	-0.70645200
C	-1.79014400	1.59147700	-0.16016200
C	-1.07853600	-1.01924800	1.10920900
C	-0.44916800	1.82368600	0.16369300
C	0.10851000	-0.30203600	1.25793400
C	0.50102000	0.67875900	0.20130600
C	-2.68308800	2.65750300	-0.07965800
C	-2.25868900	3.91927800	0.29990900
C	-0.92131600	4.14495600	0.58483300
C	-0.02157000	3.09534800	0.51757400
H	-3.72700100	2.49068100	-0.30953300
H	-2.97436900	4.72724500	0.36771900
H	-0.58162600	5.13246500	0.86591400
H	1.02504300	3.25082900	0.74231100
C	-2.98432400	-2.07940600	-1.96703800
C	-3.40292100	-0.86584500	-2.47908300
C	-3.01519600	0.30397400	-1.85840300
C	-2.21044900	-2.14619900	-0.81585800
H	-3.24528700	-2.99755200	-2.47792400
H	-3.99862900	-0.83048700	-3.38103800
H	-3.28651300	1.25731300	-2.29026700
C	-0.79373800	-1.88041600	3.35110900
C	-1.52058300	-1.79630400	2.17781900
C	0.84001600	-0.38960900	2.43739900
C	0.39944100	-1.18516600	3.47896100
H	-1.16118900	-2.48515400	4.16888700
H	-2.45781000	-2.32804900	2.08959000
H	0.97268200	-1.24854200	4.39360700
N	1.49920300	0.64196900	-0.56872900
C	2.38714600	-0.51195300	-0.57029600
C	1.88555300	-1.45518600	-1.66245900
C	3.85112700	-0.03279100	-0.73808700
C	4.05933100	0.66571200	-2.08291600
C	4.80088000	-1.22756100	-0.62167600
C	4.16519800	0.94657100	0.39755900
H	1.82727600	-0.94349600	-2.62223100
H	2.53039400	-2.32660500	-1.76395900
H	0.88206800	-1.80233100	-1.41292000
H	3.32917600	1.46267600	-2.21815600
H	5.05971200	1.09944700	-2.13299200

H	3.96253100	-0.03375100	-2.91420400
H	4.01235500	0.47466700	1.37158100
H	5.20527900	1.27251100	0.34485300
H	3.52917500	1.82978300	0.34142600
H	4.65202800	-1.75874800	0.32117200
H	4.66826900	-1.93945200	-1.43647900
H	5.83713400	-0.88660800	-0.65147600
H	1.75260900	0.18363100	2.53533300
C	-1.74458800	-3.50280200	-0.34983200
H	-2.42474100	-3.93551100	0.38529600
H	-1.69939800	-4.19022100	-1.19327000
H	-0.75897800	-3.45773700	0.10976100
H	2.34219000	-1.05331800	0.38143400

(P)-*trans* isomer (neutral_S_0 state) **Energy:** -1061.798

C	-1.79273600	0.73879300	0.35488900
C	-1.03991100	0.45364800	1.50773700
C	-0.34328800	-0.83867200	1.71957600
C	-2.02578200	-0.29715900	-0.68817400
C	0.43564100	-1.41308500	0.71057800
C	-0.95725400	-0.98530100	-1.26691100
C	0.39832400	-0.84139000	-0.67142500
C	-0.38292300	-1.46265900	2.96470400
C	0.32529600	-2.62613400	3.20647100
C	1.10098400	-3.18527900	2.20290500
C	1.14969800	-2.57932400	0.96024900
H	-0.99408200	-1.03505400	3.74836600
H	0.26572500	-3.10019300	4.17655900
H	1.65554200	-4.09578900	2.38349000
H	1.73897700	-3.01544600	0.16429300
C	-2.12903700	2.98281300	1.17328000
C	-1.43530800	2.68578100	2.33094100
C	-0.88550500	1.43061300	2.48793800
C	-2.31554600	2.03190800	0.17787800
H	-2.52497900	3.97951100	1.02555400
H	-1.29624600	3.44050600	3.09285200
H	-0.29309700	1.20694000	3.36459800
C	-3.52726900	-1.47176100	-2.17615100
C	-3.31121400	-0.56967600	-1.14911800
C	-1.17087400	-1.86896900	-2.31542500
C	-2.45283500	-2.10862200	-2.77791600
H	-4.53598200	-1.67235500	-2.51063500
H	-4.15406600	-0.07070000	-0.69121800
H	-2.61494000	-2.80233800	-3.59151900
N	1.34094200	-0.33434900	-1.33900800
C	2.66340200	-0.15693300	-0.76609200
C	3.63526700	-0.97919100	-1.60635600

C	2.98655500	1.36307300	-0.69523800
C	2.94150400	2.02021100	-2.07588500
C	4.37472200	1.55614700	-0.07855000
C	1.95353400	2.03273200	0.21799900
H	3.60929400	-0.66821100	-2.64996000
H	4.65477000	-0.89170200	-1.23464800
H	3.35592600	-2.03266100	-1.56838300
H	1.97545100	1.85955400	-2.55180100
H	3.10597000	3.09502600	-1.97953700
H	3.71624500	1.62727600	-2.73575000
H	1.93232800	1.55654000	1.20082000
H	2.19698800	3.08667200	0.36088500
H	0.94880700	1.97583300	-0.19993100
H	4.45740400	1.04211800	0.88159300
H	5.16622600	1.18888300	-0.73182100
H	4.56038700	2.61727300	0.09473900
H	-0.32028000	-2.37012500	-2.75738300
C	-3.03439500	2.45718900	-1.07764000
H	-4.10315400	2.24469900	-1.02679700
H	-2.92318800	3.53110500	-1.21988700
H	-2.64378600	1.95379500	-1.95950200
H	2.71085600	-0.52323500	0.26648700

(M)-*cis* isomer (anion_D_0 state) **Energy:** -1061.795

C	-2.12463300	-0.78611300	-0.20521900
C	-2.43388600	0.55958400	-0.44735200
C	-1.73019800	1.67873500	0.22148100
C	-1.22274600	-1.15230600	0.91648300
C	-0.31093200	1.69552900	0.31228300
C	0.07982100	-0.61490300	0.99932300
C	0.53792600	0.51822500	0.19220600
C	-2.44955600	2.82728200	0.54813000
C	-1.82817500	4.01235700	0.90061300
C	-0.43341200	4.06603000	0.87080500
C	0.30017400	2.94211500	0.57140700
H	-3.53204200	2.78842500	0.50215700
H	-2.41357600	4.88357900	1.16468400
H	0.07816100	4.99424300	1.09862200
H	1.38090200	2.97030000	0.55633000
C	-3.63139000	-1.44230500	-1.97407700
C	-3.99598900	-0.12221300	-2.16632000
C	-3.38288200	0.86834700	-1.42458600
C	-2.69204800	-1.78857700	-1.00938400
H	-4.06344200	-2.21936600	-2.59411800
H	-4.72410300	0.13887400	-2.92415700
H	-3.60397200	1.90787500	-1.62530400
C	-0.81883500	-2.55055600	2.85866800

C	-1.65561000	-2.07653100	1.85894000
C	0.92623600	-1.13362200	2.00542000
C	0.48982800	-2.07830100	2.90866100
H	-1.17709300	-3.27350600	3.57964300
H	-2.67208000	-2.44600800	1.79375700
H	1.16556100	-2.42859300	3.68021700
N	1.76497400	0.67366900	-0.29155500
C	2.55225000	-0.48809500	-0.61435100
C	2.00551400	-1.12572500	-1.90007100
C	4.05171300	-0.08376600	-0.70396500
C	4.26759000	1.00090400	-1.76100900
C	4.92200400	-1.30064800	-1.02918800
C	4.47075500	0.46015300	0.66478600
H	2.02615300	-0.40861800	-2.72180800
H	2.55424600	-2.02395300	-2.19241100
H	0.96373500	-1.40209800	-1.73429800
H	3.57665000	1.82397300	-1.58396000
H	5.29484600	1.37514200	-1.72580700
H	4.08860800	0.61543500	-2.76688000
H	4.35979800	-0.30894000	1.43434100
H	5.51686600	0.77965800	0.65588900
H	3.84047100	1.30520300	0.93934400
H	4.72483700	-2.11738000	-0.32972700
H	4.74356600	-1.67152800	-2.03934100
H	5.98228700	-1.04427500	-0.95386100
H	1.91846700	-0.71598000	2.10480800
C	-2.28585400	-3.23739200	-0.89628200
H	-2.87550700	-3.77655300	-0.15267800
H	-2.42947800	-3.73709900	-1.85513200
H	-1.24136700	-3.33578000	-0.60592800
H	2.51669800	-1.27795500	0.15209000

(M)-*cis* isomer (cation_D_0 state) **Energy:** -1061.514

C	-2.24379600	-0.49426400	-0.27749200
C	-2.20580200	0.89291800	-0.50874100
C	-1.34458800	1.83745100	0.24534900
C	-1.49295900	-1.10535500	0.84890100
C	0.00957700	1.58167300	0.48591700
C	-0.12852600	-0.87966100	1.04400300
C	0.53987000	0.21554100	0.29110300
C	-1.82297200	3.09279300	0.61097200
C	-0.99035200	4.05045000	1.16527600
C	0.35747900	3.78933100	1.35311600
C	0.86075600	2.54852100	1.01102300
H	-2.86937600	3.31721800	0.45973800
H	-1.39915000	5.01025500	1.44802700
H	1.01073700	4.54073900	1.77213000
H	1.90309900	2.31657400	1.18153400

C	-3.76380000	-0.73140300	-2.13137300
C	-3.76211800	0.63471000	-2.33246700
C	-2.97592300	1.43827100	-1.53302700
C	-3.01446300	-1.31739200	-1.11860000
H	-4.35195400	-1.36659800	-2.78032700
H	-4.34978000	1.06986800	-3.12831700
H	-2.92949600	2.50140300	-1.72147200
C	-1.40728800	-2.61564100	2.74295700
C	-2.11473000	-1.97498200	1.74083900
C	0.60041800	-1.53442000	2.03059700
C	-0.04294100	-2.41260800	2.88188000
H	-1.92671300	-3.27824200	3.42063800
H	-3.17681900	-2.14587100	1.64545700
H	0.51108700	-2.91553600	3.66108800
N	1.57572000	0.00588000	-0.36823500
C	2.54597400	-0.86936500	-0.93036700
C	2.16690400	-1.17858400	-2.37472100
C	3.98001500	-0.31301800	-0.67332600
C	4.14549300	1.05380300	-1.34061100
C	4.99489400	-1.30646300	-1.24209900
C	4.19560600	-0.18779100	0.83717100
H	2.24794100	-0.29440500	-3.00288800
H	2.82594500	-1.94816000	-2.76678400
H	1.14428900	-1.54815300	-2.42455700
H	3.41616500	1.77501100	-0.96474800
H	5.13935900	1.44777800	-1.13230000
H	4.03877300	0.99426600	-2.42302600
H	4.09230100	-1.15422300	1.33454400
H	5.20093000	0.17919000	1.03846900
H	3.49683700	0.51300200	1.29654000
H	4.85548500	-2.30566200	-0.82583400
H	4.94085600	-1.37316900	-2.32744800
H	6.00204800	-0.97976500	-0.98604000
H	1.65350400	-1.32181800	2.15918800
C	-3.04650400	-2.82090000	-1.00584400
H	-3.83787300	-3.15811100	-0.33534200
H	-3.24671600	-3.25946500	-1.98141400
H	-2.10977300	-3.23305300	-0.63628700
H	2.44690100	-1.78592500	-0.32554600

CI-optimized (neutral_S_0 state) **Energy:** -1061.691

C	2.17529900	-0.56020800	0.46912400
C	2.15105600	0.87476500	0.63967700
C	1.42321500	1.80880000	-0.29958600
C	1.55167400	-1.21143000	-0.74685300
C	0.08466100	1.53135600	-0.72830500
C	0.26360100	-0.94531900	-1.12426200
C	-0.52020200	0.16822000	-0.46042000

C	1.99168500	3.00158400	-0.65395400
C	1.28135400	3.96088200	-1.41570600
C	-0.02009200	3.70353800	-1.79151600
C	-0.61149600	2.46675300	-1.43977100
H	3.00330100	3.22925300	-0.34576000
H	1.76173500	4.89283200	-1.68438600
H	-0.58611000	4.42768000	-2.36326100
H	-1.62469200	2.25202200	-1.75357700
C	3.41478200	-0.71726700	2.56395000
C	3.42449500	0.62955000	2.69037700
C	2.77261300	1.42733400	1.72187000
C	2.78264300	-1.34525600	1.44846500
H	3.88301100	-1.34409800	3.31177800
H	3.90298000	1.10579700	3.53647400
H	2.74966000	2.49899600	1.86368300
C	1.77511200	-2.80279100	-2.56769700
C	2.31291900	-2.14936400	-1.50994400
C	-0.31825900	-1.64896300	-2.22532400
C	0.41890100	-2.56845200	-2.93180000
H	2.36739900	-3.50409700	-3.14119900
H	3.34426500	-2.32328200	-1.23490800
H	-0.01453500	-3.09822700	-3.77010900
N	-1.91357900	0.04754200	-0.33778200
C	-2.55616164	-0.25951802	0.97137622
C	-2.26601147	0.87362028	1.99148297
C	-4.08132102	-0.55027307	0.73185700
C	-4.79361773	0.67902726	0.11374176
C	-4.77136814	-0.93580137	2.06659833
C	-4.19892814	-1.74780090	-0.24748911
H	-2.66264973	1.82244428	1.64756624
H	-2.70052304	0.64154887	2.95747824
H	-1.19371636	0.98051861	2.12152660
H	-4.29538282	0.98546320	-0.80019577
H	-5.82382077	0.43185363	-0.12308277
H	-4.79915198	1.51785833	0.80141079
H	-3.71434100	-2.62833106	0.16306448
H	-5.24249480	-1.98625116	-0.42785294
H	-3.73136418	-1.51082252	-1.19698183
H	-4.24187928	-1.74866922	2.55431715
H	-4.81405473	-0.09463796	2.74968388
H	-5.78889819	-1.26177168	1.87530239
H	-1.34333100	-1.43246100	-2.49579400
C	2.78586900	-2.87558800	1.42631600
H	3.70859400	-3.26104300	0.99885100
H	2.71069900	-3.25488700	2.44100200
H	1.95572500	-3.27184300	0.85288600
H	-2.10934013	-1.18098153	1.36338293