10.1071/CH12039_AC

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Supplementary Material

Bisiminopropadienes R-N=C=C=C=N-R from Pyridopyrimidines

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Contents:

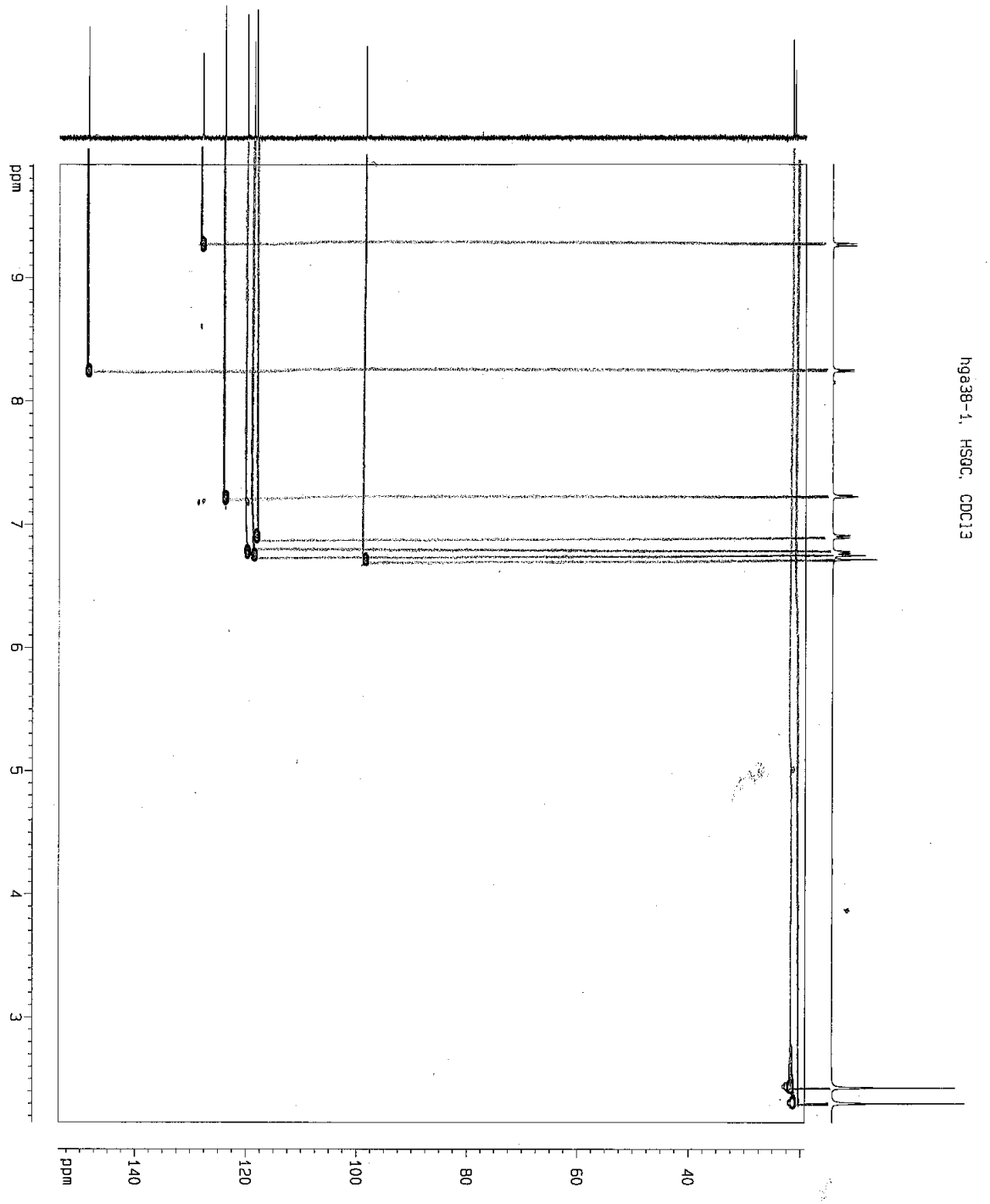


Figure S1. 2D HSQC ^{1}H-^{13}C correlation for **17a** in $CDCl_3$.

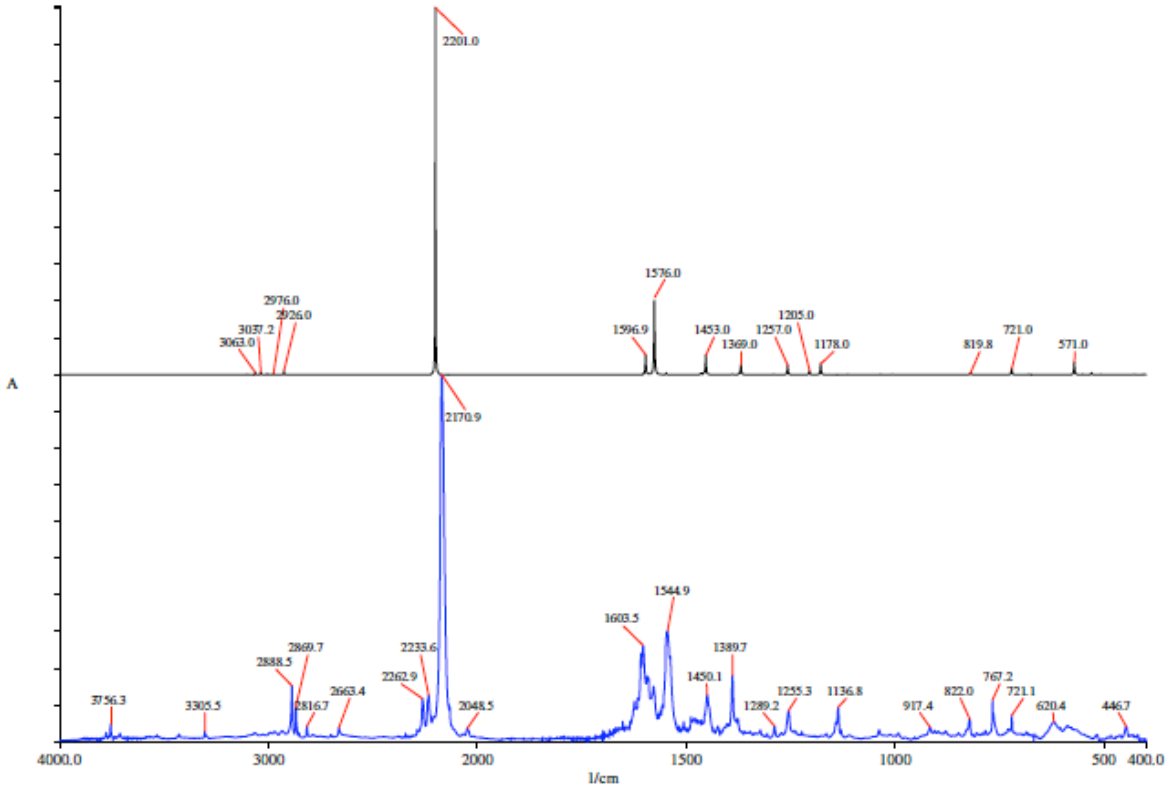


Figure S2. Calculated (top; B3LYP/6-31G**) and experimental (bottom; Ar, 10 K) IR spectra of bisiminopropadiene **20a**.

Computational Method

Calculations (a, R = CH_3) were carried out at the B3LYP/6-31G** level using the Gaussian suite of programs.[i] The temperature used is 298.15 K, and zero-point energy corrections have been applied. Calculated wavenumbers were scaled by a factor 0.9613.[ii]

As a minimum could not be found for **TS 17a-18a** at the B3LYP/6-31G** level, this reaction was optimised using the complete active space self-consistent field (CASSCF) method for the non-methylated compounds (b, R = H) (in the interest of computational speed). The CASSCF procedure used 8 electrons in 8 orbitals combined with the small atomic natural orbital (ANO-S) basis sets of Pierloot *et al.* [iii] available in the MOLCAS program[iv,v,vi], with contractions 2s1p for H, 3s2p1d for C and N, and 4s3p2d for Cl.

Table S1. **Absolute and relative energies of all species (a, R = CH_3), and imaginary frequencies of transition states (calculations at the B3LYP/6-31G** level + ZPVE).**

	HF (Hartree)	ΔE (kcal/mol)	ΔE (kJ/mol)	Imaginary Frequency (cm^{-1})
17aZ	-1258.387945	9.9	41.4	
17aE (reference)	-1258.403720	**0.0**	**0.0**	
(**TS 17a – 18a**)*	-1258.356530	29.6	123.9	-50.3
(**18a**)*	-1258.357105	29.3	122.4	
TS 18a – 19a	-1258.337974	41.3	172.6	-114.6
19a	-1258.356532	29.6	123.9	
TS 19a – 20a	-1258.318183	53.7	224.6	-158.9
20a + HCl	-797.537879	45.0	188.5	
HCl	-460.794063			

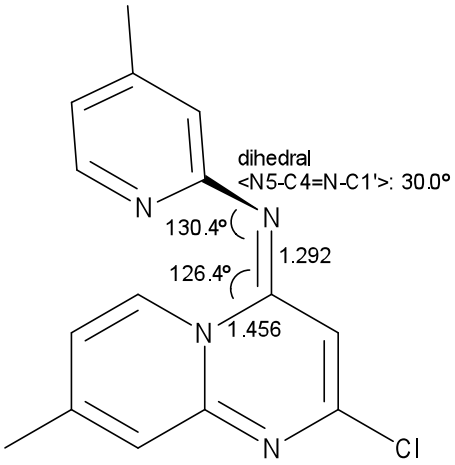
* Single point energy.

The structure and energy of TS **17a** – **18a** could not be found at the B3LYP/6-31G** level and were estimated by scanning the energy surface along the breaking C – N of **17a**, leading to an approximated structure (not a stationary point) with a C – N bond length of 2.34807 Å. Optimization converges it back to **17a**, yet a single point calculation of this TS structure yields an energy of 29.6 kcal above **17a**. E and Z in compound **17** refer to the orientation of the pyridyl group; see calculated structures below.

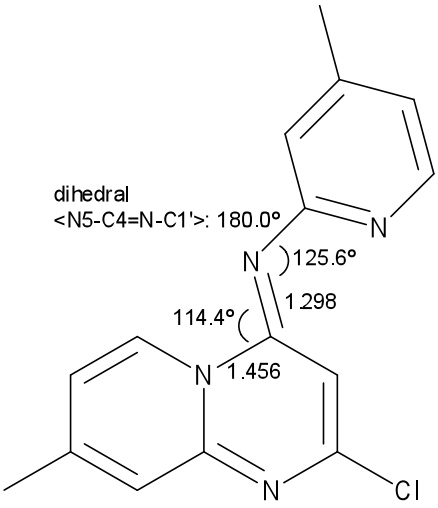
Table S2. **Absolute and relative energies for the reaction connecting 17 to 20 (b, R = H), (calculations at the CASSCF(8,8)/ANO-S level).**

	HF (Hartree)	ΔE (kcal/mol)	ΔE (kJ/mol)
17bZ	-1175.003202	6.7	28.1
17bE (reference)	-1175.013895	**0.0**	**0.0**
TS 17b – 18b	-1174.966760	29.6	123.8
18b	-1174.974950	24.4	102.3
TS 18b – 19b	-1174.950801	39.6	165.7
19b	-1174.983523	19.1	79.7
TS 19b – 20b	-1174.925614	55.4	231.8

Calculated Energies and Cartesian Coordinates (B3LYP/6-31G**)

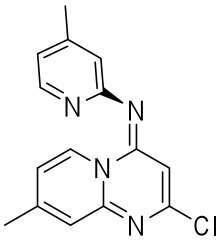


17aZ



17aE

(*Z*)-2-Chloro-8-methyl-4-(2-(4-picolinyl)-amino)-4*H*-pyrido[1,2-*a*]pyrimidine, 17aZ



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Cl	-3.874799	-2.925692	0.222014
N	0.899306	-1.365651	-0.372763
C	-2.224846	0.557765	0.032151
C	-2.657052	1.912346	0.124715
N	-0.878129	0.323704	-0.281267
C	-1.836287	2.967018	-0.177060
H	-3.691843	2.050146	0.415280
C	-0.068847	1.380650	-0.640011
C	-0.509052	2.666178	-0.607001
H	0.921301	1.117046	-0.969130
H	0.165838	3.457257	-0.913825
C	-2.299089	4.395490	-0.092897
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C	3.261493	-1.070957	-0.576135
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H	3.060330	1.450408	2.263167
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12	A	228.1	1.5	0
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27	A	605.8	27.8	4
28	A	624.6	15.2	2
29	A	639.5	13.9	2
30	A	662.2	12.8	2
31	A	672.9	21.1	3
32	A	726.1	12.3	2
33	A	732.0	19.7	3
34	A	739.2	7.3	1
35	A	760.2	10.9	1
36	A	775.1	16.2	2
37	A	794.0	20.6	3
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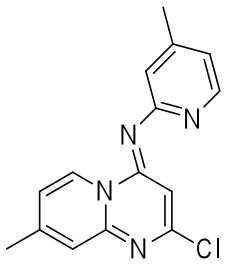
(*E*)-2-Chloro-8-methyl-4-(2-(4-picolinyl)-amino)-4*H*-pyrido[1,2-*a*]pyrimidine, 17aE



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C	-3.338774	1.884413	0.000000
N	-1.432260	0.407301	0.000000
C	-4.209173	0.825012	0.000000
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H	-1.797375	-1.619450	0.000000
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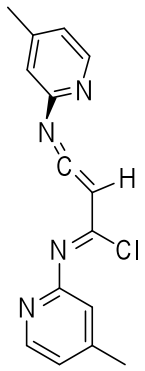
19a



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N	2.191806	-1.157133	-0.839303
C	-2.592845	0.207345	-0.291272
C	-2.748536	1.410603	0.417407
N	-3.528885	-0.291731	-1.107260
C	-3.942843	2.118710	0.310008
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C	-4.928216	1.589953	-0.537762
H	-5.414548	-0.015954	-1.888498
H	-5.879316	2.097504	-0.670351

H	0.203259	-3.365839	0.354011
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C	4.111078	0.272347	-1.000141
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C	5.132993	1.013282	-0.401306
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C	4.240104	0.273458	1.715330
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12	A	203.8	0.7	0
13	A	209.4	0.8	0
14	A	223.7	2.6	0
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16	A	299.0	0.7	0
17	A	314.0	7.3	1
18	A	360.7	5.3	0
19	A	400.0	3.8	0
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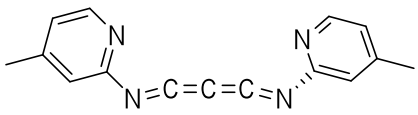
21	A	442.3	2.3	0
22	A	455.5	9.8	1
23	A	468.2	6.2	0
24	A	494.0	42.4	3
25	A	500.8	4.1	0
26	A	502.8	1.1	0
27	A	545.7	6.2	0
28	A	567.1	6.1	0
29	A	607.0	3.2	0
30	A	618.0	30.0	2
31	A	632.8	76.0	6
32	A	682.8	35.1	3
33	A	721.4	30.9	2

34	A	735.7	15.2	1
35	A	739.4	6.5	1
36	A	744.5	22.4	2
37	A	795.3	67.8	5
38	A	810.4	52.8	4
39	A	819.6	23.0	2
40	A	864.5	3.3	0
41	A	878.6	3.1	0
42	A	882.9	13.3	1
43	A	915.2	161.2	12
44	A	941.1	1.5	0
45	A	949.1	0.4	0
46	A	966.2	5.4	0
47	A	972.4	12.2	1
48	A	978.6	23.2	2
49	A	984.3	36.2	3
50	A	1023.3	3.1	0
51	A	1024.6	7.7	1
52	A	1031.1	143.4	11
53	A	1082.4	40.6	3
54	A	1093.7	0.9	0
55	A	1100.5	35.1	3
56	A	1146.4	11.3	1
57	A	1159.8	10.2	1
58	A	1238.9	46.1	4
59	A	1250.5	8.9	1
60	A	1261.1	36.5	3
61	A	1268.9	18.9	1
62	A	1276.0	4.1	0
63	A	1276.2	0.1	0
64	A	1365.9	194.0	15
65	A	1370.3	0.9	0
66	A	1371.6	1.4	0
67	A	1382.0	32.8	3
68	A	1421.7	9.0	1
69	A	1440.4	21.4	2
70	A	1440.5	8.1	1
71	A	1444.3	38.4	3
72	A	1446.4	59.1	5
73	A	1456.2	13.0	1
74	A	1456.4	40.2	3
75	A	1542.7	169.6	13
76	A	1547.1	19.2	1
77	A	1586.5	292.1	23
78	A	1590.6	154.6	12
79	A	1673.3	689.0	53
80	A	2044.3	1294.5	100
81	A	2923.0	23.6	2
82	A	2928.9	16.8	1
83	A	2979.0	15.4	1
84	A	2987.6	13.5	1
85	A	3007.6	14.6	1
86	A	3015.7	11.8	1
87	A	3037.9	28.2	2
88	A	3048.4	15.8	1
89	A	3070.3	25.5	2
90	A	3075.5	17.2	1
91	A	3080.8	3.9	0
92	A	3091.7	1.6	0
93	A	3102.4	8.8	1

20a



Atom Type	Coordinates (Angstroms) X	Y	Z
C	0.000041	-0.834898	-0.004134
C	1.258943	-0.818157	0.217945
N	2.440837	-0.908033	0.530790
C	-1.258858	-0.815952	-0.226053
N	-2.440727	-0.902595	-0.539903
C	-3.578025	-0.243708	-0.069720
C	-4.807796	-0.565051	-0.662578
N	-3.439404	0.653871	0.915220
C	-5.965276	0.072715	-0.219521
H	-4.835253	-1.303849	-1.456224
C	-4.555688	1.260545	1.333692
C	-5.822979	1.013276	0.811202
H	-4.426841	1.987189	2.133857
C	3.578029	-0.244121	0.067471
C	4.807947	-0.571849	0.656483
N	3.439123	0.664168	-0.907585
C	5.965316	0.070713	0.220058
H	4.835617	-1.319125	1.442149
C	4.555250	1.275483	-1.319624
C	5.822689	1.022605	-0.800147
H	4.426148	2.010999	-2.111603
C	7.314996	-0.243830	0.813997
H	7.987998	-0.660926	0.056513
H	7.792266	0.661075	1.205208
H	7.235914	-0.966273	1.629951
C	-7.314554	-0.233965	-0.818481
H	-7.995691	-0.639132	-0.061909
H	-7.781111	0.672562	-1.218994
H	-7.237590	-0.962629	-1.629081
H	-6.685225	1.545753	1.201591
H	6.684753	1.559640	-1.184655

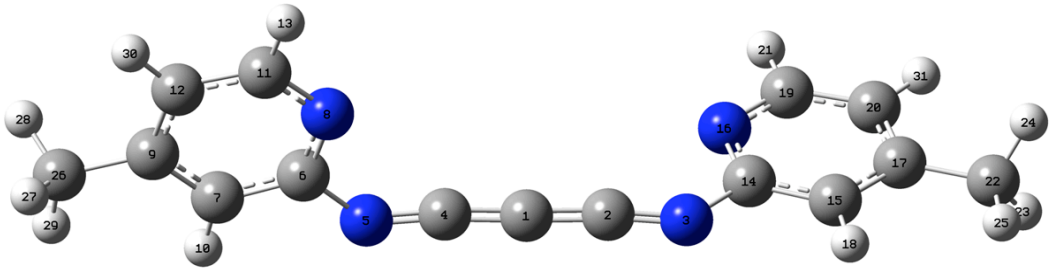
State= 1-A
HF= -797.7754897
RMSD=7.792e-09\RMSF=1.424e-06
Zero-point correction= 0.237611 (Hartree/Particle)
Sum of electronic and zero-point Energies= -797.537879

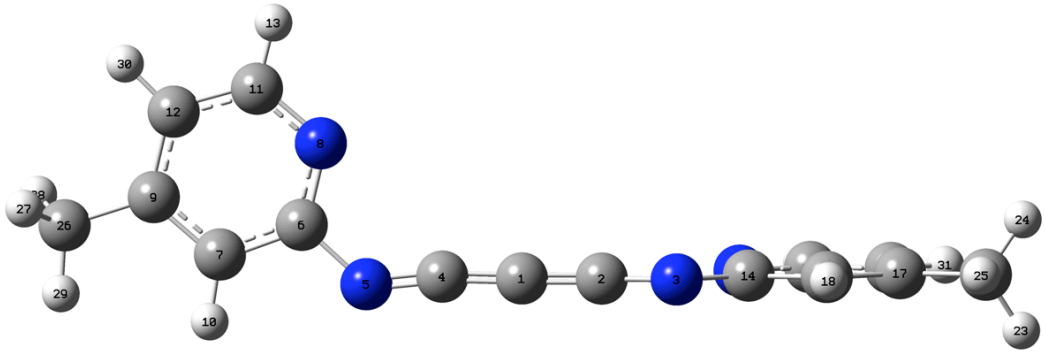
Vibrational Frequencies (scaled by 0.9613):

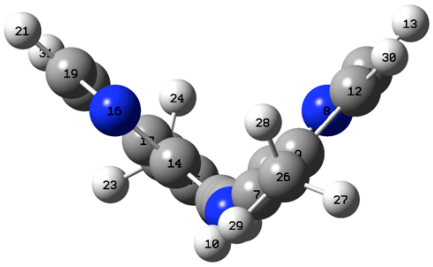
ModeNr.	Symmetry	Wavenumber	Abs.Int.	Rel.Int.
1	A	14.9	1.2	0
2	A	19.5	2.3	0
3	A	20.6	1.1	0
4	A	30.9	0.2	0
5	A	34.9	0.1	0
6	A	55.4	2.7	0
7	A	59.4	0.0	0
8	A	146.1	0.6	0
9	A	149.7	6.8	0
10	A	193.0	0.6	0

11	A	207.5	0.3	0
12	A	207.6	0.2	0
13	A	229.3	0.4	0
14	A	259.5	0.0	0
15	A	283.6	25.1	0
16	A	356.1	0.4	0
17	A	425.4	8.7	0
18	A	435.2	0.1	0
19	A	439.2	5.5	0
20	A	444.3	9.7	0
21	A	458.1	2.8	0
22	A	500.2	0.2	0
23	A	500.8	14.1	0
24	A	533.1	20.2	0
25	A	535.4	6.6	0
26	A	564.9	6.5	0
27	A	581.5	8.5	0
28	A	612.0	10.0	0
29	A	616.2	358.5	5
30	A	710.9	8.9	0
31	A	725.1	1.0	0
32	A	729.9	0.9	0
33	A	745.2	42.2	1
34	A	787.6	0.1	0
35	A	808.9	21.0	0
36	A	809.7	22.5	0
37	A	866.5	4.6	0
38	A	867.0	5.2	0
39	A	903.7	27.6	0
40	A	943.4	0.3	0
41	A	943.5	0.3	0
42	A	958.0	0.6	0
43	A	967.2	2.4	0
44	A	967.6	5.2	0
45	A	985.2	23.8	0
46	A	1004.9	0.1	0
47	A	1023.4	5.1	0
48	A	1023.4	5.0	0
49	A	1090.5	0.5	0
50	A	1093.5	0.0	0
51	A	1121.0	182.0	2
52	A	1148.7	6.1	0
53	A	1231.6	99.4	1
54	A	1254.0	2.0	0
55	A	1254.5	71.7	1
56	A	1266.9	4.3	0
57	A	1277.0	1.5	0
58	A	1280.2	3.3	0
59	A	1371.0	10.3	0
60	A	1371.1	0.3	0
61	A	1373.0	360.8	5
62	A	1390.5	23.1	0
63	A	1439.9	7.1	0
64	A	1439.9	11.5	0
65	A	1443.7	169.4	2
66	A	1445.6	29.1	0
67	A	1453.8	6.4	0
68	A	1454.6	37.0	0
69	A	1536.7	647.3	9
70	A	1543.6	27.3	0
71	A	1583.1	1612.6	21

72	A	1589.5	0.2	0
73	A	1592.9	417.0	6
74	A	2065.0	2.2	0
75	A	2203.1	7517.2	100
76	A	2928.6	46.1	1
77	A	2928.6	5.4	0
78	A	2984.6	13.5	0
79	A	2984.7	13.6	0
80	A	3013.8	14.0	0
81	A	3013.8	14.0	0
82	A	3042.1	22.5	0
83	A	3042.2	18.8	0
84	A	3073.8	27.2	0
85	A	3073.8	13.5	0
86	A	3088.3	3.1	0
87	A	3088.3	3.1	0





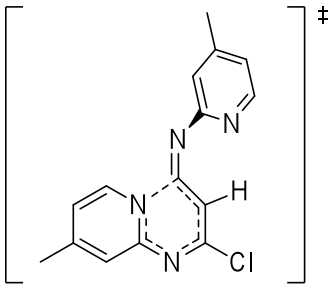


HCl

Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	0.000000	0.000000	0.071453
H	0.000000	0.000000	-1.214703

State= 1-SG
HF= -460.8007767
RMSD=1.335e-10\RMSF=3.003e-05
Zero-point correction= 0.006714 (Hartree/Particle)
Sum of electronic and zero-point Energies= -460.794063

TS connecting 17a and 18a

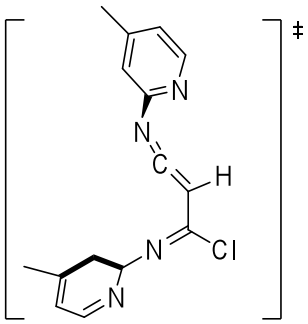


Atom Type	Coordinates (Angstroms) X	Y	Z
C	-0.890849	-2.238070	-0.185379
C	-2.278974	-1.907711	0.006847
N	-2.960232	-0.827025	0.060498
C	0.153502	-1.437054	-0.460120
Cl	-3.251179	-3.397233	0.245888
N	1.281606	-1.149693	-0.833077
C	-2.388158	0.425838	-0.085072
C	-3.217773	1.550852	0.088014
N	-1.089439	0.553730	-0.387203
C	-2.689476	2.829108	-0.051969
H	-4.261969	1.386833	0.330627
C	-0.571132	1.778766	-0.522385
C	-1.322163	2.935797	-0.368781
H	0.487645	1.824422	-0.766219

H	-0.854506	3.907734	-0.493872
C	-3.541341	4.060507	0.124890
H	-3.556164	4.661665	-0.791079
H	-4.572270	3.801390	0.377000
H	-3.146097	4.699216	0.922493
H	-0.622684	-3.284703	-0.076906
C	2.350396	-0.564068	-0.139346
C	3.572538	-0.447744	-0.815384
N	2.153276	-0.145755	1.117030
C	4.663774	0.121610	-0.159397
H	3.647715	-0.805202	-1.836719
C	3.202859	0.406615	1.736759
C	4.459641	0.561036	1.156362
H	3.025815	0.745067	2.755971
H	5.266290	1.019302	1.720884
C	6.008279	0.248228	-0.829751
H	5.941162	0.053851	-1.903006
H	6.429213	1.248601	-0.687263
H	6.722685	-0.466277	-0.404480

State= 1-A
HF= -1258.6072896
RMSD=6.184e-09\RMSF=5.411e-04
Single point energy (not a stationary point) of transition structure
obtained by scanning the breaking bond C4-N9 (energy maximum at 2.34807 Å).
Zero-point correction= 0.250760 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1258.356530
Imaginary frequency= -50.3094 cm^{-1}

TS connecting 18a and 19a

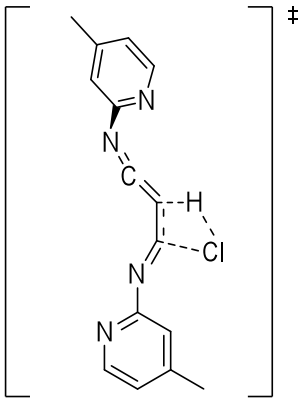


Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-3.037987	-3.368800	0.338260
N	-2.078388	-0.881083	-0.102947
N	1.584960	-1.358875	-0.928484
N	-2.327808	0.870996	-1.578195
N	2.611857	-0.831766	1.138200
C	-0.448593	-2.696299	-0.202904
C	-1.747321	-2.053365	-0.045279
C	0.629666	-1.985087	-0.513214
C	-2.311000	0.439477	-0.306499
C	-2.530141	1.283413	0.804048
C	-2.764130	2.636573	0.589494
C	-2.572646	2.174942	-1.762538
C	-2.787273	3.091284	-0.739869
C	2.595735	-0.695020	-0.191312

C	3.521731	0.054242	-0.917801
C	4.538698	0.725064	-0.230596
C	3.588802	-0.194870	1.789375
C	4.561735	0.584756	1.161297
H	-2.515622	0.864816	1.804798
H	-2.591815	2.502628	-2.800870
H	-2.973345	4.136016	-0.969429
H	-0.357255	-3.764561	-0.052032
H	3.435492	0.102401	-1.997892
H	3.597836	-0.315457	2.870688
H	5.329742	1.072145	1.754294
C	-2.996855	3.583714	1.740071
H	-2.240900	4.376906	1.753304
H	-3.973527	4.072505	1.653599
H	-2.961142	3.065792	2.701729
C	5.546556	1.575440	-0.960171
H	5.170641	2.598371	-1.081765
H	6.490356	1.635286	-0.411774
H	5.751173	1.182270	-1.959702

State= 1-A
HF= -1258.5877382
RMSD=3.076e-09\RMSF=2.449e-06
Zero-point correction= 0.249764 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1258.337974
Imaginary frequency= -114.6454 cm^{-1}

TS connecting 19a and 20a



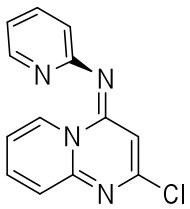
Atom Type	Coordinates (Angstroms) X	Y	Z
C	-0.196121	1.083423	-0.375228
C	0.903479	0.251454	-0.335519
N	1.815698	-0.478005	-0.305266
C	-1.447556	0.674510	-0.584045
Cl	2.055340	2.965261	0.140532
N	-2.586946	0.430258	-0.897991
C	3.141890	-0.907555	-0.192337
C	4.095886	0.081093	0.058311
N	3.361416	-2.211192	-0.338790
C	5.426309	-0.332056	0.171304
H	3.778492	1.121589	0.151872
C	4.641587	-2.586570	-0.229750
C	5.689955	-1.700934	0.018821

H	4.835784	-3.649624	-0.350725
H	6.705975	-2.077609	0.090378
C	6.520437	0.660488	0.467133
H	6.240538	1.665350	0.143165
H	6.713290	0.704724	1.545649
H	7.456822	0.378553	-0.022751
H	0.143930	2.143978	-0.185025
C	-3.730525	0.037340	-0.171119
C	-4.938537	-0.040535	-0.865155
N	-3.579002	-0.239120	1.126747
C	-6.090311	-0.420279	-0.168830
H	-4.964203	0.195065	-1.923482
C	-4.681504	-0.608897	1.784856
C	-5.941056	-0.711760	1.192130
H	-4.550908	-0.836910	2.840296
H	-6.794383	-1.020223	1.788354
C	-7.432038	-0.488818	-0.850998
H	-7.970764	0.459029	-0.734023
H	-7.327243	-0.676980	-1.922601
H	-8.057633	-1.275392	-0.420517

State= 1-A
HF= -1258.565946
RMSD=5.937e-09\RMSF=1.813e-06
Zero-point correction= 0.247763 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1258.318183
Imaginary frequency= -158.8957 cm^{-1}

Calculated Energies and Cartesian Coordinates (CASSCF/ANO-S)

17bZ



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-3.6131668	-3.2829939	-0.3947596
N	-3.0225151	-0.7713769	0.0467053
N	1.0059389	-1.3337713	-0.4806540
N	-0.8757193	0.1878300	-0.2783790
N	1.8863991	0.0486183	1.1834918
C	-1.1796372	-2.1774553	-0.5856784
C	-2.4868390	-1.9672414	-0.3177671
C	-0.2371171	-1.0860039	-0.4318730
C	-2.2339311	0.2511091	0.0341649
C	-2.7770681	1.5630649	0.3529755
C	-2.0475742	2.6703120	0.1924271

C	-0.1638054	1.3649637	-0.5240421
C	-0.6963544	2.5676427	-0.3154043
C	2.0407933	-0.5656736	0.0227184
C	3.2535456	-0.5450608	-0.6825757
C	4.3132523	0.1556287	-0.1486751
C	2.9198204	0.7075394	1.6899204
C	4.1547790	0.8050959	1.0750450
H	-3.8005722	1.5744656	0.6926759
H	0.8220372	1.2322989	-0.9152245
H	-0.1154468	3.4487221	-0.5361229
H	-0.7786409	-3.1479412	-0.8218460
H	3.3317238	-1.0800617	-1.6161868
H	2.7475065	1.1897188	2.6452861
H	4.9600311	1.3569191	1.5359971
H	-2.4651584	3.6419206	0.4155997
H	5.2593781	0.1930740	-0.6726699

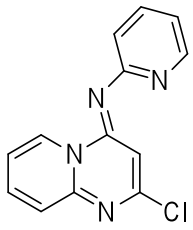
State= 1-A
RASSCF Energy= -1175.00320186
CASSCF(8,8) active space: 3 π/π^* pairs and σ/σ^* of breaking C-N bond

Natural orbitals and occupation numbers for root 1
1.978337 1.975234 1.946189 1.920774
0.079810 0.020277 0.057330 0.022049

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	0.95552	0.91302

17bE



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-2.4725636	-2.9452676	0.0000000
N	-2.7917802	-0.3515090	0.0000000
N	1.1949543	0.6562378	0.0000000
N	-1.0158172	1.2123797	0.0000000
N	2.3566521	-1.4319397	0.0000000
C	-0.5097735	-1.1291141	0.0000000
C	-1.8464326	-1.3284835	0.0000000
C	-0.0035525	0.2338192	0.0000000
C	-2.3567708	0.8651473	0.0000000
C	-3.3389184	1.9417167	0.0000000
C	-2.9693078	3.2226601	0.0000000
C	-0.6423992	2.5675129	0.0000000
C	-1.5567951	3.5561019	0.0000000
C	2.3549978	-0.1092344	0.0000000
C	3.5544240	0.6337371	0.0000000
C	4.7534553	-0.0302363	0.0000000
C	3.5384299	-2.0688433	0.0000000

C	4.7538269	-1.4323285	0.0000000
H	-4.3699157	1.6253688	0.0000000
H	0.4148302	2.7282179	0.0000000
H	-1.2280474	4.5830614	0.0000000
H	0.1917713	-1.9341162	0.0000000
H	3.4991385	1.7103571	0.0000000
H	3.4841903	-3.1502831	0.0000000
H	5.6730769	-1.9989262	0.0000000
H	-3.7094819	4.0104420	0.0000000
H	5.6847076	0.5203921	0.0000000

State= 1-A'
RASSCF Energy= -1175.01389524
CASSCF(8,8) active space: 3 π/π^* pairs and σ/σ^* of breaking C-N bond

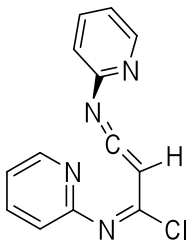
Natural orbitals and occupation numbers for root 1

1.950557	1.955797	1.924859	1.921808
0.055634	0.043276	0.070961	0.077109

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	0.93920	0.88209

18b



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-3.6111967	-2.9889985	-0.6432894
N	-2.7366187	-0.5794420	-0.7097697
N	1.1736360	-2.0729713	-0.3577277
N	-0.7129691	0.5983109	-0.9767792
N	1.9657372	-0.6031505	1.3032410
C	-1.2483563	-2.2614220	0.3746993
C	-2.4244525	-1.7215741	-0.3451889
C	0.0109018	-2.0535084	0.0323354
C	-1.9375400	0.5577498	-0.4972845
C	-2.5450571	1.6448459	0.1641870
C	-1.8169787	2.7878626	0.3477761
C	-0.0110409	1.7314648	-0.8087564
C	-0.5057385	2.8455322	-0.1539843
C	2.1034368	-1.1013091	0.0959978
C	3.1285451	-0.7532953	-0.7763708
C	4.0401748	0.1963587	-0.3521210
C	2.8506578	0.2951062	1.7051563
C	3.9033861	0.7395909	0.9196387
H	-3.5636741	1.5510599	0.5082339
H	0.9895241	1.7278991	-1.2145092
H	0.1018423	3.7310256	-0.0428096
H	-1.4477953	-2.9437848	1.1889214
H	3.1868690	-1.2181201	-1.7479140

H	2.7112893	0.6847078	2.7062740
H	4.5950187	1.4779049	1.2972395
H	-2.2484291	3.6370145	0.8601872
H	4.8495967	0.5044286	-1.0001377

State= 1-A
RASSCF Energy= -1174.97494962
CASSCF(8,8) active space: 3 π/π^* pairs and σ/σ^* of breaking C-N bond

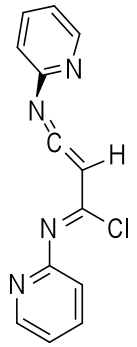
Natural orbitals and occupation numbers for root 1

1.937111	1.943222	1.931628	1.928897
0.069717	0.067633	0.056908	0.064884

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	-0.93622	0.87652

19b



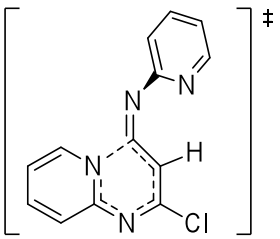
Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	2.3135181	2.2208779	0.8786526
N	1.1296059	0.0913946	-0.2180617
N	-2.2590158	1.0231959	-1.1246146
N	3.2099440	-0.3905351	-1.1322005
N	-3.5426446	0.4373427	0.7652680
C	-0.2652284	2.0311571	0.0946123
C	1.0027705	1.2794794	0.1693099
C	-1.3402612	1.5035922	-0.4680369
C	2.3494348	-0.6111123	-0.1726998
C	2.5377172	-1.5557794	0.8576362
C	3.7054773	-2.2670167	0.8645121
C	4.3526527	-1.1085832	-1.1126255
C	4.6490247	-2.0389598	-0.1545282
C	-3.2604553	0.2300723	-0.5009966
C	-3.9026112	-0.7106747	-1.2976340
C	-4.8825428	-1.4903333	-0.7094545
C	-4.4902457	-0.3051845	1.3152781
C	-5.1901453	-1.2871158	0.6300408
H	1.7728669	-1.6947303	1.6060426
H	5.0451423	-0.9027872	-1.9190521
H	5.5806853	-2.5842185	-0.1877781
H	-0.3263356	3.0110188	0.5400735
H	-3.6276109	-0.8126888	-2.3356273
H	-4.7033808	-0.1072990	2.3588904
H	-5.9527245	-1.8657434	1.1297011
H	3.8986640	-2.9975227	1.6384705
H	-5.4040225	-2.2406091	-1.2882176

State= 1-A
RASSCF Energy= -1174.98352283
CASSCF(8,8) active space: 3 π/π* pairs and σ/σ* of C-Cl bond

Natural orbitals and occupation numbers for root 1
1.930986   1.944463   1.912511   1.951943
0.047983   0.088954   0.069083   0.054079

Occupation of active orbitals:
Conf Occupation   Coef   Weight
1   22220000   -0.93595   0.87599

TS 17b – 18b



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-3.1297660	-3.2996888	0.4749761
N	-2.8978887	-0.7518903	0.2908480
N	1.1717687	-0.9300882	-1.1288426
N	-1.0615106	0.5222211	-0.4360144
N	1.9736890	-0.3064517	0.9920269
C	-0.8890700	-2.0984306	-0.3386220
C	-2.2516126	-1.8280038	0.1109151
C	0.0551835	-1.2188283	-0.6813164
C	-2.2950606	0.4763826	0.0245459
C	-3.0419596	1.6377700	0.2506488
C	-2.4568259	2.8511868	-0.0251694
C	-0.4904561	1.6992167	-0.7120063
C	-1.1479620	2.8886038	-0.5231364
C	2.2122518	-0.5382050	-0.2850257
C	3.4820382	-0.3908246	-0.8577104
C	4.5247819	-0.0011201	-0.0451244
C	2.9866662	0.0683321	1.7614312
C	4.2818574	0.2380900	1.3066913
H	-4.0480407	1.5502851	0.6297639
H	0.5177477	1.6504106	-1.0920797
H	-0.6614803	3.8242358	-0.7541261
H	-0.5760239	-3.1314029	-0.3547888
H	3.6135754	-0.5887051	-1.9099179
H	2.7466931	0.2458003	2.8033809
H	5.0674794	0.5454803	1.9804149
H	-3.0037770	3.7696201	0.1380616
H	5.5193611	0.1173477	-0.4546753

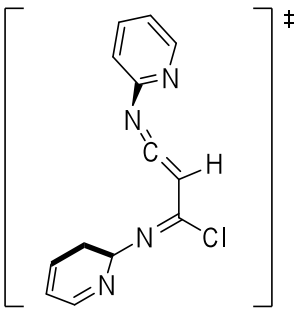
State= 1-A
RASSCF Energy= -1174.96676035
CASSCF(8,8) active space: 3 π/π* pairs and σ/σ* of breaking C-N bond

Natural orbitals and occupation numbers for root 1
1.972886   1.964891   1.946711   1.919764
0.081423   0.024767   0.050455   0.039104

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	0.95158	0.90550

TS 18b – 19b



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	-2.7648514	-3.0503955	0.4717824
N	-1.8605611	-0.6124196	0.0373621
N	1.5829705	-0.9434852	-1.3528096
N	-2.4549648	1.2663175	-1.1044438
N	2.6404097	-0.5879790	0.7388380
C	-0.2781692	-2.4103058	-0.4146080
C	-1.5641488	-1.7920904	-0.0068896
C	0.7163111	-1.6545043	-0.8495872
C	-2.0531842	0.7313890	0.0055506
C	-1.8064370	1.4625117	1.2047447
C	-2.0156102	2.8045778	1.1782879
C	-2.6616848	2.6013653	-1.1105983
C	-2.4655258	3.4160501	-0.0202595
C	2.5818693	-0.3228368	-0.5484881
C	3.4515051	0.5400850	-1.2012800
C	4.4353858	1.1611446	-0.4479790
C	3.5814494	0.0064181	1.4496432
C	4.5079296	0.8914636	0.9108211
H	-1.4689992	0.9449885	2.0891911
H	-3.0001803	3.0128650	-2.0536152
H	-2.6497759	4.4783552	-0.0763118
H	-0.1543396	-3.4793740	-0.3410068
H	3.3436116	0.7069730	-2.2616980
H	3.6034675	-0.2317471	2.5069173
H	5.2576073	1.3484703	1.5402922
H	-1.8430114	3.3984032	2.0667183
H	5.1338510	1.8428527	-0.9149969

State= 1-A
RASSCF Energy= -1174.95080053
CASSCF(8,8) active space: 4 π/π* pairs
(ketenimine HOMO/LUMO, HOMO-1/LUMO+1 and 2 π/π* imine C=N)

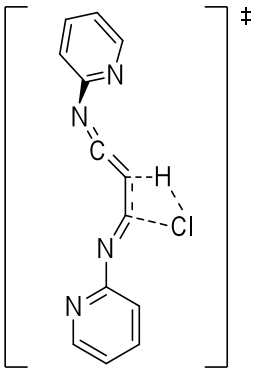
Natural orbitals and occupation numbers for root 1

1.956856	1.927484	1.938569	1.950391
0.048514	0.061436	0.073617	0.043134

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	0.94408	0.89129

TS 19b – 20b



Atom Type	Coordinates (Angstroms) X	Y	Z
Cl	1.9636898	3.0874287	0.3103672
N	1.7348146	-0.2580329	-0.4208906
N	-2.6039937	0.4817435	-1.2695212
N	3.1933117	-2.0442344	-0.4266722
N	-3.2449949	-0.3419643	0.8365204
C	-0.3141116	1.2912272	-0.5810204
C	0.8081422	0.4169951	-0.4946296
C	-1.5147604	0.8323341	-0.8923103
C	3.0480121	-0.7649315	-0.2153143
C	4.0113815	0.1406443	0.1800681
C	5.2786516	-0.3948292	0.3719770
C	4.4046707	-2.5348611	-0.2396024
C	5.4821269	-1.7490952	0.1594687
C	-3.5999674	-0.0094248	-0.3844586
C	-4.8906272	-0.1185373	-0.8781739
C	-5.8673577	-0.5895934	-0.0146272
C	-4.1789026	-0.7962328	1.6509242
C	-5.5108479	-0.9388555	1.2790002
H	3.7609297	1.1824233	0.3245564
H	4.5243044	-3.5961442	-0.4142122
H	6.4552656	-2.1953036	0.3016974
H	-0.0263231	2.3066179	-0.3080941
H	-5.1088826	0.1654138	-1.8956516
H	-3.8543324	-1.0606322	2.6496709
H	-6.2394837	-1.3102471	1.9839431
H	-6.8893880	-0.6912391	-0.3528903
H	6.0923273	0.2469187	0.6785439

State= 1-A
RASSCF Energy= -1174.92561405
CASSCF(8,8) active space: 2 π/π^* pairs and 2 σ/σ^* of C-Cl and H-Cl bonds

Natural orbitals and occupation numbers for root 1

1.939281	1.936676	1.989631	1.957200
0.066635	0.060919	0.039509	0.010150

Occupation of active orbitals:

Conf	Occupation	Coef	Weight
1	22220000	0.95631	0.91452

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