Experimental and Theoretical Investigation of the Pyrolysis Products of Iminodiacetonitrile, $(N{\equiv}CCH_2)_2NH$

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Table S1. The optimized parameters (Bond Lengths/Å and Bond Angles/Degrees) of Iminodiacetonitrile, $(N{\equiv}CCH_2)_2NH$ (I) calculated by using MP2 and B3LYP methods with 6-311++G** and aug-cc-pvdz basis sets.

Method	Basis Set	N≡C	C-C	C-N	C-H	N-H	<CCN	<CNH	<CNC
MP2	6-311++G**	1.176	1.481	1.456	1.095	1.016	116.19	110.66	115.47
	aug-cc-pvdz	1.188	1.489	1.463	1.101	1.021	116.28	110.29	115.08
B3LYP	6-311++G**	1.153	1.478	1.456	1.094	1.013	117.02	111.79	117.73
	aug-cc-pvdz	1.161	1.483	1.457	1.099	1.016	116.84	111.52	117.54

Table S2. The optimized parameters (Bond Lengths/Å and Bond Angles/Degrees) and Dipole Moments (μ/Debye) of Z-N≡CCH=NH (II) and E-N≡CCH=NH (IV) calculated by using MP2, B3LYP and CCSD methods with 6-311++G** and aug-cc-pvdz basis sets.

Method	Basis Set	N≡C	C-C	C=N	NH	CH	<CCN	<CNH	μ/Debye
MP2	6-311++G**	1.178	1.452	1.284	1.025	1.089	124.8	109.8	1.468
	aug-cc-pvdz	1.189	1.460	1.292	1.030	1.096	124.8	110.1	1.637
B3LYP	6-311++G**	1.155	1.447	1.270	1.023	1.090	125.2	111.7	1.325
	aug-cc-pvdz	1.162	1.452	1.275	1.026	1.096	125.1	111.5	1.444
CCSD	6-311++G**	1.161	1.463	1.276	1.023	1.089	124.7	110.5	1.292
	aug-cc-pvdz	1.172	1.471	1.284	1.029	1.096	124.6	110.7	1.448
Experimental[a]		---	---	---	---	--	--	---	1.41
MP2	6-311++G**	1.176	1.449	1.283	1.024	1.093	119.6	108.8	4.674
	aug-cc-pvdz	1.188	1.457	1.292	1.029	1.100	119.4	108.8	4.603
B3LYP	6-311++G**	1.154	1.445	1.269	1.022	1.094	120.5	110.5	4.268
	aug-cc-pvdz	1.162	1.450	1.275	1.025	1.100	120.3	110.2	4.168
CCSD	6-311++G**	1.161	1.459	1.276	1.023	1.093	119.7	109.3	4.294
	aug-cc-pvdz	1.171	1.468	1.284	1.028	1.100	119.5	109.3	4.238
Experimental[b]		---	---	----	----	---	---	---	4.11

a:Experimental dipole moment of II taken from Ref.23 b: Experimental dipole moment of IV taken from Ref.23.The first seven lines of data are for II; the second seven lines of data are for IV.

Table S3. The optimized Standard orientation for Iminodiacetonitrile (I) using B3LYP/aug-cc-pvdz level of theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.597712	-1.379042	0.000000
2	1	0	-1.555760	-1.026501	0.000000
3	6	0	0.085185	-0.991784	1.234092
4	1	0	-0.415097	-1.491347	2.077883
5	1	0	1.118850	-1.370908	1.194259
6	6	0	0.085185	-0.991784	-1.234092
7	1	0	-0.415097	-1.491347	-2.077883
8	1	0	1.118850	-1.370908	-1.194259
9	6	0	0.127308	0.465727	1.534612
10	6	0	0.127308	0.465727	-1.534612
11	7	0	0.127308	1.622642	1.802858
12	7	0	0.127308	1.622642	-1.802858

Table S4. The optimized Standard orientation for Z-C-Cyanomethanimine (II) using B3LYP/aug-cc-pvdz level of theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.565556	-0.584300	0.000000
2	1	0	1.660008	-0.634318	0.000000
3	1	0	-1.117987	-1.480930	0.000000
4	7	0	-0.108907	-1.666441	0.000000
5	6	0	0.000000	0.753286	0.000000
6	7	0	-0.453287	1.823774	0.000000

Table S5. The optimized Standard orientation for Ketenimine (III) using B3LYP/aug-cc-pvdz level of theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.195207	-1.241982	0.000000
2	1	0	-0.286460	-1.783216	0.939447
3	1	0	-0.286460	-1.783216	-0.939447
4	6	0	0.000000	0.060349	0.000000
5	7	0	0.314986	1.248608	0.000000
6	1	0	-0.460744	1.915970	0.000000

Table S6. The optimized Standard orientation for E-C-Cyanomethanimine (IV) using B3LYP/aug-cc-pvdz level of theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.480698	-0.601701	0.000000
2	1	0	1.576102	-0.699779	0.000000
3	1	0	0.157905	-2.465734	0.000000
4	7	0	-0.345164	-1.572917	0.000000
5	6	0	0.000000	0.766033	0.000000
6	7	0	-0.314579	1.884277	0.000000

Table S7. The scaled vibrational wavenumbers (cm^{-1}) of Z-C-Cyanomethanimine (II) and E-C-Cyanomethanimine (IV) which were calculated by using B3LYP, MP2 and CCSD methods with aug-cc-pvdz basis set. The experimental vibrational wavenumbers were reported for comparison purposes.

Assignment	B3LYP/aug-cc-pvdz		MP2/aug-cc-pvdz		CCSD/aug-cc-pvdz		Experimental	
	II	IV	II	IV	II	IV	This Work	Ref.21
N-H Str.	3440.36	3455.73	3450.83	3464.44	3457.80	3469.36	3306	----
C-H str.	3135.05	3075.85	3199.39	3141.63	3187.85	3134.01	2943	---
C≡N str.	2322.81	2336.36	2128.89	2147.51	2303.78	2315.39	2239	2250
C=N str.	1668.48	1677.79	1604.37	1622.73	1671.84	1681.40	1599	(1605)
C-H bend	1405.21	1401.61	1410.01	1390.90	1420.54	1416.00	1388	1387
CNH bend	1241.17	1237.03	1231.57	1237.51	1250.81	1250.29	1218	1218
C-C str.	920.29	912.22	921.27	916.76	919.53	915.58	904	(900)
NCC bend	616.15	619.74	597.47	601.58	606.17	609.79	---	----
CCN bend	230.17	241.98	219.56	231.76	228.77	241.23	---	---
C=N tor.	1127.52	1106.29	1123.92	1094.01	1128.08	1102.76	1095	1095
C-H O.P.	844.81	826.50	818.68	815.33	820.41	813.43	815	(800)
CCN O.P.	323.67	321.81	312.12	312.14	321.20	319.81	---	----

Table S8. The Rotational Constants A, B, and C in GHz of Z-C-Cyanomethanimine (II) and E-C-Cyanomethanimine (IV) which were calculated by using MP2, B3LYP and CCSD methods with 6-311++G**, aug-cc-pvdz and aug-cc-pvtz basis sets. The experimental microwave values[a] were reported for comparison purposes.

Method	Basis Set	A	B	C	(B+C)[b]	2{A-(B+C)/2}[b]
MP2	6-311++G**	53.9026456	4.9967386	4.5728395	0.3192	3.2768
	aug-cc-pvdz	53.1380510	4.9280139	4.5097779	0.3148	3.2302
	aug-cc-pvtz	53.8674855	5.0442182	4.6123153	0.3221	3.2715
B3LYP	6-311++G**	55.3356383	5.0676226	4.6424668	0.3239	3.3677
	aug-cc-pvdz	54.8923440	5.0231626	4.6020335	0.3211	3.3409
	aug-cc-pvtz	55.4972909	5.0898395	4.6622493	0.3253	3.3771
CCSD	6-311++G**	54.4705682	5.0101379	4.5881274	0.3202	3.3137
	aug-cc-pvdz	53.7677784	4.9433690	4.5271466	0.3159	3.2711
	aug-cc-pvtz	53.8675162	5.0442190	4.6123162	0.3221	3.2706
Experimental		**54.15600**	**5.073849**	**4.632425**	**0.3238**	**3.2891**
MP2	6-311++G**	61.2499052	4.9201288	4.5542884	0.3160	3.7701
	aug-cc-pvdz	60.4833704	4.8529953	4.4925289	0.3117	3.7243
	aug-cc-pvtz	62.1755537	4.9452685	4.5809154	0.3178	3.8301
B3LYP	6-311++G**	63.9887355	4.9723296	4.6138076	0.3198	3.9491
	aug-cc-pvdz	63.3928722	4.9299310	4.5742047	0.3170	3.9121
	aug-cc-pvtz	64.6280898	4.9831454	4.6264251	0.3205	3.9910
CCSD	6-311++G**	62.0181995	4.9308695	4.5677058	0.3168	3.8206
	aug-cc-pvdz	61.3231968	4.8649192	4.5073408	0.3126	3.7784
	aug-cc-pvtz	62.1755537	4.9452685	4.5809154	0.3178	3.8311
Experimental		**62.70034**	**4.972056**	**4.600303**	**0.3193**	**3.8636**

a:From Ref.23; b:Given in cm^{-1}. The top 10 lines are for Z-C-cyanomethanimine(II). The bottom 10 line are for E-C-cyanomethanimine(IV).

Table S9. The optimized standard orientation for the transition state (TS) using B3LYP/aug-cc-pvdz level of theory.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.186422	-1.275907	0.116709
2	1	0	0.113946	-1.458881	-0.843872
3	6	0	-1.958135	-0.639050	-0.297385
4	1	0	-2.099707	-1.060674	-1.293843
5	6	0	1.865486	0.012307	0.015478
6	7	0	2.844325	0.324004	-0.536112
7	6	0	0.666617	-0.404712	0.684728
8	1	0	0.641331	-0.298614	1.771269
9	1	0	-0.086951	1.161073	0.449165
10	1	0	-2.558171	-1.111090	0.481520
11	6	0	-1.789685	0.725312	-0.190735
12	7	0	-1.053216	1.625658	0.147828

Table S10. The Cartesian Coordinates of the imaginary frequency ($-562.45 cm^{-1}$) which was obtained as a criterion for the existence of the TS using B3LYP/aug-cc-pdz level of theory.

Centre Number	Atomic Number	X	Y	Z
1	7	-0.22	0.10	-0.10
2	1	-0.10	0.04	-0.04
3	6	0.34	-0.14	0.10
4	1	0.10	-0.09	0.10
5	6	-0.01	-0.05	0.00
6	7	-0.01	-0.02	0.01
7	6	-0.13	0.22	-0.03
8	1	0.09	-0.17	0.02
9	1	0.15	-0.74	0.16
10	1	0.13	-0.03	0.02
11	6	-0.04	0.07	-0.02
12	7	0.07	-0.10	0.03

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