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ChemPhysChem

Supporting Information

Targeting the Rich Conformational Landscape of *N*-Allylmethylamine Using Rotational Spectroscopy and Quantum Mechanical Calculations

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Supporting Information

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Appendix 1: Cartesian coordinates for the energy minima and transition states of AMA

Table S1. Cartesian coordinates of conformer I obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-2.398441	0.140305	-0.347464
H	-3.334455	-0.398834	-0.330955
H	-2.363211	1.051226	-0.930884
C	-1.334769	-0.289352	0.325400
H	-1.388512	-1.209786	0.894981
C	-0.012788	0.409515	0.345032
H	0.237228	0.690615	1.372159
H	-0.078105	1.343040	-0.233811
N	1.046020	-0.477236	-0.126628
H	0.817872	-0.795407	-1.059916
C	2.355637	0.158970	-0.123536
H	2.389862	1.101274	-0.687645
H	3.093671	-0.521454	-0.543251
H	2.646689	0.376034	0.904133

Table S2. Cartesian coordinates of conformer II obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-2.088662	0.542091	-0.135201
H	-2.895161	0.945929	0.459421
H	-2.085612	0.780874	-1.190870
C	-1.141115	-0.220614	0.401510
H	-1.153271	-0.435806	1.463974
C	-0.006511	-0.830042	-0.364641
H	-0.088554	-0.538215	-1.422566
H	-0.089653	-1.917852	-0.317398
N	1.281294	-0.465570	0.221662
H	1.996702	-1.088683	-0.126000
C	1.660343	0.916751	-0.040901
H	2.651495	1.104630	0.366561
H	0.959621	1.586009	0.454737
H	1.666198	1.171694	-1.109882

Table S3. Cartesian coordinates of conformer III obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-2.022745	-0.684707	0.043288
H	-3.096901	-0.786554	-0.004537
H	-1.438946	-1.584555	0.170277
C	-1.446412	0.511535	-0.030711
H	-2.066135	1.394399	-0.139645
C	0.027540	0.775852	0.016634
H	0.261271	1.314271	0.940925
H	0.283310	1.471510	-0.800271
N	0.833196	-0.430786	-0.012119
H	0.609883	-0.959553	-0.845924
C	2.260858	-0.150578	0.028087
H	2.597030	0.542106	-0.756068
H	2.818521	-1.079591	-0.070576
H	2.514351	0.290371	0.991954

Table S4. Cartesian coordinates of conformer IV obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	2.036856	-0.579569	0.129895
H	2.834123	-1.007341	-0.460935
H	1.996885	-0.853738	1.176384
C	1.144484	0.254835	-0.395695
H	1.209516	0.505175	-1.450653
C	0.001397	0.875039	0.359047
H	0.062170	1.962675	0.290426
H	0.079369	0.613961	1.416390
N	-1.330594	0.480944	-0.103659
H	-1.463787	0.780384	-1.061022
C	-1.600728	-0.946661	0.017972
H	-2.598836	-1.153774	-0.362804
H	-1.583412	-1.219883	1.073366
H	-0.884994	-1.590525	-0.505135

Table S5. Cartesian coordinates of conformer V obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.661984	-0.851564	-0.207748
H	-2.630277	-1.285772	-0.006705
H	-0.978468	-1.401692	-0.838055
C	-1.322833	0.329991	0.297082
H	-2.027319	0.866534	0.923263
C	-0.011483	1.030420	0.069463
H	0.333972	1.437007	1.033539
H	-0.190724	1.894545	-0.575209
N	0.997175	0.190838	-0.559098
H	1.669679	0.771330	-1.038276
C	1.684771	-0.688175	0.379016
H	2.461343	-1.242435	-0.144121
H	0.978659	-1.406043	0.790989
H	2.144183	-0.149827	1.219239

Table S6. Cartesian coordinates of conformer VI obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	2.311015	-0.171742	-0.247373
H	3.021853	-0.972058	-0.394876
H	2.640453	0.830580	-0.490769
C	1.085384	-0.398335	0.219069
H	0.790731	-1.414593	0.455230
C	0.053956	0.675820	0.420319
H	0.497144	1.644908	0.186831
H	-0.252766	0.708542	1.468707
N	-1.164666	0.521850	-0.376888
H	-0.914405	0.434370	-1.353564
C	-2.009096	-0.596369	0.023916
H	-2.888033	-0.628645	-0.617025
H	-2.349657	-0.433065	1.046447
H	-1.523858	-1.579007	-0.016780

Table S7. Cartesian coordinates of conformer VII obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.648667	-0.875376	0.182959
H	-2.628801	-1.296897	0.016540
H	-0.941553	-1.483201	0.730743
C	-1.332261	0.333751	-0.269732
H	-2.079106	0.900489	-0.816938
C	-0.014868	1.042490	-0.071542
H	-0.198693	1.928713	0.542968
H	0.326407	1.424501	-1.037580
N	1.080299	0.292535	0.515661
H	0.798055	-0.118152	1.395054
C	1.666779	-0.712448	-0.362751
H	2.443023	-1.250045	0.178386
H	2.140501	-0.209428	-1.205974
H	0.954495	-1.441286	-0.763712

Table S8. Cartesian coordinates of conformer VIII obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	2.424373	-0.170611	0.297211
H	3.355567	0.376860	0.306132
H	2.417645	-1.142253	0.773068
C	1.331726	0.324763	-0.274024
H	1.374865	1.305245	-0.738663
C	0.013629	-0.378424	-0.345133
H	0.077143	-1.335444	0.175979
H	-0.218446	-0.604287	-1.399534
N	-1.046695	0.411798	0.276984
H	-1.025938	1.353121	-0.094610
C	-2.365779	-0.169297	0.072126
H	-3.124556	0.487726	0.492030
H	-2.422934	-1.123367	0.596047
H	-2.606772	-0.353086	-0.984390

Table S9. Cartesian coordinates of conformer IX obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-2.336351	-0.152094	-0.212564
H	-3.051061	-0.947174	-0.368008
H	-2.684165	0.860773	-0.369128
C	-1.083837	-0.403179	0.154400
H	-0.773341	-1.431158	0.300666
C	-0.053535	0.655885	0.407419
H	0.200204	0.654060	1.480548
H	-0.483171	1.630149	0.175893
N	1.141734	0.474344	-0.419760
H	1.663879	1.339643	-0.430022
C	2.007799	-0.604343	0.037657
H	2.931389	-0.594459	-0.537219
H	1.527369	-1.566252	-0.133122
H	2.259753	-0.538444	1.105787

Table S10. Cartesian coordinates for the TS geometry involving the allyl torsion in the relaxation pathway for the interconversion between I+ and I- at the B2PLYP-D3(BJ)/aug-cc-pVTZ level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	2.550359	-0.179153	-0.028387
H	3.445260	0.423352	-0.073583
H	2.681656	-1.253518	-0.008904
C	1.343645	0.377211	-0.001568
H	1.254674	1.457359	-0.034558
C	0.046541	-0.381727	0.070367
H	-0.009623	-0.930969	1.023678
H	0.013308	-1.135270	-0.719517
N	-1.092485	0.507813	-0.117621
H	-1.056912	1.244951	0.575532
C	-2.366405	-0.189370	-0.022811
H	-3.182410	0.526267	-0.098157
H	-2.487749	-0.760805	0.908040
H	-2.455650	-0.887822	-0.854788

Imaginary frequency: -117.49 cm^{-1}

Table S11. Cartesian coordinates for the TS geometry involving the NH inversion in the relaxation pathway for the interconversion between I+ and I- at the B2PLYP-D3(BJ)/aug-cc-pVTZ level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-2.451808	0.001760	-0.286923
H	-3.350770	-0.571724	-0.113155
H	-2.496664	0.777758	-1.039640
C	-1.335248	-0.227733	0.397879
H	-1.309737	-1.018618	1.139699
C	-0.057424	0.527595	0.204635
H	0.240454	0.966529	1.166400
H	-0.233468	1.369493	-0.479508
N	0.994886	-0.340668	-0.250766
H	0.753723	-1.233155	-0.629373
C	2.371690	0.002262	-0.038539
H	3.007796	-0.800566	-0.404854
H	2.602960	0.154473	1.023258
H	2.658253	0.917178	-0.569780

Imaginary frequency: -577.86 cm^{-1}

Appendix 2: Calculated energetic and spectroscopic parameters for the nine conformers of AMA

Table S12. Calculated energetic and spectroscopic parameters for the nine conformers of AMA at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory

Conformer	B3LYP-D3(BJ)			
	ΔE_{ZPE}[a]	P[b]	$A/B/C$[c]	$\lvert\mu_a\rvert/\lvert\mu_b\rvert/\lvert\mu_c\rvert$[d]
I	0.0	31.7	20375/2232/2201	0.2/0.6/0.6
II	1.1	20.4	10261/3036/2635	0.4/0.2/0.9
III	1.5	17.0	14776/2689/2358	0.5/0.5/0.8
IV	2.8	10.4	9623/3159/2689	0.4/0.3/0.7
V	3.8	6.9	8866/3514/2917	0.9/0.9/0.4
VI	4.5	5.2	13597/2617/2436	0.2/0.8/0.2
VII	5.5	4.3	8694/3542/2896	0.5/0.3/0.1
VIII	4.9	3.5	21037/2222/2167	0.4/0.1/1.0
IX	9.0	0.8	14073/2606/2395	0.7/0.4/0.8

[a]Zero-point energy (ZPE) corrected relative total energies in kJ mol^{-1},[b]Populations at 298K in %, [c]Rotational constants in MHz, [d]Magnitude of the electric dipole moment components in Debye.

Table S13. Calculated rotational and quartic centrifugal distortion constants for the observed conformers of AMA at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory

Parameter	I	II	III	V
A/MHz	20135	10199	14729	8840
B/MHz	2242	3061	2703	3538
C/MHz	2213	2651	2368	2936
Δ_J/kHz	0.63	3.10	0.57	2.73
Δ_{JK}/kHz	-21.76	-23.72	-3.13	-9.93
Δ_K/kHz	433.87	87.55	36.95	23.48
δ_J/kHz	-0.09	0.91	0.10	0.75
δ_K/kHz	40.89	5.01	1.21	4.06
1.5 (χ_{aa})/MHz	4.48	3.99	3.86	1.55
0.25 (χ_{bb}- χ_{cc})/MHz	-0.38	1.94	0.75	0.27

Table S14. Percentage error* between experimental and calculated (B3LYP-D3(BJ), B2PLYP-D3(BJ) and MP2, aug-cc-pVTZ basis set) rotational and ^{14}N quadrupole coupling constants.

Parameter	B3LYP-D3(BJ)				B2PLYP-D3(BJ)				MP2			
	I	II	III	V	I	II	III	V	I	II	III	V
%A	1.9	0.9	1.6	1.1	0.7	0.3	1.3	0.8	1.8	1.6	0.7	0.3
%B	0.1	0.5	0.4	0.5	0.3	0.4	0.1	0.1	1.2	2.8	1.1	2.3
%C	0.1	0.2	0.2	0.5	0.4	0.4	0.2	0.1	1.6	2.1	1.0	2.0
%1.5 (χ_{aa})	7.4	9.0	7.6	12.7	4.0	5.2	4.1	8.8	2.4	2.2	1.9	0.6
%0.25 (χ_{bb}- χ_{cc})	22.1	7.8	11.6	14.1	4.6	3.8	5.3	15.3	28.2	4.0	2.4	28.4

*The percentage error for each constant was calculated as $\%X = (X_{calc} - X_{exp} / X_{exp}) * 100$

Appendix 3: Assigned transitions for the parent species of conformers I, II, III and V

Table S15. Assigned transitions for the parent species of conformer I+ and I-

J'	K_a'	K_c'	v'	F'	J"	K_a"	K_c"	v"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
1	1	1	1	1	2	0	2	1	2	8883.1885	-0.0102
1	1	1	0	2	2	0	2	0	3	8884.7468	-0.0137
2	1	1	0	3	1	1	0	0	2	8910.0777	0.0068
2	1	1	0	2	1	1	0	0	1	8910.9722	-0.0075
1	1	0	0	1	2	0	2	0	2	8916.0105	0.0079
1	1	0	0	2	2	0	2	0	2	8916.1878	-0.0029
1	1	0	0	2	2	0	2	0	3	8917.1124	-0.0001
1	1	0	0	1	2	0	2	0	1	8917.4438	0.0074
3	1	3	0	4	2	1	2	0	3	13267.9607	0.0090
3	1	3	1	4	2	1	2	1	3	13267.9607	-0.0063
3	1	3	0	3	2	1	2	0	2	13268.2112	0.0132
3	1	3	1	3	2	1	2	1	2	13268.2112	-0.0024
3	0	3	1	4	2	0	2	1	3	13316.3640	-0.0030
3	0	3	1	3	2	0	2	1	2	13316.3979	-0.0026
3	0	3	1	2	2	0	2	1	1	13316.5413	-0.0036
3	1	2	0	4	2	1	1	0	3	13365.2574	0.0094
3	1	2	1	4	2	1	1	1	3	13365.2574	-0.0063
3	1	2	0	2	2	1	1	0	1	13365.3001	-0.0030
3	1	2	0	3	2	1	1	0	2	13365.5181	0.0045
3	1	2	1	3	2	1	1	1	2	13365.5181	-0.0112
4	1	4	0	3	4	0	4	0	4	17616.1119	-0.0023
4	1	4	1	3	4	0	4	1	4	17616.1531	-0.0054
4	1	4	0	4	4	0	4	0	4	17616.8161	0.0032
4	1	4	1	4	4	0	4	1	4	17616.8607	-0.0003
4	1	4	0	5	4	0	4	0	5	17617.2299	-0.0031
4	1	4	1	5	4	0	4	1	5	17617.2742	-0.0041
4	1	4	0	3	4	0	4	0	3	17617.3418	0.0007
4	1	4	1	3	4	0	4	1	3	17617.3866	0.0009
4	1	4	0	4	4	0	4	0	5	17617.7947	0.0059
4	1	4	1	4	4	0	4	1	5	17617.8397	0.0025
4	1	4	0	4	4	0	4	0	3	17618.0434	0.0037
4	1	4	1	4	4	0	4	1	3	17618.0892	0.0011
3	1	3	0	2	3	0	3	0	3	17680.4810	-0.0013
3	1	3	1	2	3	0	3	1	3	17680.5251	0.0014
3	1	3	0	4	3	0	3	0	3	17680.6323	-0.0067

3	1	3	1	4	3	0	3	1	3	17680.6857	0.0043
3	1	3	0	3	3	0	3	0	3	17681.0915	0.0045
3	1	3	1	3	3	0	3	1	3	17681.1362	0.0038
3	1	3	0	4	3	0	3	0	4	17681.5945	0.0003
3	1	3	1	4	3	0	3	1	4	17681.6400	0.0032
3	1	3	0	2	3	0	3	0	2	17681.7683	-0.0033
3	1	3	1	2	3	0	3	1	2	17681.8121	-0.0011
3	1	3	0	3	3	0	3	0	4	17682.0475	0.0053
3	1	3	1	3	3	0	3	1	4	17682.0906	0.0029
3	1	3	0	3	3	0	3	0	2	17682.3818	0.0054
3	1	3	1	3	3	0	3	1	2	17682.4260	0.0040
2	1	2	0	1	2	0	2	0	2	17728.9539	-0.0087
2	1	2	1	1	2	0	2	1	2	17728.9966	-0.0048
2	1	2	0	3	2	0	2	0	2	17729.0703	-0.0041
2	1	2	1	3	2	0	2	1	2	17729.1148	0.0000
2	1	2	0	2	2	0	2	0	2	17729.2770	0.0009
2	1	2	1	2	2	0	2	1	2	17729.3209	0.0016
2	1	2	0	3	2	0	2	0	3	17729.9977	0.0015
2	1	2	1	3	2	0	2	1	3	17730.0407	0.0039
2	1	2	0	2	2	0	2	0	3	17730.2008	0.0029
2	1	2	1	2	2	0	2	1	3	17730.2402	-0.0009
2	1	2	0	1	2	0	2	0	1	17730.3866	-0.0098
2	1	2	1	1	2	0	2	1	1	17730.4291	-0.0063
2	1	2	0	2	2	0	2	0	1	17730.7108	0.0009
2	1	2	1	2	2	0	2	1	1	17730.7551	0.0018
1	1	1	0	1	1	0	1	0	1	17760.8386	-0.0174
1	1	1	1	1	1	0	1	1	1	17760.8847	-0.0129
1	1	1	0	2	1	0	1	0	1	17761.5258	-0.0029
1	1	1	1	2	1	0	1	1	1	17761.5698	0.0019
1	1	1	0	1	1	0	1	0	2	17761.6980	-0.0188
1	1	1	1	1	1	0	1	1	2	17761.7442	-0.0143
1	1	1	0	2	1	0	1	0	2	17762.3893	-0.0002
1	1	1	1	2	1	0	1	1	2	17762.4204	-0.0083
1	1	1	0	1	1	0	1	0	0	17762.9912	-0.0167
1	1	1	1	1	1	0	1	1	0	17763.0375	-0.0123
1	1	0	0	1	1	0	1	0	1	17793.7082	0.0157
1	1	0	1	1	1	0	1	1	1	17793.7313	0.0014
1	1	0	0	2	1	0	1	0	1	17793.8873	0.0066
1	1	0	1	2	1	0	1	1	1	17793.9279	0.0072
1	1	0	0	2	1	0	1	0	2	17794.7484	0.0068
1	1	0	1	2	1	0	1	1	2	17794.7893	0.0076
1	1	0	0	1	1	0	1	0	0	17795.8620	0.0176
2	1	1	0	1	2	0	2	0	2	17825.8721	0.0106
2	1	1	1	1	2	0	2	1	2	17825.9161	0.0115

2	1	1	0	3	2	0	2	0	2	17826.2649	0.0032
2	1	1	1	3	2	0	2	1	2	17826.3096	0.0062
2	1	1	0	2	2	0	2	0	2	17826.9839	0.0015
2	1	1	1	2	2	0	2	1	2	17827.0283	0.0069
2	1	1	0	3	2	0	2	0	3	17827.1879	0.0044
2	1	1	1	3	2	0	2	1	3	17827.2317	0.0064
2	1	1	0	2	2	0	2	0	3	17827.9086	0.0044
2	1	1	1	2	2	0	2	1	3	17827.9479	0.0046
2	1	1	0	2	2	0	2	0	1	17828.4165	0.0004
2	1	1	1	2	2	0	2	1	1	17828.4585	0.0031
3	1	2	0	2	3	0	3	0	3	17874.7813	0.0038
3	1	2	1	2	3	0	3	1	3	17874.8252	0.0027
3	1	2	0	4	3	0	3	0	3	17875.1241	0.0015
3	1	2	1	4	3	0	3	1	3	17875.1696	0.0029
3	1	2	0	4	3	0	3	0	4	17876.0833	0.0054
3	1	2	1	4	3	0	3	1	4	17876.1306	0.0086
3	1	2	0	3	3	0	3	0	4	17877.0623	-0.0018
3	1	2	1	3	3	0	3	1	4	17877.1049	-0.0007
3	1	2	0	3	3	0	3	0	2	17877.3939	-0.0044
3	1	2	1	3	3	0	3	1	2	17877.4392	-0.0007
4	1	3	0	3	4	0	4	0	4	17940.2185	0.0001
4	1	3	1	3	4	0	4	1	4	17940.2647	-0.0014
4	1	3	0	5	4	0	4	0	4	17940.5043	0.0015
4	1	3	1	5	4	0	4	1	4	17940.5468	-0.0031
4	1	3	0	5	4	0	4	0	5	17941.4780	-0.0006
4	1	3	1	5	4	0	4	1	5	17941.5232	-0.0027
4	1	3	0	4	4	0	4	0	4	17941.6011	-0.0079
4	1	3	1	4	4	0	4	1	4	17941.6466	-0.0068
4	1	3	0	4	4	0	4	0	5	17942.5811	-0.0038
4	1	3	1	4	4	0	4	1	5	17942.6260	-0.0035
4	1	3	0	4	4	0	4	0	3	17942.8318	-0.0040
4	1	3	1	4	4	0	4	1	3	17942.8775	-0.0029

Table S16. Assigned transitions for the parent species of conformer II

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
2	1	2	1	2	0	2	1	6730.2147	-0.0006
2	1	2	3	2	0	2	3	6730.6222	0.0002
2	1	2	2	2	0	2	2	6731.3551	0.0010
2	1	2	2	2	0	1	1	6732.7216	0.0021
1	1	1	0	1	0	1	1	7120.6793	0.0015
1	1	1	2	1	0	1	1	7121.7949	-0.0003
1	1	1	1	1	0	1	1	7122.5376	-0.0025
1	1	1	2	1	0	1	2	7122.5537	0.0009
1	1	1	1	1	0	1	2	7123.2966	-0.0010
1	1	1	1	1	0	1	0	7124.4327	-0.0010
3	0	3	2	2	1	1	1	9049.3398	-0.0010
3	0	3	4	2	1	1	3	9050.1405	0.0014
3	0	3	2	2	1	1	2	9050.5835	0.0006
3	0	3	3	2	1	1	3	9051.1482	-0.0032
3	0	3	3	2	1	1	2	9051.9502	0.0005
2	1	2	1	1	1	1	1	10973.7397	-0.0003
2	1	2	3	1	1	1	2	10975.3803	0.0011
2	1	2	1	1	1	1	0	10975.6031	0.0007
2	1	2	2	1	1	1	1	10976.2435	-0.0006
2	1	2	2	1	1	1	2	10976.9872	-0.0018
2	0	2	1	1	0	1	1	11366.0653	0.0004
2	0	2	3	1	0	1	2	11367.3108	0.0008
2	0	2	2	1	0	1	1	11367.4322	0.0019
2	0	2	1	1	0	1	0	11367.9581	-0.0003
2	0	2	2	1	0	0	2	11368.1878	0.0001
2	1	1	1	1	1	0	0	11791.6823	-0.0020
2	1	1	2	1	1	0	2	11792.6961	-0.0001
2	1	1	3	1	1	0	2	11793.4964	0.0020
2	1	1	2	1	1	0	1	11794.1976	-0.0010
2	1	1	1	1	1	0	1	11795.4389	-0.0018
1	1	1	2	0	0	0	1	12814.7056	-0.0040
1	1	0	1	0	0	0	1	13222.5839	0.0018
1	1	0	2	0	0	0	1	13224.0836	-0.0008
1	1	0	0	0	0	2	1	13226.3397	0.0013
4	0	4	3	3	1	2	2	13969.5215	-0.0007
4	0	4	5	3	1	2	4	13970.0315	-0.0005
4	0	4	4	3	1	2	4	13971.2051	0.0012
4	0	4	4	3	1	2	3	13971.7993	0.0002
3	1	3	2	2	1	2	2	16450.4128	-0.0029

3	1	3	4	2	1	2	3	16452.6913	0.0005
3	1	3	2	2	1	2	1	16452.9226	0.0027
3	1	3	3	2	1	2	2	16452.9821	0.0005
3	1	3	3	2	1	2	3	16454.5907	-0.0006
3	0	3	2	2	0	2	2	17007.0204	0.0014
3	0	3	4	2	0	2	3	17008.2525	0.0013
3	0	3	3	2	0	2	2	17008.3854	-0.0003
3	0	3	3	2	0	1	3	17009.2653	0.0018
3	1	2	3	2	1	1	3	17678.5542	0.0000
3	1	2	2	2	1	1	1	17678.9125	-0.0016
3	1	2	4	2	1	1	3	17679.1503	0.0008
3	1	2	3	2	1	1	2	17679.3524	0.0000
2	1	2	3	1	0	3	2	18097.9317	-0.0001
5	0	5	4	4	1	3	3	18545.4305	-0.0003
5	0	5	6	4	1	1	5	18545.8327	0.0000
2	1	1	2	1	0	1	1	19323.8677	0.0013
2	1	1	2	1	0	1	2	19324.6243	0.0004
2	1	1	1	1	0	1	1	19325.1088	0.0004
2	1	1	3	1	0	1	2	19325.4223	0.0002
2	1	1	1	1	0	1	2	19325.8645	-0.0013
2	1	1	1	1	0	1	0	19327.0005	-0.0015

Table S17. Assigned transitions for the parent species of conformer III

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
2	1	2	3	1	1	1	2	9788.4668	0.0114
2	1	2	2	1	1	1	1	9789.2560	0.0020
2	1	2	2	1	1	1	2	9789.3102	-0.0019
2	0	2	1	1	0	1	1	10117.0304	0.0029
2	0	2	3	1	0	1	2	10118.2164	-0.0008
2	0	2	1	1	0	1	0	10118.8810	0.0000
2	0	2	2	1	0	1	2	10119.0220	-0.0023
2	1	1	1	1	1	0	0	10460.8079	-0.0028
2	1	1	3	1	1	0	2	10461.9678	-0.0077
1	1	0	2	1	0	1	2	12176.5360	0.0129
1	1	0	1	1	0	1	0	12176.8232	-0.0123
2	1	1	2	2	0	2	2	12519.4096	-0.0022
2	1	1	3	2	0	2	3	12520.2753	-0.0060
3	1	2	3	3	0	3	3	13048.4899	0.0002
3	1	2	4	3	0	3	4	13049.1951	-0.0057
3	1	2	3	3	0	3	2	13049.6591	0.0131
3	1	3	4	2	1	2	3	14678.4624	0.0016
3	1	3	2	2	1	2	1	14678.5556	0.0034
3	1	3	3	2	1	2	2	14678.6957	-0.0067
3	0	3	4	2	0	2	3	15159.6604	0.0019
3	0	3	3	2	0	2	2	15159.7048	-0.0032
3	0	3	2	2	0	2	1	15159.8092	0.0022
3	1	2	4	2	1	1	3	15688.5774	-0.0005
3	1	2	3	2	1	1	2	15688.7864	0.0006
4	1	4	5	3	1	3	4	19563.2389	-0.0046
4	0	4	5	3	0	3	4	20179.9542	0.0037
4	0	4	4	3	0	3	3	20179.9978	0.0011

Table S18. Assigned transitions for the parent species of conformer V

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
1	0	1	2	0	0	0	1	6466.3200	-0.0015
3	1	2	4	3	0	3	4	7553.9991	0.0007
3	1	2	2	3	0	3	2	7554.0930	0.0009
2	0	2	3	1	1	1	2	7644.4622	0.0007
2	0	2	2	1	1	1	1	7644.7817	-0.0020
1	1	1	1	0	0	0	1	11705.6593	-0.0012
1	1	1	2	0	0	0	1	11705.6672	0.0043
1	1	0	1	0	0	0	1	12306.7001	-0.0006
2	1	2	1	1	1	1	0	12331.2179	0.0042
2	1	2	3	1	1	1	2	12331.3874	0.0021
2	1	2	2	1	1	1	1	12331.6874	-0.0029
2	0	2	3	1	0	1	2	12883.8106	0.0079
2	1	1	1	1	1	0	0	13533.4785	-0.0037
2	1	1	3	1	1	0	2	13533.9047	-0.0028
2	1	1	1	1	1	0	1	13534.1858	-0.0030
2	1	1	2	1	1	0	1	13534.1969	0.0043
2	1	2	3	1	0	1	2	17570.7253	-0.0011
2	1	2	2	1	0	1	1	17570.7401	-0.0043
3	1	3	2	2	1	2	1	18467.6691	0.0021
3	0	3	3	2	0	2	2	19205.6051	0.0014
3	0	3	2	2	0	2	1	19205.6197	-0.0034

Appendix 4: Relaxation pathways interconnecting specific conformers of AMA

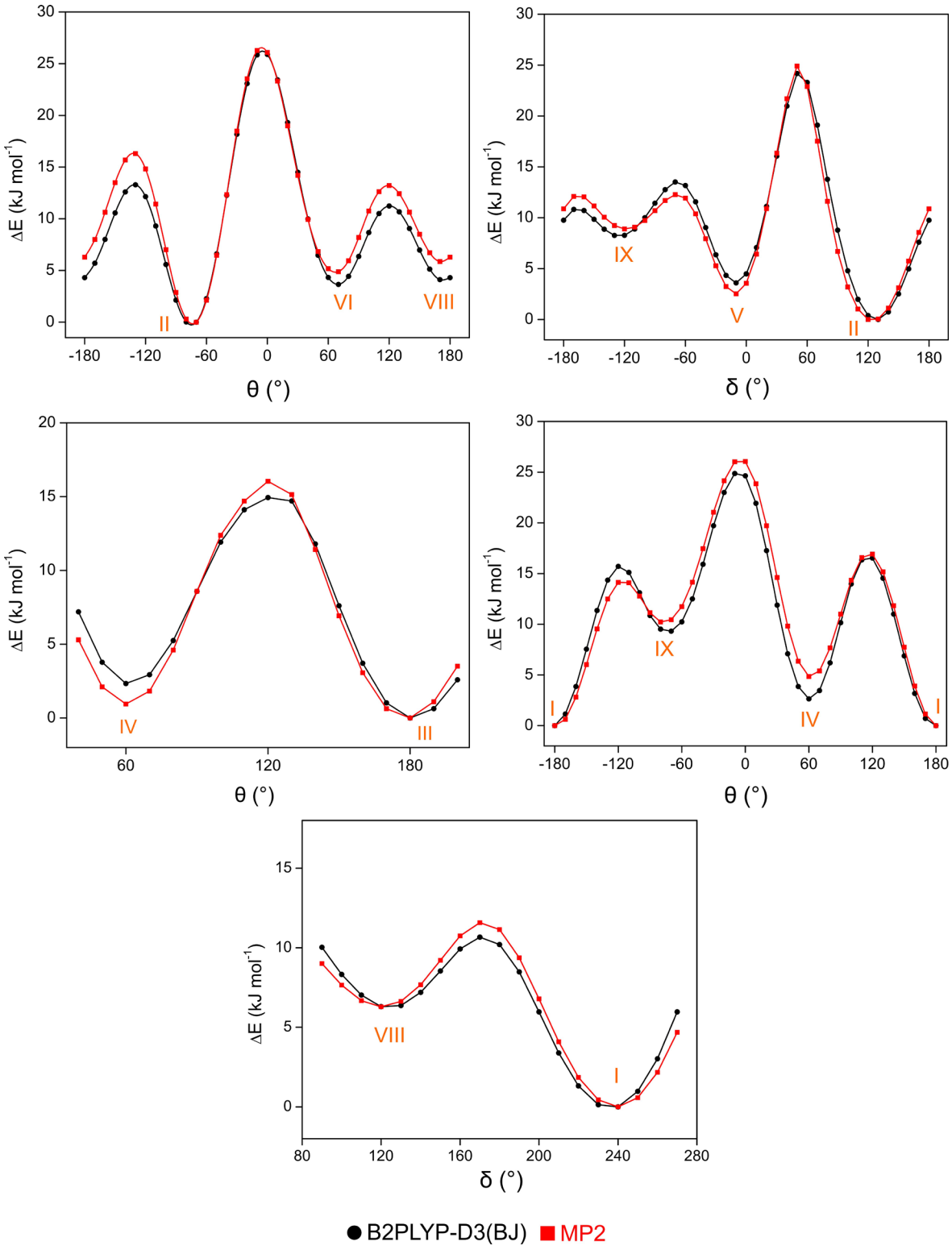

Figure S1. Possible relaxation pathways interconnecting specific conformers of AMA obtained theoretically using the MP2 and B2PLYP-D3(BJ) methods with the aug-cc-pVTZ basis set.

Appendix 5: Non-covalent interaction (NCI) isosurfaces for the conformers of AMA

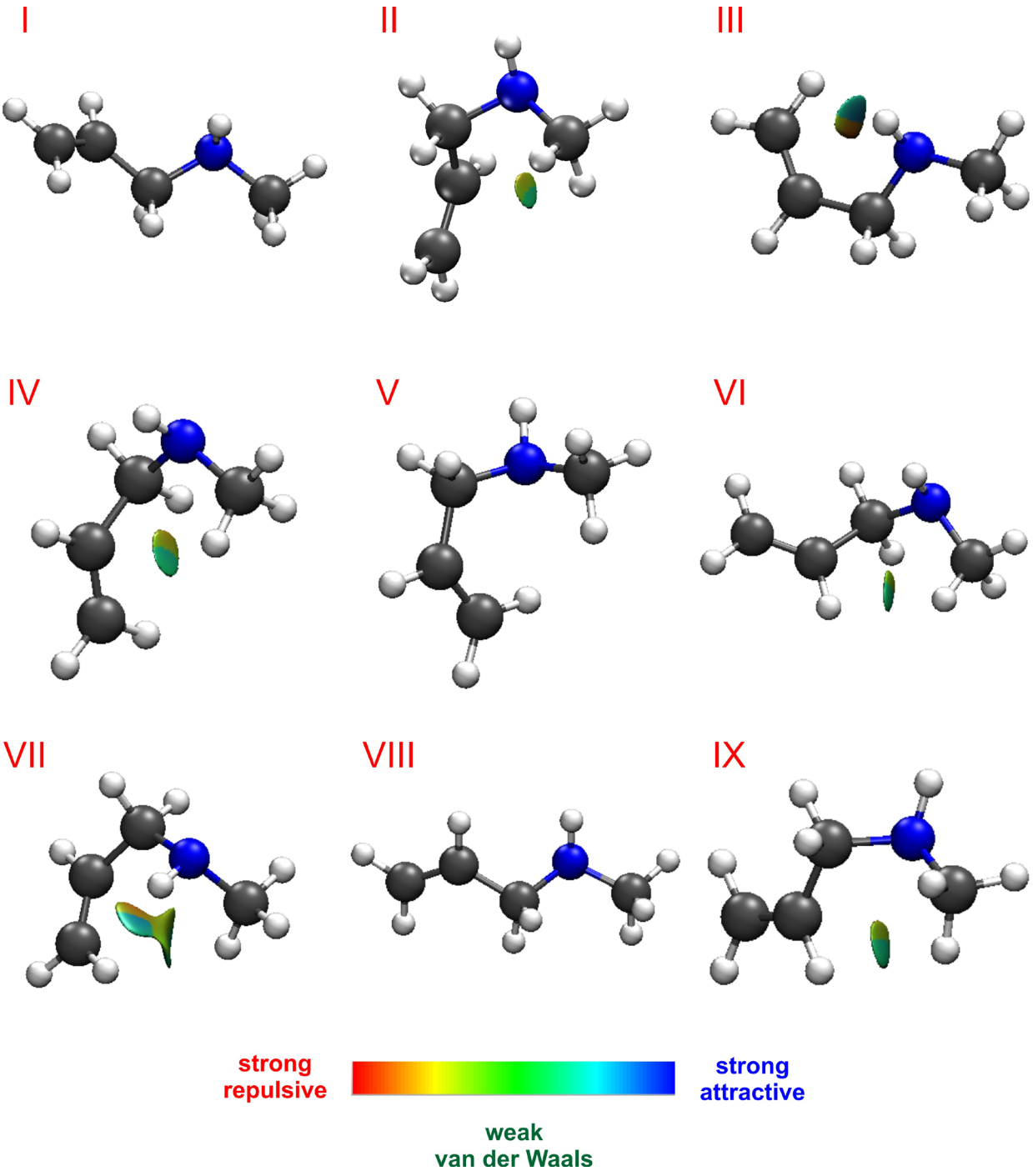

Figure S2. NCI isosurfaces (s= 0.05, colour scale of -0.02 < ρ < 0.02 au for the SCF densities) for the nine stable conformers of AMA

Appendix 6: Natural bond orbital (NBO) results for the conformers of AMA

Table S19. Charge-transfer interactions involving the lone-pair (n_N) at nitrogen exhibited by the nine conformers of AMA obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ level. The second-order perturbation energies are given in kJ mol^{-1}

Interaction	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
$n_N \rightarrow \pi^*_{C1-C2}$	2.4	2.7	0.0	5.8	0.0	6.1	0.0	0.0	0.0
$n_N \rightarrow \sigma^*_{C2-C3}$	3.2	8.5	3.5	32.4	12.6	31.8	38.0	0.0	8.2
$n_N \rightarrow \sigma^*_{C3-H}$	8.6	32.6	8.2	6.7	30.6	9.7	11.5	11.0	30.1
$n_N \rightarrow \sigma^*_{C3-H'}$	32.7	2.3	33.6	7.5	0.0	4.5	4.5	30.7	0.0
$n_N \rightarrow \sigma^*_{C4-H}$	32.2	4.2	32.6	4.5	4.4	5.1	3.9	4.2	3.3
$n_N \rightarrow \sigma^*_{C4-H'}$	4.3	9.5	4.2	9.1	9.6	8.5	10.5	10.0	11.1
$n_N \rightarrow \sigma^*_{C4-H''}$	9.7	31.8	9.9	33.6	31.5	34.7	35.1	32.0	31.8