Supporting Information

Conformational preferences of diallylamine: A rotational spectroscopic and theoretical study

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Appendix 1: Pictorial representations and cartesian coordinates for the conformers of DAA

Appendix 2: Assigned transitions for the parent species of conformers I, II, III and IV

Appendix 3: Spectroscopic parameters obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ and CCSD(T)/ANO0 levels of theory

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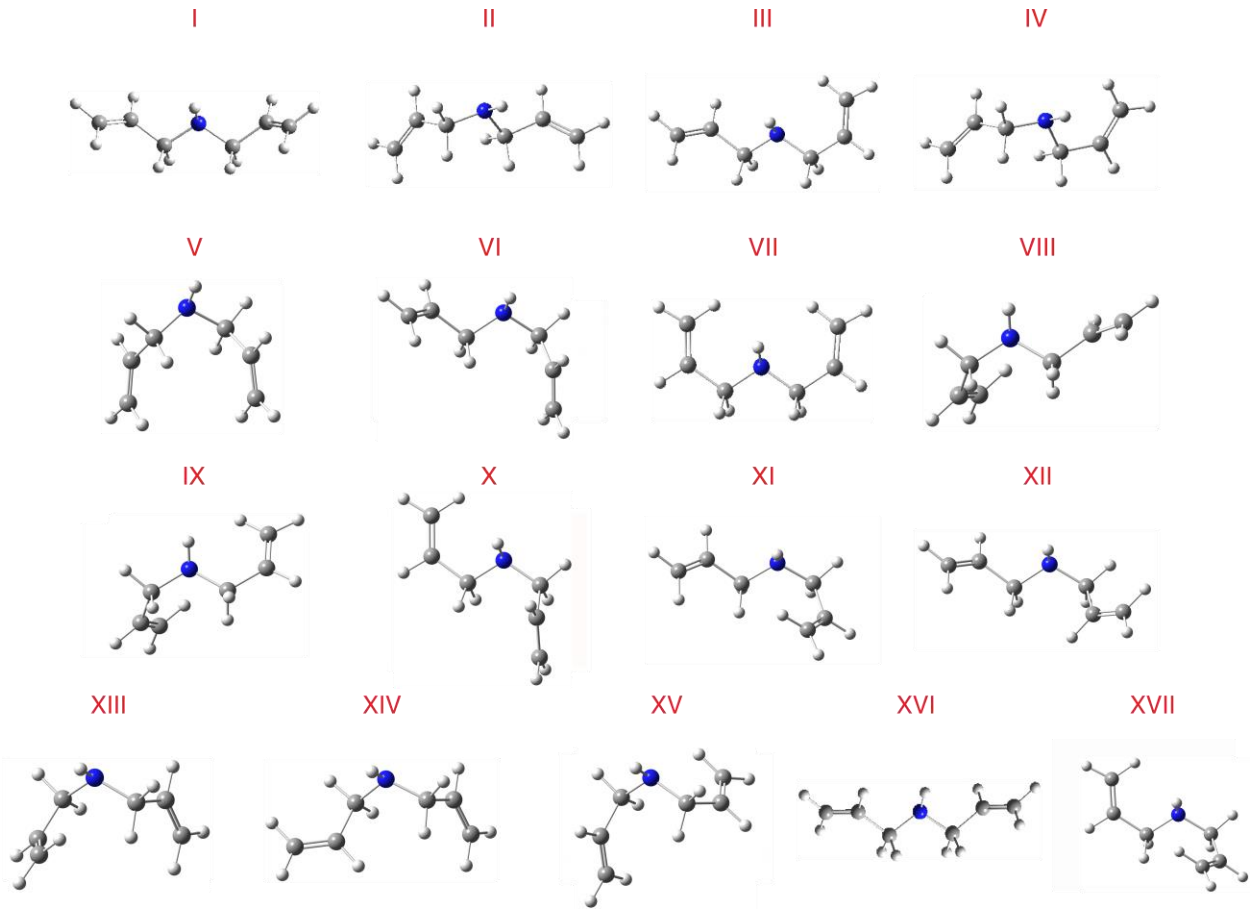
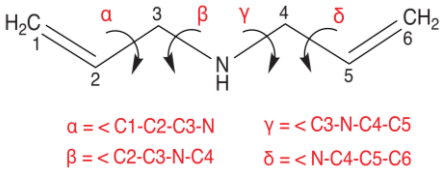
Appendix 1: Pictorial representations and cartesian coordinates for the conformers of DAA





Conformer	α	β	γ	δ
I	-123.1	-179.1	179.1	123.1
II	125.9	-74.0	178.1	122.8
III	-123.1	-179.5	179.5	-6.8
IV	126.6	-74.2	178.5	-7.3
V	125.7	-71.9	-62.3	114.2
VI	-123.5	-175.9	-61.2	117.2
VII	6.9	179.8	-179.8	-6.9
VIII	-10.9	-81.7	176.7	122.4
IX	-9.9	-81.5	175.3	-7.4
X	6.2	-176.6	-61.1	117.7
XI	-124.0	-178.3	-72.4	-8.0
XII	-123.5	-174.6	-69.6	-118.6
XIII	6.6	73.3	73.8	-125.1
XIV	119.3	72.3	71.8	-126.1
XV	-114.6	62.8	80.6	10.2
XVI	-123.0	-179.5	-172.4	-122.6
XVII	5.9	-179.5	-72.6	-8.1

Figure S1. Equilibrium structures for the 17 conformers of DAA and their corresponding dihedral angle values (degrees) obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ.

Table S1. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer I.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.000000	-0.945766	-0.283452
N	0.000000	0.066598	-0.319697
C	-1.221252	0.581057	0.292362
H	-1.280769	0.373768	1.372155
H	-1.203558	1.670449	0.181749
C	1.221252	0.581057	0.292362
H	1.280769	0.373768	1.372155
H	1.203558	1.670449	0.181749
C	-2.431421	0.031332	-0.394453
H	-2.479611	0.206072	-1.464115
C	2.431421	0.031332	-0.394453
H	2.479611	0.206072	-1.464115
C	-3.397567	-0.644311	0.213148
H	-3.365201	-0.841056	1.278164
H	-4.255968	-1.018923	-0.327569
C	3.397567	-0.644311	0.213148
H	4.255968	-1.018923	-0.327569
H	3.365201	-0.841056	1.278164

Table S2. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer II.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.569280	-1.722666	0.140240
N	-0.066501	-0.903424	-0.174397
C	-0.823393	0.297504	0.171205
H	-0.905318	0.448919	1.258834
H	-0.271523	1.154697	-0.223858
C	1.296676	-0.916151	0.352441
H	1.676054	-1.934962	0.238404
H	1.341624	-0.670290	1.424857
C	-2.187435	0.256492	-0.440312
H	-2.211025	0.135320	-1.518232
C	2.186602	0.021459	-0.406831
H	2.203382	-0.127808	-1.481591
C	-3.321069	0.343075	0.243075
H	-3.323323	0.453353	1.320985
H	-4.284355	0.314642	-0.247701
C	2.916586	0.982002	0.143330
H	3.555810	1.621386	-0.450058
H	2.902662	1.159041	1.212227

Table S3. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer III.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.107043	-0.663649	0.672947
N	-0.130931	-0.008342	-0.099323
C	-1.251099	0.900198	0.058191
H	-1.138876	1.561644	0.935515
H	-1.266691	1.571659	-0.808037
C	1.157055	0.668371	-0.205682
H	1.372928	1.319751	0.655734
H	1.111232	1.317170	-1.086618
C	-2.577003	0.209227	0.156649
H	-3.409645	0.862680	0.396176
C	2.264151	-0.323491	-0.377880
H	2.157302	-0.998958	-1.220127
C	-2.795039	-1.087885	-0.014628
H	-1.994575	-1.768409	-0.270014
H	-3.788557	-1.503432	0.080698
C	3.315523	-0.422026	0.424518
H	4.092990	-1.154493	0.255421
H	3.437671	0.234050	1.278137

Table S4. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer IV.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.750560	-1.505979	0.536254
N	-0.226221	-0.756749	0.103949
C	-0.784060	0.524559	0.498796
H	-0.659335	0.719511	1.578782
H	-0.213515	1.312942	-0.001875
C	1.195091	-0.899220	0.407757
H	1.444675	-1.957261	0.292942
H	1.440838	-0.618253	1.443985
C	-2.232772	0.680105	0.153410
H	-2.697781	1.575290	0.553671
C	2.040707	-0.096345	-0.535038
H	1.857653	-0.280810	-1.588608
C	-2.958658	-0.161389	-0.571178
H	-2.528687	-1.055028	-1.001992
H	-4.004003	0.031542	-0.768540
C	2.954785	0.788997	-0.162622
H	3.550424	1.329746	-0.885329
H	3.142400	1.000327	0.883458

Table S5. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer V.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.459390	-2.156500	0.587709
N	-0.017428	-1.477207	-0.017229
C	-1.031738	-0.697466	-0.734636
H	-0.519429	-0.046599	-1.444207
H	-1.628853	-1.401987	-1.317862
C	0.948177	-0.679458	0.740522
H	1.511872	-1.376171	1.366385
H	0.478095	0.053725	1.408802
C	-1.928276	0.126641	0.148222
H	-2.560910	-0.430400	0.834893
C	1.898294	0.028995	-0.177870
H	2.414230	-0.605199	-0.891577
C	-1.962929	1.452532	0.163060
H	-1.336638	2.036574	-0.500688
H	-2.615368	2.000488	0.829736
C	2.120832	1.336173	-0.166091
H	2.829561	1.798923	-0.839395
H	1.600807	1.988994	0.524600

Table S6. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer VI.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.276812	1.066394	1.159952
N	-0.068746	1.031047	0.169357
C	1.377950	0.999909	-0.051467
H	1.557363	1.076155	-1.126535
H	1.795190	1.899997	0.406582
C	-0.804527	-0.068543	-0.452284
H	-0.498924	-1.060663	-0.095514
H	-0.576969	-0.037602	-1.523273
C	2.079015	-0.215837	0.490675
H	2.012957	-0.357609	1.566552
C	-2.276148	0.112207	-0.250720
H	-2.683729	1.055282	-0.599478
C	2.727786	-1.109402	-0.243756
H	2.806857	-1.002220	-1.319294
H	3.206779	-1.973326	0.197033
C	-3.068537	-0.781567	0.326226
H	-4.129153	-0.607602	0.446814
H	-2.681535	-1.724800	0.693078

Table S7. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer VII.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.000000	-0.420629	0.851805
N	0.000000	0.154640	0.017665
C	-1.212227	0.948944	-0.030082
H	-1.255530	1.703726	0.775382
H	-1.205866	1.524177	-0.963022
C	1.212227	0.948944	-0.030082
H	1.255530	1.703726	0.775382
H	1.205866	1.524177	-0.963022
C	-2.467455	0.132677	0.023006
H	-3.379890	0.713197	0.112500
C	2.467455	0.132677	0.023006
H	3.379890	0.713197	0.112500
C	-2.539513	-1.190942	-0.023917
H	-1.655081	-1.803677	-0.130367
H	-3.492082	-1.699760	0.025907
C	2.539513	-1.190942	-0.023917
H	3.492082	-1.699760	0.025907
H	1.655081	-1.803677	-0.130367

Table S8. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer VIII.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.361995	-1.273244	-1.108275
N	-0.104201	-0.569471	-0.553313
C	-1.359185	-1.084351	-0.027978
H	-1.781994	-1.772238	-0.766079
H	-1.211738	-1.682899	0.886788
C	0.810222	-0.068403	0.470733
H	1.093619	-0.843713	1.198990
H	0.282075	0.709308	1.027909
C	-2.380308	-0.019719	0.265972
H	-3.247421	-0.363320	0.821485
C	2.037353	0.513954	-0.155107
H	1.862633	1.310990	-0.870270
C	-2.298183	1.251802	-0.099181
H	-1.447403	1.616978	-0.657967
H	-3.081622	1.956124	0.143554
C	3.275067	0.110287	0.098874
H	4.131570	0.568439	-0.376598
H	3.474411	-0.691290	0.800168

Table S9. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer IX.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.508014	-1.236598	1.093466
N	-0.027367	-0.597076	0.476376
C	1.343948	-1.029307	0.263342
H	1.701331	-1.500022	1.183851
H	1.420122	-1.806043	-0.516684
C	-0.790403	-0.424299	-0.747596
H	-0.878733	-1.364254	-1.319870
H	-0.237939	0.258881	-1.399253
C	2.284354	0.089394	-0.092821
H	3.270390	-0.230788	-0.414907
C	-2.164237	0.128067	-0.523716
H	-2.794447	0.144078	-1.407108
C	2.000223	1.382886	-0.035432
H	1.026559	1.726107	0.286836
H	2.735287	2.129676	-0.301565
C	-2.645170	0.577542	0.628156
H	-3.654045	0.959469	0.700241
H	-2.042184	0.591549	1.525531

Table S10. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer X.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.455586	1.061922	0.888474
N	0.250861	0.759309	-0.056243
C	0.733135	-0.595910	-0.260101
H	0.205730	-1.341364	0.355056
H	0.512929	-0.875606	-1.297092
C	-1.167728	0.951630	-0.357956
H	-1.323196	0.726700	-1.415697
H	-1.386525	2.013734	-0.223051
C	2.204828	-0.744398	-0.022077
H	2.564539	-1.767802	-0.056995
C	-2.114573	0.131204	0.475575
H	-2.079367	0.314502	1.546644
C	3.061488	0.237495	0.226771
H	2.746429	1.271459	0.253291
H	4.109895	0.033524	0.394691
C	-2.943408	-0.788703	0.000753
H	-3.598512	-1.357306	0.646999
H	-2.999055	-1.001042	-1.060575

Table S11. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XI.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.070183	0.317090	1.308128
N	0.118995	0.866614	0.459890
C	1.491602	1.022193	0.015121
H	1.476906	1.587832	-0.921716
H	2.017932	1.664092	0.729910
C	-0.808177	0.343137	-0.541547
H	-0.521417	-0.636184	-0.944507
H	-0.797157	1.045085	-1.382211
C	2.317625	-0.225109	-0.184286
H	3.297648	-0.054271	-0.621316
C	-2.192067	0.268581	0.022484
H	-2.581405	1.195754	0.430074
C	1.967798	-1.460433	0.146417
H	1.003860	-1.685984	0.584382
H	2.635989	-2.295648	-0.009748
C	-2.926090	-0.835565	0.062135
H	-3.924997	-0.840070	0.476679
H	-2.553114	-1.775046	-0.328136

Table S12. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XII.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	0.037429	0.160943	1.260528
N	0.041459	0.730004	0.422656
C	1.007469	0.194045	-0.533279
H	0.774975	-0.821303	-0.883513
H	0.981197	0.846345	-1.412580
C	-1.323811	0.881022	-0.084513
H	-1.260561	1.463050	-1.008595
H	-1.890074	1.481583	0.629947
C	2.384211	0.209160	0.054456
H	2.727988	1.175159	0.408762
C	-2.054932	-0.407862	-0.338648
H	-1.612438	-1.082938	-1.064130
C	3.160141	-0.859738	0.174530
H	2.830840	-1.836566	-0.159347
H	4.150633	-0.798150	0.604303
C	-3.173810	-0.764640	0.279316
H	-3.662082	-1.708954	0.079577
H	-3.645224	-0.115645	1.008435

Table S13. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XIII.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.804722	-1.692010	0.642491
N	-0.164645	-1.198155	0.037081
C	-0.881055	-0.431854	-0.967309
H	-0.142596	0.113443	-1.561109
H	-1.353374	-1.130065	-1.666295
C	0.819838	-0.445782	0.816733
H	1.106010	-1.077929	1.661353
H	0.426866	0.491102	1.231135
C	-1.932852	0.539411	-0.493185
H	-2.369591	1.150199	-1.278635
C	2.039169	-0.147355	-0.003203
H	2.512997	-1.009413	-0.461356
C	-2.367771	0.688010	0.750622
H	-1.966010	0.108920	1.572214
H	-3.144208	1.399515	0.994255
C	2.535182	1.067412	-0.196062
H	3.426029	1.231686	-0.786950
H	2.065894	1.942345	0.237913

Table S14. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XIV.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.576236	-1.828528	0.468828
N	-0.017345	-1.202786	-0.095761
C	-0.882785	-0.207034	-0.735575
H	-0.232741	0.495121	-1.262325
H	-1.485496	-0.711751	-1.492811
C	1.085861	-0.659837	0.697344
H	1.515708	-1.496975	1.253616
H	0.774456	0.087517	1.440619
C	-1.785709	0.535655	0.207642
H	-1.302427	1.102099	0.997318
C	2.144878	-0.066929	-0.182326
H	2.524846	-0.725601	-0.956436
C	-3.111278	0.520000	0.142187
H	-3.629730	-0.031905	-0.633458
H	-3.725783	1.058744	0.850843
C	2.612346	1.168974	-0.070375
H	3.389596	1.544977	-0.721557
H	2.234948	1.848549	0.684624

Table S15. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XV.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.114310	2.002907	0.567346
N	0.224473	1.184930	0.081182
C	0.830033	0.250278	1.020605
H	1.303731	0.832387	1.816449
H	0.086289	-0.388002	1.519734
C	-0.834447	0.621120	-0.764118
H	-0.408451	-0.197155	-1.345046
H	-1.130574	1.398104	-1.472669
C	1.871302	-0.640328	0.401171
H	2.208424	-1.451660	1.039130
C	-2.039073	0.130319	-0.010215
H	-2.599102	0.886535	0.534285
C	2.385983	-0.508071	-0.813311
H	2.072897	0.293663	-1.467903
H	3.139392	-1.191632	-1.179524
C	-2.424035	-1.137436	0.056754
H	-3.290279	-1.4432500	0.628129
H	-1.883673	-1.915971	-0.468705

Table S16. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XVI.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.111627	-0.987443	0.483148
N	-0.000893	-0.179089	-0.117626
C	-1.212197	0.633714	-0.066569
H	-1.381535	1.088513	0.922220
H	-1.077249	1.459777	-0.772849
C	1.204903	0.559866	0.252794
H	1.072571	1.096142	1.209154
H	1.390650	1.319639	-0.509651
C	-2.408481	-0.170690	-0.466509
H	-2.348863	-0.640686	-1.442442
C	2.389961	-0.346470	0.366028
H	2.296224	-1.160451	1.080224
C	-3.484426	-0.342352	0.289840
H	-3.561776	0.108143	1.272245
H	-4.327075	-0.931287	-0.045843
C	3.515939	-0.212835	-0.319760
H	4.347756	-0.890286	-0.183240
H	3.645484	0.582761	-1.043313

Table S17. Cartesian coordinates (B3LYP-D3(BJ)/aug-cc-pVTZ) of conformer XVII.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	-0.123025	0.142975	1.151471
N	-0.086025	0.673873	0.290789
C	1.272676	1.088554	-0.005093
H	1.260658	1.620179	-0.961497
H	1.575549	1.837620	0.734581
C	-0.761623	-0.038983	-0.779807
H	-0.223485	-0.938629	-1.114153
H	-0.789523	0.621945	-1.654039
C	2.342618	0.025416	-0.053792
H	3.314923	0.375852	-0.389111
C	-2.164282	-0.436566	-0.436372
H	-2.647493	-1.063377	-1.178896
C	2.202857	-1.245876	0.295642
H	1.256750	-1.647111	0.636145
H	3.033794	-1.935890	0.253101
C	-2.827726	-0.103401	0.663084
H	-3.839604	-0.446229	0.828643
H	-2.391501	0.533668	1.420018

Appendix 2: Assigned transitions for the parent species of conformers I, II, III and IV

Table S18. Assigned transitions and residuals for the parent species of conformer I.

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
10	1	10	10	10	0	10	10	8926.5588	-0.0003
9	1	9	8	9	0	9	8	8995.8154	-0.0025
9	1	9	10	9	0	9	10	8995.9199	0.0022
9	1	9	9	9	0	9	9	8996.8080	-0.0009
8	1	8	7	8	0	8	7	9059.4245	0.0001
8	1	8	9	8	0	8	9	9059.5376	0.0018
8	1	8	8	8	0	8	8	9060.4195	0.0008
7	1	7	6	7	0	7	6	9116.2708	0.0005
7	1	7	8	7	0	7	8	9116.3974	0.0014
7	1	7	7	7	0	7	7	9117.2663	0.0011
6	1	6	5	6	0	6	5	9166.2463	-0.0007
6	1	6	7	6	0	6	7	9166.3821	-0.0085
6	1	6	6	6	0	6	6	9167.2386	0.0004
5	1	5	4	5	0	5	4	9209.2601	-0.0003
5	1	5	6	5	0	5	6	9209.4274	0.0007
5	1	5	5	5	0	5	5	9210.2399	0.0008
4	1	4	5	4	0	4	4	9244.4352	-0.0001
4	1	4	3	4	0	4	3	9245.2296	-0.0010
4	1	4	5	4	0	4	5	9245.4274	0.0016
4	1	4	4	4	0	4	4	9246.1803	0.0018
4	1	4	4	4	0	4	5	9247.1713	0.0024
3	1	3	2	3	0	3	3	9272.7940	-0.0018
3	1	3	4	3	0	3	3	9273.3629	0.0014
3	1	3	2	3	0	3	2	9274.0975	-0.0017
3	1	3	4	3	0	3	4	9274.3291	0.0020
3	1	3	3	3	0	3	3	9274.9689	0.0018
3	1	3	3	3	0	3	4	9275.9333	0.0005
3	1	3	3	3	0	3	2	9276.2730	0.0024
2	1	2	1	2	0	2	2	9294.4201	-0.0041
2	1	2	3	2	0	2	2	9295.1665	0.0012
2	1	2	1	2	0	2	1	9295.8645	-0.0048
2	1	2	3	2	0	2	3	9296.0975	0.0030
2	1	2	2	2	0	2	2	9296.4759	-0.0006
2	1	2	2	2	0	2	3	9297.4078	0.0021
2	1	2	2	2	0	2	1	9297.9199	-0.0016
1	1	1	0	1	0	1	1	9309.2471	0.0022
1	1	1	2	1	0	1	1	9309.8842	0.0010

1	1	1	1	1	0	1	1	9310.2124	not included in the fit
1	1	1	2	1	0	1	2	9310.7491	-0.0001
1	1	1	1	1	0	1	2	9311.0839	-0.0021
1	1	1	1	1	0	1	0	9312.3809	-0.0038
1	1	0	1	1	0	1	2	9324.3751	0.0027
1	1	0	2	1	0	1	2	9325.5744	-0.0013
2	1	1	2	2	0	2	2	9338.8372	0.0009
2	1	1	3	2	0	2	3	9340.1497	0.0009
2	1	1	1	2	0	2	1	9340.8919	0.0002
3	1	2	3	3	0	3	3	9360.9857	0.0010
3	1	2	4	3	0	3	4	9362.1123	0.0005
3	1	2	2	3	0	3	2	9362.5075	-0.0029
4	1	3	4	4	0	4	4	9390.4086	0.0006
4	1	3	5	4	0	4	5	9391.4679	0.0016
4	1	3	3	4	0	4	3	9391.7399	-0.0003
5	1	4	5	5	0	5	5	9427.2227	-0.0012
5	1	4	6	5	0	5	6	9428.2508	-0.0013
5	1	4	4	5	0	5	4	9428.4635	0.0007
1	1	1	2	0	0	0	1	11128.8851	-0.0022
1	1	0	1	0	0	0	1	11142.5130	0.0025
1	1	0	2	0	0	0	1	11143.7156	0.0017
1	1	0	0	0	0	0	1	11145.6491	-0.0025
2	1	2	3	1	0	1	2	12932.5761	0.0003
2	1	2	2	1	0	1	1	12933.0170	-0.0040
2	1	1	2	1	0	1	1	12975.3813	0.0005
2	1	1	3	1	0	1	2	12976.6314	0.0013
3	1	3	4	2	0	2	3	14729.0549	0.0008
3	1	2	3	2	0	2	2	14815.7486	0.0004
3	1	2	4	2	0	2	3	14816.8399	0.0010
4	1	3	4	3	0	3	3	16663.3254	-0.0011
4	1	3	5	3	0	3	4	16664.3602	0.0000
4	1	3	3	3	0	3	2	16664.7181	0.0006
5	1	4	5	4	0	4	4	18518.2110	-0.0018
5	1	4	6	4	0	4	5	18519.2221	0.0000
5	1	4	4	4	0	4	3	18519.4834	0.0017

Table S19. Assigned transitions and residuals for the parent species of conformer II.

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs} /MHz	$\nu_{obs - calc}$
7	0	7	6	6	1	5	5	7852.9402	0.0010
7	0	7	8	6	1	5	7	7853.1698	0.0017
7	0	7	7	6	1	5	6	7854.6867	-0.0015
1	1	0	1	0	0	0	1	8364.8244	0.0014
1	1	0	2	0	0	0	1	8366.3269	0.0009
1	1	0	0	0	0	0	1	8368.5809	-0.0001
8	0	8	7	7	1	6	6	9696.1434	-0.0002
8	0	8	9	7	1	6	8	9696.3463	-0.0002
8	0	8	8	7	1	6	7	9697.9031	-0.0003
2	1	2	3	1	0	1	2	10350.1150	0.0006
2	1	1	2	1	0	1	1	10552.9040	-0.0014
2	1	1	2	1	0	1	2	10553.7058	-0.0008
2	1	1	1	1	0	1	1	10554.0775	0.0012
2	1	1	3	1	0	1	2	10554.4575	-0.0010
2	1	1	1	1	0	1	0	10556.0801	0.0010
3	1	2	3	2	0	2	2	12775.3187	-0.0001
3	1	2	2	2	0	2	2	12776.0637	-0.0025
3	1	2	3	2	0	2	3	12776.1913	0.0010
3	1	2	4	2	0	2	3	12776.7430	-0.0003
3	1	2	2	2	0	2	1	12777.4226	0.0012
4	1	3	4	3	0	3	3	15032.4806	-0.0005
4	1	3	5	3	0	3	4	15033.8732	0.0003
4	1	3	3	3	0	3	2	15034.3152	-0.0015
5	1	4	5	4	0	4	4	17325.5464	0.0000
5	1	4	4	4	0	4	4	17326.0549	0.0020
5	1	4	5	4	0	4	5	17326.5173	-0.0008
5	1	4	6	4	0	4	5	17326.9396	0.0009
5	1	4	4	4	0	4	3	17327.2737	-0.0007
8	2	7	7	8	1	7	7	17425.0295	0.0006
8	2	7	9	8	1	7	9	17425.1757	0.0005
8	2	7	8	8	1	7	8	17426.3356	-0.0001
7	2	6	6	7	1	6	6	17691.7885	-0.0001
7	2	6	8	7	1	6	8	17691.9493	-0.0017
7	2	6	7	7	1	6	7	17693.0769	0.0008
6	2	5	5	6	1	5	5	17926.1758	-0.0012
6	2	5	7	6	1	5	7	17926.3589	0.0010
6	2	5	6	6	1	5	6	17927.4286	0.0002
5	2	4	4	5	1	4	4	18127.7832	-0.0015
5	2	4	6	5	1	4	6	18127.9860	0.0007
5	2	4	5	5	1	4	5	18128.9687	0.0000

6	1	6	5	5	0	5	4	18230.1811	-0.0015
6	1	6	7	5	0	5	6	18230.3449	0.0016
6	1	6	6	5	0	5	5	18231.5053	-0.0004
4	2	3	3	4	1	3	3	18296.2883	-0.0010
4	2	3	5	4	1	3	5	18296.5061	0.0016
4	2	3	4	4	1	3	4	18297.3399	-0.0001
3	2	2	2	3	1	2	2	18431.4699	-0.0011
3	2	2	4	3	1	2	4	18431.6675	0.0025
3	2	2	3	3	1	2	3	18432.2172	-0.0010

Table S20. Assigned transitions and residuals for the parent species of conformer III.

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs}/MHz	$\nu_{obs - calc}$
1	1	1	2	0	0	0	1	8963.2211	-0.0012
1	1	1	1	0	0	0	1	8963.3376	0.0000
1	1	0	1	0	0	0	1	9039.9513	-0.0009
2	1	2	1	1	0	1	1	10901.2145	-0.0033
2	1	2	3	1	0	1	2	10902.5961	0.0007
2	1	2	2	1	0	1	1	10902.7841	0.0008
2	1	2	1	1	0	1	0	10903.2587	0.0003
2	1	2	2	1	0	1	2	10903.6018	0.0023
2	1	1	2	1	0	1	1	11134.3586	0.0039
2	1	1	1	1	0	1	1	11134.5617	0.0011
2	1	1	3	1	0	1	2	11135.3010	0.0007
2	1	1	1	1	0	1	0	11136.5986	-0.0023
3	1	3	4	2	0	2	3	12803.5044	-0.0006
3	1	3	3	2	0	2	2	12803.8941	-0.0015
3	1	2	3	2	0	2	2	13267.9106	0.0009
3	1	2	4	2	0	2	3	13268.6976	0.0001
3	1	2	2	2	0	2	1	13269.1560	0.0005
4	1	4	5	3	0	3	4	14666.7450	0.0008
4	1	4	4	3	0	3	3	14667.2177	0.0000
4	1	3	4	3	0	3	3	15441.1363	-0.0015
4	1	3	5	3	0	3	4	15441.8703	0.0000
4	1	3	3	3	0	3	2	15442.1422	-0.0028
5	1	5	6	4	0	4	5	16493.6075	0.0000
5	1	5	5	4	0	4	4	16494.1203	0.0005
5	1	4	5	4	0	4	4	17655.3717	0.0007
5	1	4	6	4	0	4	5	17656.0848	0.0010
5	1	4	4	4	0	4	3	17656.2802	-0.0002
6	1	6	7	5	0	5	6	18285.8876	-0.0003
6	1	6	6	5	0	5	5	18286.4172	0.0000

Table S21. Assigned transitions and residuals for the parent species of conformer IV.

J'	K_a'	K_c'	F'	J"	K_a"	K_c"	F"	ν_{obs}/MHz	$\nu_{obs - calc}$
2	1	1	2	1	0	1	1	10344.9580	-0.0034
2	1	1	3	1	0	1	2	10346.5016	-0.0033
2	1	1	1	1	0	1	0	10348.1080	-0.0015
3	1	2	3	2	0	2	2	12736.2911	0.0029
3	1	2	4	2	0	2	3	12737.7090	0.0029
4	1	3	5	3	0	3	4	15163.7672	0.0019
4	2	3	5	4	1	3	5	16659.4179	-0.0014
3	2	2	2	3	1	2	2	16793.9169	0.0011
3	2	2	4	3	1	2	4	16794.1129	0.0018
3	2	2	3	3	1	2	3	16794.6679	-0.0004
3	2	1	4	3	1	3	4	17204.4871	-0.0003
5	1	4	5	4	0	4	4	17624.4825	-0.0017

Appendix 3: Spectroscopic parameters obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ and CCSD(T)/ANO0 levels of theory

Table S22. Rotational (*A*, *B*, and *C*), quartic centrifugal distortion (D_J, D_{JK}, D_K, d_1 and d_2) and ^{14}N quadrupole coupling (χ_{aa}, χ_{bb}, χ_{cc}, χ_{bc}) constants obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ and CCSD(T)/ANO0 levels of theory.

	B3LYP-D3(BJ)/aug-cc-pVTZ				CCSD(T)/ANO0			
Equilibrium parameter	I	II	III	IV	I	II	III	IV
A (MHz)	10389	7346	8071	6842	9814	7142	7863	6677
B (MHz)	914	1090	1045	1175	912	1086	1039	1172
C (MHz)	900	1024	967	1108	896	1018	963	1104
D_J (kHz)	0.1568	0.2380	0.1514	0.3833	0.1697	0.2330	0.1535	0.3563
D_{JK} (kHz)	-12.9585	-4.3192	-4.6023	-8.9808	-12.6704	-3.7943	-4.4900	-7.6649
D_K (kHz)	384.3688	64.4822	74.754307	93.2300	340.2000	56.4200	70.6765	77.9268
d_1 (kHz)	-0.01674	-0.04545	-0.01493	-0.01417	-0.0340	-0.0442	-0.0144	-0.0176
d_2 (kHz)	0.000566	-0.001099	0.0009054	-0.004223	-0.0013	-0.0012	0.0009	-0.0004
χ_{aa} (MHz)	3.144	2.913	2.960	2.871	2.954	2.789	2.748	2.711
χ_{bb} (MHz)	1.619	2.558	0.460	2.553	1.096	2.470	0.261	2.442
χ_{cc} (MHz)	-4.763	-5.471	-3.420	-5.425	-4.045	-5.259	-3.008	-5.153
χ_{bc} (MHz)	-2.348		3.362		-2.926		3.425	

Appendix 4: Orbital overlap representations in conformers I, II, III and IV

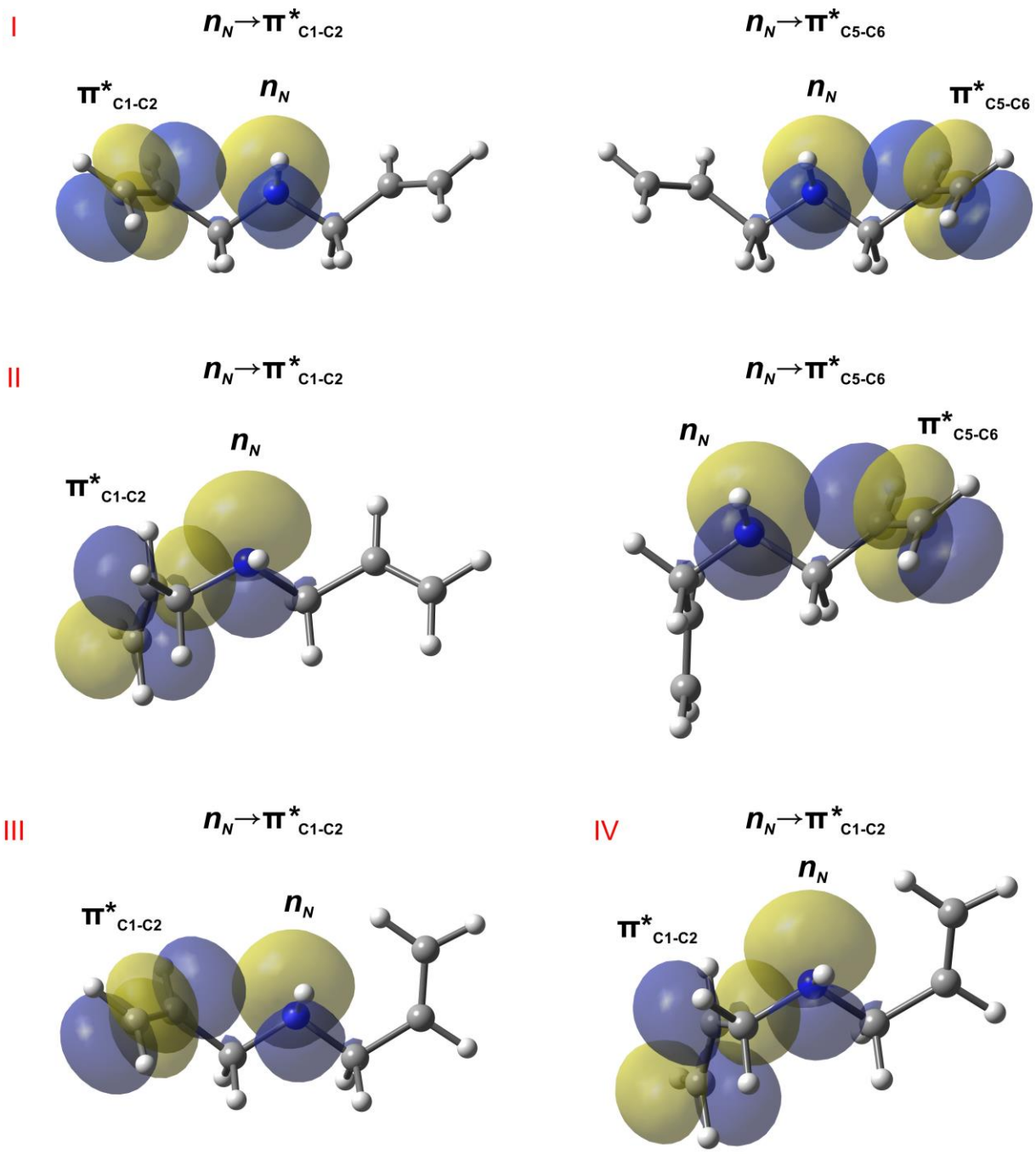


Figure S2. Pictorial representations of the orbital overlaps corresponding to the $n_N \rightarrow \pi^*_{C\text{-}C}$ hyperconjugative interactions in conformers I, II, III and IV. The presence of the interaction is confirmed by the overlap between the orbitals and the second-order perturbation energies given in Table 3 of the main text.