Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Accurate Structures and Spectroscopic Parameters of α,α Dialkylated α-Amino Acids in the Gas-Phase: a Joint Venture of DFT and Wave-Function Composite Methods

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Table S1: Ac3c Z-matrix

C
N,1,NC
H,2,HN,1,HNC
C,1,CC,2,CCN,3,CCNH,0
O,4,OC,1,OCC,2,PSI,0
O,4,O1C,1,O1CC,2,PSI1,0
H,6,HO,4,HOC,5,OMEGA,0
C,1,C1C,4,C1CC,5,TAU,0
C,1,C1C,4,C1CC,5,-TAU,0
H,8,HC,1,HCC,4,ZETA,0
H,8,H1C,1,H1CC,4,ZETA1,0
H,9,HC,1,HCC,4,-ZETA,0
H,9,H1C,1,H1CC,4,-ZETA1,0
H,2,HN,1,HNC,4,-CCNH,0

Table S2: geometrical parameters (distances in Angstrom and angles in degrees) for conformer I of Ac3c corresponding to the Z-matrix of Table S1. The experimental values of quadrupole coupling constants are: -4.485(2), 2.902(3) and 1.583(3) MHz.

Par.	MP2		rDSD/j3		rDSD/j4.		rDSD/3F12	
	fc	ae	fc	+CV2	fc	+CV2	fc	+CV2
NC	1.4320	1.4295	1.4348	1.4323	1.4328	1.4303	1.4328	1.4303
HN	1.0134	1.0123	1.0145	1.0134	1.0133	1.0122	1.0140	1.0129
HNC	109.1022	109.2344	109.8005	109.9327	109.92	110.05	109.94	110.06
CC	1.4842	1.4815	1.4902	1.4875	1.4895	1.4868	1.4895	1.4868
CCN	117.2981	117.2716	116.9579	116.9314	116.96	116.93	117.00	116.97
CCNH	57.3354	57.4763	58.1152	58.2561	58.26	58.40	58.28	58.38
OC	1.2107	1.2090	1.2101	1.2084	1.2076	1.2059	1.2080	1.2055
OCC	124.4614	124.4339	124.4494	124.4219	124.41	124.38	124.43	124.40
O1C	1.3574	1.3551	1.3569	1.3546	1.3545	1.3522	1.3550	1.3518
O1CC	113.0719	113.1173	113.3328	113.3782	113.38	113.43	113.37	113.42
HO	0.9681	0.9673	0.9679	0.9671	0.9660	0.9652	0.9670	0.9662
HOC	105.0090	105.0987	105.8904	105.9801	105.96	106.05	105.98	116.07
C1C	1.5128	1.5097	1.5163	1.5132	1.5147	1.5116	1.5148	1.5117
C1CC	117.7752	117.7622	117.8917	117.8787	117.90	117.89	117.88	117.87
TAU	146.0759	146.0830	146.0840	146.0911	146.09	146.10	146.10	146.11
HC	1.0776	1.0763	1.0804	1.0791	1.0798	1.0785	1.0806	1.0800
HCC	117.4393	117.4562	117.5375	117.5544	117.54	117.56	117.55	117.57
H1C	1.0782	1.0770	1.0809	1.0797	1.0802	1.0790	1.0810	1.0798
H1CC	114.1735	114.1831	114.4085	114.4181	114.41	114.42	114.40	114.40
ZETA	-0.71	-0.72	-0.74	-0.76	-0.77	-0.78	-0.77	-0.78
ZETA1	-143.51	-143.50	-143.25	-143.24	-143.19	-143.18	-143.23	-143.22
OMEGA	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00
PSI	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00
PSI1	180.0	180.0	180.0	180.0	180.00	180.00	180.00	180.00
Xaa	-4.634	-4.682	-4.752		-4.908		-4.870	
Xbb	2.907	2.933	2.967		3.012		3.000	
Xcc	1.727	1.748	1.785		1.896		1.869	

Table S3: geometrical parameters (distances in Angstrom and angles in degrees) for conformer II of Ac3c corresponding to the Z-matrix of Table S1. The experimental values of quadrupole coupling constants are: -3.424(1), 1.842(2) and 1.582 (2) MHz.

Par.	MP2		rDSD/j3		rDSD/j4.		rDSD/3F12	
	fc	ae	fc	+CV2	fc	+CV2	fc	+CV2
NC	1.4424	1.4396	1.4463	1.4435	1.4443	1.4415	1.4444	1.4416
HN	1.0096	1.0086	1.0110	1.0100	1.0099	1.0089	1.0106	1.0096
HNC	112.21	112.35	112.52	112.66	112.59	112.73	112.60	112.74
CC	1.5032	1.5005	1.5077	1.5050	1.5069	1.5042	1.5069	1.5042
CCN	114.10	114.14	114.04	114.07	114.06	114.10	114.09	104.13
CCNH	118.66	118.47	118.31	118.12	118.21	118.02	118.19	118.00
OC	1.2078	1.2061	1.2070	1.2053	1.2045	1.2028	1.2049	1.2032
OCC	123.37	123.36	123.47	123.46	123.45	123.44	123.46	123.45
O1C	1.3401	1.3379	1.3412	1.3390	1.3388	1.3366	1.3394	1.3372
O1CC	113.345	113.35	113.78	113.78	113.79	113.79	113.80	113.80
HO	0.9798	0.9791	0.9784	0.9777	0.9764	0.9757	0.9774	0.9767
HOC	103.83	103.89	105.00	105.06	105.20	105.26	105.18	105.24
C1C	1.5091	1.5060	1.5124	1.5093	1.5107	1.5076	1.5107	1.5076
C1CC	115.10	115.09	115.38	115.37	115.38	115.37	115.36	115.35
TAU	-33.16	-33.16	-33.20	-33.20	-33.20	-33.19	-33.20	-33.19
HC	1.0784	1.0772	1.0810	1.0798	1.0803	1.0791	1.0811	1.0799
HCC	116.14	116.15	116.32	116.33	116.32	116.32	116.31	116.31
H1C	1.0796	1.0784	1.0825	1.0813	1.0817	1.0805	1.0826	1.0814
H1CC	116.04	116.06	116.10	116.12	116.10	116.12	116.10	116.12
ZETA	-2.73	-2.73	-2.65	-2.66	-2.67	-2.67	-2.66	-2.66
ZETA1	-146.03	-146.02	-145.61	-145.59	-145.55	-145.53	-145.57	-145.55
OMEGA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PSI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PSI1	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
Xaa	-3.529	-3.568	-3.630		-3.725		-3.719	
Xbb	1.799	1.817	1.840		1.851		1.841	
Xcc	1.730	1.751	1.790		1.874		1.878	

Table S4: geometrical parameters (distances in Angstrom and angles in degrees) for conformer III of Ac3c corresponding to the Z-matrix of Table S1. The experimental values of quadrupole coupling constants are: -4.615(2), -2.940(4) and 1.675(4) MHz.

Par.	MP2		rDSD/j3		rDSD/j4.		rDSD/3F12	
	fc	ae	fc	+CV2	fc	+CV2	fc	+CV2
NC	1.4323	1.4295	1.4358	1.4330	1.4340	1.4312	1.4338	1.4310
HN	1.0124	1.0112	1.0135	1.0123	1.0124	1.0112	1.0130	1.0118
HNC	109.87	110.02	110.59	110.74	110.61	110.76	110.73	110.88
CC	1.4865	1.4838	1.4923	1.4896	1.4910	1.4883	1.4916	1.4889
CCN	121.27	121.23	120.76	120.73	120.76	120.73	120.80	120.77
CCNH	58.25	58.42	59.10	59.27	59.14	59.30	59.28	59.44
OC	1.2110	1.2093	1.2105	1.2088	1.2082	1.2065	1.2084	1.2067
OCC	125.38	125.36	125.33	125.32	125.33	125.31	125.31	125.29
O1C	1.3563	1.3540	1.3561	1.3538	1.3548	1.3525	1.3542	1.3519
O1CC	112.07	112.11	112.42	112.46	112.48	112.52	112.46	112.50
HO	0.9688	0.9680	0.9686	0.9678	0.9668	0.9660	0.9677	0.9669
HOC	104.71	104.80	105.61	105.70	105.60	105.69	105.71	105.80
C1C	1.5134	1.5104	1.5167	1.5137	1.5152	1.5122	1.5151	1.5121
C1CC	114.26	114.25	114.56	114.56	114.57	114.56	114.54	114.53
TAU	-32.72	-32.71	-32.77	-32.76	-32.76	-32.76	-32.75	-32.75
HC	1.0783	1.0770	1.0809	1.0796	1.0802	1.0789	1.0811	1.0798
HCC	116.54	116.55	116.66	116.67	116.64	116.65	116.65	116.66
H1C	1.0781	1.0769	1.0809	1.0797	1.0802	1.0790	1.0810	1.0798
H1CC	114.47	114.48	114.66	114.67	114.63	114.64	114.65	114.66
ZETA	-3.28	-3.29	-3.21	-3.22	-3.23	-3.24	-3.24	-3.25
ZETA1	-146.01	-145.99	-145.63	-145.62	-145.58	-145.57	-145.61	-145.60
OMEGA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PSI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PSI1	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
Xaa	-4.716	-4.767	-4.843		-4.952		-4.966	
Xbb	2.934	2.963	2.995		3.030		3.032	
Xcc	1.782	1.805	1.848		1.923		1.934	

Table S5: energy contributions for the Ac3c conformers. E in a.u. and ΔE in cm^{-1}

Comp. Level	Ac3c I	E(Ac3c II)	ΔE (Ac3c II)	E(Ac3c III)	ΔE(Ac3c III)
MP2/2F12	-361.0695586	-361.0679641	349.9	-361.0690686	107.5
MP2/3F12	-361.2560207	-361.2550118	221.4	-361.2555854	95.5
MP2/4F12	-361.3234408	-361.322451	217.2	-361.3230051	95.6
E_{V2}	-361.3726380	-361.371664	213.7	-361.3722030	95.4
CCSD(T)/2F12	-361.1517551	-361.1500483	374.6(24.7[a])	-361.1511042	134.5(27.0[a])
CCSD(T)/3F12	-361.3394425	-361.3382704	257.2(35.8[b])	-361.3388315	134.1(38.6[b])
ΔE_V	-0.08393772	-0.08375308	40.5	-0.08375562	40.0
MP2fc/C3	-361.1958158	-361.1949446		-361.1954565	
MP2ae/C3	-361.5413639	-361.5405323		-361. 5409921	
ΔE_{CV2}	-0.3455481	-0.3455877	-8.7	-0.3455356	2.7
E(PCS)	-361.80212382	-361.80100478	245.6	-361.80149422	138.2
E(jChs-F12)			247.0		138.8

(a) ΔE(2F12); (b) ΔE(3F12).

Table S6: PCS optimized geometry for conformer I of Aib

6 0.048735 0.584416 0.000000
7 -1.164319 1.382962 0.000000
1 -1.730511 1.148322 0.807439
6 -0.264305 -0.911787 0.000000
8 -1.368290 -1.392990 0.000000
8 0.851680 -1.673572 0.000000
1 0.554294 -2.593709 0.000000
6 0.851680 0.920137 1.254954
6 0.851680 0.920137 -1.254954
1 1.786081 0.362612 1.284857
1 1.065910 1.988367 1.255058
1 1.065910 1.988367 -1.255058
1 1.786081 0.362612 -1.284857
1 -1.730511 1.148322 -0.807439
1 0.279559 0.684722 2.154921
1 0.279559 0.684722 -2.154921

Table S7: PCS optimized geometries for the energy minimum and planar transition state of Aib conformer II

Aib conformer II: energy minimum
6 0.546368 0.013270 -0.014834
7 0.866562 1.398612 -0.389509
1 1.695663 1.723166 0.090269
6 -0.985351 -0.151494 -0.026576
8 -1.525494 -1.224150 0.023023
8 -1.663435 0.999028 -0.050994
1 -0.974307 1.692605 -0.114716
6 0.998591 -0.221204 1.423634
6 1.169011 -1.012841 -0.951540
1 0.677523 -1.205626 1.758961
1 2.087929 -0.169296 1.483205
1 2.257203 -0.955433 -0.892562
1 0.847491 -2.017118 -0.682778
1 1.042739 1.475199 -1.384025
1 0.574183 0.529570 2.092165
1 0.865365 -0.828753 -1.984300

Aib conformer II : planar transition state
6 0.096524 0.536462 0.000000
7 -1.239605 1.157719 0.000000
1 -1.383228 1.735615 0.816654
6 -0.068837 -0.997350 0.000000
8 0.871417 -1.747611 0.000000
8 -1.333617 -1.419275 0.000000
1 -1.863404 -0.593394 0.000000
6 0.871417 0.919672 1.255218
6 0.871417 0.919672 -1.255218
1 1.809608 0.369966 1.297644
1 1.083818 1.990386 1.248246
1 1.083818 1.990386 -1.248246
1 1.809608 0.369966 -1.297644
1 -1.383228 1.735615 -0.816654
1 0.297365 0.680892 2.153309
1 0.297365 0.680892 -2.153309

Table S8 : PCS optimized geometries for the energy minimum and planar transition state of Aib conformer III

Aib conformer III: energy minimum
6 -0.582490 -0.036794 -0.022295
7 -0.957434 -0.793669 -1.216345
1 -0.435132 -1.660056 -1.266738
6 0.923755 0.213271 0.025206
8 1.467882 1.284739 0.100961
8 1.625592 -0.943333 -0.040833
1 2.559785 -0.696802 -0.012169
6 -0.979670 -0.851365 1.205466
6 -1.310226 1.295816 -0.042097
1 -0.701172 -0.331328 2.123225
1 -2.059230 -0.997727 1.193656
1 -2.383051 1.109983 -0.071592
1 -1.067144 1.884395 0.840939
1 -0.746182 -0.264165 -2.054429
1 -0.493583 -1.826854 1.200695
1 -1.028256 1.881414 -0.917869

Aib conformer III: planar transition state
6 0.079992 0.579374 0.000000
7 -1.173859 1.315563 0.000000
1 -1.729144 1.073455 0.811419
6 -0.061939 -0.945033 0.000000
8 0.865328 -1.713952 0.000000
8 -1.344489 -1.369928 0.000000
1 -1.302711 -2.336526 0.000000
6 0.865328 0.958530 1.253360
6 0.865328 0.958530 -1.253360
1 1.813965 0.426018 1.287029
1 1.046128 2.032572 1.243216
1 1.046128 2.032572 -1.243216
1 1.813965 0.426018 -1.287029
1 -1.729144 1.073455 -0.811419
1 0.299427 0.713066 2.154816
1 0.299427 0.713066 -2.154816

Table S9: Energy contributions for low-energy conformers of Aib: E in a.u. and ΔE in cm^{-1}.

Comp. Level	Aib I	E(Aib II)	ΔE (Aib II)	E(Aib III)	ΔE(Aib III)
MP2/2F12	-362.2998233	-362.3000283	-45.0	-362.2986347	260.8
MP2/3F12	-362.4853240	-362.4860891	-167.9	-362.4840756	274.0
MP2/4F12	-362.5543139	-362.5551243	-177.8	-362.5530716	272.6
E_{V2}	-362.6046560	-362.6055010	-185.4	-362.6034190	271.5
CCSD(T)/2F12	-362.3921976	-362.3920853	24.6 (69.6[a])	-362.3910456	252.8 (-8.0[a])
CCSD(T)/3F12	-362.5790065	-362.5794312	-93.2(74.7[b])	-362.5777815	268.8 (-5.2[b])
ΔE_V	-0.094233320	-0.093883190	76.8	-0.094251260	-3.9
MP2fc/C3	-362.4254323	-362.4265638		-362.4242314	
MP2ae/C3	-362.7707288	-362.7719015		-362.7695247	
ΔE_{CV2}	-0.3452965	-0.3453377	-9.0	-0.3452930	0.8
E(PCS)	-363.044186	-363.044722	-117.6	-363.0429630	268.8

(a) ΔE(2F12); (b) ΔE(3F12).

Table S10: Energy contributions for the planar structures of Aib I, Aib II and Aib III species. E in a.u. and ΔE in cm^{-1} .

Comp. Level	Aib I	E(Aib II)	ΔE (Aib II)	E(Aib III)	ΔE(Aib III)
MP2/2F12	-362.2998233	-362.299641	40.0	-362.2980038	399.3
MP2/3F12	-362.485324	-362.4857924	-102.8	-362.4834987	400.6
MP2/4F12	-362.5543139	-362.554835	-114.4	-362.5524802	402.4
E_{V2}	-362.604656	-362.605218	-123.3	-362.6028180	403.3
CCSD(T)/2F12	-362.3921976	-362.3916673	116.4(76.4[a])	-362.3903543	404.5(5.2[a])
CCSD(T)/3F12	-362.5790065	-362.579113	-23.4(79.4[b])	-362.5771405	409.5(8.9[b])
ΔE_V	-0.09423332	-0.09386557	80.7	-0.09418579	10.4
MP2fc/C3	-362.4254323	-362.4260479		-362.423645	
MP2ae/C3	-362.7707288	-362.7713925		-362.768928	
ΔE_{CV2}	-0.3452965	-0.3453446	-10.5	-0.3452830	3.0
E(PCS)	-363.044186	-363.044428	-53.1	-363.042287	416.7

(a) ΔE(2F12); (b) ΔE(3F12).