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

Supplementary Information

Experiment and Theory at the Convergence Limit: Accurate Equilibrium Structure of Picolinic Acid by Gas-Phase Electron Diffraction and Coupled-Cluster Computations

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Table S1. Experimental total intensity curves $I(s)$ for picolinic acid and background lines $B(s)$.

a) Long nozzle-to-film distance L = 362.28 mm

s, Å^{-1}	$I(s)$	$B(s)$
3.6	0.530326	0.593121
3.8	0.516538	0.606476
4	0.501186	0.619831
4.2	0.508598	0.632884
4.4	0.513218	0.644956
4.6	0.54888	0.655511
4.8	0.594532	0.663786
5	0.663554	0.669321
5.2	0.734787	0.671803
5.4	0.788114	0.671184
5.6	0.811931	0.667725
5.8	0.801651	0.661848
6	0.770108	0.654054
6.2	0.725572	0.644846
6.4	0.685955	0.634723
6.6	0.649396	0.623988
6.8	0.614296	0.612837
7	0.581667	0.601503
7.2	0.553688	0.590284
7.4	0.534302	0.579478
7.6	0.523733	0.56928
7.8	0.518864	0.559748
8	0.516175	0.55087
8.2	0.514417	0.542623
8.4	0.513097	0.534973
8.6	0.513211	0.527866
8.8	0.515227	0.521199
9	0.516413	0.51482
9.2	0.51564	0.508587
9.4	0.509878	0.502409
9.6	0.501224	0.496303
9.8	0.492815	0.49034
10	0.486592	0.484588
10.2	0.484606	0.4791
10.4	0.485514	0.473875
10.6	0.486724	0.468863
10.8	0.48531	0.463989
11	0.480234	0.459184
11.2	0.471707	0.454411
11.4	0.461822	0.449652
11.6	0.450367	0.44489
11.8	0.438558	0.440126
12	0.42685	0.435367
12.2	0.415679	0.430619
12.4	0.405637	0.4259
12.6	0.398517	0.421257
12.8	0.394658	0.416738
13	0.394556	0.412397
13.2	0.397286	0.408277

13.4	0.401363	0.404396
13.6	0.405336	0.40074
13.8	0.407117	0.397258
14	0.406629	0.393888
14.2	0.403272	0.390572
14.4	0.397837	0.387296
14.6	0.391999	0.384091
14.8	0.386073	0.381001
15	0.380888	0.378065
15.2	0.376476	0.375308
15.4	0.373255	0.372747
15.6	0.370744	0.370398
15.8	0.369123	0.368289
16	0.36804	0.366457
16.2	0.366844	0.364932
16.4	0.365116	0.363731
16.6	0.362596	0.362846
16.8	0.359903	0.362233
17	0.356476	0.361827
17.2	0.35339	0.36159
17.4	0.352072	0.361509
17.6	0.352276	0.361554
17.8	0.354584	0.361598

b) Nozzle-to-film distance L = 193.94 mm

s, Å^{-1}	$I(s)$	$B(s)$
8	0.562235	0.593485
8.2	0.560096	0.586298
8.4	0.557116	0.579111
8.6	0.562228	0.571956
8.8	0.560727	0.564761
9	0.556921	0.557618
9.2	0.553633	0.550718
9.4	0.550674	0.544147
9.6	0.543338	0.537831
9.8	0.534543	0.531673
10	0.526774	0.525622
10.2	0.52615	0.519653
10.4	0.525337	0.513706
10.6	0.523849	0.507767
10.8	0.521221	0.501864
11	0.515081	0.496017
11.2	0.506819	0.490234
11.4	0.49592	0.484523
11.6	0.483327	0.478923
11.8	0.472212	0.473488
12	0.459666	0.468253
12.2	0.449356	0.463242
12.4	0.439845	0.458445
12.6	0.432877	0.453845
12.8	0.429742	0.449428
13	0.428776	0.445182
13.2	0.43102	0.441124

13.4	0.434338	0.437269
13.6	0.437679	0.433616
13.8	0.439131	0.43014
14	0.438235	0.426798
14.2	0.435134	0.423537
14.4	0.430224	0.420305
14.6	0.424774	0.417063
14.8	0.418517	0.413787
15	0.413289	0.410472
15.2	0.408491	0.407117
15.4	0.40402	0.40373
15.6	0.400779	0.40033
15.8	0.39768	0.396944
16	0.394921	0.393602
16.2	0.392222	0.390332
16.4	0.388582	0.387149
16.6	0.384095	0.384066
16.8	0.378733	0.381093
17	0.373079	0.37824
17.2	0.368424	0.375514
17.4	0.36466	0.372915
17.6	0.362411	0.370438
17.8	0.361201	0.368074
18	0.361751	0.365808
18.2	0.361971	0.363611
18.4	0.363009	0.36147
18.6	0.363092	0.359378
18.8	0.363435	0.357339
19	0.362453	0.355351
19.2	0.360349	0.353406
19.4	0.357418	0.351497
19.6	0.353745	0.349608
19.8	0.349763	0.347726
20	0.346225	0.345846
20.2	0.34283	0.343974
20.4	0.340393	0.342124
20.6	0.338454	0.340309
20.8	0.336718	0.33854
21	0.33542	0.336822
21.2	0.333974	0.335154
21.4	0.332281	0.333534
21.6	0.330425	0.331965
21.8	0.3287	0.330449
22	0.326843	0.328981
22.2	0.325241	0.327554
22.4	0.324088	0.32616
22.6	0.323004	0.324791
22.8	0.322272	0.323446
23	0.321775	0.322129
23.2	0.321505	0.320843
23.4	0.321506	0.319588
23.6	0.321074	0.318363

23.8	0.320451	0.317171
24	0.319537	0.316015
24.2	0.318225	0.314893
24.4	0.31638	0.313797
24.6	0.314434	0.312719
24.8	0.312143	0.311655
25	0.310057	0.31061
25.2	0.308365	0.309593
25.4	0.306626	0.308612
25.6	0.305567	0.307676
25.8	0.304502	0.306782
26	0.303865	0.305925
26.2	0.30316	0.305094
26.4	0.302851	0.304287
26.6	0.302268	0.303503
26.8	0.301963	0.302757
27	0.301857	0.302059
27.2	0.301398	0.301419
27.4	0.301296	0.300843
27.6	0.300779	0.300336
27.8	0.300699	0.299904
28	0.30044	0.299547
28.2	0.30031	0.299266
28.4	0.300566	0.299061
28.6	0.30045	0.298926
28.8	0.300617	0.29886
29	0.300457	0.298858
29.2	0.300318	0.298921
29.4	0.300118	0.299041
29.6	0.299774	0.299209
29.8	0.29944	0.299414
30	0.299055	0.299646
30.2	0.298476	0.299908
30.4	0.298383	0.30021
30.6	0.298261	0.300566
30.8	0.298673	0.300992
31	0.299555	0.301494
31.2	0.300591	0.30207
31.4	0.301458	0.302718
31.6	0.302937	0.303441
31.8	0.30419	0.30423
32	0.305605	0.305075
32.2	0.307049	0.305956
32.4	0.308274	0.306836

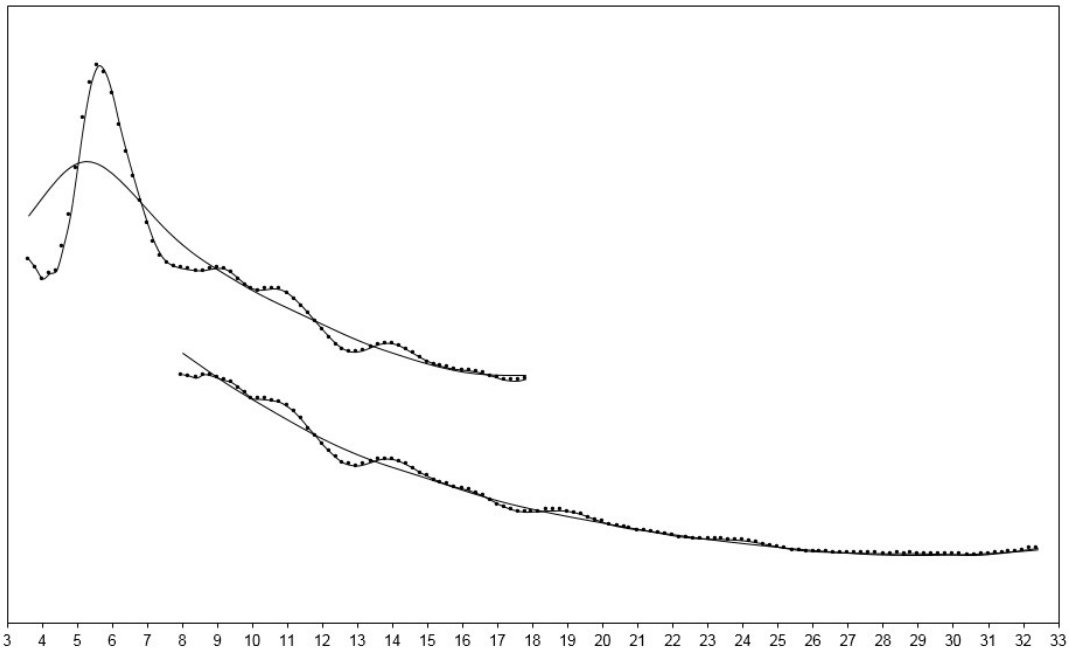

Figure S1. Experimental total intensity curves $I(s)$ (points) for picolinic acid with background $G(s)$ lines for the long (above) and short (below) nozzle-to-film distances

Table S2. Optimized geometries of the two lowest-energy conformers of picolinic acid (bond lengths in Å, bond angles in degree) [a]

Parameter r_e, $\angle_e$	B3LYP/ VTZ	MP2/ VTZ	MP2_ae/ wCVTZ	MP2_ae/ wCVQZ	CCSD(T)_ae/ wCVTZ	best estimated ab initio
ap-ap conformer						
C2−C3	1.389	1.391	1.387	1.385	1.391	1.390
C3−C4	1.387	1.389	1.385	1.384	1.389	1.388
C4−C5	1.389	1.393	1.389	1.387	1.390	1.388
C5−C6	1.390	1.392	1.388	1.386	1.391	1.390
N1−C6	1.331	1.338	1.334	1.332	1.337	1.335
N1−C2	1.336	1.342	1.337	1.335	1.340	1.338
C1−C2	1.508	1.502	1.498	1.497	1.506	1.505
C1=O2	1.202	1.208	1.205	1.203	1.203	1.201
C1−O1	1.339	1.339	1.335	1.333	1.337	1.334
C3−H3	1.080	1.080	1.078	1.078	1.080	1.079
C4−H4	1.082	1.081	1.079	1.079	1.081	1.081
C5−H5	1.081	1.080	1.079	1.078	1.081	1.080
C6−H6	1.083	1.082	1.081	1.080	1.082	1.081
O1−H1	0.977	0.978	0.977	0.976	0.974	0.973
C2C3C4	118.1	118.1	118.1	118.0	117.6	117.5
C3C4C5	118.9	118.7	118.8	118.8	119.1	119.1
C4C5C6	118.8	119.0	119.0	119.0	119.0	119.1
C1C2C3	120.7	120.5	120.4	120.5	120.3	120.3
C2C1O2	123.2	123.1	123.1	123.1	123.0	123.0
C2C1O1	113.6	113.3	113.4	113.5	113.6	113.7
C1O1H1	106.4	104.8	104.9	105.4	105.4	105.9
C2C3H3	119.3	119.1	119.1	119.1	119.4	119.4
C3C4H4	120.5	120.6	120.7	120.7	120.5	120.5
C4C5H5	121.2	121.1	121.1	121.1	121.1	121.1
C5C6H6	120.9	120.9	120.9	120.9	121.0	121.1
N1…H1	1.989	1.948	1.946	1.952	1.968	1.973
C3C2N1	123.4	123.9	123.8	123.8	124.1	124.1
C5C6N1	122.6	122.9	122.8	122.7	122.6	122.5

C6N1C2	118.2	117.6	117.6	117.7	117.6	117.8
N1C2C1	115.9	115.7	115.7	115.7	115.6	115.6
O2C1O1	123.2	123.5	123.5	123.4	123.4	123.4
C4C3H3	122.7	122.9	122.9	122.9	123.1	123.1
C5C4H4	120.5	120.6	120.6	120.6	120.4	120.4
C6C5H5	120.0	119.9	119.9	119.9	119.9	119.9
N1C6H6	116.5	116.3	116.3	116.4	116.4	116.4
ap-sp conformer						
C2−C3	1.393	1.395	1.391	1.389	1.395	1.393
C3−C4	1.387	1.389	1.385	1.383	1.389	1.387
C4−C5	1.388	1.391	1.387	1.385	1.388	1.386
C5−C6	1.392	1.394	1.389	1.388	1.393	1.392
N1−C6	1.330	1.337	1.333	1.331	1.336	1.334
N1−C2	1.334	1.340	1.336	1.334	1.339	1.336
C1−C2	1.500	1.494	1.490	1.489	1.498	1.497
C1=O2	1.208	1.213	1.210	1.208	1.208	1.207
C1−O1	1.343	1.343	1.339	1.337	1.340	1.338
C3−H3	1.080	1.080	1.078	1.078	1.079	1.079
C4−H4	1.082	1.081	1.080	1.079	1.081	1.081
C5−H5	1.081	1.081	1.079	1.078	1.081	1.080
C6−H6	1.084	1.083	1.081	1.081	1.083	1.082
O1−H1	0.968	0.969	0.968	0.967	0.967	0.966
C2C3C4	118.4	118.3	118.3	118.3	117.9	117.8
C3C4C5	118.7	118.5	118.5	115.5	118.8	118.8
C4C5C6	118.6	118.7	118.7	118.7	118.8	118.8
C3C2C1	117.9	117.6	117.6	117.7	117.5	117.7
C2C1O2	123.3	123.3	123.3	123.2	123.1	123.1
C2C1O1	113.6	113.2	113.3	113.3	113.5	113.6
C1O1H1	106.1	104.7	104.9	105.2	105.1	105.4
C2C3H3	119.4	119.2	119.2	119.2	119.4	119.5
C3C4H4	120.6	120.7	120.7	120.7	120.5	120.5
C4C5H5	121.3	121.3	121.2	121.2	121.1	121.1
C5C6H6	120.4	120.3	120.3	120.4	120.6	120.7
C3C2N1	123.4	124.1	124.0	124.0	124.3	124.2
C5C6N1	123.4	123.8	123.8	123.6	123.4	123.3

C6N1C2	117.6	116.7	116.7	116.9	116.9	117.1
N1C2C1	118.6	118.4	118.4	118.4	118.2	118.2
O2C1O1	123.0	123.4	123.4	123.4	123.3	123.3
C4C3H3	122.3	122.5	122.5	122.5	122.7	122.7
C5C4H4	120.8	120.8	120.8	120.8	120.7	120.7
C6C5H5	120.2	120.1	120.1	120.1	120.0	120.0
N1C6H6	116.2	115.9	115.9	116.0	116.0	116.0

[a] Basis sets cc-pVTZ and cc-pwCV*n*Z (*n* = T,Q) are denoted as VTZ and wCV*n*Z (*n* = T,Q), respectively.

Table S3. Optimized geometries of the *sp-sp* and *sp-ap* conformers of picolinic acid (bond lengths in Å, bond angles in degree)

Parameter r_e, $\angle_e$	B3LYP/ cc-pVTZ	MP2/ cc-pVTZ	B3LYP/ cc-pVTZ	MP2/ cc-pVTZ
	sp-sp		*sp-ap*	
C2−C3	1.394	1.396	1.395	1.397
C3−C4	1.388	1.391	1.389	1.391
C4−C5	1.386	1.390	1.386	1.390
C5−C6	1.393	1.395	1.393	1.395
N1−C6	1.327	1.336	1.329	1.337
N1−C2	1.335	1.341	1.334	1.341
C1−C2	1.502	1.497	1.511	1.504
C1=O2	1.200	1.205	1.194	1.200
C1−O1	1.360	1.359	1.362	1.362
C3−H3	1.079	1.079	1.082	1.082
C4−H4	1.082	1.081	1.082	1.081
C5−H5	1.081	1.081	1.081	1.080
C6−H6	1.084	1.083	1.084	1.083
O1−H1	0.968	0.969	0.964	0.964
C2C3C4	118.4	118.4	118.6	118.7
C3C4C5	118.7	118.6	118.6	118.4
C4C5C6	118.4	118.5	118.4	118.6
C1C2C3	121.5	121.2	121.2	121.0
C2C1O2	125.6	125.6	124.0	124.1
C2C1O1	111.8	111.4	115.3	114.8
C1O1H1	106.1	104.8	110.4	108.6
C2C3H3	120.1	120.1	120.8	120.6
C3C4H4	120.4	120.5	120.5	120.6
C4C5H5	121.3	121.3	121.3	121.3
C5C6H6	120.4	120.3	120.4	120.3
C3C2N1	123.1	123.8	122.9	123.5

C5C6N1	123.4	123.9	123.6	123.9
C6N1C2	117.9	116.9	117.8	117.0
N1C2C1	115.4	115.1	115.8	115.5
O2C1O1	122.5	123.0	120.7	121.0
C4C3H3	121.3	121.5	120.5	120.6
C5C4H4	120.8	120.9	120.9	121.0
C6C5H5	120.3	120.2	120.3	120.2
N1C6H6	116.2	115.8	116.1	115.8
N1C2C1O2	0.0	0.0	-37.8	-37.3
C3C2C1O1	0.0	0.0	-38.4	-37.8
O2C1O1H1	0.0	0.0	171.4	170.9
C2C1O1H1	180.0	180.0	-10.1	-10.6

Table S4. Experimental and calculated vibrational frequencies (cm^{-1})

Freq №		B3LYP/6-31G**[1]	MP2/cc-pVTZ	Exp [2]
1	A'	3767	3582	3464
2	A'	3237	3256	3118
3	A'	3212	3245	
4	A'	3195	3227	3056
5	A'	3169	3213	
6	A'	1849	1834	1719
7	A'	1637	1644	1612
8	A'	1631	1615	1600
9	A'	1513	1506	1459
10	A'	1472	1478	1443
11	A'	1383	1435	1347
12	A'	1333	1414	1309
13	A'	1323	1313	1294
14	A'	1208	1285	1251
15	A'	1181	1173	1203
16	A'	1152	1148	1158
17	A'	1109	1113	1088
18	A"	1072	1061	1048
19	A"	1016	1017	1009
20	A"	1012	1017	995
21	A"	986	989	966
22	A"	924	933	890
23	A"	833	834	837, 825
24	A'	790	803	801
25	A"	758	773	767
26	A"	722	751	
27	A"	655	707	676
28	A'	628	669	633, 616
29	A'	599	622	539, 499
30	A'	493	526	420
31	A"	436	441	405
32	A"	408	412	
33	A'	390	390	266
34	A'	220	218	
35	A"	152	157	
36	A"	49	98	

References:
[1] Adeoye, I.; Semire, B., Solvents Effect on Geometries and Electronic Properties of Picolinic Acid: A theoretical Study. *Int. J. Basic Appl. Sci.* 2013, **13**, 101-107.
[2] Parajón-Costa, B. S.; Wagner, C. C.; Baran, E. J. Vibrational spectra and electrochemical behavior of bispicolinate copper(II). *J. Argent. Chem. Soc.* 2004, **92**, 109-117.

Table S5. Total corrections $\Delta(r_{ij,e} - r_{ij,a})$ to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ rms vibrational amplitudes (in Å) for *ap-ap* conformer of picolinic acid.

Term	$r_{ij,a}$	$r_{ij,e} - r_{ij,a}$ [a]	$u_{ij,h1}$ [b]	$u_{ij,exp}$
O1–H1	0.990	-0.0145	0.071	0.071
C3–H3	1.094	-0.0152	0.075	0.075
C5–H5	1.095	-0.0152	0.075	0.075
C4–H4	1.096	-0.0153	0.075	0.075
C6–H6	1.097	-0.0156	0.075	0.075
C1=O2	1.208	-0.0039	0.036	0.036(4)[c]
N1–C6	1.344	-0.0064	0.044	0.042(4)[c]
C1–O1	1.345	-0.0085	0.045	0.043(4)[c]
N1–C2	1.346	-0.0062	0.045	0.043(4)[c]
C3–C4	1.396	-0.0069	0.045	0.043(4)[c]
C4–C5	1.396	-0.0069	0.045	0.043(4)[c]
C2–C3	1.398	-0.0073	0.045	0.043(4)[c]
C5–C6	1.398	-0.0071	0.045	0.044(4)[c]
C1–C2	1.513	-0.0090	0.050	0.048(4)[c]
C1 H1	1.876	-0.0182	0.096	0.096
H1 N1	2.011	-0.0386	0.162	0.162
H6 N1	2.079	-0.0128	0.096	0.096
C2 H3	2.152	-0.0137	0.099	0.099
C6 H5	2.157	-0.0132	0.099	0.099
C5 H4	2.161	-0.0128	0.098	0.098
C3 H4	2.162	-0.0128	0.098	0.098
C4 H5	2.168	-0.0131	0.098	0.098
C5 H6	2.172	-0.0140	0.097	0.097
C4 H3	2.186	-0.0121	0.098	0.098
O1 O2	2.251	-0.0065	0.053	0.055(2)[d]
C2 H1	2.278	-0.0281	0.136	0.136
C2 C6	2.309	-0.0090	0.054	0.055(2)[d]
C2 O2	2.385	-0.0082	0.060	0.062(2)[d]
C2 C4	2.388	-0.0093	0.055	0.057(2)[d]
C2 O1	2.395	-0.0165	0.060	0.062(2)[d]
C5 N1	2.396	-0.0094	0.054	0.056(2)[d]
C3 C5	2.407	-0.0099	0.056	0.058(2)[d]
C4 C6	2.407	-0.0086	0.055	0.057(2)[d]
C3 N1	2.415	-0.0089	0.054	0.056(2)[d]
C1 N1	2.420	-0.0108	0.061	0.063(2)[d]
H5 H6	2.499	-0.0134	0.159	0.159
H4 H5	2.504	-0.0118	0.160	0.160
C1 C3	2.529	-0.0111	0.067	0.069(2)[d]
H3 H4	2.535	-0.0101	0.160	0.160
H3 O2	2.596	-0.0191	0.180	0.180
O1 N1	2.644	-0.0247	0.093	0.095(2)[d]
C2 C5	2.723	-0.0106	0.061	0.063(2)[d]

H3	C1	2.726	-0.0127	0.143	0.143
C3	C6	2.755	-0.0095	0.061	0.063(2)[d]
C4	N1	2.787	-0.0087	0.063	0.065(2)[d]
C3	O2	2.879	-0.0134	0.100	0.102(2)[d]
O2	H1	3.003	-0.0139	0.091	0.091
C2	H6	3.282	-0.0156	0.093	0.093
C6	H1	3.291	-0.0378	0.168	0.168
H5	N1	3.368	-0.0153	0.094	0.094
H3	N1	3.379	-0.0152	0.094	0.094
C2	H4	3.384	-0.0154	0.093	0.093
C6	H4	3.397	-0.0148	0.094	0.094
C3	H5	3.401	-0.0158	0.094	0.094
C4	H6	3.403	-0.0155	0.093	0.093
C5	H3	3.411	-0.0153	0.094	0.094
O2	N1	3.526	-0.0057	0.061	0.063(13)[e]
C1	C6	3.662	-0.0123	0.063	0.064(13)[e]
C3	H1	3.663	-0.0253	0.139	0.139
C3	O1	3.676	-0.0120	0.065	0.067(13)[e]
H1	H6	3.712	-0.0432	0.200	0.200
C1	C4	3.785	-0.0121	0.067	0.069(13)[e]
C2	H5	3.808	-0.0166	0.093	0.093
C6	H3	3.838	-0.0155	0.093	0.093
C3	H6	3.843	-0.0162	0.093	0.093
H4	N1	3.874	-0.0148	0.095	0.095
C6	O1	3.979	-0.0231	0.098	0.100(13)[e]
H3	O1	4.030	-0.0093	0.139	0.139
C1	C5	4.228	-0.0130	0.068	0.077(12)[f]
H1	H3	4.260	-0.0230	0.166	0.166
C4	O2	4.260	-0.0118	0.101	0.110(12)[f]
H4	H6	4.310	-0.0194	0.127	0.127
H3	H5	4.328	-0.0187	0.127	0.127
C5	H1	4.383	-0.0341	0.167	0.167
H6	C1	4.491	-0.0164	0.108	0.108
C4	H1	4.528	-0.0281	0.155	0.155
H6	O1	4.547	-0.0286	0.151	0.151
C6	O2	4.671	-0.0060	0.068	0.089(20)[g]
H4	C1	4.677	-0.0157	0.110	0.110
C4	O1	4.769	-0.0132	0.073	0.094(20)[g]
C5	O1	4.892	-0.0187	0.088	0.109(20)[g]
H3	H6	4.923	-0.0204	0.117	0.117
H4	O2	4.965	-0.0163	0.149	0.149
C5	O2	5.000	-0.0086	0.087	0.109(20)[g]
H5	C1	5.311	-0.0167	0.098	0.098
H1	H5	5.363	-0.0380	0.187	0.187
H1	H4	5.579	-0.0296	0.170	0.170
H6	O2	5.580	-0.0079	0.105	0.105
H4	O1	5.754	-0.0137	0.106	0.106
H5	O1	5.932	-0.0216	0.118	0.118

H5	O2	6.073	-0.0111	0.115	0.115

[a] Calculated with the MP2/cc-pVTZ cubic force constants (see text).
[b] Calculated with the MP2/cc-pVTZ quadratic force constants (see text).
[c,d,e,f,g] Amplitudes with equal superscripts were refined in one group. Differences between amplitudes in each group were fixed at the corresponding calculated values. Other amplitudes were assumed at the calculated values.

Table S6. Total corrections $\Delta(r_{ij,e} - r_{ij,a})$ to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ rms vibrational amplitudes (in Å) for *ap-sp* conformer of picolinic acid.

Term	$r_{ij,a}$	$r_{ij,e} - r_{ij,a}$ [a]	$u_{ij,h1}$ [b]
O1–H1	0.969	-0.0143	0.069
C3–H3	1.080	-0.0153	0.075
C5–H5	1.081	-0.0152	0.075
C4–H4	1.081	-0.0153	0.075
C6–H6	1.083	-0.0156	0.075
C1=O2	1.213	-0.0035	0.038
C6–N1	1.337	-0.0064	0.044
C2–N1	1.340	-0.0062	0.044
C1–O1	1.343	-0.0090	0.045
C3–C4	1.389	-0.0071	0.045
C4–C5	1.392	-0.0069	0.045
C5–C6	1.394	-0.0070	0.045
C2–C3	1.395	-0.0071	0.045
C1–C2	1.494	-0.0084	0.049
C1 H1	1.845	-0.0163	0.101
H6 N1	2.055	-0.0130	0.096
C2 H3	2.140	-0.0150	0.099
C6 H5	2.150	-0.0131	0.099
C3 H4	2.152	-0.0129	0.098
C5 H6	2.154	-0.0145	0.097
C5 H4	2.156	-0.0126	0.098
C4 H5	2.160	-0.0129	0.098
C4 H3	2.170	-0.0115	0.098
O2 O1	2.252	-0.0108	0.053
O2 H1	2.259	-0.0200	0.139
C2 C6	2.279	-0.0091	0.053
C2 O1	2.371	-0.0095	0.064
C2 O2	2.387	-0.0083	0.059
C3 C5	2.389	-0.0102	0.056
C2 C4	2.391	-0.0087	0.055
C4 C6	2.396	-0.0088	0.055
C5 N1	2.410	-0.0089	0.055
C3 N1	2.416	-0.0090	0.055

C1	N1	2.435	-0.0074	0.063
C3	C1	2.471	-0.0132	0.065
H5	H6	2.483	-0.0140	0.159
H3	O2	2.483	-0.0603	0.181
H4	H5	2.507	-0.0112	0.160
H3	H4	2.521	-0.0091	0.160
H3	C1	2.640	-0.0189	0.141
O1	N1	2.661	-0.0315	0.104
C2	C5	2.714	-0.0100	0.061
C3	C6	2.722	-0.0103	0.061
C4	N1	2.808	-0.0083	0.064
C3	O2	2.815	-0.0340	0.100
C2	H1	3.176	-0.0131	0.095
C2	H6	3.245	-0.0158	0.093
H3	N1	3.370	-0.0162	0.095
H5	N1	3.372	-0.0148	0.094
C2	H4	3.381	-0.0148	0.094
C3	H5	3.382	-0.0160	0.094
C4	H6	3.384	-0.0159	0.093
C6	H4	3.386	-0.0148	0.094
C5	H3	3.389	-0.0151	0.094
O2	N1	3.555	0.0097	0.064
H1	N1	3.620	-0.0190	0.121
C3	O1	3.637	0.0072	0.069
C6	C1	3.650	-0.0100	0.064
C4	C1	3.745	-0.0130	0.066
C2	H5	3.794	-0.0159	0.093
C6	H3	3.800	-0.0164	0.093
C3	H6	3.805	-0.0170	0.093
H4	N1	3.889	-0.0143	0.095
H3	O1	3.961	0.0117	0.142
C6	O1	3.999	-0.0232	0.107
C4	O2	4.202	-0.0271	0.102
C5	C1	4.209	-0.0119	0.067
H4	H6	4.293	-0.0196	0.127
H3	H5	4.308	-0.0181	0.127
C3	H1	4.310	-0.0035	0.113
H3	H1	4.432	-0.0039	0.187
H6	C1	4.490	-0.0135	0.108
H6	O1	4.581	-0.0358	0.157
H4	C1	4.621	-0.0176	0.109
C6	O2	4.661	0.0045	0.070
C4	O1	4.761	0.0064	0.077
H4	O2	4.879	-0.0393	0.151
H3	H6	4.882	-0.0214	0.117
C5	O1	4.907	-0.0067	0.094
C6	H1	4.956	-0.0126	0.122
C5	O2	4.971	-0.0102	0.088
H5	C1	5.288	-0.0155	0.098
C4	H1	5.539	0.0004	0.108
H6	H1	5.549	-0.0180	0.174
H6	O2	5.583	0.0091	0.107

H4	O1	5.734	0.0101	0.111
C5	H1	5.808	-0.0040	0.110
H5	O1	5.948	-0.0091	0.124
H5	O2	6.040	-0.0125	0.116
H4	H1	6.454	0.0024	0.143
H5	H1	6.865	-0.0041	0.134

[a] Calculated with the MP2/cc-pVTZ cubic force constants (see text).
[b] Calculated with the MP2/cc-pVTZ quadratic force constants (see text).

Table S7. Energy of NBO interactions, $E^{(2)}$ in kJ mol^{-1} and natural charges on the atoms (B3LYP/cc-pVTZ)

	ap-ap conformer	*ap-sp* conformer
q(N)	-0.463	-0.391
q(O2)	-0.560	-0.591
q(O1)	-0.655	-0.643
$E^{(2)}$(LP(N)→σ*(O1−H))	22.6	
$E^{(2)}$(π(C1−C2)→ π*(O1−H1))		8.8
$E^{(2)}$(π(C1=O2)→ π*(C2−C3))	15.5	13.4
$E^{(2)}$(π(C1=O2)→ σ*(O1−H1))	3.6	
$E^{(2)}$(LP(O1)→σ*(C1−C2))	29.2	
$E^{(2)}$(π(C2−C3)→ π*(C1−O1))		7.1
$E^{(2)}$(π(C2−C3)→ π*(C1=O2))		74.0
$E^{(2)}$(π(C2−N)→ π*(C1=O2))		4.6
$\Sigma_1 E^{(2)}$		85.7
$E^{(2)}$(π(C1=O2)→ π*(C2−N))		4.2
$E^{(2)}$(π(C1=O2)→ π*(C2−C3))		13.4
$E^{(2)}$(π(C1−O1)→ π*(C2−C3))		5.9
$E^{(2)}$(LP(O1)→ π*(C2−N))		2.1
$\Sigma_2 E^{(2)}$		25.5