Supporting Information

Investigating Tautomeric Polymorphism in Crystalline Anthranilic Acid Using Terahertz Spectroscopy and Solid-State Density Functional Theory

*Sean P. Delaney, Ewelina M. Witko, Tiffany M. Smith and Timothy M. Korter**

Department of Chemistry, Syracuse University, 1-014 Center for Science and Technology, Syracuse, New York 13244-4100, United States

**tmkorter@syr.edu*

Table of Contents

Table S1. Bond lengths (Å) and RMSDs for anthranilic acid Forms I, II and III.

Form I				Form II				Form III			
		PBE				PBE				PBE	
Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)
C9-C10	1.3970	1.4003	1.3947	C2-C1	1.4660	1.4649	1.4630	C2-C1	1.469	1.4687	1.4667
C10-C11	1.3870	1.4042	1.3982	C2-C3	1.4090	1.4174	1.4127	C2-C3	1.404	1.4167	1.4117
C11-C12	1.3870	1.3986	1.3927	C3-C4	1.3710	1.3905	1.3844	C3-C4	1.377	1.3917	1.3855
C8-C13	1.4020	1.4137	1.4076	C5-C4	1.3980	1.4123	1.4067	C5-C4	1.395	1.4115	1.4061
C12-C13	1.3990	1.4092	1.4035	C6-C5	1.3710	1.3910	1.3848	C6-C5	1.372	1.3918	1.3856
C13-C14	1.5130	1.5130	1.5130	C7-C6	1.4100	1.4233	1.4172	C7-C6	1.411	1.4215	1.4163
C1-C2	1.4050	1.4122	1.4076	C2-C7	1.4180	1.4370	1.4315	C2-C7	1.418	1.4357	1.4309
C2-C3	1.3750	1.3950	1.3887	C7-N1	1.3690	1.3947	1.3678	C7-N1	1.364	1.3712	1.3684
C3-C4	1.4000	1.4070	1.4016	C1-O1	1.3270	1.3278	1.3287	C1-O1	1.326	1.3303	1.3314
C4-C5	1.3760	1.3948	1.3883	C1-O2	1.2380	1.2679	1.2585	C1-O2	1.232	1.263	1.2536
C1-C6	1.4120	1.4270	1.4224	RMSD		0.0177	0.0106	RMSD		0.0158	0.0107
C5-C6	1.4060	1.4132	1.4083								
C6-C7	1.4840	1.4867	1.4821								
C8-C9	1.3880	1.4007	1.3947								
C1-N1	1.4050	1.4117	1.4050								
C8-N2	1.4620	1.4596	1.4584								
C7-O1	1.2320	1.2578	1.2495								
C7-O2	1.3210	1.3210	1.3221								
C14-O3	1.2680	1.2872	1.2836								
C14-O4	1.2510	1.2725	1.2644								
RMSD		0.0305	0.0204								

Table S2. Bond angles (˚) and RMSDs for anthranilic acid Forms I, II and III.

Form I				Form II				Form III			
		PBE				PBE				PBE	
Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)
C8-C9-C10	119.50	119.88	119.93	C7-C2-C3	119.31	119.30	119.23	C3-C2-C7	119.30	119.22	119.12
C9-C10-C11	119.90	119.95	119.90	C7-C2-C1	121.31	121.67	121.63	C3-C2-C1	119.40	119.22	119.31
C10-C11-C12	119.90	119.63	119.62	C3-C2-C1	119.35	119.02	119.12	C7-C2-C1	121.20	121.45	121.56
C8-C13-C12	117.50	117.67	117.61	C2-C7-C6	117.72	117.93	117.93	C2-C3-C4	121.80	121.82	121.89
C9-C8-C13	121.70	121.23	121.24	C2-C7-N1	123.05	122.65	122.77	C6-C5-C4	120.90	120.82	120.75
C11-C12-C13	121.50	121.60	121.66	C6-C7-N1	119.20	119.41	119.23	C5-C6-C7	121.40	121.25	121.34
C12-C13-C14	119.30	119.31	119.25	C2-C3-C4	121.64	121.72	121.77	C2-C7-C6	117.70	118.05	118.02
C8-C13-C14	123.20	123.02	123.13	C2-C1-O2	123.79	122.76	123.12	C2-C7-N1	122.80	122.29	122.54
C1-C2-C3	121.50	121.13	121.22	C2-C1-O1	114.65	115.88	115.68	C3-C4-C5	118.80	118.84	118.87
C2-C3-C4	120.10	120.31	120.32	O2-C1-O1	121.55	121.35	121.20	C2-C1-O2	124.00	122.73	123.15
C3-C4-C5	119.40	119.19	119.16	C7-C6-C5	121.54	121.31	121.35	C2-C1-O1	114.37	115.49	115.28
C1-C6-C5	119.20	118.93	118.93	C6-C5-C4	120.77	120.74	120.77	O2-C1-O1	121.70	121.78	121.57
C4-C5-C6	121.40	121.62	121.68	C3-C4-C5	118.99	118.98	118.95	C6-C7-N1	119.40	119.61	119.39
C2-C1-C6	118.30	118.82	118.69	RMSD		0.4931	0.3895	RMSD		0.5139	0.3870
C1-C6-C7	121.00	121.28	121.21								
C5-C6-C7	119.80	119.76	119.82								
C6-C1-N1	123.00	122.53	122.49								
C2-C1-N1	118.60	118.62	118.80								
C13-C8-N2	120.50	120.18	119.97								
C9-C8-N2	117.80	118.59	118.79								
C6-C7-O1	122.90	121.79	122.29								
C6-C7-O2	115.40	115.89	115.80								
O1-C7-O2	121.70	122.32	121.91								
C13-C14-O3	117.90	117.99	118.04								
C13-C14-O4	117.30	117.62	117.74								
O3-C14-O4	124.80	124.39	124.22								
RMSD		0.4063	0.3792								

Table S3. Dihedral angles (˚) and RMSDs for anthranilic acid Forms I, II, III.

Form I				Form II				Form III			
		PBE				PBE				PBE	
Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)	Bond	Experimental	6-31G(d,p)	6-311G(2d,2p)
C6-C1-C2-C3	-0.50	-0.13	-0.08	O1-C1-C2-C3	-1.70	0.01	0.01	O1-C1-C2-C3	3.80	4.59	3.86
N1-C1-C2-C3	-178.60	-178.22	-179.88	O1-C1-C2-C7	-179.86	-178.80	-178.58	O1-C1-C2-C7	-175.40	-175.14	-175.31
C2-C1-C6-C5	0.60	0.55	0.11	O2-C1-C2-C3	177.21	179.29	179.35	O2-C1-C2-C3	-177.30	-176.11	-177.01
C2-C1-C6-C7	177.10	178.35	177.68	O2-C1-C2-C7	-1.00	0.47	0.76	O2-C1-C2-C7	3.50	4.16	3.82
N1-C1-C6-C5	178.30	178.56	178.34	C1-C2-C3-C4	-176.85	-177.40	-177.55	C1-C2-C3-C4	-177.60	-178.39	-177.67
N1-C1-C6-C7	-3.90	-3.64	-4.09	C7-C2-C3-C4	1.30	1.44	1.08	C7-C2-C3-C4	1.60	1.34	1.53
C1-C2-C3-C4	0.30	-0.31	-0.03	C1-C2-C7-C6	177.87	178.11	178.13	C1-C2-C7-C6	178.00	178.72	178.26
C2-C3-C4-C5	-0.40	0.32	0.10	C1-C2-C7-N1	-0.10	-0.54	-0.37	C1-C2-C7-N1	0.40	1.18	0.64
C3-C4-C5-C6	0.60	0.11	-0.07	C3-C2-C7-C6	-0.30	-0.70	-0.46	C3-C2-C7-C6	-1.20	-1.00	-0.92
C4-C5-C6-C1	-0.70	-0.55	-0.04	C3-C2-C7-N1	-178.30	-179.35	-178.95	C3-C2-C7-N1	-178.80	-178.55	-178.53
C4-C5-C6-C7	-177.00	-178.38	-177.65	C2-C3-C4-C5	-1.70	-1.40	-1.21	C2-C3-C4-C5	-1.10	-0.94	-1.19
C1-C6-C7-O1	6.10	5.83	4.97	C3-C4-C5-C6	1.00	0.64	0.74	C3-C4-C5-C6	0.20	0.21	0.27
C1-C6-C7-O2	-173.40	-174.16	-174.72	C4-C5-C6-C7	0.00	0.06	-0.16	C4-C5-C6-C7	0.20	0.08	0.30
C5-C6-C7-O1	-176.20	-176.39	-177.48	C5-C6-C7-C2	-0.40	-0.02	0.02	C5-C6-C7-C2	0.30	0.32	0.04
C5-C6-C7-O2	4.30	3.62	2.83	C5-C6-C7-N1	177.72	178.67	178.57	C5-C6-C7-N1	178.00	177.93	177.73
C13-C8-C9-C10	-1.50	-1.30	-1.36	RMSD		0.9536	0.9865	RMSD		0.5483	0.2078
N2-C8-C9-C10	178.70	179.17	179.14								
C9-C8-C13-C12	1.60	2.08	1.73								
C9-C8-C13-C14	-177.90	-177.58	-178.14								
N2-C8-C13-C12	-178.60	-178.40	-178.78								
N2-C8-C13-C14	1.90	1.94	1.35								
C8-C9-C10-C11	-0.10	-0.44	-0.09								
C9-C10-C11-C12	1.10	1.34	1.10								
C10-C11-C12-C13	1.00	-0.52	-0.70								
C11-C12-C13-C8	0.30	-1.16	-0.70								
C11-C12-C13-C14	179.10	178.50	179.18								
C8-C13-C14-O3	1.00	1.95	0.68								
C8-C13-C14-O4	-178.70	-178.89	-179.85								
C12-C13-C14-O3	-178.40	-177.69	-179.19								
C12-C13-C14-O4	-1.80	1.46	0.28								
RMSD		0.8920	0.8526								

Table S4. Comparison of experimental (78 K) X-ray diffraction unit cell dimensions and the solid-state DFT (PBE/6-311G(2d,2p)) derived values.

	Form I		Form II		Form III	
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
a (Å)	9.2734(15)	9.1932	11.6322(14)	11.6592	6.4900(4)	6.5375
b (Å)	10.7851(19)	10.8027	7.0969(8)	7.0141	15.1290(10)	15.0167
c (Å)	12.695(2)	12.6499	15.8282(19)	15.9157	6.9900(5)	6.9866
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	112.5430(10)	112.6684
γ (deg)	90	90	90	90	90	90
V (Å^3)	1269.7(4)	1256.27	1306.7(3)	1301.56	633.89(7)	632.91