

Supplementary information for: The crystal structures of three novel lutidine pamoate salts

Delia A. Haynes^{a,c}, Ze F. Weng^b, William Jones^a and W. D. Samuel Motherwell^b

^a Pfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW.

^b Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK CB2 1EZ.

^c present address Department of Chemistry and Polymer Science, Stellenbosch University, P. Bag XI, Matieland, 7602, Republic of South Africa, dhaynes@sun.ac.za.

Computational details

The relative stabilities of the gas phase conformations of 4,4'-Methylenebis(3-hydroxy-2-naphthoic acid) and its anionic forms were studied using Density Functional Theory. Molecular structures of **I**, **II** and **III** were geometry optimized from the crystal structure geometries using Becke's three parameter hybrid functional (Becke, 1988) with the Lee-Yang-Parr correlation functional (Lee *et al.*, 1988) (B3LYP), in conjunction with the 6-31G(d,p) basis set. The minimum of each geometry optimisation was checked as indicated by the absence of imaginary vibrational frequencies. A rigid potential energy scan was then performed on each of the optimised geometries by varying the torsion angles τ_1 and τ_2 (see Figure 1 for numbering scheme) at the same level of theory. All calculations were performed within the Gaussian 03 package (Frisch *et al.* 2004).

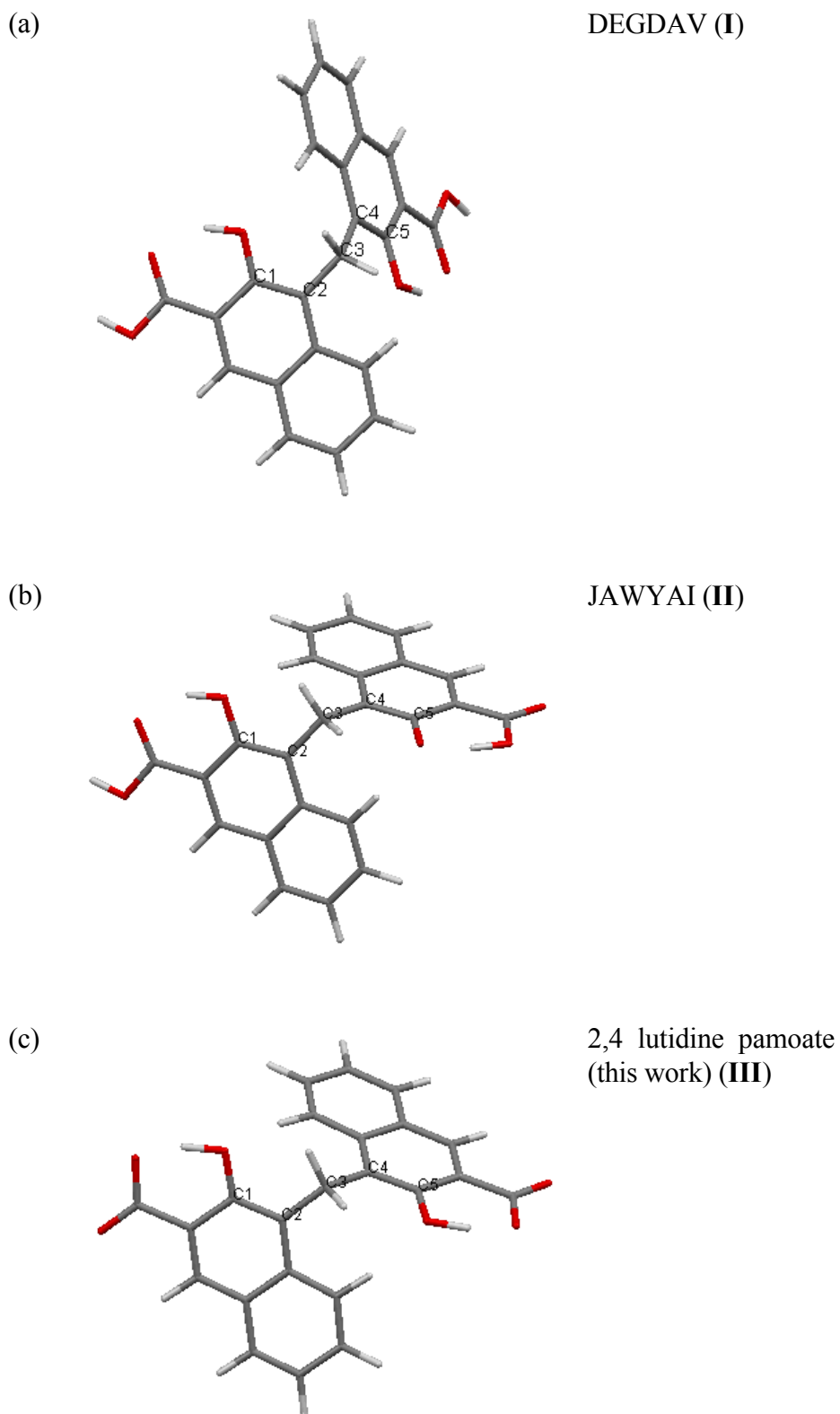


Figure S1: Molecular structures of **I**, **II**, and **III** optimised at the B3LYP/6-31G(d,p) level of theory. The torsion angles are defined as $\tau_1 = \text{C1-C2-C3-C4}$ and $\tau_2 = \text{C5-C4-C3-C2}$. For the optimised geometries: $\tau_1 = -70.5^\circ$, $\tau_2 = -70.5^\circ$ (**I**); $\tau_1 = -116.7^\circ$, $\tau_2 = -112.6^\circ$ (**II**) and $\tau_1 = -115.7^\circ$, $\tau_2 = -115.7^\circ$ (**III**).

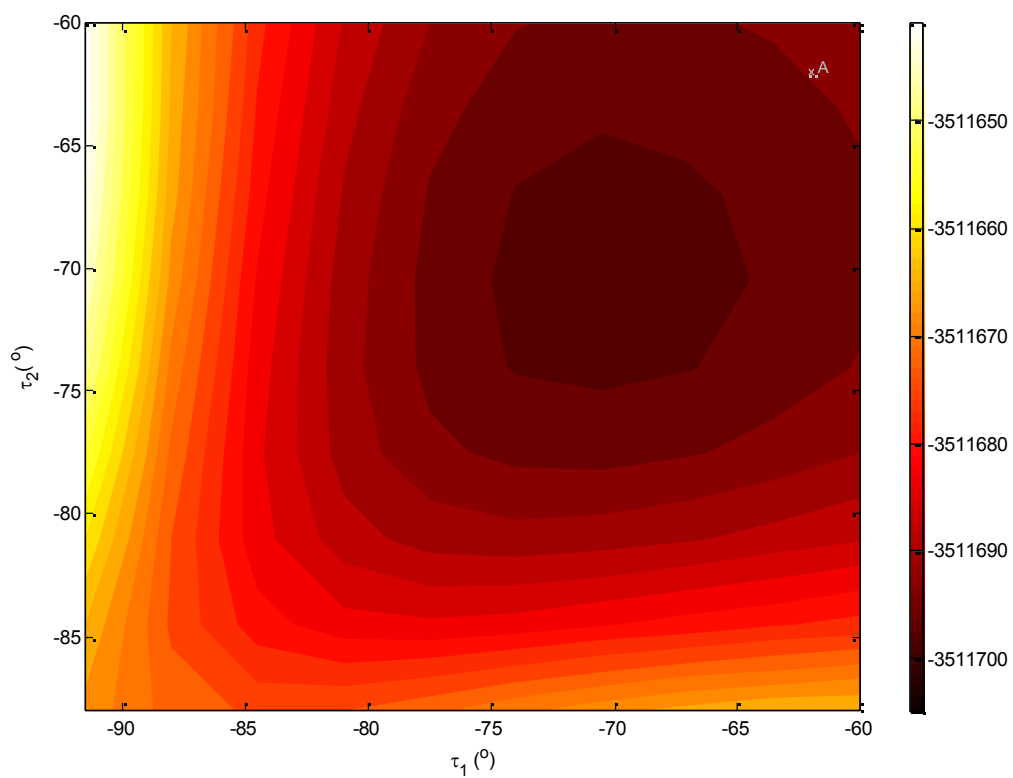
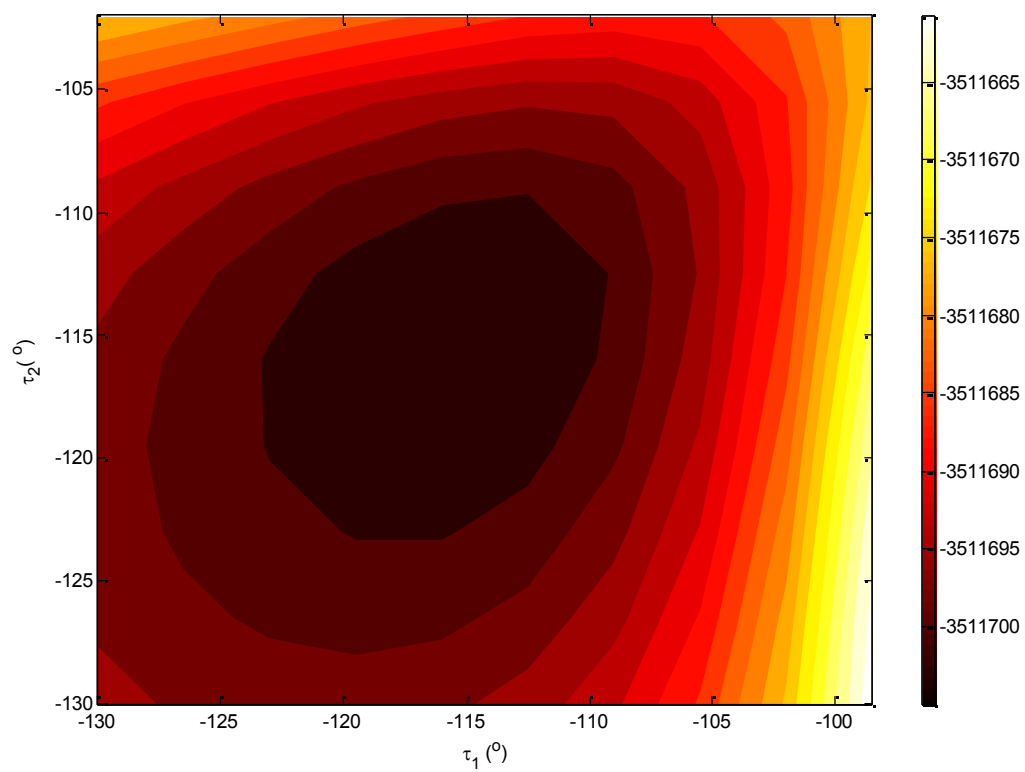


Figure S2a

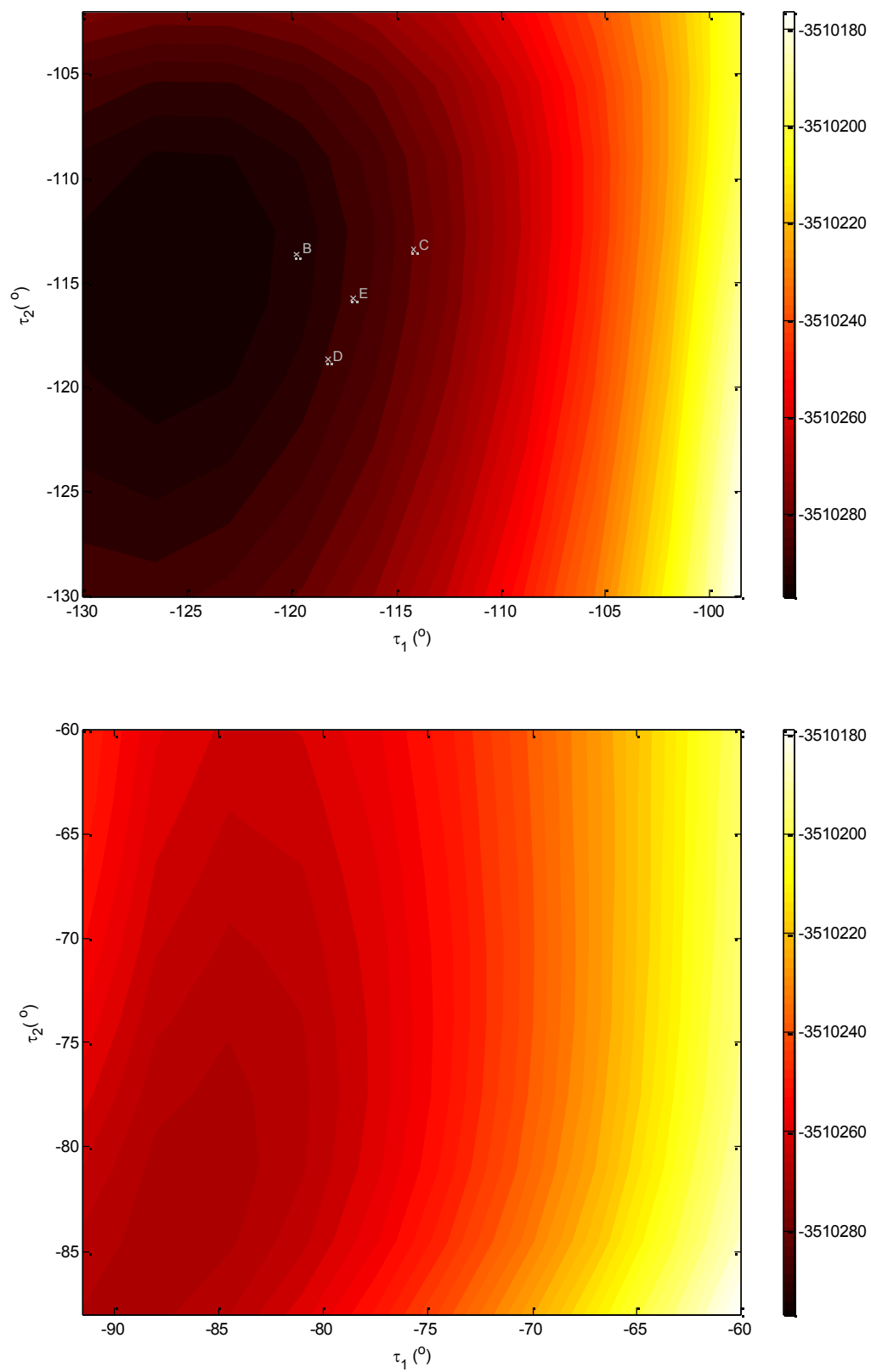


Figure S2b

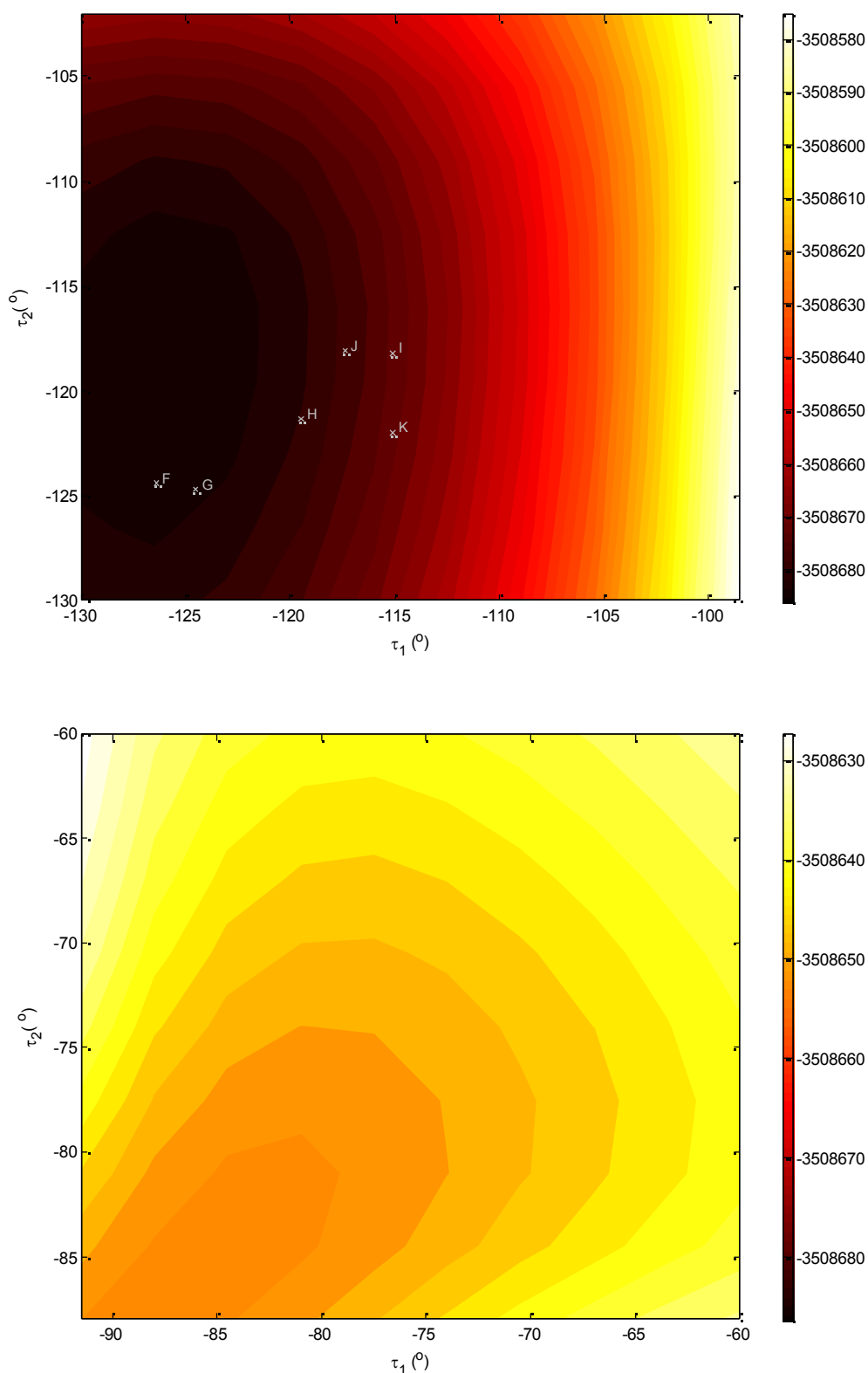


Figure S2c

Figure S2a-c: Potential energy surface scan of the optimised geometries of **I** (2a), **II** (2b) and **III** (2c) calculated at the B3LYP/6-31G(d,p) level. Torsion angles τ_1 and τ_2 are varied in increments of 3.5° , respectively, while all other bond lengths, bond angles and dihedrals are held fixed. Torsion angle of **I**, **II** and **III** from experimentally determined crystal structures are shown: A (DEGDAV, pamoic acid), B (JAWYAI 3,5-lutidinium pamoate), C (JAWXIP, 2,4-lutidinium pamoate tetrahydrofuran solvate), D (JAWXOV, 2,6-lutidinium pamoate tetrahydrofuran solvate), E (QEXJEJ, 1,10-phenanthroline-1-ium pamoate N,N-dimethylformamide solvate), F (3,4-lutidinium pamoate residue 1), G (3,4-lutidinium pamoate residue 2), H(2,3 lutidinium pamoate), I (2,4-lutidinium pamoate), J (JAWXEL, bis(2,3-lutidinium) pamoate tetrahydrofuran solvate) and K (TABMAK, bis(pyridinium) pamoate). Units are in kJmol^{-1} and contours are drawn at 2.5 kJmol^{-1} intervals.

Table S1a-c: Tabular format of Figures 1a-1c.

Table S1a

	τ_2 (°)									
		-130.00000	-126.50000	-123.00000	-119.50000	-116.00000	-112.50000	-109.00000	-105.50000	-102.00000
τ_1 (°)	-130.00000	-3511694.51931	-3511695.72704	-3511696.46218	-3511696.61971	-3511695.98959	-3511694.28302	-3511690.89612	-3511684.93624	-3511674.85432
	-126.50000	-3511695.72704	-3511697.24983	-3511698.27378	-3511698.74637	-3511698.45756	-3511696.96103	-3511693.70541	-3511687.58799	-3511676.98097
	-123.00000	-3511696.46218	-3511698.27378	-3511699.66529	-3511700.47920	-3511700.53171	-3511699.32398	-3511696.25214	-3511690.10847	-3511679.16014
	-119.50000	-3511696.61971	-3511698.74637	-3511700.47920	-3511701.68693	-3511702.08075	-3511701.21434	-3511698.37880	-3511692.36640	-3511681.41807
	-116.00000	-3511695.98959	-3511698.45756	-3511700.53171	-3511702.08075	-3511702.84215	-3511702.34330	-3511699.84908	-3511694.15174	-3511683.59723
	-112.50000	-3511694.28302	-3511696.96103	-3511699.32398	-3511701.21434	-3511702.34330	-3511702.21203	-3511700.19039	-3511695.09692	-3511685.40883
	-109.00000	-3511690.89612	-3511693.70541	-3511696.25214	-3511698.37880	-3511699.84908	-3511700.19039	-3511698.77262	-3511694.59808	-3511686.32775
	-105.50000	-3511684.93624	-3511687.58799	-3511690.10847	-3511692.36640	-3511694.15174	-3511695.09692	-3511694.59808	-3511691.78879	-3511685.56636
	-102.00000	-3511674.85432	-3511676.95472	-3511679.13388	-3511681.39181	-3511683.59723	-3511685.40883	-3511686.32775	-3511685.56636	-3511682.20572
	-98.50000	-3511658.33992	-3511659.31136	-3511660.80789	-3511662.98706	-3511665.82260	-3511669.10447	-3511672.28133	-3511674.64428	-3511675.16938

	τ_2 (°)									
		-88.00000	-84.50000	-81.00000	-77.50000	-74.00000	-70.50000	-67.00000	-63.50000	-60.00000
τ_1 (°)	-91.50000	-3511666.19017	-3511662.93455	-3511657.94610	-3511652.35378	-3511647.07653	-3511642.87573	-3511640.14521	-3511639.04250	-3511639.35756
	-88.00000	-3511671.46742	-3511673.33153	-3511672.80643	-3511670.94232	-3511668.52686	-3511666.21642	-3511664.40483	-3511663.27586	-3511662.69825
	-84.50000	-3511673.33153	-3511679.21265	-3511681.89066	-3511682.41576	-3511681.73313	-3511680.57791	-3511679.31767	-3511678.08368	-3511676.95472
	-81.00000	-3511672.80643	-3511681.89066	-3511686.77409	-3511688.90074	-3511689.39959	-3511689.05827	-3511688.13935	-3511686.93162	-3511685.56636
	-77.50000	-3511670.94232	-3511682.41576	-3511688.90074	-3511692.18262	-3511693.57413	-3511693.75792	-3511693.10154	-3511691.92007	-3511690.34477
	-74.00000	-3511668.52686	-3511681.73313	-3511689.39959	-3511693.57413	-3511695.54326	-3511695.98959	-3511695.46449	-3511694.28302	-3511692.68146
	-70.50000	-3511666.21642	-3511680.57791	-3511689.05827	-3511693.75792	-3511695.98959	-3511696.59346	-3511696.14712	-3511695.01816	-3511693.44286
	-67.00000	-3511664.40483	-3511679.31767	-3511688.13935	-3511693.10154	-3511695.46449	-3511696.14712	-3511695.75330	-3511694.67684	-3511693.23282
	-63.50000	-3511663.27586	-3511678.10994	-3511686.93162	-3511691.92007	-3511694.28302	-3511695.01816	-3511694.67684	-3511693.78417	-3511692.52393
	-60.00000	-3511662.69825	-3511676.95472	-3511685.56636	-3511690.34477	-3511692.68146	-3511693.44286	-3511693.23282	-3511692.52393	-3511691.42122

Table S1b

		τ_2 (°)								
		-130.00000	-126.50000	-123.00000	-119.50000	-116.00000	-112.50000	-109.00000	-105.50000	-102.00000
τ_1 (°)	-130.00000	-3510285.83354	-3510288.64283	-3510290.95327	-3510292.65984	-3510293.50000	-3510293.13243	-3510290.92701	-3510285.83354	-3510276.25047
	-126.50000	-3510286.41115	-3510289.53550	-3510292.18725	-3510294.20889	-3510295.36411	-3510295.31160	-3510293.28996	-3510288.27526	-3510278.53465
	-123.00000	-3510284.46828	-3510287.90769	-3510290.84825	-3510293.18494	-3510294.65522	-3510294.86526	-3510293.05367	-3510288.17024	-3510278.42963
	-119.50000	-3510279.95242	-3510283.65438	-3510286.88374	-3510289.48299	-3510291.21582	-3510291.66215	-3510290.06060	-3510285.38721	-3510275.96166
	-116.00000	-3510272.67979	-3510276.59178	-3510280.03119	-3510282.84047	-3510284.78334	-3510285.46597	-3510284.15322	-3510279.82115	-3510271.05198
	-112.50000	-3510262.33532	-3510266.35233	-3510269.92301	-3510272.91608	-3510275.06899	-3510275.98792	-3510275.01648	-3510271.26202	-3510263.49054
	-109.00000	-3510248.39391	-3510252.43718	-3510256.06037	-3510259.13221	-3510261.46890	-3510262.70289	-3510262.23030	-3510259.28974	-3510252.88352
	-105.50000	-3510230.04167	-3510233.87490	-3510237.41932	-3510240.56992	-3510243.14291	-3510244.82323	-3510245.11204	-3510243.35295	-3510238.78458
	-102.00000	-3510205.80830	-3510209.19520	-3510212.50333	-3510215.73269	-3510218.77827	-3510221.32501	-3510222.92656	-3510222.90031	-3510220.66863
-98.50000	-3510173.54091	-3510176.14015	-3510179.18573	-3510182.75641	-3510186.79968	-3510190.94797	-3510194.67618	-3510197.22292	-3510198.03682	

		τ_2 (°)								
		-88.00000	-84.50000	-81.00000	-77.50000	-74.00000	-70.50000	-67.00000	-63.50000	-60.00000
τ_1 (°)	-91.50000	-3510268.11142	-3510266.03727	-3510262.91293	-3510259.34225	-3510255.79782	-3510252.69973	-3510250.31053	-3510248.63021	-3510247.55375
	-88.00000	-3510268.68903	-3510269.47668	-3510268.74154	-3510267.00871	-3510264.82954	-3510262.65038	-3510260.65500	-3510258.92217	-3510257.45189
	-84.50000	-3510265.43341	-3510268.42648	-3510269.31915	-3510268.82030	-3510267.53381	-3510265.95851	-3510264.30444	-3510262.67663	-3510261.10133
	-81.00000	-3510259.02719	-3510263.64807	-3510265.66970	-3510266.03727	-3510265.45966	-3510264.38321	-3510263.07046	-3510261.65269	-3510260.23492
	-77.50000	-3510249.91670	-3510255.74531	-3510258.65962	-3510259.73607	-3510259.73607	-3510259.13221	-3510258.18703	-3510257.08432	-3510255.87659
	-74.00000	-3510238.54829	-3510245.29582	-3510248.94527	-3510250.59933	-3510251.09818	-3510250.94065	-3510250.31053	-3510249.47037	-3510248.55144
	-70.50000	-3510225.36828	-3510232.82470	-3510236.97299	-3510239.07339	-3510239.96606	-3510240.09733	-3510239.75602	-3510239.23092	-3510238.67956
	-67.00000	-3510210.63922	-3510218.46321	-3510222.90031	-3510225.28951	-3510226.41848	-3510226.78605	-3510226.75979	-3510226.62852	-3510226.47099
	-63.50000	-3510194.33487	-3510202.18511	-3510206.75348	-3510209.30022	-3510210.63922	-3510211.29560	-3510211.63691	-3510211.89946	-3510212.13576
-60.00000	-3510176.29768	-3510183.99040	-3510188.55877	-3510191.23678	-3510192.81208	-3510193.78351	-3510194.54491	-3510195.22754	-3510195.85766	

Table S1c:

		τ_2 (°)								
		-130.00000	-126.50000	-123.00000	-119.50000	-116.00000	-112.50000	-109.00000	-105.50000	-102.00000

τ_1 (°)	-130.00000	-3508679.86770	-3508681.44300	-3508682.49320	-3508682.93954	-3508682.54571	-3508681.04918	-3508677.84607	-3508672.04371	-3508662.22434
	-126.50000	-3508680.41906	-3508682.25691	-3508683.56966	-3508684.27854	-3508684.12101	-3508682.75575	-3508679.60515	-3508673.64527	-3508663.43207
	-123.00000	-3508678.63372	-3508680.73412	-3508682.30942	-3508683.22834	-3508683.28085	-3508682.07312	-3508678.92252	-3508672.91013	-3508662.48689
	-119.50000	-3508674.43292	-3508676.76961	-3508678.58121	-3508679.71017	-3508679.92021	-3508678.79125	-3508675.71941	-3508669.70702	-3508659.36255
	-116.00000	-3508667.63287	-3508670.17961	-3508672.14873	-3508673.43523	-3508673.75029	-3508672.72634	-3508669.73327	-3508663.90466	-3508653.98027
	-112.50000	-3508657.91852	-3508660.57028	-3508662.64442	-3508664.00968	-3508664.42976	-3508663.48458	-3508660.67530	-3508655.21426	-3508646.07752
	-109.00000	-3508644.76477	-3508647.39027	-3508649.46441	-3508650.88218	-3508651.35477	-3508650.56712	-3508648.07290	-3508643.21572	-3508635.28671
	-105.50000	-3508627.22643	-3508629.66814	-3508631.61101	-3508633.00253	-3508633.60639	-3508633.18631	-3508631.32221	-3508627.46272	-3508621.13527
	-102.00000	-3508603.88573	-3508605.88111	-3508607.58769	-3508609.00546	-3508610.00315	-3508610.37072	-3508609.63558	-3508607.40390	-3508603.20310
	-98.50000	-3508572.72105	-3508573.98129	-3508575.42531	-3508577.18440	-3508579.12727	-3508580.99137	-3508582.25161	-3508582.40914	-3508581.01763

	τ_2 (°)									
	-88.00000	-84.50000	-81.00000	-77.50000	-74.00000	-70.50000	-67.00000	-63.50000	-60.00000	
τ_1 (°)	-91.50000	-3508651.74860	-3508648.54549	-3508644.47596	-3508640.09138	-3508635.81181	-3508632.08360	-3508629.14304	-3508626.96388	-3508625.46734
	-88.00000	-3508652.85131	-3508652.03740	-3508649.91075	-3508647.02270	-3508643.84584	-3508640.80026	-3508638.06974	-3508635.75930	-3508633.76392
	-84.50000	-3508652.03740	-3508653.00884	-3508652.22119	-3508650.33083	-3508647.86286	-3508645.28987	-3508642.76939	-3508640.38018	-3508638.12225
	-81.00000	-3508649.93700	-3508652.24744	-3508652.40497	-3508651.22350	-3508649.30688	-3508647.10146	-3508644.76477	-3508642.42807	-3508640.06512
	-77.50000	-3508647.04895	-3508650.33083	-3508651.22350	-3508650.61963	-3508649.14935	-3508647.20648	-3508645.07983	-3508642.74313	-3508640.32767
	-74.00000	-3508643.87210	-3508647.88911	-3508649.33314	-3508649.14935	-3508647.99413	-3508646.31381	-3508644.23967	-3508641.92923	-3508639.54002
	-70.50000	-3508640.82652	-3508645.28987	-3508647.10146	-3508647.23274	-3508646.31381	-3508644.73851	-3508642.76939	-3508640.48520	-3508638.17476
	-67.00000	-3508638.12225	-3508642.79564	-3508644.79102	-3508645.07983	-3508644.26592	-3508642.76939	-3508640.82652	-3508638.62110	-3508636.44193
	-63.50000	-3508635.78556	-3508640.40644	-3508642.42807	-3508642.74313	-3508641.92923	-3508640.48520	-3508638.62110	-3508636.57321	-3508634.55157
	-60.00000	-3508633.79018	-3508638.14851	-3508640.06512	-3508640.32767	-3508639.54002	-3508638.17476	-3508636.44193	-3508634.55157	-3508632.63496

Table S2: Torsion angle of **I**, **II** and **III** from experimentally determined crystal structures. Definitions of torsion angles as τ_1 and τ_2 are given in Figure 1.

Molecule	Refcode	Charge	Chemical name	τ_1	τ_2
A	DEGDAV	0	4,4'-Methylenebis(3-hydroxy-2-naphthoic acid)	-62.0	-62.0
B	JAWYAI	-1	3,5-Lutidinium pamoate	-119.8	-113.6
C	JAWXIP	-1	2,4-Lutidinium pamoate tetrahydrofuran solvate	-114.2	-113.4
D	JAWXOV	-1	2,6-Lutidinium pamoate tetrahydrofuran solvate	-118.3	-118.7
E	QEXJEJ	-1	1,10-Phenanthroline-1-ium pamoate N,N-dimethylformamide solvate	-117.1	-115.7
F	this work residue 1	-2	3,4-Lutidinium pamoate	-126.4	-124.4
G	this work residue 2	-2	3,4-Lutidinium pamoate	-124.5	-124.7
H	this work	-2	2,3-Lutidinium pamoate	-119.5	-121.3
I	this work	-2	2,4-Lutidinium pamoate	-115.1	-118.2
J	JAWXEL	-2	bis(2,3-Lutidinium) pamoate tetrahydrofuran solvate	-117.4	-118.1
K	TABMAK	-2	bis(Pyridinium) 4,4'-methylene-bis(3-hydroxy-2-naphthalenecarboxylate)	-115.1	-122.0