Electronic supplementary information (ESI)

Cation□□□Cation Hydrogen Bonds in Synephrine Salts: A Typical Interaction in the Unusual Environment.

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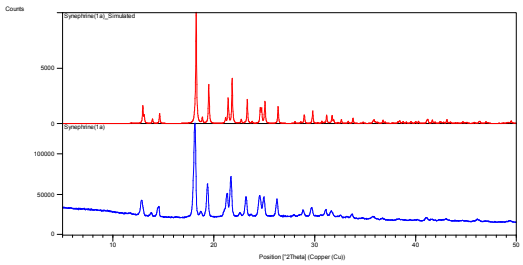
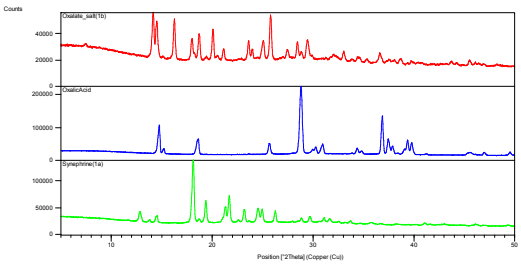
Powder X-ray Diffraction (PXRD) analysis: PXRD data was recorded using Cu-*K*α radiation over the *2θ* range 5-50□ with a step size of 0.02º at a scan rate of 2º min^{-1}.



(a)



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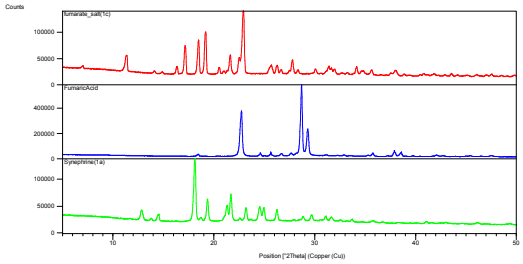

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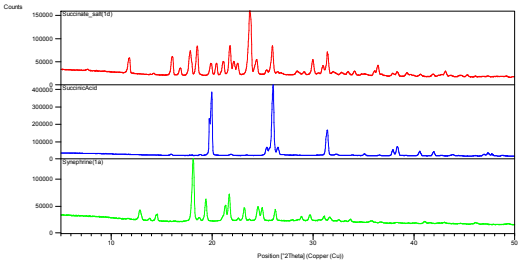

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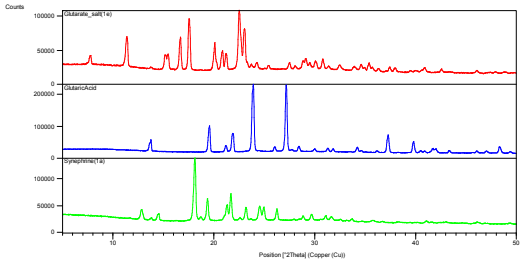

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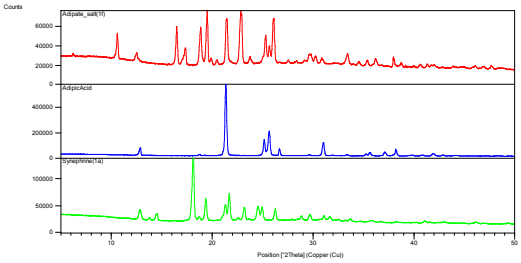
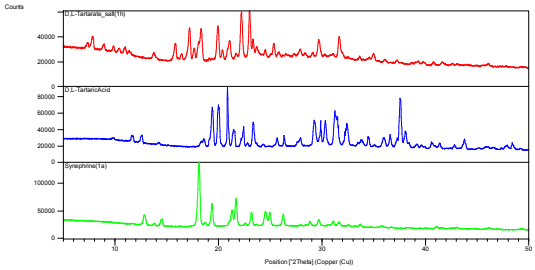
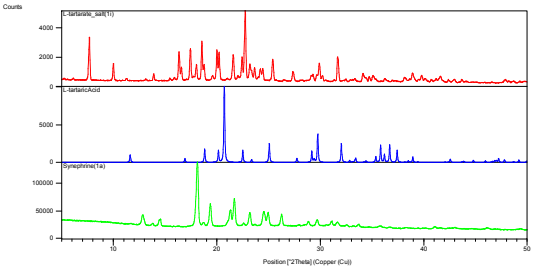


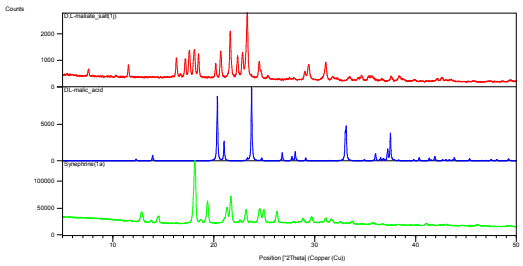
(f)



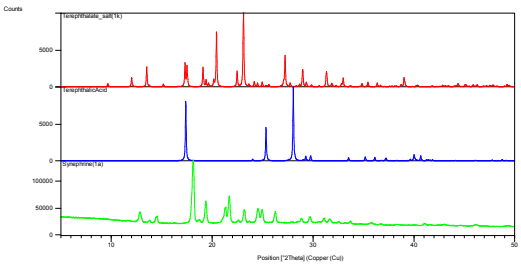
(g)



(h)



(i)



(j)

Figure S1 PXRD pattern of (a) Synephrine form I, (b) Oxalate salt, (c) Fumarate salt, (d) Succinate salt, (e) Glutarate salt, (f) Adipate salt, (g) D,L-tartarate salt, (h) L-tartarate salt, (i) DL-malate salt and (j) Terephthalate salt.

Table S1 BCP analysis of intramolecular interactions in the (±)–*p*–Synephrine–Oxalic acid salt (**1b**).

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	λ_1	λ_2	λ_3	ε	R_{ij}	d_1	d_2
C1–C2	2.080	–17.583	–14.57	–12.23	9.22	0.19	1.3937	0.6829	0.7109
C1–C6	2.072	–17.547	–14.48	–12.30	9.23	0.18	1.3949	0.7102	0.6847
C1–C7	1.718	–13.009	–11.45	–11.27	9.71	0.02	1.5180	0.7602	0.7578
C2–C3	2.069	–17.381	–14.46	–12.28	9.36	0.18	1.3930	0.7027	0.6904
C2–H2	1.816	–16.564	–16.51	–16.19	16.14	0.02	1.0886	0.7023	0.3863
C3–C4	2.096	–18.121	–14.94	–12.27	9.09	0.22	1.3971	0.6682	0.7289
C3–H3	1.826	–16.998	–16.60	–16.30	15.91	0.02	1.0874	0.7004	0.387
C4–C5	2.127	–19.265	–15.38	–12.76	8.88	0.21	1.3913	0.7140	0.6773
C5–C6	2.086	–17.568	–14.63	–12.22	9.29	0.20	1.3876	0.6896	0.698
C5–H5	1.808	–16.341	–16.42	–16.03	16.12	0.02	1.0867	0.7022	0.3845
C6–H6	1.841	–17.787	–17.26	–16.85	16.32	0.02	1.0869	0.7139	0.3730
C7–C8	1.773	–14.481	–12.24	–11.77	9.52	0.04	1.5135	0.7417	0.7718
C7–H7	1.822	–16.976	–16.79	–16.00	15.82	0.05	1.1033	0.7117	0.3916
C8–H8A	1.865	–18.965	–17.76	–17.18	15.98	0.03	1.0918	0.7208	0.3710
C8–H8B	1.855	–18.565	–17.34	–17.19	15.97	0.01	1.0931	0.7191	0.3741
C9–H9A	1.867	–18.803	–17.65	–16.97	15.82	0.04	1.0922	0.7121	0.3801
C9–H9B	1.906	–19.882	–17.77	–17.53	15.42	0.01	1.0904	0.702	0.3885
C9–H9C	1.857	–18.812	–17.73	–16.95	15.87	0.05	1.0913	0.7159	0.3755
N3–C8	1.655	–11.013	–11.20	–10.88	11.07	0.03	1.4914	0.8755	0.6159
N3–C9	1.682	–11.500	–11.57	–11.15	11.22	0.04	1.4863	0.867	0.6193
N3–H3A	2.032	–28.027	–27.26	–27.15	26.39	0.00	1.0410	0.7946	0.2464
N3–H3B	1.991	–26.403	–26.56	–26.43	26.59	0.01	1.0507	0.8048	0.2459
O1–C4	1.942	–16.186	–14.08	–13.42	11.31	0.05	1.3735	0.8397	0.5338
O1–H1A	1.922	–19.313	–28.60	–27.70	36.99	0.03	1.0141	0.7771	0.2370
O2–C7	1.786	–12.572	–12.98	–12.35	12.75	0.05	1.4253	0.8425	0.5827
O2–H2A	2.237	–29.700	–34.82	–33.85	38.98	0.03	0.9738	0.7452	0.2285
O3–C10	2.527	–20.044	–21.22	–20.93	22.10	0.01	1.2564	0.8245	0.4319
O4–C10	2.492	–18.374	–20.74	–19.62	21.98	0.06	1.2558	0.8224	0.4334

Table S2 BCP analysis of intramolecular interactions in the (±)–*p*–Synephrine–Glutaric acid salt (**1e**).

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	λ_1	λ_2	λ_3	ε	R_{ij}	d_1	d_2
C1–C2	2.06	–16.86	–14.67	–12.08	9.89	0.21	1.3972	0.6933	0.7039
C1–C6	2.10	–17.69	–15.01	–12.45	9.76	0.21	1.3920	0.6893	0.7027
C1–C7	1.70	–11.57	–11.60	–10.71	10.74	0.08	1.5158	0.7450	0.7708
C2–C3	2.08	–17.25	–14.63	–12.35	9.74	0.18	1.3905	0.6898	0.7007
C2–H2	1.89	–20.25	–16.61	–16.20	12.56	0.02	1.0860	0.6796	0.4064
C3–C4	2.14	–19.70	–15.88	–13.07	9.25	0.22	1.3919	0.6704	0.7215

C3–H3	1.86	–19.69	–16.36	–15.83	12.50	0.03	1.0871	0.6796	0.4075
C4–C5	2.12	–18.70	–15.55	–12.60	9.45	0.23	1.3935	0.7196	0.6740
C5–C6	2.09	–17.46	–14.93	–12.22	9.70	0.22	1.3850	0.6909	0.6941
C5–H5	1.84	–18.93	–16.02	–15.72	12.81	0.02	1.0863	0.6816	0.4047
C6–H6	1.85	–19.40	–16.29	–16.12	13.01	0.01	1.0909	0.6921	0.3988
C7–C8	1.63	–11.43	–11.03	–10.78	10.37	0.02	1.5187	0.7749	0.7438
C7–H7	1.82	–18.93	–16.47	–15.90	13.43	0.04	1.1056	0.7063	0.3993
C8–H8A	1.91	–21.90	–17.81	–17.04	12.96	0.05	1.0937	0.7031	0.3907
C8–H8B	1.89	–21.38	–17.66	–16.87	13.15	0.05	1.0941	0.7023	0.3918
C9–H9A	1.90	–21.90	–17.83	–17.27	13.20	0.03	1.0915	0.7084	0.3831
C9–H9B	1.88	–21.21	–17.59	–16.91	13.29	0.04	1.0922	0.7069	0.3853
C9–H9C	1.92	–22.03	–18.07	–17.52	13.56	0.03	1.0934	0.7147	0.3787
C10–C11	1.73	–13.26	–12.19	–11.54	10.47	0.06	1.5218	0.7562	0.7656
C11–C12	1.66	–11.14	–10.92	–10.85	10.62	0.01	1.5186	0.7519	0.7668
C11–H11A	1.84	–19.90	–16.42	–16.13	12.65	0.02	1.0990	0.6960	0.4030
C11–H11B	1.83	–19.25	–16.23	–16.14	13.12	0.01	1.0974	0.6975	0.3998
C12–C11	1.73	–13.81	–12.07	–11.31	9.57	0.07	1.5233	0.8012	0.7221
C12–H12	1.84	–20.47	–16.72	–16.36	12.61	0.02	1.0914	0.6857	0.4057
N3–C8	1.65	–11.34	–11.47	–11.15	11.27	0.03	1.4919	0.8764	0.6155
N3–C9	1.62	–10.46	–10.94	–10.79	11.27	0.01	1.4898	0.8773	0.6124
N3–H3A	2.06	–32.87	–27.90	–27.75	22.78	0.01	1.0399	0.8016	0.2383
N3–H3B	2.10	–34.83	–28.48	–28.35	22.01	0.00	1.0425	0.7974	0.2451
O1–C4	2.04	–19.43	–15.78	–15.39	11.74	0.03	1.3640	0.8257	0.5383
O1–H1A	2.17	–43.45	–36.57	–35.96	29.08	0.02	0.9921	0.7844	0.2077
O2–C7	1.81	–11.59	–14.02	–12.72	15.14	0.10	1.4248	0.8216	0.6031
O2–H2A	2.20	–40.98	–35.70	–35.09	29.81	0.02	0.9940	0.7772	0.2168
O3–C10	2.49	–19.06	–21.02	–20.19	22.15	0.04	1.2662	0.8361	0.4301
O4–C10	2.54	–20.81	–21.59	–21.30	22.08	0.01	1.2607	0.8313	0.4294

Table S3 BCP analysis of intramolecular interactions in the (±)–*p*–Synephrine–D,L–Tartaric acid salt (**1h**).

Bond	**ρ (eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**λ_1**	**λ_2**	**λ_3**	**ε**	**R_{ij}**	**d_1**	**d_2**
C1–C2	2.113	–18.345	–15.30	–12.60	9.55	0.21	1.3889	0.6864	0.7025
C1–C6	2.075	–17.672	–14.83	–12.44	9.60	0.19	1.3928	0.6927	0.7001
C1–C7	1.729	–13.017	–11.79	–11.21	9.99	0.05	1.5213	0.7451	0.7762
C2–C3	2.066	–16.594	–14.61	–11.96	9.98	0.22	1.3952	0.6926	0.7026
C2–H2	1.913	–22.585	–17.37	–16.68	11.47	0.04	1.0860	0.6804	0.4056
C3–C4	2.117	–18.342	–15.11	–12.46	9.22	0.21	1.3916	0.6503	0.7413
C3–H3	1.860	–19.066	–16.36	–15.64	12.93	0.05	1.0870	0.6858	0.4012
C4–C5	2.122	–18.246	–14.98	–12.50	9.23	0.20	1.3916	0.7429	0.6488
C5–C6	2.103	–18.122	–15.10	–12.56	9.55	0.20	1.3857	0.6815	0.7042
C5–H5	1.902	–20.729	–16.17	–16.13	11.58	0.00	1.0868	0.6686	0.4182
C6–H6	1.831	–18.569	–15.57	–15.46	12.46	0.01	1.0900	0.6789	0.4111
C7–C8	1.740	–14.353	–12.09	–11.64	9.38	0.04	1.5233	0.748	0.7753
C7–H7	1.935	–23.339	–17.51	–16.98	11.15	0.03	1.1027	0.6915	0.4112
C8–H8A	1.887	–22.182	–17.63	–16.87	12.32	0.05	1.0950	0.7115	0.3835
C8–H8B	1.927	–22.809	–17.66	–16.97	11.82	0.04	1.0928	0.6960	0.3968
C9–H9A	1.880	–21.646	–17.58	–16.49	12.42	0.07	1.0906	0.7050	0.3856
C9–H9B	1.938	–24.215	–18.40	–17.50	11.68	0.05	1.0908	0.7073	0.3835
C9–H9C	1.903	–22.415	–18.10	–17.01	12.69	0.06	1.0911	0.7205	0.3706
C10–C11	2.083	–18.387	–15.22	–12.59	9.420	0.21	1.3935	0.6976	0.6960

C10–C15	2.102	–18.829	–15.32	–12.86	9.35	0.19	1.3905	0.7077	0.6828
C10–C16	1.725	–13.024	–11.85	–10.98	9.81	0.08	1.5175	0.7441	0.7733
C11–C12	2.097	–18.42	–15.12	–12.71	9.42	0.19	1.3901	0.6836	0.7065
C11–H11	1.887	–21.673	–17.10	–16.59	12.02	0.03	1.0882	0.6903	0.3979
C12–C13	2.133	–19.939	–15.70	–13.24	9.00	0.19	1.3921	0.6677	0.7245
C12–H12	1.853	–19.352	–16.23	–15.71	12.59	0.03	1.0870	0.6866	0.4004
C13–C14	2.098	–18.522	–15.39	–12.47	9.33	0.23	1.3905	0.7135	0.6770
C14–C15	2.073	–18.225	–14.75	–12.95	9.47	0.14	1.3916	0.6873	0.7043
C14–H14	1.854	–18.834	–16.21	–15.33	12.7	0.06	1.0867	0.6819	0.4048
C15–H15	1.920	–22.636	–16.92	–16.74	11.02	0.01	1.0888	0.6719	0.4169
C16–C17	1.767	–16.093	–12.98	–11.9	8.78	0.09	1.5215	0.7547	0.7668
C16–H16	1.938	–24.488	–18.35	–17.47	11.33	0.05	1.1009	0.7092	0.3917
C17–H17A	1.892	–22.913	–17.73	–17.34	12.16	0.02	1.0941	0.7166	0.3775
C17–H17B	1.949	–25.627	–18.85	–17.84	11.07	0.06	1.0917	0.7089	0.3828
C18–H18A	1.767	–18.21	–17.36	–16.66	15.81	0.04	1.0927	0.7714	0.3213
C18–H18B	1.782	–18.661	–17.28	–17.15	15.77	0.01	1.0918	0.7735	0.3183
C18–H18C	1.879	–21.759	–17.75	–16.94	12.93	0.05	1.0909	0.7152	0.3757
C19–C20	1.700	–13.558	–12.44	–10.88	9.76	0.14	1.5498	0.7877	0.7621
C20–C21	1.780	–15.931	–12.92	–12.27	9.26	0.05	1.5302	0.7659	0.7643
C20–H20	1.894	–21.698	–17.00	–16.25	11.55	0.05	1.0991	0.6891	0.4099
C21–C22	1.703	–13.069	–12.04	–11.03	10.01	0.09	1.5497	0.7785	0.7713
C21–H21	1.880	–21.567	–17.28	–16.37	12.09	0.06	1.1003	0.7018	0.3985
N3–C8	1.656	–7.944	–11.55	–11.42	15.03	0.01	1.4864	0.7922	0.6941
N3–C9	1.653	–7.748	–11.49	–11.22	14.96	0.02	1.4844	0.7933	0.6911
N3–H3A	2.210	–28.64	–25.38	–25.31	22.04	0.00	1.0375	0.7177	0.3198
N3–H3B	2.108	–24.664	–23.76	–23.65	22.75	0.00	1.0412	0.7213	0.3200
N6–C17	1.611	–7.038	–11.14	–10.86	14.96	0.03	1.4964	0.7967	0.6997
N6–C18	1.599	–6.631	–11.19	–10.82	15.38	0.03	1.4913	0.7940	0.6973
N6–H6A	2.149	–24.221	–23.95	–23.75	23.48	0.01	1.0315	0.7140	0.3175
N6–H6B	2.100	–23.421	–23.15	–22.92	22.65	0.01	1.0419	0.7208	0.3211
O1–C4	2.005	–19.504	–16.08	–14.42	10.99	0.12	1.3700	0.8370	0.5329
O1–H1A	2.023	–42.270	–34.50	–33.95	26.18	0.02	1.0123	0.8066	0.2058
O2–C7	1.888	–15.825	–15.12	–13.51	12.8	0.12	1.4138	0.8298	0.5840
O2–H2A	2.233	–46.026	–37.78	–36.97	28.73	0.02	0.9840	0.7801	0.2039
O4–C13	1.992	–18.446	–15.51	–14.17	11.23	0.09	1.3651	0.8354	0.5297
O4–H4A	2.046	–41.574	–35.46	–34.74	28.63	0.02	0.9963	0.8033	0.1930
O5–C16	1.788	–13.261	–13.76	–12.02	12.51	0.15	1.4236	0.8396	0.5840
O5–H5A	2.383	–60.249	–42.19	–41.57	23.50	0.01	0.9829	0.7781	0.2049
O7–C19	2.621	–27.584	–22.69	–21.09	16.19	0.08	1.2500	0.8033	0.4467
O8–C19	2.559	–27.031	–22.15	–20.87	15.99	0.06	1.2585	0.8109	0.4476
O9–C20	1.806	–13.501	–13.92	–12.71	13.13	0.09	1.4172	0.8332	0.5840
O9–H9	2.288	–41.700	–36.72	–36.30	31.32	0.01	0.9718	0.7623	0.2095
O10–C21	1.809	–13.878	–13.81	–13.03	12.96	0.06	1.4210	0.8341	0.5870
O10–H10	2.390	–50.400	–39.56	–38.77	27.93	0.02	0.9730	0.7633	0.2097
O11–C22	2.539	–28.417	–21.31	–19.34	12.24	0.10	1.2672	0.8000	0.4672
O12–C22	2.690	–28.459	–23.57	–22.29	17.4	0.06	1.2379	0.7963	0.4416

Table S4 BCP analysis of intramolecular interactions in the (±)–*p*–Synephrine–Terephthalate salt hydrate, (**1k**).

Bond	**ρ (eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**λ1**	**λ2**	**λ3**	**ε**	**R_{ij}**	**d_1**	**d_2**
C1–C2	2.09	-17.74	-14.98	-12.59	9.83	0.19	1.3897	0.6794	0.7103

C1–C6	2.12	-18.00	-15.14	-12.72	9.85	0.19	1.3863	0.6867	0.6996
C1–C7	1.70	-12.11	-11.66	-10.79	10.34	0.08	1.5185	0.7432	0.7753
C2–C3	2.14	-18.62	-15.55	-12.63	9.56	0.23	1.3728	0.6923	0.6806
C2–H2	1.87	-19.61	-17.06	-16.66	14.12	0.02	1.0891	0.7020	0.3871
C3–C4	2.16	-19.80	-16.09	-13.08	9.36	0.23	1.3876	0.6652	0.7225
C3–H3	1.86	-20.06	-16.84	-16.33	13.11	0.03	1.0890	0.6889	0.4001
C4–C5	2.17	-19.98	-16.21	-13.1	9.33	0.24	1.3795	0.7037	0.6758
C5–C6	2.09	-17.84	-14.89	-12.7	9.76	0.17	1.3899	0.6941	0.6958
C5–H5	1.82	-18.79	-16.59	-16.09	13.89	0.03	1.0890	0.7018	0.3871
C6–H6	1.89	-20.70	-17.05	-16.79	13.15	0.02	1.0890	0.6885	0.4005
C7–C8	1.77	-14.46	-12.4	-11.95	9.88	0.04	1.5131	0.7478	0.7652
C7–H7	1.95	-22.92	-18.48	-17.52	13.08	0.05	1.0891	0.7032	0.3859
C8–H8A	1.89	-20.80	-17.52	-16.69	13.41	0.05	1.0890	0.7010	0.3879
C8–H8B	1.89	-20.72	-17.41	-16.97	13.66	0.03	1.0890	0.7048	0.3842
C9–H9A	1.90	-21.53	-17.72	-17	13.19	0.04	1.0891	0.7017	0.3874
C9–H9B	1.88	-20.69	-17.33	-16.65	13.29	0.04	1.0891	0.6979	0.3912
C9–H9C	1.94	-23.20	-18.32	-17.91	13.04	0.02	1.0892	0.7085	0.3806
C10–C11	2.08	-17.06	-14.7	-12.45	10.1	0.18	1.3909	0.6940	0.6970
C10–C14	1.72	-13.12	-12.31	-11.16	10.36	0.1	1.5136	0.7426	0.7711
C11–H11	1.88	-19.84	-16.8	-16.66	13.62	0.01	1.0881	0.6951	0.3930
C11–C12	2.10	-17.83	-15.07	-12.73	9.96	0.18	1.3893	0.7045	0.6847
C12–H12	1.87	-19.83	-17.02	-16.55	13.75	0.03	1.0868	0.6964	0.3904
C12–C13	2.12	-17.87	-15.3	-12.55	9.98	0.22	1.3899	0.6920	0.6979
C13–C15	1.75	-13.99	-12.81	-11.41	10.23	0.12	1.5055	0.7383	0.7671
N3–C8	1.67	-10.89	-11.61	-11.27	11.99	0.03	1.4876	0.8582	0.6294
N3–C9	1.66	-10.83	-11.36	-11.1	11.63	0.02	1.4835	0.8635	0.6201
N3–H3A	2.23	-41.19	-32.46	-32.17	23.44	0.01	1.0150	0.7851	0.2299
N3–H3B	2.25	-42.73	-32.49	-32.35	22.11	0.00	1.0150	0.7795	0.2355
O1–C4	2.04	-19.09	-16.07	-14.78	11.76	0.09	1.3625	0.8243	0.5382
O1–H1A	2.20	-41.49	-36.16	-35.62	30.29	0.02	0.9932	0.7769	0.2163
O2–C7	1.79	-12.88	-13.77	-12.44	13.33	0.11	1.4261	0.8359	0.5902
O2–H2A	2.25	-41.04	-35.84	-35.15	29.95	0.02	0.9929	0.7670	0.2259
O4–C14	2.62	-29.96	-24.1	-18.82	12.96	0.28	1.2575	0.7982	0.4593
O5–C15	2.61	-29.73	-24.05	-19.02	13.34	0.26	1.2625	0.8050	0.4575
O6–H6A	2.19	-38.61	-35.22	-34.77	31.37	0.01	0.9878	0.7700	0.2177
O6–H6B	2.20	-38.99	-35.21	-34.84	31.06	0.01	0.9866	0.7686	0.2180

Table S5 Bond Critical Point Analysis of Intermolecular Interactions Observed in Synephrine–Salt Forms (**1b**, **1e**, **1h,** and **1k**).

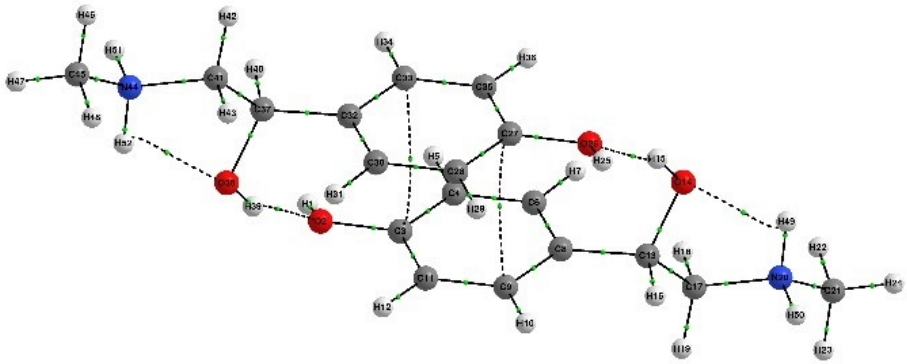
Form	Molecular Pair	Interaction	r (Å)	d (Å)	D (Å)	θ (º)	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε	$\lvert V_b \rvert / G_b$	Symm. Code
1b	Cat···Ani	O1–H1A···O3	1.01	1.60	2.61	173	0.34	5.42	0.01	1.03	1–x, 1/2+y, 1/2–z
	Cat···Ani	N3–H3B···O4	1.05	1.73	2.76	164	0.26	3.99	0.01	0.96	–x, –y, –z
	Cat···Ani	N3–H3A···O4	1.04	1.82	2.82	158	0.20	3.20	0.03	0.90	x, 1+y, z
	~~Cat···Cat~~	~~O2–H2A···O1~~	~~0.97~~	~~1.84~~	~~2.81~~	~~175~~	~~0.16~~	~~3.42~~	~~0.00~~	~~0.80~~	~~1–x, 1–y, –z~~
	Cat···Ani	N3–H3B···O3	1.05	2.38	2.97	115	0.08	1.18	0.14	0.71	x, y, z
	Cat···Ani	C8–H8A···O3	1.09	2.49	3.14	117	0.06	0.94	0.08	0.80	x, y, z

	~~Cat···Cat~~	~~C8–H8B···O1~~	~~1.09~~	~~2.51~~	~~3.40~~	~~137~~	~~0.06~~	~~0.84~~	~~0.45~~	~~0.60~~	~~1–x, 1/2+y, 1/2–z~~
	Cat···Ani	C5–H5···O3	1.09	2.58	3.30	124	0.05	0.77	1.01	0.75	1–x, 1/2+y, 1/2–z
	Cat···Ani	C9–H9B···O3	1.09	2.58	3.23	117	0.05	0.79	0.21	0.75	x, y, z
	Cat···Ani	C9–H9A···O1	1.09	2.64	3.48	133	0.04	0.59	0.13	0.67	1–x, 1/2+y, 1/2–z
1e	Cat···Ani	O2–H2A···O3	0.99	1.66	2.64	167	0.35	2.60	0.02	1.35	1/2+x, 1/2+y, z
	Cat···Ani	O1–H1A···O3	0.99	1.68	2.66	171	0.34	2.31	0.01	1.29	1/2–x, –1/2–y,1–z
	Cat···Ani	N3–H3B···O4	1.04	1.77	2.80	168	0.28	2.46	0.02	1.19	1/2+x, –1/2+y, z
	Cat···Ani	N3–H3A···O4	1.04	1.85	2.85	160	0.22	2.48	0.05	1.06	–x, y, 1/2–z
	~~Cat···Cat~~	~~C9–H9A···O1~~	~~1.09~~	~~2.26~~	~~3.32~~	~~162~~	~~0.10~~	~~1.09~~	~~0.01~~	~~0.86~~	~~1/2–x, –1/2–y,1–z~~
	~~Cat···Cat~~	~~C9–H9C···O2~~	~~1.09~~	~~2.42~~	~~3.47~~	~~161~~	~~0.07~~	~~0.75~~	~~0.03~~	~~1.00~~	~~x, –1+y, z~~
	Cat···Ani	C11–H11A···O1	1.10	2.46	3.37	140	0.06	0.79	0.20	0.75	1/2–x, 1/2–y, 1–z
	Cat···Ani	C9–H9B···O3	1.09	2.71	3.58	137	0.04	0.51	0.40	0.67	–x, y, 1/2–z
1h	Cat···Ani	O1–H1A···O11	1.01	1.59	2.59	169	0.42	1.91	0.01	1.54	x, 1+y, z
	Cat···Ani	O4–H4A···O8	1.00	1.63	2.61	168	0.35	3.38	0.01	1.21	–x, 2–y, 1–z
	Cat···Ani	N3–H3B···O7	1.04	1.72	2.76	170	0.30	1.86	0.03	1.30	x, y, z
	Cat···Ani	N3–H3A···O12	1.04	1.72	2.71	157	0.30	1.76	0.11	1.37	1+x, y, z
	Cat···Ani	O2–H2A···O11	0.98	1.79	2.77	169	0.28	1.73	0.01	1.28	–x, 1–y, 2–z
	Cat···Ani	O5–H5A···O8	0.98	1.81	2.79	177	0.27	0.59	0.01	1.67	x, y, z
	Cat···Ani	O9–H9···O1	0.97	1.83	2.80	177	0.23	2.30	0.01	1.11	–x, 2–y, 2–z
	Cat···Ani	N6–H6B···O7	1.04	1.80	2.78	155	0.22	2.65	0.09	1.00	1–x, 1–y, 1–z
	Cat···Ani	O10–H0···O4	0.97	1.84	2.78	162	0.19	2.52	0.07	0.94	x, –1+y, z
	Cat···Ani	N6–H6A···O1	1.03	2.07	3.02	152	0.14	1.26	0.16	1.00	1–x, 2–y, 1–z
	~~Cat···Cat~~	~~C9–H9A···O4~~	~~1.09~~	~~2.32~~	~~3.33~~	~~154~~	~~0.10~~	~~1.04~~	~~0.04~~	~~1.00~~	~~1–x, 2–y, 1–z~~
	~~Cat···Cat~~	~~C9–H9C···O5~~	~~1.09~~	~~2.33~~	~~3.32~~	~~150~~	~~0.09~~	~~1.06~~	~~0.17~~	~~0.94~~	~~x, y, z~~
	Cat···Ani	C18–H18A···O12	1.09	2.36	3.45	179	0.07	1.13	0.02	0.83	–x, 1–y, 1–z
	~~Cat···Cat~~	~~C18–H18C···O2~~	~~1.09~~	~~2.50~~	~~3.20~~	~~121~~	~~0.06~~	~~0.90~~	~~0.23~~	~~0.80~~	~~x, y, –1+z~~
	Cat···Ani	N6–H6A···O9	1.03	2.43	3.01	115	0.05	1.19	2.30	0.67	1–x, 1–y, 1–z
	~~Cat···Cat~~	~~N6–H6A···O10~~	~~1.03~~	~~2.40~~	~~2.95~~	~~112~~	~~0.05~~	~~1.31~~	~~1.53~~	~~0.57~~	~~1–x, 1–y, 1–z~~
	Cat···Ani	C16–H16···O11	1.10	2.73	3.79	162	0.05	0.52	0.93	0.67	x, 1+y, z
	Cat···Ani	C9–H9B···O8	1.09	2.55	3.58	156	0.05	0.60	0.35	0.67	1–x, 1–y, 1–z
	Cat···Ani	C16–H16···O12	1.10	2.65	3.60	144	0.05	0.64	4.10	0.67	x, 1+y, z
	Cat···Ani	C15–H15···O11	1.09	2.72	3.71	150	0.04	0.38	0.07	1.00	x, 1+y, z
	Cat···Ani	C5–H5···O11	1.09	2.62	3.35	124	0.04	0.72	1.55	0.50	x, 1+y, z
1k	Cat···Ani	O1–H1A··· O5	0.99	1.68	2.67	176	0.32	2.35	0.00	1.26	–x, 1+y, –1/2-z
	Wat···Ani	O6–H6A···O4	0.99	1.73	2.69	162	0.3	2.49	0.03	1.23	1/2–x, 3/2–y, –1–z
	Wat···Ani	O6–H6B···O5	0.99	1.74	2.71	166	0.29	2.56	0.01	1.18	1/2–x, 1/2–y, –1–z
	Cat···Wat	N3–H3A···O6	1.01	1.79	2.80	172	0.27	2.42	0.03	1.15	–x, 1+y, –1/2-z
	Cat···Ani	O2–H2A···O4	0.99	1.79	2.74	158	0.25	1.87	0.06	1.24	–x, y, –1/2–z
	Cat···Wat	N3–H3B···O6	1.02	1.85	2.80	154	0.2	2.43	0.1	1.00	x, 1–y, 1/2+z
	~~Cat···Cat~~	~~C9–H9C···O1~~	~~1.09~~	~~2.64~~	~~3.05~~	~~101~~	~~0.05~~	~~0.81~~	~~0.55~~	~~0.75~~	~~x, 1+y, +z~~
	~~Cat···Cat~~	~~C9–H9C···O2~~	~~1.09~~	~~2.62~~	~~3.51~~	~~139~~	~~0.04~~	~~0.54~~	~~0.18~~	~~0.67~~	~~–x, 1–y, –z~~
	Cat···Ani	C5–H5···O5	1.09	2.69	3.42	124	0.04	0.58	0.62	0.67	–x,1+y, –1/2–z
	Cat···Ani	C6–H6···O4	1.09	2.72	3.50	128	0.03	0.51	0.38	0.67	–1/2+x, 3/2–y, 1/2+z

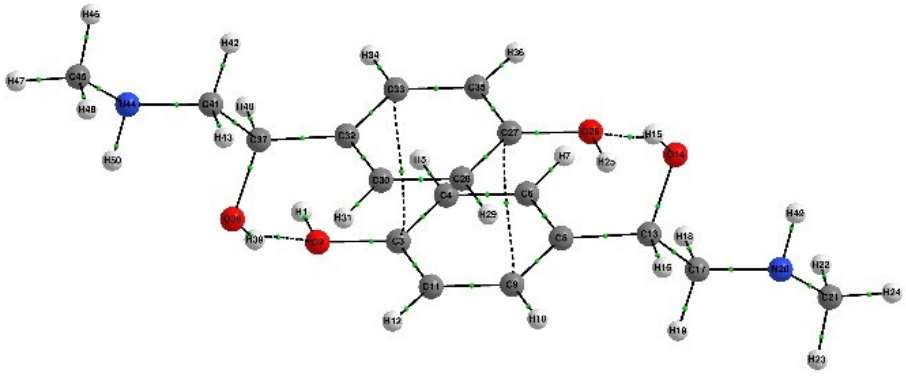
Table S6 Comparison of atomic charge for the gas phase optimized cationic and neutral synephrine O–H···O dimers derived from ESPD and AIM charge schemes.

Atom	ESPD Charges				AIM Charges			
	Charged		Neutral		Charged		Neutral	
	Dimer	Monomer	Dimer	Monomer	Dimer	Monomer	Dimer	Monomer
H1	0.45	0.45	0.45	0.43	0.61	0.60	0.59	0.58
O2	-0.66	-0.61	-0.71	-0.64	-1.17	-1.13	-1.15	-1.13
C3	0.38	0.45	0.38	0.43	0.49	0.56	0.47	0.51
C4	-0.24	-0.32	-0.22	-0.30	-0.01	-0.01	-0.03	-0.03
H5	0.16	0.16	0.11	0.13	0.05	0.04	0.01	0.01
C6	-0.18	-0.13	-0.23	-0.14	-0.01	-0.02	-0.01	-0.02
H7	0.17	0.16	0.17	0.15	0.04	0.04	0.04	0.05
C8	0.14	0.08	0.11	0.07	-0.03	-0.05	0.04	-0.03
C9	-0.20	-0.17	-0.19	-0.17	0.00	-0.01	-0.01	-0.02
H10	0.13	0.12	0.11	0.12	0.04	0.03	0.02	0.02
C11	-0.11	-0.20	-0.12	-0.22	0.01	0.01	0.00	-0.01
H12	0.13	0.18	0.12	0.16	0.06	0.08	0.05	0.05
C13	0.11	0.04	0.20	0.03	0.54	0.52	0.53	0.52
O14	-0.66	-0.63	-0.70	-0.62	-1.17	-1.15	-1.15	-1.12
H15	0.48	0.43	0.49	0.39	0.64	0.61	0.61	0.57
H16	0.07	0.10	0.02	0.07	0.01	0.02	0.00	0.01
C17	-0.23	-0.07	0.13	0.31	0.28	0.27	0.38	0.38
H18	0.13	0.09	0.03	-0.01	0.07	0.08	-0.02	-0.01

H19	0.12	0.09	0.00	-0.01	0.08	0.08	0.00	0.00
N20	0.21	0.12	-0.71	-0.76	-1.02	-1.02	-1.03	-1.03
C21	-0.29	-0.28	0.23	0.16	0.29	0.29	0.36	0.36
H22	0.17	0.17	-0.03	-0.02	0.09	0.08	-0.03	-0.02
H23	0.16	0.15	0.02	0.03	0.08	0.08	0.00	0.00
H24	0.14	0.14	-0.01	0.02	0.09	0.09	0.01	0.01
H25	0.45	-	0.45	-	0.61	-	0.59	-
O26	-0.66	-	-0.71	-	-1.17	-	-1.15	-
C27	0.38	-	0.38	-	0.49	-	0.47	-
C28	-0.24	-	-0.22	-	-0.01	-	-0.03	-
H29	0.16	-	0.11	-	0.05	-	0.01	-
C30	-0.18	-	-0.23	-	-0.01	-	-0.01	-
H31	0.17	-	0.17	-	0.04	-	0.04	-
C32	0.14	-	0.11	-	-0.03	-	-0.02	-
C33	-0.20	-	-0.19	-	0.00	-	-0.01	-
H34	0.13	-	0.11	-	0.04	-	0.02	-
C35	-0.11	-	-0.12	-	0.01	-	0.00	-
H36	0.13	-	0.12	-	0.06	-	0.05	-
C37	0.11	-	0.20	-	0.54	-	0.53	-
O38	-0.66	-	-0.70	-	-1.17	-	-1.15	-
H39	0.48	-	0.49	-	0.64	-	0.61	-
H40	0.07	-	0.02	-	0.01	-	0.00	-
C41	-0.23	-	0.13	-	0.28	-	0.38	-
H42	0.12	-	0.00	-	0.08	-	0.00	-
H43	0.13	-	0.03	-	0.07	-	-0.02	-
N44	0.21	-	-0.71	-	-1.02	-	-1.03	-
C45	-0.29	-	0.23	-	0.29	-	0.36	-
H46	0.16	-	0.02	-	0.08	-	0.00	-
H47	0.14	-	-0.01	-	0.09	-	0.01	-
H48	0.17	-	-0.03	-	0.09	-	-0.03	-
H49	0.21	0.24	0.35	0.37	0.48	0.48	0.36	0.36
H50	0.22	0.23	-	-	0.43	0.43	-	-
H51	0.22	-	-	-	0.43	-	-	-
H52	0.21	-	0.35	-	0.48	-	0.36	-



(a)



(b)

Figure S2 Molecular graph depicting bond critical point (marked in green) observed for the gas phase optimized (a) cation···cation synephrine dimer (b) neutral···neutral synephrine O–H···O dimer (Synthon **A**).

Table S7 Comparison of BCP properties for the intramolecular region of cationic (shown in red color) and neutral (*italicised*) synephrine O–H···O dimers obtained after gas-phase optimization.

Bond	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε	R_{ij} (Å)	d_1(Å)	d_2(Å)
O2–H1	2.4297	-61.8852	0.0223	0.9388	0.7784	0.1605
O2–H1	*2.4578*	*-62.0541*	*0.0224*	*0.9372*	*0.7737*	*0.1635*
O14–H15	2.3496	-60.4455	0.0214	0.9459	0.7919	0.1539
O14–H15	*2.4234*	*-61.4708*	*0.0233*	*0.941*	*0.7807*	*0.1602*
O26–H25	2.4297	-61.8852	0.0223	0.9388	0.7784	0.1605
O26–H25	*2.4578*	*-62.0541*	*0.0224*	*0.9372*	*0.7737*	*0.1635*
O38–H39	2.3496	-60.4457	0.0214	0.9459	0.7919	0.1539
O38–H39	*2.4234*	*-61.4711*	*0.0233*	*0.941*	*0.7807*	*0.1602*
N20–H50	2.2594	-40.7459	0.0037	1.003	0.7604	0.2426
N20–H50	–	–	–	–	–	–
N20–H49	2.2124	-42.4127	0.0029	1.0089	0.7775	0.2313
N20–H49	*2.2854*	*-37.3992*	*0.0483*	*0.9955*	*0.7401*	*0.2554*
N44–H51	2.2594	-40.746	0.0037	1.003	0.7604	0.2426
N44–H51	–	–	–	–	–	–
N44–H52	2.2124	-42.4125	0.0029	1.0089	0.7775	0.2313
N44–H50	*2.2854*	*-37.3992*	*0.0483*	*0.9955*	*0.7401*	*0.2554*
C3–C4	2.0898	-20.913	0.2254	1.3927	0.7259	0.6669
C3–C4	*2.0897*	*-20.8397*	*0.2343*	*1.3916*	*0.7254*	*0.6662*
C3–C11	2.1139	-21.5126	0.2267	1.388	0.7268	0.6611
C3–C11	*2.1106*	*-21.4159*	*0.2304*	*1.3879*	*0.7273*	*0.6607*
C4–C6	2.0771	-20.4528	0.2064	1.3869	0.6947	0.6922
C4–C6	*2.0675*	*-20.2724*	*0.2054*	*1.3888*	*0.7024*	*0.6864*
C6–C8	2.0536	-19.9641	0.1973	1.3953	0.6978	0.6975
C6–C8	*2.061*	*-20.1426*	*0.1906*	*1.3941*	*0.7031*	*0.691*
C8–C9	2.0653	-20.192	0.2050	1.393	0.6983	0.6947
C8–C9	*2.069*	*-20.2922*	*0.1984*	*1.3923*	*0.6899*	*0.7024*
C9–C11	2.0808	-20.6257	0.1969	1.3873	0.6949	0.6924
C9–C11	*2.0751*	*-20.4943*	*0.1995*	*1.3881*	*0.691*	*0.6971*
C4–H5	1.8804	-22.9222	0.0187	1.0699	0.6943	0.3755
C4–H5	*1.8634*	*-22.4608*	*0.0216*	*1.0713*	*0.6885*	*0.3828*
C6–H7	1.8915	-23.202	0.0127	1.0698	0.6945	0.3753

C6–H7	1.894	-23.2667	0.0133	1.0694	0.6951	0.3743
C9–H10	1.8906	-23.2109	0.0126	1.0704	0.6951	0.3754
C9–H10	1.8834	-23.0114	0.0138	1.071	0.6921	0.3789
C11–H12	1.893	-23.2848	0.0164	1.0681	0.6976	0.3705
C11–H12	1.8861	-23.0707	0.0177	1.0685	0.6943	0.3742
C13–H16	1.8896	-22.9258	0.0294	1.0847	0.7044	0.3804
C13–H16	1.8874	-22.8491	0.0306	1.0837	0.7016	0.3821
C17–H18	1.9101	-23.5553	0.0294	1.0756	0.7073	0.3683
C17–H18	1.823	-21.2931	0.0230	1.0908	0.7006	0.3902
C17–H19	1.9107	-23.6665	0.0284	1.0746	0.7072	0.3674
C17-H19	1.8678	-22.5208	0.0229	1.0807	0.6959	0.3847
C21–H22	1.9122	-23.7362	0.0317	1.0726	0.7066	0.366
C21–H22	1.8276	-21.4484	0.0268	1.0876	0.6965	0.3911
C21–H23	1.9113	-23.7177	0.0319	1.073	0.7068	0.3663
C21–H23	1.8641	-22.4156	0.0273	1.079	0.6936	0.3854
C21–H24	1.9129	-23.7813	0.0302	1.0727	0.708	0.3647
C21–H24	1.8724	-22.6446	0.0255	1.0765	0.6929	0.3837
C28–H29	1.8804	-22.9222	0.0187	1.0699	0.6943	0.3755
C28–H29	1.8634	-22.4609	0.0216	1.0713	0.6885	0.3828
C30–H31	1.8915	-23.202	0.0127	1.0698	0.6945	0.3753
C30–H31	1.894	-23.2668	0.0133	1.0694	0.6951	0.3743
C33–H34	1.8906	-23.2109	0.0126	1.0704	0.6951	0.3754
C33–H34	1.8834	-23.0115	0.0138	1.071	0.6921	0.3789
C35–H36	1.893	-23.2847	0.0164	1.0681	0.6976	0.3705
C35–H36	1.8861	-23.0708	0.0177	1.0685	0.6943	0.3742
C37–H40	1.8896	-22.9257	0.0294	1.0847	0.7044	0.3804
C37–H40	1.8874	-22.849	0.0306	1.0837	0.7016	0.3821
C41–H42	1.9107	-23.6665	0.0284	1.0746	0.7072	0.3674
C41–H42	1.8678	-22.521	0.0229	1.0807	0.6959	0.3847
C41–H43	1.9101	-23.5553	0.0294	1.0756	0.7073	0.3683
C41–H43	1.823	-21.2932	0.0230	1.0908	0.7006	0.3902
C45–H46	1.9113	-23.7177	0.0319	1.073	0.7068	0.3663
C45–H46	1.8641	-22.4156	0.0273	1.079	0.6936	0.3854
C45–H47	1.9129	-23.7813	0.0302	1.0727	0.708	0.3647
C45–H47	1.8724	-22.6445	0.0255	1.0765	0.6929	0.3837
C45–H48	1.9122	-23.7362	0.0317	1.0726	0.7066	0.366
C45–H48	1.8276	-21.4484	0.0268	1.0876	0.6965	0.3911
C8–C13	1.7077	-14.567	0.0419	1.5104	0.7388	0.7717
C8-C13	1.7121	-14.6921	0.0491	1.5121	0.7639	0.7482
C13–C17	1.6855	-14.3751	0.0467	1.5268	0.7392	0.7875
C13–C17	1.7057	-14.6873	0.0261	1.5202	0.7695	0.7506
C27–C28	2.0898	-20.913	0.2254	1.3927	0.7259	0.6669
C27–C28	2.0897	-20.8399	0.2343	1.3916	0.7254	0.6662
C27–C35	2.1139	-21.5126	0.2267	1.388	0.7268	0.6611
C27–C35	2.1106	-21.416	0.2304	1.3879	0.7273	0.6607
C28–C30	2.0771	-20.4528	0.2064	1.3869	0.6947	0.6922
C28–C30	2.0675	-20.2724	0.2054	1.3888	0.7024	0.6864
C30–C32	2.0536	-19.9641	0.1973	1.3953	0.6978	0.6975
C30–C32	2.061	-20.1425	0.1906	1.3941	0.7031	0.691
C32–C33	2.0653	-20.1919	0.2050	1.393	0.6983	0.6947
C32–C33	2.069	-20.2921	0.1984	1.3923	0.6899	0.7024
C32–C37	1.7076	-14.5669	0.0419	1.5104	0.7388	0.7717
C32–C37	1.7121	-14.6921	0.0491	1.5121	0.7639	0.7482
C33–C35	2.0808	-20.6257	0.1969	1.3873	0.6949	0.6924
C33–C35	2.0751	-20.4945	0.1995	1.3881	0.691	0.6971

C37–C41	1.6855	-14.375	0.0467	1.5268	0.7392	0.7875
C37–C41	*1.7057*	*-14.6871*	*0.0261*	*1.5202*	*0.7695*	*0.7506*
C3–O2	1.842	-5.2746	0.0710	1.3728	0.4583	0.9146
C3–O2	*1.8372*	*-5.0754*	*0.0555*	*1.3738*	*0.4583*	*0.9155*
C13–O14	1.736	-11.1074	0.0269	1.4182	0.4934	0.9248
C13–O14	*1.7112*	*-10.354*	*0.0068*	*1.4216*	*0.4921*	*0.9295*
C27–O26	1.842	-5.2745	0.0710	1.3728	0.4583	0.9146
C27–O26	*1.8371*	*-5.0753*	*0.0555*	*1.3738*	*0.4583*	*0.9155*
C37–O38	1.736	-11.1076	0.0269	1.4182	0.4934	0.9248
C37–O38	*1.7112*	*-10.3533*	*0.0068*	*1.4216*	*0.4921*	*0.9295*
C17–N20	1.5533	-12.1051	0.0106	1.5025	0.5546	0.9479
C17–N20	*1.8268*	*-17.4475*	*0.0497*	*1.451*	*0.5887*	*0.8623*
C21–N20	1.5582	-11.708	0.0048	1.4946	0.5411	0.9536
C21–N20	*1.7973*	*-16.9752*	*0.0421*	*1.454*	*0.586*	*0.868*
C41–N44	1.5533	-12.1051	0.0106	1.5025	0.5546	0.9479
C41–N44	*1.8268*	*-17.4473*	*0.0497*	*1.451*	*0.5887*	*0.8623*
N44–C45	1.5582	-11.7079	0.0048	1.4946	0.9536	0.5411
N44–C45	*1.7973*	*-16.9752*	*0.0421*	*1.454*	*0.868*	*0.586*

Table S8 Comparison of BCP properties for the intermolecular region of cationic (shown in red color) and neutral (*italicised*) synephrine O–H···O dimers obtained after gas-phase optimization.

Interaction	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	ε	R_{ij} (Å)	d_1 (Å)	d_2 (Å)	V_{cp} (kJmol^{-1}Bohr^{-3})	G_{cp} (kJmol^{-1}Bohr^{-3})
N20–H49···O14	0.1577	2.5663	0.4749	2.1522	0.9005	1.2517	–0.019	0.023
N20–H49···O14	-	-	-	-	-	-	-	-
N44–H52···O38	0.1577	2.5661	0.4750	2.1523	0.9006	1.2517	–0.019	0.023
N44–H52···O38	-	-	-	-	-	-	-	-
O38–H39···O2	0.1649	2.4157	0.0802	1.9455	0.6956	1.2499	–0.020	0.023
O38–H39···O2	*0.1377*	*1.9823*	*0.0663*	*2.0431*	*0.7485*	*1.2946*	*–0.016*	*0.018*
O14–H15···O26	0.1649	2.4157	0.0802	1.9455	0.6956	1.2499	–0.020	0.023
O14–H15···O26	*0.1378*	*1.9832*	*0.0664*	*2.0429*	*0.7484*	*1.2945*	*–0.016*	*0.018*

Table S9 NBO analysis depicting donor–acceptor delocalization for hydrogen bonds observed for the gas-phase optimized cationic (shown in red color) and neutral (*italicised*) synephrine O–H···O dimer.

Interaction involved	Donor NBO (i)	Population (n_i)	Acceptor NBO (j)	Population (n_j)	E^2 (kcal/mol)	E_j–E_i (a.u.)
O38–H39···O2	$LP1_{O2}$	1.97	$\sigma^*_{O38–H39}$	0.02	6.13	1.21
O38–H39···O2	$LP2_{O2}$	1.90	$\sigma^*_{O38–H39}$	0.02	1.95	0.95
O38–H39···O2	*$LP1_{O2}$*	*1.97*	*$\sigma^*_{O38–H39}$*	*0.01*	*3.31*	*1.25*
O38–H39···O2	*$LP2_{O2}$*	*1.90*	*$\sigma^*_{O38–H39}$*	*0.01*	*1.63*	*0.96*
O14–H15···O26	$LP1_{O26}$	1.97	$\sigma^*_{O14–H15}$	0.02	6.13	1.21
O14–H15···O26	$LP2_{O26}$	1.90	$\sigma^*_{O14–H15}$	0.02	1.95	0.95
O14–H15···O26	*$LP1_{O26}$*	*1.97*	*$\sigma^*_{O14–H15}$*	*0.01*	*3.31*	*1.25*
O14–H15···O26	*$LP2_{O26}$*	*1.90*	*$\sigma^*_{O14–H15}$*	*0.01*	*1.63*	*0.96*
N20–H49···O14	$LP1_{O14}$	1.97	$\sigma^*_{N20–H49}$	0.02	1.95	1.07
N20–H49···O14	$LP2_{O14}$	1.95	$\sigma^*_{N20–H49}$	0.02	1.20	0.78
N44–H52···O38	$LP1_{O38}$	1.97	$\sigma^*_{N44–H52}$	0.02	1.95	1.07
N44–H52···O38	$LP2_{O38}$	1.95	$\sigma^*_{N44–H52}$	0.02	1.20	0.78

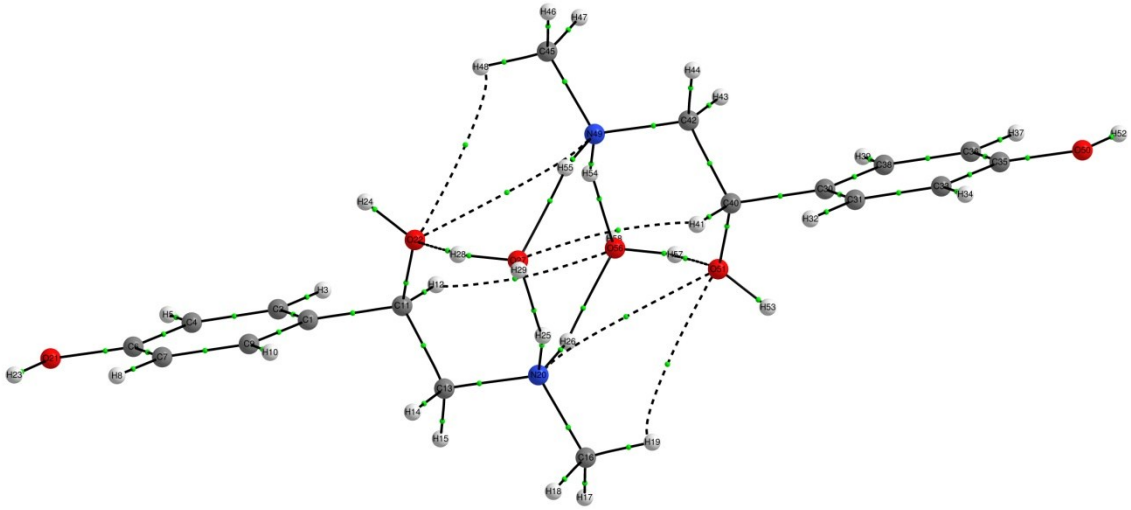


Figure S3 Molecular graph depicting bond critical point (marked in green) observed for the gas phase optimized water mediated cation···cation complex observed in **1k**.

Table S10 Intramolecular BCP properties of the water assisted tetramer observed in (□) synephrine–terepthalate salt (**1k**)

Bond	ρ (eÅ^{-3})	∇^{2}ρ (eÅ^{-5})	ε	r_{ij} (Å)	d_1(Å)	d_2(Å)
O21–H23	2.444	-62.436	0.019	0.9383	0.1606	0.7777
O50– H52	2.444	-62.435	0.019	0.9383	0.1606	0.7777
O22–H24	2.415	-61.161	0.024	0.9412	0.1614	0.7798
O51–H53	2.415	-61.153	0.024	0.9412	0.1614	0.7798
O56–H58	2.409	-61.416	0.018	0.9390	0.1597	0.7793
O27–H29	2.409	-61.418	0.018	0.9390	0.1597	0.7793
O56–H57	2.358	-60.572	0.021	0.9443	0.1547	0.7896
O27– H28	2.357	-60.569	0.021	0.9443	0.1547	0.7896
N20–H25	2.198	-41.725	0.003	1.0108	0.2321	0.7786
N49–H54	2.198	-41.714	0.003	1.0108	0.2321	0.7787
N20–H26	2.195	-41.691	0.004	1.0111	0.232	0.7791
N49–H55	2.195	-41.689	0.004	1.0111	0.2319	0.7792
C2–C4	2.103	-20.995	0.211	1.3822	0.7009	0.6813
C31–C33	2.103	-20.994	0.211	1.3822	0.7009	0.6813
C4–C6	2.088	-21.160	0.206	1.3974	0.6694	0.7280
C33–C35	2.088	-21.160	0.206	1.3974	0.6694	0.7280
C7–C9	2.081	-20.497	0.214	1.3857	0.6851	0.7006
C36–C38	2.081	-20.495	0.214	1.3857	0.6851	0.7006
C6–C7	2.075	-20.672	0.213	1.3984	0.7232	0.6751
C35–C36	2.075	-20.675	0.213	1.3983	0.7232	0.6751
C30–C31	2.044	-19.765	0.207	1.3974	0.7065	0.6909
C1–C2	2.043	-19.760	0.207	1.3975	0.7065	0.6909
C1–C9	2.039	-19.576	0.211	1.3976	0.7008	0.6968
C30–C38	2.039	-19.577	0.211	1.3976	0.7008	0.6968
C6–O21	2.013	-6.183	0.050	1.3406	0.8918	0.4488
C35–O50	2.013	-6.182	0.050	1.3406	0.8918	0.4488
C13–H15	1.909	-23.602	0.028	1.0757	0.3669	0.7087
C16–H17	1.909	-23.620	0.031	1.0732	0.3672	0.7060
C16–H19	1.909	-23.612	0.030	1.0723	0.3681	0.7042
C42–H44	1.909	-23.600	0.028	1.0757	0.3670	0.7087
C45–H46	1.909	-23.619	0.031	1.0732	0.3672	0.7060

C45–H48	1.909	-23.610	0.030	1.0723	0.3681	0.7042
C16–H18	1.907	-23.581	0.031	1.0735	0.3675	0.7060
C45–H47	1.907	-23.581	0.031	1.0735	0.3675	0.7060
C4–H5	1.906	-23.639	0.016	1.0669	0.3655	0.7014
C11–H12	1.906	-23.336	0.036	1.0818	0.3771	0.7047
C33–H34	1.906	-23.639	0.016	1.0669	0.3655	0.7014
C40–H41	1.906	-23.335	0.036	1.0818	0.3771	0.7047
C13–H14	1.899	-23.283	0.031	1.0770	0.3701	0.7069
C42–H43	1.899	-23.281	0.532	1.0770	0.3701	0.7069
C2–H3	1.890	-23.182	0.013	1.0702	0.3767	0.6935
C31–H32	1.890	-23.182	0.013	1.0702	0.3767	0.6935
C7–H8	1.887	-23.077	0.019	1.0691	0.3740	0.6951
C36–H37	1.887	-23.077	0.019	1.0691	0.3740	0.6951
C9–H10	1.878	-22.846	0.014	1.0713	0.3802	0.6911
C38– H39	1.878	-22.845	0.014	1.0713	0.3802	0.6911
C1–C11	1.724	-14.810	0.054	1.5024	0.7162	0.7862
C30–C40	1.724	-14.807	0.054	1.5025	0.7163	0.7862
C11–C13	1.702	-14.622	0.040	1.5215	0.7423	0.7791
C40–C42	1.702	-14.614	0.040	1.5216	0.7424	0.7792
C11–O22	1.593	-8.851	0.032	1.4468	0.9450	0.5018
C40–O51	1.593	-8.846	0.032	1.4467	0.9450	0.5017
C16–N20	1.581	-12.519	0.008	1.4917	0.9438	0.5479
C45–N49	1.581	-12.523	0.008	1.4917	0.9438	0.5480
C13–N20	1.570	-12.652	0.023	1.4998	0.9407	0.5591
C42–N49	1.570	-12.658	0.023	1.4998	0.9406	0.5591

Table S11 Intermolecular BCP properties of the water assisted tetramer observed in (□) synephrine–terepthalate salt (**1k**).

Bond	ρ (eÅ^{-3})	∇2ρ (eÅ^{-5})	ε	r_{ij} (Å)	d_1(Å)	d_2(Å)	Vcp (kJ/mol/Bohr^3)	Gcp (kJ/mol/Bohr^3)
N20–H26···O56	0.177	2.427	0.067	1.9434	1.2457	0.6977	-0.021	0.023
N49–H55···O27	0.177	2.438	0.066	1.9412	1.2446	0.6966	-0.021	0.023
N49–H54···O56	0.174	2.397	0.049	1.9480	1.2482	0.6999	-0.020	0.023
N20–H25···O27	0.173	2.387	0.049	1.9499	1.2491	0.7008	-0.020	0.022
O27–H28···O22	0.156	2.316	0.142	2.0484	1.2731	0.7754	-0.019	0.022
O56–H57···O51	0.156	2.315	0.142	2.0484	1.2732	0.7752	-0.019	0.022
O22···N49	0.042	0.581	1.867	3.3409	1.6276	1.7133	-0.004	0.005
O51···N20	0.042	0.579	1.863	3.3401	1.6284	1.7118	-0.004	0.005
C11–H12···O56	0.037	0.460	1.654	2.9182	1.6385	1.2797	-0.003	0.004
C40–H41···O27	0.037	0.460	1.767	2.9202	1.6392	1.2810	-0.003	0.004
C45–H48···O22	0.034	0.421	0.918	2.9538	1.6666	1.2872	-0.003	0.004
C16–H19···O51	0.034	0.420	0.924	2.9558	1.6676	1.2882	-0.003	0.004

Table S12 NBO analysis depicting donor–acceptor delocalization for hydrogen bonds (water-mediated N–H···O and cationic synephrine C–H···O dimer) observed for the gas-phase optimized tetermer.

Interactions involved	Donor NBO (i)	Population (n_i)	Acceptor NBO (j)	Population (n_j)	E^2 (kcal/mol)	E(j)–E(i) a.u.
O27-H28···O22	$LP1_{O22}$	1.978	$\sigma^*_{O27-H28}$	0.009	1.51	1.21
O27-H28···O22	$LP2_{O22}$	1.961	$\sigma^*_{O27-H28}$	0.009	2.56	0.91
N49-H54···O22	$LP1_{O22}$	1.978	$\sigma^*_{N49-H54}$	0.035	0.06	1.12
N49-H55···O22	$LP1_{O22}$	1.978	$\sigma^*_{N49-H55}$	0.036	0.17	1.12
C45-H48···O22	$LP2_{O22}$	1.961	$\sigma^*_{C45-H48}$	0.004	0.10	0.88
N20-H25···O27	$LP1_{O27}$	1.978	$\sigma^*_{N20-H25}$	0.035	4.99	0.83
N20-H25···O27	$LP2_{O27}$	1.973	$\sigma^*_{N20-H25}$	0.035	6.74	1.17

N49-H55···O27	$LP1_{O27}$	1.978	$\sigma^*_{N49-H55}$	0.036	4.62	0.83
N49-H55···O27	$LP2_{O27}$	1.973	$\sigma^*_{N49-H55}$	0.036	7.33	1.17
C40-H41···O27	$LP2_{O27}$	1.973	$\sigma^*_{C40-H41}$	0.031	0.16	1.22
N20-H26···O51	$LP1_{O51}$	1.978	$\sigma^*_{N20-H26}$	0.036	0.17	1.12
C16-H19···O51	$LP2_{O51}$	1.961	$\sigma^*_{C16-H19}$	0.004	0.10	0.88
O56-H57···O51	$LP1_{O51}$	1.978	$\sigma^*_{O56-H57}$	0.009	1.51	1.21
O56-H57···O51	$LP2_{O51}$	1.961	$\sigma^*_{O56-H57}$	0.009	2.56	0.91
N20-H26···O56	$LP1_{O56}$	1.978	$\sigma^*_{N20-H26}$	0.036	5.12	0.83
N20-H26···O56	$LP2_{O56}$	1.973	$\sigma^*_{N20-H26}$	0.036	6.85	1.17
C11-H12···O56	$LP2_{O56}$	1.973	$\sigma^*_{C11-H12}$	0.031	0.16	1.22
N49-H54···O56	$LP1_{O56}$	1.978	$\sigma^*_{N49-H54}$	0.035	4.52	0.83
N49-H54···O56	$LP2_{O56}$	1.973	$\sigma^*_{N49-H54}$	0.035	7.15	1.17

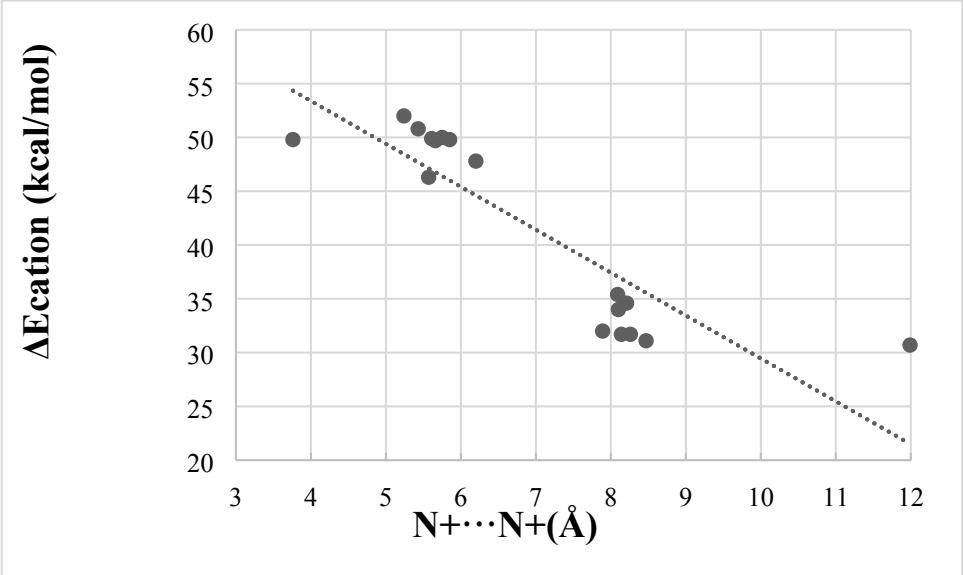
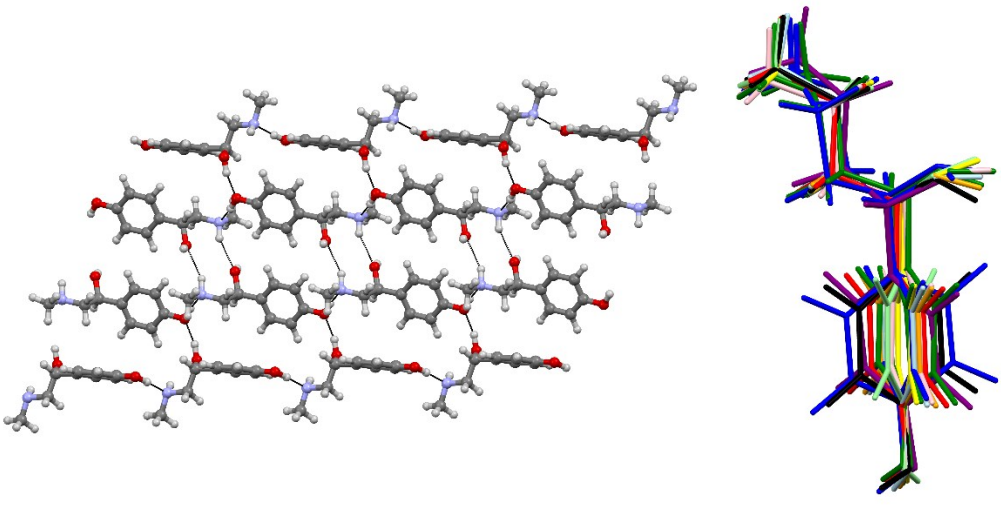
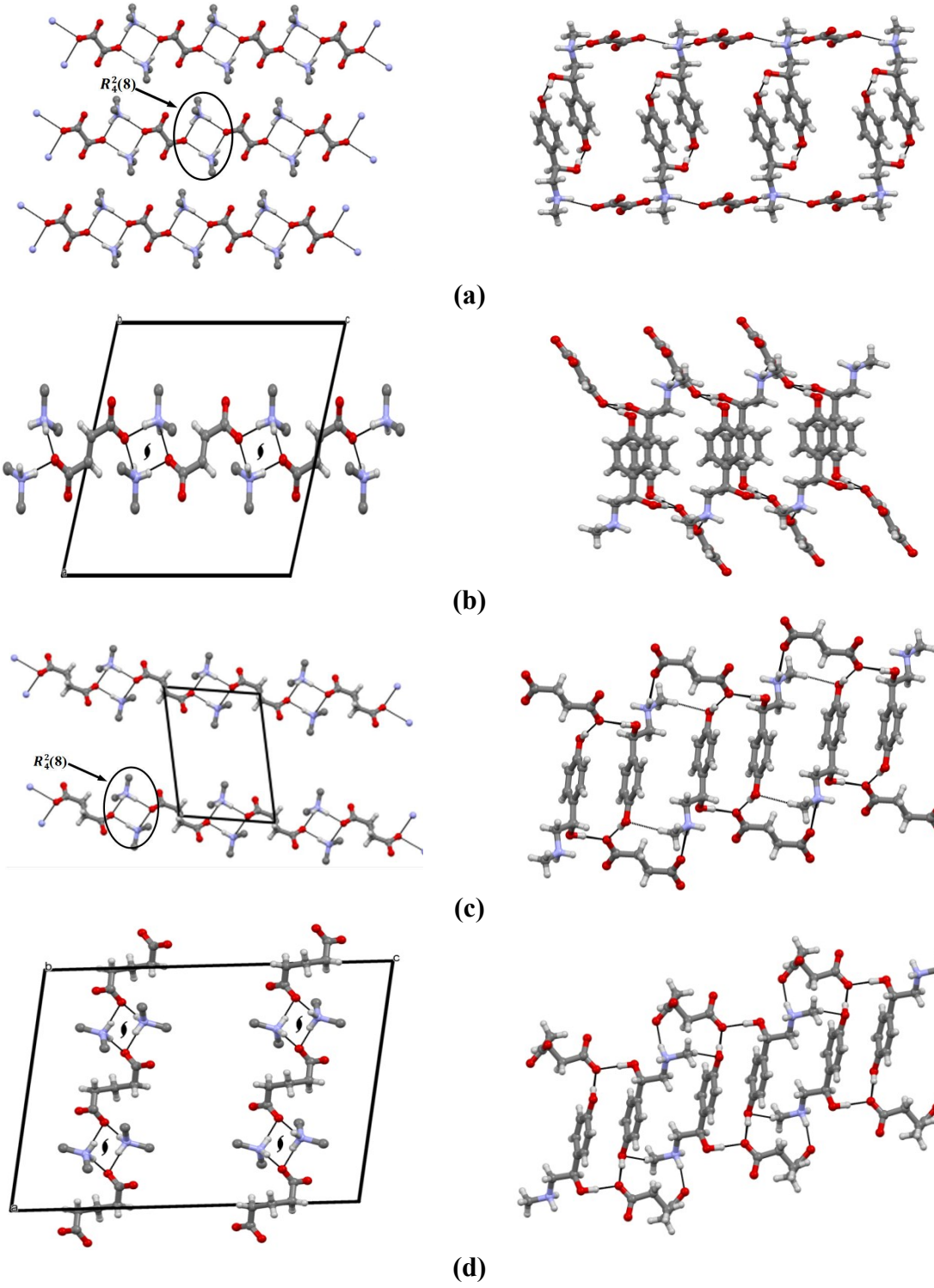


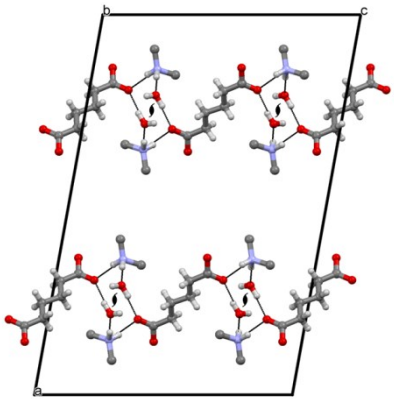
Figure S4 Variation of inter-cationic columbic repulsion estimated from ΔE_{cation} interaction energy vs distance between cationic charge centres

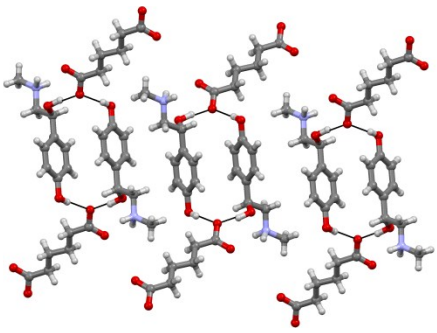


(a) **(b)**

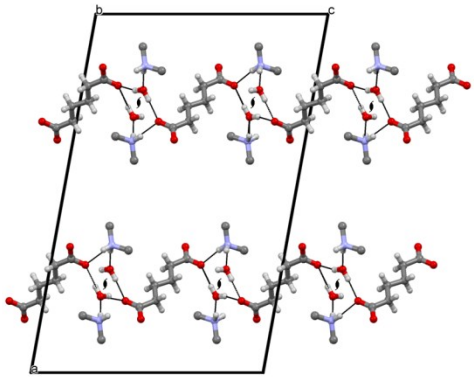
Figure S5 (a) Molecular packing in, **1a** (b) Molecular overlay of synephrine cation conformations in reported salt forms.

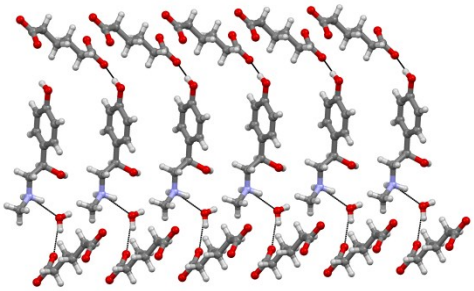




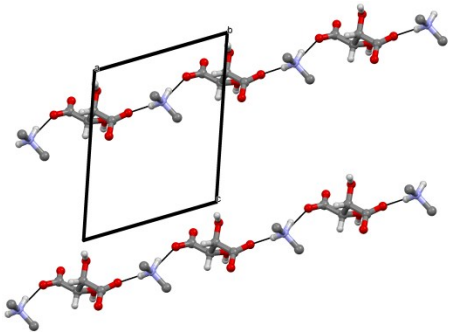


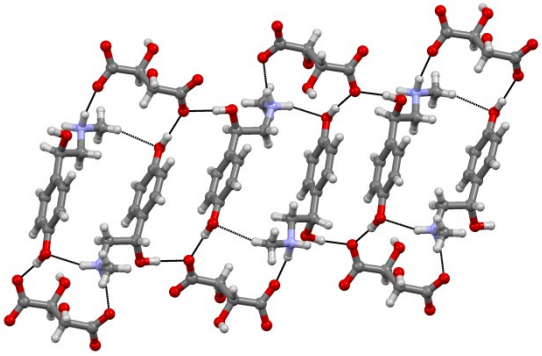
(e)



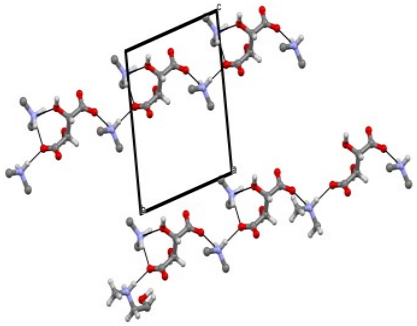


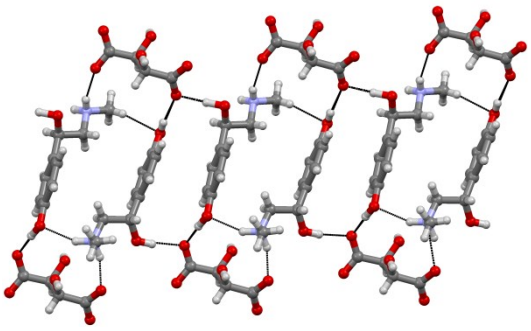
(f)





(g)





(h)

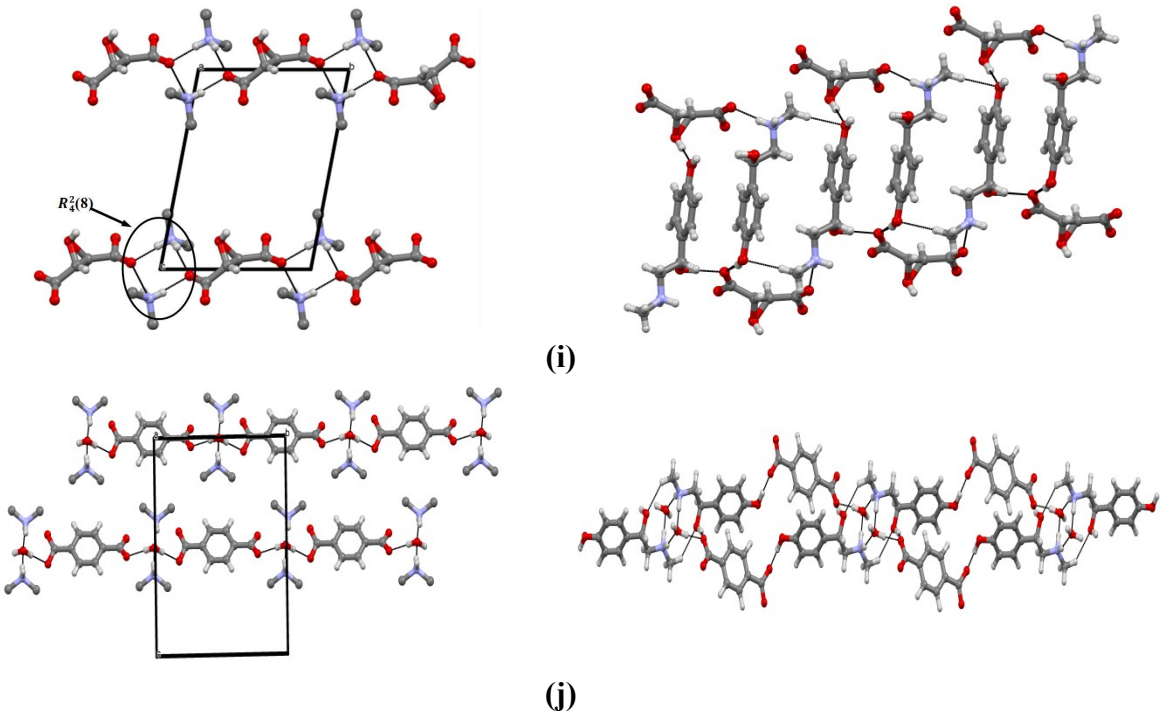


Figure S6 Crystal packing in (a) oxalate salt, **1b** (b) fumarate salt, **1c** (c) succinate salt, **1d** (d) glutarate salt, **1e** (e) adipate salt at RT, **1f** (f) adipate salt at 100 K, **1g** (g) D,L–tartrate salt, **1h** (h) L–tartrate salt, **1i** (i) D,L–maleate salt, **1j** and (j) terephthalate salt, **1k**. Symbol □ represents the top view of the 2_1-screw axis related molecular propagation.