Supporting Information for

Quadrupolar NMR Crystallography Guided Crystal Structure Prediction (QNMRX-CSP) of Zwitterionic Organic HCl Salts

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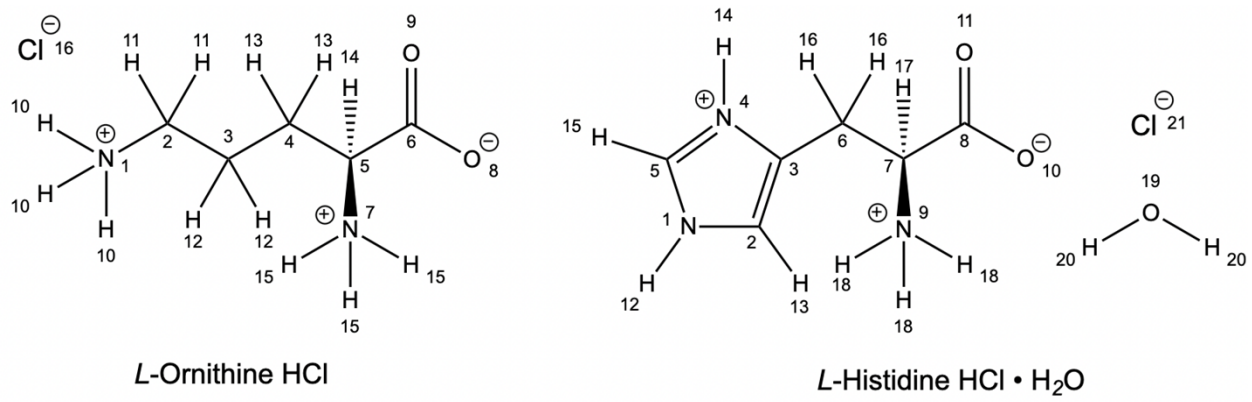
Scheme S1. An overview of QNMRX-CSP, adapted from Peach *et al.*[1] The yellow arrows indicate the path taken when starting from the known crystal structure (**§3.2**), the red arrows indicate the path taken when starting from an isolated "gas-phase" molecule (**§3.3**), and the black arrows indicate the paths taken from either starting point. The first four steps of M2 are repeated *N* times, where *N* is 10 for **Orn** and **Hist,** starting from the known crystal structure and an isolated "gas-phase" molecule.



Scheme S2. Molecular diagrams with atom positions numbered for **Orn** (left) and **Hist** (right).

Table S1. Tabulated Hirshfeld charges that were added for the **Orn** and **Hist** molecular fragments in **§3.3**, where the atom position numbers correspond to the labels in **Scheme S2**.[a,b]

Atom Position	Orn	Hist
1	–0.038	–0.028
2	–0.005	–0.002
3	–0.058	0.045
4	–0.069	–0.026
5	0.022	0.082
6	0.150	–0.100
7	–0.038	0.030
8	–0.260	0.150
9	–0.230	–0.038
10	0.100	–0.260
11	0.032	–0.230
12	0.032	0.095
13	0.032	0.045
14	0.040	0.098
15	0.100	0.054
16	–0.306	0.038
17	–	0.050
18	–	0.104
19	–	–0.246
20	–	0.096
21	–	–0.299

[a] The use of QNMRX-CSP starting from an isolated molecule requires approximate values of Hirshfeld charges to be assigned to each atomic site. Considering this, a charge database was previously constructed for small organic HCl salts.[1] This charge database could not provide approximate Hirshfeld charges for **Orn** and **Hist** as there were several functional groups present in **Orn** and **Hist** that were under-reported in the charge database. To include those functional groups several crystal structures were obtained from the Cambridge Structural Database and underwent geometry optimizations and subsequent calculations of their Hirshfeld charges. Those charges were then added to the database and the charges for **Orn** and **Hist** were determined. Minor modifications to the H and Cl Hirshfeld charges were made to obtain a net charge of zero for each structure.

[b] The following crystal structures obtained from the Cambridge Structural Database were used to calculate there Hirshfeld charges and had each of their functional groups added to the charge database: 1-Hydroxyimidazolium hydrochloride (IFUWEN), 1,3-Dihydroxyimidazolium hydrochloride (DOJLEU), 3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium hydrochloride (KERNOM03), 1,3-Dimethylimidazolium hydrochloride (JUFBUH), Imidazole-4-acetic acid hydrochloride (IMACHC), 2,3-dimethyl-1H-imidazol-3-ium hydrochloride (MAMFUF), 1,3-di-t-butyl-1H-imidazol-3-ium hydrochloride (OMEDIW), 2-(Carboxycarbonyl)imidazo[1,2-a]pyridine-1-ium hydrochloride monohydrate (PARVEL), 5-methyl-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-1-ium hydrochloride (PEQYOC), 2-Phylimidazolium hydrochloride monohydrate (PUKGAE), 1-(carboxymethyl)-3-ethyl-1H-imidazol-3-ium hydrochloride (TIGMAA), 1H-4-Hydroxymethylimidazole hydrochloride (TUQCEN), 1-ethyl-2,3-dimethyl-1H-imidazol-3-ium hydrochloride (VIPXUN01), 1,3,4,5-tetramethyl-1H-imidazol-3-ium hydrochloride (YOFKUZ02), 3-aminopropan-1-aminium hydrochloride (DUXQOF), DL-Lysine hydrochloride (DLLYSC11), Ethane-1,2-diaminium dichloride (EDAMCL09), 4-carboxybutan-1-aminium hydrochloride (VUHTUQ).

References

(1) Peach, A. A.; Fleischer, C. H.; Levin, K.; Holmes, S. T.; Sanchez, J. E.; Schurko, R. W. Quadrupolar NMR Crystallography Guided Crystal Structure Prediction (QNMRX-CSP). *CrystEngComm* **2024**, *26*, 4782–4803. https://doi.org/10.1039/D3CE01306E.